An *ab initio* study of the ionization of sodium superoxide

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**I. INTRODUCTION**

There is a significant contradiction between determinations of the Na–O₂ bond energy $D_o$ in sodium superoxide. NaO₂ was not detected in studies of the evaporation of sodium oxides with mass-spectrometric probing, an observation which implied $D_o < 112$ kJ mol⁻¹. However, recent flame modeling yielded $D_o \approx 243$ kJ mol⁻¹. Marshall *et al.* determined a lower limit to $D_o$ of 230 kJ mol⁻¹ through kinetic studies of Na + O₂ recombination and speculated that either NaO₂ was not formed in the mass-spectrometer studies for kinetic reasons, or that NaO₂ could not be detected because it might have an unstable positive ion. Very recently, Steinberg and Schofield carefully demonstrated that the mass-spectrometer results can be reconciled with $D_o = 243$ kJ mol⁻¹ on the assumption that initially formed NaO₂⁺ rapidly dissociates to Na⁺ + O₂. This communication demonstrates by *ab initio* calculations that NaO₂⁺ is indeed unstable with respect to dissociation, and fully supports the analysis of Steinberg and Schofield.

**II. METHOD**

Geometries of NaO₂⁺ in its lowest singlet and triplet states were optimized at the Hartree-Fock level using the 6-31G atomic basis set. Plane *et al.* showed this level of calculation gives good agreement with the experimental geometry for neutral NaO₂. Harmonic vibrational frequencies were derived at the minimum energy structures, and then scaled by a standard factor of 0.9. Finally, energies were calculated while incorporating a correction for electron correlation by means of Møller-Plesset fourth-order perturbation theory, at the UMP4SDTQ/6-31G//HF/6-31G level.

**III. RESULTS AND DISCUSSION**

Both NaO₂⁺ and NaO₂⁺ are loosely bound, as reflected by the large Na–O distances and low vibrational frequencies summarized in Table I. For bent C₂v NaO₂⁺ the asymmetric Na–O stretching frequency is very low (below 50 cm⁻¹, Table I) and, indeed, inclusion of polarization functions in the basis set at the HF/6-31G* level yields a C₂v structure instead. NaO₂⁺ is linear at both levels of calculation. The $r_{oo}$ distances and vibrational frequencies in the ions are very close to those for O₂ (see Table I), and the Mulliken charge on Na in both ions is +0.94. This suggests that the ions may be viewed as adducts of Na⁺ to O₂. They are isoelectronic with Ne + O₂ so strong bonding is unlikely.

The energy differences (including zero-point energy) between NaO₂ and NaO₂⁺ yield adiabatic ionization potentials (IPs) to singlet and triplet states of 8.86 and 7.35 eV, respectively. The vertical IPs (neglecting ZPE) are predicted to be 8.40 and 7.16 eV, respectively. In order to estimate the likely uncertainty in these values, $\Delta H$ at 0 K for the process Na⁺ + O₂ → Na⁺ + O₂⁺ was calculated at the MP4/6-31G/\_\_HF/6-31G level to be $-7.48$ eV. The experimental value is $-6.94$ eV. Thus likely errors in the predicted IPs are about ±0.5 eV. The *ab initio* data are illustrated on Fig. 1.

Dissociation of NaO₂⁺ to Na⁺ + O₂ is spin-allowed and the potential energy surface (PES) for this process, assuming a linear geometry is maintained, was examined in more detail. At the HF/6-31G and MP2/6-31G levels dissociation is in fact calculated to be slightly endothermic; no barriers beyond the endothermicity were located. At the MP4/6-31G level a very small barrier to dissociation was located at $r_{NaO₂} \approx 2.75$ Å; this barrier in the electronic PES is only 4 kJ mol⁻¹. Thus NaO₂⁺ will dissociate rapidly.

The conclusions are: (1) The first IP of NaO₂ is estimated to be about 7.35 ± 0.5 eV. (2) Both singlet and triplet NaO₂⁺ are unstable with respect to dissociation to Na⁺ + O₂. (3) There is a negligible barrier to the spin-
TABLE I. Energies obtained with 6-31G basis set.

<table>
<thead>
<tr>
<th>Species</th>
<th>Bond lengths/Å</th>
<th>Frequencies/cm(^{-1})</th>
<th>HF/au(^b)</th>
<th>MP4/au(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>...</td>
<td>...</td>
<td>-161.8414</td>
<td>-161.8414</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>...</td>
<td>...</td>
<td>-161.6593</td>
<td>-161.6593</td>
</tr>
<tr>
<td>O(_2)</td>
<td>(r_{OO} = 1.19)</td>
<td>1497</td>
<td>-149.5458</td>
<td>-140.7838</td>
</tr>
<tr>
<td>O(_2^+)</td>
<td>(r_{OO} = 1.09)</td>
<td>2070</td>
<td>-149.0553</td>
<td>-149.3280</td>
</tr>
<tr>
<td>NaO(_2)</td>
<td>(r_{NO} = 2.13; r_{OO} = 1.35)</td>
<td>220, 401, 1109</td>
<td>-311.4251</td>
<td>-311.6822</td>
</tr>
<tr>
<td>(A_1) NaO(_2^+)</td>
<td>(r_{NO} = 3.51, 2.35; r_{OO} = 1.19)</td>
<td>34, 158, 1606</td>
<td>-311.1323</td>
<td>-311.3567</td>
</tr>
<tr>
<td>(A_1) NaO(_2^+)</td>
<td>(r_{NO} = 2.31; r_{OO} = 1.19)</td>
<td>94, 94, 167, 1591</td>
<td>-311.2186</td>
<td>-311.4124</td>
</tr>
<tr>
<td>(B_1) NaO(_2^+)</td>
<td>...</td>
<td>...</td>
<td>-311.1590</td>
<td>-311.4190</td>
</tr>
</tbody>
</table>

\(^a\)Scaled by a factor of 0.9.
\(^b\)Hartree–Fock energy in Hartrees.
\(^c\)UMP4SDTQ/6-31G//HF/6-31G energy in Hartrees.
\(^d\)Data from Ref. 8.
\(^e\)Calculated at geometry of neutral NaO\(_2\).

allowed dissociation of \(^3\)NaO\(_2^+\). This \textit{ab initio} investigation is therefore in accord with the reanalysis of sodium oxide evaporation by Steinberg and Schofield.\(^5\)

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\(^3\)M. Steinberg and K. Schofield, Joint Conference of the Western States and Japanese Sections of the Combustion Institute, Honolulu, HI, November 1987.
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