

Studies with crossed laser and molecular beams

Experiments with intersecting beams of photons and molecules can give detailed information on the dynamics of chemical reactions at the level of individual atoms and molecules.

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During the last twenty years sophisticated microscopic experimental techniques and large-scale theoretical computations have significantly enhanced our understanding of the detailed dynamics of chemical reactions. The development of computer codes to perform lengthy and detailed computations has made it possible to clarify the connection between the first principles of quantum chemistry and the behavior of substances in the real world. Modern spectroscopy, laser technology and molecular-beam methods allow us to observe chemical reactions on the atomic and molecular levels in great detail.

One of these useful experimental techniques is the observation of chemical reactions during single collisions between individual molecules in two crossed molecular beams. The precise measurement of the angular and energy distributions of product molecules with well defined initial conditions for reactant molecules allows us to learn a great deal about the reactive collisions that transform the reactants into products. In addition to directly identifying product channels and their relative importance, one can obtain detailed information about reaction dynamics, such as the preferred orientation of reactant molecules for reaction to occur, the lifetimes of reaction complexes compared to their rotational periods, the extent of energy randomization before the decomposition of collision complexes, the distribution of excess energy among various degrees of freedom and the heights of both entrance and exit potential-energy barriers.

Clearly, one can obtain similar information

on photodissociation of molecules by replacing one of the molecular beams with a laser beam. The investigation of laser-induced unimolecular reactions is most fruitful in a strictly collision-free environment, as collisions tend to confuse the results. Kent R. Wilson and his coworkers at the University of California at San Diego have pioneered in developing photofragmentation translational spectroscopy as one technique that yields the required data. In our laboratory we have studied two types of photodissociation reaction (multiphoton dissociation of polyatomic molecules and vibrational predissociation of hydrogen-bonded and van der Waals clusters) using crossed laser and molecular beams and measuring the distribution of the directions and speeds of the products. We shall describe these experiments in more detail below.

Crossed molecular beams

Sheldon Datz and Ellison Taylor first used crossed molecular beams to study collisions of potassium and hydrogen bromide in 1955. Shortly after this, Dudley Herschbach and his coworkers studied collisions of potassium and methyl iodide in an experiment that remains a landmark. Their conclusion that KI is back-scattered with respect to K was the first dynamical information for an elementary chemical reaction derived from the observed angular distribution of product molecules. Since then, experiments with crossed molecular beams have become more and more sophisticated through the efforts of Herschbach, Datz, Richard Bernstein, Ned Green, John Ross, and other workers. The results of these experiments have led to improved understanding of many reaction mechanisms, among them the "rebound mechanism" in $K + CH_3I$, the "har-

poon mechanism" in $K + Br_2$ (through electron transfer between potassium and bromine) and the formation of long-lived complexes in exchange reactions between alkali atoms and alkali halides. The beams of reactant molecules can now be selected for specific velocity or orientation and the products can be analyzed according to mass, speed, direction, quantum state, and polarization. Further developments of the technique include John Fenn's work on developing and characterizing supersonic beams and the construction of a sophisticated "universal" molecular-beam apparatus in our laboratory.

A universal beam apparatus

The photograph (figure 1) shows one of our universal molecular-beam apparatus. Figure 2 is a schematic diagram of its working parts. Two narrow, supersonic beams collide at the center; the reaction products are identified in a rotatable quadrupole mass spectrometer. For photodissociation studies we replace one of the molecular beams with a laser beam.

The nozzles that provide the beams have adjustable temperature and backing pressure. A skimmer and a defining slit together with two stages of differential pumping serve to narrow each beam to a spread of less than 2° . The collision center and mass spectrometer are in a triply-pumped ultrahigh-vacuum region, to reduce the background to a minimum. Because the mass spectrometer has a small acceptance angle, we can measure the angular distribution of the products. One of the beams can be chopped, and the ionization signal from the mass spectrometer is detected by a gated counting system, so we can determine the velocity distribution of the products from their time of flight. We can then use these data to determine the velocity (includ-

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ing angle) and energy distributions of the products in the center of mass.

Workers in our laboratory have studied several reactions with this apparatus. For example James Valentini and Michael Coggiola investigated the reaction of iodine with fluorine. They found that the reaction



can proceed with only 4 kcal/mole of collision energy, while the generally accepted reaction path, $\text{I}_2 \rightarrow 2\text{I}$ (or $\text{F}_2 \rightarrow 2\text{F}$) followed by $\text{I} + \text{F}_2 \rightarrow \text{IF} + \text{F}$ (or $\text{I}_2 + \text{F} \rightarrow \text{IF} + \text{I}$) requires 38 kcal/mole to initiate. More recently, in a series of studies involving oxygen atoms and unsaturated hydrocarbons, a group in our laboratory found that the replacement of a hydrogen atom by an oxygen atom is the most significant of the various possible reaction channels, contrary to what had been believed. This group consisted of Richard Buss, Steven Sibner, Piergiorgio Casavecchia, Tomhiko Hirooka and Robert Bacman. These are just two examples of the sort of problems that can best be investigated with crossed molecular beams.

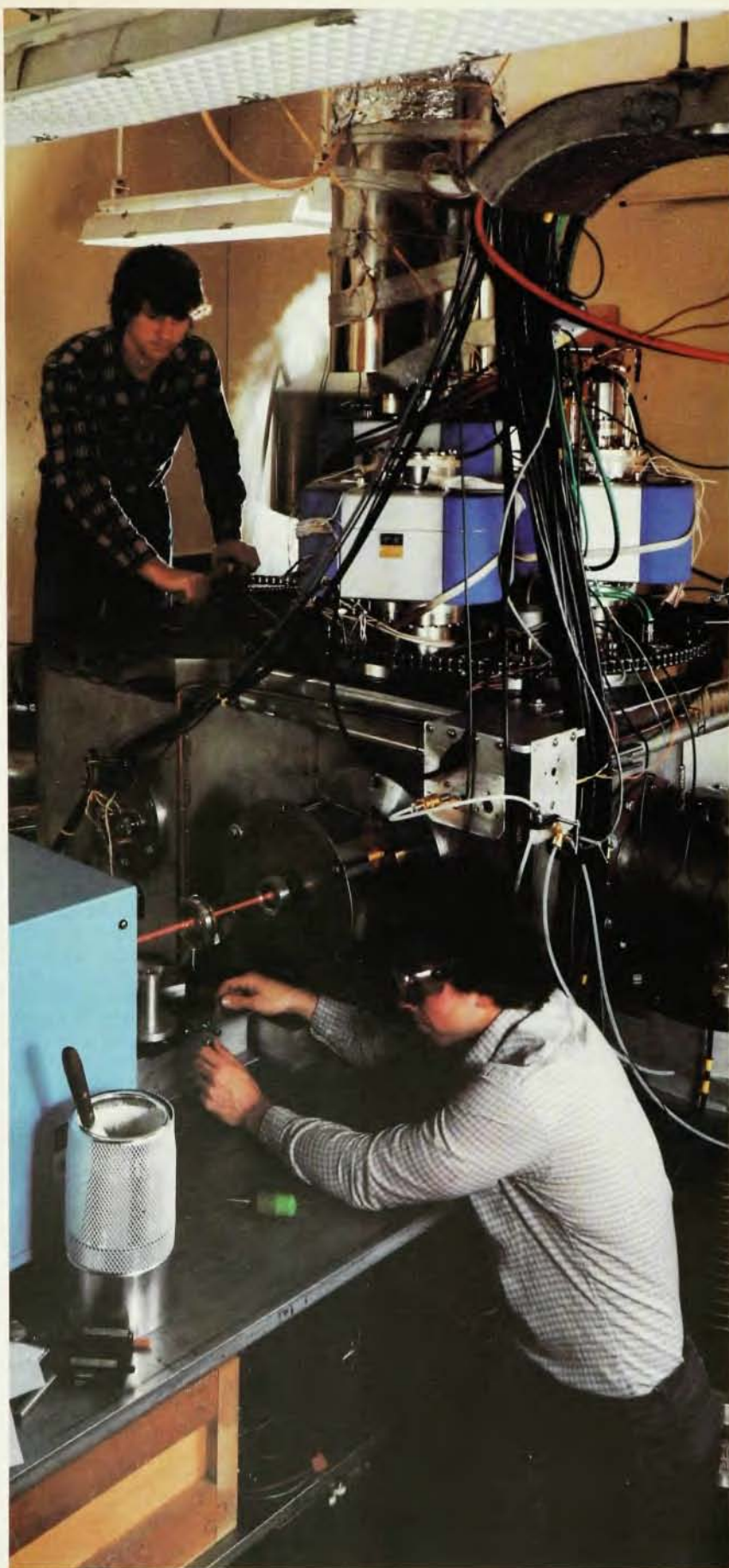
We can illustrate the use of crossed molecular beams to probe reaction dynamics with work done in our laboratory on the reaction

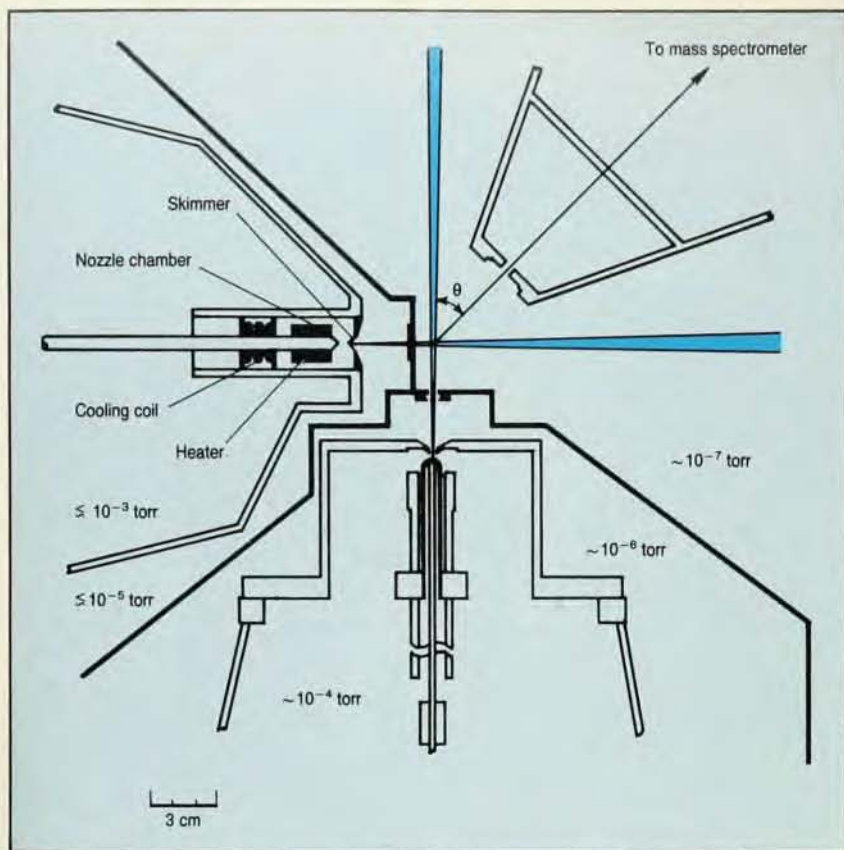


Randall Sparks, Carl Hayden, Kosuke Shobatake and Daniel Neumark collaborated on this experiment. Figure 3 shows contour maps of the speed and angular distribution of hydrogen fluoride molecules at two values of the collision energy. At the lower energy (2.0 kcal/mole) the experiments showed pronounced backward scattering of HF with respect to the incident fluorine atoms. This indicates that collisions between F and H_2 with all three atoms in a nearly collinear configuration are most effective in overcoming the energy barrier for the reaction, while F atoms approaching H_2 sideways are not likely to scatter reactively at low collision energies. Such a dependence of the potential-energy barrier on the bending angle of the F-H-H complex is now well understood and has also been found in the results of *ab initio* quantum-mechanical calculations.

One can also obtain from these results the distribution of vibrational energy in the hydrogen fluoride molecules: Because the spread in rotational excitation of the products is smaller than the spacing of vibrational levels,

Universal crossed-beam apparatus
adapted for photodissociation studies with crossed laser and molecular beams in Lee's laboratory at Berkeley. Carl Hayden and Dan Neumark are performing an experiment on the dissociation of ketene. Figure 1





Schematic diagram of a universal crossed-beam apparatus, as in figure 1, for studying the dynamics of elementary chemical reactions. The beams produced by the nozzles are supersonic and collision-free. One of the molecular beams can be replaced by a laser beam. The mass spectrometer serves as a detector for the reaction products; it can be rotated about an axis through the collision center, normal to the collision plane. Figure 2

and because the sum of vibrational, rotational plus translational energies of HF is fixed, the vibrational states are represented by well separated peaks in the velocity distribution. From the graph in figure 3a we see that the vibrational excitation in HF has an inverted distribution, with most of the molecules in states with $v = 2$ and $v = 3$. This is not surprising, and, in fact has found an application: the reaction



is a pumping mechanism for the efficient HF laser, which was first discovered by George Pimentel and his coworkers.

At the larger collision energy, 3.2 kcal/mole, there is an interesting feature in the angular distribution of the vibrational states. As figure 4b shows, the velocities of hydrogen fluoride are still sharply peaked in the backward direction for the vibrational states $v = 1$ and $v = 3$; however, for $v = 2$ the distribution is much broader, with noticeable peaks to the side. These sideways peaks appear to be the consequence of a quantum mechanical dynamical resonance. Dynamical resonances

have been predicted in one- and three-dimensional calculations of hydrogen-atom transfer reactions by Aron Kupperman and others. In a recent calculation for the reaction of F and H_2 at a collision energy of 3 kcal/mole, Robert Wyatt and his coworkers have shown that although the probability of producing the $v = 3$ state of HF is a maximum at zero impact parameter, that of the $v = 2$ state has a maximum at a finite impact parameter as a result of a dynamical resonance. Our experimental result of some sideways peaking is in qualitative agreement with their calculation.

Other techniques

Of course, the measurement of angular and velocity distributions in a crossed-beam experiment is not the only method that provides microscopic information on reaction dynamics. One can also obtain detailed information on the quantum states from analyses of

► chemiluminescence from nascent products, such as the work done by John Polanyi and his coworkers in Toronto

► the operation of tandem chemical

lasers, as is done in Pimentel's laboratory in Berkeley

► laser-induced fluorescence, a method pioneered by Richard Zare at Columbia (now at Stanford).

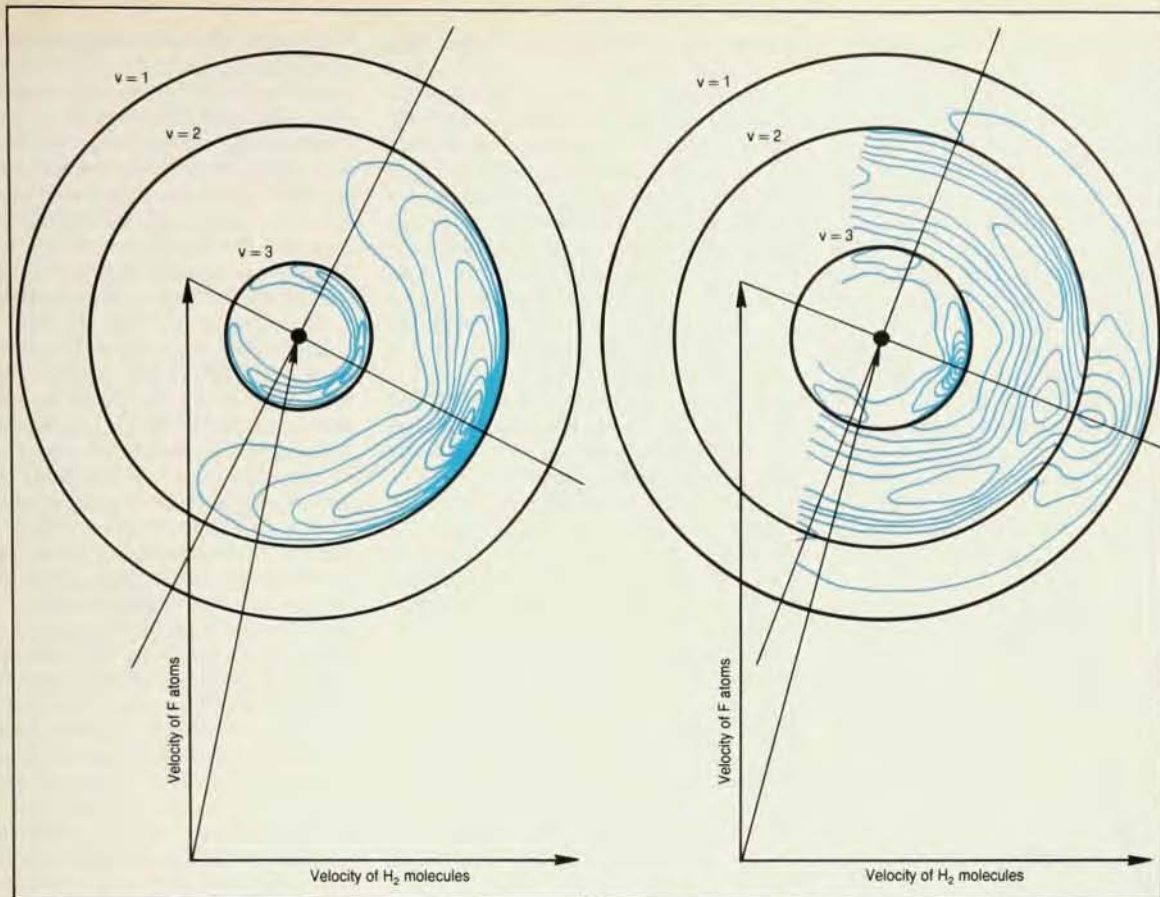
However, these methods are often applicable to only a limited range of systems. For example, laser-induced fluorescence has the sensitivity to provide detailed energy distributions in the reaction products at very low number densities; but to use this method one must already know the absorption and emission spectra of the products for identifying and probing them as well as for finding an appropriate tunable laser for selective excitation.

The molecular-beam method has the advantages that it operates in a collisionless environment with the initial conditions well specified, and that one can generally identify the reaction products in the mass spectrometer if one has properly studied the fragmentation of the products during the ionization. However, it has the disadvantage of not being able to provide detailed information about the distributions of quantum states in the reaction products, except in some special cases. In this respect, for some simple and favorable systems, a combination of the laser-induced fluorescence method (or laser-induced ionization) with the molecular-beam method may prove to be ideal for detailed studies of reaction dynamics. (See the article by Richard Zare and Richard Bernstein on page 43.)

Multiphoton dissociation

Infrared multiphoton dissociation of polyatomic molecules is not only scientifically interesting but also technologically relevant because of its potential applications to isotope separation and chemical synthesis.⁴ Here we shall discuss how the studies in our laboratory with crossed laser and molecular beams, carried out over a number of years, have led to a better understanding of many aspects of the problem.⁵ The collaborators on these experiments included Coggiola, Edward Grant, Peter Schulz, Aasmund Sudbo, Douglas Krajnovich, and Zhang Zhuangzhien. For the sake of clarity, we begin with a brief review of the multiphoton excitation process.

For the multiphoton excitation process to be efficient, each one-photon transition step must be resonant or nearly resonant.⁶ At low energies, the rotational-vibrational levels are discrete. Then, at higher energies, the density of states increases rapidly and the states blend into a quasi-continuum, as shown in the illustration on page 28. (In SF_6 , for example, the density of vibrational states is $10^3/\text{cm}^{-1}$ at 5000 cm^{-1} , and $10^6/\text{cm}^{-1}$ at $10\,000 \text{ cm}^{-1}$.) For efficient multiphoton excitation through the discrete levels into the



Velocity distribution of hydrogen fluoride from the reaction $F + H_2 \rightarrow HF + H$ at 2.0 kcal/mole (left) and 3.2 kcal/mole. The velocities of the incident molecules are shown by the arrows; the large spot marks the center of mass of the system. The contour lines

indicate the number of HF molecules as a function of speed and direction. The dashed lines labelled with vibrational quantum numbers show the maximum translational speed for which that vibrational level can be occupied with the given collision energy. Figure 3

quasicontinuum, the laser frequency must be nearly resonant with the allowed rotational-vibrational transitions. This requirement is the basis of isotope separation by multiphoton excitation and dissociation. The transition probability depends on the laser intensity and on the frequency offsets from the intermediate resonances in the multiphoton transition, and is therefore different for different initial states. Because there is an initial thermal distribution of molecules over many rotational-vibrational states, the fraction of molecules excited into the quasicontinuum is a function of the laser intensity. Only with a sufficiently high laser intensity can one excite nearly all the molecules into the quasicontinuum. Once the molecules reach the quasicontinuum, they can be readily excited further via one-photon resonant transitions. The net excitation all the way up to the dissociation level at time t depends only on the integral of the laser intensity over time, if deexcitation by collisions and spontaneous emission is negligible. This integrated intensity

$$\int_{-\infty}^t I(t') dt'$$

is often called the "laser fluence".

Above the dissociation level, the molecule begins to dissociate and the energy states form a true continuum. The molecule continues to absorb energy via single-photon resonant transitions, and its energy level in the continuum still depends only on the laser fluence as long as the dissociation rate is much smaller than the up-excitation rate. However, the dissociation rate increases rapidly with the level of excitation in the continuum and soon catches up with the up-excitation rate. The final level of excitation is then limited by dissociation, assuming that the laser pulse has enough fluence to reach that level. The multiphoton excitation process in the quasi-continuum discussed here can be described fairly well by a simple model of evenly spaced levels with rate equations governing the transitions between levels and dissociation from various levels.⁷

While this model explains why multiphoton excitation and subsequent dissociation of a polyatomic molecule can be very efficient, there are many questions about multiphoton dissociation that still need to be answered for a full understanding of the process.

► The excitation in the low-energy region is certainly mode-selective, but

does it remain so at high levels of excitation? Can the resultant multiphoton dissociation be bond-selective?

► How does the average level of excitation depend on the laser intensity, the laser energy fluence, and the molecular structure?

► Is multiphoton dissociation a truly unimolecular reaction? What are the dissociation fragments? Is the dissociation always dominated by the lowest dissociation channel?

► What are the dynamics of multiphoton dissociation? Does the molecular structure affect the dissociation dynamics?

These questions are difficult to resolve in gas-cell experiments because of confusion arising from collisions and chemical reactions. In the collisionless environment of a molecular beam, and with the measurement of the energy distribution and direction of the products, however, the situation is sufficiently clarified that the questions can be given a rather satisfactory answer.

First of all, the mere observation of multiphoton dissociation in a molecular beam shows unequivocally that it is a collisionless unimolecular dissociation process. Because the detector in our apparatus is a mass spectrometer,

we can directly identify the dissociation products. For example, we have found that SF_6 mainly dissociates into SF_5 and F, and CFCl_3 into CFCl_2 and Cl, which contradicts the earlier findings in gas-cell experiments. It turns out that in all the cases (around 30 molecules) we have studied with a high-power CO_2 laser, the major dissociation channel is always the statistically most favorable channel. Usually this is the lowest-energy channel, although in some cases, dissociation may also occur through the next higher channel.⁵ This result suggests that mode-selective excitation to high levels and subsequent

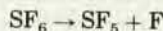
bond-selective dissociation are not likely in these cases.

Whether or not bond-selective multiphoton dissociation is possible has been the subject of a great deal of controversy; the resolution of the controversy is, of course, extremely important for chemical synthesis. For example, consider the multiphoton excitation of the carbon-hydrogen stretching vibration of the chloroform molecule CHCl_3 to an energy above the dissociation level (the resonant frequency of this mode is around 3000 cm^{-1}):

► If the energy is localized in the C-H stretch mode, the final dissociation involves breaking the carbon-hydrogen bond, leaving CCl_3 and H.

► If the mode-mode coupling is strong enough, especially at high levels of excitation, the energy fed into the molecule through one mode is quickly randomized into other modes so that the weaker C-Cl bonds tend to break first, leaving CHCl_2 and Cl.

Whether the excitation energy in the molecules is or is not randomized before dissociation can be answered for a given level of excitation by looking at the laboratory angular and velocity distributions of the dissociation products (or the translational energy distribution deduced from them) and checking the consistency of the average lifetime measured in experiments and that calculated from statistical theory.² Figure 4 shows, as an example, the velocity distribution and the translational energy distribution of SF_6 fragments obtained from our measurements. These experimental results can be compared with the prediction of the well-known statistical theory (the so-called "RRKM theory") of unimolecular dissociation.⁸ The theory assumes that the excitation energy E of each molecule is randomized in a number of accessible modes. Then, in the absence of any potential-energy barriers in the products, the translational energy distribution of the fragments is simply the probability of finding the excited molecule in a state from which the molecule will dissociate with a fragment translational energy ϵ . One can calculate this probability from the molecular properties, leaving only the excitation energy, E , as a parameter. For example, from the fit of the theoretical curves to the data shown in figure 4b, which shows results for



at a laser fluence of 7.5 J/cm^2 , one can see that the excitation energy was about 24.5 kcal/mole above the threshold for dissociation. Actually, because of the statistical nature of laser excitation,⁷ the excitation energy should have a rather wide spread, and the value of 24.5 kcal/mole is only a mean value for the dissociated molecules.

The agreement between theory and experiment in figure 4b supports the assertion that the energy in the molecule randomizes before the molecule dissociates. This idea is further confirmed by the fact that both the statistical theory and the experiment yield an average dissociation lifetime of around 10 nsec . If the excitation energy were localized in one or few modes, the dissociation lifetime could differ from this value by several orders of magnitude.

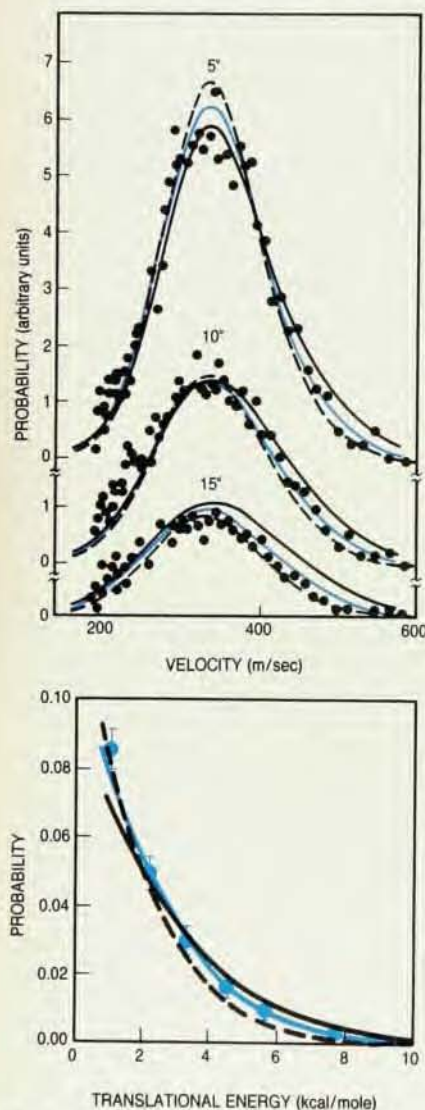
Aside from answering the question of energy randomization, the results shown in figure 4b also show that the average translational energy of SF_5 fragments is about 2.5 kcal/mole . Compared with the average excess energy of about 25 kcal/mole , it indicates that after dissociation $9/10$ of the excess energy must appear as internal energy of the fragments, mostly in the vibrational degrees of freedom of SF_5 . This corresponds to an average excitation of about 8000 cm^{-1} in SF_5 and should leave SF_5 in the excited quasicontinuum. If the SF_5 molecule is indeed in its quasicontinuum, it too will be able to absorb photons from the laser via stepwise one-photon transitions, ultimately dissociating into $\text{SF}_4 + \text{F}$. We have indeed observed SF_4 molecules in our experiments when the laser fluence was sufficiently high; the results were in fair agreement with the theoretical prediction.⁵ The onset of this secondary dissociation can provide information about the lifetime of excited SF_5 in comparison with the duration of the laser pulse.

Recently, the question of how multiphoton excitation and dissociation depend on laser intensity and energy fluence has been the focus of many discussions; however, some points appear to be proven:

► The excitation of molecules to energies above the discrete levels is a strong function of the laser intensity. Only at very high laser intensities can all molecules be excited into the quasicontinuum.

► The subsequent up-excitation in the quasicontinuum depends only on the laser fluence and the one-photon absorption cross-section.^{6,9}

Figure 5 illustrates the combined effect of the bottleneck in the initial excitation and the one-photon absorption cross section in the quasicontinuum. The curves show the dissociation yield as a function of energy fluence for several values of the laser frequency, with the shape of the laser pulse kept the same. The slope of each curve reflects, in part, how the increase in laser intensity increases the population of molecules pumped into the quasicontinuum. The intercepts of the curves, the dissociation thresholds, indicate the value of the laser fluence required to pump molecules across the quasicontinuum.



Photodissociation of SF_6 . (a) Theoretical and experimental values of the velocity distribution of SF_5 fragments produced by a laser pulse of 5 J/cm^2 . Theoretical values are for an excess energy of 13.5 (dashed line), 21.5 (color) and 32.5 (black) kcal/mole . (b) Recoil-energy distribution of SF_5 fragments produced by a laser excitation of 7.5 J/cm^2 ; theoretical curves are for excitations above E_0 of 19 (dashed line), 24.5 (color) and 30 (black) kcal/mole .

Figure 4

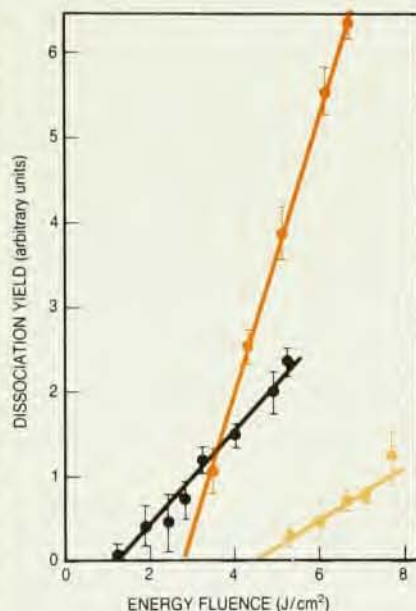
tinuum. Thus, for example, the steepness of the curves in figure 5 is for a frequency that is near the peak of an absorption band of SF_6 ; this is clearly the most effective frequency in exciting molecules over the discrete-level barrier. On the other hand, SF_6 has the largest one-photon absorption cross section at the lowest of the three frequencies used, so the dissociation threshold is also lowest for this frequency.

As we have said, excitation above the dissociation level depends on both laser intensity and fluence.^{5,10} With long laser pulses, the energy fluence may be sufficient to pump the molecules to a much higher excitation level, but the up-excitation, which is proportional to the laser intensity, is effectively terminated by the rapidly increasing rate of dissociation. The final level of excitation is then expected to be higher for higher laser intensity, and the higher level of excitation should be reflected by a distribution of translational energy of the fragments that is broader and has a larger mean value. This is actually what we have observed with SF_6 . When the excitation level is limited by the laser intensity, significant dissociation occurs during the laser pulse. The dissociation product can then absorb more photons from the laser pulse and undergo a secondary dissociation. Thus, the onset of secondary dissociation is closely associated with the intensity-limited excitation. In the case of short laser pulses with high intensity but not much fluence, the level of excitation is limited by the available fluence, even though at that level the up-excitation rate is still much larger than the dissociation rate. In the intermediate cases, both laser intensity and fluence should be important in determining the level of excitation of the dissociation molecules. Our experimental results with laser pulses of different widths and intensities agree well with the picture presented here.¹⁰

How is the intensity-limited level of excitation affected by the molecular structure? The absorption cross section in the continuum should of course be different for different molecules, but they do not differ by orders of magnitude. The dissociation rate, however, depends strongly on the molecular structure.^{5,8} For example, the excess energy $E - E_0$ (above the dissociation threshold, E_0) needed to reach lifetimes of 10^{-8} and 10^{-9} sec for N_2F_4 , CF_3Cl and SF_6 are 1, 3 and 25, and 2, 7 and 34 kcal/mole, respectively, according to the RRKM calculation. The dissociation thresholds, E_0 , for these molecules are 22.3, 81.5 and 93 kcal/mole. The RRKM theory predicts⁸ that the dissociation rate increases faster with excess energy for smaller or lighter molecules with roughly the same E_0 , and also for molecules with appreciably lower E_0 if

the molecular sizes are comparable. Thus, with the same laser pulse, the average excess energy of the dissociating molecules is expected to be higher for larger molecules with higher E_0 . This has in fact been nicely confirmed by our measurements on the translational energy distribution of fragments for a large number of molecules. For example, with 5 J/cm² and 100 ns excitation from a CO_2 laser, the average excitation levels in SF_6 , CF_3Cl , and N_2F_4 are about 22, 4, and 2 kcal/mole, respectively, above the dissociation energy.⁵

A large molecule such as SF_6 can therefore be excited to a level high above the lowest dissociation energy with a moderately intense laser pulse.



Dissociation of SF_6 as a function of energy fluence and frequency. The curves show the number of SF_5 fragments obtained for laser pulses of the same shape at wavenumbers of 934.9 cm^{-1} (black), 944.2 cm^{-1} (solid color) and 952.9 cm^{-1} (light color). Figure 5

In some cases, the average level of excitation may lie above the dissociation energies of several dissociation channels, so that the molecule can dissociate through several channels with different dissociation products. One can estimate the probability of the molecule dissociating through each channel from the RRKM statistical calculations. We have found experimentally that this is the case in a number of molecules.⁵ For example, in the dissociation of $\text{C}_2\text{F}_5\text{Cl}$, the lowest dissociation energy is for chlorine elimination, while that for carbon-carbon bond rupture is slightly higher. As one would expect, at low laser intensities chlorine elimination dominates, but with increased laser intensities the elimination process saturates, whereas

the C-C bond rupture becomes important.

In some cases, the potential-energy surface may have a hump along the dissociation coordinate. In that case, the extra potential energy is partially transformed into translational energy during dissociation, and the fragments attain a finite translational energy even at the threshold of dissociation. Thus, the observed translational energy distribution of the fragments should peak at a finite value determined by the barrier height. We have found this to be the case in a number of three-center and four-center hydrogen halide elimination reactions.⁵

From what we have discussed, we can now draw a fairly complete picture of multiphoton dissociation. The initial excitation of molecules over the discrete levels is responsible for isotopic selectivity. At low laser intensities, this initial excitation also determines the maximum dissociation efficiency that one can attain. For sufficiently high laser intensity, the dissociation yield depends only on the laser fluence, but the level of excitation above the dissociation energy still depends in general on the laser intensity. If the energy fluence of the laser does not limit the dissociation, then with the same excitation a large molecule attains more excess energy than a small molecule; most of the excess is retained by the fragments as internal energy after dissociation. Apparently, the statistical theory describes multiphoton dissociation very well, and we can therefore use it to predict, at least qualitatively, what is likely to happen to other polyatomic molecules.

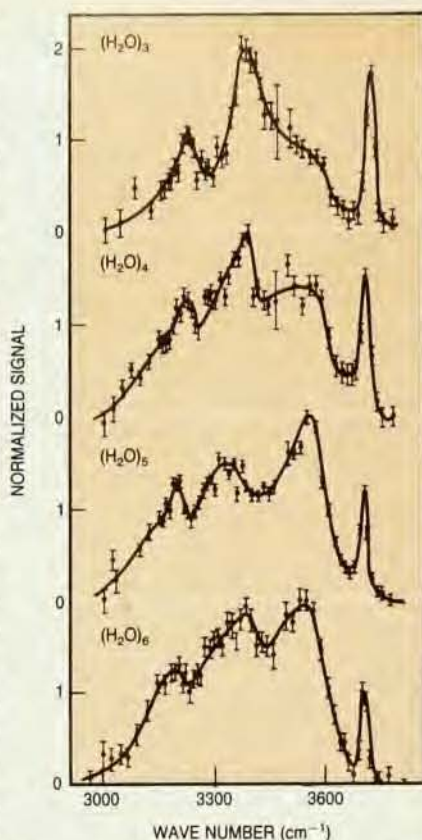
As a summary, we present an analogy that illustrates many important aspects of multiphoton dissociation. Imagine a multicompartment container that is being filled with water through one of the compartments. The container has small holes in the partition walls and slots of varying depths in the outside wall. The container is analogous to a molecule, the compartments to the vibrational modes, and water to energy. The flow of water between compartments through the holes in the partitions corresponds to energy randomization among vibrational modes, and the leaking of water through the slots in the container wall corresponds to molecular dissociation through various channels. If the slots are V-shaped the leaking rate increases rapidly as the water level goes up. The equilibration of water between various compartments depends on the filling rate and on the size of the holes in the partition walls. If the filling rate is sufficiently slow, so that water is in equilibrium among all compartments at all times, then water will eventually rise above the lowest opening and leak

out through it. On the other hand, if the filling rate is sufficiently fast, water will leak out simultaneously through more than one opening. The final water level is determined by the balance between the filling and leaking rates. If the amount of filling water is limited, the final water level may be determined by the amount of water available instead of the filling rate. Finally, only if the filling rate is much faster than the rate of water-level equilibration between compartments, can water leak out through the opening of the compartment being filled (unless of course, it has the deepest slot). The actual molecule is of course more complicated than the container we have described. Nevertheless, the picture rightly suggests that if mode-selective molecular dissociation is ever possible, it will need laser pumping in a mode fairly isolated from the other modes (presumably through frequency mismatch) and a very strong laser intensity for a very fast up-excitation.

In our experiments with a CO₂ TEA laser, typically operated at a peak power of 100 MW/cm², the rate of photon deposition is approximately 10⁹–10⁸/sec for absorption cross sections of 10⁻¹⁹–10⁻²⁰ cm². With this excitation rate, most of the molecules will not reach levels whose dissociation lifetime is much shorter than 10⁻⁹–10⁻¹⁰ sec. The fact that all our experimental results show complete energy randomization clearly indicates that when a molecule is excited to the real continuum, the time for intramolecular energy randomization must be much faster than 10⁻⁹–10⁻¹⁰ sec. In a series of chemical activation experiments, Seymour Rabinovitch and his coworkers have shown that it takes only several picoseconds to randomize the energy in chemically activated complexes.

Van der Waals clusters

In applications such as isotope separation, the energy efficiency of the dissociation yield is important. One would like to use a molecule with a relatively low dissociation energy. Clusters of molecules bound by van der Waals forces or hydrogen bonds (such as Xe:Br₂, He:I₂ and NH₃:NH₃) have very low dissociation energies. Because the weak bonds can be easily broken by collisions, the photodissociation of van der Waals molecules cannot be studied in the usual gas-cell experiments. The only viable method is to use a molecular beam. Consider (NH₃)₂ as an example. One can excite the dimer through an NH₃ bending mode, using the 10.6 micron radiation from a CO₂ laser. The dissociation energy of the hydrogen bond in this case is about 4 kcal/mole. Absorption of two laser photons (about 6 kcal/mole) is enough to break the bond with an excess energy of about 2



Vibrational predissociation spectra of hydrogen-bonded clusters of water molecules, representing the dissociation yield for single-photon excitation of the clusters. Figure 6

kcal/mole. The absorbed energy might flow back and forth between the monomer parts, cause relative motion of the two parts, and finally separate the two parts. Our experimental results show that the maximum translational energy is limited to about 2 kcal/mole, and the average translational energy is only 0.3 kcal/mole. Apparently, a large fraction of the excess energy after dissociation has appeared in the rotational degrees of freedom of the monomers, because 2 kcal/mole is not sufficient to excite even the lowest vibrational mode of NH₃.

Photodissociation in a molecular beam, is in fact, also an effective method for measurement of infrared absorption spectra of van der Waals complexes. If one excites such a complex with a single photon to a level higher than the dissociation energy, it will dissociate. Giacinto Scoles and his coworkers, as well as other groups, have obtained¹¹ the absorption spectra of these complexes by monitoring the dissociation yield as a function of the frequency of the exciting laser. This method has a great advantage over the usual gas-cell method in that the spectrum of the complexes will not be confused by that of the monomers. If, in addition, one also measures angular and velocity dis-

tributions of the dissociation products, one can also learn about the dynamics of vibrational predissociation. Recently Hoi Shin Kwok, Matthew Vernon, James Lisy and Krajnovich in our lab used a tunable parametric oscillator with 4.5 cm⁻¹ resolution to obtain the spectrum of the benzene dimer (from a beam of molecules rotationally cooled by supersonic expansion) and information on its dissociation dynamics. It is interesting to note that the spectrum of benzene dimer is like that of liquid benzene and unlike that of benzene vapor at 300 K, which is jammed with rotational bands. Because the van der Waals interaction is weak and because the rotational motion of benzene molecules in liquid is hindered even at room temperature, this result is not really surprising. We can expect that the spectrum of rotationally cooled benzene monomers (which has not been measured) is quite similar to that of the dimers.

Donald Levy and his group at Chicago have studied¹² photodissociation of van der Waals complexes by first raising them to excited electronic levels; the complex then dissociates, via vibrational predissociation, into electronically excited monomers, which decay by emitting fluorescence radiation. Levy and his group obtain the excitation spectrum by detecting the fluorescence with a high resolution tunable laser. Comparing the line positions and shapes with those of the monomer spectrum can yield a wealth of information about the van der Waals interaction, the structure of the complexes, the intramolecular energy transfer within them, and the dissociation dynamics. Very recently, Scott Anderson, Hirooka and Peter Tiedemann of our laboratory, using the rate of the autoionization process as a clock, estimated the vibrational predissociation lifetime of "vibronically" excited hydrogen-molecule dimers to be near 10⁻⁹–10⁻¹⁰ sec.

One can, of course, use this method—photodissociation with molecular beams—for measuring the absorption spectra of other molecular clusters, such as the hydrogen-bonded complexes (H₂O)_n and (HF)_n. The formation of molecular clusters is a prelude to condensation, and is thus an interesting process to investigate. In figure 6 we show the vibrational spectra of clusters of three to six water molecules obtained in our laboratory with the molecular-beam apparatus shown in figure 1. There are two distinct features in these spectra. The sharp structure around 3700 cm⁻¹ is most likely due to the vibrational motion of hydrogen atoms in H₂O that are not bonded to oxygen atoms of neighboring H₂O molecules. The relative intensity of this sharp absorption decreases as the size of cluster increases. The broad absorption

band between 3200 and 3700 cm^{-1} is due to the vibrational motion of hydrogen atoms bonded to neighboring molecules. The red shift from the 3700 cm^{-1} peak is a measure of the hydrogen bonding strength. As another example, we have found that the spectra of $(\text{HF})_3$ and $(\text{HF})_4$ show only the red-shifted absorption band between 3000 and 3700 cm^{-1} arising from the motion of hydrogen-bonded H atoms. The absence of any absorption around the 3958 cm^{-1} vibrational frequency of the HF monomer indicates that $(\text{HF})_3$ and $(\text{HF})_4$ have cyclic structures, with all the hydrogen atoms hydrogen-bonded to the fluorine atoms of the neighboring molecules. The size of the molecular clusters studied in these experiments is determined by the stagnation pressure behind the nozzle. One has to adjust this pressure very carefully to minimize contamination by larger clusters in the beam.

Other crossed-beam studies

The investigations we have described involving the infrared excitation of molecules with crossed laser and molecular beams should clearly demonstrate the power of the technique. To make full use of it, however, requires a very intense, high-resolution tunable laser and a sensitive molecular-beam apparatus. These requirements are difficult to meet, but the development of suitable lasers and molecular-beam apparatus is advancing rapidly.

For example, during the last four months, a group in our laboratory, using a Nd-YAG-laser-pumped dye laser with our new high-resolution crossed-beams apparatus, has been able to map out the electronic and vibrational-state distributions of photodissociation products of ozone from the distribution of their translational energies. This group included Randall Sparks, Lee Carson, Kosuke Shobatake, Marta Kowalczyk, Kwok and He Guozhong. In a similar experimental arrangement, Carl Hayden, Neumark, and Sparks have used a rare-gas halide laser to make an accurate determination of the energy difference between singlet and triplet CH_2 from photodissociation of CH_2CO .

We can of course think of many other cases where the optical studies of molecules can benefit from the collisionless environment of molecular beams; among them are the following:

Multiphoton dissociation: How does the excitation energy redistribute itself in the parent molecule and how is the excess energy partitioned among the various degrees of freedom in the fragments after dissociation? Both questions must be answered by probing the population distribution in various states in the absence of collisions. John Stephenson, Curt Wittig and their co-workers have used time-dependent la-

ser-induced fluorescence in a dilute-gas cell to carry such measurements. One can perform similar investigations with molecular beams, where the molecules or radicals involved can often be better characterized and where fewer assumptions are involved, for example, in the work of Karl Welge and his associates. In addition to laser-induced fluorescence, one can use photoionization and photodissociation for probing the population distribution in a molecular beam.

Chemical reactions between selectively excited molecules is an intriguing subject of great importance, with potential applications in isotope separation, laser-induced catalysis, and so forth. Here again, because of collisions, the gas-cell experiments often give confusing results. The problem can however be studied by two crossed molecular beams. Each beam can be individually excited by selective laser excitation, and one can directly monitor the reaction products from the beam collision center. One can thus study the reaction dynamics in detail by measuring the angular and velocity distributions of the reaction products. Progress in this direction is described in the article by Zare and Bernstein on page 43.

Molecular-ion spectroscopy is a field still in its early infancy. This is particularly so with respect to rotational and vibrational spectroscopy of molecular ions. The difficulty is obvious because the ion density that can be maintained is usually too low for spectroscopic studies. With new developments in ion traps for storing and generating intense pulsed ion beams, one can now attack this problem with a somewhat different approach: For example, pulses from a tunable infrared laser can synchronously excite a pulsed ion beam confined in a cylindrical octapole ion trap. One can use photodissociation of the excited ions or selected ion-molecule reactions to monitor the excitation. A tandem mass spectrometer arrangement offers a sensitive method for preparation and detection of the ions involved. It is also possible to obtain the first-order vibrational spectrum of a molecular ion by first combining it with an inert atom to form a van der Waals ion and then measuring the excitation spectrum of photodissociation of the van der Waals ions. Using such an apparatus, and as a prelude to the measurement of vibrational-rotational spectra of polyatomic molecular ions, a group in our laboratory has been able to measure the lifetime of the long-lived metastable states of $\text{O}_2^+(\text{^4}\Pi)$. This group includes Dieter Gerlich, Sandy Bustamante, Kwok and Carson.

These are only a few examples of the sort of problems for which the method of crossed laser and molecular beams can be very useful. Of course, as the experimental methods become more sophisti-

cated the equipment will become more expensive. However, the investment will be justified because the detailed information on the dynamics of chemical reactions and on elementary photochemical and photochemical processes will be extremely useful many areas of advanced technology.

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