The Peroxide-ion Fundamental Frequency

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Summary Recently published Raman data for Group IA and IIA element peroxides should be reassigned to the corresponding carbonates. The peroxide-ion frequency is shown to be near 800 cm.$^{-1}$.

BLUNT, HENDRA, and MACKENZIE[1] recently presented Raman data for several ionic superoxides and peroxides and suggested, on the basis of the lack of correlation between the frequencies and bond lengths, that the qualitative molecular-orbital picture of the bonding in these diatomic species may be grossly inadequate.[2] However, although their data for the superoxide fundamental frequencies (near 1140 cm.$^{-1}$) are in accord with previously published work,[3,4] their values for the peroxides (1054—1093 cm.$^{-1}$) are in marked disagreement with data obtained in this laboratory several years ago using 5461 Å mercury excitation and photographic recording (values near 800 cm.$^{-1}$); there are apparently no published values for comparison.

Of the eight wavenumber values for peroxides quoted by Hendra and his co-workers, seven were immediately found by reference to the available standard spectra (Raman and i.r.) to be within a few wavenumbers of the ν_1 mode of the carbonate ion in the corresponding solid metal carbonate; peroxides react rapidly with atmospheric CO_2 to yield carbonates. A sample of anhydrous Na_2O_2 (J. T. Baker Co. Analyzed Reagent)† was examined in a sealed sample tube with a Spex Ramalog instrument (6328 Å excitation) and found to show a very weak Raman band at 1141 cm.$^{-1}$

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indicative of the presence of a small amount of superoxide,[3] and two very strong bands at 738 and 794 cm.$^{-1}$ which are assigned, respectively, to the pair of identical peroxide ions within the unit cell[5,6] and to the unique peroxide ion located at the unit-cell edge; the relative intensities are indeed close to 2 : 1.

Another sample of Na_2O_2 in an open tube exposed to the atmosphere showed, within a short time, loss of intensity at the 1141, 794, and 738 cm.$^{-1}$ bands and the appearance of new bands at 1084 (carbonate), near 830 (weak), and 862 cm.$^{-1}$ (the lower hydrates of sodium peroxide). The octahydrate, obtained from an aqueous solution prepared by adding the anhydrous material slowly to ice-cold water in the absence of CO_2, showed a strong Raman band at 842 cm.$^{-1}$.

These data illustrate that the peroxide ion is subjected to widely varying environments in these several ionic lattices but they do not suggest a need for modifying the qualitative MO picture for the diatomic oxygen series. A smooth curve drawn through eight points on a graph of the fundamental frequencies against measured bond lengths for the O_2^+ and O_2 systems using data tabulated by Herzberg[7] predicts a peroxide ion frequency near 800 cm.$^{-1}$ if the bond length is 1·49 Å.[5]

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[1] F. J. Blunt, P. J. Hendra, and J. R. MacKenzie, *Chem. Comm.*, 1969, 278.

[2] G. Herzberg, "Molecular Spectra and Molecular Structure. I. Diatomic Molecules," VanNostrand, New York, 1950, p. 343.

[3] J. A. Creighton and E. R. Lippincott, *J. Chem. Phys.*, 1964, **40**, 1779.

[4] W. Holzer, W. F. Murphy, H. J. Bernstein, and J. Rolfe, *J. Mol. Spectroscopy*, 1968, **26**, 543.

[5] R. Tallman, J. L. Margrave, and S. W. Bailey, *J. Amer. Chem. Soc.*, 1957, **79**, 2979.

[6] R. G. Wyckoff, "Crystal Structure," Interscience, New York, 1963, vol. I, p. 167.

[7] Ref. 2, p. 558.