The Infrared Predissociation Spectrum of H_3^+

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Introduction

The purpose of this Account is to describe the remarkable infrared predissociation spectrum of H_3^+.[1,2] The H_3^+ molecular ion was first detected in 1911 by J. J. Thomson.[3] It is an extremely stable species with a dissociation energy of 4.355 eV (420.236 kJ mol^{-1})[4] and is one of the main constituents of hydrogen plasmas, where its suppression is of some interest for prospects of nuclear fusion. As the simplest polyatomic molecule, H_3^+ has been the subject of many theoretical studies, which have been unanimous in their conclusion that its equilibrium geometry is that of an equilateral triangle. This was first confirmed experimentally in 1978 by Coulomb explosion measurements.[4] Until recently, experimental studies of H_3^+ were confined to its chemistry, which has been extensively examined by using mass spectrometry and related techniques. Over the past eight years, however, the spectroscopy of H_3^+ and its deuterium isomers has been developed extensively, following the pioneering work of Oka[5] and Wing and his co-workers.[6] These studies have examined the lowest vibration–rotation energy levels of the ground electronic state, confirming the main conclusions of the theoretical studies.

The ground electronic state of H_3^+ has $^1A_1'$ symmetry, and it dissociates to $H_2 + H^+$. In our experiments, H_3^+ is formed by electron-impact ionization of hydrogen, the electrons being supplied either from a heated filament or by means of a plasma discharge. The predominant mechanism for the formation of H_3^+ involves the processes

$$H_2 + e^- \rightarrow H_2^+ + 2e^-$$

$$H_2 + H_2^+ \rightarrow H_3^+ + H$$
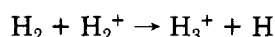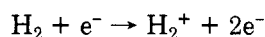
The reaction between H_2 and H_2^+ is exothermic by 1.703 eV,[7] and studies using crossed molecular beams have shown that H_3^+ ions produced in this manner possess high internal energies.[8] The H_2^+ ions formed by electron impact on hydrogen also possess high internal energies, all bound vibrational levels being populated because of favorable Franck–Condon factors, and there is good evidence that this vibrational energy is converted into internal energy of the H_3^+ product ions.

Alan Carrington was born in 1934 and obtained his B.Sc. and Ph.D. degrees at the University of Southampton, where he has remained for the major part of his career, apart from eight years in Cambridge and three years in Oxford. His research work has involved the spectroscopy of transient molecular species in liquids, gases, and ion beams. He was elected a Fellow of the Royal Society in 1971 and a Foreign Honorary Member of the American Academy of Arts and Sciences in 1987. He is at present a Royal Society Research Professor in the Department of Chemistry at the University of Southampton.

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Infrared Spectroscopy of Molecular Ions

Conventional infrared spectroscopy relies on measuring the absorption intensity of radiation transmitted through a sample. The infrared radiation from a hot source is dispersed with a prism or diffraction grating; more recently, continuously tunable (diode or F-center) lasers have been used as sources, and Fourier transform techniques have replaced traditional absorption measurements. Infrared methods have, however, required considerable modification for the successful study of ions in the gas phase because of their very high reactivity.

The difficulties have been overcome in two ways: by the continuous production of molecular ions in discharges, or by the confinement of ions in traps or beams in high-vacuum environments. In both cases, the low concentration of ionic species presents problems. The spectroscopy of ions in discharges has been greatly enhanced by the use of velocity modulation, a technique that was first applied to discharges by Gudeman, Begemann, Pfaff, and Saykally.[9] By application of an alternating high voltage between two electrodes, a discharge can be maintained coaxially with a laser beam. The ions experience an oscillating electric field; this results in an alternating drift velocity, determined by collisions with neutral species, and gives rise to frequency modulation of spectral absorption lines because of the Doppler effect. This modulation enables phase-sensitive detection to be employed, hence discriminating against all neutral (unmodulated) species present in the discharge. The technique has the added advantage that spectroscopic lines from negatively charged ions appear with the opposite phase to those from positively charged ions, because they are accelerated in the opposite direction in the same field.

Ion beams suitable for spectroscopy may be studied by mass spectrometric methods, and their use offers certain particular advantages:

1. In electron-impact ion sources, the ions are often formed with a high degree of internal excitation and can be rapidly accelerated from the source before collisional relaxation can occur. Alternatively, if internal excita-

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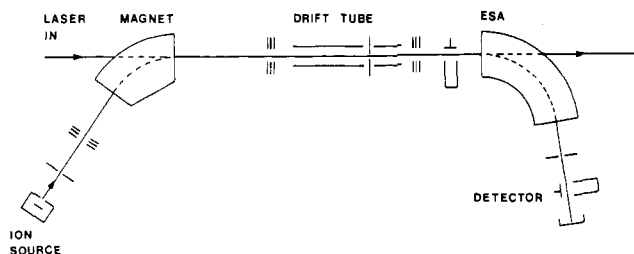
Figure 1. A simplified diagram of the modified mass spectrometer used to record the infrared photopredissociation spectrum of H_3^+. Ions formed in the source are accelerated into the magnet, where the ion of interest is mass selected. The ion beam then interacts with a collinear laser beam in the drift tube. The resulting fragment ions are separated from the main beam in the ESA and monitored with the detector (see text for details).

tion is undesirable, ions can be formed at high pressures in a discharge or chemical-ionization source where many collisions occur before acceleration.

2. Once in the accelerated beam, the ions enjoy an almost collision free environment (unless a target gas is deliberately introduced).

3. Many different molecular ions may be formed by ion–molecule reactions in plasmas and in electron-impact sources. In a mass spectrometer, however, the ion of choice may be mass selected, giving an unambiguous identification of the species studied.

A disadvantage of ion beams is that even with the maximum beam fluxes obtainable ($\simeq 10^{13}$ ions/s in our apparatus) the number of ions is often too low for normal absorption spectra to be obtained. Moreover, it is frequently found that many vibration–rotation levels are populated by the ionization process, so that the populations of individual levels are low. In these cases, the detection of resonant transitions must be accomplished by an indirect method which relies on detecting changes in ion-beam intensity (parent or fragment) occurring as a result of photon absorption. In our studies of the H_3^+ ion, for example, we monitor changes in the number of photofragment H^+ ions resulting from absorption of infrared radiation. We do not attempt to measure directly the absorption of infrared photons. However, direct infrared absorption spectra of ion beams have been reported recently by Saykally and his colleagues,[10] and such studies are likely to become more common as the techniques are improved.

Experimental Methods

Our experiments make use of an H_3^+ ion beam, formed in a modified Vacuum Generators ZAB 1F tandem mass spectrometer, a simplified diagram of which is shown in Figure 1. The ions are formed in an electron impact ionization source, the potential of which may be varied from 0 to +10 kV with respect to the rest of the mass spectrometer, which is at earth potential. The ions are therefore accelerated from the source into a magnetic mass analyzer as shown. Ion-beam potentials below 1 kV are not used because of the low beam intensities, so that for H_3^+ the ion velocities range from 2.5×10^5 to 7.9×10^5 m s^{-1}. An important modification to the spectrometer is the addition of two windows,

which allow a laser beam to be introduced collinearly with the ion beam, in either a parallel or antiparallel arrangement.

Infrared radiation is obtained from a CW carbon dioxide laser, which is line-tunable over the region 872–1094 cm^{-1}, adjacent lines being separated by typically 1 or 2 cm^{-1}. The use of an isotopic gas such as $^{13}CO_2$, as a lasing medium increases the number of lines available. In order to achieve continuous frequency coverage through the laser region, we make use of a Doppler tuning method; by changing the source potential, the velocity of the ions is scanned and therefore, via the Doppler shift, the frequency is also scanned. For light ions such as H_3^+ we obtain essentially complete coverage with the range of beam potentials and velocities available, within the limits imposed by the laser. The use of either parallel or antiparallel alignment of the ion and laser beams means that negative or positive Doppler shifts can be employed. Sweeping of the ion source potential must, of course, be coupled with synchronous sweeping of the magnetic analyzer so that continuous transmission of the H_3^+ beam is obtained.

An important advantage of using fast ion beams is a narrowing of the Doppler line width due to kinematic compression; the Doppler width of an absorption line is determined by the ratio of the velocity spread to the absolute velocity, and this ratio becomes smaller as the ion-beam velocity increases. The Doppler width is reduced, typically, by an order of magnitude compared with that obtained in conventional absorption or emission experiments.

As mentioned in the previous section, the density of ions is too small for direct absorption measurements, and an indirect method of detection must be employed. We measure changes in fragmentation of the parent ions resulting from resonant absorption of the infrared photons. The two most important situations that have arisen in our work are the following:

$$\text{(i)} \quad AB^+ \xrightarrow{h\nu} AB^{+*} \rightarrow A^+ + B$$

$$\text{(ii)} \quad AB^+ \xrightarrow{h\nu_1} AB^{+*} \xrightarrow{h\nu_2} A^+ + B$$
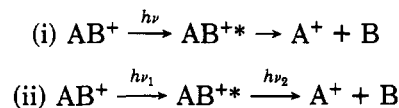
In the first case, the excited level (AB^{+*}) must lie above the lowest dissociation limit; it is therefore a quasibound level which can predissociate with an energy release which will be redistributed as kinetic energy of the fragments. The absorption line width will be determined either by the predissociation lifetime or by the Doppler width, depending on which is the larger. In the second case, a bound to bound transition at frequency ν_1 is detected through subsequent photodissociation of the upper state induced by absorption of a second photon of frequency ν_2 (which may be the same as or different from ν_1). Our work on H_3^+ is an example of type i, while our studies of the HD^+ ion[11] are of type ii.

We separate fragment ions from the main beam with an electrostatic analyzer (ESA), which then directs them onto an off-axis electron multiplier. Consequently the spectrum of H_3^+ is recorded by measuring the H^+

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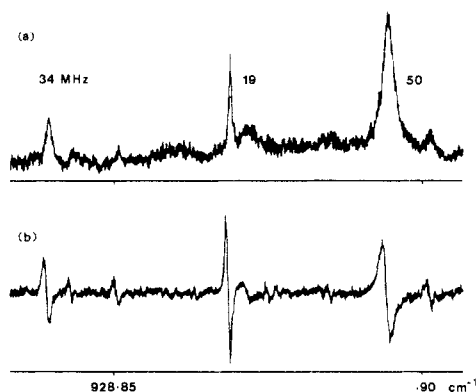
Figure 2. A small region of the H_3^+ spectrum (0.06 cm^{-1}) recorded by (a) mechanical chopping of the laser beam and (b) velocity modulation of the ion beam in the drift tube.

Figure 3. A proton kinetic energy spectrum of one line in the H_3^+ predissociation spectrum; the double peak shape is due to backward and forward scattered fragments.

ion current as a function of beam potential using a particular laser frequency. H^+ fragment ions are produced by collision-induced dissociation with the background gas, and introduction of the infrared laser beam results in a small background (off-resonance) increase in the H^+ fragment intensity. The sensitivity for detecting resonances is enhanced by means of a metal tube in the center of the apparatus, which we call the drift tube, to which a modulating voltage (7 kHz) of up to 10 V is applied. Ions entering the drift tube are velocity modulated, enabling phase-sensitive detection of the H^+ ion current to be employed. In order to reduce background noise arising from fragmentation outside the drift tube, we apply a dc offset of between ±500 V to the drift tube. H_3^+ ions which fragment inside the drift tube produce H^+ fragments with a kinetic energy different from that of the fragments formed outside. The ESA may then be set so that only fragments formed within the drift tube are collected. Note that the combined use of velocity modulation and tuning with phase-sensitive detection gives rise to first-derivative line shapes. An alternative but less sensitive method of detecting the spectrum is by mechanical chopping of the laser beam, which results in normal absorption line shapes. A small section of the H_3^+ spectrum recorded by both techniques is shown in Figure 2.

The electrostatic analyzer used in our experiments is capable of high energy resolution, so that it can be used not only to separate different fragment ions from each other but also to measure the kinetic energies of H^+ fragments. Two methods of scanning the kinetic energy are available; we may scan the ESA voltage for a given accelerating potential at which a resonant transition occurs, or we can offset the ESA voltage and scan the accelerating voltage. The first method yields a spectrum (see Figure 3) in which forward and backward scattered fragments are resolved, the separation between the corresponding maxima giving the fragment kinetic energy. The second method produces a slice of the frequency spectrum at a given fragment kinetic energy, and successive scans can be used to construct a two-dimensional spectrum[2] in which the variables are transition frequency and fragment kinetic energy.

An important aspect of our experiment which has some disadvantages is that it is intrinsically a high-resolution technique; the magnetic field must be readjusted as the source potential is scanned, and the source potential can be changed by only 1000 V before the
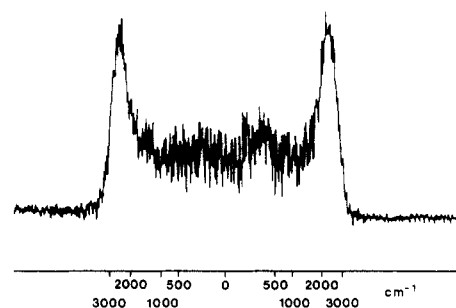
apparatus requires retuning. In order to achieve the signal to noise ratio obtained for the H_3^+ spectrum, we are restricted to a maximum scanning speed of about 1 cm^{-1}/day! With tunable lasers, much faster scanning could be achieved, but at present these have insufficient power to cause detectable increases in fragmentation. Our experiments depend upon efficient population transfer and usually require laser powers of at least 1 W.

Nature of the Observed Spectrum

H_3^+ was found to exhibit a strong and extremely dense infrared predissociation spectrum throughout the carbon dioxide laser region. This was totally unexpected, and at first there was no theoretical explanation available. Because of the intrinsically high resolution, it is extremely time consuming to scan large regions of the spectrum. Nevertheless, a complete scan was made throughout the laser region (872 to 1094 cm^{-1}), and over 26500 lines of signal to noise greater than 2:1 were measured, the spectrum taking some 2500 h to record. The measurements were made by using a laser power of 7 ± 3 W, with an output time constant of 1 s and a drift tube modulation amplitude of 7 V, and with the ESA adjusted to collect H^+ fragments with zero kinetic energy releases. However, all ion-beam slits were open at their maximum aperture in order to maximize signal intensity, giving a kinetic energy resolution of $\simeq \pm 500$ cm^{-1}.

It was important to establish that predissociation is indeed the mechanism for the observed spectrum. Three conceivable alternatives were as follows:

1. Enhanced collision-induced dissociation of the upper state on resonance. This cannot be responsible, since the addition of hydrogen gas as a collision partner *reduces* signal intensity, rather than enhancing it.

2. Direct photodissociation of the upper state on resonance. This is very unlikely since the H^+ photoproduct background for H_3^+ *off resonance* is extremely small, and further experiments using two carbon dioxide lasers showed that addition of off-resonance laser power did not enhance the intensity of the spectrum. This is in marked contrast to observations of the HD^+ spectrum when detected through subsequent photodissociation.[11]

3. Multiphoton excitation processes from bound levels. These seem to play no part in the spectrum, since detailed measurements of many line intensities at different laser powers show an essentially linear power dependence (until saturation occurs). Strong lines saturate at powers greater than 2 W, and the spectrum is considerably less dense at low powers.

Line widths vary greatly throughout the spectrum. The systematic scan of the spectrum described above was performed by using voltage modulation which discriminates in favor of the narrower lines because they have widths comparable with the modulation amplitude. Mechanical chopping of the laser beam does not discriminate in favor of narrower lines, and widths from 3 to several hundred megahertz were observed; Figure 2 shows a small section of the spectrum illustrating these features. The line-width variation is characteristic of a predissociation spectrum involving energy levels of varying lifetimes.

The geometry of the apparatus has enabled us to measure the lifetimes of some states as follows. Since we only detect molecules that fragment within the drift tube, the transitions observed must involve a lower level of sufficiently long lifetime to be extracted from the source ($\simeq 1~\mu s$) and transmitted to the detection region (drift tube) with a significant population preserved. At a beam potential of 5 kV, this implies that the initial state lifetime must be 3 μs or greater. Conversely, the final state lifetime must be short enough for the molecule to dissociate within the drift tube, and at a beam potential of 5 kV this implies that the final lifetime must be less than 0.7 μs. These aspects define an experimental lifetime window that has important consequences for the interpretation of the spectrum. The absolute lifetimes of the initial levels involved in some transitions may be determined if a transition can be observed by using two different laser lines at sufficiently different beam potentials. The ions take longer to reach the detection region at low beam potentials than they do at high beam potentials. Since the initial levels involved in transitions are excited vibration–rotation states, their populations in the ion beam will begin to decay immediately after formation; consequently a resonance line involving such a state will have reduced intensity in a spectrum recorded at a low beam potential compared with that at a high beam potential. As the ions are in a collision-free environment, first-order kinetics gives an exponential decay in the number of ions in an excited state, and since the intensity of a transition is determined by the population difference between levels, two intensity measurements of the same line for different times after formation make it possible to determine the lifetime of the state involved, provided the lifetime is sufficiently short for an observable decrease in intensity to have occurred. We have observed many examples of this effect, yielding in these cases initial state lifetimes of several microseconds;[12,13] final state predissociation lifetimes may be obtained directly from the observed line widths.

As mentioned above, the H^+ kinetic energy release for any given resonance may be determined, but to do so for all the observed resonances would require a prohibitive amount of recording time. However, sections of the spectrum have been examined in this manner. It is found that there are many resonances for which the fragment H^+ kinetic energy release is between 2000 and 3000 cm^{-1}. (See Figure 3.) Since the input energy of the photons used is only 1094 cm^{-1} at most, and since multiphoton processes do not contribute,

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these observations prove that many of the transitions that occur involve an initial level that lies *at least* 2000 cm^{-1} above the appropriate dissociation limit. In considering these results, it should be noted that a very large family of dissociation limits exists, because the H_2 fragment molecules may be produced in many different vibration–rotation levels. Unfortunately, we are unable to identify the particular dissociation channel for a given resonance.

Finally, it should be noted that the predissociation spectrum arises from only a very small proportion of the total H_3^+ beam. Most of the ions are in bound levels which lie too far below the lowest dissociation limit to contribute to the spectrum.

Pseudo-Low-Resolution Spectrum

It was soon clear that to assign the 26 500 lines was probably an impossible task, but a usual first step to take in such a case would be to examine the low-resolution spectrum. Unfortunately, due to the intrinsically high resolution obtained, it was not possible to record a low-resolution spectrum directly. It was therefore decided to construct a pseudo-low-resolution spectrum by a computer convolution of the data. This was achieved by assuming a Gaussian line shape for each measured line of the spectrum and convoluting the data with a line width of 4 cm^{-1}. Structure was immediately apparent in the convolution, and reducing the convoluted data to the strongest 1934 lines showed very clear structure, while convolution of the remaining data showed none. The pseudo-low-resolution convolution spectrum showed four peaks, at 1033.62, 978.45, 928.02, and 875.65 cm^{-1}, with an uncertainty of about 1 cm^{-1} in the peak positions. Carrington and Kennedy[2] noted that these numbers correlate remarkably closely with the calculated frequencies of the $j = 3-5$ rotational transitions in the first four vibrational levels of H_2.

In the light of subsequent theoretical work, it seems uncertain at present whether this correlation is coincidental or not. It suggests, however, that H_3^+ ions in levels close to an $H_2 + H^+$ dissociation limit might usefully be regarded as $H^+\cdots H_2$ complexes, and some of the dynamical consequences of that model (for example, the motion of H^+ relative to the H_2 core) have been investigated.

Deuterium Isotope Studies

When suitable mixtures of hydrogen and deuterium are used in the ion source, it is possible to produce intense beams of D_3^+, D_2H^+, and H_2D^+. For each ion, collision-induced dissociation results in the formation of all possible atomic and molecular fragments, but photofragment diatomic molecules are not detectable. For the mixed isotope species, both H^+ and D^+ fragments are produced by photodissociation.

D_3^+ shows a spectrum similar in type to that of H_3^+, but with a greater density of lines and less intensity. This may be a result of the same number of ions being distributed over a greater level density because of the increased mass. It should also be remembered that we are restricted to measurements in the carbon dioxide laser region.

For the mixed isotope species, predissociation spectra are also found. With D_2H^+ the possibility arises of monitoring either H^+ or D^+ fragments, and spectra of the same frequency region recorded at zero kinetic en-

ergy release by monitoring the different fragments in turn were found to be totally different, with a noticeably reduced intensity in the case of those taken by monitoring the D^+ fragments. In the case of H_2D^+, only spectra recorded by monitoring H^+ fragments could be measured, because the magnetic analyzer has insufficient resolution to differentiate between D_2^+ and H_2D^+. Consequently, attempts to measure the spectrum of H_2D^+ by monitoring D^+ ions are obscured by direct D^+ photodissociation products from D_2^+, which has an allowed electronic transition to a repulsive state.

It should also be noted that, as with H_3^+, the mixed isotope species show resonance lines with fragment kinetic energies greater than 2000 cm^{-1}.

Concluding Remarks

Assignment of the 26 500 lines observed for H_3^+ does not seem possible, and in that sense, the problems posed by the spectrum will remain unsolved for the foreseeable future. That would certainly be the view of a conventional spectroscopist, but it is perhaps overpessimistic. The traditional approach to the final analysis of a vibration–rotation spectrum is to start with an assumed molecular geometry, incorporate the relevant electronic, nuclear, and spin degrees of freedom into an effective Hamiltonian, and use the methods of quantum mechanics to calculate the energy levels, selection rules, and transition frequencies and intensities. Comparison with experiment leads to progressive refinement of the starting point, and the process is repeated until satisfactory convergence is achieved. The end product is then a set of values for the molecular constants included in the effective Hamiltonian. The major problem with highly excited H_3^+, and other molecules with substantial internal energy, is the starting point. The concept of an equilibrium geometry becomes meaningless in extreme cases of molecular nonrigidity, and it is then difficult to find a basis for spectroscopic analysis. These problems will surely be better understood as more spectra of highly excited molecules are recorded. For the H_3^+ ions studied in our work, the only certain good quantum numbers are the total angular momentum and the parity; spectroscopic analysis requires rather more than that! It is likely that as the essential molecular physics of the molecule is better understood, particularly the dynamical aspects, a better model will be found to form the basis of spectral assignment. There is also little doubt that better measurements could be made; the use of a high laser power, for example, effectively obscures any useful selection rules that might exist. For the present, however, there are a number of established facts about the spectrum which an acceptable theory must accommodate. These are as follows:

1. We observe a line density of 120 lines/cm^{-1} in the 872–1094-cm^{-1} region.

2. The initial states involved in the transitions must have lifetimes greater than ≈ 3 μs; the final states have lifetimes from 10^{-7} to 10^{-9} s. There are good reasons to suppose that both longer and shorter lived states exist.

3. Most of the states involved lie above the lowest dissociation limit for which the H_2 fragment has $v = 0$, $N = 0$. There are many long-lived states of H_3^+ lying at least 2000 cm^{-1} above this dissociation limit, and probably above higher energy dissociation limits in which the H_2 fragment is rotationally or vibrationally excited.

4. The spectrum exhibits a characteristic coarse-grained structure consisting of four well-defined maxima.

5. D_2H^+ exhibits different predissociation spectra depending on whether H^+ or D^+ fragment ions are monitored.

A number of theoretical models have been developed to account for at least some of these observations, and certain further predictions, yet to be verified experimentally, have been presented. These are reviewed in the following paper, by Pollak and Schlier.[14]

(14) Pollak, E.; Schlier, Ch. *Acc. Chem. Res.*, following paper in this issue.