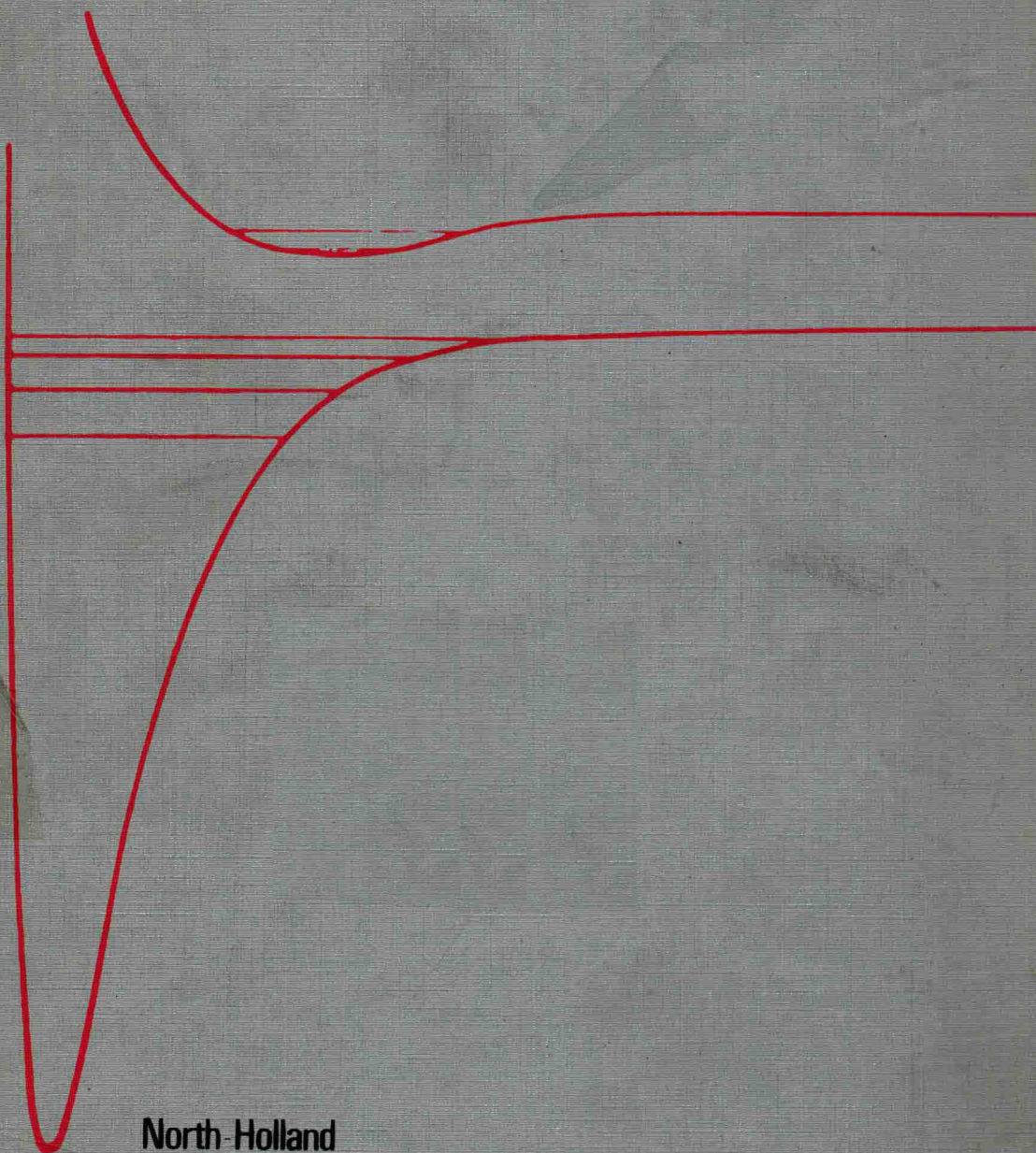


Molecular Ions: Spectroscopy, Structure and Chemistry

Edited by T.A. Miller and V.E. Bondybey



North-Holland

MOLECULAR IONS: SPECTROSCOPY, STRUCTURE AND CHEMISTRY

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MOLECULAR IONS:
SPECTROSCOPY, STRUCTURE AND CHEMISTRY

PREFACE

For many years the rich chemistry and physics of molecular ions were the almost exclusive domain of mass spectroscopists. While mass spectroscopy and related techniques can give very useful data about the existence and stability of molecular ions, they provide little information about their structures and usually cannot even differentiate between isomeric species. Recently a variety of other, structurally more sensitive experimental methods, have been applied to the study of molecular ions. Most of these techniques involve absorption or emission of photons and fall into the general area of spectroscopy. Application of these techniques has yielded a wealth of new information about molecular ions, their geometry, and their vibrational and electronic structures and their chemistry. It is this rather explosive growth of available information that has prompted us to edit this book.

We are very fortunate indeed that one of the pioneers and leading scientists in this field, Dr. Gerhard Herzberg, has agreed to contribute an introductory chapter and provide us with a historical overview of the subject. He has appropriately divided the spectroscopic study of ions into three periods - early, middle, and late. The early period was characterized by the first observations of the optical emission spectra of ions and highlighted by the interplay between the experimental ion work and the development of molecular orbital theory by Hund, Mulliken, and others. The second period, starting in about 1950, saw the observation of the optical absorption spectra of ions, the spectra of negative and polyatomic molecular ions, as well as the development of photoelectron spectroscopy. The final period, in which we find ourselves presently, can probably best be dated from the first application of lasers to the study of ions. However, the laser is but one of the recent developments which has led to remarkable advances in our knowledge about ions.

The rest of the chapters in this volume can best be described as belonging to the late (present) period of ion study. We have tried to arrange the remainder of this book in a somewhat logical fashion. The three chapters following Herzberg's historical overview deal primarily with high and very high resolution studies of some of the simplest molecular ions. Woods describes in considerable detail his efforts to obtain the spectra of di- and tri-atomic molecular ions in the microwave spectral region, and comments lucidly on the astrophysical implications of his work. Carrington and Softley move the frequency up a bit, but for the most part maintain the resolution, with their survey of the infrared spectroscopy of molecular ions. Particular attention is given to the fundamental ions HD^+ , HeH^+ , CH^+ , and H_3^+ . The latter ion, H_3^+ , is so important that our next chapter by Oka is entirely devoted to it. It is clear that the motivation for much of the high resolution work described in Chapters 2-4 is two-fold. Because of the extreme simplicity of the ions involved, a detailed experimental knowledge of their spectra and structure provides the ideal benchmark for the testing of our detailed theoretical understanding of molecular bonding. On the other hand, because of the species' very simplicity, they constitute some of the most abundant and important molecules in the universe. Thus a significant portion of the laboratory work is in support of the observation of these same ions in interstellar space. Ions like H_3^+ , HCO^+ , etc. likely play key roles in the basic underlying chemistry upon which the universe is based. All of our first four chapters comment upon the astrophysical significance of molecular ions.

Chapters 5 and 6 are the only chapters in this book which do not involve ions in the gas phase. Rather they detail how molecular ions can be isolated in cryogenic inert gas matrices for study. Chapter 5 by Andrews centers upon the study of the vibrational structure and interactions of matrix isolated ions by infrared spectroscopy. In the chapter by Bondybey and Miller, a great deal of information about the photophysics, vibrational, and electronic structure of matrix isolated ions is presented. In this case, the principal probe is electronic spectroscopy, particularly laser induced fluorescence.

In Chapter 7 by Klapstein, Maier, and Misev our steady progress towards higher frequencies and larger molecular ions is maintained. However, now the subject is the decay of excited electronic states of organic ions in the gas phase. In particular, comparison is made between electron impact excited emission and laser excited fluorescence of gaseous organic ions.

Chapter 8 by Miller and Bondybey continues the interest in laser induced fluorescence studies of organic cations, but the interest is now restricted to a number of highly symmetric benzenoid cations, e.g. $C_6F_6^+$, sym $C_6F_3H_3^+$, etc., which have electronically doubly degenerate ground states and thus are subject to the Jahn-Teller effect. The basic theory of the Jahn-Teller effect is developed and stabilization energies and distorted geometries given for several of these ions.

In the final chapter by Dunbar, the interest remains with large gas-phase molecular ions. However, unlike the previous eight chapters, the goal is now to understand the photophysics of molecular ions when they are exposed to radiation which, once absorbed, leads to their destruction (fragmentation). This is an area of much current interest for both neutral and ionic species. However, in many cases the photofragmentation of ions may provide more information than can be obtained from neutrals because of the ease of detecting ionic species.

We believe that overall the nine chapters in this book provide a good perspective upon the exciting recent developments in the understanding of the spectroscopy, structure, and chemistry of ions. We have tried to provide a balanced account ranging from the elegant high resolution spectroscopic experiments on very simple ions to a variety of lower resolution work on much more complex molecular ions. We particularly wish to thank the authors of the various chapters. Each has made outstanding contributions to the work described, and has in this present volume presented his work in a manner easily assimilable.

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INTRODUCTION TO MOLECULAR ION SPECTROSCOPY

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The field of molecular ion spectroscopy has developed in recent years into a very active subject. A detailed review of this subject as presented in this monograph seems therefore useful for those now involved in it as well as those who want to begin studies in this field or try to apply the understanding gained to other fields.

During the early period of the history of the subject it was of course by no means obvious which band spectra observed in electric discharges were due to neutral molecules and which to molecular ions. In 1922 Wien [1] showed that in a positive ray deflected by an electric or magnetic field the emission of the so-called "negative nitrogen bands" unlike the "second positive group" goes with the deflected beam; that is, the carrier of this spectrum must be the positive ion of the nitrogen molecule, N_2^+ . The designation "negative bands" of nitrogen arose from the observation that these bands occur near the cathode in the negative glow. It was then realized that bands of other molecules that are predominant in the negative glow must also be due to the corresponding positive ions. The first to be so identified were the negative bands of oxygen and carbon monoxide. These identifications were later confirmed when the doublet or quartet character of the bands assigned to the ions N_2^+ , O_2^+ and CO^+ was recognized, since for an odd number of electrons the multiplicity must be even. Other ion spectra identified in this way were those of HCl^+ , HBr^+ , BH^+ , AlH^+ and much later HF^+ . Also in the early period the spectra of the ions BeH^+ , MgH^+ , ZnH^+ , CdH^+ and HgH^+ as well as CH^+ and OH^+ were identified mainly on the basis of the observation that all of these are singlet (or triplet) spectra while the corresponding neutral molecules have even multiplicities.

The early work on molecular ion spectra just described was closely tied to the development of molecular orbital theory by Hund and Mulliken. For example, the comparison of the spectra of N_2^+ and CO^+ with that of CN made it very clear that the most loosely bound orbital in N_2 and CO must be a σ orbital while the next lowest orbitals must be π and σ since the first and second excited states of the ions are $^2\Pi$ and $^2\Sigma$. To be sure, at the time the $^2\Pi$ state of N_2^+ had not yet been observed but the similarity to CO^+ and CN left no doubt that it existed. It was actually observed first in the spectrum of the aurora by Meinel [2] and soon after in the laboratory by Dalby and Douglas [3,4].

Another interesting group of diatomic molecular ions which were studied by the same conventional methods as those mentioned in the preceding paragraphs but much more recently are the ions consisting of two inert gas atoms. Druyvesteyn [5] in 1931 was the first to notice two band groups near 4250 and 4100 Å in discharges through mixtures of He and Ne, but it was only in 1975 that it was recognized

by Tanaka, Yoshino and Freeman [6] that these band groups were due to HeNe^+ and that similar band groups corresponding to XY^+ occur in all binary mixtures of inert gases X and Y. Tanaka, Yoshino and Freeman found that these band groups occur approximately at a wavelength corresponding to the difference of the ionization potentials of X and Y, strongly suggesting that they correspond to charge exchange between the two ends of the molecule, i.e. $\text{XY}^+ \rightarrow \text{X}^+\text{Y}$. The dissociation energies are generally very small corresponding to van der Waals binding. There is one exception, the HeNe^+ ion. Its spectrum (both that of $^4\text{HeNe}^+$ and $^3\text{HeNe}^+$) has been analysed in detail [7] and shows that the ground state has a dissociation energy of 0.69 eV and an equilibrium internuclear distance $r_e = 1.30 \text{ \AA}$ indicating a much stronger bond than for any of the excited states of this molecule and all states of the other XY^+ molecules. Figure 1

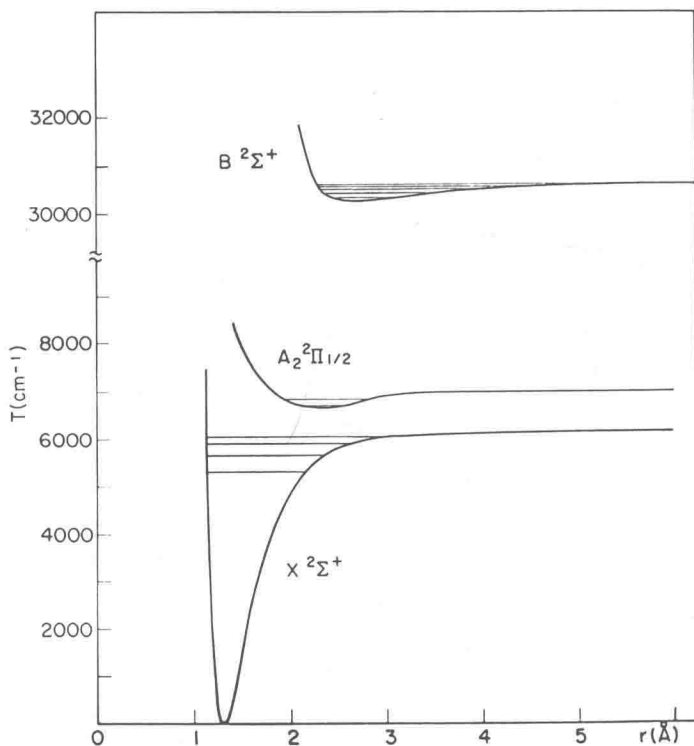


Figure 1
RKR Potential Functions of the
Three Observed States of HeNe^+

shows the potential functions of the observed states of HeNe^+ . In contrast, in HeAr^+ the dissociation energy of the ground state is only 0.026 eV [8]. The reason for this difference is clearly the interaction between $\text{B } ^2\Sigma^+$ and $\text{X } ^2\Sigma^+$ which because of the much greater proximity is much larger for HeNe^+ than for HeAr^+ .

The second (middle) period of the history of our subject starting in about 1950 but overlapping the first period just described included

the following developments:

- the observation of absorption spectra of molecular ions;
- the observation of spectra of negative ions;
- the observation of spectra of polyatomic molecular ions;
- the study of electronic states of molecular ions by means of photo-electron spectra.

A few remarks about each of these steps may be in order.

The N_2^+ ion was the first to be detected in absorption [9]. This was done by means of the flash discharge method illustrated in Figure 2. The ions produced by a mild flash discharge in the long

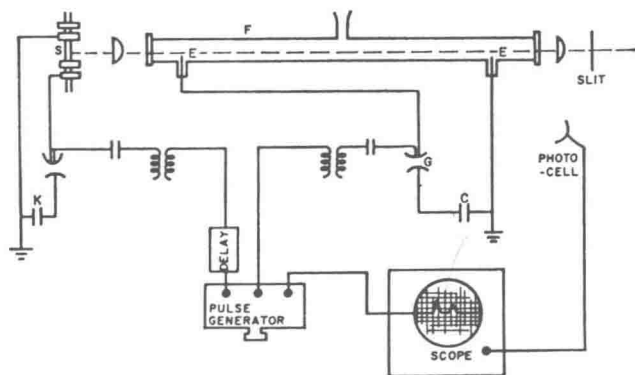


Figure 2
Flash Discharge Method for the Study of
Absorption Spectra of Molecular Ions

and fairly wide tube F were studied in absorption using the continuous spectrum produced by a second narrow flash discharge tube S as a continuous background. This second tube was triggered with a short delay after the flash in the absorption tube. Figure 3 shows

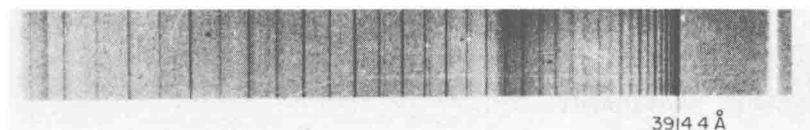


Figure 3
Absorption Spectrum of N_2^+ ($B^2\Sigma_u^+ - X^2\Sigma_g^+$)

as an example the 3914 Å band of N_2^+ in absorption. By the same method the corresponding spectrum of CO^+ at 2189.8 Å was obtained in absorption. When the absorption spectrum of a flash discharge through methane was studied (with the aim of obtaining the absorption spectrum of CH_4^+) a very simple spectrum similar to that of N_2^+ was

found near 5400 Å (both in emission and absorption) which was shown [10,11] to be due to the negative ion C_2^- . It represents the same electronic transition in this negative ion as the 3914 Å system in the positive ion N_2^+ (having the same number of electrons). In Figure 4 the electronic states of C_2^- , CN, N_2^+ and CO^+ are compared.

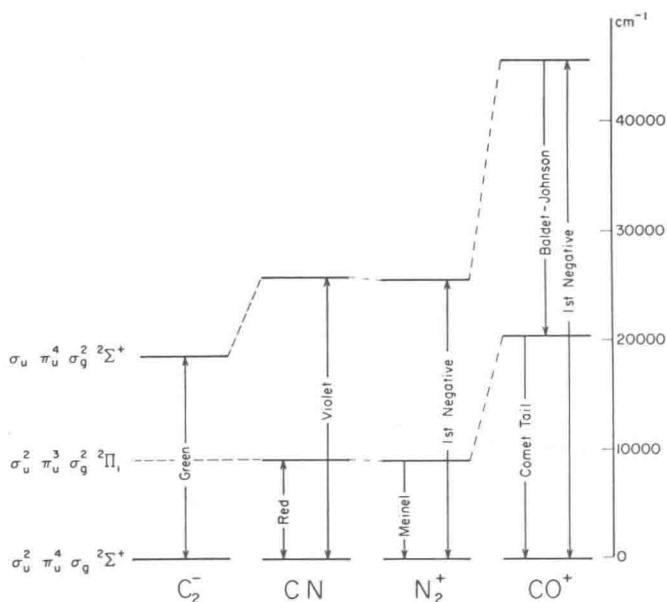


Figure 4
Observed Electronic States of 13-electron Systems

The first polyatomic ion spectrum, that of CO_2^+ , was already observed in emission in the early period of the subject [12,13,14]. In 1967 when the flash discharge method was applied to CO_2 both band systems of CO_2^+ , that is, $\tilde{A}^2\Pi - \tilde{X}^2\Pi$ and $\tilde{B}^2\Sigma - \tilde{X}^2\Pi$, were observed in absorption [9,15]. Other polyatomic molecular ions observed in this intermediate period (before the advent of laser techniques) are $C_4H_2^+$ (the diacetylene ion) studied in emission [16], N_2O^+ studied both in emission and absorption [15,17], CS_2^+ [18], COS^+ [19,20], H_2S^+ [21] and H_2O^+ [22] studied in emission only. Extensive rotational and vibrational analyses of these ions were carried out by the authors mentioned.

Toward the end of the intermediate period the method of photo-electron spectroscopy was developed by several groups, under A.N. Terenin, D.W. Turner, K. Siegbahn and W.C. Price. Here the energy levels of the ions are determined from the energies of the peaks of the photo-electrons produced by photons of short (fixed) wave lengths, usually the He line at 584 Å. At low resolution, peaks are observed which correspond to the various electronic states of the ion, at higher resolution these peaks are resolved into bands corresponding to different vibrational transitions and in a few cases at very high resolution the rotational structure is resolved.

This method has supplied data about a large number of molecular ions. A few ions of free radicals have also been studied in this way.

The first break in the rather slow development of the field of molecular ion spectroscopy came when low voltage electron beam excitation of various parent molecules was used to produce ion emission spectra. This method was pursued by a number of independent groups. In our laboratory Lew [22] discovered in this way an extensive spectrum of H_2O^+ and D_2O^+ . I tried to find in this way a spectrum of the NH_3^+ ion. Although I did observe interesting spectra in the region 2200-2400 Å which I considered as strong candidates for NH_3^+ and NH_2^+ a confirmation of this assignment is still lacking. At about the same time Maier and his collaborators in Basel, Miller and his collaborators at the Bell Laboratories, and Leach and his associates at Orsay started their detailed and comprehensive work on a large number of organic ions, especially ions of derivatives of benzene such as C_6F_6^+ , C_6HF_5^+ , etc. Of special interest is the detailed study made possible by these experiments of the Jahn-Teller effect in the degenerate electronic ground states in ions like C_6F_6^+ and $\text{C}_6\text{H}_3\text{F}_3^+$. The use of laser excitation makes possible the study of the absorption spectra of these ions. The work of Maier and Miller is fully described in the chapters contributed by these authors to this volume.

The power of laser techniques is beautifully illustrated by the study of N_2^+ by Rosner, Gailey and Holt [23] who, using the laser beam-ion beam technique, were able to resolve the hyperfine structure of the N_2^+ lines. Figure 5 shows an example from their paper.

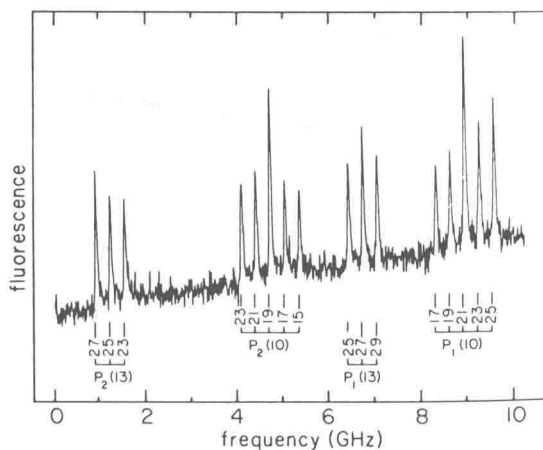


Figure 5
Fluorescence vs Doppler-shifted Laser Frequency
(with Arbitrary Origin) for a Part of the 0-1
Band of the $\text{B } ^2\Sigma_u^+ - \text{X } ^2\Sigma_g^+$ System of N_2^+

During the same period R.C. Woods and his students obtained microwave spectra of a number of triatomic molecular ions like HCO^+ , HOC^+ , N_2H^+ , HCS^+ and their isotopes, obtaining precise frequencies and rotational constants. This work will be described in the Chapter

contributed by Woods.

The addition of laser techniques has greatly aided in the further development of the subject. The use of the combination of a laser beam with a molecular ion beam of variable velocity allowed Wing and his associates to obtain for the first time an infrared spectrum of the HD^+ ion which, as was first pointed out by E. Teller, has a strong oscillating dipole moment. Here also *ab initio* calculations have been possible which show a remarkable agreement with the observed spectra. Carrington and his students have observed by a similar method many of the higher vibrational levels of HD^+ which show almost as good agreement with *ab initio* calculations as the lower observed levels (see the Chapter contributed by Carrington and Softley).

The simplest stable polyatomic molecular ion is H_3^+ which is the most prominent ion in the mass spectrum of hydrogen unless the pressure in the source is very low. The infrared spectrum of this ion could in principle be observed by orthodox methods. However the stationary concentration of H_3^+ (like that of many ions) in electric discharges is very low and its detection requires therefore more sophisticated methods. These were first applied by Oka [24] as described more fully in his Chapter. He used a difference laser and with it reached a detection limit of about $4 \times 10^{-6} \text{ cm}^{-1}$. In this way a fairly complete infrared band of H_3^+ was obtained and several molecular constants were determined. Almost simultaneously Wing and his associates [25] obtained the spectrum of D_3^+ by the use of the molecular ion-beam laser-beam technique. The same two methods were applied to the discovery of a spectrum of HeH^+ , first by Tolliver, Kyralla and Wing [26] by the beam method and later by Bernath and Amano [27] using Oka's method.

Carrington, Buttenshaw and Kennedy [28] using the ion-beam laser-beam method have recently obtained extensive spectra of H_3^+ corresponding to transitions between levels near the dissociation limit. This spectrum is still awaiting a detailed analysis.

J.D. Morrison and his students [29] have studied the spectra of the ions CH_3I^+ and CD_3I^+ using a triple quadrupole mass spectrometer with a tunable dye laser. The region studied is one in which predissociation occurs and thus a study of the absorption spectrum by detecting the photodissociation products was possible under fairly high resolution. A full analysis of this spectrum has not yet been achieved. A similar method was used by the same group for the study of the spectra of O_2^+ [30] and O_3^+ [31]. Ion-beam laser-beam studies of O_2^+ have also been carried out by Carrington's group.

Still another method, using a drift tube mass spectrometer combined with a tunable dye laser, was applied by Mosely, Cosby and their associates to the study of the absorption spectra of a number of negative ions especially O_3^- [32], [33] and CO_3^- [34]. As in the previous methods absorption is detected by way of predissociation which leads to the occurrence of product ions observed by the mass spectrometer. The observed vibrational structure allows determination of vibrational frequencies in the excited states. From the long wave length limits of the absorptions the electron affinities can be determined.

There has been an ever increasing interplay in the last 50 years between laboratory spectroscopy and astronomy [35]. This interplay has been very active with regard to molecular ion spectra. The