Interpretation of Vapor-Liquid Frequency Shift of CH Stretching Vibrations of Chloroform and Fluoroform

Katalin Tóth and Gábor Jancsó

Central Research Institute for Physics, Budapest, Hungary

Z. Naturforsch. **46a**, 49–59 (1991); received July 10, 1990

Dedicated to Dr. Karl Heinzinger on the occasion of his 60th birthday

The change in the frequency of the CH stretching vibration and in its anharmonicity constant, quadratic, cubic and quartic force constants and the equilibrium CH bond distance, on condensation, were investigated by performing model calculations for liquid chloroform and fluoroform. The interactions between the hydrogen atom and the CH oscillator, represented by a Morse potential, and the halogen atoms of its neighbor molecules were described by the sum of Lennard-Jones and Coulomb potential functions employed in molecular dynamics simulation. The calculations were carried out for different molecular arrangements in the liquid and have shown that mainly the size of the halogen atom, consequently the intermolecular distances, govern the direction of the CH vibrational frequency shift and of the change in the anharmonicity constant on the vapor-liquid transition. The pressure and temperature dependence of the CH stretching vibration was also studied for liquid chloroform. While the calculated pressure dependence is in good agreement with that observed, only the direction of the temperature dependence is in accordance with experimental observation.

Introduction

The difference in the vapor pressure of isotopically substituted molecules (vapor pressure isotope effect, VPIE) is closely related to the intermolecular forces acting between the molecules in the condensed phase and to their effect on the internal vibrations [1].

During the investigation of vapor pressure differences brought about by isotopic substitution in various haloforms [2–4] it turned out that the shift of the CH stretching frequency on condensation contributes significantly to the H/D VPIE. According to spectroscopic data the frequency of the CH stretching vibration of $CHCl_3$ and $CHBr_3$ decreases on condensation (red shift) by 14 cm^{-1} [5] and 28 cm^{-1} [6], respectively. On the other hand, in the case of fluoroform the CH vibrational frequency undergoes an increase of 27 cm^{-1} (blue shift) [7] during the vapor-liquid transition. By combining the high precision VPIE data with the above spectroscopic information we have concluded that the anharmonic constant of the CH vibration of $CHCl_3$ decreases, whereas that of $CHBr_3$ increases on condensation [8]. It is of interest to decide whether the differences in the intermolecular interactions and/or in the sizes of the haloform molecules are responsible for the differences in sign and magnitude of the shifts of the CH stretching vibrations and their anharmonicity on condensation.

Since the late fifties the changes in the vibrational spectrum of dissolved molecules caused by the intermolecular interactions in liquid phase have widely been investigated. Red shifts and an increase in the equilibrium bond distances were found for most of the CH (or OH) stretching vibrations which are due to attractive interactions [9–17]. These shifts can be offset and reversed by compressing the solution because this leads to a decrease in the mean distances between solute and solvent molecules and thus the repulsive forces become dominant.

A theoretical treatment of the effects of solute-solvent interactions on the frequencies, intensities and shapes of the infrared absorption bands of dissolved molecules was carried out by Buckingham [12–14] within the framework of second-order perturbation theory. He showed that the frequency shifts are related to the first and second derivatives of the intermolecular interaction potential with respect to the displacement of the nuclei from their equilibrium separation. However, this theory is not able to account for changes in anharmonicity constants during condensation.

Drickamer and his co-workers [9–11], who mainly studied the effect of pressure on the vibrational fre-

Reprint requests to Dr. G. Jancsó, Central Research Institute for Physics, H-1525 Budapest, P.O. Box 49, Hungary.

0932-0784 / 91 / 0100-0049 $ 01.30/0. –

quencies, described the vibration of CH bonds in the condensed phase by a potential function which was represented by the sum of Lippincott's intramolecular and a Lennard-Jones intermolecular potential function. From the equilibrium condition the changes in bond distances were calculated, while the frequency shifts were estimated from the second derivatives of the total potential function. By comparing the calculated shifts with the experimental ones they were able to obtain information on some parameters of the intermolecular potential function. Higher order derivatives, therefore changes in anharmonic force constants and anharmonicity constants were not considered in their calculations. Recently Mentel and Luck [15] carried out a high-pressure infrared spectroscopic study on OH vibrations of some fluoroalkyl alcohols and interpreted their results using a linear semiclassical model. From the maximum shifts observed they calculated OH-solvent potential parameters and found a linear correlation between the frequency shifts at ambient pressure and the well depth of the interaction potential.

Schweizer and Chandler [16] established a model calculation within the framework of statistical mechanics of liquids which accounted for the density dependence of certain vibrational frequencies, and they evaluated for the hard-sphere model the repulsive solvent-induced force exerted on a solute molecule bond. Also using the hard sphere model, Zakin and Herschbach [17] provided an analysis of pressure-induced repulsive and attractive shifts for quasi-diatomic C–H or O–H stretching vibrations as a function of solvent density.

The purpose of the present study is to understand the shifts of the CH stretching vibrational frequencies and the changes in the anharmonicity constants of haloforms on the vapor-liquid phase transition by carrying out model calculations which are similar to those of Moon and Drickamer [11]. Detailed calculations were performed for chloroform by investigating various molecular arrangements in the liquid phase; the effect of pressure and temperature on the CH stretching vibration was also studied. The intermolecular potential parameters and structural information were taken from the molecular dynamics simulation of Dietz and Heinzinger [18, 19]. It is interesting to note that the frequency shifts could directly be obtained from the molecular dynamics simulations if the molecules were regarded flexible, as was done, for example, in the case of water [20] and methanol [21].

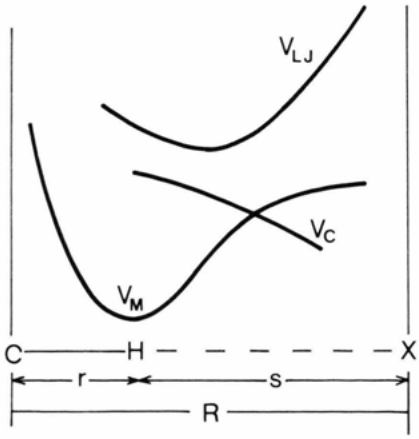

Fig. 1. Interaction between a CH oscillator and a halogen atom X. V_M: Morse potential, V_{LJ}: Lennard-Jones potential, V_C: Coulomb potential.

Method of Calculation

In our model the total interaction energy in the liquid phase is taken to be equal to the sum of pair interactions between the molecules. As for the interaction between the hydrogen atom and its surroundings in $CHCl_3$, only the H · · · Cl intermolecular interaction is taken into account because $CHCl_3$ dissolved in liquid $CHCl_3$, CCl_4 and $CFCl_3$ shows experimentally almost the same CH frequency shifts [9], indicating that they arise mainly from H · · · Cl interactions.

The potential energy of the CH bond in the liquid phase is described as the sum of intra- and intermolecular interaction energies. For the sake of simplicity, the procedure was developed first for the linear arrangement of a C–H bond and a halogen atom (Figure 1). The total potential function (V_{CH}) for this model can be written as

$$V_{CH} = V_M(r) + V_{LJ}(s) + V_C(s)\,, \tag{1}$$

$V_M(r)$ being the intramolecular potential function of the gas phase CH quasidiatomic oscillator represented by the Morse function [22]

$$V_M(r) = D\{1-\exp(-\beta(r-r_{eg}))\}^2, \tag{2}$$

where D is the bond dissociation energy referring to dissociation from the minimum of the potential energy and β is a parameter expressing the width near the minimum of the potential curve (at r_{eg}). The intermolecular potential can conveniently be given as the sum of Lennard-Jones ($V_{LJ}(s)$) and Coulomb ($V_C(s)$)

potential functions:

$$V_{LJ}(s) = 4\varepsilon\left\{\left(\frac{s_0}{s}\right)^{12} - \left(\frac{s_0}{s}\right)^{6}\right\}, \qquad (3)$$

$$V_C(s) = q_H q_{Cl}/s,$$

where s is the H–X distance, ε the depth of the minimum in the potential and q_H and q_{Cl} are partial charges carried by the hydrogen and chlorine atoms, respectively.

In equilibrium the first derivative of the total potential (V_{CH}) with respect to r is zero, so one can write:

$$2D\beta(e^{-\beta(r-r_{eg})} - e^{-2\beta(r-r_{eg})}) \qquad (4)$$
$$+\frac{24\varepsilon}{s_0}\left(\frac{s_0}{R-r}\right)^7\left\{2\left(\frac{s_0}{R-r}\right)^6 - 1\right\} + \frac{q_H q_{Cl}}{(R-r)^2} = 0.$$

This equation can be solved by the method of successive approximation for r, which gives the equilibrium bond distance in the liquid phase (r_{el}). Equation (4) was also used to calculate r_{el} as a function of the C···X distance (R), which depends on the actual value of pressure and temperature.

In order to determine the force constants of the CH stretching vibration in the liquid phase the potential energy of the CH oscillator will be expanded in a Taylor series about the equilibrium distance. Then one has for the Lennard-Jones potential

$$V_{LJ} = 4\varepsilon\left(\frac{s_0}{s_1}\right)^6\left\{\left(\frac{s_0}{s_1}\right)^6 - 1 + \left[12\left(\frac{s_0}{s_1}\right)^6 - 6\right]\frac{\Delta r}{s_1}\right.$$
$$+\left[78\left(\frac{s_0}{s_1}\right)^6 - 21\right]\frac{(\Delta r)^2}{s_1^2} + \left[364\left(\frac{s_0}{s_1}\right)^6 - 56\right]\frac{(\Delta r)^3}{s_1^3}$$
$$\left.+\left[1365\left(\frac{s_0}{s_1}\right)^6 - 126\right]\frac{(\Delta r)^4}{s_1^4}\right\} + \cdots, \qquad (5)$$

for the Coulomb potential

$$V_C = \frac{q_H q_{Cl}}{s_1}\left\{1 + \frac{\Delta r}{s_1} + \left(\frac{\Delta r}{s_1}\right)^2 + \left(\frac{\Delta r}{s_1}\right)^3 + \left(\frac{\Delta r}{s_1}\right)^4 + \cdots\right\}, \qquad (6)$$

and for the Morse function

$$V_M(r) = D\beta^2(\Delta r')^2 - D\beta^3(\Delta r')^3 + \tfrac{7}{12}D\beta^4(\Delta r')^4 + \cdots, \qquad (7)$$

where $s_1 = R - r_{el}$, $\Delta r = r - r_{el}$, $\Delta r' = r - r_{eg}$. Whereas in the vapor phase the force constants of the CH bond depend only on the parameters of the Morse function, in the liquid phase the following relationships are valid:

$$\begin{aligned} 1/2\,k_{CH} &= 1/2\,k_M + 1/2\,k_{LJ} + 1/2\,k_C, \\ g_{CH} &= g_M + g_{LJ} + g_C, \\ j_{CH} &= j_M + j_{LJ} + j_C, \end{aligned} \qquad (8)$$

where k, g, and j are the quadratic, cubic and quartic force constants, respectively. By using (5), (6) and the relationships [23]

$$k_{CH} = \left(\frac{\delta^2 V_{CH}}{\delta r^2}\right)_{r=r_{el}}, \quad g_{CH} = -\frac{1}{6}\left(\frac{\delta^3 V_{CH}}{\delta r^3}\right)_{r=r_{el}},$$
$$j_{CH} = \frac{1}{24}\left(\frac{\delta^4 V_{CH}}{\delta r^4}\right)_{r=r_{el}}, \qquad (9)$$

the force constants arising from the Lennard-Jones and Coulomb potentials can be expressed as

$$\begin{aligned} 1/2\,k_{LJ} &= \frac{4\varepsilon}{s_1^2}\left(\frac{s_0}{s_1}\right)^6\left\{78\left(\frac{s_0}{s_1}\right)^6 - 21\right\}, \\ 1/2\,k_C &= \frac{q_H q_{Cl}}{s_1^3}, \\ g_{LJ} &= -\frac{4\varepsilon}{s_1^3}\left(\frac{s_0}{s_1}\right)^6\left\{364\left(\frac{s_0}{s_1}\right)^6 - 56\right\}, \\ g_C &= -\frac{q_H q_{Cl}}{s_1^4}, \\ j_{LJ} &= \frac{4\varepsilon}{s_1^4}\left(\frac{s_0}{s_1}\right)^6\left\{1365\left(\frac{s_0}{s_1}\right)^6 - 126\right\}, \\ j_C &= \frac{q_H q_{Cl}}{s_1^5}. \end{aligned} \qquad (10)$$

The expressions for the force constants resulting from the Morse potential also contain terms proportional to $(r_{el} - r_{eg})$ (this is due to the fact that the parameters D and β in (7) refer to the vapor phase):

$$\begin{aligned} 1/2\,k_M &= D\beta^2 - 3D\beta^3(r_{el} - r_{eg}) + 7/12\,D\beta^4(r_{el} - r_{eg})^2, \\ g_M &= -1/6(-6D\beta^3 + 14D\beta^4(r_{el} - r_{eg})), \\ j_M &= 7/12\,D\beta^4. \end{aligned} \qquad (11)$$

In order to calculate the fundamental vibrational frequency (ν) defined by $\nu = \omega + 2X$, where ω and X are the harmonic frequency and anharmonicity constant, respectively, it is convenient to apply the dimensionless normal coordinate (q) system in which the potential energy can be written as

$$V_{CH} = 1/2\,hc\omega q^2 + hck_3 q^3 + hck_4 q^4, \qquad (12)$$

where ω, k_3, and k_4 are given in cm^{-1}. For a diatomic oscillator, q is given by the relation

$$q = \left(\frac{2\pi c\omega}{N_A \hbar}\right)^{1/2} \left(\frac{1}{m_C} + \frac{1}{m_H}\right)^{-1} \Delta r, \qquad (13)$$

where m_C and m_H are the atomic masses of H and C, respectively. The relationship between the anharmonic potential constants (k_3, k_4) and the anharmonicity constant (X) can be expressed as [24]

$$X = 3/2\, k_4 - 15 k_3^2/4\omega\,. \qquad (14)$$

Our method can be summarized in the following manner. After calculating the force constants (k, g, j) in the internal coordinate system as the sum of different terms arising from the Lennard-Jones, Coulomb and Morse potentials ((10) and (11)) they are rewritten in terms of dimensionless normal coordinates [25] to obtain ω, k_3, k_4. Finally the anharmonicity constant is calculated (see (14)) in order to yield the fundamental frequency (ν) by using the relation $\nu = \omega + 2X$.

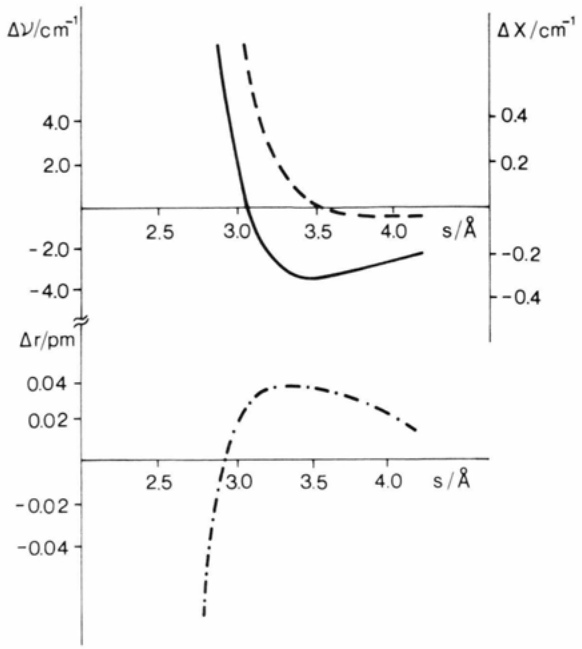

Fig. 2. Change in the vibrational frequency, anharmonicity constant and equilibrium bond distance of the CH stretching vibration of chloroform for linear C–H···Cl arrangement versus intermolecular H···Cl distance (s). $\Delta\nu = \nu_1 - \nu_g$: ——, $\Delta X = X_1 - X_g$: – – – and $\Delta r_{eq} = r_{el} - r_{eg}$: · – · – ·.

Results and Discussion

a) Linear C–H···Cl Arrangement

The calculations were first carried out for liquid chloroform with the linear C–H···Cl arrangement shown in Figure 1. The intermolecular potential parameters for the H···Cl interaction were those used by Dietz and Heinzinger in their molecular dynamics simulation [19]: $s_0 = 2.82$ Å, $\varepsilon = 5.36 \cdot 10^{-4}$ mdyne · Å, $q_H = 0.082e$, $q_{Cl} = -0.087e$. For the Morse potential parameters, β and D values of 1.852 $Å^{-1}$, and 0.7959 mdyne · Å were used [8]. The intermolecular H···Cl distance (s) was varied in the range of 2.5 Å to 4.0 Å in steps of $1.25 \cdot 10^{-2}$ Å, and at every given value of s the changes in equilibrium bond distance ($\Delta r_{eq} = r_{el} - r_{eg}$), force constants and vibrational frequency on condensation were evaluated. The values for Δr_{eq} and $\Delta\nu$ ($= \nu_{liq} - \nu_{gas}$) are plotted against s in Figure 2. As can be seen, the largest frequency shift (-3.1 cm^{-1}) is at a H···Cl distance of 3.5 Å. This value seems to be small by comparison with experiment (-14 cm^{-1}); however, one must take into account that the hydrogen atom is subjected to the influence of not only one chlorine atom in the liquid phase, since up to $s = 4.0$ Å three nearest neighbor Cl atoms were found in the molecular dynamics simulation [19]. Figure 2 illustrates that the direction of the calculated vibrational frequency shifts is in agreement with the experimental observations if the H···Cl distance is larger than 3.1 Å, which is in agreement with the results of molecular dynamics simulation [19] and neutron scattering experiments [26]. These results showed the shortest H···Cl distances to be in the range of 3 Å to 3.5 Å. It is also clear from the figure that at these distances the anharmonicity constant decreases on condensation in qualitative agreement with our earlier conclusion drawn from VPIE measurements [8].

It is important to note that, based on the experimental studies on the temperature [27, 28] and pressure [29] dependences of infrared and Raman band peaks, the CH stretching frequency in liquid chloroform increases both with increasing pressure and temperature. This is possible only when the equilibrium H···Cl intermolecular distances are in the vicinity of "s" belonging to the minimum of $\Delta\nu(s)$ function. This value is approximately 3.5 Å in this very simple model, therefore in Table 1 the results of the calculations are reported for $s = 3.5$ Å.

It is evident from Table 1 that there is a decrease of 0.2 and 0.14% in the quadratic and cubic force con-

Table 1. Calculated potential parameters and frequency shifts of the CH stretching vibration for different molecular configurations in liquid chloroform[a].

		Vapor	Liquid		
			Linear model	Conf. a[b]	Conf. b[b]
k	[mdyne/Å]	5.460	5.449	5.440	5.431
g	[mdyne/Å^2]	−5.056	−5.048	−5.042	−5.036
j	[mdyne/Å^3]	5.462	5.463	5.463	5.464
k_3	[cm^{-1}]	313.3_2	313.3	313.3_3	313.3_4
k_4	[cm^{-1}]	36.28	36.35	36.42	36.48
X	[cm^{-1}]	-62.1_9	-62.1_8	-62.1_9	-62.1_9
$\Delta\nu$	[cm^{-1}]		−3.1	−5.81	−8.23
$\Delta r_{eq} \cdot 10^4$	[Å]		3.3	6.0	8.5

[a] The calculations were performed at the minimum of the $\Delta\nu(s)$ function (see text). – [b] See Figure 6.

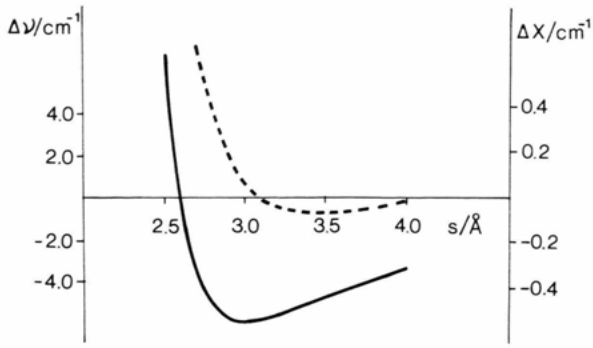

Fig. 3. Vapor-liquid shift of vibrational frequency and anharmonicity constant of the CH stretching vibration of fluoroform versus intermolecular H···F distance (s). $\Delta\nu = \nu_1 - \nu_g$: —— and $\Delta X = X_1 - X_g$: – – –.

stants, respectively, on condensation, which causes a red shift of 0.1% in the CH stretching vibration. The C–H bond distance was found to increase by $3.2 \cdot 10^{-4}$ Å in agreement with the conclusion of Moon and Drickamer [11] according to which the red shift in the frequency is accompanied by a lengthening of the bond distance. It is clear from Fig. 2 that with decreasing H···Cl distances the C–H bond begins to shorten and the CH stretching frequency undergoes a blue shift at the same time. The difference in the H···Cl distances at which the cross-over for Δr and $\Delta\nu$ takes place is caused by the dependence of Δr on the first derivative of the potential (V_{CH}), whereas $\Delta\nu$ includes terms arising from higher derivatives.

By using only the attractive part of the intermolecular potential one obtains a shift of -4.84 cm^{-1} in the CH stretching frequency, in good accord with the view that attractive forces result in red shifts [9–17]. The absolute value of the anharmonicity constant was found to increase by 0.13 cm^{-1} on condensation. The repulsive forces resulted in a frequency increase of 1.7 cm^{-1} and a 0.27 cm^{-1} decrease in the anharmonicity constant. (Note that, whereas the effect of attractive and repulsive forces is additive in the case of frequency shift, (14) shows that the additivity does not obtain for the anharmonicity constant.)

In order to understand the different signs of the vapor-liquid CH stretching frequency shifts for $CHCl_3$ and CHF_3 a calculation was performed for fluoroform by the method described above. In this case the approximation of considering only H···F atom interactions still seems to be reasonable if one takes into account that the surface area of the hydrogen atom in fluoroform is only 4% larger than that in chloroform [30]. This means that the hydrogen atom still "feels" mainly the effect of fluorine atoms in its immediate enviroment.

The intermolecular potential parameters used in the calculation are the following: $s_0 = 2.61$ Å, $\varepsilon = 2.61 \cdot 10^{-4}$ mdyne · Å, $q_H = 0.0861$ e and $q_F = -0.189$ e [31]. The parameters of the Morse potential were calculated from the values of ω and X, obtained from fundamental and overtone frequencies in the vapor phase [32] by the expressions [33]

$$D = -\frac{hc\omega^2}{4X}, \quad \beta = (8\pi^2 c\mu X/h)^{1/2}, \tag{15}$$

where μ is the reduced mass of the diatomic oscillator. For the parameters β and D, 1.743 Å^{-1} and 0.8916 mdyn · Å, respectively, were obtained. The values of $\Delta\nu$ and ΔX for fluoroform are displayed as a function of s in Fig. 3; the curves are very similar to those obtained for chloroform (Figure 2). It can be seen that a blue shift is obtained if the H···F distance is smaller than 2.6 Å. This is in agreement with the results of an MD simulation according to which the H–F radial distribution function has its first maximum at 2.7 Å [31]. Figure 3 also shows that the blue shift in the vibrational frequency should be accompanied by a decrease in the anharmonicity constant. Unfortunately, there are no experimental data available for comparison. The Lennard-Jones and Coulomb potentials as well as their sum (V_{LJ+C}) for the H···F interaction are shown in Figure 4. At a H···F distance (~2.5 Å) which corresponds to the minimum in V_{LJ+C}, the calculation gave a blue shift of 15 cm^{-1}. (In

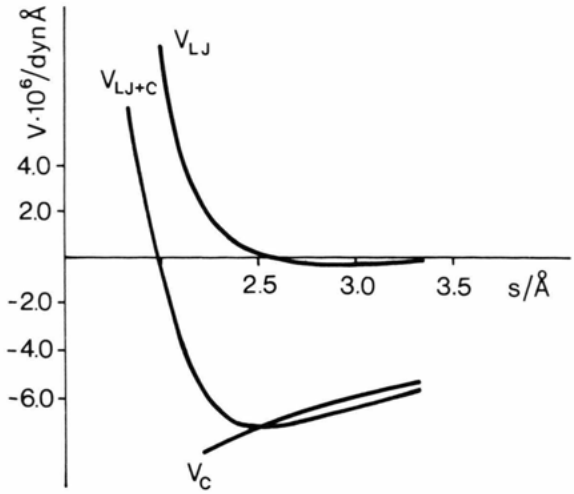

Fig. 4. Lennard-Jones (V_{LJ}) and Coulomb potentials (V_C) describing the interaction between H and F atoms in liquid fluoroform and their sum (V_{LJ+C}) versus s.

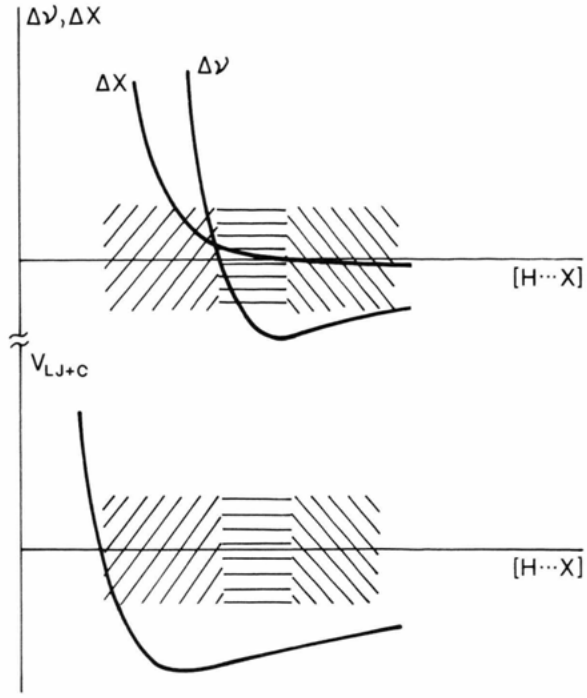

Fig. 5. Expected ranges of nearest neighbor H ··· X distances in liquid haloforms. ///: CHF_3; ≡: $CHCl_3$; \\\: $CHBr_3$.

passing we mention that the Lennard-Jones potential plays a less significant role in the vibrational frequency shift than the Coulomb potential.) This indicates that the average H ··· F distance corresponding to the closest approach of a hydrogen and fluorine atom is in the neighborhood of the minimum of the V_{LJ+C} function and that it is significantly smaller than the distance at which the minimum in the $\Delta\nu(s)$ function is situated ($\sim$3 Å). Comparison of Figs. 3 and 4 shows that the maximum red shift occurs at the inflection point distance of the potential function $V_{LJ+C}(s_{ip})$, as was pointed out by Mentel and Luck [15]. However, the frequency shift is not equal to zero at the minimum of $V_{LJ+C}(s_{min})$ since, although the first derivative of V_{LJ+C} disappears at s_{min}, the second derivative is positive and produces a blue shift. Thus the cross-over in the vibrational frequency shift occurs between s_{ip} and s_{min} where the opposite effects of the first and second derivative of V_{LJ+C} are equal to each other. Correspondingly, the statement that the blue shift is due to the predominance of repulsive forces [11] can be considered in this case as an oversimplification since the interactions between the CH oscillator and fluorine atoms are attractive even in the range of blue shifts (see Figure 4).

The shapes of the $\Delta\nu$ and ΔX vs. s curves (Figs. 2 and 3) are similar for $CHCl_3$ and CHF_3, but they are shifted towards smaller intermolecular distances in the case of fluoroform due to differences in the van der Waals radii of the halogen atoms (1.47 Å and 1.77 Å for F and Cl, respectively [30]). Furthermore, in the liquid phase the molecules are sitting at the minimum of the total intermoleclar interaction potential and the corresponding halogen-hydrogen distance ($s_{min}(V_{total})$) does not necessarily coincide with that of the minimum of the hydrogen ··· halogen interatomic potential ($s_{min}(V_{LJ+C})$), which governs the magnitude of the vapor-liquid phase transition shift of the CH stretching vibrational frequency. The difference between these distances changes with halogen substitution and increases with increasing van der Waals radius of the molecules. A change of this sort can be expected to be significant in the case of CHF_3 and $CHCl_3$ because their van der Waals volumes are 25.38 and 43.5 $cm^3 \cdot mol^{-1}$, respectively; this means that $s_{min}(V_{LJ+C})$ and $s_{min}(V_{total})$ are much closer to each other in CHF_3 than in $CHCl_3$. This suggests that the $\Delta\nu$ and ΔX vs. s functions for bromoform will be shifted to longer intermolecular distances and the difference between the distances corresponding to the minimum in V_{LJ+C} and V_{total} will increase as compared with $CHCl_3$. Since the van der Waals radius of the bromine atom (1.85 Å) is not much larger than that of the chlorine atom (1.77 Å) the change will be much

smaller than that found between fluoroform and chloroform. Accordingly, the shortest H···Br distances are expected to be larger than that of the minimum of the $\Delta\nu(s)$ function, which would qualitatively explain the different direction of the change in the anharmonicity constants of the CH stretching vibration for chloroform and bromoform on condensation. For illustration, the relative positions of the hydrogen-halogen atom distances of the closest neighbor molecules are displayed schematically in Figure 5. It can be seen that for $CHCl_3$ the anharmonicity constant decreases whereas for $CHBr_3$ it increases during the vapor-liquid transition, in agreement with what was observed experimentally [8]. Unfortunately, a potential describing the interaction between the hydrogen and bromine atoms of bromoform is not available; therefore a calculation for bromoform is not possible at present. It would also be interesting for checking the validity of our simple model to determine the pressure dependence of ν_{CH} in liquid $CHBr_3$ and to see whether with rising pressure first a minimum in red shift and then a blue shift can be observed.

b) Systems Consisting of Two $CHCl_3$ Molecules; Pressure and Temperature Dependence of ν_{CH}

A better agreement with the experimental frequency shift of the ν_{CH} vibration of chloroform can be expected by considering the effect of not only one but all three Cl atoms of an adjacent chloroform molecule on the CH oscillator. Two plausible molecule orientations were investigated: the staggered configuration (Fig. 6b) and another one which can be derived from the staggered configuration by shifting the center of the second molecule so that the C–H axis will be in line with the chlorine atom Cl_1 (Figure 6a). Of course, we do not claim that only these two configurations exist in liquid chloroform or that they represent the most probable orientations. Since there is more than one Cl atom interacting with the C–H bond, the force constants can be rewritten as

$$1/2\,k_{CH} = 1/2\,k_M + 1/2 \sum_{i=1}^{3} (k_{LJ} + k_C)_i\,,$$

$$g_{CH} = g_M + \sum_{i=1}^{3} (g_{LJ} + g_C)_i\,, \qquad (16)$$

$$j_{CH} = j_M + \sum_{i=1}^{3} (j_{LJ} + j_C)_i\,.$$

In the calculation, the projection of the forces acting between the hydrogen and chlorine atoms to the line

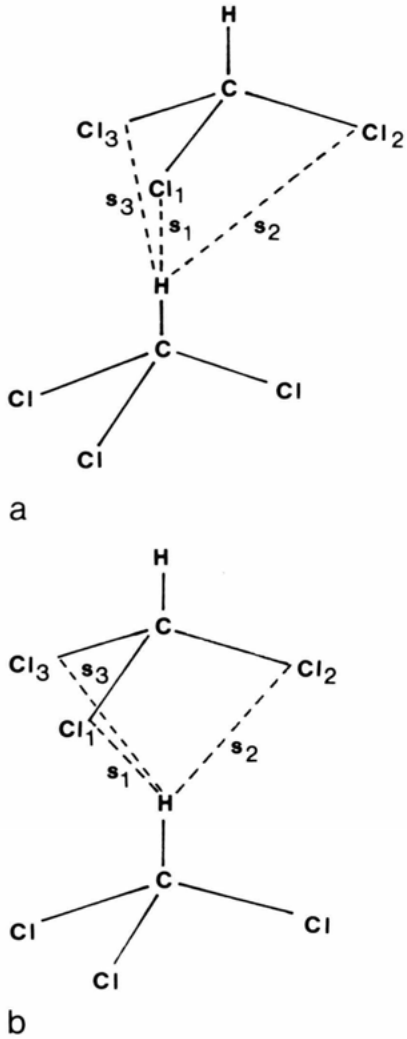

Fig. 6. Two possible orientations – used in the model calculations – of adjacent chloroform molecules in the liquid phase.

of the CH bond was considered. The shifts in the harmonic and fundamental frequencies are shown as a function of s in Figure 7. (It should be noted that s corresponds to s_1 in Fig. 6, which is equal to s_2 and s_3 in the case of the staggered configuration (Figure 6b); for the configuration shown in Fig. 6a, s_2 and s_3 are determined by the geometry of the molecule.) In the case of configuration "a" the $\Delta\nu$ function has a minimum of $-5.8\ cm^{-1}$ at $s_1 = 3.46$ Å, and in the case "b" the value of the minimum is $-8.2\ cm^{-1}$ at $s = 3.55$ Å. The agreement with experiment ($-14.0\ cm^{-1}$) is reasonable; the results of the calculations carried out

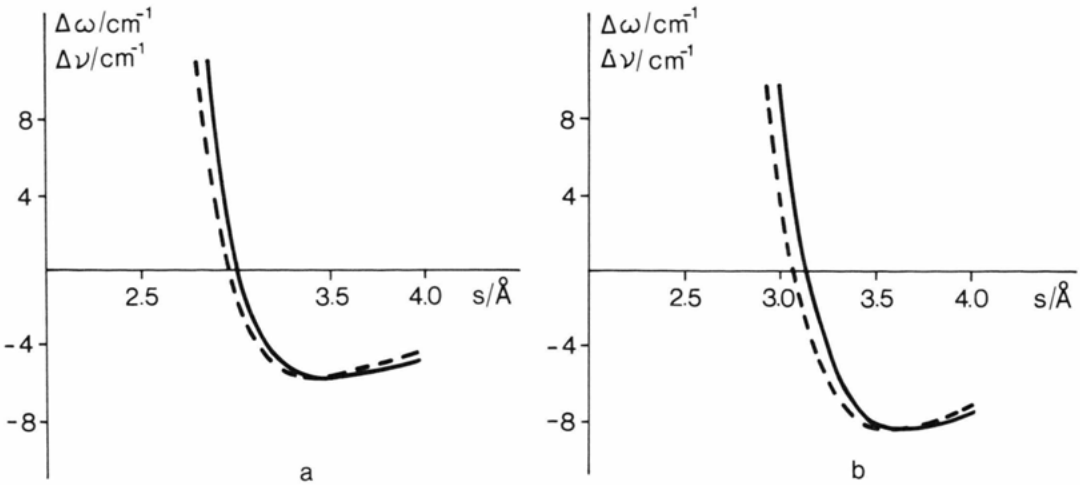

Fig. 7. Dependence of shifts in the harmonic ($\Delta\omega = \omega_1 - \omega_g$: – – – –) and fundamental ($\Delta\nu = \nu_1 - \nu_g$: ———) frequencies of the CH vibration of chloroform on the intermolecular H···Cl distance for configurations a and b shown in Figure 6.

Table 2. Calculated pressure dependence of the CH vibrational frequency in liquid $CHCl_3$ for the configuration shown in Figure 6b.

p [kbar]	ϱ [g/cm^3]	s [Å]	$\Delta\nu = \nu_1 - \nu_g$ [cm^{-1}]
0.5	1.520	3.52	−8.22
1.0	1.580	3.48	−8.13
1.5	1.620	3.45	−8.00
2.0	1.655	3.42	−7.88
2.5	1.680	3.41	−7.81
3.0	1.707	3.39	−7.64
3.5	1.735	3.37	−7.43
4.0	1.755	3.36	−7.31
4.5	1.775	3.34	−7.18

Table 3. Calculated temperature dependence of the CH vibrational frequency in liquid $CHCl_3$ for the configuration shown in Figure 6b.

t [°C]	V_t [cm^3/mol]	s [Å]	$\Delta\nu$ [cm^{-1}]
30	81.18	3.56	−8.23
40	82.25	3.58	−8.22
50	83.36	3.59	−8.21
60	84.80	3.61	−8.18

at the minimum of the $\Delta\nu(s)$ function are presented in Table 1. It can be seen that similarly to the linear arrangement the quadratic and cubic force constants decrease while the quartic force constant practically does not change on condensation.

Since there are experimental data available in the literature on the pressure [29] and temperature [27, 28] dependence of the CH stretching frequency of chloroform, a comparison with calculated values can be expected to be a sensitive test of the validity of the approximations employed in our model calculations. It has been assumed that only the intermolecular distances change with pressure or temperature but not the orientations of the molecules. The density of liquid chloroform is known in the 0.5–4.5 kbar pressure range [34], and the intermolecular H···Cl distance (s) was determined from the molar volume (V) through the relationship

$$s_P = (V_P/V_0)^{1/3}\, s_0\,, \tag{17}$$

where s_P and V_P belong to pressure P while s_0 and V_0 refer to ambient pressure and temperature. The calculations were carried out for the molecular configuration shown in Fig. 6b; the frequency shifts obtained for particular pressures are collected in Table 2. The ν_{CH} of $CHCl_3$ in the liquid phase increases with rising pressure and the pressure dependence calculated from Table 2 (0.23 cm^{-1}/kbar) is in good agreement with that observed (0.2 cm^{-1}/kbar) in the pressure range of 0–9 kbar [29].

In order to investigate the temperature dependence of ν_{CH}, the molar volume of liquid chloroform [35] and (17) were used to obtain the intermolecular H···Cl distances. The calculated vibrational frequency shifts are reported in Table 3. It was found by Raman spectroscopic measurement that the frequency of the CD stretching vibration shifts to the blue with increasing temperature by about 0.020 cm^{-1}/°C around room

temperature [27]. This is in good agreement with the value of 0.024 $cm^{-1}/°C$ for the CH vibrational frequency estimated from the temperature dependence of infrared band peaks [28]. Although the temperature dependence calculated from Table 3 (0.002 $cm^{-1}/°C$) is small by comparison with experiment, the direction of the shift agrees with the experimentally observed one. A possible reason for the poor agreement may be that in this case the neglect of any orientational change in the liquid presumably causes a larger error than in the investigation of pressure dependence. The increasing temperature does not result only in a change in the intermolecular distances but it also affects the hindered rotational motions and thus the relative orientations of the molecules; these may signficantly modify the average effect of the intermolecular interactions. The fact that the increase in T or p causes the CH vibrational frequency shift to the blue in liquid chloroform – while the intermolecular H···Cl distance (s) increases in the first, but decreases in the second case – suggests that the average, shortest H···Cl distance at ambient temperature and pressure coincides with that of the minimum in the $\Delta\nu(s)$ function, as has already been indicated in the previous section.

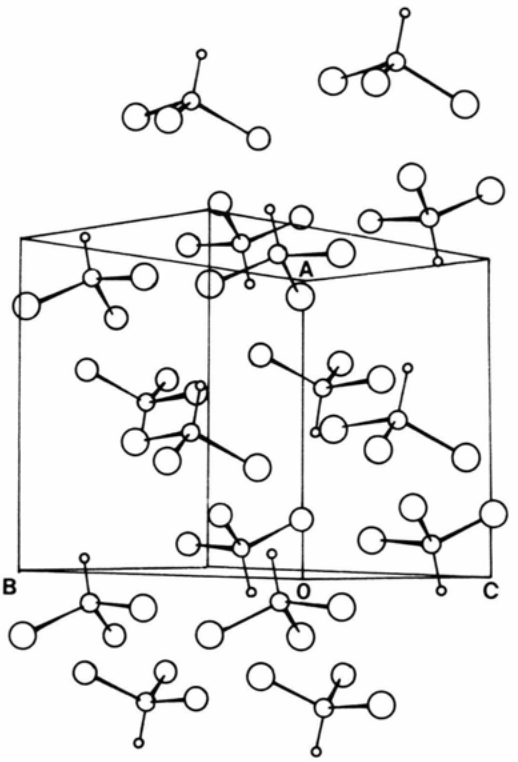

Fig. 8. Crystal structure of solid chloroform [36].

c) Quasi-crystalline Arrangement in Liquid Chloroform

In this case it is assumed that the average molecular short range order arrangement in liquid chloroform is similar to that of the solid.

The structure of solid chloroform, which forms a Pnm_a lattice, is known from X-ray diffraction [36] (see Figure 8). The X-ray data were treated by a molecular graphics program on an IBM PC, and the cartesian coordinates of a central molecule and its first 12 neighbors were calculated. For simplicity the coordinate system has been defined in such a way that the C atom of the central molecule is positioned at the origin and the H atom in the positive x direction.

In the calculations only the effect of three nearest Cl atoms has been taken into account. Using the intermolecular distances in the solid phase, a blue shift of 12.6 cm^{-1} was obtained instead of the experimentally observed red shift of 20 cm^{-1} [37]. The lack of agreement is not unexpected since molecular dynamics simulations of other liquids, mainly water [38], have indicated that an effective intermolecular potential which performs reasonably well in liquid phase does not necessarily give good results in the solid phase too.

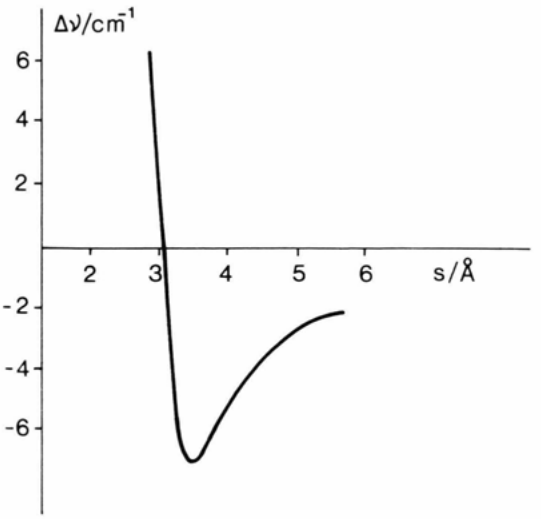

Fig. 9. Dependence of vapor-liquid shift in the vibrational frequency of the CH stretching vibration of chloroform ($\Delta\nu = \nu_l - \nu_g$) on intermolecular H···Cl distance for the quasi-crystalline structure in the liquid phase.

Judging from experimental neutron scattering [26] and molecular dynamics simulation studies [18, 19] the C···C distances in liquid chloroform are between 4.65 and 7.4 Å at room temperature. The $\Delta\nu(s)$ function resulting from the calculation carried out for this range of C···C distances is shown in Figure 9. It can be seen that the maximum in the red shift ($\sim 7\ cm^{-1}$) is at H···Cl distances where three nearest neighbor chlorine atoms around the hydrogen of the central molecule were found by MD simulation [18, 19].

Conclusion

Model calculations on the vapor-liquid shift of the frequency of the CH stretching vibration of haloforms have shown that the curves describing the dependence of the shifts on the intermolecular H···X distances have a similar shape for fluoroform and chloroform. However, the $\Delta\nu(s)$ curve for chloroform can be found at larger distances than that for fluoroform; this finding is in accordance with the different atomic radii of the two halogen atoms. In order to be consistent with the experimentally observed frequency shifts it must be assumed that the shortest H···X distances occur around the distances corresponding to the minimum of $\Delta\nu(s)$ and $V_{LJ+C}(s)$ curves in the case of $CHCl_3$ and CHF_3, respectively. The difference between the shortest H···X distance determined by the total intermolecular potential energy in the liquid phase (V_{total}) and the position of the minimum in the interatomic H···X potential function V_{LJ+C} – which is responsible for the vapor-liquid shift of the CH vibrational frequency – increases with increasing radius of the halogen atoms. Thus one can expect that in liquid bromoform the shortest H···Br distances are larger than the distance corresponding to the minimum of the $\Delta\nu(s)$ function of bromoform, this situation leading to an increase in the anharmonicity constant on condensation along with a red shift in the CH vibrational frequency (see Figure 5).

The detailed analysis carried out for the pressure and temperature dependence of $\Delta\nu_{CH}$ in liquid chloroform has given good agreement with the experimental pressure dependence, but only qualitative agreement has been obtained with the observed temperature dependence.

It seems safe to conclude that the interaction between the Morse potential of the CH stretching vibration of haloforms and the halogen atoms of the neighbor molecules as given by the interatomic hydrogen-halogen potentials used in molecular dynamics simulations describes surprisingly well the experimentally observed shifts in the vibrational frequency and anharmonicity of the CH stretching vibration on condensation.

Acknowledgement

Financial support from the Research Fund of the Hungarian Academy of Sciences is gratefully acknowledged.

[1] G. Jancsó and W. A. Van Hook, Chem. Rev. **74,** 689 (1974).
[2] G. Jancsó, Gy. Jákli, and Cs. Fetzer, Z. Naturforsch. **38a,** 184 (1983).
[3] Gy. Jákli, P. Juhász, and G. Jancsó, Acta Chim. Acad. Sci. Hung. **114,** 133 (1983).
[4] A. Popowicz, T. Oi, J. Shulman, and T. Ishida, J. Chem. Phys. **76,** 3732 (1982).
[5] J. Devaure, G. Turrell, P. V. Houng, and J. Lascombe, J. Chim. Phys. **65,** 1064 (1968).
[6] I. Rossi, N. V. Thanh, and G. Haeusler, Can. J. Chem. **47,** 3319 (1969).
[7] D. H. Rank, E. R. Shull, and E. L. Pace, J. Chem. Phys. **18,** 885 (1950).
[8] K. Tóth and G. Jancsó, Z. Naturforsch. **44a,** 355 (1989).
[9] A. M. Benson, Jr. and H. G. Drickamer, J. Chem. Phys. **27,** 1164 (1957).
[10] R. R. Wiederkehr and H. G. Drickamer, J. Chem. Phys. **28,** 311 (1958).
[11] S. H. Moon and H. G. Drickamer, J. Chem. Phys. **61,** 48 (1974).
[12] A. D. Buckingham, Proc. Roy. Soc. London **A 255,** 32 (1960).
[13] A. D. Buckingham, Trans. Faraday Soc. **56,** 753 (1960).
[14] A. D. Buckingham, Proc. Roy. Soc. London **A 248,** 169 (1958).
[15] T. F. Mentel and W. A. P. Luck, J. Phys. Chem. **94,** 1059 (1990).
[16] K. S. Schweizer and D. Chandler, J. Chem. Phys. **76,** 2296 (1982).
[17] M. R. Zakin and D. R. Herschbach, J. Chem. Phys. **89,** 2380 (1988).
[18] W. Dietz and K. Heinzinger, Ber. Bunsenges. Phys. Chem. **88,** 543 (1984).
[19] W. Dietz and K. Heinzinger, Ber. Bunsenges. Phys. Chem. **89,** 968 (1985).
[20] P. Bopp, G. Jancsó, and K. Heinzinger, Chem. Phys. Lett. **98,** 129 (1983).

[21] G. Pálinkás, E. Hawlicka, and K. Heinzinger, J. Phys. Chem. **91,** 4334 (1987).
[22] P. M. Morse, Phys. Rev. **34,** 57 (1929).
[23] T. Shimanouchi, in: Physical Chemistry, an Advanced Treatise, vol. 4 (D. Henderson, ed.), Academic Press, New York 1970, p. 233.
[24] K. Kuchitsu and Y. Morino, Bull. Chem. Soc. Japan **38,** 814 (1965).
[25] S. Califano, Vibrational States, John Wiley & Sons, London 1976, Chapter 9.
[26] H. Bertagnolli and P. Chieux, Mol. Phys. **51,** 617 (1984).
[27] R. Arndt and R. E. D. McClung, J. Chem. Phys. **69,** 4280 (1978).
[28] M. P. Lisitsa and Yu. P. Tsyashchenko, Opt. Spektrosk. **9,** 438 (1960).
[29] Y. Zhao, H. Luo, X. Lu, and G. Zou, Physica **139** and **140 B,** 526 (1986).
[30] A. Bondi, J. Phys. Chem. **68,** 441 (1964).
[31] K. Heinzinger, personal communication.
[32] G. Glocker and W. F. Edgell, J. Chem. Phys. **9,** 224 (1941).
[33] G. J. Boobyer and A. P. Cox, J. Chem. Educ. **45,** 18 (1963).
[34] J. Schroeder, V. H. Schiemann, and J. Jonas, Mol. Phys. **34,** 1501 (1977).
[35] J. A. Dean, ed., Lange's Handbook of Chemistry, McGraw-Hill, New York 1979, p. 10–127.
[36] R. Fourme and M. Renaud, C. R. Acad. Sci. Paris **263 b,** 69 (1966).
[37] M. M. Denariez, J. Chim. Phys. **62,** 323 (1965).
[38] M. D. Morse and S. A. Rice, J. Chem. Phys. **76,** 650 (1982).