H_3^+ between the stars

By Thomas R. Geballe

Gemini Observatory, 670 N. A'ohoku Place, Hilo, HI 96720,USA

The presence of H_3^+ in the interstellar medium was forecast almost four decades ago. Almost three decades ago it was asserted that its reactions with neutral molecular and atomic species directly lead to the production of many of the interstellar molecules that have been discovered by radio and infrared astronomers. With the recent detection of H_3^+ in interstellar space, astronomers finally have direct confirmation of H_3^+ as the foundation of ion-molecule interstellar chemistry. Although many questions remain to be answered, it is clear that H_3^+ is a unique tool for understanding the properties of interstellar clouds.

Keywords: infrared spectroscopy, interstellar clouds, interstellar molecules

1. Dark Clouds and the Role of H_3^+

One-half century ago astronomers were just becoming aware that interstellar space contains considerable quantities of hydrogen, in both atomic and molecular form. Almost four decades ago Martin *et al.* (1961) pointed out to astronomers that, where interstellar H_2 is ionized, H_3^+ is produced rapidly as a result of the reaction,

$$H_2^+ \ + \ H_2 \ \rightarrow \ H_3^+ \ + \ H, \tag{1.1}$$

by which H_3^+ is created in abundance in laboratory hydrogen plasmas. Molecular hydrogen is the dominant hydrogenic species in dark clouds, where dust particles prevent the penetration of ultraviolet radiation. Solomon and Werner (1971) recognized that within dark clouds cosmic ray ionisation of H_2,

$$H_2 \ + \ \text{c.r.} \ \rightarrow \ H_2^+ \ + \ e^- \ + \ \text{c.r.}, \tag{1.2}$$

is the principal means of production of H_2^+ and, through it, H_3^+. The flux of cosmic rays is such that an individual H_2 molecule is ionised roughly once per billion years. In a cloud of density 10^4 cm^{-3} the H_2^+ survives for at most a day before undergoing reaction 1.1.

At about the same time discoveries by radio and millimetre wave spectroscopists of a variety of simple molecules (including free radicals) in dark clouds (e.g., Rank *et al.* 1971) were being reported. The discoveries clearly implied the existence of an active chemistry in these cold and rarified regions. The proposal by Klemperer (1970) that an unidentified intense line at a wavelength of 3.4 mm, originally referred to as "X-ogen", was emitted by HCO^+ (later confirmed when the corresponding line of the ^{13}C isotope of that molecular ion was detected by Snyder *et al.* 1976) suggested that gas phase ion-neutral reactions, which have no activation energy barriers, could be important in dark clouds.

In 1973 Watson and, independently, Herbst & Klemperer incorporated the forgoing ideas into detailed models for the gas-phase chemistry of dark clouds, proposing networks of ion-molecule reactions as the means of production for the simple molecules observed in dark clouds. Herbst & Klemperer approximately reproduced the observed abundances of some of these molecules. These two papers revealed for the first time the fundamental importance of H_3^+. In their models as well as in those of a multitude of related papers that have followed, H_3^+ is the principal initiator of reaction chains via the generic reaction,

$$H_3^+ + X \rightarrow HX^+ + H_2, \tag{1.3}$$

where X is almost any constituent of the cloud (He, O_2 and N are exceptions). The product ion HX^+ then combines with other species through

$$HX^+ + Y \rightarrow XY^+ + H, \tag{1.4}$$

and so on, creating networks of reactions, as first detailed by Watson and by Herbst & Klemperer. Later papers enlarged and refined the early models for dark clouds (e.g., Lee *et al.* 1996) and extended and adapted the basic ideas to diffuse clouds (van Dishoeck & Black 1986). Reactions 1.3 serve as sinks for H_3^+, severely reducing its steady-state abundance, since rate coefficients of H_3^+ with the most abundant species are large. Dissociative recombination on electrons (reaction 1.3 with $X = e^-$) has a very large coefficient and is an important sink where electrons densities are sufficiently high.

2. Search strategies and early searches

Although compelling evidence for the importance of ion-molecule chemistry in the insterstellar medium has abounded since the 1970's, the ultimate test of its significance would be the direct detection of H_3^+ and the determination of its abundance. To detect H_3^+ requires spectroscopic measurements, but in which band and at what wavelength? H_3^+ has no well-bound excited electronic states, and hence no ultraviolet or visible line spectrum. Likewise, its lack of a permanent dipole moment prohibits a pure rotational spectrum, which would occur at far infrared and sub-millimetre wavelengths. The symmetric ν_1 vibration does not induce a dipole moment and thus has no associated vibration-rotation transitions. However, the asymmetric ν_2 vibration does induce a dipole moment. Following the laboratory measurements of the fundamental vibration-rotation band by Oka (1980), the ν_2 band could be used to search for H_3^+. In view of the expected weakness of the H_3^+ lines it is fortuitous that the ν_2 fundamental near 4 μm and first overtone near 2 μm (which is used for studies of planetary ionospheres) do not coincide closely with bands of astrophysically abundant molecules and, in addition, occur at infrared wavelengths which are for the most part accessible to ground-based telescopes.

Quiescent dark clouds are the most obvious sites to search for interstellar H_3^+. Since these clouds are usually very cold (typically 10–50 K), only the lowest rotational levels of the ground vibrational state of the molecule are populated and one is required to search for the vibration-rotation lines associated with those levels, in absorption against the continua of stars or protostars either embedded in the clouds or situated behind them (figure 1). Six lines are potential targets; four from

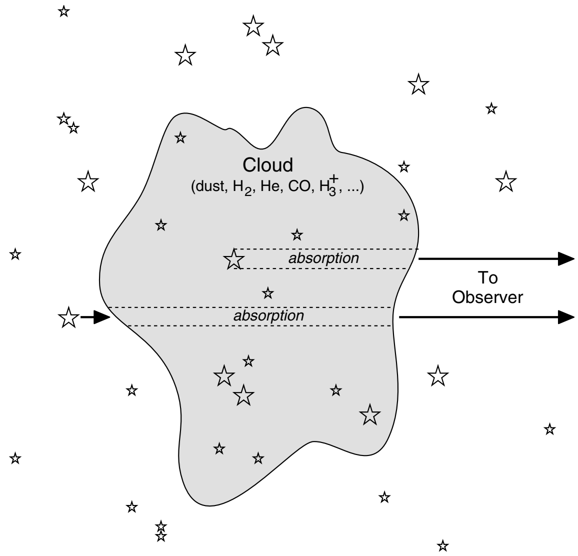

Figure 1. Absorption spectroscopy of dark clouds.

the lowest (J=1, K=1) level of para-H_3^+ and two from the lowest (J=1, K=0) level of ortho-H_3^+, which is 32.9 K higher (figure 2). Note that the J=0, K=0 level is forbidden by the Pauli exclusion principle. In a dark cloud the ortho/para ratio is thermalised by proton hops and transfers of hydrogen atoms between H_3^+ and its most frequent collision partner, H_2 (reaction 1.3 with X=H_2). The ground (para) state is more highly populated than the lowest ortho state at temperatures less than T $\approx$ 50 K. At 50 K molecules in the next lowest level (2,2) constitute less than five percent of the total. Even with essentially all of the H_3^+ in the two lowest energy levels, the narrow absorption lines from those levels are expected to be very weak because of the miniscule steady state abundance of H_3^+. Thus, detection of H_3^+ requires the use of sensitive high resolution infrared spectrometers, large telescopes, bright, yet highly obscured astronomical sources of infrared continuum, and careful attention to both wavelength calibration and the removal of atmospheric and instrumental spectral features.

The possibility of detecting interstellar H_3^+ lines in emission also should be considered. Detection of weak emission lines often is more straightforward than detection of absorption lines, because a source of background continuum radiation is not required and emission from a much larger solid angle of cloud or nebula can be observed. However, in order to detect line emission one must find environments for which not only does H_3^+ exist, but also a significant fraction of it is vibrationally excited. Within some clouds shock-excitation results from the interaction of high velocity winds, from embedded protostars or from supernovae ejecta, with the ambient gas. In the interaction zone collisional vibrational excitation of H_3^+ and subsequent line emission should occur, as they do in the case of H_2. Conditions in planetary nebulae which are ejecting extensive circumstellar molecular envelopes also can result in significant vibrational excitation of H_3^+. However, in both of these environments the columns of hot H_3^+ are very short compared to the dimensions of the cloud or nebula, making detection difficult.

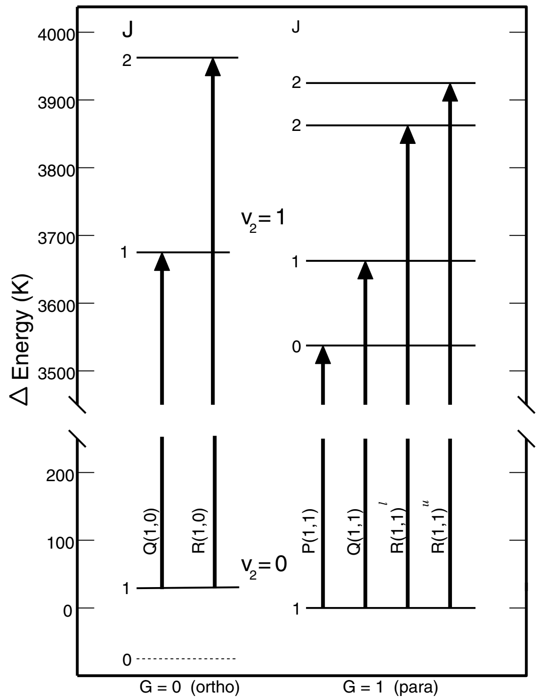

Figure 2. Vibration-rotation transitions from the lowest ortho and para states of H_3^+.

In the 1980's and the first half of the 1990's several attempts were made to detect H_3^+ in a variety of interstellar environments. All of these failed. During this period, however, the resolutions and sensitivities of infrared spectrometers improved, largely due to the advent of 2-dimensional arrays of infrared detectors. Telescope pointing and tracking accuracies and image sharpness also were considerably enhanced. Each of these improvements, along with with the experience gained from the early searches, contributed to the eventual detection of H_3^+.

3. Detection in dark clouds

The first detections of H_3^+ in interstellar space (Geballe & Oka 1996) were made toward the bright infrared sources W33A and GL2136. These objects are high mass protostars still located deep inside their natal clouds which were the targets of the search. The initial detections, obtained on 29 April 1996 at the United Kingdom Infrared Telescope (UKIRT) on Mauna Kea, were decisively confirmed on July 15 of that year. Both nights' observations utilised UKIRT's superb infrared spectrometer CGS4 (Mountain *et al.* 1990), which can obtain high resolution spectra in narrow wavelength intervals, and focussed on the closely spaced pair of ortho and para lines near 3.67 μm. The detected lines are only 1-2 percent deep, much weaker than nearby atmospheric absorption lines of methane, and can barely be discerned in the unratioed spectra (figure 3). Observing from high and dry Mauna Kea was one key to the successful detection of this line pair, as at lower altitude sites the telluric methane lines are stronger and blend with nearby lines of water vapor to make the crucial wavelengths nearly opaque. A second key was to repeat the observations at

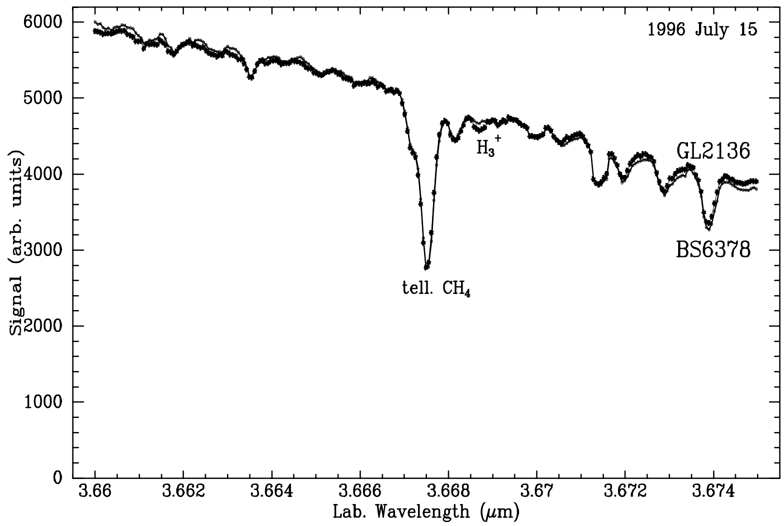

Figure 3. Raw spectra of GL2136 (thick line) and the calibration star, BS6378, in a spectral interval containing the H_3^+ ortho-para doublet, whose location is indicated.

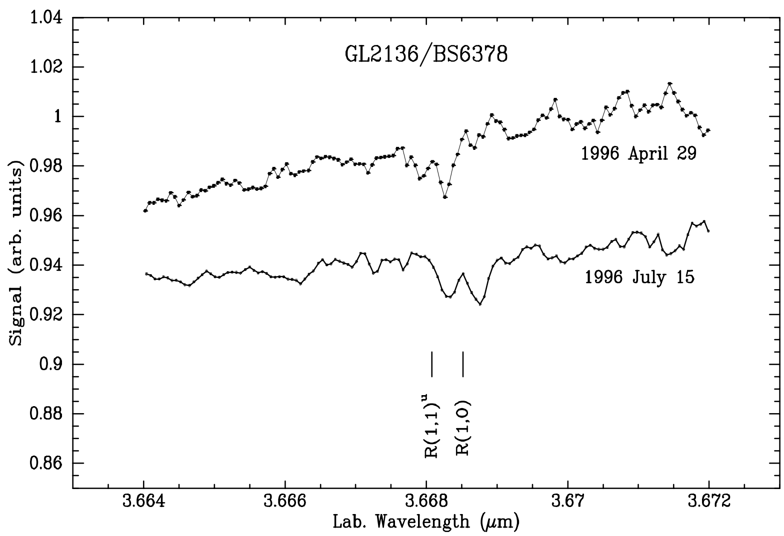

Figure 4. Ratioed spectra of GL2136 on two dates in 1996. The rest wavelengths of the H_3^+ R(1,1)^u (para) and R(1,0) (ortho) lines are indicated. The resolution is 15 km s^{-1}.

a later date, using the change in the earth's orbital velocity to change the Doppler-shift of the astronomical lines relative to the telluric lines (figure 4). The correct wavelength shift between April and July was observed, a convincing demonstration of the reality of the detection.

The measurement of lines of both ortho and para H_3^+ in a cold dark cloud allows the cloud temperature and the H_3^+ column density, N(H_3^+), to be determined directly. For the clouds in which W33A and GL 2136 are situated mean temperatures of approximately 35 K and H_3^+ column densities of 6×10^{14} cm^{-2} and 4×10^{14} cm^{-2}, respectively, were found (Geballe & Oka 1996). Molecular hydrogen, the dominant constituent of dark clouds, has not yet been detected toward W33A and GL2136. However, assuming the standard dust-to-gas ratio found in the interstellar medium, estimates of the N(H_2) can be obtained from the depth of the 9.7 μm silicate dust absorption observed toward these objects. These estimates yield values for N(H_3^+)/N(H_2) of 2×10^{-9} in each of these clouds. This compares to values of $\sim 10^{-4}$ for the most abundant non-hydrogenic molecule, CO, in dark clouds. H_3^+ indeed is a remarkably rare constituent of these dark clouds.

The detections in W33A and GL2136 have prompted searches for H_3^+ in many additional dark clouds, with detections reported in several of them (McCall *et al.* 1999; Kulesa *et al.* 1999). In all but one case, the line strengths and derived column densities are comparable to those found toward W33A and GL2136. With larger telescopes and improved spectrometers now coming into use it is likely that the number of detections will increase considerably in the next few years.

4. Testing the ion-molecule model

In the ion-molecule model of dark cloud chemistry the steady-state abundance of H_3^+ is straightforward to calculate and leads to a simple and noteworthy result. Production of H_3^+ is via reaction (1.2), where the cosmic ray ionisation rate, ζ, is thought to be $\sim 3 \times 10^{-17}$ sec^{-1} (e.g., see McCall *et al.* 1999). Destruction is via reactions of type (3); of these CO (if not largely frozen out on grains when $T < 20$ K) is the dominant reactant ($k_{CO} = 1.8 \times 10^{-9}$ sec^{-1}, Anicich & Huntress 1986), although the reaction of H_3^+ with atomic oxygen also is important. Despite a high reaction rate, dissociative recombination on electrons is unlikely in dark clouds because of the very low electron concentrations. Then, equating the rates of formation and destruction,

$$\zeta n(\mathrm{H_2}) \approx \mathrm{k_{CO} n(H_3^+) n(CO)}, \tag{4.1}$$

relating in one simple equation perhaps the three most important molecules in astronomy. Using the result from models of dark cloud chemistry that n(CO)/n(H_2) is approximately constant at 1.5×10^{-4} (Lee *et al.* 1996), this equation reduces to

$$n(\mathrm{H_3^+}) \approx 1 \times 10^{-4}\ \mathrm{cm^{-3}}. \tag{4.2}$$

That the number density of H_3^+ is *constant* in dark clouds is highly unusual; the number densities of other molecular constituents of the cloud scale as the total density. The behavior of H_3^+ derives from its rates of production and destruction both scaling with the first power of the cloud density, whereas production rates for most other molecules scale as density squared.

Thus, the fractional abundance of H_3^+, n(H_3^+)/n(H_2) $\approx 10^{-4}$/n(H_2), varies inversely with cloud density. If the cloud density is known, 10^{-4}/n(H_2) can be compared with N(H_3^+)/N(H_2), where N(H_2) has been measured or estimated (e.g. from the silicate feature). In general cloud densities are not accurately determined; however, studies of the collisional excitation of various molecular species imply that densities in the W33A and GL2136 clouds, as well as in most other clouds where

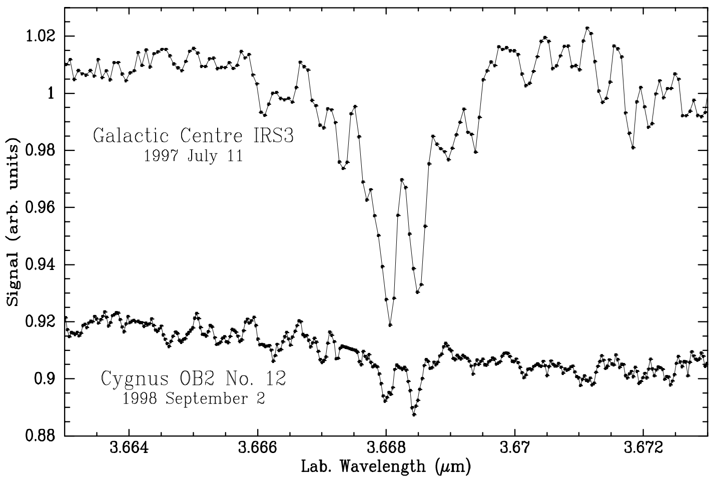

Figure 5. Spectra of the H_3^+ doublet toward the Galactic Centre source IRS3 at a resolution of 15 km s^{-1} and the reddened star Cygnus OB2 No. 12 at a resolution of 9 km s^{-1}). H_3^+ in diffuse clouds causes the narrow features seen towards the Cygnus source and probably also towards IRS3.

H_3^+ has been sought, are 10^4 – 10^5 cm^{-3}. An additional uncertainty is that densities probably vary significantly within these clouds. For the above density range $n(H_3^+)/n(H_2)$ is $10^{-8} - 10^{-9}$. The values of 2×10^{-9} for $N(H_3^+)/N(H_2)$ found toward W33A and GL2136 fall within this range, as do the values toward other sources for which H_3^+ has been detected (McCall *et al.* 1999). For clouds where only upper limits are available for $N(H_3^+)$, the upper limits on $N(H_3^+)/N(H_2)$ are greater than 10^{-9}, and hence predicted values of $n(H_3^+)/n(H_2)$ are not ruled out.

A second test is to use the observed column densities of H_3^+ to calculate the lengths of the absorbing columns of the clouds via the relation $L \approx N(H_3^+)/n(H_3^+) \approx 10^4 N(H_3^+)$. For typical column densities (e.g., 5×10^{14} cm^{-2}) the derived lengths are 1-2 pc (McCall *et al.* 1999), where 1 pc = 3.086×10^{18} cm. These are comparable to the measured linear extents of the clouds on the sky, as would be expected. Where upper limits to $N(H_3^+)$, and hence L, have been found, the results can be reasonably explained by shorter absorption columns and/or denser clouds.

Thus, although only crude checks can be made at present, the derived abundances of H_3^+ in dark clouds confirm the importance of cosmic-ray induced ion-molecule chemistry in those environments.

5. H_3^+ in diffuse interstellar gas

In the course of the aforementioned survey of dark clouds for H_3^+ by McCall *et al.* (1999), strong absorption by the 3.67 μm doublet was discovered along lines of sight to two infrared sources in the Galactic centre on 1997 July 11 (Geballe *et al.* 1999; figure 5). The visual extinction toward the Galactic centre, ∼30 mag, is comparable to those toward infrared sources in dark clouds in which H_3^+ had been found, but $N(H_3^+)$ is nearly an order of magnitude greater. The line of sight to the Galactic center, some 8 kpc long, is known to contain both dark clouds and diffuse (low density) clouds which are penetrable at least to some extent by visible radiation. (McFadzean *et al.* 1986). Thus interpretation of the spectra is not obvious, although it is clear from the velocity profile of the absorption that some of the H_3^+ is located in dark clouds known from radio/millimetre and infrared spectroscopy.

The previously unforeseen possibility that H_3^+ in low density clouds also could be detectable prompted a search (on the same night) for H_3^+ toward one of the archetypal probes of the diffuse interstellar medium, the visible star Cygnus OB2 No. 12, which is obscured by 10 visual magnitudes. The H_3^+ doublet was easily detected there (figure 5). Analysis of this spectrum and one obtained later containing an additional line yields $N(H_3^+) = 3.8 \times 10^{14}$ cm^{-2}, comparable to that in dark clouds, and T$\sim$30 K (McCall *et al.* 1998).

Understanding this result has proved more elusive than understanding the observations of H_3^+ in dark clouds. In a classical diffuse cloud H and H_2 are roughly equally abundant and there is little CO (van Dishoeck & Black 1986). Little H is ionised by ultraviolet photons except at the edges of the cloud. The H_2 within the cloud also is shielded from ionisation, which requires photons of $\geq$15.4 eV, by the ionisation of atomic hydrogen (requiring $\geq$13.6 eV photons) on the periphery. Within the cloud H_3^+ is formed in the same way as in dense clouds (reaction 1.2 followed by 1.1). Destruction of H_3^+, however, is expected to be dominated by electron recombination, because the essentially complete single ionisation of gaseous atomic carbon produces a much higher concentration of electrons than in dark clouds. (Despite depletion onto dust particles, atomic carbon is abundant in diffuse clouds and requires only $\geq$11.3 eV photons for ionisation to C^+.) Cardelli *et al.* (1996) and Sofia *et al.* (1997) have measured the abundance ratio of atomic carbon to hydrogen, z_C, to be 1.4 $\times 10^{-4}$ in diffuse clouds. As in the case of dark clouds, the density of the H_3^+-destroyer (in this case electrons, rather than CO), roughly scales with the hydrogen density. Thus, a simple expression again is obtained for the steady state density of H_3^+ (Geballe *et al.* 1999),

$$n(H_3^+) \approx \zeta/(4k_e z_C) \approx 1 \times 10^{-7}\mathrm{cm}^{-3}, \tag{5.1}$$

where $k_e = 2.1 \times 10^{-6}$ T$^{-0.5}$ cm^3 s^{-1} (Sundström *et al.* 1998) is evaluated at 30 K. Once again the density of H_3^+ is roughly constant, but in a diffuse cloud its value is roughly three orders of magnitude less than in a dark cloud. As the total gas density in a typical diffuse cloud is also a few orders of magnitude less, concentrations of H_3^+ are comparable in the two environments.

If the absorbing low density cloud or collection of clouds between Cygnus OB2 No. 12 and the earth are as described above, the aggregate absorption path length must be $\sim$ 1 kpc in order to produce the observed line strengths. This length, roughly half the 1.7 kpc distance from the earth to the Cygnus OB2 association (Torres-Dodgen *et al.* 1991), seems physically unreasonable. The mean gas density along such an absorbing path, $\sim$10 cm^{-3}, is insufficient for H_2 to be relatively abundant and hence for H_3^+ to form. It also is inconsistent with observations of C_2 (Souza & Lutz 1977; Gredel & Münch 1994), and CO (Geballe *et al.* 1999) toward Cygnus OB2 No. 12, which imply that the C_2 is located in clouds with densities at least an order of magnitude higher and that the CO exists at even higher densities. Different values for ζ and/or k_e could explain the discrepancy. The cosmic ray ionisation rate may be larger in the vicinity of an association of hot stars such as Cygnus OB2 than in an isolated dark cloud, but the difference is unlikely to be an order of magnitude. Alternatively, at low temperatures k_e may have to be considerably smaller to bring the above model into agreement with the observations.

Recently Cecchi-Pestellini & Dalgarno (2000) have suggested that much of the material obscuring Cygnus OB2 No. 12 is in clumps of gas containing both dense and diffuse components. Using a somewhat higher cosmic ray ionisation rate than adopted here, they fit the observations of H_3^+, C_2, and CO with nine such cloudlets of density 10^2 cm^{-3}, embedded in some of which are much higher density cores where most of the carbon is in the form of CO. The summed column length through these clumps is ∼60 pc, far less than the derived H_3^+ absorption length of 1 kpc for classical diffuse clouds. High resolution spectroscopy of C_2 (Gredel & Münch 1994) shows the presence of four distinct low density cloudlets along the line of sight to Cygnus OB2 No. 12, while millimetre and infrared spectroscopy of CO (Geballe *et al.* 1999) demonstrates that at least two of these contain CO and that some of the CO probably is located in dense regions. More sensitive measurements may reveal additional clumps.

6. Conclusion

The observations to date demonstrate that, as predicted, H_3^+ is an ubiquitous constituent of dark clouds. The detected column densities and upper limits are consistent with its production by cosmic ray ionisation of H_2 and destruction via reactions with neutrals which form the base of an extensive ion-molecule reaction network. Thus the detection of H_3^+ provides a crowning confirmation of the theories of Herbst & Klemperer and Watson, proposed nearly three decades ago to account for the rich chemistry observed in these clouds.

Because its density is constant in dark clouds, H_3^+ is a unique tool for astronomers, with the potential of determining two fundamental parameters: line of sight distances in the clouds and accurate values of ζ, the cosmic ray ionisation rate. However, a glance at equation 4.1 reveals that a measurement of N(H_3^+) only determines the product of ζ and the column length. More sophisticated approaches are needed to determine the values of these fundamental parameters. These could involve, for example, more detailed modelling of well-observed dark clouds to determine line of sight distances and density profiles. Direct measurements of the column densities of H_2 and CO can provide additional constraints. Alternatively, statistical studies of H_3^+ in many clouds, using background infrared sources could provide multiple line of sight distances through each cloud, to be compared with the cloud's linear extent on the sky. Whatever strategies are employed, observational progress clearly requires the use of the new and future generations of large telescopes and sensitive spectrometers, as many of the background sources will be considerably fainter than those that have been utilised to date to detect H_3^+.

The surprisingly large amounts of H_3^+ found toward the Galactic centre and especially toward Cygnus OB2 No. 12 suggest that our understanding of the physical conditions of the gas on these sight lines needs refinement. The model of Cecchi-Pestellini and Dalgarno (2000) for the material in front of Cygnus OB2 reminds us that environments intermediate between classical dark and classical diffuse clouds can exist. It also indicates that spectroscopy of H_3^+, whose steady state abundance is highly sensitive to the densities of the neutrals, H_2 and CO, and the electrons, can play a key role in characterising these environments. Measurements of H_3^+, CO and other molecules toward additional obscured stars in Cygnus OB2 along with searches for H_3^+ in additional objects obscured by diffuse gas are important next steps towards understanding these largely low density environments.

The discovery of H_3^+ toward the Galactic centre immediately suggests the possibility of detecting H_3^+ in extragalactic environments. An initial search on UKIRT is already under way, but it is clear that observations using 8-10m telescopes will be required to reach more than a few of the promising candidate galaxies. In the longer term, with telescopes such as the Next Generation Space Telescope and even larger aperture ground-based telescopes, we can anticipate that spectroscopy of H_3^+ in external galaxies, in combination with observations of CO and other molecules, will be a standard technique used to probe in detail the properties of interstellar gas in the distant universe.

I wish to thank T. Oka and B. J. McCall, not only for helpful comments during the preparation of this paper, but also for many enlightening discussions during our years of collaboration. I am especially grateful to the staff, present and past, of the United Kingdom Infrared Telescope and indeed to all of those who have supported it.

References

Anicich, V. G. & Huntress, W. T., 1986, *Astrophys. J. Suppl.*, **62**, 553.
Cardelli, J. A., Meyer, D. M., Jura, M. & Davage, B. D., 1996, *Astrophys. J.*, **467**, 334.
Cecchi-Pestellini, C. & Dalgarno, A., *Mon. Not. R. astr. Soc.*, 2000, in press.
Geballe, T. R., Baas, F. & Wade, R., 1989, *Astrophys. J.*, **342**, 855.
Geballe, T. R. & Oka, T., 1996, *Nature*, **384**, 334.
Gredel, R. & Münch, G., 1994, *Astron. Astrophys.*, **285**, 640.
Herbst, E. & Klemperer, W., 1973, *Astrophys. J*, **185**, 505.
Klemperer, W., 1970, *Nature*, **227**, 1230.
Kulesa, C. A., Black, J. H. & Walker, C. K., 1999, *Bull. Am. Astron. Soc.*, **194**, 47.09.
Lee, H.-H., Bettens, R. P. A. & Herbst, E., 1996, *Astron. & Astrophys. Suppl.*, **119**, 111.
Martin, D. W., McDaniel, E. W., & Meeks, M. L., 1961, *Astrophys. J.*, **134**, 112.
McCall, B. J., Geballe, T. R., Hinkle, K. H. & Oka, T., 1998, *Science*, **279**, 1910.
McCall, B. J., Geballe, T. R., Hinkle, K. H. & Oka, T., 1999, *Astrophys. J.*, **522**, 338.
McFadzean, A. D., Whittet, D. C. B., Longmore, A. J. & Adamson, A. J. 1989, *Mon. Not. R. astr. Soc.*, **241**, 873.
Mountain, C. M., Robertson, D. J., Lee, T. J. & Wade, R., 1990, *Proc. Soc. Photo-Opt. Industr. Eng.*, **1235**, 25.
Oka, T., 1980, *Phys. Rev. Lett*, **45**, 531.
Rank, D. M., Townes, C. H. & Welch, W. J., 1971, *Science*, **174**, 1083.
Snyder, L. E., Hollis, J. M., Lovas, F. J. & Ulich, B. L., 1976, *Astrophys. J.*, **209**, 67.
Sofia, U. J., Cardelli, J. A., Gurein, K. P. & Meyer, D. M.. 1997, *Astrophys. J.*, **482**, L105.
Solomon, P. M. & Werner, M. W., 1971, *Astrophys. J.*, **165**, 41.
Souza, S. P. & Lutz, B. L., 1977, *Astrophys. J.*, **216**, L49.
Sundström, G., Mowat, J. R., Danared, H., Datz, S., Broström, L. *et al.*, 1998, *Science*, **263**, 785.
Torres-Dodgen, A. V., Tapia, M. & Carroll, M. 1991, *Mon. Not. R. astr. Soc.*, **249**, 1.
van Dishoeck, E. F. & Black, J. H., 1986, *Astrophys. J Suppl.*, **62**, 109.
Watson, W.D., 1973, *Astrophys. J.*, **182**, L73.