Title

ULTRAVIOLET ABSORPTION STUDIES OF THE ALKALI METAL ATOM-OXYGEN MOLECULE MATRIX REACTION

Permalink

https://escholarship.org/uc/item/1203z9dq

Author

Andrews, Lester.

Publication Date

1975-09-01

Submitted to Journal of Physical
Chemistry

LBL-4164 c.1
Preprint

ULTRAVIOLET ABSORPTION STUDIES OF THE ALKALI METAL ATOM-OXYGEN MOLECULE MATRIX REACTION

Lester Andrews

September 1975

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

DISCLAIMER

LBL 4164
Shirley

ULTRAVIOLET ABSORPTION STUDIES OF THE ALKALI METAL ATOM-OXYGEN MOLECULE MATRIX REACTION

Lester Andrews*

Inorganic Materials Research Division
Lawrence Berkeley Laboratory
and
Chemistry Department
University of California
Berkeley, California 94720

ABSTRACT

Alkali metal atoms were codeposited with oxygen at high dilution in argon on a sapphire window cooled to 17 K. Ultraviolet spectra contained a medium intensity absorption near 250 nm which exhibited a long wavelength component between 269 and 275 nm for the heavier alkali metals. The 250 nm band is identified with $M^+O_2^-$ and assigned to a $\pi \rightarrow \pi^*$ superoxide transition, and the absorption near 270 nm, which increased on sample warming, is assigned to $M^+O_4^-$.

---

*The author was a Sesquicentennial Associate on leave from the University of Virginia, for the academic year 1974-75, and an Alfred P. Sloan Fellow.

INTRODUCTION

Superoxides have been of interest to chemists since the preparation of the yellow solid KO_2 in 1934.[1] The chemical properties and the absorption spectrum of O_2^- in liquid ammonia have been reported; a band at 380 nm was attributed to O_2^-.[2] However, O_2^- in alkali halide crystals absorbs at 248 nm,[3] and O_2^- produced by pulse radiolysis of oxygenated aqueous solutions exhibits a transient absorption at 240 nm.[4] This contradiction has been resolved by Czapski and Halperin who showed that the 380 nm absorption was due to NO_2^- and that O_2^- absorbs in the 240-250 nm range in several media.[5]

Using a new approach to superoxide synthesis, this author reported the preparation of $M^+O_2^-$ species using the matrix reaction of alkali metal atoms and oxygen molecules.[6-9] An ionic model for the bonding was suggested based on the agreement between the O_2^- fundamental in $Li^+O_2^-$ and in solid alkali halides.[10] This bonding picture has been confirmed by subsequent Raman[11] and ESR studies.[12,13]

In order to further characterize the $M^+O_2^-$ species, optical absorption studies were done on the alkali metal atom-oxygen molecule matrix reaction products.

EXPERIMENTAL

The cryogenic apparatus and vacuum vessel used for optical matrix isolation studies was similar to that described for previous infrared work[8] except that a Model 21 Cryodyne Cryocooler (Cryogenic Technology, Inc.) with an aluminum radiation shield was used for refrigeration of a sapphire cold window clamped to an oxygen-free hard copper block using indium gaskets. The window temperature was maintained at the lowest refrigerator temperature (10 K) or higher (up to 22 K) by a digital temperature controller using a chromel vs. gold, 0.07 atomic percent iron, thermocouple and resistance heat on the low temperature refrigeration stage. Optical quality quartz windows were affixed with Apiezon W wax to the stainless steel vacuum vessel. A Cary 14 recording spectrophotometer with a modified sample compartment was used to obtain visible spectra.

Lithium metal (Fisher Scientific Co.), sodium metal (J. T. Baker Chemical Co.), potassium metal (Baker and Adamson, Allied Chemical Co.), and a lithium metal-cesium chloride (Orion Chemical Co.) mixture were loaded into a stainless steel Knudsen cell as described previously[14] and heated to operating temperature by a resistance heater[8] in the apparatus under vacuum behind a sliding door. Operating temperatures were, respectively, 425, 230, 160, and 295°C for the Li, Na, K, and Cs atom sources. Argon matrix gas (Liquid Carbonic, 99.997%, industrial grade), and oxygen (Linde, research grade) were used without purification.

Approximately 2 mM of matrix sample was deposited on the cold sapphire plate, the absorption spectrum was recorded, and alkali metal vapor was codeposited with the gas mixture for 2-4 hr.

Absorption spectra were recorded during and after sample deposition. Most samples were frosty white in appearance indicating that all of the alkali metal was consumed by oxygen. The non-dispersed, tungsten lamp source of the Cary 14 was used to photolyse selected samples and additional spectra were recorded. Wavelength measurement of the Cary 14 was calibrated with mercury and deuterium lines.

RESULTS

Optical absorption studies of alkali metal-oxygen matrix reaction products were complicated by strong light scattering of the matrix sample with only a medium-intensity product absorption in the ultraviolet region. Observations from the individual alkali metal reactions will be described in turn.

Lithium

Three experiments were conducted with lithium, the first employed an $Ar/O_2 = 100/1$ sample. The spectrum exhibited a broad 230-250 nm shoulder on the steeply rising background, a strong band at 488 nm with shoulders at 446 and 415 nm and a broad weak band at 635 nm. The visible bands, which were destroyed by a 5 m exposure to the tungsten lamp source, are believed to be due to lithium aggregates. A similar experiment with a 50/1 sample produced a distinct shoulder with 230 and 245 nm maxima on the ultraviolet background, and no visible bands were observed.

The final experiment with lithium used an Ar/O_2 = 20/1 sample. Figure 1(a) shows the spectrum after 45 m of sample deposition; a weak feature with 235 and 245 nm maxima was observed in the ultraviolet and the visible region was free of absorption. The final spectrum after 85 m of reaction, Figure 1(b), shows band growth with the dominant absorption at 248 nm. Spectrum (c) shows that a 5 m exposure to the W lamp sharpens and slightly increases the peak at 249 nm. Sample warming to 32, 37 and 42 K and recooling to 22 K produced a slight growth in the 249 nm peak as is depicted in trace (d). However, holding the sample at 42 K for 6 m produced a marked decrease in the 248 nm peak, Figure 1(e). Finally, sample warming to 46 K reduced the 248 nm feature even more to a point weaker than the 233 nm peak which dominates the spectrum in trace (f). Since the temperatures reported in the temperature cycling operations were measured at the refrigeration stage, where the heat is applied and not at the window, the window was probably colder by at least several degrees.

Sodium

The sodium-oxygen reaction was studied in two experiments. The first, using Ar/O_2 = 200/1, is illustrated in Figure 2(a). A distinct doublet was observed at 248 and 271 nm on the steep ultraviolet background and a strong band was observed at 450 nm which is assigned to Na_2[15] along with weaker features at 403, 520, 585 and 630 nm which are believed to be due to sodium aggregates. Operation of the W lamp for 20 m destroyed the strong 450 nm band and reduced the 271 nm band to a shoulder without much effect on the 248 nm absorption.

The second sodium experiment employed an Ar/O_2 = 50/1 sample; Figure 2(b) shows that the yield of Na_2 was reduced markedly while the doublet at 250 and 269 nm increased considerably. A 14 m exposure to the W lamp decreased the resolution of the 250 nm band from the background and the 269 nm feature was reduced to a shoulder, Figure 2(c). Sample warming to 37 K and recooling to 10 K increased the background, but produced no spectral change; however, warming to 44 K reduced the 250 nm band to a shoulder while a new absorption appeared at 230 nm which is shown in Figure 2(d).

Potassium

The experiment reacting K atoms with an Ar/O_2 = 100/1 sample produced a broad ultraviolet band with a 253 nm peak and a 270 nm shoulder, which is illustrated in Figure 3(a). A 10 m exposure to W light slightly reduced the broad band, Figure 3(b). However, warming the sample to 37 K and recooling to 17 K produced a marked growth of the long wavelength part of the absorption with a peak at 272 nm, as is shown in Figure 3(c).

Cesium

Four optical studies were conducted for the Cs-O_2 matrix reaction. Matrix samples of Ar/O_2 = 200/1 and 150/1 produced a broad 250-270 nm shoulder on the ultraviolet background. Spectra from the 100/1 experiment are illustrated in Figure 4; a 275 nm band with a distinct and reproducible 255 nm shoulder was resolved from the background. As in the K experiment, exposure to the tungsten lamp reduced the band intensity, Figure 4(b). However, warming the sample to 37 K and recooling to 17 K markedly increased the 275 nm band, as is shown in Figure 4(c). A similar temperature cycle to 42 K increased the 275 nm band by 150%. Finally, cesium atoms were codeposited with an $Ar/O_2 = 50/1$ sample; the spectrum exhibited a well-defined shoulder at 255 nm on a strong 277 nm absorption which was more intense than the band in Figure 4.

DISCUSSION

The several species giving rise to the ultraviolet absorptions will be identified, and the band assignment and bonding in alkali superoxide molecules will be discussed.

Identification

The observation of ultraviolet absorption near 250 nm following the cocondensation of alkali metal atoms and oxygen, reactions known to produce the $M^+O_2^-$ species,[6-9] supports the earlier assignments[3-5] of absorptions in this region to the superoxide ion. Identification of the superoxide species responsible for the several absorption maxima at 230-233 nm, 248-255 nm and 269-275 nm in these experiments is facilitated by the previous infrared experiments where several new species were first identified.[6-9]

The primary reaction in the lithium-oxygen experiments is the direct union of the two reagents, 1.

$$\mathrm{Li} + \mathrm{O_2} \longrightarrow \mathrm{Li^+O_2^-} \qquad (\underline{1})$$

The product of reaction 1 can dimerize according to reaction 2.

$$\mathrm{Li^+O_2^-} + \mathrm{Li^+O_2^-} \longrightarrow (\mathrm{Li^+O_2^-})_2 \qquad (\underline{2})$$

Superoxide stretching vibrations at 1097 and 1048 $\mathrm{cm^{-1}}$, respectively, have been assigned to the products of reactions 1 and 2 based in part upon their behavior on sample warming.[6] The former infrared absorption decreased while the latter remained. This rationale suggests that the 248 nm absorption in $\mathrm{Li} + \mathrm{O_2}$ optical experiments is due to $\mathrm{Li^+O_2^-}$ and the 233 nm feature is due to $(\mathrm{Li^+O_2^-})_2$.

With the heavier alkali atoms, a secondary reaction product, first identified as the disuperoxide species by the use of isotopic mixtures,[8] was observed from reaction 3.

$$\mathrm{K^+O_2^-} + \mathrm{O_2} \longrightarrow \mathrm{K^+O_4^-} \qquad (\underline{3})$$

This product increased substantially upon sample warming to allow limited diffusion of the trapped species. Assignment of the 270 nm shoulder in the K experiment and the 275 nm peak in the Cs experiment, both of which grow on sample warming, to the $\mathrm{K^+O_4^-}$ and $\mathrm{Cs^+O_4^-}$ species follows. The shoulder at 255 nm on the stronger

$Cs^+O_4^-$ absorption is assigned to $Cs^+O_2^-$. The short-wavelength side of the 253 nm band in the $K + O_2$ experiment is attributed to $K^+O_2^-$.

The sodium reaction gives products related to those found with lithium and those observed only with K and Cs. The resolved shoulder at 270 ± 1 nm is probably due to $Na^+O_4^-$ although the latter is less stable than the heavier alkali analogs.[7,8] Note the absence of absorption near 270 nm in the lithium experiments; no evidence for a disuperoxide species was found in the infrared experiments with lithium.[6] Presumably the smaller lithium ion cannot stabilize the larger O_4^- anion. Following temperature cycling, the most prominent absorption in the sodium experiments appeared near 230 nm; in lithium experiments the last surviving band was observed at 233 nm. These features are probably due to $(Na^+O_2^-)_2$ and $(Li^+O_2^-)_2$, respectively.

The effect of the tungsten lamp on these samples is not completely understood since its output near 250 nm is virtually zero. Its use here simply as a diagnostic tool relates the absorptions at 269-275 nm as they all decrease upon exposure to the W lamp. Tungsten lamp radiation on the sample caused an increase in the window block temperature from 10 to 11 K.

Assignment

Assignment of the 250 nm superoxide transition draws on two pieces of information. First, the Schumann-Runge bands of O_2

beginning at 49,802 cm^{-1} involve a $\pi_u(2p)$ to $\pi_g{}^*(2p)$ transition,[16] hence a transition between these orbitals must be considered for O_2^-. Second, the O_2^- absorption at 248 nm in solid NaCl and KCl is virtually unchanged from the O_2^- absorption of the matrix-isolated $M^+O_2^-$ species, so the M^+ ion in C_{2v} symmetry is not responsible for the O_2^- transition, which must also be allowed for the ion in salt lattices. Accordingly, a $^2\Pi_g \longrightarrow {}^2\Pi_u$ transition is proposed for the 250 nm superoxide band.

Now, referring to the alkali superoxide molecular orbital diagram, Figure 5, the cation interacts more strongly with orbitals in the molecular plane, and hence they lie lower in energy than the out-of-plane orbitals. Then, the odd electron is contained in the out-of-plane $\pi_y{}^*(a_2)$ orbital and the ground state has the $\cdots b_1{}^2a_2$ molecular orbital configuration, which is in agreement with recent quantum mechanical calculations.[17] The only allowed ultraviolet transition in C_{2v} symmetry to the $\pi_y{}^*(a_2)$ orbital must originate in the $\pi_y(b_2)$ orbital. Accordingly, the $M^+O_2^-$ transition is designated $^2A_2 \longrightarrow {}^2B_2$ and is the same transition as $^2\Pi_g \longrightarrow {}^2\Pi_u$ for isolated O_2^- anion.

The transition between π_u and π_g orbitals for O_2^- has the expected relationship to this transition for O_2 which starts at 49,802 cm^{-1}. The band origin for O_2^- can be deduced from the onset of the absorption spectrum (3.8 eV) and the fluorescence spectrum

(3.0 eV);[3] a simple average predicts the non-vertical transition between lowest vibrational levels of the ground and excited electronic states to be 3.4 eV or 27,400 cm^{-1}.

Similar red shifts in the same interorbital transitions for neutrals and anions have been observed for C_2 (230 nm) and C_2^- in $M^+C_2^-$ (500 nm),[18] and Cl_2 (163 nm) and Cl_2^- in M^+Cl_2 (340 nm).[19] These anions have in common an extra electron in the orbital where the electronic transition terminates. Hence, the electron undergoing the same interorbital transition in the anion experiences extra electron-electron repulsions and a decreased effective nuclear charge as compared to the neutral molecule. Accordingly, the outer energy levels of the anion are increased, i.e. destabilized, and as a result the interorbital energy is decreased and a red shift in the electronic transition follows.

Finally, the difference between the optical bands assigned to the $M^+O_2^-$ and $M^+O_4^-$ species is worthy of comment. For the $Na^+O_2^-$ (250 nm) and $Na^+O_4^-$ (270 nm) species, this difference is 3,000 cm^{-1}. Interaction between the two precursors (O_2 and O_2^-) which form the O_4^- species, results in four π and four π^* molecular orbitals; the π are filled, the two lowest π^* are filled the next lowest π^* is half-filled. The term δ, which measures the π_y^* and π_x^* separation for $M^+O_2^-$, is approximately 3,000 cm^{-1};[13] however, δ is approximately 7,000 cm^{-1} for O_4^- which is a measure of the separation between the lowest π^* and the half-filled π^* orbitals.[20] Now, the optical transition shown in Figure 5 for $M^+O_2^-$ becomes a transition from the highest π to the half-filled π^* for $M^+O_4^-$ and a red-shift on the order of the spacing between π^* levels is expected since the transition for $M^+O_4^-$ terminates in the half-filled π^* level which is on the order of 1/2 $\delta(O_4^-)$ below the upper, unfilled π^* molecular orbital. Accordingly, the observation of $M^+O_4^-$ optical absorption in the 269-275 nm range as compared to $M^+O_2^-$ in the 248-255 nm region is consistent with the E.S.R. spectra of the two species.

Bonding

It is interesting to note the excellent agreement between the present $M^+O_2^-$ optical bands and the 248 nm absorption due to O_2^- in solid alkali halides.[3] This, too, is supportive of the ionic model for the $M^+O_2^-$ molecules, which was originally based on the agreement between the Raman spectrum of O_2^- in KCl[10] and the ν_1 infrared band[6] of $Li^+O_2^-$. The ionic model has been confirmed by complementary infrared and Raman[11] spectra of $M^+O_2^-$ and by E.S.R. spectra.[12,13]

Unfortunately, the M^+ effect on the O_2^- optical band cannot be determined as accurately as the metal effect on the vibrational spectrum. The $Li^+O_2^-$ and $Na^+O_2^-$ species absorbed at 249 ± 1 nm with $Cs^+O_2^-$ at 255 ± 2 nm and $K^+O_2^-$ was unresolved. The red shift on going from Li^+ and Na^+ to Cs^+ is not expected from the ionic model,[11] which suggests that transition wavelength varies directly with charge transfer, but it is consistent with a recent interpretation of E.S.R. spectra of the $M^+O_2^-$ species which required interaction of the cesium 5p orbitals with the valence orbitals of oxygen.[13] The net result of the cesium interaction is to force all O_2^- orbitals to higher energy, except the $\pi_y^*(a_2)$ orbitals, which cannot interact with p orbitals. The degree of interaction decreases with increasing O_2^- orbital energy so a red shift is expected in the $\pi \longrightarrow \pi^*$ transition for $Cs^+O_2^-$ as compared to the lighter alkali species whose (n - 1) p orbitals lie significantly lower in energy. It has been suggested from the E.S.R. spectrum[13] that the $\pi_x^*(b_1)$ and $\pi_y^*(a_2)$ orbitals invert for $Cs^+O_2^-$. Regardless of which π^* orbital lies lower, the transition $(\pi)^2 \longrightarrow (\pi^*)^1$ is expected to undergo a red shift due to a greater interaction between cesium 5p and $\pi(b_2)$ than $\pi^*(b_1)$, or of course, $\pi^*(a_2)$, which is consistent with the observed ultraviolet spectrum.

CONCLUSIONS

Reactions of alkali metal atoms with oxygen molecules at high dilution in argon during condensation at 17 K produced an optical absorption at 248-255 nm. This absorption, which is in agreement with earlier work on O_2^- doped into alkali halides, is identified as $M^+O_2^-$ and assigned to a π_u to π_g^* orbital transition analogous to the Schumann-Runge bands of oxygen. The $M^+O_2^-$ transition is designated $^2A_2 \longrightarrow {}^2B_2$ in C_{2v} symmetry. The marked red-shift of this transition on O_2^- as compared to O_2 is a consequence of additional electron-electron repulsions and a decreased effective nuclear charge in the anion.

Additional absorption at 269-275 nm was favored at higher O_2 concentrations and with the heavier alkali metals and upon sample warming to allow limited diffusion of the trapped species. This absorption is identified as $M^+O_4^-$, based on its parallel behavior in earlier infrared studies. The appearance of $M^+O_4^-$ some 3,000 cm^{-1} lower than $M^+O_2^-$ is consistent with their E.S.R. spectra.

Finally, it should be noted that the 300-400 nm region was free of absorption which indicates that the superoxide ion does not absorb in this region, as was first reported.

ACKNOWLEDGMENTS

This work was supported by the U.S. Energy Research and Development Administration, the University of Virginia, and the Alfred P. Sloan Foundation. The loan of a Model 21 Cryodyne by Cryogenic Technology, Inc. and a Cary 14 spectrophotometer by Professor C. B. Harris, the hospitality of Professor Leo Brewer and helpful discussions with Professor Paul Schatz are gratefully acknowledged.

REFERENCES

1. E. W. Newman, J. Chem. Phys., 2, 31 (1934).
2. J. K. Thompson and J. Kleinberg, J. Amer. Chem. Soc., 73, 1243 (1951).
3. J. Rolfe, F. R. Lipsett and W. J. King, Phys. Rev., 123, 447 (1961).
4. G. Czapski and L. M. Dorfman, J. Phys. Chem., 68, 1169 (1964).
5. G. Czapski and B. Halperin, Israel J. Chem., 5, 185 (1967).
6. L. Andrews, J. Chem. Phys., 50, 4288 (1969).
7. L. Andrews, J. Phys. Chem., 73, 3922 (1969).
8. L. Andrews, J. Chem. Phys., 54, 4935 (1971).
9. L. Andrews, J-T. Hwang and C. Trindle, J. Phys. Chem., 77, 1065 (1973).
10. J. Rolfe, W. Holzer, W. F. Murphy and H. J. Bernstein, J. Chem. Phys., 49, 963 (1968).
11. L. Andrews and R. R. Smardzewski, J. Chem. Phys., 58, 2258 (1973).
12. F. J. Adrian, E. L. Cochran and V. A. Bowers, J. Chem. Phys., 59, 56 (1973).
13. D. M. Lindsay, D. R. Herschbach and A. L. Kwiram, Chem. Phys. Letts., 25, 175 (1974).
14. R. C. Spiker, Jr. and L. Andrews, J. Chem. Phys., 59, 1851 (1973).

15. G. W. Loomis and R. E. Nusbaum, Phys. Rev., 40, 380 (1932).

16. G. Herzberg, Spectra of Diatomic Molecules, (Van Nostrand, Princeton, NJ, 1950), 2nd ed.

17. S. V. O'Neil, H. F. Schaefer, III, and C. F. Bender, J. Chem. Phys., 59, 3608 (1973).

18. W. R. M. Graham, K. I. Dismuke and W. Weltner, Jr., J. Chem. Phys., 61, 4793 (1974).

19. L. Andrews, to be published.

20. D. M. Lindsay, D. R. Herschbach and A. L. Kwiram, Paper TB3, Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, June 17, 1975, and D. M. Lindsay, personal communication, 1975.

FIGURE CAPTIONS

Figure 1. Ultraviolet spectra recorded following the condensation of lithium atoms with an Ar/O_2 = 20/1 sample on a sapphire plate at 22 K. Spectrum (a) was taken after 45 m of lithium deposition. Final spectrum (b) was recorded after 85 m of lithium deposition. Trace (c) follows a 5 m exposure to the Cary 14 tungsten lamp. Scan (d) shows the effect of temperature cycling to 42 K. Spectrum (e) was recorded after holding the sample at 42 K for 6 m. The last trace (f) followed temperature cycling of the low temperature refrigeration stage to 46 K.

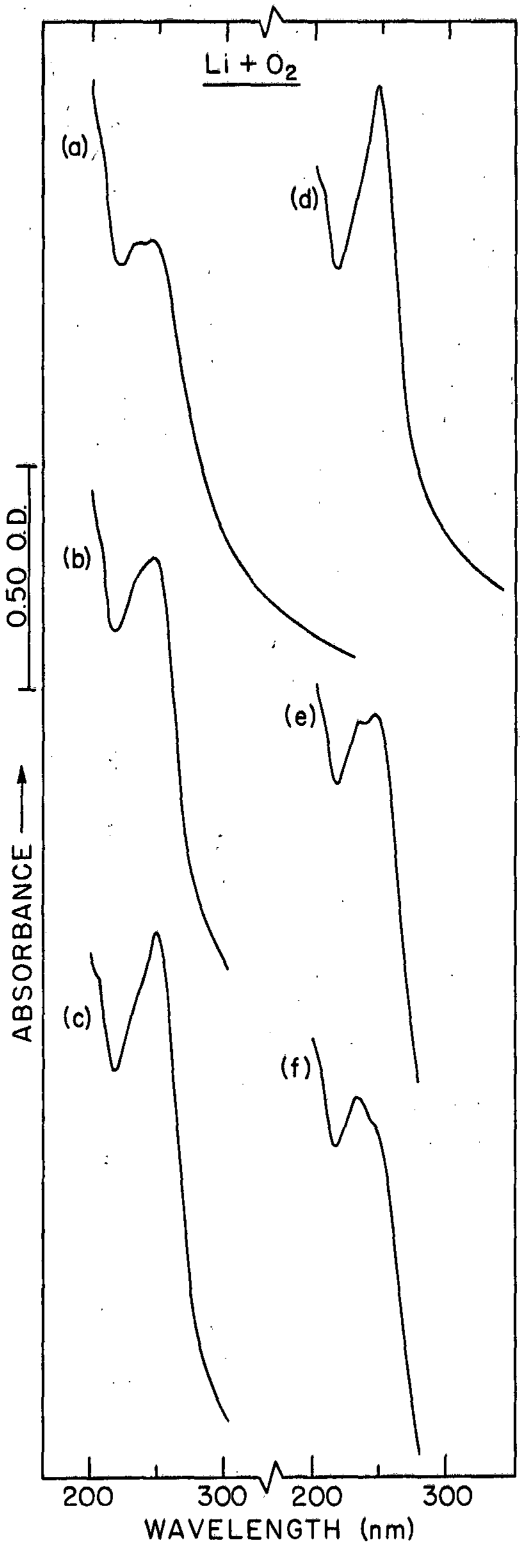
Figure 2. Optical spectra for the sodium-oxygen matrix reaction. Spectrum (a) recorded for Ar/O_2 = 200/1 sample. Spectrum (b) is final scan from Ar/O_2 = 50/1 experiment. Trace (c) follows a 14 m tungsten lamp exposure and trace (d) follows a temperature cycle to 44 K.

Figure 3. Ultraviolet spectra of the potassium-oxygen reaction products using a Ar/O_2 = 100/1 sample. Spectrum (a) is final scan after reagent deposition. Scan (b) follows a 10 m W lamp exposure, and trace (c) follows a temperature cycle to 37 K.

Figure 4. Optical spectra recorded after codepositing cesium atoms with an Ar/O_2 = 100/1 sample at 17 K. Spectrum (a) was recorded at the end of the deposition period. Scan (b) recorded

after 10 m tungsten lamp exposure and trace (c) shows the effect of a temperature cycle from 17 to 37 to 17 K.

Figure 5. Molecular orbital scheme, geometry, and optical transition for the alkali superoxide molecules.



XBL756-6490

Figure 1

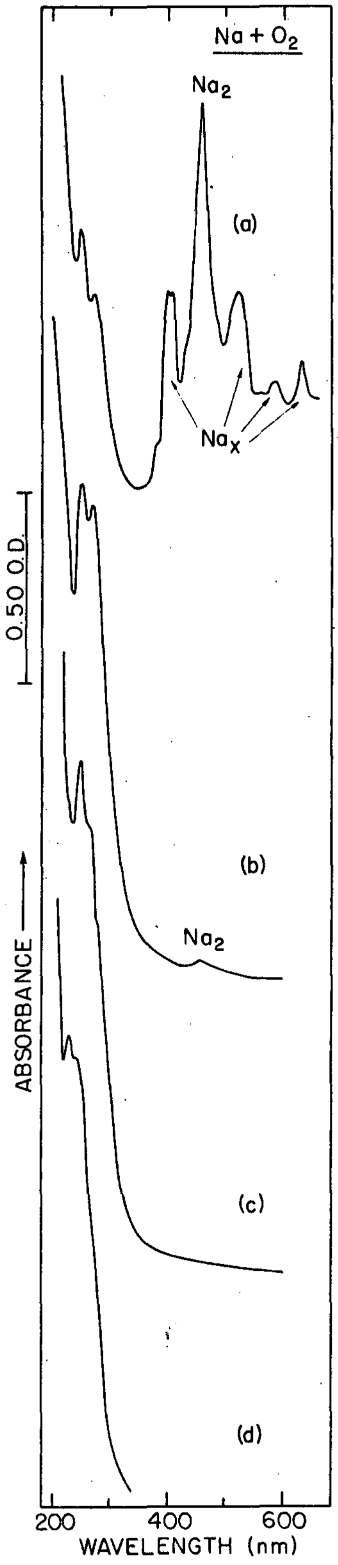

Na + O$_2$
Na$_2$
(a)
Na$_x$
0.50 O.D.
(b)
Na$_2$
ABSORBANCE
(c)
(d)
200
400
600
WAVELENGTH (nm)
XBL756-6589

Figure 2

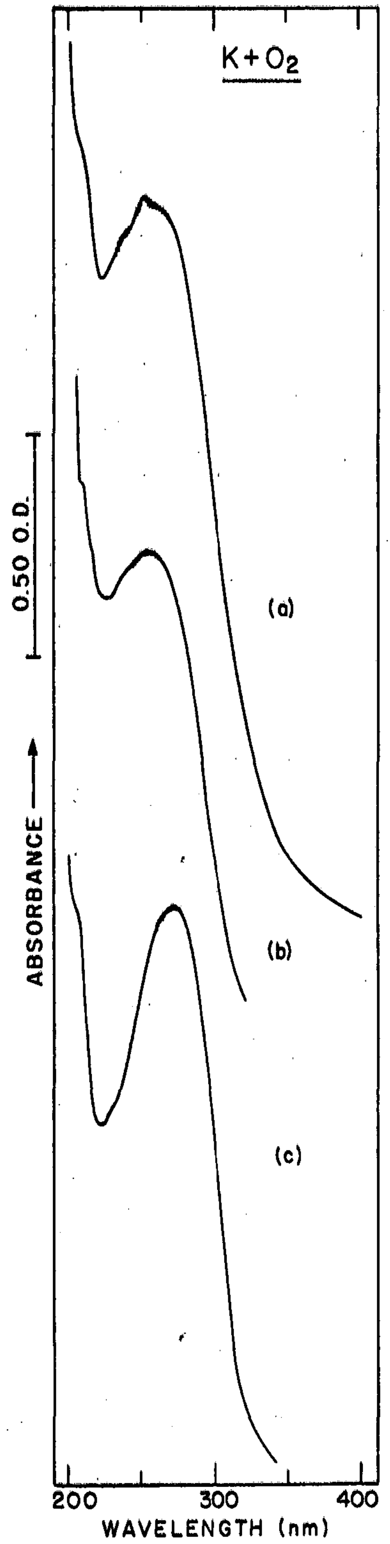
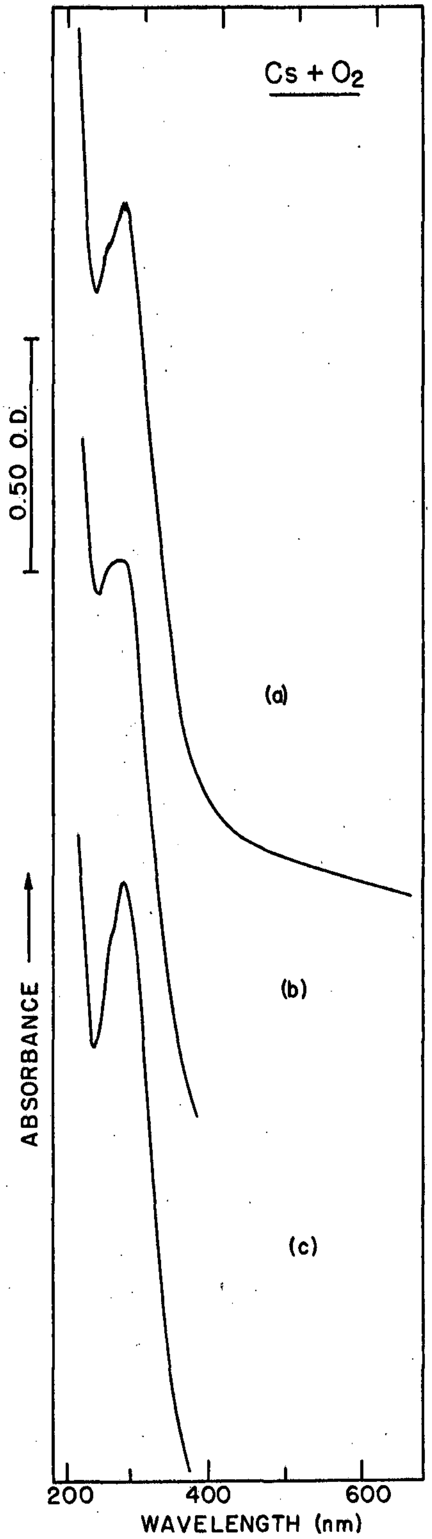

K+O$_2$
0.50 O.D.
ABSORBANCE
(a)
(b)
(c)
200
300
400
WAVELENGTH (nm)
XBL756-6484

Figure 3



XBL756-6485

Figure 4

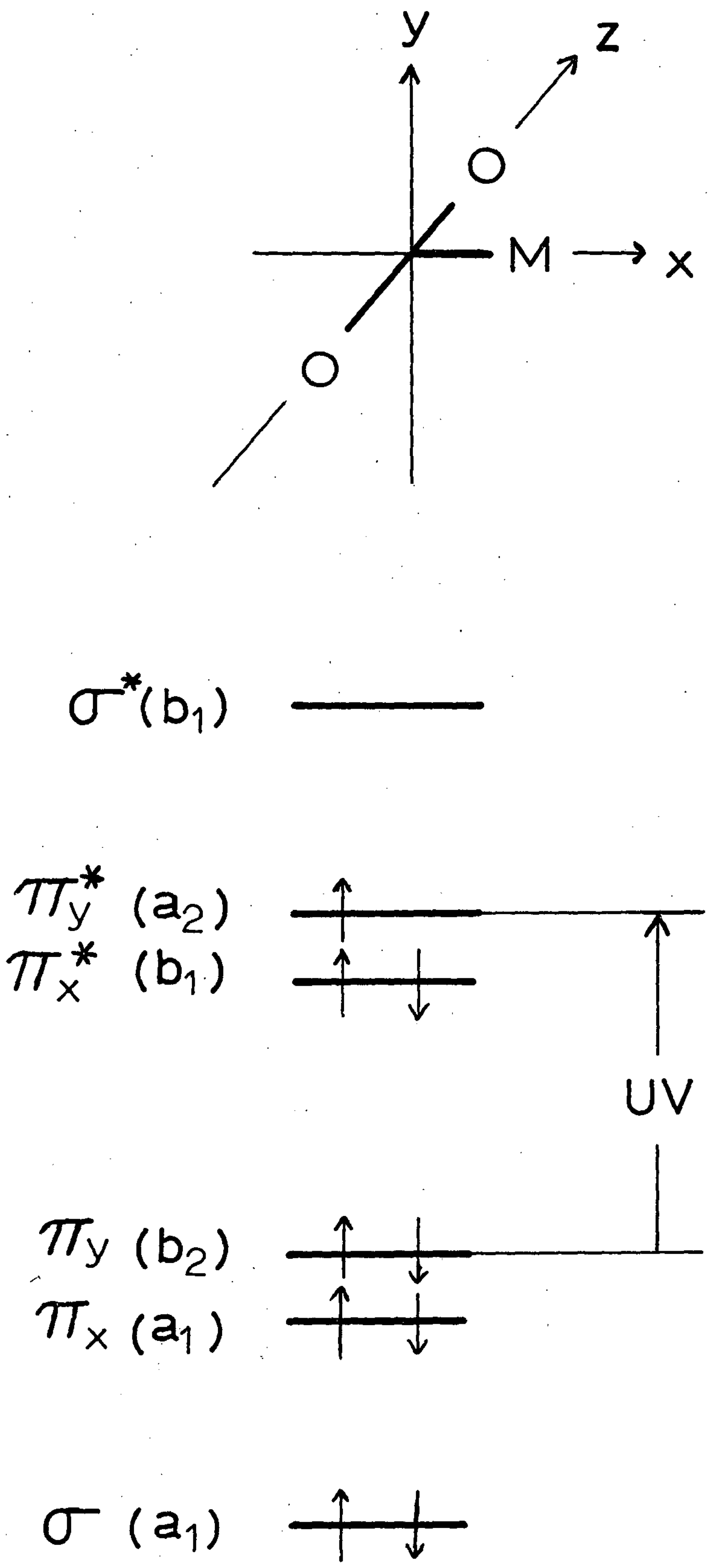


Figure 5

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720