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Collisionless decay, vibrational relaxation, and intermediate case quenching of $S_1$ formaldehyde

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The decay of fluorescence from the $4^0$ and $4^1$ levels of the $S_1(\tilde{A}^1A_2)$ state of $H_2CO$ and $D_2CO$ has been monitored as a function of pressure after selective, pulsed laser excitation. For $D_2CO$, single exponential decays modified by $4^0 \leftrightarrow 4^1$ energy transfer were observed over the entire pressure range $4 \times 10^{-5}$ to 4 Torr. The zero pressure lifetimes $\tau_0(4^0) = 7.8 \pm 0.7 \mu sec$ and $\tau_0(4^1) = 6.0 \pm 0.4 \mu sec$ are probably the radiative lifetimes. The rate of $4^1 + 4^0$ energy transfer in $D_2CO$ was found to be $(9.6 \pm 0.4) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, about three times the gas kinetic rate. For $H_2CO$ at pressures above 0.1 Torr, fluorescence decays were also single exponentials modified by $4^0 \leftrightarrow 4^1$ energy
transfer. However, in the range $2 \times 10^{-4}$ to 0.1 Torr, the decays of the individual $4^0$ and $4^1$ vibronic levels were typically biexponential. The zero pressure decay occurs on a timescale at least 20 times faster than the radiative lifetime of ~ 5 µsec. The Stern-Volmer plots of $\tau^{-1}$ vs pressure give quenching rates between $2.2 \times 10^{-9}$ and $6.5 \times 10^{-9}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ for both fast and slow components below ~ 20 mTorr. The relative amplitude of the fast component decreases rapidly with pressure and approaches zero at 0.1 Torr. The slow component plots are dramatically curved and give quenching rates of only about $2.2 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ above 1 Torr. The low pressure quenching rates and zero pressure lifetimes for H$_2$CO depend significantly on the K' rotational quantum number within $4^0$. The biexponential decays for H$_2$CO may result from variations in lifetime among the J' states excited by the laser. The large quenching rate constants and the curvature of the Stern-Volmer plots can be qualitatively understood in terms of recent mixed-state models of collision-induced radiationless decay.
I. INTRODUCTION

The formaldehyde molecule provides a seemingly ideal test system for quantitative models of radiationless transitions in small molecules. The $S_0 \rightarrow S_1$ absorption spectrum is well-resolved and individual rovibronic line assignments have been made.\textsuperscript{1} The $S_0$ and $T_1$ vibronic level densities near the $S_1$ origin at 28,188 cm$^{-1}$ are approximately 10 and 0.02 per cm$^{-1}$, respectively; these are too small for straightforward application of theories for the large molecule, statistical limit.\textsuperscript{2} Nevertheless, $S_1$ lifetimes which have been reported to date exhibit rapid non-radiative decays characteristic of $S_1 \rightarrow S_0$ intersystem crossing in the statistical limit. No lifetime lengthening characteristic of the small molecule limit has been observed. It has been found that dissociation products, $H_2 + CO$, are formed slowly compared to $S_1$ decay for 337 nm excitation and pressures greater than 0.1 Torr.\textsuperscript{3} The apparent incompatibility of these results with available theories of radiationless transitions has been underscored by recent detailed quantitative theoretical calculations.\textsuperscript{4}

The importance of collisions in radiationless transitions has been stressed in recent theoretical work.\textsuperscript{5, 6, 7} Through small changes in total energy and angular momentum, weak collisions may increase the number of effectively coupled final states for a radiationless transition. At high enough
pressure these states may become broadened into a quasi-continuum. In this paper, fluorescence lifetime measurements after laser excitation are presented for the lowest two vibronic levels of H$_2$CO and D$_2$CO. The results provide concrete examples of these pressure effects and resolve a small fraction of the experimental and theoretical questions posed by formaldehyde.

II. EXPERIMENTAL

A. Sample handling

H$_2$CO and D$_2$CO monomers were prepared as described previously. The gases were handled in a standard glass and grease vacuum line with a background pressure below 10$^{-6}$ Torr and a leak rate of less than 2 x 10$^{-6}$ Torr/min. The fluorescence cell is a 50 cm long, 5 cm i.d. Pyrex cylinder. Quartz, Brewster angle end windows and a 5 cm diameter quartz window for viewing fluorescence at 90° to the cylinder axis are attached with epoxy. The cell includes Wood's horns opposite each window and is painted black. All experiments were performed at room temperature, 22 ± 2°C.

Pressures above 1 Torr were measured to within ±1% with a 0 - 5 Torr capacitance manometer (Validyne DP-7), while pressures in the range 4 x 10$^{-5}$ to 1 Torr were measured with a 0 - 1 Torr capacitance manometer (Baratron 310-BH) whose sample side was connected directly to the fluorescence cell.
The Baratron measures pressures from $10^{-2}$ to 1 Torr to better than $\pm 1\%$; the accuracy decreases to about $\pm 20\%$ at $5 \times 10^{-4}$ Torr. At still lower pressures, leaking and/or de-gassing of the cell at a rate of $\sim 5 \times 10^{-6}$ Torr/min increased the cell pressure significantly on the timescale of a typical lifetime measurement, 5 min. Hence, an independent measurement of the formaldehyde partial pressure was obtained by comparing the peak fluorescence intensity at the low pressure with that from an accurately known pressure above $10^{-3}$ Torr under otherwise identical conditions. Tests on pressures between $10^{-3}$ and $5 \times 10^{-2}$ Torr indicated that the peak fluorescence intensity was proportional to the formaldehyde pressure to better than $\pm 7\%$. For pressures below $5 \times 10^{-4}$ Torr, this alternative measurement of the average formaldehyde partial pressure was sometimes smaller than the average Baratron reading during a measurement by as much as 30%. Thus the slow increase in the Baratron reading on a 5 min timescale was primarily due to gases other than formaldehyde. When the two measurements were substantially different, the result from peak heights is reported here. Pressures below $5 \times 10^{-4}$ Torr are in any case accurate to within $\pm 40\%$.

B. Excitation

Two different laser systems were used in this study, a $N_2$ laser-pumped dye laser and a frequency-tripled Nd:YAG laser. The dye laser consists of an oscillator and two
amplifier stages, modeled after that of Hänisch, et al. The \( N_2 \) laser is a Molecron UV-1000, 10 mJ pulses (10 nsec FWHM). A 1200 groove/mm replica grating blazed at 1.4 \( \mu \) in first order was used for wavelength selection of the oscillator output. The laser produces 5 nsec FWHM pulses of spectral width 0.02 nm FWHM. The vibrationless levels of the \( S_1 \) state of \( H_2CO \) and \( D_2CO \) were excited in the \( 4^1 \) hot band absorption using the dye BPBD (Exciton) in the wavelength range 365 - 370 nm. Typical output energy was 0.2 mJ/pulse. The \( 4^1 \) transition of \( D_2CO \) was excited by frequency doubling the 704 nm dye laser output from a mixture of Rhodamine B and Nile Blue A Perchlorate. The energy of the frequency-doubled pulses at 352 nm was several \( \mu \)J.

The Nd:YAG laser was the Raytheon SS-404, capable of delivering 250 mJ in a 15 nsec FWHM pulse at 1.06 \( \mu \). Third harmonic generation was accomplished with two KDP crystals which doubled the frequency to 530 nm and then summed the fundamental and second harmonic to yield 30 mJ pulses at 354.70 \( \pm \) 0.01 nm. Such pulses would have saturated the photomultiplier tube with scattered light. In this study, 2 mJ/pulse or less of the tripled YAG output was used to excite the \( 4^1_0 \) absorption band with 0.02 nm FWHM spectral resolution. The sample was not appreciably photolyzed at these energies on the timescale of an experiment.

The wavelength and spectral distribution of the lasers was obtained with a 1.5 m Jobin-Yvon monochromator. Its
single pass spectral resolution of \( \sim 0.005 \) nm permitted measurements of the laser linewidths of \( 0.02 \) nm FWHM. Excitation energies were measured to an absolute accuracy of \( \pm 1 \) cm\(^{-1}\) and are reported as \( \nu_{\text{vac}} \). Prior to an experiment, the dye laser was tuned to a fluorescence maximum. A particular absorption feature was reproducible to within \( 1 \) cm\(^{-1}\) from day to day. The dye laser wavelength was stable once it had been set.

The \( S_1 \) absorption spectra of \( \text{H}_2\text{CO} \) and \( \text{D}_2\text{CO} \) are well understood.\(^1\) The rotational analysis has been reported for the bands of interest here.\(^10\) At the medium resolution of the dye laser, \( \sim 2 \) cm\(^{-1}\), one can selectively excite rotational sub-bands within a vibronic band. The \( rR \) sub-bands (\( \Delta J = \Delta K = +1 \)) form heads which are quite distinct; each such head includes lines of a particular \( K' \) state and several \( J' \) states. Tables I and II list the transitions excited.

C. Detection and analysis

The fluorescence spectra of \( \text{H}_2\text{CO} \) and \( \text{D}_2\text{CO} \) from the \( 4^0 \) and \( 4^1 \) vibronic levels of \( S_1 \) are well assigned.\(^11\) In the present study, bandpass interference filters which isolate fluorescence originating from either \( 4^0 \) or \( 4^1 \) in \( \text{H}_2\text{CO} \) or \( \text{D}_2\text{CO} \) were used, as shown in Fig. 1. It was thereby possible to study collision-induced \( 4^0 \leftrightarrow 4^1 \) energy transfer. Additional Schott glass uv cut-off filters were usually used between the cell and the interference filter to further diminish scattered light intensity. In the case of \( \text{D}_2\text{CO} \) at pressures
below 10⁻³ Torr, the uv cut-off filters were often used alone in order to increase the single shot S/N. The 50% T wavelengths of the filters used were 408 nm (for 41₁ excitation) and 389 nm (for 40₀ excitation).

Fluorescence which passed through the filters at 90° to the laser beam was detected by an RCA 8575 photomultiplier tube whose nominal risetime is 2.5 nsec. The current pulse passed through a load resistor and the output voltage was digitized by a Tektronix R-7912 transient digitizer with 512 vertical and 512 horizontal channels. The time base was accurate to better than 1%. Signal averaging at 4 Hz was accomplished with a PDP-11 computer and Tektronix WDI software. The overall system response time was ~ 7 nsec using a 50 Ω load, as determined by the 1/e decay time of the scattered light from a dye laser pulse. In the tripled YAG experiments on H₂CO at 354.7 nm, the time resolution was limited by the laser pulse, which decayed with a 1/e time of ~ 13 nsec. For the microsecond D₂CO decays at pressures below 0.2 Torr, 560 Ω and 5.1 kΩ terminators were sometimes used to enhance the single shot S/N; in all cases, the response time was at least 15 times shorter than the measured decay time.

After the wavelength was set and the fluorescence cell was filled, a fluorescence intensity vs time curve was obtained by averaging 300 to 2000 laser shots, depending on the single shot S/N. The cell was then pumped and the same number of shots of scattered light were averaged under
otherwise identical conditions. The final curve was obtained by digitally subtracting scattered light from signal plus scattered light. This subtraction is important because for the lowest pressures the peak intensity of scattered light might be as much as 10 times the signal. Since the scattered light decayed rapidly on the time scale of the process of interest in most cases, this was not a serious problem. Furthermore, the subtraction process was found to give the very good digital zero crucial for analysis of the long-time behavior of the fluorescence. Both linear and semi-log plots of fluorescence intensity vs time were available from an X-Y plotter. The analysis of risetimes and decay times was performed graphically from the semi-log plots.

D. Error estimates

The combination of hardware, digital electronics, and graphical analysis permit determination of a single exponential decay time to an accuracy of better than ± 2%, assuming unlimited S/N. In practice, shot noise, synchronous rf pickup, and slight baseline errors probably limit the accuracy of the best lifetimes to ± 5%; they are reproducible from day to day within ± 5%. For H₂CO decays analyzed as a sum of two exponentials, the uncertainties are higher. At the lowest pressures which yielded reliable data, the slow lifetime τₛ of a biexponential decay is considered accurate to within ± 10%, while the fast lifetime τ₉ is accurate to
within ± 20%. The amplitude ratio \( I_f/I_s \) is accurate to within ± 25%. It is estimated that a true D\(_2\)CO lifetime of 8 µsec will be shortened by less than 3% by diffusion of excited molecules out of the viewing region of the photomultiplier tube and by quenching on the cell walls. For D\(_2\)CO at all pressures, the decay times are typically reproducible to within ± 5% due to the excellent S/N and the small amplitude of fast component contamination. The D\(_2\)CO fluorescence risetimes resulting from \( 4^0 \rightarrow 4^1 \) energy transfer are estimated accurate to within ± 10%.

III. RESULTS

A. Kinetic scheme for energy transfer

For H\(_2\)CO and D\(_2\)CO, the vibronic levels of interest are \( 4^0 \) and \( 4^1 \), an inversion doublet in the non-planar S\(_1\) state separated by only 125 cm\(^{-1}\) (H\(_2\)CO) or 69 cm\(^{-1}\) (D\(_2\)CO). In the kinetic scheme of Fig. 2, \( k_{01}^P \) and \( k_{10}^P \) are collisional energy transfer rates, while \( k_0 \) and \( k_1 \) are composite rates including all collisional and unimolecular processes, both radiative and non-radiative, which take the molecule out of S\(_1\). Higher energy vibronic levels are ignored. The vibrational energy of the \( 4^2 \) level is 543 cm\(^{-1}\) (H\(_2\)CO) or 387 cm\(^{-1}\) (D\(_2\)CO). Even if collisional energy transfer were to establish vibrational equilibrium within S\(_1\), 94% (H\(_2\)CO) or 89% (D\(_2\)CO) of the molecules would be found in the \( 4^0 \) or \( 4^1 \) levels. Although the lifetime of the \( 4^2 \) level has not been
reported, the $4^3$ level lifetime is 2 - 3 times shorter than the $4^1$ lifetime in the pressure range 0.1 - 0.6 Torr.\textsuperscript{13}

Assuming that the $4^2$ lifetimes are intermediate, significant depopulation of $4^0$ or $4^1$ via the $4^2$ or higher levels can be ruled out. Thus the system of only two excited state vibronic levels is a good approximation.

The solution to the differential equations for the three level system has been given before\textsuperscript{14} and will not be repeated in detail. Under the initial population conditions $n_0(t = 0) = \Delta n$ and $n_1(t = 0) = 0$ for the levels $4^0$ and $4^1$, the solution is of the form:

$$n_0(t) = A \exp(-\lambda_f t) + B \exp(-\lambda_s t),$$

$$n_1(t) = C [\exp(-\lambda_s t) - \exp(-\lambda_f t)],$$

where $A$, $B$, and $C$ are proportional to $\Delta n$ and depend on $k_{10}$, $k_{01}$, $k_0$, $k_1$, and the pressure $P$. In principle, the observables are the two eigenvalues, $\lambda_f$ and $\lambda_s$, and the $t = 0$ ratio of fast to slow amplitudes as a function of $P$. However, the experimental ratio $I_f/I_s$ of fluorescence amplitudes is not readily related to the kinetic parameter $A/B$ because of unknown filter factors and Franck-Condon factors. At high pressure, where vibrational equilibration is rapid compared to decay of $4^0$ and $4^1$, the square root in Eq. (18) of Ref. 14 can be expanded in powers of $[(k_{01} + k_{10})P]^{-1}$ to yield:

$$\lambda_f = (k_{01} + k_{10})P + f k_0 + (1 - f)k_1,$$

$$\lambda_s = f k_1 + (1 - f)k_0,$$
with \( f = \frac{k_{01}}{k_{01} + k_{10}} \). Equations (3) and (4) are valid for \( |k_0 - k_1| \ll (k_{01} + k_{10})P \). Microscopic reversibility gives

\[
\frac{k_{01}}{k_{10}} = \exp(-\Delta E/kT),
\]

where \( \Delta E \) is the level spacing. Thus \( f \) is 0.35 for \( \text{H}_2\text{CO} \) and 0.42 for \( \text{D}_2\text{CO} \). In this high pressure limit, the fast decay rate \( \lambda_f \) is dominated by the sum of energy transfer rates, while the slow decay rate \( \lambda_s \) is a population-weighted sum of the \( 4^0 \) and \( 4^1 \) decay rates out of \( S_1 \). In the contrasting limit of very low pressure, the decay out of \( S_1 \) is rapid and vibrational equilibration within \( S_1 \) is not approached. In this case, the same square root is expanded in powers of \( (k_1 - k_0)^{-1} \) to obtain:

\[
\lambda(4^1) = \lambda_f \approx k_1 + k_{10}P, \quad \lambda(4^0) = \lambda_s \approx k_0 + k_{01}P,
\]

where \( \lambda(4^1) \) and \( \lambda(4^0) \) label the eigenvalues which become the pure \( 4^1 \) and \( 4^0 \) decay rates in the absence of coupling.

Equations (6) and (7) are valid for \( |k_0 - k_1| \gg (k_{01} + k_{10})P \).

For \( \text{D}_2\text{CO} \), this condition requires pressures below \(~10^{-4}\) Torr.

In this low pressure limit, different single exponential decay rates are observed for \( 4^0 \) and \( 4^1 \) excitation.

**B. \( \text{D}_2\text{CO} \) results**

Two excitation wavelengths were used for \( \text{D}_2\text{CO} \), as given in Table I. By exciting the \( 4^0 \) level and observing fluorescence
through the $4^1$ filter, it was possible to measure the rate of $4^0 + 4^1$ energy transfer. In the pressure range 0.02 to 0.6 Torr, the $4^1$ fluorescence signal rises much more slowly than the laser pulse and decays as a single exponential. A typical semi-log plot is shown in Fig. 3 for the rise of fluorescence from 0.076 Torr of $D_2CO$. The deviation of the rise from exponentiality at very short times is due to a component of $4^0$ fluorescence which passes the $4^1$ filter and rises with the laser pulse; this is confirmed by the fact that the prompt fluorescence persists, while the amplitude of slowly rising fluorescence gradually decreases with pressure. Imperfect filtering affects the amplitude ratio of the slow and fast components, but not their lifetimes. The inverse $4^1$ risetimes are proportional to pressure with slope $k_{01} + k_{10} = (1.63 \pm 0.06) \times 10^{-9}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$, as shown in Fig. 4. The pressure dependence of the term $fk_0 + (1 - f)k_1$ in Eq. (3) is neglected because it is smaller than the experimental uncertainty of the overall slope. Equation (5) then yields $k_{01} = (6.7 \pm 0.3) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ and $k_{10} = (9.6 \pm 0.4) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$. Above 0.6 Torr, the risetimes are gradually distorted by the system response time, while below 0.02 Torr the amplitude of the rise becomes too small.

For $4^0$ excitation, the resonance fluorescence (as viewed through the $4^0$ filter) rises during the laser pulse and decays as a sum of two exponentials at pressures from 0.02
to 0.6 Torr. The fast component decays with a lifetime equal to the risetime of \( 4^1 \) fluorescence after \( 4^0 \) excitation; hence, it is attributed to \( 4^0 \rightarrow 4^1 \) energy transfer as in Eq. (3). The slow decay component yields the population weighted average of the \( 4^0 \) and \( 4^1 \) decay rates, as in Eq. (4). At lower pressures, the fast component gradually disappears until the decay is a single exponential below 5 mTorr.

For \( 4^1 \) excitation and observation of fluorescence through a uv cut-off filter, the decays were slightly non-exponential at pressures above 10 mTorr and the slow lifetimes agreed with those obtained from \( 4^0 \) excitation to within \( \pm 5\% \). Below 10 mTorr the decays were single exponentials and the \( 4^1 \) lifetimes gradually became distinguishable from those of \( 4^0 \). Figure 5 shows the S/N obtainable at \( 8 \times 10^{-5} \) Torr of \( \text{D}_2\text{CO} \).

The Stern-Volmer plot of \( \tau^{-1} \) vs pressure for both \( 4^0 \) and \( 4^1 \) excitation of \( \text{D}_2\text{CO} \) shown in Fig. 6 covers some five orders of magnitude in pressure. The lifetimes plotted are for the slow decay after \( 4^0 \) excitation and for the major component after \( 4^1 \) excitation. (The "fast" decay \( \lambda(4^1) \) dominates the \( 4^1 \) resonance fluorescence at pressures for which energy transfer is unimportant, Eq. (6), whereas the "slow" decay \( \lambda_S \) dominates above 10 mTorr, Eq. (4).) The linear portion of the plot from 0.1 to 4 Torr has slope \( (2.96 \pm 0.19) \times 10^{-11} \) cm\(^3\) molecule\(^{-1}\) sec\(^{-1}\) for either \( 4^0 \) or \( 4^1 \) excitation. As the pressure decreases below 0.1 Torr, the slope gradually
increases; the \(4^0\) and \(4^1\) curves are distinguishable below 5 mTorr. The limiting low pressure slopes can be estimated only very roughly as \((9 \pm 6) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}\) for \(4^0\) and \((3 \pm 2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}\) for \(4^1\). The extrapolated zero pressure lifetime \(\tau_0\) is \(7.8 \pm 0.7 \mu\text{sec}\) for \(4^0\) and \(6.0 \pm 0.4 \mu\text{sec}\) for \(4^1\). The ratio \(\tau_0(4^0)/\tau_0(4^1)\) is \(1.30 \pm 0.15\). The \(\text{D}_2\text{CO}\) results are summarized in Table I.

The linearity of the Stern-Volmer plot from 0.1 to 4 Torr gives, Eq. (4), the result \(0.42 k_1 + 0.58 k_0 = (0.30 \pm 0.13) \mu\text{sec}^{-1} + (0.96 \pm 0.06) \mu\text{sec}^{-1} \text{ torr}^{-1} P_{\text{D}_2\text{CO}}\) in the high pressure range. The slope corresponds to quenching at about one-tenth of the gas kinetic rate. The pressure dependences of \(k_0\) and \(k_1\) cannot be separated. The non-linearity of the Stern-Volmer plot below 0.1 Torr indicates a different sort of quenching process, since it is not adequately explained by the energy transfer scheme with \(k_0\) and \(k_1\) simply proportional to pressure. This is most readily seen by contradiction. A Stern-Volmer plot can be computed from the exact equations of Ref. 14 under the assumption that \(k_0\) and \(k_1\) are proportional to pressure with a slope that matches the experimental results above 0.1 Torr. The zero pressure lifetimes and the rate constants \(k_{01}\) and \(k_{10}\) are fixed by experiment. The calculation is insensitive to the partitioning of the high pressure slope between \(k_0\) and \(k_1\). The computed dependence of \(\tau_s^{-1}\) on pressure is slightly non-linear only below 10 mTorr as shown by the dotted lines in
Fig. 6, in significant disagreement with the experimental results. Variation of the kinetic constants within the experimental uncertainties cannot improve the agreement appreciably. The conclusion is that $k_0$ or $k_1$ (or both) exhibits negative curvature as a function of pressure below 0.1 Torr of D$_2$CO.

C. H$_2$CO results

The H$_2$CO lifetime results include data obtained at a variety of excitation energies, as summarized in Table II. In all cases, non-exponential decays were fit quite successfully to a sum of two exponential components, although there is no a priori reason for the decay to follow such a form. Some caution is in order here, for it is well known that slight contamination by a third component can dramatically affect the derived lifetimes of the two major components. The fast and slow lifetimes are designated $\tau_f$ and $\tau_s$, and $I_f/I_s$ refers to the experimental ratio of the fast component amplitude to the slow component amplitude extrapolated to $t = 0$.

Below 0.1 Torr, the H$_2$CO fluorescence decay was bi-exponential for most of the excitation wavelengths studied. As an example, Fig. 7 shows the decay of fluorescence from 0.0237 Torr of H$_2$CO after excitation of the rR$_0$ sub-band of $4^0_1$. The filter combination selects $4^0$ fluorescence in this case. Similar biexponential decays were observed near
25 mTorr for each of the \( rR_1 \) through \( rR_5 \) sub-bands of \( 4^0_1 \) and for tripled YAG excitation of \( 4^1_0 \). In contrast, Fig. 8 shows the decay of fluorescence from 0.0256 Torr of \( H_2CO \) after \( rR_6 \) excitation within \( 4^0_1 \). This decay is a single exponential over two decades, as is that from \( \sim 0.025 \) Torr of \( H_2CO \) after \( rR_8 \), \( 4^0_1 \) excitation.

The Stern-Volmer plot of \( \tau_s^{-1} \) vs pressure for \( H_2CO \) exhibits dramatic curvature for all wavelengths studied. Typical plots are shown in Fig. 9. The plots become linear at very low pressures, permitting accurate extrapolations to zero pressure. The low pressure slopes correspond to electronic quenching at some 10 times the gas kinetic rate. Above 0.4 Torr, all of the curves coincide within the scatter of the data, while at lower pressure there are significant variations. At high pressure, from 2 to 5 Torr, the slope of the plot is \( (2 \pm 1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \); it is not clear whether this is the limiting high pressure slope. Both the low pressure slope and the zero pressure intercept depend fairly strongly on at least the \( K' \) rotational quantum number within \( 4^0_1 \) (Fig. 10). Variations with \( J' \) would tend to be averaged out in these experiments. All of the \( rR_6 \), \( 4^0_1 \) decays were single exponentials below 0.2 Torr; they are included as slow components since their lifetimes are comparable to and blend smoothly with the other \( \tau_s \)'s. The lowest pressure data were obtained for tripled YAG excitation of \( 4^1_0 \). The S/N achieved at \( 5 \times 10^{-4} \) Torr of \( H_2CO \) is shown in Fig. 11.
Pressures below $2 \times 10^{-3}$ Torr were not readily studied in the case of dye laser excitation of $^4_1$.

It is clear from Figs. 7 and 11 that the fast component, when present, can be quite important in the 0 - 0.1 Torr pressure range. Figure 12 shows the Stern-Volmer plot of $\tau_f^{-1}$ vs pressure for the resonance fluorescence at two different wavelengths. The fast component data are relatively scattered due to the difficulty of determining $\tau_f$ consistently from limited S/N decay curves. Nevertheless, it is clear that at low pressure the fast decay rate also quenches roughly linearly at rates 10 to 20 times gas kinetic. The zero pressure lifetimes and low pressure slopes for both fast and slow components of $H_2CO$ fluorescence are summarized in Table II.

For $H_2CO$ below 0.1 Torr, the fast component of the resonance fluorescence decay is not caused by $^4_0 \leftrightarrow ^4_1$ energy transfer. For the case of $^4_1$ excitation, a careful search was made using the $^4_0$ filter for fluorescence rise-times corresponding to the fast $^4_1$ decay component. However, in the 0 - 0.1 Torr pressure range the fluorescence rose with the laser pulse. Identical biexponential decays were observed using either the $^4_0$ or $^4_1$ filter, presumably due to the imperfect blocking of $^4_1$ fluorescence by the $^4_0$ filter.

As the pressure is increased above 0.1 Torr, the rise of fluorescence observed through the $^4_0$ filter gradually becomes distinguishable from the laser pulse. In a very limited
pressure range from ~ 0.4 to 0.7 Torr the fluorescence through the $4^0$ filter has a risetime which agrees with the fast decay time of the $4^1$ fluorescence to ± 15%. In addition, the decay of the $4^0$ fluorescence is a single exponential which agrees with the $4^1$ slow lifetime within experimental error. In this pressure range, the fast component of resonance $4^1$ fluorescence is attributed primarily to energy transfer, although it may be influenced by a residual fast component of the low pressure type. It was not possible to extract meaningful energy transfer rate constants from data in so limited a pressure range. Above 0.7 Torr, both risetimes and fast decays gradually become unreliable as they blend into the finite laser pulse width. Above 1.5 Torr, the fast component of $4^1$ decay is not observed and the $4^0$ risetime is likewise faster than 10 nsec.

Further information is available from the $t = 0$ amplitude ratios $I_f/I_s$ for resonance fluorescence as shown in Fig. 13 for various wavelengths. The data are scattered due to the sensitivity of $I_f/I_s$ to the choice of both $\tau_f$ and $t = 0$. Several trends are clear. Near zero pressure, the fast component accounts for one-half to two-thirds of the decay when it is present. The ratio $I_f/I_s$ decreases rapidly in the pressure range 0 to 0.1 Torr, nearly vanishing for some wavelengths. This is the region of rapid, nearly linear quenching of $\tau_f^{-1}$, as in Fig. 12. Above 0.1 Torr, $I_f/I_s$ increases to a fairly constant value. This is the pressure range in which
the fast component is due primarily to $4^0 \leftrightarrow 4^1$ energy transfer, as argued above. Notice that although no fast component appears below 0.2 Torr for $4R_6, 4^0$ excitation, the energy transfer related fast decay indeed grows in above 0.2 Torr.

To summarize, the $H_2CO$ fluorescence decay is biexponential below 0.1 Torr for most wavelengths. The fast component is not due to energy transfer and rapidly diminishes in relative amplitude as the pressure increases to 0.1 Torr. Both $\tau_s^{-1}$ and $\tau_f^{-1}$ quench at rates much larger than gas kinetic at these low pressures. The low pressure slopes and the zero pressure lifetimes depend fairly strongly on at least the $K'$ rotational quantum number. At pressures greater than 0.2 Torr a second kind of fast component due to $4^0 \leftrightarrow 4^1$ energy transfer becomes important. The Stern-Volmer plot for $\tau_s^{-1}$ exhibits dramatic curvature below 0.2 Torr for all wavelengths.

IV. DISCUSSION

A. Comparison with other studies

Fluorescence lifetimes have been reported by Yeung and Moore (YM)$^8$ and by Miller and Lee (ML)$^{13}$ for the $4^1, 2^14^3$, and $2^24^1$ vibronic levels of $H_2CO$. In all cases, YM obtained extrapolated zero pressure lifetimes 2 to 4 times longer than those of ML. YM also reported quenching constants larger than gas kinetic, whereas ML reported no quenching. It now appears that the raw data of the two groups are quite
consistent. However, for at least the $4^1$ level, the non-
exponentiality of the decays and the extreme curvature of
the Stern-Volmer plots make the reported slopes and life-
times very sensitive to the way in which the decay curves
are recorded and analyzed and to the pressure range studied.

The $4^1$ data of ML$^{13}$ are compared with the present $\tau_s^{-1}$
data (solid line) in Fig. 14. The agreement is good above
1 Torr, but ML consistently obtain faster decay rates from
0.05 to 1 Torr. The discrepancy is apparently due to the
non-exponentiality of the low pressure decays. With poorer
S/N, ML tended to analyze only the first decade or so of the
decay, thus obtaining an "average lifetime" intermediate
between $\tau_f$ and $\tau_s$. This average lifetime is rather in-
sensitive to pressure in the range 0.05 to 3 Torr, so that
ML reported no quenching. In contrast, YM had better S/N
but discarded the early portion of the decay due to scattered
light. Thus, YM obtained lifetimes that are essentially
identical to the present results for $\tau_s$ down to 0.02 Torr.
YM reported a large quenching rate and an extrapolated
zero pressure $4^1$ lifetime 4 times longer than that of ML,
yet 30% shorter than the present result for $\tau_s$. Discrepancies
for the higher levels may well have the same origin.
Variation of low pressure lifetimes with rotational state may
also have contributed.

The $D_2CO$ results for $4^1_0$ excitation agree very well with
ML$^{13}$ over their pressure range of 0.125 to 1 Torr. In the
same pressure range, YM reported a quenching rate ~15% smaller than that obtained here. Neither previous study examined pressures low enough to observe the slight curvature of the Stern-Volmer plot below 0.1 Torr or the pure 4\textsuperscript{1} lifetime uncontaminated by collisional coupling with 4\textsuperscript{0}. The observed zero pressure D\textsubscript{2}CO lifetimes are comparable to calculated radiative lifetimes.\textsuperscript{17} The ratio of radiative lifetimes of 4\textsuperscript{0} and 4\textsuperscript{1} for H\textsubscript{2}CO is 1.4 ± 0.2,\textsuperscript{18} whereas for D\textsubscript{2}CO, the ratio of zero pressure lifetimes is 1.30 ± 0.15. ML\textsuperscript{13} report that the fluorescence quantum yield for the 4\textsuperscript{1} level of D\textsubscript{2}CO is 1.0 ± 0.2 at 4 x 10\textsuperscript{-3} Torr. The presently reported lifetimes for the 4\textsuperscript{1} level of D\textsubscript{2}CO yield
\[
\tau(4 \times 10^{-3} \text{ Torr}) = (0.83 ± 0.08) \tau_0 \leq (0.83 ± 0.08) \tau_{\text{rad}},
\]
since \(\tau_0 \leq \tau_{\text{rad}}\). Consequently, the fluorescence quantum yield at 4 x 10\textsuperscript{-3} Torr is necessarily less than 0.83 ± 0.08.

Similar comparisons at various pressures suggest a systematic error in the quantum yield calibration of 15 - 30%.

The necessity for lower pressure data on other vibronic levels of both H\textsubscript{2}CO and D\textsubscript{2}CO is now clear. A strong dependence of lifetime on rotational quantum number is not unlikely.\textsuperscript{19, 20} Previously obtained values\textsuperscript{13} of \(\tau_{\text{rad}} = \tau/\phi_{\text{fl}}\) may be in error if the Stern-Volmer plots curve between the pressures for which \(\phi_{\text{fl}}\) was measured and those for which \(\tau\) was measured, or if significant energy transfer occurred.

Shibuya and Lee\textsuperscript{21} have reported a value of 6.9 x 10\textsuperscript{-10} cm\textsuperscript{3} molecule\textsuperscript{-1} sec\textsuperscript{-1} for the H\textsubscript{2}CO 4\textsuperscript{1} + 4\textsuperscript{0} energy transfer.
rate constant within $S_1$, based on observation of changes in the fluorescence spectrum with pressure. The analogous $D_2CO$ value obtained from risetime measurements in this study is $(9.6 \pm 0.4) \times 10^{-10}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$. Recall that the $4^0 - 4^1$ energy gap in $D_2CO$ is about half that of $H_2CO$. Note that the $H_2CO$ value implies a $4^1 \rightarrow 4^0$ energy transfer rate of 0.44 μsec$^{-1}$ at 0.02 Torr, compared with typical values of ~ 4 μsec$^{-1}$ for the slow component decay rate. This confirms the conclusion that vibrational energy transfer is unimportant for $H_2CO$ at the lowest pressures studied. The two rates $k_{10P}$ and $\tau_s^{-1}$ become equal at 0.5 Torr, which compares reasonably with the onset of agreement between the lifetime of the fast component of $4^1$ decay and the risetime of $4^0$ fluorescence.

The near-resonant $4^0 - 4^1$ excited state energy transfer rate constants for $H_2CO$ and $D_2CO$ are about 2 to 3 times the gas kinetic rate. Zittel and Lineberger$^{22}$ have recently reported vibrational relaxation rates for low-lying torsional modes ($v_7$, 237 cm$^{-1}$) of the $S_1 (^{1}A_u)$ state of glyoxal, (HCO)$_2$. They found very rapid relaxation at 2 to 3 times the gas kinetic rate, roughly independent of total vibrational energy in $S_1$ for three isotopes (glyoxal - $h_2$, hd, and $d_2$). Similarly, Parmenter and Tang$^{23}$ observed nearly gas kinetic rate constants in their very thorough study of the relaxation of the $6^1$ mode of the $S_1 (^{1}B_{2u})$ state of benzene, a non-polar molecule. The emerging picture is one of very rapid relaxation of low frequency torsional and bending vibrations in excited states of polyatomic molecules.
B. Photophysics

Zero pressure behavior. An important conclusion from this study is that $\text{H}_2\text{CO}$ decays non-radiatively from $4^0$ and $4^1$ at zero pressure. Theoretical treatments of the radiative lifetime of the $S_1$ state of $\text{H}_2\text{CO}^{17}$ yield estimates of $\sim 5$ μsec. The lowest pressure data, which extend to $2 \times 10^{-4}$ Torr of $\text{H}_2\text{CO}$, are for tripled YAG excitation of $4^1_0$. These data are well fit by a biexponential decay with $\tau_f = 70 \pm 15$ nsec, $\tau_s = 430 \pm 40$ nsec, and $I_f/I_s = 2.7 \pm 0.5$. The decay does not change noticeably until the pressure is increased a factor of 5 to $10^{-3}$ Torr. Such a curve has decayed to $1/e$ of its initial amplitude at $t = 110$ nsec. The slope required to reach the estimated radiative decay rate of $\sim 0.2$ μsec$^{-1}$ at true zero pressure from the observed "$1/e$ decay rate" of 9 μsec$^{-1}$ at $2 \times 10^{-4}$ Torr corresponds to electronic quenching at $\sim 4000$ times the gas kinetic collision rate. It is possible that a very small amplitude, $\tau \geq 5$ μsec decay would appear only as a slight baseline error in these results, but an absolute upper bound on the $t = 0$ relative amplitude of such a decay is 5%. A relative amplitude greater than 2% is very unlikely. The results for various rR sub-bands of $4^0_1$ in $\text{H}_2\text{CO}$ typically extend to a few mTorr but are qualitatively similar to the $4^1_0$ results. The conclusion is that the dominant decay of the $4^0$ and $4^1$ levels of $\text{H}_2\text{CO}$ under collision-free conditions occurs on a timescale at least 20 times shorter than the estimated radiative lifetime. In
contrast, D$_2$CO decays from $^40$ and $^41$ at rates that may well be purely radiative at zero pressure.

Elert, Heller and Gelbart$^4$ have recently completed a calculation of formaldehyde dissociation dynamics from low-lying single vibronic levels of S$_1$. They suggest that the barrier to dissociation on the S$_0$ surface lies at $\approx$ 32000 cm$^{-1}$, some 4000 cm$^{-1}$ above the S$_1$ origin, so that both H$_2$CO and D$_2$CO are "small" molecules at zero pressure and merely radiate. The delayed appearance of CO product observed by Houston and Moore$^3$ might then be associated with collisional activation over the barrier. As argued in the preceding paragraph, H$_2$CO decays non-radiatively at zero pressure, in qualitative agreement with the calculations of Elert, et al. only when they place the barrier at 25000 cm$^{-1}$, slightly below S$_1$. However, for the lower barrier the CO product appears on essentially the same timescale as the S$_1$ decay, i.e., there is no time lag. A satisfactory explanation for all of the available dynamical observations is lacking at present.

**Collisional effects.** The large observed slopes of the H$_2$CO Stern-Volmer plots at low pressure correspond to electronic quenching of S$_1$ at ~10 times the gas kinetic collision rate. Following the discussion of Gelbart and Freed,$^6$ the probability of collision-induced internal conversion from an initially excited mixed rovibronic state of primarily S$_1$ character to a manifold of primarily S$_0$ final states can
be written as

$$P = \frac{\hbar}{\varepsilon} \sum_{n''j''} \left[ \int_{-\infty}^{+\infty} dt \exp(i\omega_{n''j''} t) \phi_{S_0}^{n_0j_0} + \sum_{n'j_0} C_{n'j_0j''} \phi_{S_0}^{n'j_0} \right]$$

\[ (8) \]

in a first-order time dependent perturbation theory approach. In Eq. (8), the labels $S_1$, $n$ and $j$ denote the electronic, vibrational, and angular momentum states of the zeroth order basis functions $\phi$. The basis set includes one $S_1$ vibrational level $n_0$ with its associated rotational states $j$ and the complete manifold of $S_0$ vibronic levels. The $C_{n''j''}$ are the intramolecular mixing coefficients due to vibronic coupling between the $n_0j''$ level of $S_1$ and the $n''j''$ levels of $S_0$. For Eq. (8) to be valid as the internal conversion probability, it is necessary that the total mixing $\sum_{n''j''} |C_{n''j''}|^2$ for each rotational state be much less than one. Thus, each mixed state is of primarily $S_1$ or $S_0$ character and can be labeled by the zeroth order indices $n_0j$ or $n''j''$. The intermolecular perturbation $V$ depends on the classical trajectory $R(t)$ and on the vibrational ($Q$) and angular ($\Theta$) coordinates of the formaldehyde molecules. Each Fourier transform is evaluated with frequency $\omega_{n''j''}$ corresponding to the energy separation between the initially prepared mixed state $n_0j_0$ and the final mixed state $n''j''$, and these state-to-state probabilities are
summed over final states \( n''j'' \). The resulting probability must be averaged over relative orientations and integrated over impact parameter and relative velocities to obtain the rate constant for internal conversion. If the matrix element of Eq. (8) is multiplied out, an estimate of the magnitude of this rate constant can be obtained as

\[
 k_{IC} = \left( \sum_{n'} \left| C_{n'} \right|^2 \right) k_{S_1}^{\text{rot}} + \left( \sum_{n', j_0} C_{n', j_0} \right)^2 k_{S_0}^{\text{rovib}}
 + k_{S_1-S_0} + \text{cross-terms.}
\]

Here \( k_{S_1}^{\text{rot}} \) is the rate constant for rotational relaxation from the pure \( S_1n_0j_0 \) state to all other \( S_1n_0 \) rotational states and \( k_{S_0}^{\text{rovib}} \) is an average total inelastic rate constant for transfer from a single pure \( S_0 \) vibration-rotation level to all other \( S_0 \) levels. The factor \( \sum_{n'} \left| C_{n'} \right|^2 \) is equal to the average total mixing of an \( n_0j_0 \) level of \( S_1 \), \( \sum_{n} \sum_{j} \left| C_{n'j'} \right|^2 \left/ \left( \sum_{j} 1 \right) \right. \). The factor \( \left( \sum_{n', j_0} C_{n', j_0} \right)^2 \) is the total mixing of the \( S_1n_0j_0 \) level plus cross-terms which will tend to cancel if the sum includes many coefficients of positive and negative sign. The term \( k_{S_1-S_0} \) is the total rate constant for transfer from a pure \( S_1 \) level to pure \( S_0 \) levels. The cross-terms arising from Eq. (8) should not dominate Eq. (9) and will not be explicitly considered.

At low pressure, the largest contribution to \( k_{IC} \) is
from the pure state relaxation terms $k_{S_1}^{\text{rot}}$ and $k_{S_0}^{\text{rovib}}$. The observed Stern-Volmer slopes of ~ 10 gas kinetic for $H_2CO$ can be equated to the sum of the first two terms in Eq. (9). A reasonable range for the total mixing of a typical $S_1$ level might be 0.03 to 0.3, which would imply a range of 300 to 30 gas kinetic for the sum $k_{S_1}^{\text{rot}} + k_{S_0}^{\text{rovib}}$. Microwave line broadening yields values of 12 gas kinetic for $H_2CO$ rotational relaxation rates near the $S_0$ origin, but essentially nothing is known about total inelastic collision rates for highly energetic $S_0$ rovibronic levels. It may be that very soft collisions could change the phase of an atom's vibrational motion sufficiently to cause transitions to nearby levels; the necessary energy change could be much less than 1 cm$^{-1}$.

The much smaller $D_2CO$ low pressure quenching rates can be explained in terms of the much weaker intramolecular couplings, due to poorer vibrational overlaps. Elert, et al. obtained median $S_1 - S_0$ coupling matrix elements more than 20 times larger in $H_2CO$ than in $D_2CO$. These elements are not easily related to the mixing coefficients of Eq. (8), but there is clearly a large isotope effect. The variation of low pressure slope with $K'$ in the case of $H_2CO$ (Fig. 10) might also be understood in terms of the coupling strengths. Certain pure $S_1$ rotational states may be more nearly resonant with appropriate $S_0$ levels.

At higher pressures, rapid collisional interconversion
of the $S_0$ levels may broaden them until typical widths exceed typical spacings. The result is a collision-induced statistical limit, as recently discussed by Freed\(^7\) and other workers.\(^5\)

The part of the rate constant $k_{IC}$ due to coupling of nearly isoenergetic mixed states by long-range collisions saturates at a pressure $P_{\text{sat}}$ for which $k_{S_0}^{\text{ro vib}} P_{\text{sat}} > 2\pi/\rho_{\text{tot}}$, where $\rho_{\text{tot}}$ is the total density of $S_0$ vibronic levels accessible to a given level by collisions at room temperature. For $\text{H}_2\text{CO}$, the observed $P_{\text{sat}}$ is \(\approx 0.2\) Torr (Fig. 9). Thus the product of $\rho_{\text{tot}}$ (per cm$^{-1}$) and $k_{S_0}^{\text{ro vib}}$ must be $10^5$ times the gas kinetic collision rate. The observed low pressure slopes suggest that $k_{S_0}^{\text{ro vib}}$ is in the range 30 to 300 gas kinetic, since it presumably dominates the sum $k_{S_1}^{\text{rot}} + k_{S_0}^{\text{ro vib}}$. The corresponding range for $\rho_{\text{tot}}$ is 3000 to 300 per cm$^{-1}$. The density of $\text{H}_2\text{CO}$ $S_0$ levels for six harmonic vibrational degrees of freedom at 28,000 cm$^{-1}$ is 6 per cm$^{-1}$. Anharmonicity corrections and inclusion of the accessible rotational states for each vibrational level will increase the effective density of states. There are serious limitations on both the energy and angular momentum changes that can readily occur via long-range collisions at room temperature. However, an overall density of \(\approx 10^3\) per cm$^{-1}$ is not unreasonably large.

As Freed points out,\(^7\) the term $k_{S_1-S_0}$ in Eq. (9) represents a "true" rate constant and does not saturate at high pressures. It can therefore account for the residual Stern-Volmer plot slope of \(\approx 0.1\) gas kinetic at high pressure.
for both H$_2$CO and D$_2$CO. In D$_2$CO, $k_{S_1-S_0}$ apparently dominates the overall slope above about 20 mTorr because the other terms in Eq. (9) are relatively small. The term $k_{S_1-S_0}$ corresponds to the typically observed electronic quenching$^{25}$ by hard collisions which may cause large energy changes.

The decay rate in the collision-induced statistical limit is governed by the usual Fermi golden rule rate$^7$, $^{26}$

$$\Gamma_{\text{stat}} = \frac{(2\pi/\hbar)}{\bar{v}^2} \rho,$$  

where $\bar{v}^2$ is the mean square intramolecular (collisionless) perturbation. For high pressure relaxation from a thermalized distribution of $S_1$ rotational states, the appropriate density $\rho$ is the Boltzmann average of the density of states coupled intramolecularly (without collisions) to each $S_1$ rotational state. The rate $\Gamma_{\text{stat}}$ can be obtained experimentally from a curved Stern-Volmer plot by extrapolating the linear high pressure region back to $P = 0$, i.e., by subtracting out the linear contribution of $k_{S_1-S_0}$. For H$_2$CO, such an extrapolation (Fig. 9) yields $\Gamma_{\text{stat}} = 14 \pm 2$ $\mu$sec$^{-1}$ for the population-weighted average of $4^0$ and $4^1$ rates. The corresponding D$_2$CO average (Fig. 6) is $0.30 \pm 0.13$ $\mu$sec$^{-1}$. $\Gamma_{\text{stat}}$ should vary with the initially excited vibronic level but should be independent of the perturbing molecule. Relative values of $\Gamma_{\text{stat}}$ for different vibronic levels could be compared with the non-radiative $S_1 \rightarrow S_0$ rates calculated by Yeung and Moore,$^{27}$ who assumed that the $S_0$ levels were broadened by
dissociation to the extent of forming a quasi-continuum at zero pressure.

For the simple Bixon-Jortner model of constant $S_0$ level spacing $\varepsilon$ and constant $S_1 - S_0$ intramolecular perturbation $v$, an analytical relationship between $v^2 = \nu^2$ and the total mixing $\sum_n |C_{n'j_0}|^2$ can be obtained in the weak coupling limit $v << \varepsilon$. The mixing coefficients are given by first order perturbation theory as

$$C_{n'j_0} = \nu / \left( E_{S_1} - E_{S_0} \right),$$

where the $E$'s are energies of the zeroth order $S_1$ and $S_0$ levels. The model defines $E_{S_0} = E_{S_1} - \alpha + n' \varepsilon$, with $n' = 0, \pm 1, \pm 2, \ldots$ and $0 \leq \alpha < \varepsilon$, so that $\alpha$ gives the energy offset of the equally spaced manifold relative to $E_{S_0}$. Equation (11) can be squared and summed over $n'$ to yield the total mixing

$$\sum_n |C_{n'j_0}|^2 = \pi^2 \nu^2 / [\varepsilon^2 \sin^2 (\pi \alpha / \varepsilon)].$$

If $\sin^2 (\pi \alpha / \varepsilon)$ is replaced by its average value of 1/2 and $\varepsilon^{-1}$ is replaced by $\rho$, then Eqs. (10) and (12) can be combined to yield

$$\Gamma_{\text{stat}} = \left( \sum_n |C_{n'j_0}|^2 \right) / \left( \pi n \rho \right).$$

For $H_2CO$, with $\Gamma_{\text{stat}} = 1.4 \times 10^7 \text{ sec}^{-1}$, Eq. (13) implies that $\rho (\text{per cm}^{-1}) = 4.3 \times 10^3 \left( \sum_n |C_{n'j_0}|^2 \right)$. For a range of total
mixing from 0.03 to 0.3, the density of states ranges from 130 to 1300 per cm\(^{-1}\). The corresponding range of off-diagonal matrix elements \(v\) is \(3 \times 10^{-4}\) to \(9 \times 10^{-5}\) cm\(^{-1}\), so that the weak coupling limit \(v \ll \rho^{-1}\) is preserved. Such derived densities of states are orders of magnitude larger than the harmonic oscillator level density of 6 per cm\(^{-1}\), which is divided among four symmetry representations. Both anharmonicity and Coriolis coupling\(^{29}\) of the \(S_0\) levels will increase the zero pressure density of states beyond the harmonic oscillator estimate.

Elert, et al.,\(^4\) have obtained a median \(S_1 - S_0\) matrix element of \(\overline{v} = 7.17 \times 10^{-3}\) cm\(^{-1}\) for the \(4^1\) level of H\(_2\)CO using Herzberg-Teller theory to second order. This is much larger than the estimates for \(v\) used above in the simple Bixon-Jortner model. Using \(\overline{v} = \overline{v}^2 = 5.2 \times 10^{-5}\) cm\(^{-2}\) and a symmetry allowed harmonic level density of 1.5 per cm\(^{-1}\) in Eq. (1) gives \(\Gamma_{\text{stat}}(4^1) = 9.2 \times 10^7\) sec\(^{-1}\), a factor of 6 larger than the observed average of \(4^0\) and \(4^1\) rates. It is not unreasonable to expect the \(4^1\) rate to be larger than the \(4^0\) rate. However, the corresponding total mixing, Eq. (12), is only \(2 \times 10^{-3}\), which implies, Eq. (9), that the sum \(k^{\text{rot}}_{S_1} + k^{\text{rovib}}_{S_0}\) be \~5000\) gas kinetic to match the experimental low pressure quenching rates. Such inelastic rates are uncomfortably large, and they explain why smaller total mixings (corresponding to larger \(v\)'s for a given \(\Gamma_{\text{stat}}\)) were not used in the numerical examples above.
In summary, the present work answers a few questions about formaldehyde and raises some new issues. Previous discrepancies in reported zero pressure lifetimes for H$_2$CO can be explained by the presently observed non-exponential decays and curved Stern-Volmer plots. For the $4^0$ and $4^1$ levels of $S_1$, H$_2$CO decays non-radiatively at zero pressure while D$_2$CO primarily radiates. The curvature of the Stern-Volmer plots can be qualitatively explained by a simple mixed-state model of collision-induced internal conversion; semi-quantitative comparisons suggest extremely large inelastic rate constants for interconversion of high ro-vibronic levels of $S_0$. A more critical test of the model will come from experiments using various quenchers and exciting higher vibronic levels. Fluorescence decay measurements after single rotational level excitation will clarify the role of rotational state in the non-radiative transition rate. The results suggest that pressure dependent structure might be observed in Doppler-free absorption spectra. The observation of zero pressure non-radiative decay for H$_2$CO suggests weak coupling to a dissociation continuum. Molecular beam photofragment studies might resolve the important question of whether or not photochemistry occurs at zero pressure.
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REFERENCES


16. See Fig. 4 - 39 of R.G. Miller, Ph.D. dissertation, U.C. Irvine (1975).


### TABLE I. D$_2$CO Results

<table>
<thead>
<tr>
<th>$v_{vac}$ (cm$^{-1}$)</th>
<th>Band$^a$</th>
<th>Approx. Rot. States$^a$</th>
<th>$\tau_0$ ((\mu)sec)$^b$</th>
<th>S - V Slope (cm$^3$ molec$^{-1}$ sec$^{-1}$)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>27,401</td>
<td>$4^0_1$</td>
<td>$K' = 4, J' = 5-15$</td>
<td>$7.8 \pm 0.7$</td>
<td>$(9 \pm 6) \times 10^{-10}$</td>
</tr>
<tr>
<td>28,382</td>
<td>$4^1_0$</td>
<td>$K' = 1, J' = 3-15$</td>
<td>$6.0 \pm 0.4$</td>
<td>$(3 \pm 2) \times 10^{-10}$</td>
</tr>
</tbody>
</table>

a. The notation $4^m_L^L$ indicates the $v_4'' = L + v_4' = m$ vibronic band. Within a vibronic band, the dye laser was tuned to particular $rR$ sub-band heads, for which $\Delta J = \Delta K = +1$. The approximate rotational states excited were obtained from Ref. 10 by including all assigned states within 2 cm$^{-1}$ of $v_{head}$.

b. Error limits estimated from the scatter of the data.

c. The gas kinetic collision rate is $3.15 \times 10^{-10}$ cm$^3$ molec$^{-1}$ sec$^{-1}$.

d. Least squares fit to all data above 0.1 Torr. Error limits are $\pm 2 \sigma$. 

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$^a$ The notation $4^m_L^L$ indicates the $v_4'' = L + v_4' = m$ vibronic band. Within a vibronic band, the dye laser was tuned to particular $rR$ sub-band heads, for which $\Delta J = \Delta K = +1$. The approximate rotational states excited were obtained from Ref. 10 by including all assigned states within 2 cm$^{-1}$ of $v_{head}$.

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$^d$ Least squares fit to all data above 0.1 Torr. Error limits are $\pm 2 \sigma$. 
<table>
<thead>
<tr>
<th>( \nu_{\text{vac}} ) (cm(^{-1}))</th>
<th>Band(^a)</th>
<th>Approx. ( \text{Rot. States} )</th>
<th>( \tau_0^d ) (nsec)</th>
<th>( \text{Low P Slope}^{c,d,e} ) (cm(^3) molec(^{-1}) sec(^{-1}))</th>
<th>( \tau_0^d ) (nsec)</th>
<th>( \text{Slope, P &lt; 0.1 Torr}^{d,e} ) (cm(^3) molec(^{-1}) sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>27,037</td>
<td>( 4^0_1 )</td>
<td>( K' = 1, J' = 3-10^a )</td>
<td>550 ± 90</td>
<td>((2.2 \pm 0.6) \times 10^{-9})</td>
<td>83 ± 10</td>
<td>((1.9 \pm 1.2) \times 10^{-9})</td>
</tr>
<tr>
<td>27,113</td>
<td>( 4^0_1 )</td>
<td>( K' = 5, J' = 5-11^a )</td>
<td>490 ± 90</td>
<td>((3.5 \pm 0.7) \times 10^{-9})</td>
<td>130 ± 24</td>
<td>((6.5 \pm 1.9) \times 10^{-9})</td>
</tr>
<tr>
<td>27,156</td>
<td>( 4^0_1 )</td>
<td>( K' = 7, J' = 7-11^a )</td>
<td>235 ± 22</td>
<td>((2.2 \pm 0.7) \times 10^{-9})</td>
<td>No ( \tau_f ) observed</td>
<td></td>
</tr>
<tr>
<td>28,185</td>
<td>( 4^1_0 )</td>
<td>not known(^b)</td>
<td>435 ± 15</td>
<td>((4.5 \pm 0.5) \times 10^{-9})</td>
<td>69 ± 7</td>
<td>((3.4 \pm 0.9) \times 10^{-9})</td>
</tr>
</tbody>
</table>

a. See footnote (a) under Table I.

b. For tripled YAG excitation of \( 4^1_0 \), the laser probably excites a variety of lines in the \( pP \) and \( pQ \) branches.

c. The slope from 2-5 Torr is \((2 \pm 1) \times 10^{-11}\) cm\(^3\) molec\(^{-1}\) sec\(^{-1}\) for all excitation energies. Low P slopes are reported for the linear pressure range, typically below 10 - 20 mTorr.

d. Least squares fit of data in the linear pressure range. Error limits are ± 2 \( \sigma \).

e. The gas kinetic collision rate is \( 3.25 \times 10^{-10} \) cm\(^3\) molec\(^{-1}\) sec\(^{-1}\).
Figure 1. Interference filter transmission curves. The wavelengths of maximum intensity for H$_2$CO and D$_2$CO fluorescence bands are indicated by vertical lines. A typical band has a rotational envelope of FWHM ~ 20 Å.

Figure 2. Energy level diagram and rate constants for three level kinetic scheme. The $^4_0 - ^4_1$ splitting shown is for D$_2$CO; the H$_2$CO splitting is 125 cm$^{-1}$. The $S_1$ origin lies 28,188 cm$^{-1}$ above $S_0$.

Figure 3. Rise of $^4_1$ fluorescence after $^4_0$ excitation of 0.076 Torr of D$_2$CO. The risetime due to $^4_0 + ^4_1$ energy transfer is 210 ± 20 nsec. The circles show the log plot of the difference between the data (solid line) and a fit to the function exp(-$\lambda_f t$) (dashed line), yielding $\lambda_f$ as the slope. See Eq. (2) of the text.

Figure 4. Stern-Volmer plot of reciprocal risetime of $^4_1$ fluorescence after $^4_0$ excitation. The slope of (1.63 ± 0.06) x 10$^{-9}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ is $k_{01} + k_{10}$ in the kinetic scheme. Equation (5) of the text then yields the individual rate constant $k_{10} = (9.6 ± 0.4)$ x 10$^{-10}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$. The non-zero intercept is due to the zero pressure component of $f k_0 + (1 - f) k_1$ in Eq. (3).
Figure 5. Fluorescence decay for \((8 \pm 3) \times 10^{-5}\) Torr of \(\text{D}_2\text{CO}\) following excitation to \(\text{rR}_0\) of \(4^1_0\). The fluorescence is viewed through a non-selective uv cut-off filter. The lifetime is \(5.8 \pm 0.3\) \(\mu\text{sec}\).

Figure 6. Stern-Volmer plot for \(\text{D}_2\text{CO}\) over 5 orders of magnitude in pressure. The circles are for \(\text{rR}_3\), \(4^0_1\) excitation and the triangles are for \(\text{rR}_0\), \(4^1_0\) excitation. The two sets of data are identical within experimental error above 10 mTorr. The slope is constant at \((2.96 \pm 0.19) \times 10^{-11} \text{ cm}^3\) molecule\(^{-1}\) sec\(^{-1}\) between 0.1 and 4 Torr. Below 0.1 Torr it gradually increases to the low pressure limits of \((9 \pm 6) \times 10^{-10} \text{ cm}^3\) molecule\(^{-1}\) sec\(^{-1}\) for \(4^0_1\) and \((3 \pm 2) \times 10^{-10} \text{ cm}^3\) molecule\(^{-1}\) sec\(^{-1}\) for \(4^1_0\). The dotted line shows \(\lambda_s\) computed from the kinetic model assuming linear quenching of \(k_0\) and \(k_1\) to match the high pressure slope. The computed curve reaches its high pressure slope at 10 mTorr.

Figure 7. Fluorescence decay for 23.7 mTorr of \(\text{H}_2\text{CO}\) after \(\text{rR}_0\), \(4^0_1\) excitation as observed through the \(4^0_0\) filter. The analysis yielded \(\tau_f = 70 \pm 15\) nsec, \(\tau_s = 280 \pm 30\) nsec and \(I_f/I_s = 1.2 \pm 0.3\).

Figure 8. Fluorescence decay for 25.6 mTorr of \(\text{H}_2\text{CO}\) after \(\text{rR}_6\), \(4^0_1\) excitation as observed through the \(4^0_0\) filter. The decay is a single exponential with lifetime \(160 \pm 10\) nsec.
Figure 9. Stern-Volmer plot of $\tau_{s}^{-1}$ for H$_2$CO after $4^1_0$ excitation (circles) and $\text{rR}_4$, $4^1_1$ excitation (triangles). In each case the filters selected resonance fluorescence. The two curves are identical within experimental error above 0.4 Torr. The slope from 2 to 5 Torr is $(2 \pm 1) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$. It increases dramatically to the low pressure limits of $(4.5 \pm 0.5) \times 10^{-9}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ for $4^1_0$ below 10 mTorr and $(3.5 \pm 0.7) \times 10^{-9}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ for $\text{rR}_4$, $4^1_0$ below 20 mTorr. The $4^1_0$ data extend to $2 \times 10^{-4}$ Torr of H$_2$CO.

Figure 10. Dependence of $\tau_{s}^{-1}$ Stern-Volmer plot on the rR sub-band excited within $4^0_1$. Sub-bands with quantum numbers $K' = 1, 5, \text{ and } 7$ are shown. The three curves coalesce at pressures above 0.4 Torr. The slopes are $(2.2 \pm 0.6) \times 10^{-9}$, $(3.5 \pm 0.7) \times 10^{-9}$, and $(2.2 \pm 0.7) \times 10^{-9}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ for $K' = 1, 5$ and 7, respectively.

Figure 11. Fluorescence decay for $(5 \pm 1) \times 10^{-4}$ Torr of H$_2$CO after $4^1_0$ excitation, as viewed through the $4^1_1$ filter. The decay fits a sum of two exponentials with $\tau_f = 70 \pm 15$ nsec, $\tau_s = 430 \pm 40$ nsec and $I_f/I_s = 2.6 \pm 0.5$.

Figure 12. Stern-Volmer plot of $\tau_{f}^{-1}$ for H$_2$CO after $4^1_0$ excitation with $4^1_1$ observation (circles) and after $\text{rR}_4$, $4^0_1$ excitation with $4^0_0$ observation (squares). The slopes are
(3.4 ± 0.9) \times 10^{-9} \text{ and } (6.5 ± 1.9) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1},
respectively. The $4^1_0$ data extend to $2 \times 10^{-4}$ Torr.

Figure 13. Extrapolated $t = 0 \, I_f/I_0$ for H$_2$CO after $4^1_0$ excitation (circles), $rR_4$ of $4^0_1$ excitation (squares) and $rR_6$ of $4^0_1$ excitation (triangles). In each case the filters selected resonance fluorescence. The error limits on each point are ± 25%.

Figure 14. Comparison of the $4^1_1$ decay rates of Miller and Lee (circles, Ref. 13) with the present $\tau^{-1}_s$ rates (solid line).
Fig. 1

Wavelength (Å)

Percent T

H₂CO 4° filter
H₂CO 4' filter
D₂CO 4° filter
D₂CO 4' filter

H₂CO

D₂CO

3900 4000 4100 4200 4300 4400 4500 4600

XBL779-2032
Fig. 2

\[ S_0, T_1, \text{products} \]

\[ k_i \quad k_{01P} \quad k_{10P} \quad 69 \text{ cm}^{-1} \]
Fig. 3
Fig. 4

\[ \tau^{-1} (\mu \text{sec}^{-1}) \]

vs.

\[ P_{D_2CO} (\text{Torr}) \]
Fig. 5
Fig. 6
Fig. 7
Fig. 8
Fig. 9
Fig. 10

$\tau_s^{-1}$ (µsec$^{-1}$) vs. $P_{H_2CO}$ (Torr)

- $K' = 1$
- $K' = 5$
- $K' = 7$
Fig. 11
Fig. 13
Fig. 14
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