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A Spectroscopist's View of Energy States, Energy Transfers, and Chemical Reactions

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Annu. Rev. Phys. Chem. 2007. 58:1–33

First published online as a Review in Advance on October 11, 2006

The *Annual Review of Physical Chemistry* is online at <http://physchem.annualreviews.org>

This article's doi:
10.1146/annurev.physchem.58.032806.104610

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0066-426X/07/0505-0001\$20.00

Key Words

vibrational energy transfer, bimolecular reactions, unimolecular reactions, transition states, formaldehyde, ketene, lasers

Abstract

This chapter describes a research career beginning at Berkeley in 1960, shortly after Sputnik and the invention of the laser. Following thesis work on vibrational spectroscopy and the chemical reactivity of small molecules, we studied vibrational energy transfers in my own lab. Collision-induced transfers among vibrations of a single molecule, from one molecule to another, and from vibration to rotation and translation were elucidated. My research group also studied the competition between vibrational relaxation and chemical reaction for potentially reactive collisions with one molecule vibrationally excited. Lasers were used to enrich isotopes by the excitation of a predissociative transition of a selected isotopomer. We also tested the hypotheses of transition-state theory for unimolecular reactions of ketene, formaldehyde, and formyl fluoride by (*a*) resolving individual molecular eigenstates above a dissociation threshold, (*b*) locating vibrational levels at the transition state, (*c*) observing quantum resonances in the barrier region for motion along a reaction coordinate, and (*d*) studying energy release to fragments.

GETTING STARTED

I had the good fortune to grow up on a farm in eastern Pennsylvania, where hard work produced good crops, poultry, and livestock; where I could help my father take apart, repair, and reassemble farm equipment; and where I could manufacture and experiment with gun powder. In those days, parents could still give chemistry sets to their children, and the East Coast sky was often clear enough to observe shooting stars while lying flat on the bed of a hay wagon. This constituted my first spectroscopic observations of chemistry in action. My initial in-class chemistry lab was a study of sulfur combustion carried out by placing a fumigation candle in the ink well of my third-grade desk and lighting it on departure for recess. This early initiative was not encouraged on my return from the playground.

One of Princeton Professor Hubert Alyea's renowned lectures on the marvels of chemistry at a nearby high school provided my first look at cryogenics as he exhaled through a mouth full of dry ice. By the time I finished a series of integrated courses in the physical sciences, a one-week visit by J. Robert Oppenheimer, and a challenging course in analytical/inorganic chemistry in high school (Phillips Exeter Academy in New Hampshire), I was well on my way to becoming a physical chemist. The launching of Sputnik during my first month of college (October 1957) at Harvard sharply increased federal funding for scientific research and greatly encouraged scientific career paths. That fall, the intensity of lab courses in physics and organic chemistry, a fourth-semester calculus course, and a humanities course quickly ended my aspiration to extend my high-school crew experience to intercollegiate rowing. A series of research projects in Paul D. Bartlett's personal lab at Harvard and summer jobs at Arthur D. Little and General Electric's corporate research lab deepened my interest and experimental background.

Less than three years after Sputnik, I arrived at Berkeley, newly wed to my high-school sweetheart, Penny Percival, to begin married life, Ph.D. research, and 40 years at the University of California. Graduate courses in quantum chemistry and applied math at Harvard had created a strong interest in a quantitative theoretical understanding of molecules and their quantum states. The new molecular-beam scattering work of Dudley Herschbach (1) was attractive to me. The most attractive was George Pimentel's proposal of a six-month experimental study of the infrared (IR) spectrum of methylene (CH_2) in a matrix, solid N_2 or Ar, that would be followed by molecular orbital calculations of methylene's structure and spectrum.

Methylene has humbled many spectroscopists and inspired quite a few theoreticians. My thesis work (2), 36 intense months in the lab, yielded interesting spectra of methylene precursors, diazomethane (CH_2N_2) (3–5), diazirine ($\text{c-CH}_2\text{N}_2$) (6, 7), and ketene (CH_2CO) (8). My gunpowder experience provided some preparation for the explosive properties of these molecules. Naivety led me to suggest that the second most intense band that was assigned as a fundamental vibration in both ketene and diazomethane was actually the overtone of the out-of-plane CH_2 bending vibration (4, 5, 8). The rotationally resolved spectrum of the three overlapping bends in the $400\text{--}500\text{ cm}^{-1}$ region bore this out (3). The out-of-plane bending potential has a small quadratic force constant and a relatively large quartic anharmonic constant, a

somewhat bucket-shaped potential. This was qualitatively rationalized (9) in terms of resonance structures, one planar and one with the CH_2 bent out of the plane (with a formal negative charge on the carbon and positive on the adjacent nitrogen); this discussion turned out to be the extent of the molecular orbital theory part of my thesis. It would be another 20 years before Hrvoje Petek, David Nesbitt, and Peter Ogilby observed IR spectra of methylene in the gas phase using a high-resolution laser (10). My thesis (2) described the reactivity of methylene from diazomethane or its cyclic isomer, diazirine, in solids at 20 K with isotopically labeled N_2 (6) and with diazomethane (7).

Pimentel was an exceptional scientific mentor in this thesis work; in many ways, he also replaced my father who had died during my first semester at Harvard. Pimentel's weekly group meeting was always a special learning experience. Everyone learned to be constantly questioning and skeptical of one's data and interpretations, and of the literature, always aware that Mother Nature is constantly setting traps to destroy the credibility of the unwary researcher. Discussions of new results in terms of alternative physical models let us see his exceptional intuitive insight and his strongly supportive mentoring style. During the third year of thesis work, I interviewed for faculty positions and at age 23 faced the intimidating challenge of establishing an internationally recognized research program at Berkeley entirely different from Pimentel's.

$V \rightarrow R$:

vibration-to-rotation energy transfer

$V \rightarrow T$:

vibration-to-translation energy transfer

$R \leftrightarrow T$:

rotation-to-translation energy transfer and equilibration

$V \rightarrow R, R, T$:

vibration-to-rotation of both collision partners and to translation energy transfer

$V \rightarrow V$:

vibration-to-vibration energy transfer

ENERGY TRANSFER IN COLLISIONS

During graduate work, I remained interested in molecular-beam scattering, in scattering theory and intermolecular potentials, and in collision-induced changes in vibrational and rotational quantum numbers. In my oral preliminary exam, I proposed a crossed-molecular-beams measurement of rotational excitation in collisions of HD with He. I wanted to understand how energy transfer occurs during molecular collisions, to determine any selection or propensity rules that govern quantum-number changes, and to understand these in terms of the dependence of the intermolecular potential on the vibrational and rotational coordinates of each collision partner.

An analysis of ultrasonics measurements of vibrational relaxation in methane led Cottrell & Matheson (11) to propose that for molecules with small moments of inertia, energy transfer from vibration to rotation ($V \rightarrow R$) could be more important than from vibration to translation ($V \rightarrow T$). Because rotation-to-translation ($R \leftrightarrow T$) energy transfer is much more rapid than vibrational relaxation, a direct determination from acoustic measurements is difficult. Cottrell & Matheson's idea seemed intuitively reasonable from the perspective of classical dynamical forces, semiclassical perturbation theory, and distorted-wave scattering theory. Extending this model and applying it to data from some 25 molecules produced a useful correlation that suggested the importance of $V \rightarrow R$ transfer when the rotational velocities of atoms are faster than the relative translational velocity (12). It is often the case that R in one or both collision partners and T are all important: $V \rightarrow R, R, T$. It is simply a question of which degrees of freedom cause the time-dependent force on the vibrator with the largest Fourier component at the frequency of vibration. Vibration-to-vibration ($V \rightarrow V$)

energy transfers among the modes of a single molecule may be caused by collisions with rare-gas atoms or other molecules, and vibrational energy may be transferred from one molecule to another.

ELECTRONICALLY EXCITED MOLECULES

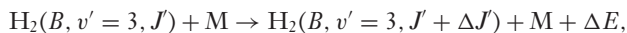
There were inspiring recent experiments on I_2 (13), OH (14), and NO (15) that used atomic resonance lamps to excite single vibration-rotation energy levels in an excited electronic state and resolved fluorescence to observe changes in quantum state induced by collisions that occurred during the radiative lifetime of the excited state.

Hydrogen

To maximize the prospect for comparison with first-principles theory, I decided to look at the hydrogen molecule in collision with $^3,^4\text{He}$ and Ne. The production of $\text{HD}(B^1\Sigma_u^+, v' = 3, J' = 2)$ by excitation with the 106.6-nm resonance line of Ar had been discovered by observing the HD spectrum resulting from an electrical discharge through an $\text{H}_2/\text{D}_2/\text{Ar}$ mixture by Mie (16) and by Tanaka and coworkers (17). Our experiments, with vacuum ultraviolet (UV) excitation at the limit of the LiF window transmission range and with a 1-m monochromator to resolve the fluorescence, required a great deal of experimental finesse and persistence from my first graduate student, Dan Akins, and my first postdoctorate fellow, Ewald Fink.

The largest collision cross section was for fluorescence quenching by HD itself, $79 \text{ \AA}^2$, much larger than the hard-sphere cross section for ground-state molecules (18). Quenching by $^3,^4\text{He}$ and Ne occurred with cross sections of 8.8, 9.9, and $3.5 \text{ \AA}^2$, respectively (18). Two decades later, experiments using a tunable vacuum UV laser for the excitation of H_2 , D_2 , and HD to any desired B -state vibrational and rotational quantum numbers showed that quenching by He occurs through the formation of an electronically excited collision complex that dissociates following curve crossing to the repulsive ground-state potential energy surface (PES) (**Figure 1**) (19). The barrier to complex formation is $250 \pm 80 \text{ cm}^{-1}$, much lower than extant ab initio calculations that ranged from 520 to 1200 cm^{-1} .

Rotational transitions among the levels of $v' = 3$,



occurred with cross sections ranging from 1 to $5 \text{ \AA}^2$ and exhibited a substantial propensity for $\Delta J = \pm 2$ over $\Delta J = \pm 1$ for rare-gas collisions (20). Normally, transitions with smaller energy changes happen with higher efficiency. Thus, notwithstanding the shift of the center of mass of HD away from its center of symmetry, the angle-dependent terms of the HD-M intermolecular potential function that are even with respect to reflection in a plane through the HD center of mass and perpendicular to the HD bond are large compared with the odd terms that cause odd ΔJ transitions. A laser study found that the collision cross sections for reorientation of the angular momentum, ΔM_J , of HD, H_2 , or D_2 were much larger, $\sim 30 \text{ \AA}^2$ (21).

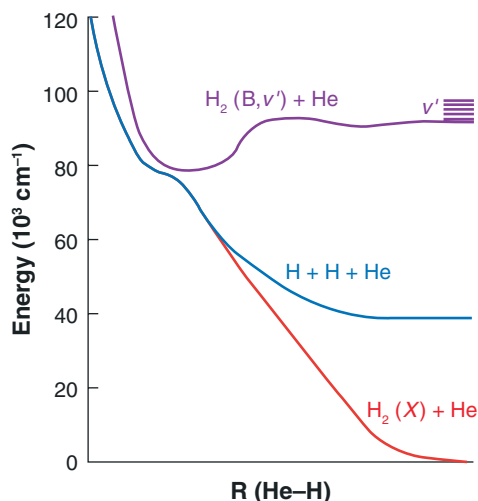


Figure 1

A schematic diagram of the potential energy surfaces involved in the quenching of *B*-state hydrogen. The excited hydrogen and helium cross a barrier on the excited potential energy surface; they then enter a deep well in which the H-H bond length grows to approximately 2 Å. At the bottom of this well, there is a seam of avoided crossing with the ground-state surface. Quenching is thought to occur when a nonadiabatic transition takes the metastable $\text{H}_2(B)\text{-He}$ complex to the ground-state surface, where the products are either $\text{H}_2(X)$ and He or two H atoms and He (19).

Loss of a vibrational quantum, $v' = 3 \rightarrow 2$, in an He or Ne collision with *B*-state HD occurred with a cross section of approximately 0.8 Å^2 ; all energetically accessible *J* levels of $v' = 2$ were populated; and on average approximately 40% of the 1092 cm^{-1} of vibrational energy is released to rotation, a clear example of $V \rightarrow R, T$ energy transfer (18). The vibrational and rotational relaxation cross sections reflect the long bond (double that of the ground state), and hence dumbbell shape, of the *B*-state hydrogen molecule. The distribution of final-state quantum numbers gives information about the nature of the energy-transfer process and the shape of the intermolecular potential function responsible for it.

Formaldehyde and Laser Photochemical Isotopic Enrichment

Because polyatomic molecules present a much greater variety of energy-transfer processes, we tried a number of sources to excite single rovibronic levels of the fluorescent singlet state of formaldehyde. Several years of severe frustration (e.g., carbon arcs that must have projected Charlie Chaplin's first films) ended in 1970 when Ed Yeung (22) used a doubled ruby laser to pump a tunable dye laser, which he then summed with ruby fundamental to generate UV. This provided the first opportunity to do chemistry with a tunable UV laser. We then carried out an extensive study of vibronically resolved lifetimes of H_2CO , HDCO , and D_2CO (23). The $^1\text{A}_2$ state of formaldehyde decays primarily by predissociation (24). Collisions result in dissociation much more

than in energy transfer, and thus rovibrational energy-transfer studies (25) did not yield state-to-state energy-transfer rate constants. Yeung (26) took advantage of the much larger absorption of the frequency-doubled ruby laser at 347.2 nm by D_2CO than by H_2CO to perform the first reported laser photochemical isotopic enrichment (27). Subsequent experiments with higher-resolution tunable lasers yielded enrichments of both ^{13}C by 80 times (28), and ^{14}C by a factor of 150 (29). The method was considered but not developed for ^{14}C dating. Steve Leone (30) was successful in photopredissociating Br_2 isotopically selectively to produce 80%–85% H^{81}Br on reaction with HI .

Lasers and $\text{V} \rightarrow \text{V}$ Energy Transfer

Working with Pimentel created a strong interest in molecular vibrations and hence in the collisional transfer of vibrational energy. In 1962, Callear and Smith (31, 32) published some nice results on vibration-to-vibration energy transfer, $\text{V} \rightarrow \text{V}$, between diatomics. There were few results or methods for making further measurements. In the early sixties, fixed-frequency lasers began to be useful sources for spectroscopic experiments (33–35). Therefore, I was constantly looking for, and experimenting with, lasers that might be useful for exciting molecular vibrations.

Methane

The observation of a strong He-Ne laser line at 2947.90 cm^{-1} (36) suggested that a nearly resonant transition of the asymmetric CH stretch of methane could be excited. Laser oscillation is shifted to a nearby line by introducing methane into the resonator cavity (37), showing that vibrational relaxation of methane might be studied optoacoustically or by laser-excited fluorescence. Jim Yardley took on this difficult experiment at the beginning of his graduate work. He built the laser, the intracavity cells and chopper, the fluorescence-collection system, and the detector and electronics for recording the phase shift between laser excitation and IR fluorescence. For IR time-resolved fluorescence detection, we used Pimentel's techniques and worked with the Santa Barbara Research Corporation to test new detector materials to optimize speed and sensitivity (38). Yardley (39) submitted the first $\text{V} \rightarrow \text{V}$ transfer-rate measurement for a polyatomic molecule in less than one-and-a-half years. Stretch-to-bend energy transfer in CH_4 was determined to require 60 collisions and bend to rotation and translation 14,000 collisions (40).

Peter Hess and Andrew Kung (41, 42) used tunable lasers to map out energy flow among all degrees of freedom for collisions with methane and with rare gases (**Figure 2**). Conversion of symmetric-stretching to asymmetric-stretching excitation requires only 11 collisions, and the number is about the same for the bending. Measurements on mixtures with rare gases, and a variety of diatomics (including HCl and DCl) and polyatomics, showed clearly that all of the available rotational and translational degrees of freedom are involved in the relaxation of the lowest-frequency bending vibration in methane. This can be understood in terms of a simple model

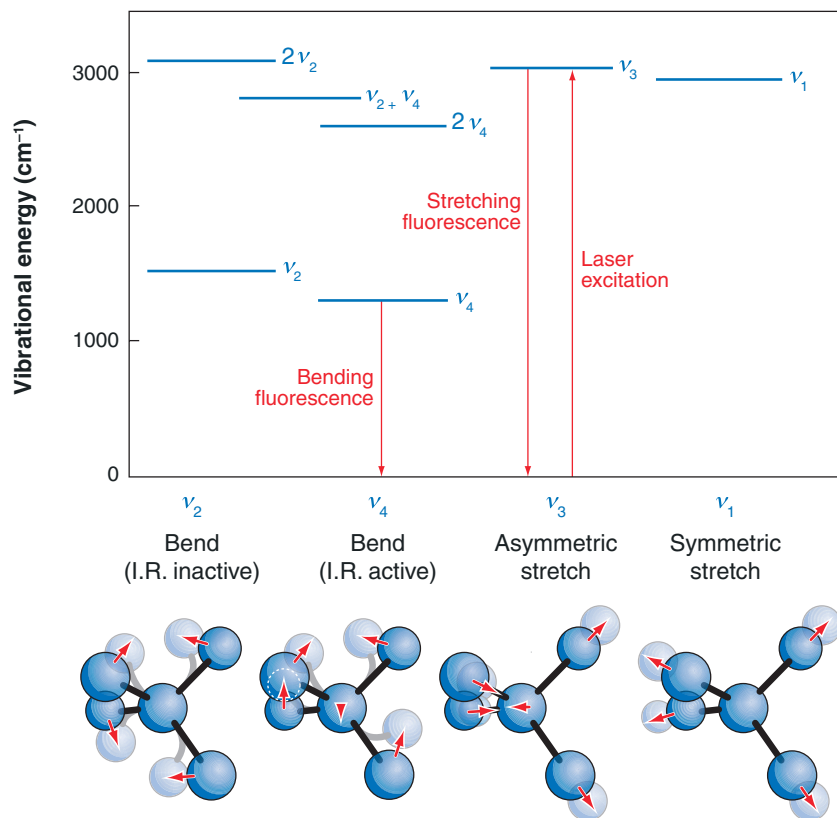


Figure 2

Vibrational energy levels of methane (33). The laser excitation and fluorescence transitions are indicated.

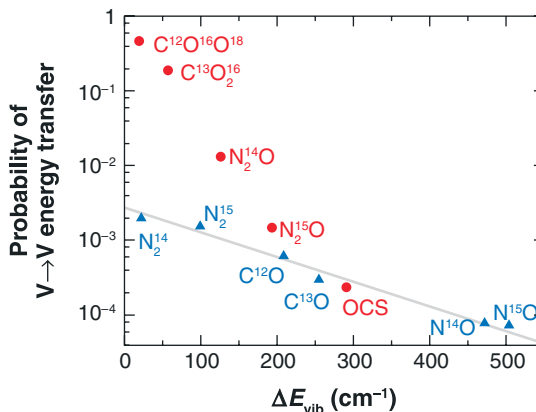
for the relative contributions of the translational and various rotational degrees of freedom (43, 44).

Carbon Dioxide

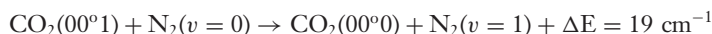
In 1966, Javan and coworkers (45) discovered that the CO_2 laser could excite the asymmetric stretch of CO_2 from the thermally populated symmetric stretch lower-laser level, and laser-excited vibrational fluorescence was easily detected. This initiated an avalanche of studies of the vibrational relaxation of the asymmetric stretch (ν_3) of CO_2 . In my lab John Stephenson, Jim Yardley, Bob Wood, Beilok Hu, Hao-Lin Chen, and Don Heller were quick to take advantage of this powerful technique. First were detailed measurements of the vibrational energy-transfer rates responsible for producing the inverted population for laser action (46). A study of ν_3 relaxation by intramolecular $V \rightarrow V$ transfers in collisions with rare gases suggested the importance of Coriolis and anharmonic mixing in the energy states of the free molecule (47). Water and its deuterated isotopomers are particularly effective in this relaxation but even more so in the relaxation of the lower-laser level, the symmetric stretch,

Figure 3

Probabilities of $V \rightarrow V$ energy transfer from the asymmetric stretch of CO_2 to stretching vibrations in other molecules (49). $\Delta E_{\text{vib}} = v_3(\text{CO}_2) - v(X)$ is the energy transferred into rotation and translation. Triangles indicate infrared inactive or weakly active vibrations for which $V' = (\mu_1 \cdot \mu_2)r^{-3}$ is negligible; circles indicate strongly infrared active vibrations.



ν_1 (48). Nearly resonant energy transfers such as



were found to have large cross sections that could be understood in terms of the oscillating dipole moment of the asymmetric stretch (ν_3) of CO_2 driving the oscillation of a nearly resonant vibration through its transition dipole or quadrupole moment (49). As these interactions are long-range compared with the repulsive potential for the collision, the cross sections may be calculated with simple but accurate models (49–51). The dipole-dipole interaction, $1/R^3$, gives cross sections that drop off much more rapidly with ΔE than the quadrupole-dipole, $1/R^4$ (**Figure 3**). Both calculated and experimental cross sections are inversely proportional to temperature for closely resonant processes (52). Transfers from the upper- to the lower-laser level of CO_2 in collisions with molecules that have vibrations approximately equal to the energy difference, such as



exhibit this same resonant transfer behavior (53).

Hydrogen Halides

Hydrogen-halide lasers provided exactly resonant sources for the excitation of hydrogen halides and launched the next wave of vibrational energy-transfer experiments (54–58). Studies of HCl in mixtures with DCl , H_2 , H_2O , and rare gases showed that in HCl-HCl and HCl-DCl collisions, vibrational energy is primarily transferred to the rotation of the vibrationally excited molecule rather than to the collision partner (**Figure 4**) (59–61). The hydrogen-bonding potential strongly favors collision model I in **Figure 4**. DCl is relaxed by HCl , with approximately double the probability per collision for relaxation by DCl ($P = 3.9 \times 10^{-5}$). Dominant participation by the lighter H atom in the relaxation would have resulted in a much larger isotopic effect. $V \rightarrow V$ transfers were also studied for many collision pairs (62).

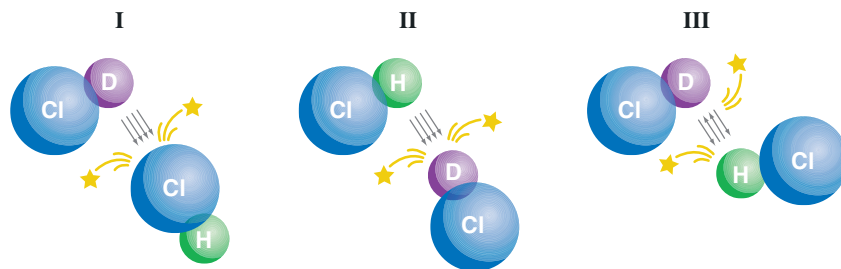
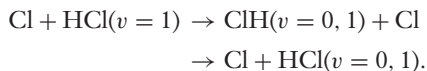


Figure 4

Collision models for vibration-to-rotation energy transfer in hydrogen chloride. Deactivation of excited DCl by an HCl collision partner is illustrated (59). In model I the impact velocity of the vibrating D atom with the collision partner is predominantly D-atom (vibrator) rotation. Energy is transferred to the rotation of the vibrator, and no rate change on isotopic substitution of collision partner H by D is expected. In model II impact velocity is taken to be entirely the rotation of the collision-partner H atom, and reduction of this velocity by the substitution of D would decrease the probability by a large amount. Energy is transferred into collision-partner rotation. Model III is a compromise between models I and II. Experiment indicates that model I plays the dominant role for HCl-HCl and DCl-DCl collisions.

Chemically Reactive Collision Partners

Norman Craig (63) took the laser-excited vibrational fluorescence experiments to the next level by using a frequency-doubled ruby laser to produce a known concentration of Cl atoms by Cl_2 photolysis and following that with an HCl laser pulse to vibrationally excite HCl. This two-laser excitation scheme allowed the study of relaxation in the potentially reactive system



The Cl atoms are approximately 2000 times more effective in relaxing HCl than are Cl_2 molecules. The rate of vibrational relaxation for DCl by Cl is 0.62 ± 0.13 times that for HCl by Cl (64, 65), even though the smaller vibrational quantum normally yields a much larger rate. This is strong evidence that the transfer is predominantly $V \rightarrow R$.

When chemical-bonding or hydrogen-bonding forces exist during a collision, there is a strong interaction with vibrations as the collision evolves and consequently relatively efficient transfer of vibrational energy. All these rates were of great value in developing the hydrogen-halide chemical lasers as practical IR sources. These studies set the stage for measuring chemical-reaction rates (66) and studying the branching between reaction and relaxation for vibrationally excited reagent molecules (67–70).

Tunable Infrared for Any Molecule

The tunable IR optical parametric oscillator liberated studies of vibrational energy transfer from the constraint of accidental coincidences between molecular absorptions and laser transitions. The LiF oscillator crystal opened up H and D stretching

fundamentals and the combination and overtone vibrations of heavier atoms to direct study (35, 71). Energy-transfer paths were studied in depth in CO (72), HCl($v = 2$) (67, 73), methane (41, 42), water (74–76), carbon dioxide and nitrous oxide (77), and their isotopomers. Dye lasers permitted the excitation of the second and third overtones of HF (78).

Progress is now limited simply by the complexity resulting from the number of possible vibrational energy transfers (79). Study of the work on carbon dioxide or methane above or on methyl fluoride by George Flynn and his group illustrates how challenging it is to measure a full set of rate constants (80) for all possible energy transfers for a polyatomic gas or a mixture of polyatomics. Nevertheless, we know a great deal about the dependence of rates on quantum-number changes, on the amount of vibrational energy to be transferred into translation and rotation, on the steepness of the repulsive intermolecular potential, on chemical- or hydrogen-bonding interactions, on long-range multipolar transition moments for nearly resonant $V \rightarrow V$ transfers, on the velocity of translation and of rotation relative to those of vibration, and so on. (79, 81). One can estimate whether inverted populations may be created and maintained in a chemically reacting mixture or in an electrical discharge. One can usually understand which degrees of freedom will be in local thermal equilibrium in a gas leaving a jet engine or in a planetary atmosphere (82).

Electronic-to-Vibration Energy Transfer

During the summer of 1973, I returned from a stimulating conference in Europe to find that Steve Leone & Frank Wodarczyk (83) had been working hard, taken the lab into a new field, and prepared a communication on the rates of $E \rightarrow V$ transfer from $\text{Br}(4^2P_{1/2})$ to HCl and HBr.

Vibrational Energy Transfer in Matrices

Jay Wiesenfeld (84), Linda Young (85–86), and Alison Abbate (87) studied the vibrational relaxation of HCl and DCl, of CH_3F , and of HCN in rare-gas matrices. The processes are similar to gas phase and could be modeled by considering the collision of the excited molecule with the cage wall (a motion corresponding to a localized phonon). The $V \rightarrow V$ transfers for the polyatomics could be understood in the same way.

BIMOLECULAR REACTIONS

Because vibrationally excited molecules are usually produced in a chemically reactive medium, it is important to understand how the dynamics of reaction and relaxation evolve together during a collision. Understanding such reactions and relaxations has been critical for the production and maintenance of inverted vibrational populations in chemical lasers. Glenn Macdonald, Steve Leone, Klass Bergmann, and Chang-Chi Mei carried out a series of measurements of halogen + hydrogen halide reaction and relaxation rates (64–68, 88–93). The endothermic reaction $\text{HCl} + \text{O}$ was studied

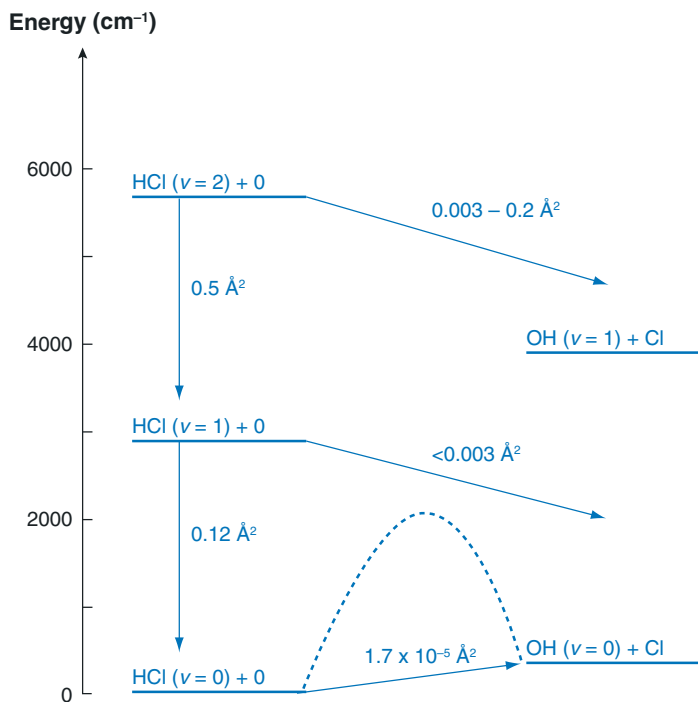


Figure 5

Summary of rate-constant information (68) for $\text{O} + \text{HCl}(v) \rightarrow \text{Cl} + \text{OH}$. Best values or ranges of effective cross sections, k/v , are given for processes shown.

$$k_0 = 2.5 \times 10^{-12} \exp(-5.9 \text{ kcal RT}^{-1})$$

$$\bar{\sigma}_0 = k_0/\bar{v} = 0.3 \exp(-2050 \text{ cm}^{-1} \text{ kT}^{-1})$$

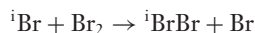
because for $\text{HCl}(v = 2, 1)$, the total energy is well above the barrier to $\text{Cl} + \text{OH}$ formation (68, 69). **Figure 5** shows the main results: Most (probably two-thirds to three-fourths) of the $\text{HCl}(v = 2)$ is relaxed to $v = 1$ rather than reacting to give OH . The relaxation rate, as for many other strongly interacting collision partners, is four times larger for $v = 2$ than for $v = 1$, in contrast to the more usual first-order perturbation theory result of probabilities linear with vibrational quantum number (72, 73). The reaction rate for $v = 2$ is approximately four orders of magnitude larger than for $v = 0$.

The $\text{Cl} + \text{HI}$ reaction cross section versus temperature peaks at 30 Å^2 near 330 K, and the cross section for hot Cl with $11.4 \text{ kcal mol}^{-1}$ of relative translational energy is nine times smaller than thermal at 295 K. The hot atom cross section increases by 25% as temperature increases from 223 to 295 K. These data suggest that the dynamics of relative translational motion is controlled by an attractive potential that brings Cl and I together (ClIH), and the reaction completes by hydrogen rotating around over a modest barrier to connect with the Cl (89, 93). For the reaction



the ground-state $\text{Br}(^2\text{P}_{3/2})$ was found to be at least four times more reactive than the excited-state $\text{Br}(^2\text{P}_{1/2})$ with 3685 cm^{-1} of excitation energy (92). A correlation diagram shows $\text{Br}(^2\text{P}_{1/2}) + \text{HI}$ connecting steeply upward to an excited electronic state of HBr on the product side, a large barrier for reaction.

By dissociating Br_2 with isotopic selectivity, the reaction rate for



was found to be half of the gas kinetic collision rate (30).

The HCO radical reacts rapidly with NO , NO_2 , and O_2 by forming a collision complex, statistically redistributing any vibrational energy, transferring the H , and dissociating to products or simply dissociating back to reactant (70, 94, 95) (**Figure 6**).

The measured rate constants for loss of vibrationally excited HCO are equal to the rate of complex formation because dissociation back to vibrationally excited HCO has negligible statistical probability. These measured loss rates are the sum of the reaction and vibrational relaxation rates. They are between two and three times larger than

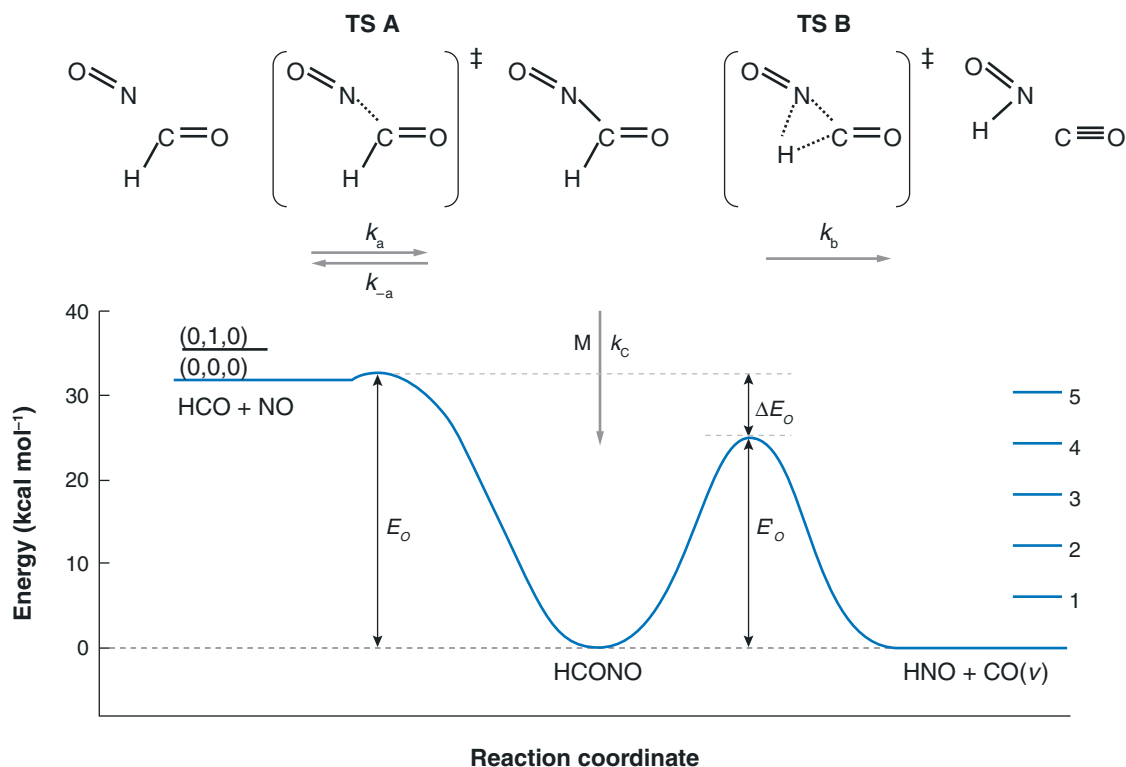


Figure 6

Schematic potential energy diagram for the collision complex mechanism for vibrational relaxation and chemical reaction of HCO (94). TS, transition state.

the reaction rate for the ground state because the complex may dissociate to reactants as well as products (70, 94).

UNIMOLECULAR REACTIONS

Formaldehyde

The attempt to observe rovibrational energy transfers in the excited state of a polyatomic led us into a long study of radiationless transitions and unimolecular reaction dynamics in formaldehyde (96–98). It was fortunate for me that during the first half of these years I learned tenacity from Joel Hildebrand (99) and the example of his iodine studies. Until Jim Weisshaar, Will Polik, and Dean Guyer were able to resolve single rovibronic levels and observe that their properties fluctuated greatly from level to level, the results were confusing. Strong collaborations with Bill Miller, Keiji Morokuma, and Fritz Schaefer were essential to developing a quantitative model (**Figure 7**) for interpreting the experimental results. The spectroscopy of formaldehyde has been reviewed in depth by Clouthier & Ramsey (100), as have the

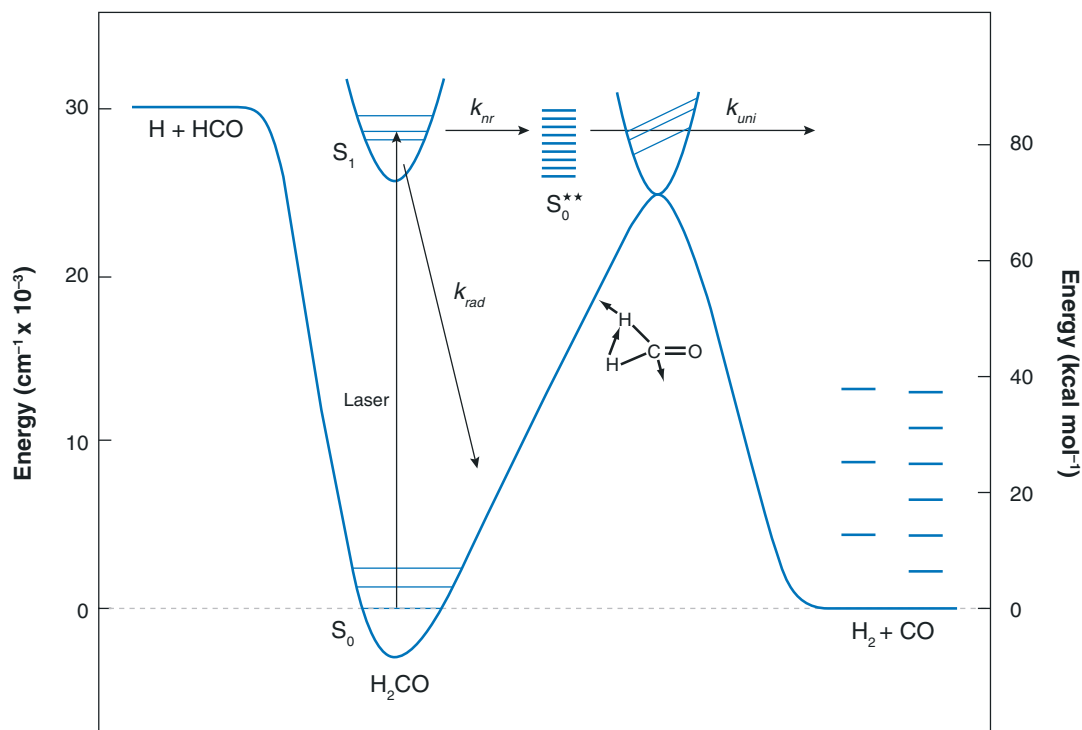


Figure 7

Energy diagram and coupling scheme for formaldehyde. The transition state geometry and reaction coordinate are shown (107). The CH bond lengths are 1.572 and 1.096 Å, $\angle \text{HH} = 110.8^\circ$, and the smaller HCO angle is 110.8° .

photochemical and photofragmentation dynamics (96, 98); thus I present only a few highlights here.

RRKM: Rice, Ramsperger, Kassel, and Marcus statistical transition-state theory

TS: transition state

Molecular eigenstates at the dissociation threshold: predissociation. The observed lifetimes of S_1 single rovibronic levels are much shorter than the radiative lifetime (approximately $10\ \mu\text{s}$ for D_2CO and at least $3\ \mu\text{s}$ for H_2CO) and fluctuate randomly from level to level (101). The lifetimes of the rotational states of the $\text{H}_2\text{CO}(S_1, 4^1)$ vibronic level vary between 3 and $0.02\ \mu\text{s}$ (102). The key to understanding these rates was realizing that the ground-singlet-state rovibrational levels (S_0^{**}) are broadened by dissociation to $\text{H}_2 + \text{CO}$, but spaced far enough apart to yield a lumpy, rather than a smooth, continuum. By Stark tuning the S_1 levels with respect to the S_0^{**} levels with a strong electric field, one can tune a single S_1 level over many S_0^{**} levels to produce a spectrum of the lumpy continuum (Figure 8) (102, 103).

Using Rice, Ramsperger, Kassel, and Marcus (RRKM) theory to calculate the dissociation rate of an S_0^{**} level, the average line width multiplied by the S_0^{**} level density (inverse line spacing) is

$$\langle \Gamma \rho(E, J) \rangle = W(E, J)/2\pi,$$

where $W(E, J)$ is the number of open channels at the transition state (TS) for dissociation on the S_0 surface (96). Thus, we can expect this lumpy or structured continuum of ground-state levels at energies from the tunneling region below the dissociation

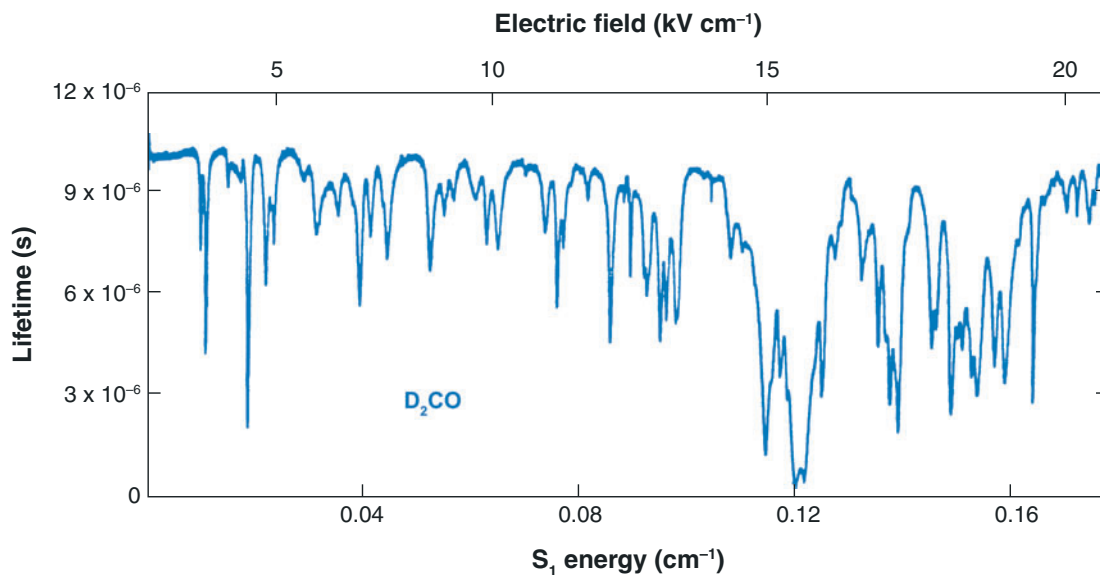


Figure 8

Stark level-crossing spectrum from 1_{10} (1) in $4^1\text{D}_2\text{CO}$ (103).

threshold up until $W(E, J) \gg 2\pi$. In the limit of strong intramolecular vibrational redistribution (IVR), the vibrational wave function of the individual S_0 levels comprises random mixtures of basis states with well-defined quantum numbers. The coupling matrix elements that determine the radiationless transition rates include vibrational Franck-Condon factors and are thus randomly fluctuating. For S_0 levels, the distributions of lifetimes, coupling matrix elements, line spacings, and line shape parameters are quantitatively linked by theory. The experiments are found to be in excellent agreement with predictions done with Bill Miller and his group (96, 104–106).

Intramolecular vibrational redistribution (IVR):

transfer of energy among the vibrational modes of a single molecule caused by anharmonic and Coriolis couplings without collisions

Dynamics of molecular product formation. Spectroscopic and molecular-beam studies of the H_2 and CO dissociation fragment-energy distributions for energies close to threshold correspond to expectations from the shape of the TS (**Figure 7**) and the strongly repulsive PES in the exit valley (107). The hydrogen propels itself from the outer p-orbital on the C atom, exerting a large torque on the CO and creating a broad distribution of $CO(v = 0, J)$ states peaking at $J = 42$ units for H_2CO and $J = 53$ units for D_2CO as measured by vacuum-ultraviolet (VUV)-excited fluorescence (108). The CO bond length at the TS (1.179 Å) and for the free molecule (1.128 Å) is comparable, and thus there is little vibrational excitation of the CO product; the population of $v = 1$ is approximately 14%. Excitation of a single line in the formaldehyde spectrum selects either an *ortho* or a *para* nuclear spin state of the two H atoms. This nuclear spin quantum number is conserved in the dissociation process, yielding the corresponding *ortho* or *para* H_2 with its odd or even values of J , respectively (109–112). The *ortho* $\rightarrow$ *para* interconversion rate, at least 0.1 min^{-1} , was too fast to be measured by depletion of the *ortho*-formaldehyde (112). The H–H distance contracts a great deal in the exit valley; the H_2 vibrational distribution, measured by coherent anti-Stokes Raman spectroscopy in Jean Pierre Taran's (109) Paris laboratory, peaks at $v = 1$ and extends to $v = 3$. H_2 rotation is excited relatively little; the rotational distribution peaks at $J = 3$ –5, accounting for less than 5% of the energy released (110). Molecular-beam time-of-flight measurements of the translational velocity show that on average 65% of the energy is released into translation (113). Doppler-resolved VUV laser-excited fluorescence of the H_2 product gives the translational energy for each $H_2(v, J)$ state, the correlation of the velocity and angular momentum vectors ($\mathbf{v} \cdot \mathbf{J}$) of H_2 , and by energy and linear momentum conservation, the J -state distribution of the $CO(v = 0, J)$ product corresponding to each $H_2(v, J)$ (110, 111).

The more energy released to H_2 vibration, the more slowly the H_2 translates and the lower the rotational excitation of the CO. Schinke (114) predicted many of these results accurately using an ab initio potential and an infinite-order sudden approximation to project the TS onto product states (115). A simple impulsive model using the ab initio geometry and vibrational wave functions at the TS or part way down the exit valley reproduces most features of the product-state distributions. The shapes of distributions depend on the shapes of the vibrational wave functions at the TS for coordinates perpendicular to the reaction coordinate (110, 116).

Extreme-motion state: a highly excited mode stable against IVR; levels close in energy have different quantum numbers requiring high-order perturbations

The out-of-plane vibration moves the dynamics out of the plane of the TS, resulting in the $\mathbf{v}$ and $\mathbf{J}$ vectors of H_2 not being completely perpendicular (111).

Branching between molecular and free-radical products. The ground state correlates smoothly to $\text{H} + \text{HCO}$ products (**Figure 7**). The triplet state, with an origin approximately 3000 cm^{-1} below S_1 , correlates to products over an energy barrier determined to be $3\text{--}6\text{ kcal mol}^{-1}$ by following the H/D product ratio from HDCO as a function of photolysis wavelength from the radical threshold (117). From statistical TS theories, one would expect that the loose TSs for free-radical products would result in a nearly 100% yield of radical products as energy increases above the radical threshold. However, the molecular-product yield remains substantial throughout the UV (118, 119). As energy increases above the radical threshold, a tail grows in on the low- J end of the $\text{CO}(v, J)$ distribution, indicating formation via a different reaction path (120). The proposed path (of near-dissociation along the radical reaction coordinate followed by H-atom return to attack on H of HCO to produce $\text{H}_2 + \text{CO}$ via abstraction $\text{H} + \text{HCO} \rightarrow \text{H}_2 + \text{CO}$) is a possibility indicated by the ab initio potential surface (121) and recently confirmed experimentally (122). It will be interesting to see whether such changes of reaction path after a loose TS occur in other molecules.

Formyl Fluoride

The PESs for formyl fluoride (123, 124) look much like those for formaldehyde (**Figure 9**). For HFCHO , the out-of-plane bending overtone ($2\nu_6$) and CO stretch (ν_2) are anharmonically coupled and form Fermi-resonant polyads that can be assigned in stimulated emission pumping (SEP) spectra up to $22,000\text{ cm}^{-1}$. These vibrations are weakly coupled to other vibrations and form quasi-stable extreme-motion (125) vibrational levels (126–129). This is different from the strongly mixed states of formaldehyde that are all coupled ergodically through the TSs to products. These extreme-motion states are relatively stable against IVR and coupled weakly to the reaction coordinate and to products. They are easily accessible via stimulated emission pumping through S_1 (124, 127, 128, 130–132).

The total density of vibrational levels is small enough that they are resolved in SEP spectra for energies near the dissociation threshold; individual polyad lines are split by coupling to nearby levels. Measured decay rates near threshold were found to increase strongly with rotational excitation; for $2_1\ 6_{15}$ the $J = 0$ level decays in 650 ns, whereas the 2_{11} rotational level decays in 16 ns (128). **Figure 10** gives a coupling mechanism for the distinctly non-RRKM unimolecular reaction dynamics (128, 132). For DFCO , IVR occurs on several timescales (132). The shortest, 25 fs, corresponds to the $\nu_2 \leftrightarrow \nu_6$ coupling. On a timescale of 0.5–4 ps, the 3566 Darling-Dennison resonance couples energy into ν_3 (HCO bend) and ν_5 (FCO bend). Weaker coupling to other background levels occurs on a 3–150-ps timescale. In marked contrast to HFCHO , the IVR dynamics of DFCO may be complete on the timescale of dissociation (132).

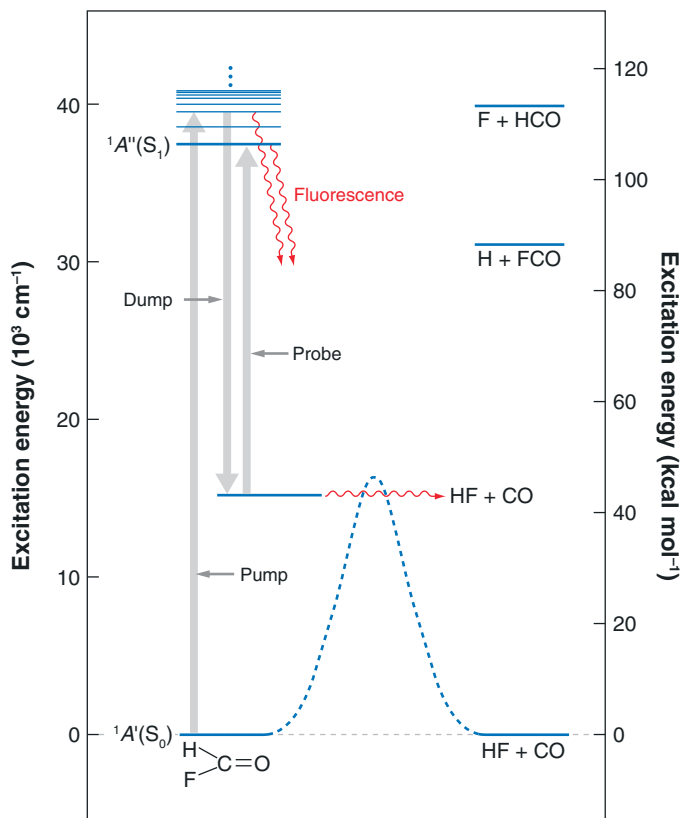


Figure 9

Energy-level diagram of HFCO and the excitation-probe scheme used in the pump-dump-probe experiment (128). The ab initio dissociation threshold for $\text{HFCO} \rightarrow \text{HF} + \text{CO}$ on the ground electronic potential energy surface is $\approx 16,500 \text{ cm}^{-1}$. HFCO molecules are excited to dissociative rovibrational levels of S_0 by stimulated emission pumping (SEP). The temporal evolution of the population in these levels is monitored by laser-induced fluorescence with a variably time-delayed third laser. The lifetimes of short-lived levels are deduced from the line widths measured in high-resolution SEP spectra. Product $\text{CO}(v, J)$ states are probed by vacuum-ultraviolet laser-excited fluorescence (130).

Ketene

Ketene held my attention even longer than formaldehyde, from my first thesis work with Pimentel, beginning in 1960, until 1998 (133). Ketene undergoes three qualitatively different unimolecular reactions (134), none of which proceeds explosively under normal laboratory conditions. The reaction thresholds are all within approximately 2000 cm^{-1} (**Figure 11**). These reactions are excellent examples for testing statistical TS theory as all appear to be slower than IVR. The reactions are (a) dissociation on the ground-state surface to singlet methylene ($^1\text{CH}_2 + \text{CO}$), (b) dissociation over a low barrier on the triplet PES to triplet methylene ($^3\text{CH}_2 + \text{CO}$), and (c) isomerization through the cyclic oxirene configuration to exchange the two carbon atoms.

The loose transition state to $^1\text{CH}_2$. The S_1 excited singlet state exhibits a continuous absorption spectrum throughout the energy range of interest for these reactions. S_1 is strongly coupled to a vibrationally excited ground state, S_0^{**} , by internal conversion; thus, the state excited by a narrow-band laser is a statistical mixture dominated by S_0^{**} . Ketene is cooled to 4 K by expansion into a vacuum chamber and excited by a tunable UV laser. When a visible laser is tuned to excite a single rovibronic level

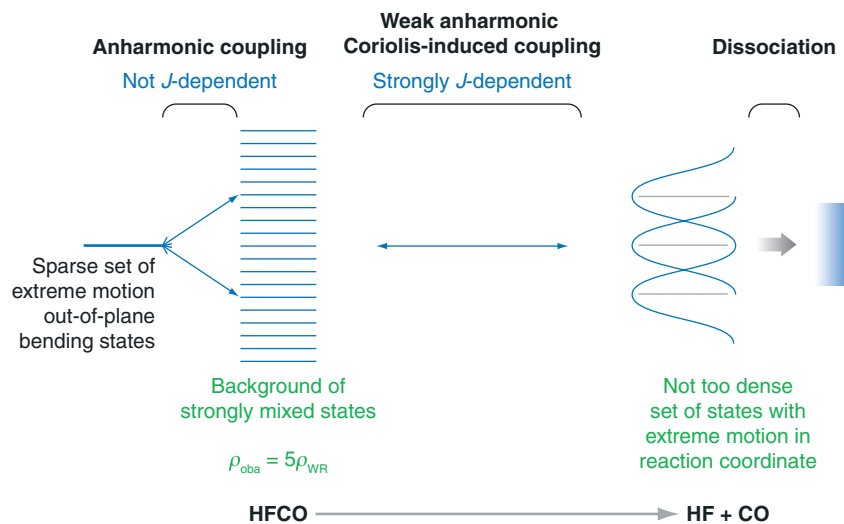


Figure 10

Coupling scheme for intramolecular energy transfer and dissociation (128).

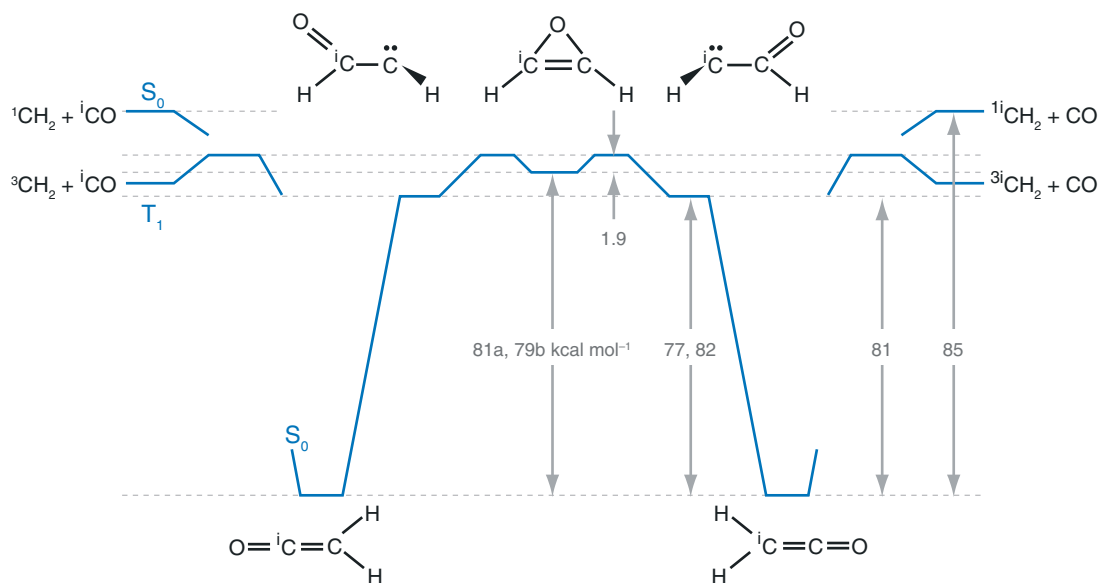


Figure 11

Energies of the $\text{C}_2\text{H}_2\text{O}$ isomers relative to ground-state ketene (134).

of singlet methylene, the fluorescence from that level increases stepwise as the UV photolysis photon energy increases through the energy threshold for each rotational state of CO being formed along with the state of $^1\text{CH}_2$ being probed, a process known as photofragment excitation (PHOFEX) spectroscopy (135–137). These steps are resolved to better than 1 cm^{-1} and show that the rate is proportional to the number of open (accessible under the constraints of conservation of energy, momentum, and angular momentum) product channels and thus equal to the phase-space-theory rate from threshold to 35 cm^{-1} above threshold.

As the UV energy increases, the dissociation to triplet methylene decreases rapidly while the singlet channels open up. This is a precise and sensitive probe of dissociation dynamics on a PES that has no barrier above the product zero-point energy, a loose TS. The variational RRKM theory predicts that the TS tightens and moves in along the reaction coordinate as energy increases. The rate constants calculated from an ab initio PES by Klippenstein et al. (138) accurately predicted from 0–6000 cm^{-1} (9000 K) the experimental PHOFEX and product-energy state distribution results from our lab (135, 136, 139), as well as the picosecond rate measurements from Zewail's (140) lab. This suggests that the variational RRKM theory can be quantitatively accurate in predicting rate constants over all temperatures of practical interest for loose TSs. A further test of the assumption of rapid IVR was carried out by selecting single ketene rotational states for dissociation by two-step excitation with a tunable IR laser to pump an overtone transition followed by dissociation with a UV laser and then by a visible laser for laser-excited fluorescence of $^1\text{CH}_2$. This showed that, except for $K = 0$ and low J , rotation about the a -axis couples to the vibrational degrees of freedom (i.e., K is mixed) (133).

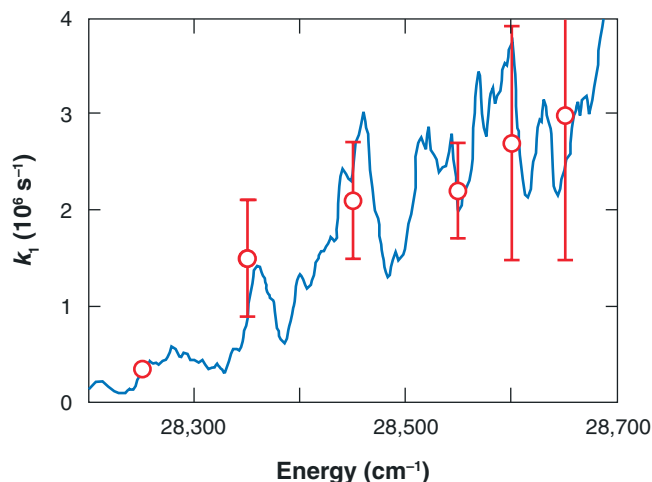
Crossing the barrier to $^3\text{CH}_2$. The dissociation of ketene on its triplet PES provides a detailed test for theories of reactions with a well-defined TS at a barrier along the reaction coordinate. I-Chia Chen (141, 142) found that the ab initio TS and PES predict a rate constant and a distribution of $\text{CO}(v, J)$ product states that agree well with experiment. By making direct nanosecond rate measurements with great care near reaction threshold, Ned Lovejoy and Sang Kyu Kim were actually able to observe the stepwise increase in rate constant, $k(E, J) = W(E, J)/h\rho(E, J)$, as the photon energy passed through each TS-level threshold, increasing W by unity (97, 143, 144). I had really not expected the TS theory to work at that level of detail. An attempt to do this experiment by selecting a single rotational level of ketene out of the 4-K distribution using a tunable IR laser to excite an overtone transition followed by a tunable UV laser for dissociation and then a VUV laser for excitation of the CO product yielded some IR spectra (145) but no useful rate constant data.

Quantum resonances: isomerization over a barrier with a well at the top. The carbon-atom-exchange reaction of ketene provides an even more strikingly quantum mechanically controlled reaction (134). Reaction is monitored by observing the CO dissociation product. When the energy is well above the top of the barrier, the rate increases smoothly with energy and is matched well by RRKM theory with ab initio parameters for the TS (146). Measurements over approximately 500 cm^{-1} near the

PHOFEX: photofragment excitation spectroscopy

Figure 12

Isomerization (k_1) rate constants derived from photofragment excitation spectroscopy data for ^{12}CO and ^{13}CO that exhibit peaks and valleys as a function of energy. The red points are experimental values of k_1 from measurements of the temporal evolution of the CO products. The error bars are 93% confidence intervals for precision (134).



top of the barrier show peaks in the rate constant spaced by approximately 80 cm^{-1} (Figure 12).

Careful ab initio calculations in the TS region show that there is a well at the top of the barrier approximately 2000 cm^{-1} deep (147). This well supports resonances (not stable states) for motion along the reaction coordinate. Quantum dynamical calculations in which the coordinates most closely coupled with the reaction coordinate are treated together in the region of the barrier reproduce the observed rate data in a qualitative way but not with an accuracy that permits assignment of specific resonances (148). This reaction is a dramatic demonstration that sometimes the TS-theory hypothesis of classical motion along the reaction coordinate is not correct.

Methyl Isothiocyanate

Methyl isothiocyanate (H_3CNCS) is a significantly toxic agricultural soil fumigant. When a full freight train car derailed into the Sacramento River, there was a major loss of aquatic life and concern regarding the ultimate fate of the material. The vapors in and near treated regions are also a concern. Media reports of photolysis of high concentrations in air suggested that H_3CNCO , the Bhopal killer, is formed. Ramon Alvarez was able to show that photodissociation in sunlight produces $\text{H}_3\text{CNC} + \text{S}$ promptly and completes in a small number of days (149).

BOND-SELECTIVE CHEMISTRY

Multiphoton Infrared Excitation

Since the invention of lasers, people have speculated about excitations that would cause a specific bond to break even if other bonds were weaker. In the mid-1970s, it was discovered that an intense IR pulse could put enough energy into a molecule through a specific normal mode for dissociation to occur. Studies with CO_2 lasers showed clearly

that IVR is rapid compared with the pulse duration, and thus the weakest bond always breaks (150). Andrew Kung built a powerful pulsed IR parametric oscillator, which he used with Hai-Lung Dai to dissociate $\text{C}_2\text{H}_5\text{Cl}$ by IR multiphoton dissociation (151). The laser was tuned throughout the region of C–H stretches; there was no indication that the bond excited was the one that ultimately broke. Approximately seven photons were required for dissociation.

High Stretching Overtones

The excitation of high overtones ($v = 5, 6$ of C–H, N–H, or O–H stretches) using visible photons to exceed the dissociation threshold with a single photon suggests the possibility of selectivity. Although the oscillator strength responsible for the spectral features corresponds to excitation of a single C–H bond, it is always the lowest energy bond that breaks (152, 153). The laser line width is much smaller than the width of overtone features in the spectrum, so a mixed eigenstate is prepared, and the dissociation behaves as predicted by RRKM theory (153). Excitation of the full overtone-feature width by a femtosecond laser might result in selective photochemistry.

Overtone excitation of liquid water gave measurable quantum yields of dissociative ionization from the second through the fourth overtone with a yield of approximately 10^{-5} near the third overtone (154). For porphine in a solid hexane matrix, the quantum yield for moving the two H atoms from one pair of N atoms to the other within the inner ring was approximately 5×10^{-4} for excitation of the combination band with one quantum each of the symmetric and asymmetric N–H stretching vibrations (155, 156). Surprisingly, IVR does not dissipate all the energy through low-frequency modes to the lattice.

Femtosecond Multiphoton Infrared

In a collaboration with Karl Kompa's group at the Max Planck Institute for Quantum Optics near Munich, a femtosecond IR pulse of 12 μJ and 140-cm^{-1} width was used to dissociate H_2CNN by excitation of the asymmetric CNN stretch at 2102 cm^{-1} (157). This mode clearly makes a large contribution to the reaction coordinate, and approximately six quanta are required to reach the dissociation threshold. Half of the singlet CH_2 product was formed with a 480-fs time constant, far faster than possible with complete IVR and consistent with directed, bond-selective dissociation. The rest of the product was formed with a 36-ps time constant, consistent with a calculated RRKM rate.

C–H Bonds in Free Radicals

The activation energy for breaking C–H bonds in free radicals is quite low because a double bond forms in the radical as the C–H bond breaks (158, 159):



In a series of experiments at Ohio State, we were able to record electronic spectra and hydrogen-atom product velocities for $\text{H}_2\text{C}=\text{CH}$ and $\text{D}_2\text{C}=\text{CH}$ by two-step ionization of H/D through the Lyman- α transition. H atoms were shown to move between the C atoms at a rate of $<1.3 \times 10^{11} \text{ s}^{-1}$. Small free radicals may well be molecules in which IVR is not always fast compared with reaction. Although we got these new experiments going within six months after moving from Berkeley in 2000, it was not possible to continue them on moving to Northwestern in 2003. Extensive work on CH_3O spectroscopy that started in Berkeley (160), and continued with Terry Miller's group at Ohio State, remains unpublished. If there is a systematic deviation from RRKM theory for these C-H bond breaking reactions, it could well have a practical effect in important chemical systems.

EPILOGUE

There are many joys to being a faculty member at one of the great research universities of the United States, and there are many people who contribute to making it so. I owe most of all to my wife, Penny. During my thesis work, she did problem sets for my thermo course, analyzed spectra, drew figures for my thesis, helped transfer liquid hydrogen into matrix isolation dewars, and, following my first explosion, stayed through the night with me for multiday experiments. She is a great partner, protector, mother, home builder, educator, author, sportswoman, and hostess to research group members, faculty colleagues, friends from around the world, and present and future university donors.

I owe a great deal to my Ph.D. mentor George Pimentel for his example, his guidance, and for signing my thesis even though I completely failed to achieve our primary goal of recording the IR spectrum of methylene. I owe a lot to his colleagues for appointing me as an assistant professor just six years after graduation from high school. As I watched my colleagues in Europe working under the direction of *the* professor well into their forties, I appreciated more and more having had the opportunity to try my own, sometimes foolish, ideas during my early twenties.

The steady flow of brilliant graduate students and postdoctorate fellows from all over the world did the research and made it invigorating, renewing, fun, and challenging. As senior research associates, Andrew Kung and Vladimir Lozovsky provided invaluable help in managing my research group. Stimulating and supportive faculty colleagues helped with research, teaching, and institution building, while setting an intimidating standard for success. Joel Hildebrand, Bruce Mahan, and Harold Johnston were excellent although very different mentors. Kenneth Pitzer, Pimentel's mentor, was kind enough to return to Berkeley from administrative assignments elsewhere in time to provide exceptional advice and insight during my terms as department chair and dean at Berkeley. Jud King was a patient and supportive boss throughout those terms, and Dean of Engineering Karl Pister was a perfect role model for a beginning dean. During my four decades at Berkeley, I published papers with 8 faculty colleagues (Bergman, Hearst, Johnston, Lee, Miller, Pimentel, Saykally, and Strauss), 50 graduate students, and approximately 70 undergraduates, postdoctoral and faculty visitors from around the world (161). PESs calculated by

Schaefer's group and many others were important for understanding our unimolecular reaction data. Collaborations with faculty colleagues from around the world were a great source of scientific benefit through joint projects and productive sabbaticals: Norm Craig, Fleming Crim, Ewald Fink, George Flynn, Robert Huber, Karl Kompa, Vladilen Letokov, Terry Miller, Hannah Reisler, Ed Schlag, Ian Smith, Jean-Pierre Taran, Soji Tsuchiya, Jürgen Troe, Curt Wittig, Jürgen Wolfrum, Keitaro Yoshihara, Zheng Qi-Ke, and many others.

By developing a deep, quantitative understanding of energy transfer and chemical-reaction processes with quantum states of reactants and products resolved and compared with dynamical models using accurate *ab initio* PES, we can predict the rates of many chemical processes with confidence. Bill Green did some of this work (96, 136, 137, 162–164) as a graduate student. Now as professor of Chemical Engineering at MIT, he models complex chemical systems computationally and makes predictions with confidence (165, 166). This will have a major impact on our ability to predict, and perhaps manage, the future of Earth's atmosphere, the performance of combustion engines with alternative fuels, and many other vitally important systems. So although I regret not controlling the work of a vice president for research well enough to maintain my own research program at full speed, I do take tremendous pleasure in the progress made in understanding energy transfer and chemical-reaction dynamics during the past 46 years.

I must admit that this is a particularly interesting time to be a vice president for research. As the institutions responsible for the creation and dissemination of knowledge, universities have an ever growing role in the era of the knowledge economy. As our research tools become ever more powerful, universities can begin to deal with some of the most challenging problems that face society and can grasp the exciting intellectual opportunities of the early twenty-first century. For example, the development of multidisciplinary research programs to look for new ways to balance the supplies and demands for energy worldwide, while maintaining Earth's environment and meeting the needs of its ever-growing population, requires people from a mix of disciplines that is available only in a research university. So at this stage in my life, I am learning less about chemistry and a great deal more about many other exciting fields in arts and humanities, social sciences, medicine, and, of course, natural sciences and engineering.

SUMMARY POINTS

1. Experiments in which the initial and final quantum states are resolved provide a detailed determination of the forces and dynamics responsible for the processes studied.
2. Calculations for dynamical models with all parameters fixed by *ab initio* computation can predict experimental reaction and relaxation rates quantitatively and are now useful for predicting the complex chemistry in the atmosphere, in chemical-processing plants and in combustion engines.

3. Anharmonic and Coriolis terms in the intramolecular potential function mix the rigid-rotor, harmonic-oscillator basis states of a molecule. The energy levels, stationary-state solutions of the Schroedinger's equation, for a free molecule with almost enough energy for a chemical bond to break are often random mixtures of basis states with comparable energies. A typical high-overtone transition is broadened over many of these states. A high-resolution laser excites a single one of these mixed states and not a pure overtone. A femtosecond laser that covers the entire broadened transition would produce a coherent ensemble of states that describes the pure overtone vibration. IVR is the dephasing that results from the range of frequencies of the wave functions of the molecular eigenstates. Bond selectivity may be possible in high-overtone photochemistry with femtosecond lasers and for C-H bond breaking in free radicals.
4. The reaction rate constant is quantitatively proportional to the sum of states, $W(E, J)$, for vibrations orthogonal to the reaction coordinate. The observed rate increases stepwise at the threshold of each energy level for two different reactions of ketene. The wave function at the TS gives the initial conditions for the dynamics of energy release in the exit valley of the PES. When single molecular eigenstates are excited, the measured rates fluctuate statistically in a quantitatively predictable way. Similarly, product energy distributions vary from eigenstate to eigenstate depending on the overlap with each of the energy-level wave functions at the TS.

ACKNOWLEDGMENTS

I thank my wife and our children, Megan and Scott, who have supported me in all things. The actual research work has been done by the brilliant students, postdoctorate fellows, and faculty colleagues that it has been my good fortune to work with. I thank them for their intense hard work and for the pleasure of admiring their progress in their own labs. I thank my faculty and administrative colleagues at Berkeley, Ohio State, and Northwestern and my program managers at NSF, DOE, Army Research Office, Air Force Office of Scientific Research, Sloan Foundation, and Guggenheim Foundation for their constant support and encouragement. I thank the editors of the *Annual Review of Physical Chemistry* for the honor of the invitation to write this chapter and Marie Heffernan, Kathy Mandell, and Caroline Carrière for assistance in preparing the manuscript.

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