Laboratory and Observational Spectroscopy of H_3^+

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1 Introduction and Historical Overview

H_3^+ is indeed a most remarkable species. As the simplest stable polyatomic molecule, it serves as a benchmark for testing out theoretical calculations for polyatomic systems. As an especially anharmonic molecule (due to the light mass of its atoms), it poses a unique challenge to laboratory spectroscopists to observe its high energy overtones and hot bands. As a completely hydrogenic species, it is arguably the second most important molecule in the universe, second to H_2, and provides a useful tool for astronomers to characterize planetary ionospheres, supernovae, and the interstellar medium.

In this prospectus, I propose additional laboratory investigations of high energy overtone bands of H_3^+, as well as new observations to detect H_3^+ in the interstellar medium.

2 A Brief History of H_3^+ (up to 1980)

H_3^+ was first discovered by J. J. Thomson[1] in 1911 as part of his "further experiments with positive rays." Using an early form of mass spectrometry, he found a positive ion with $m/e = 3$. Thomson discarded the possibility of C^{4+} on chemical grounds, but was nevertheless unsettled with the idea that H_3^+ exists. He noted that "the existence of this substance is interesting from a chemical point of view, as it is not possible to reconcile its existence with ordinary conceptions about valency, if hydrogen is regarded as always monovalent."

In 1916, a paper appeared from A. J. Dempster[2] in Chicago which demonstrated that the abundance of H_3^+ increased at higher pressures of H_2, even surpassing that of H_2^+ and H^+ under some conditions. Twenty years later, though, when deuterium was discovered, the interpretation of the H_3^+ line was questioned. In 1934, Thomson himself wrote[3] "the evidence seems to me to leave little doubt that the gas I called H_3^+ more than twenty years ago is the same as that which is now called heavy hydrogen." Thomson here refers to the alternate possibility of the line being due to HD^+.

By the end of the 1930s, there was ample evidence to support the existence of H_3^+, but little was known about this mysterious species. Henry Eyring was quoted[4] as saying that the H_3^+ problem was "the scandal of modern chemistry." By 1938, Hirschfelder had demonstrated that a triangular structure of H_3^+ was more stable than a linear one. Not until 1964, though, with the advent of modern computing, was it determined that an equilateral triangle was indeed the equilibrium structure.[5]

By the early 1970s, the astrophysical significance of H_3^+ had been recognized. Its primary role in the chemistry of the interstellar medium, as discussed below in Section 6, was highlighted in several key papers.[6–11]

In 1978, experiments were carried out at Argonne, Lyon in France, and Rehovot in Israel to

confirm the triangular geometry of H_3^+. Accelerated ($2 \sim 4$ MeV) H_3^+ ions passed through carbon foils, thus losing their electrons. The three protons then repelled each other due to Coulomb interactions, and were detected on a photographic emulsion. This was perhaps the first experiment to yield information about H_3^+ itself (as opposed to its reactions), beyond the simple fact that it exists.

3 Theoretical Background

While my interests do not primarily lie in the theory of H_3^+, it is nevertheless important to be at least familiar with the theoretical background of H_3^+ in order to understand the spectroscopy and to appreciate the interplay of theory and experiment in the case of this unique molecule.

3.1 Rigorous Quantum Numbers

Two rigorous quantum numbers for H_3^+ are, of course, the total angular momentum (F) and parity ($\pm$). These quantum numbers are rigorous because the Hamiltonian is invariant to rotation in space (space is isotropic), and because the Hamiltonian is invariant to inversion (left- and right-handed coordinate systems are equivalent), respectively.

Since H_3^+ possesses three indistinguishable nuclei (fermions), and since the Pauli principle demands that the total wavefunction of the molecule be antisymmetric with respect to permutations (12), etc. of the nuclei, the permutation operations are rigorous symmetry operations for H_3^+. Consequently, the symmetry labels of the rovibrational wavefunctions are rigorous quantum numbers. The wavefunctions may be labelled with the symmetries $\Gamma = A_1$, A_2, or E, according to their character in the permutation-inversion group S_3^* (which is isomorphic to D_{3h}).

The quantum numbers discussed above are completely rigorous, in that they depend only on the properties of space and on the Pauli principle. If the very small nuclear spin-rotation interaction is neglected, the total nuclear spin I and the rotational angular momentum J can also be considered good quantum numbers.

3.2 Approximate Quantum Numbers

There are also several approximate quantum numbers for H_3^+ that are important. These are all based on properties of the molecule itself, and are because H_3^+ is so "floppy," they are not rigorous quantum numbers when coupling terms between rotation and vibration become significant (at high J and/or high vibrational quantum numbers).

A normal mode analysis of the equilibrium geometry of H_3^+ yields (see Figure 1) a symmetric stretch (Q_1, frequency ν_1, A_1' symmetry), which is formally IR inactive, and a degenerate bending mode (Q_{2x} and Q_{2y}, frequency ν_2, E$'$ symmetry), which is IR active. Hence, we obtain two approx-

Figure 1: Top: normal modes of equilibrium H_3^+. Bottom: a useful superposition of the two degenerate normal modes, illustrating vibrational angular momentum.

imate quantum numbers, v_1 and v_2, corresponding to the number of quanta in each vibrational mode. [The limitations of the traditional formalism are belied by the fact that the $\nu_1 \leftarrow 0$ band has been observed with infrared spectroscopy.[12]]

Because the ν_2 mode is degenerate, any linear combination of its two components may be considered. It is convenient to form linear combinations with two components 90° out of phase. As can be seen in Figure 1, this leads to a vibrational angular momentum, and therefore a new approximate quantum number, l_2, where $l_2 = v_2, v_2 - 2, \ldots, -v_2$.

At least at low values of v_2 and J, then, we can label the rovibrational states as $|\mathrm{J}, \mathrm{k}\rangle|v_1 v_2^{l_2}\rangle$. However, for states with $v_2 \neq 0$ and $l_2 \neq 0$, states with different k and l_2 but the same $\mathrm{G} = |\mathrm{k} - l_2|$ will mix, and as a result at higher levels only G will be a good approximate quantum number. When mixing is not too severe, a label $|\mathrm{U}| = |l_2|$ is often used as well.

Of course, it should be kept in mind that at high enough levels, all of these approximate quantum numbers, including G, will cease to be good quantum numbers. In the final analysis (and when considering high overtone bands), the only good quantum numbers are F, $\pm$, Γ, I, and J.

3.3 Determination of Energy Levels

The traditional perturbation approach to the calculation of energy levels of a symmetric top such as H_3^+ is to use polynomials of vibrational and rotational quantum numbers with coefficients of various molecular constants. The usual approach to predicting spectra is to fit experimentally observed transitions by varying the set of molecular constants and then using these determined constants to predict higher transitions. However, since H_3^+ is so anharmonic, this process requires nearly as many parameters as there are experimentally observed transitions (since so many higher order terms must be included) — this fact implies that the fit Hamiltonian will have very little predictive power for higher transitions.

Because of this, Bawendi et al. commented that "probably the best strategy for this molecule

is to provide the *ab initio* theorists with our experimentally determined energy levels so that they can further adjust with their potentials and accurately predict new rovibrational transitions."[13] Thus, theorists use electronic structure calculations to develop a potential energy surface and solve for the eigenvalues of the motion of the three protons by using supercomputers. Then they adjust the parameters of the potential surface to try to better fit the experimental data.

In the most recent fit, for example, Dinelli et al.[14] fit nearly 1600 data points for H_3^+ and its isotopomers by adjusting 36 constants and holding 51 at the values obtained by *ab initio* methods. Their standard deviation for H_3^+ vibration-rotation energy levels was 0.015 cm^{-1}! This constitutes more than an order of magnitude improvement over pure *ab initio* potentials.

As can be seen, H_3^+ is a wonderful playground where spectroscopists and theorists meet — in 1994 and 1995, at least eleven theoretical papers reported calculations on this system.[15–25] The spectroscopists provide data for the theorists to fit to their potentials (as well as to test new *ab initio* potentials). The theorists in turn predict higher energy transitions, which guide the work of the spectroscopists in assigning new spectra. The spectroscopists feed the new transition energies back to the theorists, and the cycle begins anew.

4 H_3^+ Spectroscopy: What's Done and What's Begging to be Done

4.1 Spectroscopic Discovery of H_3^+

Because H_3^+ has no excited electronic states, it possesses no observable spectrum in the ultraviolet or visible regions of the electromagnetic spectrum. Because H_3^+ has no permanent dipole moment, it has no allowed pure rotational transitions, leaving it inaccessible to microwave spectroscopy (with the possible exception of very weak forbidden transitions[26] with $\Delta K = \pm 3$, which have yet to be observed). Therefore, in order to observe H_3^+ spectroscopically, we are consigned to look for rovibrational transitions in the infrared.

The first observation of H_3^+'s fundamental $\nu_2 \leftarrow 0$ transition did not occur until 1980, after a four year search by Oka.[27] Figure 2 shows the observed spectra of the fundamental band with water cooling (top) and liquid nitrogen cooling (bottom).

One thing that is easily noted is the complicated nature of this spectrum. We do not observe symmetrical and regular peaks in P, Q, and R bands as we see in ordinary molecules — indeed, as J becomes larger, the picture gets increasingly complicated.

Another thing to note from Figure 2 is the lack of an R(0) band. This suggests that the J=k=0 state of the vibrational ground state is unoccupied! This is a consequence the Pauli principle, which demands that the total wavefunction $\Psi \simeq \Psi_{el}\Psi_{rovib}\Psi_{nucl}$ be antisymmetric with respect to permutation.

Figure 2: Observed spectrum of the $\nu_2 \leftarrow 0$ fundamental band of H_3^+.

Year of Discovery	Investigator	Laboratory	Band	Lines Observed to Date
1980	Oka[27]	Herzberg Institute	$\nu_2 \leftarrow 0$	> 190
1989	Drossart et al.[28]	Jupiter	$2\nu_2^2 \leftarrow 0$	> 54
1991	Lee et al.[29]	Oka Ion Factory	$3\nu_2^1 \leftarrow 0$	15
1992	Xu et al.[12]	Oka Ion Factory	$\nu_1 \leftarrow 0$	9

Table 1: Discovery of H_3^+ fundamental and overtone transitions, and numbers of observed lines to date.

4.2 Recent Work

Table 1 summarizes the discovery of the fundamental and overtone bands of H_3^+. If hot bands are included, there are currently over 600 assigned spectral lines of H_3^+! However, it is noteworthy that no new overtone bands have been identified since 1992. The primary reason for this has been the lack of a powerful, tunable radiation source at the necessary wavelengths. As discussed in Section 5.2 below, this problem has recently been overcome by the development and refinement of short external cavity diode lasers. This development has paved the way to higher overtones of H_3^+.

4.3 What's Next?

One might reasonably ask "Why should we bother to pursue higher and higher overtones of H_3^+?" There are two primary motivations. The first, of course, is theoretical interest — observing higher overtones will provide a stringent test of *ab initio* calculations, probe the validity of the Born-Oppenheimer approximation, allow theorists to construct more accurate potential surfaces,

Band	Frequency	Intensity
$3\nu_2(l_2 = 1)$	7003 cm^{-1}	$\frac{1}{180}$
$\nu_1 + 2\nu_2(l_2 = 2)$	7869 cm^{-1}	$\frac{1}{270}$
$4\nu_2(l_2 = 2)$	9108 cm^{-1}	$\frac{1}{840}$
$5\nu_2(l_2 = 1)$	10883 cm^{-1}	$\frac{1}{4800}$

Table 2: H_3^+ bands to be studied in this work.

and help refine their techniques for treating polyatomic molecules. Furthermore, the barrier to linearity for H_3^+ occurs at about 10,000 cm^{-1}, so higher overtones will begin to sample linear geometries and even break the linearity barrier, providing an additional challenge for the theorists. The second motivation for this work is the need for accurate frequencies of higher energy transitions in order to characterize and identify H_3^+ in various astrophysical environments, as will be discussed in Section 6.

With these motivations in mind, I am proposing laboratory observations of four vibrational overtones of H_3^+. Table 2 lists the transitions to be examined, along with the predicted frequencies of their band origins, and their relative intensities with respect to the ν_2 fundamental.

5 Experimental Setup

5.1 Plasma Discharge

In the laboratory, H_3^+ is produced in a plasma discharge cell such as the one depicted in Figure 3. Hydrogen gas ($\sim$ 1.5 torr) flows into the tube through the multiple inlets, and the reactants are pumped out of multiple outlets with a mechanical pump. The ends of the reaction tube are sealed with CaF_2 windows mounted at the appropriate Brewster angle. An alternating current of about 150 mA at 6 kV and $\sim$ 8 kHz is applied to electrodes on either side of the cell, forming the discharge.

The plasma in the discharge cell is a highly non-equilibrium system quite different from the gas phase. Hence it is often referred to as the "fourth state of matter." The electrons may have temperatures on the order of 10^4 K, while the ions have rotational and translational temperatures on the order of room temperature. Due to inefficient energy transfer between vibrational energy and rotational and translational energy, the characteristic temperature of vibration may be on the order of 10^3 K. In our laboratory plasmas, the number density of H_3^+ is measured to be about 3 x 10^{10} cm^{-3}.

There are three key reactions involved in the chemistry of H_3^+ in this type of discharge: the

Figure 3: Liquid-nitrogen cooled multiple inlet-outlet discharge tube. The length of the tube is 1.5 m, while the inner diameter is 1 inch. A sealed vacuum jacket insulates the liquid-nitrogen from the atmosphere of the room. The bellows on the outer jacket prevent cell damage due to thermal contraction.

production of H_2^+ ions, the production of H_3^+ itself, and the destruction of H_3^+. The first reaction

$$H_2 + e^- \xrightarrow{k_1} H_2^+ + 2e^- \tag{1}$$

proceeds with a rate constant of $k_1 \sim 2.5 \text{ x } 10^{-11}$ cm^3/s in our discharge.[30] The H_2^+ ion, however, is incredibly reactive, and reacts easily with hydrogen:

$$H_2^+ + H_2 \xrightarrow{k_2} H_3^+ + H \tag{2}$$

where k_2 is a Langevin rate constant[31] of about 2.0 x 10^{-9} cm^3/s. In the plasma discharge cell, H_3^+ is primarily destroyed by wall collisions, which are limited by the ambipolar diffusion rate of 3 x 10^5 s^{-1}.

5.2 Laser Sources

For the investigation of the $3\nu_2(l_2 = 1)$ (7003 cm^{-1}) and $\nu_1 + 2\nu_2(l_2 = 2)$ (7869 cm^{-1}) overtone bands, we have purchased a New Focus diode laser which is tunable over 7650 - 8200 cm^{-1} and has a very narrow linewidth (300 kHz). The output power of the laser typically varies from 2 to 8 mW over its tuning range. With the high power and the stability of this laser, we will be able to perform ion spectroscopy with unprecedented sensitivity.

The New Focus diode lasers utilize an external cavity design, shown in Figure 4. A high-

Figure 4: Schematic of New Focus diode laser

reflection coating on one end of the diode forms one end of the cavity, while a high-reflecting tuning mirror forms the other. From the diode, the beam passes through a collimating lens and strikes a diffraction grating at near grazing incidence. The beam is diffracted toward the tuning mirror, which reflects the light back on itself for the reverse path. Part of the light from the diode is reflected, not diffracted, by the grating — this forms the output beam. The grating serves as a narrow spectral filter which forces the laser to operate in a single longitudinal mode. This is because only one of the many wavelengths of light diffracting off the grating will be exactly perpendicular to the tuning mirror, and only this wavelength will survive many round trips. The angle of the tuning mirror can therefore be adjusted to change the lasing wavelength.

For the investigation of the $4\nu_2(l_2 = 2)$ band at 9108 cm^{-1} and the extremely weak $5\nu_2(l_2 = 1)$ band at 10883 cm^{-1} [which is particularly exciting, as it lies above the barrier to linearity], we will use our group's Coherent Ti:sapphire laser, which offers an increased power of 1-2 W with a 500 kHz linewidth.

5.3 Increasing Signal-to-Noise

As illustrated in Table 2, the overtones targeted in this investigation have much lower intensities than the fundamental band. It is worth noting, however, that in the investigation of overtones we have been blessed by the anharmonicity of H_3^+, which causes these intensities to be orders of magnitude larger than those of more ordinary harmonic molecules! While the higher output power of the lasers used will help offset the weakness of these transitions, we still must employ other techniques to increase the signal-to-noise ratio.

One such technique is velocity modulation. As alluded to in Section 5.1, this involves operating the discharge with an alternating current. In an AC discharge, molecular ions are alternately accelerated towards one end of the tube, then towards the other, at a frequency of about 8 kHz. Under these conditions, an incident radiation beam of a fixed frequency in the laboratory frame of reference appears frequency modulated to the molecular ions. As the frequency of the radiation in

the molecule's frame moves back and forth across the molecule's transition, the amount of radiation absorbed rises and falls. However, neutral species are not moved by the AC potential, and have a constant absorption. By using a lock-in amplifier, then, we can easily subtract out noise due to neutral species.

Another, conceptually simpler, technique is that of multipassing. The incident laser beam is passed through the discharge cell multiple times (usually around 4) so as to increase the effective path length for absorption. Of course, when used in conjunction with velocity modulation it is important that the beam be passed through the cell in the same direction, or the modulation will be lost.

In these experiments, I will also utilize an advanced form of noise subtraction. A beam splitter will divide the laser beam into two beams of approximately equal intensity I_1 and I_2. One beam will be multipassed through the cell in one direction, while the other will be multipassed in the opposite direction. These two beams will then be sent to a new two-input autobalancing photoreceiver being developed by New Focus. This receiver outputs a signal proportional to $(I_1 - gI_2)$, where g is a constant adjusted electronically by a low frequency feedback loop so as to cancel out laser intensity noise.

One final method which will be used to increase the signal-to-noise ratio is the introduction of computer control and data collection. For the first time in the Oka Ion Factory, scans will be controlled completely by computer and all data will be collected by computer. This will allow many (N) scans to be performed over a given wavelength range, and further reduce noise by a factor of $\sqrt{\mathrm{N}}$.

Since the fundamental $\nu_2^1 \leftarrow 0$ band was observed with a signal-to-noise ratio of > 3000, we feel confident that we can detect the $3\nu_2(l_2 = 1)$, $\nu_1 + 2\nu_2(l_2 = 2)$, and $4\nu_2(l_2 = 2)$ overtones. The $5\nu_2(l_2 = 1)$ overtone will provide us with a significant challenge, and we will have to do everything possible to optimize signal-to-noise.

6 H_3^+ in Space

6.1 Astrophysical Significance of H_3^+

To appreciate the importance of H_3^+ in the universe, several things should be borne in mind. First of all, protons are far more abundant than any other nucleons — approximately 92.1% of nucleons are protons, while another 7.8% are helium nuclei. Since helium is chemically inert (the only astrophysically important compound it forms is HeH^+), the chemistry of hydrogen is dominant in the universe.

Second, a great deal of the universe's protons form molecular hydrogen. For example, the galaxy-merger system NGC 6240 (see Figure 5) emits the luminosity of 10^8 Suns in the S(1) line

Figure 5: H_2 emission from NGC 6240

alone! Molecular hydrogen has also been observed in the absorption of the light from a distant quasar by an interfering galaxy. Based on the redshift of the absorption lines, this hydrogen is about 13 billion years old![32]

Once we have molecular hydrogen, all that is needed to form H_3^+ is a source of ionization to start Reaction 1 above. In space, there are numerous ionization sources. In planetary systems, stellar winds will produce gigantic planetary magnetospheres in which charged particles are accelerated by the planet's rotating magnetic field and ionize H_2 to H_2^+. In interstellar space, the omnipresent cosmic rays provide a source of ionization.

6.1.1 Jovian Planets

While the first (unsuccessful) searches for H_3^+ in nature were in the interstellar medium, the first successful discovery of H_3^+ was an accidental one!

In late 1987, Trafton et al.[33] observed Jupiter's S(1) quadrupole transition using a grating spectrometer at the McDonald Observatory. Along with the expected emission at 2.121 μm, they also observed a strong unidentified emission feature at 2.093 μm. In late 1988, Drossart and others[28] studied this feature at higher resolution using the Fourier transform infrared spectrometer at the Canada-France-Hawaii Telescope. This emission was only observed in the auroral regions near the poles.

After a month's work, and with the help of the $2\nu_2^2 \rightarrow \nu_2$ hot band data from the Oka Ion Factory[13] and *ab initio* calculations for this band,[34] J. K. G. Watson identified the Jovian spectrum as due to the overtone $2\nu_2^2 \rightarrow 0$ band of H_3^+. In this case, as in many others, H_3^+ had spawned a close collaboration between not only theorists and spectroscopists, but astronomers as well.

In 1989, Oka and Geballe[35] observed the more intense fundamental band of H_3^+ in the Jovian ionosphere. From the relative intensities of the two bands, a temperature of about 1100 K has been

derived.[36] However, during the C fragment impact of the recent Shoemaker-Levy 9 comet-Jupiter collision, the intensities of observed hot bands suggested a temperature of 5000 K![37] Clearly, the laboratory spectra of H_3^+ that have been obtained thus far are insufficient to explain such hot phenomena.

It is also interesting to note that the ν_2 fundamental band has also been observed on Uranus[38] and on Saturn.[39] In the case of Jupiter, the observation of the spatial variations of H_3^+ using narrow-band imaging has already provided a wealth of information on the morphology and temporal variations of plasma activity in the Jovian ionosphere. It is hoped that similar observations in the future will help elucidate the nature of the Saturnian and Uranian ionospheres.

6.1.2 Supernova 1987A

In 1987, the light from an exploding star in the Large Magellenic Cloud reached Earth. Astronomers quickly began observing the supernova with various techniques, including infrared spectroscopy. By the 110th day after the first light reached Earth, strong features appeared at 3.41 and 3.53 μm, and they reached their maximum signal-to-noise ratio by day 192. In a recent paper, Miller et al.[40] fit these lines to a computed spectrum of H_3^+ in this wavelength region. Although the detection is nowhere near as convincing as that in planetary ionospheres because of the lack of rotational structure, their fit is reasonable. While their observation cannot be confirmed (until another equally bright supernova's light arrives), there is not yet another plausible explanation for these lines. Their fit of the spectrum assumes a temperature of 2050 K, yet again demonstrating the need for laboratory data on higher energy transitions.

6.1.3 The Interstellar Medium

About thirty years ago, Townes et al.[41] discovered the microwave emission spectrum of ammonia in Sagittarius B2. Since then, a host of familiar and unfamiliar [such as HC_9N] molecules have been observed in the interstellar medium. These discoveries have brought the previously nonexistent field of interstellar chemistry into the limelight.

These molecules are found in so called "dense" clouds in the interstellar medium, with densities of $[H_2] = 10^3 \sim 10^5$ cm^{-3}. These molecular clouds are now established as fertile breeding grounds for molecules, as well as the birthplace of stars.

At these low densities, two-body processes completely dominate the chemistry. Since the clouds' temperatures are very low (10–100 K), only reactions which are exothermic and have little or no activation energy can proceed at reasonable rates. Under these conditions, and with the lifetimes of the clouds estimated to be in the range of only 10^5 to 10^7 years, reactions between neutral species are unable to explain the observed abundance of molecules in dense clouds.

In the 1970s, a theory of ion-neutral reactions was advanced[6–11] to explain the extraordinarily

high abundance of molecules in dense clouds, and is now generally accepted. Ion-neutral reactions proceed with Langevin rates on the order of 10^{-9} cm^3 s^{-1}, several orders of magnitude faster than neutral-neutral reactions.

This ion-neutral reaction scheme begins with the two key reactions discussed in Section 5.1 — ionization of H_2, followed by reaction of H_2^+ with H_2 to form H_3^+. In the interstellar space, ionization is caused not by electron impact or the influence of stellar winds, but by cosmic rays, at a rate estimated[6] to be $\zeta \sim 10^{-17}$ s^{-1}.

H_3^+, with its low proton affinity of 4.4 eV, initiates the chains of chemical reactions which produce the wide variety of species in the dense clouds, through the proton hop reaction $H_3^+ + X \rightarrow XH^+ + H_2$, where X can be just about any atom or molecule present (with the notable exception of He). The most abundant reactive species X is CO, with $[CO]/[H_2] \sim 10^{-4}$.

The protonated XH^+ ions thus produced begin a network of ion-neutral reactions which produce the wide variety of molecules observed by radioastronomers. Thus H_3^+ plays a very crucial role in interstellar chemistry and hence in the chemical evolution of dense clouds, an important step in star formation.

Because of its symmetry, however, H_3^+ has no pure rotational spectrum and is therefore inaccessible to radioastronomy. We are therefore consigned to search for H_3^+ using infrared spectroscopy, which has much lower sensitivity than radio/submillimeter techniques. Since the detection of its infrared spectrum in the laboratory,[27] H_3^+ has been sought unsuccessfully in molecular clouds.[42–44]

The observation of the infrared spectrum of H_3^+ in molecular clouds would indeed be a significant breakthrough in interstellar chemistry. It would provide the most direct evidence for the the ion-neutral reaction scheme, and also would allow us to estimate absolute number densities of the most important molecular species H_2, CO, and H_3^+. Additionally, it would provide estimates of effective column lengths, and thereby measure the size of the molecular clouds. The discovery of H_3^+ in interstellar space has often been referred to as the Holy Grail of observational molecular astrophysics.

6.2 Proposed Observations

In the laboratory, we produce H_3^+ in a cell, pass monochromatic radiation through it from behind, and detect it using a broad bandpass detector. In interstellar space, though, we are clearly unable to put a laser behind the molecular clouds. However, we can select molecular clouds which have young stars embedded within them — while the visible light from the young stars does not make it out of the cloud, most of the infrared does. By selecting this type of target, we have effectively placed a continuum source behind the cloud. We then use an infrared spectrometer to look for the H_3^+ absorption lines that are expected to be strongest.

An additional trick we can use is to concentrate our telescope time on systems that are known

to be depleted in molecules that destroy H_3^+ (especially CO) — these systems will have a higher steady-state abundance of H_3^+.

While it might sound unrealistic to expect success in the search for the Holy Grail, there are reasons to believe that observational detection of H_3^+ is on the horizon.

First, the technology of infrared spectrometers has been steadily improving since the first searches for H_3^+ began in 1981. While early spectrometers had to scan over wavelength and were thus more at the mercy of atmospheric fluctuations, today's spectrometers use CCD-like arrays which enable the observation of a range of wavelengths simultaneously. Additionally, the inherent sensitivity of the detectors has improved considerably, and the resolution has increased to $\nu/\Delta\nu \sim 20000$ (or 0.136 cm^{-1} at the wavenumber of our interest) at the United Kingdom InfraRed Telescope (UKIRT). The column densities of H_3^+ that are currently predicted by models are just at the threshold of sensitivity of state-of-the-art infrared spectrometers.

Second, Oka and Geballe[45] recently reported a tentative detection of H_3^+ at 3.7 μm towards the deeply embedded young stellar objects AFGL 2136 and W33A, using the CGS4 spectrometer of UKIRT. While the signal-to-noise ratio was low ($\sim$ 2 or 3), this is nevertheless an encouraging sign that the Grail is within sight.

Third, a brand new spectrometer (named Phoenix) is just coming on line at the Kitt Peak National Observatory in Arizona. This spectrometer has five times better resolution than UKIRT, or about 0.027 cm^{-1}. This is an important development, because observed millimeter wave lines of CO indicate that the intrinsic linewidths of molecules in these sources should be $\lesssim$0.07 cm^{-1}. With Phoenix, we should be able to fully resolve H_3^+ lines, whereas UKIRT could not.

The high resolution of Phoenix will therefore allow us not only to unequivocally confirm (or refute) the detection at UKIRT, but also to detect and measure the abundance of H_3^+ in many other molecular clouds.

In pursuit of this objective, I recently participated in a ten night test and engineering run of Phoenix at Kitt Peak in late August. While we were plagued with the expected engineering and software problems, and the weather of August in Arizona was far from favorable, we were able to set up the special filter needed for H_3^+ detection and perform several short test integrations on various sources. While these observations did not detect H_3^+, an important collaboration was established with the PI of the Phoenix instrument, and we have fully characterized the instrument in this wavelength region.

We have applied for two three-night Phoenix runs in the first half of 1997 to search for H_3^+. The first run, in January, will allow us to search clouds with particularly bright infrared sources behind them. The second run, in June, will allow us to confirm or deny the tentative detections at UKIRT. Additionally, the Phoenix PI has just performed additional H_3^+ observations during his most recent test and engineering run. At the time of this writing, I am in the process of reducing the data.

In our search for H_3^+ we use the following three transitions in the $\nu_2^1 \leftarrow 0$ fundamental band which start from the lowest two rotational levels — the only levels that are appreciably populated at the low temperatures of dense clouds.

$\lvert J', k'\rangle \leftarrow \lvert J'', k''\rangle$	Wavenumber
$\lvert 2,2\rangle \leftarrow \lvert 1,1\rangle$	2726.219 cm^{-1}
$\lvert 2,1\rangle \leftarrow \lvert 1,0\rangle$	2725.898 cm^{-1}
$\lvert 2,0\rangle \leftarrow \lvert 1,1\rangle$	2691.444 cm^{-1}

7 Conclusions

H_3^+ has already made more than its share of significant contributions to astronomy and to the theory of polyatomic molecules. It seems as though its finest days, however, are yet to come. In the coming years, laboratory spectroscopists will break the barrier to linearity, and theorists will struggle to predict rovibrational energies above this barrier. If history is any predictor of the future, H_3^+ is bound to surprise astronomers again somewhere in the Universe — be it in the interstellar medium or some other as yet unforeseen place (perhaps in distant galaxies or quasars?).

Perhaps most significantly, H_3^+ has led to perhaps unprecedented collaborations between laboratory spectroscopists, theoretical chemists, and observational astronomers. Herein lies the ultimate beauty of this simple molecule.

Shortly after his discovery of its infrared spectrum, Oka wrote[46] that H_3^+ "is a beautiful jewel of nature left for the laser spectroscopist." Not to mention the theorist — and the astronomer.

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