PROSPECTS FOR THE DETECTION OF INTERSTELLAR CYANOVINYLIDENE

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ABSTRACT

Prospects for the presence and detection of interstellar cyanovinylidene, CC(H)CN, a Y-shaped isomer of cyanoacetylene, are discussed. It is proposed that CC(H)CN can arise in interstellar clouds as one of the HC3NH+ + e− dissociative recombination products, by rearrangements of the neutral chain radical HC3NH into branched species HCCCN, CC(H)C(H)N, and/or HCC(H)CN, and by the subsequent elimination of a hydrogen atom. It is deduced that the abundance of cyanovinylidene in molecular clouds should be confined between the abundances of its chain isomers HNCCC and HCNCC. Quantum chemical predictions regarding cyanovinylidene geometry, ground-state rotational constants, centrifugal distortion constants, spin–orbit coupling, IR absorption spectroscopy, and electric dipole moment are given. The spectroscopically observed molecules formyl cyanide, NC2(H)O, and propynal, HC3(H)O, with structures qualitatively resembling cyanovinylidene, served to prove the adequacy of the calculational procedures employed.

Key words: astrochemistry – ISM: abundances – ISM: molecules – molecular data – molecular processes

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1. INTRODUCTION

Ever since its discovery in space by Turner (1971), cyanoacetylene (HCCCN, 2-propynenitrile; hereafter 1) is being found in diverse environments including expanding envelopes around asymptotic giant branch (AGB) or post-AGB stars, clouds associated to H II regions, quiet dust clouds (Morris et al. 1976), and star-forming regions (Sakai et al. 2008). The abundances of the isomeric molecules HCCCN (isocyanoacetylene, 2) and CCCNH (iminopropadienylidene, 3), first postulated by Wilson (1978) and Green & Herbst (1979), and discovered in TMC-1 by Kawaguchi et al. (1992a, 1992b), are low when compared to cyanoacetylene. Approximate ratios [1]:[2] = 130:1 and [1]:[3] = 1000:1 were found in TMC-1 (Ohishi & Kaifu 1998). Similarly, Gensheimer (1997) reported [1]:[2] = 130:1 for IRC + 10216. The neutral–neutral reaction C2H2 + CN (Woon & Herbst 1997; Fukuzawa & Osamura 1997; Huang et al. 2000; Balucani et al. 2000) was recognized as the probable main gas-phase source of interstellar cyanoacetylene, while the dissociative recombination HC3NH+ + e−, thoroughly analyzed by Osamura et al. (1999) on theoretical grounds, is expected to produce, in addition to cyanoacetylene, the desired quantities of isomers 2 and 3. (Noteworthy, as pointed out by Szczepanski et al. (2005), photochemical processes within interstellar ice grains containing C2H and ammonia are likely to produce species 3 and subsequently 1.) Osamura et al. (1999) considered also the potential formation of the fourth chain isomer, CCNCH (4), a highly energetic species (Kolos & Dobrowolski 2003).

Cyanovinylidene, CC(H)CN (5), is the most probable structure (see Figure 1) among imaginable branched isomers of cyanoacetylene. The extensive quantum chemical calculations carried out by Hu & Schaefer (1993) demonstrated the separation of isomers 1 and 5 by a non-negligible energy barrier (9.2 kJ mol−1)—which permitted to consider 5 as the true minimum on the C3HN potential energy hypersurface, and there-fore as a potentially observable molecule. Indeed, Goldberg & Schwarz (1994) soon reported on its mass-spectrometric detection in a neutralization–reionization experiment. Hu & Schaefer (1993) also calculated the cyanovinylidene dipole moment, rotational constants, vibrational frequencies, and the energy of a low-lying triplet state. The present work suggests a route for the interstellar synthesis of this species, and supplies further predictions of value for future microwave and infrared searches.

2. COMPUTATIONAL DETAILS

All calculations reported here have been carried out with the Gaussian 03 suite of programs (Frisch et al. 2004). The coupled cluster method (Pople et al. 1987) was employed. Its CCSD (single and double excitations) version was used to predict the molecular structures along the reaction path, as well as for the calculation of IR absorption intensities and the values of the equilibrium electric dipole moment. The CCSD(T) variant (singles, doubles, and the perturbative treatment of triple excitations) served us in the derivation of the cyanovinylidyne geometry. Normal modes of molecular vibrations were obtained, within the harmonic approximation, through numerical second derivatives of the total energy, with respect to nuclear positions, at the Brueckner coupled cluster (Handy et al. 1989) level, BCCSD(T). This method was also employed to derive the set of independent quartic centrifugal distortion constants (which depend only on the quadratic, i.e., harmonic, part of the vibrational Hamiltonian). Anharmonic calculations, involving the numerical differentiation along normal modes, served us to obtain vibrational frequencies, vibration–rotation coupling constants, and sextic centrifugal distortion constants. These were performed at the density functional theory (DFT) level (Hohenberg & Kohn 1964; Kohn & Sham 1965), making use of the three-parameter hybrid exchange functional method and the correlation functional B3LYP (Becke 1993; Lee et al. 1988). The search for transition states (first-order saddle points) was carried out with the synchronous transit-guided quasi-Newton (STQN)
method (Peng & Schlegel 1994). The nature of stationary points (local minima or saddle points) on the potential energy surface (PES) was revealed by the absence or presence of imaginary vibrational modes. Lowest-lying molecular orbitals, occupied by inner-shell electrons, were constrained to remain doubly occupied in all calculations (“frozen core” approximation). Basis sets of the triple-zeta quality, cc-pVTZ, aug-cc-pVTZ (Dunning 1989), and TZVP (Schaefer et al. 1992) were used.

3. POTENTIAL ENERGY SURFACE CALCULATIONS

Following the capture of a slow (“cold”) electron in the interstellar environment, the ground-state HCCCNH⁺ cation turns into an odd-electron (i.e., “radical”) neutral species HCCCNH (hereafter R1) in a diffuse Rydberg state, or rather in a continuum of Rydberg states near the ionization limit. The newly formed radical is therefore rich in energy, which it cannot easily dispose of; the radiative relaxation is slow, and so are the collision-induced energy exchange processes at interstellar cloud conditions. The fate of the system is thus mostly determined by energetically feasible unimolecular transformations experienced by a highly energetic radical species of the C₃H₂N stoichiometry. A simplification of this problem, proposed by Osamura et al. (1999), consists in the confinement of such transformations to the ground-state PES. Indeed, some R1 radicals certainly pass to the ground electronic state (preserving their high internal energy content), driven by equienergetic internal conversion processes and possibly by some radiative relaxation. A more realistic approach would have to include the presence of excited valence electronic states, and consequent rearrangements of the radical therein (including the bond breaking, possibly via the predissociation), on respective PESs.

Pathways producing cyanoacetylene (1) and chain isomers 2, 3, and 4, available within the ground-state PAS of C₃H₂N after the neutralization of HCCCNH⁺, have been investigated by Osamura et al. (1999). We presently propose (Figure 2) the extension of this scheme with the creation of 5, derived at the UCCSD/TZVP level.

Initially, the N–H hydrogen of R1 can be shifted through the transition state TS1 to the neighboring carbon atom, giving rise to the Y-shaped species R2 (depicted in Figure 3, along with other C₃H₂N molecules), which in turn experiences, with the shift of another hydrogen atom to the middle carbon, the rearrangements into energy-rich radicals R3. The latter are trans (R3t, with C–H bonds pointing to opposite directions) and cis (R3c). Despite very similar electronic energies (differing by just 6 kJ mol⁻¹), trans and cis forms (the conformers) are distinctly different chemical entities: R3t is almost nonpolar and flat, while R3c features a substantial electric dipole moment and lacks any symmetry elements. The barrier between the two forms (transition state TS4) can be crossed easily (see Table 1 for all relevant energy values). Our PES analysis indicates that both R3 conformers may rearrange toward cyanovinylidene. Indeed, R3c can lose a hydrogen atom (the one in the vicinity of N) and yield 5 through the transition state TS6. An analogous process is not feasible for R3t, which species, however, can be transformed via TS5 into the cyanovinyl radical R4t, a direct (i.e., without a transition state intermediate) precursor to cyanovinylidene. Species R4t is practically equienergetic to R4c; the latter, however, does not offer an obvious exit channel to 5. Cyanovinyl radicals have been postulated by Fukuzawa & Osamura (1997), Woon & Herbst (1997), Huang et al. (2000), and Balucani et al. (2000) as important intermediate products in the C₂H₂ + CN → HC₃N reaction. Of note, R4t can be converted to R5, the most deeply bound of all C₃H₂N radicals. Radicals R4 are, just as R5 and R2, the direct precursors to cyanoacetylene (not marked in Figure 2). Somewhat unexpectedly, we did not find any direct passage between the energy minima R2 and R4; the hydrogen atom at the C(H)N terminal of R2 is more prone to detach permanently, yielding 1, than to bond to the middle carbon.

All intermediate species leading to cyanovinylidyne are easily accessible from the energetic point of view, as evident from their negative (within the convention adopted here, see Figure 2 and Table 1) electronic energies. Prior to the possible outcome of astrochemical models supplemented with the synthesis and decay of 5, one can use the current scheme for some qualitative predictions. First, it suggests the creation of 5 as less probable than that of 3. In fact, isomer 5 is expected to be slightly more stable than 3 (by 9.6 kJ mol⁻¹; Kolos & Dobrowolski 2003) — but the latter is produced directly from R1, via a simple hydrogen elimination. Therefore, as seen from the original minimum (R1), the PES curvature appears much more convoluted in the direction of 5 than in the direction of 3. Conversely, given roughly similar complexities of synthetic routes toward 4 (cf. Figure 4 in Osamura et al.’s (1999) paper) and toward 5 (this work), together with a much lower thermodynamic stability of 4 than of 5 (a difference of 121 kJ mol⁻¹; Kolos & Dobrowolski

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**Table 1**

| Species | Relative Energy (kJ mol⁻¹) |
|---------|---------------------------|
| R1      | 627.5                     |
| R2      | 648.7                     |
| R3t     | 464.6                     |
| R3c     | 458.9                     |
| R4t     | 705.2                     |
| R4c     | 705.4                     |
| R5      | 727.1                     |
| TS1     | 441.6                     |
| TS2     | 446.8                     |
| TS3     | 442.2                     |
| TS4     | 454.8                     |
| TS5     | 380.9                     |
| TS6     | 296.1                     |
| TS7     | 482.2                     |
| TS8     | 682.1                     |
| 5 + H   | 334.8                     |

**Note.** Values are relative, against HCCCNH⁺; the absolute CCSD/TZVP-derived electronic energy of this cation is −444913.2 kJ mol⁻¹.
one can anticipate species 5 to be more probable a product than 4. The abundance of cyanovinylidene in molecular clouds can thus be crudely estimated as confined between those of chain isomers HCNCC and HNCCC.

4. ROTATIONAL AND VIBRATIONAL SPECTROSCOPY

As demonstrated in an earlier study (Gronowski & Kołos 2007), experimental values of equilibrium interatomic distances in HCN, HNC, HC3N, HC2NC, and HC5N molecules were satisfactorily reproduced by combining ab initio (coupled cluster) and DFT-derived values, with appropriate scaling. The very same approach was presently adopted to the case of cyanovinylidene; the recipe involved: (1) employing CCSD(T)/aug-cc-pVTZ to obtain C–C and C–N distances (subsequently downscaled by the factor 0.9949) and all bond angles, and (2) using an unscaled B3LYP/aug-cc-pVTZ length for the C–H bond. The ensuing geometry (depicted in Figure 1) led to the following set of equilibrium rotational constants: $A_e = 72.48$ GHz, $B_e = 5432$ MHz, and $C_e = 5054$ MHz.

In the next step, the anharmonic treatment of molecular vibrations at the B3LYP/aug-cc-pVTZ level enabled us to obtain the vibration–rotation coupling constants $\alpha_i^A$, $\alpha_i^B$, and $\alpha_i^C$ (index $i$ running over all $N$ vibrational modes, with their

Figure 2. Schematic representation of molecular rearrangements relevant to cyanovinylidene synthesis within the $C_3H_2N$ potential energy surface, as derived at the UCCSD/TZVP level of theory. See Table 1 for energy values. The UCCSD/TZVP energies corresponding to remaining exit channels, not discussed here, are marked on the ordinate.

Figure 3. Geometries and equilibrium electric dipole moments for selected $C_3H_2N$ species of interest to cyanovinylidene synthesis, as derived at the UCCSD/TZVP level of theory. All structures are planar with the exception of $R3c$, where the H–C–C–N dihedral angle is 128.5°. Bond lengths given in Ångstroms, angles in arc degrees.

(A color version of this figure is available in the online journal.)

Figure 4. Geometries of the benchmark molecules formyl cyanide (right) and propynal (left) derived with the procedure identical to that applied to cyanovinylidene (cf. Figure 1). Bond lengths given in Ångstroms, angles in arc degrees.

(A color version of this figure is available in the online journal.)
degeneracy factors $d_i$). Ground-state rotational constants were then calculated by the formula

$$A_0 \approx A_e - \frac{1}{2} \sum_{i=1}^{N} d_i \alpha_i^A$$

and by analogous formulas for $B_0$ and $C_0$. Resultant values are listed in Table 2 (the complete set of $\alpha_i$ constants is available from the authors upon request).

To verify the adequacy of this approach, we have applied it to test objects—chosen from molecules similar to \( \text{5} \), yet with known rotational spectroscopy. Formyl cyanide, \( \text{NC}_2(\text{H})\text{O} \), and propynal, \( \text{HC}_3(\text{H})\text{O} \), can indeed serve as analogues of cyanovinylidyne, \( \text{NC}_2(\text{H})\text{C} \), in terms of overall structural characteristics (cf. Figures 1 and 4). With their asymmetry parameters $\kappa = (2B - A - C)/(A - C) \approx -0.99$, all three molecules closely approach the prolate symmetric top case. Table 2 summarizes the results of the present test calculations on formyl cyanide and propynal molecules, comparing the theoretical predictions, when possible, to experimental values. Apart from ground-state rotational constants, the centrifugal distortion constants are listed: quartic (harmonic BCCSD(T)/cc-pVTZ computation) and sextic (anharmonic B3LYP/aug-cc-pVTZ). The measured (Bogey et al. 1995; Costain & Morton 1959) rotational constants of test molecules match our predictions fairly well; the crucial $B_0$ and $C_0$ constants are reproduced with an accuracy ranging from 0.05% to 0.2%. For the set of five quartic centrifugal distortion constants defined by Watson’s (1966, 1967) reduced Hamiltonian formalism, the mean computational error is close to 18%. On the other hand, test calculations reveal a much lower reliability of the procedure applied here for sextic distortion constants. The whole set of cyanovinylidyne molecular constants—predicted with the same methods as those used

### Table 2

| Constant | Theoretical Method | Formyl Cyanide | Propynal | Cyanovinylidyne |
|----------|--------------------|----------------|----------|-----------------|
| $A_0$ (MHz) | CCSD(T)/aug-cc-pVTZ | 69938 | 353 | 68754 |
| $B_0$ (MHz) | combined with B3LYP/aug-cc-pVTZ (see the text) | 5007.6 4981.6 | 5010.18856 4826.223 | 6026.60 |
| $C_0$ (MHz) | | 4666.0 4499.612 | 4656.60175 | 6268.6 |
| $\Delta \delta$ (kHz) | BCCSD(T)/cc-pVTZ | 2.244 2.182 | 2.27243 | 2.0 |
| $\Delta K$ (kHz) | | -176.3 -143.1148 | -182.8 -141 | -83.31 |
| $\Delta \kappa$ (kHz) | | 8252 1016 | 7360.65 | 3339 |
| $\delta_1$ (kHz) | | 0.3960 0.3458 | 0.38974 | n/a |
| $\delta_2$ (kHz) | | 16.36 13.73 | 33.194 | n/a |
| $\phi_1$ (Hz) | B3LYP/aug-cc-pVTZ | 0.007533 | 0.00723 | 0.005782 |
| $\phi_1$ (Hz) | | -0.6498 -0.6074 | -0.202 | 0.01003 |
| $\phi_2$ (Hz) | B3LYP/aug-cc-pVTZ | 2765 | 3643 | 1062 |
| $\phi_2$ (Hz) | | 2.24443 1.8624 | 2.27243 | 2.0|
| $\phi_3$ (Hz) | | 0.002776 0.002180 | 0.002521 | n/a |
| $\phi_4$ (Hz) | | 0.06382 0.003431 | 0.0193 | n/a |
| $\phi_5$ (Hz) | | 76.56 82.17 | 1006 | n/a |
| $\mu$ (D) | | 2.7774 | n/a | 2.78 |

### Notes

Rotational constants for cyanovinylidyne isotopomers $2\text{H}$, $15\text{N}$, and $13\text{C}$ are available from the authors upon request.

* This value measured by Brown & Godfrey (1984).

### Table 3

| Symmetry | CCSD(T)/DZP | B3LYP/aug-cc-pVTZ | B3LYP/aug-cc-pVTZ | B3LYP/aug-cc-pVTZ | BCCSD(T)/cc-pVTZ | CCSD/cc-pVTZ |
|----------|-------------|--------------------|-------------------|-------------------|------------------|---------------|
| $A'$ | 3162 | 24 | 2910.3 | 2835.8 | -195.8 | 3112.5 | 2917 | 40 |
| $A''$ | 2257 | 7 | 2257.4 | 2193.6 | -31.8 | 2289.1 | 2257 | 12 | 5 |
| $A'$ | 1648 | 55 | 1663.2 | 1721.0 | -11.5 | 1672.9 | 1661 | 62 |
| $A''$ | 1021 | 1 | 974.0 | 969.4 | -4.5 | 1018.8 | 974 | 6 |
| $A'$ | 924 | 3 | 879.7 | 893.4 | -23.0 | 919.7 | 897 | 4 |
| $A''$ | 495 | 5 | 626.2 | 618.6 | -33.6 | 647.8 | 614 | 25 |
| $A'$ | 396 | 3 | 403.7 | 410.2 | -10.2 | 399.1 | 389 | 3 |
| $A''$ | 247 | 3 | 362.9 | 365.0 | -13.0 | 366.0 | 353 | 0 |
| $A'$ | 162 | 16 | 147.4 | 139.4 | -14.2 | 155.2 | 141 | 20 |

### Notes

Recommended vibrational frequencies for cyanovinylidyne isotopomers $^2\text{H}$, $^{15\text{N}}$, and $^{13\text{C}}$ are available from the authors upon request.

* Frequencies multiplied by 0.96.

* Difference between harmonic (unscaled) and anharmonic B3LYP frequencies.

* B3LYP anharmonic correction applied.
for the benchmark species—is listed in the rightmost part of Table 2.

Harmonic frequencies of 5 were calculated at the advanced ab initio level, BCCSD(T)/cc-pVTZ. Independently, both harmonic and anharmonic frequencies were found with the DFT (B3LYP/aug-cc-pVTZ). The differences between DFT-derived harmonic and anharmonic wavenumbers served us to correct the outcome of BCCSD(T). Resulting predictions are collected in Table 3, together with the values obtained by Hu & Schaefer (1993).

5. CONCLUSIONS

C$_3$H$_2$N ground-state PES analysis uncovered possible routes toward cyanovinylidene, and thus suggests dissociative recombination of HCCCNH$^+$ to be the interstellar source of this molecule. The fractional abundance of cyanovinylidene in TMC-1 can be roughly estimated as confined within the range extending from 2 x 10$^{-11}$ to 6 x 10$^{-11}$, the first of these values theoretically predicted for HCNCC by Osamura et al. (1999), and the second one coming from HNCCC observations carried out by Ohishi & Kaifu (1998). Given this rather low abundance and an expected moderate electric dipole moment of 2.77 D (about half the value of 5.67 D predicted for HNCCC), the pure rotational spectrum may not be easy to observe. In fact, the detection of cyanovinylidene in interstellar molecular clouds via microwave emission may prove to be at least as difficult as that of HCNCC; the latter has not as yet been found, even though its lower abundance can possibly be compensated with a fairly large dipole moment of 8.1 D (Osamura et al. 1999; Kolos & Dobrowolski 2003).

Cyanovinylidene IR vibrational transitions are theoretically predicted to be of medium strength, resembling those of cyanoacetylene, and are much weaker than for the imine HNCCC, where maximal intensities approach 1600 km mol$^{-1}$ (Kolos & Sobolewski 2001). Therefore, current prospects for the infrared detection of cyanovinylidene in potentially promising sources like IRC +10 216—where HNCCC was found, and yet no IR absorptions due to this isomer have thus far been revealed—seem small.

The need for further laboratory, theoretical, and observational work on cyanovinylidene is obvious. First, experimental spectra, rotational and vibrational, are indispensable, as these should eventually lead to identifications in space, particularly at microwave frequencies. Second, the proposed interstellar synthesis scheme has to be extended with the analysis of PES(s) for the electronically excited C$_3$H$_2$N system; in fact this would provide a new insight into the formation of all cyanoacetylene isomers. Also, it is desirable to include cyanovinylidyne in the models of inter- or circumstellar chemistries.

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REFERENCES

Balucani, N., Asvany, O., Huang, L. C. L., Lee, Y. T., Kaiser, R. I., Osamura, Y., & Bettinger, H. F. 2000, ApJ, 545, 892
Becke, A. D. 1993, J. Chem. Phys., 98, 5648
Bogey, M., Demyunck, C., Destombes, J. L., & Vallee, Y. 1995, J. Mol. Spectrosc., 172, 344
Botschwina, P., Horn, M., Seeger, S., & Flugge, J. 1992, Chem. Phys. Lett., 195, 427
Brown, R. D., & Godfrey, P. D. 1984, Austral. J. Chem., 37, 1951
Costain, C. C., & Morton, J. R. 1959, J. Chem. Phys., 31, 389
Dunning, T. H. 1989, J. Chem. Phys., 90, 1007
Frisch, M. J., et al. 2004, Gaussian 03, Revision C.02 (Wallingford, CT: Gaussian, Inc.)
Fukuzawa, K., & Osamura, Y. 1997, ApJ, 489, 113
Gensheimer, P. D. 1997, ApJ, 479, L75
Goldberg, N., & Schwarz, H. 1994, J. Phys. Chem., 98, 3080
Green, S., & Herbst, E. 1979, ApJ, 229, 121
Gronowski, M., & Kolos, R. 2007, J. Mol. Struct., 834, 102
Handy, N. C., Pople, J. A., Head-Gordon, M., Raghavachari, K., & Trucks, G. W. 1989, Chem. Phys. Lett., 164, 185
Hohenberg, P., & Kohn, W. 1964, Phys. Rev. B, 136, 864
Hu, C.-H., & Schaefer, H. F. 1993, J. Phys. Chem., 97, 10681
Huang, L. C. L., Asvany, O., Chang, A. H. H., Balucani, N., Lin, S. H., Lee, Y. T., Kaiser, R. I., & Osamura, Y. 2000, J. Chem. Phys., 113, 8656
Kawaguchi, K., Ohishi, M., Ishikawa, S. I., & Kaifu, N. 1992a, ApJ, 386, L51
Kawaguchi, K., et al. 1992b, ApJ, 396, L49
Kohn, W., & Sham, L. J. 1965, Phys. Rev. A, 140, 1133
Kolos, R., & Dobrowolski, J. Cz. 2003, Chem. Phys. Lett., 369, 75
Kolos, R., & Sobolewski, A. L. 2001, Chem. Phys. Lett., 344, 625
Lee, C., Yang, W., & Parr, R. G. 1988, Phys. Rev. B, 37, 785
Morris, M., Turner, B. E., Palmer, P., & Zuckerman, B. 1976, ApJ, 205, 82
Ohishi, M., & Kaifu, N. 1998, Faraday Discuss., 109, 205
Osamura, Y., Fukuzawa, K., Terzieva, R., & Herbst, E. 1999, ApJ, 519, 697
Peng, C., & Schlegel, H. B. 1994, Israel J. Chem., 33, 449
Pople, J. A., Head-Gordon, M., & Raghavachari, K. 1987, J. Chem. Phys., 87, 5968
Sakai, N., Sakai, T., Kirotta, T., & Yamamoto, S. 2008, ApJ, 672, 371
Schaefer, A., Horn, H., & Ahlrichs, R. 1992, J. Chem. Phys., 97, 2571
Szczepanski, J., Wang, H., Doughty, B., Cole, J., & Vala, M. 2005, ApJ, 626, L69
Turner, B. E. 1971, ApJ, 163, L35
Watson, J. K. G. 1966, J. Chem. Phys., 45, 1360
Watson, J. K. G. 1967, J. Chem. Phys., 46, 1935
Wilson, S. 1978, ApJ, 220, 363
Woon, D. E., & Herbst, E. 1997, ApJ, 477, 204

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