Raman Spectrum of Cl_2O_7: Assignment of the Skeletal Vibrations

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Summary The Raman spectrum of chlorine heptoxide shows a polarized band at 161 cm^{-1}, previously unreported, which is assigned to the skeletal bending mode on the basis of the depolarization ratio and normal co-ordinate calculations; a revision of the skeletal assignments is presented.

THE Raman spectrum of chlorine heptoxide was first obtained in 1938 by Fonteyne.[1] More recently the i.r. spectra of the gaseous and crystalline phases have been reported.[2] Beagley *et al.*[3] have summarized the different sets of suggested assignments for the bridge part of the molecule, and they suggest the skeletal bending mode should occur around 195 cm^{-1}, well below the lower limit of the two previous studies. In an attempt to resolve the controversy surrounding the assignment of the vibrational modes, particularly those of the skeleton, we have undertaken a study of the i.r. and Raman spectra of Cl_2O_7, and report here some of our preliminary findings.

Chlorine heptoxide was prepared by the method of Goodeve and Powney.[4] Care was taken to prevent possible injury in the event of an explosion. The final product, a colourless liquid, was sealed in Pyrex capillaries and irradiated at room temperature with a Spectra-Physics He–Ne 632·8 nm laser as the source of a Spex Model 1401 Raman spectrometer. A sample of Cl_2O_7 was placed in the laser beam at room temperature for as long as 8 h without undergoing any noticeable decomposition.

Assuming that chlorine heptoxide has the C_2 symmetry suggested from electron diffraction,[5] its 21 normal modes, all active in both the i.r. and Raman, are divided into eleven symmetric A modes and ten antisymmetric B modes. The A modes would be expected to give polarized bands and the B modes depolarized bands in the Raman spectrum. The observed Raman shifts and their assignments, which were obtained using group frequency correlations, depolarization ratios, and comparison with the assignments of the isoelectronic $S_2O_7^{2-}$ ion,[6] are shown in Table 1.

TABLE 1

Raman spectrum of chlorine heptoxide[a]

Δν (cm^{-1})	Relative intensity	Depolarization	Assignment
161	m	p	Cl–O–Cl bend
ca. 272	w	dp	ClO_3 rock
283	vvs	p	ClO_3 rock
ca. 435[b]	vw	dp	ClO_3 rock
507	m	p	ClO_3 symmetric deformation
558[b]	w	wp/dp	ClO_3 antisymmetric deformation
591[b]	w	wp/dp	ClO_3 antisymmetric deformation
699	s	p	Cl–O–Cl symmetric stretch
ca. 1019	vvw	dp	ClO_3 symmetric stretch (out-of-phase)
1048	vs	p	ClO_3 symmetric stretch (in-phase)
1275	w	dp	ClO_3 antisymmetric stretch
1305	w	dp	ClO_3 antisymmetric stretch

[a] s, m, w, v, p, and dp denote: strong, medium, weak, very, polarized, and depolarized, respectively.
[b] Depolarization ratio uncertain.

Our work differs in several respects from the earlier Raman study. First, we observe a polarized band of medium intensity at 161 cm^{-1}. This is the band which Beagley *et al.*[3] predicted at 195 cm^{-1}. In addition, depolarized components on the low frequency side of the very strong bands at 283 and 1048 cm^{-1}, respectively, were observed. Perhaps the other significant difference is in regard to the polarization of the band at 507 cm^{-1}. Fonteyne[1] reports this band to be depolarized; however, we find it to be quite polarized with ρ *ca.* 0·2.

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In assigning the three vibrational fundamentals of the Cl–O–Cl skeleton, it is expected the symmetric bend and stretch will appear as polarized bands of significant intensity in the Raman effect. The antisymmetric stretch should appear as a weak depolarized band at a higher frequency than the symmetric stretch. In view of the suggestion of Beagley *et al.*,[3] the assignment of the polarized band at 161 cm^{-1} to the skeletal bending mode appears to be a sound one. In dealing with the skeletal stretching modes, the key to the difference between this work and previous assignments[3] is the fact that all previous workers have apparently discounted the polarized character of the 699 cm^{-1} band. We find this strong band to be the most totally polarized band in the entire spectrum with a depolarization ratio of approximately zero. Therefore it cannot be the antisymmetric stretch. A more logical choice is to assign this band to the symmetric skeletal stretch. The only remaining question is the assignment of the antisymmetric stretch. By analogy with the $S_2O_7^{2-}$ assignments in Table 2 we expect the band to occur at a somewhat higher frequency than the symmetric stretch, and indeed we have observed a band at 775 cm^{-1} in the liquid i.r. spectrum. That the band is too weak for observation in the Raman effect is not surprising. The only questionable feature of this assignment is the fact that the intensity of the antisymmetric stretch is less than that of the symmetric stretch in the i.r. We believe the symmetric stretch has an unusually high intensity in the i.r. spectrum in view of the comparative weaknesses of the antisymmetric stretch and symmetric bend (the latter was not observed in the gas-phase infrared spectrum with a 15 cm path length). While we are unsure of the reason for this intensity anomaly, it is interesting to note a similar result for Cl_2O has been reported in the crystalline phase.[7] Finally, we suggest that the assignment of the skeletal bending mode in $S_2O_7^{2-}$ should be changed from 320 to 170 cm^{-1} by analogy with Cl_2O_7 (the assignment of 320 cm^{-1} corresponds to one of the original assignments[2] of 283 cm^{-1} for the bend in Cl_2O_7). The bands at 283 and 320 cm^{-1} in Cl_2O_7 and $S_2O_7^{2-}$, respectively, correspond to rocking modes of the $-XO_3$ groups in our suggested assignment.

TABLE 2

Frequency assignments for the bridge in $X_2O_7^{n-}$ (cm^{-1})

Mode	Cl_2O_7 Ref. 3	Cl_2O_7 This work	$S_2O_7^{2-}$ Ref. 6	$S_2O_7^{2-}$ This work[a]
ν_a, Antisymmetric stretch	695	775	790	790
ν_s, Symmetric stretch	595	699	730	730
ν_b, Symmetric bend	*ca.* 195	161	320	170

[a] As applied to data in ref. 6.

A full normal co-ordinate analysis of our Cl_2O_7 data and the $S_2O_7^{2-}$ data of ref. 6 has been carried out which confirms the assignments presented here. The results of this analysis and a more detailed account of our spectroscopic studies will be presented in a later publication.[8]

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