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FINAL REPORT

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Energy Paths in Chemical Reactions

Grant # AFOSR 78-3535

October 1, 1977 - September 30, 1981

This report describes research accomplishments over the period October 1, 1977 to September 30, 1981.

George C. Pimentel

George C. Pimentel
Professor of Chemistry
Principal Investigator
University of California
Berkeley, California 9472

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Research Accomplishments

RESEARCH ACCOMPLISHMENTS

1. Chemically Pumped Vibrational Lasers

During the period of the grant, three papers were published connected with the chemical pumping of HF and HCl vibrational lasers. These publications laid the groundwork for our recognition of the role of very high J states in the relaxation processes activated by chemical pumping of high v states. In the first of these (ref. 1), the results of measurements of vibrational rate constants for two different chemical laser studies and from a chemiluminescence study were critically compared. Agreement was evident among the different studies (two of them conducted in other laboratories) *when reasonable corrections were made for* V↔V and V↔R energy transfer corrections. Thus this work attracted attention to V↔R near-resonant energy transfer.

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This theme was developed further in our continued study of the ClF, ClF_3, and ClF_5 plus H_2 chemical lasers (ref. 3). The stimulated HF emission included vibration-rotation emission extending to unexpectedly high rotational states, e.g., up to v=1, J=20 and v=2, J=15, both of which emit under grating-selective conditions. The late threshold times and extended durations point to energy transfer processes involving rapid V↔R deactivation with large ΔJ coupled, probably, with V↔V up-pumping to give a cumulative increase in rotational energy.

The HCl vibrational laser emission from the $ClF-H_2$ chemical laser (ref. 11) revealed another facet of chemical pumping. Using the zero-gain and equal gain temperature methods, we determined vibrational rate constant ratios that agreed, where comparisons were possible, with comparable data available from chemiluminescence studies. With the resulting complete set of vibrational constants, a surprisal plot was obtained that could be interpreted to reveal the fraction of the exothermic energy release that occurs in the reaction entry channel. Thus, this work and its interpretation provide experimental access to this aspect of the shape of the reaction surface, previously only crudely available through extremely laborious theoretical calculations or parameter-laden classical trajectory modelling.

II. Rotational Lasers.

In view of the high J values revealed in the vibrational laser emissions, a series of studies of pure rotational laser emission from HF were initiated. The first of these (ref. 9) investigated the HF rotational laser emission obtainable from the $ClF-H_2$ chemical laser. Emission was observed from astonishingly high J values - up to $J=33\rightarrow32$ in the $v=0$ manifold and $J=30\rightarrow29$ in the $v=1$ manifold. The threshold times showed that $V\rightarrow V$ uppumping through $HF^{\dagger}- HF^{\dagger}$ collisions could not be responsible. Instead, the pumping must be attributed to the extremely exothermic branched reaction:

$$H + ClF \rightarrow HF + Cl \qquad \Delta H = -74.8 \text{ kcal/mole} \qquad (1)$$

The particular transitions observed with early thresholds, $v=0$, $J=28\rightarrow27$ and then $v=1$, $J=24\rightarrow23$ revealed the likely participation of $V\rightarrow R$ energy transfer processes involving multiquantum events.

Further study confirmed this early interpretation (refs. 13 and 18). The most easily interpreted studies were those based upon HF rotational laser emission in photoelimination lasers using CH_2CHF and CH_2CF_2 (refs 13 and 18). There was significant similarity between the laser transitions excited through photoelimination and those excited by reaction (1), which suggests similar pumping processes. With only Ar present, the earliest and most intense transitions were $J=14\rightarrow13$ in the v = 1 and 2 manifolds and adjacent transitions, 13→12 or 15→14 in v=0, 3 and 4 manifolds. These transitions are in close resonance with the rapidly equilibrated low J states of the next higher v state. Thus the importance of V→R pumping is clearly evident, in this case with v = 1 and $\Delta J \cong 10$, Again, the behavior of the much higher J state transitions, v = 0 and 1, J = 31→30 to J = 28→27, suggests a similar resonant transfer from low J states of much higher v. This inference indicates that the likely multiquantum processes extend to $\Delta v = 5$ and $\Delta J = 26$. This is probably the best evidence available that $\Delta v > 1$ multiquantum V→R channels play a role in vibrational deactivation of HF in chemical lasers. In fact this proposal provides the most reasonable model available for the extremely high v dependence for the increase of vibrational relaxation rate constant as v increases (up to $v^{2.5}$).

Further studies of the effects of deliberately added collision partners (CO, CO_2, H_2, D_2, HCl) revealed surprising differences among these molecules (ref. 18). The first two, CO and CO_2, act at modest pressures (1-25 torr) to increase the gain of almost all transitions and to bring to emission threshold many more transitions not seen with argon only. In sharp contrast, the other collision partners, H_2, D_2, and HCl, act to diminish the gain of almost all rotational laser transitions that emit with argon only. These two different types of behavior were not signalled by any earlier evidence, including apparent vibrational deactivation rates. Our new data indicate that CO and CO_2 act to move energy from vibrational excitation into rotational degrees of freedom through V→R processes, whereas H_2, D_2, and HCl remove rotational energy from HF by $R \rightarrow R'$ processes.

One additional chemical laser problem was pursued, the laser emissions near 12 microns that were observed upon flash photolysis of gaseous mixtures of dinitrogen tetrafluoride, N_2F_4, and argon. Many experiments were devoted to identification of the molecular species responsible for the emission. Despite the absence of hydrogen as a deliberately added constituent, gaseous HF emitting as a rotational laser finally seemed the most likely molecule. Careful experiments carried out in glassware that had been thoroughly exposed to D_2O showed that the glass and suprasil reaction vessel walls were the source of the hydrogen atoms.

III. Cryogenic Chemiluminescence

Cryogenic environments (e.g. solid argon at 10°K) offer a special set of conditions in which to examine the role of electronic degrees of freedom in exothermic chemical reactions. Whether chemiluminescence will be observed from a particular state when a reaction takes place depends upon, first, whether the reaction is sufficiently exothermic to permit occupancy of that state, second, whether there is a facile channel that causes entry to that state, and, third, whether competitive relaxation processes are sufficiently slow compared to the radiative lifetime to permit detectable emission. The first of these three factors is not affected by the cryogenic situation. Given enough energy, whether a particular electronic state receives population is a factor that probably is about the same under matrix conditions as in the gas phase. This is the factor we would most like to understand better, since it pertains to the chemical pumping of electronic lasers. The third factor, competing relaxation processes, acts both to increase population of a given state by non-radiative entry from a higher state and to decrease population by non-radiative drainage to lower states. The cryogenic environment affects these relaxation processes very much, generally acting to reduce significantly the non-radiative relaxation rates. Hence our studies offer a distinctive perspective and a special opportunity to examine chemical pumping of electronic states.

The photolysis of OCS in solid argon or nitrogen at 10°K provides a convenient source of a suspension of sulfur atoms. Upon slow warming, these sulfur atoms diffuse and react, either with each other to form S_2* or with other, deliberately added reactants. The reaction of ground state sulfur atoms in solid argon, krypton, xenon, and SF_6 revealed three progressions which could be identified as follows (ref. 8):

$$\begin{array}{llcl}
 & S(^2P) + S(^2P) & \rightarrow & S_2^* \quad \Delta H^\circ = -101 \text{ kcal} \qquad (2) \\
3300\text{-}5200\ \mathring{A} & S_2\ (B'\ ^3\Sigma_u^-) & \rightarrow & (X\ ^3\Sigma_g^-) \text{ and/or } B''\ ^3\Pi_u \rightarrow X \\
5580\text{-}6890\ \mathring{A} & S_2\ (A'\ ^3\Delta u) & \rightarrow & (X\ ^3\Sigma_g^-) \\
6680\text{-}8750\ \mathring{A} & S_2\ (C\ ^1\Sigma_u^-) & \rightarrow & (a\ ^1\Delta g)
\end{array}$$

These were the first observations by any technique of the latter two electronic transitions of S_2 and the first direct spectroscopic evidence that the $C^1\Sigma_u^-$ state actually lies below the $A\ ^3\Sigma_u^+$ and $A'^3\Sigma_u$ states (as is the case for O_2). These experimental results stimulated quantum mechanical calculations at the configuration interaction level, of the energy levels of S_2 and SO in good agreement with the new levels (ref. 10).

When oxygen is deliberately added, the diffusion of sulfur atoms on warming causes new progressions to appear. The most readily identified is a progression in the 3800-5000 Å region attributable to the well-known SO_2 phosphorescence (ref. 2).

$$S(^2P_2) + O_2(X\ ^3\Sigma_g^-) \rightarrow SO_2^* \qquad \Delta \overset{\circ}{H} = -137 \text{ kcal/mole} \qquad (3)$$

$$SO_2\ (a\ ^3B_1) \rightarrow (X\ ^4A_1)$$

This provides the first evidence that a sulfur atom can insert into the oxygen molecule with effectively zero activation energy.

In addition to the SO_2 phosphorescence, another new progression was observed in the spectral range 5200-7700 Å as well as a previously unobserved intense broad feature at 7816 Å (ref. 4). A variety of experimental data permitted these to be associated, respectively, with emission by SO* and by S* atoms, the latter excited by energy transfer from SO_2*.

$$S(^2P_2) + O(^2P_2) \rightarrow SO^* \qquad \Delta H^\circ = -124 \text{ kcal/mole} \qquad (4)$$

$$SO_2(a^3B_1) + S(^2P_2) \rightarrow SO_2(X^1A_1) + S('S) \qquad (5)$$

$$SO(c^1\Sigma^-) \rightarrow (a^1\Delta)$$

$$S(^1S) \rightarrow ('D)$$

This is the first observation of the c→a transition of SO and the first spectroscopic information about the $c^1\Sigma^-$ state.

These techniques were then extended to polyatomic species through chemiluminescent reactions involving methylene. The matrix suspension of CH_2 molecules was produced through in situ photolysis of diazomethane. When such a sample was warmed slowly, a red chemiluminescence appeared at 5987 Å which could be attributed to ethylene (ref. 14).

$$CH_2\ (X^3B_1) + CH_2\ (X^3B_1) \rightarrow C_2H_4^* \qquad \Delta H^\circ = -170 \text{ kcal/mole} \quad (6)$$

$$C_2H_4(Z'A, \text{ or } V^1B_2) \rightarrow (T^3A_2)$$

Both upper and lower states in the chemiluminescence are non-planar. Thus, the measurement demonstrates one of the few experimental techniques available with which to determine the energies of excited states of polyatomic molecules which cannot be detected in absorption due to radically different molecular geometries.

In addition, the infrared spectra of the photolyzed matrix (before warming) revealed absorption at 1115 cm^{-1} that is probably due to the bending mode of CH_2. This observation bears significantly on the issue of the CH_2 triplet-singlet splitting, favoring the lower, 9 kcal/mole, splitting over the higher, 19 kcal/mole value derived from photoelectron detachment studies of CH_2^-.

When oxygen was deliberately added to the diazomethane/argon matrix samples, photolysis resulted in a new chemiluminescence spectrum (ref. 12). Now slow warming produced the familiar O_2 Herzberg bands showing that oxygen atoms had been produced during photolysis. In addition, two new progressions were observed in the regions 3100-3600 Å and 3900-4900 Å. Analysis permitted these progressions to be assigned to emission from formic acid formed in reaction between CH_2 and O_2.

$$CH_2(X^3B_1) + O_2(X^3\Sigma_g^-) \rightarrow HCOOH^* \quad \Delta H° = -181 \text{ kcal/mole} \qquad (7)$$

$$3100\text{-}3600 \text{ Å} \quad HCOOH\ (a^3A'') \rightarrow (X^1A')$$

$$3900\text{-}4900 \text{ Å} \quad HCOOH\ (A'^1A') \rightarrow (A^1A'')$$

These are the first observations by any spectroscopic technique of these formic acid transitions. It is the first experimental detection of the a^3A'' state of formic acid.

These chemiluminescence studies clearly indicate that the matrix technique can provide new spectroscopic information about excited electronic states even of polyatomic molecules. It also offers some information about the role of excited states in exothermic reactions. However, this information remains somewhat ambiguous because of the probable rapidity of intersystem crossing. This implies that emission from a particular state only shows that it or a higher state not too different in energy was populated through reaction. More information on intersystem crossing rates and on quantum yields would add greatly to the significance of this type of experiments in relation to chemical pumping of electronic lasers.

IV. Vibrational Excitation of Chemical Reactions.

Two types of studies were conducted to investigate the role of vibrational excitation in chemical reactions. With a high power CO_2 laser, the chemistry of molecules excited with many photons at 1000 cm^{-1} was investigated in the gas phase. Then with single photon excitation, we have demonstrated the possibility of inducing chemical reactions in a cryogenic environment using mode-selective vibrational excitation.

The initial study of multiphoton excitation was connected with the molecular elimination of HF from fluorinated olefins.(ref. 7). The CO_2 pulsed laser beam crossed at an 8° angle the central zone of a grating-controlled, discharge pulsed HF laser. This in-cavity arrangement provided sufficient sensitivity to detect HF in the small amount produced by a single CO_2 pulse. Molecular elimination of HF was shown to occur on multiphoton excitation of vinyl fluoride, 1,1-difluoropropene, 2-fluoropropene, and t-1,2-difluoropropene. Scavenger experiments with vinyl fluoride showed that fluorine atoms, hence C-F bond rupture, played no significant role. The activation energy indicates that more than 25 CO_2 quanta were absorbed in each molecule excited to the elimination threshold. The absence of C-F bond rupture indicates that not as many as 45 quanta are absorbed. This research was the first clear evidence that molecular elimination can be caused by multiple photon vibrational excitation. The work was circulated as an AFOSR technical report but not published thereafter because before the work could be embellished and exploited, another group published a similar finding based on many repetitious exposures to CO_2 laser radiation.

The work was suspended in favor of a more sophisticated approach that again permitted analysis of products from a single pulse. The pulsed emission from a Lumonix CO_2 laser was brought to a "soft focus" in the immediate vicinity of the leak into a mass spectrometer. With gas pressures in the range of a few tenths of a torr, and a diffusion distance of 2 or 3 mm to the orifice, the vibrationally excited molecules produced by multiphoton excitation could experience a modest number of collisions - a few thousand - before entering the mass spectrometer. The intent was to permit the study of the bimolecular reactions of vibrationally hot molecules.

A test system used was 1,1-difluoro-2-chloroethylene, selected because it absorbs CO_2 radiation and it is known to eliminate both HF and HCl when excited with vacuum UV electronic excitation. The HF must be eliminated in $\alpha\beta$ elimination and HCl must come from $\alpha\alpha$. The question we posed was whether only one of these processes would occur with vibrational excitation, which approaches the elimination activation energies "from below." In fact, both HF and HCl were observed, so both channels were excited.

The desired bimolecular chemistry was observed with two systems, trifluoroethylene and butadiene. The trifluoroethylene gave a series of products that indicated chemistry between two parent molecules. The results are consistent with the interpretation that $\alpha\alpha$ elimination occurred to produce difluorovinylidine. Without hydrogen atoms, the vinylidine apparently does not rearrange because fluorine atom migration is slow. Hence the products can be associated with reaction between F_2CC and the parent F_2CCHF. Presumably because of the stability of the CF_2 molecule, one of the major products is trifluoroallene:

$$F_2CC + F_2CCHF \rightarrow CF_2 + F_2CCCHF \qquad (8)$$

The formation of CF_2 is signalled by the production of C_2F_4.

This model was verified by the addition of excess C_2H_4. In this case, allene was found as a major product instead of trifluoroallene but the C_2F_4 production was still obtained.

$$F_2CC + H_2CCH_2 \rightarrow CF_2 + H_2CCCH_2 \quad (9)$$

The multiphoton excitation of butadiene also gave products attributable to reaction between two parent molecules. The Diels-Alder product 4-vinylcyclohexene did not accumulate, but the observed products indicate that it is initially formed but with sufficient energy to fragment. Products positively identified included acetylene, ethylene,allene, and methylacetylene. Possible products were cyclopentane and ethylbenzene. It is inferred that the reaction between a multiphoton-excited butadiene and a cold butadiene molecule causes fragmentation with facile hydrogen migration. The product distribution does not resemble that obtained through pyrolysis which, at low temperature, tends to give a mixture of isomers of the dimer. At intermediate temperatures (700-800°C) the products become polycyclic, including naphthalene, anthracene, and phenanthrene as well as toluene, benzene, methane, etc. At still higher temperatures, (above 950°C), smaller molecules predominate, C_2H_2, C_2H_4, CH_4, and H_2.

Thus the experiments were successful in demonstrating the possibility of initiating bimolecular chemistry using multiphoton excitation and in revealing products distinctive for this kind of excitation.

The experiments directed toward mode selective excitation of chemical reactions in cryogenic solids has provided perhaps the most well established example of mode-selective chemistry by any technique (refs. 15 and 16). When nitric oxide and ozone are placed together in solid argon or nitrogen, they react slowly even in the cold dark (55°K environment) and with the sample at 10°K. This was shown to be due to heavy atom tunnelling (ref. 15), and this dark reaction interfered with study of vibrational enhancement. Nevertheless it was possible to demonstrate that laser excitation of the NO vibrational degree of freedom increased the rate of the cryogenic reaction.

The fluorine-ethylene reaction, however, proved to be more fruitful. No reaction occurs in a matrix at 10°K but when a tuned laser is used to irradiate a matrix sample at a frequency absorbed by $F_2 \cdot C_2H_4$ pairs, reaction does occur. Quantum yield varies over more than five orders of magnitude. It is less than 10^{-6} when ν_7, the out-of-plane bending mode, is excited. With increasing photon energy, the quantum yield Φ increases monotonically but not smoothly. It reaches 0.3 at photon energies of 4000 cm^{-1}.

When the same types of study are carried out with dideuteroethylene, there is a strong symmetry effect. The 1,2-transdideuteroethylene, which preserves the center of symmetry of ethylene, has the highest quantum yields though still below those of C_2H_4. The 1,2-cis-dideutero and 1,1-dideuteroethylenes have successively lower quantum yields for fixed photon energy.

The behavior leads us to a model of stepwise deactivation through transfer of energy into lattice phonon energy. We presume that this process shows a strong preference for the smallest steps available that are accessible through symmetry. We believe that if the molecule has g-u symmetry, then a u state excited through infrared absorption is constrained in its relaxation to successively lower u states. If relaxation is slower for larger energy gaps, then the highly symmetric molecule will have longer residence time in any given level, hence higher quantum yield.

This stepwise deactivation model implies that each state that can be excited will display a quantum yield equal to its own quantum yield plus the sum of all the states below it through which it will pass en route to complete deactivation. This accounts, then, for the monotonic increase in quantum yield with photon energies. The irregular increases, however, signal mode selectivity. If a mode is excited that has a high propensity for reaction, it will add more quantum yield to the sum than will a mode that has a low propensity for reaction. We associate high reaction propensity with excitation in out-of-plane modes but the evidence is not compelling.

There remains the question of why this cryogenic technique is successful in displaying mode selectivity when so many other attempts to find it have failed. We believe it is because the matrix has three effects that favor retention of the energy in the mode excited. First, the matrix eliminates rotational degrees of freedom, very much reducing energy level density. Second, the low temperature gives a narrow homogeneous line width, compared to the level spacing. Third, the matrix phonon modes interact sufficiently weakly to disfavor vibration-to-phonon energy relaxation. This provides long enough residence times in any given level to permit chemical reaction to compete provided there is sufficient energy to exceed any activation energy and provided the excited motion has some component of the reaction coordinate.

PERSONNEL

Principal Investigator: George C. Pimentel, Professor of Chemistry

		Present Employment
1.	Dr. Leif Fredin, Postdoctoral	Chemistry Department, Rice University, Houston TX
2.	Dr. Heinz Frei, Postdoctoral	Laboratory of Chemical Biodynamics, University of California, Berkeley
3.	Dr. Eric Sirkin, Graduate Student	Xerox Corporation, Palo Alto, CA
4.	Dr. S. Randolph Long, Graduate Student	Postdoctoral Research Appointment, Department of Chemistry, Indiana University, Bloomington, IND
5.	Dr. Yuan-Pern Lee, Graduate Student	Asst. Prof., Dept. of Chemistry, National Tsing-Hua University, Taiwan, R.O.C.
6.	Dr. Robert Stachnik, Graduate Student	Postdoctoral Research Appointment, Hanscombe Field, Newton, Mass. (Air Force)
7.	Dr. Geraldine Richmond, Graduate Student	Assistant Professor, Bryn Mawr College, PA
8.	Dr. Stella Cesaro, Postdoctoral	Research Scientist, Instituto di Chimica Fisica, Universita Roma, Italy
9.	Mr. Alvin Kennedy, Graduate Student	Graduate Student, U.C. Berkeley

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DISSERTATIONS

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The purpose of this research was to clarify the factors that need to be understood to develop chemically pumped lasers operating on electronic, vibrational, or rotational transitions. Chemiluminescence from reaction products formed at very low temperature (10-20 degrees K) has provided an effective, though as yet only qualitative, way of detecting chemical pumping into excited electronic states. Using argon and nitrogen solids as host lattices, the method was pioneered using chemiluminescence from diatomic molecules O_2, S_2, and SO. Then it was extended to polyatomics, SO_2, C_2H_4, and HCOOH. Chemical pumping HF and HCl vibrational lasers by the reaction of H_2 with ClF, ClF_3, and ClF_5 was used to determine the vibrational rate constants into particular vibrational states. The ClF-H_2 reaction was also used to excite HF pure rotational laser emission. This study and a similar photoelimination-pumped rotational laser study showed that resonant vibration-to-rotation energy transfer plays an important role in the relaxation of vibrational population inversions in HF lasers. A high energy, pulsed CO_2 laser was used to investigate the bimolecular chemistry of gaseous molecules containing high levels of vibrational excitation. Such multiphoton excitation of trifluoroethylene, for example, initiates chemistry attributable to difluoroethylidine. Similar excitation of butadiene gives products that can be recognized as fragmentation products of butadiene dimers. Another type of experiment involved single photon vibrational excitation of reactions in cryogenic matrices. Using tuned infrared lasers as light sources and infrared detection, quantum yields could be measured for the F_2-ethylene reaction. Mode-specific reaction behavior was observed.