Application of Vapor Pressure Isotope Effect to the Determination of Vibrational Anharmonicity in the Liquid Phase

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Dedicated to Professor Jacob Bigeleisen on the occasion of his 70th birthday

The experimentally observed H/D vapor pressure isotope effects in chloroform and bromoform were combined with reliable spectroscopic data from the literature in order to obtain information on the change of the potential curve of the CH stretching motion on vapor-liquid transition. The parameters studied include the Morse potential parameters, the anharmonicity constant and the harmonic, cubic and quartic force constants in both phases. While the anharmonic character of the potential energy curve of the CH oscillator of chloroform has been found to decrease on condensation, the opposite behavior has been observed in the case of bromoform.

Introduction

Since Bigeleisen worked out the theory of the vapor pressure isotope effect (VPIE) in terms of the reduced partition function ratios (RPFR) of condensed and ideal-gas phase molecules [1] numerous studies have been carried out in this field [2]. In the usual procedure the experimental results have been interpreted within the framework of the harmonic oscillator cell model by using the methodology of Stern, Van Hook and Wolfsberg [3]. This technique, which is now well established, includes the construction of vapor and condensed phase force fields (within the framework of the Born-Oppenheimer approximation), which reproduce the spectroscopically observed frequencies and frequency shifts on condensation within experimental error. These force fields are employed to calculate self-consistent sets of frequencies for the different isotopic species, which are then used for the computation of the VPIE through the RPFR's in the different phases. In the force constant calculations the observed fundamental frequencies are not corrected for anharmonicity, which means that effective ground-state force constants are obtained instead of quadratic force constants. The remarkable success of the Bigeleisen-Stern-Van Hook-Wolfsberg method seems to indicate that the anharmonic constants are very nearly the same in the vapor and condensed phases [4].

In principle anharmonicity corrections can be determined from data on the frequencies of the overtone and combination transitions in the vibration spectrum. In practice this method has been applied to all diatomic molecules in the vapor phase [5], but to very few polyatomic molecules, owing to the difficulty of obtaining sufficient data on the overtones. The situation is even worse in the condensed phase where studies have been reported only for a few molecules (see in [4]) and in addition to this the precision of the available data is rather poor. This is the main reason why the role of the anharmonicity in the condensed phase isotope effects has not been considered until quite recently, in spite of the fact that the theory of anharmonic corrections to isotopic exchange equilibria was worked out by Wolfsberg [6, 7] twenty years ago. However, in some favorable cases it was possible to obtain information on the change of anharmonicity constant on vapor-liquid transition from VPIE studies. The first system C_6H_6/C_6D_6 was originally treated by Jancsó and Van Hook [4, 8] and recently reconsidered by Van Hook [9] who concluded that there are significant shifts in both the harmonic and anharmonic CH stretching force constants on the phase change. The analysis of the vapor pressure isotope effects of chloroform [10] and bromoform [11] has shown that the anharmonicity constant of the CH stretching vibration of $CHCl_3$ decreases, whereas that of $CHBr_3$ increases on the vapor-liquid transition.

In this paper the experimentally observed VPIE's of $CHCl_3$ and $CHBr_3$ will be analysed by an alternative procedure in order to obtain information on the vapor-

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liquid shifts of harmonic and anharmonic force constants.

VPIE and Anharmonicity of CH Bond

In the case of chloroform and bromoform the most important contribution to the H/D vapor pressure isotope effect arises from the ν_1 vibration (the stretching of the CH (CD) bond), which can be considered as a diatomic oscillator [12]. Accordingly, our approach was to separate the contributions of all external and internal vibrations with the exception of the CH (CD) stretching mode from the experimentally observed VPIE. This separation was carried out by replacing the liquid phase frequencies of the ν_1 vibrations by their corresponding vapor phase values in the VPIE calculations reported in [10, 11]. Then the RPFR due to the CH/CD stretching vibration ($\ln(f_l/f_g)_{CH/CD}$) was described in the zero-point energy approximation [2]

$$\ln\left(\frac{f_l}{f_g}\right)_{CH/CD} = \frac{1}{kT}\left((E_{0H}-E_{0D})_l-(E_{0H}-E_{0D})_g\right), \tag{1}$$

where E_0 is the zero-point energy and l and g refer to the liquid and gaseous phase, respectively.

The potential energy curve of a diatomic oscillator can conveniently be represented by the Morse potential function [13]

$$V(r)=D(1-e^{-\beta\Delta r})^2, \tag{2}$$

where D is the bond dissociation energy referring to dissociation from the minimum of the potential energy, β is a parameter which expresses the width near the minimum of the potential curve and Δr is the displacement of the nuclei from their equilibrium separation ($\Delta r = r - r_e$). The Morse potential has the additional attractive feature that – as was pointed out by Wolfsberg [6, 7] – the G_0 term, which plays an important role in the anharmonicity corrections to isotopic exchange equilibria (see e.g. [14–16]), is zero for the Morse oscillator. The energy levels (E_v) can be written in closed form as

$$\frac{E(v)}{hc} = \frac{\beta}{c\pi}\left(\frac{D}{2\mu}\right)^{\frac{1}{2}}(v+\tfrac{1}{2}) - \frac{\beta^2 h}{8\pi^2\mu c}(v+\tfrac{1}{2})^2, \tag{3}$$

where μ is the reduced mass of the diatomic oscillator and v the vibrational quantum number [17]. By comparing the expansion of he Morse potential for small displacements [18],

$$V(r) \cong D\beta^2(\Delta r)^2 - D\beta^3(\Delta r)^3 + \tfrac{7}{12}D\beta^4(\Delta r)^4, \tag{4}$$

with the Taylor series expansion of the potential energy of the oscillator about the equilibrium configuration,

$$V(r) = \tfrac{1}{2}k(\Delta r)^2 + g(\Delta r)^3 + j(\Delta r)^4 + \ldots, \tag{5}$$

one obtains the following relationships between the different force constants and the parameters of the Morse function:

$$k = 2D\beta^2, \quad g = -D\beta^3, \quad j = \tfrac{7}{12}D\beta^4, \tag{6}$$

where k, g and j are the quadratic, cubic and quartic force constants, respectively. The vibrational energy levels of a CH oscillator can be expressed to a good approximation in the conventional spectroscopic notation by a function of the form

$$\frac{E(v)}{hc} = \omega(v+\tfrac{1}{2}) + X(v+\tfrac{1}{2})^2, \tag{7}$$

where ω is the harmonic frequency and X is the (first) anharmonicity constant (in cm^{-1}) [17]. These parameters can be related to those of the Morse function (cf. (3) and (7)) through the expressions

$$\omega = \frac{\beta}{c\pi}\left(\frac{D}{2\mu}\right)^{\frac{1}{2}}, \quad X = -\frac{\beta^2 h}{8\pi^2\mu c}. \tag{8}$$

Equations (6) and (8) can be used for the determination of k, g, j, D and β from ω and X. By using (1), (3) and (8) the relationship between the VPIE and the spectroscopic parameters can be given as

$$\ln\left(\frac{f_l}{f_g}\right)_{CH/CD} = \frac{hc}{kT}\left(\tfrac{1}{2}(\omega_{Hl}-\omega_{Dl}) - \tfrac{1}{2}(\omega_{Hg}-\omega_{Dg}) + \tfrac{1}{4}(X_{Hl}-X_{Dl}) - \tfrac{1}{4}(X_{Hg}-X_{Dg})\right). \tag{9}$$

Equation (9) can be simplified if one takes into account that the harmonic frequencies and anharmonicity constants of a diatomic oscillator vary in the following way with deuterium substitution [19, 20]:

$$\frac{\omega_D}{\omega_H} = \left(\frac{\mu_H}{\mu_D}\right)^{\frac{1}{2}} = \varrho, \quad \frac{X_D}{X_H} = \left(\frac{\mu_H}{\mu_D}\right) = \varrho^2. \tag{10}$$

It has been found that intermolecular interactions such as hydrogen bonding may have a slight influence on the isotopic ratios [20]; therefore we decided not to use the theoretical value for ϱ but leave it as a free parameter to be determined from the calculations. Thus (9) becomes

$$\ln\left(\frac{f_l}{f_g}\right)_{CH/CD} = \frac{hc}{kT}\left(\tfrac{1}{2}\omega_{Hl}(1-\varrho_l) - \tfrac{1}{2}\omega_{Hg}(1-\varrho_g) + \tfrac{1}{4}X_{Hl}(1-\varrho_l^2) - \tfrac{1}{4}X_{Hg}(1-\varrho_g^2)\right). \tag{11}$$

Table 1. Spectroscopic input data employed in the calculations (in cm^{-1}).

	$CHCl_3$	$CDCl_3$	$CHBr_3$	$CDBr_3$
ν_g $[\mathrm{cm}^{-1}]$	3032.9 [21]	2264 [22]	3048.3 [21]	2270 [23]
X_g $[\mathrm{cm}^{-1}]$	−62.2 [21]		−65.85 [21]	
$\nu_g-\nu_l$ $[\mathrm{cm}^{-1}]$	14 [22]	9.5 [22]	28 [21, 24]	19 [23]

Table 2. Spectroscopic and potential parameters for the CH stretching vibrations of $CHCl_3$ and $CHBr_3$ in the vapor and liquid phase.

	$CHCl_3$		$CHBr_3$	
	vapor	liquid	vapor	liquid
ω $[\mathrm{cm}^{-1}]$	3157.3	3140.2	3180.0	3159.5
X $[\mathrm{cm}^{-1}]$	−62.2	-60.6_5	-65.8_5	-69.5_9
ϱ	0.7385	0.7390	0.7363	0.7363
D [mdyne · Å]	0.7959	0.8074	0.7626	0.7124
β $[\text{Å}^{-1}]$	1.852	1.829	1.906	1.959
k [mdyne/Å]	5.460	5.401	5.539	5.468
g $[\text{mdyne/Å}^2]$	−5.056	−4.939	−5.278	−5.356
j $[\text{mdyne/Å}^3]$	5.462	5.270	5.868	6.121
k_3 $[\mathrm{cm}^{-1}]$	−313.2	−308.6	−323.6	−331.5
k_4 $[\mathrm{cm}^{-1}]$	36.27	35.38	38.41	40.59

In order to calculate the harmonic frequency, anharmonicity constant and parameter ϱ in the liquid phase we combined spectroscopically observed quantities known with high precision (fundamental and overtone frequencies in the vapor phase, shifts of the fundamental frequencies on vapor-liquid transition) with the RPFR due to the CH vibration. It can be seen from (9) and (11) that we are calculating, in fact, the changes in ω and X on vapor-liquid transition. In addition to (11) the following expressions – describing the relationship between the fundamental vibration frequency (ν) and ω, X – have been used:

$$\nu_{\mathrm{Hl}}=\omega_{\mathrm{Hl}}+2X_{\mathrm{Hl}}, \tag{12}$$

$$\nu_{\mathrm{Dl}}=\varrho_{\mathrm{l}}\,\omega_{\mathrm{Hl}}+\times 2\varrho_{\mathrm{l}}^2\,X_{\mathrm{Hl}}. \tag{13}$$

The spectroscopic data employed in the calculations are collected in Table 1. The values for ω_{Hg} and ϱ_{g} in (11) were obtained from (12) and (13) applied to the gaseous phase and are listed in Table 2.

Results and Discussion

The calculations have been carried out for 25 °C by using the values of −0.0136 and −0.0155 for $\ln(f_l/f_g)_{\mathrm{CH/CD}}$ of $CHCl_3$ and $CHBr_3$, respectively. The liquid phase harmonic frequencies and anharmonic constants are compared with those of the vapor phase in Table 2. It can be seen that the change in the anharmonicity constant on condensation contributes considerably (20–30%) to the observed vapor-liquid frequency shift of the ν_1 vibration in $CHCl_3$ and $CHBr_3$. It is interesting to note that, while in the case of $CHCl_3$ the potential function deviates less from the harmonic behavior in the liquid phase than in the vapor phase (the absolute value of X decreases by 2.5%), the opposite behavior was observed for $CHBr_3$, i.e. the anharmonicity constant increases by 5.7%. Sandorfy and coworkers have concluded from investigations on hydrogen bonded liquids that in the case of weaker interactions (e.g. secondary amines) X decreases, whereas for stronger hydrogen bonding (alcohols) the absolute value of X increases [25–27] as a consequence of hydrogen bond formation. For bromoform the effect of intermolecular interactions (mainly dispersion forces) on the CH bond can be expected to be much larger than for chloroform (the polarizability of a C–Br bond is about 40% larger than that of a C–Cl bond [28]) thus the direction of the change of the anharmonicity constant on vapor-liquid transition is in accord with the findings of Sandorfy et al.

The value of the parameter ϱ was found to be practically the same in the vapor and liquid phases and is very close to its theoretical value (0.7342). This lends further support to the assumption that in the CH (CD) stretching vibration in $CHCl_3$ and $CHBr_3$ the motion is largely localized in the CH (CD) group.

The values obtained for the Morse potential parameters (D, β) by using the expressions given in (8) are reported in Table 2. The bond dissociation energies can be compared with the available experimental data. For example, the dissociation energy obtained after correcting for the zero-point energy is about 110 kcal/mol for the CH bond of $CHCl_3$, which is in satisfactory agreement with the experimental value of 96 kcal/mol [29]. The vapor-liquid shift of parameter β, which is characteristic of the width of the potential curve in the neighborhood of the minimum, is in good accord with what has been found from the shift in the anharmonicity constant.

We now turn attention to the change of harmonic and anharmonic force constants on condensation (Table 2). The harmonic force constants of $CHCl_3$ and $CHBr_3$ decrease – as can be expected – by about 1.1% and 1.3%, respectively. The cubic and quartic force constants for $CHCl_3$ decrease by 2.3% and 3.5%, respectively, whereas for $CHBr_3$ an increase of 1.5% and 4.3% has been found. We note in passing that in the case of benzene Van Hook found a decrease in the harmonic and cubic force constants of about 0.6% and 1.6%, respectively, at room temperature [9].

It is worthwhile to look more closely at the contribution of cubic and quartic potential constants to the anharmonicity constant (X). For this purpose it is convenient to write the potential energy as an expansion in the dimensionless coordinate (q)

$$V/hc = 1/2\,\omega\, q^2 + k_3\, q^3 + k_4\, q^4, \tag{14}$$

where k_3 and k_4 are given in cm^{-1}, Q is the normal coordinate and $q = 2\pi(c\,\omega/h)^{1/2}\,Q$ [30]. The relationship between the anharmonic potential constants (k_3, k_4) and the anharmonicity constant (X) can be expressed as [30]

$$X = \frac{15\,k_3^2}{4\,\omega} - \tfrac{3}{2}\,k_4\,. \tag{15}$$

The cubic and quartic potential constants were computed from the corresponding anharmonic force constants g and j by the method described in [30, 31] and are listed in Table 2. As an example we evaluated X for the vapor phase of chloroform: the contribution of the first term in (15) to X amounts to -116.5 cm^{-1}, while that of the second term is 54.4 cm^{-1}. It is clear from these figures that the cubic and quartic potential constants are equally important (see e.g. [27]), and both constants contribute significantly to the vapor-liquid shift in the anharmonicity constant.

Conclusion

It has been demonstrated that in favorable cases it is possible to obtain information on the change of mechanical anharmonicity and anharmonic force constants on vapor-liquid transition by combining reliable spectroscopic data with the results of vapor pressure isotope effect measurements. The detailed analysis carried out for the CH stretching vibrations of $CHCl_3$ and $CHBr_3$ has shown that while in the case of $CHCl_3$ the potential curve of this vibration becomes more harmonic in the liquid phase, the anharmonic character of the potential increases in the case of $CHBr_3$.

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