Spectroscopy and Dynamics of H_3^+ in the Laboratory and in Space

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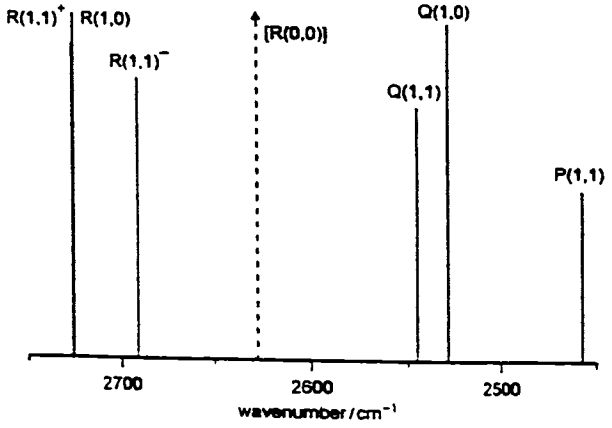
The recent detection of interstellar H_3^+ in dense[1] and diffuse[2] clouds and towards the Galactic Center[3] has revealed the remarkable abundance and ubiquity of this fundamental molecular ion which had been proposed as the cornerstone of the ion–neutral reaction scheme of interstellar chemistry.

1. The H_3^+ Spectrum

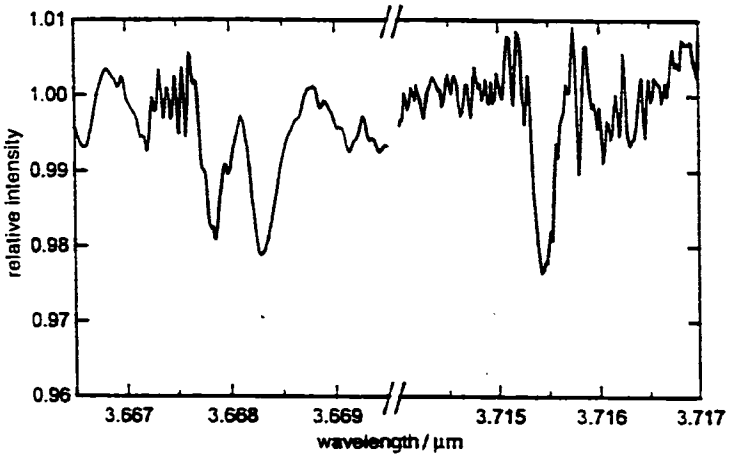
Because of the absence of electronic spectrum due to lack of well bound excited states and the absence of rotational spectrum due to the highly symmetric equilateral triangle structure, the ν_2 infrared vibration–rotation band with the origin at 2521.3 cm^{-1} is the most straightforward means to detect and study interstellar H_3^+. The band is relatively free from spectral lines of other molecules since it is lower in energy than the hydrogen stretching bands of O–H, N–H and C–H bonds and is higher than stretching bands of heavier atoms C ≡ C, C ≡ N, N= O and CO. This is clearly demonstrated in the extremely pure infrared emission of H_3^+ from Jupiter which is now used for studying plasma activities in Jovian ionospheres.[4] This freedom from other spectral lines is even more advantageous for search in interstellar H_3^+ because of relatively minor atmospheric interference.

Because of the low temperature of interstellar space and the large rotational constants of H_3^+, only the two lowest levels are significantly populated, that is, the (J,K) = (1,0) level of ortho–H_3^+ and the (1,1) level of para–H_3^+ (the (0,0) level is not allowed by the Pauli principle). We thus can use the six spectral lines shown in Fig. 1. Out of these six lines, the three R branch lines around 2700 cm^{-1} are most useful because of their relative freedom from interference and less background radiation. In particular the doublet of R(1,0) and $R(1,1)^+$ separated by 0.321 cm^{-1} is convenient for confirming detection of weak lines.



2. H_3^+ in Diffuse Clouds

Over many years since 1973 when ion–neutral chemistry was introduced as the major mechanism for the formation of interstellar molecules,[5,6] the presence of interstellar H_3^+ has been assumed. The long awaited detection of H_3^+ in molecular clouds[1] has given most direct evidence supporting such an assumption and "the sigh of relief is audible right around the world of [molecular] astronomy."[7] Our subsequent unexpected detection of strong H_3^+ absorption in diffuse clouds,[2,3] however, has introduced a new headache into interstellar chemistry. This time it is not the lack of observation but seemingly overabundance of H_3^+ that is puzzling. The H_3^+ absorption lines observed towards the direction of the highly obscured visible star Cygnus OB2 No. 12 are shown in Fig. 2.



The integrated absorption intensity gives the total H_3^+ column density of 4×10^{14} cm^{-2} which is comparable to those towards molecular clouds GL2136 (4.0×10^{14} cm^{-2}) and W33A (6.0×10^{14} cm^{-2}).

The attractive aspect of the H_3^+ spectral interpretation is that its chemistry is simple and its number density may be estimated readily. Interstellar H_3^+ is produced by cosmic ray ionization of H_2 into H_2^+ followed by the highly efficient reaction $H_2 + H_2^+ \rightarrow H_3^+ + H$ with the Langevin rate. Since the latter process is much more rapid than the former, the rate of the H_3^+ production is given by $\zeta n(H_2)$ where $\zeta \sim 10^{-17}$ s^{-1} is the cosmic ray ionization rate and $n(H_2)$ is the number density of H_2. The main destruction mechanism of H_3^+ is its recombination with an electron whose rate is $k_e\, n(H_3^+)\, n(e)$ where $k_e \sim 10^{-7}$ $cm^3\, s^{-1}$ is the recombination rate constant. Equating the production and the destruction rates, we estimate the H_3^+ number density in diffuse clouds to be

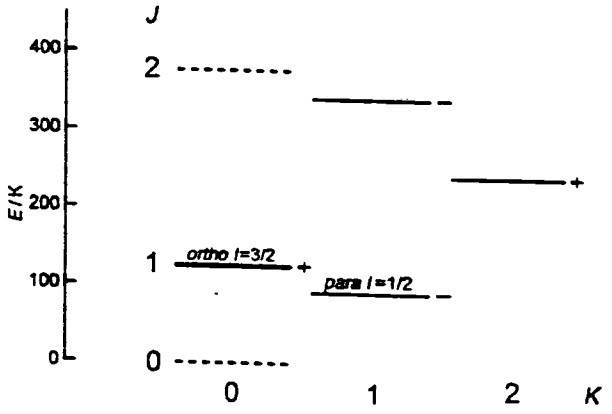
$$n(H_3^+) \sim \frac{\zeta}{k_e} \frac{n(H_2)}{n(e)} \sim 10^{-6}\, cm^{-3}$$

for $n(H_2)/n(e) \sim 10^4$. This value is two to three orders of magnitude lower than the H_3^+ number density in dense clouds. Since the observed H_3^+ column densities are comparable between the two clouds, we are led to the conclusion that the H_3^+ column length of diffuse clouds is larger than that of dense clouds by two to three orders of magnitude. Thus if we assume an isotropic distribution of clouds, the total H_3^+ is $10^4 \sim 10^6$ times higher in diffuse clouds than in dense

clouds! If we assume two dimensional isotropy, the number is $10^2 \sim 10^3$ but is still very large. This absurdity (?) may be saved if the value of the recombination rate constant k_e is lower than the reported values.[8,9,10] In this respect a better theoretical understanding of the recombination rate such as that discussed in this meeting by Guberman is very desirable. We should also be able to settle this issue observationally by studying more diffuse clouds. Such an observation is scheduled at KPNO from July 2–5 this summer.

3. Ortho–H_3^+ and Para–H_3^+

As mentioned earlier, the ground rotational levels of H_3^+ that are significantly populated in interstellar space are the (1,0) level of ortho–H_3^+ and (1,1) of para–H_3^+, as shown in Fig. 3.



Unlike in neutral molecules such as NH_3, the thermal equilibration between the ortho– and para–species of H_3^+ is very rapid because of the proton scrambling via the proton hop reaction

$$H_3^+ + \tilde{H}_2 \rightarrow H\tilde{H}_2^+ + H_2$$

and the proton exchange reaction

$$H_3^+ + \tilde{H}_2 \rightarrow H_2\tilde{H}^+ + H\tilde{H}$$

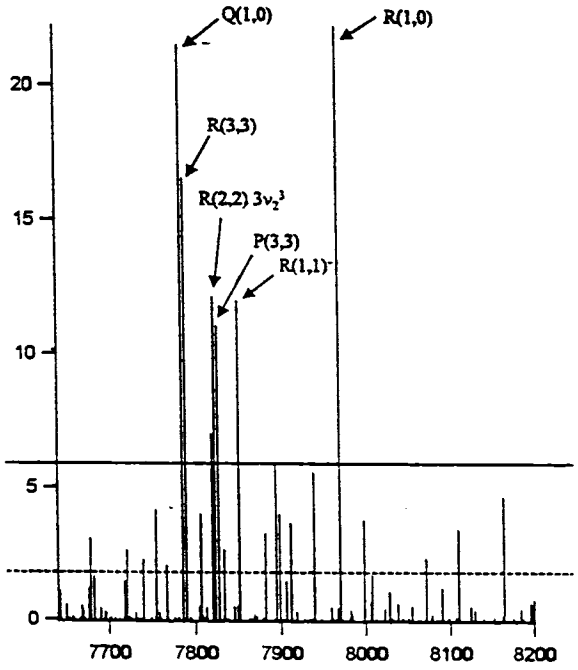
both of which have the Langevin rate. This fast thermalization allows us to measure temperature of clouds from the H_3^+ spectrum.

A laboratory study on chains of such reactions paying special attention to nuclear spin modifications[11] has led us to speculate that the equilibration of interstellar ortho–H_2 and para–H_2 is effected by the reactions with H_3^+ rather than with H^+ as hitherto assumed.[12] A model calculation is in progress to establish this idea.

4. Laboratory Spectroscopy of the $\nu_1 + 2\nu_2(2)$ Band

Being the simplest stable polyatomic system, H_3^+ provides a benchmark test for the accuracy and validity of *ab initio* variational calculations of the vibration–rotation levels. Our experimental observation for higher and higher rovibrational levels has served as a guide for these tests. The observation is also useful for future studies of hot astronomical objects.

We have set up a near infrared spectrometer covering from 7650 to 8200 cm^{-1} using a cavity controlled New Focus diode laser and applied it to observation of the $\nu_1 + 2\nu_2(2)$, combination band. A one meter plasma tube (Black Widow) with liquid N_2 cooling was used to produce H_3^+. A stick diagram of the theoretical spectrum is shown in Fig. 4. So far the six spectral lines indicated by arrows have been observed.



We are in the process of increasing the sensitivity of our spectrometer by a factor of 4 by adopting unidirectional multiple passing of two opposing beams. This will allow us to reduce the effective noise level down to the level shown in Fig. 4 by the broken line and lead us to observation of approximately 20 spectral lines.

References

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