toward the highest and lowest V_a, particularly with Pr and Sc alloys. The present study corroborates these effects for both systems RCo_2-RAl_2 and RFe_2-RAl_2.

One of the most striking features of the present investigation concerns the aberrant behavior of volumes per atom in systems containing either the rare earth Pr or the transition metal Mn. Strong negative deviations from Vegard's law are observed, particularly in systems $PrNi_2$-$PrAl_2$ and $PrCo_2$-$PrAl_2$. In these systems it appears as though deviations from the ideal binary solution behavior are due to a gradual change of valence of Pr from 3+ to 4+. The opposite is observed on Fe and Mn substitution for Al in $PrAl_2$.

It may be of interest in this connection to discuss the relevance of these findings to the problem of hydride formation. Hydrogen has been recently found to be absorbed in $CaCu_5$ type materials (*e.g.*, $LaNi_5$) easily and reversibly at a few atmospheres of pressure (van Vucht, *et al.*[25]). In $CeNi_5$, however, hydrogen did not dissolve up to relatively high pressure, presumably due to the 4+ ionic nature of Ce in this material. Judging from the findings of the present study Fe substitution may counteract ionization into the 4+ state possibly on account of size factors. Moreover, electron transfer from Al to Fe should result in a relatively filled d-shell configuration ("pseudo Ni"). This configuration appears to facilitate hydrogen take-up. Suitably substituted alloys on the basis of Ce, Pr, Fe, Ni, and Al, therefore, may become of technological interest as hydrogen storage materials.

Alloys containing Mn uniformly show positive deviations from Vegard's law. Moreover, values of V_a drop considerably toward the Mn-rich phase boundary. Magnetic studies show that Mn is either in its 3+[14] or 4+[26] state in Laves phase intermetallics. The tendencies in V_a, therefore, would seem to indicate that toward binaries RMn_2, Mn changes from the 3+ to 4+ ionic state. The pronounced step in values of V_a from C14 $PrMn_xAl_{2-x}$ to $PrMn_2$ (Th_6Mn_{23} structure) would seem to indicate considerable electronic rearrangement on both Pr and Mn. $PrMn_2$ has been investigated magnetically[27] but the situation is too complex to allow for conclusions concerning the electronic nature of both constituents.

While transition metals Fe, Co, Ni, and Cu can be considered to contribute less to the delocalized electrons than Al, Mn is of either comparable or higher valence. The stability of C14 structures $PrMn_xAl_{2-x}$ and $ErMn_xAl_{2-x}$, therefore, appears to involve different electronic criteria than the one of Fe- and Co-containing compounds.

The discontinuities in V_a between C15 and C14 materials observed most pronouncedly with Co-containing pseudobinaries indicate an improved packing efficiency which in turn suggests an ordered arrangement between T and Al. In the C14 structure ordering is possible on 2a and 6h sites. In an independent X-ray study we have shown that at the Al-rich phase boundary ordering between Al and Co does indeed occur with Co occupying site 2a. This corresponds to a superstructure of $MgZn_2$ which can be written R_2TAl_3.[28]

When T = Fe, tendencies for ordering are less pronounced. Again the transition metal tends preferentially to occupy 2a sites but now only at the Al-poor phase boundary. At the Al-rich phase boundary no deviation from random occupancy between Fe and Al was observed. Similar conclusions were also drawn on evidence from Mossbauer spectroscopy.[17] Only with the rare earths does the T element prefer the 2a site. Several examples of a superstructure to $MgZn_2$ are known, for instance, U_2Fe_3Al,[17] Nb_2Co_3Ge,[29] or Mg_2Cu_3Si,[30] but in these cases the T element occupies the 6h site.

Registry No. $ErCu_2$, 12527-58-1; $GdCu_2$, 12527-59-2; $PrCu_2$, 12310-79-1; $ErNi_2$, 12192-18-6; $GdNi_2$, 12024-74-7; $PrNi_2$, 12201-94-4; $ErCo_2$, 12017-20-8; $GdCo_2$, 12017-22-0; $PrCo_2$, 12017-40-2; $ErFe_2$, 12020-15-4; $GdFe_2$, 12023-08-4; $PrFe_2$, 12305-97-4; $ErMn_2$, 12020-20-1; $GdMn_2$, 12024-68-9; $PrMn_2$, 12311-59-0; $ErAl_2$, 12004-20-5; $GdAl_2$, 12004-26-1; $PrAl_2$, 12043-24-2.

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Halogen Nitrates

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The low-temperature infrared and Raman spectra of $I(NO_3)_3$ and the Raman spectra of liquid $ClONO_2$, $FONO_2$, FNO_2, and $ClNO_2$ have been recorded. Comparison of the vibrational spectra within the series NO_2, FNO_2, $ClNO_2$, $FONO_2$, and $ClONO_2$ allows unambiguous assignments for the halogen nitrate molecules. Raman polarization measurements show that in halogen nitrates the halogen atom is perpendicular to the ONO_2 plane contrary to previous assumptions and to the known planar structure of $HONO_2$ and CH_3ONO_2. The vibrational spectrum of $I(NO_3)_3$ is consistent with predominantly covalent nitrato ligands. However, the complexity of the spectrum suggests a polymeric structure with bridging nitrato groups. Experimental evidence was obtained for the formation of the new and thermally unstable compound $CF_3I(NO_3)_2$ in the CF_3I-$ClONO_2$ system. Attempts to convert this compound into CF_3ONO_2 were unsuccessful.

Introduction

Highly electronegative groups such as perchlorates, nitrates, fluorosulfates, or trifluoroacetates can be considered as pseudohalides. As such they either can form stable anions in the presence of suitable cations or can act as covalent ligands particularly when bonded to highly electronegative elements such as the halogens or oxygen. Whereas the vibrational spectra of the free anions are relatively well understood, those of the corresponding covalent ligands have only recently received more attention. Reliable spectra and assignments are now available for covalent perchlorates,[1-3] trifluoroacetates,[4] and fluorosulfates.[5-7] In spite of extensive infrared spectroscopic studies on halogen nitrates,[8-11] a recent paper, reporting the vibrational spectrum of CF_3OONO_2, demonstrates[12] how poorly understood these spectra are at present.

The question whether the halogen atom in $XONO_2$ is coplanar or perpendicular with respect to the ONO_2 plane added further interest to our study. The consensus[9-12] appears to favor coplanarity based on analogy with the planar structures established for the related molecules $HONO_2$[13] and CH_3ONO_2.[14] However, the assumption of a planar structure for the halogen nitrates is against our intuition. Similarly, Pauling and Brockway suggested[15] for $FONO_2$ a nonplanar structure based on low-precision electron diffraction data, although a planar structure could not be ruled out. Raman polarization measurements should clearly distinguish between a planar and a nonplanar structure provided that unambiguous assignments are available. For this purpose Raman data were also required for the closely related nitryl halides.

Another objective of this study was to characterize $I(NO_3)_3$. This interesting compound was first prepared by Schmeisser and Braendle.[16] It is unstable above 0° and no data concerning its structure have been published. Attempts were also made to synthesize the novel covalent nitrate CF_3ONO_2 which led to the synthesis of the novel compound $CF_3I(NO_3)_2$.

Experimental Section

Caution! Fluorine nitrate is shock sensitive.

Material and Apparatus. Volatile materials used in this work were manipulated in a well-passivated (with ClF_3) stainless steel vacuum line equipped with Teflon FEP U traps and 316 stainless steel bellows-seal valves (Hoke, Inc., 4251 F4Y). Pressures were measured with a Heise Bourdon tube-type gauge (0–1500 mm ± 0.1%). Nitryl chloride,[17] $ClONO_2$,[18] and FNO_2[19] were prepared by literature methods. Fluorine nitrate was prepared by direct fluorination of KNO_3 in a stainless steel cylinder.[11] The purity of volatile materials was determined by measurements of their vapor pressures and infrared spectra. Solid products were handled in the dry nitrogen atmosphere of a glove box.

The infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range 4000–250 cm^{-1}. The spectra of gases were obtained using 304 stainless steel cells of 5-cm path length fitted with AgCl windows. The low-temperature spectrum of $I(NO_3)_3$ was obtained as a dry powder between CsI plates at −196° using a low-temperature transfer technique similar to one previously reported.[20] The instrument was calibrated by comparison with standard calibration points.[21]

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880-Å exciting line and a Claassen filter[22] for the elimination of plasma lines. Sealed quartz tubes (3-mm o.d.) were used as sample containers in the transverse-viewing, transverse-excitation technique. The low-temperature Raman spectra were recorded using a device similar to one previously described.[23] Polarization measurements were carried out according to method VIII listed by Claassen, *et al.*[22]

Preparation of $I(NO_3)_3$. Resublimed I_2 (1.005 mmol) was placed into a Teflon FEP tube fitted with a stainless steel valve. Freshly fractionated $ClONO_2$ (8.20 mmol) was condensed into the tube at −196°. The mixture was kept at −45° for 1 week. The materials, volatile at −45°, were removed *in vacuo* and separated by fractional condensation. They consisted of unreacted $ClONO_2$ (2.20 mmol) and Cl_2 (3.01 mmol) in excellent agreement with the values calculated for a quantitative conversion of I_2 to $I(NO_3)_3$. The nonvolatile residue was a fluffy light yellow solid which decomposed above 0° under dynamic vacuum yielding N_2O_5 (2.05 mmol) and a tan solid residue. This residue gradually decomposed further as evidenced by the buildup of NO_2-colored fumes above the solid. An infrared spectrum of the solid after several weeks of storage at 25° did not show any absorptions characteristic for N=O double bonds.

The $ClONO_2$-CF_3I System. Chlorine nitrate (4.02 mmol) and CF_3I (1.75 mmol) were combined at −196° in a 30-ml stainless steel cylinder. The reactor was slowly warmed to −45° and kept at this temperature for 6 days. Recooling to −196° did not show any noncondensable material. Products volatile at −78° were removed *in vacuo* and separated by fractional condensation. They consisted of unreacted $ClONO_2$ (0.40 mmol) and Cl_2 (1.79 mmol) in good agreement with the amounts expected for a quantitative conversion of CF_3I to $CF_3I(NO_3)_2$. Warming of the solid residue to 25° yielded N_2O_5 (1.14 mmol), COF_2 (1.07 mmol), and CF_3I (0.65 mmol) in addition to 219 mg of a sticky solid residue of varied orange color.

Results and Discussion

Synthesis and Properties. The interaction between I_2 and excess $ClONO_2$ at −45° produced $I(NO_3)_3$ in quantitative yield according to

$$I_2 + 6ClONO_2 \rightarrow 2I(NO_3)_3 + 3Cl_2$$

Thus, this reaction offers an excellent route to high-purity $I(NO_3)_3$, contrary to a previous statement[16] that, although $I(NO_3)_3$ is formed in this system, it is not of synthetic usefulness.

The properties and thermal instability observed for $I(NO_3)_3$ are in good agreement with those previously reported[16] for the product obtained from the $ICl_3 + ClONO_2$ reaction. The evolution of 1 mol of N_2O_5/mol of $I(NO_3)_3$ in the initial stage of the thermal decomposition indicates the possible formation of $OINO_3$ as an intermediate of marginal stability at 0°

$$I(NO_3)_3 \rightarrow OINO_3 + N_2O_5$$

The subsequent slow decomposition of this intermediate involves a redox reaction in which the +V nitrogen is reduced to the +IV state (N_2O_4) with simultaneous oxidation of the +III iodine. This observation is in excellent agreement with the thermal decomposition of $I(OClO_3)_3$ which yields Cl_2O_7, lower chlorine oxides, and I_2O_5.[2]

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In the CF_3I-$ClONO_2$ system, the observed material balance is in good agreement with the reaction

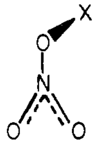
$$CF_3I + 2ClONO_2 \rightarrow CF_3I(NO_3)_2 + Cl_2$$

Again the observation of such an intermediate is in excellent agreement with the closely related $ClOClO_3$ reaction chemistry. Thus, the interaction of R_fI with $ClOClO_3$ produced $R_fI(ClO_4)_2$.[24] When R_f was $(CF_3)_2CF$ or n-C_7F_{15}, the $R_fI(ClO_4)_2$ intermediate was successfully isolated. At 40°, the n-$C_7F_{15}I(ClO_4)_2$ could be converted into R_fOClO_3 by vacuum pyrolysis. For $R_f = (CF_3)_2CF$, however, vacuum pyrolysis at 105° resulted exclusively in decomposition products. For $R_f = CF_3$, the $CF_3I(ClO_4)_2$ intermediate was not isolated; however, a quantitative yield of CF_3OClO_3 was obtainable at −45°.[24,25] Therefore, it appeared interesting to determine whether the novel compound CF_3ONO_2 could be prepared by controlled decomposition of $CF_3I(NO_3)_2$. No evidence for CF_3ONO_2 could be obtained, but CF_3I and about equimolar amounts of N_2O_5 and COF_2 were formed.

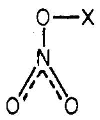
The observation of CF_3I as a decomposition product is interesting. A plausible explanation for its formation can be offered. For $R_fI(ClO_4)_2$, Raman spectra support[24] the ionic structure $[(R_f)_2I]^+[I(ClO_4)_4]^-$. If $CF_3I(NO_3)_2$ had the analogous ionic structure $[(CF_3)_2I]^+[I(NO_3)_4]^-$, as much as 50% of the originally used CF_3I might be recovered in the thermal decomposition of such an intermediate. The difficulty in obtaining CF_3ONO_2 indicates that this compound might be relatively unstable toward decomposition into COF_2. This is in good agreement with previous studies[12,26] aimed at the synthesis of R_fONO_2.

Vibrational Spectra. Figure 1 shows the Raman spectra of $ClNO_2$, FNO_2, $ClONO_2$, and $FONO_2$ and the infrared and the Raman spectrum of $I(NO_3)_3$. The observed frequencies are listed in Tables I and II.

Before the assignment of the fundamentals of the halogen nitrate molecules can be discussed in more detail, it must be established whether $XONO_2$ has structure I or II, *i.e.*, whether X is perpendicular to or coplanar with the ONO_2 plane.

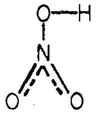


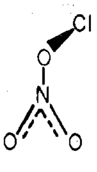
I



II

Whereas in $HONO_2$ intramolecular hydrogen bridging should favor planarity, in $HalONO_2$ the expected mutual repulsion between the halogen and the two oxygen atoms should favor the perpendicular model.





Raman spectroscopy should readily distinguish between models I and II. Both models possess symmetry C_s and nine fundamentals, but for model I three of the fundamentals are antisymmetric with respect to the symmetry plane, whereas for model II only two modes are antisymmetric.

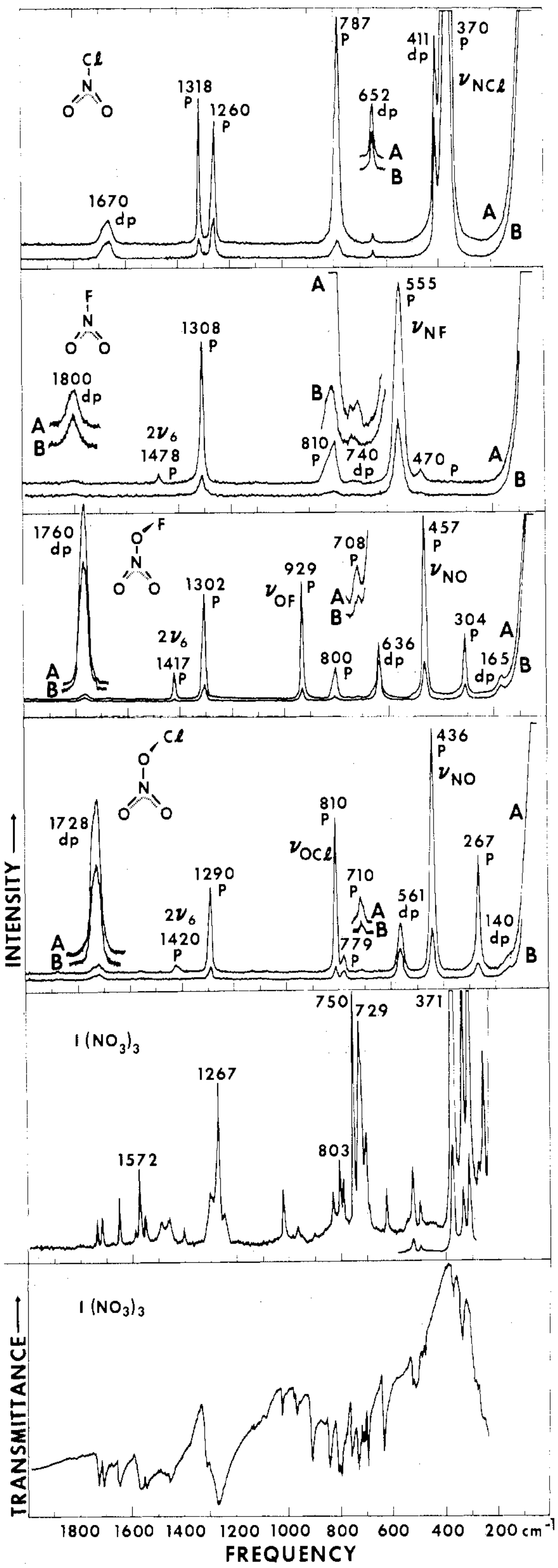


Figure 1. Raman spectra of liquid $ClNO_2$ (recorded at −110°), FNO_2 (−80°), $FONO_2$ (−100°), and $ClONO_2$ (−80°) and of solid $I(NO_3)_3$ (−90°) and infrared spectrum of solid $I(NO_3)_3$ (−196°). Spectral slit width used for the recording of the Raman spectra was 3 cm^{-1}. Traces A and B were recorded with parallel and perpendicular polarizations, respectively. The inserts represent the weaker bands recorded at higher sensitivity and larger slit width. Polarized and depolarized bands are marked by p and dp, respectively.

One mode which for model I belongs to species A″ and for model II belongs to species A′ is the antisymmetric NO_2 stretching vibration. Since no question exists concerning

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Table I. Fundamental Vibrations of NO_2, $ClNO_2$, FNO_2, $FONO_2$, and $ClONO_2$

Approx description of mode	Mode designation			Obsd freq, cm^{-1}								
	NO_2 C_{2v}	XNO_2 C_{2v}	$XONO_2$ C_s[a]	NO_2 Ir gas[b]	$ClNO_2$ Ir gas[d]	$ClNO_2$ Raman liq[e]	FNO_2 Ir gas[d]	FNO_2 Raman liq[e]	$FONO_2$ Ir gas[h]	$FONO_2$ Raman liq[e]	$ClONO_2$ Ir gas[h]	$ClONO_2$ Raman liq[e]
$\nu_{as}(NO_2)$	B_1 (ν_3)	B_1 (ν_4)	A″ (ν_7)	1618 [38][c] vs	1685 [38] vs	1670 (1),[f] 0.75[g]	1792 [41] vs	1800 (1), 0.75	1759 [39] vs	1760 (3), 0.75	1735 [41] vs	1728 (4) dp[i]
$\nu_s(NO_2)$	A_1 (ν_1)	A_1 (ν_1)	A′ (ν_1)	1318 [12] s	1286 [10] s	1318 (8), 0.15[j] 1260 (6), 0.32	1310 [12] s	1308 (7), 0.15	1301 [10] vs	1302 (59), 0.16	1292 [12] vs	1290 (30), 0.15
$\delta_{sciss}(NO_2)$	A_1 (ν_2)	A_1 (ν_2)	A′ (ν_3)	750 [10] s	793 [11] vs	787 (12), 0.07	822 [14] s	810 (21), 0.10	804 [12] s	800 (17), 0.10	780 [7] ms	779 (6), 0.45
$\nu(NX)$		A_1 (ν_3)	A′ (ν_5)		370 [2.2] vs	370 (100), 0.20	568 [1] ms	555 (100), 0.37	454 [0] ms	457 (100), 0.21	434 [2] m	436 (100), 0.21
$\delta(XNO_2)$ in-plane		B_1 (ν_5)	A″ (ν_8)		408 vw	411 (8), 0.75	560		633 [1] m	636 (31), 0.75	560 [3] s	561 (20) dp[i]
$\delta(XNO_2)$ out-of-plane		B_2 (ν_6)	A′ (ν_4)		652 [17] m	652 (0.3), 0.75	742 [20] mw	740 (1), 0.75	708 [18] m	708 (0.6), 0.40	711 [17] mw	710 (1), 0.40
$\nu(XY)$			A′ (ν_2)						928 [0] m	929 (67), 0.11	809 [6] s	810 (49), 0.07
$\delta(NXY)$ in-plane			A′ (ν_6)						303 [1] vw	304 (33), 0.24	270 vvw	267 (47), 0.10
$\tau(NX)$			A″ (ν_9)						152 vvw	165 (4), 0.75		140 (2) dp

[a] For model with *O*–Hal bond being perpendicular to ONO_2 plane. [b] E. T. Arakawa and A. H. Nielsen, *J. Mol. Spectrosc.*, **2**, 413 (1958). [c] Values listed in brackets behind infrared frequencies are observed $^{14}N-^{15}N$ isotopic shifts. [d] D. L. Bernitt, R. H. Miller, and I. C. Hisatsune, *Spectrochim. Acta, Part A*, **23**, 237 (1967). [e] Data from this study. [f] Values listed in parentheses are uncorrected Raman intensities. [g] Measured depolarization ratios; depolarized bands 0.75. [h] R. H. Miller, D. L. Bernitt, and I. C. Hisatsune, *Spectrochim. Acta, Part A*, **23**, 223 (1967). [i] The experimentally observed depolarization ratios for these two bands were slightly less than 0.75. However, we believe that these two bands are depolarized and that the observed deviation is due to either experimental conditions or interference from a trace of Cl_2 which has a highly polarized Raman band at 560 cm^{-1} and from the combination band $\nu_s(NO_2) + \nu(NX)(A') = 1726$ cm^{-1}. [j] Splitting due to Fermi resonance between ν_1 and $2\nu_6$.

Table II. Low-Temperature Infrared (−196°) and Raman (−90°) Spectra (cm^{-1}) of Solid $I(NO_3)_3$

Ir	Raman	Ir	Raman
1734 m	1734 (6)	837 m	830 (10)
1715 m	1718 (7)	805 m	803 (18)
1649 m	1649 (11)	793 m	791 (13)
1587 w, sh	1588 (3)	780 w	
1568 m	1572 (18)	775 w	775 sh
1550 m	1551 (6)	754 mw	752 (57)
1485 sh	1489 (5)	729 m	729 (50)
1457 m	1459 (6)		720 sh
1400 sh, br	1402 (4)	710 w	
1313 w		702 w	702 (22)
1300 sh	1301 (10)	690 m	690 (4)
1270 vs	1267 (34)	629 ms	627 (9)
1250 w	1249 (5)		549 sh
1024 mw	1021 (11)	525 mw	524 (14)
1010 w, sh	1008 sh	512 mw	
979 vw			498 (7)
967 mw	966 (3)	490 w	
950 sh	950 sh	478 w	
906 m	902 (1)	370 mw	370 (100)
863 w		335 m	332 (60)
			310 (93)
		280 m	282 (4)
		255 m	255 (30)

the assignment of this mode, its Raman depolarization ratio should answer the planarity question. Figure 1 and Table I show that in $FONO_2$ the antisymmetric NO_2 stretch is clearly depolarized and, hence, the fluorine atom is not coplanar with the rest of the molecule.

Additional support in favor of model I can be derived from polarization data on the XNO_2 deformational modes. For model I the ONO_2 in-plane deformation should be depolarized, whereas for model II the depolarized band should be the ONO_2 out-of-plane deformation. Application of this criterion, however, requires reliable assignments for these modes which, as stated above, were not available owing to an almost complete lack of Raman data on these and related molecules. As can be seen from Figure 1 and Table I, the combination of previously reported infrared data (including $^{14}N-^{15}N$ isotopic shifts)[11,27,28] with the Raman spectra of this study allows unambiguous assignments for all fundamentals of $FONO_2$ and $ClONO_2$. These results convincingly show that the ONO_2 in-plane deformation is depolarized and that the corresponding out-of-plane mode is polarized in agreement only with model I.

Since the assignments for the halogen nitrates are self-evident from the data given in Table I, we can limit ourselves to a comparison with previously reported assignments and some specific comments. For $ClNO_2$ only one previous reference to a Raman study was found in which only one very wide diffuse line centered at about 360 cm^{-1} was observed.[29] The observation of a depolarized line at 411 cm^{-1} in the present study confirms the previous assignment of this frequency to $\nu_5(B_1)$ based on microwave data.[30]

Similarly, our Raman data for FNO_2 are in excellent agreement with the previous assignment[27] which had been confirmed by a microwave study.[31] The observed relative Raman intensities and depolarization ratios of ν_2 and ν_3, when compared to the remaining molecules of Table I, support the conclusion[27] reached by Bernitt, *et al.*, concerning the identity of ν_2 and ν_3. On the basis of the observed $^{14}N-$

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^{15}N isotopic shifts, they chose from the two possible force fields[27,32] the one which results in ν_2 being mainly the NO_2 scissoring and ν_3 being mainly the NF stretching mode. A Raman spectrum of liquid FNO_2 has previously been reported[33] and is in fair agreement with our data. Two weak features at 470 and 710 cm^{-1}, respectively, in our Raman spectrum of FNO_2 require some comment. Both were also observed previously,[33] but the 470-cm^{-1} line was subsequently ascribed,[27] together with a line at 926 cm^{-1}, to $FONO_2$ impurity. Since our spectrum does not show any line at about 930 cm^{-1}, a different explanation for the 470-cm^{-1} band is required. It could possibly be due to the difference band $\nu_1 - \nu_2$ which could have borrowed intensity from ν_3 through Fermi resonance. The very weak polarized feature at about 710 cm^{-1} might similarly be explained by Fermi resonance between ν_2 and $\nu_1 - \nu_3$.

For $ClONO_2$ an incomplete Raman spectrum has previously been reported.[11] The five frequencies listed are in good agreement with our results. However, no polarization data were given and the fundamentals were assigned on the basis of the incorrect planar model II. Both of the two most recent assignments reported[11,12] for $ClONO_2$ need revision. Hohorst and DesMarteau assigned three and Miller, *et al.*, two fundamentals incorrectly. Both corrections involve the mode of greatest interest, the N-O stretching mode. The data of Table I (in particular the ^{14}N-^{15}N isotopic shifts and the polarization data) indicate that the similar frequencies of the NO_2 scissoring and the O-Cl stretching modes cause a strong mixing of the corresponding symmetry coordinates. The frequency of 140 cm^{-1} observed for the N-OCl torsional mode results in a barrier to internal rotation of 10.40 kcal mol^{-1} in good agreement with previous estimates and the value of 10.23 kcal mol^{-1} found for $FONO_2$.[11]

For $FONO_2$ no Raman data have been published except for the impurity bands[33] in the spectrum of FNO_2 which were attributed by others[11] to $FONO_2$. By analogy with $ClONO_2$ (see above), the previous assignments[11,12] need revision for three and two fundamentals, respectively.

Several general aspects deserve emphasis. (1) Whereas the XNO_2 out-of-plane deformation is of very low intensity in the Raman spectra and therefore difficult to detect, its first overtone was generally observed as a reasonably intense Raman band. This allows reliable identification of this fundamental. (ii) The symmetric NO_2 stretch and the NO_2 scissoring mode have very characteristic frequencies and occur in the ranges 1285-1300 and 780-820 cm^{-1}, respectively. Therefore, these two modes are useful for identifying XNO_2 groups. The XNO_2 out-of-plane deformation is moderately dependent and the corresponding in-plane deformation is strongly dependent on the mass of X. The large ^{14}N-^{15}N isotopic shifts (17-20 cm^{-1}) observed for the XNO_2 out-of-plane deformation indicates that in this mode mainly the N atom moves, *i.e.,* swings through the XO_2 plane. (iii) The NX stretching mode occurs for all compounds at a surprisingly low frequency, *i.e.,* 370-570 cm^{-1}. This is in agreement with the known thermal instability of these compounds. Contrary to the N-O stretching modes, the O-Hal stretching modes occur in their usual frequency range. They exhibit frequencies much higher than those of the N-O stretches indicating that the N-O single bond is by far the weakest bond in $ClONO_2$ and $FONO_2$.

The low-temperature spectra of $I(NO_3)_3$ (see Figure 1 and Table II) clearly show that the compound is not ionic. In the higher frequency range three clusters of bands centered at about 1570, 1270, and 800 cm^{-1}, respectively, occur, indicating the presence of covalent nitrato group. However, the number of individual bands within these clusters is too high and they are distributed over too wide a frequency range to be comfortably accounted for by a simple in-phase, out-of-phase coupling of the motions of monodentate or bidentate ligands.[3,34] It seems more reasonable to explain the complexity of the spectra by a polymeric structure involving bridging ligands as was previously suggested for the closely related compounds $I(ClO_4)_3$[2] and $I(SO_3F)_3$.[6] We suggest tentative assignments of the clusters to the following types of vibrations: 1750-1450 cm^{-1}, antisymmetric NO_2 stretches; 1300-1200 cm^{-1}, symmetric NO_2 stretches; 830-780 cm^{-1}, NO_2 scissoring; 750-690 cm^{-1}, IO stretches; 370-300 cm^{-1}, N-O stretches. The significant decrease in the N-O stretch frequencies, when compared to those in $FONO_2$ (457 cm^{-1}) and $ClONO_2$ (436 cm^{-1}), indicates increasing polarity of the Hal-O bonds within this series. This is generally true for related compounds and is caused by the increasing electronegativity difference between the halogen and the ligands with increasing atomic weight of the halogen.

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Registry No. $ClNO_2$, 13444-90-1; FNO_2, 10022-50-1; $FONO_2$, 7789-26-6; $ClONO_2$, 14545-72-3; $I(NO_3)_3$, 52760-88-0; $CF_3I(NO_3)_2$, 52760-89-1.

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