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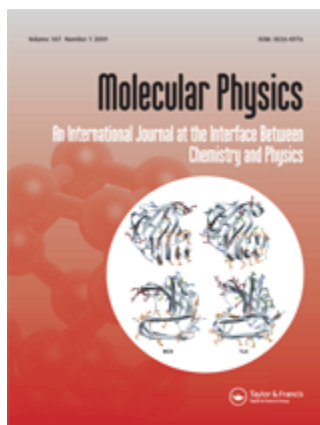
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The fundamental band vibrational shift of HCl diluted in dense Ar and Kr

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3 **The fundamental vibrational shift of HCl diluted in dense Ar and**
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5 **Kr**
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8 Antonio Padilla and Justo Pérez
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10 (Dated: January 16, 2008)
11

12 **Abstract**
13

14 The fundamental infrared band vibrational shifts of HCl diluted in dense Ar and Kr have been
15 calculated by means of molecular dynamics simulation techniques and compared with the experi-
16 mental data reported by J. Pérez et al. (J. Chem. Phys. 122, 194507 (2005)). The results have
17 been analyzed along the liquid-vapor coexistence line as in several supercritical states with good
18 agreement between the theoretical and experiemental values.
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I. INTRODUCTION

The infrared and Raman spectra of polar diatomic molecules diluted in inert dense solvents give valuable information about the intermolecular interactions, the equilibrium solvent structure and the dynamical processes involved in the vibro-rotational diatomic relaxation[1–3]. In this studies most works have been focussed on the analysis of the vibro-rotational line shape and the spectrum structure, and only a few of them have been devoted to the analysis of the vibrational shift of the whole band. The vibrational shift of the infrared and Raman bands is a solvent dependent effect which allows to obtain interesting insight about the diatomic-solvent intermolecular interactions, and the static properties of the solvent [4–7]. In this sense, while the isotropic part of the diatomic-solvent interaction has very poor effects on the spectral profile of the fundamental infrared band, the vibrational shift is very sensitive to this component of the interaction potential, and so it is an useful tool to get complementary information to the line shape studies.

A classical paper in the analysis of the effects of solute solvent interaction on the shifts of the infrared and Raman bands is that of Buckingham[8]. The basis of his work is to consider the diatomic vibration as an anharmonic oscillator and to expand the interaction energy between the diatomic and the environment as a power series of the vibrational coordinate, using a second order perturbative theory to evaluate the eigenvalues of the solvent averaged hamiltonian. More recently, Alessi et al.[7] have expanded the Buckingham's theory in order to explain the non linear dependence with the vibrational number of the shifts of the overtone bands (Buckingham's theory predicts linear behaviour).

One point of particular interest is to analyze the variation of the vibrational shift of the diatomic spectra with the experimental thermodynamic conditions. From the experimental point of view, it is difficult to evaluate the band origin because the uncertainties in the wings of the spectra produces changes in the determination of the first band moment. In a recent paper[9], we have shown that in the fundamental infrared band of HCl in liquified rare gases the band origin is systemmatically displaced from the prominent central Q branch, a result which allows to determinate absolute values of the band shift with more accuracy.

The purpose of this work is to compare the experimental vibrational shifts of HCl in dense Ar and Kr solutions with those calculated in the scope of a previously developed spectral theory [10] with the help of the molecular dynamics simulation technique to evaluate the

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3 equilibrium averages involved in the theoretical approach.
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5 In the theory the rotational and vibrational degrees of freedom of the diatomic molecule
6 are treated with a quantum approach, while the translational degrees of freedom both of the
7 diatomic and the solvent molecules are treated classically. The theoretical vibrational shift
8 is determined by the equilibrium average of the isotropic components of the diatomic-solvent
9 interaction potential depending of the vibration. For this isotropic part of the interaction
10 we have taken the functional form proposed by Marteau et al. [11] with only one adjustable
11 parameter which is obtained by fitting the theoretical and experimental vibrational shifts.
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14 The organization of the paper is as follows. In Sec. II the main theoretical aspects of the
15 calculation of the fundamental vibrational shift are developed. In Sec. III the functional
16 form of the isotropic binary potential components together with a brief summary of the
17 molecular dynamics simulation procedure are given . The theoretical and experimental
18 vibrational shifts are compared in Sec. IV and a brief summary and some conclusions are
19 collected in Sec. V.
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30 II. THEORETICAL BACKGROUND

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33 The spectral theory has been developed in Ref. [10] and we will only expose here a brief
34 summary. The results will be discussed in the scope of a simple system S constituted by the
35 rotation and vibration degrees of freedom of a representative diatomic molecule coupled to
36 a thermal bath B which collects the translational degrees of freedom both of the diatomic
37 and the solvent.
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42 We will assume that the bath average of the interaction Hamiltonian $\langle H' \rangle$ between the
43 system S and the Bath B is zero. This condition can always be achieved by redefining the
44 interaction Hamiltonian H' and the Hamiltonian H_S of the system as $H' - \langle H' \rangle$ and $H_S + \langle H' \rangle$
45 respectively, where $\langle H' \rangle$ is the bath average of the S-B interaction. It is precisely the new
46 Hamiltonian $H_S + \langle H' \rangle$ who defines the frequencies of the vibro-rotational spectral lines (the
47 normalized first order moments of the lines), introducing the term $\langle H' \rangle$ the frequency shifts
48 which are the object of our study.
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55 The $S - B$ interaction Hamiltonian H' is divided into an isotropic V_I and anisotropic V_A
56 components:
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$$58 H' = V_I + V_A$$

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The anisotropic part V_A couples the diatomic vibro-rotation with the translational motion, while the isotropic part V_I only couples the vibration with the translational motion. Because the bath is macroscopically isotropic, the bath average of the anisotropic interaction must be zero[10] $\langle V_A \rangle = 0$, and therefore the frequency shifts produced by the solvent are due to the isotropic part of the interaction $H_s + \langle V_I \rangle$ and hence associated only to the diatomic vibration.

This isotropic part of the $S - B$ interaction V_I depending of the vibration is written as a sum of effective binary potentials $v_i(Q, \mathbf{r}_p)$ **which take into account the effects of the simultaneous interaction of three or more molecules**

$$V_I = \sum_p v_i(Q, \mathbf{r}_p) \quad (2.1)$$

where Q is the vibrational coordinate and \mathbf{r}_p is the vector joining the center of mass of the diatomic and the p -solvent molecule. The binary potential $v_i(Q, \mathbf{r}_p)$ is approximated by the first two terms of its power expansion in the vibrational coordinate

$$v_i(Q, \mathbf{r}_p) = v_i^{(1)}(r_p) Q + \frac{1}{2} v_i^{(2)}(r_p) Q^2 \quad (2.2)$$

So the $S - B$ isotropic interaction can be written as

$$V_I = G_1(\{\mathbf{r}_p\}) Q + \frac{1}{2} G_2(\{\mathbf{r}_p\}) Q^2 \quad (2.3)$$

where

$$G_n(\{\mathbf{r}_p\}) = \sum_p v_i^{(n)}(r_p) \quad (2.4)$$

with $n = 1, 2$. Thus, the bath average of the isotropic potential is

$$\langle V_I \rangle = \langle G_1 \rangle Q + \frac{1}{2} \langle G_2 \rangle Q^2 \quad (2.5)$$

where $\langle G_n \rangle$ is the bath average of each coupling factor (2.4).

The Hamiltonian H_S is modeled as a cubic anharmonic oscillator coupled to a linear rotor, and the energy spectrum of the effective Hamiltonian $H_S + \langle V_I \rangle$ is calculated using a second order perturbative theory[12]. In this case, together with the usual energy terms of the isolated diatomic it appears a vibrational energy term[10] $h\omega_\nu$ with

$$\omega_\nu = \left(\nu + \frac{1}{2} \right) \left(\frac{1}{2} \langle G_2 \rangle \frac{1}{M_r \omega_e} - \frac{1}{2} \langle G_1 \rangle \frac{f}{M_r^2 \omega_e^3} \right) \quad (2.6)$$

where ν is the vibrational quantum number, M_r is the reduced mass of the diatomic, ω_e is the harmonic vibrational frequency and f is the cubic anharmonic constant of the oscillator [12]. From equation (2.6) it follows that the vibrational frequency shift with respect to the isolated molecule of the fundamental band spectra $\Delta\omega$ is given by

$$\Delta\omega = \left(\frac{1}{2} \langle G_2 \rangle \frac{1}{M_r \omega_e} - \frac{1}{2} \langle G_1 \rangle \frac{f}{M_r^2 \omega_e^3} \right) \quad (2.7)$$

an expression that also can be obtained from the work of D. W. Oxtoby et al. [13]. Eq(2.7), can be written in terms of the spectroscopic constants of the diatomic as

$$\Delta\omega = \frac{B_e}{\omega_e} \left(\langle \overline{G_2} \rangle + f_V \langle \overline{G_1} \rangle \right) \quad (2.8)$$

where B_e is the rotational constant and

$$\langle \overline{G_n} \rangle = \langle G_n \rangle R_e^n h^{-1} \quad (2.9)$$

being R_e the equilibrium intermolecular distance of the diatomic and

$$f_V = \sqrt{\frac{24 \omega_e \chi_e}{5 B_e}} \quad (2.10)$$

with χ_e the anharmonicity factor constant.

III. INTERACTION POTENTIALS AND DETAILS OF THE SIMULATION.

In order to calculate the bath average of the coupling factors (2.9) and to evaluate the vibrational shift (2.8) it is necessary to model the diatomic-solvent binary potential components $v_i^{(n)}(r)$ (2.2) ($n = 1, 2$). We will assume that the isotropic binary potential components (2.2), written as

$$\overline{v}_i^{(n)}(r) = R_e^n v_i^{(n)}(r) \quad n = 1, 2$$

are given as those proposed by Marteau et al.[11]

$$\overline{v}_i^{(1)}(r) = 4\epsilon \left(S_1 \left(\frac{\sigma}{r} \right)^{12} - S_2 \left(\frac{\sigma}{r} \right)^6 \right) \quad (3.11)$$

$$\overline{v}_i^{(2)}(r) = 8\epsilon \left(T_1 \left(\frac{\sigma}{r} \right)^{12} - T_2 \left(\frac{\sigma}{r} \right)^6 \right) \quad (3.12)$$

where ϵ and σ are the usual 6 – 12 Lennard-Jones parameters of the diatomic-solvent interaction and

$$S_2 = \frac{1}{\alpha} \left(\frac{\partial \alpha}{\partial \overline{Q}} \right)_{\overline{Q}=0} \quad (3.13)$$

$$T_2 = \frac{1}{2\alpha} \left(\frac{\partial^2 \alpha}{\partial \bar{Q}^2} \right)_{\bar{Q}=0} \quad (3.14)$$

being, α the diatomic polarizability, and $\bar{Q} = Q/R_e$

The S_i and T_i parameters are related as

$$\frac{S_1}{S_2} = \frac{T_1}{T_2} = f_r \quad (3.15)$$

where f_r is the repulsive factor, a phenomenological parameter that must be obtained by fitting the theoretical vibrational shifts to the experimental ones. The remaining parameters associated to the isotropic potential components of $HCl - Ar$ and $HCl - Kr$ are collected in Table 1.

The molecular dynamics simulations were carried out considering a single HCl molecule and 250 solvent atoms inside of a cubic box with periodic boundary conditions. In each case the size of the box was chosen to give the solvent density ρ . The equations of motion were solved by using a Leap-Frog-Verlet algorithm which includes a SHAKE technique in order to fix the diatomic bond length to $R_e = 1.275 \text{ \AA}$ and a coupling to a thermal bath in order to keep the system temperature near to the solvent value T . The time step was chosen $\Delta t = 0.25 \times 10^{-14} \text{ s}$, including each simulation run a total of 10^6 time steps. Previous to each simulation run, a long equilibration period was considered.

The binary interaction between the solvent atoms was modeled by means of a 6 – 12 Lennard-Jones potential with the parameters $\sigma = 3.405 \text{ \AA}$ and $\epsilon = 119.8 \text{ K}$ for the $Ar - Ar$ pair, and $\sigma = 3.575 \text{ \AA}$ and $\epsilon = 191.4 \text{ K}$ for the $Kr - Kr$ pair [15]. The binary interaction of the $HCl - Ar$ and $HCl - Kr$ pairs was modeled with a site-site potential whose parameters were obtained by fitting the site-site model to more accurate potentials [15]. The site-site parameters for the $HCl - Ar$ and $HCl - Kr$ pairs are collected in Table 2.

The solvent density ρ was calculated from the experimental values of the temperature T and pressure P . The densities of the liquid-vapor coexistence states were determined by means of a cubic spline interpolation of the experimental data (ρ and T) reported by Bertsev et al. [18]. For the supercritical states the densities were calculated by using the $vdW - 711$ equation of state [19]. The values are shown in tables 3 and 4. In both cases the superscript s in the temperatures denotes supercritical states, while the remaining ones are in the liquid-vapour coexistence curve.

IV. THEORETICAL-EXPERIMENTAL COMPARISON

The fundamental absorption bands of the HCl dissolved in condensed Ar or Kr in several thermodynamic states both along the liquid-vapor coexistence curve as in supercritical conditions, have been reported by J. Pérez et al. [9]. From these absorption spectra the band origin frequencies ω_{10} were obtained by means of a fit of the vibro-rotational line frequencies [9] and shown to be systematically displaced from the Q branch maximum frequency. The vibrational shifts $\Delta\omega$ were obtained from the band origin frequencies using the isotope abundance-weighted HCl molecular constants [17] $\omega_e = 2990.4 \text{ cm}^{-1}$, and $\chi_e = 0.01766$. The rotational constant $B_e = 10.589 \text{ cm}^{-1}$ was also used in the theoretical calculations.

The experimental and calculated absolute values of the vibrational shifts are plotted in Fig. 1 versus solvent temperature. The numerical values together with those of pressure and density are reported in tables 3 and 4 for $HCl - Ar$ and $HCl - Kr$ respectively.

In both cases it can be observed how the experimental vibrational shifts correspond to a red shift that decreases in absolute value with increasing temperature and decreasing density presenting a smooth behaviour on passing from the subcritical to the supercritical states. This reduction is accompanied by a diminution of the broadening of the infrared rotational spectral lines [9].

We have found that the values of the repulsive factor f_r which gives the best fit of the theoretical vibrational shifts to the experimental data corresponds to $f_r = 1.78$ for the $HCl - Ar$ and $f_r = 1.6$ for the $HCl - Kr$. As a comparison a value of $f_r = 1.5$ has been reported [11] for the $HF - Ar$ pair. **On the other hand we have compared our difference potential $\Delta v_i(r)$**

$$\Delta v_i(r) = v_i(v=1, r) - v_i(v=0, r) = \left(\frac{1}{2} v_i^{(2)}(r) \frac{1}{M_r \omega_e} - \frac{1}{2} v_i^{(1)}(r) \frac{f}{M_r^2 \omega_e^3} \right) \quad (4.16)$$

for $HCl - Ar$ with $f_r = 1.78$, where

$$v_i(v, r) = \langle v | v_i(Q, r) | v \rangle \quad (4.17)$$

with that determined from the vibrational depending potentials obtained by J. M. Hutson [20] for the $HCl - Ar$ by fitting the experimental data on high-resolution microwave, far-infrared and infrared spectroscopy, and we have found a reasonably accord between them.

In general terms it can be appreciated a good agreement between the theoretical and the experimental values of the shifts in the different thermodynamic states showing the greater relative discrepancies in the supercritical states of the HCl-Kr solution. In any case the differences are less than 10% in the remaining thermodynamic states.

Although they are not magnitudes that can be measured experimentally it is interesting to analyze the relative contribution of the linear $\Delta\omega_1 = \langle \overline{G_1} \rangle f_V B_e / \omega_e$ and quadratic $\Delta\omega_2 = \langle \overline{G_2} \rangle B_e / \omega_e$ terms of the vibrational shifts (2.8) In this approach this relative contribution depends of the variables of the solvent and so it is independent both of the solvent and the thermodynamic state, corresponding to the 64% for the linear term $\frac{\Delta\omega_1}{\Delta\omega} = 0.64$ and to the 36% for the quadratic one $\frac{\Delta\omega_2}{\Delta\omega} = 0.36$. Representative values are $\Delta\omega_1 = -10.5 \text{ cm}^{-1}$, $\Delta\omega_2 = -5.8 \text{ cm}^{-1}$ and $\Delta\omega_1 = -3.4 \text{ cm}^{-1}$ and $\Delta\omega_1 = -1.9 \text{ cm}^{-1}$ for *HCl - Kr* at $T = 135.5 \text{ K}$ and $T = 251.7 \text{ K}$ respectively.

Another point of interest is the contribution of the attractive and repulsive components of the potential. Attending to the theoretical expressions (2.8), (2.4) and (3.11-3.12) it is shown that the attractive contribution of $\overline{v}_i^{(n)}(r)$ ($n=1,2$) produces a negative shift $\Delta\omega_-$, while the repulsive contribution $\Delta\omega_+$ is positive. So the calculated vibrational shift is the difference of two contributions $\Delta\omega = \Delta\omega_+ - |\Delta\omega_-|$. The shift is negative because the absolute value of the repulsive component is greater than the attractive one. The calculated values of $\Delta\omega_-$ and $\Delta\omega_+$ for the HCl-Kr system are represented in Fig. 2 where it can be observed that both $\Delta\omega_+$ and $\Delta\omega_-$, decrease in absolute value with increasing temperature and decreasing density being greater the decreasing of the absolute value of the repulsive component.

V. SUMMARY AND CONCLUSIONS

The vibrational shift of the fundamental band of HCl in Ar and Kr solutions have been calculated using molecular dynamics simulations in the scope of a previously developed theory [7]. The results have been compared with the experimental data reported by Pérez et al. [9]. The components of the isotropic binary potential used in the calculations (2.2) have been taken as those proposed by Marteau et al. [11], with one phenomenological parameter that has been obtained by comparing the theoretical and the experimental vibrational shifts. The results cover a wide interval of both subcritical and supercritical temperatures and a reasonable agreement between the theoretical and the experimental shifts has been found

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3 in all the thermodynamic states considered. The relative contributions of the linear and
4 quadratic terms in the vibrational coordinate and of the attractive and repulsive components
5 of the potential have also been discussed.
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7 [1] D. Steele and J. Yarwood, *Spectroscopy and Relaxation of Molecular Liquids*, (Elsevier, Amsterdam, 1991).
8
9
10 [2] A. I. Burstein and S. I. Temkin, *Spectroscopy of Molecular Rotation in Gases and Liquids*,
11 (Cambridge University Press, Cambridge, 1994).
12
13 [3] M. O. Bulanin, G. Ya Zelikina and N. D. Orlova, in *Molecular Cryospectroscopy*, Edited by
14 R. J. H. Clark and R. E. Hester, (John Wiley & Sons Ltd, Chichester, 1995).
15
16 [4] J. P. J. Michels and M. I. M. Scheerboom, *J. Chem. Phys.* **103**, 8338 (1995).
17
18 [5] K. F. Everitt and J. L. Skinner, *J. Chem. Phys.* **115**, 8531 (2001).
19
20 [6] S. Roychowdhury and B. Bagchi, *J. Chem. Phys.* **119**, 3278 (2003).
21
22 [7] N. Alessi, I. S. Tolokh, S. Goldman and C. G. Gray, *Mol. Phys.* **102**, 2037 (2004).
23
24 [8] A. D. Buckingham *Transac. Farad. Soc.* **56** 753 (1960)
25
26 [9] J. Pérez, A. Padilla, W. A. Herrebout, B. J. Van der Veken, A. Calvo Hernández M. O.
27 Bulanin, *J. Chem. Phys.* **122**, 194507 (2005).
28
29 [10] A. Padilla, J. Pérez and A. Calvo Hernández, *J. Chem. Phys.* **111**, 11015 (1999).
30
31 [11] Ph. Marteau, C. Boulet and D. Robert, *J. Chem. Phys.* **80**, 3632 (1984).
32
33 [12] I. Levine, *Molecular Spectroscopy*, (AC, Madrid, 1980).
34
35 [13] **D. W. Oxtoby, D. Levesque and J.-J. Weis, J. Chem. Phys. 68, 5528 (1978).**
36
37 [14] L. Bonamy and P. N. M. Hoang, *J. Chem. Phys.* **67**, 4423 (1977).
38
39 [15] A. Medina, J. M. M. Roco, A. Calvo Hernández, S. Velasco, M. O. Bulanin, W. A. Herrebout
40 and B. J. van der Veken, *J. Chem. Phys.* **116**, 5058 (2002).
41
42 [16] M. O. Bulanin and K. G. Tokhadze, *Opt. Spectroscopy* **61**, 198 (1986).
43
44 [17] G. Guelachvili, P. Niay and P. Bernage, *J. Mol. Spectroscopy* **85**, 271 (1981).
45
46 [18] V. V. Bertsev and G. Ya. Zelikina, in *Molecular Cryospectroscopy*, Edited by R. J. H. Clark
47 and R. E. Hester, (John Wiley & Sons Ltd, Chichester, 1995).
48
49 [19] D. P. Tassios, *Applied Chemical Engineering Thermodynamics*, (Springer Verlag, Berlin 1993).
50
51 [20] **J. M. Hutson, J. Phys. Chem. 96, 4237 (1992).**
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TABLE I: Parameters of the isotropic binary potential components. (a) Obtained with the combining rules from the data of ref. 13. (b) Obtained with the combining rules from the data of refs. 13-14. (c) Obtained from ref. 15.

	$\epsilon(K)$	$\sigma(\text{\AA})$	$\alpha(\text{\AA}^3)$	$(\partial\alpha/\partial\bar{Q})_{\bar{Q}=0}(\text{\AA}^3)$	$(\partial^2\alpha/\partial\bar{Q}^2)_{\bar{Q}=0}(\text{\AA}^3)$
HCl-Ar	206.97 ^a	3.38 ^a			
HCl-Kr	262.49 ^b	3.44 ^b			
HCl			2.63 ^c	1.54328 ^c	4.165 ^c

TABLE II: Parameters of the site-site binary potential.

	H-Ar	Cl-Ar	H-Kr	Cl-Kr
$\epsilon(K)$	79.52	150.35	138.01	168.38
$\sigma(\text{\AA})$	2.41	3.44	2.55	3.53

TABLE III: Experimental and theoretical vibrational shifts of the HCl-Ar system.

$T(K)$	$P(atm)$	$\rho(g/cm^3)$	$\Delta\omega^{\text{exp}}(\text{cm}^{-1})$	$\Delta\omega^{\text{teo}}(\text{cm}^{-1})$
115.3	24.7	1.195	-10.6	-9.9
128.7	39.5	1.080	-9.2	-9.1
141.8	59.2	0.930	-8.1	-8.0
153.6 ^(s)	74.0	0.952	-7.3	-7.9
169.3 ^(s)	94.8	0.627	-5.8	-5.9
180.5 ^(s)	108.6	0.535	-5.0	-5.0
190.3 ^(s)	118.5	0.483	-4.1	-4.5

TABLE IV: Experimental and theoretical vibrational shifts of the HCl-Kr system

$T(K)$	$P(atm)$	$\rho(g/cm^3)$	$\Delta\omega^{\text{exp}}(\text{cm}^{-1})$	$\Delta\omega^{\text{teo}}(\text{cm}^{-1})$
135.5	14.8	2.289	-16.7	-16.3
154.8	24.7	2.121	-15.4	-15.0
174.7	37.5	1.912	-13.3	-13.6
194.0	51.3	1.646	-11.4	-12.0
213.6 ^(s)	67.1	1.298	-9.2	-9.7
232.8 ^(s)	88.8	0.869	-6.0	-7.1
251.7 ^(s)	99.7	0.674	-3.8	-5.3

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3 **Fig. 1** Experimental and theoretical vibrational shifts of the HCl-Ar and HCl-Kr for
4 different temperatures of the solvent.
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8 **Fig. 2** Absolute values of the repulsive $\Delta\omega_-$ and attractive $\Delta\omega_+$ contributions to the
9 shift of the potential of the HCl-Kr for different temperatures of the solvent.
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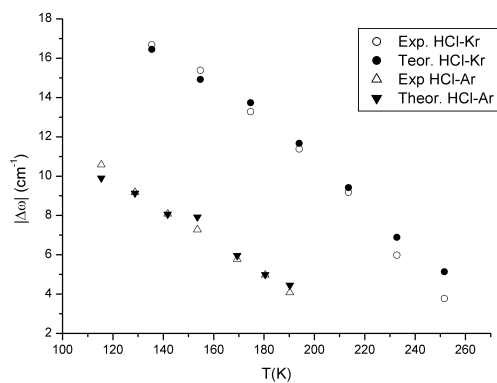


FIG. 1: Experimental and theoretical vibrational shifts of the HCl-Ar and HCl-Kr for different temperatures of the solvent.

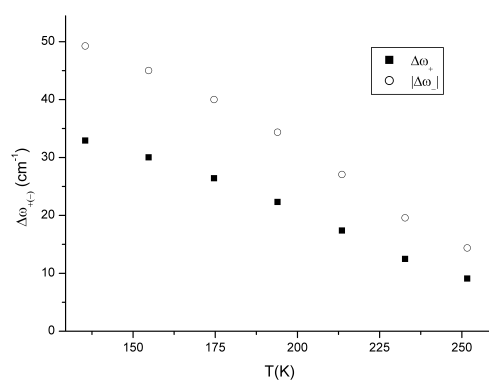


FIG. 2: Absolute values of the repulsive $\Delta\omega_-$ and attractive $\Delta\omega_+$ contributions to the shift of the potential of the HCl-Kr for different temperatures of the solvent.

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