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Semiempirical valence bond model of hyperfine interactions and bonding in RbO and CsO[a]

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The alkali hyperfine structure (hfs) splittings in the $^2\Sigma$ radicals RbO and CsO are analyzed using a semiempirical valence bond (VB) wave function similar to that used previously for the noble gas monohalides. For the alkali monoxides this wave function is $\psi = N(^2\Sigma)[\chi\mathscr{A}\Phi(M^+ \cdots O^-) + (1 - \chi^2)^{1/2}\mathscr{A}\Phi(M^{++} \cdots O^=)]$, where M and O denote the alkali and oxygen, respectively, and $\mathscr{A}$ is the antisymmetrization operator. This antisymmetrization and the effects of interatomic electron correlation in the $\Phi(M^{++} \cdots O^=)$ VB structure are the principal contributors to the hfs. At the bond distances $R_{RbO} = 4.30$ and $R_{CsO} = 4.67a_0$ the parameters $\chi = 0.9996$ and 0.9967 for RbO and CsO, respectively, give good agreement between theory and experiment for both the isotropic and anisotropic hfs. The admixture of the doubly ionized $\Phi(M^{++} \cdots O^=)$ VB structure, which produces covalent bonding involving the alkali cation core orbitals and the oxygen anion valence orbitals, is small as expected from the high energy of this structure.

I. INTRODUCTION

Investigations of the alkali monoxide radicals (MO),[1,2] especially a very definitive electron spin resonance (ESR) study,[2] have revealed an interesting change in the ground electronic state from $^2\Pi$ to $^2\Sigma$ as the size of M increases, the change occurring between KO and RbO. This reversal of the $^2\Pi$–$^2\Sigma$ energy ordering raised questions about contributions to the bonding energy of the ionic MO radicals from: (1) polarization effects,[1] which increase with cation size; and (2) covalent bonding involving the cation core electrons.[2] Similar effects have been proposed to account for bonding in the noble gas monohalides.[3–6] More recently, however, rather detailed calculations have attributed the $^2\Pi$–$^2\Sigma$ reversal to a competition between a quadrupole-like term in the Coulomb attraction between the M^+ and O^- ions, which favors the $^2\Pi$ state, and the Pauli repulsion forces between the unpaired electrons of M^+ and O^-, which favor the $^2\Sigma$ state and which become relatively more important as the size of M^+ increases.[7–9] Although these latter calculations tend to rule out core covalency effects as the dominant factor in determining the alkali monoxide ground state, they do not completely exclude its occurrence, so it is of interest to consider other ways of estimating the extent of core covalency in the molecular wave function.

The electron-nuclear hyperfine structure (hfs) data on RbO and CsO are an especially important source of information on their bond character. One way to use this data is as a test of a calculated molecular wave function, which has recently been done for CsO and XeF.[10] An alternative procedure is to use the hfs data to determine physically significant parameters, such as the relative weights of covalent and ionic bond character, in a model wave function. Obviously, *ab initio* calculation of the wave function is the more fundamental and esthetically preferable procedure, but given the great difficulty of such calculations on large many-electron radicals, the semiempirical method is an attractive alternative. In this paper, therefore, we will analyze the RbO and CsO hfs data using a semiempirical valence bond (VB) model previously applied to the noble gas monohalides.[11]

II. THEORY
A. Semiempirical VB wave function

For notational convenience and ease of comparison with previous work,[11,12] we follow as closely as possible the noble gas monohalide treatment and notation. To facilitate this we introduce for the alkali monoxide radicals, already designated MO, the additional designation AB, where A or M_A denotes the alkali and B or O_B denotes the oxygen. With this notation the ground state VB wave function for a $^2\Sigma$ MO radical has the form

$$\psi(^2\Sigma) = N(^2\Sigma)[\chi\mathscr{A}\Phi_A^+ \Phi_B^-(2p_z) + (1 - \chi^2)^{1/2}\mathscr{A}\Phi_A^{++}(mp_z)\Phi_B^=], \quad (1)$$

where N is the normalization constant, $\mathscr{A}$ is the antisymmetrization and renormalization operator, $\Phi_A^+\Phi_B^-(2p_z)$ corresponds to the simple-ionic VB structure $M_A^+\ldots O_B^-$ with the unpaired electron occupying an oxygen valence-shell $2p$ atomic orbital (AO) oriented along the z axis, and $\Phi_A^{++}(mp_z)\Phi_B^=$ corresponds to the VB structure $M_A^{++}\ldots O_B^=$ with the unpaired electron occupying a valence-shell p AO of the alkali dication similarly directed along the z axis. The z axis is the bond axis with the positive direction from M_A to O_B, which notation causes overlap

integrals involving a p_z AO of O_B to be negative. The parameter χ specifies the relative admixture of the two VB structures, the second of which represents covalent bonding involving the cation core orbitals. We are neglecting VB structures corresponding to the neutral alkali interacting with the oxygen $(M_A...O_B)$, even though such structures may be more significant energywise than the $M_A^+ {}^+...O_B^=$ structure, because, as noted previously,[2] their unpaired electron orbitals are so diffuse that unrealistically large admixtures of such structures in the wave function would be required to yield significant contributions to the alkali hfs.

In the VB structure $M_A^+...O_B^-$ the overlap of the O_B^- $2p_z$ unpaired electron AO with the s and p core AOs of M_A^+, combined with the Pauli exclusion principle, transfers a small amount of the unpaired electron density into these core AOs, thereby yielding contributions to the isotropic and anistropic hfs constants of M_A^+.[11] The VB structure $M_A^+ {}^+...O_B^=$ contributes directly to the anisotropic alkali hfs constant, and polarization of $M_A^+ {}^+$ by the negative charge on $O_B^=$, which is partly described by introducing spin-selective excitations of the $M_A^+ {}^+$ dication such as $(ms)^2(mp_z)$ $\rightarrow(ms)(mp_z)^2$, will contribute to the alkali isotropic hfs constant.[11] Finally, and very importantly in the present case where the weight of the $M_A^+ {}^+...O_B^=$ structure is likely to be very small, there are contributions to the hfs from the overlap of this structure with the simple ionic structure $M_A^+...O_B^-$.

B. Alkali isotropic hyperfine interaction

The contribution to the alkali isotropic hfs constant $(a^{(A)})$ from the $M_A^+...O_B^-$ VB structure is due to overlap which admixes small amounts of the M_A^+ core s AOs with the M_O^- $2p_z$ unpaired electron AO. (A similar overlap with the M_A^+ core p AOs is an important contributor to the anisotropic alkali hfs.) Following the previous analysis, except for anticipating that χ is so close to unity that we may approximate $N(^2\Sigma^+) = 1$ and neglect terms in $\chi(1 - \chi^2)^{1/2}$ (this approximation will be supported by the empirical determinations of χ in RbO and CsO) then the overlap contribution to $a^{(A)}$ is

$$a^{(A)}_{overlap} = (8\pi/3)K'_A\chi^2$$
$$\times \langle b^-_{2p,z} P(a_s^+; a_s^+)|\delta(\mathbf{r}_A)|P(a_s^+; a_s^+)b^-_{2p,z}\rangle, \quad (2)$$

where $\mathbf{r}_A$ is the position vector of an electron relative to nucleus A, and P is a projection operator defined by the equation

$$P(\mu; \nu) = 1 - \sum_{\substack{j = \text{principal quantum} \\ \text{numbers of occupied orbitals}}} |\mu_j\rangle\langle\nu_j|. \quad (3)$$

Also, the constant K'_A is

$$K'_A = 2\mu_\beta\mu_A/I_A, \quad (4)$$

where μ_β is the Bohr magneton, and μ_A and I_A are the magnetic moment and spin of the alkali nucleus.

The contributions to $a^{(A)}$ from polarization of the dication by the negative charge on the dianion in the VB structure $M_A^+ {}^+...O_B^=$ and, also the atomic contribution of $M_A^+ {}^+$

in this structure,[11] will be proportional to $(1 - \chi^2)$ in Eq. (1) and, thus, negligible for χ very close to unity and $(1 - \chi^2) \ll 1$ as assumed previously. We do need to consider, however, the contribution to $a^{(A)}$ from polarization overlap which is a cross term involving matrix elements of the isotropic hfs operator with the polarized $M_A^+ {}^+...O_B^=$ VB structure and the simple ionic structure $M_A^+...O_B^-$. This polarization-overlap term is proportional to $\chi(1 - \chi^2)^{1/2}$, as were certain neglected terms in $a^{(A)}_{overlap}$, but cannot be similarly neglected because the other factors in this term are considerably larger than in the overlap case. This term is calculated as described previously[11,12] except that the polarizing field of the $O_B^=$ dianion at $M_A^+ {}^+$ is $2(e^2/R^2)\Sigma_\alpha z_{A\alpha}$ instead of $(e^2/R^2)\Sigma_\alpha z_{A\alpha}$, where R is the internuclear distance and $z_{A\alpha}$ is the z component of $\mathbf{r}_{A\alpha}$. The result, again with $N(^2\Sigma^+) = 1$, is

$$a^{(A)}_{\text{pol overlap}} = 2(8\pi/3)K'_A\chi(1 - \chi^2)^{1/2}$$
$$\times \frac{2e^2\langle a_{ms}^+|z_A|a_{mp,z}^+\rangle}{R^2\epsilon(ms^+{}^+\rightarrow mp^+{}^+)} \langle b^-_{2p,z} P(a_s^+; a_s^+)|\delta(\mathbf{r}_A)|a_{ms}^+\rangle, \quad (5)$$

where $\epsilon(ms^+{}^+\rightarrow mp^+{}^+)$ is the energy required to excite an electron from the valence s to the valence p orbital of the alkali dication. The values of this quantity from atomic spectroscopy are 16.1 and 15.8 eV for RbO and CsO, respectively.[13] Also, in deriving Eq. (5) we have assumed that the alkali cation and dication have the same AOs and similarly that the oxygen anion and dianion have the same AOs, which approximations are necessary because Slater-function-based Hartree–Fock AOs for the alkali dication and oxygen dianion are not available. Judging from the analogous calculations on the noble gas monohalides,[11] where the corresponding required AOs of both the neutral and singly ionized atoms are available, this approximation, and a similar approximation made in calculating the anisotropic hfs, produces only small errors, of the order of 10% in the hfs contributions from the $M_A^+...O_B^-$, $M_A^+ {}^+...O_B^=$ cross term, and considerably less in the total hfs contants to which this cross term is a relatively minor contributor.

The isotropic hfs constants are readily calculated from Eqs. (2) and (5), the only complication being a relativistic correction to the values of the alkali s core AOs at the heavy Rb and Cs nuclei. This correction may be approximated as $a_s^+(0)_{rel} = F^{1/2}a_s^+(0)_{nonrel}$ where $F = 1.15$ and 1.39 for Rb and Cs, respectively.[14] The Hartree–Fock AOs for Rb$^+$ and O$^-$ are given by Clementi and Roetti,[15] while those for Cs$^+$ were kindly provided by the Atomic Physics group of The National Bureau of Standards.[16] The calculated alkali isotropic hfs constants may be written as

$$a^{(A)} = \chi^2 a_1 + 2\chi(1 - \chi^2)^{1/2}a_2, \quad (6)$$

where a_1 and a_2 are functions of R only. From the values of a_1 and a_2, given in Table I, one can calculate the isotropic hfs constants as functions of R and χ.

C. Alkali anisotropic hyperfine interaction

The calculation of the anisotropic alkali hfs constant $B^{(A)}_{||}$ is very similar to that described previously for the noble gas monohalides[11] except for the following modifications.

TABLE I. Coefficients for calculating the isotropic and anisotropic hfs constants of ^{87}Rb in RbO and ^{133}Cs in CsO as functions of R and χ using Eqs. (6) and (8). R is in Bohr radii and the hfs coefficients are in MHz.

Molecule	R	a_1	a_2	b_1	b_2
RbO	3.75	836	1541	97	679
	4.00	656	1199	83	611
	4.25	501	933	69	543
	4.30	468	877	66	527
	4.50	375	716	56	477
	4.75	277	553	44	416
CsO	4.00	505	873	44	366
	4.25	414	701	42	336
	4.50	329	560	37	304
	4.67	277	474	33	282
	4.75	256	441	31	272
	5.00	196	348	26	241

First, as discussed previously for the isotropic case, we anticipate that $(1 - \chi^2)^{1/2}$ will be very small, and neglect all terms in $(1 - \chi^2)$ and also neglect all terms in $\chi(1 - \chi^2)^{1/2}$ except for the off-diagonal matrix element of the anisotropic hfs Hamiltonian between the $M_A^+...O_B^-$ and $M_A^{+~+}...O_B^=$ VB structures, which term is much larger than other cross terms between these VB structures. Second, in calculating the contribution to $B_{\parallel}^{(A)}$ in the VB structure $M_A^+...O_B^-$ from overlap of the cation p AOs with the O^- $2pz$ unpaired electron AO we shall consider all cation p AOs rather than just the outermost one as did the calculations on the noble gas monohalides[11] and the diatomic halogen anions.[12] The more exact treatment is required here because overlap is the major contributor to $B_{\parallel}^{(A)}$ in the alkali monoxides, whereas it was only a minor contributor in the previous cases. The result is

$$B_{\parallel}^{(A)} = \tfrac{4}{3} K_A' \{ \chi^2 [\langle b_{pz}^- [P(a_{pz}^+; a_{pz}^+) - 1] | r_A^{-3} |$$
$$\times [P(a_{pz}^+; a_{pz}^+) - 1] b_{pz}^- \rangle + \tfrac{2}{3} R^{-3}]$$
$$- 2\chi(1 - \chi^2)^{1/2} \langle a_{mpz}^+ | b_{2pz}^- \rangle \langle a_{mpz}^+ | r_A^{-3} | a_{mpz}^+ \rangle \},$$
$$(7)$$

where $P(a_{pz}^+; a_{pz}^+)$ is a projection operator as defined in Eq. (3) and it is to be noted that the coordinates used in Eq. (1) make $\langle a_{mpz}^+ | b_{2pz}^+ \rangle$ negative. Equation (7) is readily evaluated using Hartree–Fock AOs,[15,16] the only complication being a relativistic correction, similar to that applied to the isotropic hfs constants. The correction is $B_{\parallel, rel}^{(A)} = \mathscr{R} B_{\parallel, nonrel}^{(A)}$, where $\mathscr{R} = 1.06$ and 1.14 for Rb and Cs, respectively.[14,17] Following the isotropic case, cf. Eq. (6), the results for $B_{\parallel}^{(A)}$ may be written as

$$B_{\parallel}^{(A)} = \chi^2 b_1 + 2\chi(1 - \chi^2)^{1/2} b_2, \qquad (8)$$

where b_1 and b_2 are also given in Table I.

III. RESULTS AND DISCUSSION

The calculated hfs constants in Table I are pure spin values whereas the experimental values can contain an orbital component along with the pure spin terms, and often do so for heavy nuclei with large spin orbit interactions. The orbital term, however, derives from those wave function components in which the unpaired electron is immediately

located on the heavy nucleus (as contrasted with indirectly, via overlap) as it is in the $M_A^{+~+}...O_B^=$ VB structure in Eq. (1). Since the weight of this structure will shortly be seen to be very small, as might be expected from the large energy required to create the $M_A^{+~+}$ dication, the orbital contributions to the alkali hfs can be neglected. This conclusion had previously been reached by Lindsay on the basis of a molecular orbital analysis.[18]

We shall compare theory and experiment at the calculated bond distances of $R = 4.30$ and $4.67a_0$ for RbO,[7] and CsO,[9] respectively. These values were chosen in preference to the larger values ($R_{RbO} = 4.76$, $R_{CsO} = 5.04a_0$) of Allison and Goddard[8] for reasons given by Laskowski et al.[9] The procedure is to determine at the calculated bond distance the value of χ required to yield agreement between the experimental and theoretical values of $B_{\parallel}^{(A)}$, and then calculate $a^{(A)}$ and compare it with experiment. For RbO ($B_{\parallel}^{(Rb)} = 95$ MHz) $\chi = 0.9996$, $(1 - \chi^2)^{1/2} = 0.0274$, giving $a_{theory}^{(Rb)} = 516$ as compared with $a_{expt}^{(Rb)} = 464$ MHz. For CsO ($B_{\parallel}^{(Cs)} = 78$ MHz), $\chi = 0.9967$, $(1 - \chi^2)^{1/2} = 0.0810$, giving $a_{theory}^{(Cs)} = 353$ as compared with $a_{expt}^{(Cs)} = 389$ MHz. Thus, the agreement between theory and experiment is quite good. This agreement is considerably poorer at the larger bond distances of Allison and Goddard, with the calculated isotropic hfs constants being 341 and 261 MHz in RbO and CsO, respectively. This result is additional support for the shorter set of calculated bond distances.

The empirically determined coefficients of Eq. (1) are qualitatively reasonable with the coefficient of the doubly ionized VB structure $M_A^{+~+}...O_B^=$ being quite small as expected for this high-energy structure. Furthermore, the weight of this structure is considerably greater in CsO than in RbO which is consistent with the trend found in the noble gas monohalides[11] and also the Kr...H and Xe...H interactions for hydrogen atoms trapped in noble gas matrices.[19]

These results point out the importance of overlap between nonorthogonal AOs for the hfs constants of the electron spin deficient atom in diatomic radicals where the unpaired electron density is highly concentrated on one atom of the pair. Overlap is important not only for hfs contributions from the simple ionic VB structure where the unpaired electron is located on the O atom, but also for the contribution from the doubly ionized VB structure where the unpaired electron is on the alkali, because the weight of this structure is so small that it contributes primarily as an overlap-dependent cross term with the simple ionic VB structure.

Finally, it is to be noted that the contribution of the $M_A^{+~+}...O_B^=$ VB structure to the isotropic hfs comes from polarization of the $(ms)^2(mp)^5$ $M_A^{+~+}$ species by the $O_B^=$ charge. This is an electron correlation effect of a type which is rather difficult to treat in ab initio molecular orbital calculations since it requires inclusion of a considerable number of excited configurations. Thus, although ab initio calculations are the ideal, and hopefully can someday be readily carried out on radicals of this type, semiempirical models such as the present one are also important for obtaining bonding parameters from experimental hfs data and for the insights they provide.

ACKNOWLEDGMENTS

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