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# Semiempirical model of the exchange polarization mechanism of transferred hyperfine interactions in ionic radicals<sup>a)</sup>

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This paper presents a semiempirical method for calculating metal hyperfine interaction constants in ionic radicals whose zero-order wave function places the unpaired electron completely on the anion with zero overlap between it and the relevant cation orbitals. The mechanistic basis of the calculation is spin polarization of closed-shell anion orbitals by their exchange interaction with the unpaired electron, followed by partial transfer of the resulting unpaired electron density in these anion orbitals to the cation orbitals via overlap. The exchange polarization is described by a perturbation theory expansion in anion excited states, which expansion is summed by introducing semiempirical average excitation energies. The contribution of direct exchange polarization of the cation orbitals to the cation hyperfine interactions is found to be negligible, due primarily to the very large excitation energies of the cation core orbitals. Calculated results are compared with experiment for the ionic radicals  $\text{Na}(\text{C}=\text{CH}_2)$  and  $\text{NaO}_2$ .

## INTRODUCTION

Theoretical calculations of electron-nuclear hyperfine structure (hfs) constants are vital to the interpretation of electron spin resonance (ESR) spectra in terms of the identity and structure of the observed paramagnetic species. Although first-principles hfs calculations would be most desirable, such calculations are often extremely difficult, making it necessary to resort to semiempirical methods.

Semiempirical hfs calculations have been especially useful in the case of transferred hfs interactions or, as they are also known, superhyperfine interactions. These are hfs interactions of nuclei on ligands which have zero unpaired electron density in the zeroth-order approximation to the wave function but acquire the actual nonzero density in three ways: (1) Overlap, which admixes small amounts of ligand character into the unpaired electron orbital<sup>1,2</sup>; (2) charge transfer between the ligand orbitals and the unpaired electron orbital<sup>2,3</sup>; and (3) spin polarization of either the paired ligand orbitals themselves, or other orbitals which have nonzero overlap with these ligand orbitals, by the spin-dependent exchange interaction between the paired orbitals and the unpaired electron orbital.<sup>4-6</sup> If, as often happens in ionic radicals and ionic defects in solids, the overlaps between the unpaired electron orbital and the spherically symmetric (s) ligand orbitals are zero, then only the third mechanism can account for the isotropic part of the ligand hfs. As might be expected, this third mechanism, which involves two electrons, presents considerably greater computational difficulties than the first two, which are one-electron

processes, and treatments of it have been rather limited. Here, we shall describe a semiempirical treatment of the spin polarization mechanism of transferred hfs constants of metal ion ligands which is simple enough to be applied to a wide variety of paramagnetic systems. The method, which uses a perturbation theory expansion of the spin-polarized wave function and sums over the various types of excited states in this expansion by introducing empirically chosen excitation energies, will be illustrated by calculation of the isotropic  $\text{Na}^+$  hfs constant in  $\text{Na}(\text{C}=\text{CH}_2)$ <sup>7</sup> and  $\text{NaO}_2$ .<sup>8</sup>

## THEORETICAL MODEL

We illustrate the method for the isotropic hfs of the cation nucleus in the model species  $\text{C}^+\text{A}^-$  where the cation ( $\text{C}^+$ ) has two electrons in a closed shell of 1s atomic orbitals (AOs) and the anion ( $\text{A}^-$ ) has three electrons, two in closed shell  $\sigma$  atomic or molecular orbitals (MOs), and one electron in a  $\pi$  AO or MO. (Here,  $\pi$  and  $\sigma$  are the usual designations for orbitals which are, respectively, antisymmetric or symmetric with respect to reflection in the plane of a planar molecule or a 180° rotation about the axis of a linear molecule. Such  $\pi$  and  $\sigma$  orbitals have zero and nonzero overlaps, respectively with the symmetric 1s AO. The ambiguity in this notation when the isolated anion is an orbitally degenerate linear radical with two sets of  $\pi$  orbitals is readily dealt with, as is discussed later for  $\text{NaO}_2$ .) The zero-order wave function for the ground electronic state of the  $\text{C}^+\text{A}^-$  radical is

$$\psi_0^{(0)} = \mathcal{A} c_{1s} \bar{c}_{1s} a_\sigma \bar{a}_\sigma a_\pi, \quad (1)$$

where  $\mathcal{A}$  is the operation of antisymmetrization and renormalization,  $c_i$  and  $a_j$  denote the  $i$ th orbital of  $\text{C}^+$  and the  $j$ th

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orbital of  $A^-$ , respectively, and the barred and unbarred orbitals denote "up" and "down" electron spins, respectively.

It can be shown that the isotropic hfs constant of the cation nucleus is given by the expression<sup>9</sup>

$$A_C = \frac{K_C}{S_z} \langle \psi_0 | \sum_{\mu} \delta(\mathbf{r}_{C\mu}) s_{\mu z} | \psi_0 \rangle, \quad (2a)$$

where  $\psi_0$  is the ground state wave function,  $\mathbf{r}_{C\mu}$  is the radius vector from the nucleus of  $C^+$  to the  $\mu$ th electron, and  $S_z$  and  $s_{\mu z}$  are the components of the total electron spin ( $S$ ) and the  $\mu$ th electron spin ( $s_{\mu}$ ) with respect to an arbitrary quantization direction. Also,

$$K_C = (16\pi/3)\mu_B\mu_C/I_C, \quad (2b)$$

where  $\mu_B$  is the Bohr magneton and  $\mu_C$  and  $I_C$  are, respectively, the magnetic moment and spin of the nucleus of  $C^+$ .

If Eq. (2) is evaluated using the zero-order approximation to the  $C^+A^-$  wave function, i.e., Eq. (1), the result is zero because, by definition,  $\langle a_{\pi} | \delta(\mathbf{r}_C) | a_{\pi} \rangle$  and the overlap integrals  $\langle c_{1s} | a_{\pi} \rangle$  and  $\langle a_{\sigma} | a_{\pi} \rangle$  are zero. This situation changes upon introduction of spin polarization effects. This polarization may be described formally as the admixture of various electronic excited states into the ground state wave function by the interelectron Coulomb interactions, which are given by the expression

$$G = e^2 \sum_{\mu > \nu} 1/r_{\mu\nu}. \quad (3)$$

Specifically, the cross terms between some of these excited states and  $\psi_0^{(0)}$  in the matrix element of Eq. (2) are nonzero, giving the isotropic hfs constant a first-order dependence on the exchange polarization.

Since we will eventually introduce average excitation energies to sum over the perturbation expansion in excited state functions, we must distinguish between those excited states of the many-electron  $C^+A^-$  radical due to excitation of the  $C^+$  core electrons (cation excited states) and those due to excitation of the  $A^-$  core electrons (anion excited states). The distinction is important because the excitation energy of the former will usually be much greater than that of the latter. The cation excited states are

$$\mathcal{A} c_i \bar{c}_{1s} a_{\sigma} \bar{a}_{\sigma} a_{\pi}; \quad \mathcal{A} c_{1s} \bar{c}_i a_{\sigma} \bar{a}_{\sigma} a_{\pi}, \quad (4a)$$

where  $c_i$  is an orbital of  $C^+$ , which is unoccupied in the ground state of the ion. The corresponding functions involving anion excited states are

$$\mathcal{A} c_{1s} \bar{c}_{1s} a_j \bar{a}_{\sigma} a_{\pi}; \quad \mathcal{A} c_{1s} \bar{c}_{1s} a_{\sigma} \bar{a}_j a_{\pi}, \quad (4b)$$

where  $a_j$  is an orbital of  $A^-$  which is unoccupied in its ground state. The perturbation-theory expression for the contribution of the cation excited states to  $A_C$ , up to second-order terms in overlap of cation and anion orbitals, is

$$\begin{aligned} A_C(C^+ \text{ states}) = 2e^2 K_C \sum_{i \neq 1s} \frac{\langle c_{1s} | \delta(\mathbf{r}_{C1}) | c_i \rangle}{\epsilon(c_{1s} \rightarrow c_i)} \\ \times [ \langle a_{\pi} c_i | r_{12}^{-1} | c_{1s} a_{\pi} \rangle \\ - \langle c_i | a_{\sigma} \rangle \langle a_{\pi} a_{\sigma} | r_{12}^{-1} | c_{1s} a_{\pi} \rangle \\ - \langle a_{\pi} c_i | r_{12}^{-1} | a_{\sigma} a_{\pi} \rangle \langle a_{\sigma} | c_{1s} \rangle \\ + \langle c_i | a_{\sigma} \rangle \langle a_{\pi} a_{\sigma} | r_{12}^{-1} | a_{\sigma} a_{\pi} \rangle \langle a_{\sigma} | c_{1s} \rangle ], \end{aligned} \quad (5)$$

where  $\epsilon(c_{1s} \rightarrow c_i)$  is the energy required to excite an electron from the  $1s$  orbital to the  $i$ th orbital of the cation, which energy is a positive quantity, and

$$\langle \phi_i \phi_j | r_{12}^{-1} | \phi_k \phi_l \rangle = \iint \phi_i^*(1) \phi_j^*(2) \frac{1}{r_{12}} \phi_k(1) \phi_l(2) d\tau_1 d\tau_2. \quad (6)$$

In Eq. (5) the first three terms are due to excitation of the  $c_{1s}$  electron with the same spin as the unpaired electron and the last term is due to excitation of the  $c_{1s}$  electron whose spin is opposite to that of the unpaired electron.

Similarly, the contribution of the anion-excited states to  $A_C$ , up to second order terms in the overlap of cation and anion orbitals, is

$$\begin{aligned} A_C(A^- \text{ states}) = 2e^2 K_C \sum_{j \neq \sigma} \frac{\langle c_{1s} | \delta(\mathbf{r}_{C1}) | c_{1s} \rangle}{\epsilon(a_{\sigma} \rightarrow a_j)} \\ \times \langle c_{1s} | a_{\sigma} \rangle \langle a_{\pi} a_{\sigma} | r_{12}^{-1} | a_i a_{\pi} \rangle \langle a_i | c_{1s} \rangle, \end{aligned} \quad (7)$$

where  $\epsilon(a_{\sigma} \rightarrow a_j)$  is the energy required to excite an electron from the  $a_{\sigma}$  orbital to the  $a_j$  orbital of the anion. Here, only the state produced by excitation of the  $a_{\sigma}$  electron with the same spin as the unpaired electron contributes to  $A_C(A^- \text{ states})$ .

To evaluate the sums over excited states in Eq. (5) we introduce an average excitation energy for the cation, and complete the sum over cation orbitals by adding the  $c_{1s}$  orbital to the sum and separately subtracting the terms associated with this orbital. This gives

$$\begin{aligned} A_C(C^+ \text{ state}) = \frac{2e^2 K_C}{\bar{\epsilon}(c_{1s} \rightarrow c^*)} \{ [ \langle a_{\pi} c_{1s} | \delta(\mathbf{r}_{C1}) r_{12}^{-1} | c_{1s} a_{\pi} \rangle - \langle c_{1s} | \delta(\mathbf{r}_{C1}) | a_{\sigma} \rangle \langle a_{\pi} a_{\sigma} | r_{12}^{-1} | c_{1s} a_{\pi} \rangle \\ - ( \langle a_{\pi} c_{1s} | \delta(\mathbf{r}_{C1}) r_{12}^{-1} | a_{\sigma} a_{\pi} \rangle - \langle c_{1s} | \delta(\mathbf{r}_{C1}) | a_{\sigma} \rangle \langle a_{\pi} a_{\sigma} | r_{12}^{-1} | a_{\sigma} a_{\pi} \rangle ) \langle a_{\sigma} | c_{1s} \rangle ] - \langle c_{1s} | \delta(\mathbf{r}_{C1}) | c_{1s} \rangle \\ \times [ \langle a_{\pi} c_{1s} | r_{12}^{-1} | c_{1s} a_{\pi} \rangle - 2 \langle c_{1s} | a_{\sigma} \rangle \langle a_{\pi} a_{\sigma} | r_{12}^{-1} | c_{1s} a_{\pi} \rangle + \langle c_{1s} | a_{\sigma} \rangle^2 \langle a_{\pi} a_{\sigma} | r_{12}^{-1} | a_{\sigma} a_{\pi} \rangle ] \}, \end{aligned} \quad (8)$$

where  $\bar{\epsilon}(c_{1s} \rightarrow c^*)$  is the average cation excitation energy. The terms within the first set of square brackets result from summing over the complete set of cation orbitals. The following arguments show that these terms are small compared to the terms within the second set of square brackets, which latter

terms are the  $i = 1s$  terms. First, the matrix elements of the product  $\delta(\mathbf{r}_{C1}) r_{12}^{-1}$  are zero because  $a_{\pi}$  vanishes for  $r_{C1} = 0$ . Second, the remaining terms in the first set contain the factor  $\langle c_{1s} | \delta(\mathbf{r}_{C1}) | a_{\sigma} \rangle$ , whereas the corresponding terms in the second set contain the factor  $\langle c_{1s} | \delta(\mathbf{r}_{C1}) | c_{1s} \rangle \langle c_{1s} | a_{\sigma} \rangle$ , all other

factors being the same. It is readily shown that  $\langle c_{1s} | \delta(r_{c1}) | a_\sigma \rangle \ll \langle c_{1s} | \delta(r_{c1}) | c_{1s} \rangle \langle c_{1s} | a_\sigma \rangle$  for all realistic choices of the orbitals  $c_{1s}$  and  $a_\sigma$ , the qualitative reason for this being that the overlap density  $c_{1s}a_\sigma$  is a rather diffuse quantity which is largest in the region between  $C^+$  and  $A^-$ , whereas  $\delta(r_{c1})$  is zero everywhere except at the nucleus of  $C^+$ . Thus, taking only the second  $i = 1s$  group of terms in Eq. (8) gives

$$A_C(C^+ \text{ states}) = - \frac{2e^2 K_C \langle c_{1s} | \delta(r_{c1}) | c_{1s} \rangle}{\bar{\epsilon}(c_{1s} \rightarrow c^*)} \\ \times [ \langle a_\pi c_{1s} | r_{12}^{-1} | c_{1s} a_\pi \rangle - 2 \langle c_{1s} | a_\sigma \rangle \langle a_\pi a_\sigma | r_{12}^{-1} | c_{1s} a_\pi \rangle \\ + | \langle c_{1s} | a_\sigma \rangle |^2 \langle a_\pi a_\sigma | r_{12}^{-1} | a_\sigma a_\pi \rangle ]. \quad (9)$$

To evaluate the sums over the excited states in Eq. (7) we introduce an average excitation energy for the anion, add the  $j = \sigma$  orbital to complete the sum over orbitals of  $A^-$  and subtract the  $j = \sigma$  terms separately. This gives

$$A_C(A^- \text{ states}) = \frac{2e^2 K_C \langle c_{1s} | \delta(r_{c1}) | c_{1s} \rangle}{\bar{\epsilon}(a_\sigma \rightarrow a^*)} \\ \times [ \langle c_{1s} | a_\sigma \rangle \langle a_\pi a_\sigma | r_{12}^{-1} | c_{1s} a_\pi \rangle - | \langle c_{1s} | a_\sigma \rangle |^2 \langle a_\pi a_\sigma | r_{12}^{-1} | a_\sigma a_\pi \rangle ], \quad (10)$$

where  $\bar{\epsilon}(a_\sigma \rightarrow a^*)$  is the average anion excitation energy. The following qualitative arguments, which are supported by calculations, show that the first term in Eq. (10) is small enough compared to the second term to be neglected. The basic point is that since the cation orbitals are quite compact and the anion orbitals are rather spread out, the overlap density  $a_\pi c_{1s}$  is largest in the vicinity of the cation, whereas the orbital product  $a_\pi a_\sigma$  is largest near the anion. Consequently, the exchange integral  $\langle a_\pi a_\sigma | r_{12}^{-1} | c_{1s} a_\pi \rangle$  really has the character of a Coulomb integral between charge distributions on two distinct centers. Such integrals are quite small when the centers are well separated, and the total charge of each orbital product is zero, as is the case, here, i.e.,  $\langle a_\pi | c_{1s} \rangle = \langle a_\pi | a_\sigma \rangle = 0$ , (In the limit  $\lim_{R \rightarrow \infty} \langle a_\pi a_\sigma | r_{12}^{-1} | c_{1s} a_\pi \rangle = 1/R \langle a_\pi | c_{1s} \rangle \langle a_\sigma | a_\pi \rangle = 0$ , where  $R$  is separation between  $A^+$  and  $C^-$ .) so that it is reasonable to expect that:  $\langle a_\pi a_\sigma | r_{12}^{-1} | c_{1s} a_\pi \rangle \ll \langle c_{1s} | a_\sigma \rangle \langle a_\pi a_\sigma | r_{12}^{-1} | a_\sigma a_\pi \rangle$ . Thus, we have, approximately,

$$A_C(A^- \text{ states}) = - \frac{2K_C e^2}{\bar{\epsilon}(a_\sigma \rightarrow a^*)} \langle c_{1s} | \delta(r_{c1}) | c_{1s} \rangle \\ \times | \langle c_{1s} | a_\sigma \rangle |^2 \langle a_\pi a_\sigma | r_{12}^{-1} | a_\sigma a_\pi \rangle. \quad (11)$$

Comparing the contributions of the cation and anion excitations to the cation hfs we note that the integrals in these expressions are quite similar. The integral in Eq. (11) for  $A_C(A^- \text{ states})$  is the same as one of the terms in Eq. (9) for  $A_C(C^+ \text{ states})$ . Of the remaining terms in Eq. (9), the term  $2 \langle c_{1s} | a_\sigma \rangle \langle a_\pi a_\sigma | r_{12}^{-1} | c_{1s} a_\pi \rangle$  also appeared in the expression for  $A_C(A^- \text{ states})$  and can be neglected for the reasons just discussed in that case, and calculations show that the integral  $\langle a_\pi c_{1s} | r_{12}^{-1} | c_{1s} a_\pi \rangle$  is substantially smaller than the quantity  $| \langle c_{1s} | a_\sigma \rangle |^2 \langle a_\pi a_\sigma | r_{12}^{-1} | a_\sigma a_\pi \rangle$  for realistic choices of

the orbitals  $c_{1s}$ ,  $a_\pi$  and  $a_\sigma$ . Thus, the expressions are approximately equal except for the excitation energies. Since the excitation energy of the tightly bound cation core electrons will be much greater than that of the anion core electrons, the complete isotropic cation hfs constant will be given to a good approximation by Eq. (11). This expression is quite simple involving only a one-center exchange integral and two-center overlap integrals which, unlike the two-center exchange integral, are readily calculated from Hartree-Fock AOs. Furthermore, once the exchange integrals are computed for a given radical anion, they can be used for hfs calculations on various ionic radicals containing that anion.

With the possible exception of an excited state in which the anion electron is transferred to the valence  $s$  AO of the neutral C atom, which state may be described as  $\psi(C A) = \mathcal{A} c_{1s} \bar{c}_{1s} c_{2s} \bar{a}_\sigma a_\pi$ , excitation of an anion electron to an orbital outside the valence shell of an anion is tantamount to ionizing it. For these latter states the average anion excitation energy can be estimated as follows:

$$\bar{\epsilon}(a_\sigma \rightarrow a^*) = \epsilon(a_\sigma \rightarrow a_\pi) + I + 27.2e^2/R, \quad (12)$$

where the energy units are in eV and  $R$ , the  $C^+ - A^-$  separation, is in Bohr radii. Here,  $\epsilon(a_\sigma \rightarrow a_\pi)$ , which is the energy required to excite an anion electron from the  $\sigma$  to the  $\pi$  orbital, can be estimated from spectroscopic data or Hartree-Fock calculations;  $I$  is the ionization potential of  $A^-$  or, equivalently, the electron affinity of  $A$ ; and  $27.2e^2/R$  is the point-charge approximation to the Coulomb energy of the excited anion electron in the field of  $C^+$ , it being assumed that in excited states of  $A^-$ , except for the state  $\psi(C A)$ , this electron will be almost completely out of the field of  $C^+$ . Although the state  $\psi(C A)$  may have a lower excitation energy than that given by Eq. (12), the approximation of using Eq. (12) for the average excitation energy of all states is believed reasonable for the following reasons. First, since all the anion excited states are highly diffuse in the sense that the excited electron charge cloud is widely spread out and at a considerable distance from the electron charge clouds of the anion valence AOs, excitation of the anion is likely to lead to a large number of excited states, with the weight of any particular state such as  $\psi(C A)$  being small. Second, it can be shown that the state  $\psi(C A)$  contributes to the hfs only if the  $c_{2s} \bar{a}_\sigma$  pair has the antibonding triplet spin configuration rather than the bonding singlet configuration. This will reduce somewhat the difference between the excitation energy of this state and the energy given by Eq. (12).

The extension of this model to more complex ionic radicals with more than two core electrons on the cation and several types of spin-polarizable core orbitals on the anion is quite straightforward and will be illustrated by the calculations on  $Na(C = CH_2)$  and  $NaO_2$ .

## APPLICATION AND DISCUSSION

### $Na^+(\cdot C = CH_2)^-$

Kasai identified the  $Na^+(\cdot C = CH_2)^-$  ionic radical as a product of the photolysis of Na atoms and acetylene in an argon matrix from its ESR spectrum, especially the large  $\beta$  proton hfs splittings (154 MHz) and the Na hfs splitting.<sup>7</sup>

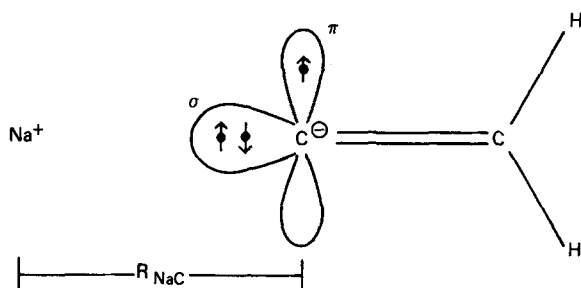


FIG. 1. Illustration of the  $\text{Na}^+(\text{C}=\text{CH}_2)^-$  ionic radical, indicating the unpaired electron  $\pi$  orbital and the spin-polarized lone-pair  $\sigma$  orbitals.

The Na splitting (34 MHz) is also rather large for a radical in which the unpaired electron has zero overlap with the  $\text{Na}^+$  AOs, cf.  $\text{NaO}_2$  (8 MHz),<sup>8</sup>  $\text{NaSO}_2$  (4 MHz),<sup>8</sup> and  $\text{NaO}_3$  (4 MHz).<sup>10</sup> The ESR-indicated structure of the radical, shown in Fig. 1, is especially interesting because its formation requires a rearrangement of one of the acetylenic H atoms during or following the transfer of an electron from the Na to the acetylene.

Calculation of the Na isotropic hfs constant using the formalism of the previous section is straightforward, the principal modification being that we must consider overlaps of the  $a_\sigma$  orbital with the  $\text{Na}^+$  1s as well as the  $\text{Na}^+$  2s AOs. Here, the  $\pi$  and  $\sigma$  anion orbitals of Eq. (1) are, cf. Fig. 1,

$$a_\pi = \phi_{C-2p\pi}; \quad a_\sigma = \chi_s \phi_{C-2s} + \sqrt{1-\chi_s^2} \phi_{C-2p\sigma}, \quad (13)$$

where the  $2p\sigma$  AO in the  $sp$  hybrid  $a_\sigma$  has its positive lobe pointing toward the  $\text{Na}^+$  ion. We shall neglect spin polarization of other core or bonding orbitals of the  $(\cdot\text{C}=\text{CH}_2)^-$  anion because these have much smaller overlaps with the  $\text{Na}^+$  AOs than does  $a_\sigma$ . Following the procedures leading to Eq. (11) but including both the  $\text{Na}^+$  1s and 2s AOs and their overlap integrals with  $a_\sigma$  gives for  $\text{Na}^+(\text{C}=\text{CH}_2)^-$  the result

$$A_{\text{Na}} = - \frac{2e^2 K_{\text{Na}} \langle a_\pi a_\sigma | r_{12}^{-1} | a_\sigma a_\pi \rangle}{\bar{\epsilon}(a_\sigma \rightarrow a^*)} \times \sum_{j=1}^2 \sum_{i=1}^2 \langle \phi_{\text{Na}^+ 1s} | a_\sigma \rangle \langle a_\sigma | \phi_{\text{Na}^+ 1s} \rangle \times \langle \phi_{\text{Na}^+ 2s} | \delta(r_{\text{Na}1}) | \phi_{\text{Na}^+ 2s} \rangle, \quad (14)$$

where the  $\phi_{\text{Na}^+ 1s}$  are the  $\text{Na}^+$  core s AOs. Using Eq. (13) for  $a_\pi$  and  $a_\sigma$ , the exchange integral becomes

$$\langle a_\pi a_\sigma | r_{12}^{-1} | a_\sigma a_\pi \rangle = \chi_s^2 \langle \phi_{C-2p\pi} \phi_{C-2s} | r_{12}^{-1} | \phi_{C-2s} \phi_{C-2p\pi} \rangle + (1-\chi_s^2) \langle \phi_{C-2p\pi} \phi_{C-2p\sigma} | r_{12}^{-1} | \phi_{C-2p\sigma} \phi_{C-2p\pi} \rangle \quad (15)$$

and calculations using  $\text{C}^-$  Hartree-Fock AOs<sup>11</sup> give 2.48 and 0.55 eV for the first and second integrals on the right-hand side of Eq. (15). Following the procedures described in Eq. (12) the average excitation energy is

$$\bar{\epsilon}(a_\sigma \rightarrow a^*) = \chi_s^2 \epsilon(\text{C}^- 2s \rightarrow \text{C}^- 2p) + \text{E.A.}(\text{C}) + 27.2 e^2/R.$$

Here,  $\epsilon(\text{C}^- 2s \rightarrow \text{C}^- 2p)$  is the energy required to promote a  $\text{C}^-$  electron from the 2s to the 2p shell,  $\text{E.A.}(\text{C}) = 1.1$  eV is the electron affinity of carbon,<sup>12</sup> and  $R$  is the separation of the Na atom from the  $\alpha$  carbon atom of the anion. Hartree-

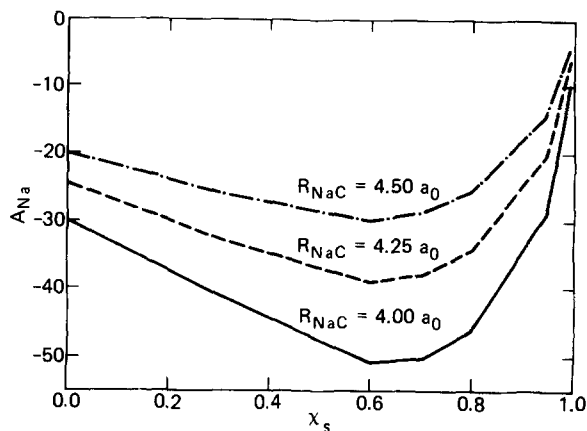


FIG. 2. Calculated values, in MHz, of the  $\text{Na}^+$  isotropic hfs constant in  $\text{Na}^+(\text{C}=\text{CH}_2)^-$  vs the  $sp$  hybridization of the lone-pair C orbitals at various values of the NaC distance.

Fock energies of the 2s and 2p  $\text{C}^-$  orbitals<sup>11</sup> give  $\epsilon(\text{C}^- 2s \rightarrow \text{C}^- 2p) = 9.4$  eV, which value is an average over the three electronic states realizable from the  $\text{C}^-(p^3)$  electron configuration. The overlap integrals and the electron densities at the Na nucleus were calculated using Hartree-Fock AOs.<sup>11</sup>

The results are shown in Fig. 2 as a plot of  $A_{\text{Na}}$  vs the hybridization parameter  $\chi_s$  for three values of  $R$ . Except for the unlikely extremes of complete  $p$  or complete  $s$  character in the hybrid  $\sigma$  orbital, a wide range of  $\chi_s$  values yield good agreement between theory and experiment<sup>7</sup> ( $|A_{\text{Na}}| = 34$  MHz) with the best agreement coming at  $R = 4.25a_0$ . This value of  $R$  is similar to that found in other ionic radicals containing  $\text{Na}^+$  such as  $\text{NaO}_2$  ( $R = 4.0a_0$ ),<sup>8</sup>  $\text{NaSO}_2$  ( $R = 4.3a_0$ ),<sup>8</sup> and  $\text{NaO}_3$  ( $R = 4.5a_0$  from the end oxygens).<sup>10</sup>

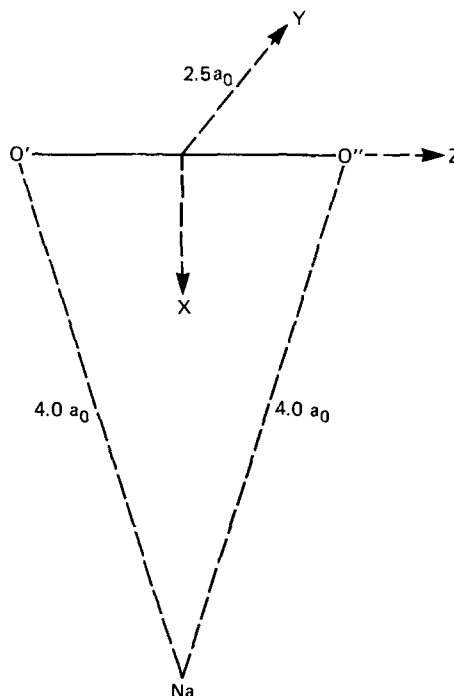


FIG. 3. Geometry and reference axes of the  $\text{NaO}_2$  radical.

It is to be noted that theory predicts  $A_{\text{Na}}$  is negative, which is the usual result for the spin-polarization mechanism of transferred hfs constants. The sign of  $A_{\text{Na}}$  has not been determined experimentally in this case, but it is reasonable to assume it is negative, as has been shown experimentally for  $\text{NaO}_2$ ,<sup>8</sup>  $\text{NaSO}_2$ ,<sup>8</sup> and  $\text{NaO}_3$ .<sup>10</sup>

### $\text{NaO}_2$

Analysis of the anisotropic  $\text{Na}^+$  hfs of  $\text{NaO}_2$  has shown that the molecular shape is an isosceles triangle ( $R_{\text{NaO}} = 4.0a_0$ ) with the unpaired electron occupying a  $\text{O}_2^- 2p\pi_g$  MO oriented perpendicular to the molecular plane.<sup>8</sup> This is the  $\pi$  MO referred to in Eq. (1), and is designated here as  $2py(\pi)_g$  following the geometry of  $\text{NaO}_2$  and the chosen reference axes shown in Fig. 3. The Na isotropic hfs is almost completely due to the spin polarization of that filled  $\text{O}_2^-$  MO which the present notation designates as  $2px(\sigma)_u$  because, although it is a  $\pi$  MO of the free  $\text{O}_2^-$  ion, it is a  $\sigma$  MO of the planar  $\text{NaO}_2$  molecule. Spin polarization of the  $2pz(\sigma)_g$  MO contributes only negligibly to the  $\text{Na}^+$  hfs because the overlap of this MO with the  $\text{Na}^+$  s AOs is very small. The spin polarization of the  $2s(\sigma)_g$  MO also contributes only negligibly to the  $\text{Na}^+$  hfs because of the small overlap of this MO with the  $\text{Na}^+$  s AOs and also its high excitation energy.

We obtain the following contribution to  $A_{\text{Na}}$  from the spin polarization of the  $2py(\sigma)_u \equiv \sigma$  MO by the  $2py(\pi)_g \equiv \pi$  unpaired electron orbital of  $\text{NaO}_2$ .

$$A_{\text{Na}} = - \frac{2e^2 K_{\text{Na}} \langle a_\pi a_\sigma | r_{12}^{-1} | a_\sigma a_\pi \rangle}{\bar{\epsilon}(a_\sigma \rightarrow a^*)} \times \sum_{j=1}^2 \sum_{i=1}^2 \langle \phi_{\text{Na}^+ i\sigma} | a_\sigma \rangle \langle a_\sigma | \phi_{\text{Na}^+ j\pi} \rangle \times \langle \phi_{\text{Na}^+ i\pi} | \delta(r_{\text{Na}1}) | \phi_{\text{Na}^+ j\pi} \rangle. \quad (16)$$

Here,

$$a_\pi = (2 - 2\langle \phi_{\text{O}'2py} | \phi_{\text{O}''2py} \rangle)^{-1/2} (\phi_{\text{O}'2py} - \phi_{\text{O}''2py}) \quad (17)$$

and

$$a_\sigma = (2 + 2\langle \phi_{\text{O}'2px} | \phi_{\text{O}''2px} \rangle)^{-1/2} (\phi_{\text{O}'2px} + \phi_{\text{O}''2px}), \quad (18)$$

where  $\text{O}'$  and  $\text{O}''$  are the two oxygen atoms of  $\text{O}_2^-$ . Expanded, the exchange integral in Eq. (16) consists of a one-center exchange-type integral and a two-center Coulomb-type integral, with all other terms in this integral cancelling. For  $R_{00} = 2.50$ ,  $\langle a_\pi a_\sigma | r_{12}^{-1} | a_\sigma a_\pi \rangle = 0.42$  eV. The average excitation energy, approximated as described in Eq. (12), is

$$\bar{\epsilon}(a_\sigma \rightarrow a^*) = E(^2\Pi_g \rightarrow ^2\Pi_u) + \text{E.A.}(\text{O}_2^-) + 27.2e^2/R_{\text{NaO}}, \quad (19)$$

where  $E(^2\Pi_g \rightarrow ^2\Pi_u) = 3.1$  eV from the spectroscopic estimate of the  $^2\Pi_g \rightarrow ^2\Pi_u$  transition in  $\text{O}_2^-$ ,<sup>13</sup> and  $\text{E.A.}(\text{O}_2^-) = 0.44$  eV.<sup>12</sup>

The calculated values of  $A_{\text{Na}}$  are given as a function of  $R_{\text{NaO}}$  for  $R_{00} = 2.5a_0$  in Fig. 4. As also shown in Fig. 4, results are virtually unchanged for  $R_{00} = 2.75a_0$  indicating that small variations in this parameter are inconsequential.

Theory agrees with experiment ( $A_{\text{Na}} = -8.1$  MHz), including, of course, the negative sign, at  $R_{\text{NaO}} = 4.1a_0$ , which agrees well with the value  $R_{\text{NaO}} = 4.0a_0$  determined

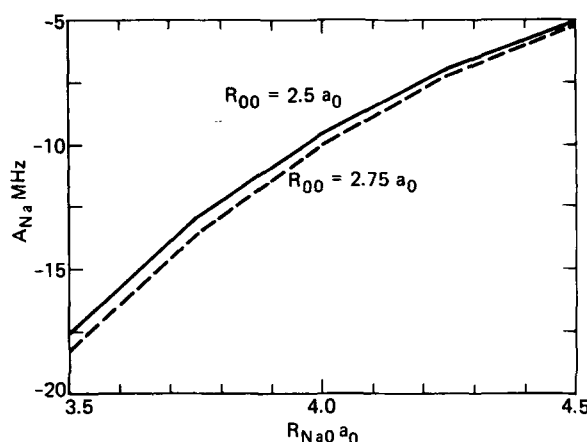


FIG. 4. Calculated values of the  $\text{Na}^+$  isotropic hfs constant in  $\text{NaO}_2$  vs  $R_{\text{NaO}}$  at two values of  $R_{00}$ .

by comparison of the anisotropic part of the Na hfs with values calculated from the unpaired electron charge density on  $\text{O}_2^-$ .

The  $\text{Na}^+$  isotropic hfs constant is considerably larger in  $\text{Na}(\text{C}=\text{CH}_2)$  than in  $\text{NaO}_2$  for two reasons. One, the exchange integral between the unpaired electron orbital and the anion " $\sigma$ " orbitals is considerably larger in  $\text{Na}(\text{C}=\text{CH}_2)$  than in  $\text{NaO}_2^-$  and, second, the  $sp$  hybrid  $\sigma$  orbital in  $\text{Na}(\text{C}=\text{CH}_2)$  has a considerably greater overlap with the  $\text{Na}^+$  s AOs than does the  $\text{O}_2^- \sigma$  orbital.

In summary, the present method, although admittedly approximate and empirical, appears to offer a simple and reasonably accurate way to estimate metal atom transferred hfs constants due to the spin-polarization mechanism in metal-ionic radicals. Given the difficulty of calculating spin-polarization hfs constants by *ab initio* and other more refined methods, the present method should be a useful approach to this problem.

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