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The Vibrational Spectroscopy and Dynamics of Weakly Bound Neutral Complexes

R. E. MILLER

A growing number of binary and tertiary van der Waals and hydrogen-bonded complexes are being studied by means of near-infrared laser spectroscopy. Studies of this type have generated a wealth of detailed structural and dynamical information that provides exacting tests of the corresponding theoretical methods. An additional incentive for the investigation of such clusters arises from the fact that they may be considered as intermediates between the gas and condensed phases of matter. As a result, these systems represent a fertile meeting ground for researchers from both fields and can often be studied with a variety of methods.

THE FIELD OF GAS-PHASE CLUSTER RESEARCH HAS GROWN tremendously over the past decade, to the point where a wide array of experimental (*1–6*) and theoretical (*7–10*) methods has been developed for the study of clusters. For the purposes of the present discussion, these clusters may be defined as a collection of two or more chemically bound molecules or atoms (or both) held together by weak van der Waals, hydrogen, or metallic type bonds. Much of the interest in these systems is therefore related to the fact that they represent intermediates between the gas and condensed phases (*6, 11*). Indeed, clusters of argon consisting of as few as three atoms have been shown to undergo modifications that are entirely analogous to the phase transition from liquid to solid (*7, 12*). For small molecular systems of this type, the "liquid" phase is more traditionally thought of as simply a "floppy" molecule that undergoes wide-amplitude vibrational motion, whereas the "solid" phase can be correlated with the rigid-molecule limit. In view of these associations, the study of clusters of this type provides a fruitful meeting ground for scientists from a wide range of fields, and these clusters are often amenable to study with techniques from both the gas and condensed phases.

From the computational standpoint, the advantages of studying clusters of finite size are obvious. Not only do these systems allow for the systematic inclusion of a larger number of intermolecular interactions, but the reduced computational effort, in comparison to the effort required for the bulk phases, makes more realistic calculations feasible. For example, the problems associated with the inclusion of periodic boundary conditions are eliminated. Through the systematic study of clusters, varying in size from two or three to perhaps several hundred molecules, detailed information can be obtained on the intermolecular interactions responsible for their existence. For example, although the structure of a binary complex depends on only a single pair interaction, the structure of a tertiary complex (*13*) may depend on not only the sum of the corresponding pair interactions but also the effects of three-body forces.

Binary and tertiary complexes also may be thought of as prototype systems in the study of photochemical processes. The interest here stems from the fact that the intermolecular bond is much weaker than all of the chemical bonds of the constituent molecules so that dissociation can occur at very low energies of excitation. For example, vibrational excitation of one of the constituent molecules in the complex is often sufficient to vibrationally predissociate the complex by breaking the intermolecular bond (*3*). This process occurs on a single electronic potential surface (*9*), at energies sufficiently low to enable essentially exact closed coupled calculations to be carried out in favorable cases (*14, 15*). As a result, it is possible to make quantitative comparisons between experiment and theory.

The intense activity in the field of gas-phase cluster research has given rise to a body of literature far too extensive and diverse to be discussed in a single article. In fact, even within the field of gas-phase infrared spectroscopy of clusters, the literature is quite extensive. As a result, what follows is not meant to be a critical review of the literature but rather a way of highlighting some of the more important aspects of these studies, with work from my laboratory used as illustrations. These results include the observation of rotational fine structure, which gives detailed structural information (*16, 17*), as well as of line broadening (*18, 19*) and photofragment distributions (*20, 21*), which give important new clues on the nature of the vibrational predissociation dynamics.

Experimental Methods

Despite its early application to the study of van der Waals molecules (*22*), gas-phase infrared spectroscopy has only recently become a method that is generally applicable to their study. These recent advances are mainly a result of the blending of tunable

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infrared laser methods and molecular beam techniques. Nevertheless, the first rotationally resolved near-infrared spectra of van der Waals complexes were obtained when standard grating spectrometers were used in conjuction with long-path-length gas cells. For example, Welsh and co-workers were able to obtain and assign the spectra of H_2–Ar, H_2–Kr, and H_2–Xe (*23*) in this way. This absorption method relies on the small equilibrium concentration of the complex of interest, which can be optimized by varying the pressure and composition of the gas as well as the temperature of the cell. Several factors limit the general application of this method, namely: (i) the limited resolution resulting from the use of the spectrometer; (ii) the low equilibrium concentration of the species of interest; (iii) the high temperature of the gas (relative to that obtained from free jet expansions), which makes the spectrum more congested; and (iv) obscuration of the spectrum of interest by the often overwhelming intensity of the monomer absorptions. With the advent of high-resolution Fourier transform infrared (FTIR) spectrometers (*24, 25*) and widely tunable infrared laser sources (*26, 27*), the resolution of these gas cell experiments has been greatly improved, thus alleviating at least some of the problems. The resolution obtained in these experiments is typically limited by a combination of Doppler and pressure broadening (*26*). Even here, however, the relatively high temperature of the gas cell limits the use of these methods to molecules with open rotational structure.

In both the visible-ultraviolet (*28*) and microwave (*1*) (and most recently in the infrared) regions of the spectrum, molecular beams have been used to overcome most of the remaining difficulties. Indeed, the collimated nature of the molecular beam can be used to greatly reduce the Doppler linewidth, whereas the lack of collisions ensures that the effects of pressure broadening are negligible. As a result, the full resolving power of the available laser systems can often be utilized. In addition, free jet expansion sources provide a convenient way of producing a wide variety of complexes in high concentrations and at supercooled temperatures. The opto-thermal detection technique (*29*) was the first infrared laser–molecular beam method used to study van der Waals complexes. It is based on the use of a liquid helium–cooled bolometer to measure the laser-induced change in molecular beam energy resulting from the vibrational excitation of the molecules. When the excited state of the system is stable, for a time that is long with respect to the molecular flight time from the laser crossing region to the detector, an increase in molecular beam energy is observed. This is shown schematically in Fig. 1A and gives rise to a "positive" bolometer signal. For complexes that vibrationally predissociate (*2, 3*) before reaching the bolometer, the result is a "negative" bolometer signal since the translational energy of the fragments is missing from the molecular beam (Fig. 1B). In the experiments carried out in our laboratory, a tunable *F*-center laser (10-mW output power) is used to vibrationally excite the molecules of interest. The high sensitivity of the bolometer detector (minimum detectable power of approximately 10^{-14} W/$\sqrt{\text{Hz}}$) makes this method applicable to a wide range of van der Waals complexes (*3, 13, 17, 18*). In practice, less than a million excited molecules per second (at 4000 cm^{-1}) are needed to detect a signal.

Although direct absorption techniques have been used to study stable molecules in molecular beams (*30*) and free jets (*31*) for a number of years, the improved sensitivity obtained with pulsed jets (*16, 32*) and pulsed slit expansions (*19*) has made it possible to study weakly bound complexes. Indeed, spectra of this type have been reported from a number of laboratories; the techniques include diode (*16*), difference frequency (*19*), and *F*-center (*32*) lasers, all of which show resolved rotational fine structure. In the case of a pinhole expansion source, however, the resolution is again limited by Doppler broadening because the laser crossing occurs in the uncollimated expansion. This situation can be improved somewhat with the use of slit nozzles that give rise to nearly one-dimensional expansions (*19*). In this case the laser is directed along the axis of the slit so that the molecular velocity along the direction of the laser beam is small.

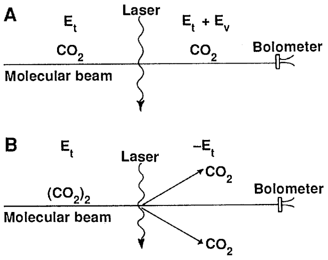


Fig. 1. (**A**) The opto-thermal detection method as applied to a stable molecule, thus yielding a "positive" bolometer signal. (**B**) Vibrational predissociation of $(CO_2)_2$ leading to the recoil of the fragments out of the beam and hence a "negative" signal. E_t, translational energy; E_v, vibrational energy.

It is important to point out that in addition to these near-infrared methods, which are based on the excitation of an intramolecular vibration of one of the constituent monomer units, a number of far-infrared techniques (*33, 34*) have been developed for studying the vibrational degrees of freedom associated with the weak intermolecular bond. Studies of this type are important since they directly probe the details of the intermolecular potential surface.

Molecular Structure from Infrared Spectroscopy

Gas-phase molecular structures for binary [and more recently tertiary (*35*)] complexes have traditionally been obtained with microwave spectroscopy (*1*). Most noteworthy are the molecular beam electric resonance and pulsed Fourier transform techniques (*1*), which have been used to obtain structures for a large number of polar complexes. In general, these structures are obtained by analyzing the rotational structure for a number of isotopically substituted complexes. Given sufficient resolution, infrared spectroscopy can also be used to make structural determinations with the added advantages that (i) it is also applicable to nonpolar species and (ii) additional information can be obtained concerning the vibrationally excited states of the molecule. The carbon dioxide (CO_2) dimer can be used to demonstrate these points.

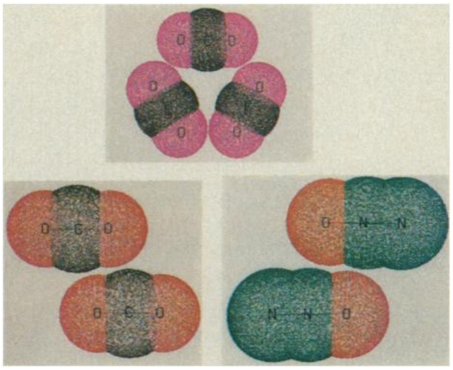
Many attempts have been made to determine the structure of this dimer by means of a variety of experimental techniques. These include two conflicting electric deflection studies, one of which indicated a polar structure (*36*) whereas the other showed no evidence for the deflection of the dimer in an electric field (*37*). In a recent infrared study of the dimer, spectra obtained for the vibrational bands, which correlate with $\nu_1 + \nu_3$ and $2\nu_2 + \nu_3$ of the monomer (*38*), unambiguously show that the geometrical structure is nonpolar. Figure 2 shows the experimentally determined structure of the CO_2 dimer, onto which are superimposed the van der Waals radii of the individual atoms. Since this "slipped parallel" geometry is similar to the molecular arrangement observed in the crystal (*39*), it is tempting to conclude that the complexes of CO_2 will simply be small "pieces" of the solid. In fact, this is not the case, as is demonstrated by the recent structural determination for the triangular CO_2 trimer (*40*), also shown in Fig. 2. The radically different structures for these two complexes suggest that the journey from the gas to condensed phases will be a very interesting and fruitful one.

In view of the similarities between CO_2 and nitrous oxide (N_2O) monomers, one might expect that the N_2O dimer structure will also be "slipped parallel." However, since the N_2O monomer is nonsymmetric, three parallel structures can be envisioned, two of which are nonpolar and possess a center of symmetry whereas the third (having the two monomer units pointing in the same direction) will have a small dipole moment. A portion of the spectrum of the N_2O dimer is reproduced in Fig. 3 along with the calculated spectrum obtained by fitting a large number of transitions to a rigid asymmetric rotor Hamiltonian. The transitions shown in the figure are associated with the perpendicular band of the dimer and can be used to emphasize a number of important points. First, the N_2O monomer transition seen at the low-frequency end of the spectrum has the opposite sign to that of the dimer transitions. This illustrates that the excited state of the dimer dissociates in a time that is short with respect to the molecular flight time.

The rotational constants obtained from the fit to the spectrum are sufficient to establish that the two monomer units are indeed parallel to one another. However, they cannot be used to differentiate among the three parallel structures. In attempting to do this it is helpful to consider the relative intensities of the various transitions. Indeed, the K-type doublets observed in the spectrum [that is, the pairs labeled $^RR_2$ (J)] reveal the presence of nuclear spin statistics, which establish a C_2 symmetry axis for the equilibrium structure. In the absence of these spin statistics the intensities of the two members of the K-type doublets should be equal. Instead, they are clearly different, with the high-frequency member of the doublet alternating with J between intense and weak. For the two centrosymmetric dimer structures the calculated spin degeneracies are 45:36 for the even to odd K_c states (each of which alternates with J between the high- and low-frequency member of the doublets). This is in excellent agreement with the observed intensity ratio, therefore eliminating the slightly polar structure. In order to differentiate between the two remaining centrosymmetric structures, rotational constants for another isotopic form of the dimer are needed. By measuring the spectrum of $(^{15}N^{14}N^{16}O)_2$, Huang and Miller have determined (*41*) that the equilibrium structure of this dimer is the one shown in Fig. 2.

The ability to obtain reliable relative intensities for the observed transitions is an important advantage in determining molecular structures. Indeed, for some favorable cases, such as CO_2–C_2H_2 (*41*), the combination of rotational constants and nuclear spin statistics can give a unique geometrical structure from a single isotopic form. In all of these structural determinations we have assumed that the weak van der Waals interactions do not appreciably distort the individual monomer units.

Fig. 2. Experimentally determined structures for $(CO_2)_3$, $(CO_2)_2$, and $(N_2O)_2$. Van der Waals radii have been superimposed on each atom.



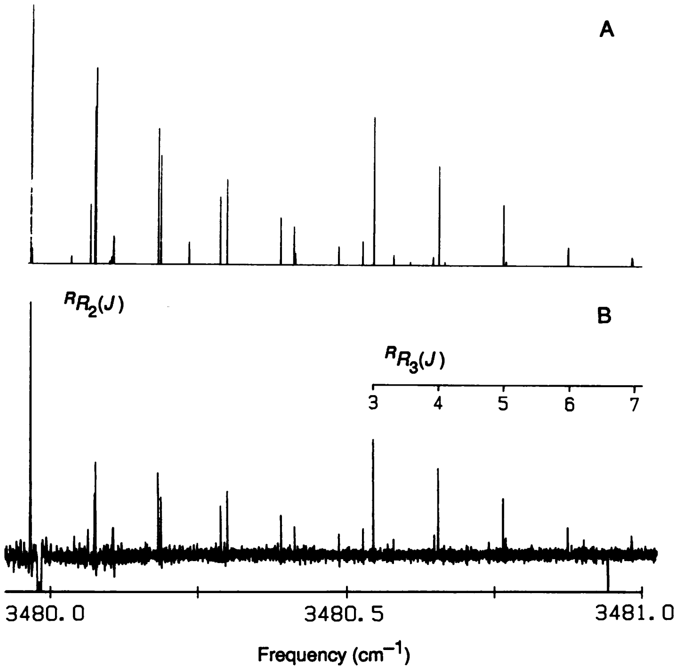
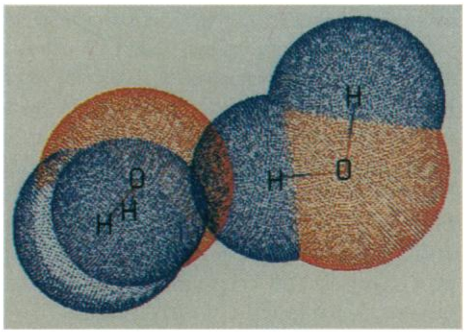


Fig. 3. A portion of the (**A**) calculated and (**B**) experimental rovibrational spectrum of the N_2O dimer. The vibrational band correlates with the $\nu_1 + \nu_3$ mode of the constituent monomer unit.

Fig. 4. The structure of the water dimer determined from microwave spectroscopy.



Hydrogen-Bonded Complexes

The water dimer is perhaps the most interesting and the most studied complex of this type, important in fields ranging from atmospheric modeling (*42, 43*) to ab initio quantum chemistry (*44, 45*). For example, considerable controversy still remains concerning the importance of the water dimer in determining the radiation balance in the lower atmosphere. On a more local scale, it has even been suggested that the dimer may play an important role in the behavior of hurricanes (*43*). The hydrogen-bonded structure of this dimer, shown in Fig. 4, was first determined experimentally from microwave studies carried out in a number of laboratories (*46, 47*). Although the more recent infrared studies have tentatively located the four O–H vibrational bands of the dimer (*48, 49*), the lack of rotational resolution in these spectra has made detailed assignments and species identification impossible.

We have recently used the apparatus discussed above to study the water dimer in the hope of obtaining rotationally resolved spectra that could be used to answer some of the remaining questions about this system and provide further tests for the existing pair potentials of water. To date, three of the four O–H vibrational bands have been observed at high resolution, and in all cases rotational fine structure has been observed. Although detailed assignment of these spectra requires the inclusion of tunneling motions between equivalent dimer geometries, several features are observed that serve to unambiguously associate it with the dimer. Since water is very light, it is likely that rotationally resolved spectra can also be obtained for complexes of moderate size. Infrared spectroscopy is particularly important in these cases since nonpolar cyclic structures are expected (*45*), and so microwave spectroscopy would be inappropriate for their study.

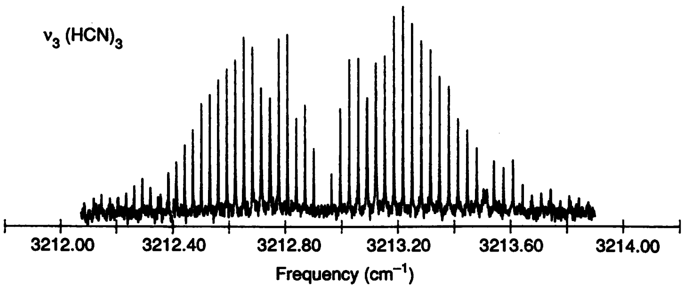
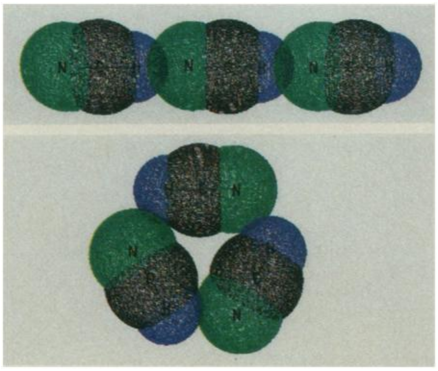


Fig. 5. The infrared spectrum associated with the "hydrogen-bonded" C–H stretching modes of the linear HCN trimer.

Fig. 6. Experimentally determined structures for the linear and cyclic isomers of the HCN trimer.



One of the most remarkable generalizations that can be made concerning the large number of structures determined to date, for both binary and tertiary complexes, is the almost universal lack of multiple isomeric forms. This is so despite the fact that the intermolecular potentials for many of these systems are not strongly anisotropic and might be expected to have more than one local minimum. For example, a semi-empirical potential for the N_2O dimer (*41*) has two local minima of comparable energy (for the two centrosymmetric structures discussed above), and yet only one is experimentally observed. Although the lack of multiple isomers may be due to the low temperatures obtained from a free jet expansion, the complete explanation undoubtedly depends on both the energetics of the clusters and the kinematics associated with the expansion.

The hydrogen cyanide (HCN) trimer is a noteworthy exception to this pattern, in that more than one isomeric structure has been experimentally observed. Both the microwave (*50*) and the infrared (*51*) studies of HCN show that the dimer is linear and that a linear trimer also exists. For example, the infrared spectrum shown in Fig. 5 corresponds to one of the trimer's hydrogen-bonded C–H stretches. It is evident from the simple *P* and *R* branch structure in this spectrum that the trimer is indeed linear, as is the molecular arrangement in the crystal, which consists of long polymer chains. In view of this, it is perhaps surprising that a cyclic isomer has also been observed under the same molecular beam conditions used to generate the linear trimer (*51*). The spectrum of this cyclic conformer is characteristic of an oblate symmetric top and can be fitted to a rigid rotor Hamiltonian to obtain the center of mass separations between the three monomer units. Figure 6 shows the two experimentally determined structures, onto which the van der Waals radii have been superimposed. The in-plane angles between the various monomer units in the cyclic isomer are not well established, whereas the out-of-plane angles are known to be small from the magnitude of the inertial defect. This complex is clearly nonpolar and hence is only observed in the infrared studies.

Recent ab initio calculations (*52*), which in fact predate the experimental measurements, also suggest that a local minimum exists on the trimer surface corresponding to a cyclic isomer. However, these calculations indicate that the linear trimer is considerably more stable. The fact that the signals observed for the two isomers are comparable, even at the low temperatures obtained in the molecular beam, suggests that their binding energies are in fact similar. The implication here is that the two hydrogen bonds in the linear trimer give approximately the same stabilization energy as the three nonlinear (and therefore strained) hydrogen bonds of the cyclic isomer. Unresolved vibrational bands are also observed for higher polymers of HCN, but for these there is no evidence for the existence of linear structures. This is most likely due to the fact that the larger complexes have more molecules in the ring so that the individual hydrogen bonds are less strained, thus making the cyclic isomers the most stable. In the crystal, the effects of molecular packing become more important than the additional stabilization that comes from the formation of the cyclic structure, thus making the linear polymer form more favorable.

Vibrational Predissociation Dynamics

As indicated in the previous sections, intramolecular vibrational excitation is generally sufficient to dissociate the weak intermolecular bond, thus making these weakly bound complexes of considerable photochemical interest. Only a single electronic surface is involved in this process, so that nearly exact dynamical calculations are often possible. In this section I give an overview of what has been learned from these infrared studies concerning the nature of this process.

Although the energy of a near-infrared photon is generally sufficient to break the intermolecular bond, the excitation energy is initially deposited into an intramolecular vibrational coordinate. As a result, before dissociation can occur, this intramolecular vibrational motion must couple to the intermolecular coordinate. It is the resulting energy "flow" that finally leads to dissociation of the complex. Our first challenge is therefore to understand the factors that are important in controlling the rate of this energy "flow."

The simplest theoretical treatments of vibrational predissociation are based on Fermi's golden rule, which can be written as

$$\tau^{-1} = (4/\hbar v_{\mathrm{cm}})[(\Psi_{\mathrm{b}}|V'|\Psi_{\mathrm{c}})]^2 \qquad (1)$$

where τ is the lifetime, V' is the portion of the molecular Hamiltonian that couples the excited state (Ψ_b) to the dissociative continuum (Ψ_c), and v_{cm} is the center of mass velocity of the fragments. This expression forms the basis of the laws for energy (*53*), momentum (*54*), and quantum number (*9*) gaps that have appeared in the literature. A general prediction of all of these laws is that the most facile dissociation channel will be the one that leads to the production of fragments having a small amount of relative translational energy. Otherwise, the localized quasi-bound state wave function (Ψ_b) has poor overlap with the rapidly oscillating continuum state wave function (Ψ_c) (that is, a short DeBroglie wavelength) associated with the fragments. This is most clearly seen experimentally in the angular distributions of the fragments. For example, dissociation of the water dimer (*20*) leads to the production of fragments that are strongly peaked in the forward direction, despite the fact that considerable excess energy is available. The implication here is that most of the excess energy is deposited into the internal (rotational or vibrational) degrees of freedom rather than into translational recoil. Although quantum mechanical calculations (*55*) support these ideas, the experimental data presently available on the internal state distributions of the fragments are limited (*56, 57*).

This is an area that will clearly receive increased attention in the future.

Consider the case of a complex that has essentially no energetically accessible fragment channels of low translational energy. It is clear from what has been said that the rate of dissociation will necessarily be slow. An excellent example of such a system is Ar–HF (*58*). Excitation of the hydrogen fluoride (HF) stretch in this linear complex gives rise to a metastable state that has a lifetime in excess of 0.3 msec, corresponding to 3.6×10^{10} HF vibrational periods. This lower limit on the lifetime is established by noting that the bolometer signal is "positive" in this case, indicating that the lifetime is longer than the molecular flight time from the laser crossing point to the bolometer. The only depositories for the excess energy (approximately 3800 cm^{-1} per molecule) are in the recoil of the fragments and the rotational degrees of freedom of the HF. For these small complexes the translational energy or momentum gaps (between the initially prepared quasi-bound state and the lowest translational energy exit channel) play an important role in determining the rate of dissociation.

Consider now what happens when the complexity of the partner in an HF complex is increased slightly, for example, to H_2–HF (*59*). For this system, the bolometer signals are found to be "negative" and the individual rovibrational transitions are homogeneously broadened by an amount corresponding to an excited-state lifetime of 27 nsec. Although the potential surface for this system is different from that of Ar–HF, such a large difference between the two does suggest that the additional rotational degree of freedom associated with H_2 contributes to the faster rate of dissociation. The reason for this may be that in Ar–HF it is difficult to conserve the total angular momentum for the case where the HF fragment is highly rotationally excited. In contrast, for H_2–HF this can be achieved by having the two diatomic fragments retreat with counterrotations, the result being that the excess energy is more easily disposed in the rotational degrees of freedom.

As the complexity of the partner in an HF complex is further increased, one finds that the lifetime changes in a much less dramatic way. For example, the lifetimes obtained for a wide range of diatomic and polyatomic partners, from H_2–HF to C_3H_6–HF, are all confined to the range 0.1 to 100 nsec. In addition, a strong correlation between the number of rotational and vibrational degrees of freedom of the partner and the lifetime of the complex is not observed. This suggests that the differences are no longer simply determined by the momentum gaps and that other factors more specific to the individual molecules must also be considered.

Thus far, the discussion of vibrational predissociation has ignored the effects of the coupling term (V') between the intramolecular vibration and the intermolecular coordinate. That is, it has been assumed that the dominant effect is simply the overlap between the two wavefunctions. Although this gives a qualitative understanding of the process and serves as a useful guide, a detailed treatment of this problem must take into account the nature of this coupling term. This fact is best emphasized by pointing out that for complexes for which more than one vibrational band has been studied, the lifetimes are strongly mode-dependent even when the vibrational energies are essentially the same. This is illustrated in Fig. 7, which shows the CH and HF rovibrational spectra of the HCN–HF complex. The large difference in the excited-state lifetimes is reflected in the linewidths associated with each. In an effort to understand this difference let us consider the structure of the complex. As expected from the simple *P* and *R* branch rotational structure seen in these spectra, the HCN–HF complex is linear, with the HF proton hydrogen-bonded to the nitrogen atom. As a result, the HF intramolecular vibration is much more strongly coupled than the C–H stretch to the intermolecular bond. Behavior of this type, which has been seen in a number of systems (*26*, *51*, *60*), can only be understood by considering the coupling term (V').

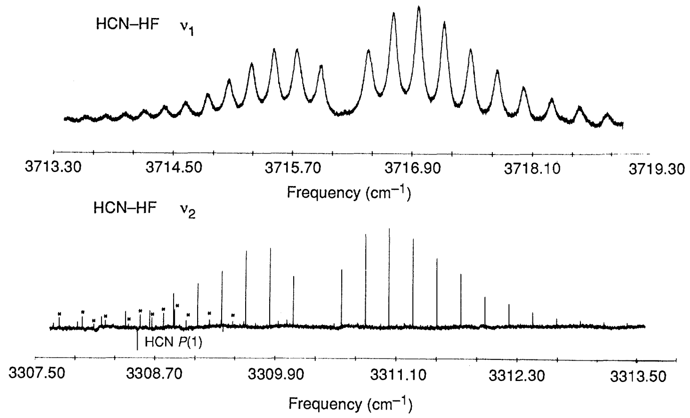


Fig. 7. A comparison between the rovibrational spectra of linear HCN–HF associated with the excitation of the HF (ν_1) and CH (ν_2) stretches. Transitions associated with the former are broad as a result of the short lifetime of the excited vibrational state.

Although it would be misleading to refer to this behavior as mode-specific chemistry, since the products of the photochemical reaction are independent of the vibrational mode excited (namely, two monomer units in all cases), these systems do show strong mode-dependent vibrational predissociation rates. As a result, one can say with certainty that the predissociation dynamics of these systems is highly nonstatistical. That is, the identity of the initially excited vibrational state is maintained for a time that is long with respect to the predissociation lifetime. In making these statements it is assumed that the effects of intramolecular vibrational relaxation are negligible, an assumption that is rather good for the systems considered here (*61*).

In view of the sensitivity of the predissociation rate to the nature of V', a prerequisite for carrying out accurate theoretical calculations is the determination of the nature of V'. One possibility is to use accurate ab initio methods to determine the intramolecular stretching dependence of the intermolecular potential. Unfortunately, the small binding energies associated with these intermolecular bonds make calculations of this type extremely difficult in all but a few favorable cases. The situation is not much better from the experimental point of view, however, since few of the experimental methods traditionally used to determine intermolecular potentials are sensitive to this stretching dependence. Fortunately, the infrared spectrum itself contains some information of this type that can at least be used to constrain the required potential surface. For example, the vibrational frequency shift associated with the formation of the complex is sensitive to the change in the intermolecular well depth upon vibrational excitation. That is to say, if the well depth increases upon vibrational excitation, which is usually the case for HF-containing complexes, the spectrum of the complex will be red-shifted from the monomer origin. This shift arises from the same intramolecular-intermolecular coupling responsible for dissociation. In fact, the vibrational predissociation lifetime is quantitatively correlated with the frequency shift, as seen in the plot shown in Fig. 8. The solid line represents a fit to the data using the functional form $\tau = K/(\text{shift})^2$. This functional form can be justified theoretically on the assumption that the translational energy released in the fragments is small so that the de Broglie wavelengths are large (*57*); this assumption now seems quite reasonable.

A second constraint on the form of the stretching-dependent intermolecular potential comes from the rotational constants determined from fitting the spectrum. In many of these linear complexes

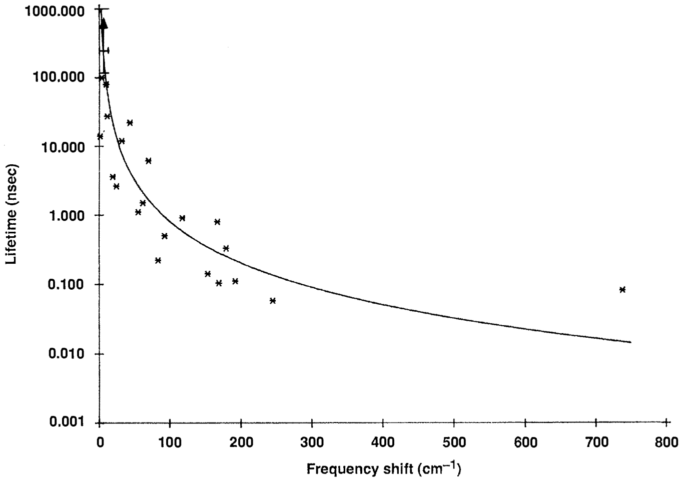


Fig. 8. Plot of the excited state lifetime versus the monomer-to-dimer frequency shift for a wide range of van der Waals and hydrogen-bonded complexes. The solid line has the functional form $\tau = K/(\text{shift})^2$.

the rotational constant is found to increase upon vibrational excitation (*20*, *57*) because of a shortening of the intermolecular bond. Data of this type are sensitive to the dependence of the position of the potential minimum on the intramolecular vibration. The stiffness of the intermolecular bond and its dependence on vibrational excitation can, in some cases, be inferred from the difference between the dipole moment of the complex in the ground and vibrationally excited states (*20*). This is due to the fact that wide-amplitude bending of a highly polar monomer subunit greatly affects the overall dipole moment of the complex. Similar information can be obtained by measuring hot-band and combination-band transitions associated with the low-frequency bending vibrations of the complex. At best, data of the type described here only give constraints on the overall potential energy surface. It remains to be seen if this will be sufficient to produce potential energy surfaces that are capable of reproducing the dynamical data now available.

Intermolecular Vibrations

Up to now, my discussion has been centered on the spectroscopy of clusters in the near-infrared region of the spectrum where the vibrations excited by the laser correlate with the vibrational degrees of freedom of the constituent monomer units. However, several far-infrared laser techniques have also been developed to directly probe the vibrational degrees of freedom associated with the weak intermolecular bond. These include direct intracavity absorption in free jets (*34*), molecular beam electric resonance (*33*), and FTIR spectroscopy (*62*). The interest in these low-frequency vibrations comes from the fact that they depend directly on the details of the intermolecular potential surface. For example, a recent far-infrared study of Ar–HCl shows evidence for the existence of a second minimum in the intermolecular potential (*34*), even though a second isomer has not been observed. A major difficulty with the far-infrared laser experiments is that the lasers are only line-tunable so that the molecule must be Startk-tuned into resonance. As a result, searching for and assigning spectra can be both challenging and taxing. This problem has recently been alleviated somewhat by making use of far-infrared–microwave mixing techniques to generate continuously tunable far-infrared radiation (*63*).

We have recently used an alternative approach to study these intermolecular vibrations in $(HCN)_2$, which is based on the observation of combination and hot band transitions in conjunction with the fundamental intramolecular vibrations already discussed. In this way, combination differences can correspond to the bending frequency in both the ground [40.7511(4) cm^{-1}] and excited [40.5520(4) cm^{-1}] "free" C–H vibrational states (where the number in parentheses is the error in the last digit). The two main advantages of this strategy are that the lasers can be easily tuned and information can be obtained on the intermolecular frequencies in both the ground and excited intramolecular vibrational states. Data of this type are of considerable value in constructing potential surfaces that include the effects of intramolecular stretching.

The Future

The application of infrared spectroscopy to the study of weakly bound complexes is still in its infancy. Nevertheless, it has already provided a wealth of information on both the structure and the dynamics of these species. The application of the various infrared methods allows for a rather complete characterization of these systems. Many more interesting complexes remain to be studied. A further challenge is in the determination of state-to-state photodissociation cross sections from the infrared methods. In principle, this would require infrared pump–infrared probe techniques, where one laser is used to dissociate the complex while a second is used to probe the internal degrees of freedom of the monomer fragments. Data of this type are needed if we are to obtain a complete characterization of this photochemical process to test the emerging theoretical methods. It remains to be seen just how well stretching-dependent potential surfaces can be constructed from the limited spectroscopic data. In practice, the ab initio methods will likely be used as a guide in constructing these potential surfaces.

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Theoretical Studies of the Energetics and Dynamics of Chemical Reactions

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Computational studies of basic chemical processes not only provide numbers for comparison with experiment or for use in modeling complex chemical phenomena such as combustion, but also provide insight into the fundamental factors that govern molecular structure and change which cannot be obtained from experiment alone. We summarize the results of three case studies, on HCO, $OH + H_2$, and $O + C_2H_2$, which illustrate the range of problems that can be addressed by using modern theoretical techniques. In all cases, the potential energy surfaces were characterized by using ab initio electronic structure methods. Collisions between molecules leading to reaction or energy transfer were described with quantum dynamical methods (HCO), classical trajectory techniques (HCO and $OH + H_2$), and statistical methods (HCO, $OH + H_2$, and $O + C_2H_2$). We can anticipate dramatic increases in the scope of this work as new generations of computers are introduced and as new chemistry software is developed to exploit these computers.

DURING THE PAST DECADE THE ABILITY OF THEORETICAL chemists to address important chemical problems has been significantly enhanced by advancements in computer technology. In 1977 the first supercomputer was introduced by Cray Research, Inc.; unfortunately, the chemistry community had only limited access to these powerful computers. In 1981 the first minisupercomputer was introduced by Floating Point Systems, Inc. The FPS-164 offered a tenth of the power of a Cray 1 supercomputer at the cost of a minicomputer (*1*); because of its speed and cost-effectiveness, the FPS-164 found widespread use in chemistry. More recently, chemists have gained access to supercomputers at the national supercomputer centers sponsored by the National Science Foundation and the U.S. Department of Energy.

During this same period revolutionary advances were made in theoretical methodology and computer algorithms for chemical computations. These developments—for example, the implementation of efficient configuration interaction (CI) algorithms based on the unitary group formalism (*2*), the development of effective many-body perturbation theory and coupled cluster techniques (*3*), and the derivation and coding of efficient techniques for computing energy derivatives (*4*) in ab initio electronic structure theory—have

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