

Vibrationally Induced Dynamics in Hydrogen-Bonded Complexes

R. E. MILLER

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599

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Introduction

It is well-known that the vibrational degrees of freedom of a polyatomic molecule play a central role in determining its unimolecular chemistry. For this reason there exists a vast literature dealing with the vibrational dynamics of polyatomic molecules over a wide range of energies.¹⁻⁵ At the high-energy extreme, where chemical bond breaking can occur, the dynamics of a large molecule often can be described in terms of statistical theories, such as RRKM theory.⁶⁻⁸ In RRKM theory, the energy is assumed to be equally distributed over all of the isoenergetic states. Even if this is not initially the case, the vibrational states are assumed to be sufficiently coupled (due to strong anharmonic and/or Coriolis interactions) so that rapid intramolecular vibrational redistribution (IVR) soon gives rise to a statistical distribution. Molecules displaying behavior of this type are often said to be in the "large"-molecule limit.

At the opposite extreme are the "small" molecules, for which intramolecular vibrational couplings are unimportant, and the vibrational states are well characterized by the normal modes (or some other set of essentially stationary states) of the molecule. As a result, these vibrational states are isolated from one another and IVR does not occur, at least on a time scale relevant to the photochemical process of interest. Between these two limits lie the "intermediate" systems for which normal modes are a good first approximation, but where a limited number of vibrational states are coupled. The effect of this vibrational coupling can be observed in experiments carried out in both the time^{4,10,11} and frequency¹²⁻¹⁷ domains. In the latter case, these couplings lead to what has been traditionally referred to as spectral perturbations.¹²⁻¹⁷ In favorable cases, the identity of all of the involved vibrational states^{14,16} can be established. The interaction between the upper state of an allowed transition and a near resonant "dark" (or optically inactive) state leads to both a frequency shift of the allowed transition and the transfer of some intensity to the transition involving the "dark" state. As a result, additional lines appear in the spectrum that would have zero oscillator strength in the absence of this coupling.^{15,18,19} As the number of coupled states increases, more transitions involving these "dark" states appear in the spectrum, until eventually a quasi-continuum of states is reached, and fine structure is no

longer observed. Under these conditions, it is difficult to differentiate between coupling to a quasi-continuum of bound states and direct coupling to the dissociative continuum. In fact, this ambiguity has led to considerable discussion of the meaning of the observed line shapes in the frequency domain when both IVR and dissociation are possible.²⁰ The problem is further complicated by the fact that in the medium to large molecule regime the rotational density of states becomes very high, so that inhomogeneous line broadening may also be important.

The "small"-, "intermediate"-, and "large"-molecule regimes can equally well be separated by using real-time experiments, as so beautifully demonstrated by Zewail and co-workers.^{4,11,21,22} In the "intermediate"-molecule regime (restricted IVR⁴), the sharing of oscillator strength between the optically active and inactive transitions gives rise to well-resolved quantum beats (beating between the fluorescence decay from more than one state), assuming that the bandwidth of the excitation laser is sufficient to encompass the coupled states in question. As the number of coupled states

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Roger E. Miller was born in Kitchener, Ontario, Canada, in 1952. He received his B.A., M.A., and Ph.D. degrees from the University of Waterloo. He then went to the Australian National University as a Research Fellow. During this period he spent time at the Max Planck Institut für Stromungsforschung and the Hahn-Meitner-Institut. In 1985 he joined the faculty of the University of North Carolina at Chapel Hill, where he is now a Professor of Chemistry. He presently holds an A. P. Sloan Fellowship. His research interests span the fields of molecular spectroscopy and dynamics.

increases, the beat pattern becomes more complex, and eventually a near exponential fluorescence decay is observed at short times. If the fluorescence lifetime is short with respect to the recurrence time, then the IVR is referred to as dissipative. This regime is clearly analogous to that which gives rise to the completely congested frequency domain spectra. In what follows, we consider the implications of these processes in the ground electronic state vibrational dynamics of a variety of weakly bonded complexes, with particular attention given to the question of the interpretation of the infrared line shapes now available for many of these systems.

Vibrational Spectroscopy of Weakly Bound Complexes

The same forces that lead to condensation of a gas at low temperature can also result in the formation of weak bonds between two or more atoms and/or molecules. Once formed, these molecules can dissociate with only modest energies of excitation. For example, excitation of a high-frequency intramolecular vibration in one of the monomer constituents can lead to the rupturing of the weak bond (vibrational predissociation (VP)).²³⁻²⁷ Due to the very nonresonant nature of the coupling between the intramolecular vibration and the intermolecular degrees of freedom, the dissociation lifetimes of these systems are generally long compared to the intramolecular vibrational period. The possibility therefore exists for other dynamical processes to occur before the molecule dissociates. In fact, considerable evidence has been gathered, from both real-time^{21,22} and frequency-domain^{15,16,28,29} experiments, which suggests that IVR can play an important role in the vibrational dynamics of some weakly bound complexes. In these cases, the competition between IVR and VP gives rise to rather complex vibrational dynamics.^{20,22}

The vast majority of data on these weakly bound complexes has come from spectra obtained in the frequency domain, usually in conjunction with free jet expansion techniques.³⁰⁻³³ Quite recently, infrared spectroscopy has become a powerful tool in the study of both the spectroscopy and dynamics of these systems.^{23,24,34-36} The generality of infrared spectroscopy results from the fact that nearly every molecule has at least one infrared-active vibrational mode. With the tunable infrared laser systems presently available, it is possible to obtain high-resolution spectra throughout the entire midinfrared region of the spectrum. In fa-

vorable cases, a large fraction of the molecules can be pumped into a well-defined excited rovibrational state, making it possible to probe the internal and translational degrees of freedom of the photofragments resulting from vibrational predissociation of a single quantum state.³⁷⁻³⁹ The combination of these state-to-state experiments and high-resolution infrared spectroscopy provides us with a very powerful approach for studying the dynamics of these weakly bound complexes.

This Account is not intended as a review of the literature on the infrared spectroscopy of van der Waals complexes, since several of these already exist.^{24,34} Instead, we will examine several issues of current interest in this field and give some indications as to what might be expected in the future. In particular, the issue of IVR versus VP in these systems will be examined in light of the most recent results.

Experimental Methods

In recent years we have seen the development of a number of important infrared spectroscopic methods which have made possible the study of a wide range of weakly bound complexes. These include the molecular beam-optothermal detection method,^{40,23,24} discussed in detail below, and direct absorption in both long path length gas cells³⁵ and free jet expansions.^{16,36} In general, the molecular beam or free jet based methods are more versatile than the cell experiments, since in the former case the molecules are cooled to very low temperatures, so that spectral congestion is largely alleviated, and the resolution is often sub-Doppler. The optothermal technique is given here as an example of a molecular beam based infrared spectroscopic method, since much of the data used to illustrate the following discussions was obtained by using this method in the author's laboratory.

The optothermal detection method⁴⁰ is based on the use of a liquid helium cooled bolometer detector (minimum detectable power of approximately 10^{-14} W) to monitor the energy of a collimated molecular beam. In the absence of laser excitation, the beam energy simply consists of the translational kinetic energy of the molecules and the surface accommodation energy. Vibrational excitation of the molecules in the beam can lead to a change in the detected energy in one of two ways. For stable species, the vibrational energy is simply transferred by the molecules to the detector, thus increasing the overall molecular beam energy. Alternatively, the molecule may dissociate upon vibrational excitation so that the resulting photofragments recoil out of the molecular beam, thus reducing the total molecular beam energy. In either case, a bolometer positioned on the molecular beam axis can be used to measure the infrared spectrum of the corresponding species by amplitude modulating and frequency scanning the laser while using phase-sensitive detection of the bolometer signal.

An important advantage of the optothermal detection method, over those based on direct absorption, comes

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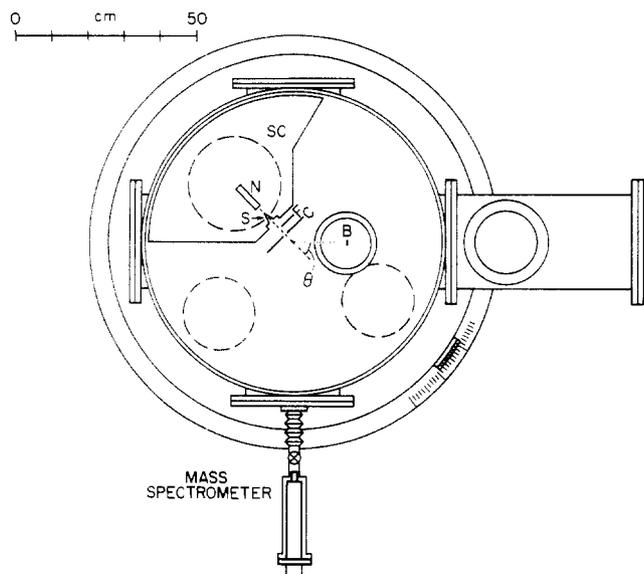


Figure 1. Schematic diagram of the molecular beam apparatus used in both the spectroscopic and angular distribution measurements: SC, source chamber; N, nozzle; S, skimmer; F, flag; C, collimator; B, bolometer; and θ , photofragment scattering angle. The laser crosses the molecular beam on the axis of rotation.

from the fact that the bolometer can be rotated about the photolysis point in order to detect the photofragments. In favorable cases, these results give detailed information on both the translational and internal degrees of freedom of the fragments.³⁷ Figure 1 shows a schematic diagram of the molecular beam apparatus which we have used for both types of experiments. When positioned at $\theta = 0^\circ$, the instrument can be used to record the infrared spectrum by simply scanning the laser. Alternatively, the laser can be fixed at the resonant frequency while the instrument is scanned in angle to record the corresponding angular distribution. An F-center laser system provides the necessary tunable infrared radiation ($2900\text{--}4400\text{ cm}^{-1}$).⁴¹

Information on the internal state distribution of the fragments can also be obtained from two-color pump-probe techniques.^{38,39} For example, pulsed infrared pump-pulsed UV probe laser methods have been used to obtain rotational-state distributions of NO produced from ground-state vibrational predissociation of systems such as Ar-NO³⁹ and NO-C₂H₄.³⁸ In a later section we will contrast the relative merits of this method with those based on angular distribution measurements.

Vibrational Coupling versus Vibrational Predissociation

Much of the confusion that has arisen concerning the relative importance of IVR and VP in the vibrational dynamics of weakly bound complexes has resulted from the low-resolution characteristic of the early infrared laser-molecular beam studies. Since the rotational fine structure was not resolved in these experiments, it was impossible to separate the contributions to the line width from homogeneous and inhomogeneous sources, let alone differentiate between IVR and VP. With the ability to obtain rotationally resolved spectra has come a much more coherent picture of the dynamics of complexes. In many cases, single rovibrational transitions

can now be observed. An example of such a spectrum is shown in Figure 2a for the C-H stretch in HCN-HF. This is clearly the spectrum of a linear complex in which the rotational structure is completely resolved and the assignment obvious. Although the observed line widths are less than the corresponding room temperature Doppler width for this species, they are somewhat broader than the limit imposed by the instrument. Close examination of the line shapes reveals that the transitions associated with the monomer are Gaussian in shape and have a width that is consistent with the laser line width and residual Doppler width, while the line shapes associated with the HCN-HF transitions are clearly Lorentzian. As is the case for a large number of binary and ternary complexes, the line widths are found to be rather insensitive to the rotational state of the molecule, although a growing number of exceptions to this rule have been found.^{42,43}

As indicated previously, broad, structureless line shapes can result either from dissociation into the continuum (VP) or from an IVR process involving a larger number of vibrational states (large-molecule limit). The question is, can we differentiate between these two processes from measurements made in the frequency domain? Strictly speaking, the answer to this question has to be no, since both give rise to identical frequency-domain line shapes. However, by looking at the large body of data now available, we can make a very convincing argument to support the claim that many of these complexes lie in the small-molecule limit (for the low excitation energies considered here), such that vibrational predissociation is primarily responsible for the observed line widths. To begin this discussion, let us consider some systems where IVR (or vibrational coupling) is clearly observed and distinguishable from the line broadening discussed above.

Perturbations due to vibrational coupling have been observed in a number of systems, including OC-HF,⁴⁴ Ar-HF,⁴⁵ NCCN-HF,⁴⁶ (HCN)₂,⁴² (N₂O)₂,⁴⁷ and (C-O₂)₂.⁴⁸ For cases where the coupling is rather weak, the individual transitions are shifted in frequency relative to what is expected from fits to the unperturbed transitions. For more strongly coupled states, the mixing can be strong enough to give the "dark" state sufficient oscillator strength to be observed in the spectrum.^{44,42} In both cases, the perturbations are highly dependent upon the rotational state since slight differences in the rotational constants of the two coupled vibrational states will cause the rotational states to tune in and out of resonance. In the case of Ar-HF,⁴⁵ where the density of vibrational states is very low, resonances of this type have been assigned to specific "dark" vibrational states of the molecule.

It is interesting to note that localized perturbations have been observed in spectra with very narrow transitions, as well as those that show extensive line broadening. Conversely, unperturbed spectra have been observed for cases where the individual transitions are

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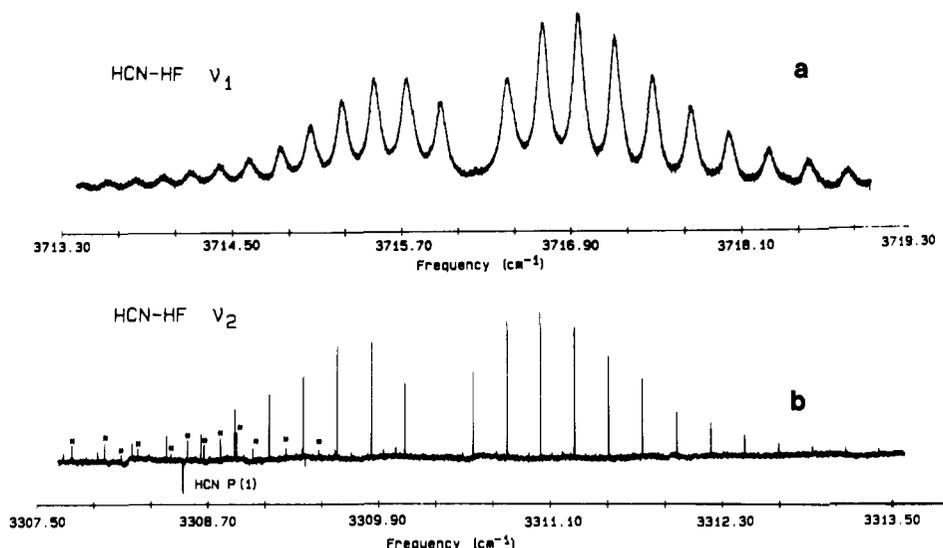


Figure 2. (a) Infrared spectrum of the C-H stretching band of the linear HCN-HF complex. (b) Spectrum of the H-F stretching mode of HCN-HF.

both narrow and broad. In no case have cluster spectra been obtained in which individual rotational transitions are split into a clump of lines.⁴⁹ As a result, in order to explain both the discrete perturbations discussed above and the homogeneous line broadening in terms of a single mechanism (IVR), we would have to assume that the transition from the "small"- to "large"-molecule limit occurs very suddenly and that, as a result, very few systems display the "intermediate"-molecule behavior. However, this seems inconsistent with the body of literature that now exists for the IVR of stable molecular species,^{4,10} which shows that the transition from the "small"- to "large"-molecule limit is smooth. That is, as the energy content of a molecule is increased, its behavior passes through all three categories.

It is also interesting to note that perturbations of the type discussed above have only been observed in binary complexes excited in the 2-3- μm frequency range, while the spectra recorded by using diode lasers at longer wavelengths show no evidence of spectral perturbations. All of this evidence suggests that these systems are indeed in the "small" to "medium" size range where intramolecular vibrational coupling is either limited to a few, relatively isolated vibrational levels, or completely absent (or, more precisely, too weak to be observed).

Further evidence exists in support of the assignment of the homogeneous line broadening to VP in the correlation that exists between the type of intramolecular vibrational mode excited by the laser, and the width of the transitions. Consider, for example, the spectrum associated with the HF stretching vibration of HCN-HF,⁵⁰ shown in Figure 2b. In this case the line width is clearly much greater than that observed for the C-H stretch. This strong mode dependence suggests that the dynamics associated with this system is far from statistical. In view of the fact that the HF is directly involved in the hydrogen bond, it is not surprising that the C-H stretch (which is remote from the hydrogen-bond coordinate) gives the longer VP lifetime. This structural correlation has now been observed in a number of systems,^{51,52} where in some cases the higher

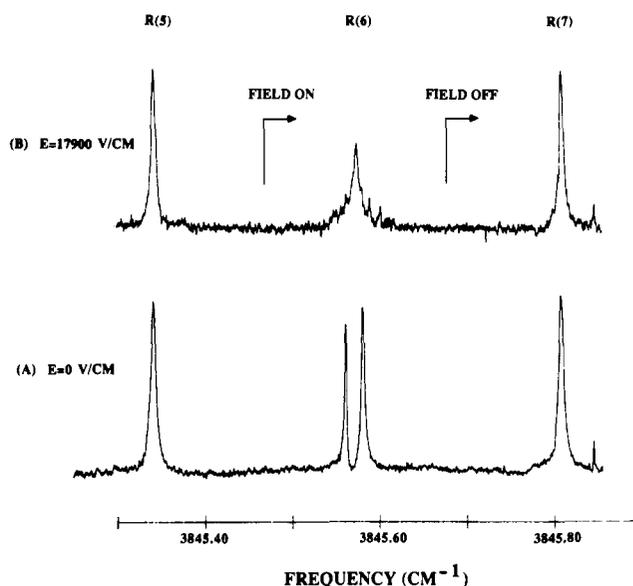


Figure 3. (a) Bottom: A portion of the R branch of OC-HF showing a strong perturbation of the R6 transition in the absence of an electric field. (b) Top: The same region of the spectrum with the field on during the scan through R6.

energy mode can even have the longer lifetime. This clearly supports the direct dissociation mechanism, where the system has some memory of the equilibrium structure up until the moment of dissociation.

The conclusion drawn from this discussion should not be that IVR is unimportant in the vibrational predissociation dynamics of van der Waals and hydrogen-bonded systems. Indeed, the recent experiments of Parmenter and co-workers²⁶ clearly show evidence for such behavior in *p*-difluorobenzene-Ar. Rather we emphasize that for "small" and "intermediate" molecules the frequency-domain observables can be used to distinguish between VP and IVR. To further illustrate this point, let us consider some recent results obtained in our laboratory for the OC-HF binary complex. Despite the very low density of vibrational states in the vicinity of the H-F stretching vibration of this molecule, the individual rovibrational transitions show substantial

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Lorentzian-type broadening. In addition, several transitions are split into two or more components as a result of localized coupling to discrete "dark" states.⁴⁴ An example of this is shown in Figure 3a for the R6 transition. As discussed in detail elsewhere,⁴⁴ the ratios of the observed line widths and integrated intensities for the two peaks are the same within experimental error. This result, taken together with the weak transition seen on the high-frequency side of R7, which is also due to coupling to other optically inactive vibrational states, suggests that the homogeneous line width associated with the dark state is much smaller than that of the H-F band responsible for the transition intensity. It is interesting to note that the R6 transition can be largely deperturbed with the application of an electric field (see Figure 3b), in which case the line width becomes comparable with that of the other unperturbed transitions. Several weak side peaks are still observed in the Stark spectrum, which must be due to a much weaker coupling to the Stark split optically inactive state. As expected, these transitions are much sharper due to the fact that they now have largely the character of the "dark" state. These strongly mode dependent line widths would clearly not be expected if the dynamics of this system were dominated by strong intramolecular coupling between a large number of vibrations, i.e., near statistical behavior.

Before leaving this subject, it is important to point out that there are systems for which the homogeneous line widths do depend upon the J and K quantum numbers. For example, in molecules that display tunneling motions, such as $(\text{HF})_2$ ⁵¹ and $(\text{H}_2\text{O})_2$,⁵³ the homogeneous line width can be quite strongly dependent upon (at least) the K rotational quantum number. Although this effect is still not well understood, this dependence is most likely associated with changes in the tunneling behavior with K and its effect on the VP dynamics. The other cases where the line widths depend upon J and/or K involve systems that show evidence of strong vibrational coupling to one or more "dark" vibrational states. The combination of wavefunction mixing and vibrational mode dependent line broadening can result in a homogeneous line width that is dependent upon the rotational state.

Up to this point our arguments concerning the interpretation of the observed line widths in the infrared frequency-domain studies have been based entirely on the spectroscopic results. In order to obtain a more comprehensive picture of the vibrational dynamics of these systems, it is clearly desirable to have information on the final states of the photofragment produced. Such state-to-state data is well-known to provide very detailed information concerning the unimolecular dynamics. In the next section we examine data of this type for the HF dimer.

Photofragment Internal State Distributions

Although the vast majority of experimental and theoretical effort in the study of binary complexes has been directed toward obtaining a detailed understanding of the structure and predissociation lifetimes of these complexes, there is clearly considerable interest in obtaining photofragment-state distributions. In excited electronic states there has been considerable

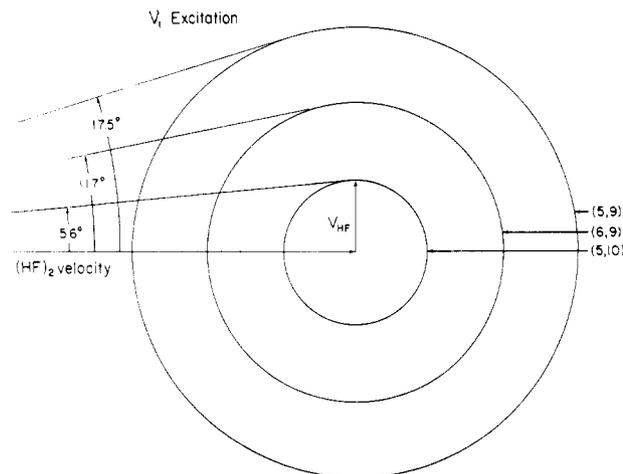


Figure 4. A Newton diagram showing the maximum laboratory scattering angles for various photofragment rotational channels.

progress in this direction,^{26,27,54} using a number of techniques. However we will continue to consider only those experiments that probe the dynamics on the ground electronic state potential surface.

The first direct experimental data dealing with the energy partitioning in photofragments (resulting from infrared excitation) came from measurements of the associated angular distributions, using both mass spectrometers,^{55,56} and bolometer detectors.⁵⁷ In all cases, the photofragments were observed to be highly peaked in the forward laboratory direction, indicating that only a small fraction of the available energy was released in the translational coordinate. These results are consistent with energy and momentum gap considerations,⁵⁸ but do not provide the desired state-to-state information, since the individual photofragment states are not resolved.

More recently, two laser pump-probe methods have been used to directly probe the rotational degrees of freedom of the NO fragments produced as a result of infrared photodissociation.^{38,39} In this case, a pulsed valve was used to generate the desired complex, while pulsed infrared and UV lasers were used to dissociate the complex and probe the fragments by laser-induced fluorescence, respectively. In this way the rotational distribution of at least the NO fragment could be obtained. For $(\text{NO})_2$ this obviously gives a rather complete characterization of the system. In general, the rotational populations obtained in this way appear to be well characterized by a Boltzmann distribution.

What is not determined in measurements of this type are the correlations between the two rotor fragments. That is to say, for any given dissociation event, the rotational states of both photofragments cannot be determined. This level of refinement in the state-to-state cross sections can be obtained in favorable cases from measurements of the photofragment angular distributions, as shown by our recent results for HF dimer.³⁷ Due to the low density of fragment rotational states, structure can be resolved in the angular distributions

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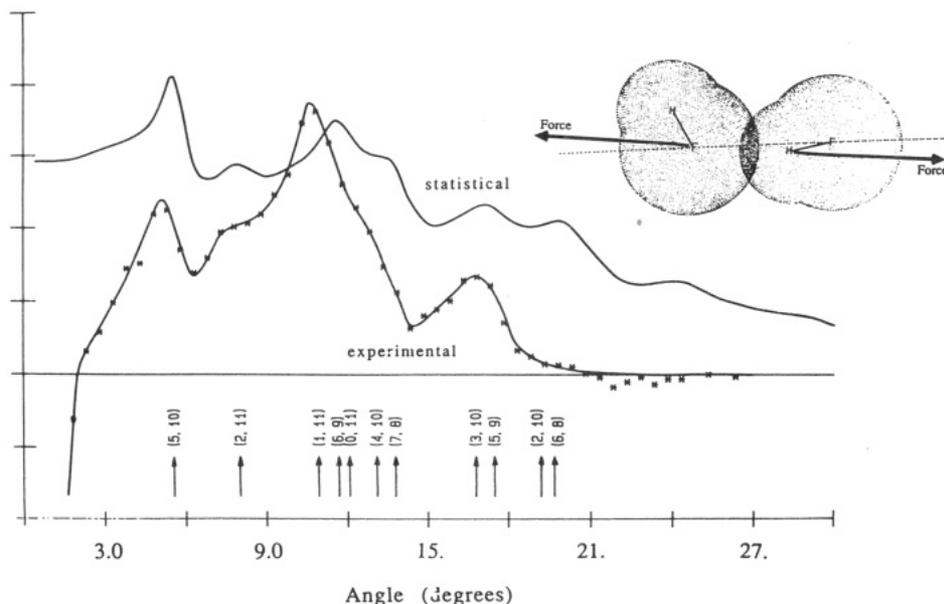


Figure 5. A photofragment angular distribution resulting from excitation of the free H-F stretch of HF dimer. The solid curve is the expected angular distribution, assuming that the final rotational channels are statistically populated. The insert shows the equilibrium structure of HF dimer and illustrates that in an impulsive dissociation the proton donor molecule becomes highly rotationally excited while the proton acceptor receives only a small torque.

measured in the laboratory frame, which can easily be assigned to individual dissociation channels. HF dimer is ideal for this type of study, owing to the large rotational constant of the monomer.

As indicated by the Newton diagram shown in Figure 4, each rotational channel for HF dimer is characterized by two rotational quantum numbers and a discrete kinetic energy release. As a result, each channel has a maximum laboratory scattering angle beyond which no photofragments can be observed. In fact, if the detector is set at a laboratory angle corresponding to the line of sight through the photolysis volume being tangent to one of the Newton spheres, there is a maximum in the detected scattered flux. The angular position and identity of the individual "cusps" can therefore be used to determine the rotational quantum numbers for both molecular fragments. An example of such an angular distribution for HF dimer is shown in Figure 5. This angular distribution results from exciting a single rotational level in the "free" H-F vibrationally excited state. When compared with a statistical calculation, such as that resulting from phase space theory (PST),⁵⁹ it is clear that the dynamics of this system is highly nonstatistical. The photofragment channels associated with the observed intensity maxima are also indicated in the figure by the vertical arrows. This assignment was obtained by varying the dissociation energy of the dimer while looking for a match between the experimental and calculated positions of the photofragment channels. In fact, a number of excited states of the dimer have been pumped, and in all cases the cusp positions are consistent with a dissociation energy (D_0) of 1062 cm^{-1} .

It is clear from the above discussion that the kinematics can be used to measure not only the photofragment rotational population distributions but also the correlations between the rotational states of the two molecular fragments. Information of this type can be used to obtain important insights into the nature of the

dissociation mechanism. In the case of HF dimer, a surprisal analysis^{60,61} shows that the preferred exit channels are those in which one HF is highly rotationally excited, while the other is in states of low J . As illustrated by the insert in Figure 5, this distribution is consistent with an impulsive dissociation mechanism (proceeding from the equilibrium structure) in which the hydrogen of the proton donor "pushes off" from the fluorine of the proton acceptor. Since the fluorine of the proton donor lies very near the center of mass of this HF molecule, the angular momentum of this fragment is expected to be small. On the other hand, the force acting on the proton donor in an impulsive dissociation is predominantly acting on the light hydrogen, which is far from the center of mass of this HF fragment. The observed correlation therefore suggests that the dissociation proceeds rapidly from a configuration reminiscent of the ground-state equilibrium structure. This is not what would be expected if, prior to dissociation, the excited HF vibrational state coupled with the bath of intermolecular vibrations via some form of IVR process, since in this case the buildup of amplitude in these intermolecular modes would tend to erase all memory of the system's equilibrium structure prior to dissociation. In this case, the two HF fragments would be less distinguishable, giving rise to a correlation in which J_1 and J_2 are more nearly equal.

Conclusions

With the advent of several new experimental methods, our understanding of both the structural and dynamical aspects of binary and ternary complexes has been greatly increased. The weak bonds associated with these systems make possible the study of unimolecular dissociation in an energy regime in which the dynamics is highly nonstatistical. This fact is reflected both in the strong intramolecular mode dependence of the vi-

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brational predissociation life times and in the state-to-state photodissociation cross sections. Coupled with the impressive advances that have been made in the fields of *ab initio* and quantum dynamical calculations, these results should soon provide us with a dynamical description of these systems at a spectroscopic level of precision. That is to say, with accurate potential energy surfaces and essentially exact quantum calculations of the dynamics, the vibrational predissociation in these systems could be described in terms of detailed vibrational coupling schemes, rather than statistical theories which tend to mask the details of the dynamics. As already demonstrated with the state-to-state experi-

ments on HF dimer, detailed information of this type provides insights into the nature of the transition state. In conclusion, although care must be taken in the interpretation of line widths obtained from the frequency-domain experiments, for the systems discussed here, there is ample evidence to suggest that direct VP is the source of this broadening.

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