Vapour Pressure Isotope Effects of Chloroform

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The vapour pressure difference between $CHCl_3$ and $CDCl_3$ is measured by differential capacitance manometry between -60 and $+60\,°C$. The results can be expressed by the equation $\ln(p_H/p_D) = 5.507 \times 10^{-3} - 6.269/T$. The vapour pressure of $CHCl_3$ between -98 and $+62\,°C$ has also been determined. The experimental H/D vapour pressure isotope effect data together with the available literature values on the $^{12}C/^{13}C$ and $^{35}Cl/^{37}Cl$ isotope effects are interpreted within the framework of the statistical mechanical theory of isotope effects in condensed systems. The results show that the anharmonicity constant of the CH stretching vibration decreases by about 4% on the vapour-liquid transition.

I. Introduction

The change in the vapour pressure brought about by isotopic substitution (vapour pressure isotope effect, VPIE) is closely related to the intermolecular forces in the condensed phase and to their effect on the internal vibrations of the molecules [1]. Recent highly precise determinations of isotopic vapour pressure differences and their interpretation in terms of the statistical theory of condensed phase isotope effects [2, 3] have given information on the temperature dependence of internal force constants [4, 5], on the nature of the interaction between the external-internal degrees of freedom of molecules in the condensed phase [4, 6], and on the origin of the deviation of isotopic mixtures from the ideal behaviour [7]. It has also been shown that VPIE studies can be utilized to estimate the dielectric correction to vibrational frequencies in the condensed phase [8, 9] and the change in the anharmonicity constants on condensation [10].

Some thirty years ago Baertschi, Kuhn and Kuhn [11] found that the distillation of chloroform leads to an about 0.08% enrichment of ^{13}C in the distillate (inverse isotope effect) whereas the heavy chlorine isotope (^{37}Cl) is enriched by about 0.01% in the still pot (normal isotope effect). Rabinovich [12] has reported that the vapour pressure of $CDCl_3$ is higher than that of $CHCl_3$ by 4% at $-40\,°C$ and the isotope effect falls off rapidly to about 1.6% at $10\,°C$. This unusually large temperature dependence of the VPIE for a nonassociated compound containing a CH bond [13] as well as the relatively poor precision of the experimental data prompted us to redetermine the vapour pressure difference between $CHCl_3$ and $CDCl_3$ in a wide temperature range. The experimental findings together with the $^{12}C/^{13}C$ and $^{35}Cl/^{37}Cl$ VPIE data will be interpreted by a model calculation in terms of the harmonic cell approximation, and an attempt will be made at estimating the vapour-liquid shift of the anharmonicity constant of the CH stretching vibration.

2. Experimental

Reagent grade chloroform (Reanal) was subjected to gas chromatographic analysis showing it to contain about 1.1% ethanol which was removed by repeated equilibration (shaking) with water. After drying over a molecular sieve the sample was distilled and stored over P_2O_5 in the dark until its use. The deuterated sample (NMR grade, Stohler Isotope Chemicals) with a nominal 100.0 at% D content showed no impurity by gas chromatographic analysis. After drying over a molecular sieve it was distilled under vacuum and stored over P_2O_5.

The apparatus and procedure used to measure the vapour pressure differences between the isotopic species are described in detail elsewhere [14, 15]. The differential capacitance manometer was calibrated against the vapour pressure of water [16, 17] and the temperature was measured by a platinum resistance thermometer. Both the differential and the absolute vapour pressure were measured to four decimal places; the uncertainty in the temperature measurement being $\pm 0.03\,°C$.

3. Results

The absolute vapour pressure measurement of chloroform covered the temperature range from -98 to $+62\,°C$. Below the melting point ($-63.5\,°C$ [18]) we took 131 data and in the liquid phase 217*. The data were fitted to the Antoine equation giving

$$\log_{10}(p_H/Pa) = 5.9105 - 346.26/(149.19 + t/°C) \quad (1)$$
$$(-98\,°C < t < -63.5\,°C)$$

in the solid and

$$\log_{10}(p_H/Pa) = 9.0459 - 1156.5/(224.97 + t/°C) \quad (2)$$
$$(-63.5\,°C < t < +62\,°C)$$

in the liquid phase. The standard deviation of the calculated $\log_{10}p$ values is about $\pm 2 \times 10^{-3}$ and $\pm 2 \times 10^{-4}$, respectively. We were unable to find any vapour pressure data in the literature for comparison with our solid phase data. The lowest temperature in the liquid phase at which we found data was $-58\,°C$ where the agreement with the old tabulated values of Stull [19] can be considered as satisfactory, our data lying 1.2% lower. At $-40\,°C$ the two vapour pressure curves cross each other, our value becomes 2% and 0.1% higher at room temperature and at the boiling point, respectively. The recent data of Boublik and Aim [20] agree with ours within the experimental errors, the difference does not exceed $0.1 - 0.2\%$ in the temperature range from -10 to $+60\,°C$. The agreement with the data from other laboratories [21, 22] can also be considered as quite satisfactory, the difference varies between 0.5 and 0.1% from $10\,°C$ to the boiling point.

For the vapour pressure differences between the pure $CHCl_3$ and $CDCl_3$ samples we took 236 data* in the temperature range from $-60\,°C$ to $+60\,°C$. The VPIE could adequately be described by the equation

$$\ln(p_H/p_D) = 5.507 \times 10^{-3} - 6.269/(T/K) \quad (3)$$
$$(213\,K < T < 333\,K),$$

where p_H and p_D are the vapour pressures of $CHCl_3$ and $CDCl_3$. The standard deviation of the calculated $\ln(p_H/p_D)$ values is about $\pm 5 \times 10^{-5}$. The vapour pressure isotope effect data can be compared with

those obtained by Rabinovich [12] who used liquid differential manometry of much lower accuracy. At low temperatures (from -40 to $-20\,°C$) his inverse VPIE is almost twice as large as ours but the difference becomes gradually smaller as the temperature increases: at the highest temperature of his measurement ($+10\,°C$) the two VPIE's differ only by 4%. At $+10\,°C$ Handa et al. [23, 24] determined the vapour pressures of $CHCl_3$ and $CDCl_3$ by separate measurements from which a value of -0.014 can be obtained for $\ln(p_H/p_D)$ in which case the agreement with our value (-0.0166) is acceptable. From the VPIE measurements the isotope effect on the triple point can also be determined since we took several data points just below the melting point too. The triple point of $CHCl_3$ was found to be $1.08 \pm 0.05\,°C$ lower than that of $CDCl_3$.

For theoretical analysis of the VPIE the ratio of the reduced partition function ratios of the liquid and gas phases (f_c/f_g) is the quantity of interest which is obtained from the experimentally observed VPIE [1, 2]

$$\ln(f_c/f_g) = \ln(p'/p) - \frac{p'V' - pV}{RT}$$
$$- \left(B_0 p + \frac{1}{2}C_0 p^2 + \ldots\right)$$
$$+ \left(B_0 p + \frac{1}{2}C_0 p^2 + \ldots\right)', \quad (4)$$

where f_c and f_g are the reduced partition function ratios for the condensed and gaseous phase, V is the molar volume in the liquid phase, B_0 and C_0 are virial coefficients and the prime refers to the lighter isotopic species. The molar volume correction turned out to amount at most ($60\,°C$) to 0.2% of the experimentally observed VPIE, thus it can be neglected. The vapour nonideality correction has been evaluated by taking $C_0' = C_0 = 0$, $B_0' = B_0$ and using the equation $B(cm^3 mole^{-1}) = B_0RT = 211.0 - 1.2437 \times 10^8 T^{-2}$ obtained by fitting to the data from Dymond and Smith [25]. The correction term amounts to 0.01% of the logarithm of the vapour pressure ratios at $-60\,°C$ but increases to 3.2% at $+60\,°C$. The experimental reduced partition function ratio (f_c/f_g) for $CHCl_3/CDCl_3$ is plotted as a function of temperature in Figure 1. The $^{12}C/^{13}C$ and $^{35}Cl/^{37}Cl$ VPIE's obtained from distillation experiments have not been corrected.

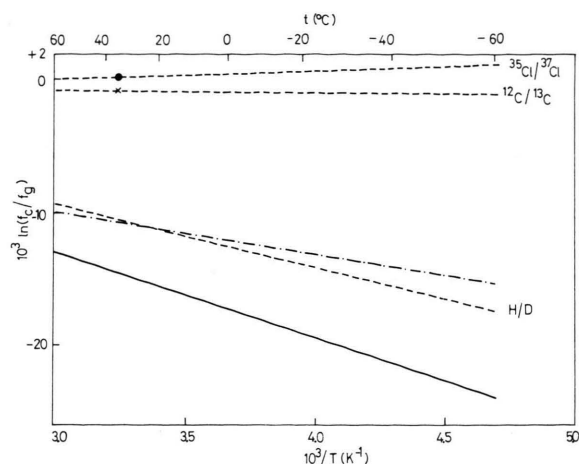* List of experimental data is available from the authors on request.

Fig. 1. Comparison of calculated and experimental reduced partition function ratios (f_c/f_g) for $CHCl_3$. ●, ×, —— experimental; —·—·— calculated from temperature independent liquid force field; — — — — calculated with temperature dependent liquid force field.

Fig. 2. Coordinate system and valence coordinates of chloroform.

4. Discussion

In the harmonic oscillator approximation with the assumption of a cell model for the liquid phase the reduced partition function ratios (f_c/f_g) are calculated from the internal and external vibrational frequencies of the isotopic molecules by the equation [1, 3]

$$\frac{f_c}{f_g} = \prod_{\text{int. freq.}}^{3N-6} \frac{(u_i/u_i')_c}{(u_i/u_i')_g} \frac{\exp((u_i'-u_i)_c/2)}{\exp((u_i'-u_i)_g/2)} \frac{(1-\exp(-u_i')_c)/(1-\exp(-u_i)_c)}{(1-\exp(-u_i')_g)/(1-\exp(-u_i)_g)}$$

$$\times \prod_{\text{ext. freq.}}^{6} \frac{u_i}{u_i'} \left[\exp\left(\frac{u_i'-u_i}{2}\right) \right] \left[\frac{1-\exp(-u_i')}{1-\exp(-u_i)} \right], \tag{5}$$

where $u_i = hc\,v_i/kT$; N is the number of atoms in the molecule; v_i is the i-th normal mode frequency in cm^{-1}.

The $3N$-6 gas phase frequencies of the different isotopic species were calculated by using the Wilson FG matrix method [26] and the force field derived on the basis of the experimentally observed vibrational frequencies and of the initial force field of Galasso et al. [27]. The internal coordinate system consisting of one CH bond stretch (D), three CCl bond stretches (d), three HCCl angle bends (β) and three ClCCl angle bends (α) is shown in Fig. 2 and the molecular parameters used for the computation of G matrices are listed in Table 1. The values of
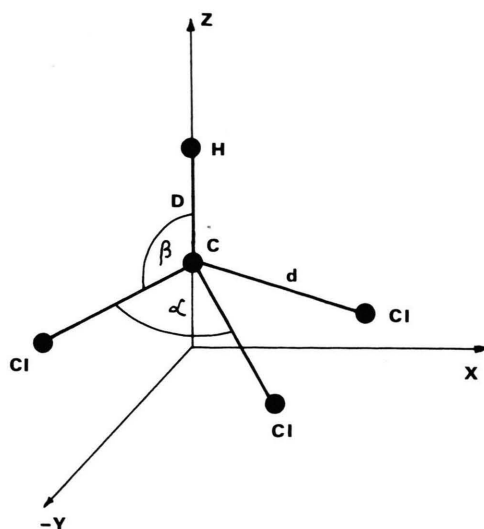
the gas phase force constants are shown in Table 2 and the calculated frequencies are compared with the observed ones in Table 3.

In order to derive the liquid force field from the gas field the observed liquid phase frequencies were applied which should be corrected for the dielectric effect [8, 9]. In the case of chloroform only the high intensity v_5 antisymmetric CCl stretching frequency has a sizeable correction [33, 34] since the intensities of the other vibrational bands are much lower than that of the v_5 vibration [35, 36]. Therefore the liquid phase force field was constructed from the F matrix for the gas phase by using the observed liquid fundamentals of $CHCl_3$ and $CDCl_3$ with the exception of the v_5 vibration. It was found, in accordance with Devaure et al. [30], that it is necessary to change some of the off-diagonal force constants too in order to describe properly the perturbations of the vapour phase frequencies brought about by the intermolecular interactions. The resulting liquid phase force constants are listed in Table 2 and the vapour-liquid frequency shifts predicted from this

Table 1. Molecular parameters of chloroform.

r_{CH}	1.100 Å	
r_{CCl}	1.758 Å	[28]
$\angle$ Cl−C−Cl	111.3°	
m_H	1.0078246 a.m.u.	
m_D	2.0141022 a.m.u.	
m_{12_C}	12.0000000 a.m.u.	
m_{13_C}	13.0033554 a.m.u.	[29]
$m_{35_{Cl}}$	34.9688531 a.m.u.	
$m_{37_{Cl}}$	36.9659034 a.m.u.	

Table 2. Gas and liquid phase force constants in unsymmetrized coordinates for chloroform[a].

	Gas phase	Liquid phase (25 °C)
f_D	4.87748[c]	4.83097[b]
f_d	3.50538	3.44861
f_{dd}	0.79775	0.76266
f_{Dd}		− 0.04829
$f_{D\alpha}$		0.25294
$f_{D\beta}$		− 0.24854
$f_{d\alpha}$		0.20449
$f_{d\alpha'}$		− 0.13551[d]
$f_{d\beta}$		0.12539
$f_{d\beta'}$		− 0.19461
f_α		0.89774
$f_{\alpha\alpha}$		− 0.18184
f_β	0.63888	0.63695
$f_{\beta\beta}$		− 0.03615
$f_{\alpha\beta}$	− 0.19414	− 0.20447
$f_{\alpha\beta'}$		− 0.11756
$f_{T_x} = f_{T_y} = f_{T_z}$		0.24090[b]
$f_{R_x} = f_{R_y}$		0.14409[b]
f_{R_z}		free rotation (see text)

[a] Bond stretching, bond-bond interaction and translational constants are in mdyne/Å, bond-angle interaction constants are in mdyne, angle-bending, angle-angle interaction and rotational constants are in mdyne · Å.
[b] These force constants are temperature dependent.
[c] The number of significant figures is retained to give satisfactory reproduction of the observed wavenumbers and to secure internal consistency in the calculations.
[d] The prime refers to the interaction between two coordinates which do not share a common C−Cl bond.

force field are compared with the observed ones in Table 4. On the frequencies corresponding to the external motions of the chloroform molecules in the liquid phase no information is available except on the frequency of the librational motion around the axis perpendicular to the symmetry axis, for which values of 45 cm⁻¹ [40, 41] and 40 cm⁻¹ [42] were found at room temperature. However, the experimentally observed values of $^{12}C/^{13}C$ and $^{35}Cl/^{37}Cl$ VPIE's

$$\ln(p_{^{12}CHCl_3}/p_{^{13}CHCl_3}) = -8 \times 10^{-4}$$

and

$$\ln(p_{CH^{35}Cl_3}/p_{CH^{37}Cl_3}) = 3 \times 10^{-4}$$

at 34.6 °C [11], which are more sensitive to the selected values of the external frequencies than the H/D isotope effect, make possible the estimation of the contributions from the external degrees of freedom. The small magnitude of the $^{35}Cl/^{37}Cl$ VPIE indicates that the rotational motion around the symmetry axis should be much less hindered than those around the perpendicular axes. Detailed analysis showed that satisfactory agreement between the calculation and measurement for the $^{12}C/^{13}C$ and $^{35}Cl/^{37}Cl$ VPIE can be achieved by assuming free rotation around the top axis and a value of 58.9 cm⁻¹ for the triply degenerate translational frequency of the $^{12}CH^{35}Cl_3$ molecule. The assumption of free rotational motion is supported by the spectroscopic investigation of Rothschild et al. [43] and also by the result obtained for bromoform in which case the rotation around the C_3 axis was found to become free already in the solid phase [44]. The $^{12}C/^{13}C$ VPIE changes very sensitively with the magnitude of the dielectric correction applied to the observed vapour-liquid shift of the ν_5 antisymmetric CCl valence vibration. The value of 3.9 cm⁻¹ for the dielectrically corrected ν_5 frequency shift obtained from the present VPIE calculation nicely agrees with those obtained by spectroscopic methods [33, 34] (see Table 4) and shows that only about one third of the vapour-liquid frequency shift is due to the direct action of the intermolecular forces on the CCl antisymmetric stretching vibration.

The external frequencies are known to decrease with increasing temperature which can be described by volume dependent force constants within the framework of quasi-harmonic approximation [45]. The same temperature independent Grüneisen parameter ($\gamma_i = -d\ln\nu_i/d\ln V$) [46] was used for the different external vibrational modes: the value of 1.99 for γ was obtained by Mizushima [47] and the temperature dependence of the liquid density was taken from [48]. There exists spectroscopic evidence that the frequency of the CH(CD) stretching vibration changes with temperature therefore the introduction of temperature dependence into the CH stretching force constant seems to be warranted just as it was in the case of benzene [4] and acetonitrile [5]. This decision is supported by the fact that most of the H/D VPIE arises from the zero-point energy

Table 3. Observed and calculated gas phase frequencies in cm^{-1}.

	CHCl$_3$		CDCl$_3$	
	obs.	calc.[a]	obs.	calc.[b]
v_1 CH (CD) stretch	3034 [30] 3033 [32] 3032.9 [31]	3033.224	2264 [30]	2264.982
v_2 sym. CCl$_3$ stretch	674.5 [30]	674.967	655.5 [30]	652.606
v_3 sym. CCl$_3$ bend	364.5 [30]	363.419	362 [30]	357.582
v_4 HCCl (DCCl) bend	1219 [30]	1219.070	913 [30]	910.781
v_5 antisym. CCl$_3$ stretch	772.5 [30] 772 [32]	773.452	747 [30]	742.201
v_6 antisym. CCl$_3$ bend	. . . .	261.651	. . . .	261.325

[a] $^{12}CH^{35}Cl_3$. − [b] $^{12}CD^{35}Cl_3$.

shift of the CH stretching vibration on condensation. Judging by Raman investigations the frequency of the CD stretching vibration shifts to the blue with increasing temperature by an amount of about 0.020 cm^{-1}/°C around room temperature [49]. This is in good agreement with the value of 0.024 cm^{-1}/°C for the CH stretching vibration estimated from the temperature dependence of infrared band peaks [35]. The vapour pressure isotope effects calculated with temperature independent and temperature dependent force constants are shown in Figure 1. It can be seen that there is a significant difference between the calculated and experimental H/D VPIE, e.g. at room temperature

Table 4. Frequency shifts on condensation ($v_{gas} - v_{liq}$) for CHCl$_3$ and CDCl$_3$ in cm^{-1} (at room temperature).

CHCl$_3$		CDCl$_3$	
obs.	calc.	obs.	calc.
v_1 14 [30]	14.0	9.5 [30]	10.0
v_2 5 [30]	5.6	4.5 [30]	5.9
v_3 −2 [30]	−1.8	−2.5 [30] 2.2 [39][c]	−2.0
v_4 3.5 [30]	3.0	4 [30]	4.8
v_5 15.5 [30] 17 [37] 3.6 [33][a, b] 3 [34][a] 8.8 [38]	3.9	13.5 [30] 23 [39][c]	1.8
v_6	0.1	1.05 [39][c]	0

[a] Frequencies corrected for dielectric effect.
[b] 6 cm^{-1} and 3 cm^{-1} were obtained on the basis of the Lorentz and of the more accurate Onsager-Bötcher model, respectively.
[c] $v_{CHCl_3, liq.} - v_{CDCl_3, liq.}$ observed by Raman difference spectroscopy.

the calculated inverse isotope effect is as much as 30% less than the measured one. In order to rationalize the experimental VPIE data such large values for the vapour-liquid shifts of the internal frequencies (e.g. of the CH stretching frequency) should be employed which would lie far beyond the experimental errors of the spectroscopic measurements. It is appropriate to emphasize that the consideration of the neglected, assumingly very small dielectric corrections would make the situation even worse.

It has been shown that the success of the methodology of the calculation of the VPIE based on (5) indicates that the anharmonicity constants do not change significantly on condensation [10]. On the other hand the available spectroscopic data show that in the case of CHCl$_3$ and CDCl$_3$ the anharmonicity constant of the CH(CD) stretching vibration might be different in the vapour and liquid phase [31, 32, 50 − 52] but it is difficult to reach any quantitative conclusion on the magnitude of the shift because of the insufficient accuracy and precision of the measurements. It seems reasonable to investigate the possibility of ascribing the discrepancy between the calculated and experimental H/D VPIE to the change of anharmonicity of the v_1 vibration on condensation. This decision is also supported by the following: the most important contribution to the H/D VPIE, as it was noted earlier, comes from the v_1 vibration and this can adequately be treated in the zero-point energy approximation; the largest anharmonicity of all the vibrations of chloroform can be expected in the case of the v_1 vibration − which can be considered as a diatomic oscillator; and the anharmonic coupling constants between this

and the other normal vibrations can be assumed to be zero [32].

The contribution of the anharmonicity corrected vibrational zero-point energy change [53] upon condensation to the H/D VPIE can be written for a diatomic CH oscillator as

$$\ln (f_c/f_g)_{CH/CD,\,anh} = \frac{hc}{kT}\left[\frac{1}{2}(\omega_{H,c} - \omega_{D,c}) - \frac{1}{2}(\omega_{H,g} - \omega_{D,g}) + \frac{1}{4}(X_{H,c} - X_{D,c}) - \frac{1}{4}(X_{H,g} - X_{D,g})\right] \quad (6)$$

where ω is the harmonic frequency, X is the anharmonicity constant [54] and c and g refer to the condensed and gaseous phase, respectively. On the other hand according to the usual procedure of the VPIE calculation the harmonic oscillator approximation — which uses the frequencies computed from vapour and condensed phase force fields obtained by reproducing the spectroscopically observed vibrational frequencies and frequency shifts within the experimental errors — gives the expression

$$\ln (f_c/f_g)_{CH/CD} \qquad (7)$$
$$= \frac{1}{2}\frac{hc}{kT}[(v_{H,c} - v_{D,c}) - (v_{H,g} - v_{D,g})],$$

where v is the fundamental frequency ($v = \omega + 2X$). Subtracting Eq. (7) from Eq. (6) and taking into account that $X_H/X_D = \mu_D/\mu_H$ [55, 56] one obtains

$$\Delta \ln (f_c/f_g) = \frac{3}{4}\frac{hc}{kT}\left(1 - \frac{\mu_H}{\mu_D}\right)\Delta X_H, \qquad (8)$$

where $\Delta \ln (f_c/f_g)$ corresponds to the difference between the observed H/D VPIE and that calculated in the harmonic oscillator approximation, μ_H and μ_D

represent the reduced mass of the CH and the CD oscillator, respectively and $\Delta X_H = X_{H,g} - X_{H,c}$.

The values of ΔX_H and ΔX_D are given and compared with the available literature data in Table 5. The ΔX_D values were obtained by using the approximation $\Delta X_H/\Delta X_D = \mu_D/\mu_H$ the application of which seems to be justified in this case since within the experimental precision X_{12} is equal to X_{23} in the liquid phase (see Table 5), hence we may assume that the second order perturbation treatment (see e.g. [56]) applies according to which the variation of the anharmonicity constant of the CH oscillator with deuterium substitution should satisfy the above relationship. While on the basis of the spectroscopic data no definite conclusion can be obtained on the shift of the anharmonicity constant of the CH(CD) stretching vibration on condensation, the VPIE calculation shows that there is an about 4% decrease in the absolute value of the anharmonicity constant at room temperature. The direction of the change is in agreement with the data available on other molecules [57] and with the conclusion, obtained by means of perturbation calculations, according to which whenever the relative shift of the vibrational frequency on condensation is less than about 0.5% the relative change in the anharmonicity constant does not exceed 5% [58]. The small but significant change in the anharmonicity constant of the CH stretching vibration (we estimated an uncertainty of ± 0.6 cm^{-1} in ΔX_H) which decreases with increasing temperature indicates that the inter-

Table 5. Anharmonicity constants for the CH(CD) stretching vibration of chloroform in the vapour and liquid phase (in cm^{-1}).

Temperature (°C)	CHCl$_3$				CDCl$_3$		
	X_{vapour}	X_{liquid}	$\Delta X_H = (X_{vap} - X_{liq})$[a]		X_{vapour}	X_{liquid}	ΔX_D[a]
− 60			− 2.7$_2$				− 1.4$_7$
− 20			− 2.6$_7$				− 1.4$_4$
0			− 2.6$_3$				− 1.4$_2$
25	− 62.2 ± 0.2 [31]	− 63.5 ± 1.3 [50][b]	− 2.5$_7$		− 33.6 [51][b]	− 32.0 ± 0.6 [52][b]	− 1.3$_9$
	− 61.5 ± 1.5 [32][b]	− 63.8 ± 1.3 [50][c]			− 34.1 [51][c]	(− 35.3)[d]	
	− 61.2 ± 2 [32][c]					− 34.7 ± 0.6 [52][c]	
60			− 2.3$_8$				− 1.2$_8$

[a] Present work.
[b] Computed from $X_{12} = v_{01} - v_{02}/2$, where v_{01} and v_{02} are the fundamental and the first overtone, respectively.
[c] Computed from $X_{23} = v_{02}/2 - v_{03}/3$, where v_{03} is the second overtone.
[d] Calculated by using $v_{01,\,liq.} = 2254.5$ cm^{-1} [30] instead of $v_{01,\,liq.} = 2251.1$ cm^{-1}.

molecular forces make the potential curve of the CH stretching vibration more harmonic in the liquid than it is in the vapour phase.

We conclude that vapour pressure isotope effect studies might provide in favourable cases informa-

tion not only on the vapour-liquid shifts (thus on the magnitude of dielectric correction) of internal vibrational frequencies but also on the influence of intermolecular interactions on the anharmonicity of vibrations.

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