Title

MOLECULAR BEAM STUDIES OF IR LASER INDUCED MULTIPHOTON DISSOCIATION AND VIBRATIONAL PREDISSOCIATION

Author

Lee, Yuan T.

Publication Date

1980-06-01

8/15/80

LBL-11105 c.2
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

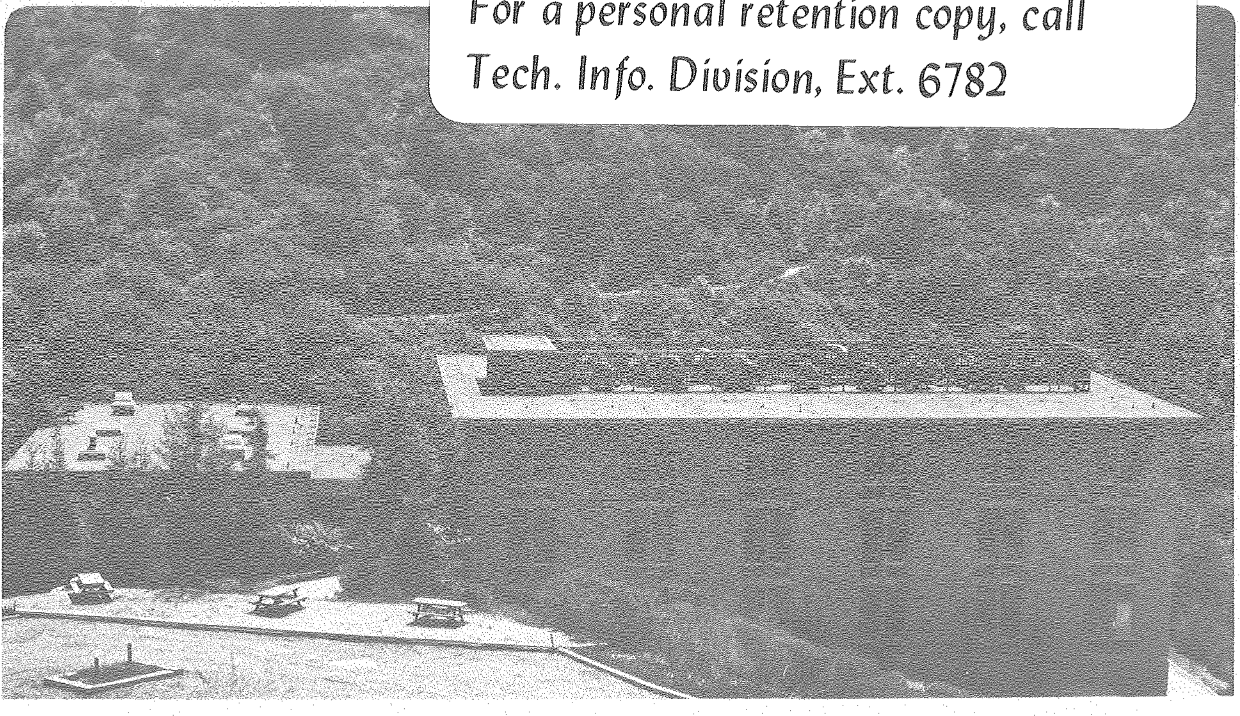
Materials & Molecular
Research Division

Submitted to Physics Today

MOLECULAR BEAM STUDIES OF IR LASER INDUCED MULTIPHOTON DISSOCIATION AND VIBRATIONAL PREDISSOCIATION

Yuan T. Lee and Y. Ron Shen

June 1980



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

submitted to Physics Today LBL-11105

MOLECULAR BEAM STUDIES OF IR LASER INDUCED MULTIPHOTON DISSOCIATION AND VIBRATIONAL PREDISSOCIATION

Crossed Laser-Molecular Beam Experiments Provide Unique Opportunity to Study Dynamics of Photophysical and Photochemical Processes in Great Detail

Yuan T. Lee and Y. Ron Shen

The understanding of the detailed dynamics of elementary chemical reactions is an important area of science which has enjoyed significant advances during the last twenty years. This remarkable progress, which enables us to understand, predict, and control many complicated macroscopic phenomena, is mainly due to the advancement of both sophisticated microscopic experimental techniques and the methodology of quantum chemistry. The availability of large scale electronic computation to quantum chemistry has certainly made possible some connections between first principles and the real world. The advancement of crossed molecular beams methods, modern spectroscopy and laser technology, on the other hand, allows us to observe chemical reactions on atomic and molecular levels in great detail.

The observation of chemical reactions under the single collision conditions of crossed molecular beams experiments is most important.[1] 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 trajectories of the reactive collisions that transform the reactants into products. In addition to the direct identification of product channels and their relative importance, detailed information about reaction dynamics can be obtained, namely;

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, the heights of both entrance and exit potential energy barriers, etc.

Clearly, similar information on photodissociation of molecules can be obtained if one of the molecular beams is replaced by a laser beam. The investigation of laser-induced primary photophysical and photochemical processes (unimolecular reactions) is often most fruitful in a strictly collision-free environment, as collisions often tend to greatly confuse the results. The direct and unambiguous identification of primary products in the photo-induced processes and the dynamic information derived from angular and velocity distributions of the products are most important for the understanding of such processes. Photofragmentation translational spectroscopy, pioneered by Wilson and his coworkers,[2] is one such example. In later sections, we shall describe in some detail, studies of two types of infrared photodissociation, namely, multiphoton dissociation of polyatomic molecules, and vibrational predissociation of hydrogen-bonded and van der Waals molecular clusters, by crossed laser and molecular beams. With laser excitation, chemical reactions of selectively excited molecules can also be studied by crossed molecular beams. Photophysics and photochemistry have long been important fields of science. As the variety and availability of lasers has improved over the years, the fields have recently bloomed into tremendous activity and productivity.

Brief History of Crossed Molecular Beams Studies

Following the first crossed molecular beams study by Datz and Taylor on K + HBr in 1955, Herschbach and coworkers did the landmark experiment on K + CH_3I. 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, crossed molecular beams experiments have become more and more sophisticated through the pioneering efforts of Herschbach, Bernstein and other workers in the field.

Results have led to improved understanding of many reaction mechanisms, such as the rebound mechanism in K + CH_3I, the harpoon mechanism in K + Br_2 through electron transfer between K and Br_2, and the formation of long-lived complexes in exchange reactions between alkali atoms and alkali halides. Many refined experiments using molecular beams have been carried out, with velocity-selected or oriented reactant molecules. Product analysis may include mass identification, angular and velocity distributions, quantum state distribution, and the polarization of angular momentum of the products. The development and characterization of supersonic molecular beams by Fenn and others and the construction of a sophisticated "universal" molecular beam apparatus with an ultrahigh vacuum mass spectrometric detector have also extended the utility and the scope of the crossed molecular beams method. It has now become one of the most powerful tools for the investigation of elementary atomic and molecular processes.

Universal Molecular Beam Apparatus

Figure 1 shows schematically one of our universal molecular beam apparatus. The nozzles, whose temperature and backing pressure can be adjusted, provide the supersonic molecular beams. A skimmer and a defining slit with two stages of differential pumping are used for each beam source to narrow the beam spread to less than 2°. The beams collide at the collision center and the reaction products are identified and measured with a rotatable quadrupole mass spectrometer in a triply differentially pumped ultrahigh vacuum chamber with an electron bombardment ionizer. The angular distribution of the products can therefore be obtained. The ion signal is detected by a gated counting system, so that the velocity distribution of the products at a given angle can also be measured by the time-of-flight method. Through a deconvolution calculation, the angular and velocity distributions, and hence the translational energy distribution, of the products in center-of-mass coordinates are finally deduced. Figure 2 is a photograph of our recently constructed high resolution crossed molecular beam apparatus.

In the photodissociation studies, one of the molecular beams is replaced by an exciting laser beam. In our work on IR multiphoton dissociation of polyatomic molecules and vibrational predissociation of van der Waals and hydrogen-bonded molecular clusters that will be discussed later, the lasers used are respectively, a CO_2 TEA laser and a Nd:YAG laser-pumped optical parametric oscillator. The molecular clusters can be formed in a beam by properly adjusting the backing pressure in the nozzle.

Examples of Crossed Molecular Beams Studies

Using the apparatus described above, Valentini and Coggiola in our laboratory studied the reaction of I_2 and F_2. They found that $I_2 + F_2 \rightarrow I_2F + F$ can proceed with only 4 kcal/mole of collision energy, while the generally accepted reaction path, $I_2 \rightarrow 2I$ (or $F_2 \rightarrow 2F$) followed by $I + F_2 \rightarrow IF + F$ (or $I_2 + F \rightarrow IF + I$) requires 38 kcal/mole to initiate. More recently, in a series of studies involving oxygen atoms and unsaturated hydrocarbons, Buss, Sibener, Cassavecchia, Hirooka, and Baseman of our laboratory found that among various possible reaction channels, the replacement of a hydrogen atom by an oxygen atom was most significant. This is contrary to what has been believed in the past. These are just two examples of reaction product identification that can best be investigated by the crossed molecular beams method.

The probing of reaction dynamics with crossed molecular beam experiments can be illustrated by the work of Sparks, Hayden, Shobatake, and Neumark in our laboratory on $F + H_2 \rightarrow HF + H$. Contour maps in Fig. 3(a) and 3(b) show the observed center-of-mass velocity and angular distributions of HF products at collision energies of 2.0 and 3.0 kcal/mole respectively. At 2.0 kcal/mole, the angular distribution shows pronounced backward scattering of HF with respect to F. This indicates that collisions between F and H_2 with all three atoms in near 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. This dependence of the potential energy barrier on the bending angle of F-H-H is well understood from ab initio quantum mechanical calculations.[3] The population distribution in the vibrational states of the HF product can also be obtained from the velocity distribution. Since the rotational excitation of HF is small , population of different vibrational states is characterized by the well separated peaks in the velocity or translational energy distribution, as required by energy conservation. We notice that the vibrational distribution of HF is inverted, with most of the products in v = 2 and v = 3. This is not surprising, since $F + H_2 \rightarrow HF + H$ is a pumping mechanism for the efficient HF laser. At a collision energy of 3.0 kcal/mole, a very interesting feature occurs. As shown in Fig. 3(b), the angular distributions of HF (v = 3) and HF (v = 1) are still sharply peaked in the backward direction, but that of HF (v = 2) is much broader with a noticeable sideways peaking. The latter appears 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. A recent calculation on F + H_2 by Wyatt and coworkers has shown that at a collision energy of 3 kcal/mole, although the reaction probability of producting HF (v = 3) is maximum at zero impact parameter, that of HF (v = 2) 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.

Comparison with 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. The analysis of chemiluminescence from nascent products, the operation of tandem chemical lasers, and the laser-induced fluorescence method can often reveal much more detailed quantum state distributions of reaction products. However, these methods are often applicable only to limited favorable systems. For example, the laser-induced fluorescence method has the sensitivity to prove detailed energy distributions in reaction products at very low number densities. Yet it requires prior knowledge of absorption and emission spectra of the products for identification and probing as well as an appropriate tunable laser for selective excitation. Then, in the analysis of the results, certain assumptions on the initial conditions must also be made, especially in the gas cell environment. The molecular beam method has the advantages that it operates in a strictly collisionless environment with the initial conditions well specified, and that the reaction products can generally be identified by the mass spectrometer if proper study is made of the fragmentation of molecules during the ionization. However, it has the disadvantage of not being able to provide detailed information about the quantum state distribution in the reaction products, except in some special cases. In this respect, for some simple and favorable systems, combining 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.[4]

IR Multiphoton Dissociation of Polyatomic Molecules

Infrared multiphoton dissociation (MPD) of polyatomic molecules is one of the most exciting problems in laser chemistry and quantum electronics in recent years. It deals with the process in which a single molecule dissociates through absorption of many photons from an intense laser pulse. The problem is not only scientifically interesting but also socially relevant because of its potential applications to isotope separation and chemical synthesis. A number of review articles on the subject have already appeared in the literature.[5] Here, we shall discuss how our crossed laser and molecular beam studies carried out over the years with Coggiola, Grant, Schulz, Sudbø, Krajnovich, Giardini-Guidoni, Huisken, and Zhang have led to a better understanding of many aspects of the problem.[6] For the sake of clarity, we shall begin with a brief review of the multiphoton excitation process.

In order for the multiphoton excitation process to be efficient, each one-photon transition step must be resonant or nearly resonant.[7] Figure 4 describes schematically the energy levels of a polyatomic molecule. 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. (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 cm^{-1}.) For efficient multiphoton excitation through the discrete levels into the quasi-continuum, the laser frequency must be nearly resonant with the allowed rotational-vibrational transitions. This is the basis of isotope searpation 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. Since there is an initial thermal distribution of molecules over many rotational-vibrational states, the fraction of molecules excited into the quasi-continuum is a function of the laser intensity. Only at sufficiently high laser intensity is it possible to excite nearly all the molecules into the quasi-continuum. Once the molecules reach the quasi-continuum, they can be readily excited further up via one-photon resonant transitions. The net excitation all the way up to the dissociation level at time t depends only on the laser energy fluence (integration of the laser intensity over time, $\int_{-\infty}^{t} I(t)dt$) if deexcitation by collisions and spontaneous emission is negligible. Above the dissociation level, the energy states form a true continuum, and the dissociation of molecules sets in. The up-excitation via one-photon resonant transitions continues and 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 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 N evenly spaced levels with rate equations governing the transitions between levels and dissociation from various levels.[8]

While the above-mentioned excitation process explains why multiphoton excitation and subsequent dissociation of a polyatomic molecule can be very efficient, there are a large number of questions about MPD which have to be answered. Among them, the more important ones are the following. 1) The excitation in the low-energy region is certainly mode-selective, but does it remain so at high levels of excitation? Can the resultant MPD be bond-selective? 2) How does the average level of excitation depend on the laser intensity, laser energy fluence, and molecular structure? 3) Is MPD a truly unimolecular reaction? What are the dissociation fragments? Is the dissociation always dominated by the lowest dissociation channel? 4) What is the dynamics of MPD? Does the molecular structure affect the dissociation dynamics? These are questions difficult to resolve in the usual gas cell experiments because of confusion arising from collisions and chemical reactions. In the collisionless environment of a molecular beam, they can however be given a rather satisfactory answer.[7]

First of all, the mere observation of MPD in a molecular beam shows unequivocally that it is a collisionless unimolecular dissociation process. Then, the mass spectrometer as a detector in the setup of Fig. 1 allows a direct identification of the dissociation products. For example, we have found that in MPD, SF_6 mainly dissociates into SF_5 and F, and $CFCl_3$ into $CFCl_2$ and Cl, in contradiction to the earlier findings in gas cell experiments. It turns out that in all cases (around 20 molecules) we have studied with a high-power CO_2 laser, the major dissociation channel is always the statistically most favorable channel, which is usually the lowest-energy channel, although in some cases, dissociation may also occur through the next higher channel.[6] This suggests that mode-selective excitation to high levels and subsequent bond-selective dissociation are not likely in these cases.

The possibility or impossibility of bond-selective dissociation in MPD has been the subject of great controversy as it is extremely important for chemical synthesis. For example, the $CHCl_3$ molecule can be excited through laser excitation of the C-H stretch vibration around 3000 cm^{-1}. If the excitation energy were localized in the C-H stretching mode, then the final dissociation of the molecule would occur via the C-H bond breaking. On the other hand if the mode-mode coupling is strong, especially at high levels of excitation, the energy fed into the molecule through one mode is quickly randomized into other modes so that in the dissociation the weaker C-Cl bond tends to break. Whether the excitation energy in the molecules is 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 5a and 5b show, as an example, the velocity distribution and the translational energy distribution of SF_6 fragments obtained from our measurements. It can be compared with the prediction of the well-known statistical (RRKM) theory of unimolecular dissociation.[9] The theory assumes that each molecule contains an excitation energy E which is randomized in a number of accessible modes. Then, in the absence of exit potential energy barriers, the translational energy distribution of the fragments, $g_E(\varepsilon)$, is simply the probability of finding the excited molecule in a phase space from which the molecule will dissociate with a fragment translational energy ε. This can be calculated from the related molecular properties. In Fig. 5b, the curves are calculated with the assumption of complete energy randomization in the 15 vibrational modes of SF_6, and $E - E_0 =$ 19, 24.5, and 30, kcal/mole respectively, where E_0 is the dissociation energy for $SF_6 \rightarrow SF_5 + F$. The middle curve describes the experimental results fairly well. Actually, because of the statistical nature of laser excitation,[8] the excitation energy should have a rather wide spread, and $E - E_0 = 24.5$ kcal/mole is only a mean value for the dissociated molecules. The agreement between theory and experiment in Fig. 5b supports the assertion of energy randomization in the molecule before dissociation. It is further confirmed by the fact that both the statistical theory and the experiment yield an average dissociation lifetime of the order of 10 nsec. If the excitation energy were localized in one or few modes, the dissociation lifetime could differ by several orders of magnitude.

Aside from answering the question of energy randomization, Fig. 5b also shows the average translational energy of SF_5 fragment to be ~2.5 kcal/mole. Compared with the average excess energy of $(E - E_0) \sim 25$ kcal/mole, it indicates that after dissociation, 9/10 of the excess energy must appear as internal energy of the fragments, namely in the rotational and vibrational degrees of freedom of SF_5. This corresponds to an average excitation of ~8000 cm^{-1} in SF_5 and should leave SF_5 in the excited quasi-continuum. The immediate consequence is that being in the quasi-continuum, SF_5 will also be able to resonantly absorb photons from the laser via stepwise one-photon transitions. It will be excited to and beyond the dissociation level, and finally dissociate into SF_4 and F. This secondary dissociation of SF_6, the onset of which provides information about the average lifetime of excited SF_6 in comparison with the laser pulse duration, has indeed been observed in our experiment when the laser energy fluence is sufficiently high, with results in fair agreement with the theoretical prediction.[6]

Recently, the question of how multiphoton excitation and dissociation depend on laser intensity and energy fluence has been the focus of many discussions. It is well proven that excitation of populations over the discrete levels is a strong function of the laser intensity. Only at very high laser intensities can all molecules be excited into the quasi-continuum. The subsequent up-excitation in the quasi-continuum depends only on the laser fluence and the one-photon absorption cross-section.[7,10] Figure 6 illustrates the combined effect of the bottleneck in the initial excitation and the one-photon absorption cross section in the quasi-continuum. With the laser pulse shape kept the same, the slopes of the curves for different laser excitation frequencies partly reflect how the increase of laser intensity increases the populations pumped into the quasi-continuum, and the dissociation thresholds are indicative of the laser fluences required to pump the populations across the quasi-continuum. In Fig. 6, the 944.2 cm^{-1} excitation is near the peak of the ν_3 linear absorption band of SF_6, and is most efficient in exciting the molecules over the discrete barrier, as evidenced by the steep slope of the curve. However, its one-photon absorption cross-section in the quasi-continuum is not as large as that at 934.9 cm^{-1}, and consequently, the dissociation threshold is higher at 944.2 cm^{-1} than at 934.9 cm^{-1}.

Excitation above the dissociation level depends on both laser intensity and fluence.[6,11] 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. Figure 7 shows how the dissociation rate increases with the excess energy $(E - E_0)$ for some molecules.[11] 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 broader translational energy distribution of the fragments with a larger mean value. This is actually what we have observed in MPD of SF_6. When the excitation level is limited by laser intensity, significant dissociation will occur during the laser pulse. Then, the dissociation product can 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 dissociating molecules. Our experimental results with laser pulses of different widths and intensities agree well with the picture presented here.[11]

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.[6,9] In Fig. 7, three representative cases are shown. The dissociation energies E_0 for SF_6, CF_3Cl, and N_2F_4

are 93, 81.5, and 22.3 kcal/mole respectively. As predicted by RRKM theory,[9] the dissociation rate increases faster with excess energy, $E - E_0$, for smaller and/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. The above picture 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/cm^2 and 100 ns CO_2 laser pulse excitation, the average excitation levels in SF_6, CF_3Cl, and N_2F_4 are about 22, 4, and 2 kcal/mole respectively,[6] above the dissociation energy.

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. In some cases, the average level of excitation may lie above the dissociation energies of several dissociation channels. Then, dissociation through several channels with different dissociation products becomes possible. The probability of the molecule dissociating through each channel can be estimated from RRKM statistical calculations. We have found experimentally that this is the case in a number of molecules.[6] For example, the two lowest dissociation channels of C_2F_5Cl are $C_2F_5Cl \rightarrow C_2F_5 + Cf$ with E_0 = 83 kcal/mole and $C_2F_5Cl \rightarrow CF_3 + CF_2Cl$ with E_0 = 97 kcal/mole. At low laser intensities, dissociation via Cl elimination dominates. With increases laser intensities, the Cl elimination process saturates, whereas the C-C bond rupture becomes important.

In some cases, the potential curve in Fig. 5 may have a hump along the dissociation coordinate. Because of the existence of such an exit energy barrier which is partially transformed into translational energy during dissociation, the fragments will 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.[6]

From what we have discussed, a fairly complete picture of MPD can now be drawn. The initial excitation of molecules over the discrete levels is responsible for isotopic selectivity. At low laser intensities, it also determines the maximum dissociation efficiency which may be attained. For sufficiently high laser intensity, the dissociation yield depends only on the laser fluence, but the level of excitation still depends in general on the laser intensity. With the same laser pulse excitation, if the energy fluence of the laser is not the limitation, a large molecule will attain more excess energy, most of which will be retained by the fragments as internal energy after dissociation. Since the statistical theory describes MPD very well, we are now in a very good position to predict, at least qualitatively, what is likely to happen in MPD of a given polyatomic molecule.

As a summary, we present here an analogy that illustrates many important aspects of MPD. Imagine a multi-compartment container, shown in Fig. 8, with small holes in the partition walls, which is being filled with water through one of the compartments. As such, the container is analogous to a molecule, the compartments to the vibrational modes, and water to energy. Then, the flow of water between compartments through the holes corresponds to energy randomization among vibrational modes, and the leaking of water through openings on the container wall corresponds to molecular dissociation through various channels. The v shape of the openings makes the leaking rate increase rapidly as the water level goes up. The following situation may arise. First, the equilibration of water in various compartments depends on the water filling rate and on the size of the holes in the partition walls. Second, if the filling rate is sufficiently slow, so that equilibration of water among all compartments is achieved at all times, as long as the water level is above the lowest holes on the compartment walls, then water will eventually rise above the lowest opening and leak out through it. The final water level is determined by the balance between the filling and leaking rates. Third, if the filling rate is sufficiently fast, the water level may rise above the second or even third lowest opening, and water will now leak out simultaneously through more than one opening. Fourth, 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. The actual molecule is of course more complicated than the container we have described, especially at high levels of excitations, where the original mode identity may have disappeared because of the strong mode-mode coupling. Nevertheless, the picture here 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 typical experiments with a CO_2 TEA laser operated at a peak power of 100 MW/cm^2, the rate of photon deposition is approximately $10^9 - 10^8$/sec for absorption cross sections of $10^{-19} - 10^{-20}$ cm^2. With this excitation rate, most of the molecules will not reach a level with a dissociation lifetime 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, Rabinovitch and coworkers have shown that it takes only several picoseconds to randomize the energy in chemically activated complexes.

In applications like isotope separation, the energy efficiency of the dissociation yield is important. One would like to use, in MPD, a molecule with a relatively low dissociation energy such as N_2F_4. Van der Waals molecules or hydrogen bonded molecular clusters (Xe:Br, He:I_2, NH_3:NH_3, etc.) in particular have the lowest dissociation energies. Photodissociation of van der Waals molecules is actually interesting in its own right. Because of the weak van der Waals bond that can be easily broken by collisions, it cannot be studied in the usual gas cell experiments. The only viable method is to use a molecular beam. Consider $(NH_3)_2$ as a example. The dimer can be excited by 10.6 μm CO_2 lasers through vibrational excitation of an NH_3 bending mode. The dissociation energy of the hydrogen bond in this case is about 4 kcal/mole. Absorption of two laser photons (~6 kcal/mole) is enough to break the bond with an excess energy of about 2 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. Figure 8 shows the translational energy distribution of monomers resulting from photodissociation of the dimers. As expected, the maximum translational energy is limited to ~2 kcal/mole, and the average translational energy is only 0.3 kcal/mole. A large fraction of the excess energy has apparently appeared after dissociation in the rotational degrees of freedom of the monomers since 2 kcal/mole is not sufficient to excite even the lowest vibrational mode of NH_3.

Vibrational Predissociation of Hydrogen-Bonded and van der Waals Molecular Clusters

Photodissociation in a molecular beam is in fact also an effective method for measurements of absorption spectra of van der Waals complexes. If in one-photon absorption, a complex is excited to a level higher than the dissociation energy, dissociation will result. The absorption spectrum can then be obtained by monitoring the dissociation yield as a function of the exciting laser frequency.[12] The 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. In addition, if in the experiment, angular and velocity distributions of the dissociation products are also measured, the dynamics of vibrational predissociation can be understood. Figure 9 shows an example of the spectrum of benzene dimers obtained by Kwok, Vernon, Krajnovich, and Lisy using a tunable optical parametric oscillator with 4.5 cm^{-1} resolution. It is interesting to note that this spectrum of benzene dimers, rotationally cooled through supersonic expansion, is practically the same as that of liquid benzene rather than the rotationally jammed spectrum of benzene vapor at 300°K. Since the van der Waals interaction is weak, and the rotational motion of benzene molecules in liquid is hindered even at room temperature, this result is not really surprising. The rotationally cooled spectrum of benzene monomers, yet to be measured, is also expected to be quite similar to that of the dimers, the difference probably being only visible if a high-resolution tunable laser beam is used so that the rotational-vibrational fine structure of the spectrum can be resolved.

Photodissociation of van der Waals complexes can also be studied by electronic excitation followed by vibrational predissociation and fluorescence of the electronically excited uncomplexed molecules, as shown by Levy and coworkers.[13] The excitation spectrum of the fluorescence can be obtained by a high-resolution tunable laser. Then, the line shifts and lineshapes in comparison with those of the monomeric molecules can yield a wealth of information about the van der Waals interaction, the structure of the complexes, the intramolecular energy transfer within the complexes, and the dissociation dynamics of the complexes. Very recently, Anderson, Hirooka, and 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 around 10^{-9} - 10^{-10} sec.

The photodissociation method using molecular beams for measuring absorption spectra of complexes can also be extended to other molecular clusters, such as hydrogen-bonded $(H_2O)_n$ and $(HF)_n$. This is important since the formation of molecular clusters is a prelude to condensation. An example is shown in Fig. 9 where the vibrational spectra of the hydrogen-bonded trimer, tetramer, pentamer and hexamer of H_2O are given. There are two distinct features in these spectra. The sharp structure around 3700 cm^{-1} is most likely due to the vibrational motion of the hydrogen atoms in H_2O which are not hydrogen-bonded to the oxygen atoms of the neighboring H_2O molecules. The relative intensity of the of this sharp absorption decreases as the size of cluster increases.

The red-shifted broad absorption band between 3200 to 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 $(HF)_3$ and $(HF)_4$ show only the red-shifted absorption band between 3000 to 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 $(HF)_3$ and $(HF)_4$ have cyclic structures, with all the H atoms hydrogen bonded to the F atoms of the neighboring molecules. In the measurement of the vibrational predissociation spectrum of a given cluster, the stagnation pressure behind the nozzle is carefully adjusted to minimize possible contamination by larger clusters in the beam.

Future Research with the Crossed Beams Technique

The physical problems discussed above involving IR excitation of molecules should clearly demonstrate the power of the crossed laser and molecular beam technique. Difficulty in the technique often lies in the requirement of a very intense, high-resolution tunable laser and a sensitive molecular beam apparatus without background. Both areas are advancing rapidly. For example, during the last four months, using a Nd-YAG laser-pumped dye laser system with our new high resolution crossed molecular beams apparatus, Sparks, Carlson, Shobatake, Kowalczyk, Kwok, and He have been able to map out the electronic and vibrational state distributions of photodissociation products of O_3 from the measurement of their translational energy distributions. In a similar experimental arrangement, Hayden, Neumark, and Sparks using a rare gas halide laser have carried out 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. Here, we shall suggest a few that are worth pursuing.

1) In the study of MPD, two important problems still require further investigation: how does a certain 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. Such measurements have been carried out in a dilute gas cell with the time-dependent laser-induced fluorescence technique by Stephenson, Wittig and their coworkers. However, in a molecular beam, the molecules or radicals under investigation can often be better characterized with fewer assumptions involved. In addition to laser-induced fluorescence, photoionization and photodissociation can also be used for probing the population distribution if a molecular beam is used.

2) Chemical reactions between molecules selectively excited is an intriguing subject of great importance with potential applications in isotope separation, laser-induced catalysis, etc. 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 the reaction products from the beam collision center directly monitored. Then, the reaction dynamics can be studied in detail by measuring the angular and velocity distributions of the reaction products. Progress in this direction is described in an article by Zare and Bernstein in this issue.[4]

3) 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 since 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. Tunable IR laser pulses can synchronously excite a pulsed ion beam which is confined in a cyclindrical octapole ion trap. Photodissociation of the excited ions or subsequent selection ion-molecule reactions can be used 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 or molecule to form a van der Waals ion and then measuring the excitation spectrum of photodissociation of the van der Waals ion. Using such an apparatus, and as a prelude to the measurement of vibrational-rotational spectra of polyatomic molecular ions, Gerlich, Bustamente, Kwok, and Carlson of our laboratory have measured the lifetime of the long lived metastable state of $O_2^+(^4\Pi)$.

These are of course only a few examples of the types of problems that the crossed laser and molecular beams method can be most helpful in exploring. This exciting area of research will undoubtedly become more active and productive in the future. As the experimental methods become more sophisticated, the investment in the research facilities will necessarily become more substantial. However, the detailed information on the dynamics of chemical reactions, and elementary photophysical and photochemical processes, will be extremely useful for the development of many areas of advanced technology. This is an important and productive field of research that should be fully explored with the most advanced facilities.

ACKNOWLEDGMENTS

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, and the Division of Advanced Systems Materials Production, Office of Advanced Isotope Separation, U.S. Department of Energy under contract No. W-7405-Eng-48.

Yuan T. Lee is Professor of Chemistry and Y. Ron Shen is Professor of Physics. Both of them are with the University of California, Berkeley, California.

REFERENCES

1. R.D. Levine and R.B. Bernstein, Molecular Reaction Dynamics, Oxford Univ. Press, 1974.
2. George E. Bush and Kent R. Wilson, J. Chem. Phys. 56, 3638 (1972).
3. M.J. Redmon and R.E. Wyatt, Chem. Phys. Lett. 63, 209 (1979).
4. R.N. Zare and R.B. Bernstein, "State to State Dynamics." This issue Physics Today.
5. See, for example, V.S. Letokhov, Physics Today, May, 1977, p. 23; N. Bloembergen and E. Yablonovitch, Physics Today, May, 1978, p. 23; book on "Multiphoton Excitation and Dissociation of Polyatomic Molecules," edited by C. D. Cantrell (Springer Verlag, to be published).
6. More details can be found in the following review articles: E.R. Grant, P.A. Schulz, Aa.S. Sudbø, M.J. Coggiola, Y.T. Lee, and Y.R. Shen, in "Laser Spectroscopy III" edited by J. L. Hall and J. L. Carlson, (Springer Verlag, 1977) p. 94; Aa.S. Sudbø, P.A. Schulz, D.J. Krajnovich, Y.R. Shen, and Y.T. Lee, in "Advances in Laser Chemistry", edited by A.H Zewail, (Springer Verlag, 1978), p. 308; P.A. Schulz, Aa.S. Sudbø, D.J. Krajnovich, H.S. Kwok, Y.R. Shen, and Y.T. Lee, Ann. Rev. Phys. Chem. 30, 379 (1979).

7. D.M. Larsen and N. Bloembergen, Optics Commun. 17, 254 (1976); R.V. Ambartzumian, N.P. Furzikov, Yu.A. Gorokhov, V.S. Letokhov, G.M. Makarov, and A.A. Puretzki, JETP Lett. 23, 217 (1976); Optics Commun. 18, 517 (1976).

8. E.R. Grant, P.A. Schulz, Aa.S. Sudbø, Y.R. Shen, and Y.T. Lee, Phys. Rev. Lett. 40, 115 (1978).

9. See, for example, P.J. Robinson and K.A. Holbrook, "Unimolecular Reactions" (J. Wiley, 1972).

10. J.G. Black, E. Yablonovitch, N. Bloembergen, and S. Mukamel, Phys. Rev. Lett. 38, 1131 (1977); J.L. Lyman and S.D. Rockwood, J. Appl. Phys. 47, 595 (1976); J.G. Black, P. Kolodner, M.J. Schultz, E. Yablonovitch, and N. Bloembergen, Phys. Rev. A19, 704 (1979).

11. P.A. Schulz, Aa.S. Sudbø, E.R. Grant, Y.R. Shen, and Y.T. Lee, J. Chem. Phys. 72, 4985 (1980).

12. H.S. Kwok, D.J. Krajnovich, M. Vernon, Y.R. Shen, and Y.T. Lee, XIth International Quantum Electronics Conference (Boston, June 1980), paper D-5.

13. See, for example, J.E. Kenny, K.E. Johnson, W. Sharfin, and D.H. Levy, J. Chem. Phys. 72, 1109 (1980), and references therein.

FIGURE CAPTIONS

Fig. 1. Experimental arrangement for molecular beam studies of dynamics of elementary chemical reactions.

Fig. 2. High resolution universal crossed molecular beams apparatus equipped with two supersonic molecular beam sources and a rotatable ultrahigh vacuum mass spectrometric detector.

Fig. 3. (a) Center-of-mass velocity space contour plot of HF product distribution from F + H_2 at 2.00 kcal/mole. (b) Center-of-mass velocity space contour plot of HF product distribution at 3.17 kcal/mole.

Fig. 4. Schematic energy levels, density of states of a polyatomic molecule in relation to the infrared multiphoton dissociation process.

Fig. 5. (a) Velocity distribution of SF_5 obtained with laser excitation of 5 J/cm^2 compared with three RRKM theoretically predicted velocity distributions. Curves are calculated assuming an excitation of $E - E_0$ = 13.5 (------), 21.5 (—— ∘ —— ∘ ——), and 32.5 kcal/mole (————————) where E_0 is the dissociation threshold energy. (b) Fragment recoil energy distribution for $SF_6 \rightarrow SF_5 + F$. Experimental data points obtained with laser excitation of 7.5 J/cm^2 are denoted by the dots. Curves are calculated from the RRKM theory assuming a molecular excitation of $E - E_0$ = 19 (—— ∘ ——), 24.5 (————————) and 30 kcal/mole (------).

Fig. 6. Energy fluence dependence of SF_6 MPD yield at three CO_2 laser frequencies.

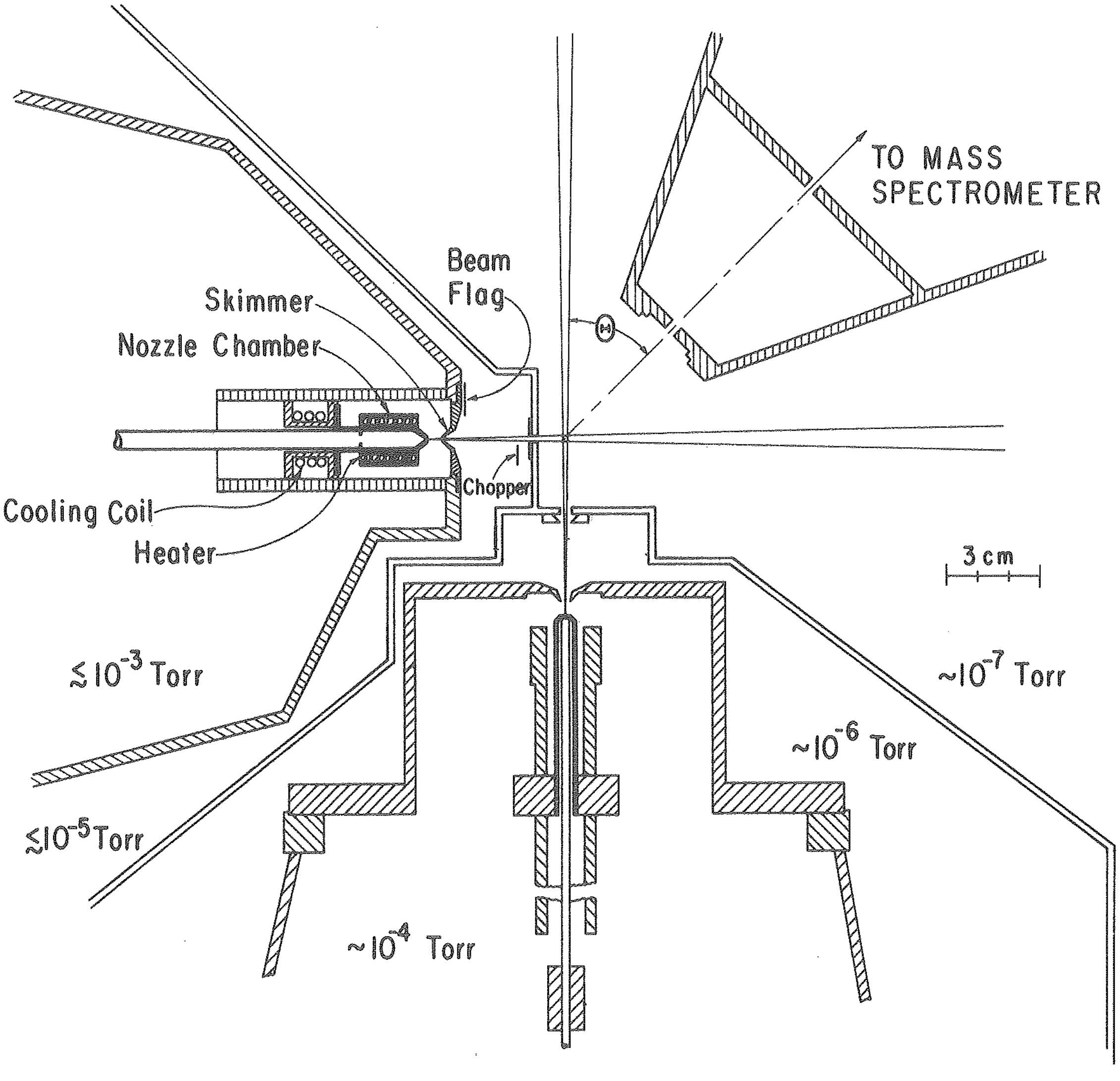
Fig. 7. Dissociation rate constants of N_2F_4, CF_3Cl and SF_6 calculated from the RRKM theory as a function of excess energy.

Fig. 8. Schematic illustration of important aspects of MPD. The multi-compartment container with small holes on the partition walls is analogous to a molecule, the compartments to the vibrational modes, and the water to energy. The flow of water between compartments through the holes corresponds to energy randomization among vibrational modes, and the leaking of water through openings on the container wall corresponds to molecular dissociation through various channels (see text).

Fig. 9. Translational energy distribution of NH_3 from $(NH_3)_2$ dissociated by pulsed CO_2 laser excitation.

Fig. 10. Single photon vibrational predissociation spectrum of $(C_6H_6)_2$.

Fig. 11. Single photon vibrational predissociation spectra of $(H_2O)_n$, n = 3,4,5, and 6.



XBL 806-10234

Fig. 1

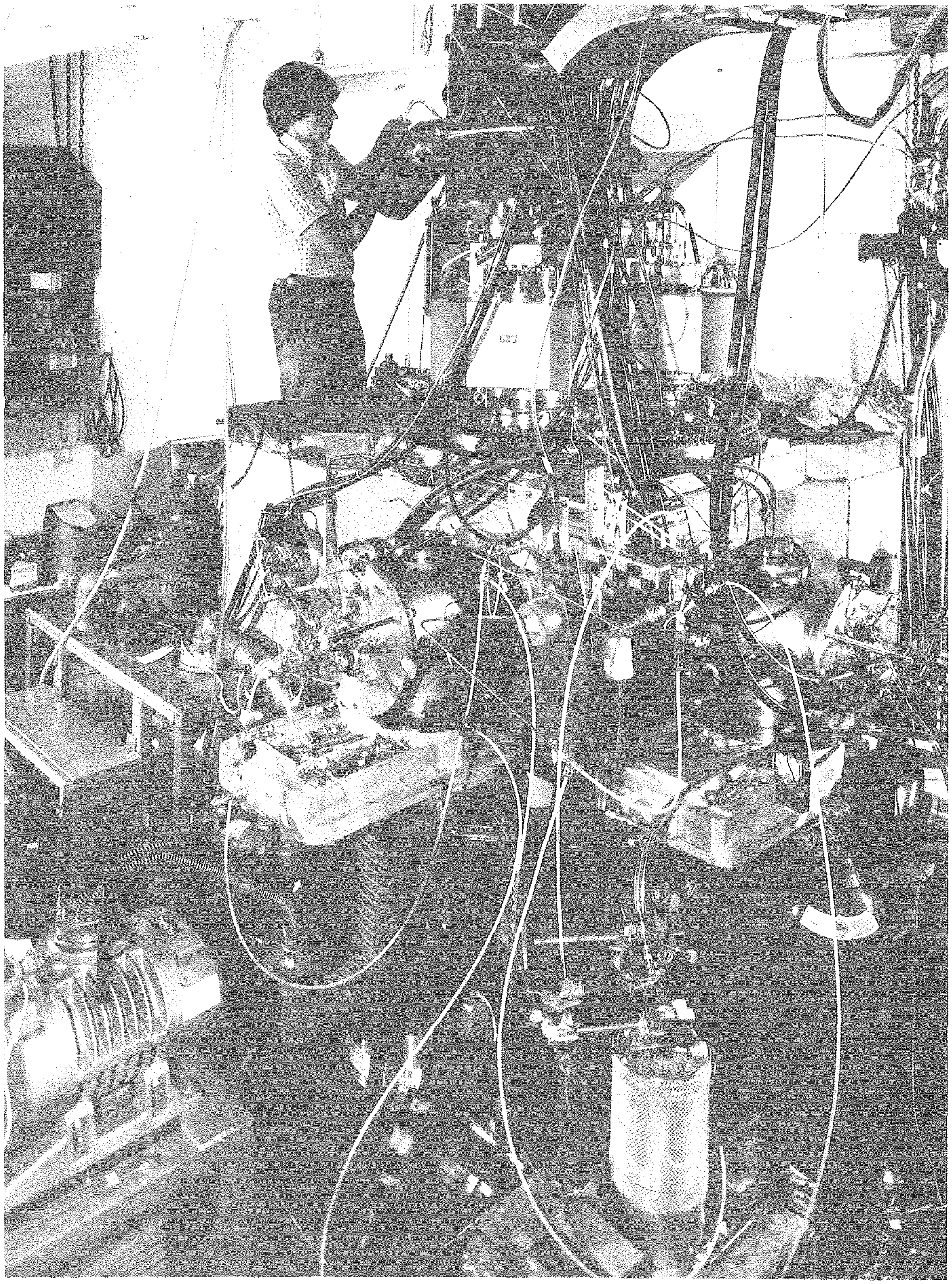
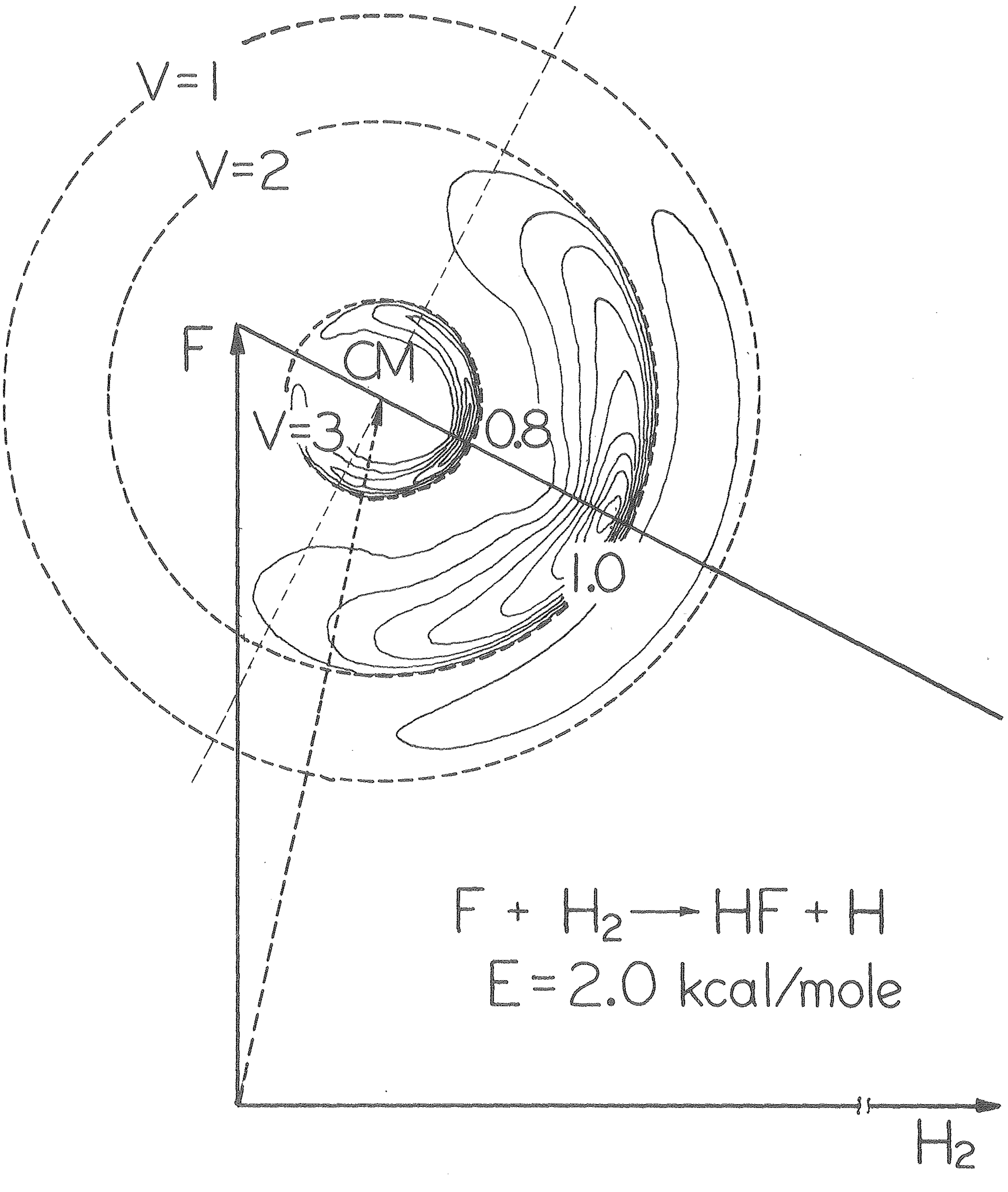


Fig. 2

CBB 801-49



XBL 7910-12374

Fig. 3a

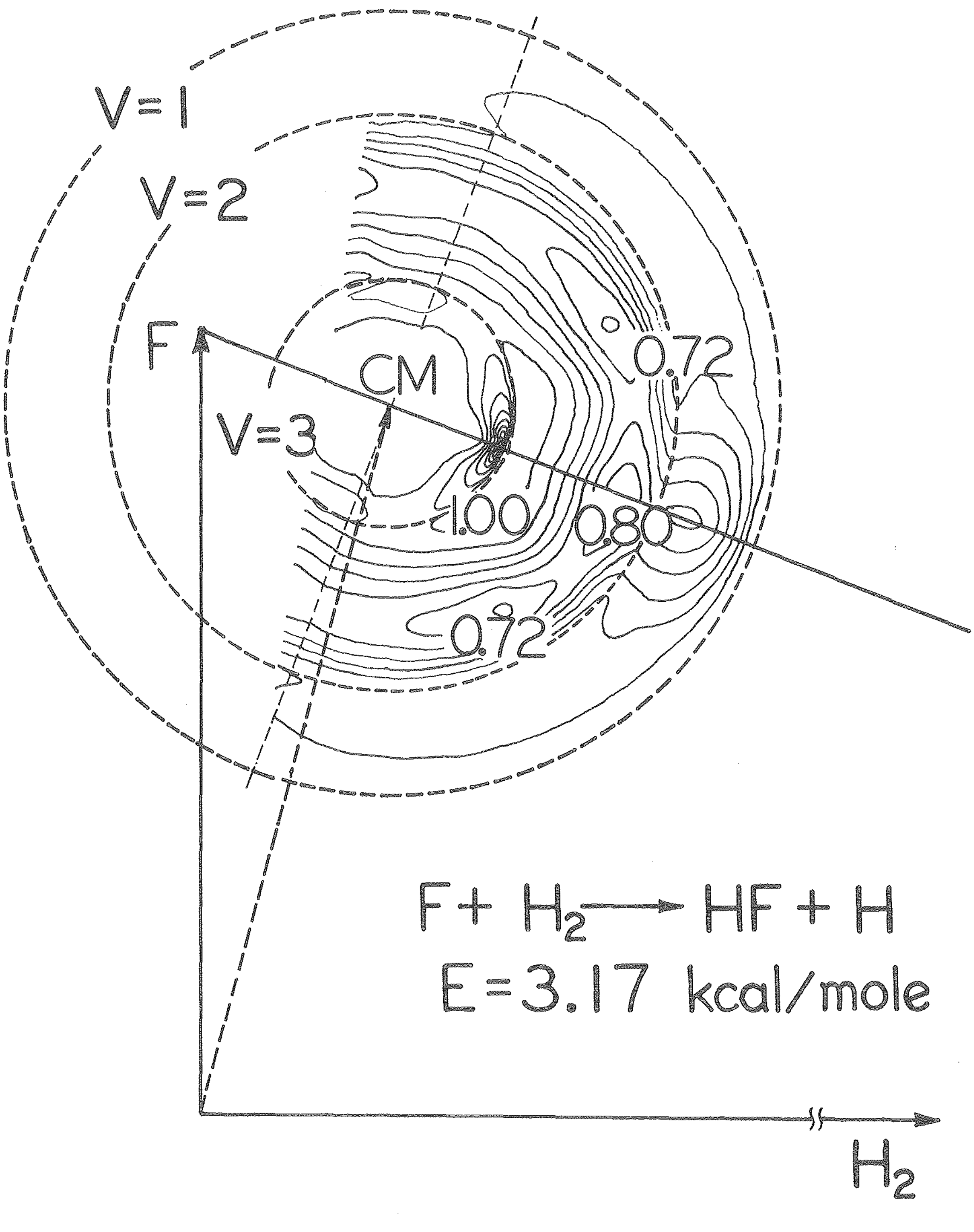
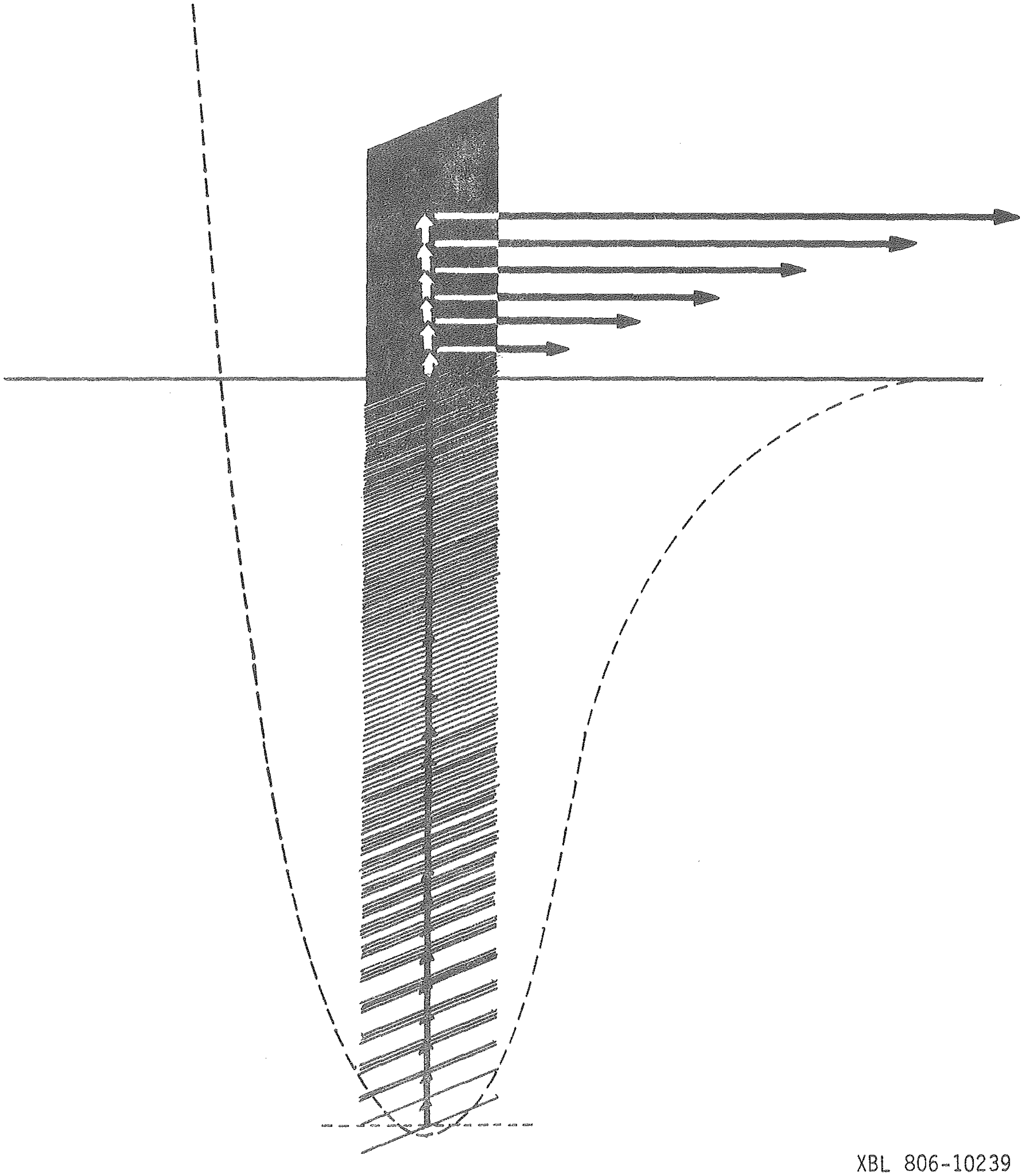
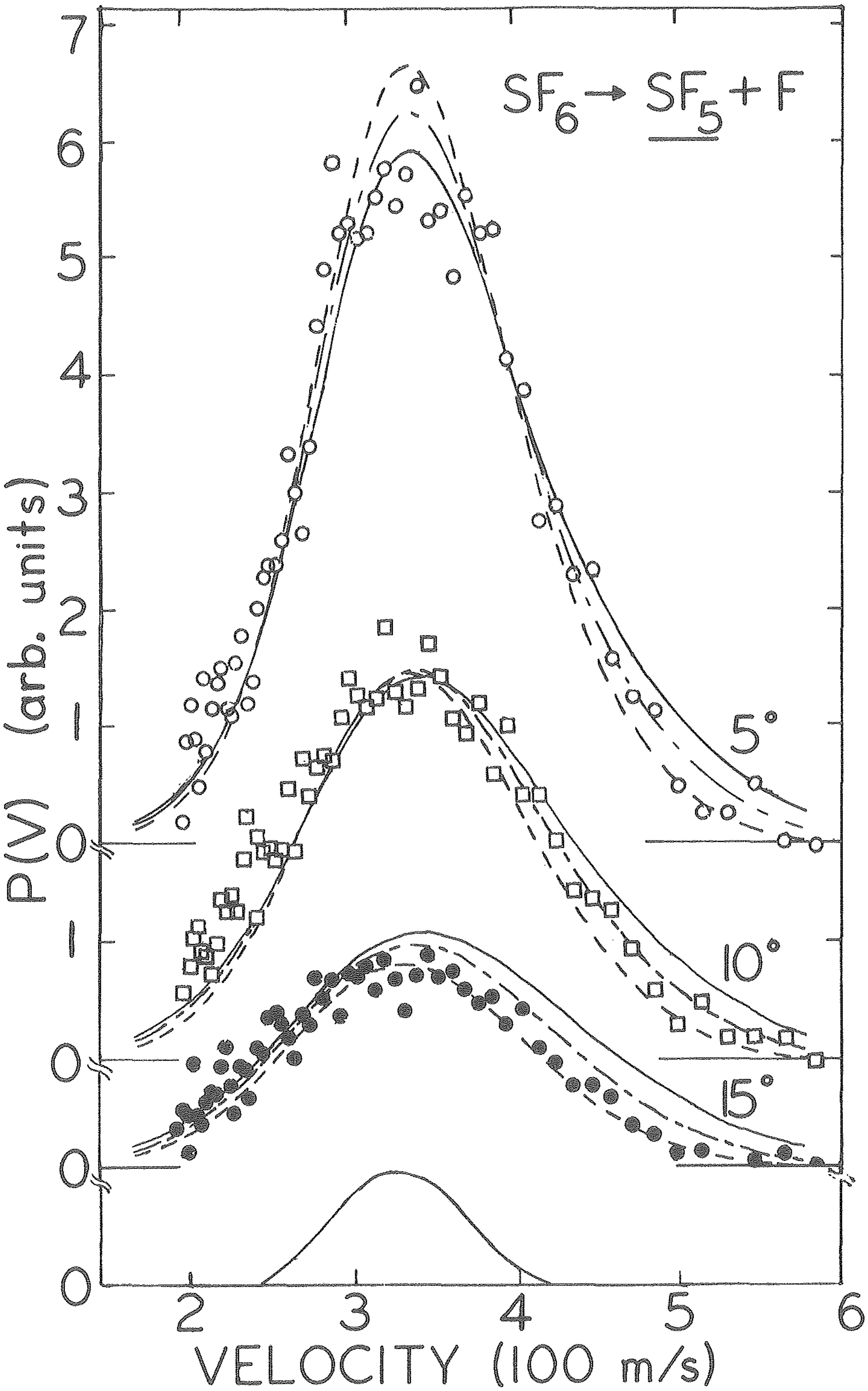


Fig. 3b XBL 7910-12376



XBL 806-10239

Fig. 4



XBL 792-8359

Fig. 5a

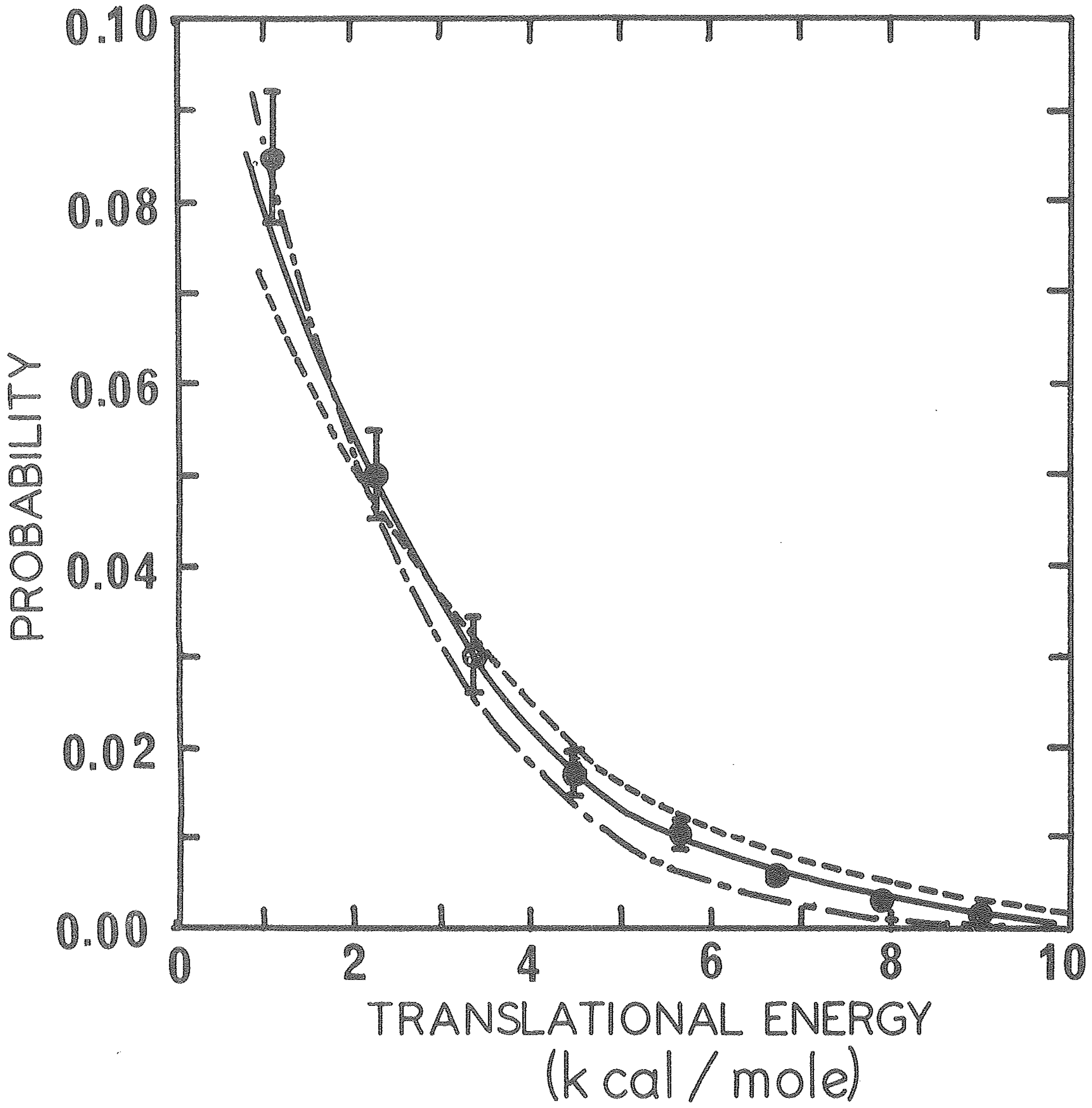
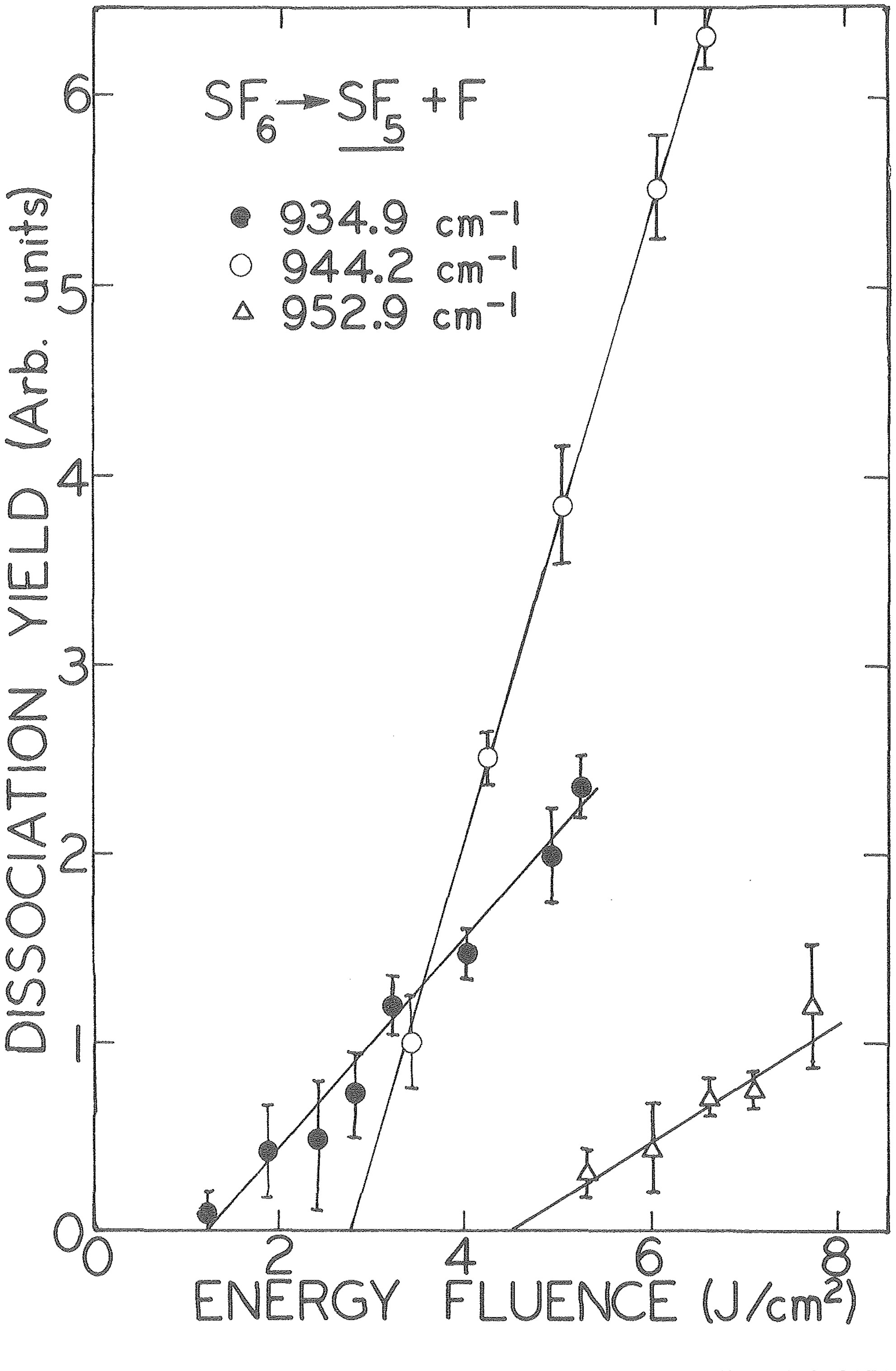


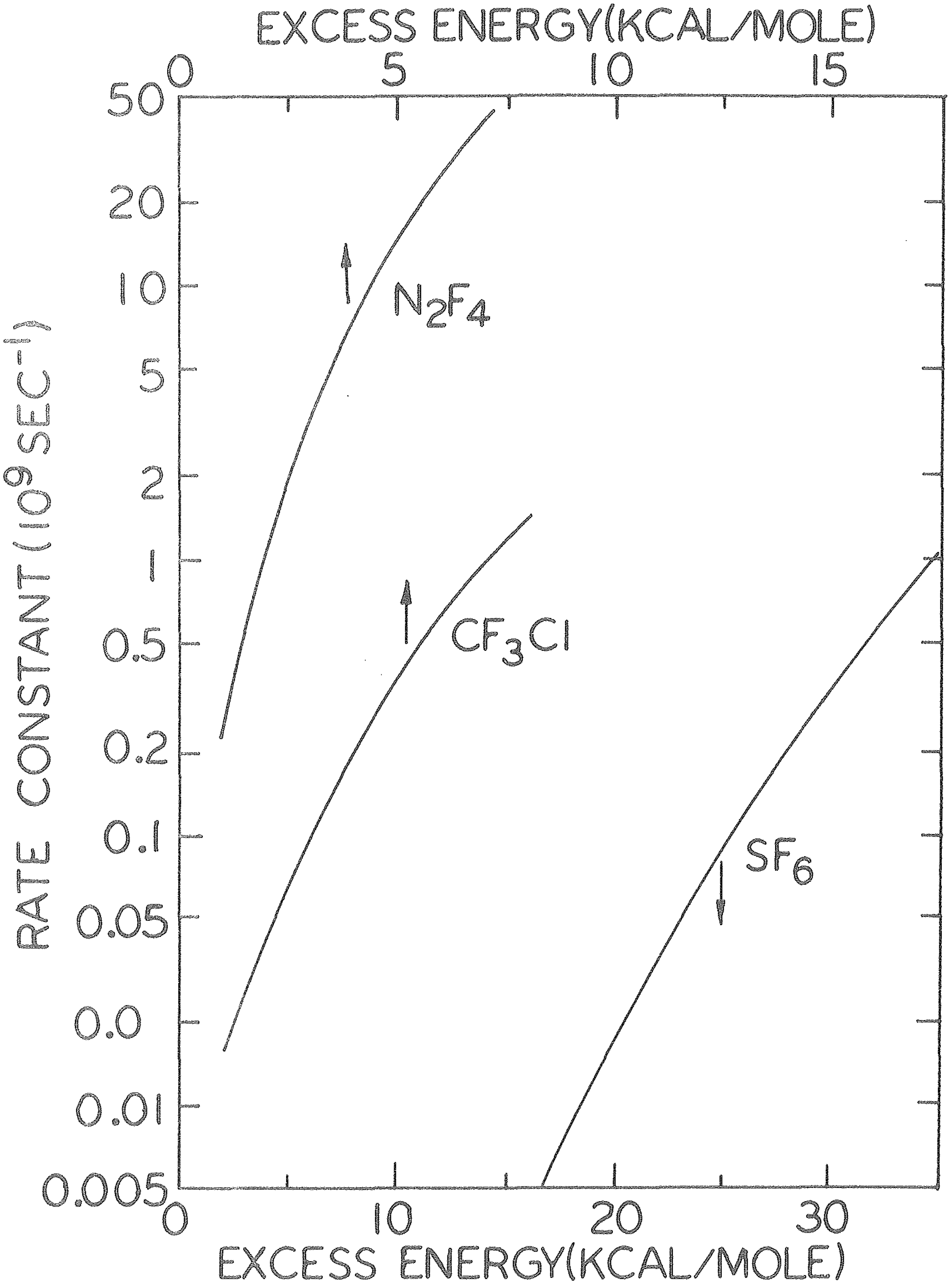
Fig. 5b

XBL 771-7431



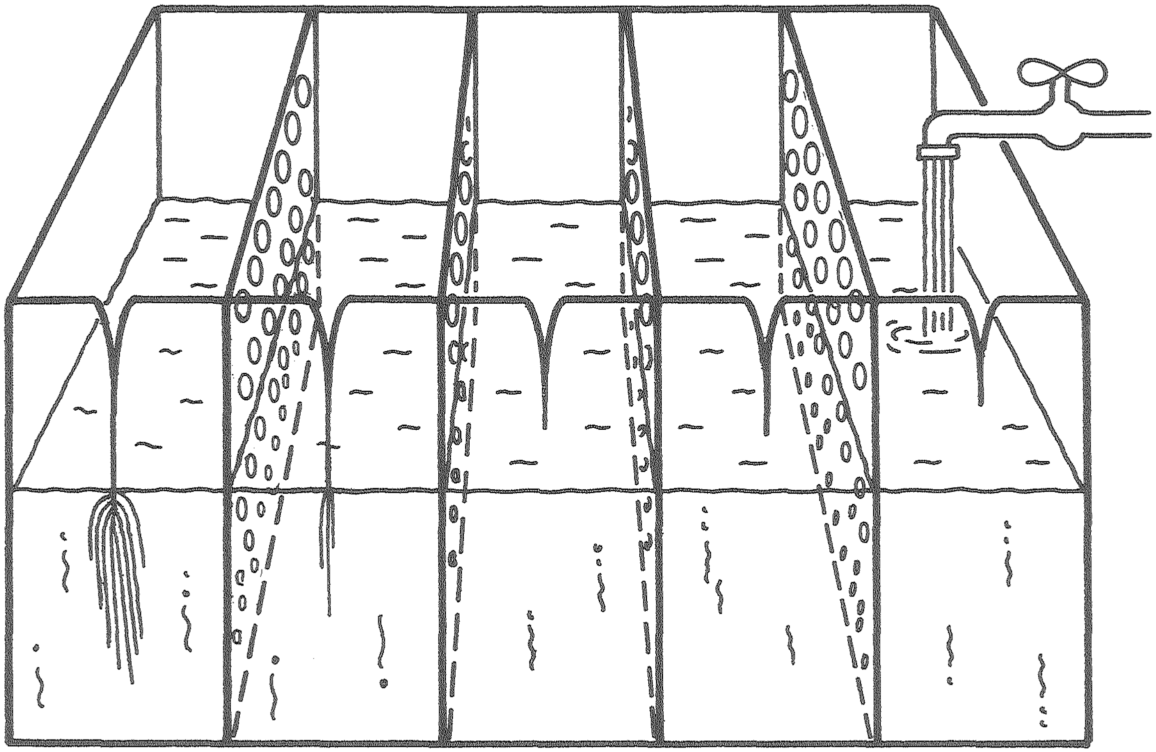
XBL 792-8358

Fig. 6



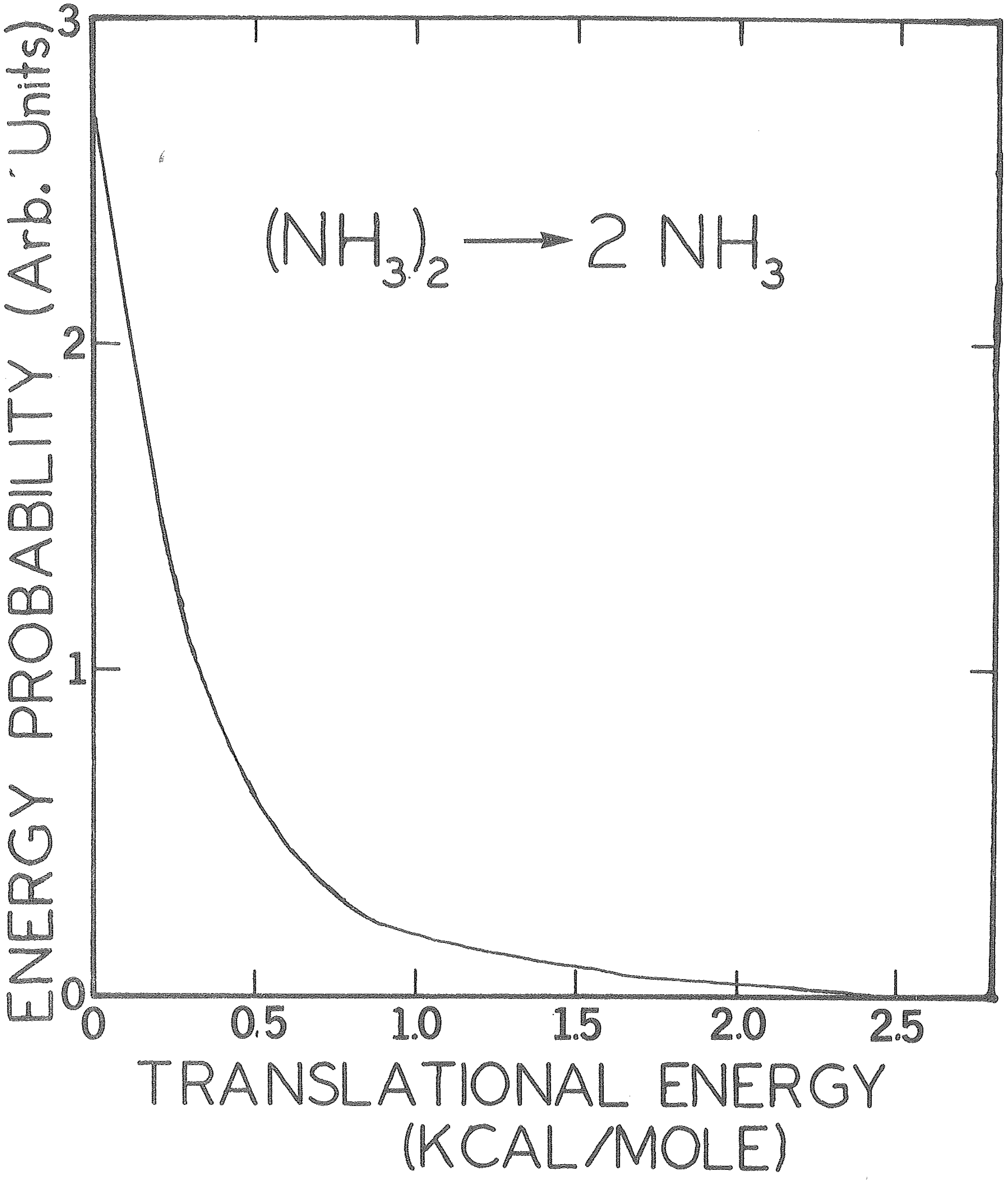
XBL 806-10238

Fig. 7



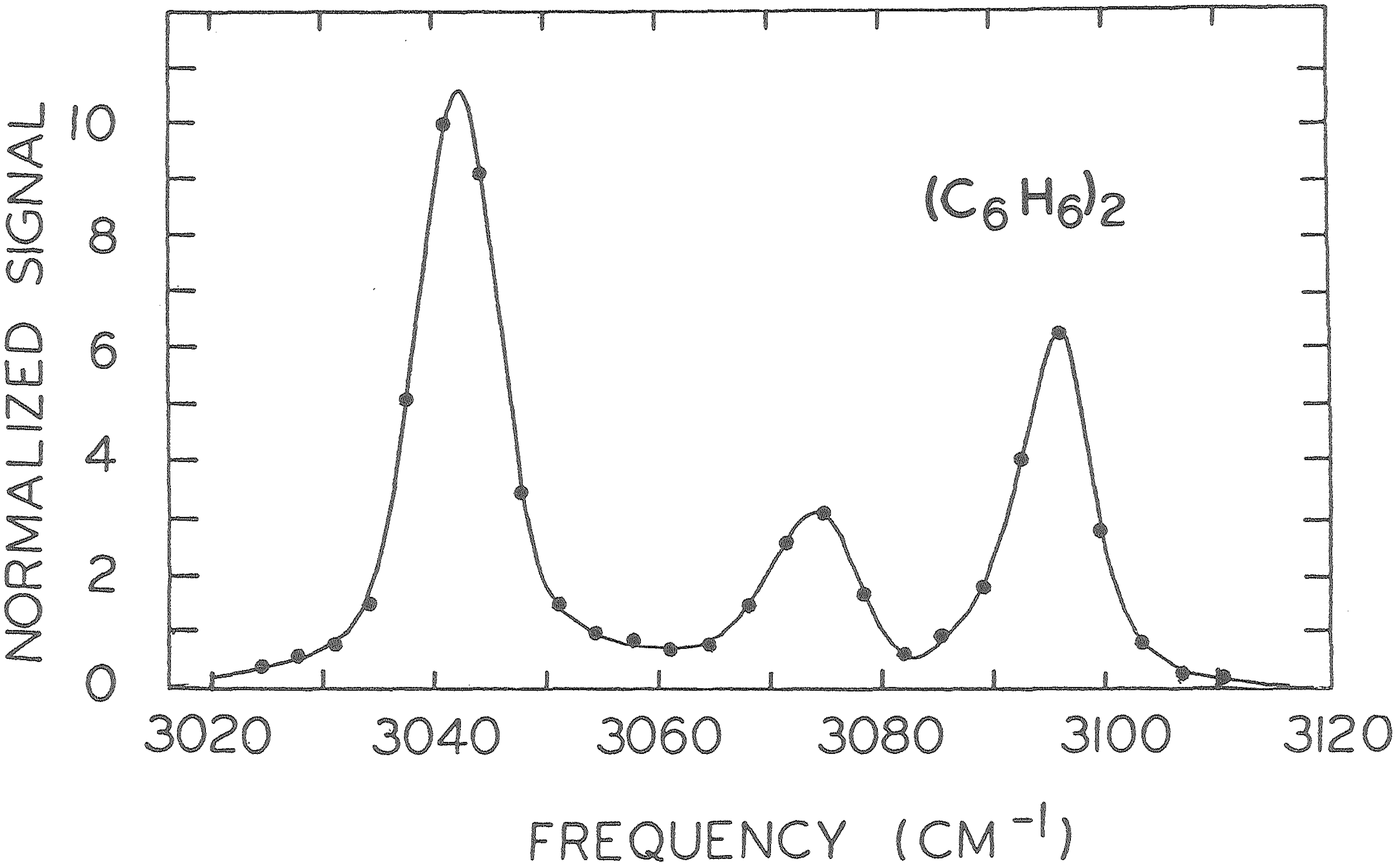
XBL 806-10237

Fig. 8



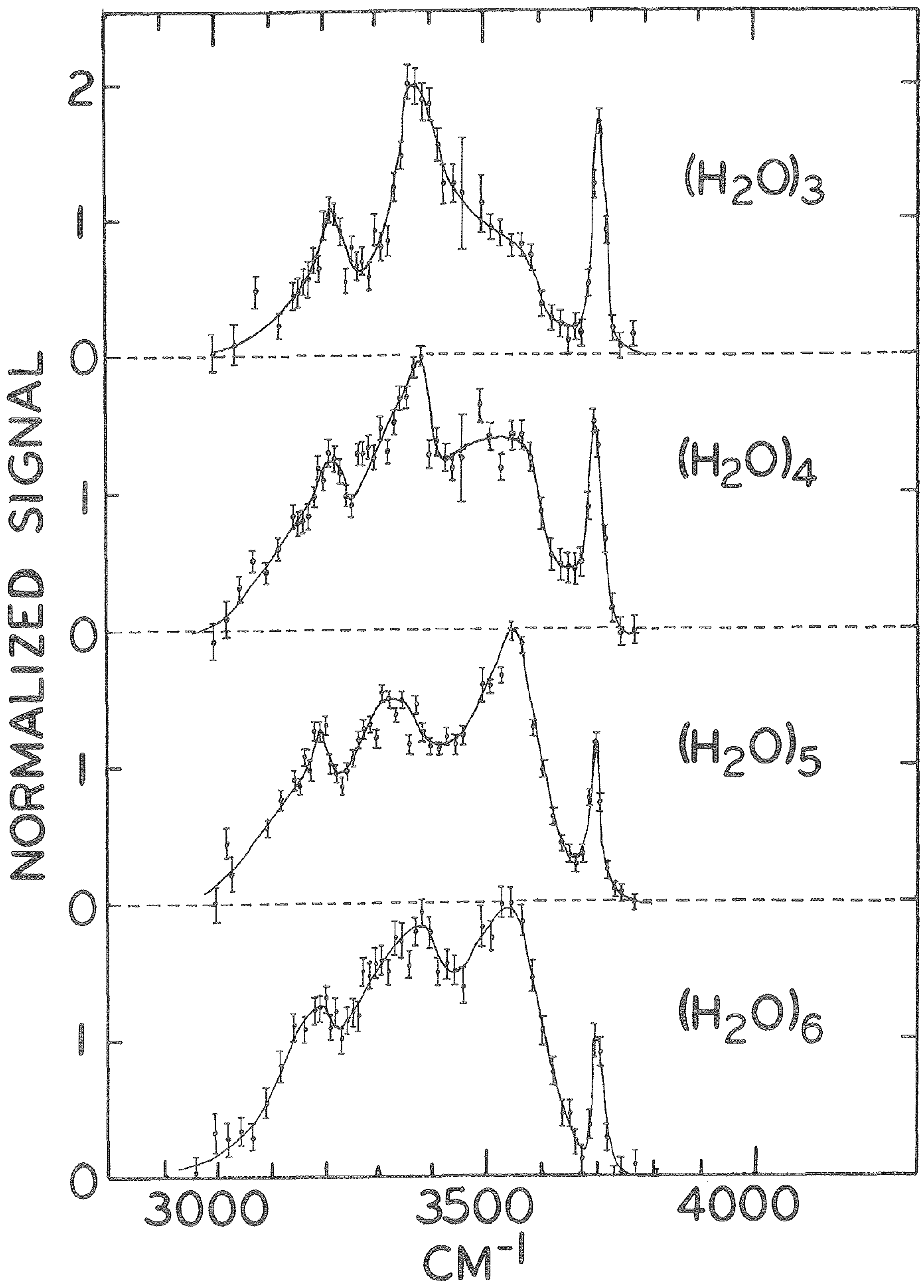
XBL 783-7705

Fig. 9



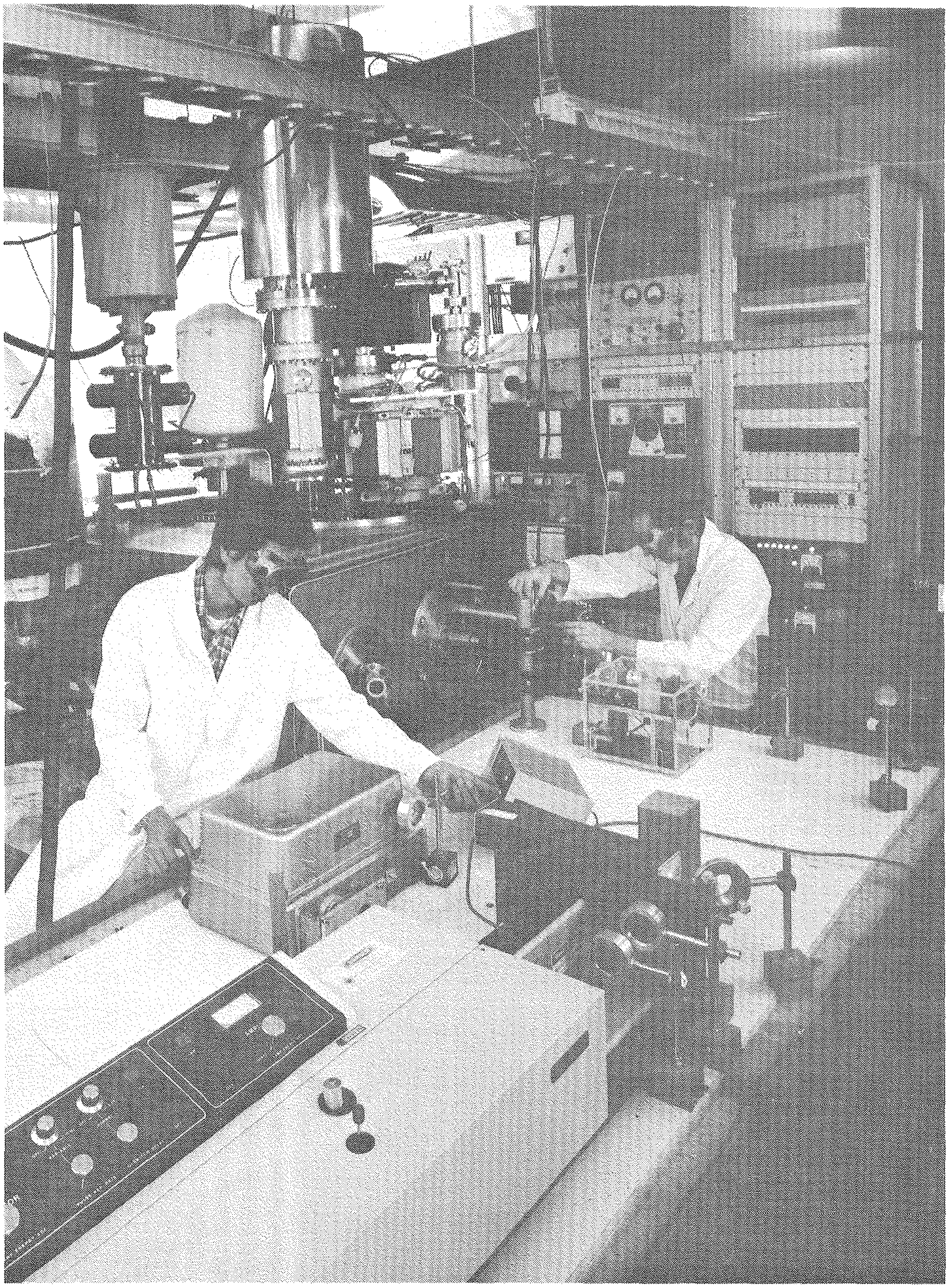
XBL 806-10236

Fig. 10

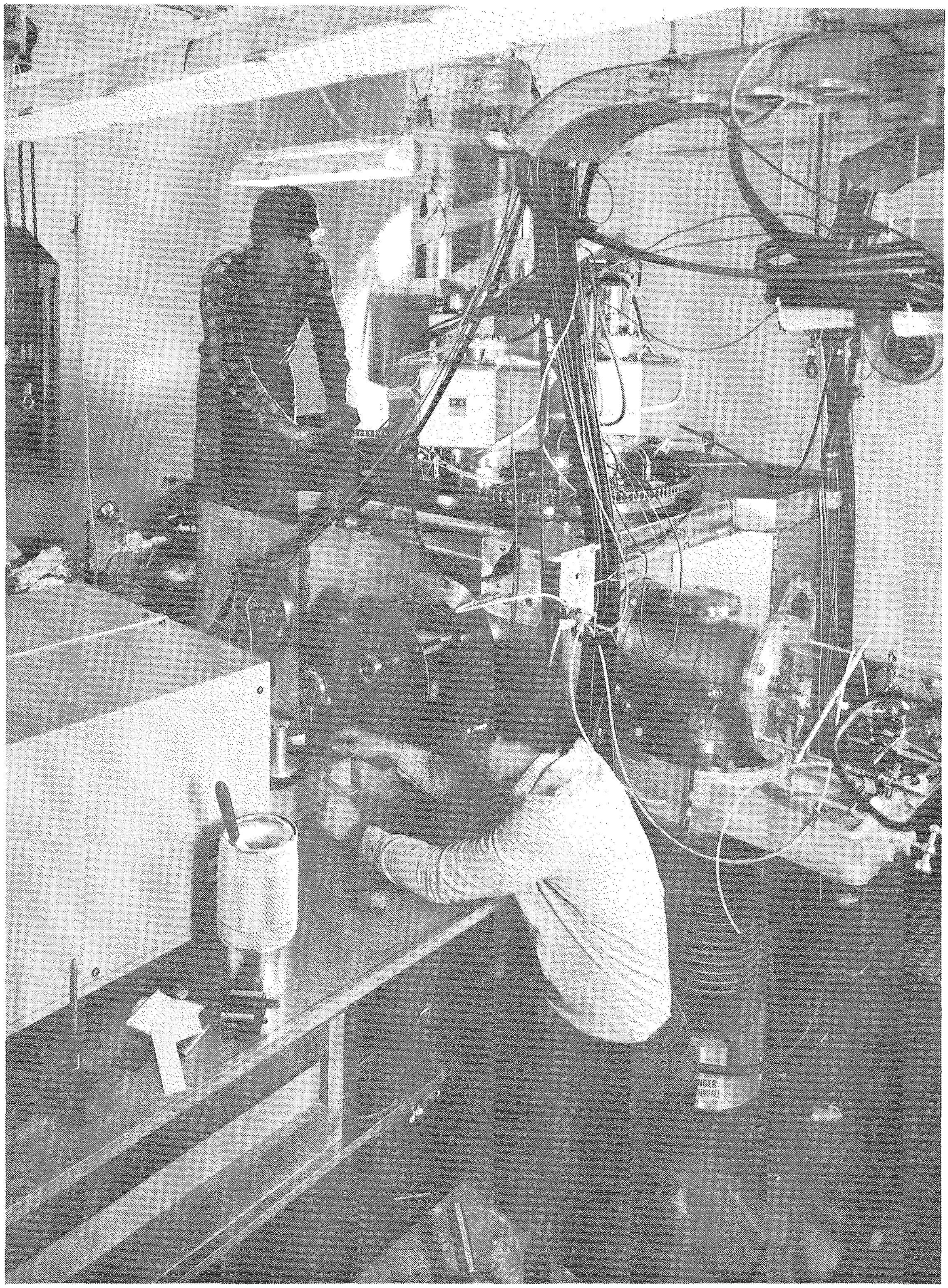


XBL 806-10235

Fig. 11



CBB 806-7058



CBB 806-7056