

## A search for interstellar $\text{H}_3^+$

By T. OKA†

*Herzberg Institute of Astrophysics National Research Council of Canada  
Ottawa, Ontario, Canada K1A 0R6*

Based on the results of recent laboratory observation of the infrared  $\nu_2$  fundamental band of the  $\text{H}_3^+$  molecular ion, the possibility of observing this important ion in interstellar space is discussed. An observation of this spectrum has been attempted with the aid of the high-resolution Fourier transform spectrometer on the 4 m Mayall telescope of the Kitt Peak National Observatory.

### 1. INTRODUCTION

The triatomic hydrogen molecular ion  $\text{H}_3^+$  is the simplest well-bound polyatomic system. According to the most recent *ab initio* calculation (Dykstra *et al.* 1978), the formation energy of  $\text{H}_3^+$  from three protons and two electrons is 36.533 eV. Subtracting from this value the Rydberg energy of hydrogen atom formation and the dissociation energy of  $\text{H}_2$  we obtain the formation energy of  $\text{H}_3^+$  from a proton and  $\text{H}_2$  of  $-4.579$  eV. This proton affinity to  $\text{H}_2$  is even greater than the dissociation energy of  $\text{H}_2$  of 4.478 eV.

Because of this high stability of  $\text{H}_3^+$ , the ion molecule reaction



is exothermic with  $\Delta E = 1.844$  eV = 178.0 kJ/mol, even though it starts from the well-bound species. The cross section for this reaction can be calculated from Langevin's formula (1905)

$$\sigma(v) = 2\pi e(\alpha/\mu)^{1/2}/v \quad (2)$$

where  $\alpha$  is the polarizability of  $\text{H}_2$ ,  $\mu$  is the reduced mass;  $\sigma \approx 1.5$  nm<sup>2</sup> for the thermal velocity  $v$  of 1 km/s for laboratory conditions and *ca.* 5 nm<sup>2</sup> for  $v = 300$  m/s for interstellar Space. Thus reaction (1) is extremely efficient and  $\text{H}_3^+$  rather than  $\text{H}_2^+$  is the dominant hydrogenic molecular ion both in a hydrogen discharge in the laboratory and in molecular clouds in space.

In the scheme of ion–molecule reactions that is now believed to be the most efficient mechanism for producing interstellar molecules (Herbst & Klemperer 1973), the  $\text{H}_3^+$  ion plays a crucial role. It acts as an efficient protonator through the reaction



Thus, for example, the important and abundant molecular ions  $\text{HCO}^+$  and  $\text{HNN}^+$  are mainly produced through this chemical reaction with  $\text{X} = \text{CO}$  and  $\text{N}_2$ , respectively. Since the proton affinities of  $\text{CO}$  and  $\text{N}_2$  are even higher than that of  $\text{H}_2$ , these reactions are exothermic. The cross sections of these reactions are similar to that for (1). In fact, (3) with  $\text{X} = \text{CO}$  is believed to be the chief destruction mechanism of  $\text{H}_3^+$  in interstellar space because of the large abundance

† Present address: Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois 60637, U.S.A.

of CO. The role of  $\text{H}_3^+$  as a protonator is so universal that as many as 70 reactions of the type of equation (3) were considered in Suzuki's (1979) treatment of chemical reactions in molecular clouds.

This ubiquitous molecular ion has been well known to mass spectroscopists since its accidental discovery by J.J. Thomson (1912). However, its astronomical observation has been hampered because of the lack of a laboratory spectrum of it in any wavelength region. The recent discovery (Oka 1980) of the infrared  $\nu_2$  band of this ion makes such an observation possible. In this paper I describe the results of the first such attempt.

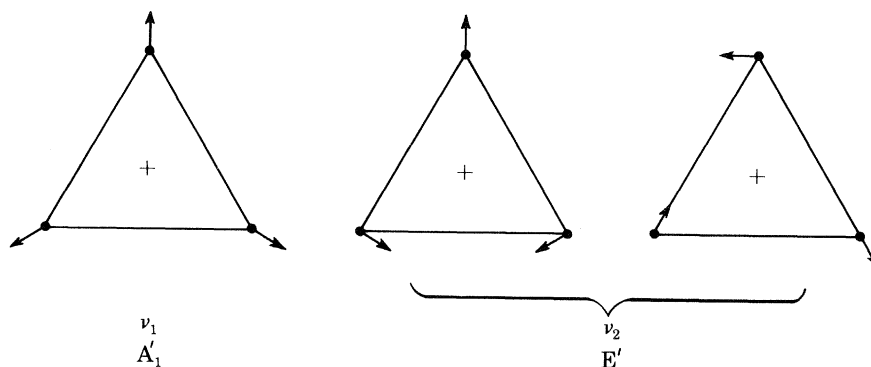


FIGURE 1. Normal coordinates of  $\text{H}_3^+$ .

## 2. LABORATORY SPECTRUM

Among the three types of spectrum of  $\text{H}_3^+$ , i.e. the electronic, the vibrational and the rotational, only the vibrational spectrum is suitable for observation. The optical spectrum of  $\text{H}_3^+$  has never been observed, probably because it dissociates when an electron is excited (Herzberg 1967). This ion possesses no dipole moment and hence no strongly allowed rotational transitions. The  $\Delta K = 3$  rotational spectrum induced by centrifugal distortion of the molecular ion (Watson 1971) is very weak and difficult to observe, although spontaneous emission processes caused by such a mechanism may be significant in discussing thermal equilibrium of interstellar  $\text{H}_3^+$  (Oka *et al.* 1971).

Because of its equilateral triangular structure,  $\text{H}_3^+$  has the totally symmetric  $\nu_1$  vibrational mode and the doubly degenerate  $\nu_2$  mode (figure 1); the former mode is infrared inactive. The vibrational transition dipole moment for the  $\nu_2$  fundamental band is calculated to be 0.156 D† from the Einstein coefficient for spontaneous emission given in the extensive *ab initio* calculation by Carney & Porter (1976). This is a large dipole moment considering the fact that the transition dipole moment of the intense  $\nu_2$  band of  $\text{NH}_3$  is 0.24 D (Shimizu *et al.* 1971).

The intensity of spectral lines in terms of the absorption coefficient is given (Townes & Schawlow 1955) by

$$\gamma = \frac{8\pi^3\nu}{3hc} n(\text{H}_3^+) f(T_{\text{rot}}, T_{\text{vib}}) \left[ 1 - \exp\left(\frac{-h\nu}{kT_{\text{vib}}}\right) \right] |\mu_{ij}|^2 \phi(\nu, T_{\text{trans}}), \quad (4)$$

† 1D =  $3.336 \times 10^{-30}$  C m.

TABLE 1. OBSERVED FREQUENCIES OF THE  $\nu_2$  BAND OF H<sub>3</sub><sup>+</sup>

transition $\nu_2(J,  K-l )_{\text{I,II}} \leftarrow (J, k)$	frequency cm <sup>-1</sup>	intensity <sup>†</sup> 10 <sup>-6</sup> cm <sup>-1</sup>
(5,1) <sub>I</sub> ← (4,1)	3029.823	0.1*
(5,2) <sub>I</sub> ← (4,2)	3024.547	0.2*
(7,6) <sub>II</sub> ← (6,6)	3015.240	0.2*
(5,3) <sub>I</sub> ← (4,3)	3014.358	0.7*
(5,4) <sub>I</sub> ← (4,4)	3008.115	0.5*
(6,5) <sub>II</sub> ← (5,5)	2956.072	0.4*
(4,0) ← (3,0)	2930.163	2.3*
(4,1) <sub>I</sub> ← (3,1)	2928.351	1.3*
(4,2) <sub>I</sub> ← (3,2)	2923.361	1.6*
(4,3) <sub>I</sub> ← (3,3)	2918.026	3.8
(5,3) <sub>II</sub> ← (4,3)	2894.610	0.7*
(5,4) <sub>II</sub> ← (4,4)	2894.488	0.5*
(4,3) <sub>II</sub> ← (3,3)	2829.923	10
(3,1) <sub>I</sub> ← (2,1)	2826.113	5.9
(3,2) <sub>I</sub> ← (2,2)	2823.136	5.0
(3,2) <sub>II</sub> ← (2,2)	2762.068	10
(2,1) <sub>I</sub> ← (1,1)	2726.219	11
(2,0) ← (1,0)	2725.898	30
(2,1) <sub>II</sub> ← (1,1)	2691.444	11
(3,3) ← (3,3)	2561.493	3.4
(2,2) ← (2,2)	2554.664	4.6
(2,1) <sub>I</sub> ← (2,1)	2552.987	1.4*
(1,1) ← (1,1)	2545.418	8.9
(1,0) ← (1,0)	2529.724	30
(2,1) <sub>II</sub> ← (2,1)	2518.207	5.6
(3,0) ← (3,0)	2509.075	3.2
(3,1) <sub>II</sub> ← (3,1)	2508.131	1.6*
(3,2) <sub>II</sub> ← (3,2)	2503.347	1.5*
(4,2) <sub>II</sub> ← (4,2)	2492.534	0.2*
(0,1) ← (1,1)	2457.90	5.9

† Calculated intensities at 200 K. Lines marked with asterisks were observed at a temperature of 450 K.

where  $n(\text{H}_3^+)$  is the density of H<sub>3</sub><sup>+</sup> per cubic centimetre,  $T_{\text{rot}}$ ,  $T_{\text{trans}}$  and  $T_{\text{vib}}$  are the rotational, translational and vibrational temperatures, respectively,  $\phi(\nu, T_{\text{trans}})$  is the Doppler broadened normalized line shape function and  $\mu_{ij}$  is the transition dipole matrix element. The absorption  $\alpha = -\ln(I/I_0)$  is given by multiplying  $\gamma$  by the optical path  $l$ . For an astronomical observation we use the column density  $n(\text{H}_3^+)l$ .

The laboratory experiment gave the values  $n(\text{H}_3^+) \approx 3 \times 10^{10} \text{ cm}^{-3}$  and  $T_{\text{rot}} \approx T_{\text{trans}} \approx 200 \text{ K}$  for a liquid N<sub>2</sub> cooled hydrogen discharge with a pressure of *ca.* 100 Pa and a current density of *ca.* 60 mA cm<sup>-2</sup>. For this condition the strongest absorption after the optical path of 32 m, that is for the column density of 10<sup>14</sup> cm<sup>-2</sup>, was about 10 %. This value agreed approximately with the value predicted from (4) on the assumption that  $T_{\text{vib}} \ll h\nu/k \approx 4000 \text{ K}$ . A linewidth (h.w.h.m.) of about 0.01 cm<sup>-1</sup> was observed and was due to the Doppler shift for the thermal velocity of H<sub>3</sub><sup>+</sup> of *ca.* 1 km s<sup>-1</sup>.

Observed frequencies are summarized in table 1. The small discrepancies between the observed frequencies given in table 1 and those given in Oka (1980) are due to more accurate calibration of frequencies in this work. Readers are referred to Oka (1980) for more details of the laboratory observation, analysis of the spectrum and molecular constants. A more detailed paper will be published soon. Here we consider only the rotational level structure of the ground

state of  $\text{H}_3^+$ , which is needed for discussing the feasibility of detecting this molecular ion in interstellar Space.

The rotational level structure of  $\text{H}_3^+$  in the ground vibrational state is shown in figure 2 in terms of three quantum numbers:  $J$  for the total angular momentum,  $K$  for the rotational angular momentum around the threefold symmetry axis and  $\pm$  for the parities of wavefunctions with respect to inversion. The level structure is similar to that of  $\text{NH}_3$  except that there is no inversion

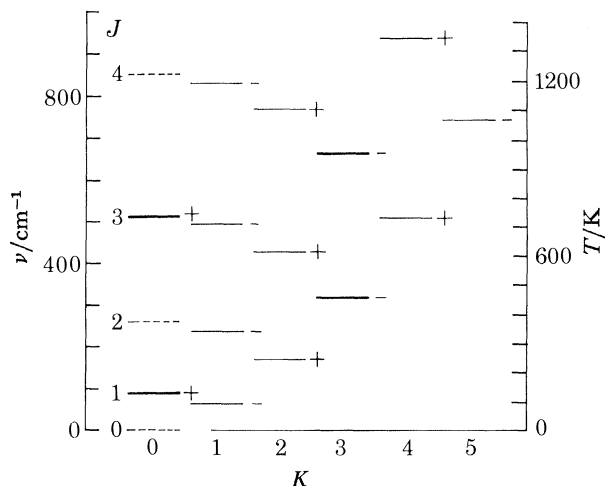


FIGURE 2. Rotational levels of  $\text{H}_3^+$  in the ground vibrational state with quantum numbers  $J$ ,  $K$ , parity  $\pm$ , and *ortho* (bold line) and *para* (thin line) specified.

doubling. In fact if one takes the lower components of the inversion doublets of  $\text{NH}_3$  one obtains qualitatively the same structure as shown in figure 2. This is natural because a planar molecule can be considered as the limiting case of non-planar molecules with the barrier of inversion set equal to 0. As in  $\text{NH}_3$ ,  $\text{H}_3^+$  molecules are composed of two spin modifications: *ortho*- $\text{H}_3^+$  with the total nuclear spin quantum number  $I = \frac{3}{2}$  and associated with levels  $K = 3n$  (shown in figure 2 with bold lines), and *para*- $\text{H}_3^+$  with  $I = \frac{1}{2}$  with levels  $K = 3n \pm 1$ . The former has a spin degeneracy  $(2I + 1)$  of 4 and the latter 2.

Because of the large rotational constants of  $\text{H}_3^+$ ,  $B_0 = 43.620 \text{ cm}^{-1}$  and  $C_0 = 20.331 \text{ cm}^{-1}$  (J. K. G. Watson, unpublished), only several lowest rotational levels are populated even for the laboratory plasma temperature of 200 K. The most populated is the  $J = 1$ ,  $K = 0$  level of *ortho*- $\text{H}_3^+$ , which is occupied by about 30 % of the total molecular ions at this temperature (note that the lowest  $J = 0$ ,  $K = 0$  level is not allowed owing to the Pauli principle). The two strongest lines listed in table 1, which are most suitable for astronomical observation, start from this most populated level. The  $J = 1$ ,  $K = 1$  level is lower than the  $J = 1$ ,  $K = 0$  level by  $23.167 \text{ cm}^{-1}$ , but is less populated because of the lower spin weight. However, this is not necessarily so in interstellar Space. If the rotational excitation temperature is below 48 K, the lowest *para*-level is more populated than the lowest *ortho*-level. It has been shown in the laboratory (Oka, unpublished) that *ortho*- $\text{H}_3^+$  and *para*- $\text{H}_3^+$  equilibrate quickly through the exchange reaction



## 3. INTERSTELLAR CONDITIONS

The results of the laboratory spectrum summarized in the previous section are translated into the language of observational astrophysics as follows: if the  $\text{H}_3^+$  molecular ions exist in a molecular cloud with a column density of  $10^{14} \text{ cm}^{-2}$ , an average velocity of  $1 \text{ km s}^{-1}$ , and a rotational excitation temperature of  $200 \text{ K}$ , we expect absorption of *ca.* 10 % at  $2725.898 \text{ cm}^{-1}$  and  $2529.724 \text{ cm}^{-1}$  provided there is an infrared source behind the molecular cloud. This value of absorption may increase by a factor of about 2 if the excitation temperature is lower, but decrease by a factor of 5 through the limited instrumental resolution of  $0.041 \text{ cm}^{-1}$  used in our observation.

We have a dilemma here. Theory predicts that  $\text{H}_3^+$  is abundant in carbon-depleted clouds with large magnitudes of optical extinction (de Jong *et al.* 1980), the type of clouds in which deuterium fractionation is efficient. Thus  $\text{H}_3^+$  must be relatively abundant in clouds such as TMC-1 and L 134; these clouds are also of low kinetic and excitation temperature. But there is no infrared source.

The most promising area of observation seems to be the Orion Molecular Cloud, in which dense molecular clouds and intense infrared sources coexist. In this source  $\text{HCO}^+$  column densities of  $2 \times 10^{15} \text{ cm}^{-2}$  with linewidth (h.w.h.m.) of *ca.*  $14 \text{ km s}^{-1}$  (plateau),  $3 \times 10^{14} \text{ cm}^{-2}$  with *ca.*  $1.1 \text{ km s}^{-1}$  (ridge I), and  $2 \times 10^{14} \text{ cm}^{-2}$  with *ca.*  $1.3 \text{ km s}^{-1}$  (ridge II) have been reported (Rydbeck *et al.* 1981). From these results and those from the laboratory it is estimated that if the ratio of column densities  $n(\text{HCO}^+)/n\text{H}_3^+$  is 10 in all regions, an absorption of 5 % is expected. The ratio in question has been predicted by Herbst & Klemperer (1973) to be from 0.07 to about 0.01. For a more depleted cloud de Jong *et al.* (1980) predict this ratio to be on the order of 1. We should also keep in mind that since the spatial resolution of an infrared telescope is much higher than that of a millimetre telescope, these estimates are subject to a large change if the millimetre observation is the result of averaging over many features.

Let us now consider the possibility of observing the  $\text{H}_3^+$  spectrum in emission. Here a comparison with the  $\text{H}_2$  quadrupole emission spectrum is useful. The rate-determining process of the production of  $\text{H}_3^+$  is the ionization of  $\text{H}_2$  into  $\text{H}_2^+$  which is converted quickly to  $\text{H}_3^+$  (equation (1)). Equating the production rate with the destruction rate through (3) we obtain (Dalgarno *et al.* 1973)

$$\zeta n(\text{H}_2) = kn(\text{X})n(\text{H}_3^+), \quad (6)$$

where  $\zeta$  is the cosmic ray ionizing flux (*ca.*  $10^{-17} \text{ s}^{-1}$ ) and  $k$  is the rate constant for (3) *ca.*  $10^{-9} \text{ cm}^2 \text{ s}^{-1}$ . For the typical CO concentration  $n(\text{CO}) \approx 10/\text{cm}^3$ , we thus obtain

$$n(\text{H}_3^+)/n(\text{H}_2) \approx 10^{-8}/n(\text{X}) \approx 10^{-9}. \quad (7)$$

This factor of  $10^{-9}$  is approximately cancelled by the intensity ratio of the dipole spectrum and the quadrupole spectrum, i.e.

$$I_\mu/I_Q \approx (\lambda/a)^2 \approx 10^9, \quad (8)$$

where  $\lambda$  is the wavelength of radiation and  $a$  is the molecular dimension (Heitler 1953). Equation (8) is confirmed by the laboratory spectrum of  $\text{H}_2$  (D. R. Rao and T. Oka, unpublished) and  $\text{H}_3^+$  (Oka 1980) as shown in figure 3.

These considerations indicate that the *absorption* of  $\text{H}_3^+$  in a molecular cloud would be similar

to that of  $H_2$ . However, the *emission* of  $H_3^+$  is expected to be much less than that of  $H_2$  because of the slow pumping by collision. The factor of  $10^9$  in (8) applies also to the spontaneous emission rate if we neglect the wavelength dependence. Thus the spontaneous emission lifetime  $t_e$  of the  $\nu_2$  state of  $H_3^+$  is on the order of 10 ms, while that of the excited state of  $H_2$  is on the order of a year. Therefore while the collisional excitation rate  $t_c$  is sufficiently fast for  $H_2$  excitation in a dense region it is far too slow for  $H_3^+$  excitation. This reduces the emission from  $H_3^+$  with respect

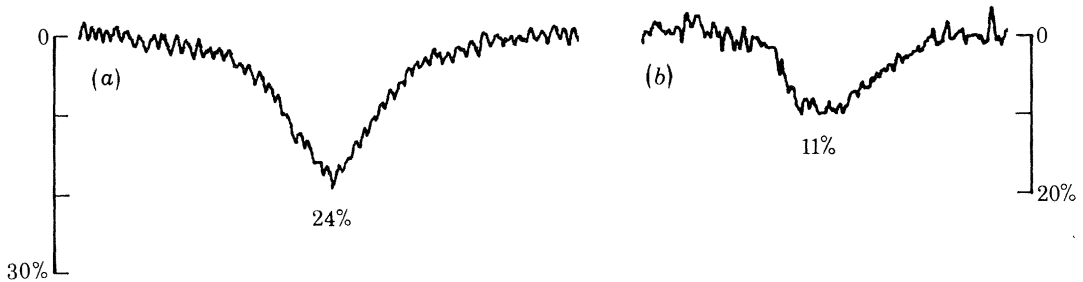


FIGURE 3. Comparison of (a)  $H_2$  and (b)  $H_3^+$  absorption lines in the laboratory. The  $H_2$   $\nu = 1 \leftarrow 0$   $Q(1)$  transition at  $4155.2540 \text{ cm}^{-1}$  with 1 atmosphere pressure and 64 m path length (column density *ca.*  $2 \times 10^{23} \text{ cm}^{-2}$ ) gives about twice as much absorption as that of  $H_3^+$   $\nu_2$   $R_0(1)$  transition at  $2725.898 \text{ cm}^{-1}$  with the column density of  $10^{14} \text{ cm}^{-2}$ , demonstrating the relation in equation (8).

to that from  $H_2$  by a factor of  $t_e/t_c = 10^{-2}n\sigma v$ . For this ratio to be appreciable we need an enormously high density of  $H_2$  of *ca.*  $10^{12}/\text{cm}^3$  or more.

The infrared emission from  $H_3^+$  inside the dark cloud at the time of formation is very low owing to the small  $\zeta$ ,  $10^{-17} \text{ s}^{-1}$ . It seems that the only possibility of observing this type of emission is that from the area where the ionization of  $H_2$  is very rapid either by intense short wavelength radiation or by shock wave.

#### 4. OBSERVATION

Observation was made for 2 days on 1981 March 23–25, with the coude Fourier transform spectrometer with high resolution (*ca.*  $0.041 \text{ cm}^{-1}$ ) on the 4 m Mayall telescope of the Kitt Peak National Observatory. A liquid He cooled narrow band filter with the centre wavenumber of  $2725.898 \text{ cm}^{-1}$  and the full width at half maximum of *ca.*  $65 \text{ cm}^{-1}$  combined with a broad band filter was used with the infrared detectors to reduce noise. This wavenumber region was chosen aiming at one of the strongest transitions  $[\nu_2, J = 2, |K-l| = 0] \leftarrow [J = 1, K = 0]$  and its satellite  $[\nu_2, J = 2, |K-l| = 1]_{\text{I}} \leftarrow [J = 1, K = 1]$  which are only  $0.322 \text{ cm}^{-1}$  apart. The former corresponds to *ortho*- $H_3^+$  and the latter *para*- $H_3^+$ . Two other transitions  $[\nu_2, J = 3, |K-l| = 2]_{\text{II}} \leftarrow [J = 2, K = 2]$  and  $[\nu_2, J = 2, |K-l| = 1]_{\text{II}} \leftarrow (J = 1, K = 1)$  are expected within the pass band of the filter used.

The search for absorption was made in seven infrared sources, the Becklin–Neugebauer source of Orion ( $10^{-14} \text{ W cm}^{-2}$ ), carbon stars IRC + 10216 ( $7 \times 10^{-13} \text{ W cm}^{-2}$ ) and CIT ( $10^{-13} \text{ W cm}^{-2}$ ), cool and hot stars  $\alpha$  Tau ( $3 \times 10^{-13} \text{ W cm}^{-2}$ ),  $\alpha$  Lur ( $2 \times 10^{-14} \text{ W cm}^{-2}$ ) and R Leo where the numbers in brackets show the infrared flux of each source at  $3.7 \mu\text{m}$ . Telluric absorption lines were removed by taking the ratio of the observed spectrum to that of  $\alpha$  CMa, which is known to have no discrete spectrum of its own. Unfortunately the spectrum of the most important source, the BN source of Orion, turned out to be not of excellent quality because of noise from the observation conditions, and the minimum detectable absorption was on the order of 20%. This

sets an upper limit on the  $\text{H}_3^+$  column density of  $5 \times 10^{14} \text{ cm}^{-2}$ . The sensitivity of the spectrometer for the other sources ranged between 5 and about 30 %.

The search for emission was made in the peak 1 position of Orion where very strong  $\text{H}_2$  quadrupole emission has been observed (Beckwith *et al.* 1978) and the compact H I region NGC 7027. The negative results set an upper limit for the emission infrared flux of  $10^{-16} \text{ W cm}^{-2} \mu\text{m}^{-1}$  at 3.6" aperture.

More observations will be attempted for this important and fundamental molecular ion.

I am grateful to S. T. Ridgway, D. N. B. Hall and W. Lenz for their assistance during my observation, and to J. K. G. Watson for reading this paper.

#### REFERENCES (Oka)

- Beckwith, S., Persson, S. E., Neugebauer, G. and Becklin, E. E. 1978 *Astrophys J.* **223**, 464.  
Carney, G. D. & Porter, R. N. 1976 *J. chem. Phys.* **65**, 3547.  
Dalgarno, A., Oppenheimer, M. & Berry, R. S. 1973 *J. Lett.* **185**, L 21.  
de Jong, T., Dalgarno, A. & Boland, W. 1980 *Astron. Astrophys.* **91**, 68.  
Dykstra, C. E., Gaylord, A. S., Gwinn, W. D., Swope, W. C. & Schaefer, H. F. III 1978 *J. chem. Phys.* **68**, 3951.  
Heitler, W. 1953 *The quantum theory of radiation*. London: Oxford University Press.  
Herbst, E. & Klemperer, W. 1973 *Astrophys. J.* **185**, 505.  
Herzberg, G. 1967 *Trans. R. Soc. Can.* **5**, 3.  
Oka, T. 1980 *Phys. Rev. Lett.* **45**, 531.  
Oka, T., Shimizu, F. O., Shimizu, T. & Watson, J. K. G. 1971 *Astrophys. J. Lett.* **165**, L15.  
Rydbeck, O. E. H., Hjalmarson, A., Rydbeck, G., Elldér, J., Olofsson, H. & Sume, A. 1981 *Astrophys J. Lett.* **243**, L 41.  
Shimizu, T., Shimizu, F. O., Turner, R. & Oka, T. 1971 *J. chem. Phys.* **55**, 2822.  
Suzuki, H. 1979 *Prog. theor. Phys.* **62**, 936.  
Thompson, J. J. 1912 *Phil. Mag.* **24**, 209.  
Townes, C. H. & Schawlow, A. L. 1955 *Microwave spectroscopy*. New York: McGraw-Hill.  
Watson, J. K. G. 1971 *J. molec. Spectrosc.* **40**, 536.