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THEORETICAL STUDY OF ISOCYANOACETYLENE AND THE ISOCYANOETHYNYL RADICAL

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ABSTRACT

Quantum mechanical calculations, using the matrix Hartree-Fock model, have been performed to obtain estimates of the rotation constants of the isocyanoacetylene molecule and the isocyanoethynyl radical which may be detectable in space. A rotation constant, B_e, of 5076 MHz is calculated for HC_2NC while for the radical C_2NC the value 5458 MHz is obtained.

Subject headings: interstellar: molecules — molecular processes — quantum mechanics

The cyanoethynyl radical, C≡C—C≡N, has been tentatively identified (Guélin and Thaddeus; Wilson and Green 1977) in the molecular envelope of the carbon star IRC +10216. This is perhaps not surprising since HCN (Snyder and Buhl 1971), CN (Jefferts *et al.* 1970), and HC≡C—C≡N (Turner 1971) are fairly common species in space and are known to be relatively abundant in IRC +10216 (Morris *et al.* 1971; Wilson *et al.* 1971; Morris *et al.* 1975). Since the hydrogen isocyanide molecule has been detected (Snyder and Hollis 1976), it is possible that the isocyanoacetylene molecule, HC≡C—N≡C, and the corresponding radical, the isocyanoethynyl radical, C≡C—N≡C, are also present in space and particularly in the molecular envelope of IRC +10216 or similar carbon star. In the present work we report quantum mechanical studies of these two species for which no laboratory data are available.

Matrix Hartree-Fock calculations have been employed to obtain estimates of the equilibrium geometries of HC_2NC and C_2NC, and thus the rotation constants, B_e, are determined. We illustrate the reliability of the Hartree-Fock model in this context by studying similar molecules for which experimental data have been reported.

Cyanoacetylene is known to be linear, and we shall assume this to be true of the isomer HC_2NC and the corresponding radical C_2NC. The isocyanoacetylene molecule is described by the molecular orbital configuration

$$X^1\Sigma^+ : 1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma^2 9\sigma^2 1\pi^4 2\pi^4 ,$$

while for the isocyanoethynyl radical we have

$$X^2\Sigma^+ : 1\sigma^2 2\sigma^2 3\sigma^2 4\rho^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma^2 9\sigma 1\pi^4 2\pi^4 .$$

A basis set of contracted Gaussian functions was used to parametrize the molecular orbitals. Two basis functions were included for each occupied *nl* shell in the separated atoms (Dunning 1970).

Assuming a linear geometry, the structural parameters were optimized by the method of alternating directions. By studying cyanoacetylene and some simpler homologous molecules, it is possible to give *qualitative* estimates of the accuracy of the present calculations. The theoretically determined bond lengths for several pertinent systems are shown in Figure 1 together with the known experimental values in parentheses. For cyanoacetylene the theoretical and experimental bond lengths are within 1%. The calculated bond lengths for HCN and HNC agree to within 0.3% and 0.5%, respectively, of the experimental values, while for the CN radical the bond length differs by 1.1%. The latter is indicative of the change in the accuracy afforded by the Hartree-Fock model on passing from closed- to open-shell systems.

More relevant for either astrophysical or laboratory studies than bond lengths is a comparison of theoretical and experimental rotation constants. This comparison is made in Table 1. For cyanoacetylene the theoretical B_e value is within 0.05% of the experimental B_0 value. For the cyanoethynyl radical, which has been tentatively identified in IRC +10216, these constants are within 0.2%. This agreement is somewhat deceptive since vibration-rotation interactions

TABLE 1

SOME THEORETICAL AND EXPERIMENTAL ROTATION CONSTANTS FOR PERTINENT MOLECULAR SPECIES

Molecule	Frequency Range	Theoretical Value	Experimental Value
HCCNC.....	MHz	5076	...
HCCCN.....	MHz	4551	4549[a]
CCNC.....	MHz	5458	...
CCCN.....	MHz	4955[b]	4947[c]
CN.....	GHz	58.20	56.69[d]
HCN.....	GHz	44.71 (44.53)[e]	44.32[f]
HNC.....	GHz	45.37 (45.43)[e]	45.33[g]

REFERENCES.—[a] Westenberg and Wilson 1950; De Zafra 1971. [b] Wilson and Green 1977. [c] Guélin and Thaddeus 1977. [d] Penzias *et al.* 1974. [e] Pearson *et al.* 1973. [f] DeLucia and Gordy 1969. [g] Cresswell *et al.* 1976; Saykally *et al.* 1976.

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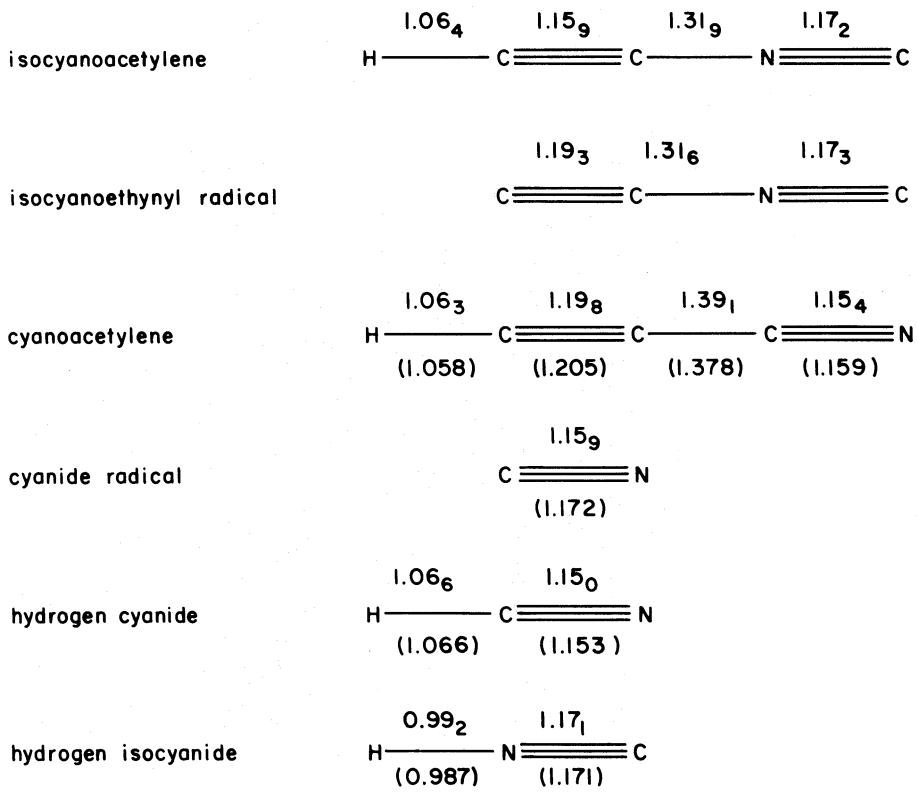

FIG. 1.—Some pertinent molecular species. The calculated bond lengths, in angstroms, are shown, and the experimental values, when available, are given in parentheses. All molecules were assumed to be linear.

typically lead to differences of about 0.5% between values of B_e and B_0. The calculated B_e values for HCN and HNC are within 0.9% and 0.1%, respectively, of the experimental B_0 values. For HCN an experimentally determined B_e constant of 44.51 GHz has been reported (Winnewisser, Maki, and Johnson 1971) which compares favorably with the present calculation. For the corresponding radical, CN, there is a 2.7% difference between the theoretical and experimental rotation constants. Again this is indicative of the accuracy which may be achieved from open-shell Hartree-Fock studies.

The calculated rotation constants, B_e, for various isotopically substituted isocyanoacetylene molecules are given in Table 2. The observation of these species can provide useful evidence for the assignment of lines. Theoretically determined rotation constants for the isocyanoethynyl radical are presented in Table 3.

Hyperfine interactions will cause additional structure in the transitions among lower rotational levels. The nitrogen nucleus has a permanent quadrupole moment which will give rise to an eqQ interaction. From data which has been reported for cyanide-isocyanide pairs (Gosh, Trambarulo, and Gordy 1953; Bolton, Owen, and Sheridan 1969; Yamada and Winnewisser 1975; Bak, Van Eijck, and Kierkegaard 1973; Kukolich 1972), we estimate eqQ to be small for the isocynaide species. For HCN we have $eqQ = -4.7$ MHz (DeLucia and Gordy 1969); for HC_3N,

TABLE 2

THEORETICALLY DETERMINED ROTATION CONSTANTS FOR ISOTOPICALLY SUBSTITUTED ISOCYANOACETYLENE MOLECULES

Molecule	B_e, MHz
HCCNC	5076
DCCNC	4697
$H^{13}CCNC$	4920
$HC^{13}CNC$	5056
$HCC^{15}NC$	5053
$HCCN^{13}C$	4909

TABLE 3

THEORETICALLY DETERMINED ROTATION CONSTANTS FOR ISOTOPICALLY SUBSTITUTED ISOCYANOETHYNYL RADICALS

Molecule	B_e, MHz
CCNC	5458
$^{13}CCNC$	5262
$C^{13}CNC$	5432
$CC^{15}NC$	5435
$CCN^{13}C$	5275

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$eqQ = -4.3$ MHz (Westenberg and Wilson 1950; De Zafra 1971); and the theoretical value of eqQ for C_3N is -4.1 MHz (Wilson and Green 1977). For HNC, on the other hand, eqQ is found experimentally to be less than 1 MHz (Cresswell *et al.* 1976). The ^{14}N nucleus has nonzero nuclear spin, and the interaction of the resulting nuclear magnetic moment with the spin of the unpaired electron in a $^2\Sigma$ radical will lead to additional structure in the lower levels.

The total energy of the cyanoacetylene molecule at its equilibrium nuclear geometry was calculated to be -168.4896 hartrees while that of its isomer, HC_2NC, was found to be -168.4595 hartrees—a difference of 0.82 eV. For the corresponding radicals C_2CN and C_2NC, the total energies were calculated to be -167.8037 hartrees and -167.7762 hartrees, respectively. The isomerization energy for the radicals is 0.75 eV.

Several members of the homologous series of compounds $H—(C{\equiv}C)_n—C{\equiv}N$ (Turner 1971; Avery *et al.* 1976) have now been detected in space. The discovery of HCN and HNC suggests that the isocyano-species may also be present. The tentative detection of the cyanoethynyl radical C_2CN (Guélin and Thaddeus 1977; Wilson and Green 1977) suggests that the radicals C_2NC, C_2C_2CN and C_2C_2NC, C_2C_2NC, $C_2C_2C_2CN$, etc., should also be searched for. Such radicals may possibly play an important role in interstellar chemical processes.

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REFERENCES

Avery, L. W., Broton, N. W., MacLeod, J. M., Oka, T., and Kroto, H. W. 1976, *Ap. J.* (*Letters*), **205**, L173.
Bak, B., Van Eijck, B. P., and Kierkegaard, C. 1973, *J. Molec. Struct.*, **18**, 429.
Bolton, K., Owen, N. L., and Sheridan, J. 1969, *Spectrochim. Acta*, **25A**, 1.
Cresswell, R. A., Pearson, E. F., Winnewisser, M., and Winnewisser, G. 1976, *Zs. Naturforsch.*, **31a**, 221.
DeLucia, F., and Gordy, W. 1969, *Phys. Rev.*, **187**, 58.
De Zafra, R. L. 1971, Ap. J., **170**, 165.
Dunning, T. H. 1970, *J. Chem. Phys.*, **53**, 2823.
Gosh, S. N., Trambarulo, R., and Gordy, W. 1953, *J. Chem. Phys.*, **21**, 308.
Guélin, M., and Thaddeus, P. 1977, *Ap. J.* (*Letters*), **212**, L81.
Jefferts, K. B., Penzias, A. A., and Wilson, R. W. 1970, *Ap. J.* (*Letters*), **161**, L87.
Kukolich, S. G. 1972, *J. Chem. Phys.*, **57**, 869.
Morris, M., Gilmore, W., Palmer, P., Turner, B. E., and Zuckerman, B. 1975, *Ap. J.* (*Letters*), **199**, L47.
Morris, M., Zuckerman, B., Palmer, P., and Turner, B. E. 1971, *Ap. J.* (*Letters*), **170**, L109.
Pearson, P. K., Blackman, G. L., Schaeffer, H. F., Roos, B., and Wahlgren, U. 1973, *Ap. J.* (*Letters*), **184**, L19.
Penzias, A. A., Wilson, R. W., and Jefferts, K. B. 1974, *Phys. Rev. Letters*, **32**, 179.
Saykally, R. J., Szanto, P. G., Anderson, T. G., and Woods, R. C. 1976, *Ap. J.* (*Letters*), **204**, L143.
Snyder, L. E., and Buhl, D. 1971, *Ap. J.* (*Letters*), **163**, L47.
Snyder, L. E., and Hollis, J. M. 1976, *Ap. J.* (*Letters*), **204**, L139.
Turner, B. E. 1971, *Ap. J.* (*Letters*), **163**, L35.
Westenberg, A. A., and Wilson, E. B. 1950, *J. Am. Chem. Soc.*, **72**, 199.
Wilson, R. W., Solomon, P. M., Penzias, A. A., and Jefferts, K. B. 1971, *Ap. J.* (*Letters*), **169**, L35.
Wilson, S., and Green, S. 1977, *Ap. J.* (*Letters*), **212**, L87.
Winnewisser, G., Maki, A. G., and Johnson, D. R. 1971, *J. Molec. Spectrosc.*, **39**, 149.
Yamada, K., and Winnewisser, M. 1975, *Zs. Naturforsch.*, **30a**, 672.

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