Electron-Spin Magnetic Moments (*g* Factors) of the Oxides LiO, NaO, and the Superoxides LiO_2, NaO_2. An ab Initio Study

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The electron-spin magnetic moments of the superoxides LiO_2 and NaO_2, as parametrized by the *g* factors, are studied at the uncorrelated (ROHF) and correlated (MRCI) ab initio levels. The present method, which uses a perturbative approach complete to second order, is based on the Breit−Pauli Hamiltonian. In the standard C_{2v} notation for the MO_2 radicals, $\Delta g_{yy} > \Delta g_{zz} \gg |\Delta g_{xx}|$, where $\Delta g_{aa} = g_{aa} - g_e$. The perpendicular component Δg_{xx}, which is small and negative, is dictated by first-order terms (ground-state expectation values). The in-plane components Δg_{yy} and Δg_{zz} are large and positive. Δg_{yy} is governed by the second-order magnetic coupling between X^2A_2 and 1^2B_2 (electron excitation from the highest b_2 MO into the $a_2(\pi^*)$ SOMO), and Δg_{zz} by the coupling with two $^2A_1$ states (excitations from the two highest a_1 MOs into π^*). The calculated data reproduce the experimental trends reasonable well. For the ground state X^2A_2, the MRCI results for Δg_{xx}, Δg_{yy}, Δg_{zz} (in ppm, with ppm $= 10^{-6}$) are −373 (−350), 56 800 (56 250), 7273 (6600) for LiO_2; and −393 (150), 110 492 (108 600), 6868 (4600) for NaO_2, with the experimental results given in parentheses (average from Ar and Kr matrices). For comparison purposes, the *g* shifts of the low-lying excited state 1^2B_2 of LiO_2 and NaO_2, as well as the magnetic coupling parameters for O_2^-, LiO, and NaO, are also reported.

Introduction

The electronic *g* factor of a radical is a fundamental quantity in electron spin resonance (ESR) spectroscopy. Values of $\Delta g = g - g_e$ relate to the change of the spin magnetic moment ($\boldsymbol{\mu}_m$) with respect to that of a free electron. The deviation from g_e depends mainly on the spin−orbit coupling (SO) of the ground state with particular excited states as well as on their energetic separation (ΔE) and magnetic overlap *L* (expectation value of the orbital angular-momentum operator). The knowledge of the *g* components provides information about the excitation energies of selected excited states.[1] The hyperfine coupling constants (hfcc's), also determined via ESR, only relate to the ground state, however. For π-radicals with little s-density on the nuclei, such as the alkali superoxides (MO_2), the hfcc's are small, and the *g* factors become the salient ESR parameter.[2]

Accurate theoretical predictions of *g* shifts have only been published recently. The different methods (e.g., multireference CI,[3,4] density functional,[5,6] MCSCF response theory,[7] and energy derivative[8]) generally reproduce the experimental results within 20% or better. Small *g* shifts are affected by larger errors, though. However, since most ESR measurements are carried out for radicals in solution or trapped in inert matrices, full agreement between theory (simulating gas phase radicals) and experiment cannot be expected.

In a series of papers from this laboratory, Δg values have been presented for MgF,[9] CO^+, H_2O^+, NO_2,[4,10] H_2CONa,[11] H_2COH,[12] O_3Li, and O_3Na,[13] both at the uncorrelated (ROHF) and correlated (MRCI) levels. The approach uses first- and second-order perturbation theory based on the Breit−Pauli Hamiltonian.[1,3,9,14] The second-order contribution is calculated via a sum-over-states (SOS) expansion. This strategy has the advantage of giving a transparent picture of the excited states responsible for the *g* shifts as well as additional information (such as excitation energies, *f* values, dipole moments) with little or no extra computational effort.

In this article, the *g* shifts of O_2^- stabilized in the alkali superoxides LiO_2 and NaO_2 will be presented, for both X^2A_2 and 1^2B_2 states. For comparison purposes, the vertical excitation energies and magnetic coupling parameters of free O_2^-, and of LiO and NaO are included. A short review of the experimental and theoretical literature on MO_2 systems which are relevant to this work, in particular on *g*-data and vertical excitation energies, is given next. More comprehensive reviews can be found in refs 15 and 16.

Literature Review

In the gas phase, the ground-state $X^2\Pi_g(3\sigma_g^2 1\pi_u^4 1\pi_g^3)$ of O_2^- lies only 0.45 eV below $X^3\Sigma_g^-(3\sigma_g^2 1\pi_u^4 1\pi_g^2)$ of O_2.[17] All electronically excited states of O_2^- lie in the $O_2 + e^-$ continuum. Information about the energetic location of a few resonant states has been provided by electron scattering experiments on O_2.[18,19]

The O_2^- anion can be stabilized (i) as an adsorbed species on surfaces,[20] (ii) as a trapped impurity in ionic crystals,[21] and (iii) as part of an ionic compound $M^+O_2^-$ (usually isolated in inert matrices).[22,23] The analytical technique most widely used to identify O_2^- is based on the electronic *g* factor obtained from ESR measurements. For O_2^- adsorbed on surfaces,[20] *g* shifts along the O−O axis, ranging from 17 000 to 100 000 ppm, were measured (with ppm $= 10^{-6}$). For O_2^- in ionic lattices,[21] much larger Δg values were obtained (from 29 000 to 520 000 ppm).

Alkali halide (AH) crystals doped with O_2^- exhibit a characteristic yellow color due to the transition $1^2\Pi_u \rightarrow X^2\Pi_g$ of O_2^-.[24,25] Pioneering work on the electronic and ESR spectra of O_2^- centers in AH crystals was carried out by Känzig and Cohen[21] in 1959, who presented a simple two-state model correlating Δg-values with the crystal-field splittings of O_2^-.

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The *g* shifts of O_2^- adsorbed on surfaces have been interpreted in the same manner.[20]

The *g* factors of MO_2 (M = Li, Na, ..., Cs) have been measured in various matrices.[22,23] For the Li and Na compounds, the largest shift has been assigned to Δg_{yy} (≈56 000 and 109 000 ppm, respectively), the component parallel to the O−O axis. This is followed by Δg_{zz} (4000 and 7000 ppm, respectively), where *z* is the C_{2v} symmetry axis. The perpendicular component, Δg_{xx}, is small and negative (≈−400 ppm on average). From the experimental Δg values, the nature of the ground state, and the approximate vertical ΔE of the two lowest electronic states of MO_2 could be obtained. Except for CsO_2, the *g* data indicated that these radicals have a X^2A_2 ground state, with 1^2B_2 lying 2000−3000 cm^{-1} higher.

For O^- adsorbed on surfaces,[20] ESR studies have found two components of Δg, with $\Delta g_{\|} \approx 0$ and $\Delta g_{\perp} \gg 0$ ($\Delta g_{\perp}$ values (in ppm) from 17 000 (ZnO) to 300 000 (KI)), indicating the existence of diatomic-like radicals.

According to ab initio studies,[26−28] several excited potentials of free O_2^- have a minimum. For R(OO) ≤ 3.3 bohr, the $1^2\Pi_u$-($1\pi_u \rightarrow 1\pi_g$) potential of O_2^- lies above $X^3\Sigma_g^-$ of O_2. In that region, the leading configuration $1\pi_u^3 1\pi_g^4$ of $1^2\Pi_u$ mixes with $1\pi_u^4 1\pi_g^2 p\pi_u$, where $p\pi_u$ is a diffuse MO.[29] Ewig and Tellinghuisen[28] calculated several electronic states of O_2^-, both in vacuo and within a simulated ionic lattice (KCl). The energetic separation and spectroscopic constants for the $X^2\Pi_g$ and $1^2\Pi_u$ states remained essentially unchanged in both cases. For the simulated ionic environment, the $1^2\Pi_u$ potential at short R retained its valence composition upon expansion of the basis set with more diffuse AOs.

The separation ΔE between the lowest $^2\Pi$ and $^2\Sigma^+$ states of the alkali oxides M−O[30] and between the lowest $^2A_2$ and $^2B_2$ states of the superoxides MO_2[31] were determined theoretically. Both MO_2 states have C_{2v} equilibrium geometries, with the R_e and ω_e values of the O_2 moiety being similar to those of O_2^-; i.e., the superoxides have the structure $M^+O_2^-$.

Potential surfaces for the X^2A_2 and 1^2B_2 states of LiO_2 and NaO_2 were reported by Alexander[32] (semiempirical) and by Schaefer and co-workers[15,16] (ab initio). The $X^2\Pi(\pi^4\pi^3)$ state of linear M−O−O splits into X^2A_2 and 1^2B_2; their relative separation is 0.72 eV for LiO_2 and 0.37 eV for NaO_2 (all data from Schaefer et al.).

Methods

1. Basis Sets and Programs Used. The basis sets used for Li and O, the 12s7p/7s4p contraction from Thakkar et al.,[33] are of quadruple-ζ quality. For Li, a d-function with exponent $\alpha = 0.15$ was added. The basis set for O was supplemented by one AO each of s($\alpha = 0.085$), p($\alpha = 0.059$), and d-type ($\alpha = 0.85$). The calculations on isolated O_2^-, however, were done with a valence-only basis set (no semidiffuse s and p AOs included). McLean−Chandler's 12s9p/6s4p contraction[34] was taken for Na, which was augmented by one semidiffuse s ($\alpha = 0.0076$) and one polarization d-AO ($\alpha = 0.175$).

The correlated calculations were carried out using a multireference configuration interaction (MRDCI) approach.[35] The frozen core approximation was used, i.e., the inner shells 1s of O and Li, and 1s2s2p of Na were left uncorrelated, and the corresponding higher-lying species discarded (i.e., 7 valence electrons were correlated for the oxides M−O and 13 for O_2^- and MO_2). Throughout this work, the MO numbering corresponds to that of the valence shell. In general, up to nine electronic states were calculated at the CI level, in two different batches of about four or five states each, depending on the particular situation. On average, the dimension of the secular equations was in the 25 000−30 000 range.

2. *g* Factor Calculations. The electron-spin magnetic moment, $\boldsymbol{\mu}_s$, of a radical is given as $\boldsymbol{\mu}_s = -\mu_B \boldsymbol{g}\cdot\mathbf{S}$, where μ_B is the Bohr magneton, **S** the spin angular momentum vector, and ***g*** a second-rank tensor called the electronic *g* tensor.[1] The *g* components can be written as $g_{ab} = g_e\delta_{ab} + \Delta g_{ab}$, with g_e = 2.002 319 corresponding to the free-electron *g* factor; δ_{ab} to the Kronecker delta; and *a*, *b* to the *x*, *y*, *z* coordinates. The electronic-charge centroid (ECC), calculated at the ROHF level, has been used here as gauge origin.[36] For C_{2v} radicals, the Δg values are diagonal in the *x*, *y*, *z* coordinates; besides, Δg_{zz} is gauge invariant.

Details concerning the theoretical evaluation of Δg values can be found in refs 1, 3, 4, 10, and 14. In short, the present method is based on a perturbative approach, complete to second order in appropriate Breit−Pauli operators. A given Δg_{ab} is calculated as the sum of two first-order terms and one second-order term. First-order contributions comprise the relativistic mass correction to the spin-Zeeman term (Δg_{RMC}) and the one- and two-electron spin-Zeeman gauge corrections (Δg_{GC-SZ}); the latter two corrections are also called *diamagnetic* contributions.[5] Both first-order terms are simply ground state expectation values. The second-order contribution, or *paramagnetic* term,[5] is calculated as a sum-over-states (SOS) expansion, where each term is directly proportional to the spin−orbit (SO) and orbital-Zeeman (L) matrix elements, and inversely proportional to the corresponding excitation energy (ΔE).

For linear radicals, the magnetic moment operator is given by $\boldsymbol{\mu}_m = -\mu_B(\Lambda + g_e\Sigma)$, the sum of the orbital ($\boldsymbol{\mu}_o = -\mu_B\,\Lambda$) and spin ($\boldsymbol{\mu}_s = -\mu_B\, g_e\, \Sigma$) contributions.[1,2,37] Λ represents the orbital angular momentum vector and Σ the electron spin vector. For an orbitally nondegenerate electronic state, the only orbital angular momentum is derived from spin−orbit mixing with excited states. For a $^2\Pi$ state, however, the quantum number Λ is ±1 and Σ is $\pm{}^1/_2$. In Hund's case (a), a $^2\Pi$ state arising from a π^3 configuration splits into the sublevels $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$, with the former lying lower. At zero order, the magnetic moment (in μ_B units) is approximately −2 for $^2\Pi_{3/2}$ and 0 for $^2\Pi_{1/2}$.[47] A $^2\Pi_{3/2}$ ground state is difficult to measure via ESR since the *g* values lie near $g_{\perp} = 4$ and $g_{\|} = 0$, and the resultant spectrum of randomly oriented molecules is smeared out.[2] For $^2\Pi_{1/2}$, both $g_{\perp}$ and $g_{\|}$ are close to zero, and therefore again an ESR spectrum can hardly be obtained.

O^- Ion: *g* Factors for the Oxides LiO and NaO ($1^2\Sigma^+$). Under the influence of an electric field of axial symmetry (*z*-axis), such as for O^- adsorbed on surfaces,[20] the ^2P level of O^- splits into $^2\Sigma^+(2\sigma^2 3\sigma 1\pi^4)$ and $^2\Pi(2\sigma^2 3\sigma^2 1\pi^3)$. In a simplified two-state model,[20] the Δg-values are

$$\Delta g_{\|} = g_{zz} - g_e \approx 0$$

$$\Delta g_{\perp} = g_{xx} - g_e = g_{yy} - g_e \approx 2\lambda/\Delta E$$

where for λ the spin−orbit constant of O has been used, and $\Delta E = E(^2\Pi) - E(^2\Sigma^+)$. This simple relation allows for estimating ΔE on the basis of $g_{\perp}$ data, and *vice versa*. Since the aforementioned experiments found $\Delta g_{\perp} > 0$, it follows that $^2\Sigma^+$ is more stable than $^2\Pi$. The estimated ΔE's for O^- adsorbed on surfaces are not higher than 0.1 eV.[20]

The oxygen atom of the oxide M−O essentially has a net charge of −1, and the M−O radical undergoes a similar axial splitting as above. Detailed ab initio calculations[30] have found that the ground state is $X^2\Pi$ for LiO and NaO, but $X^2\Sigma^+$ for KO, RbO and CsO. Since the ESR spectra of $^2\Pi$ radicals are

TABLE 1: Vertical Excitation Energies (ΔE), Spin−Orbit (SO), and Angular-Momentum (L) Matrix Elements, and Second-Order Contributions to the $\Delta g_\perp$ Values for the $X^2\Pi$ and $1^2\Sigma^+$ States of LiO and NaO[a]

		LiO ($X^2\Pi$) ($R_e = 3.167$ au)	LiO ($1^2\Sigma^+$) ($R_e = 2.984$ au)	NaO ($X^2\Pi$) ($R_e = 3.853$ au)	NaO ($1^2\Sigma^+$) ($R_e = 3.670$ au)
ΔE (eV)	ROHF	0.229	−0.111	0.050	0.041
	MRCI	0.387	−0.260	0.329	−0.230
	(CI)[b]	0.315	−0.188	0.211	−0.112
SO (cm^{-1})	ROHF	69.52	70.12	68.15	68.19
	MRCI	60.44	61.00	57.19	57.28
L (au)	ROHF	0.9678	0.9583	1.0074	1.0030
	MRCI	0.9501	0.9395	1.0048	1.0012
$\Delta g_\perp$ (ppm)	ROHF	149700	−311220	699920	826900
	MRCI	75590	−112280	88980	−127030
	(CI)[b]	92850	−155330	139400	−260720

[a] Equilibrium bond distances taken from ref 30. [b] Using corrected ΔE's (see text).

TABLE 2: MRDCI Data for Excited States of O_2^- As Calculated with a Valence Basis Set[a] (Only Valence MOs Are Counted)

u states[b]		ΔE (eV)	g states		ΔE (eV)	SO (cm^{-1})	L (au)	$\Delta g_\perp$ (ppm)
$1\pi_u \rightarrow 1\pi_g$	$1^2\Pi_u$	5.199	$2\sigma_g \rightarrow 1\pi_g$[c]	$1^2\Sigma_g^+$	6.324	−73.57	−1.1808	6999
$1\pi_g \rightarrow 2\sigma_u$[d]	$1^2\Sigma_u^-$	6.210	$1\pi_u \rightarrow 2\sigma_u$[e]	$1^2\Sigma_g^-$	9.284	−27.43	0.3285	−494
	$1^2\Delta_u$	6.272		$1^2\Delta g$	10.500	12.74	0.4489	277
	$1^2\Sigma_u^+$	6.765		$2^2\Sigma_g^+$	10.622	14.45	0.4785	332
$2\sigma_g \rightarrow 2\sigma_u$	$2^2\Pi_u$	12.510						

[a] All data relative to $X^2\Pi_g$, at R(OO) = 2.551 bohr. ΔE, vertical excitation energy; SO and L, spin−orbit and angular momentum matrix elements, respectively; $\Delta g_\perp$, second-order contribution to the perpendicular g shift. [b] The oscillator strength f is 0.074 for $1^2\Pi_u$ and 0.012 for $2^2\Pi_u$; for the other doublet states, $f \approx 0.001$. [c] ROHF data: $\Delta E = 4.807$ eV; SO = -75.17 cm^{-1}; $L = -1.1610$ au; $\Delta g_\perp = 9248$ ppm. [d] $\Delta E(1^4\Sigma_u^-) = 4.721$ eV. [e] Only the lowest doublet of each symmetry is given.

difficult to measure, it is understandable why no such spectra have been observed for LiO and NaO.[38]

The g-shifts of these M−O radicals are determined by the coupling between $^2\Sigma^+(2\sigma^2 3\sigma 1\pi^4)$ and $^2\Pi(2\sigma^2 3\sigma^2 1\pi^3)$, with 3σ and 1π being 2p(O) AOs. Excited states of charge-transfer character (i.e., those in which the unpaired electron has been transferred from O^- to M^+) have no influence on the magnetic coupling.[11,13]

We have calculated the second-order contribution (due to the electron spin) to the $g_\perp$ shift for both $X^2\Pi$ and $1^2\Sigma^+$ states of LiO and NaO. The $\Delta g_\perp$ value is proportional to (SO•L)/ΔE, where SO = $\langle ^2\Sigma^+|H_{so}|^2\Pi\rangle$ and $L \equiv \langle ^2\Sigma^+|L|^2\Pi\rangle$, thus allowing to compare the theoretical values of SO•L with the "experimental" 2λ of the two-state model.[20] When SO is given in cm^{-1} and both L and ΔE in atomic units, use a factor of 18.72 to get Δg in ppm.

The $g_\perp$ shifts of LiO and NaO are collected in Table 1. The ΔE value under the heading ROHF was calculated from differences in determinantal energies using $1^2\Sigma^+$ MOs. Our correlated *adiabatic* ΔE's of 0.370 eV for LiO and 0.329 eV for NaO are 0.073 and 0.118 eV, respectively, higher than those from Langhoff et al.[30] obtained with larger basis sets. The "corrected" energies, given as "(CI)" in Table 1, were obtained by lowering our vertical ΔE's by those amounts.

$\Delta g_\perp$ is extremely sensitive to the level of treatment. The SO matrix elements from CI wave functions are up to 20% smaller than those from ROHF; the L matrix elements are much less affected (≈2%).

The O_2^- Ion *in Vacuo*. MCSCF/CI calculations have shown, when comparing the potential curves of $X^2\Pi_g$, $1^2\Pi_u$, and $1^4\Sigma_u^-$ for O_2^- in vacuo with those in simulated ionic solids, that the corresponding values of R_e, ω_e, and ΔE change very little.[28] One important feature does change, however: the energy of low-lying excited states of "trapped" O_2^- moves below the energy of $O_2(X^3\Sigma_g^-)$, i.e., resonant states of negative ions stabilize in condensed media.[39] Thus, the magnetic coupling between $X^2\Pi_g$ and the excited states of free O_2^- is more or less preserved when this anion is placed in an ionic lattice, as in alkali MO_2 radicals, for example.

Table 2 gives the vertical excitation energies ΔE for excited states of O_2^- at R(O−O) = 2.551 bohr. The calculations have been carried out with $1^2\Sigma_g^+(2\sigma_g 1\pi_u^4 1\pi_g^4)$ SCF-MOs to ensure degenerate π_g orbitals.

Relative to $X^2\Pi_g(2\sigma_g^2 1\pi_u^4 1\pi_g^3)$, the $1^2\Pi_u(1\pi_u \rightarrow 1\pi_g)$ and $1^2\Sigma_g^+(2\sigma_g \rightarrow 1\pi_g)$ states lie at about 5.20 and 6.32 eV, respectively. The excitation $1\pi_g \rightarrow 2\sigma_u$ gives rise to excited states ranging from 4.72 to 6.8 eV. The doublet states $1\pi_u \rightarrow 2\sigma_u$ (i.e., two each of type $^2\Sigma_g^+$, $^2\Sigma_g^-$, and $^2\Delta g$) lie above 9 eV.

Only gerade states can magnetically couple with $X^2\Pi_g$; the corresponding SO and L matrix elements, and Δg values are also given in Table 2. For $1^2\Sigma_g^+$, a $|L|$ value of about 1.2 au indicates a large "magnetic" overlap between $2\sigma_g$ and $1\pi_g$, as expected for 2p MOs. A SO value of about -74 cm^{-1} is typical for O_2[40] and O_2^-.[41] However, the contribution of this state to $\Delta g_\perp$ is relatively modest (≈7000 ppm) because of its high ΔE.

The magnetic coupling of the lowest $1\pi_u \rightarrow 2\sigma_u$ states results in absolute $\Delta g_\perp$ values not higher than 500 ppm. These small contributions are due to the high ΔE (>9 eV), relatively weak SO (<30 cm^{-1}) and moderate magnetic overlap L (<0.5 au).

The $^2\Sigma_g^-$, $^2\Sigma_g^+$, and $^2\Delta_g$ states (up to $\Delta E = 16$ eV) contribute to $\Delta g_\perp$ by −501, 173, and 400 ppm, respectively, resulting in an overall contribution of 72 ppm and showing a considerable cancellation of positive and negative terms. We expect the same feature for the excited states of MO_2 occupying the $\sigma^*(2\sigma_u)$ MO.

The O_2^- Ion Stabilized in the Superoxides LiO_2 and NaO_2. (1) O_2^- in Orthorhombic Crystal Fields. When O_2^- is placed in a crystal field of orthorhombic (C_{2v}) symmetry, the degeneracy of the π orbitals is removed: π_g splits into a_2 and b_2, and π_u into a_1 and b_1. Now, π_g and σ_u can mix through their b_2 components, as do π_u and σ_g through a_1 orbitals. Table 3 summarizes the correlation between electronic states of O_2^- in $D_{\infty h}$ and C_{2v} symmetries. We use here the standard orientation for C_{2v}, in which x is perpendicular to the molecular plane, y

TABLE 3: Correlation between Doublet Electronic States of O_2^- in $D_{\infty h}$ and C_{2v} Symmetries, and Contributions to Δg_{ii} Components (Only Valence Electrons Are Counted)

$D_{\infty h}$[a]	C_{2v}[b]	Δg_{ii}
$X^2\Pi_g$ ($2\sigma_g^2 1\pi_u^4 1\pi_g^3$)	X^2A_2 ($2a_1^2 3a_1^2 1b_1^2 2b_2^2 1a_2$)	
	1^2B_2 ($2b_2 \rightarrow 1a_2$)	*yy*
$1^2\Pi_u$ ($1\pi_u \rightarrow 1\pi_g$)	1^2B_1 ($1b_1 \rightarrow 1a_2$)	*xx*
	1^2A_1 ($3a_1 \rightarrow 1a_2$)	*zz*
$1^2\underline{\Sigma}_g^+$ ($2\sigma_g \rightarrow 1\pi_g$)	2^2A_1 ($2a_1 \rightarrow 1a_2$)	*zz*
$^2\Sigma_u^-$, $^2\Sigma_u^+$, $^2\Delta_u$ ($1\pi_g \rightarrow 2\sigma_u$)	$^2B_2$ ($1a_2 \rightarrow 3b_2$)	*yy*
	$^2A_2(2)$ ($2b_2 \rightarrow 3b_2$)	
$^2\underline{\Sigma}_g^-$, $^2\underline{\Sigma}_g^+$, $^2\underline{\Delta}_g$ ($1\pi_u \rightarrow 2\sigma_u$)	$^2A_1(2)$ ($1b_1 \rightarrow 3b_2$)	*zz*
	$^2B_1(2)$ ($3a_1 \rightarrow 3b_2$)	*xx*
$^2\Pi_u$ ($2\sigma_g \rightarrow 2\sigma_u$)	$^2B_1$ ($2a_1 \rightarrow 3b_2$)	*xx*

[a] States contributing to $\Delta g_\perp$ are underlined. [b] Only singly-excited states given.

parallel to the O−O bond, and z coincides with the C_2 axis. Please note that in most experimental papers dealing with the g factors of O_2^-, the roles of the y and z axes are interchanged.

$X^2\Pi_g$ correlates with X^2A_2 and 1^2B_2, $1^2\Pi_u(1\pi_u \rightarrow 1\pi_g)$ with 1^2A_1 and 1^2B_1, and $1^2\Sigma_g^+(2\sigma_g \rightarrow 1\sigma_g)$ with 2^2A_1. Excited states arising by the promotion of an electron from a fully occupied MO into the SOMO (π_g) are the main contributors to g (upper part of Table 3), whereas those occupying the virtual $2\sigma_u$ ($3b_2$) MO should only be weakly magnetically coupled (high ΔE's and small SO and L values, cf. Table 2).

In C_{2v} symmetry, the $2b_2$ MO, mainly [$p_z(1) + p_z(2)$], is more stable than $1a_2$ [$p_x(1) + p_x(2)$] as $2b_2$ lies collinear to the z axis and therefore undergoes a stronger interaction with the crystal field than does $1a_2$, which lies perpendicular to it. For $X^2\Pi_g$-($1\pi_g^3$) in C_{2v} symmetry, the occupation $2b_2^2 1a_2$ (X^2A_2) is thus favored over $2b_2 1a_2^2$ (1^2B_2).

In second order, the g components of X^2A_2 are governed by the magnetic coupling with excited states of type $^2B_1$ for g_{xx}, $^2B_2$ for g_{yy}, and $^2A_1$ for g_{zz}. Since in C_{2v} symmetry the $^2A_1$ components of the close-lying states $1^2\Pi_u$ and $1^2\Sigma_g^+$ can mix, g_{zz} might actually involve the coupling with *two* $^2A_1$ states (rather than with only one, as has been assumed in the literature).[2,18,20,21,23] Excitations from doubly occupied MOs into the SOMO ($1a_2$) give positive contributions to Δg, whereas those into $\sigma_u(3b_2)$ contribute negatively.

For O_2^- placed in various orthorhombic environments,[20] ESR studies have found that $g_{xx} \approx g_e$ and $g_{yy} \gg g_{zz} > g_e$ (typically, Δg_{yy} is 200 000 to 500 000 ppm). In a simplified two-state model,[20] the Δg values for X^2A_2 are given by the same expressions presented for the oxides MO, namely

$$\Delta g_{xx} = g_{xx} - g_e \approx 0$$

$$\Delta g_{yy} = g_{yy} - g_e \approx 2\lambda/\Delta E$$

where λ again is the spin−orbit coupling constant of O and $\Delta E = E(1^2B_2) - E(X^2A_2)$. The large Δg_{yy} value is due to the small ΔE between the split components of $X^2\Pi_g$, which depends strongly on the perturbing crystal field. For Δg_{zz}, a similar expression as for Δg_{yy} has been derived, with ΔE assumed to be the excitation energy of $^2A_1(1^2\Sigma_g^+)$.

(2) O_2^- in LiO_2 and NaO_2. We consider now the superoxides MO_2 at the linear ($C_{\infty v}$) and bent (C_{2v}) geometries. The $D_{\infty h}$ configurations in Table 3 can be converted to $C_{\infty v}$ by substituting $2\sigma_g$, $1\pi_u$, $1\pi_g$, and $2\sigma_u$ with 3σ, 1π, 2π, and 4σ, respectively.

After minor changes, the ideas presented above for O_2^- in a C_{2v} crystal field can as well be applied to O_2^- in MO_2. First, for linear MOO the distinction between g and u is not longer valid, and therefore, the number of excited states contributing to $g_\perp$ increases (from those underlined in Table 3) by the corresponding u-states $1\pi_g \rightarrow 2\sigma_u$ ($2\pi \rightarrow 4\sigma$). However, the fact that a magnetic coupling $g - u$ is not allowed should hold approximately in the lower symmetry (i.e., small contributions to Δg due to u states). Second, the number of low-lying excited states of MO_2 is larger than those given in Table 3 for free O_2^-, as the counterion Li^+ or Na^+ has four valence MOs, namely two a_1, one b_1 and one b_2 (neglecting 3d AOs for Na^+). The analysis above holds for the X^2A_2 ground state of MO_2, with a π-type character. The 1^2B_2 excited state, formally a σ-type species, should have a similar magnetic coupling as the ground state since both are split components of $^2\Pi(M^+O_2^-)$. It is therefore of interest to study the g-shifts of 1^2B_2 as well. For 1^2B_2, the xx, yy, and zz components of Δg are governed by the coupling with $^2A_1$, $^2A_2$, and $^2B_1$ states, respectively. While Δg_{yy} again depends mostly on the $X^2A_2/1^2B_2$ coupling and thus remains the largest g shift, the roles of the other two components have to be exchanged, i.e., $\Delta g_{zz} \approx 0$ and $\Delta g_{yy} \gg \Delta g_{xx}$. The Δg_{yy} value of 1^2B_2 is negative due to a negative ΔE.

ROHF Δg Values. The uncorrelated Δg_{xx}, Δg_{yy}, Δg_{zz} (in ppm) for X^2A_2 of LiO_2 are respectively, −385, 44 818, and 7803 (corresponding first-order contributions: −384, −281, and −283 ppm). For X^2A_2 of NaO_2, the values are −426, 71 124, and 7843 (first-order: −424, −323, and −283 ppm). The SOS expansions of both radicals, which only contain one-open-shell singly excited states, comprise 36 terms of A_1, 12 of B_1, 27 of B_2, and 8 of A_2 symmetry.

First-order contributions, which are dominated by the isotropic Δg_{RMC} term (≈−290 ppm), only play a role for the small Δg component (that having the same direction as the SOMO). They become relatively important, however, for small radicals (e.g., H_2^-;[42] LiH^+, BeH^{2+}, BeH, BH^+;[43] Li_2^+, Li_2^-, Be_2^+ [44]).

The average $\langle \Delta g \rangle$, also known as Δg_{iso}, is 17412 ppm for LiO_2 and 26180 ppm for NaO_2; i.e., it increases by about 50% when replacing Li by Na. The data above indicate that the Δg_{xx} and Δg_{zz} components are practically the same for both radicals (≈−400 and 7800 ppm), whereas Δg_{yy} increases by about 60% between LiO_2 and NaO_2. As shown later, the major source of difference between the Δg_{yy} values lies in the ΔE's.

MRCI Δg Values. The second-order MRCI contributions to Δg are collected in Tables 4 and 5. Depending on the convergence pattern, from 8 to 10 excited states were included in the SOS expansions. In general, one or two states are the main contributors to the large g shifts.

For the g-shifts of LiO_2 (Table 4), the correlated results corroborate the ROHF data, namely $\Delta g_{xx} \approx 0$, $\Delta g_{yy} \gg \Delta g_{zz}$. The SOS expansion for Δg_{yy} has a large contribution due to 1^2B_2, and essentially none for the other states, justifying the two-state coupling model.[20] The small deformation of the π_g components $1a_2$ and $2b_2$ is evident by a L value close to 1.0 (Table 4). Since the energy difference is a critical parameter for evaluating Δg, we have compared our calculated adiabatic $T_e(1^2B_2)$ value with that reported in a more extensive treatment.[31] Our CI value is too high by 0.056 eV. Adjusting the vertical ΔE by the same amount, Δg_{yy} increases by about 9% (Table 4, footnote *c*).

As mentioned earlier, not one but two $^2A_1$ states give large contributions to Δg_{zz}. For LiO_2, both states are energetically close (5.531 and 5.825 eV); the corresponding SO and L matrix elements are also of a comparable magnitude (≈52 cm^{-1} and 0.82 au, respectively). The two $^2A_1$ states derive from $1^2\Pi_u$ and $1^2\Sigma_g^+$ of O_2^- (Table 3).

The second-order Δg values have also been calculated for the 1^2B_2 state of LiO_2, at the equilibrium geometry given in ref

TABLE 4: MRCI Second-Order Contributions to the *g* Shifts of the X^2A_2 State of LiO$_2$[a]

		ΔE (eV)	SO (cm^{-1})	L (au)	Δg(2o)[b] (ppm)
$^2B_1$ (Δg_{xx})	1	4.037	2.577	0.2595	84
	2	4.603	3.635	−0.1380	−56
	3	4.714	0.597	−0.0811	−5
	4	5.528	−0.158	−0.0899	1
	5	5.543	1.973	0.1143	21
	6	6.546	1.870	0.0752	11
	7	7.128	0.645	0.0091	0.5
	8	7.406	0.762	0.0051	0.5
					57
$^2B_2$ (Δg_{yy})	1	0.760	−79.078	−0.9992	52957[c]
	2	5.332	−10.026	0.0214	−20
	3	6.930	−1.569	0.0241	−7
	4	7.365	0.097	0.0299	0
	5	7.588	8.872	−0.0155	−9
	6	9.021	−0.812	0.0344	−2
	7	9.990	3.740	−0.0330	−6
	8	10.376	−0.851	0.0190	−1
					52912
$^2A_1$ (Δg_{zz})	1	4.699	−0.035	−0.1954	1
	2	4.850	0.439	0.1710	8
	3	5.531	52.432	0.8380	4047
	4	5.781	5.583	−0.2102	−103
	5	5.801	0.346	−0.0986	−3
	6	5.825	−51.821	−0.8033	3640
	7	6.708	0.375	0.2036	6
	8	7.645	1.048	−0.0935	−6
					7590

[a] Geometry from ref 31. [b] Total contribution in boldface. [c] Using $\Delta E = 0.704$ eV, $\Delta g_{yy} = 57\,162$ ppm (**57 117** ppm, total).

TABLE 5: MRCI Second-Order Contributions to the *g* Shifts of the X^2A_2 State of NaO$_2$[a]

		ΔE (eV)	SO (cm^{-1})	L (au)	Δg(2o)[b] (ppm)
$^2B_1$ (Δg_{xx})	1	2.702	−3.160	−0.3230	192
	2	3.951	−4.452	0.2407	−140
	3	4.451	1.312	0.1454	22
	4	4.680	2.911	0.2067	65
	5	4.764	1.461	0.0697	11
	6	5.278	0.306	0.1264	4
	7	5.673	0.629	−0.0260	−1
	8	5.696	2.229	−0.0313	−6
	9	7.274	−0.078	−0.0639	0
					82
$^2B_2$ (Δg_{yy})	1	0.439	−79.250	−1.0067	92523[c]
	2	4.822	−6.495	−0.0372	26
	3	6.524	1.743	−0.1079	−15
	4	6.729	3.378	−0.0497	−13
	5	8.331	−0.635	0.1514	−6
	6	8.722	−19.683	−0.0991	114
	7	9.406	−0.251	0.0274	0
	8	10.680	−4.771	−0.0524	12
	9	11.195	−1.472	−0.0673	5
					92646
$^2A_1$ (Δg_{zz})	1	3.510	−2.247	0.1265	−41
	2	3.524	8.262	0.2666	318
	3	5.079	−1.628	0.0832	−14
	4	5.244	33.585	0.4595	1499
	5	5.436	3.097	−0.1114	−32
	6	6.332	−64.248	−1.0557	5456
	7	6.848	0.263	−0.0262	−1
	8	7.218	−0.511	0.0895	−3
	9	8.052	−0.762	−0.0569	3
					7185

[a] Geometry from ref 31. [b] Total contribution in boldface. [c] Using $\Delta E = 0.367$ eV, $\Delta g_{yy} = 110\,675$ ppm (**110 798** ppm, total).

TABLE 6: ROHF and MRCI Second-Order Contributions to Δg_{yy} for the Coupling $X^2A_2/1^2B_2$, and to Δg_{zz} for the Coupling $X^2A_2/^2A_1$ of LiO$_2$ and NaO$_2$[a]

Δg_{yy}		X^2A_2[b] ROHF	MRCI	1^2B_2[c] ROHF	MRCI
LiO$_2$	ΔE	0.930	0.704	−0.439	−0.648
	SO	85.136	79.078	84.720	79.061
	L	0.996	0.999	0.999	0.999
	Δg_{yy}	45191	57162	−95730	−62073
NaO$_2$	ΔE	0.595	0.367	−0.144	−0.348
	SO	85.550	79.250	85.304	79.110
	L	1.002	1.007	1.006	1.007
	Δg_{yy}	71484	110731	−296261	−116758

Δg_{zz}		X^2A_2[b,d] ROHF	MRCI1	MRCI2	total CI
LiO$_2$	ΔE	5.333	5.531	5.825	
	SO	76.779	52.432	−51.821	
	L	1.141	0.838	−0.803	
	Δg_{zz}	8149	4046	3640	7686
NaO$_2$	ΔE	5.237	5.244	6.332	
	SO	75.977	33.585	−64.248	
	L	1.145	0.460	−1.056	
	Δg_{zz}	8239	1499	5456	6955

[a] ΔE in eV, SO in cm^{-1}, L in au, and Δg in ppm. [b] At its equilibrium geometry (ref 31), and using X^2A_2 SCF MOs. [c] At its equilibrium geometry (ref 31), and using 1^2B_2 SCF MOs. [d] Two $^2A_1$ states at the CI level, given as MRCI1 and MRCI2. See text.

31. The corresponding contributions (in ppm) to Δg_{xx}, Δg_{yy}, and Δg_{zz} are 8685, −61 454, and 59. After substituting *xx* by *zz*, the SOS expansions associated with the *g*-shifts of 1^2B_2 of LiO$_2$ exhibit similar trends as observed for X^2A_2 (Table 4). Since $|\Delta E|$ at the 1^2B_2 geometry is necessarily smaller than for X^2A_2 at equilibrium, $|\Delta g_{yy}|$ is consequently larger for the excited state.

The data in Table 5 for NaO$_2$(X^2A_2) follow the same trends as those in Table 4 for LiO$_2$(X^2A_2), i.e., small Δg_{xx} of 82 ppm, large Δg_{yy} of 92 646 ppm (governed by the coupling with 1^2B_2), and a medium Δg_{zz} component (7185 ppm) with two excited states dominating the SOS expansion. Lowering the vertical $\Delta E(1^2B_2)$ value for NaO$_2$ by 0.072 eV after comparing with Bauschlicher's data,[31] Δg_{yy} increases by about 21% (Table 5, footnote *c*). The g_{yy} shift of NaO$_2$ is about twice the value for LiO$_2$, mainly because $\Delta E(\text{NaO}_2) \approx (1/2)\ \Delta E(\text{LiO}_2)$.

The same behavior as for 1^2B_2 of LiO$_2$ is observed for that state of NaO$_2$, with second-order contributions $\Delta g_{yy} = -116\,575$ ppm, $\Delta g_{xx} = 8213$ ppm, and $\Delta g_{zz} \approx 101$ ppm. The major difference lies in the magnitude of Δg_{yy}, which is about two times larger in the Na compound.

ROHF *vs* MRCI Δg Values. Table 6 collects the dominant second-order ROHF and MRCI contributions to the in-plane components Δg_{yy} and Δg_{zz}.

The Δg_{yy} value relative to X^2A_2 or 1^2B_2 is governed by the coupling $X^2A_2/1^2B_2$. For X^2A_2, correlation *increases* Δg_{yy} by 26% for LiO$_2$ and by 55% for NaO$_2$; for 1^2B_2, correlation *decreases* $|\Delta g_{yy}|$ by 35 and 61%, respectively. At each level of treatment, the magnitude of Δg_{yy} *increases* in passing from LiO$_2$ to NaO$_2$.

The $\langle X^2A_2|H_{SO}|1^2B_2\rangle$ values for the two states of LiO$_2$ and NaO$_2$ are remarkably uniform, with a median of 85.2 ± 0.5 cm^{-1} (ROHF) or 79.1 ± 0.1 cm^{-1} (MRCI). Also, $\langle X^2A_2|L_y|1^2B_2\rangle$ has a value of about 1.0 au for both radicals. The similarity between the SO and L matrix elements shows that the structure of O_2^- is nearly independent of the counterion.

It follows from the discussion above that the major difference between the Δg_{yy} values of LiO$_2$ and NaO$_2$ lies in the ΔE's. Please note that the present "ROHF" excitation energies are not obtained from two independent SCF calculations but as difference of determinantal energies evaluated using the same set of MOs (e.g., those from 1^2B_2 when dealing with this excited

TABLE 7: Best Δ*g* Data (in ppm) Calculated in This Work for LiO_2 and NaO_2

Δ*g* data[a]		$LiO_2(X^2A_2)$	$LiO_2(1^2B_2)$	$NaO_2(X^2A_2)$	$NaO_2(1^2B_2)$
Δg_{xx}	1st	−430	−346	−475	−379
	2nd	57	8685	82	8213
	total	−373	8339	−393	7834
Δg_{yy}	1st	−315	−319	−362	−352
	2nd	57117	−61454	110854	−116575
	total	56800	−61773	110492	−116927
Δg_{zz}	1st	−317	−405	−317	−395
	2nd	7590	59	7185	101
	total	7273	−346	6868	−294
$\langle\Delta g\rangle$		21233	−17927	38989	−36462
$\langle g\rangle$		2.023552	1.984392	2.041308	1.965857

[a] 1st: corrected values (by 12%) from the corresponding ROHF first-order terms (see text); 2nd: second-order MRCI (best values from Tables 4 and 5).

TABLE 8: Experimental Δ*g* Values (ppm) and Total Magnetic Moments μ_m (in Bohr magnetons) of Alkali Superoxides MO_2 (X^2A_2), and the Best Theoretical Results for LiO_2 and NaO_2 from This Work

MO_2/matrix	Δg_{xx}	Δg_{yy}	Δg_{zz}	$\langle\Delta g\rangle$	μ_m
LiO_2/N_2[a]	−900	65500	5800	23467	1.7546
LiO_2/Ar[a]	−400	56900	6100	20867	1.7523
LiO_2/Kr[a]	−300	55600	7100	20800	1.7522
NaO_2/Ar[b]	600	108900	4000	37833	1.7673
NaO_2/Kr[c]	−100	108300	5200	37800	1.7673
KO_2/Kr[c]	−1600	116100	4500	39667	1.7690
RbO_2/Kr[c]	−2700	120400	4600	40767	1.7700
CsO_2/Kr[c]	−1000	104600	4600	36067	1.7658
LiO_2[d]	−373	56800	7273	21233	1.7526
NaO_2[d]	−393	110492	6868	38989	1.7684

[a] Lindsay and Garland (1987), ref 23. [b] Lindsay et al. (1974), ref 23. [c] Adrian et al., ref 22. [d] Best results from this work (cf. Table 7).

state). For this reason, the two ROHF values for |Δ*E*| of LiO_2 (Δg_{yy}), for example, lie too much apart (0.930 vs 0.439 eV), in contradiction with the fact that the equilibrium geometries of X^2A_2 and 1^2B_2 are quite alike. With the correlated Δ*E*'s, the discrepancy is obviously lifted (0.704 vs 0.648 eV). The same picture holds for NaO_2.

The Δ*E*'s of LiO_2 are about twice those of NaO_2. As the equilibrium bond distance R(Li−O) is shorter than R(Na−O), the Coulombic interaction O_2^-...M^+ is stronger in LiO_2, thus resulting in a higher Δ*E*.

The description of Δg_{zz} for X^2A_2 is slightly more complicated than for the Δg_{yy} component. In detail, at the ROHF level only one state, $^2A_1(2a_1 \rightarrow 1a_2)$ correlating with $1^2\Sigma^+$ of linear MO_2, contributes to Δg_{zz}. The corresponding couplings $X^2A_2/^2A_1$ in LiO_2 and NaO_2 have average values of 5.28 ± 0.05 eV for Δ*E*, 76.4 ± 0.4 cm^{-1} for SO, 1.14 au for *L*, and 8194 ± 45 ppm for Δg_{zz}. These averages lie rather close to ROHF values for the $X^2\Pi_g/1^2\Sigma_g^+$ coupling of free O_2^-: 4.81 eV, 75.2 cm^{-1}, 1.16 au, and 9248 ppm, respectively (Table 2).

The CI treatment finds $^2A_1(3a_1 \rightarrow 1a_2)$ to be also of relevance for $\Delta g_{zz}(X^2A_2)$; this $^2A_1$ state correlates with $1^2\Pi$. As seen in Table 6, for each $^2A_1$ state of LiO_2 the corresponding values of Δ*E*, SO, and *L* are of similar magnitude, thus resulting in equivalent contributions to Δg_{zz} (4046 and 3640 ppm). For NaO_2, however, one notes a clear tendency toward a stronger coupling with the higher $^2A_1$ state, as indicated by its contribution to Δg_{zz} of 5456 ppm versus 1499 ppm from the lowest $^2A_1$. Such a less severe $1^2\Sigma^+/1^2\Pi$ mixing in NaO_2 than in LiO_2 is most probably due to the larger *R*(Na−O) (i.e., a weaker $Na^+-O_2^-$ interaction).

Table 7 summarizes our best theoretical results for the *g* shifts of LiO_2 and NaO_2. The total value of each Δ*g* component combines first-order (ROHF) and second-order (MRCI) terms. As shown by Bündgen et al.[45] for the radicals O_2, SO, and NO, correlated first-order terms are in magnitude about 12% larger than the uncorrelated values. Assuming that the same trend holds for the superoxides, the first-order contributions given in Table 7 have been increased by 12% relative to the ROHF data.

The small Δ*g* components (Δg_{xx} of X^2A_2 and Δg_{zz} of 1^2B_2), which are governed by first-order terms, vary from −300 to −400 ppm. Next in magnitude one finds Δg_{zz} of X^2A_2 and Δg_{xx} of 1^2B_2, ranging from 6900 to 8400 ppm. It is seen that the coupling $X^2\Pi_g/1^2\Sigma_g^+$ of free O_2^- resulting in $\Delta g_\perp \approx 7000$ ppm (Table 2) is more or less preserved in both LiO_2 and NaO_2 for the equivalent couplings of X^2A_2 or 1^2B_2 with the $^2A_1$ manifold.

For both electronic states, the largest *g* shift is assigned to Δg_{yy} (≈57 000 ppm for LiO_2 and ≈110 000 ppm for NaO_2, both in their ground states). Since the energetically close-lying $1a_2$ and $2b_2$ MO's have similar charge-density distributions, the paramagnetic current density is optimal for rotation about the *y*(O−O) axis.

Comparison with Experimental Results

O^-, LiO, and NaO. See ref 20 for detailed information on the experimental *g* shifts of adsorbed O^- ions. Experimentalists have interpreted the *g* shifts assuming that the interaction of O^- with the surface leads to the diatomic state $^2\Sigma^+(\sigma\pi^4)$ of O^- being more stable than $^2\Pi(\sigma^2\pi^3)$. Most of the experimental $\Delta g_\perp$ values (component perpendicular to the bond O surface) for O^- adsorbed on alkali halides vary from 224 000 to 300 000 ppm. The average energy splitting pσ−pπ, calculated as $\Delta E = 2\lambda/\Delta g_\perp$, is about 0.1 eV.

No experimental *g* shifts are available for LiO and NaO since both have a $X^2\Pi$ ground state. Our theoretical values of $|\Delta g_\perp|$ and |Δ*E*| for $1^2\Sigma^+$ of LiO (0.155 500 ppm and 0.19 eV) and NaO (0.261 000 ppm and 0.11 eV) resemble those for O^- adsorbed on alkali halide surfaces.

O_2^-, LiO_2, and NaO_2. Experiments for O_2^- in ionic lattices[21] find Δg_{yy} values (component parallel to the O−O bond) from ≈300 000 to 500 000 ppm, corresponding to Δ*E*'s of less than 0.1 eV for the splitting of $X^2\Pi_g(O_2^-)$. No experimental data are available for Δg_{zz}, but our calculations on free O_2^- (Table 2) suggest that this component should lie around 7000 ppm.

In Table 8 Δ*g* values are given for MO_2 radicals (M = Li to Cs) isolated in inert matrices. The magnitude of the magnetic moment has been calculated as $|\mu_m| = {}^1/_2|\sqrt{\Sigma g_{ii}^2}|$ (in Bohr magnetons) using experimental g_{ii}'s. Our best theoretical results for the Δ*g* values and $|\mu_m|$ of the Li and Na systems are displayed at the bottom of this table.

The Δg_{yy} values for LiO_2 in Ar and Kr matrices are quite similar, with an average of 56 250 ± 650 ppm. However, Δg_{yy} for LiO_2 in solid N_2 is about 9250 ppm (16%) higher, indicating a significantly larger host-matrix interaction than in rare-gas matrices.

We suspect that Δg_{yy} measured for LiO_2/N_2 might have been tainted by an interaction between Li and N_2. According to MP2/611+G* calculations by Ramondo et al.,[46] the radical LiN_2 has a C_{2v} equilibrium geometry, like LiO_2. The $X^2\Pi_g(1\pi_u^4 1\pi_g)$ state of linear Li−N−N splits into X^2B_2 and 1^2A_2, the latter lying slightly higher. Therefore, its Δg_{yy} value is governed by the magnetic coupling $X^2B_2/1^2A_2$, in a similar fashion as it does for the alkali MO_2's.

The net charges for Li, e.g., +0.46 for LiN_2 (X^2B_2) and +0.53 for LiO_2 (1^2B_2), indicate a similar amount of electronic charge

TABLE 9: ROHF and MRCI Values of $K = \langle SO\rangle\cdot\langle L\rangle/\hbar$ (in eV) for Oxides, Superoxides, and Ozonides of Li and Na, and the Free Ions O_2^- and O_3^- [a]

radical	ROHF	MRCI	radical[b]	ROHF	MRCI
LiO ($1^2\Sigma^+$)	0.034	0.029	NaO_2 (X^2A_2)	0.044	0.041
NaO ($1^2\Sigma^+$)	0.035	0.029	NaO_2 (1^2B_2)	0.044	0.041
O_2^- ($1^2\Sigma^+{}_g$)	0.044	0.044	O_3^- (X^2B_1)	0.035	0.038
LiO_2 (X^2A_2)	0.043	0.040	LiO_3 (X^2B_1)	0.033	0.038
LiO_2 (1^2B_2)	0.043	0.040	NaO_3 (X^2B_1)	0.035	0.037

[a] For LiO and NaO, data for coupling $X^2\Pi/1^2\Sigma^+(\Delta g_\perp)$; for O_2^-, coupling $X^2\Pi_g/1^2\Sigma_g^+(\Delta g_\perp)$; for LiO_2 and NaO_2, coupling $X^2A_2/1^2B_2(\Delta g_{yy})$; for O_3^- and O_3M, coupling $X^2B_1/1^2A_1(\Delta g_{yy})$. [b] Data for O_3^- and MO_3 taken from Bruna and Grein (ref 13).

density being transferred from Li to the diatomics O_2 and N_2.[46] The bond strengths of the Li−N and L−O bonds were found to be similar.

As pointed out earlier, the SO and *L* values related to Δg_{yy} of LiO_2 and NaO_2 are essentially identical. Since the observed Δg_{yy} increases in passing from LiO_2/rare gas to LiO_2/N_2, one can infer that ΔE in the N_2 matrix is somewhat smaller. This would mean that Li^+ in the presence of both $O_2(-)$ and $N_2(-)$ is less effective in splitting $X^2\Pi_g(O_2^-)$ than in the presence of O_2^- only (as in rare-gas matrices). It would be of interest to study NaO_2 in solid N_2 to determine whether Δg_{yy} is higher in NaO_2/inert gas).

The experimental Δg_{zz} values of LiO_2 lie in the 5800−7100 ppm range. The Δg_{xx} component is found to be negative in all cases, with an average of −530 ppm.

The *g*-shifts for NaO_2/Ar were determined by Adrian et al.,[22] and for NaO_2/Kr by Lindsay et al.[23] Both sets of Δg_{yy} and Δg_{zz} data are essentially equivalent; however, a positive $\Delta g_{xx} = 600$ ppm for O_2Na/Ar does not agree with the general trend (Table 9). The Δg_{yy} component of NaO_2 (108 600 ppm) is about twice that of LiO_2, in line with a decrease in $\Delta E(X^2A_2 - 1^2B_2)$ by about one-half between both compounds.[15,16,31]

The average $\langle\Delta g\rangle$ of LiO_2 or NaO_2 appears to be independent of the host, at least for Ar and Kr matrices. For the heavier systems KO_2, RbO_2, and CsO_2, the Δg values are similar to those of NaO_2, except for Δg_{xx}, which increases slightly in magnitude.

The calculated Δg_{yy} components (about 57 000 ppm for LiO_2 and 110 500 ppm for NaO_2) agree very well with experimental data cited in Table 8 for rare-gas matrices. The theoretical g_{zz} shift (about 7300 ppm for LiO_2 and 6900 ppm for NaO_2) reproduces the value measured for LiO_2 but it is about 1700 ppm too large for NaO_2. In line with experimental observations, Δg_{xx} is calculated to be small and negative (about −400 ppm for both radicals). Compared to the rather pronounced differences seen in the *g* shifts, the magnetic moment values (Table 8) are quite insensitive parameters, varying from 1.752 to 1.755 μ_B for LiO_2, and from 1.766 to 1.770 μ_B for NaO_2 to CsO_2. For a free electron, $|\boldsymbol{\mu}_\mathbf{m}| = 1.7341\ \mu_B$.

Summary and Concluding Remarks

The paramagnetic behavior of KO_2, discovered by Neuman[47] in 1934, was the first experimental proof for the existence of the O_2^- radical. Although numerous experimental studies have been carried out on O_2^- since then, we are unaware of any ab initio study dealing with the magnetic properties of O_2^- and simple superoxides. To fill this gap, the electron-spin magnetic moments (as parametrized by the *g* shifts) of LiO_2 and NaO_2 have been here studied theoretically. Details of the vertical spectra of both radicals are found elsewhere.[48] Complementary calculations were carried out as well to determine the magnetic coupling parameters (SO, *L*, and ΔE) for isolated O_2^- and the oxides LiO and NaO. Uncorrelated (ROHF) and correlated (MRCI) wave functions, in conjunction with a perturbative approach complete to second-order of the Breit−Pauli Hamiltonian, have been used.

The superoxides MO_2 are π-radicals, with the SOMO being ascribed to the out-of-plane component a_2 of $\pi_g(O_2^-)$. The energetically close-lying component b_2 has a similar spatial charge-density distribution. This results in an optimal paramagnetic current density due to rotation about the *y*(O−O) axis, leading to a large Δg_{yy} value for both X^2A_2 and 1^2B_2.

Our theoretical results for (gas phase) LiO_2 and NaO_2 reproduce the experimental ones reasonably well. For the ground-state X^2A_2, the MRCI results for Δg_{xx}, Δg_{yy}, Δg_{zz} (in ppm) are −373 (−350), 56 800 (56 250), 7273 (6600) for LiO_2; and −393 (150), 110 492 (108 600), 6868 (4600) for NaO_2, with the experimental numbers given in parentheses (average from Ar and Kr matrices). The theoretical averages $\langle\Delta g\rangle$ deviate from the average experimental values by about 400 ppm (2%) for LiO_2 and 1200 ppm (3%) for NaO_2.

As shown below, our calculations on LiO_2 and NaO_2 confirm the two-state model used by experimentalists for Δg_{yy}, which is calculated to be inversely proportional to the energy splitting between X^2A_2 and 1^2B_2. Experimental studies in rare-gas matrices found Δg_{yy} to lie around 56 000 ppm for LiO_2, but to be roughly 2 times larger for NaO_2 to CsO_2 (from 105 000 to 120 000 ppm). This trend indicates that Li^+ is a stronger perturber of O_2^- than the other alkali cations M^+, by the simple reason that the M−O distance is shortest for LiO_2. The stronger the metal−oxygen interaction the larger the splitting ΔE (the smaller the g_{yy} shift).

In the following, we focus on the coupling between the two lowest states of LiO_2 and NaO_2. According to the MRCI data for the X^2A_2 states, a ratio $\Delta g_{yy}(NaO_2)/\Delta g_{yy}(LiO_2)$ of 1.94 lies very close to 1.92 calculated for the quotient $\Delta E(LiO_2)/\Delta E(NaO_2)$. For the 1^2B_2 states, the corresponding (MRCI) ratios are 1.88 and 1.86. In other words, the “internal” magnetic coupling of O_2^-, as measured by SO and *L*, remains unchanged in passing from LiO_2 to NaO_2 (and probably, for heavier alkali MO_2 as well). The only mentionable difference relates to the “strength” of the perturbing field exerted by the countercation, as reflected in ΔE, which in turn depends on *R*(M−O). This feature allows to separate the magnetic coupling into a part common to all members of a given family of compounds MO_2 (i.e., SO and *L*), and another part characteristic of each of its members (ΔE).

As stated earlier, the simple relation $\Delta g \approx 2\lambda/\Delta E$ has been used by experimentalists to estimate ΔE from a knowledge of Δg and λ, as, for example, $\Delta g_\perp$ for O^- adsorbed on surfaces, and Δg_{yy} for LiO_2 and NaO_2. We have found that the Δg_{yy} values of the ozonides also satisfy this equation. It is therefore of interest to compare the experimental values of 2λ with the equivalent term $\langle SO\rangle\cdot\langle L\rangle$ provided by theory.

In Table 9 we summarize the ROHF and MRCI values (in eV) for the product $K = \langle SO\rangle\cdot\langle L\rangle/\hbar$ as calculated here for M−O, MO_2, and O_2^-, and for MO_3 and O_3^-.[13] The collected data refer to the largest *g*-shift of each system, which involves the coupling between two close-lying states. In detail, the coupling involves $X^2\Pi/1^2\Sigma^+$ for the oxides $O^-(^2P)M^+$, $X^2A_2/1^2B_2$ for the superoxides $O_2^-(^2\Pi_g)M^+$ and $X^2B_1/1^2A_1$ for the ozonides $O_3^-(^2\Pi_u)M^+$. In a simple approximation, the corresponding Δg components are evaluated as $\Delta g = K/\Delta E$.

For each family of compounds, the *K* parameter is found to be internally consistent, again pointing out that the counterion has only little influence on the SO and L parameters of O_n^- ($n = 1, 2, 3$). At the MRCI level, most of the K data lie in the range 0.029−0.041 eV. Recalling that K is approximately equal to 2λ, the effective spin−orbit constant λ at the CI level ranges from 0.015 to 0.021 eV. The ROHF values of K are 10−20% larger, from 0.033 to 0.044 eV. The experimental λ is 0.0186 eV for O and 0.0236 eV for O^- (see Zeller and Känzig, ref 21). On the other hand, Che and Tench[20] used $\lambda = 0.014$ eV to fit the g data from different experimental studies.

Codeposition at low temperatures of a mixture Li/O_2 in an excess of N_2, leading to the formation of LiO_2 in a N_2 matrix, might lead to somewhat anomalous g factors in the ESR spectrum when compared with that in rare-gas matrices, as Li is able to interact with both O_2 and N_2. Additional experimental studies on the g shifts of alkali nitrides MN_2, as well as for other superoxides MO_2 in N_2 matrices, are desirable.

A general discussion on the trends expected for the g shifts of MX_2 radicals (with M = Li, Na, and $X_2 = C_2, N_2, O_2, F_2$) can be found elsewhere.[49]

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