491. *Iodine–Oxygen Compounds. Part I. Infrared Spectra and Structure of Iodates.*

By W. E. Dasent and T. C. Waddington.

The infrared spectra of some simple and complex iodates are reported and interpreted in terms of discrete iodate ions (IO_3^-) and iodato-groups ($-O-IO_2$) bonded covalently to metal atoms. The infrared spectra of HIO_3, DIO_3, and $KH(IO_3)_2$ are also reported.

During a structural investigation of a number of iodine–oxygen compounds, it became necessary to make a study, the results of which we now report, of the vibrational characteristics of the IO_3 (iodate) group, both as the free anion and in combination as a covalently bound iodato-group.

The chemistry of crystalline iodates is confused, and has been discussed by Wells [1] and others.[2,3] In particular, the early view [4] that the iodates of the alkali metals, and ammonium iodate, adopt lattices of the perovskite type has been disputed. However, the most recent studies [2,5] of sodium iodate agree that the crystal contains discrete pyramidal IO_3^- ions, stereochemically similar to the chlorate and bromate ions. This pyramidal configuration has also been established in both anhydrous ceric iodate [6] and its monohydrate,[3] and is very probable in ammonium iodate.[2]

The Raman spectra of solutions containing the iodate ion have been studied [7,8] by Shen, Yao, and Wu; a symmetrical pyramidal ion belongs to the point group C_{3v} and the four fundamental vibrational frequencies expected were observed and the following assignments made:

	ν_1 (sym. stretch)	ν_2 (sym. bend)	ν_3 (asym. stretch)	ν_4 (asym. bend)
Species	A_1	A_1	E	E
Frequency (cm.$^{-1}$)	779	390	826	330

All four fundamentals are both infrared- and Raman-active; the antisymmetric fundamentals ν_3 and ν_4 are both doubly degenerate.

We have studied the infrared spectra of a number of iodates, both simple and complex, between 4000 and 400 cm.$^{-1}$. For the simple iodates (Table 1) the frequencies ν_1, ν_3, and

---

[1] Wells, "Structural Inorganic Chemistry," Oxford University Press, 2nd edn., 1950, p. 266.

[2] MacGillavry and van Eck, *Rec. Trav. chim.*, 1943, **62**, 729.

[3] Ibers, *Acta Cryst.*, 1956, **9**, 225.

[4] For references to, and a discussion of, the early literature, see ref. 2.

[5] Naray-Szabo and Neugebauer, *J. Amer. Chem. Soc.*, 1947, **69**, 1280.

[6] Cromer and Larson, *Acta Cryst.*, 1956, **9**, 1015.

[7] Shen, Yao, and Wu, *Phys. Rev.*, 1937, **51**, 235.

[8] For references to the early spectrographic literature, see Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Supplement 2, Part I, Longmans, Green and Co., 1956, pp. 935, 936.

in a few instances ν_2, were observed. The vibration of lowest frequency ν_4, and in most instances ν_2 also, lay beyond the spectral region accessible with sodium chloride and potassium bromide optics. In all cases both ν_1 and the less intense ν_3 (often observed only as a shoulder to the ν_1 band) lay between 700 and 800 cm.$^{-1}$, their separation being within the range 20—70 cm.$^{-1}$. An unambiguous assignment of the peaks in this region was made difficult by the possible occurrence there of the overtone $2\nu_2$, its intensity amplified by Fermi resonance with the other symmetrical frequency ν_1. Several of the spectra do, in fact, display three maxima between 700 and 800 cm.$^{-1}$; that of highest frequency has been assigned to ν_3 but it is impossible to distinguish between ν_1 and $2\nu_2$, and these are included in the same column in Table 1.

In three cases (lithium, nickel, and thorium iodates) only a single maximum, at *ca.* 770 cm.$^{-1}$, was observed. It is possible that in these spectra we have failed to resolve two or more very close peaks; this is very probably the case for thorium iodate, where the band is very broad. But there is another possibility which arises if the crystal, instead of being composed of discrete IO_3^- ions, involves an octahedral arrangement of oxygen atoms equidistant from a central iodine atom. The iodate group in such a structure would have, instead of four, only two infrared active fundamentals, as is the case in the octahedral molecule sulphur hexafluoride. An early study [9] of the crystal structure of lithium iodate has in fact assigned such a configuration to the iodate group, but this work has been criticised [1,3] and cannot be regarded as certain. Elucidation of this point is impossible at this stage, but it is noteworthy that we have also observed only a single maximum, whereas a pyramidal ion should give two in the same region, in the spectra of ammonium chlorate (1070 cm.$^{-1}$), ammonium bromate (785 cm.$^{-1}$), and potassium bromate (786 cm.$^{-1}$).

TABLE 1.

Compound	ν_1 and $2\nu_2$ (cm.$^{-1}$)	ν_2 (cm.$^{-1}$)	ν_3 (cm.$^{-1}$)	Compound	ν_1 and $2\nu_2$, (cm.$^{-1}$)	ν_2 (cm.$^{-1}$)	ν_3 (cm.$^{-1}$)
$LiIO_3$	778s	404m	*a*	NH_4IO_3 ...	730s	*a*	790sh,m
$NaIO_3$ [c] ...	774s, 760s	*a*	796m	$AgIO_3$ [b] ...	705s, 695s	*a*	766m, 752m, 742m, 728m
KIO_3 [c]	750s	*a*	796m				
$RbIO_3$	757s, 741s	*a*	795sh, m	$TlIO_3$	705s	*a*	743s
$CsIO_3$	763s, 748s	*a*	773sh,s	$Ni(IO_3)_2$ ...	765s	440m, 407m	*a*
Me_4NIO_3 ...	780s, 757s	*a*	796sh,s	$Th(IO_3)_4$	770s [d]	410	*a*

s = strong, m = medium, w = weak, sh = shoulder.

a Not observed.

b The extensive splitting of ν_1 and ν_3 may mean that this compound should be grouped with those in Table 2. Anomalies in the spectra of the anions of silver salts are not unusual—see, *e.g.*, Sharp.[10]

c Spectra between 4000 and 650 cm.$^{-1}$ were also recorded by Miller and Wilkins,[11] whose results do not differ significantly from our own.

d Very broad band.

In compounds where the iodate group forms a covalent bond with another atom, the symmetry of the group is changed from C_{3v} to C_s, and the number of infrared-active fundamentals is increased from four to six. The additional two frequencies accrue from the removal of the degeneracy from the two antisymmetric fundamentals ν_3 and ν_4 of the iodate ion. This occurs in the compounds listed in Table 2, and is probably due to partial covalent bond formation (co-ordination) with the metal ion.

The two frequencies expected to result from the splitting of the degenerate ion frequency ν_4 were experimentally inaccessible, but in all cases the splitting of ν_3 was observed to give rise to two new peaks, one (ν_{3a}, the antisymmetric IO_2 stretching mode) in the range 757—808 cm.$^{-1}$, and the other (ν_{3b}, the symmetric IO_2 stretching mode) in the range 719—758 cm.$^{-1}$. The symmetrical bond stretching frequency ν_1 of the ion has, as its

---

[9] Zachariasen and Barta, *Phys. Rev.*, 1931, **37**, 1626.

[10] Sharp, *J.*, 1957, 3761.

[11] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.

TABLE 2.

Compound	ν_1 (O–I str.)	ν_{3a} (IO_2 asym. str.)	ν_{3b} (IO_2 sym. str.)	ν_{M-O} (M–O str.)	Compound	ν_1 (O–I str.)	ν_{3a} (IO_2 asym. str.)	ν_{3b} (IO_2 sym. str.)	ν_{M-O} (M–O str.)
$K_2Mn(IO_3)_6$	630s	786s	755s	480m	$Pb(IO_3)_2$	690s	770m	720s	423m
$(NH_4)_2Mn(IO_3)_6$	640s	789s	758s	479m	$Hg(IO_3)_2$	683s	757m	738	436m
$K_2Pb(IO_3)_6$	695s	783sh,m	757s	420m	$Hg_2(IO_3)_2$	650s	794, 776	719	448m
$K_2Ti(IO_3)_6$	656s	787s	757	443m	Iodoxybenzenes [12]	—	762—795	716—744	
$Fe(IO_3)_3$	697s	808m	757s	451m					

equivalent in the Table 2 compounds, an O–IO_2 stretching mode absorbing at rather lower frequencies, 630—697 cm.$^{-1}$.

The frequency ranges for the antisymmetric and symmetric stretching vibrations of the IO_2 group agree well with those recorded[12] for iodoxybenzene ($C_6H_5{\cdot}IO_2$) and its derivatives, *viz.*, 762—795 cm.$^{-1}$ (asym.) and 716—744 (sym.).

Circumstances rather similar to the above have already been reported for nitrato-[13] and carbonato-[14] complexes, in which each of the degenerate frequencies of the planar nitrate and carbonate ions gives rise to two new frequencies when the degeneracy is removed by co-ordination with a metal ion.

A better parallel to the iodate case has been recorded[15] for the pyramidal ammonia molecule, which has the same symmetry as the iodate ion (C_{3v}); partial deuteration to monodeuteroammonia changes the symmetry to C_s, with a resultant splitting of ν_3 (3414 cm.$^{-1}$) into ν_{3a} at 3378 cm.$^{-1}$ and ν_{3b} at 2444 cm.$^{-1}$.

In all the compounds listed in Table 2, a peak of moderate intensity was observed between 420 and 480 cm.$^{-1}$. Although this peak may represent the $-O{\cdot}IO_2$ bending mode corresponding to ν_2 in the iodate ion, yet it seems more likely that the absorption is due to a metal–oxygen bond-stretching vibration, since a recent study[16] of the infrared spectra of a large number of metallic acetylacetonates and benzoylacetonates records M–O stretching frequencies between 420 and 490 cm.$^{-1}$. Also, the frequencies observed (Table 2) are in the same order as those found[18] for M–F vibrations in comparable octahedral complex fluorides:

	K_2MnF_6	K_2TiF_6	K_2PbF_6
M–F (cm.$^{-1}$)	622	560	502
	$K_2Mn(IO_3)_6$	$K_2Ti(IO_3)_6$	$K_2Pb(IO_3)_6$
M–O (cm.$^{-1}$)	480	443	420

Iodic Acid.—The structure of the α-modification of iodic acid has been determined by *X*-ray diffraction.[17] The crystal consists of pyramidal IO_3 groups bound together by hydrogen bonds, and the I–O distances within the IO_3 groups, *viz.*, 1·80, 1·81, and 1·89 Å, strongly suggest that at least one I–O bond differs in character from the other two. The bond distances found in a later neutron-diffraction study,[19] *viz.*, 1·78, 1·82, and 1·90 Å, suggest that all three may be different. The symmetry of the group is there C_s, and the infrared spectrum should show the same features as those of the Table 2 compounds. This is found to be the case, but more extensive splitting of the observed frequencies is noticeable, suggesting a higher degree of interaction between one IO_3 group and others in the crystal. This is not unexpected, since in iodic acid, although the pyramidal iodate groups are distinct, there are three more oxygen atoms completing a very distorted octahedron around the central iodine, at distances noticeably shorter than those expected

---

[12] Furlani and Sartori, *Ann. Chim.* (*Rome*), 1957, **47**, 124.
[13] Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222.
[14] Gatehouse, Livingstone, and Nyholm, *J.*, 1958, 3137.
[15] Reding and Hornig, *J. Chem. Phys.*, 1955, **23**, 1053.
[16] Nakamoto, McCarthy, and Martell, *Nature*, 1959, **183**, 459.
[17] Rogers and Helmholz, *J. Amer. Chem. Soc.*, 1941, **63**, 278.
[18] Peacock and Sharp, *J.*, 1959, 2764.
[19] Garrett and Levy, quoted by Ibers, ref. 3.

for van der Waals bonds.[20] Thus ν_1 is observed as a broad band with maxima at 650m, 637m, and 577m cm.$^{-1}$; ν_{3a} at 804 cm.$^{-1}$, with shoulders at 820 and 835 cm.$^{-1}$; and ν_{3b} at 763s, cm.$^{-1}$, with shoulders at 745 and 718 cm.$^{-1}$. These maxima were essentially unchanged in deuterium iodate, whose spectrum was recorded in order to identify the frequencies assignable to O–H vibrations. In iodic acid, the O–H bond stretching frequency appears as a broad band of rather low intensity, with a poorly defined maximum at 2920 cm.$^{-1}$. In deuterium iodate this band has shifted to considerably lower frequencies (max. = 2200 cm.$^{-1}$). Two peaks of low-medium intensity at 1163 and 1101 cm.$^{-1}$ can be assigned to O–H bending modes, since these disappear in deuterium iodate, having presumably shifted to lower frequencies where the intense I–O absorption precludes their observation. A weak peak at 462 cm.$^{-1}$ in both HIO_3 and DIO_3 has not been assigned.

The spectrum of the well-known "bi-iodate," KIO_3,HIO_3, was also recorded, but a complete assignment of the observed peaks is difficult without a knowledge of its crystal structure. The complexity of the spectrum suggests that the two types of iodate group may be present. The following are the observed maxima (in cm.$^{-1}$): 2900 (very broad; O–H str.), 1170w (O–H bend.), 833w, 820m, 777sh,s, 765s, 742s, 713s, 637m, 571m.

Experimental.—Compounds for determinations of infrared spectra were dried *in vacuo* over suitable desiccants, mulled with Nujol and with hexachlorobutadiene, and smeared between rock-salt or potassium bromide plates. The spectra were recorded on a Perkin-Elmer 21 double-beam recording spectrophotometer, with sodium chloride and potassium bromide optics.

The following compounds were pure commercial samples, or were prepared by standard metathetical reactions: lithium, sodium, potassium, rubidium, cæsium, ammonium, tetramethylammonium, silver, thallous, thorium, lead, mercurous, and mercuric iodates.

Anhydrous nickel iodate was prepared [21] by heating together nickel nitrate and iodic acid in 8N-nitric acid, and ferric iodate [22] by adding ferric nitrate in 4N-nitric acid to boiling aqueous iodic acid.

Potassium hexaiodatomanganate(IV) was obtained by boiling together freshly precipitated manganese dioxide, iodic acid, and potassium iodate, according to Berg's method [23] [Found: iodometric equiv., 31·2. Calc. for $K_2Mn(IO_3)_6$: 31·1]. The corresponding ammonium salt was prepared by a similar procedure [Found: iodometric equiv., 30·3. Calc. for $(NH_4)_2Mn(IO_3)$: 30·0]. Potassium hexaiodatoplumbate(IV) was prepared [24] from lead tetra-acetate, potassium nitrate, and iodic acid in 7N-acetic acid [Found: iodometric equiv., 37·3. Calc. for $K_2Pb(IO_3)_6,2H_2O$: 38·1]. Potassium hexaiodatotitanate was prepared by a modification of the literature method [25] [Found, after being dried at 150°: iodometric equiv., 33·0. Calc. for $K_2Ti(IO_3)_6$: 32·7]. The source of titanium was a sample of $K_2TiO(C_2O_4)_2,2H_2O$ kindly supplied by Dr. W. G. Palmer.

Potassium hydrogen di-iodate (bi-iodate) was obtained by crystallising equimolar quantities of the constituents from hot water, and deuteroiodic acid from a solution of iodine pentoxide (dried for several days at 200—210°) in deuterium oxide.

One of us (W. E. D.) acknowledges with thanks the award of a Fellowship by the Nuffield Foundation.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, December 18th, 1959.*]

---

[20] Wells, *Acta Cryst.*, 1949, **2**, 128.
[21] Meusser, *Ber.*, 1901, **34**, 2432.
[22] von Endredy, *Z. anorg. Chem.*, 1934, **217**, 58.
[23] Berg, *Compt. rend.*, 1899, **128**, 673.
[24] Ray and Saha, *Z. anorg. Chem.*, 1934, **217**, 376.
[25] Ray and Saha, *Z. anorg. Chem.*, 1932, **208**, 104.