Title
VIBRATIONAL ENERGY TRANSFER IN SELECTIVELY EXCITED DIATOMIC MOLECULES

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VIBRATIONAL ENERGY TRANSFER
IN SELECTIVELY EXCITED DIATOMIC MOLECULES

Cameron John Casch
(Ph.D. thesis)

September 1978

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VIBRATIONAL ENERGY TRANSFER IN SELECTIVELY EXCITED DIATOMIC MOLECULES
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ABSTRACT
Single rovibrational states of HCl(v=2), HBr(v=2), DCl(v=2), and CO(v=2) have been excited with a pulsed optical parametric oscillator (OPO). Total vibrational relaxation rates by near - resonance quenchers were measured at 295 K using time resolved infrared fluorescence. These rates are attributed primarily to V - V energy transfer, and they generally conform to a simple energy gap law. A small deviation was found for the CO(v)+DCl(v') relaxation rates. Upper limits for the self relaxation by V - R,T of HCl(v=2) and HBr(v=2) and for the two quantum exchange between HCl and HBr were determined. The HF dimer was detected at 295 K and 30 torr HF pressure with an optoacoustic spectrometer using the OPO. Pulsed and chopped, resonant and non-resonant spectrophones are analyzed in detail. From experiments and first order perturbation theory, these V - V exchange rates appear to behave as a first order perturbation in the vibrational coordinates. The rotational dynamics are known to be complicated however, and the coupled rotational - vibrational dynamics were investigated theoretically in "infinite order" by the Dillon and Stephenson and the first Magnus approximations. Large ΔJ transitions appear to be important, but these calculations differ by orders of magnitude on specific rovibrational transition rates. Integration of the time dependent semiclassical
equations by a modified Gordon method and a rotationally distorted wave approximation are discussed as methods which would treat the rotational motion more accurately.
Dedication

To my parents and brothers,
with love, respect, and thanks
ACKNOWLEDGEMENTS

A thesis does not capture the complete image of the many and multifaceted experiences accumulated during years of work. Nor, is it possible to thank sufficiently or in commensurate manner the people who have aided me on this rite of passage.

I do wish to thank Professor C. Bradley Moore under whom this work was performed for giving rein to my independent urgings. I am indebted to Glen MacDonald and Steve Leone for experimental ideas and methods. I am happy in the remembrance of hours of debate with Jay Wiesenfeld and his abundant wealth of ideas, memories, and speculations. I will always heartfully recall the cheerful impatience, companionship, and cooking of Pauline, Linda, and Vera during the final "hours" of the writing.

This work was done under the auspices of the U. S. Department of Energy.
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INTRODUCTION

Vibrational energy transfer has engaged the attention of physical scientists since the 1920's when it was perceived that those processes could be observed. In part, perhaps, this long and sustained interest has come about because vibrational energy transfer in gases can be viewed as the simplest phenomenon in which one molecule interacts with the interior of another molecule. For chemists, vibrational energy transfer has been viewed as a simpler homologue of the all important chemical reaction.

Lasers enabled the direct observation of vibrational energy transfer via visible and infrared fluorescence, but it was not till around 1970 that the systematic variation of rates with vibrational level could be studied. In those studies populations in many vibrational levels were generated, usually by chemical reactions not lasers. However, whenever an uncontrollable, initial distribution of states is generated kinetic information is lost.

This work is primarily devoted to the study of V - V (vibration to vibration) energy transfer from diatomic molecules selectively pumped to their second (v=2) excited vibrational state. Two nearly resonant collision systems, HCl-HBr and CO-DC1, were studied. These systems were chosen because they can be observed with existing technology and because in nearly resonant systems one can study V - V transfer rates relatively free from contributions due to the slower V - R,T (vibration to rotation and translation) transfer rates. This work represents the first systematic study of a sizeable group of
collidants in which unambiguous \( v=2 \) rates can be compared with the \( v=1 \) rates. Because only a single vibrational level is initially excited detailed rate constants for the less dominant processes such as two quantum exchanges and \( v=2 \ V-R,T \) can in principle be determined. In practice, these rates are so small that upper limits could be established for them only in HCl - HBr mixtures where the fluorescence was strongest.

These measurements rely on a unique, continuously tunable infrared laser - a Nd:YAG pumped, temperature tuned, LiNbO\(_3\) optical parametric oscillator (OPO). The OPO is a pulsed source, and the energy transfer studies probe the relaxation by means of the spectrally resolved, infrared luminescence. The luminescence is weak and these experiments depend heavily on initially detecting the OPO absorption optoacoustically. The OPO absorption is detected by a microphone as a pressure increase in the gas.

This sensitive absorption spectroscopic technique was used to observe the HF dimer at 2.5 \( \mu \). At the pressures used the dimer absorption is three and a half orders of magnitude smaller than the monomer absorption. The absorption was too weak, however, to allow the intended observation of line broadening due to vibrational predissociation. Such processes can be viewed as the second half of a \( V-R,T \) collision, in a peculiar collision which manages to appear in the classically forbidden region at the bottom of the intermolecular potential well.
These experimental results combined with previous measurements indicate that simple first order perturbation reasoning predicts the manner in which single quantum V-V exchange rates scale with vibrational level. The rate constants (or thermally averaged cross section or probability) for a

\[ v + (v'-1) \rightarrow (v-1) + v' + \Delta E_{vv'} \]

exchange scale as

\[ k_{vv'} = v v' k_o (\Delta E_{vv'}) \]

where \( \Delta E_{vv'} \) is the rotationless difference of energy levels, a quantity known as the energy discrepancy. \( k_o (\Delta E_{vv'}) \) is a resonance function. A small deviation from this correlation was found in the well studied CO + DCl system.

One of the ultimate chemical purposes for these studies is to derive new information on intermolecular interactions, especially details of the intermolecular potential. Since measured cross sections are a convolution of the potential and kinematics, there is the nearly philosophical question as to whether the cross sections can be inverted to a unique representation of the potential. In 1973 there were suggestions that V-V energy transfer was primarily due to multipolar forces and that moments of the expansion might be determined from measured rates. It is now recognized that other parts of the potential give comparable contributions to the rates.

In this work an effort was made to find a representation-free description of the rates using the Massey-Mott view of energy transfer. As was previously known, most rates are less sensitive to
the energy discrepancy than they are predicted to be; especially the hydrogen and deuterium halides. In these molecules the rotational spacing is comparable to the width of the resonance function and the rotational dynamics are expected to be complicated. In this work, the effect of rotation on V - V rates was investigated theoretically using the first Magnus approximation and the Dillon and Stephenson quasi Magnus approximation. Large rotational transitions were observed as well as a decreased dependence on the vibrational energy discrepancy. However, the rotational dynamics were strongly dependent upon the method of calculation. As a result, more rigorous methods of treating the dynamics were developed, including exact integration of the time dependent semiclassical equations and a rotationally distorted wave Born approximation.
II. EXPERIMENTAL

A. Introduction

The majority of the experiments described below are laser induced infrared fluorescence measurements of vibration to vibration energy transfer in simple gases. In these experiments a single rovibrational level of a molecule was excited with a pulsed, tunable infrared laser known as an optical parametric oscillator (OPO).

Section B of this chapter describes in a summary fashion the oscillator and signal averaging equipment which have been developed with several other people in the laboratories where this work was performed. An overall view of the pieces involved in these experiments is shown in Fig. II-1. The signal averaging equipment was computer interfaced, and a large program for numerical, on-line, interactive analysis of the multiexponential fluorescence decays was written. This work clarified some questions on minor signal corrections which can be made numerically.

One of the primary difficulties encountered with a pulsed, tunable laser having relatively large (10%) pulse to pulse fluctuations in energy is the uncertainty of laser line - gas line coincidence. In earlier work absorption in a long absorption cell was used, but given the 10% energy fluctuation the OPO could be easily detuned to 50% of the absorption maximum. Finzi began the present practice of optoacoustic or spectrophone detection. In this work several new designs of spectrophone were developed for higher sensitivity. Given the high sensitivity of the method, work was performed to construct
Fig. II-1. Schematic of fluorescence and spectrophone experimental layout. Abbreviations used are BS - beam splitter, E = etalon, L = lens, M = mirror, PZT = piezoelectric translator.
Fig. II-1.
a technique for doing spectroscopy on species at low pressures. One of these spectrophones was used to detect the HF dimer, for which a simple signal averaging process with analog output was necessary. This work is described in section B.

The gas handling procedures for each of the gases is included in the following chapters.

B. Infrared Fluorescence Experiments

The laser excited infrared fluorescence technique has become well established since the original experiments of Yardley and Moore and Javan et al. Although the OPO's low energy requires care to maximize the fluorescence collection, very low intensities can be measured once the OPO beam and fluorescence detection system are aligned.

1. Nd:YAG Laser and Optical Parametric Oscillator

The experiments described below involved a single excitation source: the Chromatix doubled Nd:YAG pumped, LiNbO₃ optical parametric oscillator (OPO) shown schematically in Fig. II-2. In the course of the last eight years this tunable infrared source has provided the means of selectively exciting the fundamental and combination absorptions of several polyatomic molecules and especially in this work the overtones of several diatomic molecules.

While being a low energy (1-30μJ) source relative to several recently developed OPO's (5mJ) its very narrow linewidth (one or two longitudinal modes) and high repetition rate (75 pps) make it a unique excitation source of Doppler broadened gaslines in the region of 1.5 to 3.3μ. In the course of this work Leone's OPO and a Chromatix OPO were used.
The OPO was operated in the region of the HCl and HBr first overtone (1.7 - 1.8\(\mu\)) and the fundamentals of HF (2.4 - 2.7\(\mu\)) and HCl (3.3\(\mu\)). The YAG pumping lines, typical energies, and pulse lengths for these regions are tabulated in Table II - I. In general it was found that the Chromatix OPO operated more stably and with higher energies than the Leone OPO. The former oscillator is enclosed in a sheet metal box which stabilizes the crystal temperature by allowing sufficient conduction to reach quickly a thermal steady state while minimizing convection currents past the LiNbO\(_3\) crystal. Also, the etalon could be quickly and reproducibly inserted into the cavity.

The OPO is a photon efficient device since doubled Nd:YAG can be 90\(^\circ\) phase matched for parametric oscillation in LiNbO\(_3\). LiNbO\(_3\) absorbs doubled YAG at room temperature but not at the temperatures necessary for phase matching.

Tuning in the OPO is somewhat complicated and involves three tuning elements as seen in Figs. II-1 and -2. The center of the bandwidth is controlled by the LiNbO\(_3\) crystal temperature. This is scannable by the oven controller which contains a clock motor which in turn varies the temperature reference voltage. The longitudinal mode structure is controlled by a PZT translator attached to the output mirror. This could be ramped or manually set with a 0 - 2000 V programmable power supply. The output was narrowed with a temperature scanned solid sapphire etalon.
Table II-I. OPO Characteristics

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<td>$\lambda_{\text{pump}}$ (m)</td>
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<td>5-15</td>
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<td>10-20</td>
<td>3-10</td>
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<td>100</td>
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* Measured.
** LiNbO$_3$ scanned at 0.1 °C/min.
$^+$ calculated.
Fig. II-2. Characteristics of etalon narrowing the OPO. BW = single pass bandwidth of etalon, FSR = free spectral range of etalon.
Fig. II-2.
The gain of the OPO depends upon the pump energy, wavelengths, and cavity configuration, but generally the bandwidth of the OPO is somewhat less than the calculated one. By means of a spectrum analyzer, it has been measured to be .15 - .20 cm\(^{-1}\) in the 2.3 to 2.6\(\mu\) region.\(^2,8\) Since this is the high gain region of this OPO, this bandwidth is the maximum. The effective bandwidth of the OPO when the LiNbO\(_3\) temperature is scanned is considerably larger presumably due to thermal inhomogenities. The effective linewidth is the width of the excitation signal when the OPO is scanned through a narrow line such as a gaseous, Doppler-broadened line. Scanning at .1 \(^\circ\)C/min or approximately 1 cm\(^{-1}\)/min, the effective linewidth varies from .4 cm\(^{-1}\) at 2.7\(\mu\) to 1.0 cm\(^{-1}\) at 1.7\(\mu\). Wormhoudt et al.\(^9\) obtained an effective linewidth of .2 cm\(^{-1}\) presumably by using a slower scan motor. The PZT is ramped at \(-.05\) cm\(^{-1}\)/sec in order to fill out the effective linewidth.

The etalon is essential for stable frequency performance by the OPO. Since the mode spacing of the OPO is .025 cm\(^{-1}\) the .2 cm\(^{-1}\) or less bandwidth allows up to 15 modes to oscillate. In general the lower finesse etalons work best. The .6 cm\(^{-1}\) fsr Chromatix designed etalons were especially good, although the wavelength specifications are irrelevant. In the 1.7 to 3.0\(\mu\) region finesse 5 etalons were used. Within this .1 cm\(^{-1}\) bandwidth generally only one or two modes can reach threshold,\(^3\) so that the effective line width due to the etalon is approximately the mode spacing or .025 cm\(^{-1}\).

The oscillator goes single mode when the PZT and etalon maximum are near coincident. For a region of cavity lengths corresponding to
about half the mode separation ~.015 cm\(^{-1}\) the OPO can be scanned with the .001 cm\(^{-1}\) single mode linewidth. This region is scanned by varying the OPO cavity length with the PZT. Since the Doppler widths of most gases are less than .01 cm\(^{-1}\) in the 1.7 to 3.5\(\mu\) region, the OPO can be used to study anomalous broadening at low pressures such as vibrational predissociation in the HF dimer. Figure II-3 shows that the room temperature Doppler width of the HCl \(v = 2 + 0\) absorption can be resolved.

The above discussion has shown that the OPO has three levels of resolution if only one element at a time is tuned. Tuning more than one element generally would require a microcomputer. The resolution and range of tuning with single elements are tabulated in Table II-II.

The stability of the excitation signal is also indicative of single mode operation. It was found on occasion that the Chromatix OPO remained on a gas line from one day to the next despite temperature cycling of the LiNbO\(_3\) crystal and the etalon. This is a frequency reproducibility of one part in \(10^7\).

2. Detection and Signal Averaging Equipment

The geometry used for these experiments is depicted in Fig. II-1. The OPO is directed through a multipass fluorescence cell with a long (20 cm) focal length quartz lens. The OPO beam is good in this respect since it has a low (5 mrad) divergence and the IR beam is collinear with the visible pump beam.

The stainless steel, multipass fluorescence cell is \(2.5 \times 2.5 \times 5.0\) cm. The four windows are cemented on with Eccobond 45 epoxy. The Infrasil
Fig. II-3. OPO Doppler spectroscopy of HCl P(2). Spectrophone signal as a function of PZT voltage as the length of the etalon narrowed OPO cavity is scanned. The relative frequency scale is determined knowing that 1 fsr (.025 cm$^{-1}$) = 210 PZT units. o Experimental points; --- calculated Doppler profile fit to the center of the experimental points.
Fig. II-3.
Table II-II. OPO Single Element Tuning Ranges and Resolution

<table>
<thead>
<tr>
<th>Tuning element</th>
<th>Range (cm(^{-1}))</th>
<th>Linewidth (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNbO(_3) temperature</td>
<td>3000-6000</td>
<td>.2-1.0</td>
</tr>
<tr>
<td>Etalon</td>
<td>.2</td>
<td>.025</td>
</tr>
<tr>
<td>Cavity length</td>
<td>.015</td>
<td>&lt; .001 cm(^{-1})</td>
</tr>
</tbody>
</table>
(quartz) reflection windows are coated with a narrow (1 cm) band of silver and overcoated with TiF. The narrow band minimizes scattered light, and some 10-20 passes are typical. The upper and lower fluorescence windows were CaF\textsubscript{2}. Here and wherever possible CaF\textsubscript{2} optics are used since they transmit out to 12\mum and are resistant to water.

A fluorescence cell usable for HF was also constructed (Fig. II-4). The monel body was drilled with 1.9 cm diameter holes to form a T. Sapphire windows were mounted with Viton O ring seals. The reflection windows were coated on the internal surface with a gold strip and overcoated with CaF\textsubscript{2}. The length of the arms of the T, i.e. the distance from each window to the central region, is .5 cm. This dead length is the critical dimension when detecting \textit{v} = 1 \rightarrow 0 fluorescence, since it determines the minimum amount of self absorption which attenuates the fluorescence. With the low power of the OPO this cell is not very useful when simultaneously exciting and detecting HF \textit{v} = 1 \rightarrow 0 fluorescence. A 2.5 cm cubical quartz cell with external mirrors and a 1 mm dead length was much more efficient but was visibly etched even with low exposures (10 torr) of HF.

The fluorescence is collected with a single 5.1 cm diameter f/2 CaF\textsubscript{2} lens. While the f/2 lens with 1 to 1 focussing has four times less collection efficiency than a f/1 two lens system, Leone\textsuperscript{2} found it to give an operationally better signal. Presumably this is due to alignment problems. The f/2 lense at 10.2 cm from the fluorescence window collects only 1.5\% of the fluorescence.
Fig. II-4. HF fluorescence cell showing multipass arrangement.
Fig. II-4.

XBL 789-5869

Sapphire

Monel
At least 10 cm of space between the fluorescence cell and the
detector is necessary to be able to insert cold gas filter cells.
These cells are used to eliminate fluorescence which terminates on a
thermally populated state of the filter gas. Typically 100 torr is
used in the filter cell since this corresponds roughly to the onset
of pressure broadening of the absorption lines. Higher pressures have
the same peak line absorption.

Three infrared detectors were used. Two fast photoconductive
doped-germanium detectors with the operating characteristics listed
in Table II-III were used for the lifetimes reported in Chapters III
and IV, as well as an InSb detector. The Ge:Cu detector was also used
in an attempt to measure 1.7μ fluorescence corresponding to HCl v = 2+0
fluorescence. Santa Barbara Research does not recommend operation
of germanium detectors at these wavelengths which approach the intrinsic
absorption edge of germanium. There is a report that the response
time is slow in this region due to the long carrier lifetimes of the
germanium. However, these long response times were not observed for
times as short as .34 μsec at 1.76μ as seen in Fig. II-5. The Ge:Cu
response was compared with the subnanosecond response of a PEM type
InSb detector.

An InSb detector was resurrected in this attempt to detect the
1.7μ fluorescence. The signal lead for this planar diode detector
was reattached to the center of the element with silver epoxy. The
detector responded with low sensitivity and was not used.
Table II-III. Detector/Amplifier characteristics

<table>
<thead>
<tr>
<th></th>
<th>Ge:Cu with SBRC A320 Amplifier</th>
<th>Ge:Hg with LH0033 and Keithley 104</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field of view (sterrad)</td>
<td>4.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Load Resistor (kΩ)</td>
<td>100</td>
<td>30</td>
</tr>
<tr>
<td>Upper 3 dB freq. (MHz)</td>
<td>1.4</td>
<td>.43</td>
</tr>
<tr>
<td>Lower 3 dB freq. (Hz)</td>
<td>55</td>
<td>15</td>
</tr>
<tr>
<td>$D^*(3\mu)\text{cm}^{\sqrt{Hz/W}}$</td>
<td>-</td>
<td>$3\times10^{11}$</td>
</tr>
</tbody>
</table>
Fig. II-5. Ge:Cu detector response at 1.76 μ. The response of the Ge:Cu and an InSb PEM detector (τ < 1 nsec) are superimposed. The pulse length is determined by the OPO.
Time Response at 1.76 μ

- Ge: Cu detector
- PEM InSb

340 nsec

Fig. II-5.
Both germanium detectors were mounted in $^3$He cryostats and were generally operated at pumped $^4$He temperatures (14°K). The large Ge:Cu dewar has a filter turret so that cooled $^1$N$_2$ temperature interference filters can be changed in vacuo. The Ge:Hg dewar held a single filter. A MgF$_2$ flat at the detector temperature is also placed in front of the detector to eliminate radiation longer than 12 μ.

The signal is transiently digitized into 2048 channels with a Biomation 8100 Transient Recorder with a minimum channel spacing of 10 nsec and a maximum voltage resolution x full scale sensitivity of $2^{-8} \times .05$ V. Input signals were generally 0.5 V. The digitized signal is averaged by a Tracor Northern 575 Signal Averager. The minimum time to store a trace is ~10 msec and limits the signal averaging rate to about 80 pps.

As described in Section 4 the signal averager was interfaced to a terminal and the LBL interactive computer system to allow on-line data analysis of the fluorescence decay traces. Otherwise the trace was directly plotted on an Hewlett Packard 7004 Point Plotter and analyzed graphically. A calibrated time base was used to establish the overall time scale for each day's experiments.

3. **Amplifier Signal Distortion**

There will be systematic errors due to the response of the various amplifiers and electronic filters used. These response limitations usually arise from simple capacitive effects for which the response function, $R(\omega)$, is Lorentzian. There are phase shifts involved, so that the response function is complex. Taking the
response function for RC filters one has

\[ R_L(\omega) = \frac{1}{1 - i\omega L/\omega} \quad \text{low frequency cutoff} \]

\[ R_H(\omega) = \frac{1}{1 + i\omega /\omega_H} \quad \text{high frequency cutoff} \]

where \( \omega \) is in radians/sec (2\( \pi \) cycles/sec).

By performing the Fourier transform of the signal \( S(t) \) to frequency space, convolving the response function, and retransforming to time, the output \( S'(t) \) can be written as

\[ S'(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \omega \, e^{i\omega t} \, R(\omega) \int_{-\infty}^{\infty} d\tau \, e^{-i\omega \tau} \, S(\tau) \]

\[ = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\tau \, S(\tau) \, R^t(t-\tau) \]

where

\[ R^t(t-\tau) \equiv \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} d\omega \, e^{i\omega(t-\tau)} \, R(\omega) \]

Explicit expressions for the transforms are

\[ R_H^t(t-\tau) = \omega_H \exp[-\omega_H(t-\tau)] \, h(t-\tau) \]

\[ R_L^t(t-\tau) = \delta(t-\tau) - \omega_L \exp[-\omega_L(t-\tau)] \, h(t-\tau) \]

where \( h(t) \) and \( \delta(t) \) are the step and delta functions.

For a single exponential this implies \( \exp(-kt) \to \)

low frequency cutoff \( (ke^{-kt} - \omega_L e^{-\omega_L t})/(k - \omega_L) \)

high frequency cutoff \( (e^{-kt} - e^{-\omega_H t})\omega_H/(\omega_H - k) \)
both cutoffs $\omega_H >> \omega_L$  

$$[(\text{ke}^{-kt} - \omega_L e^{-\omega t})/(k - \omega_L) - e^{-\omega t}] \omega_H/(\omega_H - k)$$

The $\exp(-\omega t)$ is the spurious round corner found when high frequencies are lost. The negative, rising tail $-\omega_L \exp(-\omega_L t)$, is amplifier droop characteristic of low frequency cutoff.

It should be noted that the high frequency response of the system may be limited by the laser pulse length rather than the amplifiers' rise time. The time evolution of a two state system pumped by a pulsed excitation source will be

$$N_1 = (\alpha N_0) e^{-kt} \int_0^t I(\tau) e^{-k\tau} d\tau$$

where $N_1$ is the population of the state, $\alpha N_0$ represents the absorption strength, and $k$ is the relaxation rate constant of the population. Approximating the pulse by a rising and falling exponential

$$I(t) \sim \frac{E_0}{T_e - T_f} (e^{-t/T_f} - e^{-t/T_R})$$

If $T_f \frac{1}{k} >> T_R$

$$N_1 \sim \frac{\alpha N_0 E_0}{1 - kT_f} (e^{-kt} - e^{-t/T_f})$$

The rise of the fluorescence is determined by the decay of the pulse.

The numerical analysis program can remove these extraneous exponentials given the known rise and fall times of the combined amplifiers. The fall is much more troublesome since it appears as a baseline offset well before it interferes with the decay time. This baseline offset is a problem when $t=0$ relative amplitudes of a
multiexponential decay is desired. Analyzing these by hand the long time, sloping "baseline" should be used, but the amplitudes must be multiplied by the factor \((k - \omega_L)/k\). In general the minimum criterion

\[
\frac{\omega_H}{5} > k > 5\omega_L
\]

should be used in choosing an amplifier.

4. **On-Line Data Analysis**

The signal averaging equipment was interfaced to the CDC 6600 computer at Lawrence Berkeley Laboratory (LBL) to perform on-line numerical analysis of the fluorescence decay traces. In order to analyze multiexponential decay traces with a reasonable turn around time, it was originally felt that the larger computing ability of the CDC 6600 was needed rather than a minicomputer. This was largely borne out, but because of the increasing demands for interactive programming at LBL, daytime interactive analysis was not worthwhile.

The architecture of the interfacing is depicted in Fig. II-1. The Northern 575A Signal Averager is connected to the bus of a Tektronix 4010 Graphics Terminal\(^16\) for EIA RS232C bit - serial output at 2400 Baud. The RS232C bit - serial output of the terminal in turn is transmitted to the LBL interactive computer system by means of a hard wire. The terminal is equipped with a Tektronic 4912 Cassette Recorder to save the data off-line and to accept information from the LBL computer. Anything writeable on the screen can be recorded on the cassette. Also a Hewlett Packard 7004 point plotter was interfaced to the terminal so that points plotted on the terminal are plotted on
The HP. The plotter interface can be turned on and off by commands at the terminal keyboard or from the remote computer.

The LBL computer receives data through a multiplexing system. This "stop and go" reception of data required a modification of the terminal and the signal averager, since normally the signal averager outputs the contents of memory as an uninterrupted data string. The modifications 1) allowed the terminal to recognize the paper tape commands DC1 and DC3 from the computer; 2) inhibited the signal averager data transmission at the end of each line of data (8 channels of data followed by an ASCII carriage return character); and 3) uninhibited the signal averager when the terminal received a DC3 signal. The wiring changers are detailed in Reference 17.

Data traces were stored for long periods of time on the PSS mass storage system at LBL. Indefinite storage of data is made in the LBL tape library.

5. **Numerical Analysis of a Sum of Exponentials**

Fluorescence decays are generally sums of exponentials. This is a result of the weak excitation for which the kinetics are pseudo first order. An exception is certain solid state decays which exhibit a \( \exp(-k \sqrt{t}) \) component. Determining the coefficients in a signal which is a sum of exponentials is a perennial physical problem. It recurs in nuclear decays, biological growth problems, correlation spectroscopy, and spectral transmission of mixtures. While the program described below treats the fit as simply a minimization problem and uses the Simplex Method, there are specialized methods for generalized nonlinear
least square fits and for sums of exponentials fits.

Most of these techniques are least square methods. Given the experimental points \((t_i, y_i)\) we wish to find the \(N\) parameter fitting function \(y_N(t)\) which minimizes the residue of the experimental points.

\[
R_N = \sum_i \left[ y_i - y_N(t_i) \right]^2 / \sigma_i^2
\]

where \(\sigma_i^2\) is the variance of \(y_i\). The behavior of \(\sigma_i^2\) for different noise statistics is discussed below as well as the statistical meaning of \(R_N\). In the present case the fitting function is

\[
y_N(t) = \sum_j^{N/2} A_j \exp(-k_j t)
\]

As noted by Wiscombe and Evans\(^{18}\) there are three specialized techniques for fitting sums of exponentials. 1) Graphical Method. Successively faster decays are stripped off. 2) Prony's Method\(^{18}\). This is a least squares method using special properties of the residue when the amplitudes are all positive and the data are equally spaced in time. It applies the zero first derivative requirement to the amplitudes and replaces the exponentials by polynomials.

\[
\exp(-k t_i) = [\exp(-k \Delta) ]^i
\]

where \(\Delta\) is the data spacing. Using the linear dependence of the exponential sum upon the amplitudes should generally accelerate any method. An interesting result is that the method tends to find doublets for each decay constant. The method does not appear practical if many data points are used or if weighting functions are used.
3) Inverse Laplace Transform Method. In a sense this is the natural method for sums of exponentials. The time series is the Laplace transform of a discrete "frequency" spectrum.

\[
S(t) = \sum A_i e^{-k_i t}
\]

\[
\equiv \mathcal{L}[A(k)] = \int_0^\infty dk\, A(k)e^{-kt}
\]

where

\[
A(k) = \sum A_i \delta(k-k_i)
\]

A(k) is obtained from the inverse Laplace transform. For a noiseless signal A(k) would be a series of delta functions with heights equal to the amplitudes. In actuality the noise gives rise to finite width peaks. The inverse can be performed using Fourier transforms, although then are numerical instabilities.

The generalized least square methods are independent of the functional forms used to fit the data. These methods are a subset of more general optimization procedures used to minimize or maximize functions. Walsh has written a readable book which discusses these. The residue is a function of N fitting parameters and can be viewed as a N+1 dimensional hypersurface.

There are many methods for finding the minimum of the valley of the residue. 1) Grid Search Methods. This is a brute force method which fails if the initial grid is not big enough. 2) Newton's Methods. Expand the residue around the current guess presuming this guess is in the neighborhood of the minimum, and jump directly to where the minimum is suppose to be. If the expansion is first order
it is a Gauss-Newton method; if second order it is a Newton-Raphson. This procedure frequently diverges by overshooting the minimum.

3) Steepest Descent. Proceeding from an initial guess, follow the steepest descent. Typically the convergence is very slow. This is to be expected since the slope goes to zero near the minimum.

Prior to 1960 it was necessary to limit the step size in both the Newton and steepest descent methods. Powell subsequently developed a simple algorithm which determines the best step size for proceeding in a given direction. It was also recognized that the step direction in both methods are related. Various compromise directions which are simpler to evaluate and strategically better have been suggested. The general max/min methods of this type are the "quasi Newton" methods. Levenberg, Marquardt, and Powell have developed specializations to the generalized least squares problem. These are reviewed by Beale and Powell.

An important problem in these general extremization methods applied to exponential fits is the generic difference between the amplitudes and the decay constants. This can be seen even in single exponential fits. Figure II-6 plots logarithmically the residue as a function of the fit parameters. In a linear plot the valley is very unsymmetrical - a sharp wall at small amplitudes, gentle rise at large amplitudes. Methods which rely on the local contour of the residue surface do not work well on such highly nonparabolic surfaces. Most recent exponential fit programs including the present one rely on the Simplex Method which probes a region of parameter space.
Fig. II-6. Logarithmic plot of residue. a) Single exponential decay.

The integral

\[
R = \frac{\int_0^\infty dt [A e^{-kt} - A_{fit} e^{-k_{fit}t}]^2}{\int_0^\infty dt [A e^{-kt}]^2}
\]

b) Double exponential decay. It is assumed that amplitudes are equal and \(5k_1 = k_2\). The integral

\[
R = \frac{\int_0^\infty dt [(e^{-k_1t} + e^{-k_2t}) - (e^{-k_{fit}t} + e^{-k_{2fit}t})]^2}{\int_0^\infty dt [e^{-k_1t} + e^{-k_2t}]^2}
\]

is plotted. It is assumed in fitting that \(k_{fit} \leq k_{2fit}\). Equal contours are labeled by \(n\) where \(R_n = .1 \times 3^n\).
Fig. II-6.
The simplex method for max/minimizing a function is indirectly related to the linear programming simplex method. Both methods refer to the topological convex set known as a simplex. The simplex is a set of $N+1$ points in $N$ space which do not lie in an $N-1$ dimensional plane. For two dimensions this means 3 points which do not lie on a line; in three dimensions it is 4 points which do not lie in a plane, etc. Given these properties, points can be moved around on a line between them and the centroid and still remain a simplex. The simplex method is simply a systematic fashion of expanding and contracting this lasso around the extremum point. Nelder and Mead \cite{31} devised expansion and contraction rules empirically which apparently are being used in all current simplex routines. \cite{32,33} The present program includes a version of their rules which was developed by the LBL computer staff.

The rate of convergence for double exponential decays was slow when the ratio of the decays was less than 5. To make the residue map more parabolic the $\{A_i,k_i\}$ fitting parameters can be reparameterized, e.g. $\{\ln A_i, \ln k_i\}$ for the simplex minimization process. Lawrence Livermore Laboratory's "Creep" program uses the reparameterization $\{A_1/.05,k_1/20000;A_2/.4,k_2/2000;A_3=1-A_1-A_2,k_3/4000\}$ for a three exponential decay. No comparison tests with reparameterization were made.

With any of the min/max techniques an initial guess must be made, and this strongly affects the rate of convergence. Initially very rough guesses based on the signal maximum and $e^{-1}$ points relative to the maximum were used. These worked very poorly and were replaced
with the Graphical Method. This is the method used when traces were
analyzed by hand, and for traces involving only one decay this guess is
usually the converged fit. For double decays, the long decay was
determined from a fixed fraction of the decaying part of the signal.
Using a fixed fraction of the trace limits the accuracy of this guess
but foregoes the complicated procedures necessary to determine when the
ln of the longest decay is no longer linear.

Because a selective procedure was used to determine the initial
guess and allowance was made for the introduction of known exponentials
(known decay rates or amplifier corrections), explicit expressions for
each fitting function (1 decay, 1 rise + 2 decays, etc.) were used.

The flow diagram for the program is given in Fig. II-7. In
addition to the minimization process, it is necessary to establish
the baseline, the t=0 point, and the noise; to eliminate parts of the
trace with systematic noise; and to allow for digital filtering. All
these elements, which occur prior to the fitting procedure, allow that
not all the noise in a trace is random, and that some information in
addition to the fitting functional form is known.

The baseline is usually determined by eye on the terminal display
and input to the program by the terminal thumbwheels. However, the
program can determine the baseline automatically from the flat portions
of the trace prior to the t=0 point or following the last decay of
the signal. To do so, the rms noise level is computed from the end of
the trace, and the part of the trace flat relative to the noise level
determines the baseline. In infrared fluorescence experiments the
Fig. II-7. Flow chart for multiexponential decay analysis program.
See text for details.
Fig. II-7.
random rms noise \( \sigma_i \) is constant throughout the trace. Electronic problems within the Northern signal averager occasionally dropped bits of random data points, and these had a catastrophic effect on the automatic baseline and smoothing procedures.

As discussed at the beginning of this section, the program minimizes the sum of the residues which is related to the reduced \( \chi^2_v \)

\[
\chi^2_v \equiv \sum_i^n \frac{[y_i - y_N(t_i)]^2}{\sigma_i^2}/v
\]

where \( v = n - N + 1 \). \( N \) and \( n \) are the number of fitting parameters and data channels respectively. When there is only random noise on the signal, \( \chi^2_v \to 1 \) is a "perfect fit". As noted in the last paragraph, in infrared fluorescence experiments \( \sigma_i \) is independent of \( i \), i.e. is a background noise. Finzi\(^3\) has given a detailed estimate and measurement of the noise. In visible fluorescence experiments, the fluctuation of the signal intensity is \( \sqrt{\omega_o S} \) is also a noise source. \( \omega_o \) is the high frequency cutoff.

A nearly inverse relation between \( \chi^2_v \) and the signal to noise ratio was found. This odd behavior comes from systematic signal errors in the region of \( t=0 \). In traces where only the decay is fit and the rise is determined by either the laser or the amplifiers, the rise is difficult to reproduce accurately. To obtain a \( \chi^2_v \) representative of the decay, the region of the rise must be excluded. Frequently the program will not converge when it attempts to fit the rise with a single exponential. The \( t=0 \) point is most accurately determined by eye.
Rather than correct for electronic filters it would be desirable to digitally filter the signal after the experiment. *A posteriori* the time resolution is known and the effective S/N could be improved by smoothing. There are at least three criteria for a filter function: 1) noise rejection $\int_{-\infty}^{\infty} d\omega |R_p(\omega)|$; 2) ease of calculation; and 3) minimal distortion of the signal.

The simplest filter is an average over several channels. Written as a continuous sum

$$S'(t) = \int_{-\Delta}^{\Delta} dt \, S(t + \tau)$$

Rewriting this in the notation of the transform of the response function

$$R^+_f(t - \tau) = \begin{cases} 1 & \text{if } |t - \tau| \leq \Delta \\ 0 & \text{if } |t - \tau| > \Delta \end{cases}$$

Transforming to frequency space we can see there are difficulties.

$$R_f(\omega) = \frac{2}{\pi} \sin \frac{\omega \Delta}{\omega \Delta}$$

The response does not drop quickly to zero as $\omega$ increases, but rather the response oscillates. Generally $\Delta < \text{risetime}$ so that catastrophic signal distortion does not occur. However, this filter does not reject noise very well. The oscillations are characteristic of squarish filter functions. This behavior is equivalent to the "apodisation" problem in Fourier transform spectroscopy.

An electronic RC high frequency cutoff filter and the square digital filter reject noise in the same fashion. Averaging several sweeps $n_A$ the signal accrues as
\[ S = n_A S_0 \]

where \( S_0 \) is the single shot signal. The noise accrues as

\[ N = \sqrt{n_A} N_0 \]

since the noise fluctuates randomly from shot to shot. Since the noise is not correlated from one shot to the next, its frequency distribution is not changed with averaging. It is for this reason that filtering during averaging (RC) or afterwards (digital) have the same result of simply removing some frequencies. The rms noise is proportional to

\[ \left[ \int_0^\infty dw |R_F(w)|^2 \right]^{1/2} \]

Explicitly,

\[
\begin{align*}
\text{RC filter} & \quad \left[ \int_0^\infty dw \left| \frac{1}{1+iw/\omega_o} \right|^2 \right]^{1/2} = \sqrt{\frac{\omega_o \pi}{2}} = \sqrt{\frac{\pi}{2\tau_o}} \\
\text{Digital} & \quad \left[ \int_0^\infty dw \left| \frac{2}{\pi} \frac{\sin(w\Delta)}{w\Delta} \right|^2 \right]^{1/2} = \frac{1}{\sqrt{\Delta}}
\end{align*}
\]

Since we determine the best fit in a least squares sense, the least distortion is

\[ \min(k-k') \text{ and } \min(A-A') \]

where \( A' \) and \( k' \) are the least square fits of the filtered exponential \( A e^{-kt} \). A square filter operating on an exponential gives

\[ S'(t) = A e^{-kt} \frac{\sinh(w\Delta)}{2w\Delta} \text{ if } t > \Delta \]

Therefore

\[ A' = A \frac{\sinh(w\Delta)}{2w\Delta} \quad k' = k \]
There is distortion of the amplitudes but not of the rate constants if \( t > \Delta \). The first order estimate of the amplitude distortion is 
\[ 1-\left(k\Delta\right)^2/6, \] or 10% at \( k\Delta = .8 \). In terms of criteria 2 and 3 the square filter is very good.

As noted above convergence is sometimes slow. Since the initial guess generally is good it would appear that a Quasi - Newton Method may work better. Near the convergence limit, this method approaches the Newton Raphson method which attempts to jump directly to the minimum.

An alternative interesting approach is used in Dauwe's, et al. program. They apply the simplex process only to the decay constants. When the program evaluates the residue it actually determines the residue using the best amplitudes subject to the fixed rate constants. The amplitudes can be readily determined since the residue is quartic in them. That is, given fixed decay constants the amplitudes can be determined by a linear least squares process. Dauwe, et al. use the Gauss Seidel process. For cases where there are many exponentials this would not be very efficient since each amplitude adjustment takes as much time as \( m(m+3)/2 \) simplex movements treating all the parameters by the simplex method. \( m \) is the number of exponentials.

Of course, ultimately some exponentials can not be resolved. Despite the importance of exponential fits, general criteria describing resolution limits for given noise correlation functions just do not exist. The difficulty of resolving a double exponential trace is demonstrated in Fig. II-9.
C. **Pulsed Opto-Acoustic Spectroscopy**

In the early stages of this work, long path absorption cells were used to tune the OPO to molecular transitions. Absorption detection with the OPO is difficult due to the large pulse to pulse fluctuations in energy. In such circumstances an excitation method such as optoacoustic spectroscopy is preferable. One simply tunes for maximum pulse strength irrespective of the fluctuations. The spectrophone, in addition, is intrinsically more sensitive and compact. For perspective, it should be understood that only modest energies (5 - 25 \( \mu \)J) and absorption strengths \((-1 \times 10^{-2} \text{ cm}^{-1}\)) were used in these studies.

Appendix A contains a theoretical analysis of spectrophones. Much of this information was not available when this work was performed, and several erroneous paths were pursued. One of those, which is still not established in the literature, is involved with the importance of the microphone area. In most situations area is not important.

Three different spectrophones were used and several others constructed. These are described in section 1. The signal averaging equipment for doing pulsed optoacoustic spectroscopy while the OPO is scanned is described in Section 2.

1. **Microphones**

Initially the simple design described in Finzi's thesis\(^3\) was used. This phone has been the mainstay of the group for several years although it was a "spur of the moment" design.
This phone uses an 1/2" electret microphone\textsuperscript{35} in a 3/4" diameter x 1 1/2" long cylindrical cell. The cell dimensions used by Finzi were simply those of an available fluorescence cell with three removable, flanged windows. One window was replaced with the microphone. The FET preamp which comes with the microphone element was discarded as "noisy" although according to the manufacturer's specifications (1 $\times 10^{-3}$ V/(N/m\textsuperscript{2}) and 1.4 V noise) the performance is good. An Ortec 109 nuclear charge sensitive amplifier which was modified to be DC coupled was used.

The spectrophone output is the sum of two damped oscillations. The slow component is the first longitudinal resonance mode corresponding to greater absorption in the first part of the cell than in the last half. At low pressures (low absorption) this mode disappears. The other mode is a pseudo first azimuthal mode. It is "pseudo" since it is a standing wave between the wall opposite the microphone and the wall behind the microphone, not the microphone surface itself. Although the microphone responds at 17 KHz, the first radial mode at 18 KHz was not observed. The principal design problem with the cell is that there is too much wasted volume whether the phone were resonant or nonresonant.

This spectrophone was not satisfactory for the present work since the microphone sensitivity decreased when exposed to HBr, HCl, and HF. Electret foils are plastic films which contain both oriented dipoles and imbedded surface charges. They have been made by imposing strong fields\textsuperscript{36} or charging with a Tesla coil.\textsuperscript{34} The hydrogen halides
apparently breakdown the resistivity of the film and/or disorient the polarized dielectric. The 1/e time for the sensitivity appeared be approximately 100 torr hours. Also, the spectrophone did not have enough sensitivity to see CO v=0 + 2 absorption even when new.

Kreuzer in 1971 reported an optimized nonresonant spectrophone. This design is noteworthy since it uses a simply constructed microphone. This cell was copied. A support cylinder was drilled with approximately fifty 1 mm holes and covered with a thin sheet of aluminized mylar. The stainless steel support cylinder was 6 mm OD x 64 mm long. The .5 mil aluminized mylar (Type A) was coated at Lawrence Berkeley Lab. The edge of the foil was insulated from the cylinder with high voltage glyptal varnish. An AC coupled Oretc 109 preamp which has a BNC connector for detector biasing was used. The biasing voltage was optimized for sensitivity, typically 150 V. At higher voltages there appeared to be leakage currents. While these spectrophones are designed to be nonresonant the signal is the sum of two damped oscillations as seen in Figure II-8. The oscillation predominate at low pressures is the first longitudinal mode, the other is the nonresonant pulse partially cutoff by the preamplifier. The combination of the low pass filtering of the nonresonant mode and the high pass filtering of the preamp (3 dB at 350 Hz) gives rise to a very low Q (approximately 1) resonance.

This spectrophone and the next were resilient to HF attack. No loss of sensitivity was found so long as the pressure was kept below 20 torr. At higher pressures the mylar contracts and the film
Fig. II-8. Kreuzer spectrophone signal shape as a function of pressure.

Nearly single mode OPO excitation of HCl $P_{2-0}^2(2)$ line with 25 $\mu$J of energy.
Kreuzer Microphone

Volts

Time (m sec)

H Cl (torr)

1  5.4
2  2.5
3  1.3
4  1.6

Fig. II-8.
"crinkles" since the aluminum does not contract. The aluminum oxidizes and is easily rubbed off after exposure to HF and HCl, but the electrical conduction (i.e. the total capacitance) does not decrease. The aluminized mylar could be replaced with nickelized teflon.

The third spectrophone, which is a variant of the Kreuzer design, greatly simplifies construction and appears to be more sensitive. The electroacoustic element (Figure II-9) could be called an "inner surface cylindrical microphone". In this design a 5/16" ID x 1 1/2" long cylinder supports a square of aluminized mylar matched to its inner surface area. The mylar lies quite flat against the inner surface, and the signal from the aluminum side is picked up with a coil of nickel wire which is inserted into the cylinder last. This arrangement introduced fewer crinkles into the mylar than spring clips.

While construction is simple this device exhibits the many quirks of the crude device it is. Sensitivity, noise level, and signal shape vary from one version to the next.

In this design the edge of the aluminized mylar is no longer insulated. In the early versions the edges along the axis were folded up away from the support cylinder, and the edges at the end were supported on teflon tape. In some versions the mylar was made longer than the support cylinder so that the teflon was not necessary.

Some of these microphones exhibited erratic shot noise as well as a large "white" noise. The shot noise is probably due to leakage currents, although relaxation of the mylar and escaping gas from
Fig. II-9. Details of element of inner surface cylindrical microphone. See text for details.
Fig. II-9.
behind the mylar could also be responsible. In the HF spectrophones erratic noise and decreased sensitivity appeared when the HF attacked the microphone's ceramic vacuum feedthrough shortcircuiting the microphone. This was overcome by applying Krytox 240 fluorinated grease to the stupikoff surface. The white noise background is probably acoustic pickup. Very little effort was made to isolate the spectrophone acoustically.

The sensitivity of these phones varies considerably since the separation of mylar and cylinder is not controllable. Excessive trapped air or "crinkled" mylar are detrimental. In general the higher the capacitance of the microphone element the more sensitive it is. The sensitivity (volts/pressure) is

\[ V_{\text{Bias}} \cdot \frac{1}{C_m} \left( \frac{\partial C_m}{\partial p} \right) = V_{\text{Bias}} \cdot \frac{1}{r} \left( \frac{\partial r}{\partial p} \right) \]

where \( r = r_{\text{air}} + r_{\text{mylar}}/\varepsilon_{\text{mylar}} \) is the average separation of the aluminum surface and the support cylinder. Typically \( C_m = \varepsilon \text{Area}/r = 200 \text{ pf} \), hence \( r_{\text{air}} = .2 \text{mm} \) which is fairly large.

The signal shape varied as well. For many of the cells a 50 KHz resonance was seen, which roughly corresponds to the first \( \text{mnp} = 010 \) radial mode. More frequently the first longitudinal mode predominated. Lower frequency modes were observed, and these must be due to coupling of the gas within the cylinder to that outside. The cylinder is separated by 2 mm from both windows.
The absence of the nonresonant pressure pulse in the inner surface cylindrical microphone is not fully understood. As discussed in Appendix A the signal is the convolution of 1) the relaxation kinetics 2) the gas transport properties, 3) the microphone response, and 4) the amplifier response. The essential point is the filtering behavior of the gas transport kinetics. Figure II-10 is constructed for the case of the inner surface cylindrical microphone with 5 torr of HCl. The relaxation gives a high frequency cutoff of \( V_{TRHCl} / 2\pi = 680 \text{ Hz} \). The gas has a low frequency band whose width is the reciprocal of the thermal diffusion time of the cylinder. The higher bands are the acoustic resonances, and their height depends upon the beam's location in the cell and the attenuation of the beam (longitudinal modes). As shown, few of these occur at acoustic frequencies < 20 KHz, and these are \( 10^{-2} \) weaker than the 47.6 KHz resonance. The microphone frequency response is not known. The stiffness of the gas layer behind the mylar is \( K = 5 \text{ torr/.2mm} = 3.3 \times 10^5 \text{ dyne/cm}^2 \), and the mylar has a density of \( 1.3 \times 10^{-3} \text{ g/cm}^2 \), which give a lower limit of

\[
\nu_{HF} = \frac{1}{2\pi} \sqrt{\frac{K}{\rho}}
\]

or 16 KHz. As noted above, the transport behavior combined with the preamp should give rise to a low Q resonance. Including the slow relaxation, only two bumps are expected for this resonance such as seen in the Kreuzer cell (Figure II-8). That the nonresonant mode is not observed or is very weak is probably the result of the poor response of the microphone at low frequencies. Since the edges
Fig. II-10. Calculated relative frequency response of processes occurring in the inner surface cylindrical microphone. Included are V-T,R relaxation and thermal/pressure transport in HCl, as well as the microphone and preamp (Ortec 109) response. The last three processes are combined to give a nonrelaxation response. See text for discussion.
Fig. II-10.
of the microphone are loose, the pressure differential will relax quickly (100 Hz?). One should also note the uncertainty of the thermal diffusivity calculation for the hydrogen halides at low temperatures. using Table 1 - M of Hirschfelder et al. the effective cross section is at least 1.7 times the hard sphere cross section.

The Ortec 109 amplifier has four stages. The input stage is a charge sensitive amplifier such as described in Appendix A 
\( C_f = 1 \text{ pf}, R_f = 4 \times 10^8 \Omega \). This combination normally limits the response to above 400 Hz (3 dB point). As originally designed the second stage \( C_{12}, R_{42}, R_{17}, R_{18} \) on the schematic replaces the 400 Hz cutoff with 3 KHz. The last two stages are a power amp with switch selectable gain of either .3 or 3 and a line driver. Contrary to Finzi's thesis only the second stage need be modified to lower the frequency response, and 400 Hz is the lowest possible without changing the input stage. The measured 3 dB point is 350 ± 50 Hz. The noise is determined by \( Q_1 \) and \( Q_6 \). On the x 1 scale the output noise is 
\( (45 + .48 C_m') \text{nV/Hz} \) where \( C_m' \) is the combined microphone and cable capacitance in pf. The noise goes out to 3.0 MHz. \( Q_1 \) has 1.6 nV/\( \sqrt{\text{Hz}} \) of noise, while \( Q_6 \) has 150 nV/\( \sqrt{\text{Hz}} \). The overall gain on the x 1 scale is .3 \( C_m'/\text{pf} \).

One of the frustrations encountered with the different microphones was the ambiguity of the signal levels. Due to the odd wave patterns the peak signals which represent the overall sensitivity yield little information about the response of the separate elements of the spectrophone, especially the microphone. An additional complexity
is the response to longitudinal waves for which the signal gives the differential sensitivity of the first and last halves of the microphone. The rough overall sensitivities (volt/J cm\(^{-1}\)) were measured by tuning the etalon narrowed OPO to the absorptions of different molecules, measuring the peak signal. This signal is normalized for the pulse energy, absorption strength (units of cm\(^{-1}\)) presuming the OPO was operating single mode, and the molecular specific heat (C\(_v\)/k). Only the internal cylindrical microphone seemed to be noise limited by acoustic pickup. The others appeared to be amplifier limited.

The effective microphone sensitivities (V/(N/m\(^2\))) listed in Table II-IV are a more interesting feature. While numbers are available for commercial microphones, none for Kreuzer's have been reported. The microphone sensitivity is defined here as (cell cross section/preamp gain) x the overall spectrophone sensitivity. As noted in the last paragraph this number is not directly comparable to manufacturer's specifications due to the nonuniform pressure waves and diaphragm motion. Interestingly all three spectrophones are comparably sensitive overall. The Kreuzer microphone however appears to be less sensitive, perhaps due to the poor penetration of the pressure pulse through the small holes in the support cylinder.

2. Signal Averaging

Using a pulsed laser source the optoacoustic signal is the sum of several damped oscillations. It has been commonly stated mistakenly that with a pulsed source the spectrophone should be nonresonant.
Table II-IV.

<table>
<thead>
<tr>
<th></th>
<th>Capacity (pf)</th>
<th>Spectrophone Overall $(V/(J/cm^2))$</th>
<th>Microphone Effective $(V/(N/m^2))$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Finzi*</td>
<td>14</td>
<td>$1 \times 10^4 - 1 \times 10^5$</td>
<td>$10^{-3} - 10^{-2}$</td>
</tr>
<tr>
<td>Kreuzer Cell†</td>
<td>30</td>
<td>$3 \times 10^4$</td>
<td>$2 \times 10^{-4}$</td>
</tr>
<tr>
<td>Internal Microphone Cell</td>
<td>200</td>
<td>$4 \times 10^5$</td>
<td>$2 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

*measurements must include another 30 pf for cable capacitance.
The resulting signal would primarily be a single rise of the pressure corresponding to the $V - T, R$ transfer of energy and the pressure decay due to the thermal diffusion of the heat to the walls. As discussed in Appendix B and many other places the resonant phone derives its sensitivity only because of its $Q$ — its ability to store the acoustic energy. The peak intensity of a resonance in response to a single laser shot is similar in magnitude to the peak of the bulk pressure (nonresonant) rise so long as the resonance frequency is small relative to the molecular relaxation rate. The factor $2Q_j/\omega_j$ (or for the "zero frequency" mode the thermal diffusion time) is the time the pressure disequilibrium persists). As discussed in Appendix A.5, if one uses this time persistence by rectifying and integrating the signal, the peak S/N can be improved by $0.2 \frac{Q_j}{Q_{filter}}$. Hence the criterion for selecting resonant or nonresonant spectrophones is unchanged. In fact as $\frac{Q_j}{\omega_j}$ becomes long with respect to the time between pulses, the CW and pulsed methods have identical signals and noises independent of the signal processing.

In these experiments the rectification and integration were performed with a lockin amplifier followed by a gated integrator as illustrated in Figure II-11. One of the acoustic resonances was isolated with a lockin amplifier whose signal stage is a tuned $(Q_{filter} \sim 25)$ filter. With the inner surface microphone the $Q_{resonance}$ was 15 hence the signal was attenuated. The phase sensitive stage of the lockin is a phase and frequency controlled rectifier. The scalloped shaped output of the phase sensitive stage was passed
Fig. II-11. Signal averager of spectrophone with signal shape by stage.
Fig. II-11.
to a gated integrator rather than the lockin's RC integrator since usually the duty cycle ("length" of pressure oscillation/time between laser pulses) is low. The integration time of the gated integration is fixed at 3 seconds.

The complicated step is to synch the phase sensitive detector to the laser firing. The unsophisticated PAR JB-5 allows the synching by a brute force method. The Select External source for the phase sensitive reference is a tuned filter and amplifier which is intended to cleanup and frequency correct an external oscillator reference. However, the amplifier has sufficient gain and the filter high enough Q such that an external pulse generates a long lived oscillation for the reference. It is necessary to change the laser repetition rate such that the acoustic resonance frequency is a high (\( \geq 20 \)) overtone of the laser repetition rate. This is trivial with the Chromatix OPO.

Due to the low Q of the inner surface microphone it was found that equivalent S/N was obtained by using only the gated integrator and sampling one of the early peaks. This helps to discriminate against the systematic window absorptions and the setup time is much shorter. It is important to eliminate all ground loops associated with the microphone, power supply, gated integrator, and the laser synch out. This includes chasis ground loops. LED isolation couplers were very useful.
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10. Emerson and Cumming, Inc., Canton, MA, 02021, U.S.A.

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III. SINGLE QUANTUM VIBRATIONAL ENERGY TRANSFER
FROM HCl(v=2) AND HBr(v=2)

A. Introduction

While fundamental questions concerning the nature of single quantum V - V energy transfer, such as rotational dynamics and potential surfaces remain to be answered, good empirical correlations of the rates are known.² By contrast little is known about the vibrational level dependence of V - R, T or of the importance of multiquantum V - V and V - R,T transfers. With very high vibrational excitation these processes should predominate as vibrational spacings become smaller and many channels open.

To measure these detailed rates, as opposed to total relaxation rates, selective excitation of single vibrational manifolds is essential since the detailed rates require information on all the collision products. In this work we have selectively excited HCl (v=2) and HBr(v=2). These hydrogen halides can be readily pumped to v=2, and the vibrational dynamics can be monitored by their strong IR emission. Furthermore the large single quantum V - V rates suggest that strong interactions are involved and that the secondary V - R,T and V - V channels might be unusually enhanced. In this work we show this is not the case, and that the total relaxation rates are almost exclusively single quantum V - V rates.

B. Experimental

A Chromatix Nd:YAG pumped optical parametric oscillator was tuned to excite weakly either HCl(v=2) or HBr(v=2) in a multiple reflection,
static gas, fluorescence cell. Optimal excitation conditions were found by maximizing a spectrophone signal. The single mode, 300 nsec OPO pulses contained about 25 nW of energy, causing at most 0.2% excitation at the center of the beam. Only rotational lines near the Boltzmann maximum were excited. The transfer of energy to other vibrations was monitored by $\Delta v=1$ infrared fluorescence using either a 100 nsec response time Ge:Cu detector or a 300 nsec response time Ge:Hg detector. HCl($v=2 \rightarrow 1$), HBr($v=2 \rightarrow 1$), and the total fluorescence of either HCl or HBr were isolated with a combination of interference filters and 4 cm long cold gas filter cells filled to 100-200 torr.

The fluorescence is digitally signal averaged and could be saved for numerical analysis. Most of the multiple exponential decay traces were analyzed by semilogarithmic plots, but some of the double exponential decays were analyzed numerically by a SIMPLEX least squares method.²

Gases were handled in an Apiezon N greased, glass manifold. The system was frequently and carefully flamed and residual pressures were $1 - 2 \times 10^{-6}$ torr. Sample pressures were measured with a Baratron capacitance manometer and varied from 0.5 to 10 torr. The HCl was Matheson Electronic Grade (> 99.99%), and the HBr was Matheson Research Grade (> 99.6%). DCl was photolytically synthesized from Matheson Research Grade Cl₂ (> 99.95%) and an excess of Matheson C.P. Grade D₂ (> 99.5%). All condensible gases were degassed and doubly distilled, and infrared spectra indicated no contaminants. In the HCl ($v=2$) + DCl experiments, no HCl in addition to the residual HCl contaminant
was added to the DCl. The HCl contaminant was <2%.  

C. Kinetics and Results

1. Self Relaxation

In the pure gases only three vibrationally inelastic processes are possible. In HCl these are

\[ \text{HCl}(v=2) + \text{HCl}(v=0) \xrightarrow{k_e k_1} \text{HCl}(v=1) + \text{HCl}(v=1) + \Delta E_v \]  

(1)

\[ \text{HCl}(v=1) + \text{HCl}(v=0) \xrightarrow{k_2} \text{HCl}(v=1) + \text{HCl}(v=0) \]  

(2)

\[ \text{HCl}(v=1) + \text{HCl}(v=0) \xrightarrow{k_1} \text{HCl}(v=0) + \text{HCl}(v=0) \]  

(3)

Because of the reverse of process (1), rigorously the kinetics are nonlinear. However, in the limit of weak excitation, the kinetics can be linearized. The complete kinetics are

\[ \frac{dN_1}{dt} = -(k_e + k_2)N_0 N_2 + k_1 N_1^2 \]  

(4)

In the limit \( N_2^0 \ll N_0 \)

\[ N_2 \approx N_2^0 \exp[-(k_e + k_2)N_0 t] \]  

(5)

To determine the effect of the nonlinear term in Eq. (4) on the \( v=2 \) kinetics we approximate

\[ N_1^2 \approx \left( \frac{2k_e + k_2}{k_e + k_2 - k_1} \right)^2 \frac{N_0^2}{N_2} \left\{ \exp(-2k_1N_0 t) - N_2 \right\} \]
This accurately represents $N_1^2$ at times less than $(k_1 N_0)^{-1}$.

Solving,

$$N_2 \sim N_2^0 \{ (k_e + k_2 - 2k_1) \exp[-(k_e + k_2 + \delta) N_0 t] + \delta \exp[-2k_1 N_0 t] \} / (k_e + k_2 - 2k_1 + \delta)$$

where $\delta = \frac{k_e N_2^0}{N_0} \left( \frac{2k_e + k_2}{k_e + k_2 - k_1} \right)^2 << k_e$

The second very small decay is never observed, but the observed rate constant for $N_2$ is

$$\sim k_e (1 + \frac{4N_2^0}{N_0} e^{-\Delta E_V/kT}) + k_2$$

where $\Delta E_V < 0$ has the sign convention shown in Eq. (1). The observed decay rate would increase slowly with higher pump energies. Using known line strengths it, one can calculate that the maximum effect for any of the back reactions at the center of the beam in the present experiments is <0.5%. The back reaction will be ignored.

The total self relaxation rates of HCl(v=2) and HBr(v=2) were determined in pure gas samples by isolating the v=2 + 1 fluorescence with a cold gas filter cell. These rates are given in Table III-I. Since the rotational relaxation rate of these molecules, as determined from pressure broadening of lines, is ~300 times faster, the observed rate is for a rotationally thermalized distribution.

ii. V - R,T from v=2

$k_2$, the rate of V - R,T in the pure gases, can in principle be determined by observing the total fluorescence. The total fluorescence exhibits two decay times as can be determined from Eq. (5). The ratio
Table III-I. Vibrational energy transfer rates in HBr, HCl, DCl collisions at 295°K (torr⁻¹ sec⁻¹).

<table>
<thead>
<tr>
<th></th>
<th>v=2</th>
<th>v=1</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>total&lt;sup&gt;a&lt;/sup&gt;</td>
<td>V-V</td>
<td>Ref.</td>
</tr>
<tr>
<td>HBr(v)+HBr</td>
<td>(6.2±0.5±0.2)x10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>HBr(v)+HCl</td>
<td>(1.01±0.22±0.16)x10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>7.4x10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>6</td>
</tr>
<tr>
<td>HCl(v)+HBr</td>
<td>(9.3±0.6±0.4)x10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>3.6x10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>6</td>
</tr>
<tr>
<td>HCl(v)+HCl</td>
<td>(9.5±0.7±0.3)x10&lt;sup&gt;4&lt;/sup&gt;</td>
<td>6.2x10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>11</td>
</tr>
<tr>
<td>HCl(v)+DCl</td>
<td>(1.3±0.2)x10&lt;sup&gt;4&lt;/sup&gt; &lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.3x10&lt;sup&gt;3&lt;/sup&gt;</td>
<td>5</td>
</tr>
<tr>
<td>DCl(v)+HCl</td>
<td>-</td>
<td>6.4x10&lt;sup&gt;1&lt;/sup&gt;</td>
<td>c</td>
</tr>
</tbody>
</table>

<sup>a</sup>The first uncertainty is one standard deviation; the second is the 95% confidence limit for the uncertainty of the mean.

<sup>b</sup>The uncertainty is determined by the uncertainty in HCl concentration.

<sup>c</sup>Determined by microscopic reversibility from the reverse process.
of the fast decay amplitude to the slow decay amplitude is

$$\frac{A_{\text{fast}}}{A_{\text{slow}}} = \left( \gamma \frac{k + k_1}{2k + k_2} \right) - 1 \quad (7)$$

The relative sensitivity of the detection system for \( N_2 \) compared to \( N_1 \) is \( \gamma \). The relative response depends on the rotationally averaged product of Einstein coefficients \( A \), filter transmission \( F \), and detector wavelength response \( D \). \( P \) is the thermal distribution of rotational states.

$$\gamma = \frac{\sum_{j=2}^{j} P_{v}^{(J)} A_{VJ} F_{VJ} D_{VJ}}{\sum_{j=1}^{j} P_{v}^{(J)} A_{VJ} F_{VJ} D_{VJ}} \quad (8)$$

Due to self absorption of the \( v=1 \rightarrow 0 \) fluorescence, \( F_{v=1} \) is not well known. Only in the limit as the partial pressure goes to zero can one make valid measurements of the \( V - R, T \) rates. The self-absorption increases approximately exponentially with pressure. Referring to Eq. (7), \( \ln \left( (A_{\text{fast}}/A_{\text{slow}}) + 1 \right) \) was plotted versus partial pressure and extrapolated to zero pressure (Fig. III-1). As seen in Table III-II the fractional error in the extrapolated \( (A_{\text{fast}}/A_{\text{slow}}) \) is very large. The uncertainty in the radiative lifetimes, filters, and detector response are \( \pm 10\% \) and negligible by comparison. The filter and detector are nearly wavelength independent over the region of the emission. \( k_2 \) is determined from Eq. (7), and the values are listed in Table III-II. The uncertainties stated there are not statistical but an eye estimate of the range of values possible for the ratio
Fig. III-1. Ratio of the amplitudes for the fast and slow decays of the total fluorescence in (a) pure HCl and (b) pure HBr as a function of pressure.
Fig. III-1.
Table III-II. Experimental parameters for \( v=2 \) \( V-R,T \) determinations

<table>
<thead>
<tr>
<th></th>
<th>( \text{HCl}(v=2) )</th>
<th>( \text{HBr}(v=2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma(P_{HX} = 0) )^\text{a}</td>
<td>1.43</td>
<td>1.79</td>
</tr>
<tr>
<td>( A_{\text{fast}}/A_{\text{slow}} )^\text{b}</td>
<td>-0.07(\pm)0.07</td>
<td>-0.07(\pm)0.03</td>
</tr>
<tr>
<td>( V\rightarrow R,T ) rate ( k ) ( (\text{torr}^{-1} \text{sec}^{-1}) )</td>
<td>((1\pm1)\times10^4)</td>
<td>((5\pm5)\times10^3)</td>
</tr>
<tr>
<td>Total relaxation rate ( k_e+k_2 ) ( (\text{torr}^{-1}\text{sec}^{-1}) )</td>
<td>((9.5\pm0.7)\times10^4)</td>
<td>((6.2\pm0.5)\times10^4)</td>
</tr>
</tbody>
</table>

^\text{a} See Eq. (8).
^\text{b} See Eq. (7).
of the amplitudes. The data indicate though that the V -R,T rate is at most 15% of the total deactivation rate in HCl(v=2) and HBr(v=2).

iii. Relaxation in Mixtures

In the mixtures only the total deactivation rate of the initially excited species and the rate of two quantum exchange were measured. Because the two quantum exchange rate was found to be small as discussed below the total deactivation rate is simply the sum of all the single quantum transfer rates. For initially excited HCl(v=2) these channels are processes 1 - 3 and

\[
\text{HCl}(v=2) + \text{HBr}(v=0) \rightarrow \text{HCl}(v=1) + \text{HBr}(v=1),
\]

\[
\text{HCl}(v=1) + \text{HBr}(v=0).
\]

The total deactivation rates are plotted as a function of mole fraction in Figures III-2 and -3. The least square fit with the X=1 point fixed at the pure gas result are listed in Table III-1 along with the previously measured v=1 rates. As seen, all the v=2 total deactivation rates are at least two orders of magnitude larger than the v=1 V - R,T rates except for HBr(v=2) + HCl(v=0). Except for this rate all the other v=2 rates appear to be single quantum V- V exchange rates.

The deactivation of HCl(v=2) by DCl was also measured. The total relaxation rate of the residual HCl in the synthesized DCl was measured. This deactivation rate was \((1.4 \pm 0.1) \times 10^4 \text{ torr}^{-1} \text{ sec}^{-1}\). Estimating the HCl concentration at approximately 1% and allowing an error range to cover the uncertainty in the total rate, the HCl(v=2) + DCl
Fig. III-2. Total relaxation rate constant of HCl(v=2) in HCl - HBr mixtures as a function of HCl mole fraction, $x_{HCl}$. The line is a least squares fit.
Fig. III-3. Total relaxation rate constant of HBr(v=2) in HBr-HCl mixtures as a function of HBr mole fraction, $X_{\text{HBr}}$. The line is a least squares fit.
deactivation rate is \((1.3 \pm 0.2) \times 10^4\) torr\(^{-1}\) sec\(^{-1}\).

iv. Two Quantum \(v - v\) Exchange

The most favorable combination for observing two quantum exchanges among the present systems is

\[ \text{HCl}(v=2) + \text{HBr}(v=0) \rightarrow \text{HCl}(v=0) + \text{HBr}(v=2) + \Delta E_v = 637 \text{ cm}^{-1} \]

Exciting \(\text{HCl}(v=2)\) the \(\text{HBr}(v=2 + 1)\) fluorescence was isolated with filters and a cold gas filter which removed both \(\text{HCl}\) and \(\text{HBr} v=1 \rightarrow 0\) fluorescence. In these experiments no \(\text{HBr}(v=2)\) was observed within the limits placed by the small amount of \(\text{HCl}(v=2)\) fluorescence leaked by the filters. The signal corresponding to \(\text{HBr}(v=2)\) fluorescence was signal averaged for 8000 to 32,000 shots. The cell was then evacuated and refilled with an equivalent amount of \(\text{HCl}\) to give a background signal. The difference places an upper limit on the amount of \(\text{HBr}(v=2)\) present. This difference signal was compared with the \(\text{HBr}(v=1)\) fluorescence to normalize for the original amount of excitation. Table III-III lists the ratio of the \(\text{HBr}(v=2)\) peak population to the \(\text{HBr}(v=1)\) population present prior to \(V - R,T\) decay. This ratio has been corrected for the relative filter transmission and radiative lifetimes\(^4\) of \(\text{HBr}(v=2)\) and \(\text{HBr}(v=1)\) and for self absorption of the \(\text{HBr}(v=1)\) fluorescence. At the pressures used the latter is estimated (\(\sim 50\%\)) from the self absorption observed in the pure \(\text{HBr}(v=2)\) self deactivation experiments. The accuracy of these population ratios is limited by the power stability of the OPO over the time necessary to take the foreground and background \(\text{HBr}(v=2)\) traces.
Table III-III. Experimental parameters for two quantum V-V exchange. See Eq. 9.

<table>
<thead>
<tr>
<th>$P_{HBr}$</th>
<th>$X_{HBr}$</th>
<th>$\frac{Max[HBr(v=2)]}{Equil[HBr(v=1)]}$</th>
<th>kinetic correction factor</th>
<th>$\frac{k_g}{\lambda_1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.97</td>
<td>0.86</td>
<td>$3.5 \times 10^{-3}$</td>
<td>4.13</td>
<td>$&lt; 1.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>7.30</td>
<td>0.89</td>
<td>$4.8 \times 10^{-3}$</td>
<td>4.24</td>
<td>$&lt; 2.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>7.67</td>
<td>0.84</td>
<td>$2.3 \times 10^{-3}$</td>
<td>4.20</td>
<td>$&lt; 1.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>6.11</td>
<td>0.70</td>
<td>$2.5 \times 10^{-3}$</td>
<td>3.68</td>
<td>$&lt; 0.9 \times 10^{-2}$</td>
</tr>
</tbody>
</table>
To interpret this HBr(v=2) peak we must return to the kinetics since the maximum is dependent upon the rate of decay as well as the rate of formation. The kinetics are defined by the three processes

\[
\text{HCl(v=2)} + \text{M} \xrightarrow{k_{\text{HCl}}} \text{HCl(v=1)} + \text{M} \\
\text{HBr(v=2)} + \text{M} \xrightarrow{k_{\text{HBr}}} \text{HBr(v=1)} + \text{M} \\
\text{HCl(v=2)} + \text{HBr(v=0)} \xrightarrow{k_q} \text{HCl(v=0)} + \text{HBr(v=2)} \xrightarrow{k'_q} \text{HCl(v=1)} + \text{HBr(v=0)}
\]

This two level system exhibits two decay times which are approximately

\[
\lambda_1 = k_{\text{HCl}} + \delta' \\
\lambda_2 = k_{\text{HBr}} - \delta' \\
\delta' = \frac{(k_k' \times \text{HCl(v=2)} \times \text{HBr})}{(k_{\text{HCl}} - k_{\text{HBr}})}
\]

The decays, normalized to the initial amount of HCl(v=2), are exactly

\[
\frac{[\text{HCl(v=2)}]}{[\text{HCl(v=2)}]}_0 = \frac{(\lambda_1 - k_{\text{HBr}}) e^{-\lambda_1 t} + (\lambda_2 - k_{\text{HBr}}) e^{-\lambda_2 t}}{\lambda_1 - \lambda_2}
\]

\[
\frac{[\text{HBr(v=2)}]}{[\text{HCl(v=2)}]}_0 = \frac{k_q}{\lambda_2 - \lambda_1} \left( e^{-\lambda_1 t} - e^{-\lambda_2 t} \right)
\]

From Fig. III-2, 3 or Table III-I it can determined that \( \lambda_1 > \lambda_2 \) for all mole fractions. Defining

\[
G\left(\frac{\lambda_2}{\lambda_1}\right) \equiv \text{Max}[\frac{\lambda_1}{\lambda_1 - \lambda_2} (e^{-\lambda_1 t} - e^{-\lambda_2 t})]
\]

we can express

\[
\text{Max}[\text{HBr(v=2)}]/[\text{HCl(v=2)}]_0 = \frac{k_q}{\lambda_1} G\left(\frac{\lambda_2}{\lambda_1}\right)
\]
After $V-V$ equilibration the amount of $\text{HBr}(v=1)$ is

$$\text{Equil}[\text{HBr}(v=1)]/[\text{HCl}(v=2)]_0 = 2\left(1 + \frac{X_{\text{HCl}}}{X_{\text{HBr}}} e^{-\Delta E_v/kT}\right)^{-1}$$

Thus

$$\frac{k_q}{\lambda_1} = 2G\left(\frac{\lambda_1}{\lambda_2}\right) \left(1 + \frac{X_{\text{HCl}}}{X_{\text{HBr}}} e^{-\Delta E_v/kT}\right) \frac{\text{Max}[\text{HBr}(v=2)]}{\text{Equil}[\text{HBr}(v=1)]} \quad (9)$$

Table III-III contains the kinetic correction factor in brackets and upper limits placed on $k_q/\lambda_1$. Taking the smallest value, $k_q$ is less than $1 \times 10^3$ torr$^{-1}$ sec$^{-1}$.

D. Discussion

i. Single Quantum Transfer

There has been an extended concern with the vibrational dynamics of the hydrogen halides. Much of this interest stemmed from efforts to develop more efficient hydrogen halide lasers. However, it became clear from a fundamental viewpoint that the hydrogen halides exhibit an extreme behavior. The energy transfer rates are large and are relatively insensitive to the vibrational energy discrepancies.

The dynamics of systems excited with one quantum of vibrational energy have been extensively studied. Among these, $V-V$ and $V-R,T$ rates in HCl-HBr and HCl-DCl mixtures$^{5,6}$ including temperature dependences$^{7,8}$ have been determined. Recently, however, it has become appreciated that to understand the vibrational coordinate dependence of the energy transfer one must excite overtone vibrational levels.

The energy transfer rates of $\text{HCl}(v=2) + \text{HCl}$ and $\text{HBr}(v=2) + \text{HBr}$ have been previously measured. These are compared with the present measurements in Table III-IV. As can be seen, the HCl results$^{9,10,11}$...
Table III-IV. V-V exchange rates of HX(v=2) + HX(v=0) → 2HX(v=1).
Units of $10^4$ torr$^{-1}$ sec$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>HCl(v=2)</th>
<th>Ref.</th>
<th>HBr(v=2)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hopkins and Chen</td>
<td>$8.4 \pm 1.2$</td>
<td>9</td>
<td>$9.5 \pm 1.8$</td>
<td>12</td>
</tr>
<tr>
<td>Burak et al.</td>
<td>$9 \pm 2$</td>
<td>10</td>
<td>$14 \pm ?$</td>
<td>13</td>
</tr>
<tr>
<td>Ridley and Smith</td>
<td>$4.5 \pm ?$</td>
<td>14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Leone and Moore</td>
<td>$10.0 \pm 1.1$</td>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td>$9.5 \pm 7$</td>
<td></td>
<td>$6.2 \pm 5$</td>
<td></td>
</tr>
</tbody>
</table>
agree well, but the HBr results are not consistent. In Ref. 9-10, 12-14 the total quenching rate of \( v=2 \) was determined by \( V \rightarrow V \) up-pumping from \( v=1 \). In those experiments it was necessary to correct for the concentration of \( v=1 \) to allow for the back reaction. This is analogous to Eq. 6. Hopkins and Chen\(^\text{12}\) did not perform the correction, but did estimate it, and noted that the quoted rate was perhaps as much as 20% too large. In their experiments some 12 mJ of \( v=1 \rightarrow 0 \) pump radiation was used. Burak et al.\(^\text{13}\) did make the correction by estimating the initial population of \( v=1 \) from the relative intensities of \( v=2 \) and \( v=1 \) fluorescence. They did not allow for self absorption, and their estimate for the \( v=1 \) population is certainly low. However, this correction would probably not be enough to bring their results into agreement with the present results or Hopkins and Chen's lower limit. It seems more likely that the very intense scattered light in their experiments systematically affected their analysis of the HBr(\( v=2 \)) rise times.

Ridley and Smith\(^\text{15}\) have generated HCl(\( v=1-3 \)) by chemiluminescent reactions. The self relaxation and HBr relaxation rates measured for the lower states do not agree well with direct excitation experiments, and their numbers need to be rescaled.\(^\text{16}\) Ambartsumyan, et al.\(^\text{17}\) have generated HCl(\( v=3 \)) by stimulated Raman pumping but did not resolve any specific rate constants. Rotationally inelastic HCl(\( v=1 \)) + HCl, HBr collisions have been studied in a beam so that it is evident these hydrogen halide collisions can be studied with some rotational state resolution.\(^\text{18}\)
The HCl(v=2) and HBr(v=2) V - V exchange rates have been calculated by Sharma and coworkers \(^\text{19}\) and by Shin \(^\text{20}\). Both calculations are simple first order perturbation model calculations, and the predicted rates are low. They do predict the inverse relation between rates and temperature found by Burak, et al. \(^\text{14}\). Contrary to the conclusions in Ref. 14, the experimental temperature dependence does not prove the importance of an attractive potential. The calculated rate decreases because the energy discrepancy is relatively unimportant and a hard core is assumed. This is analogous to the negative temperature coefficient found in Anderson - Tsao - Curnutte \(^\text{21}\) calculations of line broadening.

When very high vibrational states are generated, one of the principal concerns is the point at which V - R,T rather than V - V transfer becomes important. As v increases the coupling between vibrational states increases for both processes. However, generally the V - R,T rates increase while the V - V rates decrease due to the smaller level spacings which cause the energy discrepancy to shrink and grow for the respective processes. To date, the relative V - V and V - R,T branching ratios for v > 1 have not been measured for ground electronic state diatom - diatom collisions.

Generally only the excited species can be experimentally observed, while the branching ratio requires information on the recipient molecule. In these experiments we have placed upper limits on the V - R,T rate from v=2 in the pure gases. As seen in Table III-II these upper limits are large compared with the v=1 rates and perhaps are an order of magnitude larger than the actual v=2 V - R,T rate. The V - R,T rates
of HCl(v=2) in collisions with reactive atoms have been measured and even with strong forces are at most eight times larger than those for v=1. While the upper limits for the v=2 rates are probably too large, they are sufficiently small to assure that the total relaxation rate is >85% V - V transfer.

There have been several measurements\(^5,7\) of the V - V exchange rate HCl(v=1) + HBr(v=0) → HCl(v=0) + HBr(v=1). The v=2 rates are faster as expected. The rates, when divided by two to account crudely for the enhanced transition moment, fall near other HX(v=1) V - V exchange rates, as seen in Fig. III - 4. The HCl(v=1) + HBr(v=1) HCl(v=0) + HBr(v=2) + \(\Delta E_v = 418 \text{ cm}^{-1}\) probability which is actually plotted using microscopic reversibility lies well above the other rates. As seen in Table III - I the v=2 total relaxation rate is only ten times faster than the v=1 V - R,T rate. It would appear that as much as 50% of the HCl(v=0) + HBr(v=2) total relaxation rate is V - R,T.

ii. Two Quantum Transfer

In contrast to the behavior of I\(_2\)\(^22\) multiquantum vibrational energy transfer in small reduced mass molecules has not been observed,\(^23-25\) except for electronically excited CO.\(^26\) Experimentally it is difficult to detect, although in HF(v=1) + NO, HI and HCl(v=1) + O\(_2\) its presence has been inferred from anomalous rates.\(^27-30\) However, in clear cut, directly excited experiments it will be possible to observed such processes if they are a significant channel for the relaxation.
Fig. III-4. Hydrogen halide - hydrogen halide V - V energy transfer rate constants normalized by gas kinetic cross section and average thermal velocity. Rates taken from Ref. 7 and this work, Ch. III and IV. The line is hand drawn and from Ref. 7.
Fig. III-4.
In the present experiment the two quantum transfer

\[ \text{HCl}(v=2) + \text{HBr}(v=0) \rightarrow \text{HCl}(v=0) + \text{HBr}(v=2) + E_v = 639 \text{ cm}^{-1} \]

has a cross section of less than \(6 \times 10^{-3} \text{ A}^2\) or less than 1% of that of the total relaxation. Similarly Douglas and Moore\(^{31}\) established that two (or three) quantum transfer from \(\text{HF}(v=4)\) such as

\[ \text{HF}(v=4) + \text{HF}(v=0) \rightarrow 2 \text{HF}(v=2) + E_v = -670 \text{ cm}^{-1} \]

constitutes less than 5% or the total relaxation rate. In \(I_2\) by contrast, \(V - R, T\) processes with up to \(\Delta v=6\) occur with a cross section greater than 1% of the total vibrationally inelastic cross section.

The two quantum exchange rate is exceptionally interesting. A lingering theoretical question of vibrational energy transfer is the limit to which the processes can be viewed as a simple perturbation at least in the vibrational coordinate. If the energy transfer is vibrationally a first order perturbation then multiquantum transitions will, at least in a convoluted fashion, give higher moments of the perturbation potential in a manner analogous to spectroscopic determinations of the dipole moment.

A tested theoretical apparatus for estimating the multiquantum processes does not exist. Bauer and coworkers\(^{32}\) estimated the \(\text{CO}(v=2) + \text{H}_2(v=0) \rightarrow \text{CO}(v=0) + \text{H}_2(v=1)\) rate by SSH first order perturbation theory which is based on an exponential repulsive force between harmonic oscillator states. The \(\Delta v=2\) matrix elements are fairly large. Using\(^{33}\) an exponential force parameter of \(\gamma/L = 4.9 \text{ Å}^{-1}\) the ratio of matrix elements for Morse oscillators are \((V_{2-0}/V_{1-0}) = .182\) and .201 for
HCl and HBr. In spite of the magnitude of the matrix elements the HCl-HBr two quantum exchange is expected to be small since it is a two quantum process in both collidants and the energy discrepancy is large. From correlations of experimental rates (such as the line in Fig. III-4) one can estimate that if first order perturbation reasoning is correct the HCl(v=2) + HBr(v=0) two quantum exchange cross section should be

\[
\left(\frac{v_{2-0}}{v_{1-0}}\right)_{\text{HCl}} \left(\frac{v_{2-0}}{v_{1-0}}\right)_{\text{HBr}} 4 \times 10^{-2} \text{ A}^2 = 5 \times 10^{-5} \text{ A}^2
\]

which is still two orders of magnitude smaller than the upper limit established here. It is interesting that for vibrational states near the bottom of the potential well the nonlinearity of the potential and the molecular anharmonicity have opposing effects on the \( \Delta v=2 \) transitions, although the nonlinearity is more important.

Of course, the vibrational dynamics may not behave as a perturbation in any sense. To construct a second order or higher perturbation theory is generally very cumbersome. Rabitz and Gordon have given second order perturbation expressions for multipolar forces and straight line trajectories such as used by Sharma and Brau. Sharma and coworkers have calculated a few second order distorted wave cross sections.

Dillon and Stephenson did develop a quasi Magnus (time perturbation) approximation for treating multiquantum V-V energy transfer. The theory allows processes with selection rules corresponding to infinite order perturbation theory. The theory however does rely on the hypothesis that the resonance behavior is determined primarily
by the initial and final states and not by the intermediate states. They further assume that the transition potential is linear in the vibrational coordinates and is vibrational quanta conserving. They employ considerable algebra to generate compact equations as the starting point for the calculations. The model concludes that the two quantum V - V exchange probability for one dimensional models such as SSH or breathing sphere will scale as

\[ P(v_1 = 2 \rightarrow 0, v_2 = 0 \rightarrow 2; \Delta E_v) = P(v_1 = 1 \rightarrow 0, v_2 = 0 \rightarrow 1; \Delta E_v)^2 \]

This is for a single relative translational energy and impact parameter. If we again use a correlation of the HCl-HBr rates (Fig. III-4) and assume the thermal average cross section scales as the detailed probabilities, Dillon and Stephenson's theory predicts the HCl-HBr two quantum exchange cross section will be \( 4 \times 10^{-5} \text{ Å}^2 \).

To establish empirically the behavior of multiquantum transitions it will be necessary to study transfer processes in ground electronic states with a minimum number of other channels. The

\[ \text{HF}(v=1) + \text{CO,NO}(v=0) \rightarrow \text{HF}(v=0) + \text{CO,NO}(v=2) \]

processes are especially attractive since both reactants and products can be readily excited, the processes are nearly resonant, and the species fluoresce strongly.
E. Conclusion

In this work we have shown that by selective excitation of a single vibrational manifold it is possible to study single quantum V - V and V - R,T and two quantum V - V transfer between diatomic molecules. In HCl, HBr and their mixtures, it has been determined that relaxation from v=2 is primarily (>85%) due to single quantum V - V transfer. It has been found that the two quantum exchange between HCl and HBr is <1% of the total relaxation rate.
CHAPTER III. REFERENCES


IV. V - V ENERGY TRANSFER FROM CO(v=2) AND DCl(v=2)

A. Introduction

Extensive investigations have demonstrated that V - V transfer is a resonance process. Early work in which the energy discrepancy, \( \Delta E_v \), could be changed only by changing collidants suggested an exponential energy gap law similar to that observed in the V - T,R plots of Lambert and Salter. More recent work has refined this qualitative description by exciting high vibrational levels. By this means, energy discrepancy is varied while retaining essentially the same potential surface, rotational spacings, and velocity distribution. Such work on HCl, HBr, and especially CO relaxation has suggested that a simple perturbation theory energy gap law such as

\[
 k_{\text{exo}} = k_{\text{hs}} N_v g(\Delta E_v)
\]

may be accurate. \( k_{\text{exo}} \) is the exothermic rate constant; \( k_{\text{hs}} \) is a hard sphere collision rate; \( g \) is a monotonic decreasing function of \( \Delta E_v \), the vibrational (i.e. rotationless) exothermicity; and \( N_v \) is the scaling factor for a linear perturbation between harmonic oscillators.

For the general diatomic-diatomic collision process

\[
 D(v) + D'(v'-1) \rightarrow D(v-1) + D'(v')
\]

\( N_v = v v' \). However, self relaxation \( (v' = 1) \) does not allow an independent variation of \( N_v \) and \( \Delta E_v \).

In the present investigation we have directly excited the vibrations of both collidants. Combining these results with the work
of Braithwaite and Smith\textsuperscript{14} and Zittel and Moore\textsuperscript{15} this independent variation of $N_v$ and $\Delta E_v$ does show a small, but significant deviation from the simple energy gap law. The nature of the deviations is consistent with qualitative perturbation arguments that a nonlinear potential in the vibrational coordinates or intramolecular rotational energy transfer in DCl are important.

B. Experimental

A Chromatix Nd:YAG - pumped LiNbO$_3$ optical parametric oscillator (OPO) was used to directly excite single rotational lines of CO($v=2$) and DCl($v=2$). The OPO was etalon narrowed to one or two longitudinal modes, and the cavity length was finely tuned to maximize the output of a Kreuzer style\textsuperscript{16} spectrophone filled with 5 torr of the appropriate gas. The OPO pulses had 20 $\mu$J in a 3 mm diameter beam, and were 100 nsec long. Gas mixtures were excited in a multiple pass fluorescence cell.

The combined CO and DCl 4.8 $\mu$ fluorescence was isolated with a wide band interference filter and detected with a 120 nsec response time Ge:Cu detector. The CO($v=1 \rightarrow 0$) and DCl($v=1 \rightarrow 0$) fluorescence could be removed with cold gas filter cells. The results reported here are based entirely on the combined CO($v=2 \rightarrow 1$) and DCl($v=2 \rightarrow 1$) fluorescence decay. Fluorescence was transiently digitized and signal averaged for 1000 - 4000 shots. Decay curves were analyzed as single or double exponentials by semilogarithmic plots.

Gas mixtures were made in a conventional glass vacuum system using Pace inductance manometers for pressure measurements. Final
pressures were measured with a Baratron capacitance manometer. CO was Matheson Research Grade; DCl was photolytically synthesized from Matheson Research Grade Cl₂ (>99.96%) and Matheson C.P. Grade D₂ (>99.5%) and was twice distilled. The system was exposed to only D compounds for several months, and gases removed after a run indicated HCl/DCl < 1% by infrared absorption. Relaxation rate constants of the \( v=2 \) levels were independent of pressure over the range 0.5 to 11 torr. At these pressures the decay of CO(\( v=1 \)) was determined by diffusion.

C. Results

Only the rates for collisional deactivation of CO(\( v=2 \)) and DCl(\( v=2 \)) are reported here. Moore and coworkers\(^{15,17}\) previously determined the kinetics of the \( v=1 \) levels. The vibrational decay of the \( v=2 \) states involves several \( V-V \) exchange and \( V-R,T \) decay channels. The \( V-V \) channels are

\[

c_{\text{CO}(v=2)} + c_{\text{CO}(v=0)} \rightarrow c_{\text{CO}(v=1)} + c_{\text{CO}(v=1)} + \Delta E_v = -27 \text{ cm}^{-1}
\]

\[

c_{\text{CO}(v=2)} + c_{\text{DCl}(v=0)} \rightarrow c_{\text{CO}(v=1)} + c_{\text{DCl}(v=1)} + \Delta E_v = 26 \text{ cm}^{-1}
\]

\[

c_{\text{CO}(v=0)} + c_{\text{DCl}(v=2)} \rightarrow c_{\text{CO}(v=1)} + c_{\text{DCl}(v=1)} + \Delta E_v = -106 \text{ cm}^{-1}
\]

\[

c_{\text{DCl}(v=2)} + c_{\text{DCl}(v=0)} \rightarrow c_{\text{DCl}(v=1)} + c_{\text{DCl}(v=1)} + \Delta E_v = -54 \text{ cm}^{-1}
\]

\[
\frac{k_2}{k'_2}
\]

Very weak excitation is used, and the reverse processes involving collisions between excited (\( v=1 \)) species are negligible. To first order, the apparent forward rate constants can be corrected for the back reaction in the pure gases by\(^{6}\)
\[
    k_{\text{obs}} = (1 + 4 \frac{n_2}{n_0} \ e^{-\Delta E_{\nu}/kT}) k_{\text{real}}
\]

where \( n_2/n_0 \) is the amount of excitation. One can calculate from known line strengths\(^{18,19} \) that less than 0.07% of the absorbing specie is excited at the center of the beam. The maximum correction for the reverse reaction is less than 0.5%. If the back reactions were important there would be a long decay component in the \( v=2 \) fluorescence corresponding to the \( V - R, T \) of the \( v=1 \) levels. No such long decays were observed, and we will ignore the reverse reactions.

Having excluded the nonlinear terms in the kinetic equations due to the back reactions, the kinetics can be solved explicitly. These are the simple kinetics of two states which undergo deactivation and \( V - V \) exchange.

The self relaxation rate constants (see Table IV-I) were determined from a least squares analysis of the pure gas measurements. In principle the \( V - R, T \) contribution to self relaxation of \( v=2 \) can be directly determined when a single vibrational manifold is initially excited as in the present experiments. This determination requires a careful analysis of the intensities of the initially excited \( v=2 \rightarrow 1 \) fluorescence and the \( v=1 \rightarrow 0 \) fluorescence as well as the time evolution. Corrections must be made for filter transmissions, radiative lifetimes, and self-absorption. In the present studies, the pressures needed to obtain good intensity ratios cause self absorption of the \( v=1 \rightarrow 0 \) emission to be too great to permit meaningful limits on the \( V - R, T \) rates. However, the total relaxation rates are at least two orders of magnitude larger than the \( v=1 \) \( V - R, T \) rates as seen in Table IV-I.
Table IV-I. Energy transfer rate constants for CO and DCI at 295°K (torr$^{-1}$sec$^{-1}$).

<table>
<thead>
<tr>
<th>Collidants</th>
<th>v=2 total$^a$</th>
<th>v=1 v-v$^b$</th>
<th>v-R,T</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(v) + CO</td>
<td>9.00 ± .25 ± .10x10$^4$</td>
<td>-</td>
<td>2x10$^{-3}$ c</td>
</tr>
<tr>
<td>CO(v) + DCI</td>
<td>1.13 ± .08 ± .03x10$^5$</td>
<td>4.7x10$^4$</td>
<td>-</td>
</tr>
<tr>
<td>DCI(v) + CO</td>
<td>4.32 ± .50 ± .19x10$^4$</td>
<td>3.6x10$^4$</td>
<td>-</td>
</tr>
<tr>
<td>DCI(v) + DCI</td>
<td>1.07 ± .10 ± .04x10$^5$</td>
<td>-</td>
<td>2.2x10$^2$ b,d</td>
</tr>
</tbody>
</table>

a. This work. The first error limits are one standard deviation, the second limits are 95% confidence limits for determination of the mean.
b. Ref. 15
c. Ref. 21,22
d. Ref. 17
While the $V - R, T$ rates of $k_{CO-DCl}$ and $k_{DCl-CO}$ have not been measured, the $k_{CO-HCl}$ rate is 1 torr$^{-1}$ sec$^{-1}$ and $k_{CO-DCl}$ and $k_{DCl-CO}$ can be estimated to be less than $5 \times 10^2$ torr$^{-1}$ sec$^{-1}$. Since other experiments have shown that even in strongly anharmonic systems the $V - R, T$ rate for $v=2$ is less than eight times the $v=1$ rate we conclude that less than 1% of the observed $v=2$ decays are due to $V - R, T$ except for $DCl(v=2) + CO(v=0)$ where it may approach 10%.

Writing out the kinetics explicitly for the mixtures in the case when $CO(v=2)$ is initially excited

$$CO(v=2) = n_2 [(1-\delta) e^{-K_1 t} + \delta e^{-K_2 t}]$$

$$DCl(v=2) = n_2 \left( \frac{k_{2}^x_{DCl}n_0}{K_1 - K_2} \right) (e^{-K_2 t} - e^{-K_1 t})$$

where

$$\delta = \frac{1}{2} \left[ 1 - (1 - 4k_{2}^x_{DCl}n_0^2)/(K_1 - K_2)^2 \right]^{1/2}$$

$K_1$ and $K_2$ are the two decay rates exhibited by the upper levels. They are nonlinear functions of the mole fractions if and only if two quantum exchange is important.

In the present experiments $CO(v=2)$ and $DCl(v=2)$ were not resolved. The decay of the joint $v=2$ fluorescence was found to be a single exponential and the decay rates were linearly dependent on mole fraction (rugs IV-1 and -2) and pressure. This suggests that the two quantum $V-V$ exchange is unimportant. However, the decay rates, $K_1$ and $K_2$, are sufficiently close at all mole fractions that they would not be resolvable. We prefer to argue that $CO - DC1$ collisions
behave like HCl - HBr collisions.\(^6\) In HCl - HBr the two quantum exchange in the exothermic direction is \(k_2 < 1 \times 10^{-3}\) torr\(^{-1}\) sec\(^{-1}\) at 295\(^\circ\)K. This is negligible compared to the measured decay rates in Figs. IV-1 and -2. In this case \(K_1\) is the observed decay rate, and is the sum of the CO self deactivation and the cross relaxation. The self deactivation measured in the pure gases is used. The cross relaxation rate constants were determined from the intercept of the mole fraction plot (Fig. IV-1 and 2). These results are given in Table IV-I.

The relaxation rate constants in Table IV-I are for rotationally relaxed vibrational manifolds. In 2\% CO in Argon mixtures at total pressures of 50 - 150 torr the CO\((v=2)\) decay was determined only by CO - CO collisions with the same rate constant as in undiluted CO. Excitation on \(R_{20}(6)\) and \(R_{20}(16)\) of undiluted CO yielded the same self relaxation rate. In all mixtures the ratio of measured vibrational relaxation time to rotational relaxation time (based on the pressure broadening cross section) is greater than 150.\(^{23,24}\) The rotational relaxation rates have been directly measured for CO and agree well with the line broadening data.\(^{25}\)

The signal to noise ratios after signal averaging were 10 - 100. The random errors for the measurements are listed in Table IV-I in terms of the standard deviation of the measurements \(\sigma\) and the 95\% confidence limits for determination of the mean \((-2.1\sigma/\sqrt{N-1})\).

Pressures were accurate to 2\% hence mole fractions to 4\%. These uncertainties fall well within the measured random errors.
Fig. IV-1. Total relaxation rate constant of CO\((v=2)\) in CO-DCl mixtures as a function of CO mole fraction, \(X_{\text{CO}}\). Error bars are one standard deviation. The line is a least squares fit.
Fig. IV-2. Total relaxation rate constant of DCI\(^{(v=2)}\) in CO-DCI mixtures as a function of DCI mole fraction, \(X_{\text{DCI}}\). Error bars are one standard deviation. The line is a least squares fit.
DCI (v=2) + DCI, CO

Fig. IV-2.

XBL 7810-11877
D. Discussion

The resonance character of V - V transfer was originally established by a Lambert - Salter type plot of probability vs $\Delta E_v$ for many homologous collidants. These plots suggested an exponential falloff in $\Delta E_v$ within homologous series. The series were characterized at that time by their chemical nature: hydrogen bonds and transition dipoles.

Since then, the resonance behavior on single potential surfaces has been probed by varying the vibrational energy for given collidants. CO(v) + CO has been extensively studied by many methods with fair consistency. CO is a very convenient molecule to work with and undergoes unambiguous V - V transfer since its V - R,T relaxation is extremely slow. HCl and HBr self relaxation have also been studied, only a few levels were accessible. In HF V - R,T is probably important.

The strongest conclusion based on this earlier work is that V - V processes appear to behave as a simple linear perturbation between harmonic oscillators. In CO, a simple perturbation - like expression fits the vibrational level and temperature dependence. Powell's expression, ignoring his explicit temperature dependence, is simply Eq. IV-1. The competition between $N_v$ and $g(\Delta E_v)$ leads to the maximum in V - V rates as a function of v for self relaxation ($v'=1$).

The present results for CO(v) self relaxation are consistent with the many previous results. The latter are tabulated in Table IV-II. The largest variation of measurements is for v=2. The lower vibrational levels are difficult to measure with any of the techniques which
Table IV-II. V-V transfer rates for CO(v) + CO(0) at 295°K (torr⁻¹sec⁻¹). a

<table>
<thead>
<tr>
<th>Reference</th>
<th>v=2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔE(cm⁻¹)</td>
<td>-26.3</td>
<td>-52.9</td>
<td>-79.3</td>
<td>-105.5</td>
<td>-131.7</td>
<td>-157.9</td>
<td>-183.9</td>
<td>-209.9</td>
<td>-235.8</td>
<td>-261.6</td>
<td>-287.4</td>
</tr>
<tr>
<td>Hancock and Smith [7a]</td>
<td>-</td>
<td>-</td>
<td>6.6(4)</td>
<td>4.3(4)</td>
<td>2.1(4)</td>
<td>1.1(4)</td>
<td>5.9(3)</td>
<td>3.6(3)</td>
<td>2.0(3)</td>
<td>1.5(3)</td>
<td>1.1(3)</td>
</tr>
<tr>
<td>Sackett, et al. [8]</td>
<td>8.6(4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stephenson [9]</td>
<td>1.1(5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Powell [10]</td>
<td>6.3(4)</td>
<td>7.4(4)</td>
<td>7.2(4)</td>
<td>5.2(4)</td>
<td>2.8(4)</td>
<td>1.3(4)</td>
<td>6.6(3)</td>
<td>3.9(3)</td>
<td>2.5(3)</td>
<td>1.5(3)</td>
<td>-</td>
</tr>
<tr>
<td>Fushiki and Tsuchiya [11]</td>
<td>6.2(4)</td>
<td>8.4(4)</td>
<td>1.0(5)</td>
<td>6.4(4)</td>
<td>3.2(4)</td>
<td>1.5(4)</td>
<td>7.4(3)</td>
<td>5.3(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liu, et al. [12]</td>
<td>-</td>
<td>7.7(4)</td>
<td>5.9(4)</td>
<td>3.9(4)</td>
<td>2.8(4)</td>
<td>1.7(4)</td>
<td>1.2(4)</td>
<td>7.9(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td>9.0(4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. (n) means x 10^n.
generate populations simultaneously in many vibrational states. The present measurement of CO(v=2) + CO(v=0) agrees with Sackett et al.'s\textsuperscript{8} more recent unpublished\textsuperscript{10b} results using an OPO and is slower than Stephenson's\textsuperscript{9} up-pumping CO(v=1) + CO(v=1) measurements. The up-pumping measurements require a correction on the number of v=1 molecules pumped,\textsuperscript{4} and we have found these results tend to be systematically high.\textsuperscript{6}

The CO(v) self relaxation rates measured here and the average of Refs. 7 and 10 are plotted in Figure IV-3. The rates have been normalized to the form of equation Eq. (1).

\[
P_{\text{exo/v}} = \frac{x_{\text{exo/v}}}{N_k} = g(\Delta E_v)
\]

This quantity will be referred to as the "linear perturbation harmonic oscillator normalization" (LPHON) probability and, according to the perturbation hypothesis, gives the collisional resonance function. For the CO(v) deactivation, this probability is a monotonically decreasing function of $\Delta E_v$.

This does not demonstrate that the parametric form of Eq. IV-1 is generally correct or that a perturbation treatment of V-V energy transfer is valid. In particular it is necessary to vary $N_v$ and $\Delta E_v$ independently, especially by excitation of both collision partners.

The present studies together with the work of Braithwaite and Smith\textsuperscript{14} and Zittel and Moore\textsuperscript{15} have measured the vibrational dependence of both molecules in CO - DCl V-V transfer. These results at a single temperature and on a single potential surface show a small but
experimentally real deviation from a simple correlation.

Figure IV-3 contains all the CO-DC1 relaxation data available. Again, the exothermic rate constants are plotted normalized by v. There appear to be two distinct branches. Caution is required since the lower branch is really defined by only two or three points and the upper branch is entirely derived from the chemiluminescent experiments of Braithwaite and Smith. Estimates of the error (15%) for the upper branch have been guessed from the deviation of the points from a smooth curve and from the error in their CO self relaxation results. The upper points are

\[ \text{CO}(v-1) + \text{DC1}(1) \rightarrow \text{CO}(v) + \text{DC1}(0) \quad v=4,12 \]

That is, they are derived from the CO(v) + DC1(0) collisions which are endothermic. The values are consistent with the exothermic members of the series as seen in Figure IV-4. The lower points are from direct excitation measurements and have the indicated errors (10%). These include the processes

\[ \text{CO}(1) + \text{DC1}(v-1) \rightarrow \text{CO}(0) + \text{DC1}(v) \quad v=1,2 \]

and

\[ \text{CO}(2) + \text{DC1}(0) \rightarrow \text{CO}(1) + \text{DC1}(1) \]

\[ ^{13}\text{CO}(1) + \text{DC1}(0) \rightarrow ^{13}\text{CO}(0) + \text{DC1}(1) \]

Note that all the plotted points are for independent, exothermic processes.

The only apparent property which characterizes all the points is that in the upper branch the DC1 quantum is larger and in the lower
Fig. IV-3. Experimental exothermic, thermally averaged V - V cross sections renormalized by hard sphere collision cross section (37.5 Å²) and by $N_v$ the linear perturbation harmonic oscillator scaler (see text).
Fig. IV-3.
Fig. IV-4. Experimental V - V transfer rate constant for CO(v) +
DCl(v=0) + CO(v=1) + DCl(v=1). References are 15 and 26.
Fig. IV-4.

CO(v) + DCI (O) → CO(v-1) + DCI (1)

Rate (sec⁻¹ torr⁻¹)

Vibrational Level (v)
the CO quantum is larger. The vibrational up-down transitions for both branches of the exothermic rates and for the corresponding endothermic rates are displayed in Figure IV-5.

This separation into branches differs from the conclusion of Braithwaite and Smith based on less data. No comparable data set exists for any collision pair except for CO(v) + NO(0) deactivation where for v ≥ 12 the V-V process goes from exothermic to endothermic. Only two endothermic points are available, but their $P_{\text{exo}/v}$ do correlate well with the other levels. However, CO and NO are rotationally and anharmonically very similar.

There are two reasonable, simple mechanisms for the presence of two branches. The first, less likely mechanism recognizes that the significant data points for the upper and lower branches are correlated with higher vibrational states of CO and DCl respectively. Does the energy transfer depend upon molecular anharmonicity? From infrared absorption intensity studies it is known that the dipole matrix elements between adjacent (Δv=1) vibrational states of CO and DCl increases less quickly with v than the LPHO matrix elements especially in DCl. Normalizing the V-V transfer rates by the experimental dipolar matrix elements decreases the separation between the branches slightly. At $ΔE_v \sim 100 \text{ cm}^{-1}$ the branches are separated by 40%. The experimental matrix elements decrease the separation by 4%.

While dipole forces are undoubtedly important in V-V transfer, it is generally agreed they do not contribute the majority of the perturbing potential in DCl and CO. Furthermore, the dipole
Fig. IV-5. Secondary vibrational transition propensities in CO-DCl collisions including DCl rotational transitions which minimize the change of translational energy.
<table>
<thead>
<tr>
<th>Process</th>
<th>More Probable</th>
<th>Less Probable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exothermic</td>
<td>DCI CO</td>
<td>DCI CO</td>
</tr>
<tr>
<td></td>
<td>VR V</td>
<td>VR V</td>
</tr>
<tr>
<td></td>
<td>↑↑↑</td>
<td>↑↑↑</td>
</tr>
<tr>
<td>Endothermic</td>
<td>DCI CO</td>
<td>DCI CO</td>
</tr>
<tr>
<td></td>
<td>VR V</td>
<td>VR V</td>
</tr>
<tr>
<td></td>
<td>↑↓↓</td>
<td>↓↓↓</td>
</tr>
</tbody>
</table>

Fig. IV-5.
normalization brings the branches closer because the dipole moment is a 
nonlinear function of the vibrational coordinates, not because of 
molecular anharmonicity. Perturbation calculations\textsuperscript{33} of $\nu - \nu$ transfer 
have generally assumed that the perturbing force is linear in the 
vibrational coordinates. Because CO is fairly harmonic and undergoes 
only small displacements during a vibration, we are primarily concerned 
with the behavior of DC1. That is, the lower branch is "too low" or 
the normalization factor is too large.

We can express the perturbation as a general power series in the 
deviation of the vibrational coordinates $r, r'$ from their equilibrium 
values, normalized by the vibrational characteristic distance 
\[ d_o = (\hbar/\mu \nu_e)^{1/2} \]
\[ \sum_{ij} v_{ij} [(r-r_e)/d_o]^i [(r'-r'_e)/d'_o]^i \]

Here $\mu$ and $\nu_e$ are the reduced mass and fundamental frequency (cm$^{-1}$) of 
the oscillator. The matrix element $\langle v(v'-1)|V|(v-1) v' \rangle$ between Morse 
oscillators is $m_{\nu_m}^{\nu_{m'}}$ where the elements of $V$ are the potential 
expansion coefficients and to second order\textsuperscript{32} 
\[ m = v^{1/2} (1,0,0) + v^{3/2} (\delta^2/2,3\delta,3) \]
\[ \delta = (\nu_e)^{1/2} \] is an anharmonicity factor. As stated above we see that 
anharmonicity increases the matrix elements via the $V_{11}$ elements, and 
if $V_{ij}/V_{11} < 0$ the nonlinearity also increases the matrix elements.

As stated above the dipolar nonlinear $V_{ij}/V_{11}$ coefficients are 
negative and tend to bring the branches together, although not 
sufficiently so. If exponential repulsive forces are assumed\textsuperscript{33} the
matrix elements are all positive and the branches would be further separated. Hence, a sum of dipolar and exponential forces also has the incorrect trend, and nonlinear $V_{ij}/V_{ll}$ much more negative than the dipolar coefficients are implied. This is a surprising conclusion since the intermolecular forces are the sum of the multipolar forces and short range forces which are roughly approximated by an exponential.

From this discussion we see that unusual forces must be invoked to reconcile the branching behavior with nonlinear forces and molecular anharmonicity if a simple perturbation model is assumed. The model is too simple to support such conclusions. However, it is important to note that in any model emphasizing the vibrational aspects of such $V-V$ energy transfer processes, the nonlinear potential terms will be more important than anharmonicity (aside from the effect of anharmonicity on the level spacing).

An alternative interpretation accepts the up-down description of the branches depicted in Fig. IV-4 and takes into account the importance of rotational transitions for vibrational energy transfer in the deuterium halides. In particular, it appears that transfer processes are somewhat enhanced when the total energy transferred from DC1, $|\Delta E_v + \Delta E_R|_{DC1}$, is minimized by intramolecular $V-R$ transfer. In Fig. IV-5 we reproduce the vibrational transitions of the two branches. We include rotational transitions in DC1 which would be necessary to minimize the energy which goes into translation. As a result, DC1 undergoes + rotational transitions in exothermic processes, etc. The endothermic processes are constructed by microscopic
reversibility as was done to construct the LPHON probability plot. As can be seen, in the more probable processes DCl vibrational and rotational transitions are opposed. Another way of stating this is, the more probable processes involve intramolecular rotational energy transfer, the less probable involve intermolecular rotational energy transfer. It is important to understand that the propensities in Fig. IV-5 are in a sense second order effects and not branching ratio rules.

This rotational model is consistent with our present knowledge of vibrational and rotational energy transfer. Generally the hydrogen and deuterium halides have large line broadening coefficients for both self relaxation and foreign gas broadening. This is indicative of the high rotational velocities of the halides at a given rotational temperature and of the large multipolar moments which control pressure broadening and rotational energy transfer. The mutual broadening coefficients of DCl and CO are not known\textsuperscript{23,24} but by analogy with CO-HCl and DCl-CO\textsubscript{2} coefficients, DCl will have a total rotational inelastic cross section of $150 \text{ A}^2$ while CO has $75 \text{ A}^2$. If we further assume that the cross section is indicative of the ability to undergo large $\Delta J$'s then it is clear that simultaneous rotational energy transfer in DCl during DCl-CO V - V transfer will be important. DCl is more likely to undergo large $\Delta J$'s and its rotational level spacing is three times larger.

First order perturbation arguments such as used with the vibrational mechanism can not be applied here since the rotational
forces are strong. Some classical trajectory calculations and some experiments on \( V - R, T \) in the halides have suggested that the vibrational energy is converted primarily internally into rotation. This enhanced \( V - R \) in hydrogen and deuterium halides is due to the large rotational spacings which give rise to a large \( \Delta E_R \) for a given \( \Delta J \). In the pseudo SSH model of Cottrell and of Moore this phenomenon is predicted because in the halides the change in (rotational) de Broglie wavelengths for a given \( \Delta E_R \) is relatively small.

The two models discussed here are highly qualitative but are compatible with available detailed calculations of \( V - V \) transfer rates. Aside from recent classical trajectory calculations of HF collisions, most of these calculations and especially for CO collisions are first order perturbation theory. It has been found that these rates can be predicted to an order of magnitude by assuming either multipolar or simplified repulsive forces. The agreement is rough, and some trends are clearly incorrect. Better agreement has been attained by assuming combined short and long range forces or by allowing semiempirically or ab initio more complicated rotational dynamics.

These latter results suggest that \( V - V \) (and \( V - R, T \)) energy transfer may be treated well by a generalized distorted wave calculation in which rotational transitions are treated in detail while the vibrational transition is treated as a perturbation between the distorted rotational - translation states. Gerber, Balint-Kurti and coworkers, and the present writer have pursued this path.
Dillon and Stephenson\textsuperscript{42} briefly considered this limit of their quasi-
Magnus approximation.

E. Conclusions

The deactivation rate of CO(v=2) and DCl(v=2) in CO-DCl mixtures have been measured. These measurements resolve the uncertainty in the many previous measurements of the CO(v=2) self relaxation rate. There appears to an anomaly in the CO-DCl V - V exchange rates. These rates cluster into sets which show a slightly different energy gap law. This behavior can be interpreted in terms of DCl simultaneous rotational transitions or in terms of a vibrationally nonlinear perturbation potential. However, more, careful measurements of the high CO(v) + DCl and DCl(v) + CO rates are indicated, including temperature dependences.
CHAPTER IV. REFERENCES

6. Chapter III.
32. The $m_1$ and $m_2$ terms are derived from H. S. Heaps and G. Herzberg, Z. Phys. 133, 48 (1952) in the limit $2\nu_X \ll 1$; cf. R. C. Herman and K. E. Shuler, J. Chem. Phys. 21, 373 (1953); 22, 481 (1954). The $m_3$ term is simply the harmonic oscillator term taken from E. B. Wilson, and J. C. Decius, and P. C. Cross, "Molecular Vibrations" (McGraw-Hill, New York, 1955) Appendix III.
46. Chapter VI.
V. OPTOACOUSTIC SPECTROSCOPY OF THE HF DIMER

A. Introduction

The HF dimer has been the object of physical chemists' curiosity for some sixty years, since the original investigations by Simons and Hildebrand on the thermodynamics of HF.\(^1\) Through 1959 it was solely on the basis of the vapor pressure, specific heat, and density measurements that the HF dimer and especially the hexamer were conjectured to be significant polymeric species in HF vapor. Although polymeric infrared absorptions were known as early as 1940 it was not till the work of Smith that bands were assigned to the dimer, tetramer, and hexamer on the basis of their pressure dependence.\(^3,4\)

Since 1960 the most significant work has been the molecular beam microwave spectroscopy investigation of Dyke, et al.\(^5\) In those studies, the bent equilibrium molecular geometry was unambiguously determined under conditions where the dimer was clearly identified by mass spectroscopy.

The great interest in the HF dimer has varied somewhat over time. The HF dimer is the simplest hydrogen bonded dimer. Of fundamental importance are the binding energy and the molecular geometry. As discussed by Pimentel and McClellan\(^6\) the geometry is especially relevant to molecular orbital vs. electrostatic views of hydrogen bonding. It is now well established that gaseous and matrix isolated HF dimer and solid HF tend to be zig-zag chains,\(^7,8\) while the hexamer and other intermediate polymers are probably rings.\(^9,10\) The binding energy of the dimer is approximately 6 kcal/mole.\(^4\)
More recently there has been interest in the dynamical properties of the dimer such as vibrational predissociation rates or low energy vibrational frequencies rather than equilibrium properties. This interest comes from two extremes. On the one hand, there has been difficulty understanding the large vibrational energy transfer rates of the hydrogen halides, especially HF, and their weak dependence on the energy discrepancy. It is probable that the strong attractive forces cause complexes (i.e. species with lifetimes $> 10^{-12}$ sec) to appear. Hence there is concern for the shape of the intermolecular potential near the attractive minimum, for mechanisms of complex stabilization, and for information which could be derived from vibrational predissociation analogous to photodissociation. On the other hand, the lifetime of the dimer when vibrationally excited, i.e. its predissociation rate, is a good case to test ergodicity of the molecule. The ergodicity is the degree to which an isolated, vibrationally excited molecule will fill all the phase space energetically open to it. Multiphoton dissociation has especially stimulated these questions.

The vibrational frequencies of the dimer are not known despite several infrared absorption studies in the gas phase and in inert matrices. Based on the geometry of Dyke, et al. there should be five in plane vibrations and one out of plane vibration. These are depicted in Fig. V-1 assuming $C_s$ symmetry. The modes are numbered by Herzberg's convention. It is assumed that the quasi symmetric HF stretch is the highest fundamental hence labeled $v_1$. However, since
Fig. V-1. Approximate normal modes and frequencies of the HF dimer.
<table>
<thead>
<tr>
<th>Mode ( \nu )</th>
<th>Frequency (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_1 )</td>
<td>4000</td>
</tr>
<tr>
<td>( \nu_2 )</td>
<td>4000</td>
</tr>
<tr>
<td>( \nu_3 )</td>
<td>450</td>
</tr>
<tr>
<td>( \nu_4 )</td>
<td>250</td>
</tr>
<tr>
<td>( \nu_5 )</td>
<td>180</td>
</tr>
<tr>
<td>( \nu_6 )</td>
<td>450</td>
</tr>
</tbody>
</table>

Fig. V-1.
the HF molecules do not interact strongly and are nearly degenerate as has been calculated for the HCl dimer. The frequencies are approximated from the numerous ab initio calculations assuming only single atom motions.

In principle, the matrix isolated dimer should be more readily analyzed since most of the rotational structure of the dimer as well as overlapping monomer lines will be frozen out. However, water and nitrogen-oxygen nearest neighbor absorptions greatly confuse the spectra. Two conflicting sets of lines at 2.5 μ have been attributed to the HF dimer. By contrast, the HCl matrix isolated dimer has been well studied and by 1973 three bands were generally accepted. In argon, v₁ = 2818 cm⁻¹, v₂ = 2787 cm⁻¹, and v₃ = 232 cm⁻¹. Recently, v₂ has been reassigned to 2856 cm⁻¹ where there is the overlying monomer P(1) absorption.

The gaseous HF dimer absorption is understood little better. attributed some five 2.5 μ bands to the dimer. The region is heavily overlaid by the monomer absorption which is very strong and which is very readily pressure broadened. There is also interfering water absorption in the 2.6 to 2.8 μ region. The dimer bands which have been resolved from the monomer absorption are depicted in Fig. V-2. The dimer absorption is centered at 3858 cm⁻¹ near the HF P(2) line.

There is substructure. Smith originally suggested that each of the regions between the monomer lines was a separate band with PQR branches. These branches are not evident in the higher resolution
Fig. V-2. High (Ref. 23) and low (Ref. 4) resolution spectra of HF dimer. The apparent noise on the high resolution spectra is real structure. The monomer absorption has been subtracted from the experimental spectra. The monomer lines are indicated along the upper scale.
HF Dimer at 300°K

Fig. V-2.
work of Herget et al.\textsuperscript{23} The latter caution that there is strong absorption under P(2) although its distribution could not be extracted. Himes and Wiggins\textsuperscript{26} have high resolution (0.35 cm\textsuperscript{-1}) spectra of the dimer absorption in the HF null gap and discuss in detail various interpretations of the substructure. In all the bands there is -0.5 cm\textsuperscript{-1} spacing of lines. It is clear by comparison to Dyke et al.\textsuperscript{5} that these are $\Delta J = \pm 1$ transitions and that $(B + C)/2$ of the excited dimer is somewhat larger than that of the ground state. There should be a $0, \pm A, \pm 3A, \ldots$ spacing of bands corresponding to $\Delta K=0, \pm 1$ transitions (A\textsuperscript{-23} cm\textsuperscript{-1})\textsuperscript{5}. It is difficult to reconcile this with Fig. V-2 unless there is a peak under the HF P(2) line or unless the 3895 and 3857 cm\textsuperscript{-1} peaks are the $\Delta K = 0$ bands of $v_1$ and $v_2$.

In the course of the energy transfer experiments (Ch. III and IV) it was realized that the OPO - spectrophone spectrometer has sufficient sensitivity to observe the HF dimer in the 2.5 $\mu$m region. While spectroscopically these absorptions are of interest because of the structural information contained in a rotational analysis, this information is more easily obtained by microwave spectroscopy. The centrifugal distortion constants yield information on the low frequency bending modes. For that reason only a rough survey of the region was planned at pressures where line broadening was eliminated so that more bands might be resolved. The primary purpose however was to isolate single lines and to measure linewidths, in the hope of finding vibrational predissociation. At 0°C, lifetimes shorter than 1 $\times$ 10\textsuperscript{-9} sec could be measured. Levy et al.\textsuperscript{27} found the HeI\textsubscript{2}* complex dissociated
when excited with $300 \text{ cm}^{-1}$ above its $300 \text{ cm}^{-1}$ potential well. When HF is excited at $2.5 \mu$ there is $2000 \text{ cm}^{-1}$ of energy above a $2000 \text{ cm}^{-1}$ potential well.

B. Experimental

An optoacoustic spectrometer was assembled using the Chromatix OPO as the light source and using an inner surface cylindrical microphone as described in Ch. II. The inner surface microphone was necessary with its higher sensitivity and its resilience to attack by HF. A 4.0 cm long version of the element in Fig. II-9 using a monel support cylinder was mounted with teflon spacers in a small version of the monel and sapphire cell shown in Fig. II-4. HF pressures were restricted to less than 50 torr to prevent shrinkage of the microphone mylar film. While the lockin rectified signal averaging was used for most of the spectra taken, a gated integrator sampling of the first acoustic peaks gave a similar signal to noise ratio and was simpler to match the gated period to the phase of the acoustic oscillation.

The HF was handled in an all monel vacuum system. Residual pressures of $1 \times 10^{-6}$ torr could be attained with $\text{LN}_2$ trapping and the 2 inch silicon oil diffusion pump. The pumping speed of the system is very poor due to the small diameter tubing and small bore valves. High pressures were roughly measured with a monel Helicoil spring gauge. Sample pressures were measured with a Baratron 310 capacitance manometer.

Water contamination of the HF was a severe problem. Since water absorbs in the peak region of HF dimer, samples should be scrupulously
dry. The vacuum system exclusive of the spectrophone was flamed and wrapped in heating tape to remove adsorbed water. Matheson lecture bottle HF (>99.9%) was used. Gas taken from the bottles always contains 10-50% noncondensible gas which is H₂. Dyke et al.⁵ suggest this is the product of the Si + HF reaction in the stainless steel lecture bottle. After degassing the HF was distilled from a chloroform slush (210⁰K) to LN₂. The water/HF ratio of partial pressures at this temperature is 4 x 10⁻⁴. The distillate was dried following Jarry and Davis.²⁸ This combined drying by baked NaF and CoF₃ has been used in most HF(v=1) vibrational relaxation measurements. Despite the drying the water content varied considerably. A relative measure of the water content could be made by comparing the spectrophone signal from the strong water absorptions between the HF P(5) and P(6) lines to the HF signal. The water contamination appeared to increase simply with contact with the vacuum system including the desiccants and especially the spectrophone itself.

An attempt was made to cool the HF cell to -15⁰C. The spectrophone was enclosed by cooling coils of 1/8 inch copper tubing which were cemented to three sides of the cell with an ordinary epoxy. The coils and cell were encased in styrofoam. A methanol/ethylene glycol mixture was cooled in a MGW Lauda refrigerator and pumped through the coils with a Micropump. N₂ was blown across the cell windows to prevent frosting. This arrangement did not work because the refrigerator vibrations overwhelmed the microphone. One could circumvent these vibrations by using a dewared cell placed in a slush
bath, but this was not attempted.

To insure that absorptions due to water were identified the early spectrophone spectra were usually recorded simultaneously with the signal of a reference water spectrophone. The later spectra were simultaneously recorded with the OPO average power. The average power was determined by splitting the OPO beam with a Ge flat. The reflected beam was detected with a PEM InSb detector and integrated. The Ge-spectrophone and Ge-PEM distances were equal. This power signal also exhibited the water lines due to atmospheric water absorption. The OPO was N₂ purged and the absorption occurred between the OPO and the PEM detector rather than in the OPO cavity.

C. Results and Discussion

Spectra of the HF R(5) to P(12) region were recorded at room temperature for HF pressures between 3 and 30 torr. Most of these spectra exhibited very strong water absorption in the region of the HF P(3) to P(6) lines as shown in Fig. V-3. The spectral resolution of the OPO is ~0.3 cm⁻¹ in this region.

In Fig. V-4 the dimer was detected in the HF null gap. This band shows the shading toward the blue previously found in Refs. 23 and 26. The atmospheric water absorption is stronger than that of the water contaminant and the water lines appear as dips. The peak of the dimer spectrum is also evident to the red of P(2).

The dimer signal level agrees with that of Smith. In Fig. V-4 the ratio of dimer to HF R(0) absorption is ~5 x 10⁻⁴. The predicted ratio is 3 x 10⁻⁴ as given by the expression
Fig. V-3. Optoacoustic spectra of the HF 2.5 μ band. Lower spectrum is 10 torr HF with a large water contaminant. Upper trace is 20 torr H₂O using a less sensitive spectrophone.
Fig. V-4. HF dimer spectrum at 295°K and 30 torr HF. The partial pressure of the dimer is -0.2 torr. The absorption at the monomer lines saturates the amplifiers. The wavenumber scale is determined by linear interpolation between the monomer lines.
\[ \frac{\alpha_2 K_2 P_1 \Delta \nu_{\text{OPO}}}{S_1} \]

where \( \alpha_2 K_2 \) is the dimer absorption in units of \( \text{cm}^{-1} \) (monomer pressure) \(^{-2} \), \( P_1 \) is the monomer pressure, \( \Delta \nu_{\text{OPO}} \) is the OPO FWHM line width, and \( S_1 \) is the line strength of the monomer line.

In principle even this small absorption is sufficiently large to measure line widths if an isolated dimer line could be found. In measuring linewidths with the OPO (see Ch. IIc) the OPO is narrowed to oscillate on only one mode. Hence the peak signal is proportional to \( S_2 / \Delta \nu_{\text{doppler}} \) where \( S_2 \) is the dimer line strength. The broad band signal scales as \( \bar{S}_2 / \Delta \nu_{\text{gas}} \) where \( \Delta \nu_{\text{gas}} \) is the average spacing between gas lines which have the average line strength \( \bar{S}_2 \). The ratio \( \Delta \nu_{\text{gas}} / \Delta \nu_{\text{doppler}} \) is \(-50\). However, in fact with a signal to noise of only 2 or 3 it would be difficult to find an isolated line.

Two essential improvements are necessary to allow these measurements. A low temperature cell, preferably able to go to 250 °K should be used. The dimer concentration will be increased by \( \times 10 \) and some of the rotational structure will be frozen out. At temperatures below 250 °K the hexamer becomes a dominate specie. The second revision is to use a different charge sensitive preamp and to detect the nonresonant pressure wave since the inner surface cylindrical microphone was originally designed for this mode of operation. It is difficult to project how much this will improve the signal.

It would appear that a two step approach should be taken. High resolution (0.06 cm\(^{-1}\)) spectra could be taken on a Fourier Transform
infrared spectrometer at 6 torr, 250 °K, and a 25 cm path length by using long signal averaging times. The monomer absorption could be determined at a lower pressure and numerically stripped off. The best previous spectrum was limited by pressure broadening to ~0.2 cm\(^{-1}\) resolution. Given a high resolution spectrum, likely lines could be selected, and line widths measured with the etalon narrowed OPO-spectrophone spectrometer.
CHAPTER V. REFERENCES

VI. THEORETICAL ASPECTS OF VIBRATIONAL ENERGY TRANSFER

A. Introduction

There have been many first order perturbation treatments of vibrational energy transfer, especially V - V energy transfer. Most of the latter have used the time dependent perturbation theory due to Zener\(^1\) which is variously known as the semiclassical approximation, the impact parameter method, or the classical trajectory method.\(^2\) There are many dynamical simplifications in addition to the calculation method that might and have been made. These include the form of the intermolecular potential, the relative translational motion, and the inclusion of rotational states.

Despite the many possible combinations of assumptions these first order perturbation calculations fall into two sets of rather exclusive assumptions. These are generally known as short range (potential) calculations and long range or multipole calculations. Despite the difference of assumptions, which are discussed shortly below, it has been generally conceded among experimentalists that both long and short range forces need to be included to explain the order of magnitude of V - V transfer rates and their temperature dependence, but that the weak dependence on the energy discrepancy \(\Delta E_v\) is not theoretically accounted for. These conclusions have been drawn from a comparison of experimental rates with simple but detailed model calculations.\(^3,4\)

In section B.1 we wish to give back-of-the-envelope level expressions for these two sets of theories and to compare the
predictions with experimental results for CO - CO and HCl - HCl collisions. The essential conclusions are those above: the predicted $\Delta E_v$ dependence is too strong. Dynamically this dependence results from the "half time" of the collision, the shorter the half time the weaker the $\Delta E_v$ dependence. From a qualitative point of view it is significant that the half times for short range and dipolar forces differ by only about a factor of two. The other significant result is that the first order perturbation transition probability is significantly less than unity even at resonance, and that hence the collision appears to be a first order perturbation at least in the vibrational coordinates. This is exploited in sections B.2 and C.

A comparison of several dipole-dipole models indicates however that the resonance functions are sensitive to the details of the models. Section B.1 also shows unhappily that several of the "dipole-dipole" models frequently referred to do not contain the complete interaction and as a result are not directly comparable. It is also found that the temporal oscillation of the interaction which arises from the anisotropy decreases the dependence on $\Delta E_v$.

The last sections of this chapter are devoted to model calculations in which rotation is treated in a manner such that "infinite order" transitions can take place. In Section B.2 the first Magnus approximation and the Dillon and Stephenson approximations are applied to HCl - HCl collisions. The assumptions of these approximations suggest that they should roughly give lower and upper limits. The first ignores resonance effects altogether while the latter
considers only the overall resonance. The Dillon and Stephenson approximation has enjoyed a great popularity with experimentalists because of its accurate prediction of HF - CO₂ V - V transfer rates. There has been no previous critique of the method and its idiosyncracies. For HCl the Dillon and Stephenson method allows large ΔJ transitions and a much smaller dependence on the energy discrepancy, but the total magnitudes of the rates are too small. This is a rather involved consequence of the nonunitarity of the Dillon and Stephenson S matrix.

Sections B.3 and C are devoted to methodology. In section B.3, it is shown that in the impact parameter method any of the degrees of freedom can be treated classically, that the expectation value of the energy is conserved, and that in principle the Gordon integration method can be applied to time dependent problems. In Section C a more rigorous approximation is derived in which the vibration is treated as a first order perturbation but the rotation is treated exactly: a rotationally distorted wave approximation.

B. Time Dependent Semiclassical Treatments

1. First Order Perturbation Theory with Model Potentials

In the impact parameter formulation of inelastic scattering, the probability of transition for a collision of velocity v and impact parameter b is

\[ P_{fi}(b,v,\omega_{fi}) = \left| \int_{-\infty}^{\infty} \frac{(f|v_{int}(t)|i)}{\hbar} \exp(i\omega_{fi} t) \, dt \right|^2 \] (1)
$V_{\text{int}}$ is the transition inducing potential whose time variation is determined by the relative motion of the collision partners. $\omega_{fi}$ is the energy lost to translation in units of $\hbar$. The relative translational energy is treated as a constant, and there is no energy constraint on the final states accessible. The approach is usually limited to exoergic processes where $kT \gg \hbar \omega_{fi}$. Endothermic rates are calculated by detailed balancing.

Experimentally (see Chaps. III and IV) it is found that the thermally averaged (translational and rotational degrees of freedom) $V - V$ energy transfer cross sections for diatom - diatom collisions at a fixed temperature scale approximately as

$$\sigma_{fi} = N_{vv}, \pi d^2 P_o \exp(-k\omega_{fi})$$

(2)

where $\pi d^2$ is the gas kinetic cross section, $N_{vv}$, is defined in Chapt. IV, and $P_o$ and $k$ are empirical numbers. To account for such an expression from Eq. (1), assuming a simple collision model in the spirit of Wittriol and Stettler, we could make the following assumptions. Only collisions at small impact parameters are important, $V_{\text{int}}(t)$ is Lorentzian in time with a half time $\tau$, and $\omega_{fi}$ is independent of rotational states. This leads to the conclusion

$$\sigma_{fi} = \left(\frac{\pi V_0 \tau \exp(-\omega_{fi} \tau)}{\omega_{fi}}\right)^2 \pi d^2.$$  

(3)

Eqs. (2) and (3) are equivalent. In this manner we have the traditional Mott and Massey interpretation that the energy falloff $k = 2\tau$ is related to the half time of the collision; and the resonant
transition probability is the maximum collision action squared,
\[ p_o = (\pi v o \tau / \hbar)^2. \]
\[ v o \text{ is } \langle f \mid v_{\text{int}}(t=0) \mid i \rangle. \]

There has been a trend to classify impact parameter perturbation calculations as short range or long range (multipolar). The assumptions commonly assumed for each are given below.

"Short range" force theories such as those of Landau and Teller,\textsuperscript{10} Nikitin,\textsuperscript{11} and Shin\textsuperscript{12} assume 1) the translation determining and the perturbing potentials are the same within a geometric factor, g. This assumption leads to the result that \( V(t=0) = g(\mu v^2/2) \), which implies a soft or compressive effective interaction\textsuperscript{13} and which accounts for the presence of only g and a distance parameter in these theories. \( \mu \) is the collision reduced mass, \( v \) the relative velocity. 2) The molecules interact via an exponential repulsive potential. 3) Only collisions at impact parameters \( b \) within the hard core regions (\( b \sim 0 \)) are considered although Shin\textsuperscript{12} has proposed an expansion for higher \( b \)'s. 4) Rotation is ignored.

Generalizing Shin's more elaborate treatment based on an orientation averaged potential,

\[ \sigma_{fi} = \pi d^2 [g_1 g_2 (2\mu v^2/\hbar)]^2 [\omega_f \tau_s \exp(-\omega_f \tau_s)]^2 \]

where

\[ \tau_s = \pi a/v \]

\[ g_i = (x_i/d_i)^2 \left[ \sum_{i} (1 - S^{-1}_{i j}) e^{S_{i j}} / \left[ \sum_{i} S^{-1}_{i j} e^{S_{i j}} \right] \right] \]

\[ S_{i j} = (d_i/a) \left[ 1 - m_{i j} / (m_{i 1} + m_{i 2}) \right] \]
\( \mu \) is the reduced mass of the collidants; \( d_k \) is the bond length, \( x_k \) is the vibrational matrix element, \( m_{k1} \) and \( m_{k2} \) are the mass of the atoms in molecule \( k \); and \( a \) is the Morse potential distance parameter.

Equation (4) is also analogous to Eq. (3), except for the \( \omega_{fi} \) factor in the resonance function.

The multipolar model of Mahan\(^{14}\) was largely worked out formally earlier,\(^{15}\) but has been further studied by Sharma and coworkers.\(^{16-17}\) 1) Electrostatic multipolar forces are assumed for the perturbing potential, and 2) the relative translation is determined by a hard sphere potential, i.e. the trajectories are straight. The transition probability 3) for all impact parameters and 4) for all rotational states are calculated. Assuming all rotational states to be degenerate, the dipole dipole cross section is approximately

\[
\sigma_{fi} = \pi d^2 \frac{2}{3} \left( \frac{\mu_1 \mu_2}{d^2 \nu h} \right)^2 \exp(-0.7 \omega_{fi} d/\nu) \tag{5}
\]

\( d \) is a hard sphere diameter. This is again analogous to Eq. (3).

In Table VI - I we compare experiment Eq. (2) with short range Eq. (4) and long range Eq. (5) expressions via the heuristic model Eq. (3). \( \tau \) is extracted from the exponential dependence on \( \omega_{fi} \). Given this \( \tau \), \( V_0 \) is found. It should be noted that this \( V_0 \) is very close to the actual \( V_{int}^{(t=0)} \) for the long and short range theories.

From this table we can see that the combined \( V_0 \) from long and short range expressions approaches the experimental \( V_0 \). However, the calculated \( \tau \)'s are too large, especially for DCl and HCl. It should
Table VI-I. Comparison of Experimental and Long and Short Range Theoretical V-V Energy Transfer Rates.$^a$

<table>
<thead>
<tr>
<th></th>
<th>Repulsive</th>
<th>Dipole-Dipole</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\nu_0$</td>
<td>$\tau^c$</td>
<td>$\pi \nu_0 \tau / h$</td>
</tr>
<tr>
<td>General Expression</td>
<td>$q_1 q_2 \frac{8 \mu v^2}{\pi^2} \frac{\pi a}{v} - \sqrt{\frac{2}{3}} \frac{1 \mu_1 \mu_2}{35 \pi d^3} \frac{0.35d}{V}$</td>
<td>$\sqrt{\frac{2}{3}} \frac{1 \mu_1 \mu_2}{35 \pi d^3} \frac{0.35d}{V}$</td>
<td></td>
</tr>
<tr>
<td>CO-CO</td>
<td>7.1(-2) 9.4 2.0(-2)</td>
<td>1.7(-1) 1.9(1) 9.6(-2)</td>
<td></td>
</tr>
<tr>
<td>DC1-DC1</td>
<td>2.5 1.1(1) 8.5(-1)</td>
<td>6.6(-2) 2.0(1) 5.4(-2)</td>
<td></td>
</tr>
<tr>
<td>HCl-HCl</td>
<td>3.3 1.1(1) 1.1</td>
<td>9.3(-2) 2.0(1) 3.9(-2)</td>
<td></td>
</tr>
</tbody>
</table>

$^a(n) = x10^n$

$^b$ Units of $10^{-15}$ erg.

$^c$ Units of $10^{-15}$ sec.
be noted that the long and short range $r$'s differ by only a factor of two, independent of temperature.

The multipolar expressions are of considerable interest because they must describe the large impact behavior and because they include molecular anisotropy in a detailed fashion. The complete impact parameter expression for the transition probability can be written

$$P = \sum_{\ell} A_{\ell} I_{\ell}$$

where

$$A_{\ell} = \sum_{\ell_1 \ell_2} C(J_1 \ell_1 J_1'; 000)^2 C(J_2 \ell_2 J_2'; 000)^2 \times \frac{(2\ell)!}{(2\ell_1+1)!(2\ell_2+1)!} \left( \frac{Q_{\ell_1} Q_{\ell_2}}{d^{\ell} v h} \right)^2$$

$$I_{\ell}(b,v,\omega; \phi) = \frac{4\pi}{(2\ell+1)} d^{2\ell} v^2 \sum_{m} \int_{-\infty}^{\infty} dt \frac{Y_{1m}(\theta)}{r^{\ell+1}} e^{i\omega t}$$

$I_{\ell}(b,v,\omega) is the resonance function.

Sharma and Brau actually calculated $I_{\ell}$ only for $b \gg d$ and $b=0$. These two resonance functions for dipole dipole interactions are plotted as curves A and B in Figure VI - 1. Curve (a) reflects the oscillations in the interaction energy which occurs as the molecules translate past each other. If this anisotropy, $Y_{2m}(\theta, \phi=0)$, is left out as in curve (c) ($\theta$ equals a constant throughout the collision or the interaction is an average over angles) the resonance functions falls off more quickly. Curves (a) and (c) have been renormalized by $(b/d)^4$ so that they depend only on the Massey parameter $x \equiv \omega b/v$. 
Fig. VI-1. Effect of anisotropy on the $\Delta E_\nu$ dependence of $V - V$ energy transfer. $x = \Delta E_\nu b/v h$. (a) Sharma and Brau

$I_2(b \geq d, x) \cdot (b/d)^4$. (b) $I_2(b=0, x)$. (c) This is (a) without part of the anisotropy ($\theta=0$). See text for definition of $I_2(b, x)$. 
Fig. VI-1.
While the anisotropy decreases the effect on the energy discrepancy, it also decreases the "maximum action." This action can be found from $I_2(b,v,\omega=0)$. In Fig. VI-2, $I_2(b,v,\omega=0)$ is plotted for several approximate dipole dipole interactions which have been used. Curve (a) is for the isotropic potential ($\theta = \text{constant}$) used by Millikan and coworkers;\textsuperscript{17} (b) only the $m = 0$ term is included following Dillon and Stephenson;\textsuperscript{6} and (c) full dipole dipole interactions with hard sphere trajectories. The region $0 < b < d$ is here treated exactly, unlike Sharma and Brau.\textsuperscript{16} Curve (d) is the more exact result of Sharma and Hart\textsuperscript{17} using trajectories on a 6 - 12 potential and is dependent upon their choice of $v$ and 6 - 12 potential parameters. As seen, the more anisotropy included ($c > b > a$) the smaller the resonance function. This figure shows that these calculations are sensitive to the exact form of the potential and that not all "multipolar theories" such as that of Lev-on, et al.\textsuperscript{19} or Dillon and Stephenson\textsuperscript{6} are necessarily comparable.

The prime objections against both long and short range theories is that the relative motion and the rotational dynamics are not treated adequately. The following section deals with the latter of these questions. In Fig. VI-3 we depict four regimes of relative motion if a central 6 - 12 potential is adequate to describe the relative motion. It is apparent from the assumptions that multipolar expressions are probably appropriate for the large impact parameters where molecular attraction is unimportant (region I). On the other hand short range theories are appropriate at the high energy, small
Fig. VI-2. \( w=0 \) resonance functions for several dipolar interactions.

(a) Sharma and Brau\textsuperscript{16}, (b) Dillon and Stephenson\textsuperscript{6},
(c) Lev-on, et al.\textsuperscript{19}, (d) Sharma and Hart\textsuperscript{17} extension of Sharma and Brau.
Fig. VI-2.
Fig. VI-3. Regimes of scattering on a Lennard Jones 6-12 potential as a function of reduced energy (E/\varepsilon) and reduced impact parameter (b/d). Collisions above the heavy line experience repulsive interactions; in the shaded region, there is an attractive well in the effective potential, but the collision lies below the centrifugal barrier. See text for explanation of I - IV.
impact parameter region II. For collisions pairs such as CO - CO at
300 °K where the attractive well depth is only 60 - 90 cm\(^{-1}\) deep,\(^{20}\)
a combination of the short and long range theories is probably
adequate. In HCl or DCl however, the "spherically averaged" well
depth is ~200 cm\(^{-1}\), and most collisions are greatly influenced by the
attractive forces. Already in curve (d) in Fig. VI - 2 where the
collision energy is 1.35 times the well depth the effects of long
collisions can be seen on the energy transfer cross section. These
attractive (III) and orbiting (IV) regions have not been systematically
studied aside from Gait's curious calculation.\(^{21}\) Dillon and
Stephenson\(^{8}\) calculated various resonance functions in these regions
but there is some question as to what they actually calculated.\(^{15}\)

2. The Dillon and Stephenson and the First Magnus Approximations

As noted in the last section, one of the principal objections to
the first order perturbation treatments of vibrational energy transfer
is the inadequate treatment of the rotational dynamics. The short
range calculations ignore rotation altogether, and the multipolar
calculations allow only \(\Delta J = \pm 1\) or \(0, \pm 2\), etc. depending upon the
particular interaction. Early on, Sharma and Brau noted that even
\(\Delta J = \pm 1\) simultaneous transitions would bring some channels into
resonance and force others far away from resonance. The calculated
resonance functions have a decadic falloff of 20 to 50 cm\(^{-1}\) while the
energy involved with an average rotational transition is ~2\(\sqrt{\frac{B_e kT}{\epsilon}}\) \(\Delta J\).
Even for \(\Delta J = 1\) transitions of CO at 300°K this is 40 cm\(^{-1}\). Generally
rotation flattens out the first order perturbation resonance functions
in the region $\Delta E_v = 0 - 2\sqrt{\frac{1}{2} kT} \Delta J$. Outside this region the resonance function approaches the rotationless limit.

From line broadening data and from multipolar perturbation calculations we expect large $\Delta J$ transitions to occur at the small impact parameters where $V - V$ as well as $V - R, T$ predominately takes place. At present it is unknown what distribution of $\Delta J$'s occurs during rotationally or vibrationally inelastic collisions for strongly interacting collidants such as HCl - HCl.

Second order perturbation theory is not expected to be much more adequate than first order approximations in light of the very large first order rotational transition probabilities. A formalism which places no restrictions on the $\Delta J$'s but which conserves probability is needed. For this reason we have used the first Magnus approximation\(^2\) which is unitary and Dillon and Stephenson's theory\(^6,7\) which is approximately unitary. These two approaches were used since they should give approximately lower and upper limits on the $\Delta J$'s which occur. In fact the Dillon and Stephenson approximation does not give an upper limit, as will be discussed below.

Both approximations can be viewed as connecting formulas from a first order perturbation integral to an infinite order transition probability. We need to define two similar matrices

$$A_{fi}(\omega) \equiv \int_{-\infty}^{\infty} dt \, V_{fi}(t) \exp(i\omega t)/\hbar$$

$$A_{fi} \equiv A_{fi}(\omega_{fi})$$
The latter matrix gives the first order perturbation expression

\[ P_{fi} \sim |\delta_{fi} - iA_{fi}|^2 \]  (7)

The first Magnus approximation is simply the exponential of the first order perturbation integrals and is the analog of the exponential Born approximations recently investigated by Tarr and Rabitz.\textsuperscript{22,23}

\[ P_{fi} \sim |\langle f|\exp(-iA)|i\rangle|^2 \]  (8)

In this approximation, high order transition probabilities are the products of single step probabilities summed over all possible pathways.

The Dillon and Stephenson approximation is

\[ P_{fi} \sim |\langle f|\exp(-iA(\omega_{fi}))|i\rangle|^2 \]  (9)

This S matrix is not unitary except in the limit when all \( \omega_{fi} \) are equal:

\[ \sum_{f} |\langle f|\exp(-iA(\omega))|i\rangle|^2 = 1 \]

Again, the higher order transition probabilities are the products of single step probabilities summed over all possible pathways; but now the single steps are controlled by the overall energy discrepancy \( \omega_{fi} \) rather than the single step energy. Essentially the Dillon and Stephenson hypothesis is 1) resonant channels can be treated by the Sudden approximation\textsuperscript{2} \[ P_{fi} \sim |\langle f|\exp(-iA(\omega=0))|i\rangle|^2 \] and 2) for nonresonant channels all elements of \( A(\omega_{fi}) \) are small, hence first order perturbation theory is valid.
In this general form the Dillon and Stephenson approximation is much more time consuming than the first Magnus approximation since \( A(\omega_{fi}) \) must be computed and exponentiated (which requires that \( A(\omega_{fi}) \) be diagonalized) for each \( fi \) pair of states. The first Magnus approximation computes and exponentiates \( A \) only once for a given \( v \) and \( b \). In practice the Dillon and Stephenson method relies on an algebraic contraction of the exponential which is only possible because \( A(\omega) \) is independent of the energy level spacings.

Dillon and Stephenson specifically invoke a dipole dipole like force. It is linear in the vibrational coordinates but allows only quantum conserving \( V - V \) transfer. Starting with dipolar anisotropy, they change the potential by \( \phi \) averaging it in a space fixed reference frame; \( \theta \) changes during the collision. Unfortunately there were many typesetting and algebra errors in the initial paper. The original expressions were "corrected" in Ref. 7, although this correction also has typesetting errors which disagree with a private communication from Stephenson. In Eq. (19) of Ref. 7, the sum should run over \( \ell = 0 - \infty \). The angular momentum algebra can be performed straightforwardly, and Eq. (20) should read

\[
\sum_{J' J'M' M} \left| \langle j_1' j_2' J' M' M | S(\omega) | j_1 j_2 J M M \rangle \right|^2
\]

\[
= \sum_{n, k = -j}^j \Delta^j_{m' m} \Delta^j_{m m} \Delta^j_{m' k} \Delta^j_{m k}
\]

\[
\times \sum_{\ell = 0}^\infty j_\ell [nK_V(\omega)]\ j_\ell [kK_V(\omega)]\ (2\ell + 1)\ (2j_1 + 1)\ (2j_2 + 1)
\]

\[
\times \left( \begin{array}{cccc}
\ell & j_1 & j_2 & J_1 \ell \\
0 & 0 & 0 & 0
\end{array} \right)\ (2j_2 + 1)\ (2j_1 + 1)\ \left( \begin{array}{cccc}
j_2 \ell & j_1 \ell \ell j_2 \ell \\
0 & 0 & 0 & 0
\end{array} \right)^2
\]
This is the transition probability summed (not averaged) over all initial and final \( m \) states. (n.b. \( j, m, m', k, n \) are Dillon and Stephenson's special vibrational quantum numbers.) Contrary to Dillon and Stephenson's results, this expression does preserve detailed balancing. This is easily shown because Eq. (10) is symmetric with respect to interchange of the primed and unprimed quantum numbers.

The pure rotational transitions due to these same forces are rigorously included by replacing

\[ \ell K_V(\omega) \rightarrow \ell K_V(\omega) + k R(\omega)/2 \quad \ell = n, k \]

This differs from Ref. 7 where an ad hoc procedure is used to allow dipole dipole \( V-V \) transfer and dipole quadrupole \( R-R \) transfer.

We are only concerned with the influence of rotation (the \( \ell \) sum in Eq. 10), and not with the multiquantum vibrational transitions \( m,k \) sums. Taking the \( K_V \rightarrow 0 \) limit, only \( \Delta v_1, \Delta v_2 = \pm 1 \) transitions are allowed

\[
\begin{align*}
\left| \langle j_1 j_2 ^{\prime} (v_1 - 1) v_2 | S(\omega) | j_1 j_2 v_1 (v_2 - 1) \rangle \right|^2 \\
\sim v_1 v_2 \left[ K_V(\omega)/2 \right]^2 (2j_1 + 1)(2j_2 + 1) \\
x \left\{ \sum_{\ell=0}^{\infty} j_\ell^2 \left[ K_R(\omega)/2 \right]^2 (2\ell + 1) C(j_1 j_1 ^{\prime} ; 000)^2 \\
x C(j_2 j_2 ^{\prime} ; 000)^2 \right\}
\end{align*}
\]

(11)

In this limit the transition probability is the product of a first order pure vibrational transition probability, the rotational degeneracy, and a rotational resonance function \( R[K_R(\omega)] \) in brackets.
The rotational resonance function is plotted in Fig. VI-4 for various $\Delta j_1$, $\Delta j_2$'s using the classical limit Clebsch Gordon coefficients. It can be seen that if $K_R$ is small only $\Delta j_1$, $\Delta j_2 = \pm 1$ are allowed; if $K_R$ is very large then large $\Delta j_1$'s are allowed. Empirically it was found that

$$|\Delta j_1|, |\Delta j_2| \leq 0.8 K_R$$

In HCl - HCl collisions $K_R \ll 52$ while in CO - CO collisions $K_R < 0.5$ at room temperature. For most molecules Dillon and Stephenson's approximation suggests that only $\Delta j_1$'s $= \pm 1$ are important unless the permanent dipole moment is greater than $\sim 0.2$ debye.

Since this is only a model calculation $K_V$ and $K_R$ were approximated by simpler functions - exponentials. The $K$'s are defined and approximated as

$$K_T(\omega) \equiv \frac{(\mu_1 \mu_2) T}{\hbar} \int_{-\infty}^{\infty} \text{dt} \frac{\cos(\omega t) P_2(\cos \theta(t))}{R(t)^3}$$

$$\sim AT \exp(-k_T \Delta E)$$

where for $b=0$

$$A_T \sim 4\pi(\mu_1 \mu_2) T / \hbar d^3$$

$$k_T \sim 2\pi c T$$

$$T \sim 0.26 \text{ d/v}$$

As can be seen in Fig. VI-2, this is a fairly accurate representation of the $\omega$ dependence.

Using $A_V = 0.27$, $A_R = 52.0$, $k_V = k_R = 0.0264 \text{ cm}$ for HCl - HCl collisions we have plotted $(K_V/2)^2 R(\omega)$ against $\Delta E_{\text{total}} = \Delta E_V + \Delta E_R$.
Fig. VI-4. Dillon and Stephenson rotational resonance function $R(K_R)$. See text for definition.
Fig. VI-4.
for a thermal distribution of rotational states at 295 °K and for several values of $\Delta E_v$. This function is also a product of a pure vibrational part which falls off exponentially in $\Delta E_{\text{total}}$ as $k^{-1}$ and a rotational part. The rotational part is shown separately in Fig. VI-5b. This latter figure is very surprising, since there is a dip at $\Delta E_{\text{total}} \sim 0$ where the vibrational part has its maximum. This dip is a direct consequence of the Dillon and Stephenson hypothesis. When a given transition is resonant, it has (approximately) the transition probability of a sudden collision. In this limit the molecules have many possible final states, and the transition to any one of those is small. Because of this behavior the Dillon and Stephenson approximation underestimates the rates.

When all the partial probabilities in Fig. VI-5a are summed, the total (i.e. the rotationally averaged) probability does fall off much more slowly than the pure vibrational part as seen in Fig. VI-5c. Furthermore, the partial probabilities which contribute strongly include very large $\Delta j$ transitions.

The Magnus approximation per se does not allow a contraction over $m$ substates in a manner analogous to the Dillon and Stephenson procedure. Even for small molecules inclusion of all $m$ substates leads to matrices which are too large to exponentiate. As a result, we have used Rabitz's effect Hamiltonian method\textsuperscript{24} which replaces the $m$ dependent Hamiltonian with one which does not depend on $m$'s. The transition integral between rotational vibrational states for a dipolar force at $b=0$ is
Fig. VI-5. Dillon and Stephenson transition probability for HCl V - V transfer. (a) The rotationally averaged partial transition probability as a function of $\Delta E_{\text{total}}$. (b) The rotationally averaged, rotational resonance function $R(\omega)$ as a function of $\Delta E_{\text{total}}$. (c) The total transition probability for first order perturbation ($K_R \rightarrow 0$) and for Dillon and Stephenson. (c) is the sum of all the (a) transitions.
Fig. VI-5.
\[
\langle j_1' j_2' v_1' v_2' | A(\omega) | j_1 j_2 v_1 v_2 \rangle = -(v_1' v_2' | \mu_1 \mu_2 | v_1 v_2 ) \\
\times \{[j_1][j_2][j_1'][j_2']\}^{1/2} \left( \begin{array}{cc} j_1' & j_1 \\ 0 & 0 \end{array} \right) \left( \begin{array}{cc} j_2' & j_2 \\ 0 & 0 \end{array} \right) \\
\times 4(2/3)^{1/2} \int_{-\infty}^{\infty} \alpha \exp(i\omega t)/(h r^3)
\]

The integral is approximated by

\[
(\pi \tau /d^3) \exp(-\tau E/h)
\]

where \( \tau \sim 0.26 \ d/V \).

\[ [j_1] = 2j_1 + 1 \]

Even with this elimination of \( m \) substates, the computer quickly saturates. If \( n \) rotational states of each vibrator are included, the coupling of two vibrational manifolds leads to a \((2n^2) \times (2n^2)\) matrix which must be diagonalized. Only a few \( n=5 \) matrices were computed. The Dillon and Stephenson procedure easily allowed \( n=11 \). This corresponds to some \( 11^4 \) partial cross sections which had to be analyzed.

In Fig. VI-6 we compare the rovibrationally inelastic probabilities of the first Magnus and the Dillon and Stephenson procedures for physical parameters corresponding to HCl \( 1 + 0' + 0 + 1' \) exchange at 300 °K. For these small matrices, the first Magnus approximation is not completely converged, and the cross sections near the outer edge show small "reflection" effects. The Magnus predicts considerably smaller cross sections as expected and exhibits slightly different selection rules. The joint rotational states are labeled with two quantum numbers \( j_T = j_1 + j_2 \) and \( j_D = j_1 - j_2 \). The \( j_T \) quantum number was
Fig. VI-6. Rotational state dependence of the first Magnus and the Dillon and Stephenson treatments of HCl V - V energy transfer. The abscissa states are the initial states, ordinate states are the final states. The HCl resonance energy is viewed as a controllable variable and is exothermic. See text for definitions of $j_T$ and $j_D$. 
Fig. VI-6.
initially viewed as an important number, since there has been a great
deal of discussion as to whether low or high rotational states
contribute more strongly to exothermic vibrational transfer rates
(these respectively correspond to large $\Delta j_1$ and small $\Delta j_1$ transitions
to make the overall process resonant). With the small $\Delta E_v$'s considered
here, there is no strong correlation between rates and $j_T$.

Referring to Fig. VI - 6, the Magnus approximation tends to
allow transitions to more final states, although with smaller
probabilities. In the sense of filling phase space, the Magnus
approximation is more statistical. The Dillon and Stephenson
approximation as advertised shows strong overall resonance effects.

When $\Delta E_v$=0, the rotational transitions are confined to near the
diagonal ($\Delta E_R$ ~ 0). When $\Delta E_v = 200 \text{ cm}^{-1}$, $\Delta j=3$ transitions in both
molecules are highly probable. In a much more extensive investigation\textsuperscript{23}
of exponential approximations similar to the Magnus approximation,
it was demonstrated that $\Delta E_{\text{total}}$ was more important than $|\Delta j_1| + |\Delta j_2|$.\textsuperscript{\textsuperscript{23}}

This calculation confirms that $\Delta j_1$'s > 1 are important, and that
these transitions can strongly influence the overall dependence on $\Delta E_v$.
Tarr and Rabitz\textsuperscript{23} have shown effectively that exponential approximations
are better than first order perturbation theory, but begin to break
down when first order state to state probabilities are of the order
of unity. As noted, the Dillon and Stephenson approximation does not
appear to treat near resonant collisions very well. As a result, one
must conclude that more rigorous treatments of the rotational dynamics
are needed, perhaps of the sort discussed in section C.
3. **Exact Integration**

During the period when this work was performed there has been a shift away from time dependent methods except for purely classical scattering calculations. This largely is a consequence of the lack of energy and momentum conservation in time dependent calculations. This is especially disastrous for state to state V - R, T and R - R calculations. Time independent scattering methods have made great strides by reducing the number of effective channels in the calculation and by the use of the Gordon integration method.\(^{25}\)

As Rabitz and Gordon\(^{26}\) have pointed out the impact parameter method is primarily useful as a perturbation technique. The full time evolution equations of the collision system can be solved, but this is not much harder and less accurate than solving the time independent equations.

In this section I would like to point out that the impact parameter method used in the last two sections is only one of a set of semiclassical approximations. In fact any of the degrees of freedom and its conjugate variable can be treated either classically or quantally. As a consequence, the channel reduction methods developed for time independent calculations\(^{27}\) can be used for time dependent calculations. For vibrational energy transfer studies it would actually be more useful to treat all the rotational as well as the translational degrees of freedom classically as recently done by Poulsen and Billing.\(^{28}\) In point of fact the proper semiclassical equations developed below do conserve energy, but only in the sense
that the expectation value is constant. Hence, one still has the well known condition that accurate cross sections are calculated only for those channels where the change in internal energy is much less than the relative translational energy.\textsuperscript{2}

The great speed of the Gordon integration method\textsuperscript{25} for the second order $\nabla^2$ time independent scattering equations suggest that it may be a useful integration algorithm for the first order $\partial/\partial t$ time dependent equations. Below we give the appropriate time dependent expressions. These were implemented as a computer code to solve the one dimensional $V - T$ problem. In practice the method was not stable, and probabilities calculated for these very weak transitions were grossly too large. Reasons for this instability are discussed.

We begin with Schrödinger's Eq. for the time dependent scattering problem

$$H\Psi = [H_O(R) + H_1(\vec{r}) + V(R,\vec{r})]\Psi = -\frac{\hbar}{i} \frac{\partial}{\partial t} \Psi \quad (1)$$

We separate the Hamiltonian according to two sets of variables. The $R$ set is treated quantum mechanically, and the $\vec{r}$ set will be treated classically. Both sets of variables are taken such that the usual commutator relations hold for conjugate variables as well as the relations

$$[\vec{r},V] = 0 \quad [\vec{p},V] = -\nabla_{\vec{r}} V$$

These are the usual relations satisfied when the $\vec{r}$'s are spatial coordinates and $V$ is velocity independent. The variables $\vec{r}$ will usually be one or more relative translation coordinates, since these
most closely behave classically, but the following equations are general. We will need the Ehrenfest relations for \( r \) and its conjugate momentum \( \pi \)

\[
\frac{d}{dt} \langle r \rangle = -\frac{i}{\hbar} \langle [r, H] \rangle = -\frac{i}{\hbar} \langle [r, H_1] \rangle
\]

\[
\frac{d}{dt} \langle \pi \rangle = -\frac{i}{\hbar} \langle [\pi, H] \rangle = -\frac{i}{\hbar} \langle [\pi, H_1 + V(r, \bar{r})] \rangle
\]

and we will write the wavefunction in a "Born Oppenheimer" form

\[
\Psi = \phi(\bar{r}, t) \psi(\bar{r}, \bar{R}, t)
\]

If \( r \) behaves classically the Ehrenfest relations can be written

\[
\frac{d}{dt} \bar{r} = \{\bar{r}, \bar{H}_1\} = \nabla_\bar{r} \bar{H}_1
\]

\[
\frac{d}{dt} \bar{\pi} = \{\bar{\pi}, \bar{H}_1\} = \langle \psi(\bar{R}, t) | \nabla_\bar{r} V(\bar{r}, \bar{R}) | \psi(\bar{R}, t) \rangle
\]

\[
= -\nabla_\bar{r} \bar{H}_1 + \langle \psi(\bar{R}, \bar{R}) \rangle
\]

(13)

where \( \bar{r} \) and \( \bar{\pi} \) are the classical values of these variables. \( \psi(\bar{r}(t), \bar{R}, t) \) has been replaced by \( \psi(\bar{R}, t) \). These are simply the classical equations of motion for \( \bar{r} \) subject to the average force \( \langle \nabla_\bar{r} V \rangle \). In the usual impact parameter approximation the \( \bar{r} \) degrees of freedom evolve independently of \( \bar{R} \). The quantal equation of motion is the usual modified Schrodinger Eq.

\[
[H_0(\bar{R}) + V(\bar{r}, \bar{R}) + \frac{\hbar}{i} \frac{\partial}{\partial t} ] \psi(\bar{R}, t) = 0
\]

(14)
As noted above these equations do conserve energy in the sense that the expectation value of the total energy is constant. We define the total energy

\[ E_{\text{tot}} = \langle H \rangle \]

which in the semiclassical limit becomes

\[ E_{\text{tot}} = \hat{H}_1 + \langle \psi | H_0 | \psi \rangle + \langle \psi | V(\vec{r}) | \psi \rangle \]

Energy conservation is shown by taking the time derivative of these three terms and summing

\[
\frac{d}{dt} \hat{H}_1 = \nabla \cdot \hat{p}_1 + \nabla \cdot \hat{\mathbf{H}}_1 = -\nabla \cdot (\hat{p}_1 \cdot \nabla) + \langle \{V, H_1\} \rangle = -\langle \{V, H_1\} \rangle = -\left( \frac{dV}{dt} \right)
\]

\[
\frac{d}{dt} \langle \psi | H_0 | \psi \rangle = -\frac{i}{\hbar} \langle [H_0, V] \rangle
\]

\[
\frac{d}{dt} \langle \psi | V | \psi \rangle = -\frac{i}{\hbar} \langle [V, H_0] \rangle + \left( \frac{dV}{dt} \right)
\]

There have been several previous studies in which large numbers of coupled equations have been integrated in time. Nielsen and Gordon\textsuperscript{30} used local symmetry properties to integrate only Eq. (14). McKenzie\textsuperscript{31} has integrated Eqs. (13) and (14) with a brute force method.

The quantum mechanical equation is calculated by expanding \( \psi(R,t) \) into the solutions of \( H_0 \) and solving the coupled first order equations for the coefficients. Letting \( \mathbf{C} \) be the vector of expansion coefficients for a particular solution, Eq. (14) can be written as
\[
\left\{ \frac{\partial}{\partial t} + \frac{i}{\hbar} \left[ H_0 + V(\vec{r}(t)) \right] \right\} \mathbf{C} = 0
\] (15)

\(H_0\) and \(V\) are the matrix representations in this basis set, hence \(H_0\) is diagonal. The solution \(\mathbf{C}\) is highly oscillatory in time.

The essence of the Gordon method is to divide the potential into sections over which the effective potential, here \(H_0 + V\) is linear in time. Over this local interval the solution is known analytically. \(\mathbf{C}\) can be quickly propagated by jumping along a series of linear sections.

To be more specific, integrating from a point \((r_0, t_0)\) we initially diagonalize the effective potential

\[
M^{-1}(t_0) \left[ H_0 + V \right] M(t_0) = \tilde{K}(t_0)
\] (16)

Tildas will be used to indicate quantities in this diagonal reference frame. We replace Eq. (15) with a local diagonal equation

\[
\frac{\partial}{\partial t} + \frac{i}{\hbar} \left[ \tilde{K}(t_0) + (t-t_0) \tilde{K}_D(t_0) \right]
\]

where

\[
\tilde{K}_D = \text{diag} \left[ M^{-1}(t_0) V M(t_0) \right]
\]

The evolution operator in this frame is simply

\[
\tilde{U}(t,t_0) = \exp \left\{ -\frac{i}{\hbar} \left[ \tilde{K}(t_0) + \frac{\tilde{K}_D}{2} (t_0)(t-t_0) \right] (t-t_0) \right\}
\] (17)

The classical variables in principle should also be integrated over this interval. The total solution to Eq. (15) is then
The size of the steps are determined by the off diagonal elements of $\dot{\mathbf{K}}$ and by the nonlinear elements $\text{diag}[\mathbf{M}^{-1} \mathbf{V} \mathbf{M}]$. The largest of these elements is compared to the linear elements to determine the step size.

The time consuming part of the calculation is the diagonalization of the effective potential. However, these are a function of the velocity and of the local gradient. Since the local gradient is a function only of the relative separation, the diagonalization need only be computed once and saved for a given separation. Similarly, the largest off diagonal elements $[\mathbf{M}^{-1} \nabla \mathbf{M}]$ are stored.

This algorithm was applied to the now standard one dimensional $V - T$ problem (harmonic oscillator + atom with a exponential repulsive force). The relative separation was treated as the classical variable, the variator was quantized. The classical motion was treated two ways: 1) it was integrated simultaneously with the quantal motion as derived above. The step size was kept small enough that a Simpson integration was sufficient. 2) The classical motion was approximated by Sharp and Rapp's expression. Ten vibrational states were included, and the matrix diagonalization was performed by the IMSL version of Householder's symmetrical to tridiagonal transformation followed by the QR method.

It was found that the computed transition probabilities were many (5 - 7) orders of magnitude too large no matter how small the
integration step size or mass parameter. The larger the step size the smaller the transition probabilities.

The method appears to be unstable for the reasons discussed by Tarr and Rabitz in a different context. The difficulty is not so much one of instability, but of a step size criterion which is difficult to establish. In this calculation it is essential that \( \hat{K} \Delta t / h \) be determined to a precision much better than \( \hat{K} \Delta t^2 \), and both of these must be precise modulo \( 2\pi \). The basic instability comes about because \( H_0 \) is very large relative to \( V \). In this calculation \( \Delta t \) was determined by the criterion

\[
O(\tilde{K}) \gg \Delta t \ O(\tilde{K}) \sim \Delta t \ O(V) \ v/a
\]

To satisfy the precision requirements

\[
h \gg O(\tilde{K}) \ \Delta t \ O(\delta \tilde{K}/\tilde{K})
\]

Hence we are precision limited whenever

\[
O(\delta \tilde{K}/\tilde{K}) \ O(\tilde{K} \Delta t / h) > O(V/\tilde{K}) \quad (19)
\]

In these calculations the three factors in Eq. (19) are \( 10^{-3}, 10^2 \), and \( 5 \times 10^{-2} \) and we are precision limited. To exploit this integration method, a method must be available to determine the precision of \( \tilde{K} \).

The above estimate of the precision is based on computing the eigenvalues and eigenvectors for \( H_0 + V \), back transforming to give a quantity mathematically equivalent to it, and comparing the diagonal matrix elements. This is not an efficient method for determining the step size.
C. Rotationally Distorted Wave Approximation for Vibrational Energy Transfer

As pointed out in section B.1 of this chapter the first order perturbation V - V and especially V - R,T transfer probabilities for most molecules are considerably less than unity. Simultaneously however, the rotationally inelastic scattering probabilities are very large. In molecules such as those studied in Chap. III and IV the V - V transfer rates are less than 2% of gas kinetic while the rotational relaxation rates are 3 - 10 times gas kinetic. These are the usual conditions of vibrational energy transfer in small molecules: the molecular anisotropy leads to complex rotational behavior while the vibration is mildly perturbed.

It would appear that a rigorous description of vibrational energy transfer, if it can be treated perturbatively at all, should be expressed in a generalized distorted wave approximation in which the distorted waves are the rotationally inelastic waves. Clearly this approximation is still very difficult to calculate for diatom diatom collisions such as HCl - HBr, given the problems experienced in the calculation of H₂ - H₂ inelastic collisions. However, with the various channel reduction methods it is possible to perform such coupled channel calculations. A rotationally distorted wave approximation will not be appropriate for some strongly coupled systems such as HF - HF.

The essential purpose of approximations such as this is to produce a model which is accurate and calculable. If we consider the
dynamics between several vibrational manifolds with \(n_1, n_2, \ldots\)
rotational states in each manifold, the effort of a close coupled
calculation scales as \(27\)
\[(n_1 + n_2 + \ldots)^3\]

With the rotationally distorted wave calculation it is only
\[n_1^3 + n_2^3 + \ldots\]
or only \(n^3\) if manifolds are treated as rotationally identical. This
can be a very large reduction considering that for HCl - HCl collisions
there are approximately 10 J states (100 m states) thermally populated
per molecule or \(10^2\) J states (10^4 m states) per joint vibrational
manifold.

Gerber\(^{37}\) and Balint-Kurti and coworkers\(^{38}\) independent of this
work previously derived this "rotationally distorted wave" approxima-
tion, specifically suggesting that the sudden approximation be used
to obtain the rotational wave. The rotationally distorted wave
approximation will not be rederived here but is given as Eq. (9) in
Ref. 38.

Here we are only concerned with the errors involved in going
from the rotationally distorted wave approximation to the less
accurate "usual" distorted wave approximation. In the latter method,
first order perturbation matrix elements are computed between transla-
tional states distorted by a spherically symmetric potential. This is
the best possible first order perturbation calculation.
We will analyze the scattering problem from the close coupled point of view. The wave function is expanded in the internal and the angular - orbital wavefunctions. Schrödinger's Eq. becomes a matrix equation for the expansion coefficients dependent only on the relative separation of the collidants.

\[ \left( \frac{d^2}{dr^2} - \frac{k^2}{r^2} - k^2 \right) U = V U \]  

(19)

at a fixed collision energy and total angular momentum. Note that in this representation V has units of \((\text{distance})^{-2}\).

We are concerned with a potential which can be written as

\[ V = V_0 + V_1 + V_2 \]

where \(V_0\) allows only quasielastic scattering, \(V_1\) allows only rotationally inelastic scattering, and \(V_2\) allows rotationally and vibrationally inelastic scattering. There is no unique division of a given potential into these three terms since part of \(V_0\) may be added to \(V_1\) and \(V_1\) to \(V_2\) and still maintain the scattering conditions. From rotationally inelastic calculations, however, it appears best to minimize the amount of quasielastic potential in \(V_1\), etc.

There are three different solutions \(U_0, U_1, U_2\) to keep track of. These respectively satisfy the matrix equation (19) with transition potentials \(V_0, V_0 + V_1, \text{and} V_0 + V_1 + V_2\). We write the \(U_i\)'s as matrices in which each column vector corresponds to a different initial entrance channel, \(U_0\) is diagonal. Each \(U_i\) must satisfy the asymptotic boundary conditions.
\[ U_i(r) \xrightarrow{r \to \infty} \sin(kr - \frac{\ell \pi}{2}) - \frac{1}{2} \frac{1}{\sqrt{k}} \exp[i(kr - \frac{\ell \pi}{2})] T_i \frac{1}{\sqrt{k}} \]  

(20)

Note that \( U_i \) and \( T_i \) are unitless. This expression has only one interpretation since \( k \) and \( \ell \) and are diagonal. It can be shown that

\[
T_i = T_{i-1} + \frac{2}{\sqrt{k}} \int_0^\infty dr \, U_{i-1}^T(r) \, V_i(r) \, U_i(r) \, \frac{1}{\sqrt{k}}
\]

(21)

where \( t \) denotes the matrix transpose. The generalized notion of the distorted wave approximation is to replace \( U_i(r) \) by \( U_{i-1}(r) \) in this expression. The rotationally distorted wave approximation is

\[
T_{RDW}^2 = T_1 + \frac{2}{\sqrt{k}} \int_0^\infty dr \, U_1^T \, V_2 \, U_1 \, \frac{1}{\sqrt{k}}
\]

(22)

It is straightforward to show the fashion in which this differs from the more familiar distorted wave approximation in which only the translationally distorted wave states are used

\[
T_{TDW}^2 = T_0 + \frac{2}{\sqrt{k}} \int_0^\infty dr \, U_0^T (V_1 + V_2) \, U_0 \, \frac{1}{\sqrt{k}}
\]

(23)

Expanding \( T_1 \) in Eq. (22) these two approximations differ by

\[
T_{RDW}^2 - T_{TDW}^2 = \frac{2}{\sqrt{k}} \int_0^\infty dr \, \{ U_1^T V_2 U_1 - U_0^T V_0 U_0 \} \, \frac{1}{\sqrt{k}}
\]
We can express $U_1(r)$ by the usual integral representation

$$U_1(r) = U_0(r) - \frac{1}{k} \left\{ [U_0(r) \int_0^\infty dr' U_0^{(+)} V_1 U_1] [U_0^{(+)} \int_0^r dr' U_0 V_1 U_1] \right\}$$

where $U_0^{(+)}$ is the outgoing wave and to agree with the normalization in Eq. (20) must have the asymptotic conditions

$$U_0^{(+)}(r) \rightarrow \exp\left[i(kr - \lambda \pi/2)\right]$$

In this representation there are two principal levels of approximation intermediate to performing the entire rotationally inelastic scattering and completely ignoring it.

(1) We can include the effect of $V_1$ to first order

$$U_1(r) \sim U_0(r) - \frac{1}{k} \left[ U_0(r) \int_0^\infty dr' U_0^{(+)} V_1 U_0^{(+)} \right] + U_0^{(+)}(r) \int_0^r dr' U_0 V_1 U_0^{(+)}$$

Even with this simplification $U_0$ and $U_0^{(+)}$ must be calculated. Sharma et al.\textsuperscript{38} have performed these second order distorted wave calculations with multipolar forces.

(2) We can further restrict that only $U_0$ is used, i.e. that the asymptotic wave which is 90° out of phase with $U_0$ is ignored.

$$U_1(r) \sim U_0(r) \left[ 1 - \frac{i}{k} \int_0^\infty dr' U_0 V_1 U_0 \right]$$
This simplification is equally severe since $U_0(r)$ does not provide a complete set of radial basis functions, hence the actual phase in each channel can not be represented. Since in some collision systems the distance of closest approach is largely determined by the anisotropic terms, the wave function based on the spherical part of the potential $V_0$ can not reproduce the actual closeness of approach. Equation (26) does include the population changes due to rotational transitions but in a multiplicative manner:

$$T = T_{1}^{TDW} + S_1 \left( \int_0^\infty \text{d}r \, U_0 V_2 U_0 \right) S_1$$

From the above discussion it is very evident that on a detailed rotational state to rotational state basis only very large calculations will yield "converged" cross section for vibrationally inelastic collisions. From Section B.1 and 2 we have shown that the moment of inertia and dipole moment do greatly influence rotationally averaged $V-V$ rates. We have not answered the hardest but most important question as to what level of approximation will yield accurate rotationally averaged rates.
CHAPTER VI. REFERENCES


Also see Ref. 18.

35. International Mathematics and Statistics Library.


Optoacoustic Spectroscopy

1. Introduction

Spectrophones have been extensively studied and developed over the last decade. This renaissance of the optoacoustic detector has paralleled the development of the laser as has its kindred method, fluorescence excitation. While the great sensitivity of the method has been realized, conflicting claims and projections have been made for its ultimate sensitivity. Furthermore, there has been some duplicated effort for lack of a general theoretical description of the many regimes in which spectrophones can be and have been operated. In a fashion, this confusion parallels the mistakes made during the fifties when the spectrophone was used to measure V - T, R energy transfer.¹

Optoacoustic spectroscopy is the complement of fluorescence excitation spectroscopy.² (See Figure 1) In both a CW or pulsed laser is tuned through a spectroscopic transition. If the excited state fluoresces or phosphoresces with good efficiency, the radiated photon can be a very sensitive measure of the absorption. If, on the other hand, the excitation energy is degraded to heat, the resulting pressure wave can be detected. In both methods sensitivity increases with laser power until saturation although in practice they frequently are limited by scattered light or stray absorption. Also, both methods give only indirect information about the initial absorption. Relaxation spreads the excitation over many states, and reexcitation processes (e.g. self absorption) can occur, obscuring the nature of the initial
There are three separate problems involved in the transformation of the light absorption into a pressure modulated electrical signal; 1) the initial absorption and energy relaxation processes which are molecular phenomena; 2) the hydrodynamic transfer of the spatially and temporally varying heating throughout a confined chamber; and 3) the mechanical - electrical transduction necessary to detect the pressure variations in the cell. The processes can usefully be viewed in terms of frequency response and frequency - dependent noise plots. Note that pulsed excitation can be viewed as a very broad bandwidth experiment. The filtering effects of the above three processes are listed in Table 1. These will be discussed quantitatively in later sections.

Spectrophones are classified according to the regime of hydrodynamic transport. They are either resonant or nonresonant. The resonant phones detect pressure oscillations at one of the resonant acoustic frequencies of the cell. With a pulsed laser the resonant spectrophone gives rise to a long, damped, oscillatory signal. The oscillation can be electronically removed, and the pulse can be integrated. Nonresonant spectrophones have spatial dimensions sufficiently small such that the acoustic resonances are beyond the range of the microphone element. The heat deposited in the gas is distributed by thermal diffusion. This low frequency response of the spectrophone will be referred to as the "zero frequency" resonance.
Fig. A-1. Schematic illustrations of (a) Optoacoustic and (b) Resonance Fluorescence spectroscopy.
(a) Spectrophone

(b) Resonance Fluorescence

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Fig. A-1.
Table 1. Spectrophone parameters and their effect on the frequency response.

<table>
<thead>
<tr>
<th></th>
<th>Filter effect</th>
<th>Frequency (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Laser Beam Size</td>
<td>low pass</td>
<td>( \frac{\text{sound velocity}}{\text{beam width}} )</td>
</tr>
<tr>
<td>Energy Relaxation Rate + Molecular diffusion</td>
<td>low pass</td>
<td>( \frac{1}{2\pi\rho T \text{relax}} )</td>
</tr>
<tr>
<td>2. Cavity: acoustic resonances thermal diffusion</td>
<td>isolated resonances low pass</td>
<td>integer ( \frac{\text{sound velocity}}{2 \times \text{cell dimer}} )</td>
</tr>
<tr>
<td>3. Microphone: mechanical capacitance Preamp</td>
<td>low pass high pass low pass</td>
<td>4-20 KHz .1-20 Hz (match microphone)</td>
</tr>
</tbody>
</table>
Spectrophones used to measure vibrational relaxation rates have been nonresonant. The small cell is filled to a pressure such that the relaxation processes occur on a time scale ($\approx l/\text{pressure}$) long compared to the damping time of the resonant waves ($\approx \text{cell dimensions}$) but short relative to the thermal and molecular diffusion time. In terms of band passes, these spectrophones work way down on the cavity's zero frequency acoustic mode. This is also the regime in which thermal lensing experiments are performed.

There are fewer restrictions on the design of spectrophones for absorption detection at high pressures (> 100 torr). Theoretically, nonresonant spectrophones have a higher detectivity. The optimum geometry is a long, small bore cell approaching the minimum focussing of the laser beam. Primarily this minimizes the heated volume. The length, which allows long cylindrical, high capacitance microphones, has a minor effect. These large area microphones are not more sensitive, they simply have a lower electrical impedance $1/\text{i}\omega C_m$. Stray signals due to window absorption are decreased by a longer cell with acoustic baffles, although using CW lasers the window absorption is best minimized by wavelength modulation rather than intensity modulation. The slower the modulation the higher the peak to peak pressure modulation.

In recent development Kerr and Atwood$^2$ and Kreuzer$^3$ made valuable contributions to the design of nonresonant phones. More recently Kreuzer$^4$ has given a still more refined treatment which includes the change in cell volume by the motion of the microphone diaphragm.
He concludes that with a perfect amplifier, S/N is proportional to the area of the microphone. Physically this happens because the thermal fluctuation of the diaphragm goes as area\(^{-1}\). Patel and Kerl\(^5\) have introduced the use of miniature microphones which have better noise characteristics than Kreuzer style\(^3\) microphones.

The above prescription is not universal, however. Generally the cell cross section is limited by microphone size and beam alignment difficulties. Furthermore, the noise is usually amplifier limited, and at present comparable performance is obtained from the small nonresonant phones and from larger resonant ones. The latter were reintroduced by Dewey, Kamm, and Hackett\(^6\) in 1973. At present typical preamps allow pressures of \(10^{-4}\) N/m\(^2\) (10\(^{-6}\) torr) with a 20 KHz bandwidth to be measured. The lowest limit of detection reported\(^5\) is

\[
\text{molecular density} \times \text{absorption cross section} \times \text{peak power} \times \text{pulse length} \times \frac{C_{\sqrt{k}}}{\text{cell cross section}}
\]

equal to \(3 \times 10^{-7}\) N/m\(^2\) with a narrow bandwidth. Rough detection limits with available lasers are \(\sim 1\) ppb at 1 atm total pressure.

Resonant spectrophones and low pressure Doppler limited spectroscopy raise many more design questions. For resonant phones the sensitivity is proportional to the width (\(\omega_j/\Omega\)) of the resonance. The width, however, depends upon surface and bulk "dissipation". At low pressures (\(\sim 10\) torr) relaxation and diffusion rates become significant. At these pressures there are many variables to be considered if the signal shape or magnitude is to be interpreted
quantitatively. In general, at a fixed total pressure the signal is linearly dependent on absorbed energy. However, the signal vs. pressure at fixed laser intensity is not linear, or more generally, does not follow a Beer's law. This comes about since both microphone sensitivity and cavity Q are pressure dependent.

In the sections below we develop a general framework which includes all the relaxation - transport kinetics and which can be used for both pulsed and chopped CW optical excitation. A unified treatment establishes that the pressure response is a simple convolution of the energy relaxation of the gas and the acoustic response function of the cell. We will then examine the acoustic response of a cylindrical cell. In Section 4 we consider pressure transducers and the limits of their performance. In section 5 we discuss trends toward optimal spectrophone (i.e. combined chamber and transducer) designs and the performance of existing devices.

2. Relaxation - Transport Equations in Gases

In this section, the general relaxation-transport equations for a gas are given and discussed. Such a general discussion, which has been outlined by several authors, has a much broader application in laser state selected experiments than just optoacoustic spectroscopy. Most closely related is thermal lensing which measures density changes via refractive index changes rather than pressure changes. The general description would be needed to describe those fluorescence experiments which exhibit diffusion of excited species or shock induced modulation of fluorescence. At low pressures, a combined gas
transport - wall deactivation occurs from which wall deactivation probabilities can be extracted. \(^{22,23}\)

The working equations are the familiar Navier Stokes hydrodynamic equations. It is important to realize that these are rigorously related down to molecular potentials for fluids with densities \(< 10^{20}/\text{cm}^3\) close to equilibrium.

The general problem of relaxation of a fluid to equilibrium is rather involved. Half of Hirschfelder, et als., monograph \(^8\) is devoted to this question. The approach uses the general statistical mechanical method. 1) Liouville's classical equation of motion \(^9\) or Heisenberg's time evolution operator \(^10\) is applied to an ensemble of systems. \(^11\) Generally the ensemble is constrained to be canonical (conservation of mass but allowable energy exchange). Further, 2) the statistical mechanical (ergodic) hypothesis is invoked: the value of an observable should equal the ensemble average. \(^12\) Together these assumptions give an equation for the time and space evolution of the single particle distribution function or of the observables themselves. These equations are differo-integral and nonlinear. A general solution would have to be numerical and would be very involved.

To proceed farther it is necessary to establish a potential function for the molecular interaction. 3) In the very early work only binary collisions were allowed (Boltzmann Eq.) \(^13\) but this restriction has been eased to treat regimes where only two body potentials are present (Kirkwood's theory). \(^14\) In this way dense gases can be treated.
Generally we are interested in at most the first three moments of the velocity distribution. These correspond to the density, mean velocity, and mean translational energy. Hirschfelder, et al. refer to the two sets of differential-integral equations for the time evolution of these quantities derived from the two treatments as the Enskog and Kirkwood "equations of change". They are formally the same.\textsuperscript{14} These equations are variously known as the continuity equation; the Newton or momentum conservation equation; and the energy conservation equation. Each specie \( i \) is a single rovibronic state.

\[
\begin{align*}
\frac{\partial n_i}{\partial t} &= -\nabla \cdot n_i (\mathbf{v} + \mathbf{\bar{v}}_i) + R_i \\
\frac{\partial \rho}{\partial t} &= -\nabla \cdot \rho \mathbf{v} \\
\frac{\partial \rho \mathbf{v}}{\partial t} &= -\nabla \cdot (\rho \mathbf{v}) - \nabla \cdot \mathbf{p} + \sum_i n_i \mathbf{x}_i \\
\frac{\partial \mathbf{v}}{\partial t} &= -\nabla \cdot \rho \mathbf{u} - \nabla \cdot \mathbf{q} - \frac{\rho}{\rho} \nabla \cdot \mathbf{v} + \sum_i n_i \mathbf{x}_i \cdot \mathbf{\bar{v}}_i
\end{align*}
\]

We use the notation\textsuperscript{15}

\( n_i \) = number density of specie \( i \)

\( m_i \) = molecular mass of specie \( i \)

\( n \) = total number density

\( \rho \) = total mass density = \( \sum_i m_i n_i \)

\( \mathbf{\bar{v}}_i \) = mean velocity of specie \( i \)

\( \mathbf{v} \) = mass averaged velocity of all species = \( \frac{1}{\rho} \sum_i m_i n_i \mathbf{\bar{v}}_i \)

\( \mathbf{\bar{v}}_i \) = peculiar velocity = \( \mathbf{v}_i - \mathbf{v} \)
\( \varepsilon_i \) = internal energy per molecule of specie \( i \)

\( u \) = total energy density

\( T = \text{temperature} = \frac{3}{kn} \sum_i m_i n_i \bar{v}_i^2 \)

\( p \) = pressure tensor = \( \sum_i n_i m_i \bar{v}_i \bar{v}_i \)

\( q = \text{heat flux} = \sum_i n_i \left( \frac{m_i}{2} \bar{v}_i^2 + \varepsilon_i \bar{v}_i \right) \).

\( X_i \) = external force per molecule of specie \( i \)

\( R_i \) = rate of inelastic scattering

These are general conservation equations and have the form

\[
\frac{\partial \vec{f}}{\partial t} = -\nabla \cdot (\vec{f} \nabla) - \nabla \cdot \vec{j} + \text{relaxation reaction source terms}
\]

where

\[
\vec{j} \equiv (\vec{f} - \bar{f}) \ (\vec{y} - \bar{y})
\]

Hirschfelder, et al. refer to \( \vec{j} \) as the flux vector. Here we have explicitly indicated that \( \bar{v} \) is the average velocity. The flux vector introduces a higher moment of the velocity distribution into the time dependence of \( f \). If \( \vec{f} \) is a vector (three components) then \( \vec{f} \vec{v} \) would be a 3 x 3 matrix. In the case of momentum \( (\vec{f} = m \vec{v}) \), the flux must be rotationally invariant and forms a tensor \( (\vec{j}) \).

The integral nature of these equations is hidden since the distribution function involved in the averages is not written explicitly. The nonlinear behavior however is obvious, and these equations have not been solved analytically.

To obtain an analytic approximation the one particle distribution is expanded in a power series (Enskog series), and perturbation
theory is performed on the Boltzmann Eq.\textsuperscript{16} This linearizes the Boltzmann Eq. The first order perturbation approximation gives the Navier Stokes Eqs. This regime is generally known as the linear region of irreversible thermodynamics. This fourth assumption 4) we have made can be stated as a weak excitation or small departure from equilibrium criterion. This requires, among many things, that the distance scale (e.g. acoustic wavelength) must be large relative to the mean free path. The fluid must appear to be a continuum.

It should be recognized that since Hirschfelder, et al.'s monograph great advances have been made in understanding the quantum Liouville Eq.\textsuperscript{17} and more general solutions to the Boltzmann Eq. When one specie is relaxing in a bath gas, the Boltzmann Eq. is a master equation which is linear.\textsuperscript{18} Under some conditions this is a simple second order differential Fokker Planck Eq. On the other hand, there are now many observable phenomenon which require the full Boltzmann Eq. or quantal treatments (optical nutation, self-induced transparency).\textsuperscript{19}

In the linear, Chapman - Enskog region expressions are found for the fluxes corresponding to the diffusion velocity, pressure tensor, and the heat flux. If there are no external forces

\[ \dot{\mathbf{v}}_i = \frac{n_i}{n_i \rho} \sum_j m_{ij} D_{ij} \left[ \nabla \left( \frac{n_j}{n} \right) + \frac{n_j}{n} - \frac{m_{ij} \mathbf{v}_i}{\rho} \right] \nabla \ln \rho + \nabla \left( \frac{1}{n_i m_i} D_i^T \nabla \ln T \right) \]  \hfill (5)

\[ \rho = \rho^0 - nD^0 \]  \hfill (6)
\[ q = -\lambda \nabla T + \sum_i n_i \frac{\nabla \cdot \vec{v}_i}{\nabla \cdot \vec{v}_i} (\varepsilon_i + \frac{5}{2} kT) + \frac{kT}{n} \sum_{ij} \frac{n_i D_{ij}^T (\vec{v}_i - \vec{v}_j)}{m_i D_{ij}} \]  

(7)

where

\[ (D)_{ij} = \text{shear tensor} = \begin{cases} -2 \frac{\partial \nabla i}{\partial x_j} + \frac{2}{3} \nabla \nabla \cdot \nabla & j \neq k \\ \frac{\partial \nabla i}{\partial x_k} & j = k \end{cases} \]

or

\[ \nabla \cdot (D) = \frac{4}{3} \nabla (\nabla \cdot \nabla) - \nabla \times (\nabla \times \nabla) \]

and

\[ p = \text{hydrostatic pressure} = nkT \]

\[ \eta = \text{shear viscosity} \]

\[ \eta' = \text{bulk viscosity} \]

\[ \lambda = \text{thermal conductivity} \]

\[ D_{ij}^T = \text{mutual thermal diffusion coefficient} \]

\[ D_{ij} = \text{diffusion coefficient} \]

\[ \gamma = \frac{C_p}{C_v} \]

\[ C_p, C_v = \text{constant pressure, volume heat capacity/molecule} \]

\[ \varepsilon_i = \text{energy of state } i \]

\[ k_{ij} = \text{thermal averaged rate constant from } j \to i \]

\[ K_T = \text{isothermal compressibility} \]

\[ \beta = \text{isobaric coefficient of thermal expansion} \]

\[ c = \text{speed of sound} = kT/m \]

\[ K = \text{thermal diffusion constant} = \lambda/\eta C_v \]

\[ K' = \text{modified thermal diffusion constant (Eq. 22).} \]
Morse and Ingard\textsuperscript{20} and Herzfeld and Litovitz\textsuperscript{21} have discussed the stress tensor.

In addition to the Chapman - Enskog restriction to near equilibrium we will also require 5) that all the gradients are small. This allows the combined conservation (Eq. 1-4) and flux (Eq. 5-7) equations to be linearized. We express quantities as the equilibrium value plus a small deviation. For example

\[ n_i \rightarrow \bar{n}_i + \delta n_i \]

Removing common terms, replacing \( u \), \( q \), and \( p \) by their definitions, and assuming 6) the gas is stationary, \((\gamma = 0)\)

\[
\frac{\partial \bar{n}_i}{\partial t} = - \bar{n}_i \nabla \cdot (\bar{v}_i + \bar{v}_i) + R_i \tag{8}
\]

\[
\frac{\partial \rho}{\partial t} = - \bar{\rho} \nabla \cdot \bar{v} \tag{9}
\]

\[
- \rho \frac{\partial}{\partial t} \bar{v}_l = - \nabla p + \frac{4}{3} \eta \nabla^2 \bar{v}_l \tag{10}
\]

\[
- \rho \frac{\partial}{\partial t} \bar{v}^t = - \eta \nabla \times (\nabla \times \bar{v}^t) \tag{11}
\]

\[
\frac{5}{2} \bar{n} \frac{\partial T}{\partial t} - \frac{\delta p}{\delta t} = - \sum_i (\epsilon_i + \frac{5}{2} kT) R_i + \lambda \nabla^2 T \tag{12}
\]

We have separated the velocity into two components

\[ \bar{v} = \bar{v}_l + \bar{v}^t \]

where

\[ \nabla \cdot \bar{v}^t = 0 \]

\[ \nabla \times \bar{v}_l = 0 \]
\( v^l \) is the usual longitudinal compressional wave. \( v^t \) is a transverse wave arising from the shearing (viscous forces) such as occurs when a wave travels parallel to a wall.

This treatment differs from Morse and Ingard's in that specific account has been made of the internal degrees of freedom. To do so we used Chapman and Enskog's treatment which applies only to a dilute - perfect - gas. If we further require that no reactions occur and that the gas is a uniform mixture,

\[
\frac{D_i T}{\partial t} = 0
\]

\[
\sum_i R_i = 0
\]

\[
\rho = \rho_0
\]

and the hydrodynamic equations simplify to

\[
\frac{\partial n_i}{\partial t} = \frac{\tilde{n}_i}{\tilde{n}} \frac{\partial \tilde{n}}{\partial t} + D \nabla^2 n_j + R_i [n_j, \tilde{n}, T]
\]

(13)

\[
\left( \frac{\partial^2}{\partial t^2} - \frac{4}{3} \eta \nabla^2 \frac{\partial}{\partial t} \right) \rho_0 n = \nabla^2 p
\]

(14)

\[
\frac{\partial}{\partial t} \left( \frac{5}{2} \eta \nabla T - p \right) = - \sum_i \epsilon_i R_i + \lambda \nabla^2 T
\]

(15)

\( n_i \) undergoes diffusion modulated by the density \( n \) and temperature oscillation. \( n - T - p \) follow the usual sound equations except for an additional heat source due to energy relaxation

\[
\sum_i \epsilon_i R_i
\]
Eq. 14 is viewed as an adiabatic acoustic wave while Eq. 15 describes a thermal diffusion wave.

A "wave" is the combined $n - T - p$ functions which satisfy the Eqs. 14 and 15. The equations can be combined to give a single fourth-order-in-space equation on $p$. Of the four solutions, two are divergent. The two linearly-independent-in-space, bounded solutions are the "waves".

The relaxation term $R_i(T,n_j)$ is a function of $T$ and the densities. Due to the restriction to near-equilibrium, the relaxation process is linear and can be written as

$$R_i = \sum_j \bar{n} \bar{k}_{ij} n_j + \bar{n} \frac{\partial k_{ij}}{\partial T} \bar{n}_j T$$

$$= \sum_i \bar{n} \bar{k}_{ij} (n_j - \frac{\partial n_j}{\partial T} T)$$  \hspace{1cm} (16)

Note that $T$ is the difference between the transient temperature and the steady state temperature $\bar{T}$.

The waves must satisfy certain boundary conditions. This is especially important in spectrophones where standing waves of only one or two periods occur. The metal walls are stiff and infinitely viscous. There is no motion of the gas relative to the wall $v = 0$

Metal walls are highly conductive, and the wall is isothermal $T = 0$. These conditions can be reexpressed as a pressure boundary condition.

In the linear regime of Eqs. 13-15
\[-\rho \frac{\partial \mathbf{v}}{\partial t} = -\nabla [p + \frac{4}{3} \frac{\eta}{\rho} \frac{\partial}{\partial t} (p - \frac{\rho}{\bar{T}} T)] - \eta \nabla \times (\nabla \times \mathbf{v}) \]

Therefore, at the wall

\[\nabla (1 + \frac{4}{3} \eta \frac{\partial}{\partial t}) p = \eta \nabla \times (\nabla \times \mathbf{v}) \]  

(17)

The viscosity is small, so that this becomes

\[\nabla p = 0\]

There is also a boundary condition on the diffusing species. At the wall, relaxation may or may not take place. Measured deactivation probabilities range over \(10^{-4} - 1\). The surface boundary condition is

\[\text{diffusion gradient of } i = \text{net flux of } i\]

Written algebraically

\[\mathbf{d} \nabla n_i \cdot \mathbf{d} \hat{\sigma} = \sum_{j} \alpha_{ij} \left[ \frac{1}{4} \eta \mathbf{v}_{j} - \frac{1}{2} \mathbf{d} \nabla n_{j} \cdot \mathbf{d} \hat{\sigma} \right] \]  

(18)

\(\mathbf{d} \hat{\sigma}\) is the surface normal vector, and \(\mathbf{v}_{j}\) is the average speed of specie \(j\). The deactivation coefficient is

\[\alpha_{ij} = \text{(probability of } j \to i \text{ transition)}\]

\[\alpha_{ii} = -(\text{total probability out of state } i)\]

Equations 13-16 with boundary conditions 17-18 form a rigorous basis for the transport-relaxation kinetics in the small signal limit. However, this scheme contains much more complexity than can be resolved in the spectrophone or thermal lensing experiment. Many of the degrees of freedom are relaxed, especially rotation. In classical, continuous fluid treatment \(R\) does not appear but is sublimated into
a frequency dependent heat capacity and bulk viscosity. In equations 14 and 15

\[
\frac{4}{3} \eta + \frac{4}{3} \eta + \eta'(\nu)
\]

\[
\frac{5}{2} \bar{\eta} + \bar{\eta} C_p(\nu)
\]

\[
n = \frac{1}{kT} (p - \frac{\tilde{\rho}}{T} T) + \bar{\eta}(K_{ij}^2 - \beta T)
\]

Equations 14 and 15 become the usual sound equations

\[
\left( \frac{\partial^2}{\partial t^2} - (\frac{4}{3} \eta + \eta') \nabla^2 \frac{\partial}{\partial t} \right) (p - \frac{\tilde{\rho}}{K_{ij}^2} T) = \frac{C^2}{\gamma} \nabla^2 p
\]

(19)

\[
\frac{\partial}{\partial t} (\bar{\eta} C_p T - p) = \lambda \nabla^2 T - \sum \epsilon_i R_i
\]

(20)

At this level of approximation the diffusion equation is decoupled from the sound equation except for the heating term.

\[
\bar{n}_i = 0
\]

\[
\frac{\partial n_i}{\partial T} = 0
\]

or

\[
\frac{\partial n_i}{\partial t} = D \nabla^2 n_i + R_i(n_i)
\]

(21)

3. Pressure Response of a Closed Cell

a. Equations of Motion

Prior to giving a solution to the transport equations it will be useful to have a qualitative understanding of the processes. The energy from the heat source is dissipated by three mechanisms. If
the energy relaxes uniformly or slowly, no pressure gradients are formed. Due to the walls there will always be temperature gradients which are dissipated slowly by 1) thermal diffusion. More frequently however, pressure gradients are generated during the relaxation process. Compression and expansion in gases is nearly adiabatic, so that the pressure gradients lead to propagating $n - T - p$ waves which are weakly dissipated by 2) viscosity and heat conduction. These dissipative forces, in gases, are very small and usually negligible for the propagating waves. The chief dissipative force for these waves is 3) the cell wall. The walls have a very high thermal conductivity which quenches the $T$ oscillation. The walls are also sticky, and all motion parallel to the wall is lost.

This concern for dissipation mechanisms is fundamental to spectrophone operation. The spectrophone cavity acts as a "pressure storage" medium. The slower the dissipation, the higher the peak response. The "storage times" are short in an absolute sense, but may be hundreds of times longer than the oscillation period of the cavity.

Morse and Ingard's book\textsuperscript{20} is the standard reference for solving the transport equations. Their usage leads to some conceptual difficulties since allowance is not made for heat sources, and the waves are presumed to be either freely propagating or standing, rather than mixed.

The transport equations (Eqs. 19-20) are second order and coupled so that there must be four solutions. Two of these are
divergent and of no interest. The solutions are subject to the boundary conditions

\[ T = 0 \]
\[ \nabla p = 0 \]

There is one simple solution, which Morse and Ingard refer to as the thermal wave. It follows a diffusion equation.

\[
\frac{\partial T}{\partial t} - K' \nabla^2 T = - \sum \frac{\epsilon_i R_i}{C_p} \]
\[ \nabla p = 0 \text{ everywhere} \quad (22) \]

\[ p = \bar{n}R \frac{1}{V} \int \frac{1}{v} \, d^3 r \quad T \]

\[ K' = (\lambda - \frac{4}{3} \eta \frac{\beta}{m \bar{n} K_T})/\bar{n}C_p \]

The expression for \( p \) is simpler here because the volume is bounded.†

Contrary to Morse and Ingard's discussion, in the present situation the thermal wave is not negligible in the bulk of the gas since there is a local heat source.

The second equation, for the propagation wave, is approximate although quite accurate. Substituting Eq. 20 for \( T \) in Eq. 21

\[
\left( \frac{\partial^2}{\partial t^2} - c^2 \nabla^2 \right) p + \sum \frac{\epsilon_i R_i}{(C_v/k)} = \nabla^2 \frac{\partial}{\partial t} \left[ \frac{4}{3} \frac{\gamma n}{m \bar{n}} p - \left( \frac{k \lambda}{C_v} - \frac{4}{3} \frac{\gamma k n}{m} \right) T \right] \]

† This differs from Morse and Ingard's solution in that \( p \neq 0 \) in zero order here. Kerr and Atwood² solve this equation but erroneously use \( K \) rather than \( K' \). Also, contrary to their claim,

\[
\frac{\delta p}{p} \neq \frac{\delta T}{T} \]

but

\[
\int d^3 n = 0 = \bar{n} \int d^3 \left( K_T p - \beta T \right) \]
The RHS is very small and vanishes as $n,\lambda \to 0$. Replacing $T$ by its zero order expression (Eq. 20 with $\lambda=0$)

$$
\frac{\partial^2}{\partial t^2} - \frac{4}{3} \frac{n}{m^2} + \frac{(\gamma-1)\lambda}{C_p n} \nabla^2 \frac{\partial}{\partial t} - c^2 \nabla^2 \right] p = - \frac{\partial}{\partial t} \sum_i \varepsilon_i R_i \tag{23}
$$

with $\nabla p = 0$ at the surface. This solution does not satisfy the other surface boundary conditions $T, \gamma = 0$ and a correction must be made for these losses (see Eq. 32).

The pressure, responding to the heat source $-\sum_i \varepsilon_i R_i$, is the sum of the solutions to Eqs. 22 and 23.

The diffusion equations Eq. 21, the thermal wave Eq. 22, and the propagation wave Eq. 23 are solved by the same technique. The spatial dependence of $n_i, T$, and $p$ is removed by expanding them in solutions which satisfy Laplace's Eq.

$$\nabla^2 s_j = -s_j s_j$$

and the respective boundary conditions. The boundary conditions are different in all three cases but this is not a serious problem. In a cylindrical cell the solutions $mnp$ are

$$J_m(\alpha_{mn}, \frac{r}{r_o}) e^{im\phi} \cos(k_p z + \delta_p)$$

where $m$ is an integer, but in general $\alpha_{mn}$ and $k_p$ are not. Having removed the spatial dependence, the time dependent equations are solved by Laplace transforming, rearranging, and inverse Laplace transforming. The frequency dependent equation is found by Fourier transforming the time dependent differential equations.
Usually only three of the spatial modes are important as shown in Figure 2.

\[ m \; n \; p \]

- on 0: axially and radially symmetric
- 0 \( n \) 1: single longitudinal mode - only with strong absorption
- 1 \( n \) 0: single transverse mode - only with off-axis pumping

b. Beam Coupling, Relaxation, and Molecular Diffusion

In this section and in section d we restrict the molecular kinetics to a simple system which is actually the most common. Section c, which deals with the cavity response, is independent of the molecular dynamics at acoustic frequencies. We assume:

1. two levels with populations \( n_0 \) = constant and \( n_1 \)
2. the laser pumping does not saturate the transition. We define
   \[ \sigma_{op} = \text{absorption cross section} \]
   \[ I(t) \; \text{or} \; I(\omega) = \text{pump intensity (photon/area time)} \]
3. a single relaxation time
   \[ k_r = k_{rad} + k_{relax} n_0 \]
4. very slow diffusion
5. total quenching at the surface
   \[ \alpha_{ll} = -1 \]
6. cylindrical cell, pumped centrally with a Gaussian beam
   (see Fig. 2)

In the usual limit that diffusion is unimportant we will see that i) heating is nearly a linear function of molecular density, ii) focusing is not critical, and iii) the signal falls off as (cell
Fig. A-2. Lowest order modes of a cylindrical spectrophone.
Fig. A-2.
cross section)\(^{-1}\).

From Eqs. 15 and 18 the kinetic equation for \(n_1\) including laser pumping is

\[
\frac{\partial n_1}{\partial t} = \alpha_{op} I(t) n_0 - k_r n_1 + D \nabla^2 n_1
\]

with the wall boundary conditions

\[-\frac{2D}{v} \nabla n_1 \cdot \hat{\phi} = n_1\]

For cylindrical symmetry this requires

\[
\frac{J_m(\alpha_{mn}^D)}{\alpha_{mn}^D J_m(\alpha_{mn}^D)} = \frac{2D}{v r_o}
\]

and

\[
\text{ctn} \left( k_p^D z_0 + \delta_p^D \right) = \frac{2D k_p^D}{v}
\]

\[
\text{ctn} \left( \delta_p^D \right) = -\frac{2D k_p^D}{v}
\]

These can be solve graphically for \(\alpha_{mn}^D, k_p^D,\) and \(\delta_p^D\). Usually the cell diameter and/or pressure is high enough such that \(2D/r_o \bar{v} + 0\), the "diffusionless" limit. In this limit the basis set is

\[
J_{mn}(\alpha_{mn}^D r_o) e^{i m \phi} \sin \left( \frac{(p+1)\pi}{z_o} z \right)
\]

where

\[
J_m(\alpha_{mn}) = 0.
\]

The numbering of the longitudinal modes is chosen such that \(p\) equals the number of nodes along the longitudinal \(z\) axis.

Expanding the excited population \(n_1\) and the laser intensity \(I\) in the spatial eigenfunctions
\[ n_{\text{mnp}} = \sigma_{\text{op}} n_0 I_{\text{mnp}} - k'_r n_{\text{mnp}} \]

where

\[ k'_r = k_r + D\left(\frac{\langle \Delta n \rangle^2 + k_p^2}{r_0^2}\right) \]

The solutions are

\[ n_{\text{mnp}}(\omega) = \frac{\sigma_{\text{op}} n_0 I_{\text{mnp}}(\omega)}{i\omega + k'_r} \]

\[ n_{\text{mnp}}(t) = \int_0^t \sigma_{\text{op}} n_0 I_{\text{mnp}}(\tau) \exp[-(t-\tau)k'_r] d\tau \]

The important quantitative results are contained in Eq. 25.

From \( n_{\text{mnp}} \) we obtain the heating function

\[ h_{\text{mnp}} = \varepsilon_1 \cdot k_{\text{relax}} n_0 \cdot n_{\text{mnp}} \]

The gas acts as a low pass filter with properties

\[ \text{Bandwidth (Hz)} = \frac{k'_r}{2\pi} \]

\[ \text{Peak response} = \left[1 + \left(\frac{k_r}{k_{\text{relax}} n_0}\right)^2\right]^{-1/2} \]

Since \( D^{\sigma n_0^{-1}} \), the peak response monotonically decreases as the molecular density \( n_0 \) decreases, while the bandwidth goes through a minimum. The minimum occurs at the cross over between bulk relaxation and surface relaxation. This occurs when

\[ \sigma_{\text{HS}} n_r \leq 1.6 (Z_{\text{relax}})^{1/2} \]

\( Z_{\text{relax}} \) is the collision number.
The coupling of the beam $I_0$ to the gas diffusion mode $S_{mnp}(r)$ is given by the orthogonality of the modes.

$$I_{mnp} = \frac{\int dr^3 I S_{mnp}}{\int dr^3 |S_{mnp}|^2}$$

For a Gaussian beam of total intensity $I_t$ (photons/sec) in the center of a cylindrical cell in the diffusionless limit $2D/\overline{v}_s \rightarrow 0$

$$I(r) = \frac{I_t}{\pi a^2} \exp\left(-\frac{r^2}{a^2}\right) \exp(-\sigma_{opn_o} z)$$

$$I_{mnp} \sim I_t \delta_{m0} \frac{1}{\pi r_o^2} \left[ \exp\left(-\frac{a_{on}}{2r_o}\right) \right] \left[ \frac{2\pi p(1-(-)^{p}) e^{-\sigma_{opn_o} z_o}}{(\pi p)^2 + (\sigma_{opn_o} z_o)^2} \right] , a < r_o$$

The radial coupling in brackets is approximately $5n \exp[-(1.5na/r_o)^2]$. This clearly shows that the modes small relative to the beam width $r_o/a_{on} << a$ are not excited. Simultaneously, harder focussing $a << r_o/n$ does not increase the excitation of the lower modes. When the beam is matched to the cell $a/r_o \sim .66$, generally only the 010 mode is excited and

$$I_{010} \rightarrow \frac{I_t}{\pi r_o^2} \approx 1.97$$

In summary, the heating goes as $(\text{cross section})^{-1}$, almost independent of the focussing. This applies to nonresonant and resonant microphones.
c. Cavity Response

The properties of acoustic cavities and their implications for optoacoustic spectroscopy are well established.24,25 As noted in section a, there are thermal and propagational waves which correspond to nonresonant and resonant spectrophone operation.

The thermal waves satisfy the same boundary conditions as the diffusion solutions do in the $2D/\nu r_o \rightarrow 0$ limit. Equation 22 becomes

$$\frac{\partial}{\partial t} T_{mnp} = -k' \left[ \left( \frac{d}{r_o} \right)^2 + k_p^2 \right] + \frac{h_{mnp}}{C_v r_o}$$

with solutions

$$T_{mnp}(\omega) = \frac{h_{mnp}(\omega)}{C_v r_o} \frac{1}{i\omega + k'} \left[ \left( \frac{d}{r_o} \right)^2 + k_p^2 \right]$$

$$T_{mnp}(t) = \int_0^t \frac{h_{mnp}(\tau)}{C_v r_o} \exp[-(t-\tau)\left[ \left( \frac{d}{r_o} \right)^2 + k_p^2 \right]]$$

The thermal pressure wave is

$$P = \sum_{mnp} \frac{V_{mnp}}{V} \bar{n} T_{mnp} \quad (29)$$

where

$$V_{mnp} = \int d^3 r \; s_{mnp}$$

Kerr and Atwood2 have shown numerically that the 010 term predominates in a centrally pumped, cylindrical cell. The calculation involves substituting Eqs. 26 and 27 for $h_{mnp}$. Because of this calculation the thermal pressure wave is frequently approximated by
where $h_0$ is the integrated heating over the cell $1/V \int d^3 r \ h$ and $1/\tau_o \sim K(\alpha_0/r_0)^2$.

Generally nonresonant phones are operated $\omega \gg 1/\tau_o$ to avoid the low frequency amplifier noise and the lower efficiency of lockins at these frequencies.

To determine the resonances we expand the pressure and heating in the orthogonal functions which satisfy the propagation mode boundary conditions

$$\left. \frac{3}{\partial r} J_m (a' \frac{r}{r_o}) \right|_{r=r_o} = 0 = \left. \frac{3}{\partial z} \cos (a' \frac{z}{r_o}) \right|_{z=z_o}$$

The propagation wave Eq. 23 becomes

$$\left( \frac{\partial^2}{\partial t^2} + \omega_i \frac{\partial}{\partial t} + \omega_j^2 \right) p_j = \frac{\partial}{\partial t} h_j$$

with solutions

$$p_j(t) = \int_0^t dt' h_j(t') G_j^h(t-t')$$

$$G_j^h(t) = (1 - \frac{1}{4Q_j^2})^{-\frac{1}{2}} \cos[\omega_j (1 - \frac{1}{4Q_j^2})^2 t + \delta_j] \exp(-\frac{\omega_j}{2Q_j} t)$$

$$\cos \delta_j = (1 - \frac{1}{4Q_j^2})^{1/2}$$

(30)
where

\[ \omega_j^2 = \frac{c^2}{\left( \frac{\zeta_{mn}}{r_0} \right)^2 + \left( \frac{\mp}{z_0} \right)^2} \]

and

\[ \frac{\omega_j}{Q_j} = \frac{\omega_j^2}{c^2} \left[ \frac{\lambda}{\gamma - 1} \frac{\lambda}{\gamma - 1} + \frac{4\eta}{3m \gamma} \right] + \left( \frac{\omega_j}{Q_j} \right) \] (31)

Recall that \( c^2 = \gamma k T/m \) and \( \omega \) is the angular frequency. Equation 23 does not include the surface losses which are now added post facto by Morse and Ingard's method.\(^{20}\) Kreuzer\(^{4}\) gives the expression for the surface loss. It should be recalled that the viscous surface losses occur when the wave moves tangentially along a wall. Expressed in terms of the gaseous mean free path \( \lambda \), the losses are approximately

\[ \frac{\omega_j}{Q_j} \sim \omega_j \left( \frac{\lambda_j}{\lambda} \right) 0(10) + \left( \frac{\lambda_j}{\lambda} \right)^{1/2} \frac{c}{v} \left[ 0(0.5) (\gamma - 1) A_c + 0(0.4) A_c^+ \right] \] (32)

For acoustic resonances <10 KHz and pressures greater than \( 10^{-1} \) torr, and cell dimensions on the order of 1 cm, only the surface losses are important for the propagational waves.

There have been several experimental investigations\(^{26,27}\) of the \( Q \) and generally half of the losses can be explained by the above mechanisms. It is unclear whether the remainder are "scattering losses" due to projections of the microphone into the cell, or due to the damping action of the diaphragm.

As shown in Eq. 32 the \( Q \) depends upon the pressure. For resonant spectrophones operated with a chopped - CW laser or with a pulsed laser and rectified integration over the pulse, this adds a stray
pressure dependence to the signal (Eqs. 26 and 30). Since the signal scales as $Q n_o$ the total pressure dependence is $\sim n_o^{3/2}$. This is in addition to the pressure dependent sensitivity of most microphones (see section 4).

d. Combined Relaxation - Cavity Response

To include the simple heat function from Eqs. 25 and 27 it is necessary to transform from the diffusion solutions $S_{mnp}(\text{wall}) = 0$ to the propagation solutions $\nabla S'_{mnp}(\text{wall}) = 0$. If

$$S_{mnp}(r) = \sum_T \sum_{n'p'} S'_{mnp'}(r),$$

then

$$h'_{mnp} = \sum_T \sum_{n'p'} h_{mnp}.$$ 

Explicitly\(^{\dagger}\)

$$\frac{T_{np}}{n'p'} = \frac{4}{\pi} \frac{(p+1)}{[(p+1)^2 - p'^2](1+\delta_{p'0})} \cdot \frac{2\alpha^{2}_{mn} \alpha'^{2}_{mn}}{\left(\alpha^2 - \alpha'^2\right) \left(\alpha'^2 - \alpha^2\right)} \frac{J_{m+1}(\alpha_{mn})}{J_{m}(\alpha'_{mn})} \quad (33)$$

A specific example is the first radial mode.

$$h_{010} = \sum_p \frac{2}{\pi(p+1)} (0.701 h_{01p} + 0.591 h_{02p} - 0.193 h_{03p} + 0.066 h_{04p} - ... )$$

Because the $S'_{mnp}$ lies "between" $S_{mnp}$ and $S_{m(n+1)p}$ there are usually two important heating terms.

\(^{\dagger}\)This uses the integral\(^{29}\)

$$\int_{0}^{\infty} dr \frac{r}{m} \left(\frac{dr}{r}\right) J_{m}(\frac{\beta r}{m}) J_{m}(\frac{\beta r}{m}) = r^{2} \left\{ \frac{\alpha J(\beta) J'(\alpha) - \beta J(\alpha) J'(\beta)}{\beta^{2} - \alpha^{2}} \right\}, \alpha \neq \beta$$

$$= \frac{r^{2}}{2} \left\{ J_{m+1}(\alpha) - \frac{2m}{\alpha} J_{m}(\alpha) J_{m+1}(\alpha) + J_{m}(\alpha) \right\}, \quad \alpha = \beta$$
These complications come about because diffusion and wall relaxation have been included. If diffusion is completely neglected in the sense 

\[ k_r \gg D(\alpha_{mn}/r_0)^2 \]  

then 

\[
h_{\text{relax}}^{n_0} = \frac{\sigma_{op}^{n_0} I_{\text{relax}}^{n_0}}{i\omega + k_r}
\]

and 

\[
h_{\text{relax}}^{n_0} = \frac{\sigma_{op}^{n_0} I_{\text{relax}}^{n_0}}{i\omega + k_r}
\]

In this limit the pressure response is simply 

\[ p_j'(\omega) = \frac{\sigma_{op}^{n_0} I_j'(\omega)}{(C\sqrt{k})} \cdot \frac{\omega_j}{\omega_j} \cdot \left[ \frac{1}{i\omega_j (\frac{\omega}{\omega_0} - \frac{\omega}{\omega_0}) + 1} \right] \cdot \frac{1}{i\omega_j (\frac{\omega}{\omega_0} + 1)} \cdot \frac{k_{\text{relax}}^{n_0}}{k_r}
\]

The frequency part in brackets can be viewed as a response function. It is the product of the resonance band-pass and the relaxation low-pass filtering. Since \( \mathcal{Q} \) generally is large (>100) the low-pass action simply attenuates the response without significantly affecting the measured \( \mathcal{Q} \). The frequency and \( \mathcal{Q} \) are changed at most by \( \pm 1/(2\mathcal{Q})^2 \). Thus, if diffusion is negligible, the peak response at a resonance is 

\[ p_j'(\omega_j) = \sigma_{op}^{n_0} \cdot I_j'(\omega_j) \cdot \frac{\mathcal{Q}_j}{\omega_j} \cdot \frac{k_{\text{relax}}^{n_0}}{(\omega_j^2 + k_r^2)^{1/2}}
\]

The comments made in section b concerning \( I_j \) generally hold for \( I_j' \) as well. For central pumping with a Gaussian beam of a cylindrical cell of radius \( r_0 \)
The time response in this limit is (assume $\omega_j^2 \gg 1$)

$$p_j'(t) = \frac{\xi \sigma_{op} n_o}{(C_v/k)} \int_0^t \int G_j^I(t-\tau) I_j'(\tau) \frac{k_{relax} n_o}{[(k_r - \frac{\omega_j}{2\Omega_j})^2 + \omega_j^2]^{1/2}}$$

where

$$G_j^I(t) = \left\{ \left[ (k_r - \frac{\omega_j}{2\Omega_j}) \cos \omega_j t + \omega_j \sin \omega_j t \exp(-\frac{\omega_j}{2\Omega_j} t) \right] - \left( k_r - \frac{\omega_j}{2\Omega_j} \right) \exp(-k_r t) \right\} \cdot \left[ (k_r - \frac{\omega_j}{2\Omega_j})^2 + \omega_j^2 \right]^{-1/2}$$

If the pulse is much faster than the kinetics, then

$$p_j'(t) = \frac{\xi \sigma_{op} n_o}{(C_v/k)} \int_0^\infty dt I_j'(\tau) G_j^I(t) \frac{k_{relax} n_o}{[(k_r - \frac{\omega_j}{2\Omega_j})^2 + \omega_j^2]^{1/2}}$$

It is apparent that with pulsed sources that a high $Q$ resonant spectrophone does not improve the signal unless 1) the signal is rectified and integrated or 2) the pulse repetition rate is very high.

The peak response to a single pulse in the usual limit that $k_r \gg \omega_j \gg \frac{\omega_j}{2\Omega_j}$ is

$$p_j'(t_{peak}) = \frac{\xi \sigma_{op} n_o}{(C_v/k)} \int_0^\infty dt I_j'(\tau) \frac{k_{relax} n_o}{k_r}$$
The small carry over from one pulse to the next enhances the signal by the factor

\[ \left[ 1 - \exp\left( - \frac{\omega_j}{2Qjr_p} \right) \right]^{-1} \]

where \( r_p \) is the repetition rate in pulses/time. In the limit \( \omega_j/2Qjr_p \rightarrow 0 \) the pulsed signal approaches Eq. (34) where

\[ \frac{1}{2} I_j(\omega_j) \leftrightarrow r_p \int_0^\infty d\tau \ I_j(\tau) \]

is interpreted as the average photon flux (photons/area time).

4. **Microphones and Preamplifiers**

Four types of microphones have been used in spectrophones: electret, solid dielectric, condenser, and piezoelectric. The first three have a metal or metalized-plastic diaphragm, parallel to a back plate, and operate as a modulated capacitance device. These have been most frequently used, primarily due to availability, and are the only ones discussed here. There are four criteria for comparing the various microphones: 1) sensitivity, 2) noise, 3) frequency response, and 4) size and allowable geometries.

The most distinguishing property of the different microphones is the type of restoring force on the diaphragm. There are four restraining forces: the tension; the pressure in the space between the diaphragm and the back plate; the electric field; and the mechanical compliance (stiffness) of the diaphragm. The smaller the restoring force, the larger the displacement for a given pressure, hence the larger signal. This is evidenced in Brüel and Kjær...
microphones which become more sensitive with age. Only the first two forces are usually important. The voltage is varied to determine the maximum response. At that point the voltage can be ignored. The mechanical compliance is usually very small, but in solid dielectric phones at lower pressures it is the limiting force. The tradeoff for high sensitivity is response time. Mechanically the diaphragm is a low pass filter with a cutoff frequency of \( \omega/2\pi = \sqrt{K_D/\rho_D} \). \( K_D \) is the restoring pressure per diaphragm displacement, and \( \rho_D \) is the diaphragm mass per area. A low \( K_D \) can be somewhat offset by a lighter diaphragm. Metal and plastic diaphragms are usually 6 - 24 \( \mu \) (.25 - 1.0 mil) thick.

Solid dielectric \(^{30}\) and condensers \(^{31}\) are the classical diaphragmed microphones which are biased with an external voltage. The condenser microphone diaphragm is tensioned and is distinctly separated from the back plate. The B & K precision microphones \(^{32}\) are condensers run at 200 V. Solid dielectric phones use a metalized dielectric sheet which is in contact with a rough back plate resulting in a higher capacitance. The tension is a negligible force. Kreuzer's microphone \(^3\) is the principal example. This allows many shapes for the microphone, but they characteristically appear to be noisy. Biasing voltages of 50 - 200 volts are typically used.

Electret microphones use a permanently polarized sheet which is metalized on one side. These are usually commercial elements since it is difficult to obtain the electret sheets commercially in small quantities. Robin reports \(^{33}\) that the sheet can be made by charging with a Tesla coil. Mylar, polyester, and teflon sheets have been used.
Since the diaphragm is permanently charged, no external voltage is necessary. Miniature electret microphones with integral FET preamps have been used. These allow small sample volumes, but the preamps may be relatively noisy (see below). \(^28\)

Electrically, microphones have some peculiar properties since they are purely capacitative sources. All microphones can be represented by a voltage source in series with the phone's capacitance \(^{32}\) (see Fig. 3). The microphone capacitance coupled to the amplifier impedance will act as a high pass filter.

The voltage source is simply
\[
\frac{\Delta C_m(t)}{C_m} V_B \text{ or } \left( \frac{1}{C_m} \frac{\partial C_m}{\partial p} \right) \delta p(t) V_B
\]

This represents the intrinsic sensitivity, usually called the open circuit sensitivity, of the microphone. For nontensioned diaphragms \(1/C_m \cdot \partial C_m/\partial p\) is independent of the area. \(V_B\) is always independent of the area, even for electrets. As a result the signal source of most microphones is independent of diaphragm area. This is certainly true of Kreuzer style phones and of electrets. Increasing the diaphragm's area increases the capacitance and is beneficial in that it reduces the source impedance. The lower the impedance, the lower the noise. Typically, \(\omega/2\pi < 20 \text{ KHz}\) and \(C_m < 100 \text{ pf}\) so that \(Z_m = 1/\omega C_m > 80 \text{ K}\). The open circuit sensitivities of commercial microphones vary only by a factor of ~10 as seen in Table 2.
Fig. A-3. (a) Microphone biasing circuit and (b) its equivalent circuit.
(a) Microphone and Biasing Circuit

(b) Equivalent Circuit

Fig. A-3.
Table 2. Commercial Microphone Characteristics

<table>
<thead>
<tr>
<th>Microphone</th>
<th>Type</th>
<th>Sensitivity (V/(N/m²))</th>
<th>Integral noise</th>
<th>Capacitance</th>
<th>Frequency Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>B&amp;K Type 4144</td>
<td>.5&quot; Condenser</td>
<td>4x10⁻² (@200V)</td>
<td>-</td>
<td>57 pf</td>
<td>8 KHz</td>
</tr>
<tr>
<td>Type 4145</td>
<td>.5&quot; Condenser</td>
<td>2x10⁻² @200V</td>
<td>-</td>
<td>-</td>
<td>20 KHz</td>
</tr>
<tr>
<td>General Radio 1962</td>
<td>.5&quot; Electret</td>
<td>1x10⁻²</td>
<td>-</td>
<td>35 pf</td>
<td>20 KHz</td>
</tr>
<tr>
<td>Sony ECM-18</td>
<td>.5&quot; Electret</td>
<td>1.4x10⁻³</td>
<td>1.4 µV</td>
<td>(FET-250 Ω)</td>
<td>17 KHz</td>
</tr>
<tr>
<td>Shigoto ME-16</td>
<td>.5&quot; Electret</td>
<td>3x10⁻³</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Knowles BT-1759</td>
<td>.2x.3&quot; Electret</td>
<td>1x10⁻²</td>
<td>4 µV</td>
<td>(FET-3.5 KΩ)</td>
<td>10 KHz</td>
</tr>
</tbody>
</table>
Two types of linear preamplifiers are used with microphones: the usual voltage follower and the charge sensitive amplifier. The schematics for these amplifiers are given in Figure 4, and the response functions are listed in Table 3. The charge sensitive amp derives its high impedance purely capacitative \( l/i\omega C_f \) rather than resistively. If is referred to as a "charge sensitive" amp since the feedback capacitor \( C_f \) integrates the current. To first order the output is

\[
v = \frac{1}{C_f} \int^t Q \, dt = \frac{Q(t)}{C_f}
\]

The charge sensitive amplifier really has two advantages. Since the amplifier behaves as a short circuit with respect to the microphone, stray capacitance is unimportant. Secondly, the frequency response is independent of the microphone. As seen in Table 3, the noise referred to the input for both amplifiers is the same. The difficulty with the charge sensitive amplifier is rather limited gain if low frequency response is needed. Since the feedback resistor is physically limited to \( \leq 10^9 \Omega \) and the microphone capacitance is typically \(< 100 \text{ pf}\), the low frequency cutoff to gain ratio is about \( >1 \text{ Hz} \). The gain is proportional to the microphone capacitance, hence its area.

\[
V_o = - \left( \frac{\Delta C_m}{C_m} \right) \left( \frac{C_m}{C_f} + i\omega R_f C_m \right)
\]

\[
\rightarrow - \left( \frac{\Delta C_m}{C_m} V_B \right) \left( i\omega R_f C_m \right), \quad \omega R_f \gg \frac{1}{C_f}
\]

The noise is the same as given in Table 3.

* Kreuzer's recent analysis of spectrophone amplifiers is limited to a mixed voltage - charge sensitive amplifier which is a nonlinear amplifier. In his Figure 3, the feedback capacitor is the \( C \) or \( C_2 \) capacitance referred to in the discussion. The response function is
Fig. A-4. Microphone with preamplifier circuits including equivalent noise sources. (a) Voltage Follower and (b) Charge sensitive preamps.
(a) Voltage Follower Preamp

(b) Charge Sensitive Preamp

\[ C_C > > C_M > > C_f \]
\[ R_B C_C > > R_f C_f \]

Fig. A-4.
There are four sources of noise in the preamp: Johnson's noise in the load resistor \( R_L \) which in the charge sensitive preamp is effectively the feedback resistor \( R_f \); the Johnson noise in the biasing resistor \( R_B \); the amplifier's shunt current noise; and the amplifier's series voltage noise. The output value of the voltage/\( \sqrt{\text{Hz}} \) noise which these induce is also listed in Table 3. The total noise is the sum of the squares.

\[
V^2 = V_B^2 + V_L^2 + V_i^2 + V_v^2
\]

The Johnson noise and the current noise are "short circuited" by the microphone's capacitance in the voltage follower, or the feedback capacitor in the charge sensitive amp. As a result they fall off as 

\[
(1 + \left(\frac{\omega}{\omega_0}\right)^2)^{-1/2}
\]

where \( \omega_0 \) is the low frequency cutoff of the microphone-preamp. Usually the components are chosen such that only the series voltage noise is important. In pulsed spectrophones where a wide bandwidth is needed, the low frequency noise is removed with a simple RC filter. Op amps such as National's LH0022 have \( V_{na} = 30 \text{ nV/\sqrt{Hz}} \) and \( i_{na} = 1 \text{ fA/\sqrt{Hz}} \) at 1000 Hz. \( V_{na} \) and \( i_{na} \) are frequency dependent and increase at low frequencies. Total noise voltages are typically 100 nV/\( \sqrt{\text{Hz}} \). Using a typical microphone sensitivity of \( 10^{-2} \text{v}/(\text{N/m}^2) \), the signal to noise ratio is limited to

\[
4 \times 10^5 \text{ \sqrt{Hz}/(N/m}^2)\]

or a noise equivalent pressure of

\[
2 \times 10^{-6} \text{ (N/m}^2\)/\sqrt{\text{Hz}} = 1.5 \times 10^{-8} \text{ torr/\sqrt{Hz}}
\]
Table 3. Response functions and noise sources for a microphone with voltage follower and charge sensitive preamps.

<table>
<thead>
<tr>
<th>Response Function</th>
<th>Voltage Follower</th>
<th>Charge Sensitive</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{\Delta C}{C} \left( \frac{V_o}{(\frac{C}{C_M}) V_B} \right) )</td>
<td>( \frac{C_M}{C} \left( \frac{1}{1 + \frac{1}{i\omega RC}} \right) )</td>
<td>- ( \frac{C_M}{C_f} \left( \frac{1}{1 + \frac{1}{i\omega R_f C_f}} \right) )</td>
</tr>
<tr>
<td>Low Frequency Cutoff (3dB-Hz)</td>
<td>( \frac{1}{2\pi RC} )</td>
<td>( \frac{1}{2\pi R_f C_f} )</td>
</tr>
</tbody>
</table>

Definitions and Restrictions

\[
R = \frac{R_L R_B}{R_L + R_B} \quad \text{and} \quad R = \frac{R_f R_B}{R_f + R_B}
\]

\[
C = C_M + C_S + C_I \quad \text{and} \quad C_C \gg C_M, C_f
\]

\[
R_B > C_C \gg R_f C_f
\]

Johnson Noise

\[
\frac{4kT}{\omega C_M^2 R}
\]

Shunt Current Noise

\[
\frac{i^2}{\omega C_M^2 na}
\]

Total Noise

\[
\frac{4kT/R + \frac{i^2}{2 na}}{\omega C_M^2} + \frac{\nu^2}{\nu_{na}}
\]

Integrated Noise

\[
\frac{4kT/R + \frac{i^2}{2 na}}{8\pi C_M^2 \nu_{LF}^2} + \frac{\pi}{2} \frac{\nu^2}{\nu_{na} \nu_{HF}}
\]

*Noise has units of Volts²/Hz and is referred to the input. The integrated noise has units Volts² and assumes simple RC filters with \( \nu_{LF} \ll \nu_{HF} \) 3dB points.
Most optoacoustic spectroscopy has been chopped - CW. The preamp signal is processed by a lock - in amplifier at the chopping frequency. The bandwidths can be made very small (> .3Hz) and with reasonable powers (~1 W) sub ppb concentrations at a atm total pressure have been detected. The relaxation processes can be examined by an analysis of the frequency dependent phase shifts in nonresonant cells.

Pulsed excitation holds no special problems for signal processing. One arrangement is illustrated in Figure 5. For spectroscopic studies one of the resonant modes ω_j or the "zero frequency" mode is isolated with a low Q bandpass filter. This removes destructive interfering resonances. This Q_filter should be less than the acoustic Q_j or the signal is attenuated by Q_j/Q_filter. If ω_j ≠ 0 the signal is rectified with a lock - in amplifier phase synchronized to the laser pulse. The scalloped - shaped output is integrated with a gated integrator. Typically k_{relax} >> ω_j >> ω_j/2Q_j >> 1/τ_o. τ_o is the gated integration period. Under these conditions the signal from the integrator at the end of the gating period is

\[ \text{Signal} \approx SP_j \frac{4}{\pi} \frac{Q_j}{\omega_j} \left[ 1 - \exp\left(-\frac{\omega_j}{2Q_j} \tau_o \right) \right] \]

S is the microphone - preamp sensitivity ∂V/∂p, p_j is the peak pressure given in Eq. 39. The signal has units of Volt sec. The integrated noise of a white noise source can be determined from the Wiener Khintchine Theorem 34

\[ \text{Noise} \approx (N_{\text{rms}}/\sqrt{\text{Hz}}) \sqrt{\tau_o} \]
Fig. A-5. Signal averaging method for pulsed, resonant spectrophones.
Fig. A-5.

XBL 789-5854
5. Towards Optimum Designs

As discussed above, under most circumstances optimization is subject to four constraints: 1) mode of pumping, 2) nature of the gas sample (i.e. pressure and temperature), 3) fixed microphone sensitivity, and 4) usually amplifier limited noise. As noted in section 4, pulsed excitation with gated integration is preferable. So long as the relaxation is fast relative to all transport phenomena, the kinetic properties of the gas can be ignored. In this regime optimization largely is restricted to signal enhancement by geometry changes.

In nonresonant cells this implies minimizing the cell volume and eliminating window absorption. Various suggestions towards this end include Patel's use of miniature microphones, Rosengren's suggestions for frequency modulation, hyperbolically - shaped cells, and wave guide cells; and intracavity laser absorption.

Resonant spectrophones have taken on several shapes, none of which probably approach the optimum. The optimization can be viewed in a plane perpendicular to the beam since the cross section should be uniform throughout the cell, otherwise the Q is inevitably low due to radial - longitudinal interference. The dimensional dependence of the signal is

\[
\frac{1}{A_{cs}} \left( \frac{Q_j}{\omega_j} \right) \propto \frac{V_c}{A_{cs}} \frac{\sqrt{\lambda_j}}{A_c} \xrightarrow{\text{length}^{+\infty}} \frac{\sqrt{\lambda_j}}{P_{cs}}
\]

\( A_{cs} \) and \( P_{cs} \) are the cell cross sectional area and perimeter, \( V_c \) and \( A_c \) are the total volume and surface areas. This suggests the optimum geometry is a flat rectangular cell with length \( l = \lambda_j/2 \). The signal
then scales approximately as \( 1/\sqrt{\nu} \). The cell can be made substantially smaller by using a heavy carrier gas such as Xe or SF\(_6\) to decrease the speed of sound. Possibly the microphone can be made resonant as well.\(^{25}\)

The choice between resonant and nonresonant cells is not so clear cut. Frequently\(^{4,35}\) the criterion has been simply stated as

\[
\min(1/\omega, \tau) \leq Q_0/\omega_j. \quad Q/\omega_j \text{ is the storage time of the resonant cell.}
\]

In a nonresonant cell the storage time is the smaller of the chopping period or the thermal diffusion time of the cell. The longer the storage time the better the S/N. Integration must be used. Section 3 and 4 systematically discuss the other design criteria which may affect the \( Q_j/\omega_j \) or \( 1/\omega \) which may be obtained.

The important concerns may be summarized as follows 1) At low pressures, care must be taken that the resonant signal is not attenuated by the slower gas relaxation rate, and generally a nonresonant cell will have a more predictable response. 2) With pulsed excitation, a nonresonant cell should be used since the inverting electronics are not needed. 3) As discussed above the optimum resonant cell may be a skinny rectangular cell. The skinny dimension is determined by the pressure (transport properties) and the long dimension is determined by the upper limit of the frequency response of the microphone. With chopped - CW sources one is limited by the available modulation speeds. 4) The lowest \( 1/\omega \) time in nonresonant cells is determined by the available amplifiers since the noise increases sharply at low frequencies.

As can be seen in the many conditions expressed throughout this appendix, the design will be strongly controlled by available resources
and the pressure regime. The nonresonant cell will usually be more sensitive and will have less susceptibility to the pressure regime. A pulsed laser should be used.
APPENDIX A

References

9. Ibid., Chapter 1.4.
10. Ibid., Chapt. 2.2
11. Ibid., Chapt. 2.1
12. Ibid., Chapt. 7.1
13. Ibid., Chapt. 7.1, 2.
14. Ibid., Chapt. 9.4
15. Ibid., Chapt. 7.4
16. Ibid., Chapt. 7.3b.