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Equilibrium Structure and HCC Bending Potential Energy Function of $^3A''$ HCCN

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The molecular parameters of the ground triplet state of cyanocarbene, $^3A''$ HCCN, have been determined in large-scale ab initio calculations using the coupled-cluster method, RCCSD(T), and basis sets of double-through-quintuple-ζ quality. The equilibrium structure of the molecule was found to be planar and bent, with the trans conformation of the HCCN chain and the parameters $r_e(\mathrm{HC}) = 1.069$ Å, $r_e(\mathrm{CC}) = 1.328$ Å, $r_e(\mathrm{CN}) = 1.186$ Å, $\angle_e(\mathrm{HCC}) = 144.9°$, and $\angle_e(\mathrm{CCN}) = 175.4°$. The potential energy function for the HCC bending motion (v_5 mode) was determined to be strongly anharmonic, with the barrier to linearity of 286 cm^{-1}. Influence of various electron-correlation effects on the shape of the HCC bending potential energy function is discussed. The rotation−bending energy levels of the HCCN and DCCN molecules were then calculated using a semirigid-bender Hamiltonian. For both molecules, the predicted patterns of rotational transitions in the excited ν_5 states agree favorably with the experimental data.

1. Introduction

Cyanocarbene, HCCN, is a cyano derivative of the simplest carbene, CH_2, and its ground electronic state is a triplet A″ state (in the C_s symmetry point group). The equilibrium structure and spectroscopic properties of cyanocarbene have been the subject of a series of papers.[1−22] In the initial experimental studies,[1−4] the spectra of cyanocarbene were interpreted as those characteristic of a linear molecule. On the other hand, the equilibrium structure of the HCCN molecule was predicted to be bent by the ab initio calculations.[5−13] The equilibrium HCC angle was computed to be about 140°, and the potential energy barrier to the linear configuration was predicted to lie in the range 2−6 kcal/mol depending on the level of theory. Malmqvist et al.[9] calculated the potential energy surface of cyanocarbene by the complete-active-space self-consistent field (CASSCF) method[23] using a polarized basis set of double-ζ quality (DZP). The CASSCF wave functions were further used in multireference contracted-configuration-interaction (CCI) calculations,[24] including additionally the Davidson correction.[25] Using the computed potential energy surface, the vibrational−rotational energy levels of the HCCN and DCCN molecules were calculated variationally and compared with available experimental data. By comparing the calculated and experimental frequencies of the HCC/DCC bending mode, Malmqvist et al.[9] estimated the potential energy barrier to linearity of cyanocarbene to be 1 ± 0.5 kcal/mol (350 ± 175 cm^{-1}). Similar molecular parameters were reported by Seidl and Schaefer,[10] based on calculations by the single-reference coupled-cluster (CCSD(T))[26] and configuration interaction (CISD) methods with polarized basis sets of double-ζ (DZP) and triple-ζ (TZ2Pf) quality. By combining the results obtained at the CCSD(T)/DZP and CISD/TZ2Pf levels of theory, the equilibrium HCC angle and barrier to linearity were estimated[10] to be 142° and 0.8 kcal/mol (280 cm^{-1}), respectively. The structure and energetics of cyanocarbene were also investigated by Francisco[12] at the QCISD(T)/6-311G(2d,2p) level of theory.[27,28] The HCCN molecule was thus predicted theoretically to be quasilinear. To our knowledge, the studies by Malmqvist et al,[9] Seidl and Schaefer,[10] and Francisco[12] are the most advanced ab initio studies reported so far in the literature.

The experimental evidence for quasilinearity of cyanocarbene came from analyses of the high-resolution rotational[14,15] and vibrational[16−22] spectra. McCarthy et al.[15] assigned the rotational transitions arising from the HCCN and DCCN molecules in excited states of the HCC/DCC bending mode, ν_5. It was found that the observed rotational spectra could not be described as those of a well-behaved asymmetric top (a bent molecule), but rather as those of a linear molecule with a low-frequency large-amplitude motion. The effective rotational constants for the ground and some excited ν_5 states were determined, and the vibrational energies were estimated from relative intensities of the vibrational satellite lines. The barrier to linearity was estimated[15] to be 240 and 220 cm^{-1} for the HCCN and DCCN molecules, respectively. The high-resolution infrared spectra of the HCCN and DCCN molecules were investigated by Curl and co-workers[16−20] and by Allen et al.[22] The fundamental wavenumber of the ν_5 mode was determined to be 74.845 cm^{-1} for DCCN[18] and 128.907 cm^{-1} for HCCN.[19] The barrier to linearity was estimated to be 280 and 300 cm^{-1} for the DCCN and HCCN molecules, respectively. In the very recent paper by Curl and co-workers,[20] the new values of 229 cm^{-1} for DCCN and 256 cm^{-1} for HCCN were reported. It is worth noting that the fundamental ν_5 frequency of cyanocarbene is lower than that for fulminic acid, HCNO, the species being a textbook example of a quasilinear molecule.[29] For the HCNO and DCNO molecules, the fundamental ν_5 wavenumber was determined to be 224.87 and 163.34 cm^{-1}, respectively.[30] In fact, the fundamental ν_5 frequency of cyanocarbene is the lowest among all of the quasilinear H*XYZ* species known in the literature,[29] making thus cyanocarbene a new type of a quasilinear molecule.

The present study was undertaken with the aim of predicting the spectroscopic properties of cyanocarbene by the ab initio approach and of gaining a deeper insight into the nature of the HCC bending motion. In this paper, we report the results of calculations near the one- and *N*-particle basis set limits. These were performed by the single-reference spin-restricted coupled-

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cluster approach, the RCCSD(T) method,[31−33] with series of the systematically expandable correlation-consistent polarized basis sets, cc-pV*n*Z,[34] up to spdfgh quality. The coupled-cluster approach in conjuction with large one-particle basis sets was shown to provide a remarkably accurate description of the electronic structure and consequently unusual vibrational dynamics of several closed-shell quasilinear species.[35−40]

2. Method of Calculation

The molecular parameters of cyanocarbene were calculated using the spin-restricted coupled-cluster method including single and double excitations and a perturbational correction due to connected triple excitations, RCCSD(T),[31−33] based on the spin-restricted Hartree−Fock (RHF) molecular orbitals as a reference wave function. The one-particle basis sets employed were the correlation-consistent polarized valence basis sets, cc-pV*n*Z.[34] The quality of the basis sets ranged from double-ζ (n = D), through triple-ζ (n = T) and quadruple-ζ (n = Q), to quintuple-ζ (n = 5). The cc-pV*n*Z basis sets provide a systematic way of enlarging the basis set. The accuracy of the results obtained with increasing quality of the one-particle basis set can thus be conveniently estimated, assuming monotonic convergence of the calculated properties toward the limit of an infinite basis set. The complete-basis-set (CBS) limits can be estimated using various extrapolation techniques.[41−45] The largest basis set, cc-pV5Z, consists of a (14s8p4d3f2g1h)/[6s5p4d3f2g1h] set for carbon and nitrogen and a (8s4p3d2f1g)/[5s4p3d2f1g] set for hydrogen, thus resulting in a molecular one-particle basis set of 328 contracted functions. Only the spherical harmonic components of the d through h polarization functions were used. In the correlation treatment, the 1s-like core orbitals of the carbon and nitrogen atoms were excluded from the active space.

The core-related correlation effects were investigated using the correlation-consistent polarized core-valence basis set of double- and triple-ζ quality, cc-pCVDZ and cc-pCVTZ.[46] The largest basis set, cc-pCVTZ, is obtained by augmenting the standard cc-pVTZ basis set with a (2s2p1d) set, and it consists thus of a (12s7p3d1f)/[6s5p3d1f] set for carbon and nitrogen and a (5s2p1d)/[3s2p1d] set for hydrogen. In the correlation treatment involving the core and valence electrons, all of the molecular orbitals were included in the active space.

The calculations were performed using the MOLPRO-2000 package of ab initio programs.[47]

The vibrational−rotational energy levels and wave functions of cyanocarbene were calculated using an approximate, semirigid-bender Hamiltonian.[48] The four-dimensional Hamiltonian describes the HCCN molecule bending at the HCC angle and rotating in space. Interaction of the HCC bending motion with the other vibrational degrees of freedom is accounted for by varying the corresponding structural parameters along the minimum-energy HCC bending path. For each rotational quantum number *N*, the rotation−bending energy levels are calculated variationally by diagonalizing the Hamiltonian matrix in a basis set consisting of products of rotational symmetric-top and HCC bending wave functions.

3. Results and Discussion

The calculated equilibrium molecular parameters of cyanocarbene are given in Table 1. For all of the one-particle basis sets employed, the equilibrium structure of the molecule was found to be planar and bent, with the trans conformation of the HCCN chain. The calculated values tend to converge to well-defined asymptotic limits with enlargment of the basis set. To estimate the CBS limit for a molecular parameter, the exponential/Gaussian extrapolation formula[42] was applied. The total energy lowering from the cc-pV5Z to cc-pV6Z basis set computed in this way is ≈4 mhartrees, whereas that to the infinite basis set is estimated to be ≈6 mhartrees. In this context, the structural parameters calculated with the cc-pV5Z basis set should be converged to better than about 0.0004 Å and 0.01° for the bond lengths and angles, respectively.

TABLE 1: Equilibrium Molecular Parameters of $^3A''$ HCCN, Determined Using the CCSD(T) Method and Various cc-pV*n*Z Basis Sets

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
r(HC) (Å)	1.0895	1.0718	1.0709	1.0706
r(CC) (Å)	1.3607	1.3356	1.3317	1.3309
r(CN) (Å)	1.2036	1.1918	1.1886	1.1879
∠(HCC) (deg)	140.49	144.08	144.55	144.56
∠(CCN) (deg)	175.06	175.21	175.32	175.33
energy + 131 (hartree)	−0.072987	−0.187281	−0.221910	−0.232458

TABLE 2: Molecular Parameters of the Linear Configuration of $^3A''$ HCCN, Determined Using the CCSD(T) Method and Various cc-pV*n*Z Basis Sets

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z
r(HC) (Å)	1.0801	1.0646	1.0643	1.0640
r(CC) (Å)	1.3188	1.2974	1.2945	1.2937
r(CN) (Å)	1.2213	1.2092	1.2056	1.2049
ΔE^a (cm^{-1})	656	367	324	313

[a] ΔE is the energy difference between the linear and equilibrium configurations.

TABLE 3: Optimized Values of the Structural Parameters^a of $^3A''$ HCCN, Determined for Various Assumed Values of the HCC Angle at the CCSD(T)/cc-pVQZ Level of Theory

	∠(HCC) (deg)						
	180	170	160	150	144.55	140	130
r(HC) (Å)	1.0643	1.0648	1.0665	1.0691	1.0709	1.0725	1.0764
r(CC) (Å)	1.2945	1.2987	1.3095	1.3236	1.3317	1.3383	1.3520
r(CN) (Å)	1.2056	1.2032	1.1976	1.1915	1.1886	1.1864	1.1825
∠(CCN) (deg)	180.0	177.94	176.30	175.41	175.32	175.47	176.47
energy (cm^{-1})^a	0.0	−41.0	−158.7	−293.9	−324.2	−295.9	44.6
energy (cm^{-1})^{a,b}	0.0	−38.8	−151.7	−283.3	−312.8	−284.2	55.1

[a] Relative to the energy of the linear configuration. [b] Calculated at the CCSD(T)/cc-pV5Z level of theory.

Table 2 lists the molecular parameters calculated for the linear configuration of cyanocarbene. Large changes are observed for the potential energy barrier depending on the size of the one-particle basis set. With the cc-pVDZ basis set, the barrier height is calculated to be quite substantial, about 2.1 kcal/mol. Upon basis set enlargement to cc-pV5Z, it decreases to about 0.9 kcal/mol. The CBS limit value we estimated using the exponential/Gaussian extrapolation formula[42] is 307 cm^{-1}.

The HCC bending potential energy function was determined by optimizing the structural parameters for various assumed values of the HCC angle. Results of the calculations with the cc-pVQZ and cc-pV5Z basis sets are given in Table 3. For the cc-pV5Z basis set, the size of the molecular one-particle basis set poses some computational problems and, therefore, the total energies were calculated for the structural parameters optimized using the cc-pVQZ basis set. As shown in Tables 1 and 2, differences between the structural parameters optimized with the cc-pVQZ and cc-pV5Z basis sets are in fact negligibly small. Differences between the calculated total energies quoted in Table 3 are thus primarily due to extension of the one-particle basis set. Moreover, these differences were computed to be quite small, not exceeding 12 cm^{-1} for the HCC angle ranging from 180° to 130°. It is worth noting that the CC bond length changes

TABLE 4: Core-Related Corrections (A − V)[a] to the Equilibrium Structural Parameters of ^{3}A″ HCCN, Determined Using the CCSD(T) Method and Various cc-pCV*n*Z Basis Sets

	cc-pCVDZ	cc-pCVTZ
r(HC) (Å)	−0.0008	−0.0013
r(CC) (Å)	−0.0016	−0.0026
r(CN) (Å)	−0.0006	−0.0019
∠(HCC) (deg)	0.21	0.37
∠(CCN) (deg)	0.04	0.08

[a] A difference between the value determined correlating all of the electrons (*A*) and the value determined correlating only the valence electrons (*V*).

TABLE 5: Total Energy[a] of ^{3}A″ HCCN (cm^{-1}) as a Function of the HCC Angle, Determined at the CCSD(T)/cc-pCVTZ Level of Theory

	∠(HCC) (deg)						
	180	170	160	150	144.55	140	130
valence-only (V)[b]	0	−47.0	−181.1	−337.1	−378.2	−357.3	−29.2
all-electrons (A)[c]	0	−45.0	−173.4	−321.5	−357.5	−332.3	−5.3
A − V	0	2.0	7.7	15.6	20.7	25.0	34.5

[a] Relative to the energy of the linear configuration, calculated with the structural parameters given in Table 3. [b] Correlating only the valence electrons. [c] Correlating all of the electrons.

substantially with the HCC angle. For the HCC angle decreasing from 180° to 140°, the difference amounts to nearly 0.04 Å. In comparison, for the HCNO molecule,[36] the CN bond length elongates by nearly 0.02 Å for the HCN angle changing in the same range.

The core-related correlation effects were computed as differences between the molecular parameters determined in calculations correlating only the valence electrons and those when all of the electrons were correlated, both calculations performed using the core-valence basis set. The core-related corrections to the equilibrium structural parameters of cyanocarbene determined with the cc-pCVDZ and cc-pCVTZ basis sets are given in Table 4. Similar calculations were also performed for the linear configuration of the HCCN molecule. Inclusion of the core-related correlation effects decreases the barrier to linearity by 22 and 21 cm^{-1} for the cc-pCVDZ and cc-pCVTZ basis sets, respectively.

The best estimate of the molecular parameters of cyanocarbene at the CCSD(T) level of theory can be determined by adding the changes in the parameters due to the core-related correlation effects to the CBS limits determined with the valence cc-pV*n*Z basis sets. The equilibrium structural parameters are calculated in this way to be r_e(HC) = 1.069 Å, r_e(CC) = 1.328 Å, r_e(CN) = 1.186 Å, $\angle_e$(HCC) = 144.9°, and $\angle_e$(CCN) = 175.4°. Considering convergence of the computed values with the basis-set size, we estimate uncertainties in the calculated structural parameters to be smaller than ±0.001 Å for the bond lengths and ±0.1° for the valence angles.

Table 5 illustrates the core-related correlation effects for the HCC bending potential energy function. Inclusion of these corrections results in a slightly steeper function. Using the CBS limit value quoted above, the best estimate of the barrier to linearity of cyanocarbene at the CCSD(T) level of theory is thus 286 cm^{-1}, being accurate to better than ±10 cm^{-1}.

TABLE 6: $N = l_5$ Rotation−Bending Energy Levels (cm^{-1}) and Changes in the Effective Rotational Constant *B* (MHz) Due to Excitation of the HCC/DCC Bending Mode, ν_5, of ^{3}A″ HCCN/DCCN (Model I)

	HCCN		DCCN	
$v_5^{l_5}$	energy/*hc*[a,c]	Δ*B*[b,c]	energy/*hc*[a,c]	Δ*B*[b,c]
0^0	0.0	0.0	0.0	0.0
1^{1e}	118.8 (128.9[d])	−23.9 (−18.164[g])	65.3 (74.8[e])	−14.6 (−8.701[g])
1^{1f}	118.8 (128.9[d])	18.2 (22.397[g])	65.3 (74.8[e])	39.7 (41.927[g])
2^2	321.5 (341.7[f])	−5.7 (1.009[g])	188.9 (208.0[f])	24.3 (30.714[g])
2^0	444.5	11.0	310.2	8.3
3^3	585.8 (625[g])	−8.0 (2.531[g])	354.4 (400[g])	35.3 (43.125[g])
3^{1e}	708.6	−12.9	474.6	0.2
3^{1f}	708.6	38.9	474.6	62.7
4^4	900.8	−10.1	553.7	45.6
4^2	1008.2	13.1	666.2	47.5
4^0	1054.5	24.8	715.8	45.7

[a] The ground-state energy level is calculated to lie 191.0 and 152.3 cm^{-1} above the minimum of the potential energy function for HCCN and DCCN, respectively. [b] The ground-state effective rotational constant *B* is 11016.4 (10986.4087, ref 15) and 9943.4 (9906.3708, ref 15) MHz for HCCN and DCCN, respectively. [c] Experimental values are given in parentheses. [d] Reference 19. [e] Reference 18. [f] Reference 20. [g] Reference 15, the vibrational energies estimated with an uncertainty of 20 cm^{-1}.

The HCC bending potential energy function computed at the CCSD(T)/cc-pV5Z level of theory was corrected for the core-related correlation effects. It was then used to calculate the rotation−bending energy levels of the HCCN and DCCN molecules by the semirigid-bender approach.[48] The spin−spin and spin−rotation interactions were not taken into account, and therefore, the fine structure of rotational transitions could not be predicted. This calculation is referred to hereafter as model I. A comparison of the theoretical predictions and available experimental data is given in Table 6. As in the experimental studies, the energy levels are labeled by the quantum numbers v_5 and l_5 describing the doubly degenerate bending mode of a linear molecule. For both HCCN and DCCN molecules, the predicted fundamental vibrational level $v_5^{l_5} = 1^1$ is underestimated by about 10 cm^{-1}, whereas the energies of the higher excited v_5 states differ from the experimental values by 20−40 cm^{-1}. Except for the 1^1 and 2^2 states, energies of the excited states were estimated experimentally[15] from relative intensities of the vibrational satellite lines in the rotational spectra and, therefore, are only accurate to 15−20 cm^{-1}. The calculated rotation−bending energy levels were then used to determine the effective rotational constant *B* for each vibrational $v_5^{l_5}$ state. These values were obtained by fitting an odd power series in $(N + 1)$ to the calculated rotational transition frequencies. The effective rotational constant *B* for the ground vibrational state of the HCCN and DCCN molecules is determined in this way to be 11 016.4 and 9943.4 MHz, respectively. The predicted values overestimate the corresponding experimental values[15] by 30 and 37 MHz, respectively. Likewise, the ground-state rotational constant *B* is predicted for the other cyanocarbene isotopomers to be 10 643.5 MHz for H^{13}CCN, 11 016.1 MHz for HC^{13}CN, and 10 676.1 MHz for HCC^{15}N. These predicted values overestimate the corresponding experimental values[14] by 27, 30, and 30 MHz, respectively. Such close agreement between the predicted and observed values of the effective rotational constant *B* is a strong confirmation of the validity of the calculated equilibrium structure of cyanocarbene. Table 6 lists also the predicted and observed changes in the rotational constant *B* due to excitation of the ν_5 mode. For the $v_5^{l_5} = 1^1$, 2^2, and 3^3 states assigned in the rotational spectra of the HCCN and DCCN molecules,[15] these changes are predicted to about ±6 MHz accuracy. The predicted patterns of rotational transitions in the excited v_5 states agree very favorably with the experimental data. Especially, the anomalous qualitative difference between the rotational spectra of the HCCN and DCCN molecules is nicely reproduced. It is worth noting that this

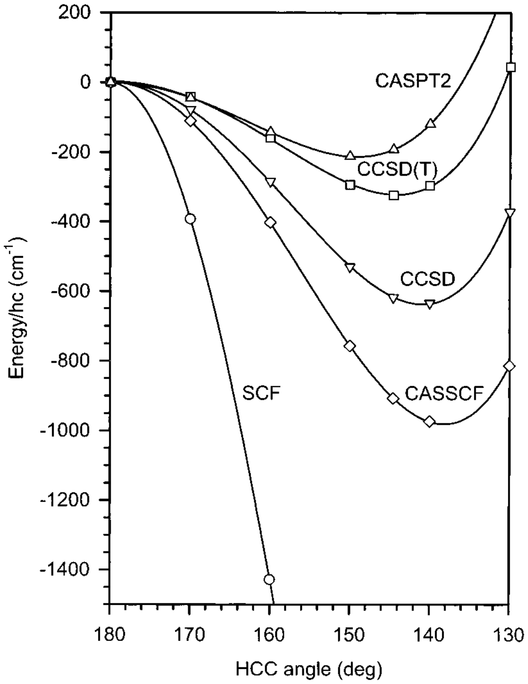

Figure 1. The (relative) total energy of cyanocarbene as a function of the HCC angle, determined using the cc-pVQZ basis set at the SCF, CASSCF, CASPT2, CCSD, and CCSD(T) levels of theory. The functions are drawn to a common scale.

TABLE 7: Total Energy[a] of $^3A''$ HCCN (cm^{-1}) as a Function of the HCC Angle, Determined Using the cc-pVQZ Basis Set at Various Levels of Theory

	∠(HCC) (deg)						
	180	170	160	150	144.55	140	130
SCF	0	−392.6	−1428.6	−2730.5	−3384.3	−3834.7	−4364.9
CASSCF	0	−110.0	−402.7	−756.7	−906.9	−972.9	−813.6
CASPT2	0	−45.2	−141.8	−211.8	−192.0	−118.5	318.9
CCSD	0	−77.3	−284.0	−529.4	−618.0	−634.1	−372.2
CCSD(T)	0	−41.0	−158.7	−293.9	−324.2	−295.9	44.6

[a] Relative to the energy of the linear configuration, calculated with the structural parameters given in Table 3.

change in the vibrational satellite pattern upon deuteration is rather unexpected and just the opposite of what was found for fulminic acid.[30] However, for the HCCN molecule, the predicted changes ΔB for the $v_5^{l_5} = 2^2$ and 3^3 states (albeit small) have the opposite sign than those observed experimentally.[15]

TABLE 8: Leading Configurations of the CASSCF Wave Function (in the Natural Orbital Representation, Weights Greater Than 0.005), Determined Using the cc-pVQZ Basis Set for the Equilibrium Configuration of $^3A''$ HCCN

configuration	weight
SCF	0.868
$(1a'') \rightarrow (3a'')$	0.018
$(1a'')^2 \rightarrow (3a'')^2$	0.008
$(8a') \rightarrow (12a')$	0.015
$(8a')^2 \rightarrow (12a')^2$	0.009

To gain a better insight into the nature of the HCC bending potential energy function, it was determined at various levels of theory, namely by the self-consistent field (SCF),[49] complete-active-space self-consistent field (CASSCF),[23] complete-active-space second-order perturbation (CASPT2),[50,51] and coupled-cluster (CCSD and CCSD(T))[31−33] approach. The calculations were performed using the cc-pVQZ basis set and the structural parameters given in Table 3. In the CASSCF and CASPT2 calculations, the reference wave function consisted of a full valence complete active space. The wave function included thus all excitations of 14 valence electrons in 13 molecular orbitals corresponding to the valence atomic sp orbitals of the carbon and nitrogen atoms, and the 1s orbital of the hydrogen atom. The calculated potential energy functions are shown in Figure 1 and are also presented in Table 7. As can be seen, the shape of the HCC bending potential energy function is due to a delicate balance between different electron correlation effects. At the SCF level, the HCCN molecule is predicted to be strongly bent. For the HCC angle ranging from 180° to 130°, the SCF total energy of cyanocarbene decreases steeply to below −4000 cm^{-1} (relative to the linear configuration). In fact, by optimizing the structural parameters at the spin-restricted SCF/cc-pVQZ level of theory, the HCCN molecule is predicted to be bent, with the equilibrium HCC angle being 130.3° and the barrier to linearity being 3480 cm^{-1}. Inclusion of the static (near-degeneracy) electron correlation effects through the CASSCF framework favors the linear configuration. At the HCC angle of 130°, the correlation energy correction amounts to about +3600 cm^{-1} (relative to that at the linear configuration). The equilibrium HCC angle is thus predicted to be 138° and the barrier to linearity decreases to 981 cm^{-1}. Leading configurations of the CASSCF wave function are listed in Table 8. The SCF configuration accounts for 87% of the multiconfiguration wave function, and there are only four excited configurations with weights greater than 0.005. Accounting for the dynamical electron correlation effects within the second-order perturbational procedure, CASPT2, favors the linear configuration as well. At the HCC angle of 130°, the correlation energy correction amounts to about +1100 cm^{-1}. At this level of theory, the equilibrium HCC angle is predicted to be 149° and the barrier to linearity decreases to only 213 cm^{-1}. The calculations at the CASSCF and CASPT2 levels of theory show thus that both the dynamical and nondynamical electron correlation are important for cyanocarbene. As shown in Figure 1, the shape of the HCC bending potential energy function at the CASPT2 level is similar to that determined by the CCSD(T) approach. Inclusion of the effects of connected single and double excitations through the single-reference spin-restricted CCSD framework favors the linear configuration, as in the case of the CASSCF and CASPT2 methods. The equilibrium HCC angle and barrier to linearity are calculated to be 141° and 637 cm^{-1}, respectively. At the CCSD(T) level of theory, the effect of connected triple excitations is found to be quite substantial, decreasing the barrier height to nearly one-half that at the CCSD level. In light of the importance of dynamical and nondynamical electron correlation effects, it would be desirable to assess the reliablity of the employed theoretical methods against results obtained with the less approximate methods as CCSDT[52] or multireference configuration interaction, MRCI. Unfortunately, for large one-particle basis sets, such calculations for cyanocarbene are beyond our computational capabilities. At the MRCI/cc-pVQZ level of theory, the reference space for the complete active space specified above consists of 644 490 configuration state functions (CSF), leading to about 32 × 10^9 singly and doubly excited configurations for the multireference wave function. Even for the internally contracted method, icMRCI,[53,54] the total number of contracted excited configurations is nearly 220 × 10^6. To circumvent this limitation, we examined the electronic wave function by comparing the weights of leading configurations of the CASSCF wave function along the HCC bending potential energy function. The spectrum of the configurations appeared to be essentially identical for the whole range of the HCC angle under consideration. For example, the weight of the SCF configuration changes steadily from 0.859

TABLE 9: $N = l_5$ Rotation−Bending Energy Levels (cm^{-1}) and Changes in the Effective Rotational Constant B (MHz) Due to Excitation of the HCC/DCC Bending Mode, ν_5, of ^{3}A″ HCCN/DCCN (Model II)

	HCCN		DCCN	
$v_5^{l_5}$	energy/$hc^{a,c}$	$\Delta B^{b,c}$	energy/$hc^{a,c}$	$\Delta B^{b,c}$
0^0	0.0	0.0	0.0	0.0
1^{1e}	154.8 (128.9^d)	−21.7 (−18.164^g)	92.6 (74.8^e)	−7.1 (−8.701^g)
1^{1f}	154.8 (128.9^d)	15.1 (22.397^g)	92.6 (74.8^e)	38.7 (41.927^g)
2^2	388.6 (341.7^f)	−6.6 (1.009^g)	241.4 (208.0^f)	28.9 (30.714^g)
2^0	477.3	8.6	326.5	22.5
3^3	679.9 (625^g)	−9.5 (2.531^g)	429.8 (400^g)	40.8 (43.125^g)
3^{1e}	768.6	−13.8	518.0	12.9
3^{1f}	768.6	35.6	518.0	71.6
4^4	1018.6	−12.0	649.7	51.7
4^2	1092.8	11.3	732.4	57.6
4^0	1128.3	22.0	770.6	58.7

[a] The ground-state energy level is calculated to lie 168.6 and 129.8 cm^{-1} above the minimum of the potential energy function for HCCN and DCCN, respectively. [b] The ground-state effective rotational constant B is 11016.4 (10986.4087, ref 15) and 9925.5 (9906.3708, ref 15) MHz for HCCN and DCCN, respectively. [c] Experimental values are given in parentheses. [d] Reference 19. [e] Reference 18. [f] Reference 20. [g] Reference 15, the vibrational energies estimated with an uncertainty of 20 cm^{-1}.

to 0.873 for the HCC angle decreasing from 180° to 130°. Therefore, it is reasonable to conclude that although the electronic wave function of cyanocarbene may have nonnegligible multireference character, the HCC bending potential energy function obtained by the single-reference CCSD(T) approach is quantitatively correct. The results just discussed indicate that for the ground electronic state of cyanocarbene, the valence correlation energy rises more steeply with decreasing HCC angle than the Hartree−Fock total energy falls. As a result, the HCC bending potential energy function becomes rather flat and strongly anharmonic.

To assess sensitivity of the computed rotation−bending energy levels to the shape of the HCC bending potential energy function, the semirigid-bender calculations were also performed with this function determined at the CASPT2/cc-pVQZ level of theory. As for model I, the HCC bending potential energy function was corrected for the core-related correlation effects, and the structural parameters were those determined at the CCSD(T) level of theory. This calculation is referred to hereafter as model II. A comparison of the theoretical predictions and available experimental data for the HCCN and DCCN molecules is given in Table 9. In contrast to the results for model I, the predicted fundamental vibrational level $v_5^{l_5} = 1^1$ is overestimated by about 20 cm^{-1}, and the energies of the higher excited v_5 states differ from the experimental values by 30−50 cm^{-1}. Since the experimental ν_5 fundamental wavenumber for both the HCCN and DCCN molecules is midway between those predicted by models I and II, the parameters of the HCC bending potential energy function may be estimated by using linear interpolation. In this way, we found the barrier to linearity and HCC equilibrium angle for the HCCN molecule to be 265 cm^{-1} and 146.3°, respectively. For the DCCN molecule, the corresponding values are 259 cm^{-1} and 146.6°. It must be pointed out that the interpolated values of the parameters can be considered as effective, as they incorporate somehow contributions from all of the small-amplitude vibrations of cyanocarbene which are not accounted for by the semirigid-bender approach. The ab initio calculated values discussed above represent equilibrium parameters. In this sense, differences between the interpolated and ab initio calculated values can be regarded as a measure of the mass-dependent, zero-point averaging effects. For the HCCN isotopomer, the interpolated barrier height is close to the effective barrier height of 256 cm^{-1} determined very recently[20] from the experimental $v_5^{l_5} = 1^1$ and 2^2 energy levels. For the DCCN isotopomer, the effective barrier height was found[20] to be 229 cm^{-1}, being 30 cm^{-1} lower than the interpolated value.

TABLE 10: Harmonic Wavenumbers (ω, cm^{-1}) of ^{3}A″ HCCN/DCCN, Determined for the Equilibrium Configuration at the CCSD(T)/cc-pVQZ Level of Theory

	HCCN		DCCN	
symm^a	ω	PED × 100^b	ω	PED × 100^b
A′	3340	99 HC stretch	2474	97 DC stretch
A′	1863	90 CN stretch, 9 CC stretch	1856	91 CN stretch, 8 CC stretch
A′	1139	87 CC stretch, 10 CN stretch	1100	89 CC stretch, 8 CN stretch
A′	581	73 HCC bend, 24 CCn bend	518	47 DCC bend, 53 CCN bend
A″	425	100 out-of-plane bend	419	100 out-of-plane bend
A′	380	76 CCN bend, 24 HCC bend	323	47 CCN bend, 53 CC bend

[a] Symmetry in the C_s point group. [b] The potential energy distribution, only contributions greater than 5 are quoted.

The effective rotational constant B for the ground vibrational state of the HCCN and DCCN molecules determined by model II overestimates the corresponding experimental values[15] by 30 and 19 MHz, respectively. It is interesting to note that for the HCCN molecule, the changes in the rotational constant B due to excitation of the ν_5 mode are predicted to essentially the same accuracy by models I and II, to about ±7 and ±8 MHz, respectively. In contrast, for the DCCN molecule, the changes predicted by model II are far closer to those observed experimentally[15] (about ±2 MHz) than the changes predicted by model I (about ±6 MHz). Therefore, we conclude that in the case of cyanocarbene, the semirigid-bender approach is not capable of predicting the HCC/DCC bending vibrational dependence of the effective rotational constant B as precisely as for the other quasilinear molecules.[37−40] Nevertheless, we hope that the agreement with the experimental data is good enough that the results reported here may be a guide to the further assignment of rotational−vibrational transitions in the cyanocarbene spectra.

The reason for such a behavior of the semirigid-bender approach is likely neglecting the small-amplitude vibrational degrees of freedom of cyanocarbene. The calculated harmonic wavenumbers and potential energy distribution of the normal modes for the HCCN and DCCN molecules are presented in Table 10. The harmonic force field of cyanocarbene was computed at the CCSD(T)/cc-pVQZ level of theory. Note that since the harmonic wavenumbers were calculated for a bent molecule model, the HCC bending harmonic frequency corresponds to the $v_5^{l_5} = 2^0$ energy level. The large discrepancy between this frequency and the energy levels quoted in Tables 6 and 9 is due to the strong anharmonicity of the HCC bending motion. The vibrational spectrum of cyanocarbene was observed in the gas phase[16−20,22] and inert-gas matrixes;[3,21] however, there are to date no experimental harmonic wavenumbers to compare with. As shown in Table 10, the calculated harmonic wavenumbers of the bending modes of cyanocarbene are similar and the bending vibrations are coupled to each other. The situation is more acute for the DCCN molecule, for which the low-frequency normal modes consist of a half−half mixture of the DCC and CCN bending vibrations. The fundamental approximation inherent to the semirigid-bender model[48]—separability of the large- and small-amplitude vibrational degrees of freedom—seems to be no longer valid in the case of cyanocarbene. A more sophisticated treatment accounting explicitly for all of the vibration−vibration and vibration−rotation interactions, advocated previously by Malmqvist et al.,[9] is necessary.

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