The sodium superoxide radical:
$\tilde{X}\,^2A_2$ and $\tilde{A}\,^2B_2$ potential energy surfaces

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The two lowest electronic states of NaO_2 have been studied using ab initio methods, including RHF SCF, CISD, Davidson-corrected CISD, UHF SCF, UMP2-UMP4, CASSCF, and CISD based on CASSCF natural orbitals, with basis sets ranging in quality from Na(11s7p/7s5p), O(9s5p1d/5s3p1d) to Na(13s10p2d1f/7s6p2d1f), O(11s7p2d1f/6s4p2d1f), i.e. from TZ+d to TZ2P+f+R. Total and relative energies, geometries, vibrational frequencies, and dipole moments of stationary points on the $\tilde{X}\,^2A_2$ and $\tilde{A}\,^2B_2$ surfaces have been determined. A C_{2v} minimum is proposed for $\tilde{X}\,^2A_2$ NaO_2 with r_e(O-O) = 1.335 and r_e(Na-O) = 2.10 Å. The analogous structure for the $\tilde{A}\,^2B_2$ state is predicted to have r_e(O-O) = 1.34 and r_e(Na-O) = 2.13 Å with an adiabatic excitation energy of T_e = 8.5 kcal mol^{-1}. Linear, $^2\Pi$ NaOO, which correlates to the $^2A_2$ and $^2B_2$ minima via C_s transition states, is predicted to be a shallow minimum lying 17 kcal mol^{-1} above the $\tilde{X}\,^2A_2$ structure but with a barrier to rearrangement of less than 1 kcal mol^{-1}. The dissociation energy of the ground state of NaO_2 is deduced to be D_0 = 38 kcal mol^{-1}, a value substantially lower than recent experimental estimates.

1. Introduction

Alkali-metal superoxide radicals (MO_2) play important roles in the chemistry of the mesosphere [1,2] and the combustion of alkali metals in oxygen-rich flames [3,4]. Allen and co-workers [5] have previously reported the results of a comprehensive ab initio quantum chemical study of the two lowest electronic states of LiO_2, including total and relative energies, geometric structures, and spectroscopic data for stationary points on both surfaces, as well as the dissociation energy D_0($Li-O_2$) of the ground state. A major portion of the investigation comprised the design of a solution to the problem of spatial symmetry breaking in the Hartree–Fock wavefunctions for alkali-metal superoxides. In this paper the the-

oretical approach developed for LiO_2 is applied to the study of the two lowest states of NaO_2.

Matrix-isolation infrared [6], Raman [7], and ESR [8,9] spectroscopic studies have established that NaO_2 in its ground electronic state has an ionic ($Na^+O_2^-$) structure of C_{2v} symmetry, for which fundamental vibrational frequencies and approximate bond lengths have been obtained (vide infra table 1). Plane et al. [10] have determined ab initio geometries and frequencies using UHF wavefunctions and the 6-31G and 6-311G basis sets. These results could be improved by the inclusion of polarization and diffuse functions in the basis set, and symmetry breaking in the UHF wavefunction invalidates [5] the Na–O antisymmetric stretching frequencies predicted therein. Marshall et al. [11] have reported a

6-31+G* UMP2 structure for NaO_2 with an O–O distance of 1.39 Å and an Na–O distance of 2.16 Å, both of which exceed the experimental estimates by ≈ 0.06 Å, as expected from an analysis of similar results for LiO_2 [5]. Much of the recent experimental and theoretical work [4,10–14] on NaO_2 has focused on the Na–O_2 dissociation energy, for which there is still much disagreement (as summarized in table VIII of ref. [12]). In the most recent report, a high-temperature flame result of 58.1(19) kcal mol^{-1} has been given by Steinberg and Schofield [13], consistent with two independent experimental bounds of $D_0(Na–O_2) \geqslant 48$ kcal mol^{-1} [10] and $D_0(Na–O_2) \geqslant 55$ kcal mol^{-1} [11]. In contrast, ab initio work appurtenant to these experimental investigations has provided $D_0(Na–O_2)$ values of 44 kcal mol^{-1} (UMP4/6-311G//UHF/6-311G) [10] and 36 kcal mol^{-1} (UMP2/6-31+G*) [11]. Finally, Schleyer [14] has obtained theoretical results at the 6-311+G* QCISD(T) level which yield $D_0(Na–O_2) = 33$ kcal mol^{-1}.

The highest occupied molecular orbitals of NaO_2 are essentially the in-plane (b_2) and out-of-plane (a_2) π^* orbitals of the O_2^- ion, the degeneracy of these orbitals being removed by the presence of the sodium cation. Thus, the two lowest-lying electronic states of NaO_2 and $\tilde{X}\,^2A_2$ and $\tilde{A}\,^2B_2$ with the respective electronic configurations $(core)^2$ $(4b_2)^2(1a_2)^1$ and $(core)^2(4b_2)^1(1a_2)^2$. The $^2A_2$ and $^2B_2$ states become $^2A''$ and $^2A'$, respectively, in C_s symmetry, and for linear NaOO geometries they correlate to the two components of a $C_{\infty v}$, $^2\Pi$ state. Few investigations have attempted to elucidate features of these potential energy surfaces other than the $^2A_2$ minimum. In his semiemprical study of NaO_2, Alexander [15] predicted that the $^2A''$ surface is quite flat with respect to changes in the Na–O–O angle near linear geometries and that the $^2\Pi$ state lies 19 kcal mol^{-1} above the $^2A_2$ minimum. As for the $^2B_2$ state, Rajasekhar et al. [2] recently predicted the $^2A_2 \to {}^2B_2$ vertical transition energy to be 8.8 kcal mol^{-1} at the 6-31G UHF level.

In summary, more rigorous and comprehensive theoretical results are needed to map out the general features of the potential energy surfaces of the two lowest electronic states of NaO_2 and, in particular, to establish the dissociation energy of NaO_2. In this letter we report on our recent investigations toward this goal.

2. Theoretical methods

Most electronic energies in this study were determined using the Hartree–Fock self-consistent-field (RHF SCF) technique [16] to obtain reference wavefunctions followed by the configuration interaction singles and doubles (CISD) method [17] to treat electron correlation. The sodium and oxygen 1s-like occupied orbitals and their virtual counterparts (three occupied and three virtual orbitals for NaO_2) were excluded in the CISD procedures, which otherwise included all single and double excitations in the Hartree–Fock interacting space. The sodium 2s and 2p orbitals were not frozen in the CI wavefunctions, in part because Langhoff et al. [18] have found that correlating the $n=2$ shell of Na significantly shortens the computed bond length for the diatomic molecule NaO. In some cases, designated CISD+Q, the Davidson correction [9] was appended to the CISD energy to estimate the unlinked cluster contribution from quadruple excitations. Final results for relative energies were obtained using unrestricted Hartree–Fock (UHF) SCF reference wavefunctions [20] and Møller–Plesset perturbation theory through fourth order (UMP2, UMP3, and UMP4(SDTQ)) [21–23], the 1s core and virtual orbitals frozen as before. While spin contamination is not a major concern for the species studied here, the spin-projected counterparts to the UMPn energies, denoted as PUMPn, are also reported [24]. In the cases labeled UMP∞, the exact correlation energy (E_{corr}) within a given one-particle basis set was estimated by extrapolating the UMP series according to the formula [25,26]

$$E_{corr} = \frac{E_2 + E_3}{1 - E_4/E_2}, \qquad (1)$$

where E_n represents the nth-order correction to the electronic energy. All UHF, UMP, and PUMP results were obtained with the GAUSSIAN88 suite of programs [27].

As discussed previously [5], single-configuration SCF wavefunctions for alkali-metal superoxides are prone to symmetry breaking. Reference wavefunc-

tions which do not suffer from this deficiency were constructed using the complete-active-space multi-configuration SCF method (CASSCF) [28] as coded in a version of the Cambridge Analytic Derivatives Package (CADPAC) [29] which implements the wavefunction optimization algorithm of Werner and Knowles [30,31]. The wavefunctions labeled CASSCF-π for $^2A_2$ NaO_2 involved three electrons in an active space comprised of four out-of-plane π orbitals ($1a_2$, $2b_1$, $2a_2$, and $3b_1$), a procedure which was selected to solve the symmetry breaking problem with minimal complexity rather than to treat electron correlation extensively. Because the SCF reference configuration is dominant in these CASSCF-π wavefunctions, dynamical electron correlation is incorporated conveniently via a single-reference CI treatment based on CASSCF-π natural orbitals [5], a method denoted here as CISD-π. Geometric structures and harmonic vibrational frequencies at the various levels of theory were found using either analytic derivative or finite difference methods [32,33]. In all cases the uncertainties in the optimum geometries and harmonic vibrational frequencies were less than 10^{-5} Å and 0.1 cm^{-1}, respectively.

Four one-particle Gaussian basis sets, designated TZ+d, TZP, TZ2P+R, and TZ2P+f+R, were employed in this study. The TZ+d basis is a Na($11s7p/7s5p$) and O($9s5p1d/5s3p1d$) set. The oxygen portion of this basis is identical to that used previously for LiO_2 [5] and is comprised of the Huzinaga–Dunning ($9s5p/5s3p$) set [34,35] augmented with a single set of Cartesian d-type polarization functions with exponent $\alpha_d(O)=0.80$ [36]. The core of the sodium basis was assembled from Huzinaga's $11s$ and $5p$ primitive sets [37] contracted in (5111111) and (311) schemes, respectively. The sodium $3p$ subshell is not well described by the p functions in this basis because they were optimized for the ^2S state of the Na atom. Hence, two sets of p functions were added with exponents $\alpha_p(Na)=0.104631$ and 0.030126, values optimized for the Na ^2P state at the RHF level. The TZP basis was constructed from the TZ+d set by appending to sodium a single set of Cartesian d-type functions with orbital exponent $\alpha_d(Na)=0.20$, as optimized with the RHF method for the $^2A_2$ state of NaO_2 at the TZ+d SCF geometry. The TZ2P+R st is a Na($13s10p2d/7s6p2d$)

and O($11s7p2d/6s4p2d$) basis derived from the Na($12s9p/6s5p$) set of McLean and Chandler [38] and the O($10s6p/5s3p$) set of Dunning [39], both of which are contractions of Huzinaga's primitives [34,37]. To each of these contracted sets, single sets of diffuse s and p functions with $\alpha_s(O)=0.0846$, $\alpha_p(O)=0.0565$, $\alpha_s(Na)=0.0101$, and $\alpha_p(Na)=0.0057$ were added in an even-tempered manner, these being designated as R, or Rydberg, functions. The sets of d-type polarization functions in the TZ2P+R basis involved the exponents $\alpha_d(O)=1.35$ and 0.45 [40] and $\alpha_d(Na)=0.4$ and 0.1, the latter values arising by doubling and halving the corresponding exponent in the TZP basis [41,42]. Finally, the largest basis used in this study, TZ2P+f+R, was constructed from the TZ2P+R set by appending a set of f functions to each atom with $\alpha_f(O)=1.40$ [43] and $\alpha_f(Na)=0.0854$ [18]. In all cases here the sets of d-type functions involved six Cartesian Gaussian components, whereas the sets of f-type functions were comprised of the seven true spherical harmonics alone.

3. Results and discussion

Theoretical results for the total energy, internuclear distances, harmonic vibrational frequencies, and dipole moment of $\tilde{X}$ $^2A_2$ NaO_2 are listed in table 1. The ionic nature of NaO_2 is apparent not only from the large values of the dipole moment, but also from the minuscule differences in the TZ+d and TZP results, i.e. the insensitivity of the predictions to the addition of a set of d-type polarization functions to the cationic sodium center. The data in table 1 are also consistent with the assertion that the O–O bond length in NaO_2 is near the 1.335 Å value proposed previously for LiO_2 [5] and with the observation that the experimental fundamental frequency ν_1 (the O–O stretch) is nearly identical in LiO_2 (1097 cm^{-1}) [43] and NaO_2 (1094 cm^{-1}) [7]. The data encapsulated in table 2 highlight these comparisons further and reveal the structural similarities between the free O_2^- ion and the superoxide moiety in the MO_2 species. The trends in r_e(O–O) and the O–O stretching frequency in going from O_2^- to LiO_2 have been discussed fully in our previous work [5]. The one consistent variation in table 2 for LiO_2 vis-á-vis NaO_2

Table 1
The total energy, internuclear distances, harmonic vibrational frequencies, and dipole moment of $\tilde{X}\,^2A_2$ NaO$_2$ at various levels of theory [a]

Method	Total energy	r_e(Na–O)	r_e(O–O)	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(b_2)$	μ
TZ+d RHF	−311.504032	2.1219	1.2976	1456	442	292 [b]	8.64
TZP RHF	−311.507359	2.1205	1.2973	1456	444	296 [b]	8.41
TZ2P+R RHF	−311.532518	2.1162	1.2872	1435	439	308 [b]	8.40
TZ+d CASSCF-π [d]	−311.532905	2.1233	1.3086	1414	443	362	–
TZ+d CISD	−311.982071	2.1394	1.3401	1281	434	c)	8.55
TZP CISD	−311.987882	2.1362	1.3401	1280	437	c)	8.28
TZ2P+R CISD	−312.046727	2.1273	1.3258	1258	434	c)	8.32
TZ+d CISD-π [d]	−311.981774	2.1393	1.3396	1284	434	364	–
6-311G UHF [e]	–	2.14	1.34	1281	439	275 [b]	8.81
6-31G UHF [e]	–	2.13	1.35	1232	445	244 [b]	6.44
6-31+G* MP2 [f]	–	2.16	1.39	–	–	–	–
experiment [g]	–	2.07	1.33	1094	391	333	–
experiment [h]	–	2.1	1.33	–	–	–	–

[a] Units: energy in hartree, bond distances (r_e) in Å, frequencies (ω_i) in cm^{-1}, and dipole moment (μ) in D.
[b] These values are expected to be anomalously small due to symmetry breaking phenomena. See text and ref. [5].
[c] Unphysical vibrational frequency due to symmetry breaking in reference wavefunction.
[d] Active space for reference wavefunction: three electrons in four orbitals (two a_2 and two b_1).
[e] Refs. [10,12].   [f] Ref. [11].   [g] Refs. [6,7].   [h] Ref. [8].

Table 2
Comparison of O–O bond lengths and bond stretching vibrational frequencies of O$_2^-$, LiO$_2$ and NaO$_2$ [a]

Method	O$_2^-$		LiO$_2$		NaO$_2$	
	r_e(O–O)	ω_e	r_e(O–O)	$\omega_1(a_1)$	r_e(O–O)	$\omega_1(a_1)$
TZ+d RHF	1.2995	1460	1.2944	1455	1.2976	1456
TZ+d CASSCF-π	1.3089	1425	1.3064	1408	1.3086	1414
TZ+d CISD	1.3466	1265	1.3412	1260	1.3401	1281
TZ+d CISD-π	–	–	1.3405	1263	1.3396	1284
proposed values	1.341 [b]	1089 [c]	1.335	–	1.335	–

[a] O$_2^-$ and LiO$_2$ data from ref. [5]; NaO$_2$ data from this work. Units: bond lengths (r_e) in Å and frequencies in cm^{-1}.
[b] Ref. [44].   [c] See footnotes to tables 4 and 5 in ref. [5].

is the shift of ω_1 toward slightly higher values, which is at variance with previous rationalizations based on the Rittner ionic model [45] but in accord with a view of enhanced charge transfer from the π^* orbital of O$_2^-$ to the metal atom M as the size of M increases [5].

The current predictions for the Na–O distance in table 1 lie in the range 2.12–2.14 Å, but these values are expected to be too large due to basis set deficiencies, as found previously for LiO$_2$ [5]. Improved theoretical estimates for the Na–O distance can be obtained by comparing the NaO$_2$ data with the corresponding theoretical bond lengths appear-

ing in table 3 for diatomic NaO. Note that the theoretical ratio $r_{\mathrm{NaO_2}}/r_{\mathrm{NaO}}$ is quite insensitive to basis set and electron correlation, a final value of 1.032 at the TZ2P+R CISD level being accepted here. The most reliable value for the true bond distance in NaO is the 2.033 Å theoretical prediction of Langhoff et al. [18] using a large atomic natural orbital basis and multireference configuration interaction wavefunctions. By multiplying our final $r_{\mathrm{NaO_2}}/r_{\mathrm{NaO}}$ ratio by the bond distance of Langhoff et al., a prediction of r_e(Na–O)=2.098 Å is obtained for NaO$_2$. Thus, we propose 2.10 Å as the Na–O distance in the sodium superoxide radical. Accordingly, the TZ+d CISD

Table 3
The total energy, bond length, and harmonic vibrational frequency of $\tilde{X}\,^2\Pi$ NaO at various levels of theory [a]

Method	Total energy	r_e(Na–O)	ω_e	r_{NaO_2}/r_{NaO}	$\omega_2(NaO_2)/\omega_e(NaO)$
TZ+d RHF	−236.666072	2.0461	515	1.037	0.858
TZP RHF	−236.670192	2.0460	518	1.036	0.857
TZ2P+R RHF	−236.689882	2.0478	511	1.033	0.859
TZ+d CISD [b]	−236.955749	2.0620	500	1.038	0.868
TZ2P+R CISD [b]	−236.999223	2.0606	498	1.032	0.871
ANO MR CI [c]	–	2.033	490	–	–

[a] Units: energy in hartree, bond lengths in Å, and frequencies in cm^{-1}. The NaO_2 data used for comparison are from table 1.

[b] See text, two core and two virtual SCF orbitals frozen in CISD procedure.

[c] Atomic natural orbital multireference configuration interaction results taken from ref. [18]. The ANO basis may be characterized as Na(20s14p6d2f/7s6p4d2f) and O(13s9p6d4f/5s5p2d1f).

r_e(Na–O) distance of 2.1394 Å is approximately 0.04 Å too long, an overestimation which compares favorably to the analogous error of 0.03 Å deduced for LiO_2 [5].

Andrews [6] has analyzed the infrared spectrum of matrix-isolated NaO_2 to find an approximate Na–O bond length. First, an O–O length of 1.33 Å was taken from the X-ray diffraction result of 1.33 ± 0.06 Å [46], and subsequently r_e(Na–O) = 2.07 Å was found using product rule calculations based on a harmonic force field analysis of the observed fundamentals. Similarly, Adrian et al. [8] have extracted the equilibrium Na–O distance from the ESR spectrum of matrix-isolated NaO_2. They also assumed r_e(O–O) = 1.33 Å and calculated Na hyperfine structure splittings for several Na–O distances, finding the best match between observed and calculated splittings for r_e(Na–O) = 2.1 Å. Considering the uncertainty of these experimental estimates, good agreement is found with the structure proposed here, viz. r_e(O–O) = 1.335 Å and r_e(Na–O) = 2.10 Å.

The effect of basis set deficiencies in describing interionic interactions in NaO_2 must also be considered in the prediction of the Na–O stretching frequencies. Once again comparisons with results for diatomic NaO are advantageous; nota bene, the constancy of $\omega_2(NaO_2)/\omega_e(NaO)$ ratio in table 3. However, the ω_e values for NaO at the TZ2P+R CISD and ANO MR CI levels differ by only 8 cm^{-1}, and thus for NaO_2 the TZ2P+R CISD $\omega_2(a_1) = 434$ cm^{-1} prediction in table 1 is seen to be quite accurate without further corrections. Anharmonic contributions of the order of 5 cm^{-1} and matrix shifts perhaps as large as 40 cm^{-1} [5] are likely sources for

much of the remaining disparity with the experimental value of 391 cm^{-1}. For $\omega_2(b_2)$, all values determined at the RHF and UHF levels are expected to be anomalously small and methodologically defective, as suggested in table 1, because the onset of spatial symmetry breaking in the electronic orbitals of these wavefunctions leads to an irremovable singularity in the quadratic force constant for antisymmetric Na–O stretching at nearby geometries in which the O–O distance is slightly elongated. This phenomenon has been fully analyzed in the case of LiO_2 by Allen et al. [5]. In contrast, the CASSCF-π and CISD-π methods are designed to avert the symmetry-breaking dilemma, and the ω_3 predictions of 362 and 364 cm^{-1}, respectively, are in good agreement with the experimental fundamental, especially if effects due to anharmonicity and matrix shifts are considered. It is thus worthwhile to report the TZ+d CISD-π quadratic force constants of $\tilde{X}\,^2A_2$ NaO_2 (in mdyn Å^{-1}) as $F_{11} = 7.759$, $F_{21} = -0.078$, $F_{22} = 0.826$, and $F_{33} = 1.098$, relative to the internal coordinates $S_1 = R(O–O)$, $S_2 = 2^{-1/2}[r(Na–O) + r'(Na–O)]$, and $S_3 = 2^{-1/2}[r(Na–O) - r'(Na–O)]$. The analysis of the experimental fundamentals of matrix-isolated NaO_2 by Andrews [6] provided similar values for the Na–O stretching constants, in particular, $F_{22} = 0.68$ and $F_{33} = 0.92$ mdyn Å^{-1}.

Theoretical data for the $\tilde{A}\,^2B_2$ state are found in table 4. Compared to analogous values for the $^2A_2$ state, the Na–O distance is 0.03–0.04 Å longer, the symmetric Na–O stretching frequency is reduced by 30–40 cm^{-1}, the O–O distance is longer by less than 0.005 Å, and the O–O stretching frequency is lowered by less than 10 cm^{-1}. Similar effects are found

Table 4
The total energy, internuclear distances, harmonic vibrational frequencies, and dipole moment of $\tilde{A}\,^2B_2$ NaO_2 at various levels of theory [a]

Method	Total energy	$r_e(Na-O)$	$r_e(O-O)$	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(b_2)$	μ
TZ+d RHF	−311.489800	2.1612	1.3009	1450	407	114 [b]	8.91
TZP RHF	−311.492955	2.1595	1.3006	1448	407	126 [b]	8.67
TZ+d CISD	−311.967429	2.1659	1.3442	1274	403	c)	8.80

[a] Units: energy in hartree, bond distances (r_e) in Å, frequencies (ω_i) in cm^{-1}, and dipole moment (μ) in D.

[b] As in the case of the $\tilde{X}\,^2A_2$ state, these values are expected to be anomalously small due to symmetry breaking phenomena. See text and ref. [5].

c) Unphysical vibrational frequency due to symmetry breaking in reference wavefunction.

for LiO_2 [5]. These trends are accounted for by the decrease in the electrostatic interaction of the Na^+ and O_2^- ions when the extra electron in O_2^- moves from an in-plane π^* orbital ($^2A_2$ state) to an out-of-plane π^* orbital ($^2B_2$ state). In NaO_2, however, the difference between the $^2B_2$ and $^2A_2$ metal–oxygen bond lengths is approximately half as large as in LiO_2, indicative of a smaller $^2B_2$–$^2A_2$ energy separation in NaO_2. Based on the geometric structure recommended above for $\tilde{X}\,^2A_2$ NaO_2 and comparisons of the data in tables 1 and 4, the final structural predictions which arise for $\tilde{A}\,^2B_2$ NaO_2 are $r_e(O–O) = 1.34$ Å and $r_e(Na–O) = 2.13$ Å.

Table 5 lists theoretical values of the $\tilde{X}\,^2A_2 \rightarrow \tilde{A}\,^2B_2$ adiabatic excitation energy. The highest quality result therein is 8.5 kcal mol^{-1}, the difference in TZ2P+R CISD+Q energies evaluated at the TZ+d CISD geometries. For comparison, Rajasekhar et al.

Table 5
Energies (in kcal mol^{-1}) of the $^2B_2$ and $^2\Pi$ states relative to $\tilde{X}\,^2A_2$ NaO_2.

Method [a]	$^2B_2$	$^2\Pi$
TZ+d RHF	8.9	9.4
TZP RHF	9.0	9.4
TZ2P+R RHF	8.5	9.3
TZ+d CISD	9.2	16.4
TZP CISD	–	16.8
TZ2P+R CISD//TZ+d CISD	8.6	15.7
TZ2P+R CISD+Q//TZ+d CISD	8.5	16.5

[a] The notation "method 1//method 2" indicates that method 1 was applied at the optimum geometry of method 2. Zero-point vibrational corrections are *not* included. Refer to table 1 for the absolute energies of $\tilde{X}\,^2A_2$ NaO_2 at its equilibrium, C_{2v} geometry. Final predictions for the $^2\Pi$–$^2A_2$ separation appear in table 8.

[2] recently found a $^2A_2 \rightarrow ^2B_2$ vertical excitation energy of 8.8 kcal mol^{-1} at the UHF level using a significantly smaller basis set. The small differential correlation energy in the NaO_2 results is also characteristic of LiO_2 [5] and is consistent with the ionic model of bonding between the metal ion and O_2^-. Our $^2B_2$–$^2A_2$ energy splitting of ≈ 8.5 kcal/mol is significantly smaller than the value of $T_e = 16.6$ kcal mol^{-1} for LiO_2 [5], in agreement with the results of Lindsay et al. [9,47], who measured the ESR spectra of matrix-isolated alkali-metal superoxides and concluded that the separation of the highest occupied b_2 and a_2 molecular orbitals decreases monotonically through the series LiO_2–RbO_2. In fact, the ESR data suggest that the $^2B_2$ state is actually lower in energy than the $^2A_2$ state in the case of CsO_2.

Other features of the NaO_2 $\tilde{X}\,^2A_2$ and $\tilde{A}\,^2B_2$ potential energy hypersurfaces are found in tables 5–7. The $^2A_2$ and $^2B_2$ states correlate, via $^2A''$ and $^2A'$ intermediate states, respectively, to the two components of a $^2\Pi$ state at linear Na–O–O geometries. This $^2\Pi$ state is a minimum on both surfaces at the RHF and CISD levels of theory, with Na–O and O–O bond lengths which are shorter than those in the $^2A_2$ state by 0.166 and 0.025 Å, respectively, at the TZP CISD level (cf. tables 1 and 6). The analogous shifts in bond lengths for LiO_2 are very similar, in particular, 0.160 and 0.026 Å [5]. Note that the contraction of the O–O distance and the increase in the O–O stretching frequency for the $^2\Pi$ state is only recovered using correlated levels of theory, indicating a large differential correlation energy effect between the $^2A_2$ and $^2\Pi$ states. Consequently, the $^2\Pi$–$^2A_2$ energy difference in tables 5 is very sensitive to the inclusion of electron correlation. The best result therein,

Table 6
The total energy, internuclear distances, harmonic vibrational frequencies, and dipole moment of $^2\Pi$ NaO$_2$ at various levels of theory [a]

Method	Total energy	r_e(Na-O)	r_e(O-O)	$\omega_1(\sigma)$	$\omega_2(\sigma)$	$\omega_{3a}(\pi)$ [b]	$\omega_{3b}(\pi)$ [b]	μ
TZ+d RHF	−311.489075	1.9585	1.3080	1330	450	77	70	9.69
TZP RHF	−311.492303	1.9546	1.3078	1327	452	92	74	9.51
TZ2P+R RHF	−311.517698	1.9576	1.2956	1308	443	72	60	9.66
TZ+d CISD	−311.955948	1.9771	1.3158	1353	438	58	56	10.07
TZP CISD	−311.961034	1.9699	1.3152	–	–	–	–	9.86

[a] Units: energy in hartree, bond distances (r_e) in Å, frequencies (ω_i) in cm^{-1}, and dipole moment (μ) in D.
[b] The degeneracy of the bending frequencies is removed due to the Renner–Teller effect [48]. Upon Na–O–O bending along the ω_{3a} and ω_{3b} modes, the $^2\Pi$ state correlates to the $\tilde{X}$ $^2A_2$ and $\tilde{A}$ $^2B_2$ surfaces, respectively.

Table 7
Total energies, geometric structures, and vibrational energies of transition states on the $\tilde{X}$ $^2A''$ and $\tilde{A}$ $^2A'$ surfaces of NaO$_2$ at the TZ+d CISD level of theory [a]

	$\tilde{X}$ $^2A''$ ($^2A_2$)	$\tilde{A}$ $^2A'$ ($^2B_2$)
energy	−311.955808	−311.955598
r_e(Na-O)	1.9997	2.0130
r_e(O-O)	1.3185	1.3225
θ (Na-O-O)	155.4	138.3
ω_1(a')	1339	1322
ω_2(a')	432	445
ω_3(a')	77i	66i

[a] Units: energy in hartree, bond distances (r_e) in Å, bond angles (θ) in deg, and frequencies (ω_i) in cm^{-1}.

16.5 kcal mol^{-1} at the TZ2P+R CISD+Q//TZ+d CISD level of theory, is within 1 kcal mol^{-1} of the final value proposed below.

The small vibrational frequencies of the $^2\Pi$ bending modes, ≈ 60 cm^{-1} at the TZ+d CISD level, suggest that the $^2\Pi$ state is only a shallow minimum. This expectation is confirmed by the transition states located on the $\tilde{X}$ $^2A''(^2A_2)$ and $\tilde{A}$ $^2A''(^2B_2)$ surfaces at the TZ+d CISD level of theory (table 7) for Na–O–O angles of 155° and 138°, respectively. The corresponding barrier heights for the rearrangement of linear Na–O–O to a C$_{2v}$ structure are only 0.09 and 0.22 kcal/mol, respectively, on the $\tilde{X}$ $^2A''$ and $\tilde{A}$ $^2A'$ potential surfaces. Alexander's [15] semiempirical $^2A''$ surface essentially agrees with these ab initio results. In comparison, the respective TZP CISD $^2A''$ and $^2A'$ barrier heights for LiO$_2$ are 1.2 and 2.0 kcal mol^{-1}, the transition structures displaying Li–O–O angles of 137° and 105°.

Table 8 details final theoretical data for the dissociation energy of NaO$_2$ and the $^2\Pi$–$^2A_2$ energy separation, all results being determined with the TZ2P+f+R basis set in conjunction with Møller–Plesset perturbation theory. While these predictions are based on UHF reference wavefunctions, all spin contaminations are reasonably small (see footnote c to table 8), and the spin-projected results do not differ significantly from their unprojected counterparts. The effect of the $^2\Pi$–$^2A_2$ differential correlation energy on the corresponding energy separation is quite apparent as ΔE is successively computed at each order of perturbation theory. The UHF value of 10.1 kcal mol^{-1} rises to 19.3 kcal mol^{-1} in second order before falling off to 17.5 kcal mol^{-1} at the UMP4(SDTQ) level. The extrapolation estimate denoted as UMP∞ in table 8 engenders a final proposal of $\Delta E = 17$ kcal mol^{-1}. Previous data for LiO$_2$ [5] show that the $^2\Pi$–$^2A_2$ energy separation is quite insensitive to the one-particle basis set; hence further expansion of the basis is expected to have little effect on the final ΔE predicted for NaO$_2$.

The dissociation energy of NaO$_2$ is one of the central, unresolved questions pertaining to this molecule [10–14]. From a theoretical perspective the dissociation energy of an ionic species MX is best determined using the equation

$$D_0(\text{M-X}) = E(\text{M}^+ + \text{X}^-) - E(\text{MX}, r_e)$$
$$+ \Delta(\text{ZPVE}) - \text{IP}(\text{M, expt}) + \text{EA}(\text{X, expt}), \quad (2)$$

because differential correlation energy effects are essentially eliminated by dissociating to M$^+$ + X$^-$ and then correcting the results with experimental values for the ionization potential (IP) of M and the electron affinity (EA) of X [5,49–51]. In table 8, dis-

Table 8
Final theoretical data (TZ2P+f+R basis) for the dissociation energy of NaO₂ and the ²Π-²A₂ NaO₂ energy separation a)

	$E(\text{Na}^+)$	$E(\text{O}^-)$	$E(\text{O}_2^-)$	$E(\text{NaO, }^2\Pi)$	$E(\text{NaO}_2, {}^2A_2)$	$E(\text{NaO}_2, {}^2\Pi)$	$\Delta E({}^2\Pi-{}^2A_2)$	$D_0(\text{Na-O})$ b)	$D_0(\text{Na-O}_2)$ b)
UHF c)	-161.665177	-74.794130	-149.650522	-236.694853	-311.545475	-311.529412	10.1	62.3	34.8
PUHF d)	-	-74.797775	-149.659225	-236.698038	-311.554002	-311.535265	11.8	62.0	34.7
UMP2	-161.785405	-75.000687	-150.112837	-236.020422	-312.129434	-312.098632	19.3	61.6	35.7
PUMP2 d)	-	-75.003551	-150.119065	-237.022717	-312.135327	-312.102485	20.6	61.2	35.5
UMP3	-161.783856	-75.006681	-150.106504	-237.026650	-312.122872	-312.096818	16.3	62.7	36.5
PUMP3 d)	-	-75.008984	-150.109750	-237.028419	-312.125813	-312.099020	16.8	62.4	36.3
UMP4 (SDTQ)	-161.786951	-75.018105	-150.139743	-237.039997	-312.158197	-312.130312	17.5	62.0	35.9
UMP∞	-161.786992	-75.019124	-150.141828	-237.040834	-312.160049	-312.132293	17.4	61.8	35.7

final proposals: $D_0(\text{Na}+\text{O}_2)=38$ kcal mol⁻¹; $\Delta E({}^2\Pi-{}^2A_2)=17$ kcal mol⁻¹

a) Total energies in hartree; ΔE and D_0 in kcal mol⁻¹. Based on the TZP CISD optimum geometries for NaO and NaO₂ and the experimental bond distance (table 2) for O₂⁻.
b) Determined via eq. (2) as described in the text, which gives (in kcal mol⁻¹) $D_0(\text{Na-O})=D_e(\text{NaO}\rightarrow\text{Na}^++\text{O}^-)-85.47$ and $D_0(\text{Na-O}_2)=D_e(\text{NaO}_2\rightarrow\text{Na}^++\text{O}_2^-)-109.38$.
c) Expectation values of S^2: O⁻, 0.770; O₂⁻, 0.793; NaO, 0.762; (NaO₂, ²A₂), 0.788; and (NaO₂, ²Π), 0.770.
d) Approximations based on the annihilation of the quartet component of the spin-contaminated, doublet wavefunction. See ref. [24].

sociation energies obtained in this manner for both $\tilde{X}\,{}^2\Pi$ NaO and $\tilde{X}\,{}^2A_2$ NaO₂ are reported. Pertinent experimental data are: IP(Na)=5.138 eV [52], EA(O)=1.462 eV [53], and EA(O₂)=0.440 eV [44]. The zero-point vibrational contributions, Δ(ZPVE), to the dissociation energies are based on the experimental fundamental frequencies reported in tables 1 and 2 for NaO₂ and O₂⁻, respectively, and the ANO MR CI ω_e value for NaO in table 3. The near constancy of D_0(Na-O) and D_0(Na-O₂) is striking as the treatment of electron correlation is improved. The main errors in the UMP∞ results (61.8 and 35.7 kcal mol⁻¹ for NaO and NaO₂, respectively) are thus expected to arise from remaining deficiencies in the TZ2P+f+R basis set. From more extensive theoretical investigations of the bond energies of LiO and NaO by Langhoff, Bauschlicher and Partridge [49,50] and previous work on the dissociation energy of LiO₂ by Allen and co-workers [5], a D_0 correction of about +2 kcal mol⁻¹ is warranted for incompleteness of the TZ2P+f+R basis. Therefore, the data in table 8 provide D_0(Na-O)=64 kcal mol⁻¹ and D_0(Na-O₂)=38 kcal mol⁻¹ as final results, the former value being in excellent agreement with the most recent experimental determination of D_0(Na-O)=63.6(10) kcal mol⁻¹ by Steinberg and Schofield [13]. However, for NaO₂ these same authors report a dissociation energy of 58.1(19) kcal mol⁻¹ as found from high-temperature flame studies [13], this value being substantially higher than the corresponding theoretical result determined here. In our view the theoretical value (38 kcal mol⁻¹) cannot be more than a few kcal mol⁻¹ in error based on previous experience [5,49,50] with the methods from which it arises. Therefore, it appears that the dissociation energies obtained from flame studies in the early 1980s by Jensen [3] and Hynes et al. [4] happen to be more accurate than later revisions. In this regard it is worth noting that as in the case of LiO and LiO₂, the theoretical dissociation energies of NaO and NaO₂ are in accord with Herm and Herschbach's [54] (see also ref. [15]) approximation $D_0(\text{M-O}_2)\approx D_0(\text{M-O})-1.0$ eV, lending further credence to a bond energy for NaO₂ near 40 kcal mol⁻¹ as a consequence of the recent experimental results [13] for D_0(Na-O). If the Herm and Herschbach estimate were to hold for the larger superoxides, the dissociation energies of KO₂ and RbO₂

would also lie near 40 kcal mol^{-1}, as indicated by previous theoretical determinations of bond energies for KO and RbO near 65 kcal mol^{-1} [49]. Accordingly, the experimental lower limit of 48 kcal mol^{-1} reported by Plane et al. [12] for $D_0(K-O_2)$ would be subject to revision toward smaller values.

Acknowledgement

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