

The Infrared Spectrum of H_3^+

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1. Introduction

Just as the most basic task of an astronomer is to find a new star, the most basic task of a spectroscopist is to find a new spectrum. But just as an astronomer is happier if an extraordinary object rather than another ordinary star is found, a spectroscopist is happier if a spectrum of some unusual species is found. And just as the new method of radioastronomy has led to the discoveries of such exotic objects as quasars, pulsars, 3K blackbody radiation and molecular clouds, we would hope that laser spectroscopy will enable us to discover new spectra of exotic species.

The H_3^+ molecular ion is the simplest polyatomic system, with two electrons keeping three protons in an equilateral triangle configuration. I consider H_3^+ as a system in which a hydrogen molecule has swallowed a proton; and it swallows with a tremendous appetite. The formation energy of the reaction ($H_2 + p \rightarrow H_3^+ + 4.8 \text{ eV}$) is even greater than the formation energy (4.5 eV) of H_2 from two hydrogen atoms. The proton is well bound to H_2 .

Because of this stability H_3^+ is the most abundant hydrogenic ion in laboratory plasma and in dark molecular clouds. However there has previously been no spectroscopic observation of this species in any range. This is probably because H_3^+ is predissociated in electronic excited states and does not have a discrete optical spectrum. The vibrational spectrum in the infrared region seems to be the only way to study this ion spectroscopically. This is a beautiful jewel of nature left for the laser spectroscopist.

2. Method

A direct infrared absorption method combining a multiple-reflection discharge cell and a frequency-tunable infrared source was chosen as the detection method [1]. A block diagram of the apparatus is shown in Figure 1.

A difference-frequency laser system developed by Alan PINE [2] was constructed and used as the frequency tunable infrared source. Mixing radiation from an Ar laser (ν_A) and that from a dye laser (ν_D) in a temperature-controlled $LiNbO_3$ crystal, we obtained an infrared radiation source with a power of a few microwatts whose frequency ($\nu_A - \nu_D$) was tunable over the range 4400 - 2400 cm^{-1} . This continuous coverage over a wide infrared region was essential in the detection and identification of H_3^+ because the spectrum extends over a region of $\sim 600 \text{ cm}^{-1}$ and the estimated accuracy of the theoretical prediction [3] was $\sim 50 \text{ cm}^{-1}$.

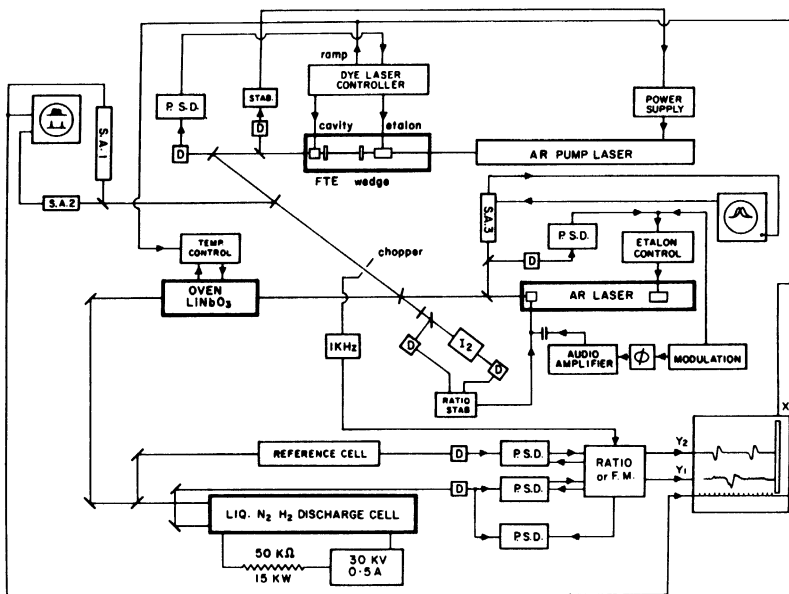


Fig.1 Apparatus

A Spectra Physics 580 dye laser pumped by a 171 Ar laser generated red to yellow radiation with a power of $20 \sim 60$ mWatts and spectral purity of $5 \sim 30$ MHz. The scanning of the etalon was locked to that of the cavity to prevent mode hops and to minimize amplitude fluctuation. The latter was further reduced to the level of less than 1% by feedback to the pump Ar laser. The dye laser output was mixed with either 5145 \AA or 4880 \AA radiation (~ 80 mWatts) from a 165 Ar laser on a dichroic mirror. The frequency of this Ar laser was modulated with an amplitude of ~ 400 MHz and a frequency of 2.5 kHz for frequency modulation of the infrared radiation. In order to do this an etalon mounted on a piezoelectric element was inserted in the Ar laser cavity and modulated synchronously with the cavity. Here also the etalon was locked to the cavity to minimize amplitude modulation.

The multiple-reflection discharge cell was 2 m long with a diameter of 2 cm and was cooled with liquid nitrogen as was done by WOODS and his collaborators for their microwave detection of molecular ions [4]. The discharge tube was sealed with two CaF_2 Brewster angle windows and placed inside a multiple reflection mirror system. This arrangement allowed easy optical alignment and a wide variation of discharge conditions. The radiation loss due to Brewster windows was less than that due to the reflecting mirrors. An absorption path of 32 meters was normally used. The discharge current density of the plasma and the pressure of H_2 varied between $40 \sim 120$ mA/cm² and $0.3 \sim 10$ Torr, respectively. For observing transitions starting from higher J levels, water was used for cooling instead of liquid nitrogen.

The overall sensitivity for the search was $\sim 1.5 \times 10^{-2}$ and the speed of scanning was ~ 8 cm¹/hr. This is by no means a high sensitivity spectroscopy

but a reading of previous papers on hydrogen discharge [5][6] convinced me that this sensitivity should be sufficient.

3. Observed Spectrum

After two years' assembling and adjusting the spectrometer and another two years' search and continuous improving of the apparatus, the first absorption line of H_3^+ was observed on April 25, 1980. It took another 8 months to reveal the whole spectral pattern between 2450 cm^{-1} - 3050 cm^{-1} . It is shown in Fig. 2 for liquid nitrogen cooling (temperature of discharge $\sim 200\text{ K}$) and ice water cooling ($\sim 450\text{ K}$).

Altogether 30 absorption lines have been observed and assigned. For liquid nitrogen cooling no other lines were observed except for the Brackett line ($n = 5 \rightarrow 4$) of the hydrogen atom at 2467.746 cm^{-1} which happened to appear with an intensity similar to that of the H_3^+ lines. For ice water cooling, many spurious lines were observed; the H_3^+ lines were identified from their intensity dependence on discharge conditions.

The spectrum was analyzed by Jim WATSON [1][7] and least squares fitted to 13 vibration-rotation parameters. The lack of any obvious regularity or symmetry in the spectral pattern in Fig. 2 is due to a large ℓ -type resonance with ℓ -doubling constant $q = -5.383\text{ cm}^{-1}$. The lower order parameters derived by Watson agree well with those predicted by CARNEY and PORTER [8] from *ab initio* calculations.

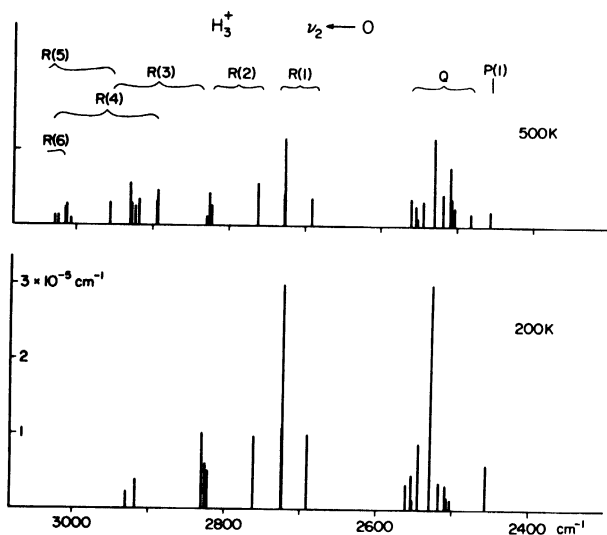


Fig.2 Observed spectrum

Shortly after my submission of the manuscript to Physical Review Letters [1], I received a telephone call from Bill WING and learned that his group has observed [9] the infrared spectrum of D_3^+ .

4. Discussion

The success of our observation of the infrared spectrum of H_3^+ seems to open the following paths for future research in various fields: (1) systematic infrared spectroscopy of molecular ions in discharges, (2) in situ monitoring of molecular ions for ion mobility measurements and ion-molecule reactions, (3) detection of H_3^+ in interstellar space.

An observation of the infrared spectrum of H_3^+ was attempted on March 23-25, 1981 with the high resolution Condé Fourier transform spectrometer on the 4 m Mayall telescope of the Kitt Peak National Observatory [10]. The result was negative. More observations will be attempted for this important and fundamental molecular ion.

References

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