

A theoretical study on the hyperfine coupling constant of the radical cations of aliphatic ethers

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Summary. The hyperfine coupling constants of the radical cations of dimethylether, oxetane (oxacyclobutane), and tetrahydrofuran (oxacyclopentane) are studied by *ab-initio* molecular orbital theories. The extraordinarily large hyperfine coupling constants of the β protons of the ethers that have been found experimentally are analyzed to conclude that an important mechanism of the hole delocalization is the spin polarization in the H–C–O–C–H σ bond. It is also found that for the ethereal systems conventional molecular orbital calculations give glaringly small spin densities but the SAC-CI calculation gives remarkably improved values.

Key words: Hyperfine coupling constants – Radical cation – Spin polarization effect – SAC-CI

1. Introduction

A prominent feature of the radical cations of aliphatic ethers is that the hyperfine coupling constants (HFCCs) of the β protons, i.e., the protons bonded to the carbon atom next to the oxygen atom are remarkably large compared with other radicals [1–3]. Specifically, the averaged HFCCs of the β protons of the radical cations of dimethylether, oxetane (oxacyclobutane), and tetrahydrofuran (oxacyclopentane) are 121, 179, and 181 MHz, respectively, which are about 1.8 times as large as those of the isoelectronic hydrocarbon radicals, isopropyl (69 MHz), cyclobutyl (103 MHz), and cyclopentyl (99 MHz) [4].

This means that the spin density of the odd electron or the positive hole in the out-of-plane p orbital of the oxygen atom extends substantially to the protons. A motivation of the present work is to clarify the mechanism of the above delocalization. As a result of the study, the delocalization is attributed mainly to the so-called spin polarization effect in the σ skeleton. Since such a hole delocalization may have to do with the electronic conduction in oxides, the present analysis in terms of *ab-initio* molecular orbital methods may be relevant for the understanding of the mechanism of the conduction.

In the present paper, we will mainly study the radical cation of dimethylether as the prototype of aliphatic ethers. In Sect. 2 computational procedure is briefly described. In Sect. 3, geometries of the radical cations are given. In Sect. 4, apparent peculiarity of the HFCCs of the ethereal cations predicted by calculations at the Hartree–Fock level will be shown. In Sect. 5, the results of various Beyond-Hartree–Fock calculations will be presented, by which the apparently anomalous HFCCs will be rationalized. Conclusions are given in Sect. 6.

2. Computational procedure

The convergence of spin density calculations is notoriously slow if the computation is based on the variational principle of the total energy. Since configuration selection deteriorates seriously the accuracy of calculated spin densities [5], any configuration selection should be avoided or minimized. We have employed various complete-active-space (CAS) type MCSCF methods to analyze the correlation effect of the valence electron. A modified version of the program HONDO7 coded by Dupuis et al. [6] was used for the calculation of MCSCF wave functions. Since the program is coded on the basis of the Graphical-Unitary-Group-Approach (GUGA) CI method, the spin densities cannot be obtained directly. Therefore, they were obtained by performing a Slater-determinant-based full CI calculation within the same active space as that for the MCSCF calculation using the converged CASSCF orbitals. The program for this full CI procedure was coded after Knowles and Handy [7]. The configuration interaction calculation for single-electron excitations (SECI) and single and double-excitations (SDCI) were also performed without any configuration selection to examine the contribution of the so-called dynamic correlation effect. Along with these orthodox MCSCF and CI approaches, symmetry-adapted-cluster-expansion configuration interaction (SAC-CI) calculations were also carried out without configuration selection. Details of the SAC-CI theory have been described in previous papers [8–10]. The SAC-CI method is found to be suited for the calculation of HFCC [5, 11] since the SAC-CI wave function satisfies the important necessary conditions such as orthogonality and Hamiltonian orthogonality to be imposed upon the states under consideration so that it takes into account the electron and spin correlations adequately [8, 9].

The choice of the basis set is crucial particularly for the calculation of the spin density because the Fermi contact constant represents a property *at* the nucleus. Usually, a large basis set is demanded to describe the vicinity of the nucleus adequately. However, such a calculation is not practically feasible for polyatomic systems such as the ethereal radical cations. We have found that Dunning's double zeta (DZ) basis set [12] is superior to other sets in this respect [5]. Throughout the present work Dunning's [9s5p/4s2p] DZ basis set was employed. Polarization functions were not included because our previous studies on several radicals [5, 11] showed that the inclusion did not improve noticeably the calculated spin density of the protons in the studied radicals.

3. Geometries

In most cases calculated spin densities depend sensitively on the molecular geometry. For the radical cation of dimethylether we employed the geometry

determined by an MP2 calculation with 6-31G* basis set.¹ One C–H bond of the methyl groups were kept in the molecular plane to restrict the radical cation to have the C_{2v} symmetry.

The geometries of oxetane² and tetrahydrofuran³ were determined by UHF calculations with the same basis set. A full optimization of the radical cation of oxetane showed that the oxygen atom was not in the C–C–C molecular plane, but the dihedral angle between the C–C–C and the C–O–C planes was ca. 2.1°. However, since the angle is small enough and since the experimental HFCCs of the four β protons are averaged values as a result of a puckering motion fast enough compared with the ESR time scale [13], we employed a geometry of C_{2v} symmetry to reduce the number of configurations for the CI calculations. The difference of the HFCCs for both the C_{2v} and the unaveraged C_s symmetries calculated by the SAC-CI method was less than 0.5% which is safely ignored.

The radical cation of tetrahydrofuran is twisted around the C_2 axis so that the environment of the two types of the β protons, axial and equatorial, are not equivalent to give markedly different HFCCs [1].

4. Hartree–Fock calculations

Table 1 shows the HFCCs of the protons for dimethylether, oxetane, and tetrahydrofuran calculated by unrestricted Hartree–Fock (UHF), annihilated unrestricted Hartree–Fock (AUHF), and restricted Hartree–Fock (ROHF) methods. The experimental values are also listed. The calculated HFCCs for dimethylether were averaged over the three protons in the methyl group. (Note that the methyl group was observed to be rotating at 4 K due to the tunneling [14].)

UHF calculations usually overestimate the experimental value of HFCC because of the spin contamination while AUHF calculations underestimate because of the insufficiency in taking into account the correlation effect. Therefore, usually the following empirical relation holds:

$$|\text{UHF}| > |\text{exptl.}| > |\text{AUHF}|$$

¹ The geometrical parameters of the radical cation of dimethylether (C_{2v} symmetry) optimized by an MP2 calculation with 6-31G* basis set. Bond distances: $r(\text{CO}) = 1.421 \text{ \AA}$, $r(\text{CH}_1) = 1.087 \text{ \AA}$, $r(\text{CH}_2) = r(\text{CH}_3) = 1.099 \text{ \AA}$. Bond angles: $\angle(\text{COC}) = 121.35^\circ$, $\angle(\text{OCH}_1) = 112.16^\circ$, $\angle(\text{OCH}_2) = 104.49^\circ$, $\angle(\text{H}_1\text{CH}_2) = 113.87^\circ$

² The geometrical parameters of the radical cation of oxetane (C_{2v} symmetry) optimized by a UHF calculation with 6-31G* basis set. Bond distances: $r(\text{OC}_1) = r(\text{OC}_2) = 1.492 \text{ \AA}$, $r(\text{C}_1\text{C}_3) = r(\text{C}_2\text{C}_3) = 1.529 \text{ \AA}$, $r(\text{C}_1\text{H}_{1a}) = 1.081 \text{ \AA}$, $r(\text{C}_3\text{H}_{3a}) = 1.079 \text{ \AA}$. Bond angles: $\angle(\text{C}_1\text{OC}_2) = 90.10^\circ$, $\angle(\text{OC}_1\text{C}_3) = 91.28^\circ$, $\angle(\text{H}_{1a}\text{C}_1\text{H}_{1b}) = 111.20^\circ$, $\angle(\text{H}_{3a}\text{C}_3\text{H}_{3b}) = 110.06^\circ$, $\angle(\text{XC}_1\text{O}) = 119.26^\circ$ where the symbol X denotes a point which is on the line bisecting the angle, $\text{H}_{1a}\text{C}_1\text{H}_{1b}$

³ The geometrical parameters of the radical cation of tetrahydrofuran (C_2 symmetry) optimized by a UHF calculation with 6-31G* basis set. Bond distances: $r(\text{C}_1\text{O}) = r(\text{C}_2\text{O}) = 1.472 \text{ \AA}$, $r(\text{C}_1\text{C}_3) = r(\text{C}_2\text{C}_4) = 1.521 \text{ \AA}$, $r(\text{C}_3\text{C}_4) = 1.535 \text{ \AA}$, $r(\text{H}_{1a}\text{C}_1) = 1.079 \text{ \AA}$, $r(\text{H}_{1b}\text{C}_1) = 1.085 \text{ \AA}$, $r(\text{H}_{3a}\text{C}_3) = 1.083 \text{ \AA}$, $r(\text{H}_{3b}\text{C}_3) = 1.081 \text{ \AA}$. Bond angles: $\angle(\text{C}_1\text{OC}_2) = 111.03^\circ$, $\angle(\text{OC}_1\text{C}_3) = 104.53^\circ$, $\angle(\text{OC}_1\text{H}_{1a}) = 104.85^\circ$, $\angle(\text{OC}_1\text{H}_{1b}) = 102.17^\circ$, $\angle(\text{H}_{3a}\text{C}_3\text{C}_4) = 111.32^\circ$, $\angle(\text{H}_{3b}\text{C}_3\text{C}_4) = 112.55^\circ$. Dihedral angles: $DA(\text{C}_2\text{OC}-\text{OC}_1\text{C}_3) = 11.41^\circ$, $DA(\text{H}_{1a}\text{C}_1\text{O}-\text{C}_1\text{OC}_3) = 125.27^\circ$, $DA(\text{H}_{1b}\text{C}_1\text{O}-\text{C}_1\text{OC}_3) = -120.15^\circ$, $DA(\text{H}_{3a}\text{C}_3\text{C}_4-\text{C}_3\text{C}_4\text{C}_1) = -118.51^\circ$, $DA(\text{H}_{3b}\text{C}_3\text{C}_4-\text{C}_3\text{C}_4\text{C}_1) = 119.71^\circ$

Table 1. The HFCCs of β protons of ethereal radical cations calculated by Hartree–Fock approximation (in units of MHz)

	UHF	AUHF	ROHF	exptl. ^a
Dimethylether	86.4	53.0	33.2	121 ^b
Oxetane	91.7	56.5	36.2	179 ^c
Tetrahydrofuran ax. ^c	127.8	81.6	54.0	249 ^d
eq. ^f	67.2	41.3	26.6	112 ^d

^a The g -factor of the free electron was used to convert the unit of experimental HFCCs from mT to MHz

^b [1]

^c [3]

^d [1]

^e Axial β proton

^f Equatorial β proton

The relation is often used for guessing HFCCs of large molecules. However, all the three ethers in Table 1 do not obey the above conventional relation. To our knowledge the unusual relation of:

$$|\text{exptl.}| \gg |\text{UHF}| > |\text{AUHF}|$$

is found only for the ethereal radical cations, which motivated us to initiate the present study.

Since the UHF wave function takes into account the electron correlation to such an extent that some of the one-electron excitation configurations based on the ROHF wave function are included [15], the fact that the experimental HFCCs of the ethereal cations exceed the UHF values implies that the electron correlation effect due to two-electron excitations and beyond them is important in the present systems, which will be examined in the following section.

5. Beyond-Hartree–Fock calculations

5.1. Radical cation of dimethylether

In order to investigate the many-electron correlation effect, first, the CASSCF approach was applied to analyze the valence electron correlation. Then, SECI and SDCl calculations were carried out to examine the so-called dynamic correlation effect. Finally, the SAC-CI calculation was performed for the quantitative discussion of HFCC of the radical cation of dimethylether.

By restricting only to the valence electron, the hole delocalization can be associated with the following two mechanisms: One is “direct spin delocalization” or “hyperconjugation”, and the other is “spin polarization” among the valence electrons. The former is depicted as the direct spin propagation through space and the latter as the preferential parallel spin alignment due to one of Hund’s rules applied to chemical bonds.

The spin density calculated by ROHF is to be associated with the “direct spin delocalization” within the Hartree–Fock approximation. There should be another “direct spin delocalization” effect originating from the electron correlation, the contribution of which to the spin density cannot be assessed by the

Table 2. The HFCCs of β protons and the total energies of the radical cation of dimethylether obtained by several methods of calculation

	HFCC (MHz)	Total energy (hartree)	Number of configurations ^a
ROHF	33.2	-153.694 094	1
MSCF-1 ^b	54.17	-153.713 370	39
MSCF-IIa ^c	79.05	-153.788 881	19,070
MSCF-IIb ^d	81.46	-153.795 398	736,464 ³
SECI	80.22	-153.726 925	153
SDCI	75.66	-153.963 692 (-153.991 842) ^f	19,605
SAC-CI	107.27	-153.968 947	1,050
exptl.	121 ^g		

^a The configurations were constructed allowing the use of the orbital symmetry of C_{2v} point group. The symmetry of the electronic structure is 2B_1

^b MSCF calculation based on five active orbitals of π type

^c MSCF calculation based on eleven active orbitals consisting five π and six σ types

^d Full-CI calculations within thirteen orbitals consisting of five π and eight σ types (see text)

^e The number of configurations without spin symmetry adaptation

^f Estimated full-CI energy using Davidson's correction

^g [1]

ROHF calculation. The assessment, however, can be made by comparing the result of the ROHF calculation with that of an MCSCF calculation which treats all the out-of-plane p orbitals as the active orbitals. The result of the MCSCF calculation is in the second row of Table 2 (MCSCF-I). In this CAS-type calculation, configurations were constructed from five electrons distributed among the five orbitals consisting of a p orbital on the oxygen atom, two p orbitals on the two carbon atoms, and the two out-of-plane pseudo π orbitals, each from the two methyl groups.

The assessment of the "spin polarization", on the other hand, can be made by including σ orbitals as the active orbitals in addition to the above five. We have included four in-plane bonding σ orbitals of $a_1(\sigma_{\text{COC}})$, $a_1(\sigma_{\text{CH}})$, $b_2(\sigma_{\text{COC}})$, and $b_2(\sigma_{\text{CH}})$, and two antibonding σ orbitals of $a_1(\sigma_{\text{COC}}^*)$, and $b_2(\sigma_{\text{COC}}^*)$. (Note that one of the three C-H bonds in the methyl group is in-plane according to the optimized geometry under the C_{2v} restriction.) The result is in the third row of Table 2 (MCSCF-IIa). The total eleven orbitals were treated as the active orbitals among which thirteen electrons were distributed. We have omitted two antibonding σ orbitals of $a_1(\sigma_{\text{CH}}^*)$ and $b_2(\sigma_{\text{CH}}^*)$ because of the computer limitation. Instead, a single full CI calculation with 736,464 Slater determinants was performed with the thirteen electrons among the thirteen orbitals (i.e., the sum of the previous eleven orbitals plus the two σ_{CH}^* orbitals) after the MCSCF calculation based on the eleven orbitals had converged. According to the result of this calculation the effect of the σ_{CH}^* orbitals to the HFCC was inferred to be relatively small. (Compare MCSCF-IIb with MCSCF-IIa in Table 2.)

The calculated HFCC increases steadily from ROHF toward MCSCF-IIb, although the value of MCSCF-IIb is still smaller than the experimental value by about 30%. The increase between MCSCF-I and ROHF by ca. 21 MHz is attributable to the "direct spin delocalization". The difference between MCSCF-IIa or IIb and MCSCF-I by ca. 27 MHz is to be associated with the "spin

polarization". It should be noted that the latter increase is much more significant than the former which indicates the importance of the "spin polarization" relative to the "direct spin delocalization" in the present system.

The MCSCF-I wave function is found to be almost single-configurational:

$$\begin{aligned} \Psi(\text{MCSCF-I}) = & 0.9936 |0\rangle \\ & + 0.0403 |\alpha(a_2(\pi_{\text{CH}_3}) \rightarrow a_2(\pi_{\text{CH}_3}^*)), \beta(a_2(\pi_{\text{CH}_3}) \rightarrow a_2(\pi_{\text{CH}_3}^*))\rangle \\ & + \dots \end{aligned}$$

In contrast, a considerable configuration mixing occurs in the MCSCF-IIb wavefunction as in the following expansion:

$$\begin{aligned} \Psi(\text{MCSCF-IIb}) = & 0.9661 |0\rangle - 0.0990 |\beta(b_1(\pi_{\text{COC}}) \rightarrow b_1(n_0))\rangle \\ & + 0.0750 |\alpha(b_2(\sigma_{\text{COC}}) \rightarrow b_2(\sigma_{\text{COC}}^*)), \beta(b_2(\sigma_{\text{COC}}) \rightarrow b_2(\sigma_{\text{COC}}^*))\rangle \\ & + 0.0688 |\alpha(a_1(\sigma_{\text{COC}}) \rightarrow a_1(\sigma_{\text{COC}}^*)), \beta(a_1(\sigma_{\text{COC}}) \rightarrow a_1(\sigma_{\text{COC}}^*))\rangle \\ & - 0.0514 |\alpha(b_2(\sigma_{\text{COC}}) \rightarrow b_2(\sigma_{\text{COC}}^*)), \beta(a_1(\sigma_{\text{COC}}) \rightarrow a_1(\sigma_{\text{COC}}^*))\rangle \\ & - 0.0505 |\alpha(a_1(\sigma_{\text{COC}}) \rightarrow a_1(\sigma_{\text{COC}}^*)), \beta(b_2(\sigma_{\text{COC}}) \rightarrow b_2(\sigma_{\text{COC}}^*))\rangle \\ & + \dots \end{aligned}$$

The symbol $b_1(n_0)$ designates the singly occupied molecular orbital (SOMO) in the reference configuration $|0\rangle$. The electron in $b_1(n_0)$ is mainly in the out-of-plane p orbital of the oxygen atom. It should be emphasized that coefficient of the configuration $|\beta(b_1(\pi_{\text{COC}}) \rightarrow b_1(n_0))\rangle$ becomes more than 10% of the coefficient of the first term. The configuration should not mix, in first-order approximation, with the Hartree–Fock configuration on account of the generalized Brillouin theorem for the open-shell Hartree–Fock theory [16]. The significant weight of the configuration originates from the inclusion of the σ correlation which is represented by the third to the sixth terms and beyond them in the right-hand side of the above equation for $\Psi(\text{MCSCF-IIb})$. It is noted that under the approximation the coefficients of the two-electron excitations in the C–O–C σ skeleton are fairly large to exceed 0.05.

The total HFCC value can be decomposed into the contributions from each configuration. It is found that the main contribution to the HFCC with the MCSCF-IIb wavefunction is from the first configuration, $|0\rangle$, which amounts to 36.8% (30.1 MHz), and the next is from the second configuration, $|\beta(b_1(\pi_{\text{COC}}) \rightarrow b_1(n_0))\rangle$, which is 15.3% (12.6 MHz). Thus, the inclusion of the second configuration is indispensable for the system under study.

In the three MCSCF calculations in Table 2, we have analyzed the electron correlation due to the valence electrons only. The difference between the MCSCF-IIb and the experimental values must, therefore, be associated with the correlation effect between the electrons in and outside the active space currently being considered. The inclusion of the so-called dynamic correlation effect by expanding the active space, however, requires a huge number of configurations. Therefore, we have limited the test to SECI and SDCl calculations but with no configuration selection. The $1s$ core orbitals of the carbon and oxygen atoms were excluded. The results of the calculations for the total 36 orbitals are given in Table 2.

Since the SECI wavefunction includes only configurations of the spin polarization type with the neglect of all the higher order excitations, the proximity of

the SECI value to that of MCSCF-IIb may be accidental. The result of SDCI turned out to be even smaller than the values of SECI and MCSCF, which indicates that the dynamic correlation due to two-electron excitations happens to be not so effective in the ether cation. This apparent ineffectiveness in improving the HFCC at the level of SDCI indicate that such approximations as the second order CI do not give the essential solution to eliminate the discrepancy between the experimental and theoretical HFCCs. In other words, correlation effects via the whole σ electrons higher than the second order are required, after all.

The CI wave function of SDCI turned out as:

$$\Psi(\text{SDCI}) = 0.94635 |\text{ROHF}\rangle - 0.07010 |\beta(b_1(\pi_{\text{COC}}) \rightarrow b_1(n_0))\rangle + \dots$$

That is, the second term is not negligible as in the MCSCF-IIb wave function although the coefficient of the second term is a little smaller than that of the MCSCF-IIb wave function. The larger coefficient of the latter comes from the rotation of the orbitals during the SCF procedure of the MCSCF calculation by which the higher order effect is renormalized efficiently. It should be emphasized that the popular, but brute-force approach of SDCI calculation does not improve the HFCC for the ethereal system.

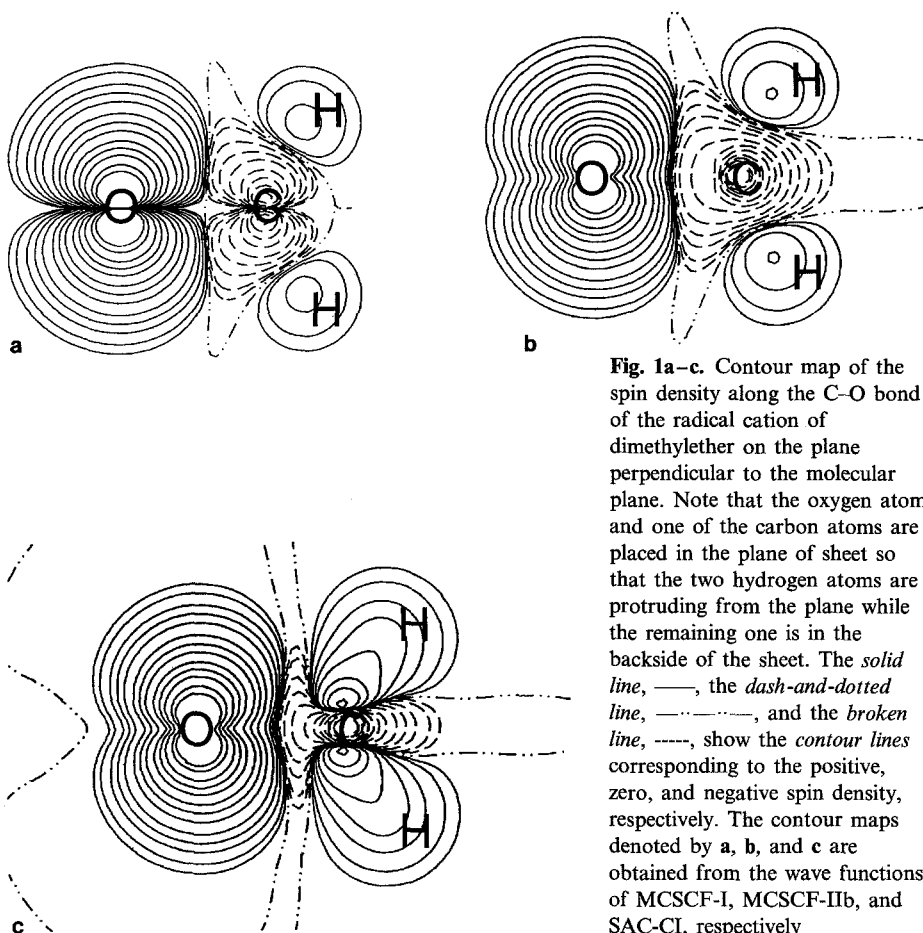
So far we have focused on the mechanism to cause the remarkably large HFCC of the ethereal cation by starting from the Hartree–Fock and going to Beyond-Hartree–Fock levels. However, from the view point of reproducing the experimental value, even the best of all, i.e., $\Psi(\text{MCSCF-IIb})$, is still unsatisfactory. In this respect the SAC-CI theory is superior to the orthodox approach as has been repeatedly emphasized [5, 11].

Table 2 includes the result of the SAC-CI calculation for the dimethylether. All of the 42 orbitals were included as active orbitals. We *did* the configuration selection at the stage of SAC calculation [5], but *not* at the stage of SAC-CI calculation. The HFCC obtained with only about one thousand configurations are much closer to the experimental values than the calculated values by the conventional methods. It should be noted that the total energy of the SAC-CI wavefunction is the lowest among all the calculations in Table 2 except that of SDCI after Davidson's correction.

Since the SAC-CI method starts from the cluster expanded wavefunction for the neutral molecule, it is difficult to expand the wave function in terms of ROHF wave functions exactly, which prevents similar arguments to those made for the MCSCF approaches. However, an approximate expansion is found to be as follows:

$$\Psi(\text{SAC-CI}) \cong 0.8949 |\text{ROHF}\rangle - 0.2768 |\beta(b_1(\pi_{\text{COC}}) \rightarrow b_1(n_0))\rangle + \dots$$

The second configuration of $|\beta(b_1(\pi_{\text{COC}}) \rightarrow b_1(n_0))\rangle$ is quite large. This is the main reason for the SAC-CI method to obtain a far better HFCC than the others. The SAC-CI calculation includes, in principle, up to triple-excitation configurations to give results of, at least, the same level as that of SDT-CI (single-double-triple-excitation CI). Moreover, since the configuration interaction calculation in the SAC-CI method is performed from the SAC wavefunction of the neutral ground state, some of the many-electron excitation configurations based on the ROHF wavefunction of radical cations have been already included automatically in the reference configurations of the CI calculation in the sense of multi-reference CI approaches [8, 9]. Therefore, it is understandable that the correlation effect due to many-electron excitations beyond the triple has been efficiently taken into account compared with other ordinary CI calculations.



The above features of the three calculations by MCSCF-I, MCSCF-IIb, and SAC-CI can be shown visually by the contour map of the spin density distribution as shown in Fig. 1 (see the figure caption for details). As for the MCSCF-I, the negative spin density in the vicinity of the carbon atom is seen with a nodal plane which is a natural consequence of the absence of the σ electron correlation. In contrast, the negative spin density on and around the carbon atom becomes nodeless in the MCSCF-IIb calculation and the positive density around the hydrogen atoms increases due to the spin polarization effect. Finally, the spin density on the carbon atom by the SAC-CI calculation is further squeezed out to result in the marked increase in the spin density at the hydrogen atoms.

5.2. Other aliphatic ethers

Comparison of the three ethers reveals the following features; from Tables 2 and 3 the total sums of the experimental HFCCs of the β protons for the three ethers are obtained as $121 \times 6 = 726$, $179 \times 4 = 716$, and $(249 + 112) \times 2 = 722$ in units of MHz. The constancy of the sum means that the overall distribution of the

Table 3. The HFCCs of β protons of the radical cations of oxetane and tetrahydrofuran (in units of MHz)

	ROHF	MCSCF ^a	SAC-CI	exptl.
Oxetane	36.2	52.7	144.8	179
Tetrahydrofuran ax.	54.0	—	182.5	249
eq.	26.6	—	85.1	112

^a MCSCF calculation based on the seven active orbitals

electron spin on the β protons is nearly constant. The corresponding sums of the HFCCs calculated by SAC-CI are obtained from Tables 2 and 3 as $107.27 \times 6 = 643.6$, $144.8 \times 4 = 579.2$, and $(182.5 + 85.1) \times 2 = 535.2$ MHz, respectively. The values are smaller than the experimental values and decrease gradually as the ethers become larger, even though no configuration selection was made at the stage of the SAC-CI calculations for all the three ethers. Since the quality of the SAC-CI method is comparable with that of SDT-CI, and since the method gives satisfactory results for other systems than the ethereal radical cations [5, 11], the discrepancy between the experimental and the SAC-CI values indicates a particular difficulty of reproducing the spin density for the present systems. Nevertheless, we should like to emphasize the remarkable improvement from ROHF to SAC-CI for oxetane and tetrahydrofuran (see Table 3) as in the case of dimethylether in Table 2. The gradual decrease of the sums of the calculated HFCCs with the increase of the size of the ethers is attributed to the increase in the configurations beyond three-electron excitations which are not included in the SAC-CI method. The non-negligible contribution from the configurations of beyond triple-electron excitations indicates a limitation of using the Hartree-Fock molecular orbital as the starting basis to describe the ethereal systems even though the superiority of the SAC-CI to the other approaches is obvious.

The MCSCF value of 52.7 MHz for oxetane is to be associated with the "direct spin delocalization" only which increases to 144.8 MHz in the SAC-CI calculation. Since the latter calculation takes into account both the "direct spin delocalization" and the "spin polarization" as well as the dynamic correlation effects, the increase of 92.1 MHz ($= 144.8 - 52.7$ MHz) amounting to ca. 64% of the SAC-CI value must be due to "spin polarization" and dynamic correlation. This relative increase is larger than the corresponding value of $(107.27 - 54.17)/107.27 \cong 49.5\%$ for dimethylether (see Table 2). The result indicates that the relative importance of the "spin polarization" and the dynamic correlation becomes larger as the ethereal system becomes larger.

Although the MCSCF calculation was not carried out for the largest ether studied (tetrahydrofuran), it is conjectured that the "spin polarization" and the dynamic correlation becomes even more important in tetrahydrofuran.

Figure 2 shows the contour map of the spin density calculated for oxetane by the SAC-CI method. The general feature is similar to that of the prototype system shown in Fig. 1c, that is, due to the increased spin polarization and higher order correlation effects the density around the two β protons is markedly enhanced at the sacrifice of the density in the vicinity of the carbon atom.

So far we have been concerned exclusively with the β protons of the radical cations of the three ethers. However, a close examination of the experimental

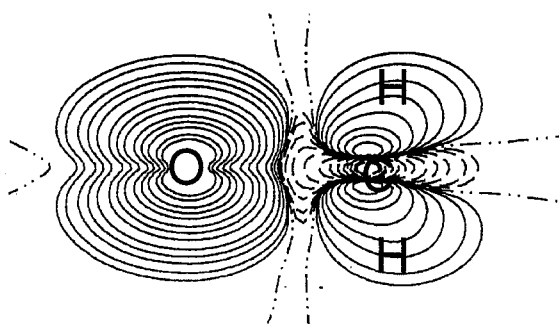


Fig. 2. The contour map of the SAC-CI spin density along the CO bond of the radical cation of oxetane on the plane perpendicular to the molecular plane

data of the ethers with those of the corresponding paraffinic radicals [4] reveals that not only the β protons but also the γ protons of the ethereal cations possess relatively large HFCCs; e.g., $a(\text{H}_\gamma)$ of the oxetane cation reported to be 30.8 MHz [3] is about ten times as large as that of the cyclobutyl radical reported as 3.1 MHz [4], although the absolute magnitude of these constants are much smaller than those of the β protons.

Table 4 shows the calculated HFCCs of the γ protons of the radical cations of oxetane and tetrahydrofuran. As for the HFCC of the γ proton of oxetane, Hartree-Fock calculations are totally useless including the prediction of the sign of HFCC, while the SAC-CI calculation gives ca. 88% of the experimental value. Difference between the values of MCSCF and SAC-CI indicates even more importance of "spin polarization" and dynamic correlation for the HFCC of γ proton compared with that of β protons. Although the experimental HFCCs of the γ protons of tetrahydrofuran have not been determined, the essential feature is considered to be the same with the case of oxetane.

The situation reminds us of arguments on long-range proton hyperfine couplings in radical ions of carbonyl compounds invoking the rule of the W -plan originally proposed in NMR analyses [17, 18]; the δ protons of the radical cations of several aliphatic carbonyls [19, 20] and the γ protons of some ketyls of aliphatic diones [17, 18] are known to have significantly large HFCCs. According to a semiquantitative theory the occurrence of the W -plan feature in ESR should be rather general to be determined by the spatial arrangement of the radical under study [22]. However, what seems interesting to us is that the absolute magnitude of the HFCCs of certain long-range protons is notably large for oxygen-containing compounds such as ethers and carbonyls. It may be that the spin delocalization is particularly intensified in oxygen-containing systems. Fur-

Table 4. The HFCCs of γ protons of the radical cations of oxetane and tetrahydrofuran (in units of MHz)

	UHF	AUHF	ROHF	MCSCF ^a	SAC-CI	exptl.
Oxetane	-6.3	-1.1	1.3	-0.7	27.1	30.8
Tetrahydrofuran ax.	-1.7	0.0	0.8	—	7.3	—
eq.	-6.1	-2.0	0.0	—	-2.0	—

^a MCSCF calculation based on the seven active orbitals

ther investigation should be made to elucidate the characteristic feature of the systems. The present analysis on the ethereal systems suggests that calculations of the spin distribution of these oxygen-containing systems may lead to a serious underestimation if the calculations are initiated from the Hartree–Fock molecular orbital and if the effect of the spin polarization and the electron correlation due to many-electron excitations are not taken into account properly.

6. Conclusion

We have shown in this paper on the ethereal radical cations the importance of the “spin polarization” as the mechanism for giving the large HFCC of the β protons. It is also found that the electron correlation effect due to configurations beyond triple-excitations is substantial for these systems. This is a reflection of the limitation of starting from the Hartree–Fock molecular orbital, especially for the calculation of spin density of the ethereal systems.

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