HIGH RESOLUTION SPECTROSCOPY OF MOLECULAR IONS

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Richard J. Saykally

Department of Chemistry, University of California, Berkeley, California 94720

R. Claude Woods

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

INTRODUCTION

Gaseous molecular ions are involved in some of the most intriguing problems in modern science. The realization of their importance in such diverse systems as the upper atmosphere, the aurora, comet tails, electrical discharges, flames, and in more conventional chemical systems, coupled with recent technological progress that has resulted in the capability to perform detailed laboratory studies of charged molecules, has precipitated a new dialogue among the disciplines of chemical physics, theoretical chemistry, aeronomy, astronomy, astrophysics, atomic physics, and plasma physics. At the center of this interaction is the field of high resolution spectroscopy. The purpose of this article is to review the progress that has been made in this area during the past decade with respect to the study of molecular ions. By "high resolution" spectroscopy we imply that rotational structure of the subject molecule is observed. Consequently our discussion emphasizes work on small molecular ions—principally diatomics and triatomics—and necessarily excludes some very interesting work on larger cationic systems. These, however, are the subjects of a current review article by Dunbar (1). We have restricted ourselves to gas phase studies, in spite of the fact that spectra of a number of molecular ions have been studied in cryogenic matrices (2), and we have excluded the beautiful (but low resolution) photo-detachment studies of negative ions (3) and photoelectron spectroscopy (4) in general. Because laser pho-

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tofragment spectroscopy of ion beams is the subject of another chapter in this volume (5) we have not emphasized this excellent work, except as it applies to specific high resolution studies.

The fundamental purpose for studying high resolution spectra of molecular ions is that of understanding their geometrical and electronic structures, for these in turn affect every other molecular property. Analysis of rotational structure directly yields moments of inertia, from which we can deduce the molecular geometry. This knowledge is essential to understanding the electronic structure. If we combine it with the results of measurements of more complicated interactions, such as spin-orbit or spin-spin splittings, hyperfine structure or lambda doubling, we can obtain a detailed characterization of the electronic wavefunction. By studying spectra of charged atoms, vital information has been obtained about their neutral counterparts. This same principle applies to molecular ions with respect to understanding the structure, bonding, stability, and reactivity of molecules in general.

Ion-molecule reactions dominate the chemistry of the upper atmospheres of planets and influence the properties of nearly all plasmas, both in the laboratory and in nature. Comprehension of the dynamics of these reactions normally requires previous knowledge of electronic structure and molecular geometry of the reactant and product ions. One of the most exciting developments of the preceding decade has been the discovery of an intricate and complex chemistry in interstellar gas clouds. The observation of molecular ions in particular has provided crucial support to the theories of Herbst & Klemperer (6) and Watson (44, 45) that regard ion-molecule chemistry as the principal vehicle for synthesis of most of the approximately 52 molecules now discovered in such regions. The importance of the interaction between astronomy in the radio, millimeter, and far-infrared regions of the spectrum and laboratory spectroscopy of molecular ions should be emphasized. It now appears very probable that a number of additional molecular ions (as well as neutral radicals) are present in the denser (10^3–10^6 cm^{-3}) clouds (7). In order to detect and definitively identify these species through astronomical observations very accurate laboratory spectra will be of great utility, or in some cases, essential.

Spectroscopic studies of molecular ions have already revealed some interesting features that are unique to these charged systems. Collisional linewidths of molecular ions have been a topic of controversy. Earlier arguments had been advanced which predicted that collision cross sections and therefore pressure-broadened (homogeneous) linewidths of ions would be 1–2 orders of magnitude larger than those of corresponding neutral molecules. This argument was based on the hypothesis that the same long-range multipole forces that cause ion-molecule reaction rates to

exceed those for most neutral systems would similarly increase the homogeneous linewidths. Such large collisional linewidths would almost certainly have precluded the observation of rotational spectra of molecular ions. Fortunately, as we discuss later in the chapter, this argument is incorrect. The electric dipole moments of molecular ions exhibit somewhat anomalous behavior in comparison to those of neutral molecules because of their dependence on the origin of the electronic coordinates. Since the physically meaningful origin is the center of mass, substitution of an isotopic nucleus, which causes a shift in the center of charge relative to the center of mass, can have a dramatic influence on the resulting ion dipole moment. Small dipole moments, of the order of tenths of a Debye, are produced through this mechanism in homopolar ions by creating the isotopically asymmetric species, eg. $^{16}O^{18}O^+$, affording the opportunity to study rotational and vibrational spectra of these otherwise nonpolar molecules. The search for spectra of molecular ions for which the neutral molecule is unstable with respect to dissociation (eg. H_3^+, NH_4^+) has led to the discovery of spectra from bound Rydberg states of the neutral. These Rydberg states may be of considerable importance regarding the chemistry of the ions in plasma environments. In addition to giving characteristic high-quality spectroscopic information for several important species, the study of molecular ion beams provides a nearly unprecedented opportunity to study molecules very near their dissociation limits with extremely high precision.

Our understanding of the properties and dynamics of molecular ions is restricted by the fact that few of them have been studied in the laboratory, which is particularly true for polyatomic ions. This is a simple consequence of the facts that ion-molecule reactions are among the fastest known chemical processes and that ions in general are short-lived in most environments because they either recombine with electrons or rapidly diffuse under the influence of small electric fields to the walls of their containers. Thus it is very difficult to create detectable concentrations of molecular ions for any length of time—especially of those species that are chemically less stable.

The status of molecular ion spectroscopy was reviewed by Herzberg in his Faraday Lecture to the Chemical Society (8) in September of 1971. As of that time 33 diatomic ions and six polyatomic ions had been studied by spectroscopic methods. All of these had been observed by absorption or emission in the visible region of the spectrum, except for H_2^+; it had become in 1968 the first molecular ion to be detected by a technique with resolution better than the optical Doppler width, through the work of Dehmelt & Jefferts (9–11).

The last decade has witnessed dramatic advances in the spectroscopy of

molecular ions. Technological breakthroughs in the areas of electronics, computer science, and molecular beams and the evolution of laser light sources have made possible sophisticated new experiments for detecting molecular ion spectra. The HCO^+ and HNN^+ ions have been established as important and ubiquitous constituents of interstellar clouds by the powerful new radio astronomy techniques that have been used to detect them. Recently CO^+ and HCS^+ have likewise been observed in interstellar clouds. Microwave spectroscopy has been successful in detection of rotational spectra of CO^+, HCO^+, HNN^+, and HCS^+ and the determination of precise structures for HCO^+ and HNN^+. Ion beam spectroscopy has produced vibrational spectra of HD^+, HeH^+, and $D_3{}^+$ and high resolution electronic spectra of CO^+, H_2O^+, $O_2{}^+$, and CH^+. Far infrared laser magnetic resonance spectroscopy has been used to measure pure rotational spectra of HBr^+. Most recently, vibrational absorption spectra of $H_3{}^+$ have been detected with a tunable infrared difference frequency laser system. In addition, optical spectra have been observed for a number of other ions by laser-induced fluorescence methods employing ion traps, flowing afterglows, and ion beams, and by more conventional absorption and emission spectroscopy.

A list of the molecular ions studied with techniques producing at least rotational resolution is presented in Table 1. In the following pages we survey these experiments and summarize the results that have been obtained from them. We begin with studies of molecular ions in non-mass-specific sources, viz. electrical discharges, interstellar clouds and afterglows, and then consider the experiments done on mass-selected ions.

EMISSION AND LASER-INDUCED FLUORESCENCE SPECTRA OF MOLECULAR IONS

Emission spectroscopy of molecular ions in electrical discharges and with electron impact excitation has traditionally provided the cornerstone of our understanding of molecular ion structures. In many cases elegant laser and charged-beam techniques for studying ions are quite impotent without the existence of data from previous optical spectroscopy work; emission spectroscopy has provided the broad overview and general understanding needed to design and interpret newer experiments, while the latter have revealed the intimate details. In this section we discuss the recent progress made in the study of rotationally resolved emission spectra of molecular ions. We also include here the closely related studies of ions by laser-induced fluorescence (LIF), electron-impact excited fluorescence and chemiluminescence in sources with no mass selectivity, viz. afterglows, supersonic expansions, and electron-excited gases. Two reviews

Table 1   Molecular ions studied with rotational resolution

No.	Ion	Ground state	Method of detection[a]
1.	AlH^+	$^2\Sigma^+$	Optical emission (12)
2.	AsO^+	$^1\Sigma^+$	Optical emission (12)
3.	AsS^+	$^1\Sigma^+$	Optical emission (12)
4.	$BeAr^+$	$^2\Sigma^+$	Optical emission (12)
5.	$BeKr^+$	$^2\Sigma^+$	Optical emission (12)
6.	BeH^+	$^1\Sigma^+$	Optical emission (12)
7.	BH^+	$^2\Sigma^+$	Optical emission (12), chemiluminescence (40)
8.	BO^+	unknown	Optical emission (12)
9.	C_2^+	$^2\Pi_u$	Optical absorption (12)
10.	C_2^-	$^2\Sigma_g^+$	Optical absorption (12)
11.	CCl^+	$^1\Sigma^+$	Optical emission (12)
12.	CdH^+	$^1\Sigma^+$	Optical emission (12)
13.	CH^+	$^1\Sigma^+$	Optical absorption (12, 15), ion beam electronic (103), ion trap LIF (99, 100), chemiluminescence (37–40)
14.	$C_4H_2^+$	$^2\Pi_g$	Optical emission (13)
15.	Cl_2^+	$^2\Pi_{3/2g}$	Optical emission (12)
16.	CN^+	$^1\Sigma^+$	Optical emission (12)
17.	CO^+	$^2\Sigma^+$	Microwave pure rotational (61, 76), ion beam electronic (77), ion beam LIF (115), ion trap LIF (100, 102), MM astronomy (78)[b]
18.	CO_2^+	$^2\Pi_g$	Optical emission (13, 16, 17)
19.	CS^+	$^2\Sigma^+$	Optical emission (12)
20.	CS_2^+	$^2\Pi_g$	Optical emission (13)
21.	F_2^+	$^2\Pi_g$	Optical emission (12)
22.	H_2^+	$^2\Sigma_g^+$	RF-optical double resonance (9–11)
23.	HD^+	$^2\Sigma^+$	Ion beam infrared vib-rot (104), ion beam infrared doub res (114)
24.	H_3^+	$^1A_1$	Infrared laser vib-rot (95)
25.	D_3^+	$^1A_1$	Ion beam infrared vib-rot (108)
26.	H_2D^+	$^1A_1$	Ion beam infrared vib-rot (120)
27.	HBr^+	$^2\Pi$	Laser magnetic resonance (94), optical emission (12)
28.	HCl^+	$^2\Pi$	Optical emission (12)
29.	HCO^+	^1A	Microwave pure rotation (64, 65), MM astronomy (58, 63, 66, 67)[b]
30.	HCS^+	^1A	Microwave pure rotation (80), MM astronomy (79)[b]
31.	HF^+	$^2\Pi$	Optical emission (12)
32.	HNN^+	^1A	Microwave pure rotation (71, 72), MM astronomy (69, 70, 73)[b]

Table 1   *Continued*

No.	Ion	Ground state	Method of detection[a]
33.	H_2O^+	$^2A_1$	Ion beam electronic (114), optical emission (13, 19)
34.	HeH^+	$^1\Sigma^+$	Ion beam infrared vib-rot (107)
35.	H_2S^+	$^2A_1$	Optical emission (13)
36.	$HeNe^+$	$^2\Sigma^+$	Optical emission (18)
37.	$HgAr^+$	$^2\Sigma^+$	Optical emission (12)
38.	HgH^+	$^1\Sigma^+$	Optical emission (12)
39.	LaF	unknown	Optical emission (12)
40.	MgH^+	$^1\Sigma^+$	Optical emission (12)
41.	N_2^+	$^2\Sigma_g^+$	Optical emission (12, 24), ion trap LIF (100, 102)
42.	NH^+	$^2\Pi$	Optical emission (12)
43.	NNO^+	$^2\Pi$	Optical emission (13)
44.	NO^+	$^1\Sigma^+$	Vib-rot emission spectrum (41)
45.	O_2^+	$^2\Pi_g$	Ion beam electronic (103, 110–112), optical emission (12, 14)
46.	OCS^+	$^2\Pi$	Optical emission (13)
47.	OH^+	$^3\Sigma^-$	Optical emission (12)
48.	P_2^+	$^2\Pi_{3/2}$	Optical emission (12)
49.	PF^+	$^2\Pi$	Optical emission (12)
50.	PH^+	$^2\Pi$	Optical emission (12)
51.	SH^+	$^3\Sigma^-$	Optical emission (12)
52.	SiH^+	$^1\Sigma^+$	Optical emission (12)
53.	SiO^+	$^2\Sigma^+$	Optical emission (12)
54.	TaO^+	unknown	Optical emission (12)
55.	YF^+	$^2\Delta$	Optical emission (12)
56.	ZnH^+	$^1\Sigma^+$	Optical emission (12)
57.	ZrO^+	unknown	Optical emission (20, 121)

[a]Original references for optical emission and absorption work prior to 1975 are given in (12) and (13).
[b]MM = millimeter.

cover optical spectroscopy of diatomic (12) and polyatomic (13) molecular ions up to about 1975. We summarize here the most important developments since that time.

Several ions observed earlier by classical optical methods have been examined in more detail. New work has been done on the $b^4\Sigma_g^- - a^4\Pi_u$ First Negative System of O_2^+ observed in emission (14) from discharges through helium with a trace of oxygen. This is closely connected with the ion beam results on O_2^+, and additional references are given in papers

cited in that section. The $A^1\Pi - X^1\Sigma$ system of CD^+ was studied in a hollow cathode discharge (15), the $A^2\Pi_u - X^2\Pi_g$ bands of CO_2^+ were studied in a hot cathode discharge (16), the ^{14}C and ^{18}O isotopes of CO_2^+ were observed and analyzed (17), and spectra involving the $B^2\Sigma^+$, $A^2\Pi$, and $X^2\Sigma^+$ states of $HeNe^+$ excited in a hollow cathode were examined in detail for the first time (18). Extensive work has been done on H_2O^+ observed in emission from a hot filament discharge (19). Two new ions have been observed in emission from discharges, ZrO^+ (20, 121) and LaF^+ (21). Electron impact excited emission studies of radical cations of numerous polyatomic molecules have been done by Maier (22, 23). While this group has concentrated principally on obtaining spectra for larger polyatomic systems, such as the halobenzenes, partial rotational resolution has been obtained for the haloacetylenes and increases in sensitivity are expected to yield rotationally resolved spectra of several cations in the future. Cossart-Magos et al (24) have observed emission from several cations ranging in size from N_2^+ to halobenzenes using a discharge source developed by Cossart (25) with a liquid nitrogen-cooled cathode and a large transverse magnetic field to confine the ions near the electrodes. Both the Maier (22) and Leach (26) groups have developed sophisticated photon-ion coincidence counting techniques to measure lifetimes and quantum yields of molecular ions. Cossart (27) has reviewed the different types of sources that have been used to excite emission spectra of molecular ions.

Emission spectra of H_3 and D_3 have been discovered by Herzberg (28) in liquid nitrogen-cooled hollow cathode discharges. The transitions occur between Rydberg states of the neutral molecules, which have repulsive $^2E'$ ground states. H_3 and D_3 are formed in the negative glow region of the discharge by recombination of H_3^+ and D_3^+ with electrons. Analysis of the spectra found near 5600 Å, 6025 Å, and 7100 Å indicates that the molecules have an equilateral triangular geometry with unresolved doublet spin structure (29, 30). The molecular constants closely approximate calculated values for ground states of H_3^+ and D_3^+, as expected, since these Rydberg states correspond to an electron loosely bound to an H_3^+ (D_3^+) core. Details of the electronic structure were revealed by analysis of the lambda doubling and Jahn-Teller perturbations and the line broadening caused by predissociation from lower levels of the 5600 Å and 6025 Å bands, assigned as parallel bands of an oblate symmetric top (30). Similar Rydberg states have been recently assigned to the NH_4 molecule by Herzberg (116) and related molecules, eg. H_3O and CH_5, should also have analogous states. Spectra of these species would give us the first spectroscopic information on structures of the corresponding molecular ions, as well as on the neutrals.

Another development in emission spectroscopy of ions first reported by Rockett & Brundin (117) and Robbin et al (118) for N_2^+, and used by Carrington & Tuckett (31) to study N_2^+, N_2O^+, and CO_2^+, makes use of controlled electron impact ionization of a supersonic molecular beam to produce excited molecular ions with very low translational and rotational temperatures. Spectra of N_2^+, N_2O^+, and CO_2^+ were obtained with rotational temperatures near 20 K. The extreme cooling in the supersonic beam simplifies the emission spectra tremendously, and consequently will be most valuable when applied to complicated polyatomic ions.

Laser-induced fluorescence spectra of N_2^+ molecular ions generated in a He flowing afterglow by Penning ionization were first observed in 1975 by Engelking & Smith (32). Miller, Bondybey, and co-workers (33–35) have used this approach to obtain rotational resolved LIF excitation spectra for N_2^+, O_2^+, and CO^+ in flowing afterglows. They generated Ar metastables in either a DC discharge or a 2450 MHz cavity discharge and mixed them with reactant gases in a concentric flow tube. Time-resolved detection of fluorescence excited with a pulsed dye laser allowed radiative and collisional lifetimes to be measured. In a clever series of experiments (33, 35), they showed that vibrational relaxation of the excited $A^2\Sigma^+$ states of isoelectronic CN, CO^+, and N_2^+ through collisions with rare gas atoms have extremely large cross sections, and found the mechanism for vibrational energy transfer to be internal conversion between vibrational levels of the upper state and high vibrational levels of the ground state. The fact that the cross sections for N_2^+ was a factor of 10 larger than for CO^+ or CN showed that A-X perturbations, which are symmetry forbidden in N_2^+, are not important in the process. In later work, Miller, Bondybey, and co-workers (36) studied LIF spectra of halobenzenes by this technique, but without rotational resolution.

The final technique to be considered in this section is chemiluminescence spectra of molecular ions. Ottinger (37, 38) and co-workers developed the CLIMAX (Chemiluminescent Ion-Molecule Atom Exchange) method on the reaction $C^+ + H_2 \rightarrow CH^+ + H$. C^+ ions were generated in a commercial ion source, mass filtered, and accelerated into the collision chamber, where they encountered H_2 target gas at 10 mTorr pressure. Light emitted from the reaction in a perpendicular direction was dispersed and monitored by a photon counting system. The $A^1\Pi–A^1\Sigma^+$ transition was observed in high-J lines for both CH^+ and CD^+. More recently, Ottinger & Kusunoki (39, 40) have observed three new bands involving the $a^3\Pi$ state, located 1 eV above ground, and have discovered a new state of BH^+ generated in the reaction of B^+ with H_2. It seems very probable that other molecular ion spectra will be observed in this same manner. In a related development, Zwier et al (41) observed unresolved

infrared chemiluminescence from molecules that had undergone vibrational excitation as a result of fast exothermic ion-molecule reactions occurring in a flowing afterglow apparatus. They found that the chemiluminescence from some ions, including NO^+, is about as intense as that from neutral products. It seems that the use of a high-resolution spectrometer instead of the filters that were actually employed could lead to the observation of vibration-rotation spectra of a number of interesting ions. Because the flowing afterglow can employ mass selection of reactant ions and mass spectroscopic detection of products, as well as modulation of ion flow velocities, identification of the emitting species can be made independently from assignment of the spectra. The signals detected so far are quite weak, but with some improvements, like cryogenic cooling of the afterglow and narrow-band detection, the signal/background could be enhanced considerably.

MICROWAVE SPECTROSCOPY OF IONS: RADIO ASTRONOMY AND LABORATORY DISCHARGE STUDIES

Ten years ago pure rotational spectra, which usually occur in the microwave region of the electromagnetic spectrum, were completely unknown for molecular ions, and the possibility of obtaining them had seldom even been discussed. Today microwave spectra have been obtained for four ions (CO^+, HCO^+, HN_2^+, and HCS^+), and for each of these detection has been possible both by radioastronomy and by absorption spectroscopy in laboratory glow discharges. In most cases the identical transitions have been studied by the two techniques. Because of this one-to-one correspondence in the species observed, we discuss both techniques together in this section, even though the instrumentation and the nature of the chemical environment are very different indeed.

Radioastronomy began as a very exciting application of the results of high resolution spectroscopy. In the late 1960s a number of simple, well-known molecules, e.g. H_2O, NH_3, and OH (42), were observed in the interstellar medium, using transitions that had been previously measured and assigned by laboratory microwave spectroscopy. The resolution and measurement accuracy of microwave spectroscopy are intrinsically so high and the transition frequencies so characteristic that such interstellar molecules could be identified with complete assurance with the observation of even one or two transitions. By now the list of molecules found by radio astronomy has grown to more than 50 entries (the largest is HC_9N) (43), and most of these are found in so-called "dense" molecular clouds

($\sim 10^5$ molecules/cm^3) that are totally opaque to optical astronomy due to absorption and scattering by dust grains. This extensive and intricate chemistry was completely unanticipated, but is now thought to be explained by a complicated mechanism that relies heavily on ion-molecule reactions (6, 44, 45). Thus, the ions play a pivotal role even in the production of the neutral molecules, and their observation and study is particularly helpful in testing the validity of proposed kinetic schemes. Radioastronomy is no longer just a user of high resolution spectroscopic results, but also a producer, i.e. an important technique for obtaining new spectra. Several interstellar molecules, including the three ions HCO^+, HN_2^+, and HCS^+, as well as the radicals C_3N (46), C_2H (47), and C_4H (48a–c) and the unstable isomer HNC (49, 50), were first detected by radioastronomy (usually by accident) and later identified solely from the astrophysical spectra or from some combination of laboratory and astrophysical data or ab initio calculations. From the instrumental point of view radioastronomy of ions is absolutely no different from radioastronomy of neutrals; it is never even clear whether an ion or neutral is being observed until the spectrum is completely assigned. The instrumental details of radioastronomy have been reviewed elsewhere (51a,b).

Laboratory studies of the microwave spectra of molecular ions have been carried out at the University of Wisconsin in a glow discharge spectrometer first described by Woods (52, 53). This straightforward absorption experiment is distinguished primarily by the nature of the cell and its absorbing medium, which is the plasma of a DC glow discharge, suitable for the production of many transient species, including molecular ions. The discharge tube that has been used for the ion work so far is 15 cm in diameter and 4 m long and is driven by a power supply capable of providing up to 1 amp of current at voltages to 3 kV. Gas mixtures can be pumped through this tube using either a large throttled diffusion pump or a large mechanical pump, and cooling can be provided by a flow of liquid nitrogen (or tap water) through plastic tubing that is in thermal contact with the outer wall of the pyrex discharge tube. Overall pressures are those typical for microwave spectroscopy (5–150 mTorr) and the attainable ion densities are near 10^{10}/cm^3. The translation, rotational, and vibrational temperatures of the ions are not entirely well characterized at present, but have been discussed recently, along with other considerations bearing on the absorption intensity and spectrometer sensitivity, by Woods (54). The fractional ionization in the discharge is near 10^{-5} and loss of this factor in concentration relative to ordinary stable molecules does mean that spectra of ions are fairly weak and that sensitivity is the main limitation (usually the only one) to their detection and study. Sensitive modulation methods, either Zeeman or source frequency modulation,

must be used along with computer-controlled signal averaging (55) to obtain adequate signal-to-noise ratios. In the most recent scheme the tone burst frequency modulation method of Pickett (56), along with his digital phase detector (57), are used, since these permit the klystron source to be modulated and phase locked simultaneously. Thus the frequency sweep becomes totally digital. With a computer-programmed frequency synthesizer providing the reference, the frequency is controlled, accurate, and stable to 1 kHz (1 part in 10^8) at each step in the scan. The detector is either a silicon point-contact diode or a sensitive Schottky barrier diode.

Previous results from optical spectroscopy and theoretical ab initio calculations have both played a major role in assigning and predicting the microwave spectra of ions and will continue to do so. Microwave spectra depend directly on molecular structure, which is a property well predicted by ab initio calculations. Such calculations, even at rather modest levels of approximation, e.g. SCF with a double zeta basis, will typically yield bond distances good to about 1%, which leads to frequency predictions of 2% accuracy. This is still 2–4 GHz for typical millimeter wave transitions— too large for a search with adequately high sensitivity to be practical. The very best state of the art calculations with large basis sets and extensive configuration interaction may be considerably more precise (bond distances to .003 Å) and (when available) can provide a practical starting point for a microwave search. The ab initio calculations can also provide dipole moments or hyperfine constants that are of great help in understanding or identifying microwave spectra. Spectroscopic constants obtained from high quality classical optical spectroscopy on diatomic or triatomic ions can predict microwave transitions with a precision of 20–200 MHz, i.e. better than the best ab initio calculations.

In 1970 Buhl & Snyder (58) discovered the first interstellar unidentified line at 89,189 MHz and gave the name X-ogen to the mysterious species responsible. Shortly afterward Klemperer (59) proposed that X-ogen was in fact HCO^+ on the basis of arguments that ions should be fairly abundant in interstellar sources and an estimation of the HCO^+ rotational constant from an empirically deduced structure. Only a single unsplit line was observed (as expected for HCO^+) and conclusive identification was not possible without further information. An extensive ab initio calculation at the CI level by Wahlgren et al (60) in 1973 gave strong support to Klemperer's identification, but unequivocal confirmation was still lacking. In 1974 the first successful laboratory microwave observation of an ion, namely CO^+, was carried out by Dixon & Woods (61). The frequency of the strongest component of the $N = O \rightarrow 1$ doublet near 118 GHz was predicted from the best available optical spectroscopic constants (62), yielding a search region of about 300 MHz. A long tedious search of

this region with a room temperature carbon monoxide discharge failed to yield any spectrum, but when it was repeated with liquid nitrogen cooling, the CO^+ transition was just barely detected. A 10% mixture of CO in helium proved a better source of CO^+ and permitted accurate measurement of the two lines to be made. These agreed very well with the optical predictions. The definitive resolution of the X-ogen mystery came in 1975 from two sources. Snyder et al (63) reported observation of the long sought $H^{13}CO^+$ line by radioastronomy, and, independently, Woods et al (64) reported detection of the original X-ogen transition in a laboratory hydrogen-carbon monoxide discharge at liquid nitrogen temperature, making it abundantly clear that Klemperer's identification had been right all along. By the following year the laboratory measurements had been extended to a total of six isotopic species, yielding a complete substitution "r_s" structure for HCO^+ (65). The $H^{13}CO^+$ frequency was in excellent agreement with the astrophysical measurement (63), and the frequencies for DCO^+ and $HC^{18}O^+$ made it possible for radioastronomers to detect and identify them (66, 67). The DCO^+ astrophysical observation (66) was especially interesting in that it showed an extremely high chemical fractionation in favor of deuterium and allowed the distribution of deuterium within the galaxy to be probed to some extent. In 1976 a very high quality CI calculation on HCO^+ was published by Kraemer & Dierckson (68). They calculated not only equilibrium bond distances but anharmonic potential constants and the vibration-rotation interaction corrections, providing overall frequencies for the various isotopes in excellent agreement with experiment. Their bond distances and those of Wahlgren et al (60) agree beautifully with the r_s values from microwave spectroscopy. In 1975 Turner accidentally discovered a triplet of lines near 93,173 MHz (69), which was soon identified as HN_2^+ by Green et al (70) on the basis of ab initio calculations of its rotational constant and quadrupole coupling constants. The hyperfine pattern in conjunction with the ab initio results were sufficient to identify HN_2^+ with certainty using only the astronomical data. The laboratory observation of this HN_2^+ triplet in a hydrogen-nitrogen discharge was soon reported by Saykally et al (71). The laboratory measurements of HN_2^+ were then extended to a total of six isotopic forms to yield another "r_s" structure (72). The astrophysical spectrum of HN_2^+ was greatly improved by Thaddeus & Turner (73), who used a dark dust cloud source and obtained sufficient resolution to observe and measure the quadrupole hyperfine splittings from both nitrogen nuclei. Using the frequency that had been obtained in the laboratory (74), Snyder et al (75) were able to detect DN_2^+ in the interstellar medium, again revealing dramatic deuterium enhancement by chemical fractionation. In 1977 Piltch et al (76) extended the laboratory observations

of CO^+ to the $C^{18}O^+$ and $^{13}CO^+$ isotopic forms, with the latter providing
^{13}C hyperfine coupling constants in excellent agreement with those of
Carrington et al (77) obtained from ion beam laser spectra. Just recently
CO^+ has been detected by radioastronomy by Erickson et al (78). The
$N = 1 \leftarrow 2$ transition was observed, since the molecular oxygen absorption
makes the earth's atmosphere almost opaque at the frequency of the
$N = 0 \rightarrow 1$ lines. A low concentration is predicted for CO^+ in interstellar
clouds because it reacts readily with the very abundant H_2. The most
recent addition to the list of ions studied by microwave techniques is
HCS^+. The $J = 1 \leftarrow 2$ transition at 85,347 MHz was discovered in Sagit-
tarius B2 as an unidentified line by Thaddeus, Guélin & Linke (79), who
eventually located several other transitions in a clear linear molecule pat-
tern and assigned the spectrum to HCS^+ on the basis of ab initio calcula-
tions of the structure, astronomical distribution, and the lack of any viable
alternative. Gudeman et al (80) have now seen the $J = 1 \rightarrow 2$ transition in
laboratory discharges in helium-carbon monoxide-hydrogen sulfide mix-
tures at a frequency (85,347.90 ± .03 MHz) that closely matches the as-
trophysical one (85,347.90 ± .3 MHz). In the same paper Thaddeus,
Guélin & Linke (79) also report radioastronomical detection of spectra
from another linear (or near-linear) molecule, which they conclude is
most likely to be either $HOCO^+$ or $HOCN$. A definitive assignment will
require some further information.

In laboratory discharges pressure broadening normally determines the
observed linewidth; since it is a sensitive probe of intermolecular forces,
the linewidth parameter $(\Delta\nu/P)$ is of considerable interest. This param-
eter has been studied extensively for neutral molecules, but the case of an
ion spectrum broadened by collisions of the ion with neutral molecules
provides a new theoretical and experimental challenge. Before laboratory
microwave spectra of ions had been obtained there was some pessimism
that the linewidth would be very much greater (a factor of 20 perhaps) for
an ion because of the long-range nature of the monopole-dipole force (81,
82). On the other hand, Woods et al (83) had argued that the linewidth
parameter would be similar or only slightly larger for an ion than for a
comparable polar neutral. Experiments have supported the latter conclu-
sion. A measurement of $\Delta\nu/P$ for HCO^+ broadened by collision with H_2
in a liquid nitrogen-cooled discharge has been reported by Anderson et al
(84) and studies with other partners and at other temperatures are now
being carried out. It is hoped that a quantitative theoretical analysis can
be developed that is capable of producing linewidths in agreement with
the experimental ones. The linewidth measurement is of special note in
that it provides an example of the investigation of dynamical effects by
high resolution spectroscopy of ions.

Dipole moments of molecules can normally be measured in microwave experiments to great precision utilizing the Stark effect, but for ions this has not yet proven feasible. The plasma of an electric discharge behaves as a conductor, and electric fields adequate for a measurable Stark perturbation will not penetrate it without excessive current. Similarly, ions in beam environments are strongly deflected by electric fields. Thus, precise measurements of dipole moments for ions remains a challenge for the experimentalist with no viable method yet identified. Less precise spectroscopic determinations, e.g. from absolute intensities, saturation effects, or double resonance, appear quite difficult and may not be worth the effort, since the precision attainable probably cannot compete with that available from good ab initio theoretical calculations. With relatively modest CI calculations dipole moments accurate to $\pm .2$ D can be obtained for neutrals and presumably for ions (85, 86).

It is quite likely that several additional ions will be detected by radioastronomy in the next few years, but there are some definite limitations. Only certain atoms (H, N, O, C, S, and a few others) occur with adequate abundance to produce observable quantities of ions, and the best present models of interstellar chemistry predict only a few ions to have large enough steady-state concentrations to be observed with current technology. Some increase in receiver sensitivity is inevitable, but eventually a level of signal strength must come [Thaddeus has called it the confusion limit (87)] where there are lines from something at almost every frequency and assignment or even resolution of them becomes impossible. A great many ions are potential candidates for laboratory microwave studies and as the production of them becomes better understood (e.g. through mass spectrometric studies), the prediction of their frequencies from theory or other spectroscopic methods improves, and the available spectrometer sensitivity increases, more of them will surely be observed.

PURE ROTATIONAL SPECTROSCOPY
OF MOLECULAR IONS
BY LASER MAGNETIC RESONANCE

Far infrared (FIR) (50–1000 μm) laser magnetic resonance (LMR) spectroscopy was invented in 1968 by Evenson et al (88). It has subsequently evolved into one of the most powerful methods for high resolution spectroscopy of open-shell molecules in the gas phase. So far 20 molecules and two atoms have been detected by LMR, including 18 ground state neutral radicals (9 diatomics, 7 triatomics, and 2 polyatomics), 4 metastable ex-

cited electronic states of diatomics, the ^3P ground states of C and O atoms, and the molecular ion HBr^+.

FIR LMR was reviewed in 1980 by Evenson et al (89). The experiment consists mainly of a fixed-frequency optically pumped FIR laser operating in the range 30 cm^{-1}–200 cm^{-1} as a light source and a large electromagnet to tune appropriate energy levels of a paramagnetic gaseous sample into resonance with the laser frequency. The sample is generated inside the laser cavity with either a low pressure flame or a DC discharge. The laser power is monitored as the magnetic field is scanned, producing the LMR spectrum. With this technique one obtains an impressive combination of sensitivity and resolution; for example, pure rotational transitions can be detected for OH radical densities of 5×10^5 cm^{-3}—a much lower detection limit than any other spectroscopic method except laser-induced fluorescence. The resolution is normally limited by the pressure broadened linewidth, typically 10 MHz at the usual operating pressures near 1 torr. Sub-Doppler resolution can be obtained in favorable cases because the sample is located inside a standing wave radiation field, making saturation dip measurements possible. LMR is most sensitive for detecting pure rotational transitions of light paramagnetic molecules, especially hydrides that are usually inaccessible to microwave spectroscopy, and is for that reason quite complementary to microwave techniques. Frequency coverage is provided by about 1000 optically pumped laser lines throughout the FIR. Typically a transition must lie within 1% of these laser frequencies for it to be tuned into resonance by available magnetic fields (20 kGauss).

The development of an LMR spectrometer employing a positive column plasma to generate molecular ions inside the laser cavity has been described by Saykally, Lubic & Evenson (90). The discharge spectrometer consisted of a 7.6 cm diameter by 38 cm long quartz far-infrared gain cell pumped transversely by a 2.3 meter CO_2 laser with a 30 W single line output power and a 5 cm diameter by 58 cm long intracavity sample region; these two regions were separated by a polypropylene beam splitter. The sample region was centered inside the bore of a 5 cm diameter by 33 cm long solenoid magnet cooled by liquid nitrogen and capable of producing 6 kGauss fields with a 1% homogeneity over a 15 cm length. Because this arrangement produced an axial magnetic field, only $\Delta M = \pm 1$ transitions could be observed. A DC glow discharge was maintained between a water-cooled cathode located in a sidearm outside of the optical cavity and a cylindrical copper anode located about 3 cm from the beam splitter. The discharge was generally operated near 1 torr pressures with about a

100 l/min flow of gases at currents of 50 mA. This produced a plasma density of 10^8–10^{10} cm^{-3}. Discharges of this nature exhibit electron temperatures of 20,000–30,000 K. Studies of neutral molecules in discharges have shown that their translational and rotational temperatures are generally close to the wall temperature (300 K), while vibrational temperatures can exceed several thousand degrees. Such information is much more difficult to obtain for ions in discharge environments, but one must consider the possibility that they can behave quite differently from neutral molecules under these conditions.

Preliminary experiments produced LMR spectra of ground-state O atoms (91) and metastable excited electronic states of O_2 (92) and CO (93) in glow discharges. Detection of pure rotational transitions in the HBr$^+$ molecular ion was reported by Saykally & Evenson (94) in 1979. The $J = 3/2 \rightarrow 5/2$ and $J = 5/2 \rightarrow 7/2$ transitions in the $\Omega = 3/2$ spin component of the $X^2\Pi$ ground electronic state were observed in a discharge through 1% HBr in He at currents of 15 mA and pressures near 1 torr. Because bromine has two equally abundant isotopes, each with a spin of 3/2 and large nuclear electric quadrupole and magnetic dipole moments, two sets of hyperfine quartets were observed for every M_J state, with each line further split into a doublet by the small lambda doubling. The proton hyperfine splitting was too small to resolve. The $J = 3/2 \rightarrow 5/2$ transition of DBr$^+$ (in a DBr/He discharge) and the $J = 5/2 \rightarrow 7/2$ transition of HBr$^+$ in v = 1 were also detected under the same conditions. Most transitions have been assigned and are being analyzed by nonlinear least squares regression. When this analysis is completed, one expects to obtain a great deal of information about the electronic structure of HBr$^+$. This is a particularly unusual case, in that there exist two nuclear spins and quadrupole moments, fine-structure interactions, and four isotopic species with which to probe the structure of a molecule with a net charge. Comparisons with the isovalent species SeH, SH, OH, and TeH, and with neutral HBr will be very interesting.

While very high levels of sensitivity and resolution are the positive aspects of LMR spectroscopy, there are problems with regard to analyzing the spectra. Because high magnetic field values are often used, a large number of interactions must be included in the Hamiltonian of even a simple molecule to reproduce the experimental accuracy, necessitating tedious and expensive calculations. Nevertheless, when these are properly done, the accuracy of molecular eigenvalues and molecular constants obtained from LMR spectra is nearly as good as those from microwave spectroscopy. There are numerous molecular ions which seem well suited for study by laser magnetic resonance, and future work should surely result in the detection of rotational spectra for some of them.

DIFFERENCE FREQUENCY INFRARED LASER SPECTROSCOPY OF MOLECULAR IONS

The technique developed most recently by T. Oka (95, 96) for observing molecular ion spectra is, like the microwave spectroscopy experiment, very simple in principle. Tunable, coherent infrared radiation was passed through an absorption cell that contained a live discharge and the vibration-rotation spectrum of the very important H_3^+ ion was detected directly.

The tunable infrared source was a difference-frequency laser system of the kind developed by Pine (97). A dye laser pumped by a multimode argon ion laser generated monochromatic radiation between blue and red wavelengths. This radiation was combined on a dichroic mirror with monochromatic light from a second argon ion laser operating single-mode either in the blue (4880 Å) or green (5145 Å). These two laser beams were passed through a temperature-controlled $LiNbO_3$ crystal, which then generated a difference frequency in the infrared over the range from 4400 to 2400 cm^{-1} with powers of 1–2 μW. This difference frequency was tuned by scanning the dye laser frequency. With etalon cavity-locking of the dye laser it was possible to scan 2 cm^{-1} without mode hopping. The resolution was limited by the bandwidth of the dye laser to about 10 MHz. The frequency of the infrared radiation was modulated by varying that of the single mode Ar^+ laser at 2.5 kHz with an amplitude of $\sim$400 MHz using piezoelectric mounts on the end reflector and on the mode selecting intracavity etalon.

The H_3^+ ions were generated in a liquid nitrogen-cooled 2 m multiple reflection discharge cell operating at a hydrogen pressure of 1 torr and current densities near 60 mA/cm^2. An InSb detector was used with a phase-sensitive amplifier to detect the absorption signals. The sensitivity of this system with an effective path length of 32 m was about 1.5×10^{-2}, corresponding to a minimum detectable absorption coefficient of 4×10^{-6} cm^{-1}, as determined by observing the $v = 0–1$ electric quadrupole spectrum of D_2.

A continuous scan of the region from 2800–2460 cm^{-1} produced nine lines assigned to H_3^+, which were predicted from the ab initio results of Carney & Porter (98). From the known path length and sensitivity of the spectrometer and the calculated transition moment of 0.156 D, the observed signals imply a H_3^+ density near 3×10^{10} cm^{-3}. The translational and rotational temperatures of H_3^+ in the discharge were estimated to be near 200 K.

This first spectroscopic detection of H_3^+ is very significant since it opens the door to systematic infrared spectroscopy of molecular ions in

discharges, and in addition, will provide the basis for a search for H_3^+ and its isotopes in interstellar space. Since H_3^+ is the cornerstone of the ion-molecule chemistry of interstellar clouds, astrophysical detection will constitute an important step to understanding these objects. H_3^+ has the structure of an equilateral triangle, and as such is nonpolar, making detection of rotational transitions very difficult. However, the isotopic variant H_2D^+ has a small dipole moment (0.6 D) resulting from the shift of the center of mass from the center of charge, and is a potential candidate for a search by radioastronomy. The experimental data obtained for H_3^+ can now be used as a calibration for theoretical calculations of H_2D^+ rotational transitions, which should result in accurate predictions of astrophysically important emission lines. Furthermore, infrared astronomy has advanced to the point where direct detection of H_3^+ vibrational spectra may now be possible by using infrared telescopes.

RF-OPTICAL DOUBLE RESONANCE SPECTROSCOPY OF TRAPPED IONS

Mass spectroscopy has been an immensely useful tool for the study of molecular ion chemistry. The utilization of techniques from mass spectroscopy to create, manipulate, and detect ions in molecular spectroscopy experiments has resulted in some impressive work on important molecular ions. The first such experiments were carried out by Dehmelt & Jefferts two decades ago on the H_2^+ ion (9–11).

Their approach was to create the H_2^+ molecules by electron impact ionization of H_2 in an rf quadrupole ion trap at pressures near 1×10^{-9} torr, induce optical transitions to the dissociative $^2\Sigma_u^+$ excited electronic state with polarized UV light, and measure the fine and hyperfine structure of H_2^+ by inducing rf transitions between different $|F\,M_F>$ states, which in turn caused changes in the photodissociation rate and thus in the ratio of H^+ to H_2^+ ions observed in the trap. Three dimensional containment of ions was achieved by creating an electric field in which the ion experiences a force proportional to its displacement from the center of symmetry of the trap. The trap itself consisted of two hyperbolic disc electrodes spaced 25 mm apart and contained in a cylindrical tantalum mesh electrode 118 mm in diameter; rf and DC bias voltages were applied to the cylinder, determining depth and secular ion oscillation frequency for the parabolic well. Ion densities were measured by driving their secular motions with a second rf field between the disc electrodes, which then removed them from the trap. An 800 eV electron beam with 70 mA of

intensity was used to ionize the H_2 during a 50 msec pulse. Both H^+ and H_2^+ were simultaneously trapped at a total ion density near 1×10^7 cm^{-3}. The ionization cycle was followed by a 120 msec irradiation cycle in which a 500 W high-pressure mercury arc operating as far as 2500 Å into the ultraviolet produced light that was then polarized parallel to the static magnetic field (H_0) and passed through a quartz window into the ion trap. The sequential extraction of the remaining H_2^+ and the H^+ formed in the photodissociation reaction $H_2^+ + h\nu \rightarrow H^+ + H(1s)$ was performed in the final 200 msec cycle. The ratio of H^+/H_2^+ counts was formed by a particle multiplier and stored in a multichannel analyzer as the frequency of the rf magnetic field (H_1) was swept.

The key to this experiment was the variation in photodissociation rates of different $|F M_F >$ states in a magnetic field. The photodissociation cross section has the orientational dependence $\sin^2 \theta$, where θ is the angle between N, the rotational angular momentum, and E, the ultraviolet electric field vector, averaged over the precessional motion of N. Calculations showed a threefold variation in this cross section among the 30 sublevels of the rotational levels $N = 0$, 1, and 2 (Hund's Case B). When an rf transition between the sublevels is saturated the net photodissociation rate becomes the average of the individual rates, and the effect is to increase the production of H^+ photoproduct.

Approximately 30 rf transitions were observed for both *ortho* and *para* H_2^+ in the vibrational states v = 4–8 with linewidths of 200 to 750 Hz determined by the magnetic field inhomogeneity. The resolution was subsequently improved, with linewidths near 5 Hz obtained (122). Analysis of these precise data provided accurate values for the nuclear spin-electron spin, electron spin-molecular rotation, and nuclear spin-molecular rotation interactions, which were valuable tests of theoretical calculations on this simplest of all molecules. The frequency of the astrophysically interesting $(F_2, F) = 3/2, 5/2 \rightarrow 1/2, 3/2$ transition was extrapolated to the v = 0 state value of 1404.3 MHz. Several searches have been made for this line in interstellar sources, but so far without success.

This technique has not yet been expanded to other molecular ions. For other than hydrogenic molecules the ion densities will be distributed over many more states, and given the rather low signal-to-noise ratios observed for H_2^+; this in itself seems to preclude observation of rf spectra of such ions. Microwave-optical double resonance detection using a narrow-band dye laser as a light source for state-specific excitation appears to be more favorable in these cases. Laser-induced fluorescence (LIF) studies of molecular ions in similar rf quadrupole traps have indeed produced some interesting results. These are discussed in the next section.

LASER-INDUCED FLUORESCENCE SPECTRA
OF TRAPPED MOLECULAR IONS

The technology of rf quadrupole ion trapping has been combined with laser-induced fluorescence methods to carry out electronic spectroscopy studies on mass-selected molecular ions by Mahan and co-workers (99–102). A three dimensional ion trap similar to that used in the rf-optical double resonance work was designed to store molecular ions for several milliseconds. A nitrogen-pumped dye laser was used in conjunction with gated photon counting detection to record the excitation spectrum of ions generated in the trap by electron impact. The ion trap itself consisted of a hollow cylindrical mesh center electrode and a pair of circular end caps separated by 2 cm and held at ground potential. The field produced with this configuration was a close approximation to that in the hyperbolic electrode trap described earlier. A low trapping frequency (1 MHz) was used to maximize the number density of ions in the trap, which is proportional to the inverse square of this frequency. The maximum number of ions that can be trapped is determined by the point when the resulting space charge cancels the trapping potential. For a well depth of 19 volts, appropriate for the case of N_2^+, approximately 3×10^7 ions could be stored.

Ions were created in the trap by pulsed electron impact ionization of parent gas at pressures of 10^{-5}–10^{-6} torr with a pulse width of several milliseconds. Following ionization, a delay of several hundred microseconds was used to allow the mass selection to stabilize and to allow excited electronic states of the ions to decay. Then a 10 nsec, 1 cm^{-1} bandwidth pulse from the nitrogen-pumped dye laser was passed through the ion region. The laser-induced fluorescence emitted at right angles to the laser beam was collected and focused into a cooled gated photomultiplier tube. The signal from the photomultiplier was amplified and fed into a photon counting system. After collecting the fluorescence, the ions were pulsed out of the trap and counted by an electron multiplier. The entire sequence was repeated about 40 times per second under computer control. This system allowed the temporal behavior of fluorescence to be monitored, so that radiative lifetimes could be determined for the trapped ions with a resolution of several nanoseconds.

The rf-driven motion of ions in the trap gave rise to translational temperatures near 5000 K and correspondingly large Doppler widths. While this placed severe limits on the resolution attainable, it still allowed rotational resolution of light ions. Because the ions are usually produced and sampled under collision-free conditions, the intensities of the LIF spectra reflect the populations of ground state ions after excitation and initial

cascading. Since electron excitation does not appreciably disturb the angular momentum of the neutral molecules, rotational temperatures of the ions were generally near-ambient, except in the case of fragment ions, where an exothermic "kick" could cause rotational and vibrational excitation. The ion vibrational populations generally reflected the Franck-Condon factors for both impact ionization and decay of excited ionic states. High vibrational states can be populated in this process. If a background gas, such as Ar, is added to the trap, collisions with the energetic ions convert translational energy into rotational excitation, producing $T-R$ equilibration near $5000°$ for $N_2{}^+$ at an Ar pressure of 10^{-3} torr. This has been quite useful for obtaining high-J spectra of $N_2{}^+$ (101, 102).

Thus far, laser-induced fluorescence and radiative lifetime measurements have been made with this system for CH^+, CD^+, $N_2{}^+$, CO^+, $BrCN^+$, H_2S^+, $ClCN^+$, and 1,3,5-trifluorobenzene cation (102). This work has afforded an appraisal of the advantages and disadvantages of the method. The advantages include the ability to measure nascent populations resulting from the ionization process and precise radiative lifetimes of excited molecular ions, the availability of a controlled number of collisions with background gas available, and the general complementarity that fluorescence spectroscopy provides to conventional emission spectroscopy. The disadvantages are principally the large Doppler widths and the low ion densities. It appears that this technique will be of greatest value for the dynamical study of ionization and collisional energy transfer processes rather than as a true high resolution spectroscopy method. Extension to numerous molecular ion systems will very likely be made—especially as tunable UV lasers become available.

LASER SPECTROSCOPY OF MOLECULAR ION BEAMS

A fast beam of molecular ions offers many of the same advantages possessed by an rf-quadrupole ion trap, viz. collisionless environment, definite mass selectivity, and easily determinable numbers of ions, as well as the added features of velocity control (and hence the ability to frequency shift or modulate via the Doppler effect), tight collimation, and directional control of the ions. Several experiments have successfully exploited these properties for obtaining high resolution spectra of molecular ions by allowing fast ion beams to interact with intense laser radiation. Indirect effects of the photons on the ion beam were utilized as a means of detection, but in one case the photons themselves were detected. We shall consider experiments in which rotationally resolved spectra of molecular ions were detected by predissociation and multi-photon dissociation of the

ions, by the effects of laser photons on charge exchange and ion-molecule reactions, and by laser-induced fluorescence. The subject of molecular ion beam spectroscopy was rather thoroughly reviewed by Carrington in 1979 (103). We do not attempt to reproduce his analysis, but rather we concentrate on highlights in this area and on more recent developments.

Fast ion beams have been used in atomic and molecular physics for nearly a decade, principally in beam foil and photodissociation studies, but also for some high resolution spectroscopy experiments on atoms. The development of fast ion beams for molecular spectroscopy was pioneered by Wing et al (104), who observed the first infrared spectrum of a molecular ion in 1976. They used the large controllable Doppler shifts resulting from the fast ion motion to tune vibration-rotation transitions in HD^+, which are allowed by the mass asymmetry-induced electric dipole moment, into resonance with a line-tunable (5.3–6.0 μm) CO laser. The transitions were detected by their effects on the rate of the charge transfer reaction between HD^+ and a buffer gas. The HD^+ ions were produced by electron impact on an equal mixture of H_2 and D_2 at low pressure. Under these conditions the beam consisted of about 40% HD^+ with a Franck-Condon vibrational population and a Boltzmann rotational distribution near the wall temperature of the source (320 K). The ions were extracted from a small hole in the anode of the source into a system of electrostatic lenses and accelerated to several kilovolts of energy. In a region of constant potential the ion beam was crossed at an angle of 11 mrad by the beam from a 1 W CO laser. The ions then passed through a gas target, became partially neutralized through charge exchange, and were detected by a Faraday cup. The beam accelerating voltage was swept from 1 to 10 kV, producing a Doppler tuning in HD^+ of 1.5 to 5.0 cm^{-1}. At resonance the chopped laser power transferred population between two initially unequally populated vibrational states that had different cross-sections for charge exchange (by a few percent), causing a small (3 ppm) change in the beam current which was synchronously detected at the chopping frequency. The beam noise was shot-effect limited; observed signal-to-noise ratios were about 3 to 1 with a 1 sec time constant. The resolution was limited by the Doppler width caused by an energy spread of 0.5 eV in the ion beam. Because a beam accelerated to high velocity experiences a kinematic compression of the initial velocity spread, the observed linewidths of HD^+ (7 to 25 MHz) were about 10 times less than the normal Doppler width.

Seven transitions among the levels v = 0–3 of the $^2\Sigma^+$ ground state were observed. The extremely high resolution resulted in measurement of fine and hyperfine structure with an accuracy exceeding that of existing calculations. The 1 ppm measurement accuracy was sufficient to allow a

test of quantum electrodynamic (QED) theory and to refine the values of several fundamental constants, e.g. the electron/proton mass ratio, if improved non-QED calculations could be made. This work did stimulate such theoretical calculations (105, 106, 119).

The charge exchange scheme for indirect detection of infrared photons is rather general, making this a widely applicable technique. The limitations arise in the small sizes of the signals, caused by the combination of small variation in charge exchange cross section with vibrational state and small differences in population among vibrational states of ions in these beams. In spite of the low signal-to-noise ratios and consequent tedious searches required to observe ion beam vibrational spectra, two other ions of fundamental significance to both physics and chemistry, HeH^+ and D_3^+, have since been detected by this method. Five transitions in $v = 0–2$ of the ground $^1\Sigma^+$ state were observed in 1979 for HeH^+ (107), providing similarly precise data for this simple heteronuclear two-electron system. Experimental frequencies deviated from theoretical values by about 0.2 cm^{-1}, and were two orders of magnitude more precise than existing theoretical results.

In 1980 Shy et al (108) reported the measurement of eight transitions in the ground $^1A_1'$ state of D_3^+ with a precision of 0.3 ppm at the same time Oka reported his results for H_3^+. The D_3^+ measurements compared favorably with the ab initio calculations of Carney & Porter (98) after adjustments were made of $+8.9$ cm^{-1} and $+1.6\%$ in their vibrational frequencies and rotational energies, respectively. Recently, this group has also observed the H_2D^+ isotopic species by the same technique (120).

While fast molecular ion beams have been used for photodissociation studies with visible lasers since 1972, it was not until 1976 that high resolution electronic spectroscopy of ion beams was carried out. Carrington & Sarre (109) reported the first such work in a study of the CO^+ spectrum. Aside from the fact that an argon ion laser operating at 4579 Å was used to induce transitions between electronic states of the ion, their experiment was virtually identical to that of Wing and his collaborators. Kinematic compression produced a resolution of 90 MHz, sufficient for resolution of hyperfine structure in many open shell molecules. The signals resulting from the charge exchange detection method were substantially stronger for these electronic transitions than the signals obtained in the IR by Wing et al (104, 107, 108). In addition, the incorporation of mass selection at the ion source made unambiguous assignment of the ion possible. Carrington, Milverton & Sarre (77) reported a thorough study of $^{13}CO^+$ in 1978, in which they observed for the first time the ^{13}C hyperfine structure in an electronic spectrum. A detailed analysis of the fine and hyperfine splittings provided a characterization of the electronic

wavefunction of $^{13}CO^+$ in both the ground and excited $^2\Pi$ states that fit very well with the simple picture of bonding in this molecule, viz. that in the ground state both the positive charge and the unpaired electron are localized in an sp hybrid nonbonding orbital on the carbon atom.

The use of predissociation of molecular ion beams as a means to detect electronic spectra with rotational resolution was demonstrated by Carrington et al (110) and Cosby et al (111) on O_2^+, and by Carrington on CH^+ (103). In this case, predissociation of the upper state of an electronic transition produces fragment ions at a rate that is fast enough to permit their detection, but not so fast as to broaden the lines much. The mass-selective detector was set to transmit only the fragment ions, which were produced only when the electronic transition was Doppler-tuned into resonance with the laser. Because the optical spectrum was thus detected with zero background, this method was much more sensitive than charge exchange. Linewidths were generally limited by the predissociation rate but were still not much larger than the 100 MHz residual Doppler width in the beam. The first high-resolution study of predissociation in O_2^+ was that of Carrington, Roberts & Sarre (110). In the ion source used, approximately 30% of the O_2^+ was present in the metastable $a^4\Pi_u$ state. Carrington et al (110) Doppler tuned the 4965 Å line of an argon ion laser into resonance with absorption transitions in the (4,1) band of the $b^4\Sigma_g^- - a^4\Pi_u$ system (the First Negative System) and observed the O^+ fragments produced. Twenty-four lines were observed and analyzed, producing a set of molecular constants for these states. The data suggested that predissociation of the $b^4\Sigma_g^-$ state occurs through a coupling with a $a^4\Sigma_g^+$ state. Subsequent work by Cosby et al (111) using a tunable dye laser and photofragment kinetic energy analysis gave a much more extensive survey of the First Negative System, including 359 transitions in the (4,4), (4,5), (5,5), and (3,3) bands. These data were combined with existing emission spectra and analyzed to produce a new accurate set of constants and Dunham coefficients for the $b^4\Sigma_g^-$ and $a^4\Pi_u$ states. Additional details of this O_2^+ predissociation study are given by Moseley & Durup (5) in this same volume. Very recently, Carre et al (112) published another investigation of the same system of O_2^+ by Doppler-tuned laser predissociation spectroscopy of a fast ion beam produced by a low energy accelerator instead of the more conventional mass spectrometer ion sources. They report achievement of O_2^+ beam intensities near 10 μamps accelerated to maximum energies of 100 kV with about the same kinematic compression ratio as in the "conventional" beams, whereas the latter sources typically produce 100 namp beams of up to 10 kV energy. Clearly, this method offers advantages in sensitivity and tunability; technical problems were encountered with the accelerator voltage stability and

absolute beam energy measurement, but these can probably be overcome. These accelerators could contribute substantially to molecular ion spectroscopy in the future. One of the major deficiencies in the predissociation method for detecting spectra in ion beams is that one must rely on previous electronic spectroscopy both to design the experiments and to interpret the results. This is illustrated by the work of Carrington (103) on CH^+. Only two rotational lines assigned to CH^+ were found, using an argon ion laser and detecting C^+ fragments. The electronic states involved in the transition could not even be identified. This is most unfortunate, since CH^+ is of considerable importance in astrophysics.

The use of variations in ion-molecule reaction cross sections with electronic state was explored as a means of detecting electronic spectra of ion beams by Carrington et al (113). The potential advantage of this approach relative to the similar charge exchange scheme is that an ion-molecule reaction could in principle be chosen to be endothermic for the lower state and exothermic for the upper state, thus producing a large change in density of a monitored product ion at resonance. Such an experiment was reported for determination of rotational components of electronic transitions in CO^+ and H_2O^+ (113). After Doppler-tuning these ions into resonance with the argon ion laser, the beam velocity was retarded to energies of a few volts, and the ions were allowed to react with H_2 gas. The corresponding reactions were

$$CO^+ + H_2 \rightarrow HCO^+ + H \quad \text{and} \quad H_2O^+ + H_2 \rightarrow H_3^+ + OH.$$

The product ions were then reaccelerated into the mass analyzer and detected as before. For H_2O^+ one rotational line of the $A^2A_1 \rightarrow X^2B_1$ transition was detected and assigned on the basis of earlier optical studies as the $2_{12} \leftarrow 3_{22}$ F_1 transition in the $(0,12,0) \leftarrow (0,0,0)$ band. A series of transitions in CO^+ was detected by this method. Subsequent work showed that the detection mechanism was actually due to the charge exchange reaction $CO^+ + H_2 \leftarrow CO + H_2^+$ rather than the ion-molecule reaction mentioned above. While the ion-molecule detection scheme seems very promising, in practice one must overcome the problem of a serious loss in beam flux when the ions are decelerated. If this could be accomplished, ion-molecule reactions would provide a much more sensitive way to detect both electronic and vibrational transitions than the charge exchange approach.

Carrington's most recent work (103, 114) has been to obtain vibration-rotation spectra of HD^+ in vibrational states near the dissociation limit by use of two-photon photodissociation with infrared lasers. HD^+ is formed by electron impact with appreciable populations in all 22 of its vibrational levels. One laser (CO or CO_2) induces transitions from the highest vibra-

tional states $v = 18$–21 into the repulsive excited electronic state; another laser induces transitions between lower vibrational states and these higher ones. The H^+ or D^+ photoproduct is detected. These spectra will provide interesting and detailed information on properties of this fundamental molecule near its dissociation limit. In principle, the approach can be extended to many other molecular ions as well.

The first laser-induced fluorescence (LIF) spectra of a molecular ion beam was obtained for CO^+ by Brown et al (115) in 1979. They used an ion beam system nearly identical to that of Carrington et al (77, 109, 110) to produce CO^+. A pulsed dye laser illuminated the beam coaxially. The fluorescence excitation spectrum was recorded by monitoring the photons emitted in the interaction region with a photomultiplier and photon counting system. The excitation spectrum of the $A^2\Pi$–$X^2\Sigma^+$ system was observed with a rather low signal-to-noise ratio after 50 hr of signal averaging. Variation of the accelerating voltage changed the transit time of the ions through the observation region, allowing the first measurement of the radiative lifetime of the $A^2\Pi$ state (7.4 $\pm$ 1 μsec). This method is potentially applicable to a large number of molecular ions, and kinematic compression will result in linewidths that are much narrower than LIF spectra of either ion traps or conventional sources. These advantages would seem to be outweighted by the low sensitivity relative to that obtained with the indirect detection schemes; however, LIF of ion beams might well produce valuable complementary information.

SUMMARY

We present a list of all molecular ions studied with rotational resolution in Table 1. Fifty-four different ions have been observed up until this time, not including the HD^+, H_2D^+, and D_3^+ isotopes. Eleven of these are polyatomic ions; only one is a negative ion (C_2^-). Only one ($C_4H_2^+$) contains more than three atoms. These observations are firm evidence that the field of molecular ion spectroscopy is in a very early stage of its evolution.

Up to 1974, only one ion (H_2^+) had been observed with resolution better than the optical Doppler width (and therefore with capability to resolve hyperfine structure). By now the number has grown to 13 ions detected by seven different high resolution techniques. This is indicative of the progress that has been achieved in molecular ion spectroscopy. Such progress is a result of both the development of sophisticated technology needed to study ions and a substantially heightened interest in the field, spawned in turn, by the discovery of ions in interstellar clouds, the rapid evolution of ab initio theoretical chemistry, and the ability and

desire to measure chemical reactions—in particular, ion-molecule reactions—on a state-to-state basis.

In the coming decade developments in high resolution spectroscopy of molecular ions should continue at a rapid pace. The presently available experimental techniques are clearly capable of producing spectra and much valuable information about a number of new ions, and further technological progress and experimental innovation should accelerate the acquisition of data and increase the quality of the information that can be derived. Negative ion studies will very likely become feasible in this time period, and perhaps some work on multiply charged ions will too. Our understanding of the properties and behavior of molecular ions should increase dramatically as a result of these efforts.

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