PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

The abundance and excitation of interstellar H_3^+

John H. Black

Phil. Trans. R. Soc. Lond. A 2000 **358**, 2515-2521
doi: 10.1098/rsta.2000.0664

10.1098/rsta.2000.0664

THE ROYAL SOCIETY

The abundance and excitation of interstellar H_3^+

By John H. Black

Onsala Space Observatory, Chalmers University of Technology,
S-439 92 Onsala, Sweden

Observations of interstellar H_3^+ test a central part of theories of ion–molecule chemistry in space. It is possible to measure the abundances of cold H_2, of H_3^+, and of CO in the same parcel of gas by means of infrared absorption spectroscopy toward obscured stars. The observed populations of the lowest rotational levels of H_2 and H_3^+ confirm that reactive collisions tend to thermalize the ortho- and para-nuclear-spin species in interstellar clouds. The rotational population distributions in CO provide diagnostic information on physical conditions (density and kinetic temperature). Taken together, observations of these three molecules make it possible to infer the rate of ionization in neutral, molecular clouds by penetrating cosmic rays or X-rays. Recent observations and their interpretation are summarized. The prospects for detecting weak, pure rotational transitions of H_3^+ are considered.

Keywords: interstellar molecules; infrared spectroscopy; molecular ions

1. Infrared absorption spectroscopy

The H_3^+ molecular ion plays a pivotal role in interstellar gas-phase chemistry. Because it lacks strong transitions in other parts of the electromagnetic spectrum, interstellar H_3^+ is best studied through the technique of infrared absorption spectroscopy. Lines of the ν_2 fundamental vibration–rotation band at wavelengths of 3.6–4.1 µm are formed in cold interstellar gas that lies between the observer and a background star. The star must be bright enough for spectroscopy at high resolution (preferably a resolving power $R = \lambda/\delta\lambda \approx 10^5$ or higher) despite the extinction of light by the interstellar dust particles that accompany the molecular gas. The value of H_3^+ as a chemical and physical diagnostic tracer is greatly enhanced by the fact that both H_2 and CO are also observable by the same technique at wavelengths between 2 and 5 µm. Thus it is worthwhile to summarize the general features of high-resolution infrared absorption spectroscopy that make this technique so valuable in the study of dilute astrophysical gases such as interstellar clouds.

First, the tests of interstellar chemical theory are direct and more readily interpreted than those posed by mm-wave emission-line observations. Even though cold H_2 in thick interstellar clouds is detectable only by means of its quadrupole transitions, its abundance is sufficiently higher than those of H_3^+ and CO that its strongest $v = 1 \leftarrow 0$ absorption lines are at worst only a few times weaker than those of the CO first overtone band $v = 2 \leftarrow 0$ at nearly the same wavelength and those of the ν_2 fundamental band of H_3^+. The first direct detection of cold H_2 in a thick interstellar cloud was an important advance in interstellar studies (Lacy *et al.* 1994). Not only did it confirm the expected large concentrations of H_2, but it also offered a direct calibration of the CO/H_2 abundance ratio. CO and its isotopomers are widely used as surrogate tracers of molecular hydrogen.

Second, various other non-polar molecules that lack radio frequency spectra are observable through infrared absorption spectroscopy. Among the important non-polar species detected in interstellar clouds in this way are CH_4, C_2H_2, and CO_2 (Lacy *et al*. 1989, 1991; van Dishoeck *et al*. 1996).

Third, it is possible to measure and compare directly the amounts of gaseous and solid forms of the same species, e.g. H_2O, CO, CO_2, and CH_3OH.

Fourth, the analysis and interpretation are easier for weak absorption lines than for radio frequency emission lines. For weak absorption lines the relationship between integrated intensity and column density of absorbers is linear. In practice, while the quadrupole lines of H_2 are usually weak in this sense, the interstellar lines of CO in its $v = 2 \leftarrow 0$ band are often somewhat saturated, so that the derived column densities are sensitive to the Doppler velocity dispersion. The absorbing gas toward a point-like background source can be modelled as a one-dimensional atmosphere, unlike the emitting gas sampled by the more extended beam of a radio telescope. Over a restricted wavelength range, all absorption measurements probably refer to exactly the same absorbing column.

Because interstellar lines are often weak and narrow (Doppler full-width at half-peak of the profile $\Delta V \approx 1\ \mathrm{km\ s^{-1}}$), high resolution is essential. For example, consider the case where the total column density of H_3^+ is $N(H_3^+) = 4 \times 10^{14}\ \mathrm{cm^{-2}}$, the fractional population in the ortho ground level† $(J, G) = (1, 0)$ is 0.40, and the linewidth is $\Delta V = 1.665\ \mathrm{km\ s^{-1}}$. The equivalent width (integrated intensity) of an absorption line is

$$W_\lambda = \int (1 - \exp(-\tau))\, \mathrm{d}\lambda,$$

where τ is the optical depth, which includes corrections for stimulated emission in the interstellar radiation field. For the ν_2 $(J', G', U') \leftarrow (J'', G'') = (2, 1, +1) \leftarrow (1, 1)$ line at wavelength $\lambda = 3.6685\ \mu\mathrm{m}$, the equivalent width is $W_\lambda/\lambda = 1.50 \times 10^{-6}$ in this example. At line centre the optical depth is $\tau = 0.29$, which yields an easily detectable 29% absorption when the line profile is resolved. In practice, existing spectrometers have resolving powers $R = \lambda/\delta\lambda \approx 10^5$ so that such lines with $c/\Delta V \approx 1.8 \times 10^5$ are not fully resolved. In this regime of astronomical spectroscopy, the true sensitivity of an observation is limited by the resolution as well as by the aperture of the telescope and the noise characteristics of the telescope-plus-spectrometer system. There is an additional advantage of high resolution, $R \geqslant 10^5$: when telluric atmospheric absorption is dominated by narrow lines, too, their removal from the astronomical spectrum is simpler and more accurate than at lower resolution.

2. The abundance of interstellar H_3^+

In the conventional theory of interstellar ion chemistry, H_3^+ is formed by cosmic-ray-induced ionizations of H_2,

$$H_2 + \text{cosmic ray} \rightarrow H_2^+ + e + \text{cosmic ray},$$

---

† Rotational levels in triangular H_3^+ are labelled with the quantum numbers of total angular momentum J, its projection along the symmetry axis G, and the vibrational angular momentum U. In the degenerate bending mode ν_2, the vibrational angular momentum takes on values $|\ell_2| = v_2, (v_2 - 2), \ldots,$ so that $G = |K - \ell_2|$ and $U = \pm|\ell_2|$ for the upper and lower levels of each ℓ-doublet.

followed by the rapid reaction,

$$H_2^+ + H_2 \rightarrow H_3^+ + H.$$

The destruction of H_3^+ is accomplished by dissociative recombination,

$$H_3^+ + e \rightarrow \text{products},$$

by reactions with abundant oxygen-bearing species,

$$H_3^+ + CO \rightarrow HCO^+ + H_2,$$
$$H_3^+ + O \rightarrow OH^+ + H_2,$$

and by other less important reactions. In steady state, the resulting number density of H_3^+ can be written

$$n(H_3^+) \approx \frac{1.8\times10^{-5}[\zeta/10^{-17}]}{\left[\dfrac{x(\mathrm{e})}{2\times10^{-6}}\right]\left[\dfrac{50}{T}\right]^{1/2} + \left[\dfrac{x(\mathrm{CO})}{3\times10^{-4}}\right] + 0.5\left[\dfrac{x(\mathrm{O})}{3\times10^{-4}}\right]}\ \mathrm{cm}^{-3}$$

in molecular gas. The fractional abundances of free electrons, CO and O, by number relative to H_2 are $x(\mathrm{e})$, $x(\mathrm{CO})$ and $x(\mathrm{O})$, respectively, and ζ is the effective rate of ionization of H_2 (s^{-1}) to produce H_2^+. It has been assumed that dissociative recombination is rapid, with a rate coefficient $k_{\mathrm{DR}} \approx 1\times10^{-7}(300/T)^{1/2}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$ for ground-state ions (Larsson (1997) and references therein). This formula predicts a concentration of H_3^+ that is independent of total density. It also identifies two limiting cases. When the electron fraction is small, $x(\mathrm{e}) \ll 10^{-4}$, as expected in thick, dense molecular clouds, then $n(H_3^+) \approx 1.8\times10^{-5}[\zeta/10^{-17}]\ \mathrm{cm}^{-3}$. In the diffuse and translucent clouds, where one expects $x(\mathrm{e}) \approx 5\times10^{-4}$, the concentration of H_3^+ is predicted to be rather smaller, $n(H_3^+) \approx 7\times10^{-8}[\zeta/10^{-17}]\ \mathrm{cm}^{-3}$ at $T = 50$ K.

3. H_3^+ in dense molecular clouds

The interstellar absorption lines of H_3^+ had been sought unsuccessfully for many years (Oka 1981; Geballe & Oka 1989; Black *et al*. 1990) before Geballe & Oka (1996) reported detections toward the infrared sources W33A and AFGL 2136. Since that time, McCall *et al*. (1999) have presented measurements of H_3^+ toward six infrared sources. A similar study of six molecular clouds has been carried out with the Phoenix spectrograph on the 2.1 m telescope of Kitt Peak National Observatory (C. A. Kulesa & J. H. Black 2000, unpublished data). Preliminary results can be summarized for three of the sources with fully analysed data, AFGL 2591, AFGL 490, and NGC 2024 IRS2. H_2 is measured in its $v = 1 \leftarrow 0$ S(0) line toward all three; the resulting column densities in the $J = 0$ ground level of para hydrogen lie in the range $N(H_2) = (2-4)\times10^{22}\ \mathrm{cm}^{-2}$. Upper limits on the amount of H_2 in $J = 1$ are found for the first two clouds. A marginal detection toward NGC 2024 IRS2 is consistent with an ortho/para ratio of 0.25, which is the expected ratio for thermalized populations at temperature $T = 48$ K. Toward that source, the kinetic temperature of the gas is well determined by the rotational population distribution of CO: $T = 44$ K. H_3^+ is measured in its para and ortho ground levels toward all three sources. The observations are in harmony with ortho/para ratios in both H_2 and

H_3^+ that are thermalized at the same temperature inferred from the CO rotational populations. This confirms that reactive collisions of H_2 with H^+ and H_3^+ are able to equilibrate the ortho and para populations (Dalgarno *et al*. 1973) even in thick, dense molecular clouds. The fractional abundance of CO is directly measured with values in the range $x(\mathrm{CO}) = (2\text{–}5) \times 10^{-4}$. The column density of H_3^+ is measured directly, the hydrogen density can be estimated from the abundance and excitation of CO, and the destruction rate of H_3^+ can then be estimated from the observed CO abundance. According to the simple theory outlined above, it is thus possible to solve for the ionization rate. The derived values are in the range $\zeta \approx (0.8\text{–}2.0) \times 10^{-17}\ \mathrm{s}^{-1}$, similar to what is expected for the spectrum of cosmic rays observed near Earth.

4. H_3^+ in the diffuse interstellar medium

The discovery of H_3^+ in the diffuse interstellar medium toward Cygnus OB2 No. 12 (McCall *et al*. 1998) was unexpected. The interstellar clouds that have been studied traditionally by optical absorption spectroscopy toward background stars are thin enough that ultraviolet starlight can photoionize most of the gaseous carbon, sulphur, silicon, iron, and magnesium. The resulting electron fraction, $x(\mathrm{e}) = n(\mathrm{e})/n(\mathrm{H_2}) > 10^{-4}$, should be high enough that H_3^+ is destroyed rapidly by dissociative recombination, rather than by reactions with O and CO as in the thick, dense molecular clouds. As emphasized by McCall *et al*. (1998) and Geballe *et al*. (1999), the column density $N(\mathrm{H_3^+}) = 3.8 \times 10^{14}\ \mathrm{cm}^{-2}$ implies that the ratio ζ/k_{DR} be at least 10 times larger than its widely adopted value. Cecchi-Pestellini & Dalgarno (2000) have constructed a model of the interstellar line of sight to Cygnus OB2 No. 12 in which dense concentrations of molecular gas within the diffuse clouds combine to produce the observed absorbing column of H_3^+ at $\zeta = 6 \times 10^{-17}\ \mathrm{s}^{-1}$. Absorption spectra provide further constraints on CO and C_2 molecules in the same column (Geballe *et al*. 1999; Gredel & Münch 1994), although the resolution of the existing spectra is inadequate to provide an accurate description of the conditions in distinct cloud components.

There is an alternative possibility to explain the large abundance of H_3^+ toward Cygnus OB2 No. 12, which takes account of the very special environment surrounding that unusual star. The Cygnus OB2 association is one of the most remarkable concentrations of hot, luminous stars in the Galaxy. Star No. 12 itself has a bolometric luminosity of $2 \times 10^6\ \mathrm{L}_\odot$ that places it among a handful of so-called hypergiant stars. For reference, the luminosity of the Sun is $\mathrm{L}_\odot = 3.8 \times 10^{26}$ W. The hotter stars in the association maintain a very large (*ca.* 100 parsec radius), low-density ($n(\mathrm{e}) \approx 30\ \mathrm{cm}^{-3}$ on average) photoionized nebula. Based on the stellar data of Massey & Thompson (1991), the total output of the association is approximately 6×10^{50} hydrogen-ionizing photons per second. It is quite likely that the nebula is density-bounded rather than ionization-bounded, which means that it leaks hydrogen-ionizing photons into the surrounding neutral gas. Moreover, several of the O-type stars of Cygnus OB2 are among the most powerful stellar X-ray sources in the Galaxy and have large mechanical luminosities in the form of stellar winds (Waldron *et al*. 1998). Any molecular gas lying within a few hundred parsecs of Cygnus OB2 No. 12 is probably ionized by ultraviolet light and X-rays at a rate that is significantly larger than the typical cosmic-ray rate. Massey & Thompson (1991) also suggest that a large fraction of the extinction and gaseous column density seen toward Cygnus OB2 No. 12 is circumstellar rather than truly interstellar. In that case, an important component of the absorbing column may well be located within the zone of enhanced ionization around the association. If so, then the enhanced abundance of H_3^+ in this direction would reflect directly the high ionization rate rather than a more general property of an interstellar line of sight that extends over 1740 parsecs between us and the association. Thus it is important to determine whether the H_3^+ is close to the Cygnus OB2 association or distributed over the entire line of sight to star No. 12. With the advent of high-resolution spectrographs on optical telescopes of 8–10 m diameter, it is now feasible to make crucial observational tests between competing explanations. For example, it would be instructive to search sensitively for interstellar absorption lines of the reactive ions OH^+ and H_2O^+, which should be good tracers of enhanced ionization in dilute molecular gas. Further attempts should be made to observe H_3^+ in other diffuse lines of sight.

5. Pure rotational emission lines of H_3^+

As pointed out by Pan & Oka (1986), the distortion-induced rotational transitions of H_3^+ may be of astrophysical interest. It is worthwhile to discuss the difficulties of observing these intrinsically weak lines. With one exception, the distortion-induced rotational transitions occur at wavelengths between 24 and 254 μm, for low-lying levels within 1000 cm^{-1} of ground. Warm molecular clouds in the Galaxy almost always exhibit intense continuous radiation due to thermal emission of dust particles at these wavelengths. It is the intensity contrast of line and adjacent continuum that will limit the detectability of the IR lines of H_3^+ in practice. This is illustrated with a specific example: the giant molecular cloud complex Sgr B2 near the Galactic Centre. The total column density of molecular hydrogen averaged over an angular scale of 1 arcmin toward Sgr B2 is approximately $N(H_2) \approx 10^{24}\ \mathrm{cm}^{-2}$ (Lis & Goldsmith 1990). On this scale the radiating dust has an average temperature $T_d \approx 32$ K and an average optical depth of $\tau \approx 1$ at a wavelength $\lambda = 100$ μm. Although there exist numerous molecular condensations of higher density and temperature within the Sgr B2 complex, average values of density $n(H_2) = 1.7 \times 10^5\ \mathrm{cm}^{-3}$ and gas temperature $T \approx 40$ K are appropriate on the scale of 1 arcmin, which corresponds to 2.5 parsecs. Geballe *et al*. (1999) have observed large column densities of H_3^+ toward stars near the Galactic Centre, $N(H_3^+) \approx 2 \times 10^{15}\ \mathrm{cm}^{-2}$. If this column density is adopted for the Sgr B2 cloud, then the implied abundance of H_3^+ is consistent with cosmic-ray ionization of H_2 at a rate $\zeta \approx 3 \times 10^{-16}\ \mathrm{s}^{-1}$. A multi-level excitation calculation has been carried out for H_3^+ under the above conditions with an assumed linewidth of 20 $\mathrm{km\ s}^{-1}$. As described previously (Black 1998) the transition probabilities and line frequencies have been adopted from Neale *et al*. (1996). A naive model of inelastic collision rates has been adopted with a typical downward rate coefficient of $2 \times 10^{-10}\ \mathrm{cm}^3\ \mathrm{s}^{-1}$. Reactive collisions of H_3^+ with H_2 that change nuclear-spin species have also been included (cf. Uy *et al*. 1997). Under these circumstances, the four lowest rotational states, $(J, G) = (1, 1)$, (1,0), (2,2), and (2,1), have populations that are nearly thermalized at the kinetic temperature. The $(2, 2) \rightarrow (1, 1)$ transition has a predicted wavelength of 95.08 μm. Its peak intensity in this model of the Sgr B2 cloud is $I_{\mathrm{line}} = 0.014$ Jy nsr^{-1}, where 1 Jy = $10^{-26}\ \mathrm{W\ m}^{-2}\ \mathrm{Hz}^{-1}$ and nsr stands for one nanosteradian (10^{-9} sr). The calculated intensity of the thermal dust continuum radiation is $I_c = 272$ Jy nsr^{-1} at the same wavelength. It is clearly not feasible to detect such a weak line in the presence of such a strong continuum. Line/continuum ratios of the other rotational transitions are similarly small.

There is an unusual distortion-induced rotational transition between the levels $(J, G) = (4, 4)$ and (3,1), which are accidentally very close to each other. The transition frequency is estimated to be 217.78 GHz, based on the comparison of experimental and *ab initio* energy levels for which the differences range between 7.261 and 7.268 cm^{-1} (Dinelli *et al*. 1997). The upper state lies 438 cm^{-1} in energy above the lowest state of H_3^+. Interestingly, this mm-wave transition is the only possible rotational transition out of the upper level (4,4), while two transitions of much higher probability can drain population out of the lower level (3,1). As pointed out previously (Black 1998), this means that the populations of these two states will naturally become inverted whenever the density is too low for the populations to be quenched by collisions. Thus it is conceivable that this transition might appear as a cosmic maser. Large column densities $N(H_3^+) \geqslant 10^{17}\ \mathrm{cm}^{-2}$ and high temperatures $T \gg 100$ K are probably required in order to achieve appreciable gain in such a maser. Such conditions are, in fact, expected to occur in molecular gas surrounding active galactic nuclei such as quasars and radio galaxies, where the 217.8 GHz maser line as well as the quasi-thermal far-infrared lines might be detectable (Black 1998). In the case of a molecular cloud like Sgr B2 discussed above, the predicted intensity of the 217.8 GHz line is less than 1 μK in units of radiation brightness temperature. For comparison, the rich mm-wave spectrum of Sgr B2 is confusion-limited at a level of 10 mK or higher.

Although a simple estimate suggests that the 217.8 GHz rotational line will not be easily detectable in the ionosphere of Jupiter where infrared line emission of H_3^+ is so intense, it might be rather stronger in the ionospheres of some giant, extrasolar planets. A giant planet lying closer than one astronomical unit to its parent star is expected to have a greatly distended atmosphere compared with Jupiter. Depending upon the extreme ultraviolet flux of the star and the magnetospheric properties of such a planet, it might also have an even thicker, warmer ionosphere than Jupiter. In that case, interferometric searches for maser emission in the H_3^+ 217.8 GHz line might offer an interesting method of detecting such an atmosphere.

6. Future prospects

It is now possible to use the H_3^+ ion as a powerful diagnostic probe of interstellar molecular gas. Observations of the interstellar absorption spectra of H_3^+, H_2, and CO can already be made with high-resolution spectrographs on telescopes of 2.1 m aperture toward a small sample of highly obscured stars. In 2001 the Phoenix spectrograph, with a resolving power $R = \lambda/\delta\lambda \approx 10^5$, will move to the 8 m Gemini South telescope. In 2003 the Cryogenic Infrared Echelle Spectrometer (CRIRES) with $R \geqslant 10^5$ is scheduled to go into operation at the 8.2 m UT4 unit of the Very Large Telescope of the European Southern Observatory. With the increased light-gathering power of these large telescopes, direct observations of interstellar H_2 and H_3^+ will become routine and will be possible toward a much greater variety of stars within and behind molecular clouds.

Research in atomic and molecular astrophysics at Onsala Space Observatory is supported by the Swedish Natural Science Research Council and the Swedish National Space Board. A grant from the Chalmers Foundation is also gratefully acknowledged.

References

Black, J. H. 1998 Molecules in harsh environments. *Faraday Discuss.* **109**, 257–266.

Black, J. H., van Dishoeck, E. F., Willner, S. P. & Woods, R. C. 1990 Interstellar absorption lines toward NGC 2264 and AFGL 2591: abundances of H_2, H_3^+, and CO. *Astrophys. J.* **358**, 459–467.

Cecchi-Pestellini, C. & Dalgarno, A. 2000 H_3^+ in diffuse interstellar gas. *Mon. Not. R. Astr. Soc.* **313**, L6–L8.

Dalgarno, A., Black, J. H. & Weisheit, J. C. 1973 Ortho–para transitions in H_2 and the fractionation of HD. *Astrophys. Lett.* **14**, 77–79.

Dinelli, B. M., Neale, L., Polyansky, O. L. & Tennyson, J. 1997 New assignments for the infrared spectrum of H_3^+. *J. Mol. Spectrosc.* **181**, 142–150.

Geballe, T. R. & Oka, T. 1989 An infrared spectroscopic search for the molecular ion H_3^+. *Astrophys. J.* **342**, 855–859.

Geballe, T. R. & Oka, T. 1996 Detection of H_3^+ in interstellar space. *Nature* **384**, 334–335.

Geballe, T. R., McCall, B. J., Hinkle, K. H. & Oka, T. 1999 Detection of H_3^+ in the diffuse interstellar medium: the Galactic Center and Cygnus OB2 Number 12. *Astrophys. J.* **510**, 251–257.

Gredel, R. & Münch, G. 1994 Complex interstellar absorption lines of C_2 in the Cygnus OB2 association. *Astron. Astrophys.* **285**, 640–644.

Lacy, J. H., Evans II, N. J., Achtermann, J. M., Bruce, D. E., Arens, J. F. & Carr, J. S. 1989 Discovery of interstellar acetylene. *Astrophys. J.* **342**, L43–L46.

Lacy, J. H., Carr, J. S., Evans II, N. J., Baas, F., Achtermann, J. M. & Arens, J. F. 1991 Discovery of interstellar methane: observations of gaseous and solid CH_4 absorption toward young stars in molecular clouds. *Astrophys. J.* **376**, 556–560.

Lacy, J. H., Knacke, R., Geballe, T. R. & Tokunaga, A. T. 1994 Detection of absorption by H_2 in molecular clouds: a direct measurement of the H_2:CO ratio. *Astrophys. J.* **428**, L69–L72.

Larsson, M. 1997 Dissociative recombination with ion storage rings. *A. Rev. Phys. Chem.* **48**, 151–179.

Lis, D. C. & Goldsmith, P. F. 1990 Modeling of the continuum and molecular line emission from the Sagittarius B2 molecular cloud. *Astrophys. J.* **356**, 195–210.

McCall, B. J., Geballe, T. R., Hinkle, K. H. & Oka, T. 1998 Detection of H_3^+ in the diffuse interstellar medium toward Cygnus OB2 No. 12. *Science* **279**, 1910–1913.

McCall, B. J., Geballe, T. R., Hinkle, K. H. & Oka, T. 1999 Observations of H_3^+ in dense molecular clouds. *Astrophys. J.* **522**, 338–348.

Massey, P. & Thompson, A. B. 1991 Massive stars in Cyg OB2. *Astron. J.* **101**, 1408–1428.

Neale, L., Miller, S. & Tennyson, J. 1996 Spectroscopic properties of the H_3^+ molecule: a new calculated line list. *Astrophys. J.* **464**, 516–520.

Oka, T. 1981 A search for interstellar H_3^+. *Phil. Trans. R. Soc. Lond.* A **303**, 543–549.

Pan, F.-S. & Oka, T. 1986 Calculated forbidden rotational spectra of H_3^+. *Astrophys. J.* **305**, 518–525.

Uy, D., Cordonnier, M. & Oka, T. 1997 Observation of ortho–para H_3^+ selection rules in plasma chemistry. *Phys. Rev. Lett.* **78**, 3844–3847.

van Dishoeck, E. F. (and 17 others) 1996 A search for interstellar gas-phase CO_2. Gas:solid state abundance ratios. *Astron. Astrophys.* **315**, L349–L352.

Waldron, W. L., Corcoran, M. F., Drake, S. T. & Smale, A. P. 1998 X-ray and radio observations of the Cygnus OB2 association. *Astrophys. J. Suppl.* **118**, 217–238.