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# The Spectroscopy of Very Cold Gases

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*Summary.* The technique of supersonic free jet spectroscopy can be used to study the structure and dynamics of molecules which have been cooled to far below their boiling points but which remain in the gas phase. Cooling of the internal degrees of freedom, the molecular rotations and vibrations, produces a highly resolved and greatly simplified molecular spectrum. The principles of the technique are discussed and its utility is demonstrated by two examples: the spectroscopy of porphyrins in the gas phase and the photochemistry of van der Waals molecules.

Spectroscopy is one of the chemist's most powerful tools for probing the microscopic details of the structure of molecules and the dynamics of chemical processes. Molecular gas-phase spectra are rich and full of structure, and the information content is high if the spectra can be understood. Unfortunately, in many cases nature has provided too much of a good thing. In all but the smallest molecules, a very large number of quantum states are populated at ordinary laboratory temperatures, each populated state may contribute several features to the spectrum, and the complete spectrum is therefore a composite of an enormous number of individual lines. Therefore under ordinary conditions many molecular spectra cannot be resolved into their individual components, and they appear to consist of broad, uninteresting features. Even in favorable cases where the spectrum can be resolved into its individual components, there may be so many lines that it is uninterpretable.

One source of the complexity in gas-phase molecular spectra is rotational fine structure. The rotational motion of molecules produces a set of energy levels that are separated by energies proportional to the reciprocal of the moment of inertia of the molecule. For light diatomic molecules rotational energy spacings are on the order of 1 $cm^{-1}$, but since the moment of inertia increases as the square of the size of the molecule, these spacings become very small as the molecular size increases (*1*). Rotational energy level spacings in simple aromatic compounds can be $10^{-1}$ to $10^{-3}$ $cm^{-1}$. Energy levels that are within a few $kT$ (*2*) of the lowest level will have a significant population, and therefore even molecules of moderate size and weight will have tens of thousands of populated rotational levels at room temperature.

A second source of complexity in molecular spectra is the population of excited vibrational levels. In a diatomic molecule there is only 1 degree of freedom, and since vibrational energy level spacings are usually hundreds or thousands of reciprocal centimeters, the ground state (zero point) vibrational level is frequently the only one that is significantly populated. As the molecular size increases the number of vibrational degrees of freedom increases, and at least some of the vibrational energy level spacings decrease. In molecules of moderate size, significant contributions to the molecular spectrum come from excited vibrational levels. This problem, as well as the rotational problem, is only aggravated by the fact that larger molecules have very low vapor pressure and must be heated to produce an observable gas-phase concentration.

## Supersonic Free Jets

Cooling the sample is an obvious solution to the problem of overly complex molecular spectra, and this is a standard spectroscopic technique. The easy availability of liquid helium has had a tremendous impact on the range of problems that can be attacked by molecular spectroscopy, and this once exotic substance is now one of the spectroscopist's standard chemicals. There are, however, some limitations on the use of ordinary refrigerants. Since gases condense as they are cooled, one must either limit the amount of cooling or be prepared to work on solid samples. Even room temperature may be too cold for the gas-phase study of many species, and essentially all substances are solids at the temperature of liquid helium. The spectroscopy of solids is an area of tremendous interest in its own right, but there are times when one wishes to study an isolated molecule free of external perturbations, and in these cases standard cooling techniques cannot be used.

During the last several years we have been using the technique of supersonic free jet spectroscopy to study the spectra of very cold gases (*3*). In a supersonic free jet, molecular vibrations and rotations are cooled to temperatures far below the molecule's freezing point. Nevertheless, little, if any, condensation occurs, and it is possible to study the spectra of internally cold isolated gas-phase molecules.

A supersonic free jet is formed when a gas at high pressure is allowed to expand through an orifice or nozzle into a vacuum (*4*). In the absence of viscous forces, heat conduction, and shock waves, the expansion is isentropic, and an isentropically expanding substance must cool.

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From a microscopic point of view, the expansion converts random thermal motion in the static gas into directed motion in the expanding gas as shown in Fig. 1. The enthalpy necessary for directed mass flow is supplied by the enthalpy that had been associated with the random thermal motion of the static gas, and therefore the enthalpy associated with the random motion is reduced in the expansion and the gas is cooled.

*Translational cooling.* The cooling that is produced directly in a supersonic expansion is a cooling of the translational motion. The translational temperature can be defined by the width of velocity distribution in the gas. In a static gas the velocity distribution in one direction reaches a maximum at zero velocity, since motion in the forward direction is just as likely as motion in the reverse direction. As shown in Fig. 2, when a static gas is cooled the velocity distribution narrows but the maximum remains at velocity $v = 0$. In a supersonic expansion the velocity distribution narrows but the maximum shifts to a nonzero value since the flow is preferentially in one direction. The translational temperature is determined by the width of the velocity distribution, not by its peak position. The distribution width is the physically interesting quantity since it determines the relative energy of collisions in the expanding gas. The gas may be moving with a high flow velocity, but if all molecules are moving at about the same velocity, collisions between them in the expanding gas will be of low energy (*5*).

The local speed of sound is proportional to the square root of the translational temperature and therefore decreases as the expansion proceeds. The local conditions are frequently described in terms of the Mach number, $M$, which is the flow velocity divided by the local speed of sound. Since the flow velocity is increasing and the speed of sound is decreasing, the Mach number increases. Past the throat of the nozzle $M > 1$ and the flow is supersonic.

As enthalpy is transferred from random motion to directed flow, the speed of sound decreases and the flow velocity increases. In the unreachable limit, all random enthalpy would be converted to flow enthalpy, the translational temperature and speed of sound would be zero, and the Mach number would be infinite. However, even in this limit, only the finite amount of initial random enthalpy would be converted to directed mass flow, and the limiting flow velocity would still be finite. In a real expansion the flow velocity rapidly approaches its limiting value and is almost constant during the rest of the expansion. In an expansion of helium initially at room temperature the limiting flow velocity is $2 \times 10^5$ centimeters per second, only a factor of 1.7 larger than the speed of sound in the static gas.

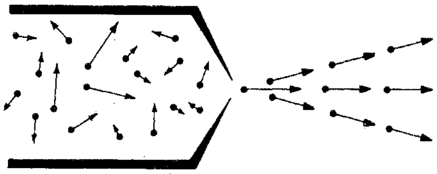


Fig. 1. Molecular velocities before and after expansion through a nozzle. Each arrow represents the magnitude and direction of the velocity of an individual molecule. The randomness in direction and magnitude that is characteristic of a hot static gas is converted into directed flow after the nozzle.

*Rotational and vibrational cooling.* If only the translational motion of a gas were cooled, a supersonic expansion would be of little use to a spectroscopist interested in cooling the internal molecular motions. However, at least in the early stages of the expansion, there are collisions between molecules, and these collisions tend to cool the vibrational and rotational degrees of freedom. In effect, the vibrating and rotating molecule finds itself in a translationally cold bath and the internal degrees of freedom are cooled by collisions just as if they had been immersed in liquid helium. In expansions that we have used we have achieved a Mach number of 150, corresponding to a translational temperature of 0.04 K, and even lower translational temperatures have been obtained by others (*6*). Thus, even by modern cryogenic standards, a supersonic expansion is not a bad refrigerant.

*Absence of condensation.* Simply obtaining low temperatures is not the object of the technique. To be useful, these temperatures must be produced in the gas phase with little or no condensation. This is possible in a supersonic expansion because the molecule of interest is in contact with the cold bath for only a short time. As the expansion proceeds downstream, the translational temperature decreases but the molecular density also decreases. Since the cooling of the internal degrees of freedom requires collisions with the cold bath, the nontranslational cooling stops when the density becomes too low to allow a significant number of collisions. Therefore the limiting temperature of the nontranslational degrees of freedom in the collision-free region is determined more by kinetics than by thermodynamics. Degrees of freedom that equilibrate rapidly with the translational bath will be extensively cooled; those that take a long time to equilibrate will remain hot.

The equilibration between translation and rotation is very fast, and it is possible to cool the molecular rotational motion to a very low temperature. Under conditions where the translational temperature is ~0.1 K, the rotational temperature will be less than 1 K (*7*). In a static gas translational-vibrational relaxation is much slower, and the final vibrational temperature in a supersonic jet is substantially higher than the final translational temperature. There is, however, appreciable vibrational cooling. We are finding that the low-energy collisions in the cold downstream portion of a supersonic expansion are very much more effective at vibrational relaxation than room temperature collisions (*8*). Therefore vibrational cooling in a supersonic expansion is much more efficient than would have been predicted from room temperature collision studies.

Condensation is a slow process both in a static gas and in a supersonic expansion, and it is this fact that makes the supersonic free jet so useful for spectroscopists. Cooling requires only two-body collisions, while condensation requires three-body (or higher) collisions to form nuclei around which condensation can take place. Ultimately condensation will occur, and this determines how cold a jet can be produced. A common method for limiting condensation is the use of a seeded mixed-gas expansion. If a small quantity of the molecule of interest is mixed with a large amount of a carrier gas, such as helium, and the mixture is expanded to form a supersonic free jet, most of the collisions will be between carrier gas atoms. When helium or other rare gases are used as carriers, the interatomic forces are much weaker than they would have been in a pure molecular expansion, and condensation is greatly reduced.

## Spectroscopic Methods

In principle, any type of spectroscopy that has been used to study static gases may be used to study samples cooled in a supersonic expansion, but in practice the spectroscopic method must be tailored to the properties of a free jet or molecular beam. If lasers were not available, supersonic jet spectroscopy would be at best a curiosity which could be demonstrated in a few favorable cases but which lacked general utility. Supersonic free jets are rarefied and small, hence their use involves a loss of sensitivity due to their low density and short path length. In part this is offset by the fact that only a few states are populated in the cold jet, and therefore the intensity that was distributed among a large number of spectral lines in the static gas is compressed into a few lines in the jet. However, even with this advantage the small number of molecules requires that a large number of photons be used if the experiment is to be successful for any but the most favorable cases.

The advantage of lasers is not just that they are powerful. The property of greatest importance is the brightness, the power per unit frequency per unit solid angle. Because it is possible to design lasers with very narrow frequency bandwidths, all of the laser photons can be used to pump a given spectral line even though the intrinsic resolution of a supersonic jet experiment is much higher than that of a static gas experiment. Moreover, the small divergence and cross-sectional area of a laser beam means that all the power can be delivered to the small volume occupied by the cold molecular jet.

*Laser-induced fluorescence.* Several forms of spectroscopy have been used to study molecules cooled in supersonic expansions. Most of the work to date has been with laser-induced fluorescence spectroscopy, either fluorescence excitation spectroscopy or dispersed fluorescence spectroscopy. The fluorescence excitation spectrum is a plot of the total number of fluorescent photons emitted by a molecule as a function of the frequency of the laser used to excite the fluorescence. As the frequency of the exciting laser is tuned through an absorption frequency, the molecule can absorb a laser photon and be pumped to an excited electronic state. Only when this has occurred can it emit a fluorescent photon as it returns to the ground electronic state, and the fluorescent photon is used only as an indicator to signal that the molecule had absorbed a photon at a particular frequency. Therefore the information contained in the fluorescence excitation spectrum is similar to that contained in the absorption spectrum. However, in favorable cases this is a much more sensitive way of doing an absorption experiment.

The dispersed fluorescence spectrum is taken by tuning the exciting laser to a particular absorption frequency, fixing the laser frequency, and measuring the number of emitted photons as a function of the frequency of the emitted photon. This provides the usual emission spectrum and has the advantage that the emission spectrum of a single excited level can be studied without the congestion produced when many levels are excited simultaneously by a broadband source.

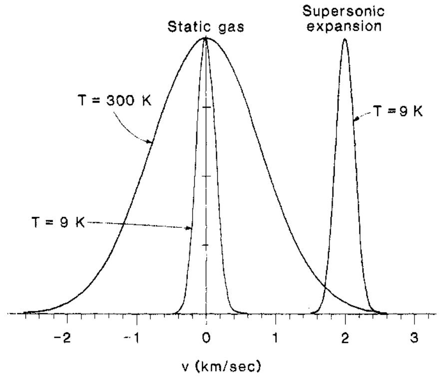


Fig. 2. Distribution of parallel velocities for helium in a static gas at room temperature, a static gas at 9 K, and a supersonic expansion at 9 K (Mach 10).

Laser-induced fluorescence is extremely sensitive if the molecule to be studied has a high fluorescence quantum yield. There are, however, nonradiative processes by which an excited molecule can return to its ground state, and if these are fast compared to radiation, the molecule will not fluoresce or will fluoresce with only a very small quantum yield. Moreover, even in cases where fluorescence can be detected, not all excited states of a given molecule have the same quantum yield, and the strength of a particular line in the fluorescence excitation spectrum will be the product of the absorption strength and the quantum yield. This may be a help or a hindrance in extracting information about the molecule. Spectral intensities are frequently used in assigning and analyzing molecular spectra, and the quantum yield dependence complicates the analysis. On the other hand, if something is known about the absorption strength either from theory or from other experiments, the observed intensity of a fluorescence excitation line can be used as a measure of the quantum yield, a quantity that is interesting to know but frequently difficult to measure.

*Nonfluorescence spectroscopy.* Several types of spectroscopy other than fluorescence have been used to study molecules cooled in supersonic molecular beams. There is a large body of literature describing the radio-frequency or microwave spectra of cold molecules (*9*). Most of this work utilizes the fact that the trajectory of a polar molecule through a series of inhomogeneous fields depends on the rotation, hyperfine, and magnetic quantum state of the molecule. Therefore, spectroscopic transitions between these quantum states will alter the molecular trajectory, and detection of particles that have traversed the new trajectory (or loss of particles from an old trajectory) can be used to signal a spectroscopic transition. A recent and apparently very powerful technique, Fourier transform microwave spectroscopy (*10*), has been used to directly detect the absorption of microwave energy.

Raman spectroscopy has been used to study cold supersonic jets. Ordinary noncoherent Raman spectroscopy (*11*) has been used to study jets of carbon dioxide, and coherent anti-Stokes Raman spectroscopy (CARS) has recently been observed by a number of groups (*12*). Undoubtedly the entire family of coherent Raman scattering techniques will be applicable to cold supersonic jets.

Direct optical absorption has now been observed in supersonic free jets (*13*). In molecules with large absorption coefficients, absorption can be detected directly even though the path length and number density of the sample are small. Additional sensitivity can be achieved by placing the supersonic free jet inside the laser cavity and detecting the effect of molecular absorption on the output power of the laser (*14*). Another promising method is the use of slit nozzles rather than circular apertures (*15*). The supersonic jet that emerges from a slit is extended in one direction perpendicular to the flow axis, and if the laser propagates along this extended direction, a greatly increased path length can be achieved.

One very promising spectroscopic technique that was recently developed and applied to supersonic molecular beams is multiphoton ionization spectroscopy (*16*). In this technique one photon (or several) is used to pump transitions between electronic states of a molecule. A second photon (or several more) is then used to ionize the excited electronic state populated by the first photon. Therefore a charged-particle detector, perhaps including mass analysis, can be used to signal the absorption of a photon between two bound states of a neutral molecule.

In the original multiphoton ionization experiments, a single laser was used to provide both pump and ionizing photons. More recently, two different lasers have been used, allowing the power and frequency of the pump and ionizing photons to be independently varied. Moreover, by using two lasers a time delay can be imposed between excitation and ionization, and dynamics of the excited intermediate level can be studied.

## Porphyrin Spectroscopy

Two problems that we have studied with supersonic jets are the spectroscopy of porphyrins and the photochemistry of van der Waals molecules. These two areas of research illustrate some of the advantages of supersonic cooling. In both cases we investigated the molecule of interest by laser-induced fluorescence excitation and dispersed fluorescence spectroscopy.

Porphyrins and related macrocyclic molecules such as phthalocyanines are of considerable interest because of their physiological importance and their importance in many technical applications, such as their use as dyestuffs. These molecules have negligible vapor pressure at room temperature, but they can be heated to several hundred degrees Celsius without decomposing. At temperatures just below their decomposition point, they have vapor pressures in the range $10^{-2}$ to $10^{-1}$ torr, and this is sufficient to allow their gas-phase spectra to be observed either in a static gas or in supersonic expansion. The static-gas spectra of porphyrins have been extensively studied (*17*), but because of the size of the molecule and the elevated temperature of the sample, only a limited amount of detail can be resolved. The spectral features are usually several hundred reciprocal centimeters wide, and in general it has been impossible to resolve vibrational structure.

*Fluorescence excitation spectrum.* A mixture of a few parts per million of a porphyrin in an inert carrier gas such as helium can be prepared by passing preheated helium over a hot sample of the porphyrin. If the resulting hot mixture is then expanded through a nozzle, the porphyrin cools internally but remains a gas. The fluorescence excitation spectrum (*18*) of free base phthalocyanine cooled in this way is shown in Fig. 3. Also shown is the static-gas absorption spectrum from the data of Eastwood *et al.* (*19*). In the cold spectrum the sharp lines have a width of less than 1 cm$^{-1}$, and it is clearly possible to resolve individual vibrational features.

The spectral congestion in the region around 16,700 cm$^{-1}$ is intrinsic to the molecule and cannot be cooled out. Metal-bearing porphyrins and phthalocyanines have fourfold symmetry and the excited electronic state involved in the visible spectrum is orbitally degenerate. Substitution of two hydrogens for a metal atom to form free base phthalocyanine breaks the fourfold symmetry and slightly splits the formerly degenerate state into two closely spaced electronic states called $S_1$ and $S_2$. To a first approximation, transitions are allowed only to the zero-point level of each electronic state and to a few excited vibrational levels. The very strong feature at 15,132 cm$^{-1}$ is a transition to the zero-point level of the lower electronic state ($S_1$), and the weaker but well-resolved features in the region 15,100 to 15,500 cm$^{-1}$are to a few excited vibrational levels of $S_1$. However, the zero-point level of the second excited electronic state ($S_2$) is close in energy to a large number of excited vibrational levels of $S_1$ and can mix and share absorption intensity with these many levels of $S_1$. Transitions that would be forbidden in the absence of this mixing become allowed, and this produces the very crowded spectrum. This is an excellent example of what is and is not possible with a supersonic expansion. If spectral congestion is due to initial population of a large number of states, cooling will simplify the spectrum. If it is caused by many transitions from a single initial state to a large number of final states, then cooling will not help. Spectra due to transitions high up on an excited potential surface where the density of vibrational levels is large are likely to be complicated even in a cold sample.

*Dispersed fluorescence spectrum.* The dispersed emission spectrum (*20*) of free base phthalocyanine is shown in Fig. 4. This spectrum was obtained by tuning the exciting laser to the strong absorption feature at 15,132 cm$^{-1}$. The emission spectrum consists of a very strong sharp feature at the same frequency as the exciting laser, plus several weaker features to the low-frequency side of the exciting frequency. The strong feature is due to a transition from the initially excited zero-point level of $S_1$ to the zero-point level of the ground electronic state ($S_0$). The weaker features are transitions from the zero-point level of $S_1$ to excited vibrational levels of $S_0$. The width of the individual emission features is due to the resolving power of the apparatus and is not intrinsic to the molecule.

In Fig. 5 we show the dispersed emission spectrum that results when the absorption feature at 15,925 cm$^{-1}$ is excited. The positions of the features in this spectrum are similar to those in Fig. 4. However, the features in Fig. 5 are appreciably broader than those in Fig. 4 even though the two spectra were taken with the same instrumental resolving power. When the molecule is excited at 15,925 cm$^{-1}$, the transition is to a vibrational level of $S_1$ with 793 cm$^{-1}$ excess vibrational energy in addition to the 15,132 cm$^{-1}$ necessary to excite the zero-point level of $S_1$. At this level of excitation the density of excited vibrational levels can be very high in a large molecule such as phthalocyanine. This dense set of levels can serve as a heat bath for vibrational relaxation of the excess vibrational energy. Therefore emission will not be from a single excited vibrational level but from a large number of relaxed vibrational levels, and this broadens the emission spectrum. The phenomenon is similar to that which occurs in a molecule trapped in a solid matrix. In the latter case, excess vibrational energy originally placed in the molecule is relaxed into the phonons of the lattice, and emission usually takes place from the relaxed zero-point level. In the case of gas-phase phthalocyanine, the vibrational relaxation is intramolecular, and the many vibrational degrees of freedom allow the molecule to act as its own heat bath. This intramolecular vibrational relaxation will occur in any large molecule with sufficient excess vibrational energy. However, the effect can only be observed by taking advantage of the increased resolution and simplification of the cold gas-phase spectrum.

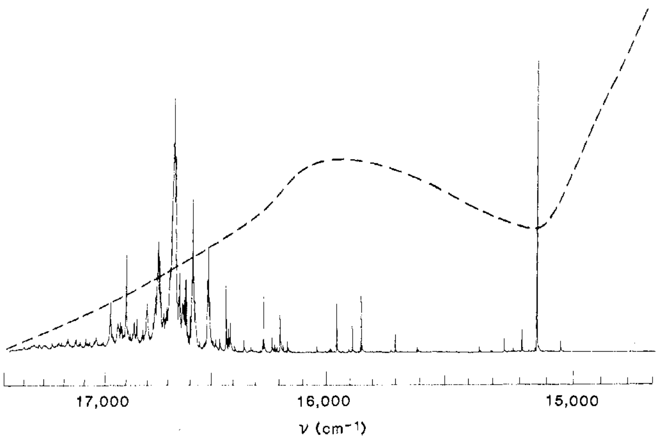
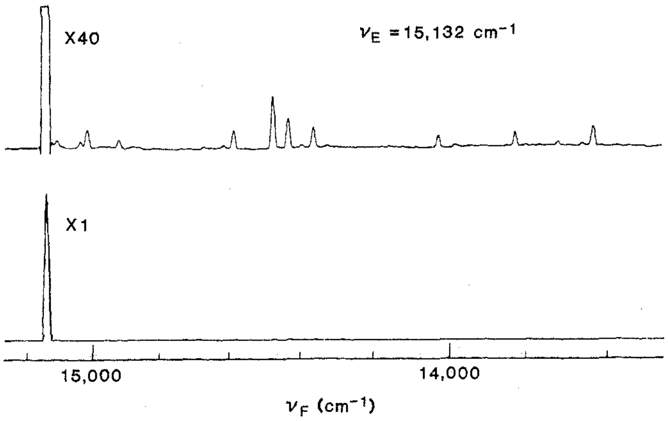


Fig. 3. Fluorescence excitation spectrum of free base phthalocyanine cooled in a supersonic free jet. The dashed curve is the static-gas absorption spectrum from (*19*).

## Van der Waals Photochemistry

A second problem that we investigated by supersonic jet spectroscopy is the photochemistry of van der Waals molecules (*21*). These are molecules that are bound, at least in part, by van der Waals forces. Because van der Waals forces are weak, they do not produce stable bound molecules under ordinary laboratory conditions. Roughly speaking, the kinetic energy of two colliding gas-phase molecules is given by $kT$. At room temperature $kT$ is larger than the binding energy produced by van der Waals forces, and any van der Waals molecule that might form would be destroyed by essentially every two-body collision. However, in a supersonic jet, where the translational temperature can be much less than 1 K, even the weakest van der Waals forces produce binding energies that are much larger than $kT$, and under these conditions van der Waals molecules are stable and can be studied spectroscopically just as chemically bound molecules can be studied at room temperature.

Van der Waals molecules can be dissociated by irradiating them with light of the appropriate frequency, and the mechanism of this photochemical reaction can be studied in great detail. When the molecule absorbs a visible or ultraviolet photon it is excited electronically. At the same time the excited electronic state may be vibrationally excited, with excess vibrational energy stored either in the relatively high-frequency vibrations of the chemical bonds or the relatively low-frequency vibrations of the van der Waals bonds. Since van der Waals bonds are weak, a few quanta of chemically



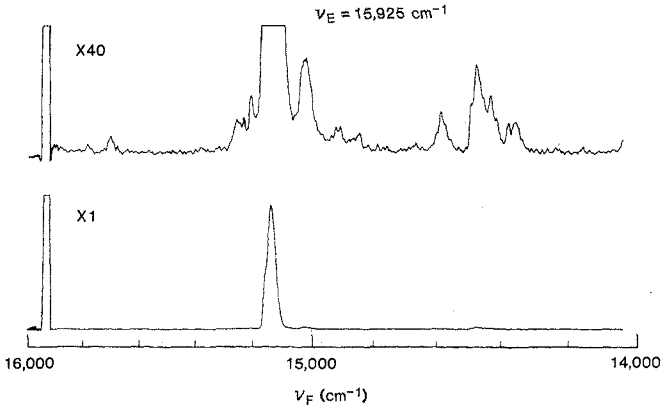
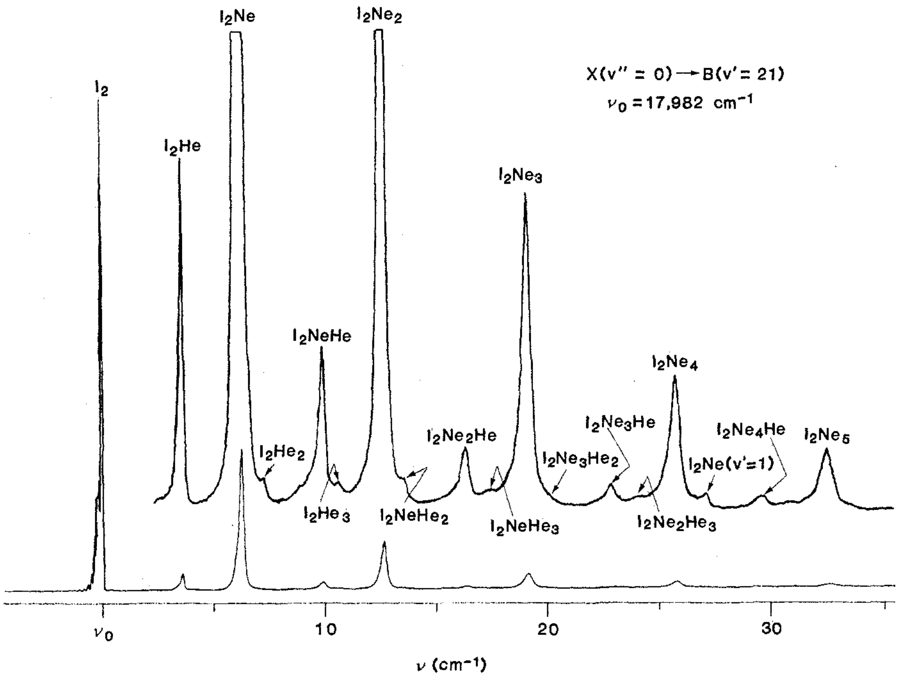


Fig. 4 (left). Dispersed fluorescence spectrum of the free base phthalocyanine excited at 15,132 cm$^{-1}$. The upper and lower traces were taken at high and low sensitivity, respectively. The spectral resolution was 9 cm$^{-1}$. The feature at the exciting wavelength is mostly fluorescence, with a small amount of scattered laser light; $\nu_E$ and $\nu_F$ are the frequencies of excitation and fluorescence, respectively. Fig. 5 (right). Dispersed fluorescence spectrum of free base phthalocyanine excited at 15,925 cm$^{-1}$. The upper and lower traces were taken at high and low sensitivity, respectively. The spectral resolution was 9 cm$^{-1}$. The strong feature at the exciting wavelength is scattered laser light.



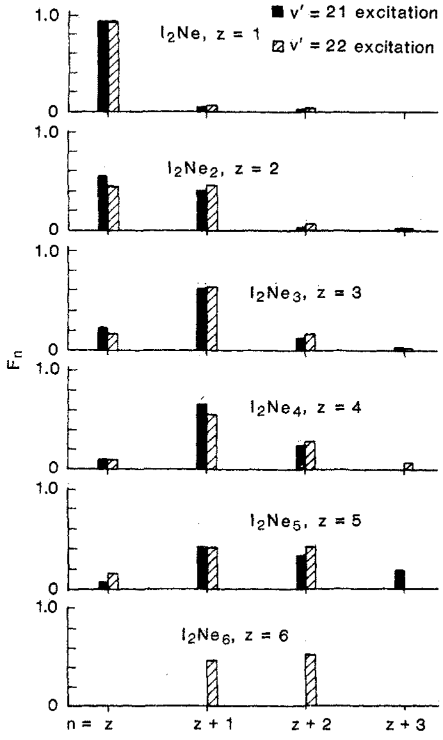


Fig. 6 (left). Fluorescence excitation spectrum of a supersonic expansion of iodine in a mixture of neon and helium. Assignment of the various van der Waals species formed in the expansion is shown. Fig. 7 (right). Relative cross sections for the process $I_2Ne_z(v')^* \rightarrow I_2^*(v'-n) + z$Ne for the complexes $I_2Ne$ to $I_2Ne_6$ excited to vibrational levels $v' = 21$ and $v' = 22$. The ordinate is the fraction $F_n$ of the population predissociating through an $n$-quantum channel.

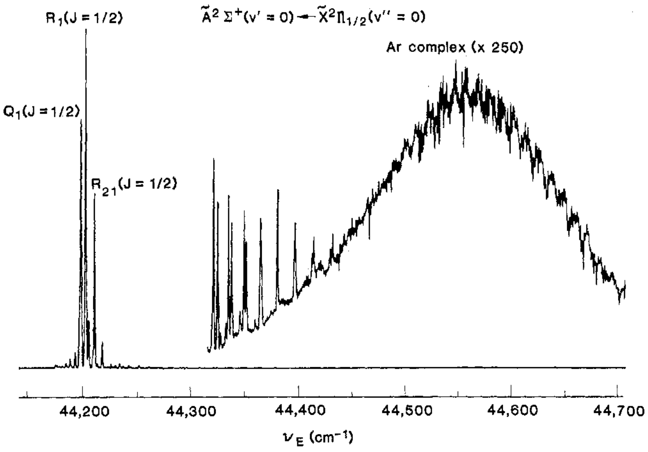


Fig. 8. Fluorescence excitation spectrum of a mixture of 2 percent NO in Ar taken at 75 nozzle diameters downstream with a backing pressure of 3 atmospheres. The upper trace is identical to that directly below it but is scaled as indicated.

bound vibrational energy may be more than the entire van der Waals binding energy. Therefore a small amount of excess vibrational energy initially stored in a chemically bound vibrational mode can dissociate the molecule if it is transferred to the van der Waals bond. Since the required excess energy is so small, the initial excitation can be very precise, involving the population of a single vibrational and even rotational level.

*Photodissociation lifetimes*. We used two spectroscopic probes to study the dynamics of the photodissociation of weakly bound molecules. The dissociation process limits the lifetime of the excited state of the van der Waals molecule, and the uncertainty principle requires that this finite lifetime produce a spectral line of increased width. By measuring the line width of the fluorescence excitation spectra of iodine–rare gas van der Waals molecules, we have been able to infer the amount of time that is required before energy flows from the initially excited storage mode, the I–I stretch, to the dissociating mode, the $I_2$–rare gas stretch (*22*). In iodine–rare gas molecules the time is on the order of tens to hundreds of picoseconds, and this means that in these molecules the vibrational energy will remain in the storage mode for hundreds of vibrational periods before transferring to the dissociating mode.

*Product state distributions*. Our second probe of the dissociation dynamics is the internal product state distribution of the electronically excited $I_2^*$ fragment produced in the photodissociation reaction (*23*). If the van der Waals molecule is initially excited so that the storage mode contains more energy than is necessary to break all the van der Waals bonds, there is a question of how the excess energy distributes itself among the various degrees of freedom of the products. In the case of iodine–rare gas complexes there are three possible product degrees of freedom: the iodine stretching vibration that initially held the energy, the rotational motion of the $I_2^*$ fragment, and the kinetic energy of the recoiling fragments.

The fluorescence excitation spectrum obtained from an expansion of a mixture of a few parts per million of $I_2$ and a few percent of neon in a helium carrier gas is shown in Fig. 6. As seen in Fig. 6, a large number of van der Waals molecules containing varying numbers of helium and neon atoms bound to an iodine core are produced in this expansion. The assignment of the spectral lines to particular molecules is based primarily on the spectral shift between the free-$I_2$ line and the van der Waals line. The principle of these assignments has been discussed elsewhere (*23*).

The internal state distributions of the products of iodine–rare gas photodissociation can be measured by tuning the exciting laser to the different absorption frequencies shown in Fig. 6 and observing the dispersed fluorescence spectra of the product $I_2^*$. We have done this for a number of van der Waals molecules (*23*), and the results for a series of iodine-neon complexes are shown in Fig. 7. For the smallest complex, $I_2Ne$, the dominant dissociation process involves loss of only one quantum of vibrational energy from the storage mode. As the complexes become larger, the number of vibrational quanta per dissociating neon increases. For example, in the case of $I_2Ne_6$, the six-quantum channel is not observed and the eight-quantum channel has the largest cross section. The extra energy per atom to dissociate the larger complexes is believed to be necessary because of the increasing number of nondissociating van der Waals modes in the larger complexes.

*Direct photodissociation*. The dissociation process in iodine–rare gas clusters is a predissociation. That is, the initial excitation is to a quasi-bound state, and some finite period of time must pass between the excitation and the dissociation. Most van der Waals molecules that we have studied predissociate from quasi-bound levels. Recently, however, we observed (*24*) the direct dissociation of van der Waals molecules consisting of NO bound to helium, neon, or argon. The fluorescence excitation spectrum of NOAr is shown in Fig. 8. The sharp strong features to the low-frequency side of the spectrum are assigned to free NO, but the broad weak feature peaking near 44,550 cm$^{-1}$ is believed to be due to NOAr. The spectroscopic transition observed here is from a bound level of the ground electronic state of the complex to a repulsive continuum in the upper electronic state. As soon as the complex is excited, the forces between the argon atom and the NO molecule switch from being attractive to being repulsive, and the molecule dissociates during the first vibrational period.

## Conclusions

Supersonic free jets and molecular beams can be used to cool the internal degrees of freedom of a molecule to temperatures far below the molecule's freezing point, but this internal cooling can be done with little or no condensation. In this way it is possible to prepare a molecular sample consisting of isolated gas-phase molecules with very low translational, rotational, and vibrational temperatures. At these low temperatures only a few rotational and vibrational states are appreciably populated, and therefore only a few states contribute lines to the molecular spectrum. This leads to a tremendous simplification of the molecular spectrum compared to that of a static gas at ordinary laboratory temperatures, and this simplification allows the resolution and analysis of the spectra of large molecules whose static-gas spectra are extremely complicated.

Two areas where supersonic cooling has been used to simplify the optical spectrum are the study of porphyrins and related molecules and the study of the photochemistry of van der Waals molecules. The use of supersonic cooling changes the gas-phase spectrum of a porphyrin from a broad unresolved electronic band hundreds of reciprocal centimeters wide to a sharp spectrum where individual vibrational features are easily resolved. We have made use of the increased resolution to pump individual vibrational features and to follow the intramolecular vibrational relaxation that occurs by measuring the broadening that it produces in the emission spectrum. Without the spectral simplification produced by supersonic cooling, it would be impossible to pump individual vibrational features, and it would be impossible to detect broadening in the emission spectrum.

Van der Waals molecules are unstable at ordinary laboratory temperatures, and therefore the low translational temperature in a supersonic jet is essential for their study. Because the spectra of van der Waals molecules are well resolved in the cold jet, it is possible to deposit energy in a specific quantum state and then to measure the rate at which this energy moves into and breaks the weak van der Waals bond. It is also possible to measure the excess energy distribution in the quantum states of the products of the photochemical reaction, and in this way one may follow a simple photochemical event in great detail. Once again, without the increased resolution produced by supersonic cooling, it would be impossible to make these measurements even it if were possible to produce the van der Waals molecule in the first place.

Supersonic jet spectroscopy is intimately connected with laser technology. The technique is now widely used by physical chemists and laser physicists, and as lasers become more reliable and easier to use, it should become increasingly attractive to scientists in other disciplines who use optical spectroscopy as a tool. The availability of fairly reliable high-power pulsed lasers has already extended the useful spectral region into the ultraviolet and near infrared, and has made available various nonlinear spectroscopic techniques such as multiphoton ionization spectroscopy and coherent Raman spectroscopy. These new spectroscopic techniques will make the use of supersonic jets attractive in a growing number of areas. Anyone who now uses gas-phase spectroscopy (including mass spectroscopy) might consider whether supersonic cooling would be an advantage. Even some problems where condensed-phase spectroscopy is now used might be better attacked through the cold gas phase.

### References and Notes

1. The unit of energy used in this article is the reciprocal centimeter, the energy of a photon with a 1-cm wavelength. Roughly speaking, electronic energy level splittings are $10^4$ to $10^5$ $cm^{-1}$, corresponding to visible or ultraviolet light; vibrational energy level splittings are $10^2$ to $10^3$ $cm^{-1}$, corresponding to infrared light; and rotational energy level splittings are $10^{-3}$ to 1 $cm^{-1}$, corresponding to radio or microwaves.
2. The quantity $kT$ is Boltzmann's constant ($1.38 \times 10^{-16}$ erg per degree) multiplied by the temperature in kelvins. In more meaningful terms, for an energy $E$ of 1 $cm^{-1}$, $E/k = 0.7$ K. One can get a qualitative feeling for which levels contribute to a molecular spectrum by assuming that a level contributes if its excitation energy in reciprocal centimeters is less than the temperature in kelvins.
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