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Authors
Frei, H.
Pimentel, G.C.

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H. Frei and G.C. Pimentel

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Chemistry on Ground and Excited Electronic Surfaces
Induced by Selective Photo-excitation in Matrices

Heinz Frei and George C. Pimentel

Chemical Biodynamics Division, Lawrence Berkeley Laboratory
University of California, Berkeley, CA 94720
1. Introduction

Tunable laser light sources have opened new opportunities for clarification of the course of chemical reactions. Both on ground and excited electronic surfaces, it is now possible to initiate chemical reactions at precisely controlled initial energies and excitations. In principle, such possibilities bring the reaction coordinate and the activated complex closer to experimental reach.

The earliest attempts to develop these possibilities have revealed the rapidity of intramolecular energy redistribution and the necessity to understand these processes better. Some of these important but diversionary processes are either muted or inactive in cryogenic matrix environments. We shall discuss here a number of types of experiments that show that a cryogenic matrix offers a unique environment for the study of selective, photo-induced chemistry.

One special function of a matrix is to hold together a pair of potentially reactive molecules in a "sustained collisional complex"). This permits convenient and leisurely infrared spectroscopic study of these reactive pairs before and after selective excitation and in the absence of diffusion and thermally induced reactions. Of course, the diagnostic power of the IR spectral regions for matrix samples derives from the narrow band widths and the fact that essentially all molecules are vibrational chromophores (with the sole exception of homonuclear diatomics). Furthermore, prolonged photolytic exposure is possible, so low extinction coefficients and/or low quantum yields can be dealt with. For systems with low activation energies, one may attempt to stimulate reactions on the electronic ground state surface by selective excitation of fundamental, overtone, or combination vibrations using mid- or near-IR photons. Both for vibrationally stimulated and selective electronically induced chemistry, infrared monitoring of product growth allows detailed study of
quantum efficiencies to reaction, branching ratios, and sequential processes. Of course, the possibility of trapping transient intermediates and studying them by UV/visible and infrared spectroscopy makes the cryogenic technique a very valuable tool for such elucidation of reaction pathways.

There are limitations of the matrix technique that must be recognized. There is little known about the molecular orientations in the "sustained collisional complex" nor is it yet clear how much this can be controlled either by matrix cage size or elevated temperatures. Furthermore, there is no certainty that all intermediate species can be stabilized—experience shows that for exothermic reactions, this is a sensitive function of the competition between deactivation and continued reaction. Some bimolecular systems of interest cannot be studied because of prereaction during deposition (even with dual jet deposition). Careful attention must be paid to the degree of isolation and to reactant cluster size. Finally, there always remains the need for judgment and circumspection as we relate matrix reaction pathways to those of the gas phase.

This article surveys recent work in the field of selective photo-induced reactions in cryogenic solids, with focus on contributions from our laboratory. We will start with a brief review of vibrationally stimulated reactions in matrices, with special focus on evidence for mode selective chemistry (Sect. 2). This will be followed by a discussion of selective vibronically induced bimolecular reactions with red and near infrared photons (Sect. 3). A few examples of chemistry induced by photo-excited group III B metal atoms, which permit initiation of reactions on excited hypersurfaces not accessible by direct excitation of the reactants, will be presented in Section 4. Then, we will discuss the study of a UV wavelength controlled photoisomerization, of fundamental importance both for molecular energy and information storage (Sect. 5).
2. **Infrared Laser Induced Chemistry**

A cryogenic matrix is a unique environment for vibrational stimulation of reactions with low electronic ground state barriers (a few kcal/mole), since under such conditions the $kT$ energy available to the reactants is very small. As a consequence, thermal reactions are suppressed, hence high energy conformers may be stabilized and accumulated for convenient spectroscopic study. The first such process, the cis-trans isomerization of nitrous acid induced by excitation of the OH stretching mode with broad band infrared light, has been discovered in this laboratory more than 25 years ago [1]. However, new IR induced processes in matrices have been discovered only in the past ten years, reflecting the growing interest in vibrational photochemistry and the increasing availability of tunable infrared laser sources. We have reviewed progress in this field very recently [2], so will summarize here only briefly.

Beyond the well established IR laser induced interconversions of Fe(CO)$_4$ [3] and prototype cases with one conformational degree of freedom like nitrous acid [1,4] and 1,2-difluoroethane [5], an increasing number of vibrationally stimulated isomerizations of more complex molecules with two or more internal rotations are reported. Among these, the 2-haloethanols have been studied most extensively, 2-fluoroethanol under selective laser excitation [6], and all of them under globar irradiation [7]. An exciting feature of the vibrationally induced isomerization common to all 2-haloethanols is the one order of magnitude higher efficiency of the Gg$'-+Tt$ interconversion upon OH stretch excitation when compared with the $\nu$(OH) induced, reverse Tt $\rightarrow$ Gg' process (the capital letter in the designation Gg' determines the conformation about the C-C bond, the lower case letter the conformation about the C-O bond).
This is opposite to what is expected from energy considerations, since the OH stretching level of the less stable trans isomer, measured relative to the gauche ground vibrational state, lies several hundred cm\(^{-1}\) above the \(\nu(\text{OH})\) level of the gauche form in the case of all 2-haloethanols. This suggests that the OH stretching mode couples with the delocalized CC, CO torsional overtones in the gauche form much more strongly than in the trans form, most probably because of the weak intramolecular hydrogen bonding interaction in the former. Such conformer specificity in vibrationally induced interconversion processes has also been found in systems with three internal rotational degrees of freedom like ethylene glycol [8], 2-nitroethanol [9], and 2-aminoethanol [10]. This effect constitutes a very sensitive probe for conformer dependence of vibrational mode mixing.

A striking illustration of the use of IR induced conformational interconversion in matrices for mapping of high energy valleys on the electronic ground state surface of flexible molecules is the very recent first synthesis of the trans form of a carboxylic acid by Gunthard and coworkers [11]
Key to the elucidation of this complex conformational interconversion of glycolic acid was a vibrational analysis based on specific $^{18}$O and $^{13}$C substitution. Although the isotopic shifts are small, they can be measured very precisely due to the sharpness of the vibrational absorptions of matrix isolated molecules. This example demonstrates that IR induced isomerization of matrix isolated molecules is a unique tool for conformational analysis.

The recent discovery of vibrationally stimulated rotamerization of an unsubstituted alkane shows that IR induced isomerizations in matrices are not limited to any group of molecules with particular substituents. Rasanen and Bondybey have found that excitation of the CH stretching modes of a mixture of gauche and trans n-butane in solid neon results in efficient conformational interconversion [12]. Broad band globar source irradiation leads to a photostationary state consisting of about 90% trans n-butane, indicating that the quantum efficiency to gauche $\rightarrow$ trans interconversion exceeds that of the reverse trans $\rightarrow$ gauche process by a factor of eight. The effect of selective deuteration on the isomerization rates suggests a strong mode-selective effect: excitation of the terminal methyl groups appears to be substantially more effective in promoting internal rotation than irradiation of the methylene CH stretching modes, although the energies of these two modes are similar.

Examples of vibrationally induced bimolecular reactions in cryogenic matrices are far more sparse than isomerizations. We would like to discuss here briefly our most recent case of an IR laser induced chemical reaction, that of allene with molecular fluorine [13].

$$\text{CH}_2=\text{C}=\text{CH}_2 + \text{F}_2 \rightarrow \text{CH}_2=\text{CF}-\text{CH}_2\text{F (cis, gauche)}$$

$$\quad \rightarrow \text{CH}_2=\text{C}=\text{CHF} + \text{HF}$$

$$\quad \rightarrow \text{HC=C-CH}_2\text{F} + \text{HF}$$
In a search for vibrational transitions that might stimulate the reaction, we
irradiated suspensions of allene and fluorine in solid nitrogen and rare gas
matrices at 12 K with light from grating controlled cw CO₂, cw CO, or
continuously tunable cw F-center lasers. Concentrations of reactants were
selected so that about 10-20% of all allene molecules would have an F₂ molecule
as a nearest neighbor. The laser frequency was tuned to an infrared absorption
attributable to one of these allene-fluorine nearest neighbor pairs, whose
position was located in advance by a concentration study and then later
confirmed by the observed loss of absorption upon chemical reaction. Reactant
loss and product growth upon infrared irradiation was monitored by FT-IR
spectroscopy, and assignment of bands to the cis and trans forms of
2,3-difluoropropene product was made on the basis of IR laser induced
interconversion of the two rotamers.

$2\nu_{10}$, the overtone of the CH₂ wagging motion at 1696 cm⁻¹, is the lowest
frequency infrared absorption of allene selective excitation of which led to
reaction with fluorine. From the product absorbance growth curve obtained
through prolonged CO laser irradiation at 1696 cm⁻¹, a rate constant was
derived by fitting the measured curve to a first order rate law. That allowed
calculation of a quantum yield $\phi$ to reaction of $8 \times 10^{-5}$. As in the case of our
earlier study of the vibrationally induced ethylene-fluorine reaction [14], we
encountered a general increase of $\phi$ with the energy per exciting photon, as
shown in Fig. 1. The increase is large, covering four orders of magnitude for
transitions between 1700 and 3100 cm⁻¹, but it is not smooth. For example, the
quantum yield increases by a factor of 30 from $\nu_{6}$ at 1955 cm⁻¹ to $2\nu_{9}$ at 2002
cm$^{-1}$, while excitation at much lower frequency, 1696 cm$^{-1}$, induces reaction with an efficiency only nine times below that at 1955 cm$^{-1}$. A qualitatively similar, albeit less spectacular, observation was made in the case of an Ar matrix: $\phi(2\nu_9)/\phi(\nu_6) = 2.4$ [13]. While the general increase of the quantum yield with the energy of the exciting photon may originate for the most part from vibrational cascading during relaxation, which results in access to an increasing number of (reactive) vibrational states as the molecule is excited at higher and higher energies, the steep increase of $\phi$ from $\nu_6$ to $2\nu_9$ must reflect some distinct advantage of $2\nu_9$ over $\nu_6$ in promoting reaction. First, there is no vibrational state in the 47 cm$^{-1}$ interval between the two levels, hence the entire change of $\phi$ from $\nu_6$ to $2\nu_9$ can be attributed to a higher quantum yield to reaction of the $2\nu_9$ vibrational state. Second, the known Fermi resonance interaction between $2\nu_9$ and $\nu_6$ suggests an extra short residence time of the molecule in the upper state, implying that the high quantum efficiency originates from a high chemical reactivity of $2\nu_9$, i.e. a mode specific effect. This can easily be interpreted in terms of the nuclear distortions involved: The CH$_2$ rocking overtone, $2\nu_9$, distorts the sp$^2$ hybridized methylene groups of allene toward the CH$_2$F-CF=CH$_2$ product tetrahedral structure, while it is hard to visualize how the asymmetric CCC stretching mode $\nu_6$ can contribute to the reaction coordinate. This is a very interesting result in view of the prevailing experimental evidence indicating rapid randomization of vibrational energy on the time scale of chemical reaction, and shows that selective infrared excitation of chemical reactions in a cryogenic matrix environment opens up a way to learn about types of vibrations that facilitate reaction.

The products of the allene-fluorine reaction, propargyl fluoride, fluoroallene, and 2,3-difluoropropene, are consistent with concerted addition of F$_2$ to the allene C=C bond, forming a highly vibrationally excited,
electronic ground state CH₂=CF-CH₂F intermediate. The branching ratio is determined by the competition between stabilization of this hot intermediate through transfer of the excess vibrational energy to the matrix environment, or elimination of HF. The postulated, vibrationally hot difluoropropene intermediate is also consistent with the lack of observation of a mode selective behavior with respect to product branching. Randomization of the vibrational energy of the intermediate is expected to be much faster than elimination of HF, hence the nature of the excited allene mode is not expected to influence the product ratio. However, the branching between elimination and stabilization changed dramatically when conducting the allene-fluorine reaction in different matrices, indicating substantial differences in the effectiveness of matrices to deactivate the hot intermediate. Interestingly, the branching between the two elimination products, fluoroallene and propargyl fluoride, also varied strongly with the matrix material. Although the origin of this matrix effect is not fully understood, the fact that product branchings can be influenced by the choice of the matrix bears considerable interest in the search for means to control chemical reaction pathways.
3. **Selective Vibronic Excitation of Bimolecular Reactions with Near-Infrared Light**

Control of an electronically induced bimolecular reaction is most likely achieved when it can be induced by excitation of a reactant into the bound region of an excited electronic state, especially in cases in which the excited vibronic level lies below the lowest dissociation limit. This tends to favor direct, molecular mechanisms over multistep, atom or free radical reactions induced by dissociation or predissociation of a reactant, with their propensity to cause secondary chemistry. A prototype reactant for chemistry of a small molecule in excited, bound states is molecular oxygen in the $^1\Sigma^+$ state ($\tilde{\nu}_{00}=13100$ cm$^{-1}$), both situated well below the dissociation limit to ground state atoms ($D_0^0=41000$ cm$^{-1}$) [15]. $O_2(^1\Sigma^+)$ is a particularly interesting reactant due to its long lifetime and strong electrophilic character, which makes its chemistry distinctly different from that of the remarkably unreactive, though radical-like $^3\Sigma^-$ ground state molecule [16]. We have probed the chemical reactivity of selective vibronically excited $^1\Delta_g$ and $^1\Sigma^+$ oxygen with substituted furans and molecular fluorine in order to explore low-energy reaction pathways of these systems.

The first two members of the $O_2$ $^1\Delta_g$, $v' + ^3\Sigma_g^-$, 0 vibronic progression could be observed by near infrared Fourier transform spectroscopy of solid $O_2$ at 12 K. Fig. 2 shows the 0-0 and the 1-0 transition of the $\alpha$-phase at 7990 and 9480 cm$^{-1}$, respectively [17]. These transitions, both spin and electric dipole forbidden for the isolated molecule, become enhanced in the solid $\alpha$-phase by about two orders of magnitude [18]. This enhancement has been interpreted by Bhandari and Falikov in terms of factor group selection rules for interacting $O_2$ molecules in the $\alpha$-$O_2$ unit cell, which lead to electric dipole allowed transitions between substates classified according to the $D_{2h}$ symmetry of $O_2$. 
Fig. 3 shows the two electric dipole allowed transitions of \((O_2)_2\) to the \((^1\Delta_g, ^3\Sigma_g^-)\) manifold. These factor group selection rules also predict electric dipole allowed transitions for the \(^1\Sigma_g^+, v' = 3\Sigma_g^-, 0\) progression in solid \(\alpha\-O_2\), but we were not able to detect any of its members by FT-IR absorption spectroscopy. However, we did observe this progression in Ar and \(O_2\) matrices by means of the near infrared laser induced reaction of \(O_2\) with 2,5-dimethylfuran [17]. Fig. 4 shows a plot of the endoperoxide product yield, measured by the growth of the CO stretch absorption at 1120 \(\text{cm}^{-1}\) over equal time intervals, as a function of the cw dye laser irradiation frequency in a matrix dimethylfuran/\(O_2/\text{Ar} = 1/15/85\). This laser "reaction excitation spectrum" reveals the first two members of the progression, \(^1\Sigma_g^+, 0 + ^3\Sigma_g^-, 0\) at 13100 and \(^1\Sigma_g^+, 1 + ^3\Sigma_g^-, 0\) at 14500 \(\text{cm}^{-1}\). Relative absorbances of the 0-0 and 1-0 transitions can be determined (except for a factor determined by the relative quantum efficiencies to reaction upon excitation of the two states) from measured product absorbance growths, irradiation times, and laser intensities, which puts the peak absorbance of the 1-0 transition 25 times below that of the 0-0 transition. Plainly, direct excitation of \(^1\Sigma_g^+\) vibronic levels does induce addition of \(O_2\) to 2,5-dimethylfuran, but no conclusion can be drawn from this experiment with respect to the reactive state, i.e. whether \(O_2\) reacts in the \(^1\Sigma_g^+\) state or, after relaxation, in a lower lying \(^1\Delta_g\) vibronic level.

In order to determine the reacting \(O_2\) state(s), we measured the relative quantum yields to chemical reaction of dimethylfuran with \(O_2\) upon selective excitation to \(^1\Delta_g\) and \(^1\Sigma_g^+\) vibronic levels. Excitation of \(O_2\) to the \(^1\Delta_g\), \(v' = 0\) and \(^1\Delta_g\), \(v' = 1\) levels gave the same quantum yields to reaction, and an estimate of the absolute quantum efficiency led to a value around one. Assuming the physical quenching time of \(O_2\left(^1\Delta_g\right), 0\) with a nearest neighbor dimethylfuran molecule in an Ar matrix to be the same, or shorter, than that measured by Crone
and Kugler for $O_2(1\Delta_g)$ isolated in solid Ar, 85 sec [20], the high quantum yield to reaction would imply a half life to $O_2(1\Delta_g) +$ dimethylfuran reaction of 10 sec or less. With this half life, and a frequency factor equal to $10^{12}$ sec$^{-1}$, a typical phonon frequency, classical Arrhenius behavior would require an activation energy no higher than 720 cal mole$^{-1}$. This is two thirds of the gas phase value of 1070 cal mole$^{-1}$, close enough to permit interpretation of the reaction of dimethylfuran with vibrational ground state $O_2(1\Delta_g)$ in terms of thermal barrier crossing even in the cryogenic environment. On the other hand, in pure solid $O_2$, Akimoto and Pitts estimated a nonradiative lifetime of $O_2(1\Delta_g, 0)$ around one microsecond or less [21], orders of magnitude shorter than in Ar. With this lifetime, the high quantum yield to reaction in solid $O_2$ requires a reaction time of 0.1 $\mu$sec or less which, if explained in terms of thermal reaction, would imply a barrier no higher than 300 cal. This would represent an unusually large discrepancy between gas phase and matrix barrier, and because of that we prefer interpretation in terms of $O_2$ molecular tunneling on the singlet hypersurface through a barrier with the gas phase value [17]. In any event, the fact that all observed quantum yields to reaction upon selective $1\Delta_g$ and $1\Sigma_g^+$ vibronic excitation are around one prevents determination of the reacting vibronic state. The high reaction efficiency would be observed even if relaxation among the singlet states down to the $1\Delta_g, \nu' = 0$ level were faster than reaction, i.e. even if all reaction would occur from the $1\Delta_g$ ground vibrational level.

Laser reaction excitation spectroscopy also unveiled a vibronic progression of oxygen in solid Ar in the red spectral range with bands at 15830 and 17300 cm$^{-1}$. These are assigned to the 0,0 and 1,0 members of the $(O_2)_2 (1\Delta_g, 1\Delta_g) + (3\Sigma_g^-, 3\Sigma_g^-)$ one photon, two-molecule transition first observed by Ellis and Kneser in the absorption spectrum of liquid oxygen [22]. The fact that these
transitions were observed in a matrix of the composition dimethylfuran/O_2/Ar = 1/2/100 with its low concentration of reactive dimethylfuran \((O_2)_2\) clusters demonstrating the high sensitivity of the laser reaction excitation technique. The factor group selection rules indicate that this transition, too, is electric dipole allowed (Fig. 3 and reference [19]).

The frequencies of the first two members of the \((O_2)_2\) \(\left(1^1_g, 1^1_g\right) + \left(3^3_g, 3^3_g\right)\) progression coincide with the corresponding absorptions of \((O_2)_2\) isolated in solid neon measured earlier by Goodman and Brus with the laser fluorescence excitation technique [23]. Both laser fluorescence and laser reaction excitation spectroscopy are very sensitive, complimentary techniques to monitor weak vibronic absorptions in condensed phase. We expect bimolecular reaction excitation spectroscopy to be a particularly useful tool when searching for weak absorptions in condensed phase, reactive samples where rapid nonradiative relaxation would quench laser-induced fluorescence.

FT-IR analysis of product spectrum in the range 4000-400 cm\(^{-1}\), including analysis of the peroxodic \(^{18}\)O counterpart, allowed empirical vibrational mode assignment and confirmation of the endoperoxide structure of the product. Thanks to the long wavelength of the exciting red and near infrared photons, no excitation of the product endoperoxide occurred, hence the product spectrum and the growth kinetics could be studied in complete absence of secondary photolysis.

In contrast to the singlet oxygen-furan system, our cryogenic laser technique allowed us to uncover a strong vibronic dependence of the quantum yield to reaction of singlet \(O_2\) with molecular fluorine [24]. We found the singlet \(O_2\) induced reaction pathway when searching for new, low-energy paths of
the reaction
\[ F_2 + O_2 \rightarrow O_2F + F \quad \Delta H^O(298) = +31 \text{ kcal mole}^{-1} \]
\[ + O_2F_2 \quad \Delta H^O(298) = +8 \text{ kcal mole}^{-1} \]

The first of these reactions, induced in a cryogenic matrix by mercury arc radiation, has been used in this laboratory [25], and independently by Arkell [26], about two decades ago to generate and study spectroscopically the elusive \( O_2F \) radical. In those experiments, the near UV and blue light emitted by the Hg arc source initiated reaction by dissociating \( F_2 \) into ground state atoms through excitation of the molecule into the \( \Pi_u \) repulsive state. Now we were interested in finding the lowest energy photons capable of promoting the reaction, with the goal of achieving control over the \( O_2F/O_2F_2 \) product branching. Given the \( \Delta H^O \) of 31 kcal mole\(^{-1} \) for the more endothermic \( O_2F+F \) channel, we expected, for example, \( O_2(\Sigma_g^+, v'=2) \) or \( O_2(\Delta_g) \) to carry enough energy to initiate reaction with \( F_2 \).

The \( F_2+O_2 \) laser reaction excitation spectrum in Fig. 5a demonstrates that it is indeed possible to induce chemical reaction with photons in the red spectral range with energies as low as 14500 cm\(^{-1} \). Each point of the solid curve represents the growth of the integrated absorbance of the \( O-O \) stretching mode of \( O_2F \) in solid oxygen at 12 K during an irradiation period of 15 minutes at 280 mW cm\(^{-2} \) cw dye laser intensity. The 70 cm\(^{-1} \) \( ^{18}O \) shift of the peak at 14600 cm\(^{-1} \) (determined by laser photolysis of a suspension of \( F_2 \) in solid \( ^{18}O_2 \)) is in agreement with that calculated for the \( O_2(1\Sigma_g^+, 1+3\Sigma_g^-) \) transition, and the coincidence with the corresponding band in the \( O_2+\text{dimethylfuran} \) laser reaction excitation spectrum (Fig. 5b) supports this assignment. On the other hand, we were not able to induce \( F_2+O_2 \) reaction by excitation of any of the lower lying \( O_2 \) vibronic transitions, the ground vibrational level of the \( \Sigma_g^+ \) state at 13250 cm\(^{-1} \), or the \( v'=0 \) and \( v'=1 \) levels of the lower lying \( \Delta_g \) state.
We estimate that excitation of $O_2 \, 1\Sigma_g^+, \, v' = 0$ is at least 180 times less effective in promoting reaction with $F_2$ than $O_2 \, 1\Sigma_g^+, \, v' = 1$. Goodman and Brus' laser fluorescence study of the nonradiative relaxation pathway of selective vibronically prepared oxygen dimers in a neon matrix permits a conclusion about the reactive $O_2$ vibronic state [23]. These authors found that an $O_2 \, (1\Sigma_g^+, \, v' = 1)$ molecule with an $O_2 \, (3\Sigma_g^-, \, 0)$ ground state nearest neighbor relaxes directly to the $v' = 0$ level of the $1\Sigma_g^+$ state, without cascading through intermediate $1\Delta_g$ or $3\Sigma_g^-$ vibronic levels. This, combined with our observation that $O_2 \, (1\Sigma_g^+, \, 0)$ did not promote $F_2 + O_2$ reaction, establishes the optically excited $O_2 \, 1\Sigma_g^+, \, v = 1$ level as the reactive state. Together with our recent direct observation of $O_2 \, (1\Sigma_g^+)$ in room temperature solution [27], this reopens the search for the elusive $O_2 \, (1\Sigma_g^+)$ chemistry in condensed phase. More generally, it shows that laser induced cryogenic photochemistry is a valuable tool for the search of low energy reaction pathways of bimolecular systems.

Quite to our surprise, the $O_2F$ reaction excitation profile showed a minimum in the spectral range around 15900 cm$^{-1}$ where, according to the dimethylfuran + $O_2$ spectrum (Fig. 5b), the $(O_2)_2 \, (1\Delta_g, \, 1\Delta_g)$, $0 \rightarrow (3\Sigma_g^-, \, 3\Sigma_g^-)$, $0$ transition absorbs. The $O_2F_2$ excitation profile, on the other hand, exhibits a peak at this frequency. Quantitative analysis of absorbance growth (decrease) upon irradiation at 15900 cm$^{-1}$ revealed that excitation of the $(O_2)_2 \, (1\Delta_g, \, 1\Delta_g)$ transition induces reaction of $O_2F$ with $F$ atoms to form $O_2F_2$, but very little or no $F_2 + O_2$ reaction. Excitation of the $(1\Delta_g, \, 1\Delta_g)$ transition turns out to be at least two orders of magnitude less efficient in inducing $F_2 + O_2$ reaction than excitation of the lower energy $1\Sigma_g^+, \, v' = 1$ state. This surprising finding is most probably a manifestation of an extremely efficient relaxation process of $(O_2)_2 \, (1\Delta_g, \, 1\Delta_g)$ which is not accessible to $O_2 \, (1\Sigma_g^+, \, 1)$. There is spectroscopic evidence for picosecond exchange of $1\Delta_g$ quanta between two nearest
neighbor $O_2$ molecules isolated in solid neon [23], and the exchange of $^1_A^g$ excitation between oxygen molecules colliding in the gas phase is known to be close to gas kinetic [28]

$$O_2 (^1_A^g) + O_2 (^3_S^-) \rightarrow O_2 (^3_S^-) + O_2 (^1_A^g)$$

Hence, in solid oxygen, we can expect the 16000 cm$^{-1}$ ($O_2$)$_2$ ($^1_A^g$, $^1_A^g$) quanta to decay very fast into separate 8000 cm$^{-1}$ $O_2$ $^1_A^g$ quanta, a process that is endothermic possibly by a few cm$^{-1}$, but certainly not more than 17 cm$^{-1}$ [23].

$$O_2 (^1_A^g) + O_2 (^3_S^-) \rightarrow O_2 (^1_A^g, ^3_S^-) + O_2 (^1_A^g)$$

As mentioned above, the energy of $^1_A^g$ 8000 cm$^{-1}$ quanta does not suffice to induce reaction with $F_2$. An analogous break-up of the $O_2$ $^1_S^+$, $v' = 1$ quantum through energy transfer to a nearest neighbor, ground state $O_2$ molecule, however, is inhibited by an endothermicity of 150 cm$^{-1}$ which exceeds $kT$ at 12 K by far,

$$O_2 (^1_S^+, 1) + O_2 (^3_S^-, 0) \rightarrow O_2 (^1_S^+, 0) + O_2 (^3_S^-, 1)$$

$$\Delta E = +150 \text{ cm}^{-1}$$

We conclude that the inhibition of this relaxation process gives vibrationally excited $O_2 (^1_S^+)$ sufficient lifetime to react with $F_2$.

The most striking difference between the reaction excitation spectra of $F_2 + O_2$ and dimethylfuran + $O_2$, Fig. 5, is a continuous absorption clearly visible in the $F_2 + O_2$ profile which is absent in the furan + $O_2$ case, hence cannot be due to absorption of molecular oxygen. The onset of the absorption is around 15000 cm$^{-1}$, and it continuously increases through the red, yellow, and green spectral range. All experimental evidence points to $F_2$ as the absorber despite the fact that the absorption extends more than 200 nm to longer wavelengths than in the electronic spectra of $F_2$ reported in the literature ($\lambda_{max} = 285$ nm, with tail extending to 450 nm [29]). According to ab initio potential energy curves for the lowest excited electronic states of $F_2$ [30]
shown in Fig. 6, the new, red fluorine absorption is either due to excitation to the $^{1}{\Pi}_{u}$ state, or to the repulsive limb of the weakly bound, hitherto unobserved $^{3}{\Pi}_{0}^{+}{u}$ state. Two arguments point to $^{3}{\Pi}_{0}^{+}{u}$ as the absorbing state. First, the $^{3}{\Pi}_{0}^{+}{u}$ transition has the more favorable Franck-Condon factors (Fig. 6), and, second, there is an enhancement of the absorption by nearest neighbor ground state $O_2$ molecules [24]. The latter can easily be explained by removal of the spin forbiddeness of the $F_2 : ^{3}{\Pi}_{0}^{+}{u} + ^{1}{\Sigma}^{+}$ transition by interaction with $O_2$

$$F_2 \cdot O_2 : ^{3}(^{3}{\Pi}_{0}^{+}{u}, ^{3}{\Sigma}^{g}) \rightarrow ^{3}(^{1}{\Sigma}^{g}, ^{3}{\Sigma}^{g}),$$

but no such enhancement is expected in the case of the spin allowed excitation to the $^{1}{\Pi}_{u}$ state. The unveiling of the lowest triplet state of molecular fluorine again shows how laser reaction excitation spectroscopy in matrices can be used to locate very weak electronic transitions.
4. New Chemistry on Excited Haloethene Hypersurfaces

Unique chemistry may occur on excited electronic hypersurfaces not accessible by direct optical excitation, for example on surfaces originating from reactant states with triplet spin multiplicity. Such surfaces may be reached, however, by use of triplet excited sensitizers like Hg(\(^3\)P), and mercury atom sensitization of gas phase reactions has been used to this end quite extensively. Key to the understanding and control of the chemical reaction pathways, made available through Hg(\(^3\)P) initiation is the elucidation of the mechanism, and in particular the role played by the excited metal atom. Does Hg(\(^3\)P) initiate reaction by transient formation of chemical bonds, or does it merely transfer its electronic energy to a reactant? In the former case, there might be reaction products unique to Hg(\(^3\)P) inducement, and not attainable by other triplet sensitizers. Matrix isolation, uniquely suited for stabilization of transient intermediates, offers a direct, convenient probe for Hg(\(^3\)P) atom participation through chemical bonding. In addition, well established metal atom-matrix deposition techniques allow comparison with \(^3\)P induced chemistry of the other group IIB metals Cd and Zn. Since the latter have their higher energy, \(^1\)P\(_1\) \(\rightarrow\) \(^1\)S\(_0\) absorptions at wavelengths longer than 200 nm, these metals permit convenient study and elucidation of differences between singlet and triplet metal atom induced chemistry.

An interesting example is provided by the \(^3\)P mercury, cadmium, and zinc induced reactions of 2-chloro-1,1-difluoroethene in krypton matrices [31]. Krypton is most convenient for the study of Hg(\(^3\)P) induced chemistry since the matrix shift brings the \(^3\)P\(_1\) \(\rightarrow\) \(^1\)S\(_0\) optical absorption into coincidence with the output maximum of our 1000 W Hg-Xe arc lamp at 250 nm. While gas phase Hg(\(^3\)P) sensitized decomposition of fluoroethenes leads to HF elimination [32], no
evidence was found for hydrogen halide elimination in the matrix study. Instead, FT-IR spectral record of reactions of CF₂=CHCl·Hg(³P) and CF₂=CDCl·Hg (³P) pairs (Fig. 7) revealed products with vibrational spectra resembling that of the ethene parent, but with the bands shifted 30-70 cm⁻¹ to lower frequencies. These shifts, in particular that of the C=C stretching mode, are substantially smaller than those observed for metal-ethene complexes like C₂H₄·Cu, C₂H₄·Ag, and C₂H₄·Au [33], but close to shifts of group IIB metal insertion products reported in the literature [34]. This points to Hg(³P) involvement through chemical bonding rather than through mere energy transfer, and comparison of product and reactant spectra showed that the excited mercury atom inserts into the C-Cl bond, constituting the first example of a photochemically prepared mercury-haloethene

While Zn ³P₁ + ¹S₀ (300 nm) and Cd ³P₁ + ¹S₀ (316 nm) induced chemistry of CF₂=CHCl gave analogous insertion products, excitation of the easily accessible ¹P₁ states of these metals (Zn:212 nm, Cd:226 nm) did not lead to any reaction despite their higher energies relative to the ³P state. This indicates that the observed M(³P) induced chemistry is associated with a triplet reaction surface not accessible through ¹P₁ excitation of the metals.

An interesting question opened by the observed product specificity concerns the factors that control the reaction pathway. Fig. 8 shows an
energy diagram for the matrix reaction of $\text{CF}_2=\text{CHCl} \cdot \text{Hg}(^3\text{P})$, which is based on thermochemical and UV spectral data available for the related ethene and a few haloethene systems [31]. Assuming the equilibrium geometry of chlorodifluoroethene in its lowest triplet state to be twisted like in the case of $T_1$ ethylene [35], reaction of Hg($^3\text{P}$) with the planar haloethene on a triplet surface requires surpassing of a barrier associated with internal rotation around the CC bond. Taking again $T_1$ ethylene as a guide, we estimate triplet state barriers to internal rotation to be around 30 kcal mol$^{-1}$ [35] (dotted lines in Fig. 8). With these reaction heat, triplet state energy, and barrier estimates, the observed product selectivity can be explained by restriction to a triplet reaction pathway. Under spin conservation, insertion of Hg($^3\text{P}$) into the C-Cl bond can proceed with the available energy, whereas insertion into the C-H or C-F bond would require substantial activation. Similarly, the energy diagram (Fig. 8) shows that spin conserving hydrogen halide elimination to produce either triplet HX or triplet excited acetylenic products would be endothermic. Hence our observation of only one reaction channel, C-Cl bond insertion, is consistent with a triplet surface pathway.

The three isomers of dichloroethene, cis-1,2, trans-1,2, and 1,1-dichloroethene have electronic absorptions at longer wavelengths than chlorodifluoroethene, with tails extending to approximately 235 nm. Hence we were able to compare Hg($^3\text{P}$) induced chemistry of these haloolefins with reaction promoted by direct photo-excitation at $\lambda > 200$ nm. We found substantial differences in product distribution, indicating effective control of the reaction pathway by the method used for reactant excitation (direct vs. Hg atom mediated initiation) [36].

Direct photolysis of cis and trans 1,2-dichloroethene with unfiltered Hg-Xe arc radiation at $\lambda > 200$ nm in solid Kr led to cis-trans isomerization
and, in the case of cis-1,2-dichloroethene, to HCl elimination (to form hydrogen chloride-chloroacetylene hydrogen bonded complexes). Optical excitation of 1,1-dichloroethene at $\lambda > 200$ nm resulted in isomerization to the cis and trans form, and again elimination of HCl. Energy requirements strongly suggest that the observed photochemistry (isomerization plus HCl elimination, but no expulsion of Cl$_2$) is the result of a restriction of the reaction path to excited singlet states [36].

In contrast, Hg(3P) induced chemistry of the dichloroethenes in Kr gives products consistent with reaction on a triplet surface not accessible by direct optical excitation of the energetically higher olefin $S_1$ state. The cis isomer and 1,1-dichloroethene undergo isomerization, but also Cl$_2$ elimination, a reaction channel not observed in the case of direct photoexcitation. In contrast to photolysis in the absence of Hg, only little HCl elimination could be detected. The energy diagram, Fig. 9, shows that among the triplet elimination pathways only one is exothermic, namely the one leading to HC=CH + Cl$_2$; while the H$_2$ and HCl elimination pathways are endothermic. Therefore, the observed elimination product branching can be rationalized on the bases of spin conservation coupled with energy requirements. This also gives an explanation for Hg atom insertion into the C-Cl bond without insertion into the C-H bond in the case of 1,1-dichloroethene and the cis isomer; only the carbon-chlorine bond reaction gives a product that can be reached on a triplet pathway with a barrier below the energy of the C$_2$H$_2$Cl$_2$+Hg(3P) reactant pair (Fig. 9).

It is remarkable that the photoexcitation of trans-CHCl=CHCl•Hg pairs did not result in any elimination or metal atom insertion at all, in contrast to the behavior of the cis isomer. This indicates that simple energy transfer from CHCl=CHCl•Hg(3P) to $^3$(CHCl=CHCl)•Hg(^1S) is not involved in Cl$_2$
elimination and the insertion reaction, since if it were, the cis and the trans isomer would give identical products. Rather, the excited Hg atom appears to interact with the cis isomer in a way not possible in the case of the trans, opening up a reaction pathway unique to the cis form.

A change of the product distribution in the presence of Hg atoms was also observed in the case of the UV photolysis of trichloroethene [37]. Direct irradiation of the olefin at λ > 200 nm gave HCl elimination, while chemical reaction initiated by Hg(3P) resulted in elimination and Hg atom insertion into the C-Cl bond to produce trans-CHCl=CCl-HgCl, similar to the case of the dichloroethenes. Again, these differences between direct and Hg atom mediated initiation of the reaction can most easily be explained by differences between excited singlet and triplet surface chemistry [37].

The participatory role of the excited metal atom found in the dichloro, trichloro, and chlorodifluoroethene - group IIB metal initiated photochemistry motivated us to explore other systems, like the vinyl and ethyl halides [37,38]. Hg(3P) induced reaction of CH2=CHF, CH2=CHCl, and CH2=CHBr, and Zn and Cd initiated chemistry of CH2=CHCl, mostly in krypton, gave HX elimination in all cases. Infrared spectra revealed that the expelled hydrogen halide is engaged with acetylene, the other photo-fragment, in a hydrogen bonded complex identical to the C2H2·HX complexes prepared previously by Andrews and coworkers through direct VUV photolysis of the vinyl halide precursor [39]. In addition, metal atom insertion into the C-Cl and C-Br bond occurred, but not into the C-F bond. Assuming our estimates of reactant and product triplet energies to be correct, this outcome in terms of insertion products is again consistent with a spin conserving, triplet reaction pathway; CH2=CHCl·Hg(3P) and CH2=CHBr·Hg(3P), with the vinyl halide in its planar configuration, has sufficient energy to undergo metal atom insertion, while CH2=CHF·Hg(3P) does
not carry enough energy to undergo C-F bond insertion (Fig. 8 and Ref [37]). However, reactant product excited state energies give no immediate clue as to what pathway may lead to HX elimination. These systems are under further study.

Reaction of CH$_3$-CH$_2$X•Hg(3P) pairs gave HX elimination (ethyl chloride and bromide) and, to less extent, H$_2$ elimination in the case of the chloride and fluoride. Excited Hg atom insertion was only observed into the C-Cl and C-Br bond, but not into the C-F bond, no surprise in the light of the haloethene results. However, in contrast to the haloethenes, chemical reactivity in the case of ethyl chloride appeared not to be limited to CH$_3$-CH$_2$Cl•Hg nearest neighbor pairs. The asymptotic growth of the C$_2$H$_4$•HCl product alone indicates that 16% of all ethyl chloride molecules react, a far higher percentage than represented by the statistical fraction of CH$_3$-CH$_2$Cl•Hg nearest neighbors. A possible reason is energy transfer between Hg(3P) and non-nearest neighbor ethyl chloride molecules, leading to excitation of the chloride to its lowest triplet state.
5. Azirine-Nitrile Ylide Photoisomerization

Azirine-nitrile ylide systems

\[
\begin{align*}
\text{hv} & \quad \text{hv}' \\
\begin{array}{c}
\text{2H-azirine} \\
\text{I}
\end{array} & \quad \begin{array}{c}
nitrile ylide \\
\text{II}
\end{array}
\end{align*}
\]

constitute prototypes of reversible photo-induced isomerizations which can be controlled by the wavelength of the exciting photon. Although systems of this type have been studied by visible/UV absorption techniques [40], there is little definitively known about the structure of the high energy ylide form, mainly due to the lack of structurally informative infrared data. Moreover, the energy pathway of these photo-initiated interconversions has not yet been elucidated. This is despite the intriguing possibility that these systems exhibit adiabatic, upper state surface chemistry of interest to photon conversion.

Favored systems for the determination of the structure of the high energy ylide form and the wavelength study of the interconversion are those with small substituents \( R, R' \), like \( H \) or \( \text{CH}_3 \), since these substituents would interfere the least with arizine and ylide vibrational modes and electronic chromophores. However, such small azirines and ylides tend to be reactive and unstable at room temperature. A cryogenic matrix, then, offers an ideal environment for the study of their IR spectra and monitoring of wavelength dependent photochemistry initiated with tuned UV radiation.

The simplest system, \( R = R' = H \), might be attainable through the cryogenic
reaction of NH radicals with acetylene. In fact, Jacox and Milligan have initiated this reaction in solid Ar by photolyzing HN₃ (to from NH + N₂) in the presence of C₂H₂ [41]. The only product observed was ketenimine, CH₂=C=NH, but these authors postulated the isomeric 1H-azirine (III) as an undetected intermediate

(\( R = R' = H \))

\[
\begin{align*}
& \text{1H-azirine} \\
& \text{III}
\end{align*}
\]

Assuming the initial reaction step to be addition of NH the triplet bond, the observed ketenimine implies H atom migration between the two carbons. So, if undesired isomerization to ketenimine is to be suppressed, H has to be replaced by a substituent that is less amenable to migration and/or acts as a sink for the excess energy of the hot azirine as it is generated upon NH addition, e.g. a methyl group. Therefore, we attempted an azirine synthesis by photolyzing hydrazoic acid in the presence of dimethylacetylene (DMA), with the hope of being able to trap the 1H-azirine III or the isomeric 2H-azirine I (\( R = R' = \text{CH}_3 \)).

Mercury arc photolysis of dimethylacetylene/HN₃ suspensions in Ar and Xe gave more than one product in both matrices as inferred from absorbance growth behavior [42]. In Ar, two bands were observed in the region around 2000 cm⁻¹, which is characteristic for multiple bond stretching motions of possible product structures.
The growth behaviors of the two absorptions at 2031.5 and 2007.9 cm\(^{-1}\) were identical, indicating that they probably originate from one and the same species. Comparison of the observed \(^{15}\)N and D isotope shifts with those predicted by the diatomic approximation for the stretching motions of the structures above led to assignment to a Fermi doublet of 3,3-dimethylketenimine,

\[
\begin{align*}
\ce{CH3} & \quad \ce{C==C==N} & \quad \ce{CH3} \\
\ce{C==C==N} & \quad \ce{CH3}
\end{align*}
\]

This product also appeared in Xe, but only as a minor by-product relative to the principal product N-methyl-1-amino-propyne,

\[
\begin{align*}
\ce{CH3} & \quad \ce{C==C==N} & \quad \ce{CH3} \\
\ce{C==C==N} & \quad \ce{CH3}
\end{align*}
\]

The structure of this main product was established by a band at 2038.6 cm\(^{-1}\), which did not exhibit an \(^{15}\)N shift and hence was assigned to \(v(\text{C=O})\), and observation of a strong absorption at 870 cm\(^{-1}\) with an \(^{15}\)N isotope shift of 14 cm\(^{-1}\) characteristic for the C-N stretching motion. There is an additional set of product bands both in Ar and Xe, so close that they most probably originate from one and the same product. Since it does not possess an absorption in the 2000 cm\(^{-1}\) region, this molecule cannot have a cumulene or triple bond, which suggests a cyclic azirine structure, I or III. The lack of a C=N stretching absorption around 1700 cm\(^{-1}\), combined with observation of a strong band around 890 cm\(^{-1}\) featuring \(^{15}\)N and D-shifts characteristic for an N-H bending motion points to the 1H-azirine form III. We believe that it is formed in the initial reaction step, with its yield determined by the competition between deactivation of the hot 1H-azirine and rearrangement to ketenimine (Ar) and/or
N-methyl-l-amino-l-propyne (Xe). If this identification is correct, it is the first spectral detection of a l-azirine.

Although the cryogenic reaction of NH with dimethylacetylene apparently did not lead to the desired 2H-azirine-nitrile ylide pair, the strong dependency of the rearrangement path on the matrix material is a most interesting finding. We believe that it is the heavy atom induced spin-orbit coupling by Xe which is responsible for the observed difference in product branching between the two matrices. In the gas phase, UV photolysis of HN$_3$ produces 95% of NH in its excited $^1\Delta$ state, and it is reasonable to assume that in an inert gas matrix, too, a substantial fraction of photodecomposing HN$_3$ produces NH in the $^1\Delta$ excited state. Spin-orbit coupling induced by Xe can be expected to increase the rate of crossing from the initial singlet reaction surface to a triplet surface somewhere along the reaction coordinate. This might be early in the reaction through Xe catalysis of the NH $^1\Delta$ + $^3\Sigma^+$ relaxation, which would enhance the triplet reaction pathway connected with vibrationally excited NH ($^3\Sigma^+$) in Xe relative to the NH ($^1\Delta$) singlet reaction path favored in Ar. At the other extreme, NH ($^1\Delta$) may react rapidly with DMA to form singlet excited lH-azirine followed in Ar by rearrangement on the singlet surface to form ketenimine but in Xe, through matrix-induced intersystem crossing to give triplet lH-azirine. The triplet lH-azirine would then isomerize to N-methyl-l-amino-l-propyne. While the present data do not discriminate between these two extremes, (or the possible singlet-triplet crossings between), the reaction is a fascinating prototype that shows the influence and control that can be exerted by the matrix environment on excited state reaction paths.

In our next attempt to synthesize a nitrile ylide in a cryogenic matrix, we took 3-phenyl-2H-azirine (IV) as starting material. This azirine has the advantage that it can be stored indefinitely at toom temperature, and then be
suspended in a cryogenic solid by standard matrix deposition techniques. 
Irradiation in solid nitrogen with Hg arc light around 250 nm resulted in 
interconversion to a single new product. Subsequent photolysis of the product 
at longer wavelengths, around 350 nm, allowed nearly complete recovery of the 
2H-azirine form [43].

Specific isotopic labeling of this photochromic system with $^{15}$N, D, and $^{13}$C turned out to be crucial for elucidation of the nitrile ylide structure. We 
obtained the isotopically modified species by synthesis of azidostyrene from 
labeled styrene or labeled sodium azide, followed by UV induced elimination of 
$N_2$ in the matrix to give the nitrile ylide product in high yield.

The triple bond/cumulene stretching region around 1900 cm$^{-1}$, shown in 
Fig. 10 for six isotopic species, was found to contain the most decisive 
information about the structure of the ylide form. This spectral region, which 
is free of vibrational absorptions of the aromatic ring, exhibits only one band 
in the case of two of the six isotopes, C$_6$H$_5$-C$_2$HDN (Fig. 10C) and C$_6$D$_5$-C$_2$H$_2$N 
(Fig. 10F). This shows that there is a single ylide structure, and the monodeutero isotope result, in addition, suggests that the nitrile ylide 
possesses two equivalent CH bonds (otherwise one would expect two skeletal 
stretching frequencies in the 1900 cm$^{-1}$ region). This rules out possible 
cumulene and triple bond structures shown in Fig. 11, namely VI and VIII. While 
N-phenylketenimine, IX, has been identified as a photostable side product of the 
matrix photolysis of azidostyrene (it does not absorb around 1900 cm$^{-1}$), the 
ketenimine structure, X, could be ruled out on the basis of other isotope data,
in particular the lack of NH modes with their characteristic $^{15}\text{N}$ and D frequency shifts [43].

Key to the distinction between the remaining ylide structures V and VII are the isotope shifts of the 1900 cm$^{-1}$ stretching absorption. Determination of these shifts from the spectra shown in Fig. 10 is rendered difficult by the appearance of doublets (multiplets) in the case of $\text{C}_6\text{H}_5\text{-C}_2\text{H}_2\text{N}$ (Fig. 10A), $\text{C}_6\text{H}_5\text{-C}_2\text{H}_2^{15}\text{N}$ (Fig. 10B), $\text{C}_6\text{H}_5\text{-C}_2\text{D}_2\text{N}$ (Fig. 10D) and $\text{C}_6\text{H}_5\text{-C}^{13}\text{CH}_2\text{N}$ (Fig 10E). Since the $d_1$ and $d_5$ species have only a single absorption in that spectral range, and all components of the multiplets of the other isotopic species showed uniform photolysis behavior, we are confident in attributing the splittings to Fermi resonances between combinations of skeletal vibrations and the multiple bond stretching mode. This interpretation is strongly supported by the fact that the calculated discrepancy between the unperturbed stretching frequency and the closest combination is on the order of 1-2 cm$^{-1}$ for the isotopes which exhibit multiplets around 1900 cm$^{-1}$ ($d_0$, $^{15}\text{N}$, $d_2$ and $^{13}\text{C}$), but larger, 8-9 cm$^{-1}$, in the case of $d_1$ and $d_5$ species which do not show splittings. Taking the location halfway between the two most prominent features of $d_0$, $^{15}\text{N}$, $d_2$, and $^{13}\text{C}$ as the unperturbed stretching frequency, we have determined the isotope shifts and compared them with those calculated for structures V and VII in terms of the diatomic approximation [43]. Substantially better agreement was obtained for the nitrile ylide structure V than for the structure VII. Hence we conclude that the isomer of 3-phenyl-2H-azirine obtained upon irradiation at 250 nm is the nitrile ylide with the linear heterocumulene skeleton V, which has double bonds of about equal force constant and the nitrogen in the center position.

With the structures of this azirine-nitrile ylide photochromic system now established, we are interested in learning about the energy pathway of the photo-
induced isomerization. We have begun measuring the yields of the azirine + ylide and the reverse, ylide + azirine interconversion in solid nitrogen as a function of irradiation wavelength using a continuously tunable, pulsed laser source. From these yields and the UV spectra of the two isomers, wavelength dependent quantum yields to isomerization will be determined, and from them we hope to be able to deduce the shape of the excited reactive surface of this system. If successful, this would be a prototype study that shows how to map reaction surfaces of electronically excited molecules.

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List of Figure Captions

Fig. 1: C₃H₄ + F₂: logarithm of the quantum yield to reaction as a function of the vibrational frequency. Error bars denote uncertainties of relative quantum efficiencies.

Fig. 2: Near infrared spectra of the transitions (a) ¹Δ₂g, 0 + ₃Σg⁻⁻, 0 and (b) ¹Δ₂g, 1+ ₃Σg⁻⁻, 0 of solid α-oxygen at 12 K.

Fig. 3: Electric dipole allowed transitions of interacting O₂ molecules in solid α-oxygen (see Ref. 19).

Fig. 4: Laser reaction excitation spectra of (a) O₂: ¹Σg⁺⁻, 0 + ₃Σg⁻⁻, 0 and (b) O₂: ¹Σg⁺⁻, 1+ ₃Σg⁻⁻, 0 of matrices DMF/O₂/Ar = 1/15/85 at 12 K. DMF: dimethylfuran.

Fig. 5: (a) Laser excitation spectrum of the reaction F₂+O₂ in the red spectral range. Matrix F₂/O₂ = 1/50. (b) Laser excitation spectrum of the reaction 2,5-dimethylfuran + O₂. Ordinate: growth of the integrated absorbance of the 1330 cm⁻¹ band of dimethylfuran endoperoxide (DMFO₂). Matrix DMF/O₂ = 1/100.

Fig. 6: Potential energy curves of low lying electronic states of F₂ according to ab initio calculations by Cartwright and Hay (Ref. 30).

Fig. 7: FT-IR difference spectrum: 7 hour Hg ³P₁ photolysis in a matrix Kr/CDFE/Hg = 8000/80/1 at 12 K. Product features are marked by arrows. CDFE: 2-chloro-1,1-difluoroethene.
Fig. 8: Energy diagram for the matrix reaction between Hg$^{3p}$ and 2-chloro-1,1-difluoroethene.

Fig. 9: Energy diagram for filtered photolysis of cis-dichloroethene in Kr with Hg present.

Fig. 10: Infrared spectra of six ylide isotopic species in the 1900 cm$^{-1}$ region.

Fig. 11: Possible cumulene and triple bond structures for the ylide photoisomer.
Fig. 2

\[ 1\Delta_g,1 \leftrightarrow 3\Sigma_g^{-},0 \]

\[ 1\Delta_g,0 \leftrightarrow 3\Sigma_g^{-},0 \]

Absorbance

9900 cm\(^{-1}\) 9700 9500 9300

9478

8500 cm\(^{-1}\) 8300 8100 7900

7989
\( \text{O}_2 \) unperturbed manifold

\[
\begin{align*}
(1\Delta_g, 1\Delta_g) \\
1\Sigma^+ & \quad (1\Sigma_g, 3\Sigma_g) \\
1\Delta_g & \quad (1\Delta_g, 3\Sigma_g) \\
3\Sigma^- & \quad (3\Sigma_g, 3\Sigma_g)
\end{align*}
\]

\( (\text{O}_2)_2 \) \( D_{2h} \)

\[
\begin{align*}
1\text{Ag} & \quad 1\text{B}_{2u} \\
1\text{B}_{1g} & \quad 1\text{Ag} \\
3\text{B}_{2u} & \quad 3\text{B}_{1g} \\
3\text{B}_{2u} & \quad 3\text{B}_{1g} \\
3\text{B}_{3u} & \quad 3\text{B}_{2u} \\
5\text{Ag} & \quad 3\text{B}_{3u} \\
1\text{Ag} & \quad 1\text{Ag}
\end{align*}
\]

\( v = 0 \)

Fig. 3
DMF/O\textsubscript{2}/Ar = 1/15/85

Fig. 4
Fig. 5
\[ E(\text{cm}^{-1}) \]

**Fig. 6**

- \( \text{F}_2 \)
- \( 1\Pi_u \)
- \( 3\Pi_{0+u} \)
- \( 3\Pi_{1u}, 3\Pi_{2u} \)
- \( X^1\Sigma_g^+ \)

- \( (\text{O}_2)_2(1\Delta_g, 1\Delta_g)0,0 \)
- \( \text{O}_2(1\Sigma_g^+, 1) \)
- \( \text{O}_2(1\Sigma_g^+, 0) \)

*Graphical representation of energy levels.*
Fig. 10
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