

A multireference configuration interaction study of the hyperfine structure of the molecules CCO, CNN, and NCN in their triplet ground states

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The hyperfine structures of the isoelectronic molecules CCO, CNN, and NCN in their triplet ground states ($X^3\Sigma^-$) are investigated by means of *ab initio* methods. The infrared frequencies and geometries are determined and compared with experiment. Configuration selected multireference configuration interaction calculations in combination with perturbation theory to correct the wave function (MRD-CI/ B_k) employing extended atomic orbital (AO) basis sets yielded very accurate hyperfine properties. The theoretical values for CCO are in excellent agreement with the experimental values determined by Smith and Weltner [J. Chem. Phys. **62**, 4592 (1975)]. For CNN, the first assignment of Smith and Weltner for the two nitrogen atoms has to be changed. A qualitative discussion of the electronic structure discloses no simple relation between the structure of the singly occupied orbitals and the measured hyperfine coupling constants. Vibrational effects were found to be of little importance.

I. INTRODUCTION

The isoelectronic molecules CCO, CNN, and NCN are reactive triplet radicals. They are linear in their $X^3\Sigma^-$ electronic ground states. Many experimental¹⁻¹¹ and theoretical¹²⁻¹⁹ investigations have been performed for these interesting molecules. Most of the studies consider the structure and the vibrational frequencies. In 1966, CNN was produced from irradiation of cyanogen azide and isolated in argon and nitrogen matrices by Milligan and Jacox¹ and studied via infrared spectroscopy. They determined the three fundamental frequencies to be at 393, 1241, and 2847 cm^{-1} , but some doubts existed with regards to the larger frequency. Based on *ab initio* calculations, DeKock *et al.*¹² concluded that the largest frequency found by Milligan and Jacox is indeed the first overtone of the fundamental. Similar results as obtained from the complete active space self-consistent field (CASSCF) calculations of DeKock *et al.* have been reported using density functional theory (DFT).¹⁹ DeKock *et al.* also calculated the geometry and the frequencies of CCO. For this molecule, the matrix isolation spectrum has been recorded by Jacox *et al.*⁴ The experimental confirmation of 1419 cm^{-1} as the third true fundamental of CNN was measured by Wurfel *et al.*⁵ by laser-induced fluorescence (LIF) of the radical in an argon matrix.

In 1960, Jennings and Linett⁸ observed an emission line at a wavelength of about 329 nm from a vaporization of various hydrocarbons into nitrogen atoms. They assigned it to NCN molecules. Herzberg and Travis⁹ investigated the NCN system produced by photolysis of diazomethane. They confirmed the assignment of Jennings and Linett and deduced that the NCN molecule is a linear symmetric molecule with a $^3\Sigma_g^-$ electronic ground state. The ultraviolet (UV)

absorption spectrum and the infrared frequencies were measured by Milligan *et al.*^{2,3}

The hyperfine Hamiltonian, i.e., the interaction of the electron spin with the spin of the nuclei, is normally divided into an isotropic and an anisotropic part.²⁰ The isotropic part is proportional to the electron spin density at the position of the various nuclei and is also known as the Fermi contact term

$$A_{\text{iso}}(N) = \frac{8\pi}{3} g \beta_N \beta_e g_N \frac{1}{S} \times \left\langle \Psi \left| \sum_{k=1}^n \delta(r_k - r_N) s_z(k) \right| \Psi \right\rangle, \quad (1)$$

where the term in the bra ket is the total spin density $\langle \delta(r_N) \rangle$ of the electrons at the location of the nucleus N . The term g is the g value for the electrons in the radical, while β_N is the Bohr magneton. In the present work, g was set to the value for the free electron g_e . The quantities g_N and β_N are the nuclear g factor and the value for the nuclear magneton, respectively.

The anisotropic part describes the dipole-dipole interaction between I and S. Its Cartesian components are defined in a molecule-fixed coordinate system as

$$A_{ij}(N) = g_N g_e \beta_N \beta_e \frac{1}{S} \times \left\langle \Psi \left| \sum_{k=1}^n \left(\frac{3ij - r^2 \delta_{ij}}{r^5} \right)_{ck} 2s_{zk} \right| \Psi \right\rangle \quad (2)$$

with $i, j = x, y, z$; ck indicates that A_{ij} is formulated with respect to the center N .

Using the isotopic molecules $^{13}\text{C}^{12}\text{C}^{16}\text{O}$, $^{12}\text{C}^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{15}\text{N}^{15}\text{N}$, $^{12}\text{C}^{14}\text{N}^{14}\text{N}$, and $^{13}\text{C}^{15}\text{N}^{15}\text{N}$, the hyperfine structure of CCO and CNN was investigated experimentally by Smith and Weltner¹¹ in noble gas matrices at 4 K. Hyperfine

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coupling constants (hfcc's) could be measured for all centers except the oxygen. In the case of CNN, not all of the expected lines could be resolved due to line broadening. Furthermore, only the absolute values of A_{\perp} could be determined.

Although some questions concerning the magnetic hyperfine coupling constants of these molecules are still open to the authors' knowledge, only a few theoretical studies of the hyperfine structure of these radicals have been performed. Beside the intermediate neglect of differential overlap (INDO) calculations performed by Olsen and Burnelle,¹³ small configuration interaction (CI) calculations for CNN by Cai *et al.*¹⁵ also exist. While the *ab initio* calculation of the anisotropic part is known to be simple, reliable determination of the isotropic part (also known as the Fermi contact term) is very complicated. To obtain reliable values careful selection of the atomic orbital (AO) basis set is necessary.²¹⁻²³ Furthermore, highly correlated wave functions are required. Carmichael²⁴ proposed the use of quadratic configuration interaction of the singles and doubles excitations with approximate triple excitation [QCISD(T)]²⁵ for the calculation of hfcc's. Coupled cluster calculations with single and double excitations [CCSD(T)]²⁶ yield similar results. The use of the multireference configuration interaction method (MR-CI) turned out to be problematic^{27,28} since a large amount of higher than double excitations are very important. Therefore large reference spaces are necessary to obtain good agreement with experimental values, which leads to very large MR-CI spaces. If truncated MR-CI methods are applied, the convergence of the isotropic hfcc's with respect to the number of selected configurations is very slow. Recently, one of the authors²⁹ has shown that selected MR-CI can yield very accurate hfcc's if the influence of the discarded configurations is taken into account using the B_K method³⁰ (MRD-CI/ B_K). The hfcc's obtained with the MRD-CI/ B_K treatment are comparable to those calculated from unselected MR-CI calculations since use of the B_K correction accelerates the convergence of the isotropic hfcc's with respect to the selected configuration. The theory and extensive testings are reported in Refs. 29 and 31-36. As shown for H_2CN (X^2B_2) and H_2CO^+ (X^2B_2) MRD-CI/ B_K , QCISD(T) and CCSD(T) give equivalent results.³¹

In many cases, the configuration interaction treatment in which only the single excitations with respect to the Hartree-Fock configurations (CIS) are taken into account gives quantitative agreement with the experimental results. CIS calculations are inexpensive, which could open a possibility for handling large molecules. However, as shown in a previous study, the success of CIS is due to error cancellation,^{34,37} which in some cases, e.g., H_2CN (X^2B_2), does not even out. The performance of this method for triplet states is not as predictable, since two electrons interact with the electronic core.

The present study concentrates on two points. First, the hyperfine structure of the molecules CNN, CCO, and NCN is studied using the MRD-CI/ B_K method and comparisons among the three molecules are made. The influence of spin polarization effects is investigated as well. Second, CIS calculations are performed to test whether they are suitable for

TABLE I. Structure and vibrational frequencies of CNN ($^3\Sigma_u^-$), NCN ($^3\Sigma_g^-$), and CCO ($^3\Sigma_u^-$).

	Method	r_{X-X}^a	r_{C-X}	ν_3 (cm ⁻¹)	ν_2 (cm ⁻¹)	ν_1 (cm ⁻¹)	Reference
CNN	CASSCF	1.223	1.241	1461	1177		12
	DFT+G	1.204	1.261	1586	1282	383	18
	DFT+G	1.205	1.253	1469	1235	389	19
	QCISD ^b	1.231	1.237	1537	1205	390	
	Expt.			1424	1241	393	1
	Expt.			1419	1235	396	5
NCN	CASSCF		1.245	1319	1246		12
	QCISD ^b		1.245	1411	1247	437	
	Expt.		1.232	1475		423	2,9
CCO	CASSCF	1.367	1.170				12
	CISD	1.379	1.161				12
	QCISD ^b	1.371	1.173	2046	1099	354	
	Expt.			1978	1074	381	4

^aFor CNN, X stands for the nitrogen atoms, while it represents the carbon atoms in the case of CCO.

^bUHF-QCISD/6-31G* calculations.

the calculation of triplet molecules. In addition, since no experimental structure is known for CNN the geometries and IR frequencies of all three molecules are calculated with the QCISD method to obtain a consistent set of geometrical parameters.

II. GEOMETRIES AND IR FREQUENCIES

The electronic structure of the ground state of the CNN and CCO molecules is $^3\Sigma_u^-$ with the following configuration:

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2(6\sigma)^2(7\sigma)^2(1\pi_x)^2(1\pi_y)^2 \\ \times (2\pi_x)^1(2\pi_y)^1,$$

while NCN has a $^3\Sigma_g^-$ ground state with the electronic configuration

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(3\sigma_g)^2(2\sigma_u)^2(4\sigma_g)^2(3\sigma_u)^2(1\pi_u)^4 \\ \times (1\pi_g)^2,$$

For technical reasons, the calculations for CNN and CCO were performed in C_{2v} symmetry, while for NCN, the D_{2h} symmetry was imposed. As stated in the Introduction, most geometrical parameters and IR frequencies are well known. Since the authors are not aware of any experimental structure for CNN, a consistent set of geometries for the hyperfine calculations was needed; the geometry was recalculated using QCISD/6-31G* calculations. For the UHF-QCISD²⁵ calculations, the Gaussian 90 program³⁸ was used. The results of these calculations are displayed in Table I. They are similar to the results of the density functional calculation by Murray *et al.*¹⁹ The frequency ν_3 is the asymmetric stretch vibration in the case of CNN, which was first assigned at 2847 cm⁻¹. The later theoretical clarification by Schaefer, which was experimentally substantiated by Wurfel *et al.*,⁵ leads to half the value (1419 cm⁻¹), indicating that Milligan and Jaccox had found the first overtone of the vibration. In the case of CCO, no such interpretational problems occurred. The QCISD method achieved similar results as the DFT calcula-

tions by Dixon and DeKock¹⁸ and Murray *et al.*¹⁹ All frequencies are in reasonable agreement with the infrared measurements of Jacox *et al.*⁴

According to the QCISD calculations, the bond distances in CCO are both ~ 1.23 Å, indicating similar double bond character of both bonds. In contrast, the C–N bond in CNN is shorter (1.17 Å) than the N–N bond (1.37 Å). This is due to the partial triple bond character of the C–N bond, as is also indicated by a larger frequency (about 2000 cm^{-1}) for the asymmetric stretch vibration. Since the geometry seems to be relatively insensitive to the applied theoretical treatment, the geometries optimized with the QCISD method were used to investigate the hyperfine properties.

III. HYPERFINE STRUCTURE

A. Technical details of the calculations

The calculation of the hyperfine properties and the B_K calculations were performed with a modified version of the MRD-CI program package of Peyerimhoff and Buenker³⁹ using the Table CI algorithm.⁴⁰ The selected MRD-CI wave function was corrected with a modified B_K (Ref. 30) treatment.

In all MRD-CI and MRD-CI/ B_K calculations carried out in this study, natural orbitals obtained from preliminary MRD-CI calculations were used as the one-particle basis. The reference configurations in the calculations were selected according to two criteria. First, the squared coefficients of the reference configuration should be larger than 0.002 in the final wave functions, and second, their importance in the spin density matrix was analyzed. The number of reference configurations obtained with this procedure was between 50 and 60. For CNN and CCO, about 13.5×10^6 configurations were generated from these reference sets, while for NCN, the MR-CI space consisted of about 6.5×10^6 configurations.

The sum of the squared coefficients of the reference configurations were consistently ~ 0.90 . The number of selected configurations was approximately 30 000 in all MRD-CI calculations. All single excitations with respect to the main configurations were included in the B_K correction. The relaxation of the coefficients of higher excitations is less important, so that inclusion of those configurations having coefficients larger than 0.04 into the B_K treatment was found to be sufficient.²⁹

As shown in previous studies,²³ for spin density calculations, the AO basis set should be of triple zeta plus polarization or better quality. Furthermore, it should contain a tight and a diffuse *s* function. The Chipman AO basis,^{23,41} which contains diffuse *s* and *p* functions and *d* polarization functions was augmented by a tight *s*-function, with exponent 28 191.9 for carbon, 40 030.9 for nitrogen, and 51 962.3 for oxygen. In the cases of H_2CN and H_2CO^+ , this AO basis set yielded equivalent results to larger AO basis sets.

We also performed CIS calculations since Chipman³⁷ has shown that the CIS method predicts reliable results for hyperfine structures of doublet states in most cases. For the CIS and CISD calculations (CI including single and double excitations with respect to the Hartree–Fock configuration),

unselected spaces were used. These calculations were performed using the MELDF-X programs.⁴² For the CIS and CISD calculations, canonical orbitals were used as the one-electron basis.

B. Results of the hyperfine calculations

In Table II, the results of the hyperfine calculations are collected. A comparison with the experimental data for $A_{\perp} = A_{\text{iso}} - \frac{1}{2}A_{zz}$ and $A_{\parallel} = A_{\text{iso}} + A_{zz}$ is given. The isotropic hfcc A_{iso} is also included because its strong dependence on the theoretical method is the reason for the variations of A_{\perp} and A_{\parallel} according to the treatment. Since the anisotropic term A_{zz} is nearly constant with respect to the theoretical method, it is not given. For all calculations, the QCISD/6-31G* optimized geometries in Table I were used.

A comparison of the theoretical values with the experimental findings shows that only the MRD-CI/ B_K treatment yields reliable quantitative hfcc's for all the investigated molecules. Employing this method, all results lie within the experimental error bars. The CIS method again reaches qualitative agreement with the experimental results. The deviations are between 0 and 6 MHz (0%–20%) with the exception of the C_{α} center in $C_{\alpha}C_{\beta}O$ for which much larger errors were found. The value of A_{\perp} deviates more than 12 MHz ($\sim 23\%$) from the experimental value (43.7 vs 57 ± 3 MHz); for A_{\parallel} , an error of 15 MHz ($\sim 71\%$) is found. A comparison with the MRD-CI/ B_K treatment shows that the CIS calculations yield values for the isotropic hfcc of C_{α} which are much too low (17.3 vs 30.7 MHz).

Consistent with other studies, the agreement with experimental data deteriorates dramatically when double excitations are also taken into account. The CISD method yields deviations of more than 40 MHz. The reasons for the differences between CIS and CISD were studied in a previous investigation.³⁴ For truncated MRD-CI calculations in which the most important higher excitations are accounted for, the situation improves to some extent. However, the influence of the discarded configurations is found to be substantial. If their influence is included via the modified B_K treatment, almost perfect agreement with the experimental findings is obtained; in all cases, the deviations from the experimental data lie within the experimental error bars. Again the most remarkable example is the C_{α} center of $C_{\alpha}C_{\beta}O$, where the B_K corrections improve the isotropic hfcc from -7.8 MHz (MRD-CI) to 30.7 MHz (MRD-CI/ B_K). Due to this improvement, A_{\perp} increases from 17.9 to 56.3 MHz (exp. 57 ± 3 MHz), while the value of A_{\parallel} goes from -50.3 to -20.7 MHz (exp. -17 ± 3 MHz).

Considering the excellent agreement between theory and experiment for CCO, it became obvious during the analysis of the $CN_{\alpha}N_{\beta}$ values that the assignment of the experimental hfcc's to N_{α} and N_{β} was wrong. In their original work, Smith and Weltner assigned the A_{\perp} value of 35 MHz to the N_{α} center, while $A_{\perp} = 19$ MHz was attributed to the N_{β} center. According to our work, this assignment clearly has to be interchanged.

The hfcc's of the NCN molecule are not known experimentally. The absolute values $A_{\perp}(^{13}\text{C})$ and $A_{\parallel}(^{13}\text{C})$ are found to be much larger than the absolute values found for C_{β} of

TABLE II. Theoretical hyperfine coupling constants (in megahertz) for CCO ($^3\Sigma_u^-$), CNN ($^3\Sigma_u^-$), and NCN ($^3\Sigma_g^-$) from the MRD-CI/ B_K calculations ($A_{\perp} = A_{\text{iso}} - \frac{1}{2}A_{zz}$, $A_{\parallel} = A_{\text{iso}} + A_{zz}$).

$C_{\alpha}C_{\beta}O$	C_{α}			C_{β}			O		
	A_{iso}	A_{\perp}	A_{\parallel}	A_{iso}	A_{\perp}	A_{\parallel}	A_{iso}	A_{\perp}	A_{\parallel}
CIS	17.3	43.7	-35.5	-33.8	-32.4	-36.6	-26.6	-43.3	6.8
CISD	-8.0	17.9	-59.7	-34.8	-32.0	-40.2	-5.2	-17.7	19.8
MRD-CI	-7.8	17.9	-59.3	-34.0	-31.7	-38.7	-12.7	-26.8	15.7
MRD-CI/ B_K	30.7	56.3	-20.7	-30.7	-29.6	-32.9	-23.8	-41.3	11.2
Expt. ^a		57(3)	-17(3)		-26(3)	-32(3)			
$CN_{\alpha}N_{\beta}C$	C			N_{α}			N_{β}		
	A_{iso}	A_{\perp}	A_{\parallel}	A_{iso}	A_{\perp}	A_{\parallel}	A_{iso}	A_{\perp}	A_{\parallel}
CIS	36.9	51.2	8.4	-16.8	-20.0	-10.5	25.3	43.6	-11.3
CISD	-7.6	2.3	-28.2	-13.1	-14.9	-9.4	8.0	26.6	-29.2
MRDCI	11.4	24.8	-15.2	-18.8	-21.4	-13.7	9.6	27.1	-25.6
MRDCI/ B_K	35.3	52.9	-0.1	-22.3	-25.8	-15.3	19.3	35.4	-13.0
Expt. ^{a,b}		50(5)			-19(5)			35(5)	
NCN ^c	C			N					
	A_{iso}	A_{\perp}	A_{\parallel}	A_{iso}	A_{\perp}	A_{\parallel}			
CIS	-64.4	-77.2	-38.6	14.7	28.1	-12.1			
CISD	-44.3	-54.2	-24.75	1.6	13.6	-22.3			
MRDCI	-61.0	-72.9	-37.2	8.2	20.9	-17.2			
MRDCI/ B_K	-73.8	-86.9	-47.8	14.1	27.1	-11.8			

^aReference 11. The numbers in parentheses are the experimental errors and the signs of the experimental values were taken from the theoretical calculations.

^bThe nitrogen centers have been interchanged.

^cValues for ^{14}N .

$C_{\alpha}C_{\beta}O$ ($A_{\perp} = -86.9$ vs -29.6 MHz; $A_{\parallel} = -47.8$ vs -32.9 MHz). The reason for the difference lies in both the strong decrease in A_{iso} (-30.7 vs -73.8 MHz) and the strong increase in the anisotropic constants A_{zz} (-2.2 vs 26 MHz).

In the electronic ground state of all three molecules, the singly occupied molecular orbitals (SOMOs) represent the two components of the π^* orbital. The shapes of the respective π_x^* components are given in Figs. 1–3. The nodal plane which determines the antibonding character of the SOMOs cuts through the C–O bond in CCO and through the N–N bond in CNN. For NCN, the SOMO is located at the N centers due to symmetry reasons. The π^* character of the SOMOs prevents them from contributing to the isotropic hfcc's of the various centers, so that the isotropic hfcc's are determined by spin polarization effects. This explains the small absolute values and the varying signs found for the calculated isotropic hfcc's. In all three molecules, the end standing centers possess positive spin density at the position of the atomic centers (keep in mind that the g_N value of ^{17}O is negative), while the central atom has negative spin density. Using the MRD-CI/ B_K method, for CNN, the calculated spin densities are -0.14 for N_{α} , 0.12 for N_{β} , and 0.06 for the C center, while for CCO, one obtains 0.05 for C_{α} , -0.05 for C_{β} , and 0.08 for the oxygen center. For NCN, the spin density at the carbon center is -0.13 and 0.09 at the nitrogen centers. This behavior can be related to the density of the SOMO around the centers. For both molecules, the SOMO is delocalized over the whole molecule, but its density around the inner center (negative spin density) is some-

what smaller in comparison to both outer centers (positive spin density). However, a simple correlation between the density of the SOMO and the isotropic hfcc of a given center is not obvious. For example, the change of the sign in the isotropic hfcc's of both nitrogen centers in CNN is not ac-

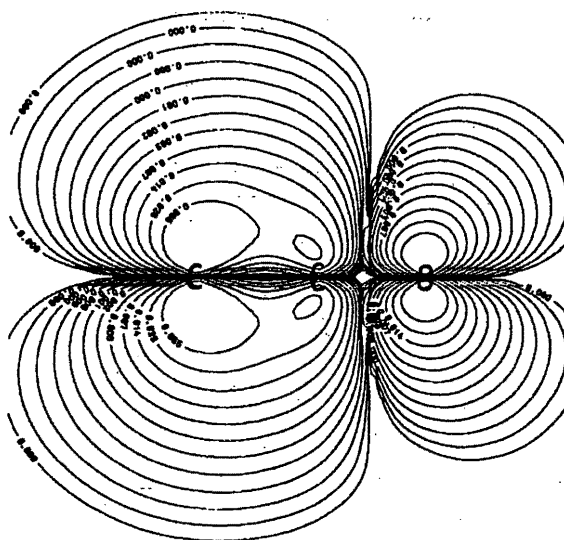


FIG. 1. The shape of the singly occupied molecular orbital (π_x^* component) of CCO ($X^3\Sigma_u^-$).

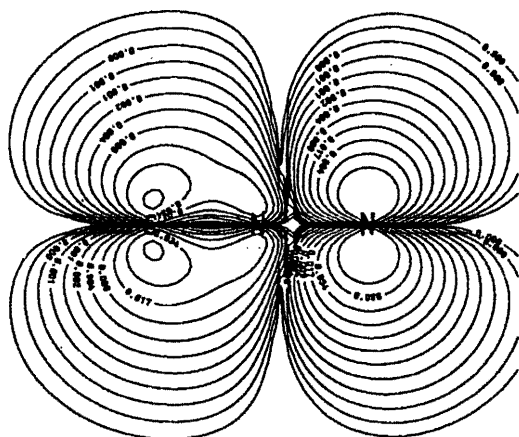


FIG. 2. The shape of the singly occupied molecular orbital (π_x^* component) of CNN ($X^3\Sigma_u^-$).

accompanied by a dramatic difference in the density of the SOMO around the given centers. The above analysis shows that all contributions to A_{iso} arising from the spin polarization of the various doubly occupied shells (valence shell and of the $1s$ orbitals) are important and will contribute with different signs. The SOMOs of CNN and CCO have similar shapes which leads to an equivalent behavior.

The analysis of the correlation between the density of the SOMOs around the various centers and the isotropic hfcc's makes the smaller values of A_{iso} for the carbon in NCN than that of C_β in $C_\alpha C_\beta O$ plausible, since in NCN, both nodal planes go through the carbon center.

In unperturbed electronic states, the influence of the nuclear motion on the hfcc's is small in most cases. Exceptions are those molecules in which the character of the SOMO changes from π type to σ type due to the vibrational motions. To check this influence, we performed test calculations for NCN using the CIS approach. However, averaging

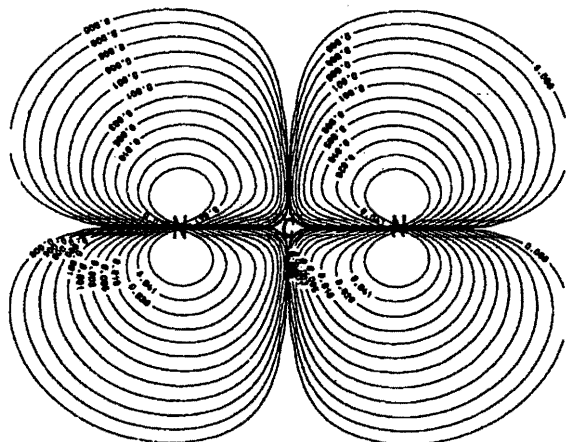


FIG. 3. The shape of the singly occupied molecular orbital (π_x^* component) of NCN ($X^3\Sigma_g^-$).

over the bending vibration shifted the calculated isotropic hyperfine coupling constants by only 0–4 MHz, i.e., they are smaller than the experimental uncertainties. Therefore, only small changes are expected if the vibrational motion were to be taken into account.

IV. SUMMARY AND CONCLUSION

The infrared frequencies and the hfcc's were calculated for the electronic ground state of the isoelectronic triplet molecules CCO ($X^3\Sigma_u^-$), NCN ($X^3\Sigma_g^-$), and CNN ($X^3\Sigma_u^-$). The geometries and IR frequencies were obtained with the QCISD method. The bond distances in CNN have been found to be nearly equal. In CCO, the C–O bond distance is shorter than the C–C bond distance, resulting in a higher asymmetric vibrational stretch frequency (calculated at 2046 cm^{-1}) than in CNN. These results are in agreement with recent experimental and theoretical work.

For the hyperfine coupling constants, CIS, CISD, MR-CI, and MRD-CI/ B_K calculations were performed. Using the CIS method, qualitative agreement with the experimental data is obtained. The deviations from the experimental values are between 0 and 6 MHz (0%–20%), with exception of the hfcc's for the C_α center of $C_\alpha C_\beta O$ for which a much larger error is found (30%–70%). Excellent agreement between theory and experiment is found if the MRD-CI/ B_K method is used. All theoretical values then lie within the error bars of the experimental data. The tentative assignment of the hfcc's to the two nitrogen atoms in CNN given by Smith and Weltner¹¹ had to be changed. The parameters of NCN and the hfcc's of the oxygen center of CCO (^{17}O), which are yet experimentally unknown were predicted. An analysis of the spin polarization effects was carried out. A correlation between the density of the SOMO around the given center and isotropic hfcc is found. However, it becomes clear that all contributions to A_{iso} arising from the spin polarization of the various doubly occupied shells (valence shell and $1s$ orbitals) are important and will be of different signs.

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