Mean Amplitudes of Vibration of ClF_2O^+ and BrF_2O^+

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Z. Naturforsch. **57a**, 837–838 received July 22, (2002);

Mean amplitudes of vibration of the two title cations have been calculated from vibrational spectroscopic data in the temperature range between 0 and 1000 K. Their bond characteristics are discussed on the basis of the obtained results and by comparison with known data for some related species.

Keywords: ClF_2O^+; BrF_2O^+; Mean Amplitudes of Vibration; Bond Properties.

Chlorine trifluoride oxide, ClF_3O, and the corresponding bromine species, BrF_3O, form adducts with different Lewis acids such as BF_3, AsF_5 or SbF_5, generating species containing the ClF_2O^+ or BrF_2O^+ cations [1, 2]. Recently, we have calculated the mean amplitudes of vibration and discussed the bond properties of the two mentioned oxides [3] and, in order to complement this study we have now made a similar investigation for the derived cations.

The structure of these species can be formally derived from an sp^3 hybridization of the central halogen atom, generating a pyramidal geometry of C_s symmetry.

Christe et al. investigated the vibrational spectrum of ClF_2O^+ [4], whereas that of BrF_2O^+ was reported by Bougon et al. [2]. Both studies confirmed the pyramidal C_s geometry, and the vibrational data of these authors were used in our calculations.

The mean amplitudes of vibration were calculated by the method of the characteristic vibrations of Müller et al. [5] (cf. also [6, 7]. For ClF_2O^+, the following geometrical parameters were used: $d(\text{Cl–O}) = 1.41$ Å; $d(\text{Cl–F}) = 1.62$ Å; $<\text{F–Cl–F} = 93°$ and $<\text{O–Cl–F} = 108°$ [4], whereas for BrF_2O^+ they were estimated as follows: $d(\text{Br–O}) = 1.57$ Å; $d(\text{Br–F}) = 1.75$ Å; $<\text{F–Br–F} = 93°$ and $<\text{O–Br–F} = 106°$.

Table 1. Calculated mean amplitudes of vibration (in Å) of ClF_2O^+.

T(K)	$u_{\text{Cl–F}}$	$u_{\text{Cl–O}}$	$u_{\text{F····F}}$	$u_{\text{F····O}}$
0	0.0436	0.0340	0.062	0.045
100	0.0436	0.0340	0.062	0.045
200	0.0438	0.0340	0.066	0.047
298.16	0.0450	0.0341	0.071	0.049
300	0.0400	0.0341	0.071	0.049
400	0.0471	0.0344	0.078	0.053
500	0.0496	0.0349	0.085	0.057
600	0.0523	0.0356	0.091	0.061
700	0.0551	0.0365	0.097	0.064
800	0.0579	0.0375	0.103	0.068
900	0.0607	0.0386	0.109	0.072
1000	0.0634	0.0397	0.114	0.075

Table 2. Calculated mean amplitudes of vibration (in Å) of BrF_2O^+.

T(K)	$u_{\text{Br–F}}$	$u_{\text{Br–O}}$	$u_{\text{F····F}}$	$u_{\text{F····O}}$
0	0.0413	0.0347	0.068	0.054
100	0.0413	0.0347	0.068	0.055
200	0.0417	0.0347	0.074	0.058
298.16	0.0432	0.0349	0.083	0.063
300	0.0433	0.0349	0.083	0.063
400	0.0456	0.0355	0.092	0.069
500	0.0484	0.0364	0.100	0.075
600	0.0514	0.0376	0.109	0.080
700	0.0544	0.0389	0.117	0.086
800	0.0573	0.0404	0.124	0.091
900	0.0601	0.0419	0.131	0.096
1000	0.0629	0.0434	0.138	0.101

The results of the calculations, in the temperature range between 0 and 1000 K, are shown in Tables 1 and 2.

As it can be seen, the X–O bonds are particularly strong, as reflected by their relatively low mean amplitudes of vibration and weak temperature dependencies. A comparison with the values calculated previously for the related F_3XO oxides [3] shows a reinforcement of this bond in the present cases, in agreement with the presence of the positive charge. In the case of ClF_2O^+, for which force constants were calculated [4], these calculations show the same trend, i.e. $f(\text{Cl–O}) = 11.21$ mdyn/Å for ClF_2O^+ and $f(\text{Cl–O}) = 9.37$ mdyn/Å for F_3ClO.

The mean amplitudes of the X–F bonds are comparable, but slightly lower than those determined for the equatorial X–F bonds in the related

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F_3XO oxides [3], also pointing to a reinforcement of this bond on going from the molecule to the cation.

The X–O and X–F mean amplitude values for both XF_2O^+ cations are also comparable to those calculated for the isoelectronic SF_2O and SeF_2O molecules [8]. These strong analogies, also remarked from the overall spectroscopic behaviour [4], suggest similar structure and bonding properties of these molecules and the two investigated cations. This fact indicates that an essentially covalent bond model using sp^3 hybridized halogen atoms can describe the bonding in these XF_2O^+ species. Bond models involving semiionic three-center, four electron p-p σ bonds, as suggested for the axial F–X–F bonds in the F_3XO oxides [3], are not possible owing to the absence of such linear F–X–F groups in these related cations. On the other hand, and in agreement with these different bonding characteristics, the mean amplitude values for these axial bonds are remarkably higher [3] than those found in the present cases.

Finally, it may be commented that the amplitude values of the non bonded F ···· O pairs are comparable to those calculated in the case of the F_3XO oxides, whereas those of the F ···· F pairs are also similar, but somewhat higher than those determined for the F(ax) ···· F(eq) interactions in the same oxides [3].

Acknowledgement

This work was supported by the "Consejo Nacional de Investigaciones Científicas Técnicas de la República Argentina", the author being a member of the Research Career of this organism

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Verantwortlich für den Inhalt: A. Klemm
Satz und Druck: Konrad Triltsch, Print und digitale Medien GmbH, Ochsenfurt/Hohestadt