Microwave Spectroscopy at the Dissociation Limit

Alan Carrington

An ion beam technique has been developed that combines some of the methods of mass spectrometry and molecular spectroscopy and is designed for the study of molecular ions at energy levels lying very close to the lowest dissociation limit. Microwave radiation is used to drive spectroscopic transitions, and electric field dissociation of the weakly bound levels provides a high degree of state selection for sensitive detection of the spectra. The analysis of the spectra requires unconventional approaches to the description of the long-range levels and their spectroscopic study and provides stringent tests of ab initio theories.

Molecular spectroscopy is the method of choice for determining the shapes, sizes, and internal dynamics of small molecules, particularly in the gas phase, in which the molecules are free and undistorted by the intermolecular interactions that are characteristic of condensed phases. A number of generalizations that are almost always true can be made. For example, ultraviolet and visible spectroscopy probe the motions of the electrons within a molecule; in the infrared, molecular vibrations can be studied; and in the microwave, molecular rotations are investigated. The radiofrequency region allows the investigation of interactions between the electrons and nuclei that are classed as hyperfine interactions.

In the gas phase at room temperature, the largest population of molecules is usually to be found in the ground vibrational level of the ground electronic state, so that rotational and vibrational spectra invariably involve transitions within or from this level. The spectra, commonly taken in the microwave or infrared, are interpreted in terms of an effective Hamiltonian containing "molecular constants" that can, in turn, be related to structural parameters of the molecule concerned. The energy levels can be represented analytically and in a diatomic molecule, for example, the spectra yield values of vibrational and rotational constants, defined within the harmonic oscillator approximation. Spectra involving higher vibrational or rotational levels are interpreted by the addition of anharmonic corrections to the initial effective Hamiltonian. This process, however, becomes increasingly unsatisfactory as we proceed up a potential well because the number of parameters can exceed the number of measurements. Electronic absorption spectra are somewhat different; although transitions usually involve the lower levels of the ground electronic state, the relevant vibrational or rotational levels of the excited electronic state are not necessarily the lowest. Because experimental measurements often involve a molecule at or near its ground-state equilibrium configuration, ab initio theoretical calculations also tend to concentrate on this region, often with little attention given to the long-range part of the potential. Because these are the regions that are most relevant to reaction dynamics, one could often wish for theory that is good at all internuclear separations, not just their equilibrium values. Almost all theoretical calculations are performed within the framework of the Born-Oppenheimer approximation.

To a molecular spectroscopist, all of the above will rightly be classified as stating the obvious. It is summarized here, however, because my work conforms to almost none of these generalizations. My aim was to study the spectra, structure, and dynamics of molecules in energy levels that lie very close to the lowest dissociation limit. I addressed the question of how to describe the first few vibration-rotation levels by starting from the dissociation asymptote and proceeding downward in energy, which is in sharp contrast to most studies, which start at the bottom of a potential well and work upward. Do the rules that work so well in describing spectroscopy and structure at or near the ground-state equilibrium configuration still have value in the near-dissociation region? The answers vary from one system to another. My work encountered problems similar to those found in the study of weakly bound neutral van der Waals molecules and molecular Rydberg states.

The experiments were confined to ionic systems, for entirely experimental reasons. I made use of many of the standard techniques of mass spectrometry but with an important addition, electric field dissociation, which provides a high degree of state selectivity and detection sensitivity, without which the measurements would not be possible. Except for hydrogen ion beams, which are very strong, the parent ion beam fluxes were in the range of 10^8 to 10^{10} ions s^{-1}, of which probably only 10^3 to 10^5 occupied the near-dissociation levels that were of interest. All of the spectroscopic work described here involved microwave radiation, because the density of closely spaced levels near the dissociation limit is expected to be high, and therefore there is always likely to be a microwave spectrum. Microwave line widths are small, so that subtle details of the spectra are revealed. Experimentally, it is easy to couple microwave radiation to an ion beam; and with modern microwave synthesizers, frequency scanning, modulation, and computer control are straightforward.

Experimental Methods

Ions were produced by electron bombardment and accelerated to potentials of up to 10 kV to form a beam. In most cases, I used a flowing gas or gas mixture, but I also had the ability to inject a neutral molecular beam into the ion source. Ions of different mass were identified with a magnetic sector (Fig. 1), and the ion of choice was then selected by fixing of the magnetic field. The ion beam passed through a 40-cm length of rectangular waveguide, where it was exposed to tunable amplitude-modulated microwave radiation, and then through an electric field lens. The lens was a very simple three-element structure; the first and third plates were at earth potential, whereas a positive or negative potential was applied to the center plate. The second and third plates were separated by only 1 mm, so that the strongest electric field (up to 40 kV cm^{-1}) was established between them. Dissociation of weakly bound levels occurred in this field, producing fragment ions that were separated with an electrostatic sector according to their different kinetic energies, and detected with an electron multiplier. Resonant microwave transitions induced in the waveguide resulted in population transfer between different levels, producing changes in the fragment ion intensity. These changes were recorded by detection of the changes in the electron multiplier output current. The microwave frequency range available was 4 to 170 GHz. Spectral linewidths were determined primarily by the transit time of the parent ion beam through the

---

The author is in the Department of Chemistry, University of Southampton, Hampshire SO17 1BJ, UK.

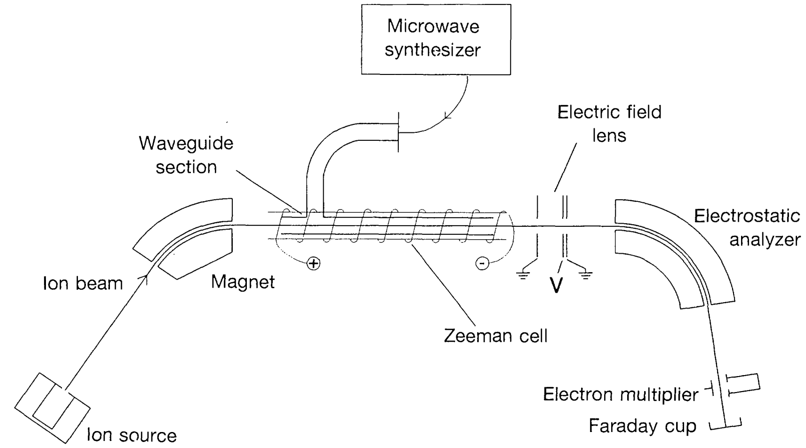

Fig. 1. Schematic diagram of the ion beam apparatus.

waveguide; they were 1 MHz or less.

The unique part of the ion beam apparatus is the electric field lens. Weakly bound levels of different dissociation energies undergo fragmentation at different positions within the lens, where the electric fields and potentials are different. The range of electric fields can also be varied by changing the potential applied to the center plate. The ideal situation is one in which the upper level involved in a transition fragments, whereas the lower does not. Spectroscopic transitions between the two levels transfer population from the lower level to the upper, so that an increased fragment ion current is produced and detected. The problem is that until a resonance is observed, the ideal lens or electrostatic analyzer voltages are unknown. Consequently, the search problem was three-dimensional, in that I needed to scan microwave frequency, lens potential, and electrostatic analyzer voltage.

Two other aspects of the experimental methods were important. The first involves passing a current through a solenoid wound around the waveguide; the axial magnetic field produced often results in Zeeman splittings of a microwave line, from which I could determine total angular momentum quantum numbers (*J*). Zeeman splittings also enabled me to determine the g factors giving the magnetic moments of the two levels involved in the transition. The second important aspect involves the use of a second microwave frequency so that, ideally, two transitions can be driven simultaneously. These double-resonance experiments allowed me to determine whether two spectroscopic transitions involved a common energy level. They also enabled me to access energy levels that lie too far below dissociation to be detected by single-photon spectroscopy.

Results

To date, I have studied 11 different systems (Table 1). For six of these systems, the spectra have been fully assigned and interpreted with high accuracy; the remaining five are still under active investigation. I have no doubt that many other systems will be detectable, including further polyatomic systems.

How are the high-lying near-dissociation levels in these long-range complexes populated? In the case of H_2^+ and its deuterium isotopomers, the desired populations arise directly from electron impact ionization. This is because the potential energy curve for H_2^+ is displaced to larger internuclear distances than that of H_2, so that vertical ionizing Franck-Condon transitions from the ground vibrational level of H_2 access all of the bound levels of H_2^+, including the highest vibration-rotation level [with vibration (v) = 19 and rotation (N) = 1], which is bound by only 0.215 cm^{-1}. Because the ions, once formed, are ejected from the ion source into a high vacuum system to form a beam, there is very little opportunity for collisional relaxation. Similarly, the near-dissociation levels of Ne_2^+, discussed later, are populated by direct vertical ionization of the Ne_2 neutral precursor, formed in a nozzle-beam expansion.

Five of the complexes listed in Table 1 contain helium, which presents some especially favorable opportunities. Electron bombardment of ground-state He atoms results in direct ionization but also in electronic excitation to a metastable triplet state, lying 19.818 eV above the ground state. These energetic He atoms can undergo associative ionization, either with ground-state He atoms (to form He_2^+ molecular ions) or with other substrates, such as Ar atoms or even H_2 molecules. The excess energy in the excited He atoms often leads to substantial population of the highest energy levels of the long-range ionic complexes. Most of the complexes formed in this way and studied by me contain a helium atom, but I recently discovered that if N_2 is the substrate partner, N_2^+ ions in which the highest bound levels are populated can be observed by the microwave techniques discussed here. In the same system, I was also able to observe microwave transitions of the long-range $He \cdots N^+$ complex, a fragmentation product. Helium absorbs electron energy and acts as an energy sink in the ion source; this energy is then available for a range of secondary processes.

$H \cdots H^+$, $D \cdots D^+$, $D \cdots H^+$, and $He \cdots He^+$

H_2^+, the simplest of all molecules, has been and still is the subject of a large number of theoretical studies and few experimental measurements. Before my own interest, the only spectroscopic study was an elegant radiofrequency investigation of hyperfine transitions within the v = 4 to 8 vibrational levels by Jefferts (*1*). The paucity of experimental spectroscopic studies is easy to understand: H_2^+ has no electric dipole moment, so that vibrational and rotational spectroscopy are not possible; and although the molecule is well bound in its ground electronic state (with a dissociation energy D_e of 22,529 cm^{-1}), the first excited electronic state is essentially repulsive. Other excited states lie at very high energies, so electronic spectroscopy does not seem feasible. Add to these physical difficulties the fact that H_2^+ is extremely chemically reactive, particularly with H_2 itself, and one can understand why H_2^+ was for many years a theoretician's molecule.

It has, in fact, been known for 55 years that the first excited electronic state of H_2^+ is not repulsive at all internuclear distances

Table 1. Long-range complexes studied by ion beam microwave spectroscopy to date.

Long-range complexes				
$He \cdots He^+$	$H \cdots H^+$	$D \cdots D^+$	$D \cdots H^+$	$He \cdots H_2^+$
	$He \cdots Ar^+$	$He \cdots Kr^+$	$He \cdots N^+$	
	$Ar \cdots Ar^+$	$Ne \cdots Ne^+$	$N \cdots N^+$	

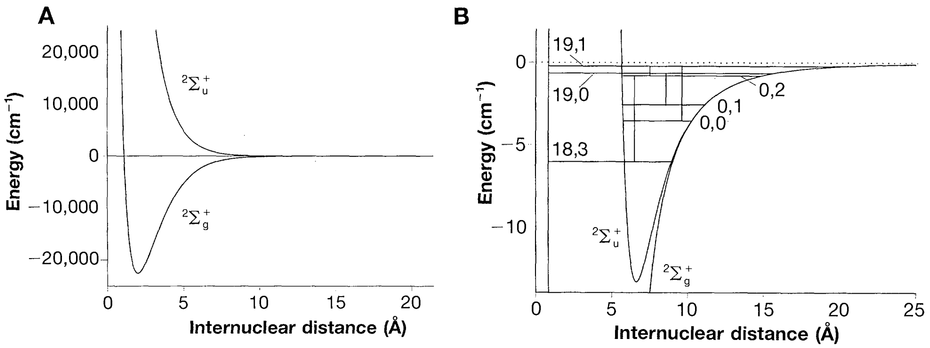

Fig. 2. (**A**) Potential energy diagram (*4*) for H_2^+ showing the bound ground electronic state ($^2\Sigma_g^+$) and repulsive first excited electronic state ($^2\Sigma_u^+$). (**B**) Potential energy curves for the ground and first excited states of H_2^+ in the near-dissociation region, with the vertical scale expanded by a factor of 5000. The long-range minimum in the excited state potential can now be seen, as well as the near-dissociation vibration-rotation levels for both states. Electronic transitions between the two states, which I have observed, are also shown.

(*2*). When a proton and a hydrogen atom approach each other, the first interaction between them is an attractive force arising from polarization of the H atom charge distribution and a resulting electrostatic interaction with the H^+ nucleus. This charge/induced-dipole interaction, the most fundamental interaction between an ion and a neutral species, atomic or molecular, is also known as the Langevin interaction. In the lowest excited state of H_2^+, it results in a long-range minimum in the potential at an internuclear separation r_e of 12.5 Bohr radii (a_0); the potential well has a depth of 13.3 cm^{-1} and supports three bound vibration-rotation levels (*3*). Figure 2A shows the potential energy curves for the ground and first excited states of H_2^+, first calculated by Teller (*4*), as they appear in standard textbooks on spectroscopy (*5*). Figure 2B, however, shows the near-dissociation region for both states; and on this magnified scale, the long-range minimum in the excited state potential can be seen; the bound vibration-rotation levels for both states also are shown.

There is therefore the possibility of resolved electronic transitions between the high levels of the ground electronic state and the van der Waals or Langevin long-range levels. These transitions should occur in the microwave region, and using electric field dissociation as the detection method, I have observed all four of the transitions accessible within the frequency range studied (*6*). An example of the spectra obtained (Fig. 3) illustrates a common feature of these experiments: Doppler-shifted parallel and antiparallel replications of a microwave absorption line were always observed. Moreover, when high-frequency radiation was coupled into a waveguide appropriate for lower frequencies, microwave propagation occurred in more than one mode, each of which had its own characteristic phase velocity and Doppler shift. This Doppler replication is very useful, enabling rest frequencies to be determined with high accuracy. These measurements provided the first characterization of the van der Waals minimum in the long-range $H \cdots H^+$ interaction and the first measurements of rotational separations in the ground state of H_2^+. After progressive refinement (*7*), the theory agreed with experimental results to within 3 MHz.

I was able to perform similar measurements on the $D \cdots D^+$ complex (*8*), where there are more microwave resonances (15 in all), because of the increased molecular mass. I have also made a similar study of the $He \cdots He^+$ system (*9*), obtaining the first spectrum of the helium molecular ion in its predominant naturally occurring isotopic form $^4He^4He^+$. These studies of H_2^+ and He_2^+ contravene the generalization that microwave spectroscopy is the study of rotational motions. These transitions are electronic, and they involve very large internuclear separations (31 a_0 in the highest ground-state level of H_2^+ and 18.3 a_0 in the highest van der Waals level of He_2^+). The helium ion also illustrates one of the features of many ab initio calculations introduced at the beginning of this review. The fundamental vibration-rotation band of the heteronuclear species $^3He^4He^+$ has been measured by Yu and Wing (*10*). Several different ab initio calculations give equally satisfactory quantitative accounts of the $v = 1 \leftarrow 0$ band, but they predict different numbers of bound vibrational levels; the electronic spectrum I saw would not exist if the predictions of these calculations were correct. The potentials calculated by

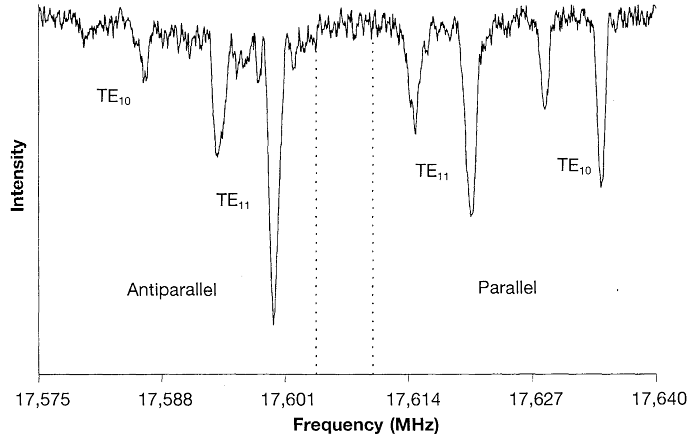

Fig. 3 (left). (0,2) to (19,1) microwave resonance from H_2^+ showing a doublet hyperfine splitting and microwave mode Doppler structure. The vertical dashed lines indicate the positions of the rest frequencies. The transition responsible for this resonance is between the highest bound levels of both the ground and excited electronic states. TE, transverse electric.

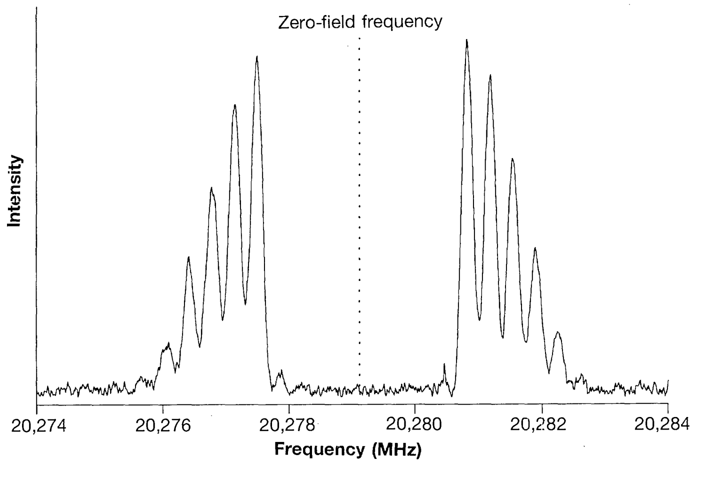

Fig. 4 (right). Zeeman splitting of a microwave line from $He \cdots Ar^+$ in a field of 4.44 G. The multiplet structure shows that the resonance arises from a $J = 7/2$ to 5/2 transition. The position of the zero-field resonance is shown.

Knowles (*9*) are the most accurate at both short and long range but still require a small semi-empirical adjustment to bring the predicted electronic transition frequencies into coincidence with those measured experimentally. Comparing the three-electron (He_2^+) with the one-electron (H_2^+) molecule, I conclude that the electron correlation problem that arises in the former limits the accuracy of the theoretical predictions. For the one-electron molecule, agreement between experiment and theory is on the order of 1 MHz; for the three-electron molecule, it is 100 MHz, after the semi-empirical scaling referred to above.

The heteronuclear system $H^+ \cdots D$ is very different from the corresponding homonuclear systems. Whereas in the latter, the ground and first excited electronic states are degenerate at the dissociation limit, the $H^+ + D$ and $H + D^+$ dissociation limits are separated by almost 30 cm^{-1}. There is, therefore, no microwave electronic spectrum, but in compensation there is the possibility of probing vibrational and rotational transitions, because the HD^+ ion in its long-range levels has a large electric dipole moment, arising from the large separation between the centers of charge and mass. Using electric field dissociation to produce H^+ fragments from the highest vibration-rotation levels of the ground state, I have detected and measured a number of rotational transitions (*11*). The microwave absorption lines show well-resolved hyperfine structure arising from interaction of the unpaired electron with both the proton and the deuteron nuclei. The principal mechanism for hyperfine coupling is the Fermi contact interaction, which provides a measure of the *s* electron density at each nucleus. A fascinating observation is that in the more strongly bound levels, the electron density is the same at both nuclei, as the Born-Oppenheimer approximation requires, but in levels that approach the $H^+ + D$ dissociation limit, the electron density becomes increasingly concentrated at the deuteron nucleus. In its highest bound level, the ion may be represented accurately by the formula $H^+ \cdots D$. This shows a complete breakdown of the Born-Oppenheimer approximation, but ab initio calculations (*12*) that go beyond the Born-Oppenheimer level by treating the nonadiabatic effects correctly, and also include relativistic effects, are in excellent agreement with experimental results. It is important to recognize that, in contrast to the heteronuclear HD^+ molecule, the electron cannot distinguish between the two nuclei in the homonuclear species H_2^+ and D_2^+.

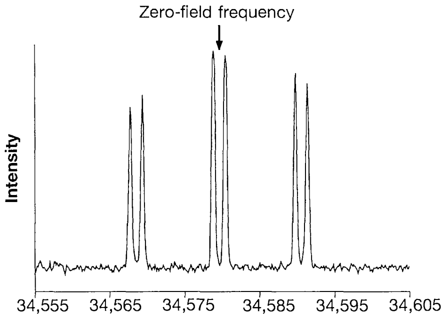

Fig. 5. Zeeman splitting of a microwave line from $Ne \cdots Ne^+$ obtained with a magnetic field of 6.66 G. The multiplet structure shows that the resonance arises from a $J = 3/2$ to $3/2$ transition. The position of the zero-field resonance is shown.

$He \cdots Ar^+$ and $He \cdots Kr^+$

The progressive interaction between experiment and ab initio calculations has been crucial in the understanding of the long-range species discussed in the previous section. The $He \cdots Ar^+$ complex presented a very different situation initially, because no sufficiently accurate ab initio calculations were available, and previous studies of electronic emission spectra provided only limited information that was relevant to my studies. The Ar^+ atomic ion has two fine-structure states, the $^2P_{3/2}$ state being 1431 cm^{-1} lower in energy than the $^2P_{1/2}$ state; there are, therefore, two dissociation limits that might be relevant. I detected 68 microwave resonances (*13*), using electric field dissociation to produce Ar^+ fragments, and in most cases was able to observe the Zeeman splittings produced by an axial magnetic field (Fig. 4). The number and relative intensities of the Zeeman components in Fig. 4 show that the microwave resonance must arise from a $J = 7/2$ to $5/2$ transition, and the *g* factors for the two levels were also obtained. I performed similar studies on almost all of the observed resonances and, with the additional information from double-resonance observations, was able to determine the pattern of energy levels lying up to 10 cm^{-1} below the $He + Ar^+(^2P_{3/2})$ dissociation asymptote. These levels could be labeled with parity and *J* values, but not, from experiment alone, vibrational or electronic quantum numbers. The solutions were provided with the use of a coupled-channel theory (*14*) that dealt with the coupling of the three electronic states correlating with the two dissociation limits. By optimizing the values of the potential parameters, it was possible to calculate the energies, *J* values, and *g* factors of the near-dissociation bound levels and to obtain an accurate convergence of experiment and theory. Unlike a more conventional spectroscopic analysis, there was no effective Hamiltonian linking experiment and theory. All of the near-dissociation levels were identified, the highest level lying only 14 MHz from the first dissociation asymptote. The energy levels were found to conform fairly closely to Hund's case (*c*), in which the components $|\Omega|$ of the atomic electronic angular momentum J_a along the internuclear axis are good quantum numbers. The observed microwave transitions were of all possible types: rotational, vibrational, Ω-doubling, and electronic. A similar analysis has been performed for the $He \cdots Kr^+$ long-range complex (*15*), which provides the first authentic example of Hund's case (*e*) coupling; electronic angular momentum projection quantum numbers (Ω) are not defined for this coupling case, the atomic angular momentum J_a remaining a good quantum number.

$Ne \cdots Ne^+$, $He \cdots N^+$, $N \cdots N^+$, and $He \cdots H_2^+$

N_2^+ is probably the most extensively studied molecular ion, both spectroscopically and theoretically. The remaining three ions discussed in this section have not previously been detected in any region of the spectrum. The point where the spectra are assigned has not yet been reached, but each raises different problems that are novel and interesting.

Ne_2^+ is the first species to be studied with the nozzle beam injection method (*16*), and it provides the best signal-to-noise resonances I have yet observed. So far, over 100 resonances have been measured (*17*) (Fig. 5 shows an example). The highest observed *J* value is 9/2, which shows that the ion beam is rotationally cold, as one might expect because the Ne_2 precursor is produced in a skimmed nozzle beam. I am in the process of establishing the pattern of near-dissociation levels, using double resonance, Zeeman splittings, *g* factors, and numerical relations between transition frequencies. The problem resembles a sophisticated jigsaw puzzle in which the task is to find all the pieces, as well as to connect them in the right order. I believe that levels are being observed that correlate with either of the two dissociation asymptotes, involving Ne^+ in its $^2P_{3/2}$ or $^2P_{1/2}$ states. Final assignment will define the long-range potential and probably also the dissociation energies of the electronic states involved.

$He \cdots N^+$ appears, not surprisingly, to have a much sparser near-dissociation pattern of energy levels. The N^+ ion in its ground-state electron configuration has three fine-structure components, $^3P_0$, $^3P_1$, and $^3P_2$, which are split by spin-orbit coupling. I have observed four microwave resonances (*18*), three of which show triplet ^{14}N hyperfine structure, whereas the fourth is unsplit. It should be possible to establish the correlations between molecular levels and the three dissociation asymptotes, but more resonances must first be observed and their Zeeman behavior studied. The $N \cdots N^+$ system is even more complicated; the lowest dissociation limits resemble those of $He \cdots N^+$ but occur in three doubly degenerate pairs because of the homonuclear symmetry. I have observed 11 microwave resonances so far (*17*), which exhibit ^{14}N hyperfine splitting characteristic of either ortho or para nuclear spin states. Although the observed spectra must necessarily be electronic, a disconcertingly large number of possibilities exists. These include Σ to Σ, Σ to Π, and Π to Π transitions, involving doublet, quartet, or sextet spin states.

Perhaps my most exciting recent observation (*19*) is the detection of microwave resonances from the long-range complex $He \cdots H_2^+$. The ion-molecule reactions involving helium and hydrogen neutral or ionic species are benchmark reactions that have been extensively studied, both experimentally and theoretically. The HeH_2^+ so-called "collision complex" occupies a pivotal position in understanding these reactions, and a number of potential surface calculations have been described. These may be divided into those that deal accurately with the short-range parts of the potential (*20*) and those that deal accurately with the long-range interactions (*21*). The interpretation of this spectrum is going to require the best of both worlds. I have observed 10 resonances so far, and for the energy levels involved, the H_2^+ component appears to be an essentially free rotor within the complex. Resonances involving *ortho*-H_2^+, which exhibit a sextet proton hyperfine structure characteristic of two equivalent protons, and those involving *para*-H_2^+, which show, as expected, no hyperfine structure, can be very clearly distinguished. There must be further resonances to be discovered, and it must be possible to perform sufficiently accurate calculations for this three-electron system to provide an unambiguous interpretation of the spectrum. Success in that endeavor will also help provide a better understanding of the ion-molecule reaction dynamics.

Conclusions

These experiments are extremely time-consuming. I calculate that a blind search in which microwave frequency, electric field potential, and electrostatic analyzer voltage are varied systematically would take 308 days. Moreover, until the first microwave resonance line is observed, one cannot be sure that the near-dissociation energy levels are populated. Fortunately, the apparatus is extremely stable, and computer-controlled searches can be conducted, unattended, for several days. Some of the complex resonances, with microwave mode or nuclear hyperfine structure, may themselves require several days of signal averaging. In these circumstances, it is difficult to find a satisfactory compromise between completing the recording of existing spectra and searching for new species. I have no doubt that these techniques have the sensitivity and generality to tackle many more long-range complexes. I also note that although this work is concerned with microwave spectroscopy, the methods developed would be even more sensitive and general with shorter wavelength–tunable radiation sources, which would probe the more strongly bound levels.

The analysis of the spectra for each molecular species has required a new approach. They all have open-shell ground states with electron spin degeneracy, and most of them also have orbital degeneracy. There are no spectral regularities to aid in assignment, and usually the available theory does not help in the initial understanding. In heteronuclear species, it is not, at first, known what types of transitions are being observed nor what quantum numbers are useful. I am unable to represent the energy levels analytically or to define molecular constants. In the long run, therefore, only direct partnerships between theory and experiment can lead to successful conclusions. Given the resolution and accuracy of these experiments, almost unprecedented demands are being made on ab initio theory, which must be accurate for all internuclear separations and molecular geometries. Ultimately, the main goal is not precise agreement of theory and experiment but further clarification of the molecular physics involved in long-range interatomic and intermolecular forces. This work represents an intimate contact point between spectroscopy, structure, and the dynamics of ion-atom or ion-molecule reactions at thermal energies.

REFERENCES AND NOTES

1. K. B. Jefferts, *Phys. Rev. Lett.* **20**, 39 (1968); *ibid.* **23**, 1476 (1969).
2. C. A. Coulson, *Proc. R. Soc. Edinburgh* **A61**, 20 (1941).
3. J. M. Peak, *J. Chem. Phys.* **50**, 4595 (1969).
4. E. Teller, *Z. Physik.* **61**, 458 (1930).
5. See, for example, fig. 166 in G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, NJ, 1950).
6. A. Carrington *et al.*, *J. Chem. Soc. Faraday Trans.* **89**, 603 (1993).
7. R. E. Moss, *Mol. Phys.* **80**, 1541 (1993).
8. A. Carrington, D. I. Gammie, A. M. Shaw, S. M. Taylor, *J. Chem. Soc. Faraday Trans.* **91**, 1887 (1995).
9. A. Carrington, P. J. Knowles, C. H. Pyne, *J. Chem. Phys.* **102**, 5979 (1995).
10. N. Yu and W. H. Wing, *Phys. Rev. Lett.* **59**, 2055 (1987).
11. A. Carrington, I. R. McNab, C. A. Montgomerie, J. M. Brown, *Mol. Phys.* **66**, 1279 (1989); A. Carrington *et al.*, *J. Chem. Phys.* **98**, 5290 (1993).
12. R. E. Moss, *Mol. Phys.* **78**, 371 (1993).
13. A. Carrington *et al.*, *J. Chem. Phys.* **102**, 2379 (1995).
14. J. M. Hutson, *Comp. Phys. Commun.* **84**, 1 (1994).
15. A. Carrington *et al.*, *J. Chem. Phys.*, in press.
16. A. Carrington, A. M. Shaw, S. M. Taylor, *Chem. Phys. Lett.* **241**, 611 (1995).
17. A. Carrington, D. I. Gammie, A. M. Shaw, S. M. Taylor, unpublished work.
18. ———, *Chem. Phys. Lett.*, in press.
19. ———, J. M. Hutson, *ibid.* **260**, 395 (1996).
20. D. R. McLaughlin and D. L. Thompson, *J. Chem. Phys.* **70**, 2748 (1979); J. Tennyson and S. Miller, *ibid.* **87**, 6648 (1987); V. Spirko and W. P. Kraemer, *J. Mol. Spectrosc.* **172**, 265 (1995).
21. M. F. Falcetta and P. E. Siska, *Mol. Phys.* **88**, 647 (1996).
22. I thank my former collaborators in this work, whose names appear in the list of references. I owe particular debts to the present members of my group, namely A. Shaw, S. Taylor, and D. Gammie. On the theoretical side, I thank R. E. Moss, J. M. Brown, J. M. Hutson, P. J. Knowles, and M. M. Law for their advice or collaboration. I thank the Royal Society for a Research Professorship and recurrent financial support, and the Engineering and Physical Sciences Research Council for grants toward the purchase of apparatus.