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Librational and Torsional Modes in Hydroxylammonium, NH₃OH⁺, Salts Studied by Inelastic Neutron Scattering and Infrared Spectroscopy

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Inelastic neutron scattering spectra of the hydroxylammonium halides and sulphate together with Raman and infrared data on these systems are reported. The two librational/torsional modes of the NH_3OH^+ ion about the N-O axis have been identified and, with a plausible assumption for the internal barrier, the external barriers to rotation calculated.

This work, like that¹ on the salts N_2H_5Cl and N_2H_5Br , represents an extension of the studies of molecular librations and torsions in the much more symmetric ions^{2,3} $N_2H_6^{2+}$ and $CH_3NH_3^+$. Torsions and librations are distinguished here as oscillations about internal or external axes, respectively. The most thorough and extensive study of the infrared spectra of the hydroxylammonium halides so far reported⁴ is due to Frasco and Wagner, extending from 4000 to 400 cm⁻¹. We have extended these measurements to 200 cm⁻¹ and below in some cases.

The crystal structures of NH₃OHCl and NH₃OHBr have been determined by X-ray diffraction by Jerslev⁵ and that of NH₃OHCl by X-ray and neutron diffraction by Padmanabhan *et al.*⁶ The salts are isomorphous and belong to the space-group $P2_1/c$. The --NH₃ group is in the form of an undistorted triangular pyramid in the NH₃OHCl crystal. The average of the N-H distances is 1.044 ± 0.012 Å and the H-N-H and O-N-H average bond angles are 109.4 ± 0.7 and $109.9\pm0.7^{\circ}$, respectively; within experimental error this corresponds to the tetrahedral angle. Each nitrogen atom has four closest Cl⁻ neighbours, one of them virtually along an extension of the O-N bond and the others with approximately three-fold symmetry round the nitrogen. The N-H…Cl angles are 153-157°. A similar but more regular grouping of chloride ions about a nitrogen is found in hydrazinium dichloride.' Each oxygen atom in NH₃OHCl has two closest chloride ion neighbours, one of them along an extension of the N-O bond. The other is hydrogen bonded to the oxygen and the bond O-H…Cl is of length 3.042 Å and is much more bent (144°) than the H-H...Cl bonds. The arrangement of the chloride ions round an individual NH_3OH^+ is shown in fig. 1.

The crystal structure of the unstable NH₃OHI is unknown. NH₃OHF has orthorhombic symmetry⁸ and is not isostructural with the chloride and bromide.

EXPERIMENTAL

Hydroxylammonium chloride, NH_3OHCl , was obtained as the AnalaR grade material from Hopkins and Williams. Hydroxylammonium sulphate, $(NH_3OH)_2SO_4$, was purchased as a laboratory grade reagent from B.D.H. Hydroxylammonium bromide, NH_3OHBr , was



FIG. 1.—Coordination of chloride ions round the hydroxylammonium ion in hydroxylammonium chloride.

prepared⁴ from aqueous hydroxylammonium sulphate and excess aqueous barium hydroxide. The precipitated barium sulphate was removed by filtration and the solution distilled to give a solution of hydroxylamine to which aqueous hydrobromic acid was added and the resulting solution was evaporated to dryness. The solid NH_3OHBr was recrystallised from alcohol.

Hydroxylammonium iodide, NH₃OHI, was prepared from stoichiometric quantities of aqueous hydroxylammonium sulphate and barium iodide and the precipitated barium sulphate removed by centrifuging. The resulting solution was evaporated under reduced pressure at 0 °C and in the dark. The salt is both light and heat sensitive.

Hydroxylammonium fluoride, NH₃OHF, was made⁷ by adding anhydrous liquid hydrogen fluoride to anhydrous solid hydroxylammonium chloride and removing the hydrogen chloride produced and the excess hydrogen fluoride by pumping.

Hydroxylammonium sulphate was deuterated by three crystallisations from deuterium oxide. In each case 2 g of the salt was added to 20 cm^3 of deuterium oxide (Prochem, 99.8% D) in a nitrogen atmosphere box. After complete solution of the compound, the solvent was removed by pumping at room temperature using a vacuum line. Two further applications of the same volume of deuterium oxide were used to reduce the percentage hydrogen present to very close to that of the deuterium oxide used. This would mean 0.21% of residual hydrogen. The infrared spectra in the region above 3000 cm^{-1} clearly showed the absence of significant amounts of hydrogen.

The time-of-flight energy gain i.n.s. spectra of NH_3OHCl and NH_3OHBr at ambient temperature were measured on the 4H5 spectrometer⁹ at the DIDO reactor. The data were treated using standard computer programmes^{10,11} to produce graphs of

$$\lim_{\alpha \to 0} P(\alpha, \beta) = 2\beta \sinh\left(\frac{\beta}{2}\right) S(\alpha, \beta)/\alpha,$$

where $\alpha = hQ^2/2kMT$, $\beta = h\omega/kT$, k is Boltzmann's constant, T is the absolute temperature, M is the mass of the scattering atom, Q is the momentum transferred to the neutron, ω is the frequency of the transition and $S(\alpha, \beta)$ is the "Scattering Function".

The neutron energy loss spectrum of NH_3OHCl at liquid nitrogen temperature was obtained using the inverted beryllium filter (b.f.d.) spectrometer¹² at the PLUTO reactor. All other neutron energy loss spectra were obtained from the new inverted beryllium filter (b.f.d.) spectrometer at the DIDO reactor. Descriptions of these spectrometers have been given before. The true transition frequencies have been obtained from the band maxima in the b.f.d. spectra by using the correction factors of Gamlen *et al.*¹²

Infrared spectra of the salts, as nujol mulls between caesium iodide plates, were obtained at room temperature and at liquid nitrogen temperature in the range $4000-200 \text{ cm}^{-1}$ on a Perkin–Elmer 577 infrared spectrometer and, in the region below 200 cm^{-1} , as nujol mulls between polyethylene plates on a Beckman RIIC FS-720 far-infrared interferometric spectrometer. Raman spectra were recorded on a Cary 82 Raman spectrophotometer, using a Spectra-Physics argon-ion laser.

For the neutron scattering studies, NH₃OHF was contained in an airtight cell with PTFE windows and NH₃OHI was contained in a sealed silica cell. All other compounds were contained in aluminium sachets.

RESULTS

INELASTIC NEUTRON SCATTERING RESULTS.

The $\lim_{\alpha\to 0} P(\alpha, \beta) = 2\beta \sinh(\beta/2)S(\alpha, \beta)/\alpha$ against energy curves obtained from the time-of-flight spectra of NH₃OHCl and NH₃OHBr at room temperature are shown in fig. 2 and 3. The inverted beryllium filter spectrum of NH₃OHCl at liquid nitrogen temperature obtained from the PLUTO spectrometer is shown in fig. 4. Fig. 5, 6, 7 and 8 show, respectively, the inverted beryllium filter spectra of NH₃OHBr, NH₃OHI, NH₃OHF and (NH₃OH)₂SO₄ at liquid nitrogen temperature obtained from the DIDO spectrometer.



FIG. 2.— $\operatorname{Lim}_{\alpha \to 0} P(\alpha, \beta)$ for NH₃OHCl plotted against wavenumber obtained from the time-of-flight spectrum. This function is proportional to the density of states.

The bands found in these spectra and the weak bands found in the Raman and the cold infrared spectra of these salts are summarised in table 1 for the halides and in table 2 for the sulphate.

By far the strongest band in all the i.n.s. spectra is the sharp peak which can be identified as an $-NH_3$ torsion. This band occurs only very weakly in the infrared

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	F ⁻	CI⁻					
i.n.s. (b.f.d.) (80 K)	i.r. (80 K)	assignment	i.n.s. (b.f.d.) (80 K)	Raman (r.t.)	i.n.s. (t.o.f.) (155 K)	i.r. (80 K)	assignment
	875	VOH				590	v _{OH}
463	477	$\nu_{\rm NH_3}$	338	333 253	320	358	$\nu_{\rm NH_3}$
364	385	$\nu_{OH} \leftarrow \nu_{NH_3}$	248sh	217	220sh		$\nu_{\rm OH} \leftarrow \nu_{\rm NH_3}$
250	275	$\nu_{\rm trans}$ (lattice)	193	191	190	194 <i>br</i>	$\nu_{\rm trans}$ (lattice)
150		$\nu_{\rm lib}(\perp)$		159	130		. ,
		in the second se	117	133			$ u_{ m lib}(\perp)$
				129			
				111			
				89			

Table 1.—O	BSERVED	LOW	VIBRATIO	ON FREG	QUENCIES	IN	THE
н	YDROXYL	АММС	DNIUM H	ALIDES	(cm^{-1})		

		\mathbf{Br}^-		Ι-				
i.n.s. (b.f.d.) (80 K)	i.n.s. (t.o.f.) (155 K)	Raman (r.t.)	i.r. (80 K	assign- () ment	i.n.s. (b.f.d.) (80 K)	i.r. (80 K)	assign- ment	
616 567			542	$ u_{ m OH}$	~500	460	$\nu_{\rm OH}$	
					278		$ u_{ m NH3}$	
324	300		320	$ u_{ m NH_3} $	177		ν_{trans}	
240	217sh	209		$v_{OH} \leftarrow v_{NH}$	93		$\nu_{\rm lin}(\perp)$	
198	184	172		$\nu_{\rm trans}$ (lattice)				
		141		· · · ·				
114	113	115		$ u_{ m lib}(\perp)$				
		83						
		74						
		56						

spectra of the halides taken at liquid nitrogen temperature and is not observable in their room temperature infrared spectra. The -OH torsional mode occurs at considerable higher frequency, as is to be expected from the shorter $O-H\cdots Cl$ hydrogen bond and the much lower moment of inertia of the -OH group compared with the $-NH_3$ group. Where we have extended the inelastic neutron scattering studies to sufficiently high frequencies to observe this band, it is considerably weaker than the $-NH_3$ torsion. This is to be expected since only one third of the number of protons move in the -OH torsion compared with the $-NH_3$ torsion and the



FIG. 3.—Lim_{$\alpha \to 0$} $P(\alpha, \beta)$ for NH₃OHBr plotted against wavenumber obtained from the time-of-flight spectrum. This function is proportional to the density of states.



FIG. 4.—Beryllium filter detector (b.f.d.) spectrum of NH₃OHCl from the PLUTO spectrometer. The figures marked on the peaks give the true vibrational frequencies in cm⁻¹. 311 monochromating plane of aluminium used.



FIG. 5.—B.f.d. spectrum of NH₃OHBr from the DIDO spectrometer. \triangle , 111 monochromating plane of aluminium used; +, 311 monochromating plane of aluminium used. The figures marked on the peaks give the true vibrational frequencies in cm⁻¹.



FIG. 6.—B.f.d. spectrum of NH_3OHI from the DIDO spectrometer. 111 monochromating plane of aluminium used. The figures marked on the peaks give the true vibrational frequencies in cm⁻¹.

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FIG. 7.—B.f.d. spectrum of NH₃OHF from the DIDO spectrometer. △ and —, 111 monochromating plane of aluminium used; + and - - -, 311 monochromating plane of aluminium used.



FIG. 8.—B.f.d. spectrum of $(NH_3OH)_2SO_4$ from the DIDO spectrometer. 111 monochromating plane of aluminium used. The figures marked on the peaks give the true frequencies in cm⁻¹.

salt		\mathbf{F}^{-}	Cl-	Br ⁻	I-	SO_4^{2-} (site I)	SO ₄ ²⁻ (site II)
$ u_{ m lib} $	found	150	117	114	93	148	126
$(\perp \text{ to } N-O \text{ axis})$	calculated	175	128	122	105	161	143

TABLE 2.—CALCULATED AND OBSERVED VALUES FOR THE WHOLE BODY LIBRATION OF THE HYDROXYLAMMONIUM ION PERPENDICULAR TO THE N–O AXIS (cm^{-1})

amplitude of the -OH torsion is considerably less than that of the $-NH_3$ torsion. However, the band due to the -OH torsion is quite strong in the infrared spectra.

Since infrared and Raman studies have indicated that in the rather similar systems N₂H₅Cl and N₂H₅Br there is a degree of mixing^{13,14} between translational modes and the two librational modes which have axes perpendicular to the N—N axis, a similar situation is very likely for the hydroxylammonium halides. The lower frequency modes in the i.n.s. spectra of the hydroxylammonium salts can be assigned (i) as a weak difference band $\nu_{OH} \leftarrow \nu_{-NH_3}$, which is absent from the far-infrared spectra, (ii) as a band which corresponds to the lattice translational modes and is seen as a strong band in the far-infrared and (iii) a band which corresponds to whole body librations about an axis perpendicular to the N—O bond and is absent in the infrared spectrum. For this last band, calculations, based on the crude assumptions that (i) the motion is simple harmonic, (ii) that the force field is the same for this mode and the —NH₃ torsion and (iii) that the relative moments of inertia are $I_{NH_3} = 3$ a.m.u. Å²; $I_{\perp} = 21$ a.m.u. Å², give the values in table 2, where the values found in the i.n.s. spectra are given for comparison. For the halides the values are in reasonable agreement considering the crudity of the assumptions.

In the case of NH₃OHCl a puzzling feature is the discrepancy between the frequencies of the weakly infrared active $-NH_3$ torsion at 358 cm⁻¹ (77 K) and the i.n.s. frequency for the same band at 338 cm⁻¹ (77 K). A factor group analysis for the crystal indicates that each mode should have four components in the lattice (2 Raman and 2 i.r. active)

$$\Gamma_{\rm NH_3(tor)} = A_g(R) + B_g(R) + A_u(i.r.) + B_u(i.r.).$$

The Raman spectrum of a single crystal of NH₃OHCl in this region shows simply a broad hump centred on ca. 327 cm⁻¹ at room temperature but on cooling to 77 K this sharpens to two bands at 338 and 331.5 cm⁻¹. Thus the Raman and i.n.s. data are in good agreement but the i.n.s. band is not wide enough to cover the infrared frequency adequately. We have, therefore, in potential barrier calculations for the chloride used the data based on the Raman and i.n.s. frequencies.

The general situation in the hydroxylammonium sulphate, $(NH_3OH)_2SO_4$, is more complex (table 3). From the inelastic neutron scattering spectrum we conclude that there are two $-NH_3^+$ torsions, indicating that there are at least two distinct $HONH_3^+$ sites in the crystal lattice. These bands appear at 370 and 420 cm⁻¹ in the liquid nitrogen temperature infrared spectrum of $(NH_3OH)_2SO_4$ and are stronger in the infrared than the corresponding $-NH_3$ torsions in the halides. They can actually be seen in the room-temperature infrared spectrum. The normally infrared inactive $\nu_2(E)$ frequency¹⁵ of the SO_4^{2-} ion also appears at 470 cm⁻¹ in the infrared spectrum, presumably because of site symmetry effects, but of course is not seen in the i.n.s. spectrum because of the low neutron scattering cross-sections of sulphur

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	(1	NH ₃ OH) ₂ S(D₄	(ND ₃ OD) ₂ SO ₄			
i.r. (80 K)	Raman (r.t.)	i.n.s. (b.f.d.) (80 K)	assignment	i.r. (80 K)	Rama (r.t.)	n assignment	
648		656br	$\nu(OH)$			······································	
625	625		$\nu(SO_4)$	650br		contains $\nu(SO_4)$ and shifted peak from	
610	607		(60.)	609		$MH_3 OH at 910$	
600	007		$\nu(\mathrm{SU}_4)$	577		$\nu(30_4)$	
468	472 453		$\nu(SO_4)$	481		$\nu(OD)$	
422	155	427	$\nu(\mathbf{NH}_2)$	466	470	$\nu(SO_4)$	
372		378	ν (NH ₂)	451	448	$\nu(OD)$	
288	250	286			228		
190vbr	203	219	$\nu_{\rm max}$ (lattice)	190br	182	$v_{\rm e}$ (lattice)	
170701	148	21/	$\nu_{\rm trans}(1000)$	17001	142	$\nu_{\text{trans}}(\perp)$	
	126	134	$\nu_{\rm lib}(\perp)$		124	$\nu_{\rm lib}(\perp)$	
	94		10(-)		93	no (—)	
	67				67		
	46				45		

TABLE 3.—OBSERVED LOW FREQUENCIES AND VIBRATIONAL ASSIGNMENTS IN HYDROXYLAMMONIUM SULPHATE (cm^{-1})

and oxygen. The -OH torsional mode is probably associated with the very broad band that appears at ca. 656 cm⁻¹ and above in the i.n.s. spectrum. In the infrared spectrum the -OH torsion is not resolved very clearly from the $\nu_4(F)$ mode of the sulphate ion,¹⁵ which appears to be split by site symmetry effects. In the best infrared spectrum that we obtained in this region there are four bands at 600, 610, 625 and 648 cm^{-1} . On deuteration, two new bands appear at 481 and 451 cm⁻¹ (see table 2) and we attribute these to $\nu(OD)$. The situation is complicated because other bands have shifted into the 600-650 cm⁻¹ region but $\nu(OD)$ at 451 cm⁻¹ is clearly identified with the peak at 600 cm^{-1} in the spectrum of the undeuterated compound, which has disappeared on deuteration. This corresponds to a deuteration shift of 1.330. The peak at 648 cm⁻¹ is probably the strongest candidate for the other -OHtorsion and its displacement to 481 cm^{-1} corresponds to a deuteration shift of 1.347.

DISCUSSION AND CALCULATIONS

The shapes of the barriers to rotation may be surmised, at least for the chloride and the bromide, by inspection of the environment⁵ of the two rotor groups. Fig. 1 shows the coordination round the two ends of the NH_3OH^+ ion in hydroxylammonium chloride. The $-NH_3^+$ end of the molecular ion appears to be H-bonded to three Cl⁻ ions, which are arranged in a roughly trigonal pattern. The -OH end has only one Cl⁻ in a suitable position for H-bonding. We may conclude that (a) the internal rotation barrier must be predominantly three-fold, (b) the external barrier for the $-NH_3^+$ group must also be predominantly three-fold since ca. 120° rotations will give the same equilibrium configuration of three H-bonds to chloride ions and (c) the situation for the -OH group is more complex. There is only one chloride ion to which the hydrogen of the -OH can point and be H-bonded.

In previous papers¹⁻³ reasonable success was achieved using a simple harmonic model in the calculation of approximate barrier heights from torsional energy translations, for systems involving two co-axial rotors. The same model will be applied here. It is based on the assumption that for a cosine potential the bottom parts of the well (which will include the two lowest energy levels) can be approximated by a simple harmonic potential.

Re-arranging and quoting the results derived earlier,² one can write

$$\bar{\nu}_1^2 = \frac{1}{2}K\{(d_{\rm A} + d_{\rm B}) + [(d_{\rm A} - d_{\rm B})^2 + d_{\rm I}^2]^{1/2}\}$$
$$\bar{\nu}_2^2 = \frac{1}{2}K\{(d_{\rm A} + d_{\rm B}) - [(d_{\rm A} - d_{\rm B})^2 + d_{\rm I}^2]^{1/2}\}$$

where $\bar{\nu}_1$ and $\bar{\nu}_2$ are observed $0 \rightarrow 1$ torsional frequencies in cm⁻¹, $K = \hbar/8\pi^2 c$, $d_A = (n_A^2 \bar{V}_A + n_1^2 \bar{V}_I)/I_A$, $d_B = (n_B^2 \bar{V}_B + n_1^2 \bar{V}_I)/I_B$, $d_I = -2n_1^2 \bar{V}_I/(I_A I_B)^{1/2}$, $n_x =$ barrier multiplicity, $\bar{V}_{A,B}$ = external barrier at rotor A or B in cm⁻¹, \bar{V}_I = internal barrier in cm⁻¹ and $I_{A,B}$ = moment of inertial of rotor A or B. The value $(n^2 \bar{V})$ appears in these equations as a pseudo-force constant, whose relationship to *n* and \bar{V} is clearly established for symmetric three-fold barriers. In the present situation for the -OH group it seems reasonable to assume that the bottom of the well may be nearly parabolic in shape, but it clearly is not safe to assume a cosine shape for the higher parts of the potential, so the pseudo-force constant should not be broken down into *n* and \bar{V} components.

Values of $I_{\rm NH_3} = 2.907$ and $I_{\rm OH} = 0.9125$ a.m.u. Å² are taken for the moments of inertia of the $-\rm NH_3$ and $-\rm OH$ groups about the N-O axis, based on their geometries in NH₃OHCl.⁶

Rearranging the two equations gives

$$\left[\frac{\bar{\nu}_1^2 + \bar{\nu}_2^2}{K}\right] = d_{\rm A} + d_{\rm B} = X$$
$$\left[\frac{(\bar{\nu}_1^2 - \bar{\nu}_2^2)^2}{K^2} - d_1^2\right]^{1/2} = d_{\rm A} - d_{\rm B} = Y.$$

The experimental band centre frequencies may now be substituted, leaving two equations with three unknowns: $\bar{V}_{\rm NH_3}$, \bar{V}_1 and $F_{\rm OH}$ (where F is the pseudo-force constant = $n^2_{\rm OH} \bar{V}_{\rm OH}$). To proceed further a range of values for one of the unknowns must be estimated. This is best done for the smallest unknown, \bar{V}_1 , from a knowledge of the internal barriers in other compounds. One crude estimate would be to argue that since the internal simple harmonic barrier in N₂H₆²⁺ was found to be 632 cm⁻¹ in the chloride and 610 cm⁻¹ in the bromide² and since in NH₃OH⁺ the interactions between the hydrogen of the rotors have been reduced from three to one, the barrier might be expected to be approximately a third of the value in N₂H₆²⁺, *i.e. ca.* 210 cm⁻¹. This is almost certainly an underestimate since (a) it assumes that the lone pairs in the oxygen atom have no significant effect and (b) it ignores the decrease in charge in passing from N₂H₆²⁺ to NH₃OH⁺ which is likely to increase the barrier. A better method is to proceed as follows: the values for the cosine barriers in CH₃OH, ¹⁶ CH₃CH₃¹⁶ and CH₃NH₃⁺³ are, respectively, 374, 1024 and 857 cm⁻¹. We would expect the internal barrier in NH₃OH⁺ to be lower than in CH₃OH and the reduction might reasonably be given by

$$\frac{\bar{V}_{\rm NH_3OH^+}}{\bar{V}_{\rm CH_3OH}} = \frac{\bar{V}_{\rm CH_3NH_3^+}}{\bar{V}_{\rm CH_3CH_3}}$$

whence $\bar{V}_{\rm NH_3OH^+} = 313 \text{ cm}^{-1}$. This is a value for the cosine barrier and the simple harmonic approximation might well produce a value 10% lower. Hence the simple harmonic value for the internal barrier in NH₃OH⁺ is probably close to 300 cm⁻¹ and certainly lies in the range 200–400 cm⁻¹. We have therefore taken values of $\bar{V}_{\rm I}$ of 200, 300 and 400 cm⁻¹ and substituted them into the appropriate equations to find values of $d_{\rm A}$ and $d_{\rm B}$. Further calculation to find $\bar{V}_{\rm NH_3}$ and $F_{\rm OH}$ must then follow two separate possibilities, namely case A in which $d_{\rm A}$ involves $\bar{V}_{\rm NH_3}$ and $d_{\rm B}$ involves $F_{\rm OH}$ and case B in which $d_{\rm A}$ involves $F_{\rm OH}$ and $d_{\rm B}$ involves $\bar{V}_{\rm NH_3}$. The results obtained are given in table 4.

TABLE 4.—CALCULATED VALUES OF THE BARRIER TO ROTATION OF $-NH_3^+$ and the pseudo-force constant for -OH motion in hydroxylammonium salts for different values of the internal barrier for both cases A and B. Moments of inertia taken: $I_{NH_3} = 2.907$, $I_{OH} = 0.9125$ a.m.u. Å²

	torsional	$\bar{\nu}_{ m OH}$	875	590	567	500	648	600
	frequencies	$ar{ u}_{ m NH_3}$	463	338	324	278	427	378
		values of	i					
		$ar{V}_{ m I}$ /cm $^{-1}$	\mathbf{F}^{-}	Cl-	Br^{-}	\mathbf{I}^-	$SO_4^{2-}(I)$	SO_4^{2-} (II)
		200	14 464	6444	5932	4553	7821	6670
	$\bar{V}_{\rm NH_3}/{\rm cm}^{-1}$	300	14 349	6308	5792	4403	7685	6531
		400	14 228	6156	5636	4230	7534	6375
case A								
	$F_{\rm OH}$	200	9843	4468	3972	2495	8153	6025
	$/\mathrm{cm}^{-1}\mathrm{rad}^{-2}$	300	8986	3670	3183	1737	7354	5236
		400	8146	2917	2443	1043	6598	4495
		200	3921	2019	1843	1320	3323	2570
	$\bar{V}_{\rm NH_2}/{\rm cm}^{-1}$	300	3836	1955	1783	1270	3259	2509
	1413	400	3758	1907	1739	1243	3210	2465
case B								
		200	39 628	16 970	15 523	11 629	20 860	17 608
	$F_{ m OH}$	300	38 685	15 968	14 511	10 587	19 859	16 598
	$/\mathrm{cm}^{-1}\mathrm{rad}^{-2}$	400	37 725	14 921	13 452	9481	18 815	15 539

It must now be reasoned as to which case is the most sensible. The coordination of halide ions round the $-NH_3^+$ group is fairly similar to that in the $N_2H_6^{2+}$ and $CH_3NH_3^+$ salts, where the external barriers to $-NH_3^+$ torsion have been found to be^{2,3} $N_2H_6Cl_2$, ca. 3500 cm^{-1} ; N_2H_6Br , ca 2800 cm^{-1} ; β -CH₃NH₃Cl, ca. 3250 cm^{-1} ; β -CH₃NH₃Br, ca. 2650 cm^{-1} . On this basis the barrier heights given for the $-NH_3^+$ torsion in case A look remarkably high, particularly when it is borne in mind that the N···H···Cl distances in the hydrazinium chloride are rather shorter than in hydroxylammonium chloride. Case B produces much more reasonable values for the external barrier heights to $-NH_3^+$ torsion, lower than those in the hydrazinium dihalides. The values of F_{OH} produced by case B also look reasonable. They are more than half the values for F_{NH_2} in the $N_2H_5^+$ halides (61% for the chloride, 54% for the bromide).¹ This is to be expected since two H-bonds are involved in the $-NH_2$ group and only one in the -OH group.

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