INFRARED SPECTROSCOPY OF MOLECULAR IONS

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ABSTRACT

In this course of three one-hour lectures, I cover the three main features of molecular ion spectroscopy using tunable infrared sources and discharges, (I) production of ions, (II) spectroscopy of molecular ions, and (III) analysis of infrared ion spectra. There are four subject matters that play major roles in this course: (1) Molecular ions with its tremendous activity and challenge (2) Infrared laser spectroscopy with its high sensitivity and resolution. (3) Plasma full of ions and mystery, and (4) Interstellar space with a high degree of ionization and inexhaustible richness.

I. PRODUCTION OF MOLECULAR IONS

1.1. Introduction

Let us take the hydrogen molecule H₂ as the starting point, a stable, neutral system with two protons and two electrons. We can produce charged species, i.e., molecular ions, by subtracting or adding an electron or a proton. The simplest way to make an ion from H₂ is to knock off an electron to produce H₂⁺. This occurs in the laboratory plasma through electron bombardment and in space through cosmic ray ionization and photoionization due to star radiation. Radiofrequency spectroscopy of H₂⁺ by Dehmelt and Jefferts and infrared spectroscopy of HD⁺ by Wieg, Ruff, Lamb and Spezceski are the classic work on the ionic species. We can also attach an electron to H₂⁺ we then obtain H₂⁻. This anion is known to exist in spite of the negative electron affinity of H₂⁻.
Instead of subtracting and adding an electron to produce the cation and anion, we can do it also by adding and subtracting protons. We then obtain $\text{H}_2^+$ and $\text{H}^-$ from $\text{H}_2$. The whole situation can be summarized in a diagram shown in Figure 1.

![Diagram of ions]

While $\text{H}_2^+$ and $\text{H}_2^-$ produced by subtracting or adding an electron are paramagnetic radical ions and chemically very active, $\text{H}_3^+$ and $\text{H}^-$ are isoelectronic to $\text{H}_2$ and therefore diamagnetic and quite stable. They are called protonated and deprotonated ions. These ions have been known to mass spectroscopists over many years but their spectroscopy has not been conducted successfully until very recently.

Some of you may think that these ionic species are unstable and are very rare exotic species in the nature. They are rare in the terrestrial atmosphere. However our terrestrial atmosphere is an exception in nature. The universe as a whole is much more highly ionized; atomic and molecular ions are abundant and play important roles in various aspects of astrophysics. For example, since the work of Bethe and Hylleraas, stability of the hydrogen atom anion $\text{H}^-$ is well-known. The $\text{H}^-$ ions exist abundantly around the sun and its absorption of the solar radiation is the major cause for the sun's opacity as initially noted by Wildt and shown conclusively by a series of papers by Chandrasekhar and his colleagues.

The stability of protonated hydrogen $\text{H}_3^+$ has been well known since its discovery by J.J. Thomson. Although it is yet to be discovered in space, it is the most important ingredient in our understanding of ion-molecule reaction schemes of dense molecular clouds. Ab-initio calculations show the energy relation

\[ * \text{It is none other than J.J. Thomson who discovered } \text{H}_3^+ \text{ in 1912. For the long history of } \text{H}_3 \text{ see Reference 4.} \]
\[ H_3^+ = H_2 + p - \Delta H_e \]

with \( \Delta H_e = 4.59 \text{ eV} \) \(^{17,18}\). The large value of \( \Delta H_e \) (proton affinity) shows the stability of this ion.

In general protons attach to any stable molecule or atom to produce stable protonated ions, in other words the proton affinities of stable molecules are always positive. A convenient list of proton affinity is found in Ref. 19. Some typical values are: \( \text{H}_2 \) 4.4 eV, \( \text{He} \) 1.9 eV, \( \text{CH}_4 \) 5.4 eV, \( \text{NH}_3 \) 8.8 eV, \( \text{H}_2\text{O} \) 7.3 eV, \( \text{CO} \) 6.1 eV, \( ^3\text{N}_2 \) 4.9 eV, \( \text{HCN} \) 7.5 eV, \( \text{C}_2\text{H}_2 \) 6.5 eV. On the contrary electron affinities of most stable molecules are negative. Values of electron affinity are found in Reference 20.

Because of the large proton affinities protonated ions are quite stable. For example, if we use a thermodynamical argument the exothermicity of

\[ \text{H}_2\text{O} + p \rightarrow H_3^+ \]

reaction is so large at room temperature (\( \Delta H = 7.3 \text{ eV} \approx 290 \text{ kJ} \)), that the ratio of \( H^+ \) to \( H_3^+ \) in solution is \( 10^{-130} \). Hence Sidgwick's remark,21 "in 10\(^7\) universes filled with a normal acid solution there would be one unsolvated hydrogen ion". Because of this stability, protonated ions have been well-known to mass spectrosocists. However, their spectra had never been observed in any spectral region until 1970 when radio astronomers Snyder and Buh122 observed the microwave emission of unknown species and named it X-ogen. This caught laboratory spectrosocists by surprise and (although Klemperer correctly conjectured23 the carrier of the emission line to be protonated carbon monoxide HCO\(^+\)), it took five years until in 1975 the spectral line was identified in the laboratory of Woods and his group.24 As is often the case, the message came from the sky.

### 1.2. Molecular Ions

We can extend the manoeuvre shown in Fig. 1 and obtain a great many fundamental molecular ions as shown below. Fig. 2 summarizes molecular ions containing hydrogen atoms and one heavy atom; we limit ourselves to carbon, nitrogen and oxygen which are highly abundant in nature. The most well studied ones are of course the stable species \( \text{CH}_3 \), \( \text{NH}_3 \) and \( \text{H}_2\text{O} \). They are the most fundamental examples of spherical top, symmetric top, and asymmetric top, respectively, and much of our knowledge on spectroscopy has been obtained from the enormous amount of studies on these molecules.25,26 From each of these stable species we obtain free radicals \( \text{CH}_3 \), \( \text{CH}_2 \), \( \text{CH} \), \( \text{NH}_2 \), \( \text{NH} \), \( \text{OH} \) which have also been studied spectrosocopically.26,27 Now the subjects of this course are the charged species, cations and anions produced from the
neutral species. There are so many of them as seen from Fig. 2 and each gives a fascinating spectrum.

Some of these ions (diatomic cations CH⁺, NH⁺, OH⁺ and H₂O⁺) have been studied through their electronic spectra prior to the present activity of molecular ion spectroscopy. We use laser infrared spectroscopy: infrared because all these ions absorb infrared radiation strongly and laser spectroscopy because of its high sensitivity and resolution.

Figure 2 is extremely rich in its content and we can have a lot of fun looking at it in various ways. First of all if you draw vertical lines between the group of carbon, nitrogen, and oxygen compounds, we have isoelectronic species connected. The species in the groups CH-NH⁺, CH⁺-NH⁺-OH⁺, CH₂-CH₂⁺-CH₂⁺-H₂O⁺, CH₂⁺-H₂O⁺, CH₂⁺-NH₃⁺, CH₂⁺-CH₂⁺-H₂O⁺, CH₂⁺-NH₃⁺, have some number of nuclei and electrons and usually have the same geometrical and electronical symmetry and multiplicity. For example, CH⁺-NH⁺-OH⁺ all have 3Π ground state (although CH⁺ is yet to be observed), and CH₂⁺-NH₂⁺-H₂O⁺ all have the C₃ᵥ pyramidal structure of 1A₁ electronic symmetry with double minimum potential and inversion (although this is yet to be experimentally observed for CH₂⁺).
We can show isoelectronicity in a wider sense when we consider protonation and deprotonation. For example, \( \text{CH}_3^+ - \text{CH}_3^- \), \( \text{NH}_4^+ - \text{NH}_3^- \), \( \text{H}_2\text{O}^+ - \text{H}_2\text{O}^- \), \( \text{OH}^+ - \text{OH}^- \) are isoelectronic and have singlet ground states. The species in the group \( \text{CH}_3^+ - \text{CH}_3^- \), \( \text{NH}_4^+ - \text{NH}_3^- \), \( \text{H}_2\text{O}^+ - \text{H}_2\text{O}^- \) have all doublet ground states. The series \( \text{CH}_3^+ - \text{CH}_3^- \), \( \text{NH}_4^+ - \text{NH}_3^- \), \( \text{H}_2\text{O}^+ - \text{H}_2\text{O}^- \) have triplet ground states except for \( \text{CH}_3^+ - \text{CH}_3^- \) which has a singlet ground state (\( \text{CH}_2 \) too has almost a singlet ground state).

For the analysis of rotational structure of the spectrum, we group the species in Fig. 2 according to the number of protons. For example we can look at \( \text{CH}_3^+ - \text{CH}_3^- \), \( \text{NH}_4^+ - \text{NH}_3^- \), and \( \text{H}_2\text{O}^+ - \text{H}_2\text{O}^- \). \( \text{CH}_3^+ \) is a rigid planar molecule whereas \( \text{CH}_3^- \) and \( \text{NH}_4^+ \) are "planar with low frequency out of plane vibration." \( \text{NH}_3^- \), \( \text{H}_2\text{O}^+ \) and \( \text{CH}_3^- \) (yet to be studied) are pyramidal with inversion splitting (\( \text{NH}_3^- 0.8 \text{ cm}^{-1} \), \( \text{H}_2\text{O}^+ 55 \text{ cm}^{-1} \)). If we look at the \( \text{CH}_3^+ - \text{CH}_3^- \), \( \text{NH}_4^+ - \text{NH}_3^- \), \( \text{H}_2\text{O}^+ - \text{H}_2\text{O}^- \) series, they are all "bent but the rigidity of bending varies from well bent molecules (\( \text{H}_2\text{O}, \text{H}_2\text{O}^- \), \( \text{NH}_4^+, \text{NH}_3^- \)) to quasi-linear molecules (\( \text{CH}_3^+, \text{CH}_3^- \)). We are currently studying the \( \nu_3 \) fundamental band of \( \text{NH}_2^+ \) but it looks like this ion is even more quasi-linear than \( \text{CH}_2^+ \).

We can extend Fig. 2 to more complicated ions. Figure 3 lists the similar species containing two heavy atoms. Again we can discuss various molecular properties systematically using such figures. We

Fig. 3. Molecules, free radicals, ions containing CO, CN and OC.
can extend such figures to more complicated molecules. Among the molecular ions appearing in these figures, the following ions have been studied since 1983 through their infrared spectra: CH$_3^+$, NH$_2^+$, NH$_3^+$, OH$^+$, H$_2$O$^+$, H$_2$O$^-$, OH$^-$, HCOH$^+$, C$_2$H$_5^+$, C$_2^-$, H$_2$NH$^+$, CO$^+$, HCO$^+$. Spectra of many other ions will be discovered in the near future. Spectroscopy and chemistry is much enriched through these studies.

1.3. Ion Kinetics

Langevin Rate. The Langevin rate is one of the most fundamental concepts which is indispensable in the discussion of ion kinetics (Langevin, 1905). In the laboratory discharge and in interstellar space an ion collides mostly with neutral molecules. If the polarizability of the neutral molecule is $a$, the energy of interaction between the ion and the molecule (charge-induced dipole interaction) is

$$ W = -\frac{1}{2} a E^2 = -\frac{a e^2}{2r^4} $$

(1)

where $E = e/r^2$ is the Coulomb electric field of the ion at the position of the neutral molecule. The collision cross section for such an interaction is $^9$

$$ \sigma = \frac{\alpha^2}{m v} \approx 10^2 \text{A}^2. $$

(2)

for a typical velocity $v$. This large cross section and the corresponding rate constant

$$ k = \sigma v = \frac{\alpha^2}{m} e \approx 10^{-9} \text{cm}^3/\text{sec} $$

(3)

are called the Langevin cross section and the Langevin rate constant, respectively. This large rate constant applies both to many ion-molecule reaction rates and to a relaxation process such as rotational energy transfer. Thus in the laboratory where the typical concentration is $\approx 10^7$ cm$^{-3}$, the rate is $\approx 10^7$/sec; in space where the typical concentration is $\approx 10^6$ cm$^{-3}$, the rate is $\approx 10^{-5}$/sec. We note in Eq. (3) that $k$ is independent of velocity and thus temperature. Maxwell used this potential for his calculation of the transport process for sheer mathematical convenience. The Langevin rate for rotational relaxation leads to pressure broadening on the order of $\approx 10$ MHz/torr Vibrational relaxation without chemical reaction is several orders of magnitude slower.
Ionization  In the laboratory plasma, molecular ions are initially produced through ionization by electron bombardment. Since the electron temperature of the plasma (typically 2-3 eV (20 eV - 30,000K) is considerably less than the ionization potential of molecules (typically 12-15 eV) the ionization occurs through the tail of the energy distribution of thermal electrons. If a Boltzmann distribution is assumed the rate constant can be calculated from

\[ k = \int_0^\infty \sigma(\epsilon) v \, dn(\epsilon) \]  

(4)

where \( v = \sqrt{2e_0} \) is velocity of electrons and the energy distribution of electron is

\[ dn(\epsilon) = \frac{2}{\sqrt{\pi}} \left( \frac{e_0}{kT} \right)^{1/2} e^{-\frac{e_0}{kT}} d\left( \frac{e_0}{kT} \right) \]  

(5)

The cross section \( \sigma(\epsilon) \) as a function of electron energy is often approximated as a linear function of \( \epsilon \)

\[ \sigma(\epsilon) = a\epsilon - b. \]  

(6)

The experimental values of \( a \) and \( b \) can be found from the \( \sigma(\epsilon) \) curve in the compilation by Kieffer.\textsuperscript{55} The value of \( k \) is typically \( 2 \times 10^{-5} \) cm\(^3\) sec, that is, if we have \( 10^{11} \) cm\(^3\) of electron density a molecule is ionized 0.2/sec. For plasma with a pressure of 1 torr the ion production is on the order of \( 10^{14} \) cm\(^3\) sec, that is, \( 10^{10} \) ion pairs are produced per cm\(^3\) per second. Once ions are formed they react with neutrals with the large Langmuir rate, that is \( 10^{-5} \) sec.

Recombination  Because of the long range Coulomb interaction, the electronic recombination usually occurs much faster than the Langmuir rate. The typical value of the recombination rate constant is \( 10^{-7} \) cm\(^3\) sec. We can find electron recombination rates in Ref. 38 and 35. So, for an electron density of \( 10^{14} \) cm\(^3\), the recombination rate to be on the order of \( 10^9 \) sec. At the Royal Society Meeting in London (March, 1987), David Smith surprised us by announcing that the \( H_2^+ \) recombination is at least \( 10^4 \) times slower than previously believed. 36 This will radically change the ion kinetic argument in hydrogen dominated plasmas both in the laboratory and in space.

In a laboratory plasma the dominating ion destruction mechanism is often not the electron recombination in the plasma but the electron recombination at the wall after ambipolar diffusion. Because of the light mass and high temperature, electrons diffuse in the plasma
faster than atomic and molecules ions by say 10^3. In order to preserve quasi-neutrality in the plasma, cations move with the electrons towards the wall. The data for this is found in Ref. 39. In the last few years, there has been mounting evidence that ambipolar diffusion is much faster than previously believed.40 In a recent plasma diagnostics of H₂ and He discharges,41,42 we have used diffusion rates of 10^5 cm/sec. Thus destruction of ions by ambipolar diffusion is more significant than that by electron recombination if the diameter of the discharge tube is on the order of a few centimeters.

1.4. Degree of Ionization

Laboratory Plasma

The ion concentration in a laboratory plasma can be estimated from the simple formula

\[ \frac{I}{S} = nev. \]  

(7)

From the measured current density I/S we can determine the electron concentration n if we assume the electron drift velocity v. The drift velocity in various discharges can be found in Ref. 32. We usually find the value like I/S ~ 0.2 A/cm², v ~ 10⁵ cm/sec and n ~ 10¹¹/cm³. From the overall neutrality this must also be the number density of cations (the densities of molecular anions probably are smaller).

This ion concentration agrees with what we expect from the ion kinetics in the previous section. Using the ion production rate of \( \sim 10^{10}/\text{cm}² \) sec and destruction rate by ambipolar diffusion of \( \sim 10^7 \) sec (i.e. lifetime of \( \sim 10^{-3} \) sec) we obtain the steady state ion concentration of \( \sim 10^{14}/\text{cm}³ \). Since the pressure of the gas is \( \sim 3 \) Torr, the fraction of ion (which we call degree of ionization) is typically \( \sim 10^{-3} \). This is a typical value for a glow discharge. Depending on the main component of the gas the degree of ionization varies. For example, in an Ar discharge the electron drift velocity is smaller and thus the degree of ionization is larger by an order of magnitude. The degree of ionization is also larger in hollow cathodes and in negative glow, due to larger current density and/or small electron drift velocity.

Astronomical Plasma

The degree of ionization in various astronomical objects have wide ranging values depending on the energy of the object. Inside the star and cosmic ray, of course, the electrons are completely stripped from nuclei - the fully ionized plasma. In the solar corona, where the temperature is \( \sim 2\times10⁶ \) K, highly charged atomic ions are observed. As we go towards lower temperature, planetary nebula - diffuse cloud - dense cloud, the degree of ionization decreases.
In the dense clouds which we are most interested in, the star radiation is completely shielded and the ionization occurs through cosmic ray bombardment. The universal cosmic ray flux is fairly well established to be $\zeta = 10^{-17}/\text{sec}$. This should be compared with 0.2/sec given earlier for the laboratory plasma. The degree of ionization in dense clouds can be estimated by equating the production rate and the destruction rate by electron recombination.

$$\zeta[X] = k [X^+] [e].$$ \hspace{1cm} (8)

We have

$$[X^+] = [e] = \frac{[X]}{k} \sim 10^{-3}/\text{cm}^3$$ \hspace{1cm} (9)

if we use $k = 10^{-7} \text{ cm}^3/\text{sec}$ and density $[X] = 10^9/\text{cm}^3$. This gives the degree of ionization $[X^+]/[X] \sim 10^{-7}$. We note that even the least ionized part of the universe has degrees of ionization comparable to that of laboratory plasma (as we mentioned earlier, planetary atmosphere is exceptional because of the high molecular concentration). If we use $[X] = 10^{10}/\text{cm}^3$ in Eq. (9) we obtain $[X^+]/[X] \sim 10^{-3}$.

1.5. Production of Specific Ions

As we have seen, we have a pretty good idea about how much charged species we can produce in a discharge. To produce a specific ion, however, is more difficult. Plasma chemistry is almost alchemy. There is not much logic before the execution of the experiment; we just try to see if it works. The simplest is the production of $H_3^+$ in the $H_2$ discharge, through the ion-molecule reaction

$$H_2^+ + H_2 \rightarrow H_3^+ + H.$$

(10)

The reaction is very exothermic (1.8 eV) with a large Langevin cross section of $H_3^+$, and therefore $H_3^+$ is the dominant ion in a pure hydrogen discharge.

The simple hydride cations are produced by the hydrogen extraction reaction,

$$X^+ + H_2 \rightarrow HX^+ + H.$$

(11)

For the oxygen series the extraction reactions occur efficiently throughout the chain

$$O^+ \rightarrow OH^+ \rightarrow H_2O^+ \rightarrow H_3O^+$$

which are all exothermic with the Langevin rates. For the nitrogen
series with the chain

\[ \text{N}^+ \rightarrow \text{NH}^+ \rightarrow \text{NH}_2^+ \rightarrow \text{NH}_3^+ \rightarrow \text{NH}_4^+ \]  

(13)

all reactions are very efficient except for the last reaction \( \text{NH}_3^+ \rightarrow \text{NH}_4^+ \) which has a barrier and has a rate constant which is lower by a factor of 10^3. The individual reaction rates can be found conveniently in the table of ion-molecule reactions by Albritton.47 These reactions are very important in the ion chemistry scheme in interstellar space and are used a great deal in the literature.13,14,15 The series of work by Hantzen16,17,18 is particularly informative. Because of the chains shown in Eqs. (12) and (13), it is easy to produce much \( \text{H}_2\text{O}^+ \) and \( \text{NH}_4^+ \). They are sometimes called "end of the food chain" ions. In order to produce plasmas which have abundant intermediate ions such as \( \text{CH}^+, \text{H}_2\text{O}^+, \text{NH}^+, \text{NH}_2^+, \) etc. we use a large amount of \( \text{He} \) to slow down the reaction reaching the end of the chains.49,50

The chain of reactions for carbocations is more complicated,

\[ \text{C}^+ / \text{CH}^+ + \text{CH}_2^+ \rightarrow \text{CH}_3^+ / \text{CH}_4^+ \rightarrow \text{CH}_5^+ \]  

(14)

This chain has two hangups.51 As a result of these hangups, \( \text{CH}_3^+ \) is relatively easy to produce.

The diatomic carbon chain

\[ \text{C}_2^+ \rightarrow \text{C}_2\text{H}^+ \rightarrow \text{C}_2\text{H}_2^+ \rightarrow \text{C}_2\text{H}_3^+ / \text{C}_2\text{H}_4^+ \]  

(15)

also has a hangup.51 The last reaction \( \text{C}_2\text{H}_3^+ \rightarrow \text{C}_2\text{H}_4^+ \) goes only for vibrationally excited \( \text{C}_2\text{H}_3^+ \). Therefore \( \text{C}_2\text{H}^+ \) and \( \text{C}_2\text{H}_2^+ \) are relatively abundant in hydrocarbon discharges.55 A major difficulty in the production of carbo-ions results from efficient polymerization. Almost all reactions between carbocations and neutral hydrocarbons such as \( \text{CH}_2^+ + \text{CH}_4(\text{C}_2\text{H}_2, \text{C}_2\text{H}_3, \text{etc.}) \) have the Langemeyer cross sections and produce polymeric hydrocarbons eventually leading to a large amount of soot deposited on the wall of the discharge tube. The method we use to cope with this difficulty is to simply dilute the discharge gas mixture with a large amount of \( \text{He} \). Helium also increases the efficiency of ion production through Penning ionization56 and, because of its high ionization potential, tends to increase the electron temperature in the plasma thus helping to fragment larger carbon compounds. For example, for the spectroscopy of \( \text{CH}_3^+ \) or \( \text{C}_2\text{H}_3^+ \) we used a gas mixture of \( \text{He}: \text{H}_2: \text{X} = 700:20:1 \) (X=\( \text{CH}_3, \text{C}_2\text{H}_4, \text{C}_3\text{H}_6\text{etc.} \)) with a total pressure of 47 Torr. A more detailed discussion of carbon chemistry appears in Refs. 54 and 57.
For the spectroscopy of carbo-ions we have found it useful to use various multiple-inlet-outlet discharge tubes. We use an air-cooled discharge tube (nicknamed "spider"), a water cooled tube ("tarantula") and a liquid nitrogen tube ("black widow") depending on purposes. The water cooled tube is schematically shown below in Fig. 4.

![Diagram](image)

**Figure 4.**

A fresh mixture of gases is introduced into the discharge tube through the eight inlet ports. From the color of the discharges we note that fresh chemical reactions occur in the region of the inlet ports. In the usual single inlet-outlet cell, the fresh reaction tend to occur at electrodes, depositing a large amount of soot in that area. The reaction chain of Eq. (14) plays an important role in interstellar chemistry as seen from Fig. 5 provided by A. Dalgarno. 50, 59

There are many other reactions which form specific molecular ions. For example the universal reaction

\[ X + H_3^+ \rightarrow HX^+ + H_2 \]

(16)

occurs very efficiently in a hollow cathode discharge. Amano has been extremely successful in using this reaction in a hollow cathode discharge tube with \( X = \text{O}_2, \text{N}_2, \text{OCS}, \text{CH}_3\text{CN} \) to produce \( \text{HCO}^+ \) (Ref. 60), \( \text{HNCO}^+ \) (Ref. 61), \( \text{HCCO}^+ \) (Ref. 62), \( \text{CH}_3\text{CNH}^+ \) (Ref. 63) and \( \text{HCCONH}^+ \) (Ref. 63). The reaction of Eq. (16) is also universal in interstellar
space and leads to HCO\textsuperscript{+}, HN\textsubscript{2}\textsuperscript{+} and numerous other molecular ions observed by radio astronomers. In Suzuki's treatment of chemical reactions in molecular clouds\textsuperscript{15} as many as 70 reactions of this type have been considered.

Negative ions can also be produced in abundance in discharges as has been demonstrated recently by the detection of OH\textsuperscript{-} and NH\textsubscript{2}\textsuperscript{-} infrared spectrum in discharges.\textsuperscript{64,65} The production of negative ions is optimized under different discharge conditions from that for cations. For example, metal coating the wall of a discharge cell increases the concentration of OH\textsuperscript{-} at least an order of magnitude.\textsuperscript{66} Recently M. Polak, M. Gruebele and R.J. Saykally have been extremely successful in producing polyatomic negative ions by using the general reaction

\[ \text{XO} + \text{NH}_2^- \rightarrow \text{XN}^- + \text{H}_2\text{O}. \] (17)

Using N\textsubscript{2}O, CO\textsubscript{2} and OCS, they have obtained spectra of N\textsubscript{3}\textsuperscript{-} (Ref. 67), NCO\textsuperscript{-}(Ref. 68) and NCS\textsuperscript{-} (Ref. 69).

Obviously there are a great many more ways to produce other ions.
II. INFRARED SPECTROSCOPY OF MOLECULAR IONS USING FREQUENCY TUNABLE LASER SOURCES

Infrared spectroscopy is the most universal spectroscopic method to study the simple fundamental ions discussed so far. There are cases such as $\text{H}_3^+$ for which no stable electronic excited state exists. Even if there are excited states, they are often predissociated and do not give discrete spectra. Thus few hydride ions would show discrete electronic spectra. On the other hand, almost all molecular ions (except for some homonuclear diatomics) absorb infrared strongly.

In discussing the experimental aspect of spectroscopy there are two major factors — sensitivity and resolution. Comparing the two neighboring spectral ranges, i.e., microwave and visible, the traditional grating infrared spectroscopy had been inferior in both of the two attributes. The availability of monochromatic sources and the relative ease of electronic controls of various elements has made microwave spectroscopy an extremely sensitive ($\Delta I/I < 10^{-7}$) and high resolution technique. In the visible-ultraviolet region, fluorescence spectroscopy and the photographic method has made the spectroscopy also extremely sensitive. Many large grating visible and UV spectrometers had near Doppler limited resolution of $\Delta v/\nu \sim 10^{-6}$. In the grating infrared spectrometer the sensitivity has been typically $\Delta I/I \sim 10^{-5}$ and the resolution $\Delta v/\nu \sim 10^{-5}$. This situation has been changed radically with the advent of laser spectroscopy and Fourier transform spectroscopy (I shall not touch on the latter here). The sensitivity of laser infrared spectroscopy by using a suitable modulation is comparable to that of microwave, and the resolution using sub-Doppler techniques is $\sim 10^{-9}$. This increase of a factor of $\sim 10^4$ both in sensitivity and resolution has made the infrared spectroscopy much more powerful than before. A great many things are now possible. Ion spectroscopy is only a small part of it. We have not really understood the impact of this yet.

2.1. Frequency Tunable Laser Infrared Sources

Although it is already more than a quarter century since Maiman first operated his laser, it is only in the last ten years or so that frequency tunable infrared sources have become available to practicing spectroscopists. A review by Pine contains useful information on various sources and spectroscopy using them. Following are brief sketches of various sources in relation to molecular ion spectroscopy.

Difference Frequency Laser System

This non-linear optical method of generating frequency tunable infrared radiation was initially operated by Boyd and Ashkin, and developed by Pine into a very powerful spectroscopic tool. Radiation from a dye laser ($\nu_D$) and radiation from a single-mode Ar ion laser ($\nu_A$) are mixed in a LiNbO$_3$ crystal. Their planes of
polarization are perpendicular to each other. The infrared difference frequency \( v_{IR} \) is generated when the energy balance

\[ v_{IR} = v_A - v_D, \]

and the momentum balance condition

\[ k_{IR} = k_A - k_D, \]

are satisfied. The latter (phase matching) is achieved for a special value of temperature for collinear \( k_A \) and \( k_D \) through the temperature dependence of the dielectric constants of the birefringent LiNbO\(_3\) crystal. (Note \( k = h\nu/c(T) = h\nu/\text{cn}(T) \) where \( \text{cn}(T) \) is the temperature dependent refractive index). The frequency of infrared is tuned by tuning the dye laser frequency. The monochromatic (\( \Delta\nu \approx 2 \text{ MHz} \)) radiation obtained has power of \( 1 \sim 500\text{\mu W} \) which is sufficient for linear spectroscopy (Note that the noise equivalent powers of high sensitivity detectors are typically \( 10^{-10} \sim 10^{-11} \text{ Watts} \)).

The advantage of this source is its wide and continuous coverage (2.2\( \sim \)4.2\( \mu \)m) of the important infrared region. Practically all hydrogen stretch vibrations fall in this region. This radiation source was indispensable for my first work on \( \text{H}_3^+ \) (Ref. 5) and still is the most powerful tool in our laboratory. The spectrometer used for the \( \text{H}_3^+ \) spectroscopy is shown below in Fig. 6.
This type of spectrometer is used now by Amano in Ottawa and in Chicago for molecular ion spectroscopy. An extension of the frequency coverage is being attempted using LiIO₃. It will then cover a wide wavelength region of 2-5.6 μm albeit with less power.

Color Center Laser

The color center laser was invented by Mollenauer and Olson in 1974. It has become well-known among high resolution spectroscopists through the beautiful and energetic work of Saykally and his colleagues. It is the infrared version of the dye laser. Pumped by a Kr ion laser, it generates tunable infrared radiation over a wide range of 2.3-3.45 μm with high power (2.5 - 100 mWatts). This radiation source covers the N-H and O-H stretching regions and much of the C-H stretch also. The available high power makes this source particularly attractive for non-linear experiments such as sub-Doppler spectroscopy and double resonance spectroscopy. Color center lasers are used for ion spectroscopy in Saykally's laboratory in Berkeley and in Urban's laboratory in Bonn. The extensive electronic and computer control of this system by the latter group and by Curl and his colleagues is noteworthy.

Diode Lasers

The semiconductor lasers are commercially available from 3 to 30 μm. The advantage of diode lasers is that they are relatively low priced, easy to operate, they generate a fair amount of power (10 μW-1 mW) of low amplitude noise, and their frequency is easily modulated. They are the only frequency tunable infrared sources which cover more than three octaves (if a sufficient number of diodes are available). This infrared source was indispensable for the detailed studies of the ν₂ vibration-inversion mode of H₂O in which three bands between 10-30 μm had to be studied. The disadvantage of this source on the other hand is the narrow and patchy coverage of an individual diode laser and their rather unpredictable optical quality.

Diode lasers are used for ion spectroscopy by McKellar in Ottawa, Davies in Cambridge, Destombes in Lille, Kawaguchi and Hirota in Okazaki, Sears in Brookhaven, Saykally in Berkeley, and in Chicago. Perhaps there are come more people doing this.

Microwave Modulation Sidebands on CO₂ Laser Lines

The 10 μm radiation from a CO₂ laser (v₁) and microwave radiation (vₚ) are mixed in a CdTe crystal to generate sidebands at v₁+vₚ. This technique, developed by Bonek and Magerl, provides a relatively simple way to produce tunable infrared radiation with high spectral purity and sufficient power (1-3 mWatts) for sub-Doppler spectroscopy. While this source is not very suitable for the search of new ion spectra, it allows very high resolution observation.
(Δν/ν 10^-9) of a known spectrum. The experimental set up is shown in Figure 7.

![Diagram of CO₂ microwave sideband sub-Doppler spectrometer with multiple path.]

Figure 7. CO₂ microwave sideband sub-Doppler spectrometer with multiple path.

This approach has recently been applied to the H₃O⁺ ion spectroscopy.

2.2. Increasing the Sensitivity

We saw earlier that the number concentration of ions in typically 10^7/cm³. Since the infrared absorption coefficient for the hydrogen stretching vibration of simple molecules (such as the ν₁ band of CH₄) is on the order of 0.1 cm⁻¹/Torr, we are dealing with absorption coefficient on the order of 3 x 10⁻⁶ cm⁻¹. If a path length of 1m is used the absorption is 3 x 10⁻⁴. This is too small for the traditional grating spectroscopy but is sufficiently large for laser spectroscopy. In fact the existence of charge usually makes the transition moment larger and ion absorptions are often more than the above value. We have seen <20% absorption due to ArH⁺ using a 2m path length. In favorable cases we can detect ions with number concentrations on the order of 10⁶/cm³.

One complication in infrared spectroscopy is that, unlike electronic spectroscopy, many bands appear overlapped in the same wavelength region. Thus, for example, the spectra of the C-H stretching vibrations of CH₂⁺, HCCH⁺, and C₂H₃⁺ appear intermixed with those of stable neutral hydrocarbons CH₄, HCH₃, C₂H₄, C₂H₆ ... and a great many others which are always produced abundantly in plasmas regardless of
which hydrocarbon discharge is used. Since the ions are a very small fraction of neutrals this causes a serious problem of detection and assignment. The ingenious method of velocity modulation invented by Gudeman, Saykally and others\textsuperscript{75,81} is a very powerful tool to avoid this difficulty and, at the same time, to increase sensitivity. Let us first start from the drift velocity of ions in plasmas.

**Ion Drift Velocity**

In plasmas ions are always under acceleration by the discharge electric field $E$ which is typically 10 V/cm in a positive column. At the same time ions are decelerated upon collisions with neutrals. So on the average ions move from anode to cathode with a constant speed. We write the ion drift velocity $v_d$ phenomenologically as

$$v_d = \frac{KE}{K}$$

(20)

where the proportionality constant $K$ is called mobility. Equating the drift velocity to the diffusion velocity formula $v_d = \frac{(D/N)(dN/dz)}{D}$, we obtain the Einstein relation

$$K = D \frac{6}{\pi a^2}$$

(21)

between the mobility $K$ and the diffusion constant $D$.\textsuperscript{56} Using the Langevin cross section of Eq. (2) we obtain

$$K = \frac{3}{4 \pi a^2} \left( \frac{3}{2} \right)^{1/2}$$

(22)

from the Chapman-Enskog theory\textsuperscript{38,85} of diffusion.

In order to have a more microscopic picture, it is instructive to consider a hypothetical one-dimensional model. The acceleration of a single ion is

$$m \ddot{z} = eE \quad \text{or} \quad \dot{z} = v_0 + \frac{eE}{m} t$$

(23)

An ion with zero initial velocity will have a velocity $v_0 t$ after a time interval $t$ ($v = eE/m$). Suppose it collides after this time interval with a neutral molecule with zero velocity and with mass $m_0$. The velocity of an ion after the collision will be $v_0 t$ from momentum conservation where $\rho \equiv m/(m+m_0) < 1$. The ion starts from this initial velocity now and gets accelerated. After another time $\Delta t$, it has the velocity $(1+\rho) \rho^\Delta t$ and collides with a neutral. If we continue this argument we find that after many collisions, the ion speed approaches

$$v = (1 + \rho + \rho^2 + \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots) \rho^\Delta t = \frac{\rho^\Delta t}{1-\rho}$$

just before the final collision. If we substitute the expressions of $\rho$ and $\rho$ given earlier and $\Delta t = (n \sigma v)^{-1}$ with the Langevin cross
section of Eq. (2) we obtain
\[ v = \frac{1}{2\pi N} \frac{1}{v_{\mu_s}} E \] (25)

The value of mobility thus obtained has the same \( \mu \), \( \alpha \) dependence as that in Eq. (22); its value is larger than that in Eq. (22) by about 20%. Eq. (25) gives the value just before the collision, the average velocity is
\[ \bar{v} = \frac{2m + m_0}{2(m + m_0)} v = KE \] (26)

While this simplistic picture requires much extension taking into account the three dimension and the stochastic nature of collision (see the simplified one-dimensional picture and its extension in Chandrasekhar's article on Brownian motion\(^{36} \)), we can obtain from it a basic picture and orders of magnitude of the microscopic motion. We can calculate approximate values of velocity from Eqs. (25) and (26) for various combinations of molecular ions and neutrals. We see from the discussion leading to Eq. (24) that, if \( \rho \ll (m + m_0) \) it takes many collisions for the ion to reach the steady state while if \( \rho < 1 \) \( (m < m_0) \) the ion is slowed down by each collision but reaches the ultimate speed by the time the next collision occurs.

Spectroscopic Measurements of Ion Drift Velocity

The traditional method of measuring ion drift velocity has been to use time-of-flight drift tubes employing a mass spectrometer as the detector.\(^39 \) The high sensitivity ion spectroscopy has introduced an additional method to measure this quantity. The advantage of this new method compared with the traditional one is that it is in situ and non intrusive and it can be carried out with high spatial resolution. The basic setup is shown in Figure 8. The radiation from a diode laser is

Fig. 8. Doppler-shift discharge cell and optical arrangement.
split into two counter propagating beams with a beam splitter detected with two separate Hg CdTe detectors. For ions moving from with velocity \( v \), the two radiations appear blue shifted and red shifted by \( v/c \). Thus we have Doppler shifted spectra as shown below in Figure 9.

![Doppler-shift spectrum](image)

The Doppler shifted line in Fig. 9 is the F(5) fundamental transition of \( \text{ArH}^+ \) at 2479.411 cm\(^{-1}\). We observed this spectrum using a He:Ar:H\(_2\) mixture of 50:3:1 with the total pressure of 0.3 Torr, the discharge electric field was 5.3 V/cm. We clearly see from Fig. 9 that \( \text{ArH}^+ \) ions are drifting from anode to cathode with the velocity of \( \approx 512 \) m/s and that this speed is comparable or larger than the random velocity of the molecular ions in the discharge. Such a measurement gives ion mobility in discharges. For more details of these results see Ref. 85.

Velocity Modulation

Early in 1983 Gudeman, Begemann, Pfaff and Saykally published a paper in which they used AC glow discharge applied to the fundamental band of HOD\(^+\). Their apparatus is shown below in Fig. 10. In the AC discharge the molecular ions are accelerated back and forth by the alternating electric field thus frequency modulating the absorption line through Doppler effect. This modulation is effective for molecular ions since, as we see from Fig. 9, the Doppler shift is comparable to the Doppler linewidth due to the random velocity. Suppose we use the velocity modulation with frequency of 10 kHz, that is, an ion is accelerated for a time interval of \( 5 \times 10^{-5} \) sec to one direction and then to the other. The ion will collide with neutrals about \( 10^4 \) times during the time interval (a pressure broadening of 30 MHz is used in this estimate). The ion reaches its ultimate velocity of Eqs. (24)-(26) after \( 1 \times 10^4 \) collisions. The velocity is on the order of \( \approx 500 \) m/sec, that is, the ion moves a few centimeters in its plasma and changes direction. This method allows us to discriminate ion lines from much stronger neutral absorption and at the same time
increase the sensitivity of detection. From my viewpoint this is the most important technical development for ion spectroscopy after introduction of the tunable infrared source. More details of this method can be found in the review by Gudeman and Saykally.

Other Methods

Several other methods have been utilized to increase sensitivity and discrimination of molecular ion spectroscopy. Kawaguchi, Yamada, Saito and Hirota developed the magnetic field modulation method exploiting the sensitivity of molecular ion absorption to a magnetic field. Since the magnetic field varies the plasma conditions in general, the neutral absorption lines are also affected by the magnetic field but the effect on ion lines is more drastic. This method is particularly useful for cases when the velocity modulation method is not applicable such as for a hollow cathode discharge used very effectively by Amano and his colleagues.

The traditional method of noise subtraction has been revived and used very effectively for ion spectroscopy. The laser beam is split into two parts, one for spectroscopy and the other for reference and detected by two matched infrared detectors. The signals from the two infrared detectors are electronically combined with opposite phase to subtract noise. This method is particularly effective for a color center laser and a difference frequency laser system where the
amplitude noise of the laser is larger (a few percent). Improvements on sensitivity of 10⁻¹⁻¹₀ have been reported.

The method of White multiple path cell\textsuperscript{90} is also adapted to the ion spectroscopy to increase the absorption path length. For ion spectroscopy without using velocity modulation such as that for \( \text{H}_2^+ \) or hollow cathode discharge,\textsuperscript{5,69,88} usual White cell arrangement\textsuperscript{11} is used and increase the path by \( \text{S-16} \). When the velocity modulation method is used, it is necessary to arrange a unidirectional multiple path as shown in Figure 11. Using the arrangement we typically gain sensitivity by a factor of \( \sim 4 \) (Ref. 57,54).

![Diagram of a multiple path cell setup]

2.3. Spectroscopy of Molecules Under Acceleration

There is a qualitative difference between translational motion of neutral molecules in normal spectroscopy and that of molecular ions in discharge spectroscopy. In normal spectroscopy a molecule is moving with a uniform velocity between collisions and if it resonates with the laser radiation the resonance is interrupted only by collision. In ion spectroscopy, however, the ions are under acceleration between collisions and, depending on the condition, the resonance may not last for the whole collision interval. This fact introduces a new source of uncertainty broadening which I call here "transit" broadening (the quotation mark is to discriminate this effect from the usual transit time broadening which is much smaller).

The calculation of this new broadening is simple. The velocity of an ion under acceleration is given as

\[ v = v_0 + \frac{eE}{m} t. \]  

(27)

The variation of velocity during the collision interval \( \Delta t \) is \( v = \frac{eE \Delta t}{m} \), which means the variation of resonance frequency is

\[ v = \frac{eE}{m \lambda} \Delta t \]  

(28)

where \( \lambda \) is the wavelength of radiation. If we compare this with the
usual equation of uncertainty broadening

\[ \Delta \nu = \frac{1}{2\pi \Delta t}, \]  

(29)

we find that they are inverse in their \( \Delta t \) dependence. If \( \Delta t \) is short \( \Delta \nu \)
is determined from Eq. (29), but if \( \Delta t \) is long, the ion moves out of
resonance after some time interval \( \delta t \) which is shorter than \( \Delta t \). I
speculate that the value of \( \delta t \) is obtained by equating Eq. (28) and
(29) for that value of \( \delta t \), that is

\[ \delta t = \sqrt{\frac{m_A}{2\pi eE}}, \]  

(30)

which means the uncertainty broadening

\[ \delta \nu = \sqrt{\frac{eE}{2\pi m_A}}, \]  

(31)

Some numerical examples are given below.

<table>
<thead>
<tr>
<th>ion</th>
<th>( \lambda(\mu) )</th>
<th>E(V/cm)</th>
<th>( \delta \nu ) (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2^+ )</td>
<td>4</td>
<td>15</td>
<td>31</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}^+ )</td>
<td>10</td>
<td>20</td>
<td>9</td>
</tr>
<tr>
<td>( \text{OH}^+ )</td>
<td>100</td>
<td>3</td>
<td>1.2</td>
</tr>
<tr>
<td>( \text{H}_3\text{O}^+ )</td>
<td>1000</td>
<td>1</td>
<td>0.6</td>
</tr>
</tbody>
</table>

One additional subtlety; if the coordinate displacement of the
ion \( \delta z \) during the time \( \delta t \) is smaller than the wavelength of the radia-
tion, the radiation cannot sense the off-resonance (Dicke narrow-
ing\(^92,93\)). Thus for the last case of the above numerical examples, \( \delta \nu \)
will be smaller than the calculated value.

The numerical examples indicate that very low electronic field
discharge is required for sub-Doppler saturation spectroscopy of
molecular ions.

I have run out of the paper allotted to me and I have to cut the
chapter on the analysis of ion spectra. While in principle, the
analysis of ion spectra is not different from that for usual molecules,
there are certain cases where unexpectedly rich and irregular spectral
features are observed because of (paradoxically) simplicity of the
species (\( \text{H}_3^+ \) see Refs. 5,12,94) and because of non-rigidity of the
species (\( \text{C}_2\text{H}_5^+ \) see Ref. 54). Readers are referred to review
articles\(^9,95\) for more sources.
References

30. J.C. Maxwell, Phil. Trans. R. Soc. 157, 49 (1867).
63. T. Amano, private communication.