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VIBRATIONAL SPECTRA AND FORCE CONSTANTS FOR THE MOLECULAR SERIES $NH_{3-n}Cl_n$

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ABSTRACT

The IR spectrum of NCl_3 has been remeasured in an N_2 matrix and reassigned. Force constants have been calculated by ab initio methods for the molecular series $NH_{3-n}Cl_n$. For the still unknown $HNCl_2$, the force field was used to calculate the expected vibrational frequencies which may prove helpful for finding spectroscopic evidence for this molecule.

INTRODUCTION

Some time ago, force constants of the molecular series $NH_{3-n}F_n$ were calculated by ab initio methods [1]. For H_2NF, unknown at that time, the expected vibrational frequencies were calculated from its ab initio force field. Recently, when this molecule was synthesized, this prediction was shown to be fairly correct and it was helpful for the identification of the compound and the assignment of its vibrational spectrum [2]. As the vibrational spectrum of H_2NCl is now completely known and could be used for a force field calculation [3], it seemed worthwhile to treat the series $NH_{3-n}Cl_n$, in which one member, $HNCl_2$, is still missing, in the same way. To obtain more reliable results, the vibrational spectrum of NCl_3, hitherto only known in solution [4,5], in which a frequency shift due to intermolecular interaction cannot be excluded, was remeasured in an N_2 matrix - analogous to H_2NCl.

EXPERIMENTAL

NCl_3 was obtained by feeding gaseous chlorine into 2 mol NH_4Cl in aqueous solution for 1 h. The evolved NCl_3 gas was dried in a $CaCl_2$ cylinder and frozen

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at a cold surface at −78 °C. After the reaction was stopped, the cooling device was slowly warmed up to room temperature, which caused the surplus chlorine to evaporate through the $CaCl_2$ cylinder. About 0.5 ml of almost Cl_2-free NCl_3 remained on the bottom of the cooling device. It was frozen at −196 °C. *Caution!* During these operations, *violent explosions* can occur, therefore, *extreme precautions* are mandatory.

To obtain the matrix spectrum, the vessel containing the NCl_3 was connected to a helium evaporation cryostat. By warming up the vessel slowly, the NCl_3 was transported in a stream of N_2 onto a sample holder, where it was frozen in the N_2 matrix at 10 K. $^{15}NCl_3$ was prepared in the same way from $^{15}NH_4Cl$ (95%), obtained from Stohler Co.

Infrared spectra were recorded with a Perkin Elmer instrument 580 B; a maximum resolution of 0.8 cm^{-1} was achieved.

VIBRATIONAL SPECTRUM OF NCl_3

The matrix IR spectra of NCl_3 (Fig. 1) confirm essentially the earlier spectroscopic work of Jander, Engelhardt and co-workers carried out in organic solvents [4,5]. In the low frequency region only, an additional combination band is observed, which suggests a different assignment of a deformation mode. The combination band $\nu_3-\nu_4$ at 385 and 371 cm^{-1} respectively, found by Bayersdorfer et al. [5] was not observed in the matrix spectrum. Instead, there is a band at 365.2 and 364.8 cm^{-1}, which we assign to $\nu_2(\delta_s NCl_2)$. The band at 351.5 and 349.5 cm^{-1}, also found by Bayersdorfer et al. [5] and assumed to be ν_2 is of somewhat lower intensity and is therefore reassigned as the combination $\nu_2+\nu_4-\nu_1$, which is enhanced by Fermi resonance with ν_2 at ca. 365 cm^{-1}. The intensity ratio of these two bands is 100:81.5 ($^{14}NCl_3$) and 100:79 ($^{15}NCl_3$). From these ratios and the measured frequency values the frequency difference of unperturbed ν_2 and $\nu_2+\nu_4-\nu_1$ can be calculated [6] to be only 2 cm^{-1} for $^{14}NCl_3$ and 1.8 cm^{-1} for $^{15}NCl_3$. This close vicinity of the coupling vibrations is the reason for the strong enhancement of the combination band.

The combination $\nu_2+\nu_4$ at 608 cm^{-1} could only be seen as a shoulder of the strong ν_3 band for $^{14}NCl_3$ in solution [5]. For a thin layer of the matrix, both vibrations could be observed as clearly separated bands at 644 and 622 cm^{-1} for $^{14}NCl_3$. Again, Fermi resonance must be assumed for $\nu_2+\nu_4$ and ν_3, but this time the intensity ratio is only 100:4.6, giving a 1 cm^{-1} shift for the unperturbed vibrations to 643 and 623 cm^{-1}. For $^{15}NCl_3$ (632.3 and 618 cm^{-1}) the resolution is less and the intensity ratio cannot be determined exactly. It can only be estimated to be between 100:20 and 100:35. This gives a frequency correction of 3.0 ± 0.7 cm^{-1} with 629.2 cm^{-1} for ν_3 and 621 for $\nu_2+\nu_4$ of $^{15}NCl_3$, in the unperturbed state. In Table 1, our assignment for NCl_3 is compared with the earlier one [5].

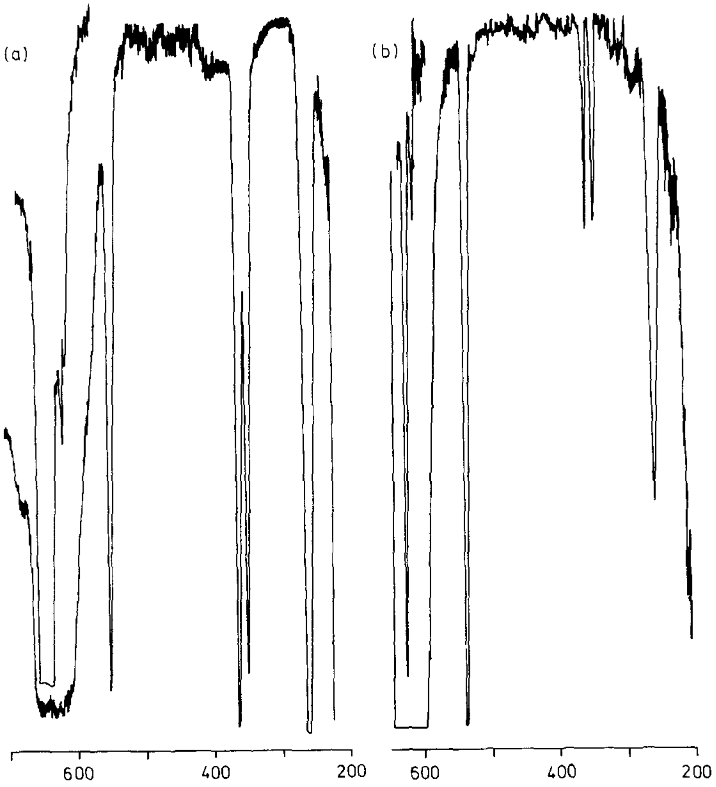

Fig. 1. Matrix IR spectra of: (a) $^{14}NCl_3$ and (b) $^{15}NCl_3$ in an N_2 matrix at 10 K.

TABLE 1

Vibrational spectra of $^{14}NCl_3$ and $^{15}NCl_3$ (in cm^{-1})

Infrared (solution) [4,5]		Infrared (N_2 matrix) (this work)		Corrected for Fermi resonance		Isotopic shift	Assignment
$^{14}NCl_3$	$^{15}NCl_3$	$^{14}NCl_3$	$^{15}NCl_3$	$^{14}NCl_3$	$^{15}NCl_3$		
643	627	644	632.3	643	629.2	13.8	$\nu_3(E)$ (ν_{NCl}asym.)
608	n.b.	622	618	623	621	2.0	$\nu_2+\nu_4$ (E)
520-540	510-530	554.4	541.7			12.7	$\nu_1(A_1)$ (ν_{NCl}sym.)
385	371						$\nu_3-\nu_4$ (E)
349	349	365.2	364.8	359	358	1.0	$\nu_2(A_1)$ (δ_{NCl_3}sym.)
		351.5	349.5	357	356.2	0.8	$\nu_3+\nu_4-\nu_1$ (A_1)
258	258	263	262.8			0.2	$\nu_4(E)$(δ_{NCl_3}asym.)

CALCULATION OF FORCE CONSTANTS

As for H_2NCl [3], the force fields for $HNCl_2$ and NCl_3 were calculated ab initio according to Pulay's force method [7,8] with the TEXAS program [9]. A 4-21G basis set was used for nitrogen [10], a 4-3-21G basis set for chlorine, similar to the 3-3-21 basis set of Oberhammer and Boggs [11], but fitting better to the 4-21G basis sets for the second row elements [12]. An additional *d* function was used for nitrogen (with exponent 0.8) and chlorine (with exponent 0.6).

Table 2 contains the calculated geometrical data for the series $NH_{3-n}Cl_n$ which are compared with the experimental results. They are in good agreement; however, it should be noted that for the NCl distance the experimental data give a 1 pm shortening for NH_2Cl compared with NCl_3, but the ab initio results give a 1 pm lengthening, with $NHCl_2$ fitting this trend.

Table 3 gives the ab initio force constants calculated for the series $NH_{3-n}Cl_n$. All constants show consistent and plausible trends within this series, with all comparable coupling constants being of identical sign and similar magnitude. For NCl_3 and H_2NCl [3], an iteration of the diagonal force constants to fit the experimental frequencies was performed as usual. For NH_3, the ab initio force field obtained by Pulay and Meyer [13] with the least sophisticated basis set (7-31) was adapted to the anharmonic frequencies of NH_3 [17], to give comparable values.

Calculating a GVFF for NCl_3 using the isotopic frequency data for $^{14}NCl_3$ and $^{15}NCl_3$ may be a good check for the validity of the ab initio calculation. The results are given in Table 4. It should be noted that a total adaption of both isotopic shifts was neither possible in species A_1 nor in species E. In species A_1 the force field was chosen to reproduce $\Delta\nu_1$ as closely as possible, as this is the more accurate quantity, $\Delta\nu_2$ being influenced by Fermi resonance, though an attempt was made to correct for it. A better fit for $\Delta\nu_2$ would shift

TABLE 2

Geometrical data for the series $NH_{3-n}Cl_n$

	NH_3		NH_2Cl		$NHCl_2$	NCl_3	
	Calc. [13]	Exp. [14]	Calc. [3]	Exp. [15]	Calc.	Calc.	Exp. [16]
r_{NH} (pm)	100.1	101.2	101.2	101.9	101.2		
r_{NCl} (pm)			176.0	174.8	175.2	174.9	175.4
$\angle NH_2$ (deg)	107.57	106.68	105.64	106.42			
$\angle HNCl$ (deg)			103.36	103.50	103.32		
$\angle NCl_2$ (deg)					109.70	108.6	107.8

TABLE 3

Force constants for the series $NH_{3-n}Cl_n$ (consistent with energy in aJ, bond lengths in Å = 100 pm and angles in radians)

	NH_3		H_2NCl [3]		$HNCl_2$		NCl_3		
	Ab initio [13]	Diagonal iteration	Ab initio	Diagonal iteration	Ab initio	Extrapolation	Ab initio	Diagonal iteration	GVFF
Symmetrical species									
$F(\nu_{NH})$	7.587	6.504	7.393	6.155	7.395	6.157			
$F(\nu_{NCl})$			4.165	3.593	4.361	3.870/3.384	4.461	3.959	3.462
$F(\delta_{NH_2})$	0.592	0.453	0.804	0.603					
$F(\delta_{HNCl})$			1.016	0.753	1.101	0.816			
$F(\delta_{NCl_2})$					1.522	1.295/1.381	2.061	1.754	1.870
$F(\nu_{NH}/\nu_{NCl})$			−0.041		−0.074				
$F(\nu_{NH}/\nu_{NH_2})$	0.600		0.362						
$F(\nu_{NH}/\delta_{HNCl})$			0.108		0.074				
$F(\nu_{NH}/\delta_{NCl_2})$					0.086				
$F(\nu_{NCl}/\delta_{NH_2})$			0						
$F(\nu_{NCl}/\delta_{HNCl})$			0.769		0.630	0.630/0.502			
$F(\nu_{NCl}/\delta_{NCl_2})$					0.620	0.620/0.494	1.105		0.881
$F(\nu_{NH_2}/\delta_{HNCl})$			−0.018						
$F(\delta_{NCl_2}/\delta_{HNCl})$					0.079				
Asymmetrical species									
$F(\nu_{NH})$	7.762	6.428	7.439	6.195					
$F(\nu_{NCl})$					3.551	2.167/2.417	3.431	2.094	2.335
$F(\delta_{NH_2})$	0.787	0.640							
$F(\delta_{HNCl})$			1.000	0.642	0.920	0.591			
$F(\delta_{NCl_2})$							1.466	1.144	1.107
$F(\nu_{NH}/\delta_{NH_2})$	−0.205								
$F(\nu_{NH}/\delta_{HNCl})$			−0.032						
$F(\nu_{NCl}/\delta_{HNCl})$					0.486	0.486/0.681			
$F(\nu_{NCl}/\delta_{NCl_2})$							−0.440		−0.618

F_{12} to even lower values, close to its minimum at 0.8, but increase $\Delta\nu_1$ to ~14 cm^{-1}. In comparison to the ab initio calculation, a reduction of F_{12} from 1.11 to 0.88 seems to be tolerable within the inaccuracy of the ab initio method due to the small basis set used and the neglect of configuration interaction. However, as F_{12} is close to the minimum value (0.79), its uncertainty also causes a relatively large uncertainty (~0.5) for F_{11}. In species E, $\Delta\nu_3$ and $\Delta\nu_4$ are absolutely incompatible. $\Delta\nu_4$ is best adapted at $F_{34}=-0.4$, but $\Delta\nu_3=-1.1$ even at the largest margin (14.5 cm^{-1}) set by the Fermi resonance correction. Whereas the solution generated by $\Delta\nu_4$ is close to the ab initio result, that produced by $\Delta\nu_3$ is far removed. We calculated a third solution leveling out $\Delta\nu_3$ and $\Delta\nu_4$, which gives F_{34}==0.62, which may be assumed as just tolerable in comparison to the ab initio result (−0.44). We also calculated the force field

TABLE 4

Force field for NCl_3 (units as in Table 3)

	Ab initio	Ab initio			Method of stepwise coupling	Experimental Frequency shifts
		Diagonal iteration	GVFF(I)	GVFF(II)		
A_1: F_{11}	4.461	3.959	3.462		3.422	
F_{12}	1.105	1.105	0.881		0.872	
F_{22}	2.061	1.754	1.870		1.894	
E: F_{33}	3.431	2.094	2.838	2.335	2.027	
F_{34}	−0.440	−0.440	−1.080	−0.618	−0.395	
F_{44}	1.466	1.144	1.186	1.107	1.164	
$\Delta\nu_1$	11.57	10.33	12.72			12.7
$\Delta\nu_2$	3.62	3.07	2.51			1.0
$\Delta\nu_3$	23.02	17.51	15.02	16.84		13.8 (14.5)
$\Delta\nu_4$	0.52	0.45	1.47	0.72		0.2

by the method of stepwise coupling [18], which is known to give a good approximation to species containing only one stretching and one deformation mode [19]. The results confirm the solutions with F_{12}=0.88 (A_1) and F_{34}=−0.40 (E).

VIBRATIONAL SPECTRUM EXPECTED FOR $HNCl_2$

To calculate the normal vibrations for the as yet unknown $HNCl_2$, its force field was derived from the ab initio data by reducing the diagonal constants by the same amount as was found for the other molecules of the series $NH_{3-n}Cl_n$. The reduction factors for one constant, derived in different molecules (e.g. $F(\nu_{NH})$ from NH_3 and H_2NCl or $F(\nu_{NCl})$ from H_2NCl and NCl_3) are in good agreement. Another force field was obtained by using the GVFF results for NCl_3 (with F_{34}=−0.62 in the E species, as the other probable limit of force field besides the modified ab initio solution). In this case, the coupling constants between the NCl stretchings and the deformations were also corrected to the GVFF values for NCl_3. The frequency calculations show that these variations of the force constant matrix are only of minor influence on the normal vibrations of $HNCl_2$, which are stable within a 10 cm^{-1} margin, with the only exception of ν_{NCl} asym. (E), for which a difference up to 30 cm^{-1} is obtained. This is an indication that the calculated spectrum given in Table 5 should be a good approximation to the real one and should be helpful for its identification. One unusual feature is the interchange of ν_{NCl} sym. and asym. compared

TABLE 5

Calculated normal vibrations (cm^{-1}) for $HNCl_2$

A'	3336 (ν_{NH}), 960-970 (δ_{HNCl}), 630-640 (ν_{NCl}sym.), 290-300 (δ_{NCl_2})
A''	1185-1195 (δ_{HNCl}), 580-610 (ν_{NCl}asym.)

TABLE 6

Stretching force constants of the series $NH_{3-n}Cl_n$ (force constants in aJ $Å^{-1}$, distance in pm) compared with those of the series $NH_{3-n}F_n$ from refs. 1 and 2

	NH_3	H_2NCl [3]	$HNCl_2$	NCl_3
f_{NH}	6.45	6.18	6.16	
r_{NH} exp.	101.2	101.9		
r_{NH} calc.	100.1	101.2	101.2	
f_{NCl}		3.59	3.02/2.78	2.71/2.52
r_{NCl} exp.		176.0		174.9
r_{NCl} calc.		174.8	175.2	175.9
	NH_3	H_2NF	HNF_2	NF_3
f_{NH}	6.54	6.04	5.64	
r_{NH} exp.	101.2	102.0	102.6	
r_{NH} calc.		101.8		
f_{NF}		4.47	4.57	4.16
r_{NF} exp.		143.34	140.0	136
r_{NF} calc.		140.0		

with NCl_3, which is due to the coupling of these vibrations with deformational modes for $HNCl_2$.

DISCUSSION OF STRETCHING FORCE CONSTANTS

Though the force field of NCl_3 is still not exactly known, and this correlates with similar uncertainties for $HNCl_2$, a discussion of the stretching force constants is possible, as most of the effect on the NCl stretching constants in symmetry space turns out to affect only the NCl/NCl coupling constant, if transferred to internal coordinates, with a less than 10% variation of f_{NCl} itself (Table 6). Thus, the trend of this constant within the molecular series remains the same, with only a slightly different amount of change.

By substituting H by Cl in NH_3, the NH stretching force constant is decreased by ca. 4%. This is in agreement with a ~1 pm increase of the bond length and conforms with the results obtained for the series $NH_{3-n}F_n$ [1], for which a 15% decrease of the force constant and a 2 pm lengthening was found.

Going from NX_3 to HNX_2, an increase of ca. 10% is observed for f_{NX} both in the fluorine and chlorine series, but proceeding from HNX_2 to H_2NX, the NF stretching constant remained almost constant [1,2], whereas f_{NCl} increases by about another 20%. An explanation for this different behaviour cannot be given as yet, but the overall effect of an increase of the NX constant by reducing the number of X atoms remains the same in both series. For the fluorine compounds, this is in contrast to the NF bond length, which increases in this direction too, which is rather unusual, as one is inclined to assume an increase of the stretching force constant, if the bond distance becomes shorter [20], though one should keep in mind the different meaning of these data correlated to the potential energy curve [21]. An explanation for the opposite trend in the $NH_{3-n}F_n$ series was given only recently [22] by the effect of negative hyperconjugation and by the fact that for a highly polar bond the bonding potential consists of a covalent and an electrostatic part, of which the covalent one gives a constant contribution to the stretching force constant, but the electrostatic one shifts it considerably in the direction of higher values by increasing attraction.

For the series $NH_{3-n}Cl_n$, the NCl bond distance remains almost constant. The experimental results suggest a very slight increase with decreasing number of Cl atoms, whereas the data calculated by the ab initio method show a similarly small decrease, which cannot account for the change of the NCl stretching force constants. Thus, similar arguments as for the $NH_{3-n}F_n$ series may also hold for the chlorine compounds, though the effect seems to be smaller here.

Note added in proof: Recently, H.G. Mack, D. Christen and H. Oberhammer, J. Mol. Struct., 190 (1988) 215, published a new ab initio calculation for the series $NH_{3-n}F_n$ with a much more sophisticated MP2/6-31G** basis set. Though this gives a better adaption to the experimental data, the trends of stretching force constant changes within the series remained the same as in our earlier publication [1] and therefore the conclusions drawn in the present discussion remain valid.

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