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

Paul Marshall
Department of Chemistry, University of North Texas, P. O. Box 5068, Denton, Texas 76203-5068

(Received 15 July 1991; accepted 2 August 1991)

I. INTRODUCTION

There is a significant contradiction between determinations of the Na–O_2 bond energy D_o in sodium superoxide. NaO_2 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}.[1,2] However, recent flame modeling yielded $D_o \approx 243$ kJ mol^{-1}.[3] Marshall *et al.* determined a lower limit to D_o of 230 kJ mol^{-1} through kinetic studies of $Na + O_2$ recombination and speculated that either NaO_2 was not formed in the mass-spectrometer studies for kinetic reasons, or that NaO_2 could not be detected because it might have an unstable positive ion.[4] 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 NaO_2^+ rapidly dissociates to $Na^+ + O_2$.[5] This communication demonstrates by *ab initio* calculations that NaO_2^+ is indeed unstable with respect to dissociation, and fully supports the analysis of Steinberg and Schofield.

II. METHOD

Geometries of NaO_2^+ in its lowest singlet and triplet states were optimized at the Hartree–Fock level using the 6-31G atomic basis set.[6,7] Plane *et al.* showed this level of calculation gives good agreement with the experimental geometry for neutral NaO_2.[8] 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 $^1NaO_2^+$ and $^3NaO_2^+$ are loosely bound, as reflected by the large Na–O distances and low vibrational frequencies summarized in Table I. For bent C_s $^1A_1$ NaO_2^+ 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 C_{2v} structure instead. $^3\Sigma$ NaO_2^+ is linear at both levels of calculation. The r_{OO} distances and vibrational frequencies in the ions are very close to those for O_2 (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 O_2. They are isoelectronic with $Ne + O_2$ so strong bonding is unlikely.

The energy differences (including zero-point energy) between NaO_2 and NaO_2^+ 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, ΔH at 0 K for the process $Na^+ + O_2 \rightarrow Na + O_2^+$ was calculated at the MP4/6-31G//HF/6-31G level to be -7.48 eV. The experimental value is -6.94 eV.[9] Thus likely errors in the predicted IPs are about ± 0.5 eV. The *ab initio* data are illustrated on Fig. 1.

Dissocation of $^3\Sigma$ NaO_2^+ to $Na^+ + O_2$ 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 $r_{NaO} \approx 2.75$ Å; this barrier in the electronic PES is only 4 kJ mol^{-1}. Thus $^3\Sigma$ NaO_2^+ will dissociate rapidly.

The conclusions are: (1) The first IP of NaO_2 is estimated to be about 7.35 ± 0.5 eV. (2) Both singlet and triplet NaO_2^+ are unstable with respect to dissociation to $Na^+ + O_2$. (3) There is a negligible barrier to the spin-

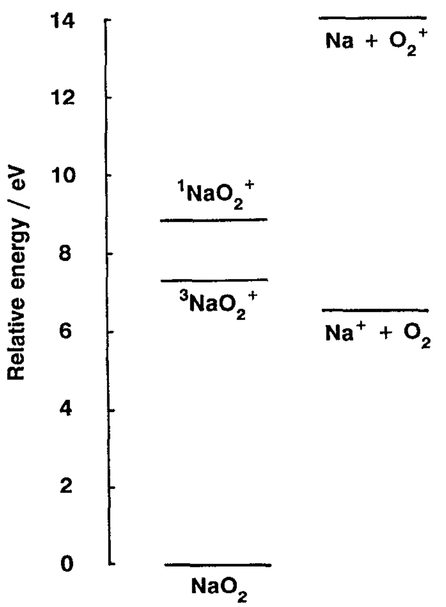

FIG. 1. Relative energies of sodium superoxide, ions and dissociation fragments calculated at the UMP4SDTQ/6-31G//HF/6-31G level.

TABLE I. Energies obtained with 6-31G basis set.

Species	Bond lengths/Å	Frequencies/cm^{-1} [a]	HF/au[b]	MP4/au[c]
Na	···	···	−161.8414	−161.8414
Na^+	···	···	−161.6593	−161.6593 [d]
O_2	$r_{OO} = 1.19$	1592	−149.5458	−149.7838
O_2^+	$r_{OO} = 1.09$	2070	−149.0553	−149.3280
NaO_2	$r_{NaO} = 2.13$; $r_{OO} = 1.35$	220, 401, 1109	−311.4251	−311.6822 [d]
$^1A_1$ NaO_2^+	$r_{NaO} = 3.51, 2.35$; $r_{OO} = 1.19$	34, 158, 1606	−311.1323	−311.3567
$^1A_1$ NaO_2^+	[e]	···	−311.0845	−311.3736
$^3\Sigma$ NaO_2^+	$r_{NaO} = 2.31$; $r_{OO} = 1.19$	94, 94, 167, 1591	−311.2186	−311.4124
$^3B_1$ NaO_2^+	[e]	···	−311.1590	−311.4190

[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 $^3NaO_2^+$. This *ab initio* investigation is therefore in accord with the reanalysis of sodium oxide evaporation by Steinberg and Schofield.[5]

ACKNOWLEDGMENTS

This work was supported by the R. A. Welch Foundation (Grant No. B-1174) and the UNT Organized Research Fund.

[1] D. L. Hildenbrand and E. Murad, J. Chem. Phys. **53**, 3403 (1970).
[2] R. H. Lamoreaux and D. L. Hildenbrand, J. Chem. Phys. Ref. Data **13**, 151 (1984).
[3] M. Steinberg and K. Schofield, Joint Conference of the Western States and Japanese Sections of the Combustion Institute, Honolulu, HI, November 1987.
[4] P. Marshall, A. S. Narayan, and A. Fontijn, J. Phys. Chem. **94**, 2998 (1990).
[5] M. Steinberg and K. Schofield, J. Chem. Phys. **94**, 3901 (1991).
[6] W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, *Ab Initio Molecular Orbital Theory* (Wiley, New York, 1986).
[7] M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. A. Robb, J. S. Binkely, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, and J. A. Pople, GAUSSIAN 90 (Gaussian, Pittsburgh, 1990).
[8] J. M. C. Plane, B. Rajasekhar, and L. Bartolotti, J. Phys. Chem. **93**, 3141 (1989).
[9] M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF Thermochemical Tables*, 3rd ed. [J. Phys. Chem. Ref. Data **14**, Supplement No. 1 (1985)].