Correlation between Structural, Infrared and Nuclear Quadrupole Resonance Data of Iodates *

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The peculiarities of the structure and the IR and NQR spectra of acid iodates and pyroiodates which contain the I_2O_5 group are reported. Based in this, the results for several iodates that contain organic cations are considered.

Key words: Iodates, NQR and IR spectroscopy, Structure.

Introduction

After two papers with incorrect data on NQR of I_2O_5 [1, 2], numerous papers on various classes of iodates were stimulated by three papers on iodine-127 NQR of α-HIO_3 [3–5]. Based on NQR data, Herlach [6] indicated that none of the alkaline metal iodates have a perovskite structure, as was confirmed by further structural studies on iodates. At present we know the structure, infrared spectra and NQR of (i) simple iodates of metals having various valencies (ii) complicated iodates whose chromatoiodate $CrIO_6$ type heteroions represent CrO_4 tetrahedra which are connected with the IO_3 group via oxygen bridges, (iii) complex iodates $M^I M^{IV} (IO_3)_6$, where M^I is an alkaline metal, NH_4 or H, and M^{IV} is Sn, Ge, Ti, Zr, Pb or Mn, (iv) acid iodates that contain the HIO_3 group, and (v) pyroiodates that contain the groups I_2O_5 and IO_3. We shall consider the peculiarities of these crystals and their correlation with NQR data (Table 1) and IR spectra, and then we shall discuss based on their NQR data, the peculiarities of the structures of several iodates with organic cations.

1. Correlation of Structure and NQR and IR Spectra Data

The iodate group is a triangular pyramid with an iodine atom in the vertex and three oxygen atoms in the base. The distance of I–O is approximately 1.81 Å, and the angles at the vertex are ca. 100°. The I–O distance is greater than the double bond length $I = O$,

which equals 1.78 Å, and smaller than the single bond length (1.99 Å). The sum of van der Waals radii of iodine and oxygen is 3.5 Å. In crystal structures of iodates, besides these three closest atoms the iodine atom is surrounded by another three (rarely with two of four) oxygen atoms with an I–O distance of 2.6 up to 3.2 Å. This causes a distorted octahedral environment of iodine. In a pure form this occurs in case of $RbIO_3$ [7] where the three closest I–O bonds measure 1.807(3) Å, the three weaker I…O bonds 2.753(3) Å, and the apex angles O–I–O 99.63°. In α-$LiIO_3$ the situation is similar [8].

Axial symmetry of the IO_3 group brings about a zero EFG tensor asymmetry parameter η on iodine (see Table 1 for $RbIO_3$ and [9] for α-$LiIO_3$).

A slight deviation of η from zero for α-$LiIO_3$ [10] may be explained by the formation of $Li_{1-x}H_x IO_3$ solid solutions during α-$LiIO_3$ growth from acid solutions [11].

Close axial symmetry and hence small values of η are observed for other alkaline metal- and ammonium iodates. The quadrupole coupling constant of alkaline metal iodates is approximately 1000 MHz. A weak (< 5%) but regular decrease at the transition from Li to Cs is observed, which demonstrates the decrease of ionic contribution with increasing ionic radius and a decrease of the cation polarizing capabilities. This shows that the EFG is mainly due to covalent iodine-oxygen bonds [9, 12].

Various iodate group interactions may cause a departure of a regular pyramid. Such interactions can be (i) stronger bonds of the iodate group oxygen with the metal, (ii) even stronger bonds O…I, the lengths of which can vary between 2.2 and 2.5 Å (these bonds can be considered as intermediate between first and second coordination spheres [13]), (iii) covalent bonds,

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which can be carried out via oxygen as well as hydrogen bonds observed in acid iodates and crystalline hydrates. These interactions appear in changes of the asymmetry parameter and quadrupole coupling constant. Thus, when going from alkaline metal iodates to metal iodates with higher valencies, the bond covalency between the oxygen and metal increases, and this causes an increase of both the asymmetry parameter and quadrupole coupling constant. A correlation between these values and metal valencies 'n' takes place [9, 14]:

$$\eta = 0.111\,n - 0.095\,,$$
$$e\,Q\,q\,(\text{MHz}) = 23.24\,n + 974.57\,. \qquad (1)$$

The great value of one of the two non equivalent iodine atoms in the $AgIO_3$ structure asymmetry parameter is somehow unexpected (see Table 1).

The explanation is found in a peculiarity of the $AgIO_3$ structure [15]. Normal $I(1)-O$ and $I(1)...O$ is observed in one of the two non equivalent iodate groups (1.78–1.81 Å) and (2.74–2.99 Å) respectively, while in the other one at usual $I(2)...O$ bonds (2.71–2.77 Å) somewhat unusual bonds $I(2)-O(6)$ (1.80 Å), $I(2)-O(1)$ (1.85 Å) and $I(2)-O(2)$ (1.85 Å) are observed. Such a lengthening is due to the existance of short contacts of two oxygen atoms of the $I(2)O_3$ group with silver ions $Ag(1)-O(1)$ (2.38 Å) and $Ag(2)-O(3)$ (2.37 Å). While the average distance from other five oxygen atoms of each silver ion is 2.60 Å. Thus, a strong deviation from the correlation (1) may indicate unusual bonds, which causes the distortion of the iodate group.

Even grater distortions of the iodate group are observed on covalent bond formation with oxygen atoms. The iodic acid HIO_3 can serve as an example. The non-equivalent $I-OH$ bond length for α-HIO_3 is 1.90 Å, and for the other two 1.79 Å. Though the $I-OH$ bond is much longer than the other two, due to the hydrogen bonding this bond is still shorter than the single bond. It is interesting to note that in acid iodates the $I-OH$ bond may be both longer and shorter than in pure HIO_3, depending on the strength of the hydrogen bond and other structure peculiarities.

The structure of acid sulphate-iodate of potassium has been determined by X-ray diffraction [16]. Observing an $I-O$ bond length of 1.90 Å in the iodate group, the authors [16] concluded that this group represents an HIO_3 molecular and suggested the formula $HIO_3 \cdot K_2SO_4$. The structure of this crystal has

Table 1. Data on iodate iodine-127 NQR of various compounds.

Compound	T/K	v_1 MHz	v_2 MHz	η	$e\,Q\,q_{zz}$ MHz
$RbIO_3$	300	145.44	290.88	0.0000	969.60
NH_4IO_3	300	147.24	294.41	0.0135	981.40
$AgIO_3$	77	148.31	291.96	0.1112	975.64
		153.58	306.73	0.0329	1022.66
α-HIO_3	77	203.12	330.84	0.4337	1141.03
β-HIO_3	77	192.88	326.40	0.3849	1118.30
$HIO_3 \cdot K_2SO_4$	300	236.44	340.30	0.5796	1199.94
β-$KIO_3 \cdot HIO_3$	300	146.97	289.08	0.1142	966.14
		154.77	305.87	0.0964	1021.48
		193.06	304.45	0.4732	1055.99
		193.40	315.40	0.4322	1087.54
$KIO_3 \cdot HIO_3 \cdot KCl$	300	148.40	291.50	0.1188	974.44
		208.17	302.60	0.5682	1065.07
$K_2[Ge(IO_3)_6]$	77	194.74	314.43	0.4445	1086.09
	293	192.96	310.05	0.4505	1071.87
$KCrIO_6$	77	205.34	313.24	0.5125	1092.93
I_2O_5	77	217.75	329.02	0.5236	1149.95
		249.03	357.58	0.5822	1261.42
	300	216.53	323.47	0.5367	1132.84
		245.24	346.84	0.5994	1226.95
$HIO_3 \cdot I_2O_5$	77	178.03	316.35	0.3172	1074.91
		213.55	308.24	0.5763	1086.31
		221.35	318.57	0.5796	1123.32
	300	177.46	312.02	0.3325	1062.11
		210.00	303.30	0.5756	1068.79
		221.98	313.42	0.6014	1109.04
$RbIO_3 \cdot I_2O_5$	77	155.90	301.70	0.1616	1010.93
		252.10	319.03	0.7247	1152.35
		257.23	324.51	0.7282	1172.85
$KIO_3 \cdot I_2O_5$	77	162.60	308.15	0.2084	1036.03
		259.75	319.80	0.7557	1161.22
		264.02	331.75	0.7327	1199.93
$2\,KIO_3 \cdot I_2O_5$	77	160.02	303.35	0.2078	1019.84
		166.45	305.92	0.2644	1033.69
		245.18	319.90	0.6903	1148.82
		266.60	327.25	0.7592	1188.95

been determined once again in [17]. For the iodate group the following bond lengths have been obtained: $I-O(1)$ (1.916 Å), $I-O(2)$ (1.796 Å), $I-O(3)$ (1.799 Å), which undoubtedly is HIO_3. Besides, there exists a short contact between iodine atom and one of the sulphate group oxygen atoms $I...O(4)$ (2.495 Å) (while the bond $S-O(4)$ is simultaneously lengthening). This was the basis for the author of [17] to suggest the formula $K_4H_2(I_2S_2O_{14})$, which from our point of view is not as clear. The $I-O$ bond lengths obtained in [17] are in better agreement with the NQR data for $HIO_3 \cdot K_2SO_4$ (see Table 1), as the values of η and $e\,Q\,q$ are maximal for this crystal among all those obtained for HIO_3 now in use. This shows the weakness of the hydrogen bond and maximal distortion of the HIO_3 group (see also [18], where the spectroscopic and thermal behaviour of this crystal has been studied).

From the aforesaid it can be seen that the bond length is sufficiently sensitive and reflects the state of the iodate group. In X-ray structural works, in the presence of iodine atom it is difficult to localize the hydrogen atom. The bond lengths in the iodate group are the bases for IO_3, HIO_3 and hydrogen bond recognitions [13]. Values of eQq for the IO_3^- group are usually lower than 1050 MHz, whereas for the covalently bonded IO_3 group (HIO_3 etc.) they are higher than 1050 MHz. The asymmetry parameter η is more sensitive. This is why the correlation between η and nonequivalent (the longest bond lengths $D(I-O)$ seems well grounded [19]:

$$D(A) = 0.2103\,\eta + 1.812\,. \tag{2}$$

There exists another approach to connecting η and eQq with iodate group distortion [20, 21], namely with variation of IO_3 apex angles. In [10] an attempt has been made to justify this connecting. Without denying the role of angle variation, we note the inconvenience and insufficient justification of this approach, that may lead to incorrect conclusions. A correlation between the I–O stretching frequencies and the lengths of these bonds [22] was also established, which can be expressed by the relation [23]

$$\nu(\text{cm}^{-1}) = 3256 - 1380\,D(A)\,. \tag{3}$$

From (2) and (3) a correlation between the asymmetry parameter and the stretching frequency of the longest bond can be obtained:

$$\nu(\text{cm}^{-1}) = 755 - 290\,\eta\,. \tag{4}$$

From the example of $\beta - KIO_3 \cdot HIO_3$, the sensitivity and efficiency of the NQR method in revealing fine peculiarities of hydrogen bond can be seen. Insufficient accuracy of the X-ray experiment on the structure of β-$KIO_3 \cdot HIO_3$ [24] lead the authors of [25] to the conclusion that at room temperature there exist dimers $H(IO_3)_2$ with $\bar{1}$ symmetry, similar to that obtained for α-$KH(IO_3)_2$. However, the NQR data show that despite the strong hydrogen bond $IO_3 \ldots HIO_3$ [26] one can easily distinct IO_3 and HIO_3 groups, and hence there are no dimers with $\bar{1}$ symmetry. This indicated the necessity of another more accurate determination of the β-modification structure, which was carried out in [27]. This neutron diffraction study of β-$KIO_3 \cdot HIO_3$ reveals $IO_3 \ldots HIO_3$ grouping with nonsymmetric hydrogen bond in full accordance with the NQR data.

One other interesting example of acid iodates is the potassium biiodate-chloride [28]. According to NQR data it may be concluded that an HIO_3 group ($\eta = 0.5682$) and a sufficiently distorted IO_3 group ($\eta = 0.1188$) exist. However, here the distortion of the IO_3 group is not so much due to hydrogen bond (in this case the same values of η for HIO_3 as in β-$KIO_3 \cdot HIO_3$ could be expected), than due to strong $I \ldots O$ bond with 2.536 Å length between the iodine HIO_3 and oxygen IO_3 group, which leads to appropriate lengthening of the I–O bond in IO_3 [29].

In Table 1, NQR data for $K_2Ge(IO_3)_6$ are given as an example of alkaline metal hexaiodatometalate $M^I M^{IV}(IO_3)_6$, where M^I is alkaline metal, NH_4 or H and M^{IV} is Sn, Ge, Ti, Zr, Pb or Mn. The crystal structure of $K_2Ge(IO_3)_6$ has been determined [30] from $M^I M^{IV}(IO_3)_6$ isomorphous compounds [31]. In the $Ge(IO_3)_6^{--}$ ion, the central Ge atom is surrounded by six oxygen atoms at equal 1.901 Å distances which form a regular octahedron. At two usual bonds 1.796 Å and 1.801 Å, the iodate groups have one longer bond 1.861 Å due to covalent bond formation between one oxygen atom with the central Ge atom. All the iodate groups are crystallographically equivalent. In accordance with structural data, on each transition (ν_1 and ν_2) only one line is observed, the values η and eQq of which correspond to the appropriate parameters of α-HIO_3.

The $CrIO_6^-$-chromatoiodate heteroion represents a CrO_4 tetrahedron and an IO_3 group, covalently connected via a common bridge oxygen atom $O_3Cr-O-IO_2$ [32]. The I–O bond length with the bridge oxygen (1.899 Å) longer than the two other ones (1.742 Å and 1.787 Å), and the iodate group represents a distorted covalently bonded grouping. The values η and eQq of Table 1 could be expected on the basis of correlations (1) and (2).

The I_2O_5 iodic anhydride [33] has a structure somewhat remaining that of the chromatoiodate ion. Here two iodate groups are connected via the common oxygen atom, the bonds of which are close to the single bond $O_2I-O-IO_2$. The iodine atoms of this group, however, are crystallographically inequivalent. One of the iodine atoms has an additional intrachain bond $I \ldots O$, whereas the other one has also an interchain bond $I \ldots O$. In the I_2O_5 structure, the shortest $I \ldots O$ bond length is only 2.23 Å. As it was expected, the asymmetry parameters of I_2O_5 are very high (Table 1). Appropriate pairs of line ν_1 and ν_2 are determined by the two-frequency method. In the structure of anhydro-iodic acid, $HIO_3 \cdot I_2O_5$ (HI_3O_8) [34], it was found

that the groups I_2O_5 and HIO_3 are hydrogen bonded with each other. Thus, in the NQR spectra, two lines on each transition could be expected, the asymmetry parameters of which are characteristic for the I_2O_5 group ($\eta = 0.5756$ and $\eta = 0.6014$), and one line of which is characteristic for HIO_3 group ($\eta = 0.3325$). The checking by the two-frequency method revealed the "mixing up" of two lines in the $HIO_3 \cdot I_2O_5$ NQR spectra (see Table 1). We have listed on such a possibility in [35]. HI_3O_8 full NQR spectra have been obtained by the authors of [20] independently of us [19, 35, 36]. However, from our point of view these authors, without having the full I_2O_5 NQR spectra and assuming a connection between eQq and the apex angles of the pyramid, have assigned incorrectly the line with 221 MHz frequency to the HIO_3 group, and lines with 178 MHz and 213 MHz frequencies to the I_2O_5 group.

The structures of potassium and rubidium pyroiodates given in Table 1 are unknown. Nevertheless, on the basis of NQR data we may find their structure. The I_2O_5 groups in these compounds approach maximal distortion. The bond lengths $I-O-I$ in the bridges approach the maximum for single $I-O$ bonds (1.99 Å). The asymmetry parameter, that corresponds to this length (on (2) $\eta \sim 0.85$) is close to those observed in these compounds. At the same time we have an essential value of η for the IO_3 group. As far as very short bonds between alkaline metal and the IO_3 group oxygen are unprobable, we can suppose very short $O \ldots I$ bonds between the IO_3 group oxygen and the I_2O_5 group iodine atoms. Thus, $KIO_3 \cdot I_2O_5$ and $RbIO_3 \cdot I_2O_5$ could be formally considered as salts of anhydro-iodic acid HI_3O_8, where the $I_3O_8^-$ ion is expressed as a unit. Similar conclusion can be made in connection with $2KIO_3 \cdot I_2O_5$ when considering $K_2I_4O_{11}$.

2. On Structure of Several Iodates with Organic Cations

In Table 2 several iodates with organic cations [23, 37–40] are given, where only the crystal structure of guanidinium iodate $C(NH_2)_3IO_3$ is known [41]. Values of η and eQq are calculated from an equation obtained by A. F. Volkov [42] (see also [43]) on the basis of NQR frequency measurements:

$$\frac{(1-\eta^2)^2}{(3+\eta^2)^3} = \frac{343}{10\,800} \cdot \frac{[(a-1)(a+2)(2a+1)]^2}{(a^2+a+1)^3}, \quad (5)$$

$$eQq_{zz} = 20\,v_1 \sqrt{\frac{a^2+a+1}{21\,(3+\eta^2)}}, \quad \text{where} \quad a = \frac{v_2}{v_1}.$$

Tetramethylammonium (TMA) iodate is characterised by a rather greater than ammonium iodate asymmetry parameter. Nevertheless, the value of eQq is smaller. This could be expected from the common behaviour of eQq decrease while increasing the cation radius in the series of alkaline metals [9].

TMA iodate dihydrate has an even greater asymmetry parameter than the anhydrous one at approximately the same value of eQq, which apparently is connected with additional distortion of the iodate group due to hydrogen bonds with water molecules. In the range of 77 K up to room temperature, no phase transition is observed, however, in anhydrous TMA iodate the authors of [44] found a phase transition near 210 °C.

In acid TMA iodate the HIO_3 group is characterised by a sufficiently great asymmetry parameter ($\eta = 0.5245$), whereas the IO_3 group is characterised by relatively lower values ($\eta = 0.0576$), which allows

Table 2. Data on iodate iodine-127 NQR of compounds with organic cations, the structures of which are mainly unknown.

Compound	T/K	v_1 MHz	v_2 MHz	η	eQq_{zz} MHz
$N(CH_3)_4IO_3$	77	146.72	297.50	0.0885	969.87
	300	140.28	278.09	0.0829	928.26
$N(CH_3)_4IO_3 \cdot 2H_2O$	77	149.18	290.75	0.1427	973.16
	300	141.22	276.33	0.1311	924.29
$N(CH_3)_4IO_3 \cdot HIO_3$ H_2O	77	150.79	300.29	0.0576	1001.64
		202.28	305.42	0.5245	1067.61
$(NH_2)_2CO \cdot HIO_3$	77	158.28	311.64	0.1107	1041.37
		159.20	312.86	0.1172	1045.76
		160.29	319.47	0.0518	1065.48
		162.51	309.75	0.1965	1040.45
$C(NH_2)_3IO_3$	77	156.08	306.10	0.1240	1023.49
		160.52	314.60	0.1261	1052.03
	298	152.12	298.40	0.1233	997.71
		156.00	306.90	0.1135	1025.66
α-En $\cdot 2HIO_3$	77	150.72	296.21	0.1170	990.10
	293	145.69	288.46	0.0885	963.06
β-En $\cdot 2HIO_3$	77	149.81	297.82	0.0684	993.67
	293	146.12	289.90	0.0790	967.56
En $\cdot 3HIO_3$	77	155.75	307.68	0.0980	1027.60
		161.00	309.64	0.1751	1039.13
		223.13	324.26	0.5681	1141.37
En $\cdot 6HIO_3$	77	159.95	312.76	0.1332	1046.26
		197.32	316.10	0.4542	1093.36
		222.10	325.37	0.5593	1143.60
	293	156.72	307.64	0.1210	1028.49
		194.24	309.96	0.4589	1072.86
		216.71	317.66	0.5587	1116.36

En – ethylendiamine ($H_2NCH_2CH_2NH_2$)

us to suppose that the hydrogen bond is relatively weak and short I...O contacts are absent.

There are four inequivalent iodine atoms in the unit cell of hydroiodate of urea, none of which enters the HIO_3 group. On proton transition from the HIO_3 group to urea, uronium cation formation can be concluded. The mean values of η and eQq for uronium iodate are close to of those of the guanidinium iodate.

Both iodate groups in α- and β-En $\cdot$ 2 HIO_3 are equivalent, and the values of η and eQq are typical for the IO_3 group, and not for the HIO_3 group, which certifies on ethylendiamine protonation with ethylendiammonium iodate formation. The difference between the α and β modifications are apparently due to different conformations of ethylendiammonium [23].

Addition of one more HIO_3 molecule in En $\cdot$ 3 HIO_3 causes the formation of a hydrogen bond

of HIO_3 ($\eta = 0.5681$) with an IO_3 group, as a result of which the formerly equivalent IO_3 groups become inequivalent. The hydrogen bond, and perhaps the I...O bond as well distort this IO_3 group, the asymmetry parameter of which increases up to 0.1751. The NQR spectrum of En $\cdot$ 6 HIO_3, that consists of three lines on each transition, can be explained if we assume that there are two IO_3 groups ($\eta = 0.1332$) which have given their protons to the ethylendiamine, together with which two HIO_3 molecules form an equivalent hydrogen bonded grouping ($\eta = 0.4542$) and, at last two more HIO_3 molecules from hydrogen bonds with HIO_3 which in their turn are connected with IO_3 groups. $IO_3...HIO_3...HIO_3$ groupings are being formed from both sides of ethylendiammonium cation. The IR spectra [23] are in good agreement with such a description and correlate with NQR data.

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