Infrared and Raman Studies of Crystalline I_2O_5, $(IO)_2SO_4$, $(IO)_2SeO_4$ and I_2O_4

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Crystalline samples of the iodine oxides I_2O_5 and I_2O_4 are studied by infrared and Raman spectroscopy in the region $4000-30$ cm^{-1} while only the Raman spectra are discussed for $(IO)_2SO_4$ and $(IO)_2SeO_4$. The spectra of I_2O_5, $(IO)_2SO_4$ and $(IO)_2SeO_4$ are interpreted on the basis of recent single crystal X-ray data, and force fields for these molecules are derived. A discussion of various centrosymmetrical, structural models for I_2O_4 has been based upon spectroscopical interpretations.

The history of iodine oxides and oxoacids extends back to the earlier days of chemistry. Until about 1960 the main attention was focused on synthetical, analytical and other chemical aspects of these compounds. At that time, a number of spectroscopic studies in this field appeared.[1–4] However, the interpretation of these data was hampered by the lack of reliable structural data. An exception is the more recent spectroscopic study of Sherwood and Turner[5] on HIO_3, $NaIO_3$, HI_3O_8 and I_2O_5. Except for I_2O_5, these authors had access to accurate structural data.

Earlier, the crystal structures have been reported for I_2O_5,[6] $(IO)_2SO_4$ and $(IO)_2SeO_4$.[7] The present communication aims at extending the knowledge on these compounds to include the vibrational properties in relation to structure. For I_2O_4 nobody has so far been able to grow single crystals large enough for structure determination. Hopefully, the spectral analyses, including force constant calculations, should contribute to elucidate the bonding in I_2O_5, $(IO)_2SO_4$ and $(IO)_2SeO_4$ and be helpful in solving the I_2O_4 structure.

EXPERIMENTAL

The samples of I_2O_5, $(IO)_2SO_4$, $(IO)_2SeO_4$ and I_2O_4 were prepared as described previously.[6,8]

The infrared spectra were recorded with Perkin-Elmer models 225 ($4000-200$ cm^{-1}) and FIS-3 ($400-45$ cm^{-1}) spectrometers. Nujol mulls and polyethylene pellets were prepared, and optical windows of KBr or Si were used at room temperature and in a conventional cryostat at liquid nitrogen temperature. For the Raman studies a Cary 81 spectrometer equipped with helium–neon (Spectra Physics 125 A) and argon ion (CRL 52 G) lasers were employed.

The samples employed in the Raman studies were sealed in pyrex tubes on a vacuum line. For infrared studies the samples were handled in a dry box.

RESULTS

The observed infrared and Raman frequencies of I_2O_5 with assignment of the fundamentals in terms of approximate localized vibrations are listed in Table 1 together with the calculated values. A factor group analysis is given in Table 2, and the force constants are listed in Table 3. For $(IO)_2SO_4$ and $(IO)_2SeO_4$ the observed Raman frequencies, the calculated fundamentals and the assignments are presented in Table 4. The infrared and Raman spectra of I_2O_4 are shown in Figs. 1 and 2, while the observed and calculated wave numbers and the interpretations are listed in Table 5.

DISCUSSION

Iodine pentoxide [I_2O_5]

Spectral features. The present infrared and Raman data (Table 1) are in reasonably good agreement

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Table 1. Infrared and Raman spectral data for crystalline I_2O_5.

IR Obs.	IR Calc.[a]	Raman Obs.	Raman Calc.	Interpretation
835m[b]	835	834w	834	I=O stretch
820m	832	831w	833	I=O stretch
800m	812 ⎱ 809 ⎰	810vs	812 ⎱ 809 ⎰	I=O stretch / I=O stretch
755s	751	748w	751	I=O stretch
720s	745 ⎱ 741 ⎰	724s	745 ⎱ 741 ⎰	I=O stretch / I=O stretch
670m	737	693vs	737	I=O stretch
587s	611 ⎱ 611 ⎰	607m	611 ⎱ 610 ⎰	I−O stretch / I−O stretch
510vw		535vw		combination band
	422 �️	433w	422	I−O stretch
415m	{	412vw		combination band
	421 ⎰	401w	421	I−O stretch
357m	367	377m	367	IO_2 def.
340m	353 ⎱ 352 ⎰	361w	353 ⎱ 352 ⎰	IO_2 def. / IO_2 def.
327m	342	323m	342	IO_2 def.
305w	332 ⎱ 331 ⎰	300s	332 ⎱ 331 ⎰	IO_2 def. / IO_2 def.
	282 ⎱ 281 ⎰	288m	282 ⎱ 281 ⎰	torsion / torsion
276s	256 ⎱ 250 ⎰	263w	256 ⎱ 250 ⎰	IO_2 def. / IO_2 def.
222m	226	202w	226	IO_2 def.
205m	210	193w	210	IO_2 def.
180m	199 ⎱ 198 ⎰	176w	200 ⎱ 198 ⎰	IO_2 def. / IO_2 def.
153w	133	146s	140	I⋯O stretch
122s	126	109s	116	I⋯O stretch
109m	95	97m	95	I−O−I bend
87m	68	80vs	72	I−O−I bend
81m		65m		lattice mode
60w	55[c]	59s ⎱ 47s ⎰	55[c]	torsion

[a] Calculated with force constants from Table 3. [b] s, strong; m, medium; w, weak; v, very. [c] Six torsional vibrations are calculated between 58 and 54 cm^{-1}.

with earlier work [5] when the different temperatures used are taken into account. Thus, our peaks at 327, 276 and 109 cm^{-1} can easily be split into doublets, separated by 4 − 8 cm^{-1} as previously observed [5] at 77 K. In the region 760 − 700 cm^{-1} we believe that the discrepancies are caused by humidity in Sherwood and Turner's [5] samples, since our spectra approached theirs when the samples were exposed to atmospheric moisture. Our bands at 222 and 205 cm^{-1} were reported [5] at 233 and 212 cm^{-1}, respectively. The peak [5] at 390 cm^{-1} was not observed in this study.

With few exceptions, our Raman spectrum of I_2O_5 is in good accordance with the earlier data.[5] While the Raman bands have normal widths, most of the infrared bands were extremely broad. This may partly be due to the large number of possible combination bands with appreciable intensities in the infrared spectra.[9]

Structure. The mutual exclusion between infrared and Raman bands confirms the centrosymmetric unit cell.[6] Since the work of Sherwood and Turner

Table 2. Correlation table for crystalline I_2O_5.

Molecular group C_1				Site group C_1	Space group C_{2h}^5 $(Z=4)$				
Active in	Rot.	Transl.	Vibr.	Symmetry species	No. of internal vibrations	No. of external vibrations	N_{tot}	Active in	No. of acoustical modes
IR, R[a]	3	3	15	C_1———C_1 $\Big\langle$ A_g	15	6	21	R	O
				B_g	15	6	21	R	O
				A_u	15	5	20	IR	1
				B_u	15	4	19	IR	2

[a] IR, infrared active; R, Raman active.

was based on preliminary structural data,[10] the spectroscopic deductions can be extended further. I_2O_5 belongs to the space group $P2_1/c$ (C_{2h}^5) with four molecules in the unit cell (*cf.* Fig. 1 of Ref. 6). Thus, the fundamental optical vibrations will involve 21 external and 60 internal modes. There is no mirror plane in the molecular unit (proposed in Ref. 1) and the molecular as well as the site symmetry is C_1 (Table 2).

Four I=O bonds are present within each I_2O_5 unit (Fig. 1 of Ref. 6) rather than three assumed by Sherwood and Turner.[5] As indicated by the broken lines in this figure there are strong intermolecular forces between the I_2O_5 units. The shortest

intermolecular I···O distance is 2.23 Å compared with 1.99 Å for a normal I—O bond.[6] When the additional I···O interactions of the IO_2 end groups (2.23 Å $\leq$ I···O $\leq$ 2.72 Å) are taken into account, the three-dimensional network of the I_2O_5 structure appears.[6]

Force field calculations. The **G** matrix was based on the geometry adopted from the X-ray structure[6] assuming separate molecular I_2O_5 units. In the preliminary calculations diagonal force constants were adapted from related molecules,[11] and some obvious off-diagonal elements were introduced to account for the interactions between various I to O single and double bonds. These preliminary

Table 3. Force constants for I_2O_5, $(IO)_2SO_4$, $(IO)_2SeO_4$ and I_2O_4.

Type	I_2O_5	$(IO)_2SO_4$	$(IO)_2SeO_4$	I_2O_4
I=O stretch	5.0[a]			
I—O stretch	2.45	2.45	2.45	2.45
S—O(Se—O) stretch		7.2	5.3	
I—O—I and O—I—O bend	0.62	0.62	0.62	0.62
O=I—O bend	1.1			
O=I=O bend	1.6			
O—S—O(O—Se—O) bend		2.2	1.5	
torsion	0.08	0.08	0.08	0.08
mol—mol int.[b]	0.5	0.8	0.8	
I—O, I—O int.	0.45	0.45	0.45	0.45
I—O, I=O int.	0.5			
I=O, I=O int.	0.5			
S—O, S—O(Se—O, Se—O) int.		0.46	0.4	
I—O, I—O—I int.	0.2	0.2	0.2	0.2
S—O, O—S—O(Se—O, O—Se—O) int.		0.7	0.3	
O—S—O, O—S—O int. } O—Se—O, O—Se—O int. }		0.4	0.4	

[a] In units of mdyn $Å^{-1}$ (stretch constants), mdyn rad^{-1} (stretch-bend interactions) and mdyn $Å$ rad^{-2} (bending and torsion constants). [b] Stretch constant for intermolecular "bonds" between I and O.

frequencies were used as an aid for the vibrational assignments. Later, without introducing additional interaction constants, the force field was refined by a least squares program to minimize the deviations between the observed and calculate wave numbers. At first, the four I_2O_5 molecules of the unit cell were treated as independent. Later, intermolecular interaction forces were introduced between I and O atoms separated by distances shorter than 2.50 Å. Force constants of 0.5, 1.0 and 1.5 mdyn/Å for these intermolecular bonds were employed in different sets of calculations. The best fit was obtained for k = 0.5 mdyn/Å (designated mol − mol int. in Table 3). This value seems quite reasonable for the weaker I$\cdots$O interactions compared with the intramolecular I−O and I=O stretching force constants.

The internal, fundamental frequencies (originally) accidentally degenerate for the four I_2O_5 molecules) were increasingly split into A_g and B_g and into A_u and B_u when larger intermolecular interactions were introduced. However, even for k = 1.5 mdyn/Å the $A_g − B_u$ and the $A_u − B_g$ fundamentals remain approximately degenerate due to the lack of interaction between the two molecules of the unit cell correlated by the inversion centre.

A complete normal coordinate calculation for the entire unit cell, taking a variety of physical interactions into account, was beyond the scope of this study. Our final force constants are listed in Table 3, while the calculated wave numbers, showing an average deviation of 13 cm^{-1}, are listed in Table 1.

The I=O bonds have been ascribed a total bond order of 1.91,[6] the weakening resulting from the intermolecular interactions. For the I−O bonds a bond order of 1.21 has been evaluated.[6] Thus, compared to a value of 2.45 mdyn/Å for I−O bonds the force constant of an I=O of 5.0 mdyn/Å is probably somewhat higher than expected. With the strong intermolecular interactions it is difficult to calculate these force constants accurately.

Assignments. 23 infrared and 29 Raman active peaks were observed which is only about 60 % of the optically active modes of the I_2O_5 unit cell. The broad infrared bands probably comprise overlapping neighbour bands as revealed at low temperatures.[5] Moreover, several low bending and torsional vibrations may be unobserved, hidden by the Rayleigh wing in the Raman, or having low intensities in the far infrared region.

The previous assignments of the I=O double bond stretching vibrations[5] between 670 and 845 cm^{-1} were supported by our force constant calculations.

The symmetric and asymmetric I−O−I stretching vibrations are strongly coupled because of the large bond angle (139.2°). They are assigned to bands in the 610−400 cm^{-1} region. The very weak Raman and infrared bands at 535 and 510 cm^{-1}, respectively, were explained as combination bands. The rather low Raman intensity of the I−O−I symmetric mode is unexpected, and this may reflect the contribution of partial ionic character of the bonds.

Various deformation modes involving the IO_2 end units, are expected below 400 cm^{-1}, as suggested by the potential energy distribution. Among the fundamentals of this type, 16 of 24 have been assigned to bands between 377 and 176 cm^{-1}. Like methylene groups, they may be divided into scissor, wag, twist and rocking modes, but the force constant calculations reveal that they are strongly coupled. The four I−O−I bending modes were attributed to bands around 100 cm^{-1}.

A separation of the observed low frequency infrared and Raman bands into internal and lattice modes cannot be made without great ambiguity, and the earlier interpretations[5] lack experimental

Table 4. Raman spectral data for crystalline $(IO)_2SO_4$ and $(IO)_2SeO_4$.

$(IO)_2SO_4$		$(IO)_2SeO_4$		Interpretation
Obs.	Calc.^{a}	Obs.	Calc.	
1290vw ^{b}		1158vw		
1140vw				
1077m	1066 ⎱			S−O_4 stretch
	1065 ⎰			S−O_4 stretch
1040m	1064			S−O_4 stretch
965vw	969			S−O_4 stretch
919vw				

Table 4. Continued.

		844w	846	Se$-$O$_4$ stretch
			816	Se$-$O$_4$ stretch
		812s	816	Se$-$O$_4$ stretch
			816	Se$-$O$_4$ stretch
776w				Impurity I$_2$O$_4$
649s	666			SO$_4$ bend
	634		634	I$-$O stretch
	634		634	I$-$O stretch
627m	615			SO$_4$ bend
		602w		
	614			SO$_4$ bend
	575		575	I$-$O stretch
583w				
	575		575	I$-$O stretch
542w				
		525w		
494s	510			SO$_4$ bend
		489w	487	SeO$_4$ bend
	448			SO$_4$ bend
	434		434	I$-$O stretch
428vs				
	434	417s	434	I$-$O stretch
			432	SeO$_4$ bend
		406s	423	SeO$_4$ bend
	398		398	I$-$O stretch
408s		396vs		
	398		398	I$-$O stretch
		378m	387	SeO$_4$ bend
350w		359w		
		316w	294	SeO$_4$ bend
	281		268	I$\cdots$O stretch[c]
283w		274w		
	278		253	I$\cdots$O stretch
207m	197	204s	197	O$-$I$-$O bend
179m	197	178s	197	O$-$I$-$O bend
	142		141	(IO)$_2$ torsion
		143w		
	138		138	(IO)$_2$ torsion
	120			I$\cdots$O stretch
113m	118		117	I$-$O$-$I bend
		108m		
	116		116	I$-$O$-$I bend
			108	I$\cdots$O stretch
	106	96w	106	I$-$O$-$I bend
100w				
	105		106	I$-$O$-$I bend
83s	89	87vs	77	I$\cdots$O stretch
68m		55w		lattice mode
	21		21	(IO)$_2$ torsion
	14		15	(IO)$_2$ torsion

[a] Calculated with force constants from Table 3 for one SO$_4$ or SeO$_4$ group and two IOIOI chains. [b] For abbreviations, see Table 1; b, broad. [c] I$\cdots$O stretch involves O in SO$_4$ or SeO$_4$ and I in (I$-$O) chains.

support. Therefore, we do not feel tempted to make distinction between a monomeric and polymeric structure on this criterion. With four monomeric I_2O_5 molecules in the unit cell, 16 I=O stretching vibrations should occur. As apparent from Table 1, 12 infrared and Raman bands observed between 850 and 670 cm^{-1} are attributed to I=O stretching modes, whereas 8 observed bands may correspond to I−O stretching vibrations. Thus, the number of vibrational bands observed for I_2O_5 is consistent with the quasi-monomeric structure.[6]

Iodosyl sulfate [(IO)$_2$SO$_4$] and iodosyl selenate [(IO)$_2$SeO$_4$]

Spectral data. Infrared spectra of iodosyl sulfate and selenate have been published previously,[2] but only stretching frequencies for the SO_4 and IO groups were presented. Our samples reacted with optical windows of KBr, CsI or polyethylene, and decomposed in the infrared beam. These problems probably originate from $H_2SO_4(H_2SeO_4)$ remaining to stabilize the samples.[7] Moreover, the recorded spectra contained some infrared bands due to other iodine oxides. Therefore, our infrared data offered no decisive information in the low frequency region.

The Raman samples were kept in sealed glass tubes and the spectra were of good quality, having sharp and symmetrical peaks. A very weak Raman band at 776 cm^{-1} in the (IO)$_2$SO$_4$ sample probably corresponds to the strongest Raman band of I_2O_4. No I_2O_4 impurity was detected for (IO)$_2$SeO$_4$.

Structure. The unit cells of symmetry $C2/c$ (C_{2h}^6) for (IO)$_2$SO$_4$ and (IO)$_2$SeO$_4$ contain four molecular units,[7] and can be transferred to a primitive cell conserving the basic symmetry elements (mirror glide plane and centre of inversion). With two formula units in the primitive cell we expect 54 vibrational modes, of which 51 should be optical (42 internal and 9 lattice vibrations). The structure[7] comprises sandwich-like layers of infinite (IO)$_n$ helices linked together by $SO_4(SeO_4)$ tetrahedra. While the molecular unit has only C_1 symmetry, the (IO)$_n$ chains and the $SO_4(SeO_4)$ groups may, as a first approximation, be looked upon as having higher symmetry. However, the angle distortions of the SO_4 tetrahedra[7] may be large enough to perturb the triply degenerate vibrational levels.

Force field calculations. Diagonal force constants for the (IO)$_n$ entities were adopted from I_2O_5 and for

the SO_4 groups from Schultze *et al.*[12] Only a few coupling constants were introduced, but certain structural aspects were considered. Thus, the parameter n of the (IO)$_n$ chain was varied up to $n = 15$. A large number of I−O stretching vibrations in the regions 650−550 and 455−390 cm^{-1} were predicted from the calculations. The bending modes were scattered over a wide spectral range (260−100 cm^{-1}) and many low frequency vibrations should occur.

The variations of the I−O stretching and bending frequencies were relatively small when the $SO_4(SeO_4)$ groups were taken into account. Considerably lower S(Se)−O stretching and O−S(Se)−O bending diagonal force constants had to be employed for SeO_4 compared to SO_4 (*cf.* Ref. 12). An improved fit was obtained when the S(Se)O$_4$ stretch−stretch, stretch−bend and bend−bend interaction constants were introduced. For simplicity, T_d symmetry was assumed for the $SO_4(SeO_4)$ group. The splitting of the S(Se)−O stretching modes would probably increase when a more refined molecular model is taken into account.

Only the force constants involving the S(Se)O$_4$ group were varied by a least squares program. The final set of force constants are listed in Table 3. It refers to one S(Se)O$_4$ group and two (IO)$_n$ spiral chains.

Assignments. All the observed Raman bands for (IO)$_2$SO$_4$, except those at 1290, 1140, 919, 776, 542 and 350 cm^{-1} were interpreted as fundamentals. As mentioned, the band at 776 cm^{-1} is probably caused by I_2O_4. The bands at 1290, 1140, 919 and 350 cm^{-1} were excluded as fundamentals because of the discrepancy with the calculated values. The 542 cm^{-1} band may be an I−O stretching mode. Our calculations indicate that the asymmetric I−O stretching modes lie around 600 cm^{-1} while the symmetric vibrations occur around 400 cm^{-1}.

For an SO_4 group with T_d symmetry, four Raman active vibrations are expected ($A_1 + E + 2F_2$). The larger number of Raman bands observed in the appropriate SO_4 stretching (1080−960 cm^{-1}) and bending (650−460 cm^{-1}) regions is consistent with a lower site symmetry as found by X-ray diffraction.[7] The reported[2] infrared bands at 1035 and 673 cm^{-1} were not confirmed in the present Raman spectra.

The (IO)$_2$SeO$_4$ spectrum can be assigned correspondingly, and all the Raman bands except those at 1158, 525 and 316 cm^{-1} were considered as fundamentals. The I−O vibrations for the two

compounds were quite similar (Table 4). Also, the SeO_4 stretching and bending modes were split as a result of the lack of perfect tetrahedral symmetry. The average deviations between the observed and calculated frequencies were 9 and 12 cm^{-1} for $(IO)_2SO_4$ and $(IO)_2SeO_4$, respectively.

Iodine dioxide [I_2O_4]

An infrared spectrum of I_2O_4 in the region 400 -144 cm^{-1} has been reported,[3] in complete agreement with our spectra. To our knowledge, no Raman data have been published previously.

Spectral data. Unlike the infrared spectra of I_2O_5, $(IO)_2SO_4$ and $(IO)_2SeO_4$, that of I_2O_4 has well defined, relatively sharp and symmetrical bands (Fig. 1). After cooling with liquid nitrogen, some of the bands show correlation splitting with peak separations of 10 cm^{-1} or less.

As apparent from the wave numbers listed in Table 5, there is mutual exclusion between the infrared and Raman bands with only one or two accidental degeneracies. Since molecular units with an inversion centre may be excluded (see below), the observations are interpreted in terms of a centrosymmetric, crystallographic unit cell.

With four I_2O_4 units in the unit cell, 72 fundamentals are expected, of which 48 are internal fundamentals and 21 optical lattice modes. In polymeric structures the lattice modes become
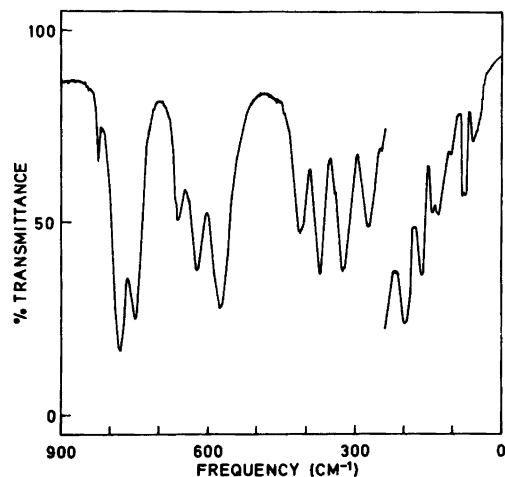

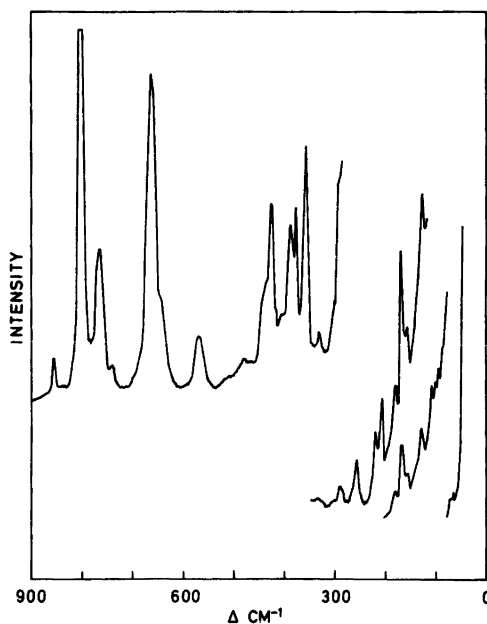*Fig. 1.* The IR spectrum of I_2O_4 (900 – 240 cm^{-1}, Nujol mull, 250 – 50 cm^{-1} polyethylene pellet).

Fig. 2. The Raman spectrum of I_2O_4 at ambient temperature.

internal vibrations. The relative number of I = O and I − O stretching modes will also be influenced.

The observed infrared and Raman bands for I_2O_4 are generally found in the regions around 775, 600, 400, 350 and below 200 cm^{-1}. As for I_2O_5, the existence of I = O and I − O stretching bands as well as bending and torsional modes should be substantiated.

Structure. Since detailed structural analyses of I_2O_4 have hitherto not been successful, we hoped that the vibrational spectra would give additional information. Strong interactions between the I_2O_4 units (as also indicated by the very low solubility in all solvents tried so far), as well as several low frequency fundamentals, make a detailed unit cell analysis difficult to carry out. It may, however, be possible to settle questions as; (a) the existence of I − I bonds, (b) the approximate number of I = O and I − O bonds, and (c) the occurrence of polymeric structure.

The presence of I − I bonds should give rise to very intense Raman bands around 250 – 200 cm^{-1} resulting from stretching vibrations. Since no such bands were observed, I − O − I linkages between the iodine atoms appear likely. Force field calculations, chemical evidence from the preparation of I_2O_4 *via*

Table 5. Infrared and Raman spectral data for crystalline I_2O_4.

IR		Raman	Calc.[a]	Interpretation
350 K	95 K	300 K		
825 w[b]	827 w	830 w		
	800 m		805[c]	
779 s	775 s	775 s		IO_3 stretch
750 s	753 s		775[c]	
	738 s	741 w		
		714 vw		
668 w	669 m		668	
662 m	664 m			
	627 m	637 m	641	
623 m	619 m	617 vw	604	I−O stretch
576 s	576 s			
	567 m		569	
		543 w		
		490 vw		
	462 vw			
	422 s		400	
413 m	414 s	415 vw	387	I−O stretch
		401 m	373	
375 m	376 s		365	
	367 s	361 m		
		350 m	358[c]	IO_3 bend
326 m		332 m	320[c]	
		305 vw		
275 m				
250 vw		262 m	268	
		230 s	236	
226 vw				
210 m				O−I−O bend
203 m		191 s	186	
		180 s		
167 m		161 w		
144 m		154 s	161	$(IO)_n$ torsion
		138 s	138	
134 m			134	I−O−I bend
		128 m	126	
107 vw		128 m	126	
		100 m	115[d]	
83 m		82 w		
78 m		74 vw		lattice mode
69 w				
62 w		58 w		

[a] Calculated with force constants from Table 3 for an $(IO)_n$ chain with nine atoms. [b] For abbreviations, see Table 1. [c] From Ref. 11. [d] Calculated torsional frequencies below 50 cm^{-1} are omitted.

$(IO)_2SO_4$ or $(IO)_2SeO_4$,[8] the structure of other iodine oxides, and the Mössbauer results[13−15] support this deduction.

In this case, the number of I=O and I−O stretching frequencies seem to be a valuable criterion, both types of bonding can be deduced from the spectra. Five infrared and three Raman bands between 830 and 735 cm^{-1} can easily be interpreted as I=O stretching modes. In the 670 to 400 cm^{-1} region 9 IR and 6 Raman bands are

possible $I-O$ stretching fundamentals. If four isolated I_2O_4 units occur in the unit cell, each having three $I=O$ bonds, the number of $I=O$ and $I-O$ stretching modes should be 12 and 8, respectively. If on the other hand, one assumes two $I=O$ bonds per I_2O_4 unit, the corresponding numbers should be 8 and 16, respectively. Allowing some IR combination bands, and weak or overlapping Raman fundamentals, the latter alternative is more consistent with the spectral data.

Force field calculations excluded models involving $I-I$ bonds. Moreover, structures with $(IO)_n$ chains having an additional $I=O$ bond at each iodine atom seem unlikely. The best fit between the observed and calculated fundamental frequencies was obtained with a model consisting of an $(IO)_n$ chain to which iodate groups were added.

In line with this, the powder X-ray and neutron diffraction data indicate a centrosymmetric unit cell with four I_2O_4 units. Two non-equivalent iodine atoms have been suggested for I_2O_4 from Mössbauer studies,[13-15] one resembling the iodine in IO_3 groups and the other being interpreted as belonging to IO groups. However, the preparational procedures in Refs. 13 – 15 attach some uncertainty to the actual composition of the measured samples.

As a conclusion two extreme models can be considered for I_2O_4:

(1) The I_2O_4 structure resembles that of I_2O_5.[6] It consists of intra- and intermolecular bonds which in the extreme version are entirely covalent. Per I_2O_4 unit there are three $I=O$ and two $I-O$ (one $I-O$ $-I$ bridging unit) bonds. The four I_2O_4 units in the primitive cell are linked by secondary bonds.[6]

(2) An ionic structure consisting of IO^+ (or $(IO)_n^{n+}$) and IO_3^- ions. The actual charges on these ionic species are not essential in this model, and some degree of covalency may be tolerated to make the situation match that in $(IO)_2SO_4$.[7]

We believe that I_2O_4 might have a bonding between the two extremes specified above. The I_2O_4 structure is probably composed of $(IO)_n$ helices resembling those in $(IO)_2SO_4$[7] with pyramidal IO_3 groups attached to neighbouring iodine atoms through a secondary bonding arrangement. The bridging $I-O-I$ and $I\cdots O=I$ framework leads to a centrosymmetrical arrangement as in I_2O_5.[6] On this basis it should be appropriate to use the designation iodosyl iodate.

The single or double bond lengths are likely to be approximately the same as in the corresponding structural fragments of $(IO)_2SO_4$ and I_2O_5. The

force field calculations strongly favour a non-planar conformation of the I_2O_4 sub-units with $O-I-O$ bond angles of $90-100°$ and $I-O-I$ of $130-140°$. The double-bonded oxygen atoms of the IO_3 groups probably form secondary bonds to iodine atoms on neighbouring $(IO)_n$ chains and IO_3 groups. In this way four coordination may be obtained for iodine in the chains and five or six coordination (distorted octahedron) for iodine in the IO_3 groups.

The latter inferences are consistent with information obtained from the Mössbauer studies.[13-15] Further indications pointing in the same direction are the yellowish colour and the diamagnetic properties of I_2O_4.

The observed IR and Raman data are compared with the frequencies calculated for an $(IO)_n$ helix containing 9 atoms, using the force constants from Table 3. As apparent from Table 5, the agreement is generally good (the $I-O$ distances were set equal to 2 Å, the $I-O-I$ and $O-I-O$ bond angles were 135 and 100°, respectively). In addition, the four vibrations localized to the IO_3 group (two stretching and two deformation modes) are adopted from Ref. 11. Except for a few weak lines all the bands not assigned to $(IO)_n$ helices can be interpreted as either IO_3 stretching or bending vibrations. Compared to IO_3 groups with C_{3v} symmetry[11] the large number of bands observed in the regions $830-730$ cm^{-1} and $370-300$ cm^{-1} are consistent with a lower IO_3 site symmetry because of strong bonding interactions with neighbouring groups.

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