Title
VIBRONIC SPECTRA OF THE OZONIDE ION IN THE MATRIX-ISOLATED M+03- SPECIES

Author
Andrews, Lester.

Publication Date
1975-06-01

Submitted to Journal of Chemical Physics

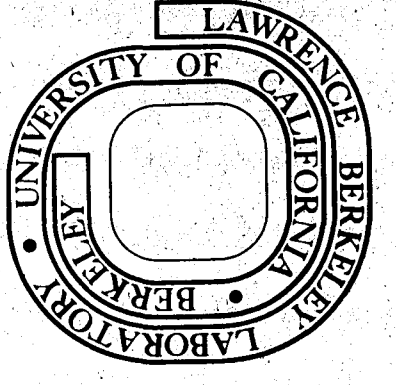
LBL-3961
Preprint c. 1

VIBRONIC SPECTRA OF THE OZONIDE ION IN THE MATRIX-ISOLATED $M^+O_3^-$ SPECIES

Lester Andrews

June 1975

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



DISCLAIMER

LBL-3961

VIBRONIC SPECTRA OF THE OZONIDE ION IN THE MATRIX-ISOLATED $M^+O_3^-$ SPECIES

Lester Andrews*

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

ABSTRACT

Matrix reactions of alkali metal atoms and ozone molecules at high dilution in inert gases produced a clear yellow film during condensation at 10-22 K on a sapphire plate which yielded vibronic spectra of the $M^+O_3^-$ species. Best resolution of up to 14 vibronic bands spaced 800-900 cm^{-1} apart was obtained for the lithium and sodium compounds. These bands formed a strong progression in ν_1' and the first six bands exhibited the presence of a weaker progression in ν_2'. The band origin was located at 17,730 cm^{-1} for $Li^{+16}O_3^-$ and $Li^{+18}O_3^-$ in solid krypton. Harmonic and anharmonic vibrational constants were determined graphically for the excited electronic state.

*The Author is a Sesquicentennial Associate on sabbatical leave from the University of Virginia, and an Alfred P. Sloan Fellow.

Introduction

The visible absorption spectrum of O_3^- has been observed very recently in studies of the matrix-isolated $Na^+O_3^-$ species produced by photolysis[1] and of $K^+O_3^-$ dissolved in liquid ammonia[2] and of the radiolysis products of solid $KClO_3$.[3] These investigations lacked sufficient intensity and/or resolution to identify the band origin although Bates and Pigg[3] used an empirical relationship to assign vibronic quantum numbers and predict the band origin.

The direct matrix reaction of alkali atoms and ozone has proven to be an excellent method of stabilizing the ozonide ion as the $M^+O_3^-$ species for infrared[4] and resonance Raman[5] investigations. Similar optical studies have been done with the aim of resolving an extensive vibronic progression and locating the band origin.

Experimental

The cryogenic apparatus and vacuum vessel used for optical matrix isolation studies was similar to that described for previous infrared work[6] 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. 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.

Ozone and ozone-18 were synthesized by tesla coil discharge of $^{16}O_2$ (Linde, research grade) and $^{18}O_2$ (Isomet Corp., 99.85%) in a pyrex finger immersed in liquid nitrogen and affixed to a stainless steel vacuum system.[7] Oxygen was removed by repeated evacuation of the condensed ozone. Matrix samples of ozone (Matrix/ozone = 100/1) were prepared using standard manometric techniques and were deposited at the rate of 2 mM/hr. Matrix gases, argon (Liquid Carbonic, 99.997%, industrial grade), krypton (Air Reduction Co., research grade), xenon and nitrogen (Matheson, research grade) were used without purification.

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[4] and heated to operating temperature by a resistance heater[6] 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.

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. The samples were clear yellow in appearance indicating that all of the alkali metal was consumed by ozone. The best samples looked like a Corning #3385 yellow-glass filter. The non-dispersed, tungsten lamp source of the Cary 14 was used to photolyse the ozonide samples and additional spectra were recorded.

Wavelength measurement of the Cary 14 was calibrated with mercury and deuterium lines. Band positions were measured to the nearest 0.1 nm in

several scans which were averaged and reported in wavenumbers. The Li data are accurate to 10-20 cm^{-1}, depending upon band intensity and resolution, the Na data are accurate to 20-30 cm^{-1}, and the Cs data are accurate to 30-40 cm^{-1}.

Results

The most extensive and best resolved vibronic data were obtained for the lithium-ozone reaction which are contrasted in Fig. 1 for N_2, Ar, Kr, and Xe matrices. Note the gradual shift of the band origin to longer wavelength with increasing matrix atomic weight. Also shown in Fig. 1 are the spectra recorded following exposure of the sample to the tungsten lamp IR source. The wavenumbers of the peaks in the vibronic progressions are listed in Table I.

Lithium atoms were reacted with $^{18}O_3$ in a krypton matrix experiment. The $^{16}O_3$ and $^{18}O_3$ isotopic spectra are contrasted in Fig. 2. Note the coincidence of the band origins and the increasing separation between the 0→5 and 0→10 vibronic bands for each isotopic species.

Sodium atoms were reacted with $^{16}O_3$ and $^{18}O_3$ in argon matrix experiments. Owing to the presence of strong visible absorptions due to Na_2 and Na_x in matrices, these samples were exposed to the tungsten lamp to bleach out any absorption due to sodium species. The Na + $^{16}O_3$ spectrum was 1.5 O.D. before a 20 min exposure to W light through Corning #5562 glass (transmits 340-520 nm) which reduced the band to 0.50 O.D.; this is illustrated in Fig. 3 along with the other alkali ozonide spectra. The Na + $^{18}O_3$ spectrum was 0.72 O.D. as deposited and a 7 min exposure to the tungsten lamp reduced the band to 0.42 O.D. The sodium ozonide isotopic spectra are contrasted in Fig. 4 on an expanded scale to

illustrate the changing band contours in the vibronic progressions. Table II gives the vibronic data for the sodium ozonide species.

The poorest vibronic resolution was found for the K + O_3 reaction in both argon and krypton matrices; the former is shown in Fig. 3. The band peaks at 436.5±0.2 nm and has an origin near 535±5 nm.

Cesium atoms were reacted with ozone in argon and krypton matrix experiments. The argon matrix spectrum is illustrated in Fig. 3 and the partially-resolved vibronic peaks are listed in Table II. The analogous krypton spectrum exhibited a similar amount of vibronic resolution and the peaks were red-shifted 2.0 nm.

Discussion

The electronic spectrum of chlorine dioxide, which is isoelectronic with the ozonide ion, has been studied extensively and it provides a good model for discussion of the present vibronic spectra of O_3^-. The ClO_2 absorption between 500 and 400 nm has been attributed to the $^2B_1 \rightarrow {}^2A_2$ transition between symmetrical states in C_{2v} symmetry.[8] Ozonide ion is a symmetrical species[4] with a O-O-O bond angle near 111°; chlorine dioxide has a bond angle of 118° in the ground electronic state.[8] It is reasonable to assign the ozonide spectrum in the same region to the same transition.

The vibrational structure of the ClO_2 band consists of a long, strong progression in ν_1' and a short progression in ν_2'. It is clear from the spacings between the major ozonide vibronic peaks, which run from approximately 900 to 800 cm^{-1} with increasing quantum number, that the major absorption produces a strong progression in ν_1'. Raman spectra of these

species exhibited a strong ν_1'' fundamental at 1010 cm^{-1}.[5] However, the fourth band spacing is irregular, which indicates interference with another vibrational mode in the excited electronic state, as suggested by Giguere and Herman.[2] This interference can be clearly seen in the vibronic spectra of Fig. 4. Notice that the second band in each isotopic progression gives the appearance of a partially resolved doublet and the third and fourth bands are broadened, probably containing unresolved features. Notice how the blue shoulder on the fifth, sixth, and seventh bands decreases in intensity. These shoulders fall approximately 300 cm^{-1} to the blue of the major peaks; it is suggested that $\nu_2' \approx 300$ cm^{-1} for O_3^- and that the shoulders are due to combination or overlapping progressions in ν_1' and ν_2'. The irregularity in band spacing is probably due to overlapping of the short progression in ν_2' with the long progression in ν_1' of O_3^-.

Comparison of the lithium experiments with $^{16}O_3$ and $^{18}O_3$ in krypton matrices clearly shows the 0→0 transition to be 17,730±10 cm^{-1} as this band is isotopically invariant whereas the other $^{18}O_3$ product bands are red-shifted from their $^{16}O_3$ counterparts. The difference between 0→5 isotopic bands is 230 cm^{-1} and the 0→10 difference is 441 cm^{-1}.

It is likewise apparent that the band origin in the $Na^{16}O_3$ and $Na^{18}O_3$ species is near 550 nm although the band is not as well-defined as its lithium counterpart. Also, the differences between isotopic bands for the sodium species extrapolate back to a band origin at 551 nm. The vibrational numbering given in Tables I and II is based on the isotopic location of the band origin.

The vibronic data in Tables I and II were treated graphically by plotting the vibrational energy per quantum $(G(v_1') - G(0)/(v_1')$ <u>vs.</u> the quantum

number (v_1'). Figure 5 illustrates three of these plots; it is seen that the data fit very well for higher quantum numbers where interference with v_2' is not present and error in the vibrational energy per quantum is divided by the quantum number. The slope of these straight lines is $-\omega_1 x_1'$ and the intercept is $\omega_1' - \omega_1 x_1'$. These excited-state vibrational constants are listed in Table III for several $M^+O_3^-$ species and matrices.

The harmonic and anharmonic vibrational constants for $M^{+16}O_3^-$ and $M^{+18}O_3^-$ can be checked against the theoretical ratio. The harmonic ratio ($^{18}\omega_1'/^{16}\omega_1'$) is 0.9497 for $Na^+O_3^-$ and 0.9466 for $Li^+O_3^-$ which compare favorably with the calculated ratio 0.9428 and the ground state ratio from resonance Raman data[5] of 0.9441. The anharmonic ratios are more sensitive to error, but the observed ratios 0.890 and 0.902 are near the calculated value of 0.889 and the ground state ratio 0.893.

Note the smooth trend in ω_1' and $\omega_1 x_1'$ for $Li^+O_3^-$ in Ar, Kr, and Xe matrices and the red shift of the band origin from N_2, Ar, Kr to Xe. The vibrational constants for $Li^+O_3^-$ in N_2 fall between the Ar and Kr values. Nitrogen appears to be a good matrix for lithium atom reactions with a reactive molecule like ozone, even though lithium atoms will react with the nitrogen matrix if given no alternative.[9] The excited state vibrational constants for $Na^+O_3^-$ in argon are slightly less than the ground state constants determined from the resonance Raman spectrum,[5] which, along with the observation of a strong progression in v_1' in absorption, indicates a longer O-O bond in the excited electronic state, as compared to the ground state, owing to the promotion of an electron into an antibonding orbital.

The excited-state vibrational constants for the matrix isolated $Li^+O_3^-$ and $Na^+O_3^-$ species reported here are near the average values computed for O_3^- in solid $KClO_3$.[3] The present constants are more accurate since they were determined from a complete vibronic spectrum rather than average band spacings.

The values of ω_1' for $Li^+O_3^-$ for four different matrices range from 908.5 cm^{-1} in argon to 877.3 cm^{-1} in xenon with nitrogen at 897.2 cm^{-1}. This is a larger intramatrix shift than is normally observed for intraionic modes or modes within a covalent molecule for a ground electronic state. For example, ν_3 of O_3^- in $Li^+O_3^-$ was observed at 814 cm^{-1} in N_2 and 811 cm^{-1} in Ar[4] and ν_3 of O_3 ranged from 1040 cm^{-1} in Ar to 1030 cm^{-1} in Xe.[7,10] It appears that the more polarizable excited electronic state of the ozonide ion is interacting more strongly with the matrix than the ground electronic state which is responsible for the larger effect on ω_1' as the matrix size and polarizability are changed.

The matrix also played a role in the relative yields of the lithium-ozone reaction. The least stable $Li^+O_3^-$ species was produced in smaller yields in the argon matrix as compared to larger yields in N_2, Kr, and Xe matrices which are known to interact more strongly with ionic molecules, i.e. they produce greater matrix shifts for molecules like LiO.[12]

It is of interest to note that the best vibronic resolution was achieved with the $Li^+O_3^-$ species where the cation is closest to the anion. Perhaps the close cation inhibits the anion bending mode which allows the observation of a more pure ν_1' progression. In infrared studies of $M^+O_3^-$ species, ν_2 was observed only for $K^+O_3^-$, $Rb^+O_3^-$, and $Cs^+O_3^-$.[4] In studies

of $Ca^+O_3^-$ where the cation lies even closer to O_3^-, resolution of the ν_1' progression was observed as for $Li^+O_3^-$.[11]

Finally, this work reflects on ozonide chemistry. For comparable argon matrix experiments, the least stable $Li^+O_3^-$ species was produced in lowest yields of the four alkali reactions studied and $Li^+O_3^-$ was photodecomposed more completely by a fixed exposure to the Cary 14 tungsten lamp. In contrast, the more stable $K^+O_3^-$ and $Cs^+O_3^-$ species were produced in larger spectroscopic yields and these compounds were more resistant to photolytic decomposition. Since the output of this lamp is primarily in the visible and near infrared, more evidence is presented for an underlying continuous absorption.[1,4] Owing to this continuous absorption, photolytic methods of producing $M^+O_3^-$, like the technique of Jacox and Milligan,[1] are limited in the amount of ozonide that can be stabilized.

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 are gratefully acknowledged.

References

1. M. E. Jacox and D. E. Milligan, J. Mol. Spectrosc., 43, 148 (1972). A review of the earlier literature is presented by these authors.
2. P. A. Giguere and K. Herman, Can. J. Chem., 52, 3941 (1974).
3. J. B. Bates and J. C. Pigg, J. Chem. Phys., 62, 4227 (1975).
4. R. C. Spiker, Jr. and L. Andrews, J. Chem. Phys., 59, 1851 (1973).
5. L. Andrews and R. C. Spiker, Jr., J. Chem. Phys., 59, 1863 (1973).
6. L. Andrews, J. Chem. Phys., 54, 4935 (1971).
7. L. Andrews and R. C. Spiker, Jr., J. Phys. Chem., 76, 3208 (1972).
8. A. W. Richardson, R. W. Redding, and J. C. D. Brand, J. Mol. Spectrosc., 29, 93 (1969) and references therein.
9. R. C. Spiker, Jr., L. Andrews, and C. Trindle, J. Amer. Chem. Soc., 94, 2401 (1972).
10. L. Brewer and J. L-F. Wang, J. Chem. Phys., 56, 759 (1972).
11. L. Andrews, unpublished results.
12. R. C. Spiker, Jr. and L. Andrews, J. Chem. Phys., 58, 702 (1973).

TABLE I

Vibronic Band Positions (cm^{-1}) Observed for $Li^{+}O_3^{-}$ in Different Matrices

$0 \rightarrow v_1'$	N_2	Ar	Kr($^{16}O_3$)	Kr($^{18}O_3$)	Xe
$v_1' = 0$	17,947	17,825	17,730	17,730	17,603
			895	864	
1	18,840	18,734	18,625	18,594	18,488
			883	838	
2	19,716	19,616	19,508	19,432	19,369
			863	807	
3	20,602	20,500	20,371	20,239	20,218
			806	774	
4	21,468	21,336	21,177	21,013	21,022
			849	783	
5	22,302	22,183	22,026	21,796	21,872
			815	788	
6	23,127	23,010	22,841	22,584	22,666
			811	780	
7	23,918	23,821	23,652	23,364	23,496
			828	756	
8	24,746	24,643	24,480	24,120	24,313
			798	756	
9	25,575	25,445	25,278	24,876	25,094
			791	752	
10	26,337	26,219	26,069	25,628	25,927
			726	750	
11	27,115	26,998	26,795	26,378	26,695
			814	700	
12	27,917	27,747	27,609	27,078	27,488
13	---	28,506	---	---	28,201

TABLE II

Vibronic Band Positions (cm^{-1}) Observed for $Na^{+}O_3^{-}$ and $Cs^{+}O_3^{-}$ in Solid Argon

$0 \rightarrow v_1'$	$Na^{+16}O_3^{-}$	$Na^{+18}O_3^{-}$	$Cs^{+16}O_3^{-}$
$v_1' = 0$	18,182±50	18,182±50	18,090±50
1	19,001	18,976	19,059
2	19,901	19,837	19,905
3	20,783	20,678	20,747
4	21,552	21,409	21,547
5	22,412	22,212	22,366
6	23,272	23,026	23,159
7	24,085	23,798	23,952
8	24,888	24,576	24,759
9	25,694	25,329	25,556
10	26,490	26,103	26,364
11	27,285	26,860	27,027
12	---	27,594	---

TABLE III

Band Origins (cm^{-1}) and Harmonic and Anharmonic Vibrational Constants (cm^{-1}) for $M^+O_3^-$ Species in Matrices

		$0 \rightarrow 0$	ω_1' [a]	$\omega_1 x_1'$ [b]
$Li^+O_3^-$	(N_2)	17,947±10	897.2±1.0	5.20±0.20
	(Ar)	17,825	908.5	6.15
	(Kr)	17,730	888.7	5.19
	(Xe)	17,603	877.3	4.30
$Li^{+18}O_3^-$	(Kr)	17,730±10	841.2	4.68
$Na^+O_3^-$	(Ar)	18,182±50	878.0	4.29
$Na^{+18}O_3^-$	(Ar)	18,182±50	833.8	3.82
$Cs^+O_3^-$	(Ar)	18,090±50	902±4	8±1

[a] Uncertainty in ω_1' is ±1.0 cm^{-1} unless otherwise noted.

[b] Uncertainty in $\omega_1 x_1'$ is ±0.20 cm^{-1} unless otherwise noted.

Figure Captions

Fig. 1. Vibronic spectra of matrix-isolated $Li^{+}O_3^{-}$ in the visible region. (a) Li atoms codeposited with O_3 in N_2 (N_2/O_3 = 100/1) at 10 K for 243 min; second spectrum follows 7 min exposure to W lamp. (b) Li atoms codeposited with O_3 in Ar at 10 K for 213 min; second spectrum follows 5 min exposure to W lamp. (c) Li atoms codeposited with O_3 in Kr at 17 K for 245 min; 5 min W lamp. (d) Li atoms codeposited with O_3 in Xe at 22 K for 210 min; 5 min W lamp.

Fig. 2. Vibronic spectra of $Li^{+16}O_3^{-}$ and $Li^{+18}O_3^{-}$ in solid krypton at 17 K. (a) Li atoms codeposited with $^{16}O_3$ in Kr (Kr/O_3 = 100/1) for 245 min. (b) Li atoms codeposited with $^{18}O_3$ in Kr ($Kr/^{18}O_3$ = 100/1) for 284 min.

Fig. 3. Visible spectra of matrix-isolated $M^{+}O_3^{-}$ species produced by codepositing alkali atoms with ozone in argon (Ar/O_3 = 100/1). (a) Li, 3.5 hr. (b) Na, 2 hr followed by 20 min of W lamp photolysis through Corning # 5562 glass which transmits 340-520 nm. (c) K, 1.5 hr. (d) Cs, 3 hr.

Fig. 4. Expanded scale vibronic spectra of $Na^{+16}O_3^{-}$ and $Na^{+18}O_3^{-}$ in solid argon.

Fig. 5. Plot of vibronic data for $Li^{+16}O_3^{-}$ in argon and krypton matrices and $Li^{+18}O_3^{-}$ in solid krypton. The ordinate represents the vibrational energy per quantum and the abscissa is the vibrational quantum number.

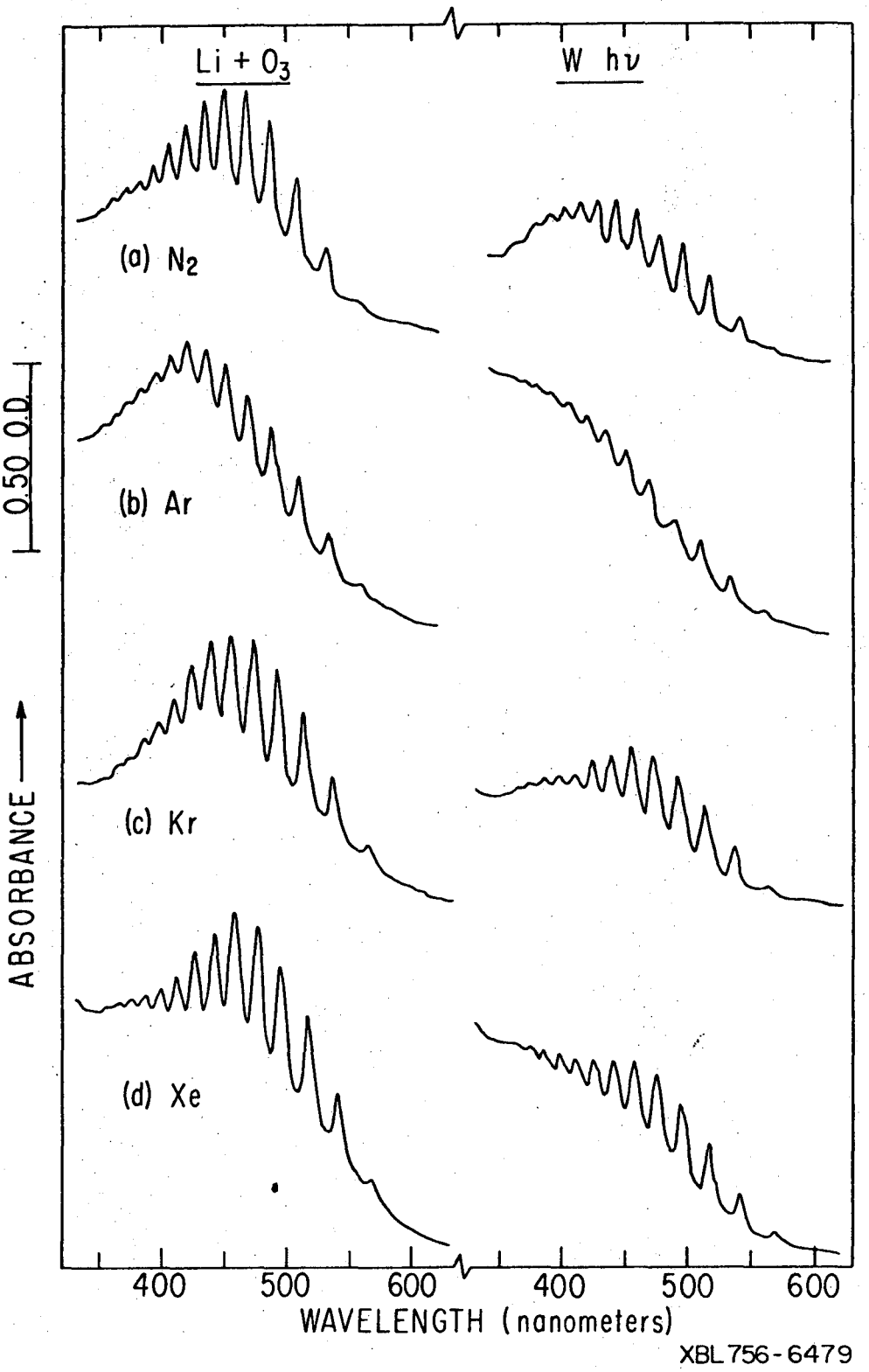


Fig. 1.

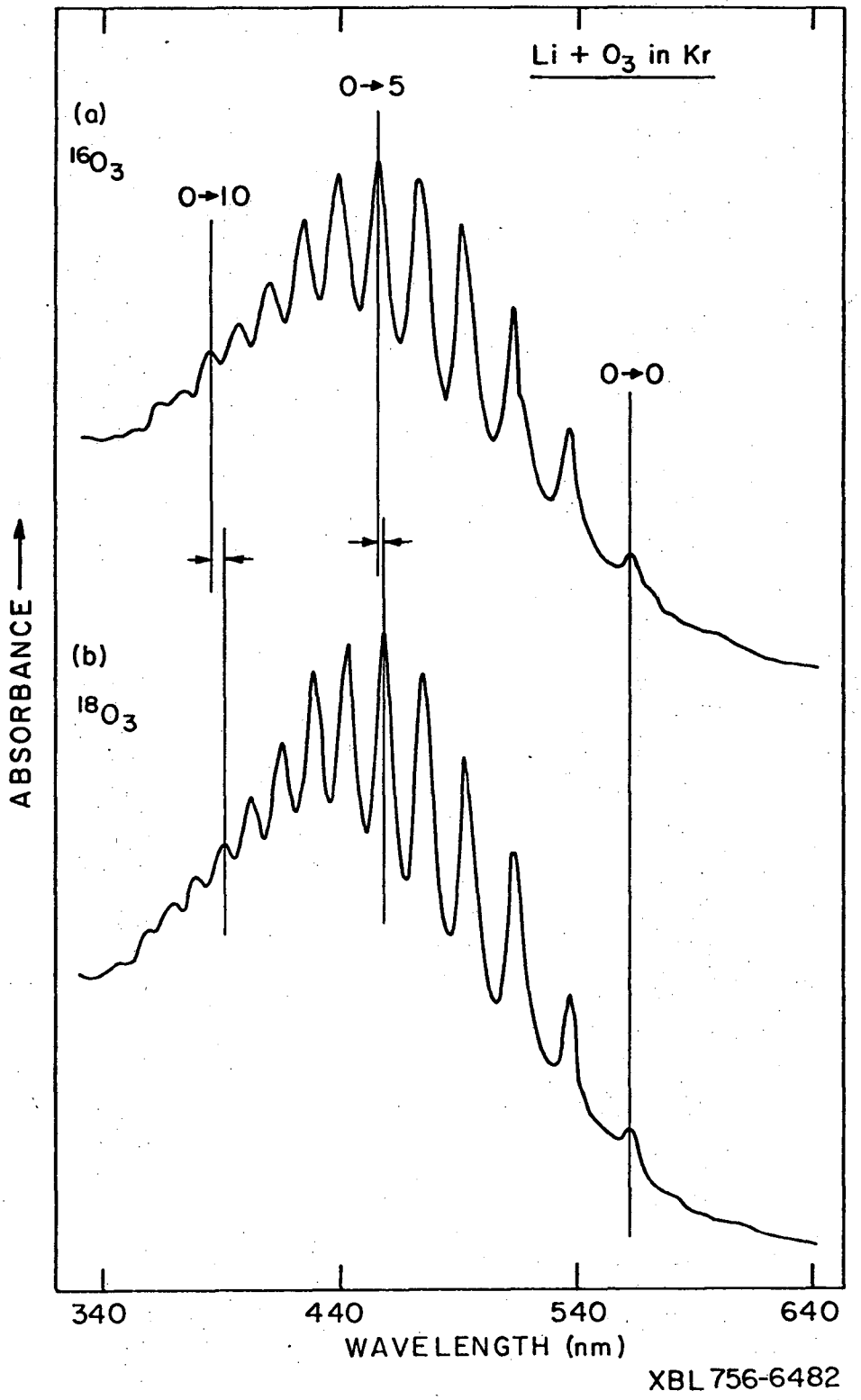

Li + O3 in Kr
0→5
(a)
16O3
0→10
0→0
(b)
18O3
ABSORBANCE
340
440
540
640
WAVELENGTH (nm)
XBL 756-6482

Fig. 2.

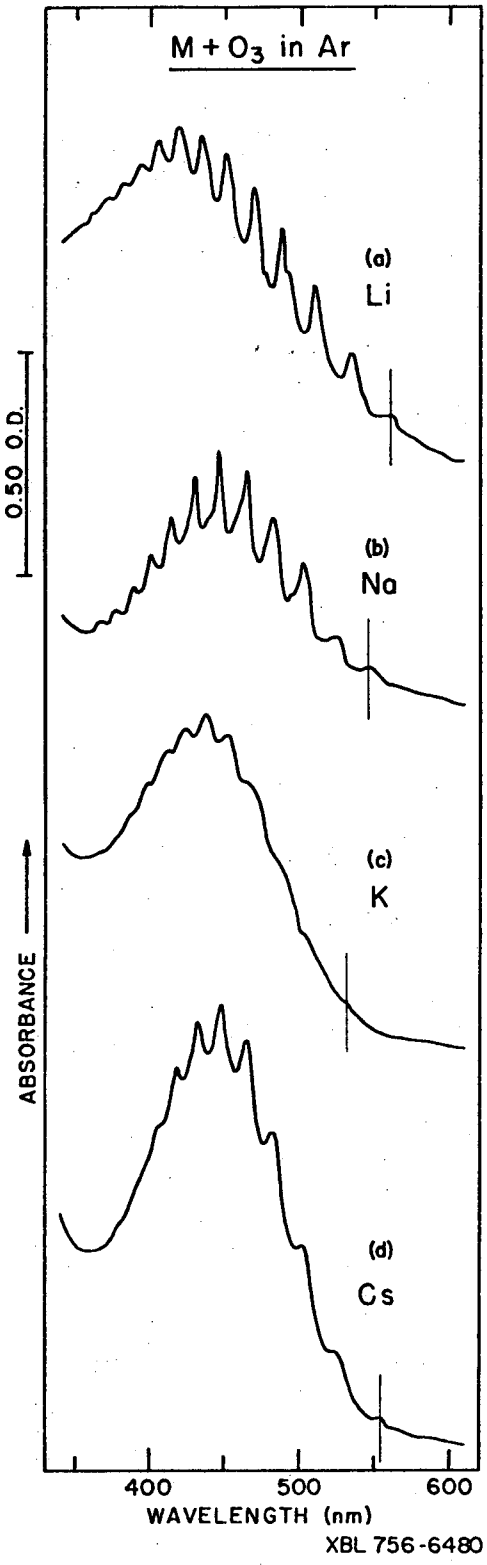


Fig. 3.

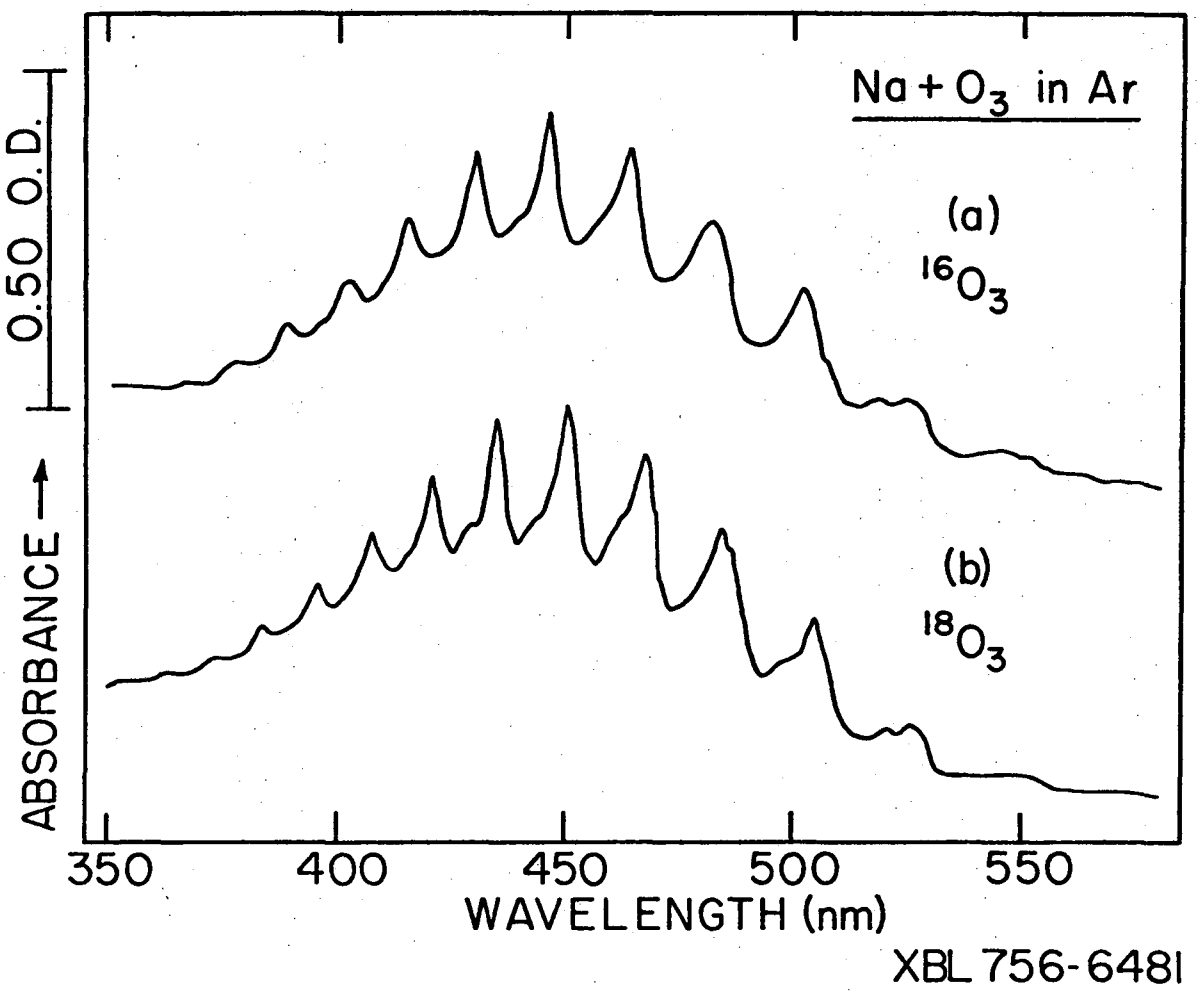

Na + O3 in Ar
(a)
16O3
(b)
18O3
0.50 O.D.
ABSORBANCE →
350
400
450
500
550
WAVELENGTH (nm)
XBL 756-6481

Fig. 4.

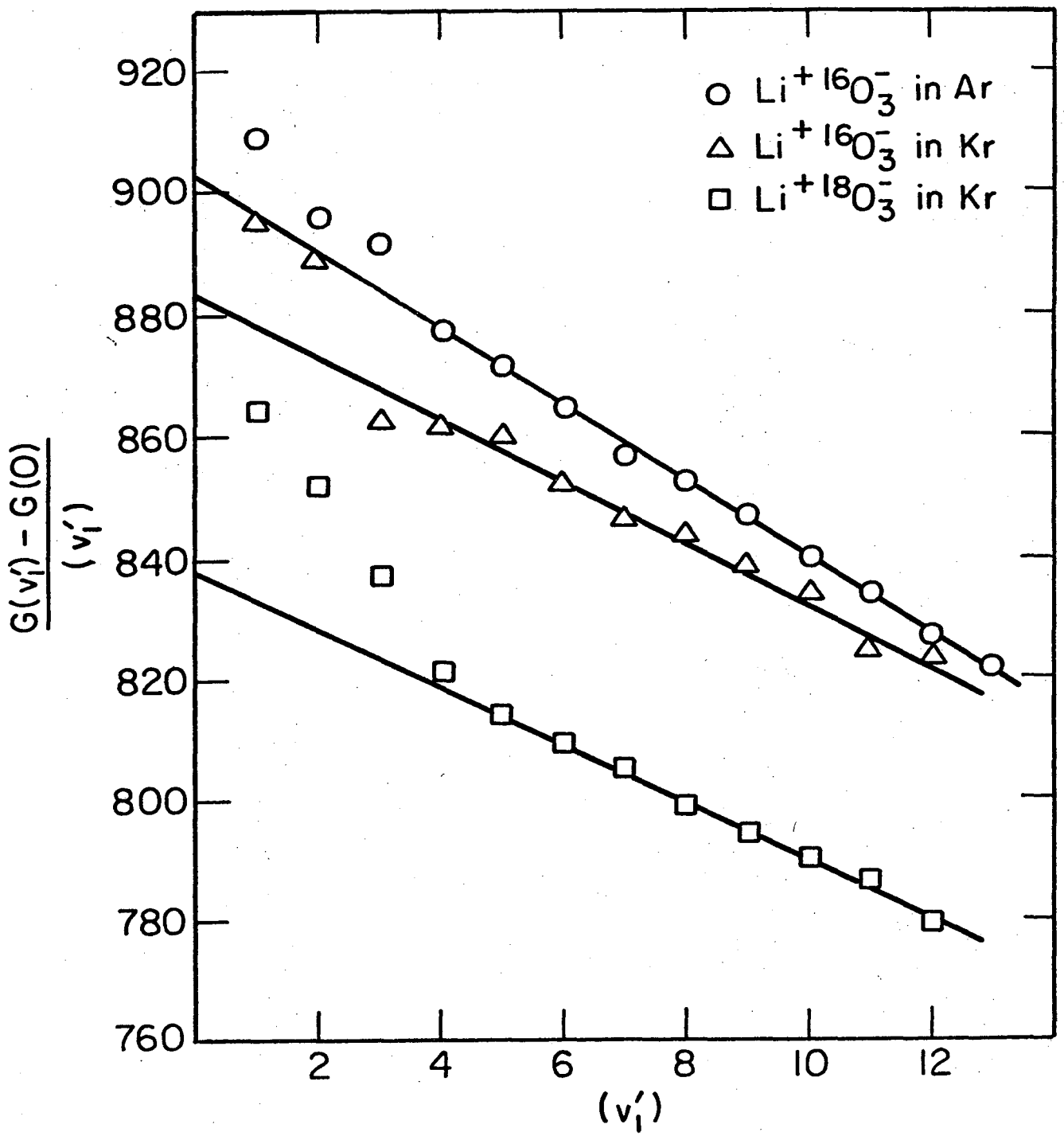


Fig. 5.

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