Vibrational line shifts of hydrogen halides in a rare gas environment: HF/DF and HCl/DCl in Ar matrices and clusters

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Abstract

Vibrational frequency shifts of fundamental and higher excitations of HF/DF and HCl/DCl in a rare gas environment are calculated using vibrationally dependent atom–molecule potentials. For both octahedral and icosahedral geometry corresponding to a substitutional site in fcc matrices and in medium sized clusters the shift is monitored for an increasing number of up to ten solvation shells. Saturation is reached for the fifth octahedral and for the third icosahedral shell. Good agreement with matrix experiments is found for the shift of the fundamental frequency, while the potential used here does not extrapolate well for the higher excitations of HCl.

1. Introduction

The spectroscopy of molecules isolated in rare gas matrices offers an interesting possibility to study the intermolecular interaction of solute–solvent systems. The most fundamental difference in infrared spectra of molecules in a rare gas environment as compared to those of free molecules is the change of vibrational and rotational energy levels resulting in shifts or splittings of characteristic absorption frequencies. For reviews on infrared spectroscopy of small molecules in rare gas matrices see for example Ref. [1,2]. Among the best studied systems are HCl/DCl [3–7] and to a lesser extent also HF/DF molecules [8–11] in solid Ar. The matrix induced red shift of the fundamental transition of HF is approximately three times as large as that of HCl (-42 cm^{-1} versus -14 cm^{-1}). It is noted that for HCl [7] and DCl [6] also higher vibrational transitions could be observed showing an essentially unchanged shift of the $1 \rightarrow 2$ and $2 \rightarrow 3$ transition.

In recent years the concept of vibrational line shifts has also been extended to the field of van der Waals clusters where the dependence of spectroscopic properties of chromophores on an increasing number of solvent atoms is studied. Beginning from the dimer, the most important questions are: (a) up to what number of particles are size effects dominant, and (b) when is the bulk limit reached. Recent experiments have been focussing on hydrogen halides in small clusters with up to $n = 4$ Ar atoms for HFAr$_n$ [12,13] and up to $n = 2$ for HClAr$_n$ [14]. These data motivated further theoretical studies of these systems especially dealing with the question of nonadditive forces [15,16]. Other workers predicted line shifts of HFAr$_n$ for larger aggregates up to one solvation shell ($n = 12$) and beyond ($n = 13, 14$) [17–20].

The purpose of the present communication is to calculate frequency shifts of HF and HCl both in Ar ma-

trices and in medium sized Ar clusters of up to 10 complete solvation shells. Special emphasis is devoted to the different solvent geometries of rare gas matrices and clusters. As is known from theory [21] and from electron diffraction experiments [22], icosahedral structures are energetically favored over cubic geometries up to cluster sizes in the order of one to two thousand particles. In this study, for both octahedral (O_h) and icosahedral (I_h) growth sequences of the rare gas solvent corresponding to a shellwise buildup of face centered cubic (fcc) lattices and icosahedral clusters (see Fig. 1), line shifts are monitored as a function of the number of solvation shells.

Our model assumptions about the solute–solvent geometry and the potential energy functions are given in Section 2. The results for the vibrational line shifts of the systems HF/Ar and HCl/Ar are presented and compared with experimental work in Section 3. The relation of the present investigation to other theoretical work and final remarks can be found in Section 4.

2. Model

Due to the roughly comparable van der Waals radii of HF, HCl, and Ar, it is reasonable to assume the hydrogen halide molecule occupies a single substitutional site in an otherwise perfectly symmetric fcc crystal which is of octahedral symmetry. However, it is noted that the smaller HF molecule may also occupy a distorted interstitial site [11] which is not considered here. Similarly, for the icosahedral clusters we assume the solute molecule to occupy the central site of the cluster which can be justified for systems containing particles of comparable sizes where the solute–solvent pair interaction is stronger than the pure solvent interaction.

In the following we make the assumption of pairwise additivity of interactions between the molecular impurity and the rare gas atoms. On the other hand, it would be inaccurate to assume that the Ar–HX (X = F, Cl) interaction can be decomposed into interatomic pair terms. The interactions of Ar–HF and Ar–HCl are among the most thoroughly studied atom–molecule potentials. Based on microwave and infrared spectroscopy of van der Waals dimers, anisotropic potential energy surfaces have been developed [23,24] and used in previous studies of HF in Ar matrices [11]
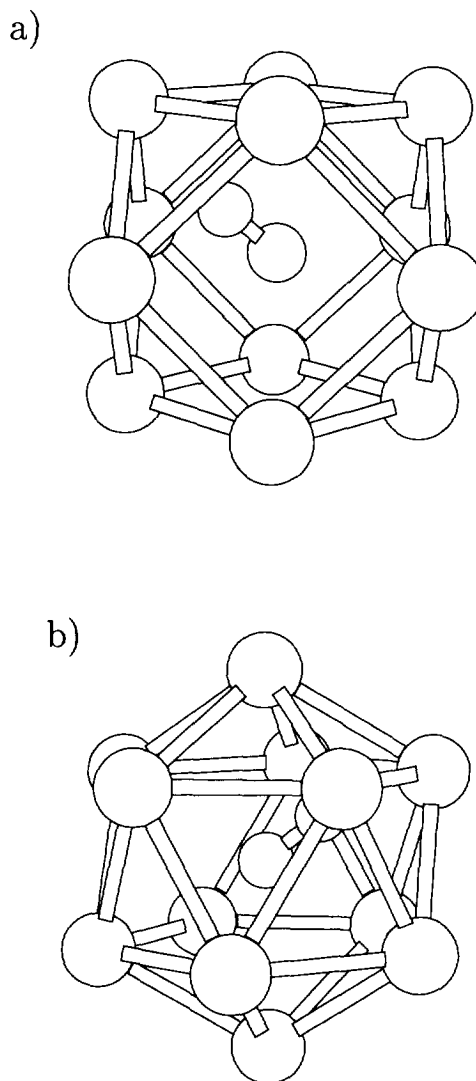

Fig. 1. (a) Octahedral, and (b) icosahedral structure of the first argon solvation shell around the HX molecule.

and in small Ar clusters [15,17–20,16]. The essential feature of these potentials, used also in the present study, is that they adiabatically depend on the vibrational state of the molecular partner and thus allow direct calculations of vibrational line shifts without having to resort to perturbational approaches [25].

The argon interaction determines the size of the solvent cage via a balancing of the Ar–Ar and Ar–HX forces. In order to obtain a model that is consistent with experimental data on the level of pair potentials

we proceed in a similar way as in computer simulations of liquids [26,27]. An effective pair potential implicitly accounting for three-body effects is modeled by a Lennard-Jones potential function. The minimum energy distance is chosen to be r_m = 387.2 pm which reproduces the nearest neighbour distance of 376.0 pm of pure Ar at T = 20 K [28] using the method of lattice sums [29]. A well depth of ϵ = 1 kJ/mol was chosen in accordance with effective pair potentials used in liquid state simulations (see also Section 4).

Using these two types of pair potentials, a simple procedure was carried out to allow for a local distortion of the matrix. The nearest neighbour distance was varied such as to minimize the total interaction energy of the guest molecule and the atoms of its first solvation shell. Because HF is slightly smaller than Ar, there is a competition between the shrinking effect of the HF–Ar attraction and the repulsion among the twelve Ar atoms. This leads to a nearest neighbour distance of 374.7 pm and 360.7 pm for the octahedral and the icosahedral symmetry, respectively. Due to the repulsion between the larger HCl molecule and the unrelaxed solvent the cage formed by the direct neighbours is expanded to 384.5 pm (O_h) or to 376.6 pm (I_h). It has to be noted that the different cage sizes resulting for the O_h and I_h geometry are due to the different number and distances of Ar–Ar pair interactions in the first solvation shell.

Based on these geometries, vibrational frequency shifts are evaluated in the following way. Keeping the rare gas environment rigid, the shift is simply calculated in two steps. First, the interaction energy E_v between the diatomic HX molecule in the vibrational state v and all the solvent particles at positions r_i is calculated,

$$E_v = \sum_{i=1}^{n} V\left(\mathrm{HX}(v), \mathrm{Ar}(r_i)\right) \ . \qquad (1)$$

Here, V is the atom–molecule potential function. This energy is then averaged over an isotropic distribution of orientations of the molecule. In the second step, the wavenumber shift is directly obtained from the difference of the energies for the initial and the final vibrational state of the hydrogen halide molecule

$$\Delta_{v \to v+1} = \frac{E(v+1) - E(v)}{hc} \ . \qquad (2)$$
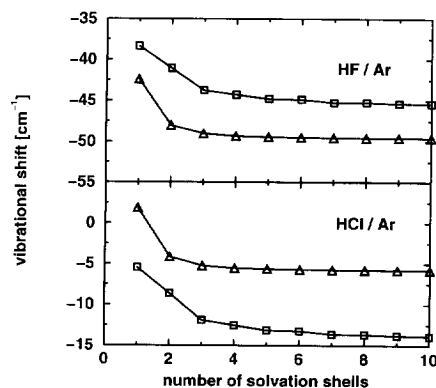

Fig. 2. Shift of vibrational wave number of the fundamental transition of HF/Ar and HCl/Ar versus the number of solvation shells. The squares show the octahedral, the triangles show the icosahedral structures.

Here, h represents the Planck constant and c is the speed of light.

3. Results

First, we want to investigate the dependence of the vibrational wavenumber shift of the fundamental excitation on the number of solvation shells. Using the relaxed geometries as described above, shifts of the HF and HCl vibration have been calculated for up to ten complete solvation shells. The results for both octahedral and icosahedral growth are shown in Fig. 2. It can be seen that the absolute shifts are very different. The red shifts are much larger for HF than for HCl which is due to the different electronic structure of the molecules giving rise to different vibrational dependence of multipole moments and polarizabilities. Furthermore, we observe that the HF frequency shift is larger for icosahedral than for octahedral solvation. Interestingly, this difference in the calculated line shifts for clusters of an equal number of solvation shells is mostly caused by the size of the cage as discussed above. Thus, the larger red shift of HF in an icosahedral than in an octahedral environment is caused by the smaller cage. The reverse is observed for HCl where the larger red shift for octahedral solvation is due to the larger cage for O_h geometry. Assuming an identical size of the cage one would obtain almost equal line shifts for the O_h and I_h symmetries.

This is not obvious because in either case, due to the anisotropy of the atom–molecule potentials, there is a complicated tradeoff of the individual contributions of the 12 Ar atoms of the first solvation shell to the line shift.

Another important feature is the convergence of the vibrational line shifts with increasing number of solvation shells (see Fig. 2). Although the absolute rate of convergence is comparable for HF and HCl it is clear that the relative convergence is much slower for HCl due to the longer range of the interaction with the solvent particles. Going from 1 to 10 layers of Ar atoms the shift of HCl in an octahedral environment increases by a factor of almost three, and for icosahedral clusters the effect changes even qualitatively, from a blue shift to a red shift. It is found that for octahedral solvation five shells are needed to obtain a result coinciding with the value for ten shells within 1 cm^{-1}. This degree of convergence is reached for icosahedral symmetries already after the third shell. The reason for this is the different shellwise buildup scheme of octahedra vs. icosahedra. In the latter case the kth filled shell consists of $10k^2 + 2$ particles at a radius of kd where d is the nearest-neighbour distance. On the other hand, the octahedral buildup pattern is more complicated. The shells with radii of $\sqrt{k}d$ are closer together but are more sparsely filled than for the icosahedral buildup, with the number of solvent atoms per shell varying from 6 to 48 for $1 \leqslant k \leqslant 10$ [29].

In the following we discuss in more detail the results for two different situations, namely the shifts in infinite fcc matrices and in icosahedral clusters with only the first solvation shell. Our values for the vibrational wavenumber shifts of HF/DF and HCl/DCl in fcc Ar matrices (site symmetry O_h) are summarized in the left part of Table 1 for both the undistorted and the distorted solute–solvent geometry, and are compared with experimental values. Our results have been obtained for ten solvation shells corresponding to 200 solvent atoms which is a very good approximation for the bulk case. It can be seen in Table 1 that for each of the molecules relaxation of the matrix leads to an increase of the red shift. While this effect is of minor importance for HF/DF it increases the matrix shift for fundamental excitation of HCl/DCl by a factor of almost two. A comparison with the experimental matrix values shows that the results for HCl/DCl in an unrelaxed matrix largely deviate from the experiment,

while for the relaxed geometry there is good agreement within 5% and 13% for the hydrogenated and deuterated species, respectively.

Experimental data for higher vibrational transitions can be obtained from the differences of fundamental and overtone excitations reported for HCl [7] and for DCl [6]. The comparison of the values for the $v = 1 \rightarrow 2$ transition with our calculations is less favorable. The results for relaxed matrices only account for 43% of the HCl shift and 73% of the DCl shift. For the next higher vibrational transition ($v = 2 \rightarrow 3$) of HCl we obtain even a blue shift of 1.2 cm^{-1} which is not at all consistent with the experimental observation [7] of a red shift of 12.8 cm^{-1}.

The right part of Table 1 gives our results for clusters with one complete solvation shell comprising of 12 Ar atoms around the HX molecule (site symmetry I_h) for which no experimental line shift data are available. Again, for HF the shrinking of the Ar cage does not effect the red shift significantly. For the relaxed geometries, we find for HFAr$_{12}$ red shifts which are about 3 cm^{-1} smaller than those for HF in Ar matrices. In the case of HClAr$_{12}$ we predict small blueshifts strongly increasing with the vibrational quantum number. Due to the small change in the nearest-neighbour distance upon icosahedral cage relaxation, the calculated shift is only slightly larger for the relaxed than for the unrelaxed solvent arrangement.

4. Discussion

The good agreement of our results for the fundamental vibrational excitation $v = 0 \rightarrow 1$ of hydrogen halide molecules with the corresponding experimental values of matrix isolated molecules indicates the high quality of Hutson's atom–molecule potential energy functions [23,24]. This has been found previously for HF in fcc Ar [11] while HCl shifts have been calculated here for the first time using these potentials. The poor agreement for the $v = 1 \rightarrow 2$ transition (see Table 1) suggests that there may be deficiencies in the extrapolation of the Ar–HCl potential which was originally obtained by fitting to spectroscopic data for $v = 0$ and $v = 1$ only [24]. On the contrary, the Ar–HF potential which is based on data for $v = 0$, $v = 1$, and $v = 2$ [23] was shown to extrapolate well for $v = 3$ [30].

Table 1
Vibrational line shifts (in cm^{-1}) of HF/DF and HCl/DCl in bulk Ar matrices (O_h) and in clusters with one solvation shell of 12 Ar atoms (I_h). The experimental values for the matrix line shifts are taken from the following references: Refs. [8–11] for HF, Refs. [9–11] for DF, Refs. [4–7] for HCl, and Refs. [3–6] for DCl

v		O_h				I_h	
		HF	DF	HCl	DCl	HF	HCl
$0 \to 1$	undistorted	−44.8 [a]	−32.5	−7.3	−6.3	−37.9	+2.5
$0 \to 1$	relaxed	−45.4	−32.9	−13.9	−11.1	−42.4 [b]	+1.9
$0 \to 1$	experiment	−43.1...−41.3	−29.9...−28.9	−14.9...−14.5	−11.9...−10.9	−	−
$1 \to 2$	undistorted	−45.8	−33.0	+0.8	−2.1	−39.0	+9.9
$1 \to 2$	relaxed	−46.5	−33.4	−6.4	−7.3	−43.6	+9.3
$1 \to 2$	experiment	−	−	−14.8 [c]	−10.0 [d]	−	−

[a] A value of −43.8 cm^{-1} was calculated in Ref. [11].
[b] A value of −42.46 cm^{-1} was obtained in quantum calculations of Ref. [18].
[c] Calculated from overtone measurements, see Ref. [7].
[d] Calculated from overtone measurements, see Ref. [6].

Again we stress here the importance of cage relaxation. As can be seen from our results, a small change of the nearest-neighbour distance sometimes leads to a significant change of the vibrational frequency shifts. While this effect is small for HF it is important for the larger HCl molecule (see Table 1). Hence, also the choice of the argon interaction potential which governs the exact size of the solvent cage plays an important role in the calculation of line shifts. Although there are high-quality gas-phase potentials in the literature, e.g. the HFD–C potential of Aziz et al. with $r_m = 375.9$ pm and $\epsilon = 1.191$ kJ/mol [31] we chose a Lennard-Jones potential with a 3% larger value of r_m and a 16% smaller value of ϵ as an effective pair potential. It approximately accounts for many-body effects on a pairwise level because all the calculations presented here are based on the assumption of pairwise additive atom–molecule forces. Most importantly, this potential correctly reproduces the lattice constant of crystalline argon [28] and is similar to effective pair potentials used in computer simulations of liquids [26,27]. Although the cohesive energy of 8.61 kJ/mol deviates from the experimental value of 7.72 kJ/mol [32] we did not further decrease the value of ϵ in order not to overestimate the strength of the Ar–HX interaction relative to that of Ar–Ar.

Publications on the effect of three-body forces appeared recently in the literature. Cooper and Hutson showed that the effect of non-additive forces on low frequency van der Waals modes of Ar_2HCl is signif-

icant [15]. Via the geometry of the aggregate non-additive contributions to the forces can also influence the vibrational line shifts as has been investigated by Lewerenz [16]. For small clusters $HFAr_n$, $n = 1 \ldots 4$, he showed that these effects are of the order of 0.5 cm^{-1}. Since the geometry of complete solvation shells is primarily dictated by closest packing, it is assumed to be not as sensitive to small changes in the interaction as the structure of smaller clusters which are much more floppy. This justifies the use of effective pair potentials adopted here.

In the present study, the convergence of the vibrational frequency shift towards the bulk limit is investigated. Unlike the assumptions drawn in Ref. [13] and Ref. [18], the latter based on the near coincidence of the line shift for the icosahedral $HFAr_{12}$ aggregate with the matrix value (see Fig. 2), our main finding is that saturation of the line shift is not yet reached after closing the first solvation shell. Although the strength of the solute–solvent interaction decreases rapidly from shell to shell this is partly compensated by the growing number of particles per shell. In order to reach convergence within 1 cm^{-1}, five octahedral or three icosahedral shells are needed.

Another interesting aspect is a methodological comparison of our approach with those found in the literature. In our method, vibrational frequency shifts are simply represented by the energy difference of the cluster with the hydrogen halide molecule being in the v and in the $v + 1$ state. Apart from the orientation of

the molecule which is isotropically averaged here our approach is identical to that of Liu et al. [17]. Indeed, quantum calculations for both octahedral [11,?] and icosahedral [18] symmetry show that the rotational part of the ground state wave function of HF in Ar is almost identical to that of the free molecule, i. e. spherically symmetric. Accordingly, the result of Liu et al. of 44.70 cm^{-1} for the red shift of HFAr$_{12}$ [17] is close to our value. In subsequent studies the same authors recalculated this value by means of a quantum five-dimensional bound state calculation [18–20]. An explicit quantum treatment of the (coupled) translation and rotation of the molecule in a rigid solvent environment yielded a red shift of 42.46 cm^{-1} which is practically identical to the result of the present work. This may indicate that quantum effects do not dominate line shifts of systems with closed solvation shells. The relative smallness of rotation–translation coupling is further confirmed by calculations of Friedmann and Kimel for HCl in Ar who showed that its contribution to the total vibrational frequency shift is in the order of 1 cm^{-1} [25].

On the other hand, a comparison of the classical [17] and quantum mechanical [18–20] results of Liu et al. reveals that quantum effects are of major importance for HFAr$_n$ with $n \leqslant 8$. This is especially true for $n = 1$ where the classical value overestimates the experimental one by about 100 %. For these systems large amplitude motions of the solute molecule with respect to the Ar solvent make it necessary to carry out full quantum calculations. Indeed, the experimental values for HFAr$_n$, $n \leqslant 4$, [12–14] could be reproduced in a number of studies using various techniques such as discrete variable representations [18–20], and diffusion Monte Carlo [16].

One quantum effect which may be important for the closed shell systems investigated here is the zero point vibration of the breathing mode of the solvent cage in HXAr$_{12}$. As has been shown in semiclassical simulations of Ar$_{13}$ by Fredj et al. this may lead to a non-negligible increase of the cluster radius even for relatively low temperatures [34]. For example, the 1% increase of the cage radius for $T = 5$ K [34] changes the calculated frequency shift for HCl from +1.9 to −1.9 cm^{-1} while the HF red shift is reduced by only 0.9 cm^{-1} which demonstrates the importance of quantum effects of the Ar atom motion on vibrational frequency shifts.

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