

Vapour pressure isotope effects in liquid hydrogen chloride

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Abstract. The difference between the vapour pressures of HCl and DCl has been measured over the temperature range 170–203 K by a differential manometric technique in a precision cryostat. In this range the vapour pressure of HCl is higher than that of DCl by 3.2% at 170 K, decreasing to 0.9% at 200 K. The reduced partition function ratios f_l/f_g derived from the vapour pressure data can be described by the equation $\ln(f_l/f_g) = (3914.57 \pm 10)/T^2 - (17.730 \pm 0.055)/T$. The experimentally observed H–D vapour pressure isotope effect, together with the values on the ^{35}Cl – ^{37}Cl isotope effect available in the literature, is interpreted in the light of the statistical theory of isotope effects in condensed systems by using spectroscopic data of the vapour and liquid phases. The results indicate that the rotation in liquid hydrogen chloride is hindered. Temperature-dependent force constants for the hindered translational and rotational motions were invoked in order to obtain better agreement between the model calculation and experiment.

1. Introduction

Over the last few years, the excess thermodynamic functions of a number of binary liquefied gas mixtures have been determined in this laboratory. Recently, we have decided to start a programme on the thermodynamics of a variety of pure isotopic species and their mixtures. The results for the vapour pressure isotope effect (VPIE) of methane and tetradeuteriomethane have already been published (Calado *et al* 1989) and the data on their mixtures will be reported soon (Calado *et al* 1991).

Hydrogen chloride was selected as one of the systems to be studied next. The VPIE of HCl and DCl has been determined together with the deviations of their mixtures from the ideal behaviour.

In this paper we shall report the differences between the vapour pressures of hydrogen and deuterium chloride in the liquid phase, from 170 to 203 K. The VPIE has been previously determined in the solid and liquid phase between 152 and 201 K by Lewis *et al* (1934) and from 138 to 165 K by Chihara and Inaba (1976) and in the liquid phase from the triple point to 226 K by Henderson *et al* (1986).

The ^{35}Cl – ^{37}Cl isotope effect has been determined by Rayleigh distillation at 167, 173 and 181 K (Matveev *et al* 1959) and by distillation at 185 K (Gverdsiteli *et al* 1958). The chlorine VPIE is approximately one order of magnitude smaller than that of H–D.

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The only attempt to interpret the H–D VPIE was that of Wolff *et al* (1968), who carried out approximate calculations for the solid phase using spectroscopic data; however, the agreement with experiment is not satisfactory.

The purpose of the present work is to confirm the existing experimental data on the difference between the vapour pressures of HCl and DCl in the temperature range covered by our investigation and to interpret the H–D and ^{35}Cl – ^{37}Cl VPIE within the framework of the statistical mechanical theory of condensed-phase isotope effects using spectroscopic information.

2. Experimental details

Samples of HCl (from Air Liquide) were purified by fractional distillation in a low-temperature column. The final purity with respect to non-isotopic impurities was checked after two distillations by measuring the triple-point vapour pressure. This yielded a value of 13.804 ± 0.007 kPa to be compared with the value of 13.811 ± 0.009 kPa recommended by Staveley *et al* (1981). This means that the purity of our sample is at least 99.99%.

Deuterium chloride was prepared by reacting heavy water (Aldrich; 99.9 at.% D) with silicon tetrachloride (Aldrich; 98% purity). Great care was taken not to contaminate the reactants, which were always handled under an argon or a helium atmosphere. Traces of water in the silicon tetrachloride were removed using molecular sieves. The crude DCl gas obtained in the reaction was purified by double fractional distillation in the low-temperature column, and the triple-point vapour pressure measurement yielded a value of 12.555 ± 0.013 kPa. The isotopic purity of the DCl sample was determined by mass spectroscopy and was found to be 97.3 at.% D. Assuming that the triple-point pressure is a linear function of the mole fraction of DCl, one would obtain for the triple-point pressure of pure DCl 12.522 ± 0.013 kPa, which compares quite well with the value of 12.521 kPa given by Henderson *et al* (1986).

The difference between the vapour pressures of HCl and DCl was measured in a differential apparatus previously described elsewhere (Calado *et al* 1989), using a high-precision differential manometric technique.

The cryostat was cooled to the working temperature range (170–203 K) using liquid nitrogen. The samples of normal and deuterated hydrogen chloride were condensed separately into the two cells where they occupied about 30% of the available cell volume. The vapour pressure difference was determined with a Datametrix model 572 capacitance manometer with 0.13 Pa resolution. The absolute vapour pressure of DCl was monitored simultaneously using another capacitance sensor, a Datametrix 570 with 3.4 Pa resolution and a Texas Instruments fused quartz Bourdon gauge (resolution, 4 Pa). The calibrations of the capacitance manometers had been previously checked against a primary standard (mercury manometer).

The temperature was measured in the ITS-90 using a four-wire platinum resistance thermometer connected to an integrating digital multimeter (Prema 6031) with a resolution of 0.001 K. The temperature scale was calibrated against the known vapour pressure of HCl (Wagner-type equation proposed by Henderson *et al* (1986)) with an accuracy of ± 0.01 K.

3. Results

The difference between the vapour pressures of the HCl and DCl samples was measured at 40 temperatures (corresponding to eight independent runs) in the temperature range from 170 to 203 K. These Δp -values were corrected for 100% isotopic purity and are presented in table 1, together with the logarithm $\ln(p'/p)$ of the vapour pressure ratio, where the prime always refers to the lighter isotope species. To calculate this last quantity the Wagner-type equation for the vapour pressure of HCl (Henderson *et al* 1986) and the experimental Δp -values were used. The VPIE is normal ($p' > p$) and decreases from 3.2 to 0.9% between 170 and 200 K.

Table 1. VPIE of hydrogen chloride ($\Delta p = p_H - p_D$).

T (K)	Δp (kPa)	$10^5 \ln(p_H/p_D)$	T (K)	Δp (kPa)	$10^5 \ln(p_H/p_D)$
175.85	1.2390	2638	175.83	1.2366	2635
182.32	1.4891	2099	181.70	1.4633	2142
187.53	1.6663	1724	187.59	1.6659	1717
193.38	1.8080	1350	193.42	1.8068	1346
199.25	1.8575	1021	199.31	1.8521	1015
178.66	1.3507	2394	170.18	1.0039	3156
184.76	1.5740	1914	176.17	1.2418	2588
190.69	1.7490	1513	181.71	1.4616	2138
196.32	1.8424	1177	190.63	1.7505	1519
201.02	1.8203	916	202.35	1.8269	861
170.04	0.9983	3170	170.68	1.0254	3112
176.22	1.2454	2587	175.86	1.2346	2626
181.72	1.4620	2138	184.90	1.5728	1897
190.48	1.7437	1526	193.40	1.8061	1347
199.23	1.8542	1021	199.87	1.8469	984
172.97	1.1196	2896	171.17	1.0435	3060
178.78	1.3479	2371	177.65	1.3099	2478
184.60	1.5654	1922	183.88	1.5526	1991
190.46	1.7416	1526	192.78	1.8116	1397
199.21	1.8460	1017	199.24	1.8560	1021

In order to test the internal consistency of our data and to compare them with those from other workers (Lewis *et al* 1934, Henderson *et al* 1986), the vapour pressure values for DCl were calculated and fitted to an equation of the type

$$\ln[p \text{ (kPa)}] = A/T \text{ (K)} + B + CT \text{ (K)}. \quad (1)$$

The fit yielded $A = 17.7281 \pm 0.0002$, $B = (-6.1217 \pm 0.059) \times 10^{-3}$ and $C = -2253.6 \pm 2.1$. The agreement of the vapour pressures calculated from equation (1) with the values of Henderson *et al* (1986) is excellent (within 0.03%), while those of Lewis *et al* (1934) exhibit a larger scatter (figure 1).

For theoretical analysis the important quantity is the ratio of the reduced partition function ratios for f_l/f_g of the liquid phase to the gas phase, which can be obtained

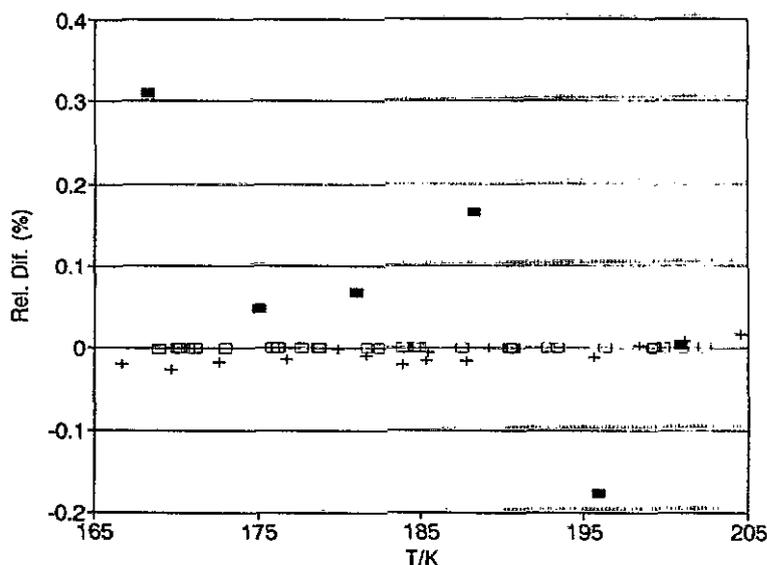


Figure 1. Comparison of the vapour pressures of DCl obtained from equation (1), with other measurements: \square , this work; +, data of Henderson *et al* (1986); \blacksquare , data of Lewis *et al* (1934). Rel. dif. (%) = $\{[\text{measurement} - \text{value from equation (1)}] / \text{value from equation (1)}\} \times 100$.

from the experimentally observed VPIE using the equation (Jancsó and Van Hook 1974)

$$\ln(f_1/f_g) = \ln(p'/p) - (p'V' - pV)/RT + B'p' - Bp \quad (2)$$

where V is the molar volume in the liquid phase and B is the second virial coefficient. The values for the molar volumes of HCl and DCl were taken from the data of Henderson *et al* (1986). For the virial coefficient the data from Schramm and Leuchs (1979) were used; they found that $B_{\text{HCl}} = B_{\text{DCl}}$ within their experimental precision. The correction terms for the liquid molar volume and the non-ideal vapour phase amount to 0.3% and 4.2%, respectively, of the logarithm of the vapour pressure ratios at the highest temperature (200 K). The ^{35}Cl - ^{37}Cl VPIEs obtained from distillation experiments have not been corrected (the magnitude of the correction is much smaller than the scattering of the experimental data).

The experimental partition function ratio values are plotted as a function of temperature in figure 2 and they can be adequately described by the equation

$$\ln(f_1/f_g) = (3914.57 \pm 10)/T^2 (\text{K}^2) - (17.730 \pm 0.055)/T (\text{K}). \quad (3)$$

The variance of the fit is 9.8×10^{-9} for $\ln(f_1/f_g)$.

4. Discussion

In the harmonic oscillator approximation with the assumption of a cell model for the liquid phase, the reduced partition function ratios f_1/f_g are calculated from the

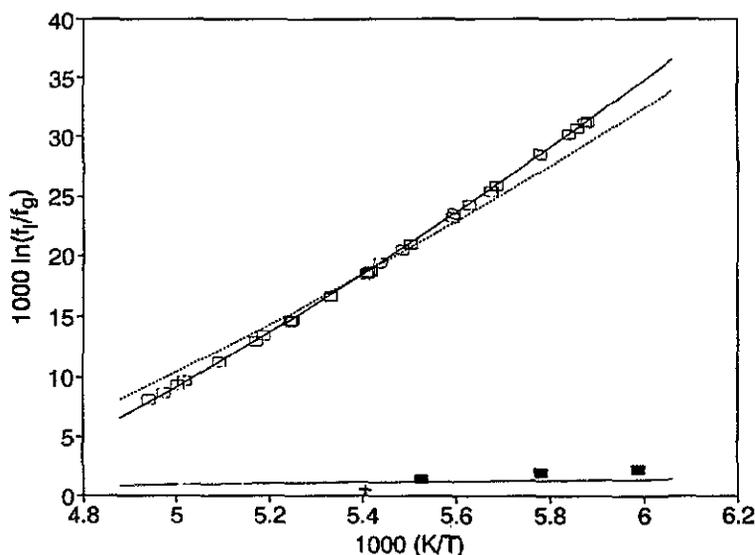


Figure 2. Comparison calculated and experimental reduced partition function ratios f_i/f_g : \square , $\text{H}^{35}\text{Cl}-\text{D}^{35}\text{Cl}$, experimental points; —, $\text{H}^{35}\text{Cl}-\text{D}^{35}\text{Cl}$, fit to the experimental data (equation (3)); - - -, $\text{H}^{35}\text{Cl}-\text{D}^{35}\text{Cl}$, calculated with temperature-independent external frequencies (the line calculated with temperature-dependent external frequencies is superimposed on the experimental line); \blacksquare , $\text{H}^{35}\text{Cl}-\text{H}^{37}\text{Cl}$, data of Matveev *et al* (1959); +, $\text{H}^{35}\text{Cl}-\text{H}^{37}\text{Cl}$, data of Gverdtsiteli *et al* (1958); \cdots , $\text{H}^{35}\text{Cl}-\text{H}^{37}\text{Cl}$, calculated with temperature-dependent external frequencies.

internal and external vibrational frequencies of the isotopic molecules by the equation (Stern *et al* 1963, Jancsó and Van Hook 1974)

$$\frac{f_i}{f_g} = \prod_{\text{internal frequency}}^{3N-5} \frac{(u_i/u'_i)_i \exp[(u'_i - u_i)_i/2] [1 - \exp(-u'_i)_i] / [1 - \exp(-u_i)_i]}{(u_i/u'_i)_g \exp[(u'_i - u_i)_g/2] [1 - \exp(-u'_i)_g] / [1 - \exp(-u_i)_g]} \times \prod_{\text{external frequency}}^5 \frac{u_i}{u'_i} \exp\left(\frac{(u'_i - u_i)}{2}\right) \frac{1 - \exp(-u'_i)}{1 - \exp(-u_i)} \frac{1}{f_{\text{nclr}}} \quad (4)$$

where $u_i = hc\nu_i/kT$; N is the number of atoms in the molecule, ν_i is the i th normal mode frequency in reciprocal centimetres and f_{nclr} represents the term for non-classical rotation in the gas phase (Bigeleisen *et al* 1967).

In the case of hydrogen chloride the contribution of the HCl stretching vibration to f_i/f_g can be expressed to a very good approximation in terms of the zero-point energy shifts of an anharmonic diatomic oscillator:

$$\ln(f_i/f_g) = (hc/kT) \left[\frac{1}{2}(\omega'_i - \omega_i) - \frac{1}{2}(\omega'_g - \omega_g) + \frac{1}{4}(X'_i - X_i) - \frac{1}{4}(X'_g - X_g) \right] \quad (5)$$

where ω is the harmonic frequency and X is the anharmonicity constant in reciprocal centimetres (Tóth and Jancsó 1989). The change in the anharmonicity on vapour-liquid transition can be estimated from the fundamental and first overtone frequencies observed in the vapour and liquid phases (table 2) using the relationship $X = \nu_{02}/2 - \nu_{01}$. The calculation gives -50 and -51 cm^{-1} for $X_{\text{H}^{35}\text{Cl}}$ in the two

Table 2. Spectroscopic parameters and moments of inertia of hydrogen chloride employed in the calculations. ν_{01} and ν_{02} are the fundamental and first overtone frequencies, respectively; the subscripts g and l refer to the gas and liquid phases, respectively. The temperatures in parentheses are the observation temperatures.

Parameter (units)	H ³⁵ Cl	D ³⁵ Cl	H ³⁷ Cl
$\nu_{01,g}$ (cm ⁻¹)	2885 ^a 2886 ^b	2091 ^a	
$\nu_{02,g}$ (cm ⁻¹)	5668 ^c		
$\nu_{01,g} - \nu_{01,l}$ (cm ⁻¹)	100(160 K) ^d 100 (188 K) ^b 102.5 (170 K) ^c 91;101 (160 K) ^f	64;71 (160 K) ^f	
$\nu_{02,l}$ (cm ⁻¹)	5470 ^b		
ω_g (cm ⁻¹)	2990.946 ^a	2145.150 ^a	
r_e (Å)	1.274 ₄ ^g		
Dielectric correction	10.6 ^b		
$I \times 10^{40}$ (g cm ²)	2.641 870	5.136 028	2.645 874

^a Pinchas and Laulicht (1971).

^b Chesnoy *et al* (1979).

^c Benedict *et al* (1957).

^d Hettner (1934).

^e Perchard *et al* (1972).

^f Oehme and Klostermann (1989); the first number refers to the maximum frequency, and the second number to the first moment of the Raman peak.

^g Van Horne and Hause (1956).

phases; thus the anharmonicity constants can be considered as being the same in the vapour and liquid phases within experimental precision. This is in agreement with the conclusion of Chesnoy *et al* (1979) who found that the anharmonicity is preserved in the liquid phase. The values of the anharmonicity constants obtained for $X_{\text{H}^{35}\text{Cl}}$ and $X_{\text{D}^{35}\text{Cl}}$ in the vapour phase through $\nu_{01} = \omega + 2X$ should obey the relationships $\omega_{\text{D}^{35}\text{Cl}}/\omega_{\text{H}^{35}\text{Cl}} = (\mu_{\text{H}^{35}\text{Cl}}/\mu_{\text{D}^{35}\text{Cl}})^{1/2}$ and $X_{\text{D}^{35}\text{Cl}}/X_{\text{H}^{35}\text{Cl}} = \mu_{\text{H}^{35}\text{Cl}}/\mu_{\text{D}^{35}\text{Cl}}$ (Herzberg 1965), where $\mu_{\text{H}^{35}\text{Cl}}$ and $\mu_{\text{D}^{35}\text{Cl}}$ are the reduced masses of the H³⁵Cl and D³⁵Cl oscillators. The ratio of the X -values and the ratio of the μ -values were found to be 0.511 and 0.514, respectively. On the basis of the above considerations, equation (5) can be simplified to

$$\ln(f_l/f_g) = -\frac{1}{2}(hc/kT) \left\{ (\omega'_g - \omega'_l) \left[1 - \left(\frac{\mu'}{\mu} \right)^{1/2} \right] \right\}. \quad (6)$$

The force constant for the stretching vibration was calculated from ω_g for H³⁵Cl given in table 2 and then it was used to calculate the gas-phase frequencies for D³⁵Cl and H³⁷Cl.

In order to obtain the HCl stretching force constant in the liquid phase, it is necessary first to correct the observed vapour-liquid frequency shift (100 cm⁻¹) for

Table 3. Gas and liquid-phase force constants for hydrogen chloride. The large number of significant figures is required to ensure consistency in the calculations.

	Gas phase	Liquid phase (183 K)
HCl stretching force constant (mdyn Å ⁻¹)	5.16276	4.86008
Degenerate translational force constant (mdyn Å ⁻¹)		0.033913 ^a
Translational force constant (mdyn Å ⁻¹)		0.086816 ^a
Librational force constant (mdyn Å)		0.040550 ^a

^a These force constants are temperature dependent (see text).

the dielectric effect brought about by the dielectric properties of the liquid medium surrounding the absorbing molecule (Jancsó and Van Hook 1977a, b). The value of 10.6 cm⁻¹ obtained by Chesnoy *et al* (1979) for the dielectric correction is relatively small when compared with the rather large shift in the HCl stretching vibrational frequency on condensation. The values of the calculated gas- and liquid-phase force constants and frequencies are given in tables 3 and 4, respectively.

To calculate the contribution of the external modes to the reduced partition function ratio a cell model is adopted for the liquid phase, in which the three translational and two rotational degrees of freedom are subject to 'harmonic' restoring forces (Stern *et al* 1963). The assignment of the liquid-phase frequencies observed by neutron inelastic scattering (Boutin and Safford 1965) can be based on the corresponding lattice vibrations observed in the low-temperature orthorhombic (phase III) and high-temperature cubic (phase I) phases. The experimentally observed external frequencies are collected in table 5. The lattice frequencies in solid phase III were assigned by comparing the corresponding HCl and DCl frequencies; the translational modes of HCl do not change their frequencies on deuteration, while the rotational modes show large red shifts (Anderson *et al* 1963-4, Ito *et al* 1969), owing to the large difference between the moments of inertia of HCl and DCl (see table 2). The liquid-phase frequencies of 40 and 64 cm⁻¹ can reasonably be assigned to the hindered translational motions. The lower frequency can be ascribed to the doubly degenerate hindered translation, while the higher frequency can be assumed to correspond to the translational motion, which involves a change in the distance of the hydrogen bond (Ito *et al* 1969).

Table 5. Observed external frequencies for HCl.

	Solid						
	Phase III				Phase I		Liquid (at 183 K)
Translational external frequency (cm ⁻¹)	59 ^a	55 ^b			56 ^c	48 ^c	40 ^c
	87	84	86 ^d	71 ^e	80	72	64
		133	109		160		
Librational external frequency (cm ⁻¹)	221	218	217	223	208	200, 200 ^b	208
		290	296				

^a Wang and Fleury (1970).

^b Ito *et al* (1969).

^c Boutin and Safford (1965).

^d Anderson *et al* (1963-4).

^e Hornig and Osberg (1955).

Table 4. Calculated gas- and liquid-phase (at 183 K) frequencies.

	H ³⁵ Cl		D ³⁵ Cl		H ³⁷ Cl	
	Gas	Liquid	Gas	Liquid	Gas	Liquid
HCl (DCI) stretching frequency ^a (cm ⁻¹)	2990.946	2901.946	2145.115	2081.284	2988.682	2899.749
Degenerate translational frequency (cm ⁻¹)		40.000		39.452		38.934
Translational frequency (cm ⁻¹)		64.000		63.123		62.294
Librational frequency (cm ⁻¹)		208.000		149.178		207.843

^a Harmonic frequency ω .

The frequencies observed at 200 and 208 cm^{-1} in the solid phase I and the liquid phase, respectively, are assigned to the hindered rotations by analogy with the corresponding band of the low-temperature phase. The librational frequencies in the high-temperature solid and liquid phases are the same within experimental error (about 8 cm^{-1}), which corroborates the observation that the average environment of the solid near the triple point resembles that of the liquid (Calado *et al* 1975, Oehme and Klostermann 1989). Since HCl can be considered to be weakly associated in the liquid phase (see, e.g., West (1939) and Swenson and Cole (1954)), the fairly high value for the hindered rotational frequencies is due to a very small value of the moment of inertia of the HCl molecule.

The external force constants obtained from the translational and rotational frequencies are listed in table 3, while the corresponding frequencies of D^{35}Cl and H^{37}Cl are reported in table 4.

In the original derivation of equation (4), classical values were used for the rotational partition functions in the vapour phase (Bigeleisen 1961). However, for HCl this cannot be considered as a good approximation in the temperature range covered by the present investigation. The contribution of the non-classical rotation (f_{nclr}) to f_i/f_g can be given as

$$\ln f_{\text{nclr}} = (Q_{\text{qm}}/Q_{\text{cl}})_{\text{rot}}(Q'_{\text{qm}}/Q'_{\text{cl}})_{\text{rot}}^{-1} \quad (7)$$

where Q_{qm} and Q_{cl} are the quantum mechanical and classical rotational partition functions, respectively (Bigeleisen *et al* 1967). By using the appropriate expressions for the Q -values (Herzberg 1965) and the moments of inertia given in table 2, the following equations were obtained:

$$\ln f_{\text{nclr,H-D}} = -2.48/[T(K)] \quad (8)$$

$$\ln f_{\text{nclr}^{35}\text{Cl}-^{37}\text{Cl}} = -7.7 \times 10^{-3}/T(K)]. \quad (9)$$

Table 6. Comparison of calculated and experimental reduced partition function ratios f_i/f_g for hydrogen chloride. The values in parentheses were calculated with temperature-dependent force constants (see text).

T (K)	$10^4 \ln(f_i/f_g)$					
	Internal contribution	Translational contribution	Rotational contribution	Non-classical rotational contribution	Total calculated value	Experimental value
$\text{H}^{35}\text{Cl}-\text{D}^{35}\text{Cl}$						
170	-1065	6 (6)	1207 (1225)	146	294 (312)	312
185	-979	5 (5)	1025 (1025)	134	185 (185)	185
200	-905	4 (4)	881 (869)	124	124 (92)	92
$\text{H}^{35}\text{Cl}-\text{H}^{37}\text{Cl}$						
170	-2.9	11.5 (12.2)	3.7 (3.8)	0.5	12.8 (13.6)	22 ^a (167 K)
185	-2.6	9.7 (9.7)	3.1 (3.2)	0.4	10.6 (10.7)	19.3 ^a (173 K) 14 ^a (181 K)
200	-2.4	8.3 (7.7)	2.7 (2.7)	0.4	9.0 (8.6)	4-6 ^b (185 K)

^a Matveev *et al* (1959).

^b Gverditsiteli *et al* (1958).

In order to illustrate the relative magnitudes of the contributions of the HCl stretching vibration (equation (6)), hindered translations and rotations (equation (4)) and the non-classical rotation in the vapour phase (equations (8) and (9)) to f_l/f_g they are compared with the experimental values at three different temperatures in table 6. As can be expected in the case of $\text{H}^{35}\text{Cl}-\text{D}^{35}\text{Cl}$ the higher vapour pressure of H^{35}Cl arises mainly from the differences between the hindered rotational frequencies of H^{35}Cl and D^{35}Cl , while for $\text{H}^{35}\text{Cl}-\text{H}^{37}\text{Cl}$ the contribution of the hindered translational motions plays a more important role.

Although the agreement between the experimental and calculated values can be considered satisfactory at this point, better agreement can be expected by taking into account the temperature (density) dependence of the internal and external frequencies in the liquid phase.

The temperature dependence of the 0–2 vibrational transition was studied by West (1939) in the liquid state, between -100 and 52°C . It was shown by Chesnoy *et al* (1979) that this peak is not dominated by the first overtone, but it is mainly due to simultaneous 0–1 transitions of two molecules. Accordingly one can obtain a value of about $-0.09\text{ cm}^{-1}\text{ K}^{-1}$ for the temperature dependence of the HCl stretching vibration in the liquid phase. This shift is of relatively small magnitude and comparable with the experimental uncertainties of the observed vapour–liquid frequency shifts (table 2). Furthermore it is possible that the observed temperature variation is due to changes in the dielectric correction with temperature; therefore the introduction of a temperature-dependent stretching force constant does not seem to be warranted.

The hindered translational frequencies are known to decrease in general with increasing temperature and this effect can be described by density-dependent force constants. On the assumption of the same volume dependence for the different translational force constants, an average value of 1.07 for the Grüneisen parameter ($\gamma_i = -d \ln(\nu_i)/d \ln(V)$) (Slater 1939) has been evaluated from the molar volume change on solid–liquid transition (Simon and Simson 1924) and from the translational frequencies observed in the solid phase I and the liquid phase (table 5). It can be seen in table 6 that the application of temperature-dependent hindered translational force constants affects only the $^{35}\text{Cl}-^{37}\text{Cl}$ reduced partition function ratio.

The largest contribution to the H–D VPIE arises from hindered rotational frequencies, but unfortunately the precision of the spectroscopic data do not allow one to obtain the Grüneisen parameter from the changes observed on solid–liquid transition. Therefore the temperature dependence of the hindered rotational frequencies was determined by reproducing the experimental data on the H–D VPIE (in figure 2 no distinction is made between calculation and experiment). The frequencies were found to decrease with increasing temperature and their shift is adequately represented by the equation $\nu_{\text{rot}} = 227.221 - 0.1036T(K)$. By using this equation and the liquid density of HCl (Henderson *et al* 1986), one can obtain a value of 0.24 for the Grüneisen parameter of the hindered rotation in the temperature range 170–200 K. This would correspond to a frequency shift of 7 cm^{-1} on solid–liquid phase transition, which is less than the experimental error in inelastic neutron-scattering measurements (Boutin and Safford 1965), and the small magnitude of the shift is in harmony with the conclusion drawn from Raman scattering studies that the rotational dynamics vary continuously from the solid to the liquid (Oehme and Klostermann 1989). On the basis of the present VPIE data, one can conclude that the free rotation of the hydrogen chloride molecules in the liquid phase (at least below 200 K) can definitely

be excluded, since this would result in an inverse VPIE ($p_{\text{DCl}} > p_{\text{HCl}}$) of about 0.078 at 200 K, instead of the observed normal isotope effect of 0.0104. This finding lends support to the same conclusion drawn by Chesnoy *et al* (1979) from a comparison of the Raman and infrared spectra of hydrogen chloride.

The agreement between the calculated and experimental ^{35}Cl - ^{37}Cl VPIEs is satisfactory (see figure 2), especially if one considers the precision of the data obtained by distillation techniques.

It seems reasonable to conclude that the experimental data obtained on the differences between the vapour pressures of HCl and DCl in the present work and those available in the literature on the ^{35}Cl - ^{37}Cl isotope effect can adequately be rationalized in terms of the statistical mechanical theory of isotope effects in the condensed phase, by using spectroscopic information on the gaseous and liquid phases. The model calculation has demonstrated that the most important contributions to the difference between the vapour pressures of HCl and DCl arise from the hindered rotational motions in the liquid phase and from the shift of the HCl stretching vibration on condensation. Our data indicate that rotation is not free in liquid HCl. The ^{35}Cl - ^{37}Cl VPIE which is one order of magnitude smaller is governed mainly by the differences between the hindered translational motions of the H^{35}Cl and H^{37}Cl molecules.

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