Mean Amplitudes of Vibration of $[NH_3F]^+$ and $[NH_3Cl]^+$

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The mean amplitudes of vibration of $[NH_3F]^+$ and $[NH_3Cl]^+$ were calculated from known spectroscopic and structural data in the temperature range between 0 and 1000 K. The results are compared with those of related species and the bond peculiarities are also briefly discussed. Mean amplitude values for the NH_4^+ cation, at some selected temperatures, are also reported.

Key words: $[NH_3F]^+$; $[NH_3Cl]^+$; Mean Amplitudes of Vibration; Bond Properties.

The interesting $[NH_3Cl]^+$ cation could recently be prepared and characterized in the form of its $[NH_3Cl](BF_4)$, $[NH_3Cl](AsF_6)$ and $[NH_3Cl](SbF_6)$ salts [1]. Similar salts the respective fluorine containing cation $[NH_3F]^+$ were described some years ago [2]. Therefore, in order to attain a wider insight into the vibrational and bonding properties of these two cations, we have performed the calculation of its mean amplitudes of vibration, using the known spectroscopic data [1, 2].

These calculations were made with the method of the characteristic vibrations of Müller et al. [3] (cf. also [4, 5]). The necessary molecular parameters for the $[NH_3Cl]^+$ cation [d(N-Cl) = 1.74 Å; d(N-H) = 1.02 Å; ∠H-N-H = 109.8°; ∠H-N-Cl = 109.1°], obtained by DF theoretical calculations, were taken from the paper of Schneider et al. [1]. For the $[NH_3F]^+$ cation the following values, also obtained by DF calculations [6], were used: d(N-F) = 1.37 Å; d(N-H) = 1.04 Å; all angles = 107.8 °. For comparative purposes we have also performed a similar calculation for the NH_4^+ cation, using reported Raman data of crystalline NH_4Cl [7] and a tetrahedral bond angle.

The results of the calculations of $[NH_3X]^+$, in the temperature range between 0 and 1000 K are shown in Tables 1 and 2. Data for NH_4^+ at some selected temperatures are presented in Table 3.

Table 1. Calculated mean amplitudes of vibration (in Å) of $[NH_3F]^+$.

T (K)	u_{N-H}	u_{N-F}	$u_{H...H}$	$u_{H...F}$
0	0.0795	0.0454	0.125	0.065
100	0.0795	0.0454	0.125	0.065
200	0.0795	0.0454	0.125	0.065
298.16	0.0795	0.0457	0.125	0.065
300	0.0795	0.0457	0.125	0.065
400	0.0795	0.0466	0.125	0.066
500	0.0795	0.0479	0.126	0.067
600	0.0796	0.0496	0.127	0.068
700	0.0798	0.0515	0.128	0.069
800	0.0800	0.0535	0.130	0.071
900	0.0804	0.0555	0.132	0.072
1000	0.0809	0.0576	0.134	0.074

Table 2. Calculated mean amplitudes of vibration (in Å) of $[NH_3Cl]^+$.

T (K)	u_{N-H}	u_{N-Cl}	$u_{H...H}$	$u_{H...Cl}$
0	0.0752	0.0468	0.122	0.082
100	0.0752	0.0468	0.122	0.082
200	0.0752	0.0470	0.122	0.082
298.16	0.0752	0.0480	0.122	0.083
300	0.0752	0.0480	0.122	0.083
400	0.0752	0.0499	0.122	0.084
500	0.0752	0.0523	0.123	0.086
600	0.0753	0.0550	0.124	0.088
700	0.0754	0.0578	0.125	0.091
800	0.0755	0.0606	0.126	0.094
900	0.0757	0.0634	0.128	0.097
1000	0.0760	0.0662	0.130	0.100

A comparison of the results for the two cations shows some interesting trends. The N-H bonds of $[NH_3Cl]^+$ present lower mean amplitudes of vibration in the full temperature range, pointing to somewhat stronger N-H bonds for this species in comparison to $[NH_3F]^+$. On the contrary, a comparison of the two different N-halogen bonds shows a stronger bond (lower mean amplitudes of vibration) in the case of $[NH_3F]^+$. This behavior implies that the reinforcement of the N-F bond causes a concomitant weakening of the N-H bonds of this cation. On the other hand, the presence of a relatively strong N-F bond in this cation is not totally unexpected as short and strong bonds of this type have also been observed in other related species [6].

Besides, a comparison of the mean amplitudes the non-bonded pairs, shows that both cations present practically identical values for the H···H pairs, whereas those corresponding to the H···X pairs are slightly higher for $[NH_3Cl]^+$.

Table 3. Calculated mean amplitudes of vibration (in Å) of NH_4^+, at some selected temperatures.

T (K)	u_{N-H}	$u_{H...H}$
0	0.0762	0.123
298.16	0.0762	0.123
400	0.0762	0.123
600	0.0763	0.125
800	0.0765	0.128
1000	0.0771	0.132

It is worth comparing the obtained values with those of NH_4^+ and other related species. For example, the parent NH_3 molecule presents a mean amplitude of vibration of 0.0725 Å for the N-H bonds at 298 K [8]. This figure suggests that the addition of the halogen atom to the NH_3 skeleton causes a slight weakening of the N-H bond. A similar weakening is observed if one proton is added to NH_3. Interestingly, the non-bonded $H \cdots H$ pairs of ammonia present practically the same amplitude values as those calculated here (0.1200 Å at 298 K [8]), and these values are also comparable to those obtained for NH_4^+. A further comparison with the respective NX_3 molecules shows that in these species the N-X bonds have somewhat higher mean amplitudes than in the now investigated $[NH_3X]^+$ cations (in NF_3, $u_{N-F} = 0.04781$ Å; in NCl_3, $u_{N-Cl} = 0.0688$ Å, both at 298 K [9]).

On the other hand, in the structurally related tetrahedral CH_4 molecule the C-H bonds show a mean amplitude of 0.0775 Å at 298 K [8], i.e., an intermediate value to those calculated here for the $[NH_3X]^+$ cations. As expected, the NH_4^+ cation presents somewhat stronger bonds than the isoelectronic neutral CH_4 molecule [4].

Comparisons can also be made with the mean amplitudes calculated at 298 K for the isoelectronic CH_3X molecules [8]. The values are as follows: for CH_3F, $u_{C-H} = 0.0777$ Å and $u_{C-F} = 0.0451$ Å; for CH_3Cl, $u_{C-H} = 0.0761$ Å and $u_{C-Cl} = 0.0485$ Å. As can be seen these values are comparable to those determined for $[NH_3F]^+$ and $[NH_3Cl]^+$, respectively, at the same temperature and show the same general trends.

Some additional comparisons with available data for species containing N-F and N-Cl bonds also show that the now obtained mean amplitudes lie in characteristic ranges for this type of bonds. For example the u_{N-F} values calculated at 298 K for NF_2Cl: 0.04975 Å [9], $NFCl_2$: 0.05156 Å [9], ONF: 0.04226 Å [8], and FNO_2: 0.0498 Å [10]; and the u_{N-Cl} values calculated at the same temperature for NF_2Cl: 0.05022 Å [9], $NFCl_2$: 0.05268 Å [9], and $ClNO_2$: 0.0452 Å [10].

To conclude, the bonding characteristics of the interesting $[NH_3X]^+$ cations with X = F, Cl are comparable to those of the isoelectronic CH_3X molecules. In the cation and the molecule, the N-Cl (or C-Cl) bond is somewhat weaker than the N-F (or C-F) bond. In contrast, the bonding to the hydrogen atoms is somewhat stronger in the chlorine compounds. The strength of these bonds is comparable to that found in NH_4^+ and CH_4, and they are somewhat weaker than in NH_3.

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