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Difficulties in *ab initio* CI calculations of the hyperfine structure of small radicals

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Two of the radicals whose ab initio hyperfine properties exhibited unusually large (30%) deviations from experiment in a recent study of such properties have been reexamined. Inclusion of vibrational averaging effects, MCSCF orbitals and large CI reference spaces resulted in a reduction of the deviation from experiment to 14% for the formaldehyde radical cation. New experimental data on the methoxy radical shows a much larger proton isotropic hyperfine value than previous experimental and theoretical studies. The best current calculations were unable to resolve the discrepancy. The ethyl radical was also included in this study since good experimental beta proton data is available for comparison.

Key words: Proton hyperfine — Spin densities — Formaldehyde cation — Methoxy — Ethyl — 1,3-butadiene

1. Introduction

A recent *ab initio* study [1] of hyperfine coupling constants in ten small radicals found differences between theory and experiment to be generally less than 10%. However, for the isoelectronic series H_2CN, H_2CO^+ and H_2BO as well as the related acetaldehyde radical cation, $H_3C\text{-}CHO^+$, the best extended basis set configuration interaction (CI) calculations yielded proton isotropic values which differed from experiment by 20%-45%. In the case of H_2CO^+, the effects of variations in basis sets, geometries and types of CI were explored, but with little overall improvement in the computed properties.

Among the four radicals showing poor agreement with experiment the unpaired spin is predominantly localized on a nucleus at least one atom removed from the hydrogens at which the proton isotropic hyperfine constant, a_H, is being measured. A counter-example which seemed to indicate that theory could, at least in one case, successfully predict a_H for beta protons was the methoxy radical, H_3CO. There the final theoretical value was within 8% of the gas phase experimental value.

In this work we reexamine some aspects of the previous calculations on the formaldehyde radical cation and the methoxy radical, where new experimental evidence has very recently become available. Additionally we look at the ethyl radical as yet another small molecule possessing beta protons for which good experimental data are available.

2. Formaldehyde radical cation

One potential source of error in computing a_H which was partially addressed in the previous work was the choice of geometry used for evaluating the spin properties. An indication of the sensitivity of a_H to geometry is given by the fact that a 0.05 Å decrease in the CO bond length can result in a 70 MHz increase in a_H.

Since an experimental geometry for the cation is not available, the previous study examined various *ab initio* SCF and multiconfiguration SCF (MCSCF) optimized geometries. Small split valence basis sets (3-21G and 4-31G) were chosen because these gave good results for the neutral formaldehyde. The MCSCF configuration list, which included all possible excitations of the 11 valence electrons among the 10 orbitals in the conceptual minimal valence space, numbered 6818. No excitations were allowed out of the carbon and oxygen inner shells. A slight (0.01 Å) lengthening of the CO bond was observed along with a 0.04 Å lengthening of the CH bonds and a 4 degree decrease in the HCH bond angle relative to the SCF optimized geometry. Reoptimization of the CO bond length at the estimated full CI level with a polarized basis set resulted in a 0.02 Å shortening compared to the SCF value.

In an effort to further probe the convergence of the geometry with respect to basis set we have performed a full 10-orbital/11-electron MCSCF geometry optimization using a $[5s, 3p, 1d/4s, 1p]$ contraction of the $(10s, 5p, 1d/8s, 1p)$ even-tempered basis [2, 3]. The contracted basis set consisted of the tightest portions of the Hartree-Fock $1s$ and $2p$ AO's plus additional diffuse primitives and could be designated (61111, 311/5111). All MCSCF natural orbital (NO) calculations were done with GAMESS [4]. Spin properties were evaluated for multiconfiguration wavefunctions with the MELD programs written in this laboratory. As seen in Table 1, the introduction of polarization functions significantly shortens the CO bond and lengthens the CH bond compared with the 3-21G MCSCF results. The accompanying increase in a_H, from 275 to 331 MHz, represents a 20% effect.

Further increasing the number of polarization functions produced only small variations in the geometry. This was demonstrated by means of a $[5s, 3p, 2d, 1f/4s, 2p, 1d]$ set. Polarization exponents were optimized at the singles and doubles CI (SD-CI) level in atoms [5]. Since the size of this basis precluded

Table 1. Formaldehyde radical cation isotropic hyperfine values (MHz) at various geometries with the [5*s*, 3*p*, 1*d*/4*s*, 1*p*] basis

Nr.	R(CO)	Geometry R(CH)	HCH	Orbital basis	No. active Orbitals	CI	Energy	a_H
1.	1.234	1.081	123.6[a]	MCSCF NO's	10	SD	−113.6587	251
						full	−113.6681	272
					52	SD	−113.8201	226
						MR SD	−113.8317	240
2.	1.242	1.117	120.2[b]	MCSCF NO's	10	full	−113.6692	275
3.	1.208	1.123	119.1[c]	MCSCF/K-orbitals	10	SD	−113.6604	306
						SDTQ	−113.6703	330
						full	−113.6706	331
					15	SDTQ	−113.7361	317
				Canonical/K-orb.	10	full	−113.6548	278
					15	SD	−113.7134	221
						SDTQ	−113.7253	270
4.	1.198	1.117	123.0[d]	MCSCF NO's	10	full	−113.6704	333
					52	MR SD	−113.8339	288
	Experiment							372

[a] Optimal 4-31G SCF geometry

[b] Optimal 3-21G MCSCF geometry

[c] Optimal [5*s*, 3*p*, 1*d*/4*s*, 1*p*] MCSCF geometry

[d] Optimal [5*s*, 3*p*, 2*d*, 1*f*/4*s*, 2*p*, 1*d*] 10-orb./11-electron K-orbital CI geometry

the use of an analytical gradient MCSCF procedure, a CI geometry optimization was performed using canonical occupied/K-orbital virtual orbitals [6] and a quadratic interpolation scheme. K-orbitals have been shown to mimic the set of frozen natural orbitals.

The effects of vibrational averaging in H_2CO^+ were estimated by averaging the quadratic correction to a_H over harmonic zero-point vibrations for the six normal modes obtained with a 3-21G MCSCF wavefunction. Second derivatives of a_H along these normal modes were computed at the MCSCF level with the $[5s, 3p, 1d/4s, 1p]$ basis. The overall effect was to increase a_H by a small amount (about 4% or 12 MHz) with the largest contributions arising from the HCH bend and the CO stretch modes. If this 12 MHz correction was applied together with a 20 MHz correction for the known basis set deficiency to the 10-orbital/11-electron MCSCF value for the final geometry listed in Table 1 the resulting 365 MHz value of a_H would be in excellent agreement with the 372 MHz experimental value of Knight et al. [7].

In light of the previous difficulties it is tempting to quit at this point and assume that the problem has been essentially solved. Unfortunately a little additional analysis reveals that this is not entirely true. Comparing the best value for a_H reported in the previous study (249 MHz) with the value obtained from the 10-orbital/11-electron MCSCF wavefunction at the *s, p, d, f* geometry (333 MHz) reveals an increase of 84 MHz. An MCSCF calculation at the final geometry used in the previous study demonstrates that only about 7% (23 MHz) of this improvement can be attributed to changes in geometry.

Restricting the MCSCF active space to the 10 orbitals suggested by conceptual minimal basis set considerations appears to result in a skewing of the proton isotropic hyperfine parameter towards larger values than might otherwise be obtained. It so happens that in this case the shift brings the computed properties more in line with experiment. An indication of the magnitude of this shift can be seen in Table 1 where the 10 orbital SD-CI property at geometry 1 is 25 MHz larger than the SD-CI using all 52 basis functions. When higher order excitations are included in the CI, the number of configurations increases so rapidly that it is difficult to accurately discern any trends in a_H as a function of the number of involved orbitals. A SDTQ-CI at geometry 3 using an active space of the 10 MCSCF NO's plus 5 K-orbitals provides some evidence that a_H would decrease as the active space is increased even at the full CI level. This CI involved almost 61 000 spin-adapted configurations.

Another effect contributing to the 84 MHz difference between the present best value of a_H and the previous best value is the use of MCSCF orbitals as opposed to canonical/K-orbitals. At geometry 3 the use of MCSCF NO's increases a_H from 278 to 331 MHz for a difference of 53 MHz. This difference between MCSCF NO's and K-orbitals is most noticable for the 10 orbital active space since the MCSCF procedure doesn't define those orbitals not occupied in the MC configuration list. As excitations are allowed into more and more of the complete set of 52 functions the differences between MCSCF NO's and K-orbitals decreases. As seen in Table 1 even a modest increase in the size of the active space, from 10 to 15, decreases the difference from 53 to 47 MHz.

Yet another part of the 84 MHz difference may originate in the failure of our previous calculations to incorporate the effect of important higher order excitations. The purpose of performing multireference singles and double CI (MR SD-CI), as opposed to HF SD-CI, is to attempt to recover some of the correlating effect of these extremely numerous configurations in an efficient manner. Even with the MR SD-CI approach, the extended basis sets employed in the previous study made it necessary to select, via second order perturbation theory, a subset of the generated configurations. Table 1 shows a 10–20% increase in a_H due to triple and quadruple excitations depending on the type of orbitals and the size of the active space. Whether or not these excitations are included in the MR SD-CI's depends on two factors: 1) the configurations must first be generated as a single or double excitation from one of the reference configurations. 2) one of the various perturbation selection schemes must view the configurations as important enough to keep.

Both criteria are more likely to be met if the zeroth order reference space is large enough to contain all important contributors to the final wavefunction. One indication of whether most "important" configurations have been included is the ability of the zeroth order wavefunction to qualitatively reproduce the property of interest. In the previous study diagonalization of the 13 dimensional reference space yielded a zeroth order wavefunction which had an associated value of $a_H = 174$ MHz at geometry 1. In the present study the reference space has been expanded to 106 spin-adapted configurations over MCSCF NO's, whose lowest root has an a_H of 256 MHz. This value is close to the 272 MHz of the 10-orbital/11-electron full MCSCF.

MR SD-CI calculations with this reference space yielded a value of $a_H = 240$ MHz at geometry 1 and 288 MHz at geometry 4. Approximately 27 000–33 000 spin-adapted configurations were selected from among the 1 026 707 generated singles and doubles. Second order perturbation theory estimates that 98% of the total possible MR SD correlation energy was variationally recovered. Correcting the 288 MHz value for basis set deficiency at the nucleus and vibrational averaging effects yields a final value of 320 MHz, which is 14% lower than the experimental value of 372 MHz.

3. Ethyl radical

The findings of previous ab initio calculations of the isotropic hyperfine coupling constants for the ethyl radical are shown in Table 2. Chipman [8] has performed UHF and projected UHF (PUHF) calculations using a wide variety of small to medium size basis sets. Results from only the 6-31G and $(9s, 5p/4s)$ are given in the table since these were the two largest sets and because the other sets gave qualitatively similar values. As expected from perturbation theory arguments and past experience, most of the UHF numbers are larger in absolute magnitude than experiment while most of the PUHF numbers are too small.

Table 2. Previous *ab initio* calculations of the isotropic hyperfine coupling constants in the ethyl radical

Method	Basis	Ref.	Isotropic hyperfine coupling constants (MHz) H-alpha	H-beta	C-alpha	C-beta
UHF	6-31G	[8]	−152.3	74.0	303.5	−74.0
	(9*s*, 5*p*/4*s*)		−123.3	66.4	196.2	−71.2
PUHF	6-31G		−49.6	44.3	104.5	−24.1
	(9*s*, 5*p*/4*s*)		−40.0	40.6	68.4	−23.3
SE-CI	[4*s*, 2*p*/2*s*]	[9, 10]	−66.7	54.9	108.5	−45.1
PO			−72.9	56.3	126.4	−51.3
SAC-CI	[4*s*, 2*p*/2*s*]		−51.0	62.8	66.1	−36.4
Experimental		[23, 24]	−62.8	75.4	110 (98)[a]	−38.1

[a] Planar equilibrium value for *a*(iso) estimated from temperature dependent hyperfine interaction data, Ref. [13]

The results of single excitation CI (SE-CI), pseudo-orbital (PO) and symmetry adapted cluster CI (SAC-CI) calculations by Ohta et al. [9] and Nakatsuji et al. [10] were based on the SCF geometry of Pacanski and Dupuis [11] and are listed in Table 2. The PO method is close to SE-CI with the exception that in the former the spin polarization effects of single excitations are included self-consistently. The SAC-CI method recovers additional correlation energy.

As in the case of the formaldehyde radical cation, there is no available experimental geometry for the ethyl radical. Pacanski and Dupuis have reported double zeta (DZ) basis set restricted Hartree-Fock (RHF) optimal geometries for both the staggered and eclipsed forms. In the staggered structure the two hydrogens on the radical center are reportedly bent 6 degrees out-of-plane.

The Carnegie-Mellon Quantum Chemistry Archive [12] lists an optimal 6-31G* unrestricted Hartree-Fock (UHF) staggered geometry with essentially the same bond lengths as those listed by Pacanski and Dupuis but with the out-of-plane angle increased to 13.6°. This difference is due to the looser convergence criterion employed by the latter authors. When the RHF optimization with the Pacanski-Dupuis basis set was repeated using a convergence criterion of 0.0003 hartree/bohr for the maximum component of a cartesian gradient the out-of-plane bend angle increased to agree with the 6-31G* UHF value and the energy decreased by 0.00002 hartree. An appreciation of the very small amounts of energy involved here can be seen in the fact that forcing the hydrogens 14 degrees back into plane raises the UHF energy of the system by only 0.00028 hartree.

Although the RHF and UHF methods produced equivalent geometries for the ethyl radical, for the methyl radical, which should be a similar case, the experimentally observed D_{3h} conformation is a transition state on the 6-31G* RHF potential surface with an imaginary frequency for out-of-plane bend of 258 i cm^{-1}. With a UHF wavefunction this normal mode has a real frequency of 295 cm^{-1}.

We have performed a 13-orbital/13-electron MCSCF geometry optimization of the staggered conformation using the 6-31G** basis. This choice of number of orbitals and electrons corresponds to the conceptual valence space and parallels what as was done for H_2CO^+. Because of the large number of active orbitals and electrons it was necessary to restrict the types of excitations to singles and doubles. The geometry optimization proceeded very slowly, presumably due to a substantial nonquadratic component of the potential surface.

Because of the slowness in convergence the geometry optimization was halted when the largest component of the gradient was 0.0005 hartree/bohr. Since several geometries, with out-of-plane bend angles ranging from 0°–10°, satisfied this criterion it was not possible to unambiguously define "the" optimal geometry although the force at all angles was in the direction of a flatter methyl group. The variation in energy as a function of angle is about 0.0002 hartree over this range. A "planar" structure is shown in Fig. 1. The lowest computed MCSCF energy was obtained for a structure with a 7 degree out-of-plane bend angle. However, in light of the very small amounts of energy involved it is quite possible that the use of more sophisticated wavefunctions may produce either a planar or a nonplanar geometry. The liquid phase EPR work of Griller et al. [13] is consistent with a planar conformation having an out-of-plane bending frequency of 500 cm^{-1}.

Isotropic hyperfine coupling constants for the ethyl radical were evaluated for various out-of-plane bending angles. All other bond lengths and angles were taken from the near optimal 6-31G** MCSCF geometry. Our findings, presented in Table 3, show a slight decrease in a_H as the hydrogens are bent 10° out-of-plane. This is in qualitative agreement with the temperature dependence of the liquid EPR results of Griller et al. The variation in the alpha and beta carbon parameters are not listed because the small size of the carbon basis set makes such results questionable.

A K-orbital MR SD-CI at the "planar" geometry using a much larger basis set produced moderately better proton results. When the computed values of a_H are corrected for the basis set error the alpha and beta proton hyperfine coupling constants are respectively 3% and 24% lower than experiment.

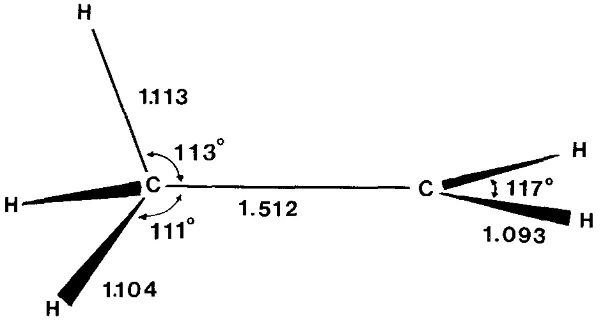

Fig. 1. The 6-31G** MCSCF geometry for the ethyl radical ($^2A'$)

Table 3. Ethyl radical isotropic hyperfine values (MHz)

Out-of-plane angle[a]	Basis	Wavefunction	Isotropic hyperfine constants			
			C (alpha)	C (beta)	H (alpha)	H (beta)
0.0	6-31G**	RHF	0.0	0.0	0.0	27.7
		singles CI	110.1	−36.9	−71.0	58.3
		13-orb./13-el. SDTQ-CI (MC NO's)			−91.8	49.6
	Extended[b]	RHF	0.0	0.0	0.0	29.8
		singles CI	97.1	−40.0	−77.2	55.3
		MR SD-CI	51.4	−32.5	−59.5	55.4
10.0	6-31G**	13-orb./13-el. SDTQ-CI (MC NO's)			−88.7	49.2

[a] The angle formed by the midpoint of the radical center hydrogens and the two carbons
[b] $(13s, 7p, 2d/10s, 2p) \rightarrow [8s, 5p, 2d/6s, 2p]$ contraction. $E(\mathrm{SCF}) = -78.6181$

4. Butadiene

The ambiguity associated with the ethyl radical optimal geometry is not unique. Although it is now widely recognized that changes in basis set or type of wavefunction (RHF, UHF, MCSCF, etc.) will result in minor variations in optimized bond lengths and angles, the possibility of qualitative differences is sometimes overlooked.

An example of the potential difficulties can be seen in the recent report [14] of a minimum corresponding to gauche-1,3-butadiene (twisted) as the second stable conformer of 1,3-butadiene. SCF geometry optimizations using DZ and DZ polarization basis sets predict the C=C—C=C dihedral angle to be in the 33°–38° range. The gauche form was lower in energy than *s*-cis-1,3-butadiene (planar) by 0.43 and 0.71 kcal/mol respectively. SD-CI calculations at the SCF geometries increased this difference to 0.81 and 0.82 kcal/mol. The planar structure was determined to be a transition state at the SCF level.

We have reoptimized the cis form of butadiene using a 10-orbital/10-electron full MCSCF wavefunction based on the Dunning-Hay [15] $(9s, 5p/4s)$ to $[3s, 2p/2s]$, or split valence (SV) contraction. The 10 orbitals include three CC sigma and two pi bonds plus their antibonding counterparts. A geometry optimization begun with the optimal twisted parameters converged to a planar structure, shown in Fig. 2, with an energy of −155.0134 hartree. If the dihedral angle is constrained to be 33 degrees and the remaining geometrical variables are optimized the resulting energy is only 0.0002 hartrees higher.

Energy differences obtained from several choices of basis set, geometry and type of wavefunction are given in Table 4. The MR SD-CI's employed a 3 space orbital product reference space that included $\pi \rightarrow \pi^*$ excitations. These configurations entered the final wavefunction with expansion coefficients on the order of

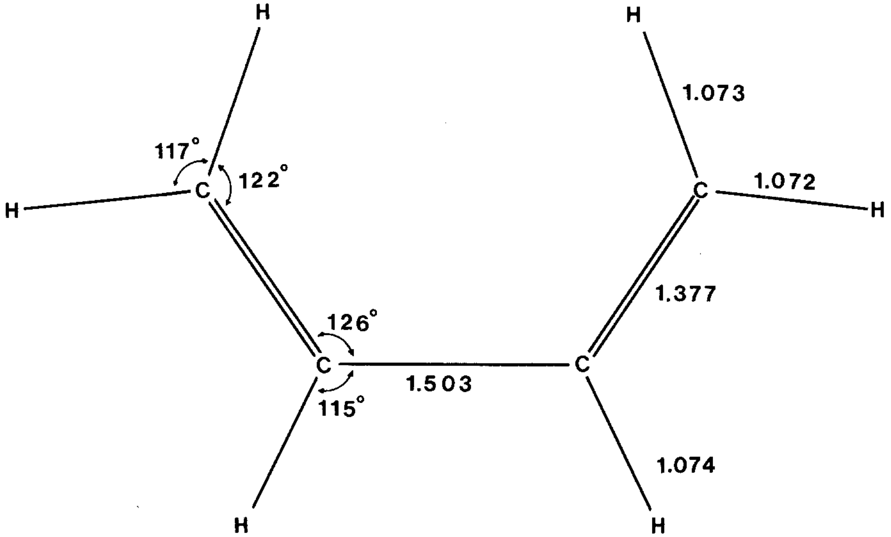

Fig. 2. The Dunning-Hay SV basis MCSCF geometry for gauche-1,3-butadiene (2*A*)

Table 4. Energy differences between gauche (twisted) and *s*-cis (planar) 1.3-Butadiene

Basis	Geometry	Wavefunction	*E* (planar)	*E* Difference[a]
SV	Opt. DZ SCF[b]	RHF	−154.87205	−0.00069
		10-orb./10-el. MCSCF	−155.00972	−0.00007
			−155.19837	−0.00130
		MR SD-CI	−155.20570	0.00002
	Opt. MCSCF[c]	10-orb./10-el. mCSCF	−155.01337	0.00019
DZ	Opt. DZ SCF	RHF	−154.87252	−0.00069
		HF SD-CI	−155.20190	−0.00130
DZP	Opt. DZP SCF	RHF	−154.94653	−0.00129
		HF SD-CI	−155.43809	−0.00130
		est. MR SD-CI	−155.4483	−0.0011
		est. full CI	−155.5252	−0.0003

[a] *E* (twisted) − *E* (planar), i.e. a positive value indicates the planar structure is lower in energy

[b] The optimal DZ and DZP structure, as well as the RHF and HF SD-CI values are taken from Ref. [14]

[c] Because no stationary point was discovered which corresponded to a twisted structure, the energy of the twisted structure was taken from a geometry optimization where the C=C—C=C dihedral angle was fixed at 33 degrees

0.1. While it would be tempting to conclude that the SCF geometry optimizations led to the incorrect structures, the only conclusion which seems warranted is that all results should be viewed with a certain amount of skepticism when energy differences as small as a fraction of a millihartree are involved. It is certainly possible that inclusion of polarization functions may well reverse the conclusion of the SV MCSCF optimization.

5. Methoxy radical

After publication of our previous results for the methoxy radical, CH_3O, new data came to our attention. In a preliminary analysis of the gas-phase microwave spectrum of the methoxy radical Endo et al. [16] reported a new geometry and new beta proton hyperfine coupling constants. With the CH bond length assumed to be 1.0937 Å, the rotational constants led to an essentially C_{3v} geometry with a CO bond length of 1.376 Å and an OCH angle of 108.3°. The average beta proton hyperfine coupling constant was found to be 119 MHz. By comparison, Russell and Radford [17] had previously reported an a_H of 65 MHz. We had reported a MR SD-CI value of 60 MHz at a CO bond length of 1.44 Å.

Recent *ab initio* calculations of the bond length by first order CI [18], many body perturbation theory [19] and generalized valence bond CI [20] give about 1.41 Å, while UHF [21] is reported to give 1.386 Å. Ohta [22] has verified that 6-31G* UHF gives a CO bond length of 1.383 Å for both the $^2A'$ and $^2A'' C_{2v}$ states with very little geometry distortion between them. The UHF energy was −114.4207 for $^2A'$, −114.4206 for $^2A''$ and −114.4201 for both states at the C_{3v} "average" of the separately optimized C_{2v} geometries. This UHF wavefunction gave 78 MHz for a_H in the C_{2v} distorted structure and 76 MHz for the C_{3v} structure.

We report here a calculation at the experimental C_{3v} geometry with a $[8s, 6p, 2d/6s, 2p]$ basis. The carbon basis was taken from our previous work on methylene, while the oxygen and hydrogen bases came from previous work on the water molecule with the exception that the Dunning exponents were used for the oxygen *d* orbitals. Table 5 summarizes the results at various levels of theory. Because of the degeneracy of $^2A'$ and $^2A''$ when symmetry and equivalence

Table 5. Methoxy radical results at the experimental geometry[a] with an $[8s, 6p, 2d/6s, 2p]$ basis

Wavefunction	Energy	a_H (MHz)
RHF ^2E	−114.4661	35.3
$^2A'$	−114.4674	33.3
$^2A''$	−114.4674	33.3
Singles CI $^2A'$	−114.4780	67.8
Multi-ref. Singles CI[b] $^2A'$	−114.4867	73.5
SDT-CI[c] $^2A'$	−114.5375	77.6
SD-CI[d] $^2A'$	−114.7635	65.3
2 state selection SD-CI[e] $^2A'$	−114.7556	77.5
Experiment		119

[a] $R(CO) = 1.376$ Å, $R(CH) = 1.0937$ Å (assumed), OCH angle = 108.3 degrees

[b] The reference space consisted of both the $^2A'$ and $^2A''$ states

[c] The same reference space as above but excitations were limited to the first $8a'$ and $3a''$ orbitals

[d] The same reference space as above but excitations are allowed into the entire orbital space

[e] The second state corresponds to a $(6a')^2(7a') \rightarrow (6a')(7a')^2$ excitation

restrictions are imposed, most of the CI's have been based on $^2A'$ calculations. As was found above for the formaldehyde radical cation, calculations based on limited excitation levels from the SCF configuration do not give a good spin density. The best result, when corrected for basis set deficiencies, is still only 67% of the most recent experimental value.

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