The Laser Raman Spectra of Salts containing the Anions O_2^- and O_2^{2-}

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Summary Oxygen–oxygen stretching frequencies for peroxides and superoxides of Group IA and IIA elements are presented and their relationship to bond orders discussed.

EXPERIMENTAL factors, particularly in cases of coloured, photosensitive, or insoluble species, have limited the versatility of the Raman method. The advent of laser sources has now largely removed such limitations. In symmetrical molecules vibrational modes in which $\partial\mu/\partial q$ (μ = dipole moment, q = normal co-ordinate) is zero are not active in absorption but frequently give rise to prominent features in the Raman spectrum.

We have studied the oxygen–oxygen stretching frequencies in the peroxides and superoxides of the metals of Groups IA and IIA. *X*-Ray crystallography has established that both these types of oxide contain discrete "O_2" species and consideration of the stoicheiometry indicates that peroxides contain an O_2^{2-} ion, superoxides an O_2^- ion. A number of such peroxides and superoxides have been prepared[1,2] and examined with the Cary 81 Raman spectrometer powered by the helium–neon laser.

TABLE

	ν(O–O)	O–O (Å) (ref. 3)
H_2O_2(l)	880[4]	1·48 ± 0·01
Li_2O_2(s)	1093	
Na_2O_2(s)	1081	1·49 ± 0·01
K_2O_2(s)	1062	
Rb_2O_2(s)	1054	
MgO_2(s)	1088	
CaO_2(s)	1086	1·48
SrO_2(s)	1073	
BaO_2(s)	1061	1·49 ± 0·04
KO_2(s)	1146	1·28 ± 0·02
RbO_2(s)	1141	
O_2(g)	1555[3]	1·211

The trends in vibrational frequency may be explained by making reference to a MO theory. In neutral O_2 the electronic configuration

$$KK(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p)^2(\pi y 2p)^2(\pi y^* 2p)^1(\pi z^* 2p)^1$$

is generally accepted.

On this simple basis it can be said that the neutral oxygen molecule displays a formal bond order of two since it has an "excess" of four bonding electrons over antibonding electrons. In forming the anions O_2^- and O_2^{2-} extra electrons must be added to antibonding orbitals. Thus, the "bond order" may be considered to be reduced by one half for each electron added, *i.e.* in O_2^- the "bond order" should be approximately $1\frac{1}{2}$, and in O_2^{2-} approximately unity. This effect should be reflected in the bond-dissociation energies, interatomic distances, and frequencies of the stretching vibrations for the bond (even though the connection between this quantity and the others is a little tenuous). The data strongly suggest that this view of the bonding is at least qualitatively correct, since as bond order is reduced the interatomic distances increase and stretching frequencies decrease. Nevertheless, several striking features are of interest.

Thus, although the –O–O– system in both K_2O_2 and H_2O_2 may formally be assigned a bond order of 1, the O–O stretching frequencies in the two compounds differ by some 200 cm.$^{-1}$ whereas the O–O distances are virtually identical.[3] It is true that on the one hand the species studied is anionic and is part of a rigid crystal lattice while on the other it is the covalent molecular component of a hydrogen-bonded liquid, but the frequency shift observed is still unduly large. This may be indicative of some fundamental differences in the nature of the bonding between the oxygen atoms in the two cases. Similar behaviour is observed for the –C≡C– bond in acetylides. Thus the C_2^{2-} species present in calcium carbide may formally be assigned a C–C bond order of 2 as in the alkenes, but again the stretching frequency differs considerably in the two classes of compounds. In CaC_2 (solid) and Ag_2C_2 (solid) laser Raman bands are observed at Δν 1860 and 1798 cm.$^{-1}$, respectively,[6] whereas the C=C stretching frequency in alkenes generally falls within the range 1620—1680 cm.$^{-1}$.

Even more striking is the effect of decreasing the charge on the –O–O– system as represented by the progression $O_2^{2-} \rightarrow O_2^- \rightarrow O_2$. The shift in O–O stretching frequency associated with the first step is of the order of 80—100 cm.$^{-1}$ with the potassium and rubidium compounds examined. This is not unduly large in the light of a variation of up to 40 cm.$^{-1}$ resulting from changes in crystal structure and in cation size and charge. It is, however, associated with a dramatic change of nearly 15% in the interatomic distance.[3] This change is nearly three times that associated with the frequency difference between superoxide ion and molecular oxygen, more than 400 cm.$^{-1}$.

The above phenomena are not susceptible to simple explanation but they do demonstrate hazards inherent in equating vibrational frequencies or force constants directly with functions of bond energies unless due allowance be made for the microscopic environment of the bonded atoms or for changes in bonding which may occur when proceeding from one molecular species to another.

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[1] E. Thorpe, "Dictionary of Applied Chemistry," 4th edn., Longmans, London, 1954.
[2] J. Newton Friend (ed.), "Text Book of Inorganic Chemistry," Griffin, London, 1914—1937.
[3] A. F. Wells, "Structural Inorganic Chemistry," Oxford Univ. Press, Oxford, 1962, pp. 406—409.
[4] K. Nakamoto, "Infrared Spectra of Inorganic and Co-ordination Compounds," Wiley, New York, 1963, p. 97.
[5] Ref. 4, p. 72.
[6] F. Blunt and J. R. Mackenzie, unpublished work.