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PAPER

Solute–solvent interactions in cryosolutions: a study of halothane–ammonia complexes†

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The formation of C–H...N bonded complexes of halothane with ammonia has been studied using infrared and Raman spectroscopy of solutions in the liquid rare gases argon, krypton and xenon, of supersonic jet expansions and of room temperature vapor phase mixtures. For the solutions and for the vapor phase experiments, the formation of complexes with 1 : 1 and 1 : 2 stoichiometry was observed. The complexation enthalpy for the 1 : 1 complex was determined to be -20 (1) kJ mol^{-1} in the vapor phase, -17.0 (5) kJ mol^{-1} in liquid xenon and -17.3 (6) kJ mol^{-1} in liquid krypton. For the 1 : 2 complex in liquid xenon, the complexation enthalpy was determined to be -31.5 (12) kJ mol^{-1} . Using the complexation enthalpies for the vapor phase and for the solutions in liquid xenon and krypton, a critical assessment is made of the Monte Carlo Free Energy Perturbation approach to model solvent influences on the thermodynamical properties of the cryosolutions. The influences of temperature and solvent on the complexation shifts of the halothane C–H stretching mode are discussed.

1. Introduction

The volatile anesthetic halothane, CF_3CHBrCl , is a proton donor that can give rise to C–H...X bonded complexes. The study of its complexes with model Lewis bases not only results in new insights into the binding of this anesthetic to larger biomolecules,^{1–3} but also leads to new knowledge about the nature of C–H...X hydrogen bonds.^{4–6} This is owed to the fact that the C–H bond in halothane can exhibit both red- and blue-shifting behavior depending on the proton acceptor studied.^{4–9}

In a previous study, of the halothane benzene complex,⁶ a *blue* shift of $+8 \text{ cm}^{-1}$ was observed for the CH stretching vibration upon complexation at low temperatures in a supersonic jet-expansion and a *red* shift of -8 cm^{-1} at room temperature for mixtures in the vapor phase. Between the same two experimental conditions a larger difference has been observed¹⁰ for the complexation shift of the CH stretching band of chloroform in its complex with ammonia, where a shift from the monomer frequency by -38 cm^{-1} was found in the supersonic jet expansion, against -17.5 cm^{-1} in the room temperature vapor phase.

In this study, data for the complexes of halothane with ammonia, NH_3 , have been collected at different experimental

conditions: infrared and Raman spectra of mixtures in solutions of liquid argon (LAr), liquid krypton (LKr) and liquid xenon (LXe) were recorded and infrared spectra of the isolated complexes in the vapor phase were obtained using equilibrium gas cells and using jet-expansion techniques. The experiments were supported by *ab initio* calculations and Monte Carlo simulations. Special attention was devoted to the behavior of the halothane CH stretching mode, and, as will be shown below, also for this complex a large difference in complexation shift between the jet, equilibrium vapor phase and solution experiments was found.

2. Experimental details

The samples of halothane (racemic, 99%) and NH_3 (99.98 and 99.9%) were obtained from Sigma Aldrich and Lancaster Synthesis, and from Air Liquide and Praxair, respectively. All samples were used without further purification. The solvent gases argon, krypton and xenon used for the cryosolution measurements were supplied by Air Liquide and had a stated purity of 99.9999, 99.998 and 99.995%, respectively. The helium used as a carrier gas in the jet expansions was also obtained from Air Liquide and had a stated purity of 99.996%.

Infrared spectra of the cryosolutions and of the room temperature vapor were recorded on a Bruker IFS 66v Fourier transform spectrometer. Mid-infrared spectra were obtained using a Globar source in combination with a Ge/KBr beam splitter and a LN_2 -cooled broad band MCT detector. The far-infrared spectra were recorded using a $6 \mu\text{m}$ Mylar beam

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splitter in combination with a LHe-cooled Si bolometer. The interferograms were averaged over 500 scans, Blackman-Harris three-term apodized and Fourier transformed to yield spectra with a resolution of 0.5 cm^{-1} . The experimental set-up used to investigate the solutions in liquid noble gases has been described before.¹¹ Liquid cells equipped with a path length of 1 and 7 cm and equipped with wedged Si or CaF_2 windows were used to record the spectra. Vapor phase infrared spectra were recorded using cells with path lengths of 7 and 21 cm.

Raman spectra were recorded using a Trivista 557 spectrometer consisting of a double $f = 50\text{ cm}$ monochromator equipped with a $2000\text{ lines mm}^{-1}$ grating, a $f = 70\text{ cm}$ spectrograph equipped with a $2400\text{ lines mm}^{-1}$ grating, and a back-illuminated LN_2 -cooled CCD detector. The 514.5 nm line of a Spectra-Physics argon ion laser was used to excite the spectra, with the power set to 0.8 Watt. Signals related to the plasma lines were removed by using an interference filter. The frequencies were calibrated using Neon emission lines; they are expected to be accurate to within 0.5 cm^{-1} . The experimental set-up used to investigate the solutions has been described before.^{11,12} A home-built liquid cell equipped with four quartz windows at right angles was used to record the spectra.

The infrared set-up used in the jet experiments has been described in detail before.^{12–15} In the current study, the expansion formed by using a $600\text{ mm} \times 0.2\text{ mm}$ nozzle was probed by a mildly focused FTIR beam. The gas pulses used typically lasted approximately 140 ms. The number of scans varied between 30 and 100. The build-up of background pressure was limited by using vacuum recipients with volumes up to 23 m^3 , and by introducing sufficiently long waiting periods, up to 1 min, before entering the next gas pulse. The experimental set-up was connected to a Bruker Equinox 55 spectrometer, equipped with the appropriate optical filters and with a large area InSb detector.

Geometries, complexation energies and harmonic vibrational frequencies were obtained from *ab initio* calculations using Gaussian09.¹⁶ During all calculations, effects due to BSSE were corrected for using counterpoise-corrected gradient techniques.¹⁷ Corrections for zero-point vibrational and thermal influences were performed using standard statistical thermodynamical approximations.¹⁸ The Monte Carlo Free Energy Perturbation (MC-FEP) simulations used to estimate the solvent effects were performed using a modified version of BOSS 4.1,¹⁹ as described before.²⁰

3. Results

3.1. *Ab initio* calculations

For the 1 : 1 complexes, MP2/6-311++G(d,p) geometry optimizations were carried out starting from different relative positions of the molecules involved. The calculations converged to three different complexes that are formed *via* different types of interactions, *i.e.* either *via* a $(\text{C})\text{--H}\cdots\text{N}$ hydrogen, a $\text{C--Br}\cdots\text{N}$ halogen, or a $\text{C--Cl}\cdots\text{N}$ halogen bond. The complexation energies $-D_e$, including corrections for BSSE, are -21.4 , -12.4 and -7.0 kJ mol^{-1} , respectively. These results are in line with previous ones where it was found that the $\text{C--H}\cdots\text{X}$ hydrogen bonded isomer has a significantly larger complexation energy than that of the halogen bonded complexes.^{6,8} It is evident

Fig. 1 MP2/6-311++G(d,p) equilibrium geometries for the 1 : 1 (left) and 1 : 2 (right) complexes of halothane with ammonia.

that also with NH_3 the hydrogen bonded species is predicted to be preferentially formed in the experiments. The equilibrium geometries of the hydrogen bonded complexes are shown in Fig. 1. The harmonic vibrational frequencies, infrared intensities and Raman scattering activities are summarized in Table ST1 of the ESI.†

The hydrogen bond in the 1 : 1 complex is characterized by a $\text{N}\cdots\text{H}$ bond length of 2.250 Å , and a near-linear $\text{C--H}\cdots\text{N}$ bond angle of 172.4° . The equilibrium geometry is predicted to have a staggered conformation. The energy difference between the global minimum and the geometry in which the N--H bonds are eclipsed with bonds in halothane equals 0.14 kJ mol^{-1} . The complexation with NH_3 induces an elongation of the C--H bond in the proton donor, by approximately 0.0042 Å , and yields a complexation shift for its stretching mode of -63.6 cm^{-1} . The calculated infrared intensities for that mode are 3.4 km mol^{-1} in the monomer and 172.8 km mol^{-1} in the complex, an increase by a factor of 51. It is of interest to note that for the 1 : 1 complex, significant absorptions, both of 43 km mol^{-1} , are calculated for the infrared bands at 225.7 and 232.5 cm^{-1} , which are due to the librational modes of the NH_3 moiety.

Similar to the complexes of chloroform with NH_3 ,¹⁰ clusters can be formed that contain one molecule of halothane coupled to an oligomeric chain of ammonia molecules. Therefore, geometry optimizations were initiated for the 1 : 2 complex, starting from different relative positions of the monomers involved. All calculations converged to the cyclic equilibrium structure shown on the right hand side in Fig. 1. To rationalize the cooperative effects in the 1 : 2 complexes, geometry optimizations and frequency calculations were also made for the NH_3 dimer: the results are in line with literature data²¹ and are not discussed here.

The $(\text{C})\text{--H}\cdots\text{N}$ hydrogen bond in the 1 : 2 complex has a length of 2.170 Å and shows an angle of 165.2° with the C--H bond. Its length is smaller than the 2.250 Å obtained for the 1 : 1 complex: this causes the shift of the CH stretching from its monomer value to increase to 109.8 cm^{-1} . The $(\text{N})\text{--H}\cdots\text{N}$ hydrogen bond in the 1 : 2 complex has a length of 2.294 Å and shows a bond angle of 158.7° . It is longer than the 2.262 Å obtained for the ammonia dimer, suggesting a weaker hydrogen bond. This is somewhat unexpected because in general cooperativity between two hydrogen bonds tends to strengthen both. The reason for the present anomaly lies in the ring closure in the 1 : 2 complex *via* weak $\text{C--Br}\cdots\text{H}$ and $\text{C--Cl}\cdots\text{H}$ secondary interactions between hydrogen atoms of the second NH_3 molecule and the chlorine and bromine atoms of halothane, the interatomic distances being 3.354 and 3.371 Å , respectively: these attractive interactions deform the $(\text{N})\text{--H}\cdots\text{N}$ hydrogen bond away from linearity, thereby weakening it in comparison to the hydrogen bond in the ammonia dimer.

Table 1 MP2 complexation energies $-D_e$, in kJ mol^{-1} , for the C-H...N bonded isomers of halothane-NH₃ and halothane-(NH₃)₂

	Halothane-NH ₃	(NH ₃) ₂	Halothane-(NH ₃) ₂
6-311++G(d,p)	-21.40	-11.1	-41.0
aug-cc-pVDZ	-22.06	-10.64	-43.50
aug-cc-pVTZ	-22.91	-11.96	-46.20
aug-cc-pVQZ	-23.29	-12.17	-47.15
CBS-limit	-23.86(8)	-12.74(4)	-48.8(6)

To account for the effect of the basis set size, single point calculations were performed for the 1 : 1 and the 1 : 2 complexes, at the MP2/aug-cc-pVXZ (X = D, T and Q) levels, using the equilibrium geometries of the 6-311++G(d,p) basis set. In addition, the complete basis set (CBS) limits were obtained from the plot of the calculated energies for the different basis as a function of $1/n$, with n the number of basis functions.²² The resulting values for the different complexation energies and the CBS-limits are summarized in Table 1. It can be seen that for the 1 : 2 complex, the extrapolation leads to a CBS-limit of $-48.8 \text{ kJ mol}^{-1}$. This value is significantly larger than the sum of the complexation energies of -23.9 and $-12.7 \text{ kJ mol}^{-1}$ calculated for halothane-NH₃ and (NH₃)₂, respectively. The contribution of the cooperative effects in the 1 : 2 complex, therefore adds up to approximately 25% of its binding energy.

3.2. Vibrational spectra

The spectra of halothane in the vapor phase and in different cryogenic environments have been discussed before.^{6,8} The spectra of NH₃ dissolved in cryogenic solutions have also been investigated in some detail before.^{23,24} These studies show that in the cryosolutions the NH₃ monomer bands are relatively broad and show some rotational structure, and that the spectra remain relatively simple if diluted solutions are studied.

However, increasing the concentration of NH₃ or lowering the temperature of the solution drastically complicates the spectra, due to the occurrence of self-associated species.

In this study, liquid rare gas solutions of mixtures of halothane and ammonia have been studied. Mole fractions ranged from 2.0×10^{-4} to 1.1×10^{-2} for halothane and 2.0×10^{-4} to 2.4×10^{-2} for NH₃. In the vibrational spectra, bands signaling the formation of complexes have been observed. Their frequencies, proposed assignments and complexation shifts are summarized in Table 2.

Panel A of Fig. 2 shows infrared spectra of the CH stretching, $\nu_{\text{CH}}^{\text{hal}}$, region, recorded in LAr, LKr and LXe, in jet-expansions and in the equilibrium gas phase, while panel B gives Raman spectra in the same region of solutions in LXe, at variable temperatures. For LKr and LXe and for the equilibrium gas phase infrared spectra recorded at different temperatures are shown: for each environment, the intensities have been adjusted so as to make equal the relative intensity of the sharper high frequency transition. From the Raman spectra, for which also the spectra of the single monomer solutions are shown, it is immediately obvious that the sharp transition, near 3000 cm^{-1} , is due to monomer halothane. This leaves the broader component at lower frequencies, near 2950 cm^{-1} , to be assigned to a complex between halothane and ammonia. This assignment is evidently supported by the temperature behavior of the low frequency band. It may be remarked that the profile of the complex band is very similar to that of the corresponding band in the infrared spectra. In the cryosolutions the differences in solvent influence from LAr to LXe shift the monomer band to lower frequencies. The behavior of the complex band is different: from LAr to LKr the complex band shifts upward, but from LKr to LXe it shifts downward. The explanation is that while the monomer frequency shifts to the red from LAr to LKr, the complexation shift decreases: at the midpoints of

Table 2 Characteristic vibrational frequencies and complexation shifts, in cm^{-1} , for the complex of NH₃ with halothane observed for a solution in LXe at 203 K, in LKr at 203 K and in LAr at 133 K. For comparison, the complexation shifts derived from the MP2/6-311++G(d,p) harmonic force field calculations have been added

	Assignment	LXe			LKr			LAr			Calc
		ν_{monomer}	ν_{complex}	$\Delta\nu$	ν_{monomer}	ν_{complex}	$\Delta\nu$	ν_{monomer}	ν_{complex}	$\Delta\nu$	$\Delta\nu$
CF ₃ CClBrH	ν_{16} (³⁷ Cl)	199.9	198.7	-1.2							-1.1
	ν_{15}	227.9	230.4	2.5							2.9
	ν_{14}	310.7	311.0	0.3							0.2
	ν_{13} (³⁵ Cl)	360.9	360.8	0.1							0.2
	ν_{13} (³⁷ Cl)	364.3	364.5	0.2							0.2
	ν_{12}	520.0	520.3	0.3	520.1	520.8	0.7				0.8
	ν_{11}	551.5	551.0	-0.5	552.2	551.4	-0.8				-0.6
	ν_{10}	663.5	663.2	-0.3							-0.4
	ν_9	715.5	713.1	-2.4							-2.6
	ν_8 (³⁵ Cl)	809.8	805.6	-4.2							-2.6
	ν_8 (³⁷ Cl)	811.1	807.2	-3.9							-2.6
	ν_6	1128.7	1137.2	8.5							12.1
	ν_5		1181.3								-6.5
	ν_2	1309.7	1329.6	19.9							42.8
			1340.6	30.9							42.8
NH ₃	ν_1	3001.2	2956.7	-44.3	3011.2	2967.1	-44.1	3013.7	2960.2	-53.5	-63.6
	ν_4	1617.7	1616.2	-1.5							-0.1
	ν_3		3414.7			3422.8			3425.2		-11.5
	ν_2	959.8	1022.4	62.6	955.9	1020.1	64.2		1021.6		58.9
	ν_1	3316.0	3313.5	-2.5		3320.5			3324.2		-5.9
	$2\nu_4$	3204.0	3208.0	4.0							
Librational mode			223.0								

Fig. 2 Vibrational spectra in the C–H stretching region of mixtures of halothane and NH_3 . (A) Infrared spectra in solution in LAr, LKr, and LXe, in jet expansions and in the vapor phase. The temperature of the cryosolutions are 123 K for LAr, and, in each case from top to bottom, 183, 189, 195 and 201 K for LKr and 183, 193, 203, 213 K for LXe. The temperatures of the vapor mixtures are 223, 258 and 293 K. The sharp bands in the 223 K spectrum are due to ammonia. (B) Raman spectra of a solutions in LXe; the temperatures for traces *a* to *d* are 183, 193, 203 and 213 K; traces *e* and *f* are the single-monomer spectra of halothane and ammonia, respectively.

the respective temperature intervals the complexation shift is -55 cm^{-1} in LAr (128 K), -49 cm^{-1} in LKr (173 K), and -42 cm^{-1} in LXe (228 K).

In the spectrum of the jet expansion a structured band is found about 55 cm^{-1} below that of the monomer. Its structure remains unaltered when the concentrations of halothane and ammonia in the gas mixture are varied, suggesting that the feature is due to a single complex. The reason for its structured contour, however, is not understood at present. Also for the equilibrium gas phase a broad, almost featureless band on the low frequency side of the monomer transition is observed, and it is clear from Fig. 2A that its temperature behavior is as expected. We note that at the lowest gas phase temperatures, the step on the low frequency slope of the dimer band found in the jet spectrum starts to appear. This supports a rovibrational band structure origin. Comparison with the other environments shows that in the higher temperature gas phase the complexation shift is significantly smaller than in the other phases: at 300 K the complexation shift is close to -30.5 cm^{-1} , while at the lowest temperature studied, 223 K, the shift has increased to approximately -35.5 cm^{-1} . We will return to this point in a later paragraph.

At comparable monomer concentrations the relative intensity of the 1 : 1 complex band is significantly smaller in the Raman spectra than in the infrared spectra. This is in line with the *ab initio* calculations that predict that the complexation raises the Raman scattering coefficient of ν_1^{hal} by a factor of 3, from 62 to $180 \text{ Å}^4 \text{ amu}^{-1}$, much less than the increase by a factor of 51 for the corresponding infrared intensity.

The higher temperatures of the solutions in liquid xenon, combined with the characteristics of the solvent, allow the study of solutions with higher concentrations. The effect of the increase of the concentrations on the spectra in the ν_1^{hal} region

Fig. 3 Infrared spectra of the CH stretching region for concentrated solutions in LXe, recorded at 203 K. The spectrum of the mixed solution and rescaled single-monomer spectra of halothane and NH_3 are shown in traces *a*, *b*, and *c*, respectively. The spectrum of the complexes obtained by subtracting traces *b* and *c* from trace *a*, are shown in trace *d*. Trace *f* shows the spectrum obtained by subtracting from trace *d* the rescaled spectrum of the 1 : 1 complex recorded at lower concentrations given in trace *e*.

is illustrated in Fig. 3. It can be seen that the monomer transition has been strongly reduced in relative intensity, and that on the low frequency side of the now familiar 2950 cm^{-1} band a shoulder is apparent. Traces *e* and *f* show the individual components as obtained using subtraction procedures. The concentration behavior of the new component, at 2920 cm^{-1} , suggests that it must be due to a complex with a stoichiometry that differs from that giving rise to the 2950 cm^{-1} transition. We assign it to a 1 : 2 complex involving one halothane molecule and two NH_3 units.

The stoichiometry of the complexes was confirmed from a concentration study, at 203 K in LXe, in which the linearity of the relation of the intensity of a complex band with products of the monomer intensities is investigated.¹¹ The relations are illustrated in Fig. SF1 of the ESI.† For the 2950 cm^{-1} band the χ^2 values of the linear regressions, with the halothane : ammonia stoichiometry indicated in brackets, are 0.007 (1 : 1), 6.368 (1 : 2), 62.605 (1 : 3) and 19.224 (2 : 1). These results clearly confirm our assignment that the 2950 cm^{-1} band belongs to a 1 : 1 complex. The χ^2 values for the 2920 cm^{-1} band are 1.72 (1 : 1), 0.13 (1 : 2), 0.29 (1 : 3) and 23.88 (2 : 1), supporting that this band originates in a 1 : 2 complex. It may be remarked that in the spectra of jet-expansions containing larger concentrations of NH_3 a second absorption due to complexes emerges near 2916 cm^{-1} . This frequency agrees well with that of the band assigned to the 1 : 2 complex in LXe and the new band is, therefore, assigned accordingly. The shift relative to the jet-cooled halothane monomer band is

-101 cm^{-1} . The near-doubling of the shift from the 1 : 1 to the 1 : 2 complex is to be compared to the doubling observed in the chloroform/ammonia case.¹⁰ The magnitude of the shifts is significantly smaller for chloroform ($38, 77\text{ cm}^{-1}$), pointing at a softer C–H bond and stronger interaction for haloethane.

Complex bands are also observed for several other haloethane vibrations. For instance, the complexation with NH_3 is found to induce blue shifts of $+31.1$, $+60.9$ and $+8.5\text{ cm}^{-1}$ for the CH bending vibrations, ν_2^{hal} and ν_4^{hal} , and for the CF_3 antisymmetric stretching mode, ν_6^{hal} , respectively. This behavior is similar to that of other haloethane complexes.^{5,8,9} In addition, a new band assigned to the CF_3 antisymmetric stretching mode ν_5^{hal} arises at 1181.3 cm^{-1} , i.e. at a frequency slightly below that of the multiplet assigned to the ν_5^{hal} mode in the monomer. The appearance of a multiplet structure for the monomer, with bands at 1194.3 , 1180.3 , 1172.4 , 1183.2 and 1169.4 cm^{-1} , and the occurrence of a single band due to the complex are related to Fermi or Darling–Dennison resonances which are present in the monomer but strongly reduced in the complex, similar to what was observed in the haloethane dimethyl ether complex.⁸ In the spectra of the mixed solutions new bands due to the C–Br, the C– ^{35}Cl and the C– ^{37}Cl stretching modes ν_9^{hal} and ν_8^{hal} are also found, the complexation shifts for these modes being -2.4 , -4.2 and -3.9 cm^{-1} , respectively.

Complex bands have also been observed in the Raman spectra of the mixed solutions. The frequencies of these bands, and the complexation shifts derived, nicely match those of the infrared studies and need no further comment.

The infrared spectra of solutions in LXe containing moderately low concentrations of NH_3 are characterized by a broad absorption in the NH stretching region. This absorption contains contributions of overlapping transitions due to $\nu_1^{\text{NH}_3}(\text{A}_1)$, $\nu_3^{\text{NH}_3}(\text{E})$ and $2\nu_4^{\text{NH}_3}(\text{A}_1, \text{E})$, the band centers and the relative intensities of which are difficult to determine.²⁴ In the Raman spectra two relatively sharp bands, at 3316.0 and 3204.0 cm^{-1} , due to the $\nu_1^{\text{NH}_3}(\text{A}_1)$ and $2\nu_4^{\text{NH}_3}(\text{A}_1)$ transitions are present. In the infrared spectra of the mixed solutions new sharp features due to the $\nu_1^{\text{NH}_3}(\text{A}_1)$ and $\nu_3^{\text{NH}_3}(\text{E})$ modes in the complex are observed at 3313.5 and 3414.7 cm^{-1} . In the Raman spectra, new features due to the complex are observed near 3313.5 cm^{-1} and 3208.0 cm^{-1} . The first feature, obviously, is related to the same transition as that causing the complex band in the infrared; the second feature is assigned to the $2\nu_4^{\text{NH}_3}(\text{A}_1)$ transition in the complex.

The region of the ammonia umbrella vibration, $\nu_2^{\text{NH}_3}$, for mixtures in LXe is shown in Fig. 4. Due to the hindered rotation in LXe, monomer NH_3 exhibits a P, Q, R structure,²⁴ the Q branch of which can be seen at 962 cm^{-1} . The broad high frequency absorption constitutes the R branch, with the weak maximum near 1055 cm^{-1} most likely due to higher aggregates, as observed in matrix infrared spectra²⁵ and NH_3 aerosols.²⁶ In the spectra of the mixture, shown in trace *a* of Fig. 4, a new band is found at 1022 cm^{-1} , which is assigned to the $\nu_2^{\text{NH}_3}$ mode of the 1 : 1 complex. Its narrow width contrasts with the broad, nearly free rotational contour of the same mode in monomer ammonia.

In Fig. 5, the far-infrared spectrum of a mixed solution in LXe is compared with those of the corresponding single

Fig. 4 The infrared spectrum of the ν_2 region of ammonia for mixed solutions in LXe containing haloethane and ammonia. Trace *a* shows the spectrum of the mixture at 203 K; traces *b* and *c* are the rescaled spectra of the single-monomer solutions containing ammonia and haloethane, respectively, at 203 K. Trace *d* is the spectrum of the complex, obtained by subtracting the monomer spectra from the spectrum of the mixture. The band at 938 cm^{-1} , indicated by an asterisk, is an impurity in the solvent.

monomer solutions. The spectrum of the complex, obtained by subtraction, is given in trace *d*. The broad, structured band in the $200\text{--}100\text{ cm}^{-1}$ range in the mixture and the monomer ammonia solution is due to the rotation of the ammonia monomer inside the solvent cavity.^{27,28} The weak sharp transitions in trace *d* are due to haloethane modes, as is clear from comparison with the monomer haloethane spectrum, trace *c*. Trace *d* also shows a prominent broad absorption band with

Fig. 5 Far-infrared spectra for a mixed solution in LXe containing mole fractions of 9×10^{-3} of haloethane and 4×10^{-3} of NH_3 . The spectrum of the mixed solution is given in trace *a*. The (rescaled) spectra of the single-monomer solution of NH_3 and haloethane are shown in traces *b* and *c*, respectively. The spectrum of the complex, obtained by subtracting traces *b* and *c* from trace *a*, is shown in trace *d*.

maximum near 220 cm^{-1} . It is assigned to the librational modes of the complex, calculated at 226 and 233 cm^{-1} . The high frequency tailing of the 220 cm^{-1} band suggests the presence of a weak transition near 260 cm^{-1} , and close inspection of the $450\text{--}400\text{ cm}^{-1}$ region, not shown in Fig. 5, shows the presence of a weak broad band near 420 cm^{-1} . These bands are assigned to the librational modes of the 1 : 2 complex, in reasonable agreement with their calculated frequencies of 445 and 297 cm^{-1} .

3.3. Relative stability

Information on the relative stability of the complexes was obtained from temperature studies between 213 and 298 K for mixtures in the vapor phase, between 183 and 203 K for the solutions in LKr and between 183 and 213 K for the solutions in LXe. The relatively high temperatures for LKr were required, as little or no spectral features due to monomer NH_3 could be observed at temperatures below 183 K . The complexation enthalpies were established using the Van't Hoff relation, as described before.¹¹ Typical Van't Hoff plots for the complexes are shown in Fig. 6. The resulting complexation enthalpies for the 1 : 1 complexes are $\Delta_{\text{compl}}H^\circ(\text{LKr}) = -17.3(6)\text{ kJ mol}^{-1}$, $\Delta_{\text{compl}}H^\circ(\text{LXe}) = -17.0(5)\text{ kJ mol}^{-1}$ and $\Delta_{\text{compl}}H^\circ(\text{vap}) = -20(1)\text{ kJ mol}^{-1}$. The complexation enthalpy for the 1 : 2 complex in LXe equals $-31.5(12)\text{ kJ mol}^{-1}$.

Fig. 6 Van't Hoff plots for the 1 : 1 (circles) and 1 : 2 (triangles) complexes of halothane with NH_3 observed in the vapor phase, in LXe and in LKr.

3.4. Intensity ratio $\epsilon_{\text{compl}}/\epsilon_{\text{mon}}$

It was pointed out above that the *ab initio* calculations predict an important increase in the infrared intensity of the halothane ν_1 vibration upon complexation. This was verified experimentally by measuring the ratio of the integrated band areas, $\epsilon_{\text{compl}}/\epsilon_{\text{mon}}$, using a procedure described before.^{11,29} Resulting values for LKr and LXe are $9.0(8)$ and $8.8(4)$. The analysis for LAr could not be pursued due to problems with the limited solubilities of halothane and ammonia. The values for LKr and LXe, within their error margins, agree favorably with each other, and suggest that for the complex studied little or no effect of the solvent on the intensity ratios is present. These values differ significantly from the *ab initio* value of 51, but this is in line with observations for previously investigated halothane complexes. Contributing to this effect is the fact that the *ab initio* value is calculated taking account only of the first derivative of the dipole moment, while for the intensity of the halothane CH stretch the second and third dipole moment derivatives are not negligible.⁸ Another contribution may be expected from the thermal excitation, which weakens the hydrogen bond in the solvent. Unfortunately, no reliable intensity ratio is available from the jet spectra. The decrease in monomer intensity upon ammonia addition is, however, consistent with an order of magnitude intensity increase in the complex. This supports the importance of higher dipole derivatives.

4. Discussion

The availability of experimental complexation enthalpies in vapor and rare gas solutions allows an evaluation of the solvation corrections we have been applying^{20,30} to extract energetic stability information from complexation enthalpies determined in rare gas solutions. In short, for each of the species involved in the complexation reaction, MC-FEP calculations are used to derive the Gibbs energy of solvation. From the variation with temperature of that quantity the entropy of solvation is derived, and this, combined with the Gibbs energy leads to the enthalpy of solvation. The latter are then used to calculate the solvation contribution to the solution value of the standard complexation enthalpy. Unfortunately, for the solutions in LKr, a warning is in place, as can be seen as follows. The solutions in LXe were investigated between 169 and 224 K . In that interval the variation of the density of the solvent is linear with temperature. Due to solubility problems of ammonia in the lower temperature range available in LKr, however, the solutions in that solvent had to be studied between 183 and 203 K , whereby the upper limit approaches the critical temperature of LKr, 209.4 K . In that interval, the density/temperature relation is strongly non-linear. It is evident that the temperature evolution of the solvation Gibbs energy will be closely related to the evolution of the density of the solution and the experience is that in an interval where the density of the solvent decreases linearly with temperature, the Gibbs energy also varies linearly, making its slope stable across the interval, so that a reliable value for the solvation entropy may be expected. In the other case, the slope, and, therefore, the solvation entropy, becomes strongly dependent on the temperature. In that case the simulations must be quite

accurate in order to predict the correct thermodynamic characteristics of the solvent and of the solvation process. It must be considered that the accuracy of the present Monte Carlo calculations may fall short of this requirement, due to its limitations such as the inherent binary approximation and the somewhat unsophisticated nature of the intermolecular potential used. It must, therefore, be expected that the predictions made in this study for the solutions in LKr will be less accurate than those for the LXe solutions. The Monte Carlo Gibbs energies of solvation for halothane, ammonia and for the 1 : 1 complex in LKr calculated in this study are given as a function of temperature in Fig. 7. It can be seen that, in agreement with what was said above, they vary linearly with temperature in the lower temperature range, up to about 190 K. It is also clear that at higher temperatures in all cases the relation becomes non-linear. It was found difficult to fit the calculated points of Fig. 7 with a straightforward polynomial, and, therefore, the first derivative of the curves had to be established using interpolation. This was done at 193 K, the mid-point of the experimental interval. The resulting standard Gibbs energies are compared with those calculated for the LXe solutions at 198 K in Table 3. Also given in that table are the standard solvation entropies and enthalpies and the solvation contributions to the standard complexation Gibbs energies $\Delta\Delta_{\text{sol}}G^\circ$, entropies $\Delta\Delta_{\text{sol}}S^\circ$ and enthalpies $\Delta\Delta_{\text{sol}}H^\circ$, at the

Fig. 7 Monte Carlo Gibbs energies of solvation in LKr of ammonia (a), halothane (b) and of the 1 : 1 complex between halothane and ammonia (c), as a function of temperature.

Table 3 Solvation Gibbs energy $\Delta_{\text{sol}}G^\circ$, in kJ mol^{-1} , solvation entropy $\Delta_{\text{sol}}S^\circ$, in $\text{J K}^{-1} \text{mol}^{-1}$, solvation enthalpy $\Delta_{\text{sol}}H^\circ$, in kJ mol^{-1} , of halothane (Hal), ammonia and their 1 : 1 complex, and solvation contributions to the 1 : 1 complexation Gibbs energy $\Delta\Delta_{\text{sol}}G^\circ$, in kJ mol^{-1} , entropy $\Delta\Delta_{\text{sol}}S^\circ$, in $\text{J K}^{-1} \text{mol}^{-1}$, and enthalpy $\Delta\Delta_{\text{sol}}H^\circ$, in kJ mol^{-1} , in LXe, at 198 K and in LKr, at 193 K

		$\Delta_{\text{sol}}G^\circ$	$\Delta_{\text{sol}}S^\circ$	$\Delta_{\text{sol}}H^\circ$
Hal	LXe	−20.9	−72.6	−35.2
	LKr	−17.3	−133.3	−43.0
NH ₃	LXe	−7.2	−30.0	−13.1
	LKr	−5.7	−45.6	−14.5
Hal·NH ₃	LXe	−26.0	−95.0	−44.8
	LKr	−21.3	−159.7	−52.1
		$\Delta\Delta_{\text{sol}}G^\circ$	$\Delta\Delta_{\text{sol}}S^\circ$	$\Delta\Delta_{\text{sol}}H^\circ$
	LXe	2.1	7.1	3.5
	LKr	1.8	19.2	5.5

respective midpoint-temperatures. It can be seen that, in agreement with expectations, the solvation Gibbs energies in LXe are more important than in LKr. In contrast, the solvation enthalpies show the opposite order. In view of the complex phenomena involved in the solvation, no attempts were made to rationalize the latter order. It can also be seen that the combined solvation effects on the individual species result in positive influences on the complexation Gibbs energy, by 2.1 kJ mol^{-1} in LXe and by 1.8 kJ mol^{-1} in LKr. This weakening of the complex in solution must be assigned to the loss of solvation, mainly for spatial reasons, when the individual monomers form the 1 : 1 complex. The most important data in Table 3 are the influences of the solvation on the complexation enthalpy $\Delta\Delta_{\text{sol}}H^\circ$. They can be seen to be 3.5 kJ mol^{-1} for the LXe solutions, and the significantly larger 5.5 kJ mol^{-1} for the LKr solution. These data were used to transform the experimental solution complexation enthalpies into vapor phase enthalpies, at the respective midpoint temperatures. In this way extrapolated vapor phase standard complexation enthalpies, $\Delta_{\text{compl}}H^\circ$ of $−20.5$ (5) kJ mol^{-1} for the LXe solutions, and $−22.8$ (6) kJ mol^{-1} for the LKr solutions, are found. To allow comparison with the experimental vapor phase complexation enthalpy, corrections must be applied so that extrapolated values are obtained that correspond to a temperature of 256 K, the midpoint of the experimental vapor phase temperature interval. These corrections were calculated, using the *ab initio* structures and vibrational frequencies of the species, to be 0.9 kJ mol^{-1} , and lead to final extrapolated vapor phase values $\Delta_{\text{compl}}H^\circ(\text{vap,LXe}) = −19.6$ (5) kJ mol^{-1} and $\Delta_{\text{compl}}H^\circ(\text{vap,LKr}) = −21.9$ (6) kJ mol^{-1} .

The value derived from the LXe measurement corresponds pleasingly well with the experimental gas phase value, $−19.9$ (11) kJ mol^{-1} . This result is taken to validate the procedure applied to derive the extrapolated vapor phase value, whereby it is realized that the goodness of the result is owed in part to the fact that the corrections are relatively small. For the LKr result, the error margins of extrapolated and experimental values do not overlap. This, in our opinion, reflects the less reliable values for the solvation entropies of the species calculated in LKr, due to, as was said above, the less evident temperature range that had to be used experimentally.

Another aspect that deserves attention is the behavior of the halothane CH stretching frequency upon complexation, in vapor as well as in solution. In Fig. 8A are given the observed values of the complexation shift relative to its value in the monomer under the same circumstances, $\Delta_{\text{compl}}\nu/\nu_{\text{mon}}$, as a function of temperature. In it, we have positioned the relative shift for the jet-experiments at the estimated temperature of 50(20) K.³¹ It can be seen that the shift observed under equilibrium vapor phase conditions decreases quasi linearly with decreasing temperature. If this trend is extrapolated linearly, the jet-shift is predicted to occur at a meaningless negative temperature. Therefore, despite the somewhat uncertain position of the jet-shift in Fig. 8A, it is clear that at lower temperatures the evolution of the relative shift must become nonlinear. This trend is not uncommon, as we have observed a similar behavior for the complexes of halothane with benzene.⁶ There, the temperature variation of the shift was proposed to be due to the increase with temperature of the

Fig. 8 Relative complexation shifts $\Delta_{\text{comp}}/\nu_{\text{mon}}$ of the halothane CH stretching fundamental in the 1 : 1 complex with ammonia. (A) Experimental data obtained from equilibrium vapor phase experiments, jet-expansions and solutions in LAr, LKr and LXe. (B) Values derived from Monte Carlo simulations of the van der Waals dynamics of the 1 : 1 complex in the gas phase.

population of the low-frequency van der Waals modes of the complex. That proposition was supported with a model that focused on the influence of the van der Waals stretching mode. For the present study we have adapted the procedure to take into account the influence of the other van der Waals vibrations as well, in the following way. At each temperature, a Monte Carlo simulation of the dynamical behavior of the complex was set up in which the intermolecular distance and the relative orientation of the rigid monomers were varied simultaneously, and the energy of the complex was calculated using dispersion corrected DFT calculations at the ω B97XD/aug-cc-pPVD level. The DFT-type of calculation was selected in order to keep acceptable the amount of cpu-time. Depending on the temperature, random distance variations between 0.05 to 0.1 Å, and random angle variations between 2.5° to 10° resulted, *via* application of the Metropolis algorithm to the DFT energies, in an acceptance ratio of 40%. Of the accepted structures, one in every 20 was used for further analysis. The latter consisted in DFT-optimizing the structure of the halothane moiety of the complex, at the same level as above, while keeping the van der Waals parameters and the structure of the ammonia moiety fixed. For the halothane structure thus obtained, the CH stretching frequency was determined from a one-dimensional harmonic oscillator model for which the force constant was obtained from DFT calculations in which only the C–H bond length was varied. By using appropriate binning of the obtained frequencies, the distributions at temperatures between 10 and 300 K shown in Fig. 9 were obtained. The weighted average over a distribution was used as the predicted frequency for the corresponding temperature. Transformed to relative shifts, they are shown as a function of

the temperature in Fig. 8B. The noise on the shifts is caused by the rather limited number of configurations collected in the Monte Carlo simulations, imposed by the calculation effort spent on the Metropolis algorithm. It can, nevertheless, clearly be seen that the relative shift becomes more important as the temperature is lowered, and that the relation is nonlinear. From the ordinate values given in panels A and B of Fig. 8, it follows that the calculated shifts are larger than the experimental ones. An explanation for this was not explicitly pursued, but most likely is the consequence of the approximate nature of the model. The present result differs from that for the halothane–benzene complex,⁶ where the calculated shifts underestimate the observed ones: this emphasizes the importance of accounting for all van der Waals modes. Except for the lowest temperatures, below 2.5 K, the calculated points can be satisfactorily fitted with a quadratic polynomial. This characteristic was used in an attempt to more accurately fix the vibrational temperature in the jet-experiment. In this, the experimental points were fitted with quadratic polynomials for which the temperature of the jet was set at values between 30 and 70 K. Even at the limiting temperatures the equilibrium shifts in the 210–300 K range were reproduced with only marginally higher uncertainties. This forces the conclusion that these calculations do not allow a preference for one of the vibrational jet-temperatures used.

Finally, the relative shifts of the same mode observed in solution must be rationalized. The temperature range used for the LXe solutions can be seen in Fig. 8A to partly overlap with that for the equilibrium gas phase, and it is clear that in the region of overlap (i) at any temperature the shift in solution is larger than the one in the gas phase and (ii) the shift/temperature relation has a higher slope in solution. As to the first point, some insight comes from the model for the interpretation of solvent shifts put forward by A. D. Buckingham.^{32–35} Applied to the present problem, the Hamiltonian that describes the isolated CH stretching mode consists of a term H_a which is the Hamiltonian for the localized anharmonic CH stretching vibration of monomer halothane in the vapor phase. To that term is added a potential $U(Q_1)$ that describes the influence of the solvent and/or of the ammonia molecule. For the present purpose we make the approximation that this term consists of a sum, the first term, $U_{\text{sol}}(Q_1)$, giving the contribution due to the solvent, and a second term, $U_{\text{am}}(Q_1)$, giving the influence of the ammonia molecule in the 1 : 1 complex. To keep things simple, it is assumed that $U_{\text{am}}(Q_1)$ is the same for the vapor phase and for the solution. For $U_{\text{sol}}(Q_1)$ we distinguish two contributions. The first describes the specific interactions between the halothane hydrogen atom and the solvent atom in closest contact with it. That contribution contains the influence of, among other phenomena, the overlap of the solvent atom electrons with the antibonding $\sigma(\text{CH})^*$ orbital. The second contribution is due to the polarization of the solvation shell by the halothane dipole moment, in particular the Q_1 -depending contribution. The latter is proportional to the value of $(\partial\mu/\partial Q_1)_0$ for the C–H stretching. The two contributions have a different impact. The former tends to lower the frequency when monomer halothane is dissolved in a rare gas solution. In view of the absence of direct overlap of solvent atom electron cloud with the $\sigma(\text{CH})^*$ orbital, this contribution will be significantly reduced in the complex.

Fig. 9 Frequency distributions, at the temperatures indicated, of the halothane C–H stretching mode, as derived from the Monte Carlo simulations of the van der Waals dynamics of the 1 : 1 complex with ammonia. The monomer vibrational frequency calculated at the same level is 3008.4 cm^{-1} .

Because of the stabilizing effect of the solvation shell the second contribution will lower the frequency of both monomer and complex, but much more so for the latter as a consequence of its much higher value of the dipole derivative, $(\partial\mu/\partial Q_1)_0$. Although there are yet no theoretical data supporting this, from the larger complexation shift of $\nu_1(\text{halothane})$ in the solutions for a given temperature, it must be concluded that the shift due to the solvent polarization in the complex outweighs the direct interaction shift. As to the second point, we interpret the higher slope of the shift/temperature relation in solution as a density effect. As was referred to above, the density of the liquid rare gases decreases significantly over the limited temperature interval in which the liquid is the stable phase. It is self-evident that the solvent-influence on vibrational shifts is reduced as a consequence of this. Therefore, it must be expected that the shift of ν_1^{hal} develops with increasing temperature towards the vapor phase shift: this can be clearly seen to be the case in the overlap-region in LXe. As the above population effect is operative in both solution and vapor phase, the added density effect in solution makes that the slope of the relation in solution must be higher than that in the vapor phase. It is in principle possible to put this to the test *via*,

for instance, measurements in the supercritical region of LXe, but results in that region have not yet been obtained.

The absence of vapor phase data in the temperature interval where solutions in liquid argon and krypton were studied prevents us from ascertaining that the evolution of ν_1^{hal} is completely similar to what occurs in LXe. However, the data in panel A of Fig. 8 suggest that for reasonable assumptions on the behavior of the vapor phase relation in the 50–200 K interval, such as the quadratic behavior of the data as in panel B, the frequencies in the solutions will be below the vapor phase values and even that the slopes of the solutions will exceed the vapor phase values. It can further be seen that in temperature intervals common to two solvents the shifts in liquid argon are smaller than in LKr, and those in LKr are smaller than in LXe. This characteristic supports the above conclusion that the solvent polarization is the dominant contribution to the observed vapor–solution shifts.

5. Conclusions

In this study we have investigated the interactions between halothane and ammonia, using vibrational spectroscopy of

mixtures in the gas phase, in jet expansions and in cryosolutions, exploiting the complementary nature of the different techniques. The formation of 1 : 1 and 1 : 2 complexes has been observed. The complexation shifts of the vibrational transitions agreed with values calculated using *ab initio* techniques to such an extent that the conclusion that the calculated structures are representative for the observed complexes is justified. Complexation enthalpies have been derived in various media and have been used to demonstrate the validity of the procedure applied to transform *ab initio* complexation energies into complexation enthalpies in cryosolutions. The differences between the halothane C–H stretching frequency of the complex in room temperature vapor, in low temperature jet expansions and in cryosolutions have been explained as due to differences in the relative thermal populations of the van der Waals modes of the complex.

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