

# Resonance Raman Spectrum of the Matrix Isolated Ozonide Ion in the Species $M^+O_3^-$

Lester Andrews

Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901. Received January 15, 1973

**Abstract:** The products of matrix reactions of ozone and alkali-metal atoms on a 16°K copper wedge have been studied using argon and krypton plasma excitation. The Raman spectra are characterized by a fundamental at 1011–1018  $\text{cm}^{-1}$  below the exciting lines depending upon the alkali reagent and a regular progression of overtones using blue-green excitation. Substitution of  $^{18}\text{O}_3$  confirms the assignment of these bands to  $\nu_1$  of the ozonide ion. The fundamental and regular overtone progressions in  $\nu_1$  of  $\text{O}_3^-$  are probably due to the resonance Raman effect.

Alkali-metal ozonides have been prepared by reaction of ozone gas with the anhydrous alkali hydroxide<sup>1</sup> or the superoxide.<sup>2</sup> Pure lithium ozonide has not been synthesized; however, the heavier alkali ozonides exhibit increasing thermal stability with increasing alkali atomic weight. The crystalline alkali-ozonide compounds are stable only when stored in hermetically sealed containers at low temperatures; upon warming the ozonide decomposes to the superoxide and oxygen gas.<sup>3</sup> Accordingly, vibrational spectroscopic study of ozonide compounds is a difficult task using conventional techniques. Nevertheless, two groups<sup>4,5</sup> have recently reported Raman bands at 1010–1020  $\text{cm}^{-1}$  for polycrystalline  $\text{KO}_3$  and  $\text{CsO}_3$  using 6328 Å He-Ne excitation. Both groups point out the thermal instability of the ozonide species and its decomposition to the superoxide.

A detailed infrared study of the products of alkali-metal atom-ozone cocondensation matrix reactions has been recently conducted in our laboratory.<sup>6</sup> The ozonide ion in the  $M^+O_3^-$  species exhibited a very intense antisymmetric oxygen-oxygen stretching mode near 800  $\text{cm}^{-1}$  and a weak valence angle bending mode near 600  $\text{cm}^{-1}$ . In a recent article, Jacox and Milligan<sup>7</sup> reported the  $\nu_3$  mode and an electronic band system at 5100–3700 Å for  $\text{O}_3^-$ ; these workers produced the  $M^+O_3^-$  molecule by photolysis of  $M\text{-O}_2\text{-N}_2\text{O}$  argon matrix samples. Owing to the importance of ozone and its reactions in atmospheric chemistry, we deemed it desirable to obtain the complete vibrational spectrum of the ozonide anion. Recent Raman work on M plus  $\text{O}_2$  matrix systems has yielded excellent Raman spectra of the superoxide ion<sup>8,9</sup> in the species  $M^+O_2^-$ . The results of analogous experiments involving alkali-metal atom-ozone matrix reactions are briefly reported here.

## Experimental Section

Ozone- and oxygen-18-enriched ozones were synthesized by

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Tesla coil discharge of oxygen gas in a Pyrex finger immersed in liquid nitrogen using  $\text{O}_2$  pressures of less than 100 Torr.<sup>6</sup> Samples of ozone in argon ( $\text{Ar}/\text{O}_3 = 100$ ) were deposited from a stainless steel vacuum system onto a tilted copper block at 16°K for 4 hr, and a 1- $\mu$  vapor pressure beam of alkali atoms was codeposited with this gas mixture for 3 hr. These samples were a deep orange color which is characteristic of the ozonide anion; the argon-ozone sample itself was frosty white in appearance.<sup>10</sup> Laser excitation spectra were recorded using several argon and krypton plasma laser lines and techniques and instrumentation described previously.<sup>8-11</sup>

## Results and Discussion

In a Raman study<sup>10</sup> of argon matrix isolated ozone, the  $\nu_1$  fundamental was observed as a strong full-scale band at 1104  $\text{cm}^{-1}$  using approximately 15 mW of 4880-Å radiation and the  $0.3 \times 10^{-9}$  A range. When alkali-metal atoms were codeposited with the argon-ozone sample, the ozone feature at 1104  $\text{cm}^{-1}$  was very weak; however, much stronger features appeared near 1020  $\text{cm}^{-1}$  full scale on the  $1 \times 10^{-9}$  A range. This represents a reversal in the precursor/product intensity ratio of 10/1 observed for  $\text{O}_2/\text{O}_2^-$ ; a ratio of approximately 1/30 was observed in  $\text{O}_3/\text{O}_3^-$  experiments. It was immediately noticed that the 1020  $\text{cm}^{-1}$  product features were more stable to laser photolytic decomposition than ozone itself, although the new 1020- $\text{cm}^{-1}$  bands did undergo laser photolysis, in agreement with the polycrystalline ozonide work where 4880-Å irradiation caused decomposition of the ozonide sample.<sup>4</sup>

Site splittings for the new features were observed depending on the particular alkali-metal reagent; the most intense component was observed at 1012  $\text{cm}^{-1}$  for Li, 1011 for Na, 1004 for K, 1026 for Rb, and 1018 for Cs using 4880-Å laser excitation. In the reaction of  $^{18}\text{O}_3$  with Cs atoms, the new product feature shifted 56 to 962  $\text{cm}^{-1}$ . Reaction of a  $^{16,18}\text{O}_3$  isotopic mixture (55%  $^{18}\text{O}$ ) produced a sharp five-component multiplet which is consistent with the assignment of this new band to  $\nu_1$ , the symmetric O-O stretching mode of the ozonide ion in the  $M^+O_3^-$  species. The symmetrical mixed isotopes 16-18-16 and 18-16-18 were unresolved; they contributed a single feature of intensity appropriate for their added statistical weights.

Owing to the great intensity of the  $\text{O}_3^-$  emission bands and the proximity of the laser excitation lines to the electronic band for  $\text{O}_3^-$ , it was suspected that the observations might be due to a resonance effect. Examination of the overtone region yielded a series of sharp bands regularly decreasing in intensity. The

- (10) L. Andrews and R. C. Spiker, Jr., *J. Phys. Chem.*, **76**, 3208 (1972).
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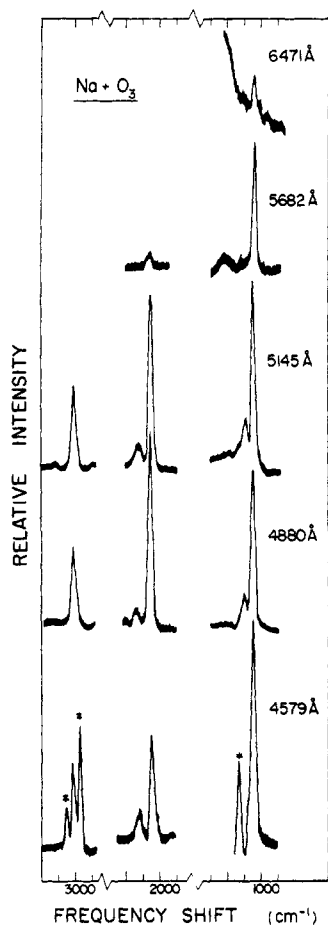


Figure 1. Emission spectra observed from products of matrix reactions of sodium atoms ( $\text{Ar}/\text{Na} \sim 200$ ) codeposited at  $16^\circ\text{K}$  with ozone ( $\text{Ar}/\text{O}_3 = 100$ ). All spectra were scanned at  $20 \text{ cm}^{-1}/\text{min}$  using a 3-sec rise time,  $250 \mu$  slits,  $0.1 \times 10^{-9} \text{ A}$  range, and  $5 \text{ \AA}$  pass dielectric filters except where otherwise noted:  $6471 \text{ \AA}$ , approximately  $45 \text{ mW}$  of power at the sample;  $5682 \text{ \AA}$ ,  $30 \text{ mW}$ , 1-sec rise time;  $5145 \text{ \AA}$ ,  $120 \text{ mW}$ ,  $0.3 \times 10^{-9}$  range;  $4880 \text{ \AA}$ ,  $20 \text{ mW}$ ,  $1 \times 10^{-9}$  range, 1-sec rise time;  $4579 \text{ \AA}$ ,  $30 \text{ mW}$ , no dielectric filter,  $\text{Ar}^+$  fluorescence bands denoted by \*.

cesium ozonide vibrational data for the  $\nu_1$  fundamental, first, second, and third overtones respectively were  $1018, 2026, 3024,$  and  $4012 \text{ cm}^{-1}$  for  $^{16}\text{O}_3^-$  and  $962, 1915, 2859,$  and  $3795 \text{ cm}^{-1}$  for  $^{18}\text{O}_3^-$ . The fundamental and overtones can be nicely reproduced with a two-constant energy level expression making the single mode or diatomic approximation.<sup>12</sup> Vibrational constants are  $\omega_1 = 1028.2 \text{ cm}^{-1}$  and  $X_{11} = 4.95 \text{ cm}^{-1}$ .

Figure 1 contrasts sodium ozonide Raman spectra for the fundamental and two overtones using five different laser exciting lines. The red  $6471\text{-\AA}$  krypton plasma line produced a weak fundamental at  $1011 \text{ cm}^{-1}$  and no overtones were detected. Yellow  $5682\text{-\AA}$  excitation produced a strong fundamental and a weak first overtone with about 10% of the fundamental intensity. As is shown in the figure, intense first and second overtones were observed at  $2013$  and  $3002 \text{ cm}^{-1}$

(12) See, for example, G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed, Van Nostrand, Princeton, N. J., 1950, p 93.

using the  $5145\text{-}$  and  $4880\text{-\AA}$  argon plasma laser lines; note that the first overtone is more intense than the fundamental in the  $4880\text{-\AA}$  spectrum. First and second overtones were observed with  $4579\text{-\AA}$  excitation with lower intensities relative to the fundamental than were observed for  $5145$  and  $4880 \text{ \AA}$ . Depolarization ratios of  $0.8\text{--}0.9$  were determined for the fundamental and overtones. Argon matrix isolated ozone produced a  $\nu_1$  depolarization ratio of  $0.6$ . Clearly this latter value is too high; this may arise from preferential orientation of the molecules in the matrix sample. The lack of randomization of molecular orientations has been observed for  $\text{NO}_2$  and  $\text{CuF}_2$  in argon matrices using esr techniques.<sup>13</sup> Accordingly the high depolarization ratios for the ozonide fundamental and overtones observed here may be due to the effect of molecular orientation.

Kiefer and Bernstein<sup>14</sup> have described the experimental characteristics of resonance Raman and pre-resonance Raman spectra. The salient feature of the present spectra using  $5145\text{-}, 4880\text{-},$  and  $4579\text{-\AA}$  excitation is the regular intensity pattern in the progression of vibrational bands. As Figure 1 shows, the intensity in the vibrational progression falls off monotonically in the  $5145\text{-}$  and  $4579\text{-\AA}$  spectra; in the  $4880\text{-\AA}$  spectrum, the intensity increases from the fundamental to the first overtone then decreases to the second overtone. This regular intensity behavior in the vibrational progression markedly contrasts resonance fluorescence spectra where the intensity in the progression can be erratic, depending upon Franck-Condon overlap integrals.

Accordingly, the  $4579\text{-}, 4880\text{-},$  and  $5145\text{-\AA}$  laser excitation spectra with regular vibrational progressions are better described as resonance Raman;<sup>14</sup> these excitation wavelengths fall within the reported electronic band.<sup>7</sup> Since the  $5682\text{-\AA}$  excitation is close to the absorption band, the observed intensity enhancement may arise from the preresonance Raman effect. The  $6471\text{-\AA}$  spectrum is ascribed to the Raman observation of the  $\nu_1$  mode of the ozonide anion.

The present Raman spectra for the  $\text{M}^+\text{O}_3^-$  species demonstrate the usefulness of the matrix reaction technique to produce and stabilize observable quantities of unstable species for laser examination. The ozonide Raman fundamentals near  $1010 \text{ cm}^{-1}$  in the matrix isolation study agree with He-Ne observations on polycrystalline ozonides. The matrix host moderates the photodecomposition of the  $\text{M}^+\text{O}_3^-$  molecule and allows the resonance Raman spectrum of  $\text{O}_3^-$  to be observed using argon ion excitation.

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