# Determination of the Absolute Photolysis Cross Section of Sodium Superoxide at 230 K: Evidence for the Formation of Sodium Tetroxide in the Gas Phase

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The absolute cross section for the photodissociation process  $NaO_2 + h\nu \rightarrow Na + O_2$  has been measured at 230 K by the technique of pulsed excimer laser photolysis of NaO<sub>2</sub> followed by laser-induced fluorescence of the resulting Na fragment, yielding  $\sigma(193 \text{ nm}) = (4.0 \pm 2.1) \times 10^{-18} \text{ cm}^2$ ,  $\sigma(248 \text{ nm}) = (3.9 \pm 2.2) \times 10^{-18} \text{ cm}^2$ , and  $\sigma(308 \text{ nm}) = (1.7 \pm 1.0) \times 10^{-18}$  $cm^2$ . These results are interpreted by ab initio calculations on the excited electronic states of NaO<sub>2</sub> and by reference to the matrix-isolated UV absorption spectrum of NaO2, which indicate that photodissociation occurs via excitation from the ground  ${}^{2}A_{2}$  state to three  ${}^{2}B_{1}$  states, with absorption maxima at 309, 248, and 163 nm. The lowest excited state correlates with Na( ${}^{2}S$ ) + O<sub>2</sub>( ${}^{3}\Sigma_{g}^{-}$ ), and the upper states correlate with Na( ${}^{2}S$ ) + O<sub>2</sub>( ${}^{1}\Delta_{g}$ ). The photodissociation cross section from 150 to 400 nm is derived and employed to calculate a photolysis rate of  $J(NaO_{2}) = (4.8 \pm 2.9) \times 10^{-3} s^{-1}$  in the upper atmosphere above 70 km. The atmospheric significance of this rate is discussed. The experimental study also indicates that another sodium oxide is formed, with a significantly larger cross section at  $\lambda = 248$  nm. We conclude that this is NaO<sub>4</sub>. A discussion of its stability and ab initio calculations of its possible structure are presented.

#### Introduction

Sodium superoxide has been the subject of much experimental<sup>1-9</sup> and theoretical<sup>10,11</sup> interest and is considered to play an important role in the chemistry of sodium in the upper atmosphere.<sup>12-16</sup> Nevertheless, the photochemistry of the molecule has received little attention, apart from a preliminary study by Andrews,<sup>1</sup> who observed the ultraviolet absorption spectrum of NaO<sub>2</sub> ( $\lambda_{max} = 248$ nm) in a matrix isolation study. We believe that the present study is the first investigation of the photolysis of  $NaO_2$  in the gas phase:

$$NaO_2 + h\nu \rightarrow Na + O_2 \tag{1}$$

NaO<sub>2</sub> has been observed by IR,<sup>2,4</sup> Raman,<sup>2,3</sup> and ESR<sup>6</sup> spectroscopy of the molecule formed when Na and O2 are coadsorbed onto an inert gas matrix at low temperatures. This has enabled the force constants and the geometry of the molecule to be ob-

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tained. The formation of NaO<sub>2</sub> in the gas phase has been inferred from the observation that the reaction between Na and  $O_2$  is termolecular, implying a recombination process.<sup>7-9</sup> NaO<sub>2</sub> is known from matrix isolation studies,<sup>2-6</sup> as well as the semiempirical calculations of Alexander<sup>10</sup> and our recent ab initio study,<sup>11</sup> to exist as an ion pair,  $Na^+(O_2)^-$ , in an isosceles triangular  $(C_{2\nu})$  configuration. In the ground  ${}^2A_2$  state of the molecule the alkali-metal outer s electron is almost completely transferred into the  $3\pi$  antibonding orbital of the O<sub>2</sub>.<sup>10,11</sup>

As in the case of our recent study<sup>9</sup> of the gas-phase recombination reaction

$$Na + O_2 + M \rightarrow NaO_2 + M$$
 (2)

a primary motivation for the present work is to understand the chemistry of sodium in the mesosphere. The major source of atmospheric sodium is considered to be meteoritic,<sup>12</sup> and a layer of free atomic Na has been observed a few kilometers wide at an altitude of about 90 km.<sup>13</sup> A number of recent atmospheric models<sup>14-16</sup> have concluded, now that reaction 2 has been demonstrated to be fast,<sup>7-9</sup> that the principal sink for Na immediately beneath this layer is NaO<sub>2</sub>.

An important question arises, however, as to the stability of NaO<sub>2</sub> with respect to photodissociation during the daytime. We have shown recently that the bond energy of  $NaO_2$  is only about 202 kJ mol<sup>-1,11</sup> Thus, if low-lying excited states of  $NaO_2$  exist that are photochemically accessible from the ground state, the molecule could have a photodissociation spectrum well into the visible region ( $\lambda < 590$  nm) and a high rate of photolysis in the mesosphere.

In this paper, the absolute photolysis cross section of NaO<sub>2</sub> is determined at the excimer laser wavelengths 193, 248, and 308 nm. This is followed by a set of ab initio calculations on the four lowest excited states of NaO2 that are spectroscopically accessible from the ground state, computed at the equilibrium geometry of the  ${}^{2}A_{2}$  ground state which we determined previously.<sup>11</sup> This information, combined with the published UV absorption spectra of  $NaO_2$  isolated in an inert gas matrix<sup>1</sup> and  $O_2^-$  isolated in solid NaCl,<sup>17</sup> is then used to estimate the photodissociation cross section from 150 to 400 nm, and hence the photolysis rate in the meso-

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sphere. Finally, experimental evidence for the formation of NaO<sub>4</sub> is discussed and a theoretical calculation of a possible structure is presented.

#### **Experimental Measurements**

Absolute photolysis cross sections were determined by the technique of pulsed excimer laser photolysis of NaO<sub>2</sub> followed by laser-induced fluorescence (LIF) of the resulting Na atoms. The NaO<sub>2</sub> was made in situ through reaction 2 by flowing together Na vapor and  $O_2$ . The pulsed laser/laser-induced fluorescence technique is based on that of Silver et al.<sup>18</sup> The principle is now described. Invoking the Beer-Lambert law in the limit of low light absorption, the expression for the photolysis laser photon flux per pulse which is absorbed and leads to photolysis of NaO<sub>2</sub> at wavelength  $\lambda$ ,  $I_{abs}(\lambda)$ , reduces to

$$I_{abs}(\lambda) = I_0(\lambda)\sigma(\lambda)[NaO_2]l$$
(3)

where  $I_0(\lambda)$  is the incident laser flux per pulse,  $\sigma(\lambda)$  is the absolute photolysis cross section at wavelength  $\lambda$ , and l is the path length over which the absorption occurs.  $I_{abs}/l$  is equal to the concentration of nascent Na atoms created by the pulse, which is in turn proportional to the measured LIF signal,  $I_{\rm fp}$ , when the probe laser is triggered. In the absence of  $O_2$  the measured LIF signal,  $I_{fo}$ , will be proportional to the total Na atom concentration, equivalent to the concentration of  $NaO_2$  after titrating with  $O_2$ . In fact, a small correction arises because of the different diffusivities of Na and NaO<sub>2</sub>, which thus have slightly different loss rates through deposition on the walls of the reaction chamber. Since  $I_{\rm fn}$  and  $I_{\rm fo}$  are measured with the same geometrical light collection factor and detection sensitivity, it follows that

$$I_{\rm fp}/I_{\rm fo} = (I_{\rm abs}(\lambda)/l)/[\rm NaO_2] = \sigma(\lambda)I_0(\lambda)$$
(4)

Thus,  $\sigma(\lambda)$  can be determined absolutely by measuring the ratio  $I_{\rm fp}/I_{\rm fo}$  and monitoring  $I_0(\lambda)$ .

The experimental system used for this study has been described in detail elsewhere.<sup>19-21</sup> Figure 1 is a schematic showing the modifications required for the present study. Briefly, the stainless steel reactor consists of a central cylindrical reaction chamber at the intersection of two sets of horizontal arms which cross orthogonally. These arms provide the optical coupling of the lasers to the central chamber where the  $NaO_2$  is photolyzed, as well as the means by which the flows of the reagents and the bath gas enter the chamber. The central chamber is enclosed in a cryogenic compartment which was filled with powdered "dry ice" to cool the chamber to 230 K. The temperature of the gases flowing through the reactor was monitored by a thermocouple permanently inserted into the chamber about 1 cm below the path of the laser beams. Because of the importance of this study to the chemistry of meteoritic sodium in the atmosphere, the photolysis cross sections were all measured at this temperature.

One of the side arms of the central chamber was independently heated to act as a source of atomic sodium vapor. A second thermocouple was inserted directly into this side arm in order to measure the temperature of this heat pipe precisely (Figure 1). A spiral wick of stainless steel mesh (gauge 150) was inserted into the heat pipe which was first run in the heat pipe oven mode<sup>9,21,22</sup> to purify the sample of Na metal. The Na vapor was then entrained in a flow of He  $(f_1)$  and carried into the central chamber where it was mixed with a flow of  $O_2/He(f_2)$ , producing NaO<sub>2</sub> through reaction 2. The temperature of the heat pipe was usually set at 570 K (and controlled to within  $\pm 2$  K), where the equilibrium Na vapor concentration is  $2.1 \times 10^{14}$  cm<sup>-3</sup>,<sup>23</sup> though we



Figure 1. Schematic of the experimental system used to determine the absolute photolysis cross section of NaO<sub>2</sub>: B, scattered light baffle; C, cryogenic compartment; E, Suprasil end window set at the Brewster angle; F, furnace around the heat pipe;  $f_1$  = flow of He;  $f_2$  = flow of He or O<sub>2</sub>(CO)/He; P, photomultiplier tube; T1, thermocouple in the central chamber; T2, thermocouple in the heat pipe.

have estimated<sup>19</sup> that less than 0.005% of this would have reached the central chamber because of condensation on the cool walls of the heat pipe adjacent to the central chamber.

A vertical side arm on the reaction chamber provides the coupling for the photomultiplier tube (Thorn EMI Gencom Inc., Model 9816QB) which monitored the LIF signal. This signal was captured with a gated integrator (Stanford Research Systems, SR250) interfaced to a microcomputer. The Na atoms were selectively pumped on one of the D-lines at  $\lambda = 589.0$  nm (Na- $(3^{2}P_{3/2})$ -Na $(3^{2}S_{1/2})$ ) by a nitrogen-pumped dye laser (Laser Science Inc., Model VSL-337; laser dye Rhodamine 6G, bandwidth  $\approx 0.01$  nm). Only nonresonant LIF was then measured at  $\lambda = 589.6$  mn (Na( $3^2P_{1/2}$ )-Na( $3^2S_{1/2}$ )) by placing a very narrow band interference filter (Janos Corp.; maximum transmission = 589.6 nm, fwhm = 0.2 nm) in front of the photomultiplier tube. This procedure greatly reduced scattered laser light and improves the detection sensitivity significantly.

An excimer laser (Lambda Physik Model EMB 201/204) was employed as the photolysis source at  $\lambda = 193$ , 248, and 308 nm. This was beam-steered from a remote laboratory into the reactor, passing through a pair of Suprasil windows set at the Brewster angle. An iris placed before the first window was used to accurately shape the center of the beam to a cylinder of diameter 0.5 cm. The laser photon flux  $I_0(\lambda)$  was determined with a new factory-calibrated pyroelectric joulemeter (Molectron, Model J3-05) which was temporarily positioned in front of the dye laser to measure the beam pulse emerging from the reaction chamber. A correction was then applied for scattering losses from the second

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TABLE I: Absolute Photolysis Cross Sections of NaO<sub>2</sub>

wavelength/nm	cross section/ 10 <sup>-18</sup> cm <sup>2</sup>	sample size	laser energy/ mJ cm <sup>-2</sup>
193	$4.0 \pm 2.1$	22	0.4-1.2
248	$3.9 \pm 2.0$	16	2.1-4.9
308	$1.7 \pm 1.0$	9	0.3-1.2

window in order to determine the photon flux per pulse in the photolysis region of the reactor. In these experiments the excimer and dye lasers were arranged to be collinear (Figure 1), with the dye laser protected from the excimer beam by a dichroic filter (Newport Corp., Model 10QM20HL1). The diameter of the dye laser was carefully maintained to be  $\approx 80\%$  that of the excimer using a beam expander and iris.

The timing of the experiment was controlled by a pulse delay generator (Stanford Research Systems, Model DG535). Since the nascent Na atoms produced in the excimer pulse are in a large excess of  $O_2$ , it is essential to trigger the probe laser with minimal delay to avoid loss of Na through reaction 2, which would lead to an underestimation of the photolysis cross section. Under the typical conditions in this study ( $[O_2] = 2 \times 10^{15}$  cm<sup>-3</sup>, [He] =  $3 \times 10^{17}$  cm<sup>-3</sup>) and with  $k_2(230 \text{ K}) = 1.3 \times 10^{-30}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>,<sup>9</sup> the delay of 4  $\mu$ s which was adopted corresponds to a loss of <1% of the nascent Na.

To determine an absolute cross section, the following procedure was employed. First, the Na/He flow  $(f_1 = 100 \text{ sccm})$  was switched on and mixed with a flow of pure He ( $f_2 = 50$  sccm), and the value of  $I_{fo}$  was determined by averaging  $10^3$  dye laser pulses. The Na flow was then titrated with  $O_2$  by mixing into flow  $f_2$  a mixture of  $O_2/He$  but keeping the total  $f_2$  constant at 50 sccm. This ensured that the ratio of the flows and their mixing pattern in the central chamber were maintained. The O<sub>2</sub> concentration was raised in the reactor until the Na atom concentration was reduced by a factor of more than  $10^3$ . The base line signal was then measured by averaging a further 10<sup>3</sup> laser shots. This base line takes account of any residual atomic Na and the scattered laser light signal being slightly offset from zero. Finally, the excimer laser was turned on to photolyze the NaO<sub>2</sub>, and  $I_{fp}$ was measured from the average of a further 10<sup>3</sup> pulses and corrected if the base line was not zero. The laser photon flux,  $I_0(\lambda)$ , was measured before and after determining  $I_{\rm fp}/I_{\rm fo}$ . The cross section,  $\sigma(\lambda)$ , then followed from eq 4.

Materials. Oxygen (Liquid Carbonic, 99.995%) was trapped at 77 K before use. Helium (Matheson, 99.9999%, "Matheson Purity") was used without further purification. Carbon monoxide (Matheson, 99.5% minimum purity) was first trapped in 15X molecular sieve at 77 K to remove metal carbonyls. Sodium metal spheres (Aesar/Johnson Matthey) were cleaned with solvent and then refluxed in the heat pipe oven for several hours before use.

#### **Results and Discussion**

The photolysis cross sections at  $\lambda = 193$ , 248, and 308 nm are listed in Table I. This table also records the number of determinations of the cross section from which the mean cross section and standard deviation were derived and the range of laser energy fluxes at each wavelength. These measurements were all made with a total pressure in the reactor of between 5 and 12 Torr (the significance of this is discussed below). The uncertainties in the measurements, reflected by the standard deviations, are probably caused by the combination of the relatively small cross sections and the modest excimer laser energy fluxes which resulted from the unavoidable physical separation of the excimer laser from the reactor. In view of these uncertainties, corrections for differences in the diffusion rates of Na and NaO<sub>2</sub> are not included, since this is a minor effect.<sup>18</sup>

While examining possible systematic errors in this experimental procedure, we demonstrated that the measured cross section was unchanged as the total Na concentration entering the central chamber was varied by a factor of about 5, which was achieved by varying the temperature of the heat pipe. However, when the total pressure in the reactor was raised to between 12 and 20 Torr,  $\sigma(248 \text{ nm})$  increased significantly, as shown in Table II. By

TABLE II: Absolute Photolysis Cross Sections of  $NaO_4/NaO_2$  at High Reactor Pressures

wavelength/nm	cross section/10 <sup>-18</sup> cm <sup>2</sup>	sample size	
193	$2.6 \pm 1.8$	5	
248	$15.2 \pm 0.9$	20	
308	$2.1 \pm 2.0$	5	

contrast,  $\sigma(193 \text{ nm})$  and  $\sigma(308 \text{ nm})$  showed only a slight decrease and increase, respectively. Thus, this observation is not the result of an experimental artifact and most probably results from the formation of another sodium oxide under these conditions. The higher total pressure in the reactor extends the reaction time of the gas mixture in the reactor and, by raising  $[O_2]$  and [He], increases the rate of further recombination reactions. Since the concentration of  $NaO_2$  in the reactor is less than  $10^{11}$  cm<sup>-3</sup>, the clustering of NaO<sub>2</sub> molecules to form species such as the peroxide,  $Na_2O_2$ , will be too slow. The most likely explanation is the recombination between  $NaO_2$  and  $O_2$  to form  $NaO_4$ . The ancillary evidence for this is presented at the end of this paper. Within the uncertainty of the low-pressure measurements, the cross sections did not show any significant trend when the total pressure was varied between 5 and 12 Torr, and we believe that under these conditions of short residence times and slow recombination rates the formation of further oxides beyond the superoxide is limited and that the cross sections listed in Table I describe the photolysis of NaO<sub>2</sub>. The standard deviation in the measurement at each wavelength is then assumed to be the standard error in the cross section.

Further experiments were carried out using a xenon flash lamp with a 320-nm short wavelength cutoff filter, which established that negligible photolysis occurs at longer wavelengths. We also investigated the possible production of Na(<sup>2</sup>P) as a photofragment but failed to observe D-line emission at  $\lambda = 589.6$  nm when the dye laser was switched off. Finally, we tested for NaO produced by the alternative photodissociation pathway:

$$NaO_2 + h\nu \rightarrow NaO + O$$
 (5)

A large concentration of CO ( $\approx 4 \times 10^{15}$  cm<sup>-3</sup>) was added to the mixture in the reactor. This would be expected<sup>25</sup> to react in less than about 20  $\mu$ s with any NaO formed during the excimer pulse:

$$NaO + CO \rightarrow Na(^{2}P,^{2}S) + CO_{2}$$
 (6)

The resulting Na( $^{2}P$ ) would then be detected by D-line emission with the probe laser off. Furthermore, the total Na produced in reaction 6 would be in addition to that formed by reaction 1 and result in an increase in the measured cross section with the probe laser on. However, neither of these effects was observed at 193 or 248 nm, so that reaction 5 does not appear to be significant above 190 nm. It should be noted that this test for reaction 5 does rely on the absence of possible reactions between NaO<sub>2</sub> and CO:

$$NaO_2 + CO \rightarrow NaO + CO_2$$
 (7)

or

$$NaO_2 + CO + He \rightarrow NaCO_3 + He$$
 (8)

Reaction 7 would recycle NaO<sub>2</sub> back to Na via reaction 6 and would prevent complete titration of Na in the presence of O<sub>2</sub> and CO under the conditions of this study.<sup>25</sup> Thus, reaction 7 must be very slow,  $k_7 < 10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. While reaction 8 cannot be ruled out, it would be rather a coincidence if NaO<sub>2</sub> and NaCO<sub>3</sub> had similar cross sections at both 193 and 248 nm.

# Theoretical Calculations on the Excited States of NaO<sub>2</sub>

The ground-state  ${}^{2}A''$  surface of NaO<sub>2</sub> contains two minima, corresponding to a linear A–O–O molecule ( $C_{wv}$ ) and to an isosceles triangular geometry ( $C_{2v}$ ). Our recent ab initio study<sup>11</sup> and the semiempirical study of Alexander<sup>10</sup> have demonstrated that the absolute energy minimum corresponds to the  ${}^{2}A_{2}$  surface

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	Mu	Illiken electron population	<i>E</i> (HF/6-31G)/	vertical	corresponding
state	te $q_{\rm Na}$	<i>q</i> o	hartrees	energy/kJ mol <sup>-1</sup>	wavelength/nm
<sup>2</sup> A	2 0.74	-0.37	-311.42506		
<sup>2</sup> B	0.84	-0.42	-311.41103	36.8 (E <sub>1</sub> )	3250
<sup>2</sup> B	-0.02	0.01	-311.391 90	$387.1 (E_2)^a$	309ª
<sup>2</sup> B	0.85	-0.43	-311.19165	619.7 (E <sub>1</sub> )	193
<sup>2</sup> B	-0.02	0.01	-311.18649	733.7 (E <sub>4</sub> ) <sup>a</sup>	163ª

<sup>a</sup> Calculated with respect to Na(<sup>2</sup>S) + O<sub>2</sub>(<sup>3</sup>Σ<sub>a</sub><sup>-</sup>), E(HF/6-31G) = -311.3871 hartrees, and  $D_0(Na-O_2) = 202$  kJ mol<sup>-1.11</sup>





b) Molecular Orbitals and Allowed Spectroscopic Transitions





Figure 2. Qualitative molecular orbital diagram of NaO<sub>2</sub>: (a) molecular geometry and axis definition under  $C_{2\nu}$  symmetry; (b) molecular orbitals and allowed spectroscopic transitions, which are indicated E1–E4. Molecular orbitals which correlate with those of  $O_2^{-}(^2\Pi_g)$  are indicated parenthetically.

in  $C_{2\nu}$  geometry. The molecular orbitals of the <sup>2</sup>A<sub>2</sub> state<sup>11</sup> are illustrated qualitatively in Figure 2. There is strong experimental<sup>1-6</sup> and theoretical<sup>10,11</sup> evidence that this state is predominantly ionic, and so the occupied molecular orbitals are essentially those of O<sub>2</sub><sup>-</sup>. In Figure 2, the MOs that correlate with O<sub>2</sub><sup>-</sup> (or O<sub>2</sub>) are labeled accordingly.

Very little is known about the excited states of NaO<sub>2</sub>. Alexander<sup>10</sup> has tabulated the states of NaO<sub>2</sub> that will arise from combining the neutral and ionic ground/excited states of Na and O<sub>2</sub>. In this study, we consider only those excited states of the molecule to which there is an allowed transition from the <sup>2</sup>A<sub>2</sub> ground state, under the group selection rules of  $C_{2v}$  symmetry.<sup>24</sup> The first four such transitions are illustrated in Figure 2.

We have carried out Hartree–Fock (HF) calculations on each of these states, using the standard split-valence 6-31G basis set available within the GAUSSIAN 86 set of programs.<sup>26</sup> We found previously<sup>11</sup> that an SCF optimization on the <sup>2</sup>A<sub>2</sub> ground state of NaO<sub>2</sub> using this basis set produced a geometry and set of vibrational frequencies in very good agreement with experiment. The present calculations were performed at the geometry of the ground state that we determined in that study.<sup>11</sup> The results of

the calculations are listed in Table III, together with the ground state for comparison. Included in Table III are the Mulliken charges on the Na and O atomic centers for each of the five states. The energy differences between the ground and excited states therefore correspond to the vertical spectroscopic transitions. The  ${}^{2}B_{2}$  and the second  ${}^{2}B_{1}$  state are ionic. Their energies with respect to the  ${}^{2}A_{2}$  state (i.e.,  $E_{1}$  and  $E_{3}$ ) were calculated by simple difference of the HF energies. The  ${}^{2}B_{2}$  is only 3073 cm<sup>-1</sup> above the ground state, in excellent agreement with an experimental value of 2770 cm<sup>-1</sup> determined by ESR spectroscopy on matrix-isolated  $NaO_2$ .<sup>6</sup> The second <sup>2</sup>B<sub>1</sub> state, designated as transition E<sub>3</sub> in Figure 2, corresponds to a  $\pi_u$  to  $\pi_g^*$  transition in O<sub>2</sub><sup>-</sup>. Indeed, this is the transition assigned by Andrews<sup>1</sup> to the absorption peak at 248 nm in matrix-isolated NaO<sub>2</sub>, virtually unchanged from the O<sub>2</sub>absorption at 248 nm in solid NaCl and KCl.<sup>1,17</sup> In Table III it will be seen that the calculated  $E_3$  in this study corresponds to  $\lambda$  = 193 nm. This is reasonably close considering that these calculations do not include correlation energy effects.

The first and third <sup>2</sup>B<sub>1</sub> states are clearly covalent (see Table III). In order to calculate their energies with respect to the <sup>2</sup>A<sub>2</sub> state (i.e., E<sub>2</sub> and E<sub>4</sub>), we have constructed an isogyric cycle<sup>11,27,28</sup> to increase the likelihood of cancellation of electron correlation. Thus, the energies of these states are determined with respect to the HF energies of the neutral fragments, and our recent bond energy  $D_0(Na-O_2)^{11}$  is used to obtain the energy with respect to  $NaO_2(^2A_2)$ . Inspection of Figure 2 indicates that an excitation of the Na 3s electron from the b<sub>2</sub> to a virtual a<sub>1</sub> orbital produces the lowest <sup>2</sup>B<sub>1</sub> state, and this correlates with  $Na(^2S) + O_2(^{3}Z_g^{-})$ . This transition occurs at  $\lambda = 309$  nm. The third <sup>2</sup>B<sub>1</sub> state involves an excitation from the a<sub>2</sub> to a virtual b<sub>1</sub> orbital, correlating with  $Na(^2S) + O_2(^{1}\Delta_g)$ , and corresponds to an absorption at  $\lambda = 163$  nm.

#### Construction of the Photodissociation Spectrum of NaO<sub>2</sub>

We have measured the photodissociation cross section of NaO<sub>2</sub> at three discrete wavelengths. We now proceed to assemble a spectrum by combining this information with the theoretical calculations described above. Although this is an imprecise procedure, an immediate consideration is to estimate the photolysis rate of NaO<sub>2</sub> in the mesosphere and assess its significance. Figure 3 is a correlation diagram illustrating the relationship between the electronic states of NaO<sub>2</sub> that were considered above. The vertical energies of the excited states above the  ${}^{2}A_{2}$  minimum are the theoretical values listed in Table III. The absolute energies between the fragments on the right-hand side of Figure 3 which correlate with these states of  $NaO_2$  are obtained from ref 1, 11, 17, and 24. The curves correlating the states of  $NaO_2$  to the fragments are qualitative but serve an illustrative purpose. The evidence that the second  ${}^{2}B_{1}$  state, correlating with Na<sup>+</sup>( ${}^{1}S$ ) +  $O_2^{-}(^2\Pi_u)$ , is bound and displaced from the minimum of the  $^2A_2$ state comes from a study of the absorption and fluorescence spectra of O<sub>2</sub><sup>-</sup> trapped in salt crystals.<sup>1,17</sup> Clearly, in the case of NaO<sub>2</sub> it must undergo an avoided crossing with the third  ${}^2B_1$  state, as illustrated. This means that the second  ${}^{2}B_{1}$  state will correlate adiabatically with Na(<sup>2</sup>S) + O<sub>2</sub>(<sup>1</sup> $\Delta_g$ ). Thus, absorption in the broad band centered at 248 nm, which has been observed in

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**Figure 3.** Potential energy diagram for the first five states of NaO<sub>2</sub> in the  $C_{2\nu}$  configuration. The relative energies of the states at the ground-state minimum and of the dissociated fragments are known from experiment or calculation (see text). The avoided crossing between the second and third <sup>2</sup>B<sub>1</sub> states is circled.

matrix-isolated NaO<sub>2</sub> and corresponds to a  $\pi$ - $\pi$ \* transition in O<sub>2</sub><sup>-1</sup> will lead to photodissociation provided that the probability of an adiabatic transition is reasonably high. This probability, which may be estimated by the Landau-Zener formalism,<sup>29</sup> becomes large if the velocity of the recoiling fragments is small as they move through the crossing region. This will probably apply here since the vertical transition to the second <sup>2</sup>B<sub>1</sub> state and the curve crossing have similar energies (Figure 3). By contrast, a transition to the third <sup>2</sup>B<sub>1</sub> state, which is much higher in energy, will leave the system with a high recoil velocity at the crossing point. In this case, a nonadiabatic transition to the lowest <sup>2</sup>B<sub>1</sub> state will result in straight dissociation to Na(<sup>1</sup>S) + O<sub>2</sub>(<sup>3</sup>\Sigma<sub>g</sub><sup>-</sup>).

Thus, three absorption maxima are expected in the photodissociation spectrum. The middle peak, which in the remaining discussion is considered to be centered at the experimental wavelength<sup>1,17</sup> of 248 nm, will have the same shape as that observed in the studies of Andrews<sup>1</sup> and Rolfe et al.<sup>17</sup> We have fitted a peak with the same half-width as in those studies to the present measured  $\sigma(248 \text{ nm})$ , as shown in Figure 4. The peak centered at 163 nm, which is in a spectral region obscured in the UV absorption study of Andrews,<sup>1</sup> was therefore arbitrarily fitted with the same half-width to the measured  $\sigma(193 \text{ nm})$  in the present study. Note that this absorption peak has very little influence on the photolysis rate because of the relatively small solar flux at  $\lambda < 200 \text{ nm}.^{30}$  The surface of the lowest  ${}^2B_1$  state will be much flatter in the region vertically above the  ${}^{2}A_{2}$  minimum (Figure 3), and the corresponding spectral peak has therefore been fitted by a peak with a narrower half-width, by analogy with the NaCl(A-X) transition at 260 nm.<sup>18</sup> By coincidence, the three excimer laser lines occur at appropriate wavelengths for this fitting procedure. The overall photodissociation spectrum is illustrated in Figure 4.



Figure 4. The photodissociation spectrum of NaO<sub>2</sub> from 150 to 400 nm. The three absorption peaks are indicated as follows:  $(--) \lambda_{max} = 309$  nm;  $(--) \lambda_{max} = 248$  nm;  $(--) \lambda_{max} = 163$  nm. The overall spectrum is the solid line. The experimental points from the present study are illustrated at  $\lambda = 193$ , 248, and 308 nm.



Figure 5. The vertical profile of the major first-order formation and loss rates of NaO<sub>2</sub> at noon in the upper atmosphere, illustrating the significance of  $J(NaO_2)$ . T = 200 K;  $k(Na+O_2+N_2) = 4.7 \times 10^{-30}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>;  $k(NaO+O) = 1 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>; the midday O atom profile is taken from ref 15.

## Calculation of the Mesospheric Photolysis Rate

The photolysis rate may now be calculated by convoluting the photodissociation spectrum in Figure 4 with the measured spectrum of solar intensity on the edge of the atmosphere from 150 to 400 nm.<sup>30</sup> This yields a photolysis rate of  $J(NaO_2) = (4.8 \pm 2.8) \times 10^{-3} s^{-1}$ . The stated error includes the uncertainties in the cross sections measured in the present study (Table I). This rate applies down to altitudes of about 70 km, since atmospheric absorption at higher altitudes by O<sub>2</sub> in the Schumann-Runge bands only affects wavelengths below 190 nm where the solar intensity is much weaker.<sup>30</sup> It should be noted that a value of  $J(NaO_2) \approx 8 \times 10^{-3} s^{-1}$  is obtained by putting a smooth curve through the three measured values of  $\sigma(\lambda)$  to generate a crude photodissociation spectrum. This value is at the upper uncertainty limit of our present estimate using the synthetic spectrum in Figure 4.

In order to assess the importance of  $J(NaO_2)$  on the mesospheric chemistry of Na, Figure 5 illustrates a comparison between this rate  $(J(NaO_2) = 4.8 \times 10^{-3} \text{ s}^{-1})$  from 70 to 100 km with the rate of formation of NaO<sub>2</sub> (i.e., reaction 2,  $k_2(200 \text{ K}) = 4.7 \times 10^{-30}$ cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>)<sup>9</sup> and the postulated rate of chemical loss through reaction by O atoms:

$$NaO_2 + O \rightarrow NaO + O_2$$
 (9)

Recent models of Na chemistry<sup>14-16</sup> have concluded that the rate constant for reaction 9 lies in the range  $k_9(200 \text{ K}) = 10^{-14}-10^{-13} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>. Other reactions of NaO<sub>2</sub>, such as with H atoms, are not included since their rate constants are unknown and current models indicate that they are of less importance than reaction 9.<sup>15</sup> Using the higher value for  $k_9$ , Figure 5 indicates that above 85 km this reaction will become a more important loss

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Figure 6. The relative photodissociation spectrum tentatively assigned to NaO<sub>4</sub> from 220 to 400 nm. The solid line is the absorption spectrum of NaO<sub>4</sub> in a matrix-isolation study (ref 1), fitted to the experimental cross sections at 248 and 308 nm.

term for  $NaO_2$  than daytime photolysis. (The daytime O atom density profile is taken from ref 15.) However, between 80 and 65 km where the O atom concentration falls off by more than an order of magnitude,<sup>15</sup> the photolysis of NaO<sub>2</sub> is the dominant loss term. NaO<sub>2</sub> will still be in excess over Na, as the formation rate via reaction 2 greatly exceeds  $J(NaO_2)$  below 85 km. However, the daytime photolysis should produce a marked diurnal maximum in the layer of atomic Na below 85 km. This diurnal variation will be much greater than that caused by reaction 9 when the O atom concentration below 85 km decays at night.<sup>15</sup> In fact, a midday maximum in the lower part of the Na layer is consistent with the recent lidar (laser radar) study of Clemesha et al.,<sup>31</sup> who observed such a maximum below 82 km in the early afternoon.

# The Formation of NaO<sub>4</sub> in the Gas Phase

The sodium tetroxide molecule, NaO<sub>4</sub>, has been identified in matrix experiments from its IR, Raman, and ESR spectra.<sup>2-4,6</sup> And rews<sup>1</sup> assigned NaO<sub>4</sub> a UV absorption maximum at  $\lambda = 270$ nm in a matrix study where NaO<sub>4</sub> was formed from the reaction between  $NaO_2$  and  $O_2$ . The large cross section at 248 nm measured in the present system under high-pressure conditions (see Table II) is consistent with the absorption peak of NaO<sub>4</sub> assigned by Andrews.<sup>1</sup> Figure 6 shows a satisfactory fit of that absorption peak shape to our cross section measurements at 248 and 308 nm. Note that the absorption spectrum of NaO<sub>4</sub> below 210 nm in the matrix study<sup>1</sup> was obscured so that the shape of the spectrum in the region of 193 nm is unknown. And rews<sup>1</sup> observed that  $NaO_4$ photolyzed much more readily than NaO<sub>2</sub>, which is also consistent with the much larger cross section observed in this study under conditions where NaO<sub>4</sub> is likely to form. It must be stressed, however, that the  $NaO_4$  cross sections listed in Table II are only limits: our current experimental system is not suitable for determining the extent of the conversion of  $NaO_2$  to  $NaO_4$ , which may be restricted thermodynamically at 230 K or limited kinetically by the concentrations of  $O_2$  and He and the residence time in the present reactor. Thus,  $\sigma(248 \text{ nm})$  in Table II is almost certainly a lower limit.

The structure of NaO<sub>4</sub> has not been completely resolved from the matrix isolation studies<sup>2-4,6</sup> although most evidence points to an  $(O_2-O_2)^-$  entity in the cis or trans conformation, with a Na<sup>+</sup> counterion. We have therefore carried out an ab initio geometry optimization of NaO<sub>4</sub> at the Hartree-Fock level. The structure shown in Figure 7 was obtained by using the 6-31G\* basis set. Less flexible basis sets, which do not include d orbitals on the atoms to add polarization, failed to yield an optimized structure. At this level of theory we did not find a stable minimum for other





Figure 7. The optimized geometry (HF/6-31G\*) of ground-state  $NaO_4(^2A_2)$ . The Mulliken electron populations are indicated as a signed number adjacent to each atomic center.

structures of NaO<sub>4</sub> that have been postulated previously,<sup>2-4</sup> including a disuperoxide  $(O_2NaO_2)$  and  $Na^+(trans-O_4)^-$ . The  $NaO_4(^2A_2)$  ground-state structure in Figure 7 illustrates the Mulliken charges on the atoms in the five-membered ring structure. The molecule is clearly ionic,  $Na^+(cis-O_4)^-$ . In contrast to the most recent ESR studies on NaO4,6 which concluded that  $r(O_2-O_2) \ge 1.8$  Å, the ab initio calculations yield  $r(O_2-O_2) =$ 1.3 Å, implying a stronger bond between the  $O_2$  moieties. It may be that the matrix-isolated  $NaO_4$  has a different structure from  $NaO_4$  in the gas phase. Indeed, Lindsay et al.<sup>6</sup> observed that the degree of formation of NaO<sub>4</sub> from NaO<sub>2</sub> was sensitive to the inert gas from which the matrix was formed. Also, our optimized geometry may well be basis set dependent, and employing more flexible basis sets may lead to other structures. Calculations are planned to investigate such possibilities.

The proposed appearance of NaO4 in the reactor at a temperature of 230 K puts a lower limit on its stability with respect to  $NaO_2$  and  $O_2$ . A simple statistical mechanical calculation with the moments of inertia and vibrational frequencies from the present ab initio calculation on NaO4 and pertinent data on NaO2 and  $O_2$  from ref 11 and 23 indicates that  $D_0(NaO_2-O_2) \ge 60 \text{ kJ mol}^{-1}$ . This may be compared with experimental estimates for the enthalpy of dissociation of  $O_4^-$  into  $O_2$  and  $O_2^-$ , which range from 4 to 56 kJ mol<sup>-1</sup>.<sup>32-35</sup> The degree of stabilization conferred by the Na<sup>+</sup> counterion is hard to predict. Ager and Howard<sup>36</sup> recently discussed the probable formation of  $NaO_4$  in the mesosphere and estimated a value of  $D_0(NaO_2-O_2) = 42 \pm 21 \text{ kJ mol}^{-1}$ .

In conclusion, we believe that there is good evidence that NaO<sub>4</sub> is formed in the gas phase at temperatures as high as 230 K. We are currently building a new experimental system that will permit us to work at much lower temperatures and prepare  $NaO_4$  in a more quantitative fashion than is possible in our present reactor. These new studies should provide a more conclusive test for the formation of  $NaO_4$  in the gas phase at temperatures well above those in matrix isolation studies, together with estimates of the dissociation enthalpy of NaO<sub>4</sub> to NaO<sub>2</sub> and O<sub>2</sub>, and the absolute photodissociation spectrum of the molecule.

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