Theoretical study of electron spin resonance parameters: H_2CN and H_2CO^+

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The hyperfine structure of the two isoelectronic molecules H_2CN and H_2CO^+ in their electronic ground state ($X\,^2B_2$) is studied. The influence of the atomic orbital (AO) basis sets, of the correlation treatment, and of the equilibrium geometry on the obtained hyperfine properties is investigated. It is found that the multireference double excitation-configuration interaction (MRD-CI)/B_K treatment in which an MRD-CI wave function is corrected by a modified B_K method yields equivalent results to quadratic CI [QCISD(T)], coupled cluster single doubles [CCSD(T)], or Brueckner doubles [BD(T)]. Uncertainties in the equilibrium geometries are found to be the major source for discrepancies between theoretically and experimentally determined isotropic hyperfine coupling constants (hfccs). For the heavier centers, the calculated values of the isotropic hfccs agrees nearly perfectly with experimental values ($\approx 1\%–2\%$). The calculated values for the hydrogens are too low, but using the equilibrium structure suggested by Yamamoto and Sato [J. Chem. Phys. **96**, 4157 (1992)], the best estimate deviates by less than 3%.

I. INTRODUCTION

The isotropic hyperfine coupling constants (hfccs), also known as Fermi contact terms (A_{iso}), are found to be quite sensitive in *ab initio* treatments. The difficulties arise since only those orbitals which possess a nonvanishing value at the position of the nucleus in question *and* a net spin density contribute to A_{iso}. Due to the interaction between the unpaired electrons and all other electrons, doubly occupied shells can also influence A_{iso}. Since the contribution from various shells are similar in magnitude, but differ in sign, a balanced description of these spin polarization effects for all shells is essential. Restricted Hartree–Fock (RHF) calculations are inappropriate because spin polarization effects are neglected. If the unrestricted Hartree–Fock (UHF) method is used, the calculated isotropic hfccs are much too large because spin polarization effects are overestimated. In the case of the configuration interaction (CI) approach, higher than double excitations were also found to be important.[1,2] Therefore, in the framework of the multireference configuration interaction (MRCI) approach, the isotropic hfccs depend strongly on the number of reference configurations, and if configuration selected MRCI calculations are used, they also depend on the number of selected configurations. The two isoelectronic molecules H_2CN ($X\,^2B_2$) and H_2CO^+ ($X\,^2B_2$) are two systems which are well-known for difficulties in the calculation of their isotropic hfccs.

Experimentally, the interest in the methylene imino radical (H_2CN) is guided by its importance as a chemical intermediate in some ballistic propellants and, e.g., for the formation of HCN in the clouds of Jupiter. A discussion of recent theoretical and experimental work on this radical may be found in the review article by Marston and Stief.[3]

In 1962, Cochran *et al.*[4] detected H_2CN for the first time using electron spin resonance (ESR) experiments. Many further ESR studies have been reported. In different matrices, the isotropic hfcc values of the protons ranged from 255 (Ref. 5) to 240 MHz, while $A_{iso}(^{14}N)$ varied between 42 (Ref. 6) and 26.6 MHz. A recent microwave investigation of Yamamoto and Saito[1] yielded the first experimental gas phase hyperfine parameters for the hydrogen and the nitrogen centers. For the protons, $A_{iso}=233.2$ MHz was found, while 25.9 MHz was given for the nitrogen center. This shows that matrix effects shifts both parameters by about 10% to higher values. Based on the measured rotational constants, Yamamoto and Saito suggested three possible equilibrium geometries which will be discussed later on.

Less experimental information is available for H_2CO^+ ($X\,^2B_2$). In particular, a microwave investigation of this molecule is missing, and to the best knowledge of the authors, no experimental geometry has been reported. As for H_2CN, matrix effects are large. The isotropic hfccs of the protons range from 372.1 MHz (Ref. 6) measured in a neon matrix to 253 MHz (Ref. 8) found in sulphuric acid at 77 K. For the carbon center, only one value (109 MHz) was reported by Knight and Steadman.[6]

Both molecules were considered in the theoretical studies of Feller and Davidson[9-12] which renewed the interest in the *ab initio* studies of ESR parameters.[13] Although the calculations seem to be at a high level of sophistication, the calculated isotropic hfccs deviate about 30%–50% from the experimental values. The methylene iminio radical (H_2CN) was later reinvestigated by Chipman, Carmichael, and Feller[14] in the following abbreviated as the CCF study, using single excitation CI (CIS) and the quadratic CI [QCISD(T)] (Ref. 15) method, as well as configuration selected MRCI calculations. The values predicted by configuration selected MRCI calculations were

too small for all centers (deviations of up to 40% from the experimental results) although very large reference spaces (146 configurations) were used. The study shows clearly that configuration selection was one of the major error sources. Although more than 450 000 configuration state functions (CSFS) were selected, convergence of the isotropic hfccs with respect to the selection threshold was not reached. Using unselected MRCI was impossible because the size of the MRCI space was $\sim 33\,000\,000$. The QCISD(T) method, first used in the calculation of isotropic hfccs by Carmichael,[16] yielded much better agreement. For the heavier centers, the agreement is nearly perfect, a deviation of less than 3 MHz is found, but the description of the isotropic hfcc of the hydrogen center turned out to be very complicated. The QCISD(T) method deviated by about 14% (22 MHz) from the experimental value, while a deviation of about 24% (48 MHz) was found for the configuration selected MRCI. The H_2CN radical was also considered in the study of Cave, Xantheas, and Feller[17] in the following abbreviated as the CXF study. In the CXF study, averaged coupled-pair functional (ACPF) and quasidegenerate variational perturbation theory (QD-VPT)[18] were used to estimate the influence of parts of those excitations not included in the MRCI approach. However, even for $A_{iso}(H)$, these contributions were found to be less important (4–6 MHz).

The present paper is devoted to some questions which are important for an understanding of the remaining differences between the experimental and theoretical hfccs. For the formaldehyde radical cation (H_2CO^+), calculations employing similarly sophisticated methods as used in the CCF study are missing. For H_2CN, the geometry used in the recent studies was obtained at a rather low level.[19] While vibrational effects as shown in the CCF study are less important (2–4 MHz) because the isotropic hfccs depend nearly linearly on the internal coordinates, the equilibrium geometry does indeed seem to be very important. The values for $A_{iso}(H)$, e.g., changes by about 20 MHz if they are calculated at the different equilibrium geometries obtained with fourth-order Møller–Plesset (MP4/6-31G**)[20] and generalized valence bond-configuration interaction/double zeta polarization GVB-CI/DZP.[21] Furthermore, it still remains unsolved why the configuration selected MRCI calculations of Feller and Davidson yield such poor agreement with the experimental values.

Recently, one of the present authors has successfully calculated the isotropic hfccs of a number of small systems[22–27] using the MRD-CI/B_K method. In the MRD-CI/B_K approach, a selected MRCI wave function is perturbationally corrected using a modified B_K treatment.[24] The modified B_K treatment extrapolates to the results of an unselected MRCI wave function, as has been shown in previous calculations on the boron and nitrogen atoms[22] and for the CH radical.[24] These publications also contain the exact formulation of the method and test calculations in which the modified B_K treatment is compared to the unselected limit. In the present study, the MRD-CI/B_K approach will be used to address the questions mentioned above. In addition, the method will also be compared to

TABLE I. The definition of the AO basis sets used in the various calculations.

	Chipman basis	Reference
Carbon center	$(9s5p) \rightarrow [5s3p]$	Huzinaga (Ref. 41)
	$+1s$ function (0.0479)	1
	$+1s$ function (28 217.82)	30
	$+2d$ functions (0.28/1.12)	1
Nitrogen center	$(9s5p) \rightarrow [5s2p]$	Huzinaga (Ref. 41)
	$+1s$ function (0.0667)	30
	$+1s$ function (39 350.32)	30
	$+1p$ function (0.0517)	2
	$+2d$ functions (0.37/1.48)	2
Oxygen center	$(9s5p) \rightarrow [5s2p]$	Huzinaga (Ref. 41)
	$+1s$ function (0.0862)	30
	$+1s$ function (52 962.288)	1
	$+2d$ functions (0.55/2.2)	
Hydrogen center	$(5s) \rightarrow [3s]$	Huzinaga (Ref. 41)
	$+1s$ function (0.0483)	30
	$+1s$ function (850.8678)	1
	$+1p$ functions (1.0)	
	Duijneveldt basis	
Carbon center	$(13s8p) \rightarrow [8s5p]$	
	$+2d$ functions (1.097/0.318)	
Nitrogen center	$(13s8p) \rightarrow [8s5p]$	
	$+2d$ functions (1.654/0.469)	
Oxygen center	$(13s8p) \rightarrow [8s5p]$	
	$+2d$ functions (2.314/0.645)	
Hydrogen center	$(9s) \rightarrow [7s]$	
	$+2d$ functions (1.407/0.388)	Duijneveldt (Ref. 29)

various other treatments such as Møller–Plesset perturbation theory, QCISD(T),[15] coupled cluster methods, and the Brueckner doubles method BD(T).[28]

II. METHODS OF CALCULATION

In the present study, two types of AO basis sets are used. The first originates from the Duijneveldt basis,[29] while the second was given by Chipman.[30] It is somewhat smaller than the first one, but optimized for spin property calculations. Both are explained in Table I and will be denoted Duijneveldt and Chipman bases for short.

The geometry optimizations were performed using the MR-CISD[31] and MR-ACPF[32] programs of the COLUMBUS package.[33] The reference space for MRCI and MR-ACPF consists of all excitations in the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) pair of B_1 and B_2 symmetries and the singly occupied orbital. In both the multiconfiguration self-consistent field (MCSCF)-CISD and MCSCF-ACPF calculations, the described reference space corresponds to the active space of the MCSCF calculation. Both a MR-CISD and a MR-ACPF were performed using the MCSCF orbitals (second order CI). The geometry optimizations were done using a finite differentiating scheme.

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 Buenker[34] using the Table CI algorithm.[35] Comparing the wave function of a configuration selected MRCI calculation and an

TABLE II. Results of geometry optimization of H_2CN using different methods. The CISD results were corrected according to the normalized Davidson extrapolation (Ref. 40). The Dujneveldt AO basis was used for the CISD calculation.

Method	R_{CN} (pm)	R_{CH} (pm)	ϕ_{HCH}	Reference
MNDO	123.3	111.4	126.1	42
ROHF/DZP	124	114	119	47
ROHF	124.3	108.4	119	19
GVB-CI	126.8	110.6	121	21
MP4	123	109.5	122	20
CISD/DZP	123.8	108.5	120	43
QCISD/6-31G**	125.9	109.2	121.5	
SF-CISD	124.7	108.9	121.0	
SF-ACPF	125.5	109.2	121.2	
MR-CISD	125.8	109.4	121.1	
MR-ACPF	125.8	109.4	121.1	
MCSCF-CISD	125.6	109.4	121.1	
MCSCF-ACPF	125.6	109.4	121.1	
Saito1	126.1	108	122.3	7
Saito2	124.7	111	116.7	7
Saito3		114		7

unselected MRCI calculation, two types of differences are obvious. First, the unselected MRCI wave function contains more expansion terms. The resulting effect on a property obtained as an expectation value will be called the direct effect. Second, since the neglected configurations interact with the configurations included in the configuration selected MRCI wave function, the coefficients of the selected configurations differ if the configuration selected MRCI wave function is compared to the wave function of an unselected MRCI calculation. Due to the more indirect nature, we called this the indirect effect. A more detailed description of the various effects are given in Ref. 2. In previous studies, it could be shown that the indirect effect is more important than the direct effect for the isotropic hfccs and that the B_K (Ref. 36) treatment is able to incorporate the former effect.[22–24] Details of the modified B_K method were described in previous papers.[22–24]

In the calculations of the hfccs, the reference configurations were selected according to two criteria. First, the squared coefficient of this configuration should be larger than 0.001 in the final CI wave function, and second, the importance to the spin density matrix was analyzed. To obtain faster convergence of the CI expansion, natural orbitals were used as the one-particle basis. Estimates of the spin densities via CI with only the single excitations (CIS) were obtained with the help of the MELDF-X program.[37] The hyperfine coupling constants of the various CI wave functions were calculated as expectation values.

For the unrestricted Hartree–Fock (UHF), unrestricted Møller–Plesset (UMP), UHF-QCISD(T),[15] UHF-CCSD(T),[38] and the UHF-BD(T)[28] calculations, the Gaussian92 program[39] was used. The correlation energy is calculated in the presence of small Fermi contact fields at each $(0.5 \times 10^{-3}$ a.u.) nucleus in turn, and the corresponding spin densities are derived by finite-field perturbation theory.

TABLE III. The influence of the geometry on the isotropic value of the hyperfine coupling constant in H_2CN (in megahertz) using the CIS method and the Chipman AO basis without peak functions. The energy (given in Hartrees) obtained by the SR-ACPF method on the geometry is also reported.

R_{CN} (pm)	ϕ_{HCH}	$A(C)$	$A(N)$	$A(H)$	E_{ACPF}
116.4	121.2	−84.6	12.8	233.7	−93.870 876 97
125.5	121.2	−72.0	15.9	167.7	−93.882 717 44
127.0	121.2	−70.2	15.5	158.3	−93.882 454 11
137.6	121.2	−64.5	13.5	104.2	−93.870 000 52
125.5	115	−65.8	36.3	153.1	−93.879 217 50
125.5	120	−71.5	15.8	164.8	−93.882 583 44
125.5	125	−74.6	19.9	177.3	−93.881 350 66
125.5	130	−77.8	17.2	192.6	−93.875 226 82

III. METHYLENE IMINO RADICAL

The problems arising in the calculation of the electronic structure of the methylene imino radical (H_2CN) in its electronic ground state $X\,^2B_2$ can already be seen in the results of the geometry optimizations using different methods given in Table II (upper part). The MP4/6-31G** calculations of Adams et al.[20] predict a C–N bond distance of about 123.8 pm, whereas the GVB-CI calculation of Bair and Dunning[21] predict a much longer distance (126.8 pm). The importance of the geometry for the calculation of hfccs can be seen in Table III. Changing the CN distance by only 1.5 pm from 125.5 to 127.0 pm shifts $A_{iso}(H)$ by about 10 MHz. The isotropic hfcc of hydrogen is also sensitive to the angle Φ_{HCH}. Both effects can be explained easily by considering the shape of the singly occupied orbital (SOMO) depicted in Fig. 1. If the CN bond is shortened or the HCH angle is widened, the hydrogens are moved towards higher density regions of the SOMO, which causes an increase in $A_{iso}(H)$. The microwave study of Yamamoto and Saito[1] could not establish a final geometry. Assuming CH distances of 108, 111, and 114 pm, they suggested the three possibilities presented in Table II as Saito1, Saito2, and Saito3. In view of the large differences in the equilibrium geometries given in the literature, a reoptimization of all geometrical parameters using different methods was carried out. The values are given in Table II (middle part). Comparing the results, it is obvious that at least a single reference SR-ACPF optimization is necessary. QCISD(T), SR-ACPF, MR-ACPF, MR-CISD, MCSCF-CISD, and MCSCF-ACPF yield nearly identical
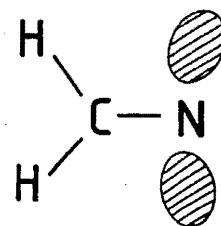

FIG. 1. The shape of the singly occupied molecular orbital (SOMO) in H_2CN ($X\,^2B_2$). The SOMO of H_2CO^+ ($X\,^2B_2$) is similar.

TABLE IV. A comparison of this study with other theoretical studies on H_2CN. The ROHF geometry of McManus et al. (Ref. 19) was used throughout. The isotropic hfccs (A_{iso}) are given in megahertz.

Method	$A_{iso}(^1H)$	$A_{iso}(^{13}C)$	$A_{iso}(^{14}N)$
SCI[a]	166.0	−68.3	24.1
SDCI[b]	152.3	−49.3	6.4
MRD-CI[b] (86[c]; 10[d])	169.3	−61.7	12.9
MRD-CI[b] (86[c]; 1.0[d])	173.6	−65.8	14.2
MRD-CI[b] (86[c]; 0.1[d])	184.8	−71.1	17.6
MRD-CI[a] (146[c]; 0.1[d])	187.0	−72.0	17.0
QCISD[a]	211.4	−75.6	24.6
QCISD(T)[a]	211.1	−77.8	26.0
MRD-CI[e] (28[c]; 2.0[d])	166.7	−56.1	10.1
MRD-CI/B_K (28[c]; 2.0[d])	204.1	−76.0	26.7
MRD-CI[e] (72[c]; 1.0[d])	171.9	−55.7	11.0
MRD-CI/B_K (72[c]; 1.0[d])	212.1	−75.0	26.6
Experiment	233.2	−80.9	25.9

[a]Carmichael, Chipman, and Feller (Ref. 14).
[b]Cave et al. (Ref. 17).
[c]Number of configurations in the reference space.
[d]Selection threshold 10^{-6} hartree.
[e]Present work using the Duijneveldt AO basis.

TABLE V. The isotropic hyperfine values of H_2CN using the MRD-CI/B_K method with different geometries (in megahertz).

Geometry	$A(C)$	$A(N)$	$A(H)$	Energy[a]
Saito1	−73.0	26.4	193.9	−93.808 732
Saito2	−81.1	25.7	219.1	−93.809 112
ROHF (Ref. 19)	−75.0	26.6	212.1	−93.808 212
MCSCF-ACPF	−78.0	26.0	207.9	−93.809 434
Exp. (Ref. 1)	−80.9	25.9	233.2	

[a]Calculated with the MCSCF-ACPF method using the Duijneveldt basis.

values, while SR-CISD deviates slightly. The optimized geometry lies between the geometries Saito1 and Saito2. The rotational constants obtained with the MCSCF-ACPF geometry also agree with experiment to 1%.

In the present study, the isotropic hfccs are calculated using the MRD-CI/B_K method. In order to discuss its ability to predict the isotropic hfccs and to study the reasons responsible for the poor agreement found in the configuration selected MRCI calculation in the CCF[14] and CXF[17] studies, an investigation was performed at the geometry used in both previous works. The results are summarized in Table IV along with the outcome of the previous investigations. Let us first focus on the hydrogen center because it is the most difficult property. Using the uncorrected MRD-CI wave function obtained with a selection threshold of $T_{CI} = 10^{-6}$ hartree, the isotropic hfccs obtained in the present study are similar to those of the previous works using the same level of sophistication (86 reference configurations, $T_{CI} = 10^{-6}$ hartree). If the number of variationally handled configurations is enlarged by decreasing T_{CI}, $A_{iso}(H)$ increases slowly, but even for the largest MRCI calculation performed in the CCF study ($T_{CI} = 10^{-7}$ hartree, 446 932 CSFs selected), no convergence is reached in $A_{iso}(H)$ (see also Figs. 1 and 2 of the CCF study). If instead of enlarging the variationally handled space, the indirect effect of the neglected configurations is estimated by the B_K method $A_{iso}(H)$ jumps by about 40 MHz (MRD-CI: 171.9 MHz; MRD-CI/B_K: 212.1 MHz) towards the experimental results. Similar effects can be seen for the isotropic hfccs of the carbon and the nitrogen centers. This shows clearly that the reason for the failure of the configuration selected MRCI wave function in predicting reliable isotropic hfccs for H_2CN lies in the slow convergence of A_{iso} as a function of T_{CI}. The indirect influence of the neglected configurations, which is incorporated by the B_K treatment, is very important and

cannot be neglected in the calculation of isotropic hfccs. This is consistent with a recent study which investigated the contributions of various excitation classes.[2] As found for the CH radical,[24] the QCISD(T) gives very similar results to the MRDCI/B_K method.

Before we discuss the influence of the equilibrium geometry, let us focus on the effects arising from excitations not included within our treatment. The value of $A_{iso}(H)$ increases from 204 to 212 MHz if the reference space is enlarged from 28 to 72 CSFs. Similar trends are found in the CCF and CXF studies. Further enlargement of the reference space should lead to an increase in A_{iso} of about 4–6 MHz. This can be seen from the calculation using 146 reference configurations and is supported by the CXF study in which up to 375 reference configurations were used in combination with a double zeta polarization (DZP) AO basis set.

Another uncertainty in the theoretical predicted isotropic hfccs arises from the equilibrium geometry of H_2CN. As discussed above, vibrational effects are of little importance.[14] Table V lists the isotropic hfccs calculated at different structures, namely, the equilibrium structure obtained from the MCSCF-ACPF calculation and two geometries suggested from the microwave study of Yamamoto and Saito[1] (Saito1, and Saito2). The third structure given by the experimental investigation was not included, because at the level of SR-ACPF, it is higher in energy by about 700 cm^{-1}. The ROHF structure given by McManus et al.[19] is included to compare the results to those given in Table IV. The geometrical parameters of the various structures can be taken from Table II. The energetical differences between the structures Saito1, Saito2, and MCSCF-ACPF are smaller than 160 cm^{-1}, indicating the very flat nature of the potential energy hypersurface around the equilibrium geometry of the molecule. The MCSCF-ACPF structure has the lowest energy, but the Saito1 structure is only 70 cm^{-1} higher in energy. The changes in the isotropic hfccs calculated at the various geometries are significant. Comparing both experimental structures $A_{iso}(H)$ varies by about 26 MHz, while a change of 8 MHz is found for $A_{iso}(C)$. For both centers, the variation consists of about 10% of the absolute values, while the isotropic hfccs of the nitrogen center are less sensitive. The values obtained for the MCSCF-ACPF structure are between the calculated and both experimental geometries, being closer to the values of the Saito1 structure. The variations in $A_{iso}(H)$ and $A_{iso}(C)$ arise due to two opposite trends. Go-

TABLE VI. Anisotropic hyperfine coupling constants (in megahertz) of H_2CN (X^2B_2). The values of the present work were obtained with the Duijneveldt AO basis in combination with the MRD-CI/B_K method.

	Hydrogen			Carbon		Nitrogen	
	T_{aa}[a]	T_{bb}	T_{ab}	T_{aa}	T_{bb}	T_{aa}	T_{bb}
Saito1[b]	10.4	−3.8	±3.8	16.2	2.9	−46.3	79.3
Saito2[b]	8.9	−3.7	±2.8	16.9	0.9	−45.3	77.9
MCSCF-ACPF[b]	9.5	−3.7	±3.1	16.7	1.7	−45.7	78.5
MRCI[c]	8.7	−2.2	±4.2	16.0	1.7	−44.0	76.4
Exp.[d]	8.3±0.1	−2.2±1.3				−45.1±0.1	80.4±0.1

[a]For a comparison with the experimental results, the elements of the hyperfine tensor are given within the principal axis of the inertial tensor with T_{aa} lying along I_a which in the present molecule correspond to the twofold symmetry axis. T_{bb} lying along I_b is the second element of the hyperfine tensor in the molecular plane. The last diagonal element (perpendicular to the molecular plane) can be obtained from the fact that the anisotropic tensor is traceless. The outer diagonal elements T_{ab} for carbon and oxygen are zero by symmetry; for the hydrogen centers, they possess different signs.
[b]The various geometrical parameters can be taken from Table II.
[c]Reference 10.
[d]Reference 7.

ing from the Saito1 structure to the Saito2 structure, the CN distance shortens and the HCH angle decreases. While an increase in the absolute value of A_{iso}(C) results from the first modification (Table III), a decrease is found for the second. Similar effects exist for the hydrogen center. Summarizing, we expect an uncertainty of about 5% for the isotropic hfccs of H_2CN from innacuracies in the equilibrium geometry. Using the Saito2 structure, A_{iso}(H) calculated in the present study deviates only 6% from the experimental value, while a deviation of 11% is found using the MCSCF-ACPF structure, although both geometries are very close in energy (ΔE=70 cm^{-1}). For A_{iso}(C), the agreement with the experimental value is good. Using the MCSCF-ACPF structure, a deviation of 3% is found, while an error of only 0.2% is obtained at the Saito2 structure. For A_{iso}(N), which is insensitive to geometrical variations, the agreement is excellent (0.2%). To decrease the uncertainties in the isotropic hfccs, a very accurate equilibrium geometry, perhaps obtained by combining experimental and theoretical results,[48] is necessary. The influences of higher excitations not taken into account in the present study (4–6 MHz), or of vibrational effects [3 MHz (Ref. 14)] are less important. The inability of selected MRD-CI studies to predict isotropic hfccs is due to the neglect of the indirect contributions of those configurations not included in the configuration selected MRCI wave function, which in the present study has been incorporated via the B_K correction.

TABLE VII. Results of geometry optimization of H_2CO^+ using different methods.

Method	R_{CO} (pm)	R_{CH} (pm)	ϕ_{HCN}	Reference
ROHF/4-31G	123.4	108.1	123.6	10
ROHF/DZP	119	110	124	47
ROHF/6-31G**	121	109	124.7	
MCSCF/TZP	120.8	112.3	119.1	10
UMP2/6-311++G**	119.5	111.1	122.5	
QCISD (T)/6-31G**	121.1	111.4	122.0	

The anisotropic hfccs are given in Table VI. All theoretical values were calculated using the MRD-CI/B_K method, but as already discussed in several works,[2,12] they are quite insensitive to the method of calculation. We have therefore left out of tabulating all results given in the literature. Only the study of Feller and Davidson is included for comparison. The dependence on the geometry is also less prominent.

IV. FORMALDEHYDE RADICAL CATION

The geometry optimization of the formaldehyde radical cation (H_2CO^+) turned out to be less sensitive to the level of correlation treatment. The results of the geometry optimizations are given in Table VII. The atomic distance of the C–O bond is ~121 pm with the QCISD(T)/6-31G** calculation, which is shorter than the C–N bond distance in H_2CN, indicating stronger double bond character in H_2CO^+. The QCISD(T)/6-31G** calculation gave very similar results to the MR-ACPF treatments in the case of the H_2CN molecule, so further calculations

TABLE VIII. The isotropic hyperfine values of H_2CO^+ in its ground state (X^2B_2) using different methods and basis sets (in megahertz). The QCISD(T)/6-31G** optimized geometry was used throughout.

Method	AO basis	A(C)	A(O)	A(H)
MRD-CI/B_K	Chipman	−102	−58	306
MRD-CI/B_K	Chipman+Peak	−107	−63	318
UMP2	Chipman+Peak	−108	−53	295
UMP3	Chipman+Peak	−102	−61	271
UMP4	Chipman+Peak	−101	−54	293
QCISD	Chipman+Peak	−112	−67	313
QCISD(T)	Chipman+Peak	−108	−66	319
CCSD	Chipman+Peak	−111	−69	309
CCSD(T)	Chipman+Peak	−107	−65	317
BD	Chipman+Peak	−110	−70	306
BD(T)	Chipman+Peak	−108	−67	318
MRD-CI	Chipman+Peak	−86	−44	284
MRD-CI/B_K	Chipman+Peak	−107	−63	318
MRD-CI/B_K	Duijneveldt	−104	−67	324

TABLE IX. Reported results of the isotropic hyperfine values (in megahertz) of H_2CO^+ in the ground state (X^2B_2).

Method	AO basis	$A(C)$	$A(O)$	$A(H)$	Reference
MRCI	ETG	−67	−39	224	9
SAC-CI	DZ	−81	−37	328	45
SAC-CI	STO	−78	−39	312	46
CCSD	DZP	−104	−59	280	44
MRD-CI+B_k	Duijneveldt	−104	−67	324	
Exp.				253	8
Exp.			−109	372	6

were not performed. In Table VIII, the effects of different types of correlation treatment and of different AO bases on the isotropic hfcc sets are studied. Let us first focus on the AO basis set. Upon addition of Gauss functions with very high exponents ("peak functions") to the Chipman basis, the value of the hydrogens is enlarged by about 12 MHz (MRD-CI/B_K calculations with and without peak). A further increase of 6 MHz is found if the AO basis set suggested by Duijneveldt[29] also used in the H_2CN calculation is employed. However, the differences are small, so that the Chipman+Peak AO basis was chosen to study the influence of the correlation treatment. According to the calculated isotropic hfccs, the methods can be divided into three groups. In terms of the absolute values, the uncorrected MRD-CI treatment gives the smallest isotropic hfccs. The large deviations from the experimental results are due to the neglect of the indirect effects as already discussed for H_2CN. Better results are obtained with Møller-Plesset perturbation theory (UMP2-UMP4). However, the series of the Møller-Plesset perturbation theory (UMP2-UMP4) shows similar behavior as found for the CH molecule.[24] The UMP2 values are surprisingly good, but comparing UMP2, UMP3, and UMP4, some sort of error cancellation is obvious. Best agreement with the experimental results is obtained in the last group of correlation treatments consisting of QCISD(T), CCSD(T), BD(T), and MRD-CI/B_K. All treatments yield very similar results. According to the present study, the MRD-CI/B_K results obtained with the Duijneveldt basis set should be the theoretically most founded.

A comparison of the present study to theoretically predicted isotropic hfccs taken from the literature and the experimental results is presented in Table IX. It contains the values given by Feller and Davidson (MRD-CI/ETG),[9] which are much too small. Another study was performed by Nakatsuij and co-workers[45,46] using the symmetry adapted cluster-CI (SAC-CI) method in combination with very small AO basis sets. While $A_{iso}(H)$ seems to be quite good, the values obtained for both heavier centers are also too small, so that some sort of error cancellation can be assumed. Especially, the size of the AO basis sets used in the latter studies seem to be insufficient. In difference to the other theoretical investigations mentionend in Table IX, Nakatsuji and Izawa[46] used Slater type orbitals (STOs) for the calculation of the isotropic hfccs. They claimed that the inadequacy of the calculation of Feller and Davidson was due to the use of Gaussian type orbitals (GTOs). This is contrary to the present study, which shows clearly that not the use of GTOs, but rather the neglect of the indirect effects is the reason for worse agreement with the experimental data. A comparison of the CCSD and CCSD(T) calculations performed in the present work with the study of Sekino and Bartlett[44] reveals that the standard DZP AO basis set is not flexible enough for the calculation of spin densities.

The isotropic hfccs obtained in the present work agree better with the experimental values given by Knight and Steadman[7] obtained in a neon matrix than with those of Symons and co-workers measured[8] in sulphuric acid. This is in keeping in line with the intuitive assumption that the influence of the environment is smaller in the Ne matrix. For the carbon center, the agreement is very good (104 vs 109 MHz), while for $A_{iso}(H)$, a deviation of 48 MHz (12%) is found. From the experience obtained with H_2CN, two major sources of errors have to be considered. First, it can be expected that, as for H_2CN, the isotropic hfccs obtained in gas phase experiments will be smaller in magnitude than those measured in matrices. Uncertainties in the theoretically determined isotropic hfccs arise from inaccuracies in the equilibrium geometries. Errors in the correlation treatment or the influence of the vibrational motion should be of lesser importance (<10 MHz). The anisotropic hfccs are given in Table X along with the experimental values. Since the anisotropic hfccs do not depend so strongly on the quality of theoretical treatment, we did not include all theoretical calculations for comparison.

TABLE X. Anisotropic hyperfine coupling constants (in megahertz) of H_2CO^+ (X^2B_2). The values of the present work were obtained with the Duijneveldt AO basis in combination with the MRD-CI/B_K method.

	Hydrogen			Carbon		Oxygen	
	T_{aa}[a]	T_{bb}	T_{ab}	T_{aa}	T_{bb}	T_{aa}	T_{bb}
ESR/Ne matrix[b]	4.2±0.9	5.0		10.3±0.9	4.2±0.9		
ESR/sulphuric acid[c]	4.5	−2.8					
MRD-CI[d]	7.0	3.4	±11.2	8.4	8.1	140.8	−263.2
Present work	5.8	3.3	±10.9	9.0	10.1	135.3	−240.4

[a]Notation (see Table VII).
[b]Reference 8.
[c]Reference 6.
[d]Reference 10.

V. CONCLUSION

In the present paper, some open questions regarding the disagreement between the theoretically and experimentally determined isotropic hfccs of H_2CN and H_2CO^+ are investigated using the MRD-CI/B_K method. Generally the study shows that the failure of configuration selected MRCI calculations in predicting isotropic hfccs correctly is due to the slow convergence of the isotropic hfccs with respect to the number of configurations actually taken into account. As already shown in previous studies,[22-24] the error can be corrected if the indirect influence of the neglected configurations is considered via a modified B_K method. For both molecules, the MRD-CI/B_K method gives comparable results to QCISD(T), CCSD(T), and BD(T). However, it should be noted that from the computational point of view, the MRD-CI/B_K method is less expensive. For H_2CN, discrepancies between experiment and theory are due mainly to uncertainties in the molecular geometry. The energies of two geometries [Saito1 and Saito2 (see Table IV)] suggested as equilibrium structures by Yamamoto and Saito differ only by 160 cm^{-1} (MCSCF-ACPF calculation), while the corresponding isotropic hfccs differ by 10% of the absolute value. The equilibrium structure obtained from a MCSCF-ACPF optimization lies between both structures. Using the Saito2 structure, the calculated values of the isotropic hfccs for H_2CN are $A_{iso}(^1H)=219$ MHz, $A_{iso}(^{13}C)=81.1$ MHz, and $A_{iso}(^{14}N)=25.7$ MHz. If for the hydrogens the influence of further error sources such as vibrational effects (<2-3 MHz) and missing correlation effects (4-6 MHz) are included, the disagreement between experiment and theory is less than 3%. For H_2CO^+, the agreement is somewhat worse—48 MHz in the case of $A_{iso}(H)$, but only 5 MHz for the carbon center. However, in addition to uncertainties arising from the equilibrium structure, we expect that the isotropic hfccs determined from gas phase experiments will be somewhat closer to the theoretical results than those obtained in the matrices.

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[1] D. M. Chipman, Theor. Chim. Acta 76, 73 (1989).
[2] B. Engels, Theor. Chim. Acta 86, 429 (1993).
[3] G. Marston and L. J. Stief, Res. Chem. Intermediates 12, 161 (1989).
[4] E. L. Cochran, F. J. Adrian, and V. A. Bowers, J. Chem. Phys. 36, 1938 (1962).
[5] D. Banks and W. Gordy, Mol. Phys. 26, 1555 (1973).
[6] L. B. Knight and J. Steadman, J. Chem. Phys. 80, 1018 (1984).
[7] S. Yamamoto and S. Saito, J. Chem. Phys. 96, 4157 (1992).
[8] M. C. R. Symons, Tetrahedron 39, 615 (1973); S. P. Mishra and M. C. R. Symons, J. Chem. Soc. Chem. Commun. 1975, 909.
[9] D. Feller and E. R. Davidson, J. Chem. Phys. 80, 1006 (1984).
[10] D. Feller and E. R. Davidson, Theor. Chim. Acta 68, 57 (1985).
[11] D. Feller and E. R. Davidson, J. Chem. Phys. 88, 7580 (1988).
[12] D. Feller and E. R. Davidson, in Theoretical Models of Chemical Bonding, edited by Z. B. Maksic (Springer, Berlin, 1991).
[13] N. M. R. Atherton, Electron Spin Resonance (Wiley, New York, 1973).
[14] D. M. Chipman, I. Carmichael, and D. Feller, J. Phys. Chem. 95, 4702 (1991).
[15] J. A. Pople, M. Head-Gordon, and K. Raghavachari, J. Chem. Phys. 87, 5968 (1987).
[16] I. Carmichael, J. Chem. Phys. 93, 863 (1990); J. Phys. Chem. 95, 108 (1991).
[17] R. J. Cave, S. S. Xantheas, and D. Feller, Theor. Chim. Acta 83, 31 (1992).
[18] R. J. Cave and E. R. Davidson, J. Chem. Phys. 89, 6798 (1988).
[19] H. J. McManus, R. W. Fessenden, and D. M. Chipman, J. Phys. Chem. 92, 3781 (1988).
[20] G. F. Adams, D. R. Yarkony, R. J. Bartlett, and G. D. Purvis, Int. J. Quantum Chem. 23, 437 (1983).
[21] R. A. Bair and T. H. Dunning, J. Chem. Phys. 82, 2280 (1985).
[22] B. Engels, Chem. Phys. Lett. 179, 398 (1991).
[23] B. Engels, Quantenmechanische Berechnungen von Magnetischen Hyperfeinkopplungskónstanten in Molekülen (Habilitation, University of Bonn, 1992).
[24] B. Engels, J. Chem. Phys. (in press).
[25] M. Staikova, B. Engels, M. Peric, and S. D. Peyerimhoff, Mol. Phys., (in press).
[26] B. Engels and M. Peric, J. Chem. Phys. 97, 7629 (1992).
[27] M.-B. Huang, H. U. Suter, B. Engels, S. D. Peyerimhoff, and S. Lunell, J. Phys. Chem. (to be published).
[28] N. C. Handy, J. A. Pople, M. Head-Gordon, K. Raghavachari, and G. W. Trucks, Chem. Phys. Lett. 164, 185 (1989); K. Raghavachari, J. A. Pople, E. Replogle, M. Head-Gordon, and N. C. Handy, Chem. Phys. Lett. 167, 115 (1990).
[29] F. B. Duijneveldt, Technical Report RJ945, IBM Research Laboratories, San Jose, CA, 1971.
[30] D. M. Chipman, J. Chem. Phys. 91, 5455 (1989).
[31] H. Lischka, R. Shepard, F. B. Brown, and I. Shavitt, Int. J. Quantum Chem. Symp. 15, 91 (1981).
[32] R. J. Gdanitz and R. Ahlrichs, Chem. Phys. Lett. 143, 413 (1988).
[33] R. Shepard, I. Shavitt, R. M. Pitzer, D. C. Comeau, M. Pepper, H. Lischka, P. G. Szalay, R. Ahlrichs, F. B. Brown, and J.-G. Zhao, Int. J. Quantum Chem. Symp. 22, 149 (1988).
[34] R. J. Buenker and S. D. Peyerimhoff, Theor. Chim. Acta 35, 33 (1974); 39, 217 (1975); R. J. Buenker, S. D. Peyerimhoff, and W. Butscher, Mol. Phys. 35, 771 (1978).
[35] R. J. Buenker and R. A. Phillips, J. Mol. Struct. (Theochem.) 123, 291 (1985), and references cited therein
[36] Z. Gershgorn and I. Shavitt, Int. J. Quantum Chem. 2, 751 (1968).
[37] MELDF-X was originally written by L. McMurchie, S. Elbert, S. Langhoff, and E. R. Davidson; it has been modified substantially by D. Feller, R. Cave, D. Rawlings, R. Frey, R. Daasch, I. Nitzche, P. Philips, C. Jackels, and E. R. Davidson.
[38] R. J. Bartlett, J. Phys. Chem. 93, 1697 (1989).
[39] M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, Gaussian 92, revision B, Gaussian, Inc., Pittsburgh, PA, 1992.
[40] S. R. Langhoff and E. R. Davidson, Int. J. Quantum Chem. 8, 61 (1974); I. Shavitt, F. B. Brown, and P. G. Burton, ibid. 31, 507 (1987).
[41] S. Huzinaga, Approximate Atomic Functions I (University of Alberta, Edmonton, Canada, 1971); J. Chem. Phys. 42, 1293 (1965).
[42] M. J. S. Dewar and S. Olivella, J. Chem. Soc. Faraday Trans. 2 75, 829 (1979).
[43] V. Barone, F. Lelj, N. Russo, Y. Ellinger, and R. Subra, Chem. Phys. 76, 3781 (1983).
[44] H. Sekino and R. J. Bartlett, J. Chem. Phys. 82, 4225 (1985).
[45] T. Momose, H. Nakatsuji, and T. Shida, J. Chem. Phys. 89, 4185 (1988).
[46] H. Nakatsuji and M. Izawa, J. Chem. Phys. 91, 6205 (1989).
[47] A. Hinchcliffe, J. Mol. Struct. 67, 101 (1980).
[48] P. Botschwina, M. Horn, S. Seeger, and J. Flügge, Mol. Phys. 78, 191 (1993).