

there are no documented cases of dangerously acidic precipitation from the high Arctic, but the effects of air pollutants may be particularly serious in the Arctic in the decades ahead [see the review by L. A. Barrie, *Atmos. Environ.* **20**, 643 (1986)]. The role of sulfate aerosols in reducing visibility at temperate latitudes is reviewed by J. Trijonis, in (26a), chap. 4.

107. F. H. Bormann and G. E. Likens, *Bioscience* **37**, 370 (1987).
108. For this review, a number of scientists contributed prepublication copies of their recent work or advice on recent publications. These include C. Asbury, L. A. Barrie, F. H. Bormann, P. Brezonik, D. F. Charles, R. B. Cook, C. S. Cronan, P.

J. Dillon, F. Elder, J. N. Galloway, E. Gorham, R. J. Hall, N. J. Hutchinson, D. Jeffries, D. Landers, G. E. Likens, R. A. Linthurst, K. H. Mills, J. Nriagu, J. P. Smol, M. E. Thompson, K. Webster, D. Whelpdale, and R. F. Wright. The manuscript was critically reviewed by L. A. Barrie, P. Brezonik, D. Charles, R. Cook, P. J. Dillon, F. Elder, J. N. Galloway, E. Gorham, R. J. Hall, R. E. Hecky, R. H. Hesslein, K. H. Mills, M. A. Turner, and D. Whelpdale. D. S. Jeffries also provided Fig. 1. E. Marshall provided invaluable assistance with the bibliography and D. Laroque assisted in keeping the manuscript updated. Supported by the Canadian Department of Fisheries and Oceans.

Infrared Laser Spectroscopy of Molecular Ions

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The development of new techniques for infrared laser spectroscopy of molecular ions has resulted in an explosion of high-quality data for important charged molecules. Velocity modulation laser spectroscopy, which exploits the motions of charged particles in electrical plasmas to eliminate interference from neutral absorbers, is rapidly producing a large body of new results for both positive and negative molecular ions. This information will have an important impact on chemistry, biology, and astrophysics.

THE STRUCTURES, PROPERTIES, AND DYNAMICS OF charged molecules are of substantial contemporary interest because of their crucial roles in such diverse and timely contexts as plasma processing of semiconductor devices, electron and proton transfer in biological systems, the formation and evolution of stars and planetary systems from interstellar dust clouds, and the chemistry and physics of planetary atmospheres. Although perhaps not seeming to be qualitatively different from their neutral counterparts, molecular ions do, in fact, present a unique set of difficult challenges to both theoreticians and experimentalists. As a consequence, it is only recently that these species have become amenable to detailed investigations. Technological innovations, such as the development of tunable infrared lasers and the explosion of large-scale computer technology, have certainly been necessary ingredients for this surge of progress, but new intellectual advances have actually been the seminal elements in the "molecular ion revolution."

In his *Science* article (1) entitled "Methylene: A paradigm for computational quantum chemistry," H. F. Schaefer described the recent advances made in ab initio quantum chemistry that have resulted in the availability of accurate and reliable theoretical predictions to guide the design and interpretation of molecular ion spectroscopy experiments. The principal impediment to experimental investigations of molecular ion spectra is simply the difficulty of obtaining sufficient concentrations to produce a detectable interaction with electromagnetic radiation. This difficulty is the result of both the inherently high chemical reactivity of charged molecules

and the elementary fact that like charges repel each other. The problems associated with producing detectable concentrations of ions have limited the spectroscopic information previously available to either optical emission spectra, which were obtained for a variety of diatomic and a few polyatomic ions, or to infrared spectra measured in highly perturbative condensed-phase environments. High-resolution techniques, such as microwave and infrared laser spectroscopy, which yield far more detailed information for individual unperturbed molecules in the gas phase (the distribution of electrons in a molecule, precise molecular geometries, and barriers to internal motions, for example) were considered inapplicable to this entire class of molecules. Even more serious was the fact that the molecular ions of greatest importance possess closed electron shells, and do not exhibit accessible electronic spectra. Then, nearly 15 years ago, two independent experimental breakthroughs occurred that dramatically changed this situation and began the molecular ion revolution.

One of these experiments, carried out by Wing and co-workers (2), combined infrared laser excitation of a velocity-tuned ion beam with sensitive mass spectroscopic detection of the ions themselves to indirectly measure the vibration-rotation spectrum of a few very simple ions (HD^+ , HeH^+ , and D_3^+) with extreme precision. Because the concentration of ions in such a beam is so small, the effects of the infrared radiation were detected by monitoring changes induced in the ion current that resulted when ions transferring their charge through collisions with a buffer gas underwent vibrational transitions. This indirect (mass spectrometric) approach has since been developed by Carrington, Moseley, and others into a general technique for measuring spectra of molecular ions in the ultraviolet-visible region as well as in the infrared. A considerable body of interesting structural and dynamical information has been obtained as a result of this important development.

Woods and co-workers (3) pioneered the other major experimental breakthrough somewhat earlier by directly measuring rotational absorption spectra of a series of simple ions (CO^+ , HCO^+ , and HNN^+) generated in an electrical discharge. By overcoming the technical problems associated with using such violent means to produce the ions, spectroscopists could take advantage of the high concentrations of ions that exist in electrical discharges because of the mutual shielding effects of electrons and ions. Direct absorption spectroscopy of several kinds of laboratory plasmas has subsequently been used for studies of many molecular ions in the microwave, infrared, and visible regions.

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Another serious difficulty concomitant to measuring absorption spectra of ions in plasmas is that the ions in these media are often outnumbered by neutral species by as much as a million to one. Hence spectra of charged molecules in discharges are often completely obscured by the much stronger absorptions of neutral molecules. This article deals principally with a technique developed by Gudeman and others in my research group at Berkeley that overcomes this problem, and has consequently allowed spectroscopists to study some of the most important molecular ions at an unprecedented level of detail.

Velocity Modulation Spectroscopy

To effectively use the relatively high concentrations of ions that exist in a plasma for making spectroscopic measurements in a general way, one must ultimately be able to detect ionic absorption signals in the presence of a large background from the more abundant neutral molecules. Such selective detection of ions in plasmas has been accomplished in three ways. Foster *et al.* (4) have developed a discharge modulation method in which the current of a hollow cathode plasma is switched on and off, resulting in a modulation of the concentration of both ions and short-lived neutral molecules in the plasma. Modulation of the axial magnetic field used to confine a negative glow plasma has been shown by Hirota and co-workers (5) to produce a corresponding concentration modulation of the ions, whereas neutral concentrations are affected only slightly. My group has developed a different approach (6) based on exploitation of the fact that the ions in a positive column plasma are accelerated by the axial plasma electric field to a net drift velocity of about 500 m/sec, which is superimposed on their random thermal motion. This net drift velocity causes the ions to exhibit a small Doppler shift in their spectral transitions. By rapidly reversing the

polarity of the discharge, spectral transitions can be Doppler-shifted in and out of coincidence with monochromatic laser radiation. As a result, the detected laser power is modulated at the same frequency at which the polarity is switched; electronic processing yields first-derivative absorption spectra of ionic transitions, whereas the much stronger absorptions of the more abundant neutral species are electronically rejected because they do not exhibit the Doppler switching effect. We call this technique "velocity modulation spectroscopy." As we shall see, the velocity modulation method possesses a significant advantage over the other two techniques in that positive and negative ion absorptions are automatically distinguished and identified as a result of the opposite velocities of positive and negative charges in an electric field. This feature, coupled with the high suppression of neutral absorptions, has led to the most recent breakthrough in molecular ion spectroscopy—vibrational absorption spectroscopy of negative ions—which will be discussed later in this article.

A schematic of the Berkeley velocity modulation experiment is presented in Fig. 1. Tunable infrared laser radiation, from either a color center laser (2850 to 4200 cm^{-1}) or from a lead-salt diode laser (350 to 3000 cm^{-1}), is directed through a velocity modulation discharge cell onto a suitable detector. The detector output is preamplified, subtracted against a reference beam to suppress low-frequency amplitude fluctuations in the laser power, and demodulated at the discharge frequency to yield the first-derivative line shapes characteristic of velocity modulation spectra. The laser frequency is measured to high accuracy with a combination of calibration gases and wavemeters. A microcomputer controls the scanning of the laser and the data processing. Both laser systems are capable of measuring extremely weak absorptions (as small as 1 part in 10^6) with an accuracy limited by the Doppler line widths (one part in 10^6).

The velocity modulation plasma cells are usually 1 cm by 100 cm, operate at pressures in the range 1 to 50 torr, and can be cooled to

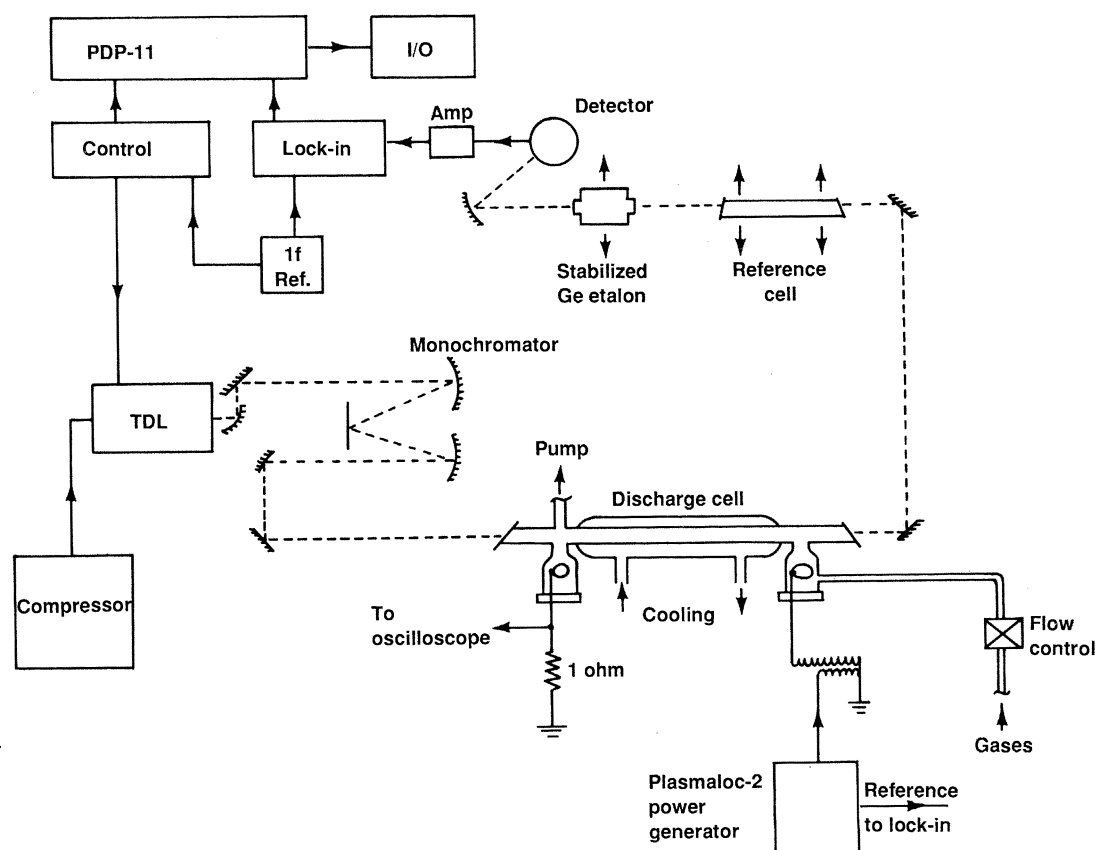
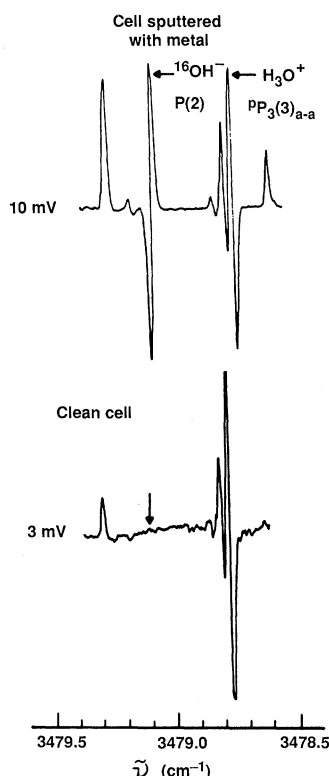


Fig. 1. Schematic diagram of the Berkeley diode laser velocity modulation spectrometer. This system operates in the range of 350 to 3000 cm^{-1} ; a similar color center laser spectrometer operates over 2850 to 4200 cm^{-1} . See text.

Fig. 2. Top trace shows opposite symmetry of derivative line shapes for a cation (H_3O^+) and anion (OH^-) obtained with the velocity modulation technique. The comparison with bottom trace indicates the large enhancement found in OH^- concentration when the cell walls are coated with metal.



77 K if desired. Ion densities as high as 10^{13} ions per cubic centimeter can be achieved when the plasmas are driven at 500 W. Studies of the dynamics of positive ions have shown that their rotational temperatures (300 to 800 K) are in equilibrium with the neutral gas kinetic temperature, which exceeds the cell wall temperature because of the finite thermal conductivity of the gas mixtures. Ion translational temperatures are somewhat higher (1000 K) due to accelerating effects of the plasma electric fields; vibrational temperatures vary dramatically with the particular ion, but are often several thousand degrees.

Over the past few years several research groups have employed the velocity modulation technique in studies of infrared spectra of some of the most fundamental positive ions (H_3O^+ , NH_4^+ , H_3^+ , CH_3^+ , and C_2H_3^+ , for example). The goals of this work are to determine accurate molecular geometries and potential function information. In 1985 Lineberger and his co-workers (7) applied his elegant indirect method of laser autodetachment spectroscopy to obtain the first vibration-rotation spectrum of a negative ion (NH^-). Shortly thereafter Owrutsky *et al.* (8) made the first direct observation of the vibrational absorption spectrum of a negative ion (OH^-) using the velocity modulation method. Since then several fundamental negative ions have been studied at Berkeley, Chicago, Okazaki, and Cambridge with this approach (OH^- , SH^- , NH_2^- , N_3^- , NCO^- , NCS^- , CCH^- , and FHF^-). Some 55 positive and negative ions have now been observed by infrared laser spectroscopy (9). Considering that the first high-resolution vibrational absorption spectrum of a molecular ion (H_3^+) was observed by Oka only 7 years ago (10), this indicates the amazing rate of progress being made in this field.

Molecular Cations— H_3O^+

At present, over 45 positive ions have been investigated by infrared laser techniques, most within the last 3 years. Several recent

review articles summarize the results obtained in these studies (9, 11, 12). Of these molecular cations, the hydronium ion (H_3O^+) is of the greatest intrinsic interest, as a consequence of its crucial roles in chemical and biological systems. Hydronium ion, in various stages of hydration, had been investigated exhaustively by spectroscopic and diffraction methods in condensed phase environments, as well as with theoretical calculations. This work showed H_3O^+ to have a pyramidal geometry, similar to its isoelectronic neutral counterpart NH_3 . Nevertheless, its structure and vibrational frequencies could be only crudely extracted from the low-resolution studies. Infrared laser spectra of H_3O^+ were first observed in 1983 by Begemann *et al.* (13) using the velocity modulation technique. Subsequently, several other groups have studied vibrational spectra of this ion with similar methods. All four fundamental vibrations of H_3O^+ have now been measured accurately, and all but the very weak symmetric stretch have been analyzed in detail. The symmetric bending vibration, or "umbrella motion," has been investigated most thoroughly. By combining the available spectroscopic data with high-quality numerical calculations, Bunker *et al.* (14) have obtained a good approximation for the molecular structure and effective potential function for this umbrella vibration.

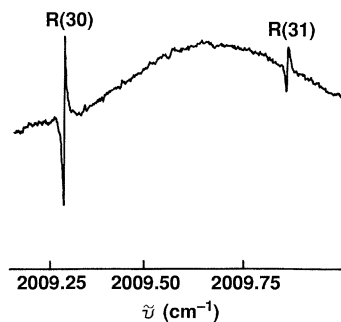
Of particular interest in these studies is the nature of the inversion tunneling in H_3O^+ . Ammonia has traditionally been the prototypical example of this textbook demonstration of the wave nature of matter, in which the hydrogen atoms move coherently from one pyramidal configuration to its mirror image analogue by tunneling through the potential energy barrier to planarity. This tunneling motion manifests itself as small splittings in vibrational or rotational spectra, which can be observed with high-precision laser techniques. The magnitude of the tunneling splittings observed in different quantum states characterizes the potential surface on which the hydrogen tunneling motion takes place. In NH_3 the potential energy barrier to inversion is about 2000 cm^{-1} , resulting in ground-state tunneling splittings of about 1 cm^{-1} . The hydronium ion has a much lower barrier to inversion ($\sim 900\text{ cm}^{-1}$) and consequently exhibits much larger ($\sim 50\text{ cm}^{-1}$) tunneling splittings, which have been predicted with high accuracy from the infrared laser studies (15). The low inversion barrier in H_3O^+ allows the hydrogen atoms to undergo very large amplitude vibrations in the tunneling coordinate (the umbrella motion). The standard mathematical theories of molecular vibrations are based on a small oscillation approximation and cannot accurately describe such "floppy" molecules. Considerable effort is currently being directed toward the development of new theoretical approaches for describing such complex types of molecular motion, which are appearing ever more frequently in modern chemical problems.

Proton transfer in aqueous systems is of ubiquitous importance, yet a detailed understanding of the mechanism of this process does not exist. It is thought that rapid tunneling of protons between nearly equivalent positions in hydrogen-bonded water molecules is the principal feature of proton transfer dynamics, which must be thoroughly understood if a valid description of this process is to be attained. A complete mathematical comprehension of the much simpler inversion tunneling motions in H_3O^+ itself is a prerequisite for this. In particular, the effects of other vibrational motions on the hydrogen tunneling rate must be understood.

Molecular Anions

The capabilities of velocity modulation laser spectroscopy become most obvious in the study of vibrational spectra of negative ions. Figure 2 shows a portion of the spectrum of OH^- observed (8) with a color-center laser near 3500 cm^{-1} in an electric discharge through

Fig. 3. Adjacent rotational lines in the asymmetric stretching band of N_3^- exhibiting 2:1 intensity alternation characteristic of molecules with a center of symmetry.



a mixture of H_2 and H_2O . In this same region H_2O itself absorbs strongly, as does the H_3O^+ cation. The OH^- absorption is immediately identified by its opposite first-derivative symmetry relative to the H_3O^+ absorption. The undifferentiated features at the beginning and end of the scan are residual strong absorptions from neutral species—probably excited vibrational states of H_2O —which are mostly eliminated by the velocity modulation detection method. The three principal attributes of velocity modulation spectroscopy—high sensitivity, high suppression of neutral absorptions, and the ability to distinguish between positive and negative ion absorptions—have allowed us to study negative ions by direct absorption spectroscopy in quite a general way.

In some cases it has been found that the presence of a thin metal coating on the discharge cell wall enhances the concentrations of negative ions—by a factor of several hundred for OH^- . This interesting effect is also evident in Fig. 2. The concentrations of positive ions are not dramatically affected by the metal coating, nor have such enhancements been observed for neutrals. A somewhat weaker metal enhancement of the concentration of the amide ion (NH_2^-) (16) was found in a NH_3 discharge, and slight enhancement (more than a factor of 5) was found (17) for N_3^- generated in $\text{NH}_3/\text{N}_2\text{O}$ discharges. No such metal enhancement was found (12) for SH^- , FHF^- , CCH^- , NCO^- , or NCS^- in the plasmas used to generate them. The mechanism responsible for this effect is not clear at present, but it probably involves surface production of the negative ions either by direct attachment to the corresponding neutral radicals or by dissociative attachment to the parent molecules. Copper, platinum, and iron have all produced large enhancements of OH^- and NH_2^- , and hence the nature of the metal does not appear to be critical. This effect clearly deserves further study, as the properties of certain plasmas used in semiconductor processing might be favorably directed if the nature of such effects were understood.

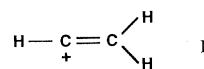
To illustrate the type of information available from these laser spectroscopy studies, we discuss some results obtained for the azide anion (17). N_3^- is an important synthetic reagent in organic and inorganic chemistry. The electron binding energy (2.76 eV) had been measured by Brauman and co-workers (17) with laser photo-detachment methods in an ion cyclotron resonance cell. All previous spectroscopic studies on the ion were carried out in crystals and solutions. In solution, infrared and Raman studies indicated a linear centrosymmetric structure, whereas both symmetric and nonsymmetric structures were observed in crystals. A bond length of 1.12 to 1.16 Å was estimated from X-ray crystallography.

Polak and Gruebele in my group (17) recently carried out a study of the infrared laser spectrum of N_3^- . The anion was generated in a discharge through NH_3 and N_2O , taking advantage of the extensive knowledge of anion chemistry obtained in the flowing afterglow studies of Bierbaum, DePuy, and their co-workers at Colorado (19). In this case, N_3^- is formed in the reaction of NH_2^- with N_2O . Excellent theoretical predictions made by Botschwina (20) indicated

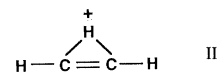
the position and large intensity of the asymmetric stretching vibration, which was observed near 1986 cm^{-1} with the diode-laser velocity modulation spectrometer. A portion of the R-branch is shown in Fig. 3. From this scan alone it is clear that an isolated N_3^- ion does indeed have a centrosymmetric structure, in that the adjacent rotational lines in the asymmetric stretching band exhibit a 2:1 intensity alternation, a consequence of the fact that the molecule possesses a center of symmetry. From an analysis of the infrared laser spectrum, a very accurate bond length of 1.18840 ± 0.00008 Å was determined, along with an asymmetric stretching frequency of 1986.467 ± 0.002 cm^{-1} .

Carbonium Ions and Carbanions

One of the most interesting frontiers of molecular spectroscopy is the incipient field of nonclassical ion spectroscopy. These species severely challenge our comprehension of molecular structure and dynamics, as they force us to describe the effects of both coupled large-amplitude motions and complex quantum tunneling effects (hydrogen migration tunneling) in their spectra. The prototypical nonclassical carbonium ion is the vinyl cation (protonated acetylene) C_2H_3^+ . Two distinct structures are possible for this molecule, the “classical” structure (I), in which naive concepts of valence are maintained



and the “nonclassical” structure (II), having a three-center C-H bond:



Detailed calculations by Schaefer and co-workers (21) and results from condensed phase studies indicate that the nonclassical form is the more stable, but that the classical form is only slightly higher in energy. Furthermore, each of these forms has six equivalent structures (different labeling of protons), such that the total potential surface has 12 minima, among which the hydrogens can tunnel. In anticipation of high-precision laser spectroscopy studies becoming possible for this molecule, Hougen (22), and Bunker and co-workers (23) have formulated elegant theories of the proton migration tunneling effects on the vibration-rotation spectrum of C_2H_3^+ . Oka's group at Chicago (24) has recently measured extensive infrared spectra in hydrocarbon discharges with velocity modulation spectroscopy; in addition to obtaining rigorous assignments of spectra for CH_3^+ and C_2H_2^+ they have assigned a considerable number of transitions to protonated acetylene, according to Hougen's model. When this project is brought to fruition, it will represent a major advance in our understanding of molecular structure and dynamics. Spectra of other nonclassical carbonium ions, such as CH_5^+ and C_2H_5^+ , are currently being sought at Chicago, Berkeley, and elsewhere.

Gruebele and Polak (25) have recently carried out a study of the prototype carbanion CCH^- by diode-laser velocity modulation spectroscopy at Berkeley. Like carbonium ions, these species are of substantial importance in organic chemistry, and have interested physical chemists for many years as well. In addition, CCH^- is probably the best candidate for the first negative ion to be studied in the interstellar medium, by virtue of its large calculated dipole moment (3.2 D) and the likelihood of a substantial abundance in at least some interstellar sources.

In this study CCH^- was generated in a discharge through NF_3 and C_2H_2 , taking advantage of the known reaction $\text{C}_2\text{H}_2 + \text{F}^- \rightarrow$

$\text{C}_2\text{H}^- + \text{HF}$. Twelve rotational lines in the C-C stretching vibration were measured with a diode laser, yielding a vibrational frequency of $1758.621 \pm 0.003 \text{ cm}^{-1}$ and a rotational constant of $1.38145 \pm 0.00026 \text{ cm}^{-1}$ for the ground state. Given this precise data, the lowest pure rotational transition of CCH^- is calculated to occur at $82.828 \pm 0.015 \text{ GHz}$. Searches for this transition with millimeter astronomy are under way. The detection of this rotational transition will open the door to investigation of the negative ion chemistry that occurs in interstellar clouds—a subject about which there has been considerable speculation, but little in the way of verifiable conclusions.

Future Prospects

The progress in molecular ion spectroscopy during the last decade, while certainly interesting and valuable in its own right, should be viewed as but the foundation for the next generation of theory and experiments in this field. Future studies of molecular ion spectra by some of the newly developed techniques promise to give us important insights into dynamical phenomena that pervade much of chemistry.

For example, a great deal of effort is being expended to achieve laser control of chemical reactions—the “holy grail” of laser chemistry. Obviously, such a development would have enormous economic and intellectual implications, but no meaningful success has as yet emanated from this work. Attempts to localize a large enough excitation in a particular bond or vibrational mode of a molecule to initiate a chemical reaction are universally frustrated by the phenomenon of IVR (intramolecular vibrational redistribution of energy)—the energy rapidly spreads out into other degrees of freedom of the molecule, simply heating the molecule. This, in turn, is a consequence of the couplings that exist between the various vibrational modes in molecules at high excitation energies, or more correctly, it is a result of the breakdown of the “normal mode” or “local mode” approximations that are employed to avoid the intrinsic and complicated many-body nature of polyatomic vibrations. A detailed understanding of molecules at high levels of excitation must be developed in order to design ways to overcome the IVR problem. Two classes of ions that will be studied in the next generation of molecular ion spectroscopy—cluster ions and nonclassical ions—exhibit the same kinds of many-body phenomena in their ground and low-lying vibrational states as do such highly excited molecules. Because of the hydrogen migration tunneling in nonclassical ions like C_2H_3^+ and the coupled internal motions in cluster ions like H_5O_2^+ , traditional theories cannot correctly describe their energy levels. Dynamical (permutation-inversion) symmetry theories must be incorporated into the formalism to simplify the many-body problem. By studying these types of molecular ions in detail by precise laser methods, we can gain considerable insight into the general many-body problem that arises for vibrationally excited molecules.

Hydrogen-bonded cluster ions like H_5O_2^+ and H_7O_3^+ are also simple prototypes for the study of proton transfer. If the internal proton motions in these ions can be understood in detail, considerable insight will be gained in comprehending this process as it occurs in the liquid state. Impressive success have already been realized in obtaining infrared spectra of these cluster ions by Lee’s beautiful ion trap experiments (26) at Berkeley.

Perhaps overshadowed by these seemingly grandiose scenarios, a great deal of important and interesting structural data will be obtained for many cation and anion systems. This information will continue to have a critical impact on the field of astrochemistry; more importantly, it expands the foundation for our increasingly sophisticated understanding of chemical bonding.

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