

## THEORETICAL MICROWAVE SPECTRAL CONSTANTS FOR $C_2N$ , $C_2N^+$ , AND $C_3H^1$

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### ABSTRACT

Theoretical microwave spectral constants have been computed for  $C_2N$ ,  $C_3H$ , and  $C_2N^+$ . For  $C_2N$  these are compared with values obtained from optical data. Calculated hyperfine constants are also presented for HNC, DNC, and  $HCNH^+$ . The possibility of observing these species in dense interstellar clouds is discussed.

*Subject headings:* interstellar: molecules — line identifications — molecular processes

### I. INTRODUCTION

In the past 10 years spectral lines of over 50 molecular species have been identified in radio observations of interstellar gas clouds. The vast majority of these are well known, stable species, and identifications were based on precisely measured laboratory frequencies. However, physical conditions in interstellar space are substantially different from those which are obtained in the laboratory, and one might expect to find more exotic species as well (for example, reactive free radicals which have too short a lifetime under laboratory conditions to be studied easily). Thus, the identification of mostly familiar compounds could be primarily a selection effect since one can conveniently search only for molecules with known spectral constants. In fact, to date microwave spectra of at least six species have been identified in interstellar clouds prior to having been measured in the laboratory. These are the molecular ions  $HCO^+$  (Buhl and Snyder 1970; Klemperer 1970) and  $HN_2^+$  (Turner 1974; Green, Montgomery, and Thaddeus 1974); the free radicals  $C_2H$  (Tucker, Kutner, and Thaddeus 1974),  $C_3N$  (Guélin and Thaddeus 1977), and  $C_4H$  (Guélin, Green, and Thaddeus 1978); and the metastable isomer HNC (Snyder and Buhl 1971). In the absence of measured spectral constants, these identifications have relied on several clues: models of interstellar chemistry (see, e.g., Herbst and Klemperer 1973) which predict that some of these species should be quite abundant, fine structure and hyperfine structure "fingerprints", and theoretical estimates of spectral constants. The identifications of  $HCO^+$  (Woods *et al.* 1975),  $N_2H^+$  (Saykally *et al.* 1976a), and HNC (Arrington and Ogrzylo 1975; Saykally *et al.* 1976b) have been confirmed by subsequent laboratory measurements.

Several dozen interstellar spectral lines are currently unidentified, and it is likely that at least some of these arise from transient species which have not yet been measured in the laboratory. The difficulty in identifying such lines should be apparent; however, once

identified the radioastronomical data provide precise spectral constants which further our understanding of the structure of these important reactive species. As noted, theoretical, i.e., quantum chemical predictions of spectral constants have played an important role in previous identifications. As part of an ongoing program in this laboratory to identify other reactive species in space, we have been computing spectral constants for a number of likely interstellar species. The present paper presents results for  $C_2N$ ,  $C_3H$ , and  $C_2N^+$ . Also reported here are some previously unpublished results for hyperfine coupling constants in HNC and  $HCNH^+$ .

### II. CALCULATIONS

Methods for obtaining approximate solutions to the molecular Schrodinger equation have been extensively studied. By using more and more elaborate trial wavefunctions it is possible, in principle, to approach the exact solution. Also, it has been well documented that certain less sophisticated levels of approximation provide relatively good accuracy for various molecular properties due to cancellation of errors. In the present work different levels of approximation have been chosen for various molecular properties to achieve a reasonable compromise between accuracy and computational cost; a similar strategy proved useful in our earlier work (Green, Montgomery, and Thaddeus 1974; Wilson and Green 1977).

#### b) $C_2N$

The CN radical is a well known component of the interstellar gas, being one of the few molecules identified in optical absorption spectra. It has now also been extensively observed at radio frequencies (see, e.g., Turner and Gammon 1975). More recently the  $C_3N$  radical has been identified in radioastronomical observations (Guélin and Thaddeus 1977). In terms of molecular structure,  $C_3N$  is obtained from CN by the addition of a very stable acetylenic  $C_2$  group. Further, CN is the radical obtained by removing a hydrogen

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atom from HCN which is abundant in interstellar space, and  $C_3N$  is the radical obtained by removing a hydrogen atom from  $HC_3N$  (cyanoacetylene) which is also abundant in space. The presence of CN and  $C_3N$  suggests that the intervening member,  $C_2N$ , may also be present.

$C_2N$  differs somewhat from CN and  $C_3N$  in that it cannot be described by a canonical valence bond electronic structure (i.e., tetravalent carbon and trivalent nitrogen). Lack of a standard valence bond structure does not necessarily imply an unstable or even a less stable structure; in fact,  $C_2N$  is known experimentally to exist as a stable, albeit extremely reactive radical. However, it is easier to predict molecular structure and spectral constants for species with a standard valence bond structure. For example, Guélin and Thaddeus (1977) were able to estimate the rotation constant for  $C_3N$  to within a few percent based on “standard” bond lengths for normal valence bond structures. Quantum chemical calculations are thought to be equally accurate in either case, but it would be highly desirable to have more experimental data for molecules with nonstandard electronic structures against which theoretical calculations could be tested. The possibility that radioastronomical data might provide precise information is enticing.

An optical absorption spectrum attributed to the  $C_2N$  radical has been obtained by Merer and Travis (1965) in the flash photolysis of diazoacetonitrile,  $HC(CN)N_2$ . From these spectra they were able to ascertain that the electronic ground state is  $X^2\Pi$ , with an effective rotation constant  $B_{\text{eff}} = 0.3981 \text{ cm}^{-1} = 11.93 \text{ GHz}$ , and a spin-orbit constant  $A = 40.34 \text{ cm}^{-1}$ . Since  $B/A$  is small, the rotational levels are well described by Hund’s case (a), see, e.g., Herzberg (1950). The ground state is  $^2\Pi_{1/2}$ , with the  $^2\Pi_{3/2}$  rotational ladder starting about 60 K higher in energy. The rotational energy levels are given for the  $^2\Pi_{1/2}$  state by

$$E_{1/2}(J) = B_{1/2}J(J+1) - DJ^4, \\ J = 1/2, 3/2, 5/2, \dots, \quad (1a)$$

and for the  $^2\Pi_{3/2}$  state by

$$E_{3/2}(J) = B_{3/2}J(J+1) - D(J+1)^4, \\ J = 3/2, 5/2, 7/2, \dots, \quad (1b)$$

where

$$B_{1/2} = B_{\text{eff}}(1 - B_{\text{eff}}/A), \quad (2a)$$

$$B_{3/2} = B_{\text{eff}}(1 + B_{\text{eff}}/A), \quad (2b)$$

and the centrifugal distortion constant is measured to be  $D = 8 \times 10^{-3} \text{ MHz}$ .

The twofold electronic degeneracy of each rotational level is split by the rotational motion into lambda doublets, with  $\Delta J = \pm 1$  transitions allowed within each ladder only from lower-to-lower and upper-to-upper levels. When the lambda-doublet split-

ting follows the “pure precession” approximation—which is often valid—it is given by

$$\Delta W_{1/2}(J) = a(J + 1/2), \quad (3a)$$

$$\Delta W_{3/2}(J) = b(J^2 - 1/4)(J + 3/2), \quad (3b)$$

where

$$a = 4AB/\Delta E_{\Pi\Sigma} \approx 80 \text{ MHz}, \quad (4a)$$

$$b = 8B^3/\Delta E_{\Pi\Sigma} \approx 0.02 \text{ MHz}, \quad (4b)$$

with  $\Delta E_{\Pi\Sigma}$  the energy to the lowest excited  $^2\Sigma$  state. Thus, lines in the  $^2\Pi_{1/2}$  ladder would be doublets at  $\nu_{1/2}(J \rightarrow J-1) = 23.62J \pm 0.040 \text{ GHz}$ , and lines in the  $^2\Pi_{3/2}$  ladder would be unresolved blends at  $\nu_{3/2}(J \rightarrow J-1) = 24.10J \text{ GHz}$ . However, Merer and Travis (1965) observe highly irregular lambda doublings, of comparable size for  $^2\Pi_{1/2}$  and  $^2\Pi_{3/2}$ ; although the splittings are near the limit of their frequency resolution they appear to be on the order of a few to a few hundred MHz. Therefore, the doublet splittings are not well represented by equations (3) and (4) and must be considered poorly known at this time. (To calculate the magnitude of the lambda doubling ab initio requires a detailed knowledge of the interaction with excited electronic states. The pure precession case arises when this is dominated by a single  $^2\Sigma$  state with appropriate orbital configuration. In  $C_2N$  it is known that there are at least two low-lying  $^2\Sigma$  states which must be considered and possibly a  $^4\Sigma$  as well. It is difficult to obtain accurate ab initio estimates in such cases.)

Finally, each level will be split into three hyperfine components due to the nuclear spin  $I = 1$  of the nitrogen. The hyperfine interactions of a nitrogen nucleus in a  $^2\Pi$  molecule are described by a number of coupling constants. A discussion of the analogous case of NO  $X^2\Pi$  is given by Neumann (1970), and his notation will be followed here. As discussed below, the various hyperfine coupling constants for  $C_2N$  are less than about 10 MHz. Since the hyperfine splittings decrease rapidly for higher rotational levels, it seems unlikely that hyperfine structure will be resolved in radioastronomical observations.

Calculations for the equilibrium bond lengths (and hence the rotation constant) of  $C_2N$  have been reported by Thomson (1973) who obtained self-consistent field (SCF) wavefunctions using two different Slater-type (screened exponential) basis set expansions: double zeta, and double zeta plus polarization. It is generally found that the former (smaller) basis set gives the most reliable bond lengths within the SCF approximation, with errors typically on the order of one percent. For this system little difference was found between bond lengths predicted by the two different basis sets. To accurately compute properties which depend on details of the electronic charge distribution, such as dipole moment and hyperfine constants, it is desirable to use large basis sets. We have repeated the calculations of Thomson, including computation of

TABLE 1  
CALCULATED PROPERTIES FOR  $C_2N X^2\Pi^a$

PROPERTY	BASIS SET		
	DZ	DZ + P	BA + P
$r_{CC}$ (bohr).....	+2.784	+2.784 <sup>b</sup>	+2.784 <sup>b</sup>
$r_{CN}$ (bohr).....	+2.187	+2.187 <sup>b</sup>	+2.187 <sup>b</sup>
$\mu$ (debye).....	+1.1 (1.2)	+1.0	+1.2
$eqQ$ (MHz).....	-4.7 (-6.2)	-4.7	-4.7
$eq_2Q$ (MHz).....	+2.3	+2.3	+2.4
$a$ (MHz).....	+10.5	+10.6	+10.9
$c$ (MHz).....	-5.4 (-12.0)	-5.4	-5.5
$d$ (MHz).....	+12.3	+12.4	+12.7
$b + c/3$ (MHz).....	0.0 <sup>c</sup> (15.2)	0.0 <sup>c</sup>	0.0 <sup>c</sup>

<sup>a</sup> From self-consistent field calculations, except for DZ values in parentheses which are from limited configuration interaction calculations; see text for discussion of expected accuracy.

<sup>b</sup> Bond lengths fixed at values optimized in the DZ calculation.

<sup>c</sup> Constrained to vanish in the SCF formalism.

the hyperfine coupling constants. In addition we have used an even larger basis set labeled  $BA + P$ , which approaches the infinite basis limit, in order to test further the dependence of properties on the expansion basis set. The larger calculations were performed at the equilibrium bond lengths determined in the DZ calculations. Results are presented in Table 1.

Based on standard molecular structure arguments,  $C_2N$  is expected to be linear. Further, a linear symmetry is indicated by the assignment of the spectral data to a  $^2\Pi$  electronic state. Thomson (1973) assumed this symmetry in his work. Nonetheless we have performed a few calculations for slightly nonlinear configurations using a Gaussian double zeta basis set with the conclusion that the linear structure is, in fact, most stable.

From these calculations it is possible to obtain a simple picture of the bonding in  $C_2N$ . The CN group has a triple bond very similar to that in HCN, with a length quite typical of such bonds. The CC bond is somewhat shorter than the 2.9 bohr typical of single bonds in hydrocarbons; however, single bonds next to triple bonds are generally shorter, e.g., 2.76 bohr in  $H_3CCN$  (Merer and Travis 1965), which is quite close to the value calculated for  $C_2N$ . Two of the "extra" three-valence electrons on the end carbon are paired in a  $\sigma$  orbital which points out the back of the molecule, leaving the unpaired electron in a  $\pi$  orbital. The electron density in this nonbonded lobe counteracts the normal  $^+CN^-$  polarity, resulting in a relatively small dipole moment. The rotation constant is predicted to be 11.3 GHz, about 5% smaller than the experimental value; this can be contrasted with analogous calculations for CN which predict a value about 3% too large and for  $C_3N$  which are within 1% of the experimental values.

It is always somewhat difficult to estimate errors in computed properties. It is apparent from Table 1 that

the dipole moment and hyperfine constants are not very sensitive to the basis set, so the remaining errors are due to neglect of correlation effects (configuration interaction) in the SCF model. To estimate these effects limited configuration interaction (CI) calculations were performed, including about 100 singly excited and 100 doubly excited configurations (see, e.g., Green 1974). These calculations used the double zeta (DZ) basis set, and results are given in parentheses next to the DZ SCF values in Table 1. The dipole moment is seen to change only slightly in the CI calculation, and its true value is estimated to be  $\mu = 1.3 \pm 0.2$  Debye. Some of the hyperfine constants are seen to change appreciably due to CI. In particular, the Fermi contact term,  $b + c/3$ , is unrealistically constrained to vanish in the SCF approximation. Hyperfine constants can be very sensitive to details of the charge distribution, and therefore are difficult to predict accurately with approximate wavefunctions; the best computed values in Table 1 are probably accurate to 25%. The important point, however, is that hyperfine constants for  $C_2N$  are all less than about 10 MHz and hyperfine splittings are not likely to be resolved in interstellar observations.

#### b) $C_3H$

$C_3H$  is isoelectronic with  $C_2N$ . The species CH,  $C_2H$ , and  $C_4H$  have all been observed in interstellar spectra. The rotational, fine, and lambda doubling structure of  $C_3H$  are expected to be similar to the isoelectronic  $C_2N$ . The hyperfine structure due to the hydrogen nucleus of spin  $I = 1/2$ , however, will be different from that in  $C_2N$ , but will be analogous to that in CH  $X^2\Pi_r$ . In fact, the rotation, fine structure, and lambda doubling in  $C_3H$  are also analogous to that in CH, although quantitative differences are substantial since  $B/A$  is much larger in CH.

There do not appear to have been any previous theoretical studies of this species. We have performed self-consistent field calculations for  $C_3H$  in a manner analogous to those for  $C_2N$ . The bond lengths were optimized using a Slater-type DZ expansion basis set. The possibility of a nonlinear structure was considered using a Gaussian DZ basis set with the conclusion that the equilibrium structure is linear. The dipole moment and hyperfine coupling constants were computed using a larger, double zeta plus polarization (DZ + P) basis at the optimized bond lengths. Results are shown in Table 2.

The rotation constant predicted from the calculated bond lengths is  $B = 10.8$  GHz. From comparison with the  $C_2N$  results, the estimated error in this quantity is about 4% with the true value probably being larger than the calculated value. The computed dipole moment is probably accurate to half a debye and is therefore much larger in magnitude than that of  $C_2N$  with a corresponding enhancement of the rotational line strength for this species. As in  $C_2N$ , there is a nonbonding electron pair protruding away from the

TABLE 2  
CALCULATED PROPERTIES FOR  $C_3H X^2\Pi^a$

PROPERTY	BASIS SET	
	DZ	DZ + P
$r_{C,C_2}$ (bohr) .....	2.685	2.685 <sup>b</sup>
$r_{C_2,C_1}$ (bohr) .....	2.281	2.281 <sup>b</sup>
$r_{C,H}$ (bohr) .....	2.002	2.002 <sup>b</sup>
$\mu$ (debye) .....	3.2	3.1
$a$ (MHz) .....	10.7	11.0
$c$ (MHz) .....	12.9	12.3
$d$ (MHz) .....	6.5	6.9

<sup>a</sup> From self-consistent field calculations; see text for a discussion of estimated accuracy.

<sup>b</sup> Bond lengths fixed at values optimized in DZ calculations.

end carbon, and this produces the large dipole moment whose polarity is  $^-C_3H^+$ . The predicted hyperfine constants are estimated to be accurate to about 50%. The Fermi contact term,  $b + c/3$ , which is constrained to vanish in the SCF approximation, is likely to have a value of less than 10 MHz from comparison with the *CI* calculations for  $C_2N$ . As in  $C_2N$  the hyperfine structure is probably not resolvable in radio-astronomical observations.

The spin-orbit constant of  $C_3H$  is likely to be within 10% of the value found in  $C_2N$ , i.e.,  $A = 40 \pm 4 \text{ cm}^{-1}$ . Horsley and Hall (1973) have calculated the spin-orbit constant for  $C_2N$  from a SCF wavefunction assuming additive single center atomic contributions and obtaining a value within 10% of experiment. The accuracy of this model suggests little change on passing from  $C_2N$  to  $C_3H$ , since the dominant contribution is from the unpaired  $\pi$  electron whose charge density is 90% on the end carbon atom, and since this orbital is quite similar in the SCF description of both radicals.

#### c) $C_2N^+$

Hartquist and Dalgarno (1979) have predicted from a model of gas-phase ion molecule chemistry in interstellar clouds that  $C_2N^+$  may be one of the most abundant molecular ions. However, their computed abundance may be overestimated by an order of magnitude or more since  $C_2N^+$  is produced in their model predominantly by reaction of  $C^+$  with HCN, and the latter is predicted to have abundances much greater than observed (Hartquist, private communication). Also, these authors assumed that  $C_2N^+$  is not rapidly depleted by reaction with  $H_2$ ; however, data for this reaction appear to be poorly known at present. A similar, although somewhat more sophisticated model calculation of Mitchell, Ginsburg, and Kuntz (1978) also predicts relatively large abundances of  $C_2N^+$  under certain conditions.

There does not appear to be any experimental or theoretical information available for  $C_2N^+$ . We have performed SCF calculations using a Slater-type DZ basis to predict the equilibrium geometry, dipole

TABLE 3  
CALCULATED PROPERTIES FOR  $C_2N^+ X^1\Sigma^+{}^a$

Property	Value
$r_{CC}$ (bohr) .....	+2.677
$r_{CN}$ (bohr) .....	+2.213
$\mu$ (debye) .....	+3.3
$eqQ$ (MHz) .....	-6.6

<sup>a</sup> From self-consistent field calculations; see text for a discussion of estimated accuracy.

moment, and nitrogen quadrupole coupling constant. Results are presented in Table 3. This ion has a closed-shell  $^1\Sigma^+$  ground state. For such cases the predicted rotation constant,  $B = 11.7 \text{ GHz}$ , is expected to be accurate to about 1%. The predicted dipole moment and quadrupole coupling constant are expected to be accurate to better than about 20%.

#### d) $HCNH^+$

The  $HCNH^+$  ion is thought to play a key role in interstellar chemistry. In particular, it is thought to be the immediate precursor of HCN and HNC, both of which are quite abundant; and this assumption has been used to justify the observation that the metastable isomer, HNC, although about half an electron volt less stable than HCN, is nonetheless of comparable abundance (see, e.g., Green and Herbst 1979). Explanations of the observed enhancement of the deuterated species, DCN and DNC, have also involved the  $HCNH^+$  ion. Models of gas phase ion molecule chemistry in interstellar clouds indicate that  $HCNH^+$  may have a large enough equilibrium abundance to be detected by direct radiofrequency observations. Pearson and Schaefer (1974) have performed SCF calculations, similar to those presented above to predict the equilibrium geometry of  $HCNH^+$ . They estimate that the  $J = 1-0$  transition will occur at about 74.8 GHz with an estimated uncertainty of about 1%. The rotational line strength is proportional to the square of the dipole moment; a recent *CI* calculation (Haese and Woods 1979) predicts  $\mu = 0.2$  debye with an expected accuracy of 0.1 debye.

Identification of  $HCNH^+$  in radioastronomical data would be greatly facilitated by the presence of resolvable nitrogen nuclear-quadrupole hyperfine structure, which would provide a characteristic triplet of lines with relative intensities 3:5:1. Therefore the value of the coupling constant is of some interest. Recall that  $eqQ$  is about 5 MHz, which is readily resolved in HCN, but too small to be easily resolved in HNC. We have performed SCF calculations to predict  $eqQ$  for  $HCNH^+$ . The internuclear distances were fixed at the equilibrium values obtained by Pearson and Schaefer (1974), and two different, relatively large Slater-type basis sets were used, giving  $eqQ$  of  $-0.7 \text{ MHz}$  and  $-0.4 \text{ MHz}$ , respectively. It is likely that the true value is  $eqQ = -0.5 \pm 0.5 \text{ MHz}$ , and is

therefore too small to be resolved except possibly in certain sources with very narrow linewidths (see, e.g., Thaddeus and Turner 1975).

### e) HNC

A strong interstellar signal at 90.665 GHz was observed by Snyder and Buhl (1971) which could not be attributed to any species known in the laboratory. Following a suggestion of Herzberg, this signal was tentatively identified as the  $J = 1-0$  transition of HNC, the metastable isomer of HCN. Large-scale, state-of-the-art quantum calculations of Pearson *et al.* (1973) were consistent with this identification, but the estimated uncertainty of about 0.2% precluded a definite assignment. A further problem was that these calculations predicted a nitrogen nuclear quadrupole coupling constant  $eqQ = 0.9$  MHz with an estimated uncertainty of 50%. If accurate, this would suggest an observable splitting, or at least a detectable broadening of the interstellar line which was not observed (see, e.g., Snyder and Hollis 1976).

We realized that this apparent conflict could be resolved by noting that Pearson *et al.* (1973) had probably underestimated the error in their calculated  $eqQ$ . Their expansion basis set, while quite accurate for bond lengths, was likely to be poor for predicting  $eqQ$ . Further, errors in calculated properties such as dipole moments and hyperfine coupling constants tend to be absolute, rather than relative; the error of more than a MHz (about 25%) found by Pearson *et al.* (1973) in an analogous calculation for  $eqQ$  in HCN suggested that the error in HNC could easily be 100% of the predicted value. To obtain a more reliable theoretical estimate, we performed SCF calculations for HCN and HNC using very large Slater-type basis sets. Our results—which have been quoted previously by Snyder and Hollis (1976), Snyder, Hollis, and Buhl (1977), and Frerking, Langer, and Wilson (1979)—are presented in Table 4. It is seen that  $eqQ$  is predicted to be very

TABLE 4  
CALCULATED PROPERTIES FOR HCN AND HNC<sup>a</sup>

Property	HCN	HNC
$\mu$ (debye).....	+3.29 (2.98) <sup>b</sup>	2.86
$eq_N Q_N$ (MHz).....	-4.44 (-4.71) <sup>b</sup>	0.04 (0.29 ± 0.04) <sup>c</sup>
$eq_D Q_D$ (MHz).....	+0.20 (0.19) <sup>b</sup>	0.27

<sup>a</sup> From large basis set SCF calculations; experimental values are in parentheses.

<sup>b</sup> Delucia and Gordy 1969.

<sup>c</sup> Frerking, Langer, and Wilson 1979.

close to zero, with an estimated uncertainty of  $\pm 0.3$  MHz.

The line at 90.665 GHz has, of course, now been unequivocally identified as HNC, based on laboratory measurements of the transition frequency (Arrington and Ogryzlo 1975; Saykally *et al.* 1976b). Very recently, the nitrogen hyperfine splitting has been resolved in an interstellar source by Frerking, Langer, and Wilson (1979); these authors discuss problems with earlier astronomical determinations and obtain a value of  $eqQ = +0.3$  MHz, in agreement with theory. Also given in Table 4 are calculated values for the dipole moments and deuterium nuclear quadrupole coupling constants in DCN and DNC. From comparison of theory and experiment for HCN, it appears that for HNC  $eq_D Q_D = 0.27 \pm 0.02$  MHz. A recent configuration interaction calculation (Haese and Woods 1979) gives the dipole of HNC as  $\mu = 3.1 \pm 0.1$  debye.

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### REFERENCES

- Arrington, C. A., and Ogryzlo, E. A. 1975, *J. Chem. Phys.*, **63**, 3670.  
 Buhl, D., and Snyder, L. E. 1970, *Nature*, **228**, 267.  
 DeLucia, F. C., and Gordy, W. 1969, *Phys. Rev.*, **187**, 58.  
 Frerking, M. A., Langer, W. D., and Wilson, R. W. 1979, *Ap. J. (Letters)*, **232**, L65.  
 Green, S. 1974, *Adv. Chem. Phys.*, **25**, 173.  
 Green, S., and Herbst, E. 1979, *Ap. J.*, **229**, 121.  
 Green, S., Montgomery, J. A., and Thaddeus, P. 1974, *Ap. J. (Letters)*, **193**, L89.  
 Guélin, M., and Thaddeus, P. 1977, *Ap. J. (Letters)*, **212**, L81.  
 Guélin, M., Green, S., and Thaddeus, P. 1978, *Ap. J. (Letters)*, **224**, L27.  
 Haese, N. N., and Woods, R. C. 1979, *Chem. Phys. Letters*, **61**, 396.  
 Hartquist, T. W., and Dalgarno, A. 1979 in *Proceedings of the Gregynog Conference on Giant Molecular Clouds*, ed. P. Solomon (New York: Pergamon).  
 Herzberg, G. 1950, *Spectra of Diatomic Molecules* (New York: Van Nostrand).  
 Horsley, J. A., and Hall, J. A. 1973, *Molec. Phys.*, **25**, 483.  
 Klemperer, W. 1970, *Nature*, **227**, 1230.  
 Merer, A. J., and Travis, D. N. 1965, *Canadian J. Phys.*, **43**, 1795.  
 Mitchell, G. F., Ginsburg, J. L., and Kuntz, P. J. 1978, *Ap. J. Suppl.*, **38**, 39.  
 Neumann, R. M. 1970, *Ap. J.*, **161**, 779.  
 Pearson, P. K., Blackman, G. L., Schaefer, H. F., Roos, B., and Wahlgren, U. 1973, *Ap. J. (Letters)*, **184**, L19.  
 Pearson, P. K., and Schaefer, H. F. 1974, *Ap. J.*, **192**, 33.  
 Saykally, R. J., Dixon, T. A., Anderson, T. G., Szanto, P. G., and Woods, R. C. 1976a, *Ap. J. (Letters)*, **205**, L101.  
 Saykally, R. J., Szanto, P. G., Anderson, T. G., and Woods, R. C. 1976b, *Ap. J. (Letters)*, **204**, L143.  
 Snyder, L. E., and Buhl, D. 1971, *BAAS*, **3**, 388.  
 Snyder, L. E., and Hollis, J. M. 1976, *Ap. J. (Letters)*, **204**, L139.  
 Snyder, L. E., Hollis, J. M., and Buhl, D. 1977, *Ap. J. (Letters)*, **215**, L87.  
 Thaddeus, P., and Turner, B. E. 1975, *Ap. J. (Letters)*, **201**, L25.  
 Thomson, C. 1973, *J. Chem. Phys.*, **58**, 841.  
 Tucker, K. D., Kutner, M. L., and Thaddeus, P. 1974, *Ap. J. (Letters)*, **193**, L119.  
 Turner, B. E. 1974, *Ap. J. (Letters)*, **193**, L83.

Turner, B. E., and Gammon, R. H. 1975, *Ap. J.*, **198**, 71.

Wahlgren, U., Liu, B., Pearson, P. K., and Schaefer, H. F. 1973,  
*Nature*, **246**, 4.

Wilson, S., and Green, S. 1977, *Ap. J. (Letters)*, **212**, L87.

Woods, R. C., Dixon, T. A., Saykally, R. J., and Szanto, P. G. 1975,  
*Phys. Rev. Letters*, **35**, 1269.

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