Laser-Induced-Fluorescence Studies
of Fragment Ions: CH^+ and CD^+

Anthony O'Keefe
Department of Chemistry
and
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

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In the course of writing a thesis and trying to summarize several years of work I've found, as many others have, that the most difficult section to write is this one. It is hard to adequately express appreciation for the many things so many have done for me.

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Anthony O'Keefe

Abstract

The dynamics of ion-molecule interactions within a mass selective rf quadrupole ion trap are studied for several ion-molecule systems. Laser induced fluorescence is used as a probe of the internal energy distributions of molecular ions under collision free conditions and under controlled collision conditions. The effects of collisions at near thermal energies (0.3-0.5 eV) are easily understood in terms of processes such as charge transfer and other energy transfer mechanisms.

The $\text{A}^1\Pi - \text{X}^1\Sigma^+$ system of CH^+ and CD^+ has been examined under collision free conditions. The ions were produced from methane through electron impact ionization/dissociation. The observed energy distributions reflect the dynamical partitioning of dissociation exothermicity, excepting short lived electronic states. Many new transitions belonging to this electronic system have been observed and a reliable vibrational frequency for the $\text{X}^1\Sigma^+$ state has been obtained. The radiative lifetimes of CH^+ and CD^+ $\text{A}^1\Pi(v=0)$ states have been measured and a revised oscillator strength for the A-X transition has been derived from this data.

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CHAPTER I

Introduction

The study of molecular ions has been an important area of both physics and chemistry for many years. In addition to the pure spectroscopic interest in molecular ions, there exist many compelling practical reasons for the physicist to study such species. For example, if the astronomer is to model the behavior of interstellar clouds he must have at his disposal an accurate set of molecular properties for the predominant molecular species.¹ It is often the case that such species are ionized by the high energy background radiation and through charge transfer, and so such ionic species must be thoroughly studied and their properties characterized before accurate models of interstellar processes can be devised. From the standpoint of a chemist, molecular ions are of primary interest due to the role they play in many chemical processes. The attractive long range charge induced dipole potential results in generally higher cross sections for interaction between ions and polarizable neutrals. For this reason ion-molecule reaction rates tend to be much higher (typically a factor of 10 or more) than those found in neutral-neutral reactions. Clearly then, ion-molecule reactions are important in the chemistry of discharges, plasmas and, in fact, any chemical system in which ions are present in significant quantity.

It is thus clear that molecular ions are of great importance in several fields of study, and one would then expect that a vast amount of information pertaining to such species would have been accumulated. Significantly though, a surprisingly meager amount of spectroscopic data is available for any molecular ion, and when data are available they are

usually of low resolution. Several reasons for this dearth of information become apparent when the techniques commonly used to study molecular structures are considered. Almost any high resolution molecular study involves some form of spectroscopy. For most spectroscopic techniques to be successful rather large sample densities must be achieved, a requirement which is extremely difficult to fulfill for ionic species. The strong repulsive coulomb force felt between ions of like charge limits the practical ion densities which can be achieved in most experiments to values which fall below the detection limits of most spectroscopic techniques. Much higher ion densities can be obtained within a discharge plasma due to the compensating presence of both positive ions and free electrons. The high pressures at which discharges are operated (~1 Torr) result in a large number of ion-molecule reactions which have the unfortunate effect of scattering the ionic population distribution among many species. An excellent example of how diverse the ion population within a discharge can be is provided by the first observation of C_2^- , which was observed in a discharge through CH_4 .²

The problems associated with the study of molecular ions have been the focus of intensive study in the last decade. Many new techniques have been developed which provide greater flexibility and higher sensitivity than previously possible.³ One such technique is the flow tube apparatus developed by Miller and Bondybey⁴ in which molecules, diluted in a fast flow of rare gas buffer atoms, are ionized through Penning ionization by metastable rare gas atoms mixed into the flow. Following ionization the ions, which are rapidly thermalized through collisions with the buffer gas, are probed with a tunable dye laser pulse and the subsequent laser induced fluorescence monitored. There are several

attractive features to this approach. Relatively high ion densities ($\sim 10^8$ ions/cc) can be obtained and, since the parent molecules are dilute in the buffer gas flow, ion-molecule reactions are minimized. The limitations of this approach are related to the fact that the only control over the ion formation process is the choice of the metastable rare gas atom. This is, in practice, limited to either He* or Ne*. It is significant that this technique has not been able to produce any fragment ions in densities sufficient to obtain excitation spectra. In addition, because the ions undergo a large number of collisions before they are probed by the laser beam, any dynamical information pertaining to the ionization process, which may manifest itself in the ro-vibronic product distributions, is lost.

Another technique, which shows great promise, is the guided ion beam-octupole trap developed by Teloy and Gerlich.⁵ In this approach ions are directed through an octupole arrangement of electrodes to which an rf voltage is applied. (In this sense the arrangement may be thought of as an extension of the conventional quadrupole ion lens). By placing potential caps at the ends of such an octupole pipe a "bottle" is formed within which ions can be confined. Since this approach involves the active storage of the ions (as opposed to the diffusion limited storage of the flow tube technique), ions may be formed and stored under collision free conditions, preserving any dynamical information which may reside in their internal state distributions.

Over the past few years we have developed a technique with which we can study ions in the gas phase under well-defined conditions.⁶⁻⁹ The approach involves the use of an rf quadrupole ion trap of the type described by Benalin and Audoin.¹⁰ The use of such a device permits the

spacial isolation of ions with a specific charge to mass ratio for time periods limited only by collisions with background neutral molecules. Once the ions have been trapped within the quadrupole electrode arrangement a short duration (~ 10 nsec) laser pulse from a tunable dye laser is passed through the ion cloud. Subsequent laser induced fluorescence is monitored at right angles to the laser axis. The experiment is operated at low pressures so that ion-molecule collisions occur on a relatively infrequent ($< 1 \text{ msec}^{-1}$) basis; a feature which has permitted the measurement of natural radiative lifetimes of excited electronic states.

This dissertation will be presented in several sections. Following this introduction, in which the reasons for the present investigation will be offered, a brief description of the apparatus and general experimental arrangement will be given. A detailed description of most experimental details may be found in the work of Grieman;⁶ however, several modifications have been made which will be described here. Following the experimental section the results of several diagnostic studies of trapped molecular ions will be presented. These results and the accompanying discussion should provide the framework with which the details of the observed spectra of molecular ions can be anticipated and analyzed. This section will also report the strong vibrational state dependence of the charge transfer reaction

as studied by laser induced fluorescence of reactant N_2^+ . These results raise the enticing possibility of using an ion trap arrangement such as this one in the study of ion molecule reactions on a state by state basis.

Finally, an analysis of the spectra observed for $\text{CH}^+(\text{CD}^+)$ produced in the electron impact dissociation of $\text{CH}_4(\text{CD}_4)$ will be presented. This ion is of substantial importance in interstellar processes as well as combustion chemistry. It is believed to play a fundamental role in the production of many important molecular species within the interstellar clouds. Klemperer and Solomon¹ have given a detailed analysis of interstellar processes involving CH^+ which are believed to have significant impact upon the molecular composition of the interstellar clouds. There have been several other recent reviews of the chemistry of CH^+ in the interstellar medium.¹¹⁻¹³ Several reactions have been proposed as sources of CH^+ . The two mechanisms commonly held to be most significant in the production of the ion are

in which the collision complex is stabilized through the emission of radiation, and

where the CH_2^+ formed here can undergo a series of involved reactions leading to the production of CH^+ . The dynamics of the reaction of C^+ with H_2 has been studied in the collision energy range from 2 to 14 eV,¹⁴ and the presence of a long lived CH_2^+ intermediate was found.

Our understanding of the important chemical and physical processes involving CH^+ in the interstellar medium is reduced somewhat due to the fact that ions produced through processes (1) and (2) (or others) can undergo rapid reaction with other species present. The list of reactions affecting the concentration of interstellar CH^+ is already extensive and,

perhaps, incomplete. The abundance of CH^+ , or even the relative abundance of CH^+ to CH , cannot be accounted for by the reactions and reaction cross sections now known.

The CH^+ radical is believed to be the precursor of CO , CN and many other molecular species. The role played by CH^+ in the production of various molecular species has been examined by Dalgarno,¹² and Dalgarno and Black.¹³ The chemistry involved in these processes is intimately related to the relative concentrations of the species involved. These concentrations must be inferred from the analysis of observed line strengths and known or calculated oscillator strengths. For CH^+ a large uncertainty has existed in the radiative lifetime of the $\text{A}^1\Pi$ state. Since the $\text{A}^1\Pi - \text{X}^1\Sigma^+$ transition has been used to monitor interstellar CH^+ this uncertainty manifests itself in a large uncertainty in stellar abundance and, in turn, leads to great confusion over the relative importance of certain molecular species in the interstellar medium. This uncertainty is not due to the lack of theoretical and experimental study, but to the inconsistent nature of the results. Until recently (Grieman *et al.*),⁷ the only experimental method which had proven useful in the high resolution study of electronic transitions of molecular fragment ions was emission spectroscopy. Radiative decay rates obtained with this technique are subject to errors which are often difficult to identify or estimate. The cascading of population from highly excited electronic states and the rapid spacial dissipation of ions due to electrostatic repulsion can lead to distortions in the observed radiative lifetime of a given electronic level. The results presented here provide important experimental verification of the potential curves for CH^+ calculated by Green *et al.*^{15,16} in that both the calculated shapes of the potential

curves of interest here and transition oscillator strengths based upon these curves are in good agreement with those deduced in the present study. The measurement of CH^+ transition oscillator strengths has been the goal of numerous experimental investigations over the past decade with essentially no agreement among the various experiments or between experiment and the calculations of Yoshimine et al.¹⁷ The approach used in this study is fundamentally different from those used in earlier studies and is free from the problems which have plagued earlier work. The results presented here are encouraging and suggest the possibility of studying the temporal dynamics not only of excited electronic states in ions, but those of the much longer lived excited vibrational levels within a stable electronic state.

CHAPTER II

Experimental

The ion trap used in this study was one of cylindrical geometry which has been described in detail elsewhere.¹⁰ This configuration was selected instead of the more general hyperbolic geometry in an effort to minimize electric field distortion introduced by the presence of laser beam entrance and exit holes in the electrode. The trap consists of a cylindrical center electrode and two flat end electrodes, positioned at opposite ends of the cylinder. The general configuration is illustrated in Figure 1. The details of trap operation will be briefly outlined here. Further details may be obtained in the references already cited.

The principles of operation are an extension to three dimensions of those involved in a conventional quadrupole ion lens. Application of an rf voltage to the center electrode creates a pseudo-potential in which ions are trapped regardless of their charge to mass ratio. By floating the applied rf voltage at some D.C. bias level a selectivity in the charge to mass ratios which are confined in the potential well is introduced. The degree of selectivity is determined by the relative magnitudes of the D.C. and rf voltages. By varying the rf amplitude, at a fixed D.C. to rf ratio, the mass selection window may be shifted to different values, with ions of larger masses being trapped for greater applied voltages.

Given the general design of the trap, the depth of the pseudo-potential well can be expressed as¹⁸

Figure 1. Schematic representation depicting a vertical slice of the quadrupole ion trap used in the present study. A radio frequency voltage is applied to the center ring electrode while the top and bottom electrodes are maintained at ground potential. Ions, spacially confined to the enclosed region, possess a nearly Gaussian density distribution peaking at the center of the trap.

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$$\bar{D} = \frac{eV^2}{4Z_0^2 M f^2} \frac{6.109 \times 10^{-3} V^2 \text{ volts}}{Z_0^2 M f^2 \text{ cm amu MHz}} \quad (3)$$

Here $\bar{D}$ is calculated in volts, V is the maximum A.C. voltage between the electrodes, Z_0 is half the minimum separation of the cap electrodes, M is the ion mass in amu, and f is the applied field frequency in megahertz. For example, in the present study of CH^+ the values for these parameters are $Z_0 = 1$, $V = 200$, $M = 13$ and $f = 1$, and the corresponding well depth is 19 volts. The well depth determines the number of ions which can be trapped, since the trap reaches its maximum capacity when the space charge potential cancels the trapping potential. At this point the maximum concentration of ions is given by¹⁸

$$n_{\text{max}} \left(\frac{\text{ions}}{\text{cc}} \right) = \frac{1.66 \times 10^6 \bar{D}}{Z_0^2} \quad (4)$$

Thus for a well depth of 19 volts we find that 3×10^7 ions can be trapped. When the instrument is operated as a mass spectrometer the total capacity of the trap is smaller by a factor which is difficult to calculate; however, the variation of laser induced fluorescence intensity with increasing mass selectivity for ions such as N_2^+ and CO^+ indicates an ion density drop by a factor between 2 and 5. In the present study, the fragmentation pattern of CH_4 necessitated the use of bias conditions capable of discriminating between ions differing by only 1 amu.

Ions are created within the trap by electron impact ionization of a selected background neutral gas which is introduced into the vacuum chamber through a variable leak valve and which is maintained at a pressure of from 10^{-6} to 10^{-5} Torr. Fragment CH^+ was generated by the electron impact dissociation of CH_4 (approximately 2-3% of the total ion

products), and CD^+ was produced analogously from CD_4 . The trap has been found to attain maximum ion density after a 2 msec electron pulse from an electron gun producing an average e^- beam current of 10 μ amp at 100 eV.

The electron gun consists of a resistively heated 1 cm strip of 0.25 mm diameter thoriated tungsten wire mounted on a ceramic base and enclosed within a metal shield which is floated at the center electrode potential. This shielding serves to reduce scattered light emitted from the hot filament. One of the focusing lenses also serves as an electron shutter through the application of a high voltage pulse to the lens element.

While the trapping potential operates continuously, the remainder of the experiment is operated in a pulsed mode at a repetition rate of 10-40 Hz. The remainder of the experiment is then most easily described by considering one experimental cycle which consists primarily of three parts: ion creation and confinement, excitation of the ions, and fluorescence signal detection. The timing sequence may be schematically represented as a series of pulses as in Figure 2.

The experiment begins with the initiation of the electron beam which creates ions for a period of several milliseconds. The electron gun is then gated off and a delay period of several hundred microseconds ensues. During these times any necessary mass selection of the ions is allowed to stabilize, and any excited electronic states which have been created are permitted to relax radiatively. Radiative relaxation of excited vibrational levels within stable electronic states is expected to be slow on the time scale of an experimental cycle. The pressure range in which we operate allows little or no collisional effects. After the delay period, a 10 nsec, 1 cm^{-1} bandwidth laser pulse from a Molelectron

Figure 2. Schematic representation of the timing sequence of an experimental cycle.

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DL-200 dye laser pumped by a Molectron UV-1000 nitrogen laser is passed through the ion cloud. Laser induced fluorescence is then monitored at right angles to the laser beam. A lens and mirror system directs some of the fluorescence through the wire mesh end electrodes to a cooled RCA 8575 photomultiplier tube.

In addition to fluorescence, scattered laser light may also reach the detection system. In order to minimize this background radiation, the laser beam is collimated to about 0.5 cm diameter with two lenses and directed through 0.5 meter arms (Fig. 3) containing light baffles on the entry and exit side of the trap. In addition to the baffle system the 10 nsec laser pulse allows the use of gated detection techniques to reduce the effects of scattered laser light.

A signal from a trigger photodiode initiates a fluorescence detection gate. The initiation of the detection gate can be variably delayed with respect to the laser pulse, and its duration can be varied between 0.1 and 10 μ sec. The duration of the gate is primarily determined by the radiative lifetime of the species being investigated. The fluorescence detection gate and the signal from the PMT are sent to a gated single photon counting system which consists of an L.R.S. 621-BL discriminator and a 100 MHz counter (Ortec Model 770).

After the fluorescence detection, the experimental cycle is completed by pulsing the ions out of the trap to an electron multiplier. In order to get a consistent ion signal from cycle to cycle a high voltage pulse must be synchronized with the rf trapping potential and applied to the bottom trap electrode. The resulting ion signal is measured by an L.R.S. 227-sg integrator and is used to normalize the fluorescence signal. The fluorescence signal is also normalized with respect to laser power which

Figure 3. Experimental arrangement used in the frequency scanning experiments. The depicted arrangement and timing sequence are discussed in the text.

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is measured by a photodiode and the gated integrator. The final signal gathered by the integrator is used to calibrate the laser wavelength. Calibration is accomplished with the use of the optogalvanic effect¹⁹ in which the laser beam is directed into a hollow cathode discharge lamp containing neon. The fluorescence excitation spectrum is then calibrated with respect to Ne metastable transitions which are known throughout the visible region.

The timing of an experimental cycle is controlled by a series of logic circuits. The detection gates initiated by this timing circuitry are generated by Tektronix P.G. 501 pulse generators. The timing and gating logic are not shown in Figure 3 in the interest of clarity. An on-line PDP-8f computer is responsible for the overall control of the experiment. At the end of an experimental cycle, the computer gathers the signals from the integrator and initiates a new cycle. After a pre-determined number of cycles the computer retrieves the signal from the counter and advances the laser wavelength by a preset increment. Typically the signal is averaged over several hundred laser pulses before advancing the wavelength. The computer normalizes the data, stores them on a disk, and produces a hard copy graph of the spectrum.

The $\text{CH}^+(\text{CD}^+)$ spectra were produced under the following experimental conditions. The ions were created from $\text{CH}_4(\text{CD}_4)$ at a background pressure of 10^{-5} Torr with an ionization period of 2.0 msec. The fluorescence detection gate was 1 μsec in duration and was initiated 200 nsec after the laser pulse. The fluorescence signal was averaged over 500 laser pulses at each wavelength and the wavelength was advanced by $0.1 \text{ \AA}$ increments.

In the determination of radiative lifetimes, the experimental arrangement is modified somewhat. Control of the experimental timing is shifted from the computer to an internally controlled pulse cycle. The timing sequence is unchanged when operating in this mode, but the laser wavelength remains fixed, and the signal is collected continuously. The output signal from the PMT is fed into a discriminator and then into a Tracor Northern NS 575 digital signal averager with a Biomation time base.

This system provides a 10 nsec channel width which is suitable for the radiative decay rates encountered in the present studies. The Biomation time base is triggered by the pulse which initiates the detection gate in the normal mode of operation. The total width of the signal averager's time base in these studies was 1024 channels; i.e., 10.24 μ sec.

For the collection of frequency scanned spectra, the nitrogen laser is used as a pump source for the dye laser because such lasers possess relatively high duty cycles. The fluctuations in laser power are corrected for on a shot to shot basis as discussed earlier. For measurements of fluorescence decay rates, however, it is desirable to maintain a steady laser power level throughout each determination. The frequency tripled output of a Quanta Ray Nd:YAG laser was found to vary in output power by only a few per cent and was used as the dye laser pump for all decay rate measurements.

For radiative decay measurements the dye laser is tuned into resonance with a strong transition in the vibronic band under study. The resulting fluorescence signal as a function of time is then accumulated in the signal averager for a period of several hundred thousand experimental cycles. The dye laser is then detuned from resonance, typically by several $\text{\AA}$, and a background signal is subtracted for an equivalent time period. Data from the signal averager are then transferred to a PDP-8 computer for

analysis. The experimental arrangement is schematically depicted in Figure 4.

Figure 4. Diagram depicting the experimental arrangement used for the measurement of radiative lifetimes.

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CHAPTER III

Trap Dynamics

While the LIF spectra at several molecular ions (N_2^+ , CO^+ , H_2S^+ , $BrCN^+$, $C_6H_3F_3^+$ and $C_6F_6^+$) had been obtained in the first two years of trap operation²⁰ certain features in the observed spectra raise questions which indicate the need for a study of the dynamics of ion confinement. For example, the rotational distributions of the ions, when resolved, were consistently "hotter" than expected.

Certain aspects of rf quadrupole ion trap dynamics have already been studied by Knight and Prior²¹ who examined the spacial and velocity distributions of Li^+ trapped in a quadrupole ion trap quite similar to that used in the present study. They determined the radial ion spacial distribution to be nearly gaussian, peaking at the center of the trap with a $1/e$ width of ~ 1 cm. In addition, they made measurements of the ion doppler width which suggested a roughly Maxwellian distribution characteristic of a translational temperature of ~ 5000 K. This high translational temperature arises from the interaction between the ions and the rf fields used to trap them. At the relatively low frequencies used here (~ 1 MHz) the ions experience a force which drives them at roughly the same frequency oscillation as that of the applied rf field.

A portion of the $(0,0)$ band of the $N_2^+ B^2\Sigma^+ - X^2\Sigma^+$ system is presented in Figure 5. The measured line width for well resolved rotational components of this band is $\sim .18 \text{ } \overset{\circ}{\text{A}}$, of which approximately $\sim .15 \text{ } \overset{\circ}{\text{A}}$ can be attributed to the laser bandwidth. Thus the residual line width, which is due to the doppler broadening of the ions, can be characterized by a translational temperature of 5,000-10,000 K.

Figure 5. Laser induced fluorescence (LIF), spectrum of the N_2^+ $B^2\Sigma_u^+ - X^2\Sigma_g^+$ (0,0) band obtained under collision free conditions. Three vibronic bands can be discerned in the spectrum and the R-branch even N components are indicated by an overhead dash.

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Although the translational energy of the ions is determined by the trap fields the distribution of internal energy within the ions is determined by other factors. For example, the rotational state population distribution in an ion produced through the direct electron impact ionization of its parent neutral (i.e., produced without molecular fragmentation or rearrangement) is essentially determined by the population distribution in the parent neutral since the ionized electron cannot efficiently carry off large amounts of angular momentum. If there were strictly no change in angular momentum upon electron impact ionization of the molecule the rotational distribution would be determined by the B'' value of the molecule being ionized. Thus, for N_2^+ produced through ionization of N_2 gas we should expect an essentially room temperature rotational population distribution. The rotational temperature of the band observed here has been measured by Grieman⁶ to be ~ 360 K, in agreement with expectation. More precisely, the temperature must be calculated using the B'' of the neutral since the thermalization of levels occurs before ionization. For this reason the temperature determined in Reference 6 must be scaled by the ratio of $B N_2(X^1\Sigma_{v=0})$ to $B N_2^+(X^2\Sigma_{v=0}^+)$

$$T = 360 \cdot \frac{1.998}{1.932} = 372 \text{ K.}$$

In contrast to this case, the vibrational distribution of an ion formed by the electron impact ionization of its parent neutral (as before) will be determined by the wavefunction overlap of the various vibronic levels of the ion and that of the initial neutral state. Such distributions can not be characterized by an equilibrium temperature and may, in some cases, exhibit vibrational level population inversion. Often, the vibrational population distribution peaks at some low vibrational level

of the ionic ground state (after electronic relaxation) and slowly tails off for higher and higher vibrational states. An example of this is provided by the case of CO^+ , whose A-X electronic system has been studied using our technique. A portion of the (2,0) band of the $\text{A}^2\Pi - \text{X}^2\Sigma$ system is reproduced from Reference 6 in Figure 6. This band system is not as well resolved rotationally as in the case of N_2^+ due to the greater number of overlapping sub-bands for such an electronic transition. However, the variation in line intensity appears to be that expected for a room temperature distribution of rotational population. To illustrate the non-thermal nature of the vibrational distributions of electron impact produced ions, the spectra shown in Figure 7 are presented. These bands, which are part of the same $\text{A}^2\Pi - \text{X}^2\Sigma$ system as that shown in Figure 6, have not been previously observed. They originate in highly excited (12,000-16,000 cm^{-1}) vibrational levels of the $\text{CO}^+ \text{X}^2$ potential. If the CO^+ were thermalized to a room temperature vibrational distribution the intensity of the (7,7) band would be 10^{-10} times that of the (4,5) band. The intensities of these bands relative to the (2,0) band is estimated to be $\sim .02-.05$.

A portion of the (1,1) band of N_2^+ (B-X system) is apparent in Figure 5 where the rotational components have been identified. The assignment given in Figure 5 are made using the molecular constants of Dick et al.²² who studied the B-X system using emission spectroscopy. The rotational population distribution of the (1,1) band is identical to that of the (0,0) band, as expected. The intensity of the (1,1) band relative to the (0,0) band is approximately a factor of 5 lower reflecting the difference in population. Although it is not accurate to describe the vibrational distribution of N_2^+ with a temperature, the population ratio

Figure 6. LIF spectrum of the $\text{CO}^+ \text{A}^2\Pi - \text{X}^2\Sigma (2,0)$ band.

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Figure 7. LIF spectrum of the $\text{CO}^+ \text{A}^2\Pi - \text{X}^2\Sigma$ (7,7) and (4,5) bands. The relative intensities of these bands and the (2,0) band reproduced in Figure 6 underscore the non-thermal nature of the vibrational population distribution of CO^+ .

of $v''=1$ to $v''=0$ may be characterized by an effective temperature which, for $N_2^+(X^2\Sigma^+)$ $\omega_e = 2207\text{ cm}^{-1}$, is $\sim 2070\text{ K}$.

Thus what we have stored within the ion trap is an ion population whose energy modes are all characterized by different temperatures. It is of interest to examine the effect of collisions upon these distributions and to examine the rate of energy redistribution within the ions. Very little information regarding such processes in ionized systems is currently available. What we would like to do, then, is to use LIF to monitor the ro-vibronic distributions of the trapped ions and to vary the experimental conditions such that the ions being probed have experienced a controlled number of collisions with some selected partner. If the experimental timing (see Fig. 2) is kept constant the collision rate may be varied by changing the background neutral density, i.e., the pressure. Several different types of experiments can be performed in this fashion. First, the effect of collisions with "structureless" particles (i.e., inert gas atoms) can be examined. In addition the interaction of the trapped ions with other molecules can be studied to see if the increased energy level density of the neutral molecule will affect the rate of energy redistribution. Finally, collisions which have a high probability of leading to reaction can be studied to see if the degree of excitation of the ion affects the rate of reaction.

As a model case such studies were performed on the N_2^+ ion using the B-X electronic system as a monitor (see potential curves in Fig. 8). This system was chosen for several reasons. In addition to the large oscillator strength of this system (as indicated by its short radiative lifetime of $\sim 60\text{ nsec}$) the structure of the vibronic bands is tight enough to simultaneously monitor several bands yet open enough to resolve

Figure 8. Potential energy curves for several electronic levels of N_2 and N_2^+ . A similar ordering of electronic states is found for CO^+ .

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individual rotational components. Initial studies were performed using Ar gas as a collision partner. The collision rate can be estimated using a Langevin collision cross section provided the limitations of such an approximation are observed. A Langevin cross section will provide a reasonably accurate measure of the true collision cross section as long as the collision energy is low. This restriction arises because the Langevin cross section is basically a measure of the charge induced dipole attractive potential in the ion-molecule system. When the collision energy becomes much greater than the charge induced dipole well depth only the repulsive part of the potential is sampled. Such potential well depths are typically a few tenths of an eV. While the Langevin model predicts a continuously decreasing cross section with increasing energy, the "true" cross section must approach a hard-sphere value. At 5000 K the translational energy of the ions is ~0.4 eV and so we should expect the calculated cross section to be a lower bound.

The expression for the Langevin cross section is

$$\sigma_L = \pi e (2\alpha/E)^{1/2} \quad (5)$$

where e is the elementary charge, α is the polarizability of the neutral collision partner, and E is the relative collision energy. If N_2^+ has an energy of 0.42 eV (~5000 K) and the Ar is at room temperature then $\sigma_L \approx 43 \text{ \AA}^2$, which is essentially a hard sphere cross section.

The average number of collisions per second, N , which an ion undergoes is

$$= \sigma_L \langle V_{rel} \rangle \rho \quad (6)$$

where $\langle V_{rel} \rangle$ is the average relative velocity, and ρ is the density of

neutrals in the trap (which is always greater than the ion density by more than four orders of magnitude). Substituting Equation (5) into this expression and recognizing that $\langle v_{\text{rel}} \rangle = (2E/\mu)^{1/2}$ results in the expression

$$N = 2\pi e(\alpha/\mu)^{1/2} \rho \quad (7)$$

where μ is the reduced mass of the collision partners. In the discussion of collision processes important in these experiments a convenient unit of time is 1 msec and a convenient reference density is the density at room temperature and 10^{-5} Torr. Using these units, we find

$$\# N_2^+ - \text{Ar collisions/msec}/10^{-5} \text{ Torr} = 0.24$$

and

$$\# N_2^+ - N_2 \text{ collisions/msec}/10^{-5} \text{ Torr} = 0.27.$$

The LIF spectrum of $N_2^+(B^2\Sigma_u^+ \rightarrow 2\Sigma_g^+(0,0))$ obtained under collision free conditions is shown in Figure 9. The delay between the end of the 1 msec ionizing electron pulse and the laser probe pulse was 0.5 msec. Figures 9b, c and d show the spectra obtained as successively greater amounts of Ar were introduced to the vacuum chamber while the N_2 pressure was held constant at 10^{-5} Torr. While an analysis of the variation of intensity as a function of rotational level can provide an estimate of the rotational temperature of the ground state ion, care must be taken in this case to avoid lines in which members of both R and P branches overlap.²³ Examination of Figure 9 reveals the strong presence of P branch lines which overlap closely with members of the R branch. The presence of these lines is manifested in an apparent splitting of the R branch lines, noticeably so for lines of odd N. Under the high collision conditions used to produce the spectrum shown in Figure 9d, it would not

Figure 9. LIF spectra of $N_2^+ B^2E_u^+ - X^2E_g^+ (0,0)$ band. Figures a, b, c, and d show the rotational distribution of N_2^+ after 0, 2, 10, and 20 collisions respectively. The arrow in Fig. (a) denotes the (1,1) band head.

be unreasonable to expect the rotational population of the $X^2\Sigma_g^+$ state to be equilibrated to the temperature characteristic of the ion velocity, that is, $T_{\text{ROT}} \approx 4000\text{--}6000$ K. A crude check of the effective temperature which describes the rotational distribution of Figure 9d can be made using the expression²⁴

$$N_{\text{max}} = 0.5896 \sqrt{\frac{T}{B} - \frac{1}{2}}. \quad (8)$$

For an expected "thermalized" temperature of 5000–6000 K and a $N_2^+(X^2\Sigma v=0) B = 1.932 \text{ cm}^{-1}$, $N_{\text{max}} \sim 24\text{--}26$. The (0,0) band R branch line positions for these high N values are slightly to the blue of the (1,1) bandhead (see Fig. 5). These levels certainly appear to be the most intense individual lines in the spectrum if the strongly overlapped lines (overlapping R & P branch lines) located at $\sim 3895 \text{ \AA}$ are excluded. Thus, the observed distribution is at least consistent with the expected final "temperature" derived from the observed doppler width. It is important to point out that in discussing the relationship between the ion translational temperature and that of the ions' internal modes, the mass of the collision partner plays a crucial role. Since the ion motion is largely determined by the rf trap fields the average ion speed is large. The relative collision energy is then determined by the reduced mass of the collision system.

Clearly, since the rotational radiative relaxation times are very long compared to ion-molecule collision periods, the N_2^+ ions would thermalize to the same final characteristic temperature, regardless of buffer pressure, given enough collisions. Thus what we see in Figures 9a–9d are rotational-vibrational distributions, far from equilibrium with the ion translational distribution, at various stages of attainment of this equilibrium. The ability to control the collision rate allows

us to freeze out the internal energy distributions and study them on a collision by collision basis.

As stated earlier, the ions are created during a 1 msec period and the spectra shown in Figure 9 are taken .5 msec following the end of this period. Thus, each N_2^+ ion has experienced on the order of 0.3 collisions with background i_2 gas, resulting in the spectrum shown in Figure 9a. As the Ar pressure is increased the N_2^+ ions undergo an additional 2, 10, and 20 collisions with Ar resulting in Figures 9b through 9d, respectively. (The stated Ar pressures are uncorrected ionization gauge readings; the true pressures are approximately 80% of these readings.)

From the above discussion it is clear that N_2^+ -Ar collisions are responsible for the changes in rotational distributions observed here. While rotational excitation in the N_2^+ -Ar system has not been investigated theoretically, the N_2 -Ar system has been.²⁵ The studies on N_2 -Ar, performed at a lower collision energy, indicate that $|\Delta N| > 2$ have appreciable cross sections and that smaller impact parameters favor successively greater ΔN 's. These results are consistent with our observations of rapid T to R energy transfer with large changes of rotational angular momentum accompanying each collision.

As mentioned already the (1,1) band appears in the LIF spectrum of N_2^+ with approximately 20% of the intensity seen in the (0,0) band. This intensity ratio is characteristic of a thermal distribution at ~2070 K, and so, the energetic-collisions with Ar atoms would be expected to shift the vibrational population into $v''=1$. Although very little is known about V-T processes in molecular ions the energy transfer rate is expected to be much lower than the R-T energy transfer rate. Thus, very

little actual change in the relative intensities of the (0,0) and (1,1) bands would be expected to occur for the relatively low collision conditions of Figure 9 a-d. What is in fact observed is a marked decrease in the (1,1) band intensity with increasing N_2^+ -Ar collisions. The (1,1) bandhead (marked with an arrow in Fig. 9a) has virtually disappeared after 20 collisions with Ar (Fig. 9d) while the (0,0) band retains significant intensity. One possible explanation for this intensity loss would be the shifting of rotational population in $N_2^+(X^2\Sigma_{v=1}^+)$ to highly excited levels (as seen in the (0,0) band) resulting in the spreading out of the bandhead.

An alternative explanation involves the selective charge transfer from $N_2^+(v''=1)$ to Ar. The I.P. of Ar is 15.755 eV and the vertical I.P. of N_2 is 15.576 eV. The addition of one quantum of vibrational energy ($2207\text{ cm}^{-1} \approx 0.274\text{ eV}$) to N_2^+ raises its energy to 15.85 eV, thus making the charge transfer to Ar exothermic by 0.09 eV. The N_2^+ present in $v''=0$ is too low in energy to ionize Ar. While the extra energy required could be supplied by the collision such E-T transfer processes are usually low cross section processes at these collision energies and energy defects.

Large cross sections for charge transfer are seen in cases where the energy defect, or the difference in energy between the charge donor and the charge acceptor, is small. To test the hypothesis that rapid charge transfer is selectively depleting vibrationally excited states of N_2^+ , similar experiments were performed using Ne as the collisional partner. The ionization potential of Ne ($\sim 21.6\text{ eV}$) is some 6 eV above ground state N_2^+ , and so, no effect attributable to charge transfer should be observed. The use of Ne as a collision partner results in a

somewhat lower relative collision energy due to its lower mass, and as a result, the degree of rotational excitation of N_2^+ will be less than that found in the Ar experiments. Nevertheless, a significant amount of rotational excitation of N_2^+ was achieved (somewhat more than that observed in Fig. 9c) while the apparent intensity of the (1,1) band remained constant. Thus, it would seem that rapid charge transfer from $N_2^+(X^2\Sigma_{v=1})$ to Ar is responsible for the intensity depletion of the (1,1) band. The measurement of absolute reaction cross sections is beyond the scope of this study; however, it is useful to make some estimates of reaction cross sections for the processes observed here. Such estimates will prove useful in understanding the relative importance of such processes. Under the conditions of high buffer gas pressure the amount of N_2^+ formed and trapped will be reduced somewhat since it constitutes a smaller fraction of the initial ion cloud and a significant amount of mass selection occurs after the electron ionization pulse. Thus, only the relative intensities of the (0,0) and (1,1) bands can be determined here, and it is not possible to obtain a true absolute cross section. If one assumes that other factors influencing the measured N_2^+ LIF signal affect $v'=0,1$ equally then cross sections may be estimated from the relative variation in intensity of the two bands. Although an accurate integrated intensity measurement of the (1,1) band would be difficult to make given the low signal levels obtained in the present study an estimate of the charge transfer cross section can be made using resolved rotational components. If one assumes that the (1,1) bandhead intensity has dropped to $\sim 1/e$ of its initial intensity after 20 collisions (Fig. 9d) then, using the Langevin collision cross section,

$$\sigma_{C.T.} \sim \sigma_L/20 = 2.1 \text{ \AA}^2.$$

This value seems rather small for a near thermal energy exothermic charge transfer cross section given the modest energy defect of 0.09 eV. Cross sections which are one to two orders of magnitude larger than this value ($2.1 \text{ \AA}^2$) are commonly found for such reactions. The most reasonable explanation for this is the rather poor Franck-Condon overlap between the $v=1$ level of $N_2^+(X^2\Sigma^+)$ and $v=0$ $N_2(^1\Sigma^+)$ which must be the final state if the overall reaction is to be exothermic.

The interaction of N_2^+ with neutral N_2 molecules should be interesting in light of the obvious energetic resonances present. Aside from the expected rotational excitation of trapped N_2^+ we should also observe the effects of inelastic charge transfer between N_2^+ and N_2 . The spectrum of N_2^+ presented in Figure 10 shows the same spectral region as displayed in Figure 5, however, the trapped N_2^+ have undergone ~ 1 collision with background N_2 . Comparison of Figures 5 and 10 indicates a striking change in the relative band intensities. In addition to the expected rotational excitation of the (0,0) band (compare with Fig. 9b) the (1,1) band intensity has decreased to a level between that observed in Figure 9b and c. The spectral region around the (1,1) band is shown in greater detail in Figures 11 and 12 for the collision free and single collision cases respectively. Members of the (1,1) R branch are identified in Figure 10 as well as an observed perturbation for $R_{12}-R_{14}$ resulting in a wide splitting of the N sublevels. This perturbation has been observed previously and has been ascribed to the interaction between the $N_2^+ A^2\Pi_{(v=11)}$ and $B^2\Sigma_{v=1}^+$ levels.²⁶ The nearly complete quenching of $N_2^+(X^2\Sigma_{v=1}^+)$ after essentially one collision with N_2 stands in sharp contrast to the N_2^+-Ar system. Since the collision energy of the $N_2^+-N_2$ system is large, direct collisional deactivation of the excited ions is

Figure 10. LIF spectrum of N_2^+ covering the same spectral region as in Figure 5. The state distribution seen here is that resulting from a single $N_2^+ - N_2$ collision.

XBL 818-11095

Figure 11. LIF spectrum of N_2^+ showing the (1,1) band in greater detail. The spectrum was obtained under collision free conditions. Even N levels of the (0,0) and (1,1) R-branches are designated above.

XBL 818-11094

Figure 12 LIF spectrum of N_2^+ showing the same spectral region as in Figure 11. This spectrum was recorded after the trapped N_2^+ had experienced a single collision with neutral N_2 .

not a feasible explanation; certainly not when the high deactivation probability is considered. A likely candidate for the process responsible are the reactions

These processes are attractive for several reasons. Franck-Condon factors favor the formation of $N_2^+(X^2\Sigma_v^+, v=0)$ from ground state N_2 . In addition, the channel leading to $N_2(X^1\Sigma_v^+, v=1)$, while endothermic by $\sim 150 \text{ cm}^{-1}$, is close to being thermoneutral and should have a substantial probability of occurring. As before, the determination of a genuine charge transfer reaction cross section is difficult; however, if the previously discussed limitations are born in mind, a lower limit to the true cross section can be obtained. If the integrated intensity of the (0,0) band is assumed to be roughly constant the intensity of the (1,1) band may be determined by direct comparison. (Obviously, since we are looking at a process which produces $N_2^+(X^2\Sigma_v^+, v=0)$ this assumption is incorrect; however, the error should be tolerable for the estimates to be made here.) Since many of the intense even N lines of the (1,1) band R branch overlap with members of the (0,0) band this comparison is best made using the strongest odd N lines (e.g., $N=7$ and 9). Comparison between figures 5 and 10 reveals an estimated $1/e$ drop in intensity for the (1,1) band. Since the spectrum shown in Figure 9 was obtained under conditions in which the trapped N_2^+ has experienced a single $N_2^+-N_2$ collision, the estimated cross section for process 9 is simply the calculated Langevin collision cross section:

$$\sigma_{\text{deactivation}} \approx \sigma_L. \quad (10)$$

Since $\alpha_{N_2} \approx \alpha_{Ar}$ this cross section is essentially the same as that calculated for N_2^+ -Ar collisions;

$$\sigma_{\text{deactivation}} \approx 43 \text{ \AA}^2.$$

A final bit of consideration should be given to the possibility of observing reactive collisions using this technique. While, in principle, molecular ions resulting from ion-molecule reactions could be studied using our technique, no such systems have been studied to date. Still, reactions are important to the processes discussed here since they can result in severe ion population depletion. Reactions of N_2^+ with H_2 , D_2 and F_2 were examined in a fashion similar to the N_2^+ -Ar collision experiments. The collision rate was controlled by varying the background neutral pressure and the LIF spectrum recorded after a controlled number of collisions. The N_2^+ - H_2 (D_2) reaction system has been studied in the past²⁷ and is known to have a rate constant of $2 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$ for the reaction

The observed effect of collisions on the LIF spectrum of N_2^+ was a rapid, uniform decrease in signal intensity. A similar effect was observed when H_2 was replaced by D_2 as the collision gas. No significant degree of vibrational selectivity was observed in the rate of signal decrease. The N_2^+ - F_2 system was studied since the ionization potential of F_2 , 15.7 eV, lies between the lowest two vibrational levels of N_2^+ ($X^2\Sigma^+$), as does the IP of Ar. Thus the possibility exists to see a vibrational effect due to the competition of reaction and charge transfer. The results obtained are presented in Figure 13, in which the rapid loss of

Figure 13. LIF spectra obtained for N_2^+ showing the effects of collisions with F_2 . The rapid decrease in signal intensity of both the (0,0) and (1,1) bands indicates the greater importance of reactive channels as opposed to charge transfer.

intensity (comparable to the $H_2(D_2)$ study) is apparent. No selectivity is observed in this collision system either, indicating that the reactive channels are far more efficient in removing N_2^+ than is the charge transfer channel. These results demonstrate that only a few (~ 5) collisions are necessary to significantly deplete the ion population in the trap when reaction can occur. It seems fair to conclude from the N_2^+ -Ar collision data that simple collisional destabilization of the ion trajectories is not a significant problem in this respect.

Summary

The experiments discussed here provide a basis upon which a detailed understanding of the trapping dynamics may be pursued. It is clear that many more experiments could be carried out which would aid in our understanding of the trapped ions behavior, however, at this stage we can already make several observations. The initial distribution of vibrational and rotational energy in primary ions (ions formed by direct electron impact which do not undergo fragmentation) can be easily understood and predicted. The occurrence of collisions, however, can dramatically alter this distribution through several processes. Direct collisional effects are observed in the population distribution of rotational levels. Since the collisions occur at an energy of 0.4 eV, the observed change in the distribution is that of rapid heating. In contrast to this observation, essentially no heating of vibrational distributions was observed. Since V-T transfer rates are generally much smaller than R-T rates this observation is in keeping with expectation. When collisions did alter the vibrational population distribution the effect is most likely the result of charge transfer. Estimated charge transfer cross sections vary

considerably; however, transfer occurring on a single collision basis has been seen. Finally the loss of ions through ion-molecule reactions has been examined and has been found to be rapid in many cases.

These results have several ramifications for the study of new ions using this technique. For spectroscopic purposes the rotational heating effect may be a useful aid. Highly excited levels of ions may be populated in this fashion and studied to observe, for example, rotational predissociation. In order to study the energy distributions of an ion formed, for example, through electron impact fragmentation, collision free conditions must be used. Large changes in rotational and vibrational distributions can evidently occur on virtually every collision. Collisions leading to reaction can also deplete the ion population in the trap resulting in a diminished signal. For these reasons the trap is best operated at pressures at or below 10^{-5} Torr and storage times (before laser excitation) should not exceed 1-2 msec. These considerations were of great importance in the present study of CH^+ and CD^+ , a highly reactive species.

CHAPTER IV

Laser Induced Fluorescence Studies of CH^+ and CD^+

A) Introduction

The CH^+ radical has been the subject of numerous experimental and theoretical investigations since its spectroscopic identification by Douglas and Herzberg.²⁸ This small, reactive radical is of great importance in combustion reactions and atmospheric chemistry and is believed to play a fundamental role in the creation of many small molecules within the interstellar clouds. The first spectroscopic observation of this ion was made in spectra of the interstellar medium,²⁹ the observed transitions belonging to the $\text{CH}^+ \text{A}^1\Pi \rightarrow \text{X}^1\Sigma^+$ system. Since this initial observation and identification the CH^+ radical has been observed through this electronic transition in many parts of the interstellar medium¹¹⁻¹³ as well as comets in our own solar system.³⁰ Because this transition is a relatively strong one it has been used extensively as a probe of CH^+ abundance¹¹⁻¹³ in space directly and as an indirect measure of such things as the $\text{C}^{13}/\text{C}^{12}$ abundance ratio.³¹ Such measurements are based upon a presupposed knowledge of the transition oscillator strength which, for the $\text{CH}^+ \text{A}^1\Pi - \text{X}^1\Sigma^+$ system, is not well-known. The measurements of the $\text{CH}^+ \text{A}^1\Pi$ state radiative lifetime, presented later in this chapter, provide the first direct, unambiguous measurement of this quantity. This quantity can be easily related to the transition oscillator strength, resulting in revised estimates of interstellar CH^+ densities which are nearly a factor of two larger than earlier estimates.

From a spectroscopic standpoint CH^+ is interesting for several reasons. While the $\text{A}^1\Pi$ state of the ion has been carefully characterized

(the lowest 5 vibrational levels have been seen in emission) only $v''=0,1$ have been seen in the $X(1^1\Sigma^+)$ state. Thus, not only are the vibrational frequencies of the X state in doubt but the dissociation energy of the ion as well (an uncertainty which affects estimates of D_0 for neutral CH as well). The LIF spectra presented here provide new information on many highly excited rotational levels of several vibrational states of the ion as well as the first observation of a new vibrational level in $CD^+(X^1\Sigma^+)$. The vibrational frequency determined here for CD^+ can be used to calculate the corresponding frequency in CH^+ through isotope relations.

The ions studied, CH^+ and CD^+ were formed through the electron impact ionization and dissociation of CH_4 and CD_4 . A limited amount of spectra was collected using C_2H_2 as a source gas. The use of C_2H_2 as a source gas resulted in a somewhat weaker overall signal relative to that found using CH_4 as a source. This is somewhat surprising given the fact that electron impact ionization of C_2H_2 produces more CH^+ than that of CH_4 (6% vs 3%). Since reactions of CH^+ with both C_2H_2 and CH_4 are expected to be rapid this difference in signal intensity is perhaps best explained as being due to loss of CH^+ through charge transfer to C_2H_2 (not energetically possible for CH_4). The large cross sections seen in the experiments with N_2^+ lend plausibility to this explanation; however, no direct evidence exists. To minimize the effects of collisions upon the trapped ions low background pressures ($\sim 10^{-5}$ Torr) and short ion residence times (~ 2 msec) were used.

The observed vibrational and rotational population distributions can be used to probe the dissociation dynamics of the ionic precursor (CH_4^+ in this case) if some estimate of the initial dissociating states identity can be made. In the case of CH^+ some plausible guesses as to

the identity of the initial CH_4^+ state can be made and the product energy distributions of CH^+ and CD^+ can be understood using a simple dissociation model.

B) Spectroscopic Results

Laser induced fluorescence spectra were obtained for the (0,0) and (2,1) bands of CH^+ and for the (0,0), (2,1) and (1,2) bands of CD^+ . Representative portions of the spectra obtained are presented in Figures 14-16. As discussed in the experimental section the line frequencies were determined by comparison with known optogalvanic lines obtained from a Ne discharge. The vacuum frequencies for the Ne^* transitions were obtained from a paper by Paschen³⁴ and all observed CH^+ and CD^+ transitions referenced to at least two Ne^* lines to minimize errors due to non-linearities in the wavelength drive of the dye laser. Observed line frequencies are tabulated in Tables I, II, III and IV. Because no new lines belonging to the 2+1 band of CH^+ were observed, we have omitted this band from the tables. Assignments for lines belonging to the CH^+ band system were based upon the rotational constants of Douglas³² which accurately reproduced low J components of each band but increasingly overestimated transition frequencies at higher J. It is clear that for a diatomic hydride such as CH^+ , high J levels of a band system may not fit a Dunham expansion formula unless higher order correction terms are included (i.e., H_v terms). Using the molecular constants of Douglas we calculated H_v constants for each band system but could not obtain adequate agreement between calculated and observed frequencies. Therefore, an weighted least squares fit of all observed line frequencies was used to produce a new set of molecular constants given in Table IV. The doubling constant, q_0 , was found to be identical to that deduced by Douglas and Morton: $q_0 = 0.038 \text{ cm}^{-1}$.

Figure 14. LIF spectrum of the $\text{CH}^+ \Lambda^1\Pi - X^1\Sigma^+ (0,0)$ and $(2,1)$ bands.

XBL 815-9550

Figure 15. LIF spectrum of the $\text{CD}^+ \text{A}^1\Pi - \text{X}^1\Sigma^+$ (0,0) and (2,1) bands.

XBL 808-11413

Figure 16. LIF spectrum of the $\text{CD}^+ \text{A}^1\Pi = \text{X}^1\Sigma^+ (1,2)$ R-branch bandhead.

XBL 815-9549

Table I. Observed line frequencies (in cm^{-1})
for the $\text{CH}^+ \text{A}^1\Pi + \text{X}^1\Sigma^+(0,0)$ band

J	R branch	Q branch	P branch
0	23619.85 ^a	--	--
1	23637.71	23591.89	--
2	23650.48	23581.77	23536.26
3	23658.14	23566.56	23498.57
4	23660.52	23546.23	23455.87
5	23657.55	23520.70	23408.37
6	23649.10	23489.92	23355.9
7	23635.01	23453.76	23298.4
8	23615.1	23412.16	23235.8
9	23589.2	23365.0	23168.2
10	23557.1	23311.9	23095.3
11	23518.6	23253.3	23017.0
12	23473.5	23188.1	22933.2
13	23422.0	23117.4	22843.9
14	23362.8	23039.5	22748.4
15	23296.2	22955.0	22647.5
16	23222.2	22863.0	22540.0
17	23139.9	22763.8	
18	23049.1	22658.1	
19	22950.6	22544.2	
20	22842.0		
21	22724.5		

^a Entries quoted to two decimal places are the more accurate values from Douglas and Herzberg.²⁸ Those with one are from this measurement. The two data sets were used as listed here in the least-squares reduction.

Table II. Observed line frequencies (in cm^{-1})
for the $\text{CD}^+ \text{A}^1\Pi \leftarrow \text{X}^1\Sigma^+(2,1)$ band

J	R branch	Q branch	P branch
0	24105.67	--	--
1	24112.90	24091.05	--
2	24116.01	24083.28	-- ^a
3	24115.80	24071.90	24039.15
4	24111.49	24056.70	24013.15
5	24103.30	24037.65	23983.24
6	24091.05	24014.69	23949.84
7	24075.02	23987.85	23912.44
8	24054.90	23957.16	23871.31
9	24031.0	23922.42	23825.4
10	24003.6	23883.75	-- ^b
11	23972.1	23840.82	23724.4
12	23937.5	23793.8	23667.0
13	23897.1	23741.0	
14	23853.0	23681.0	
15	23802.2	23621.0	
16	23753.0		
17	23687.9		
18	23606.8		

^a Entries quoted to two decimal places are the more accurate values from Antić-Jovanović *et al.*³³ Those with one are from this measurement. The two data sets were used as listed here in the least-squares reduction.

^b Missing entries were weak or overlapped and not resolved.

Table III. Observed line frequencies (in cm^{-1})
for the $\text{CD}^+ \text{A}^1\Pi + \text{X}^1\Sigma^+(0,0)$ band

J	R branch	Q branch	P branch
0	23760.03 ^a	--	--
1	23769.83	23744.90	--
2	23776.93	23739.48	23714.63
3	23781.35	23731.40	23694.20
4	23783.00	23720.62	23671.10
5	23782.02	23707.10	23645.35
6	23777.90	23690.86	23616.94
7	23771.10	23671.86	23585.96
8	23761.53	23650.05	23552.25
9	23748.90	23625.40	23516.0
10	23733.31	23597.88	23477.0
11	23714.65	23567.38	23435.8
12	23692.1	-- ^b	23390.3
13	23667.5	23497.8	23343.6
14	23639.4	23458.4	23292.8
15	23608.2	23416.2	23239.4
16	23573.5	23370.2	
17	-- ^b	23320.9	
18	23493.2	23269.1	
19	23448.0	23212.2	
20	23397.9		
21	23345.3		
22	23286.9		
23	23219.3		

^a See footnote a to Table II.

^b See footnote b to Table II.

Table IV. Observed line frequencies (in cm^{-1})
for the $\text{CD}^+ \text{A}^1\Pi \leftarrow \text{X}^1\Sigma^+(1,2)$ band

J	R branch
0	20991.7
1	20998.3
2	21009.3
3	21012.8
4	21014.1
5	21011.5
6	21005.3
7	20996.9

The rotational constants for CD^+ obtained in emission studies by Antić-Jovanović *et al.*³³ were found to be adequate in reproducing low J components of each band for this isotopic species but, again, predicted line frequencies too high for lines of increasing J (e.g., 5.8 cm^{-1} too high for the $0,0\text{ R}_{15}$ line). An unweighted least squares fit of all observed transition frequencies produced the set of molecular constants given in Table v.

The great difficulty encountered in attempting to fit high J components of each band with molecular constants derived using lower J terms is most likely due to the unusual nature of the $A^1\Pi$ potential curve for both CH^+ and CD^+ . The nature of this potential is best understood if one examines the corresponding potential in the iso-electronic species BH . This molecule has been the subject of careful emission studies³⁵ and has been determined to possess a barrier in the rotationless potential curve of the $A^1\Pi$ state.³⁶ Early calculations³⁷ indicated that the $A^1\Pi$ state arising from $B(^2P) + H(^2S)$ is initially repulsive in nature, but a strong interaction between this curve and an attractive curve arising from $B(^2D) + H(^2S)$ overcomes the repulsion and gives rise to the observed bound state.

While it might be expected that the $A^1\Pi$ state of CH^+ might exhibit similar behavior, the appearance of a potential maximum is by no means assured. The presence of the attractive charge-induced dipole force means that at large R values, $A^1\Pi$ may well exhibit attractive behavior. If the interaction with the attractive curve arising from the $C^+(^2D) + H(^2S)$ asymptote becomes strong before the repulsive nature of the $A^1\Pi$ curve overcomes the charge-induced dipole attraction, the result is a bound potential curve with unusual R dependence but no potential maximum.

Table V. Molecular constants (in cm^{-1}) for the CH^+ (0,0) band and calculated vibrational frequency for the $X^1\Sigma^+$ state

V_{00}	23596.88 (1)
B^{RP}	11.4546 (20)
D^{RP}	.00207 (5)
H^{RP}	$3.31(10) \times 10^{-8}$
B^{Q}	11.4148 (20)
D^{Q}	.00205 (5)
H^{Q}	$3.15(10) \times 10^{-8}$
B''	13.9344 (20)
D''	.00141 (5)
H''	$6.77(10) \times 10^{-8}$
ω_e	2850.1
$\omega_e x_e$	52.9

* Numbers in parentheses represent a one standard deviation uncertainty in the last digits of each constant.

The calculations of Green et al. suggest that, in fact, there is no actual barrier in the rotationless curve. These results are confirmed by the more recent calculations of Saxon et al.³⁹

As is apparent upon examination of the spectra reproduced here, we have observed no laser induced fluorescence which is not attributable to the particular ion under study. The present study covered the wavelength region from 4130 Å to 4400 Å. A thorough search throughout this wavelength region was conducted for any possible interfering species such as background neutral fluorescence or transitions originating in metastable levels of CH^+ populated in the ion formation process. No such interference was found. The recent photodissociation studies of Cosby et al.^{40,41} suggest that the $^3\Pi$ state of CH^+ ($T_e \approx 9200 \text{ cm}^{-1}$) is, in fact, populated to some extent in the electron impact ionization of CH_4 , although the relative amount of population in the singlet and triplet manifolds is difficult to estimate from the available data. If the analysis of Carre⁴² is correct then transitions belonging to the $^3\Sigma + ^3\Pi$ system might be expected to appear strongly only below 3700 Å, thus leaving the spectral regions under study here free from interference.

The rather broad distribution of rotational population, as reflected in the intensity of high J levels, provides a probe of the reaction exothermicity since the ions are maintained in a collision free environment. While portions of the (0,0) and (2,1) bands have been previously observed for both CH^+ and CD^+ ,^{28,33} no transitions involving $v'' \geq 2$ have been reported.⁴³ While only a few members of the R branch in the region of the (1,2) bandhead were observed in the present study, spectroscopic constants for the $X^1\Sigma^+$ ($v=2$) state may be obtained because the upper state ($A^1\Pi(v=1)$) is already well characterized.

Initial estimates of $B''v=2$ and $D''v=2$ can be obtained from existing constants. The values are then varied until the calculated differences in line frequencies most closely match the observed differences. Once the rotational constants have been determined in this fashion, the separation between the band origin and the band head can easily be calculated through the relation²⁴

$$\Delta V = \frac{-(B + B'')^2}{4(B' - B'')} \quad (12)$$

The band head of the (1,2) band as determined in this study occurs at 21014.1 cm^{-1} .

Such an analysis results in a rotational constant of $B'' = 7.22 \text{ cm}^{-1}$, and a resulting band origin of $V = 20983.0 \text{ cm}^{-1}$. Observed line frequencies for this band are tabulated in Table IV. The agreement between observed and calculated line frequencies is not as good for this band as for the other observed bands of either CD^+ or CH^+ . This is due largely to the low signal level and subsequent poor signal to noise ratio of the (1,2) band.

Previous optical emission studies of CH^+ and CD^+ have resulted in the observation of only the lowest few J levels of each observed band. This is due in part to the strong optical interference by other molecular species in the excitation region, and to collisional relaxation of high rotational levels. Since both of these complications are avoided in the present study many previously unobserved rovibronic components of each band studied here have been observed. These high rotational levels provide a sensitive probe of the rotational molecular constants. While the large Doppler width of the trapped ions results in a spectral resolution of $\sim 1 \text{ cm}^{-1}$, the large number of lines observed increases the accuracy

with which the molecular constants may be determined. High resolution emission studies^{32,33} of CH^+ and CD^+ have observed up to $J''=7$ for the $\text{CH}^+(0,0)$ band and up to $J''=11$ for the corresponding band in CD^+ . The chemiluminescence studies of Ottinger⁴⁴ on the $\text{A}^1\Pi - \text{X}^1\Sigma^+$ system of both CH^+ and CD^+ seem to have extended the list of observed transitions but poor spectral resolution ($\sim 35 \text{ cm}^{-1}$) prevented the refinement of existing molecular constants. The present study has extended the list of observed rotational components out to $J=22$ and $J=24$ for the $(0,0)$ bands of CH^+ and CD^+ respectively. The observed frequencies of the $(0,0)$ and $(2,1)$ bands have been reported⁷ as well as direct measurements of the $\text{A}^1\Pi_{v=0}$ radiative lifetime for both CH^+ and CD^+ .⁹ The molecular constants derived from these data as well as those obtained from the previously unobserved $(1,2)$ band of CD^+ are summarized in Tables V and VI. These molecular constants were obtained using a weighted least squares fit of all observed members of each band. The relative weighting of new lines observed in the present study to those seen under higher resolution in the emission studies was adjusted empirically until the calculated line frequencies agreed with experimental determined values to within the reported error limits. These error limits are approximately 0.05 cm^{-1} for the low J components observed in emission spectra and $\sim 0.5 \text{ cm}^{-1}$ for new lines observed in this study.

The observed low intensity of the $(1,2)$ band of CD^+ is due primarily to the low populations of excited vibrational levels of the ion. The corresponding band in CH^+ is expected to be much weaker due to the large increase in vibrational energy. While we have not observed this band it is possible to predict its molecular constants using isotope relations. Values arrived at in this fashion are listed in Table V.

Table VI. Molecular constants for the (0,0), (2,1) and (1,2) bands of CD^+ . Values in cm^{-1} and Å units

	(0,0)	(2,1)	(1,2)
r	23747.54(2)*	24094.87(5)	20983.0(5)
B ^{RP}	6.2520(5)	5.4911(7)	5.855
D ^{RP}	5.818(10) $\times 10^{-4}$	8.667(10) $\times 10^{-4}$	5.7 $\times 10^{-4}$
H ^{RP}	2.77(25) $\times 10^{-7}$	2.40(20) $\times 10^{-6}$	-
B ^Q	6.2392(5)	5.4805(5)	5.840
D ^Q	5.818(10) $\times 10^{-4}$	6.48(10) $\times 10^{-4}$	5.7 $\times 10^{-4}$
H ^Q	2.95(25) $\times 10^{-7}$	8.60(30) $\times 10^{-7}$	-
B _e [']		6.447(5)	
$\alpha_e^{'}$		0.39(2)	
R _e [']		1.241(3)	
B ^{''}	7.5828(5)	7.4015(7)	7.22(1)
D ^{''}	5.819(10) $\times 10^{-4}$	1.126(10) $\times 10^{-4}$	.0012(4)
H ^{''}	3.81(10) $\times 10^{-7}$	4.28(5) $\times 10^{-6}$	-
B _e ^{''}		7.763(7)	
$\alpha_e^{''}$		0.18(2)	
R _e ^{''}		1.116(3)	
ω_e		2092	
$\omega_e \chi_e$		28.5	

* See footnote, Table V.

Several interesting features are apparent in the spectra presented here. Examination of the spectra reveals a linewidth noticeably larger than the bandwidth of the dye laser. The source of this broadening is the large doppler profile of ions stored in a trap such as this.

Another interesting feature which is evident in both spectra is the high rotational temperature of the ions even in the absence of such collisional effects. This stands in contrast to the apparently much cooler rotational distribution observed in emission studies. One may infer from published emission photographic plates and tabulations of observed lines a rotational temperature of 350 to 400 K for ions created in the $A^1\Pi$ state, whereas, in the present study, rotational distributions corresponding to temperatures of 1500 K are seen for the $X^1\Sigma^+$ state (see following section). This broad rotational distribution is not the result of high energy ion-neutral collisions involving $CH^+(CD^+)$ of the type mentioned above as the experimental conditions under which these spectra were obtained provide an essentially collision free environment for the ions. Thus, this distribution reflects the initial product state distribution of $CH^+(CD^+) X^1\Sigma^+$ created in the electron impact fragmentation of methane (excepting possible radiative contributions from short lived electronic states). The cooler distributions characteristic of the emission studies are most likely the result of the many thermalizing collisions which may occur at the high pressures employed.

The presence of transitions originating in $v''=1$ is evident in the spectrum of CH^+ shown in Figure 14. The vibrational spacing for a hydride such as CH^+ is expected to be large (2856 cm^{-1} in this case) and so a large amount of vibrational excitation is indicated. Laser induced fluorescence spectra were also recorded for the $0+0$ band of this transition

using C_2H_2 as a source of CH^+ . It was found that the apparent rotational and vibrational population distributions are essentially identical to those obtained using CH_4 as a source.

Examination of the spectra obtained for CD^+ yields similar conclusions. The rotational distribution is quite broad (as is expected for a much smaller B_0) with a characteristic temperature of ~ 1500 K. The presence of transitions originating in $v''=1$ is more pronounced in this case (as expected) permitting a more accurate determination of the molecular constants than for CH^+ . An analysis of the observed product energy distributions will be presented in the following two sections.

C) Product Energy Distributions

Since the ions are stored under collision free conditions, the rotational and vibrational population distributions, as deduced from the laser induced fluorescence intensities, reflect the dynamical partitioning of reaction exothermicity. If the distribution of energy among all dissociation products were measured, a detailed analysis of the dissociation dynamics would be possible. In the present study, however, only one fragment of the methane dissociation has been probed. The combination of these results and results obtained in mass spectrometric studies can provide some insight into the dissociation process.

The spectra obtained in Figures 14-16 are normalized to variations in laser power with frequency, and so, the relative line intensities may be used to calculate a rotational temperature. It is possible, however, that the formation of CH^+ occurs via more than one dissociation path and the observed intensity distribution actually the superposition of several distributions. The relative absorption intensities of rotational components within a vibronic band can be approximated by the expression

$$I \approx K_{\text{abs}} S_J \exp\left[-\frac{B''J''(J''+1)hc}{kT}\right] \quad (13)$$

where K_{abs} is a constant for a given vibronic band, assuming constant R-centroid, and S_J is the appropriate Hönl-London line strength coefficient for each rovibronic component. Since we are exciting CH^+ from a 1Σ state to a 1Π state, $\Delta\Lambda = +1$. The Hönl-London factors for the R, P, and Q branches which are appropriate for this case are²⁴

$$S_J^R = \frac{(J''+2+\Lambda'')(J''+1+\Lambda'')}{4(J''+1)} \quad (14a)$$

$$S_J^P = \frac{(J''-1-\Lambda'')(J''-\Lambda'')}{4J''} \quad (14b)$$

$$S_J^Q = \frac{(J''+1+\Lambda'')(J''-\Lambda'')(2J''+1)}{4J''(J''+1)} \quad (14c)$$

A plot of $\ln(I/S_J)$ vs $J''(J''+1)$ yields a straight line with a slope of $-B''hc/kT$ if the distribution of rotational population can be characterized by an equilibrium temperature.

It is reasonable to expect the dissociation exothermicity of $\sim 1_4$ in the production of CH^+ to be essentially the same as that of CD_4 producing CD^+ . It is of interest to compare the distribution of rotational and vibrational energy in both CH^+ and CD^+ . The rotational temperatures of both $\text{CH}^+(\nu''=0)$ and $\text{CD}^+(\nu''=0)$ have been determined by an analysis of the plots shown in Figures 17 and 18 respectively. As can be seen in the plots, the observed rotational distributions are essentially single temperature distributions corresponding to a rotational temperature of 1500 K. The rotational distributions in higher vibrational levels of the fragment ions are more difficult to ascertain due to the lower intensities of these bands. The (2,1) band of CD^+ is of sufficient intensity due to its smaller vibrational spacing to permit an analysis of its

Figure 17. Rotational temperature of the $\text{CH}^+ \text{X}^1\text{L}^+(v=0)$ level as determined by the intensity variation of the (0,0) band.

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Figure 18. Rotational temperatures of the $\text{CD}^+ \text{X}^1_2^+$ $v=0, 1$ levels.

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rotational temperature. The result, shown in Figure 18 is identical to that obtained for the (0,0) band of CD^+ , although the absolute intensities are lower due to differences in Franck Condon factors.

The observed intensities of transitions belonging to the $\text{CH}^+(2,1)$ band are too low to determine a reliable rotational temperature; however, the strongest members of this band originate in $J'' = 6-8$. This observation is consistent with a rotational temperature identical to that of the (0,0) band.

These results are rather different from those obtained by Cody et al.⁴⁵ for the internal energy distributions of the CN radical produced through the photolysis of C_2N_2 . In that study it was found that the rotational temperature of the radical product decreased slightly with increasing vibrational excitation, reflecting the partitioning of the finite dissociation exothermicity.

In addition to the measurement of rotational energy distributions of CH^+ and CD^+ , vibrational populations can be ascertained if the Franck-Condon factors for the relevant vibronic bands are known or can be estimated. Components of both the (0,0) and the (2,1) bands of both CH^+ and CD^+ are easily discerned in Figure 14 and 15. Franck-Condon factors for many bands in the A-X system have been calculated by several authors.^{16,44,46} Using those calculated by Gerard et al.⁴⁶ the relative transition strength of the (0,0) to the (2,1) bands should be 2.6 and 2.2 for CH^+ and CD^+ , respectively. Since the rotational population distributions of the $v'' = 0$ and $v'' = 1$ levels of CD^+ have already been shown to be the same we may estimate the vibrational population distribution by weighting the observed transition intensities of corresponding rovibronic components by their calculated transition strengths. Sever.

members of the R and Q branches of both bands were used to make the comparison since these bands are the strongest in a ${}^1\Pi - {}^1\Sigma$ transition (see Eq. 14). The result, for CD^+ , is a population ratio of the $v''=0$ level to the $v''=1$ level of ~ 1.1 . The vibrational frequency of the $CD^+ X^1\Sigma^+$ state is $\sim 2035 \text{ cm}^{-1}$ which indicates a vibrational temperature of $\sim 3 \times 10^4 \text{ K}$. If the rotational population distribution of $CH^+ X^1\Sigma^+ (v''=1)$ is the same as that of the $v''=0$ level then the vibrational temperature based upon Franck-Condon factors and observed intensity ratios is the same as that of CD^+ within estimated uncertainties in the intensity measurements.

If the distribution of vibrational energy were truly equivalent to a temperature of $3 \times 10^4 \text{ K}$, then the intensity of the $(0,2)$ band based upon the Franck-Condon factors of Gerber *et al.* would be approximately 40% of that seen for the $(0,0)$ band. Careful measurements in search of the $(1,2)$ band of CD^+ resulted in the observation of the band presented in this paper, but only after extensive signal averaging. While the calculated Franck-Condon factors involving $v''=1$ have not been verified experimentally, the observed intensity variation would require the $(1,2)$ Franck-Condon factor to decrease by roughly an order of magnitude. Thus, it would appear to be more plausible to attribute the intensity variation to real population differences. This would mean that the vibrational distribution of product $CH^+(CD^+)$ produced by the dissociation of $CH_4(CD_4)$ is non Boltzmann. The relation between the product vibrational state population and the active dissociation mechanisms of CH_4 will be examined later.

D) Discussion

In order to understand the fragmentation processes which lead to the production of CH^+ it is useful to examine the photoelectron data available on methane. Numerous studies have been performed which have provided molecular orbital energies for $\text{CH}_4^{+47,48}$ as well as mass spectrometric branching ratios of parent and fragment ions.⁴⁹⁻⁵² The photoelectron bands observed experimentally are indicated in Figure 19a, along with their assignments. The ion is initially formed in the $(1a_1)^2 (2a_1)^2 (1f_z)^5$ configuration with an appearance potential of 12.7 eV. The large width of this band is due to the combination of a large change in equilibrium geometry and the Jahn-Teller induced distortion of the ion.⁵³ At approximately 10 eV higher energy a second band, corresponding to the configuration $(1a_1)^2 (2a_1)^1 (1f_z)^6$, is seen with an onset at 22.3 eV. In the remaining discussion these states will be referred to as $(1f_2)^{-1}$ and $(2a_1)^{-1}$ respectively (as in Fig. 19). The equilibrium geometries of these two states, as calculated by Meyer,⁵⁴ show both to be of tetrahedral structure with a C-H bond length of 2.15 Å for the $(1f_2)^{-1}$ state. This bond distance is to be compared with the 1.09 Å C-H bond length of ground state neutral CH_4 . This increase in bond length reflects the removal of a bonding electron in the formation of the ion. The removal of an electron from the $(2a_1)$ orbital results in an increase in the C-H bond length to 2.23 Å. Such a large change in the equilibrium bond length accompanying ionization will surely result in a large degree of vibrational excitation in the newly formed ion. The consequences of this vibrational excitation are seen in Figure 19b, in which the product branching ratio is plotted as a function of ionization energy. As soon as the formation of CH_3^+ becomes energetically allowed, at about 14 eV,⁵² the branching ratio of CH_4^+ to CH_3^+ drops to 1, a value that remains nearly unchanged for most

Figure 19. Photoelectron spectra of CH_4 and observed mass spectrometric branching ratios of ionization products (taken from Refs. 47-52).

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of the $(1f_2)^{-1}$ band profile.

At the high energy limit of the $(1f_2)^{-1}$ band the formation of CH_2^+ becomes energetically allowed;⁵² however, the branching ratio of CH_4^+ to CH_3^+ changes only slightly due to the poor geometrical overlap of ground state CH_4 with the highly vibrationally excited levels in $\text{CH}_4^+ (1f_2)^{-1}$ which decay to produce CH_2^+ . The branching ratio does not change significantly until the $(2a_1)^{-1}$ is reached. The onset of the $(2a_1)^{-1}$ band coincides with the appearance potential of the CH^+ fragment as well as a marked increase in the production of CH_2^+ . An additional state at ~30 eV has been observed by several investigators^{47,48} and has been ascribed to CH_4^+ in the configuration $(2a_1)^2, (1f_2)^4, (3a_1)$ by Appel⁵⁵ although it has recently been suggested that the doubly charged methane ion appears at this potential.⁵⁶ In either case, this band corresponds to the removal of two bonding electrons from the $(1f_2)$ orbital and the resulting state should be strongly dissociative. The abrupt increase in the production of H^+ which occurs in this energy region is consistent with this interpretation. The rate of CH^+ production increases gradually in this region and levels off around 40 eV.

The distribution of energy among the fragmentation products in general, and CH^+ in particular, will depend upon the details of the dissociating state of CH_4^+ . While this study has not selected particular dissociating states by using controlled ionization energy, etc., we may infer from the photoelectron spectra and the fragment branching ratios that a major fraction of CH^+ is produced following excitation of the $\text{CH}_4^+ (2a_1)^{-1}$ level. The doubly excited state at 30 eV might also be considered as a source of CH^+ ; however, this is not likely since the mass spectroscopic product branching ratio of CH_4^+ shows no significant change at this energy.

The thermodynamic threshold for the production of CH^+ through the reaction

is 19.3 eV.⁵² This value is a full 3 eV below the observed appearance potential for CH^+ , offering the possibility for considerable internal excitation of the products which is consistent with the observations made in the present study. At approximately 4.5 eV above the threshold for the process indicated in Equation 15, a new process,

becomes energetically allowed. Since a significant amount of CH^+ is produced following ionization of methane by electrons with energies of 23.3 eV or greater, it would seem that both processes (15) and (16) can contribute to its formation. The large amount of rotational excitation in the CH^+ fragment, however, requires that the loss of 3H in Equation (16) occurs non-symmetrically. On the basis of simple kinetic arguments the first step in the dissociation process leading to the production of CH^+ is probably hydrogen atom elimination. The loss of H_2 as a first step should be much less likely since this process may be considered a three center elimination as opposed to the two center hydrogen atom elimination.

In any unimolecular dissociation resulting in two products (CH^+ and H_2 in this case) the maximum kinetic energy of the two fragments may be calculated from simple classical mechanics. Any internal excitation (vibrational or electronic) will result in a reduced kinetic energy, but the exact partitioning of internal excitation will depend upon the

details of the potential energy surfaces involved. If one assumes that the dissociation exothermicity of CH^+ production from CH_4 is essentially the same as that of CD^+ production from CD_4 then the similarity in the rotational temperatures of CH^+ and CD^+ is easily understood. A simple analysis shows that the maximum kinetic energy of the CH^+ and CD^+ produced from CH_3^+ and CD_3^+ , respectively, are nearly the same with the CD^+ kinetic energy being slightly larger. While the fragment kinetic energies have not been measured in this study, the rotational population distributions resulting from the dissociation "kick" have been studied and the same qualitative trends observed. While the vibrational population distribution could be modeled using approximations such as the impulse approximation for the collisional excitation of a classical anharmonic oscillator⁵⁷ the unusual distribution actually observed suggests the importance of more detailed potential surface factors.

The absence of product CH^+ below 22.3 eV simply reflects the inability of CH_4 to absorb energy between ~17 eV and 22.3 eV. The efficiency of energy absorption is reflected in the intensity profiles seen in the photoelectron spectra (Fig. 19a). When CH_4^+ is formed in the $(2a_1)^{-1}$ state it must be assumed to be highly vibrationally excited due to the large change in equilibrium bond length. The subsequent decomposition of these vibrationally excited levels is seen in the sudden increase in CH_2^+ production as well as the onset of CH^+ production.

Since there are several eV released in the formation of CH^+ it is energetically possible to produce CH^+ in the $A^1\Pi$ state ($T_e = 2.98$ eV).⁵⁸ It is clear from the analysis of the internal energy distributions of CH^+ that some of this excess energy is channeled into vibrational and rotational excitation of the fragment. The CH^+ produced in the $A^1\Pi$

state radiates quickly⁹ ($\tau \approx 800$ nsec) down to the $X^1\Sigma^+$ state. Such radiative relaxation very nearly preserves the rotational distribution since $\Delta J = 0, \pm 1$ for such a transition. The vibrational distribution of $CH^+ X^1\Sigma^+$ produced through radiative relaxation of the A state will be largely determined by Franck-Condon factors, resulting in a relationship between vibronic populations which will, in general, be non-Boltzmann. Since the product distribution of electronic states was not determined in the present investigation, the initial vibrational distributions of either electronic state cannot be determined from the observed band intensities. It is interesting, however, to note that the rotational distributions of $v''=0$ and $v''=1$ for both CH^+ and CD^+ can be characterized by a single temperature to within the accuracy of our intensity measurements. This would imply that either the $CH^+(CD^+)$ is formed predominantly in a single electronic state, or that the product rotational distribution is very nearly independent of the vibrational/electronic energy distribution.

E) Radiative Lifetime Measurements

By tuning the dye laser into resonance with a strong optical transition and examining the time behavior of the resulting fluorescence (averaging over a suitable number of laser shots) the excited states' radiative lifetime may be obtained. Since the collision rate, under typical operating conditions, is low, the observed decay rate will not be distorted for states which may decay through electric dipole allowed transitions (typically $\tau = 10$ nsec - 10 μ sec). Since the ion trajectories within our ion trap have not been well characterized, it is conceivable that the measured decay rates could be distorted through ion diffusion in and out of the optical viewing region. For this reason we studied several well characterized systems with both short and long radiative lifetimes.

The isoelectronic ions, N_2^+ and CO^+ , are both of great importance in interstellar as well as atmospheric chemistry. These isoelectronic species share a common ordering of electronic states (for the lowest three levels), and so, it is of interest to study both ions and to draw comparisons between them. In addition, the radiative lifetimes of excited states in these ions range from 55 nsec ($B^2\Sigma$ state of CO^+) to 10 μ sec ($A^2\Pi_u$ state of N_2^+) providing convenient test points for our system's ability to accurately measure lifetimes in this range. The potential curves (for the electronic states of interest here) are reproduced in Figure 8 for N_2^+ . The potential curves for both ions have the same general form, a low lying $^2\Pi$ state, nested deeply in the $X^2\Sigma$ well, and a $^2\Sigma$ state at higher energy.

The $B^2\Sigma - X^2\Sigma$ systems of both N_2^+ and CO^+ have been thoroughly studied in the past.^{26,59} The radiative lifetime of $N_2^+ B^2\Sigma_u^+(v=0)$ is 60 nsec for low N levels, and the corresponding value for CO^+ is 55 nsec. Because these lifetimes are so short they will not be significantly distorted by space charge repulsion effects. The build-up of high positive ion density results in the rapid depletion of ions from the viewing region as the ion cloud expands. This effect is only important for radiative lifetimes greater than a few hundred nsec. Thus, the values previously measured for the $B^2\Sigma$ state of N_2^+ and CO^+ should be reasonably accurate. A test of our technique's ability to accurately measure short radiative lifetimes is presented by the study of either of these states. The $B^2\Sigma_u^+(v=0)$ level of N_2^+ is easily accessed using our dye laser and was studied as a test case. Perturbations of the $N=40-45$ levels of the $N_2^+ B^2\Sigma_u^+(v=0)$, caused by the $N_2^+ A^2\Pi$ state, have been reported to increase the radiative lifetimes of these levels by as much as 20 nsec.²⁶

Measurements of the radiative lifetime of several levels in the $B^2\Sigma_u^+(v=0)$, including some of the reportedly perturbed levels, were made, and the results are summarized in Table VII. The perturbed levels proved to have easily measurable increases in radiative lifetime, up to 17 nsec above the unperturbed value of 60 nsec, in agreement with the earlier reports. Typical results for the $N=32$ level of $N_2^+\Sigma_u^+(v=0)$ are reproduced in Figure 20.

To test the sensitivity of our technique in the measurement of much longer radiative lifetimes we studied several levels in the $A^2\Pi$ state of both CO^+ and N_2^+ . The variation of radiative lifetime with vibrational level in the $A^2\Pi$ state of CO^+ has been the subject of several experimental studies, the results of which are summarized in Table VIII. In contrast to the short radiative lifetimes found in the $B^2\Sigma$ state of this ion, the $A^2\Pi$ state lifetime is on the order of several μ sec and, hence, will be subject to large perturbations due to electrostatic repulsion if steps are not taken to confine the ions or to reduce the space charge effect. Several groups have attempted to deal with the effect of positive space charge buildup, both theoretically and experimentally.^{60,61} The poor agreement between these studies reflects the difficulties involved in modeling the space charge effects. Because the ion trap used in the present study confines the ions to a small volume for periods of many msec, the perturbations caused by the electrostatic repulsion of the ions can be avoided. The use of a laser to selectively excite a particular level in the upper state removes the possibility of population cascading which would result in the distortion of the decay rate through a lengthening of the observed radiative lifetime. The results obtained here for the $v' = 1, 2, 3$ and 4 levels of $CO^+ A^2\Pi$ are presented in Table VIII.

Table VII. Experimental radiative lifetimes for
selected rotational levels of $N_2^+ B^2\Sigma_u^+$

N'	Lifetime (nsec)
30	58
31	60
32	60
33	62
42	79
43	77

Figure 20, Decay rate of electronically excited N_2^+ . The laser excitation of the $B^2_{\Sigma_u^+}(v'=0)$, $N' = 32$ yielded the data shown here. A least squares fit to the data resulted in a value of 60 nsec for the radiative lifetime of this level.

The trends in lifetime variation with v' are in agreement with the other studies although the results we obtain are some 30% higher than those of Curtis and Erman.⁶¹

As noted by Holland and Maier,⁶² the lifetime of an excited electronic level with vibrational quantum number v' can be approximated as

$$\tau_{v'}^{-1} \approx \sum_{v''} g_{v',v''} \bar{R}_e^2 \omega_{v',v''}^3, \quad (17)$$

where $\bar{R}_e$ is the electronic transition moment. They have calculated the relative τ_{rad} 's for levels $v' = 0-8$ in the $\text{CO}^+ A^2\Pi$ state using the assumption of constant R_e , and have normalized these values to their measured ones. These values are presented in Table VIII for comparison.

The $A^2\Pi$ state of N_2^+ , with vibronic lifetimes of ~ 10 μsec , presents the greatest challenge to our technique. The strongest vibronic bands in the system are deep in the red ($\sim 8000 \text{ \AA}$), which is a poor spectral region for lasers. In addition, because the transition is so weak, high laser powers are required to induce significant excitation. The (5,0) band of this system was studied and the decay rate of its laser induced fluorescence recorded. This resulted in the value of $\tau_{(v'=5)} = 9.3 \pm 1.0$ μsec which is in good agreement with the results of Holland and Maier,⁶² and of Peterson and Moseley.⁶³

The technique discussed here may prove to be most useful in the study of fragment ions, particularly those fragment ions which are produced only in small quantities. Ion densities achieved using this technique are limited only by fixed experimental parameters, and thus comparable densities of any chosen ion may, in principle, be attained.

The radiative lifetime of the $A^1\Pi(v'=0)$ state of CH^+ has been the subject of numerous studies due to its great importance in the chemistry

Table VIII. Measured Radiative Lifetimes (in μsec) the $\text{CO}^+ A^2\Pi$ State for $v' = 0-4$

v'	A	B	C	D	measured ^E	calc
0	calc(3.96) ^a	3.82(+0.19)	2.85(+0.2)	4.6(+0.5)		3.85
1	3.51(+0.1)	3.58(+0.18)		3.8(+0.5)	3.49(+0.24)	3.41
2	3.25(+0.1)	3.09(+0.15)		3.1(+0.7)		3.09
3	2.90(+0.1)	2.85(+0.14)			2.78(+0.19)	2.84
4	2.60(+0.15)	2.69(+0.13)			2.63(+0.18)	2.66

^a This value is calculated by scaling our measured value for $\tau_{(v'=1)}$ by the ratio of $\tau_{v'=0}$ to $\tau_{v'=1}$ calculated by Holland and Maier.⁶²

Explanation of Table Headings

A. Results of the present study; B. Results of Möhlmann and DeHeer;⁶⁰ C. Result (for $v' = 0$) of Curtis and Erman;⁶¹ D. Results of study by Bondybey and Miller;⁷⁰ E. Measured and calculated results of Holland and Maier.⁶² The calculations are based upon the assumption of constant $\bar{K}_e$.

of interstellar clouds. The early studies of Smith⁶⁴ and Anderson⁶⁵ resulted in radiative lifetimes which were ~ 70 nsec. Subsequent investigations^{66,67} pushed the value up to several hundred nsec. Recent studies by Erman⁶⁸ in which attempts were made to neutralize space charge effects resulted in a radiative lifetime for the $A^1\Pi(v'=0)$ state of 630 nsec. Some of these studies suffer from poor spectral resolution and, in several cases, have likely been distorted due to the presence of overpowering impurity signals. Those studies which resolve specific rotational components of the transition are still subject to a large distortion due to electrostatic repulsion. The effect can be quite large for fragment ions, such as CH^+ , since the fragment is typically formed in small quantities ($CH^+ \approx 3\%$ of total ionization from CH_4) and high ion densities must be formed to produce a measurable signal. These high ion densities result in large space charge effects.

Relatively high densities of CH^+ ions can be generated in our trap ($\approx 10^6$ /cc) and, as in the previously discussed studies, the effects of space charge repulsion are avoided. We have carried out studies of the decay rate of the $A^1\Pi(v'=0)$ state of both CH^+ and CD^+ . In each case the (0,0) R branch bandheads were excited and total fluorescence monitored as a function of time. The results are tabulated in Table IX. The result obtained for $CH^+ A^1\Pi(v'=0)$, 815 nsec (Fig. 21), is some 30% higher than the closest previously determined value. This value, 630 nsec, was arrived at using the modified high frequency deflection (HFD) technique developed by Erman⁶⁹ in which low energy electrons are injected into the ionization region to reduce the space charge generated by the positive ions. This technique has considerably reduced the effect of electrostatic repulsion; however, the actual extent of the effect's reduction is not well documented. Even with the space charge neutralization

Table IX. Measured radiative lifetimes for
the CH^+ and CD^+ $A^1\Pi_{(v'=0)}$ state

	Lifetime (nsec)		
	A	B	C
CH^+	815(+25)	630(+50)	250
CD^+	820(+50)		

Explanation of columns: A. Results obtained using laser excitation of trapped ions (present study). B. Results obtained using space charge neutralization technique (Erman⁶⁸). C. Results obtained using electron beam phase shift technique (Brooks and Smith⁶⁷).

Figure 21. Radiative decay rate of the $A^1\Pi_{(v'=0)} J=3$ level of CH^+ .

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this technique results in a radiative lifetime for the $\text{CO}^+ \text{A}^2\Pi(v'=0)$ state of 2.85 μsec which is more than 1.0 μsec lower than the presently determined value of $\tau_{v'=0} = 3.96 \mu\text{sec}$.

Examination of the results tabulated in Table VIII reveals rather good agreement between the values of τ_{rad} obtained by Mohlmann and DeHeer,⁶⁰ Holland and Maier⁶² and those obtained in the present study. These studies were all made under low collision conditions (10^{-5} - 10^{-2} Torr). The results obtained by Bondybey and Miller⁷⁰ were obtained in a high pressure study (~ 1.0 Torr) and thus involve the extrapolation of measured values back to zero pressure. If the radiative lifetimes of the $\text{CO}^+ \text{A}^1\Pi(v'=0)$ state obtained in the low pressure experiments are averaged together the result is $\tau_{(v'=0)} = 3.88 \mu\text{sec}$. If a correction factor, based upon the ratio of this average value for the $\text{CO}^+ \text{A}^2\Pi(v'=0)$ radiative lifetime to the value measured using the HFD technique, is applied to the HFD result for $\text{CH}^+ \text{A}^1\Pi(v'=0)$, the result,

$$\tau = \frac{3.88}{2.85} \cdot 630 \text{ nsec} = 858 \text{ nsec}, \quad (18)$$

is in excellent agreement with the result obtained using the technique described here.

If the oscillator strength of the $\text{CH}^+ \text{A}^1\Pi - \text{X}^1\Sigma^+ (0,0)$ band, as determined by Eriman,⁶⁸ $f_{0,0} = 7.2 \times 10^{-3}$, is scaled by the ratio of the radiative lifetime determined using the HFD technique to that determined here, the result is

$$f_{0,0} = \frac{630}{815} \cdot (7.2 \times 10^{-3}) = 5.57 \times 10^{-3}. \quad (19)$$

This result is within $\sim 15\%$ of the $f_{0,0}$ calculated by Yoshimine et al.¹⁷

The oscillator strengths of molecular transitions can be used to make estimates of column densities and relative abundances of molecules and ions in the interstellar medium. Because CH and CH^+ are believed to be so important in the formation of many interstellar molecules, the correct modeling of their formation and chemistry is of fundamental significance. To be acceptable, any theory dealing with the formation of CH and CH^+ must accurately account for the observed abundances of these species. Thus, it is imperative to obtain precise determinations of the actual abundances of these molecular species through independent means. Recent measurements of CH^+ column density⁷¹ used an $f_{0,0}$ value of .014, based upon the studies of Brooks and Smith.⁶⁶ Using the revised value of $f_{0,0}$ as determined in the present study the revised column densities are $N = 2.8 \times 10^{13}$, 4.0×10^{13} , and $3.0 \times 10^{13} \text{ cm}^{-2}$ toward 20 Tau, ζPer , and ζOph , respectively.

CHAPTER V

Conclusions

The experiments described here have, hopefully, demonstrated the usefulness and versatility of the ion trap in the spectroscopic and kinetic study of molecular ions. Rather than reviewing the already demonstrated abilities of this technique it would be somewhat more enlightening to reflect upon the technical limitations of the apparatus in its present state. The limitations of the approach are by no means absolute experimental limitations, but will certainly challenge the clever experimentalist in finding solutions. Clearly, as each of the problems is addressed and overcome the range of new studies open this technique will expand introducing, of course, a whole new set of problems.

The first handicap to be mentioned is the spectral range over which LIF studies could be successfully carried out. Throughout most of the studies discussed in this thesis the tunable dye laser was pumped by a nitrogen laser resulting in an accessible wavelength range of from 3650-7500 Å. The extension of this range into the ultraviolet is an obvious direction in which to move since many new electronic states and many new ions will become accessible. This idea needs little discussion since the required laser technology is already available.

A more formidable problem is the reduction of the spectral line width, which is largely due to doppler broadening resulting from the driven motion of the ions. Several approaches to this problem have been considered. Operating the ion trap at significantly higher frequencies

(15-25 MHz) would certainly uncouple the ion motion from the trapping fields but only with a great reduction in ion density (see Eq. 3, Chap. II). Most double resonance pumping schemes involve a great loss of signal and so are not of much use in the problem at hand. It is conceivable that the ion motion may display some motion synchronous with the trapping field voltage in which case the doppler width may be decreased by suitable timing of the laser pulse.

Other areas for future development, such as new approaches to ion production, offer many possibilities and will hopefully direct the way to new areas of study. As each area is studied it is clear that significant modifications may be called for. I hope that all such developments will be actively pursued in the hope of maintaining the experiment at the limits of its potential.

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