Transition from Hydrogen Bonding to Ionization in (HCl)$_n$(NH$_3$)$_n$ and (HCl)$_n$(H$_2$O)$_n$ Clusters: Consequences for Anharmonic Vibrational Spectroscopy

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Anharmonic vibrational frequencies and intensities are calculated for 1:1 and 2:2 (HCl)$_n$(NH$_3$)$_n$ and (HCl)$_n$-(H$_2$O)$_n$ complexes, employing the correlation-corrected vibrational self-consistent field method with ab initio potential surfaces at the MP2/TZP computational level. In this method, the anharmonic coupling between all vibrational modes is included, which is found to be important for the systems studied. For the 4:4 (HCl)$_n$-(H$_2$O)$_n$ complex, the vibrational spectra are calculated at the harmonic level, and anharmonic effects are estimated. Just as the (HCl)$_n$(NH$_3$)$_n$ structure switches from hydrogen-bonded to ionic for $n = 2$, the (HCl)$_n$-(H$_2$O)$_n$ switches to ionic structure for $n = 4$. For (HCl)$_2$(H$_2$O)$_2$, the lowest energy structure corresponds to the hydrogen-bonded form. However, configurations of the ionic form are separated from this minimum by a barrier of less than an O−H stretching quantum. This suggests the possibility of experiments on ionization dynamics using infrared excitation of the hydrogen-bonded form. The strong cooperative effects on the hydrogen bonding, and concomitant transition to ionic bonding, makes an accurate estimate of the large anharmonicity crucial for understanding the infrared spectra of these systems. The anharmonicity is typically of the order of several hundred wavenumbers for the proton stretching motions involved in hydrogen or ionic bonding, and can also be quite large for the intramolecular modes. In addition, the large cooperative effects in the 2:2 and higher order (HCl)$_n$(H$_2$O)$_n$ complexes may have interesting implications for solvation of hydrogen halides at ice surfaces.

Introduction

Recently, there has been considerable work on the issue of spontaneous dissociative ionization of molecules in small clusters and on surfaces. This work is motivated both by fundamental questions regarding solvation in small systems and by practical questions regarding the role of ice particles in atmospheric chemistry. The calculations and experiments necessary to study these issues also happen to be near the frontier of our technical ability.

High resolution spectroscopic studies of hydrogen-bonded dimers have been possible for almost thirty years. There is a considerable literature devoted to the hydrogen halide, water and ammonia dimers. The structures, tunneling frequencies, and much of the infrared spectra have been precisely measured. There is less data, especially in the infrared region, on mixed dimers and higher clusters. One difficulty, from an experimental point of view, is that the infrared spectra of such species are extremely anharmonic, and this makes the search for such spectra using molecular beam methods quite difficult. Of course, it is exactly this high degree of anharmonicity that makes the spectra so interesting. Thus it is highly desirable to improve the accuracy of theoretical predictions of the infrared spectra in order to facilitate experimental work.

There is a long history regarding the ab initio calculation of infrared spectra, and the casual user of common programs might be led to believe that such calculations are now routine. Indeed,

there has been a tremendous amount of work on the ability of increasing basis set sizes and correlation corrections (together with the use of empirical scaling factors) to produce agreement between experiment and theory.[1] However, this is the case only in nearly harmonic systems. In the case of weakly bound complexes, anharmonic effects are very significant and have to be accounted for explicitly. Recently, our group has shown that the errors due to incomplete analysis of anharmonicity are often much larger than the errors due to incomplete basis sets or correlation corrections.[2,3] These anharmonicity corrections are especially important for hydrogen-bonded systems, for which small atomic motions could induce significant charge transfer, i.e., structures with much increased partial charges on some of the atoms.

In this paper, we examine two systems in considerable detail: ammonia/hydrogen chloride clusters and water/hydrogen chloride clusters. Each of these systems has previously been studied by both experimental and theoretical techniques. However, the role of anharmonicity has not been explicitly considered in these previous studies, with the exception of work of Del Bene and Jordan on the 1:1 H$_3$N···HCl complex.[4,5]

Tao[6] has recently performed high level ab initio calculations on the structures of (HCl)$_n$(NH$_3$)$_n$, where $n = 1$, 2, and 4. Tao and colleagues[7,8] have also studied the role of one, two, or three water molecules on the bonding between NH$_3$ and HF, HCl, and HBr. It was shown that the structure of the (HCl)$_n$(NH$_3$)$_n$ complexes changes from hydrogen-bonded to ionic between $n = 1$ and $n = 2$. Tao points out that although the hydrogen bond is significantly stronger than the ionic bond for the mixed dimer, ionic bonding is more effective in the mixed tetramer due to the fact that ionic bonding, unlike hydrogen bonding, is not

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directional. Thus, in the mixed tetramer there can be considered to be four ionic bonds, where only two hydrogen bonds would be possible. Although the mixed dimer is hydrogen-bonded, the calculated harmonic H−Cl vibrational frequency changes from 3091 cm^{-1} in free HCl to 2598 cm^{-1} in the mixed dimer.[7] This dramatic shift indicates that already for the mixed dimer the bonding strongly perturbs the individual constituents of the complex. Also, the large shift probably accounts for the fact that the infrared spectrum of NH$_3$−HCl has yet to be measured in the gas phase. Cherng and Tao[9] also performed similar studies for (HF)$_n$(NH$_3$)$_n$ and (HBr)$_n$(NH$_3$)$_n$ and showed that the transition from hydrogen bonding to ionization occurs at $n = 2$ for HBr and $n = 4$ for HF. In addition, Tao and colleagues,[7,8] as well as Biczysco and Latajka,[10] found that solvation of the NH$_3$−HCl by two water molecules is enough to ionize the complex. Only one water molecule is necessary to stabilize the ionic form of NH$_3$−HBr, and three water molecules are necessary to induce the ionization of NH$_3$−HF. Del Bene and Jordan[4] have examined the effect of anharmonicity on the NH$_3$−HX bonds by creating a two-dimensional potential energy surface at the MP2 ab initio level and solving for the vibrational functions on this reduced dimensionality surface. They found that the effect of anharmonicity grows substantially when going from HF to HCl to HBr complexes with NH$_3$.

Vibrational spectra for H$_3$N−HCl have been measured in nitrogen,[11] argon,[12] and neon[13] matrices, but the assignment of these spectra is difficult.[11] The H−Cl stretching frequency is found to be extremely sensitive to the matrix environment, ranging from 2084 cm^{-1} in Ne, to 1371 cm^{-1} in Ar, to 705 cm^{-1} in N$_2$. Del Bene and Jordan[4] analyzed the perturbation of the H$_3$N−HCl complex by three Ar and three Ne atoms and found only a very small effect (40 cm^{-1}) of rare gas atoms on the H−Cl frequency. However, they note that the presence of Ar atoms stabilizes the proton-shared region of the potential energy surface of H$_3$N−HCl with a longer H−Cl bond. This proton-shared hydrogen-bonded structure may become more stable than the "normal" gas-phase hydrogen-bonded structure as the number of Ar atoms increases. This may lead to the unusually large Ar matrix effect as compared to the presumably smaller Ne matrix shift. In their more recent study, Jordan and Del Bene[5] showed that external electric fields stabilize more polar (proton-shared and ionic) structures, which may explain the effects of different matrix environments on the structure and vibrational frequencies of the H$_3$N−HCl complex.

HCl solvated by a small number of water molecules has also received considerable attention. The microwave spectrum of HCl−H$_2$O was first reported in 1983.[14] The structure of the dimer is clearly that of a hydrogen-bonded species. However, the data were not sufficient to probe the effect of the hydrogen bonding on the H−Cl bond length. The change in the H−Cl bond length still cannot be determined from a more complete study of 14 isotopomers, although the more compete data helps to map out the bending potential and determines the dipole moment of the complex to be 3.44 D.[15] The dipole moment is 0.81 D more than the sum of the dipoles of the constituents, and analysis of the hyperfine structure shows that the enhancement is mainly localized to the HCl constituent. A matrix isolation study of HCl(H$_2$O)$_n$ complexes suggests that complexation by four waters is not enough to induce dissociation of the HCl.[16] Ab initio calculations of HCl(H$_2$O)$_n$ complexes[17−19] show that $n = 1−3$ clusters have nonionic associated structures, while all isomers with $n=5$ already have dissociated structures. The case of $n = 4$ is intermediate, with both associated and dissociated structures found.

There have recently been a variety of studies to understand the interaction of hydrogen halides with ice surfaces.[20−23] Although the theoretical studies generally conclude that isolated hydrogen halide molecules dissociate on contact with ice surfaces, there are some disagreements regarding the exact mechanism, which probably varies among the hydrogen halides. So far, the experimental evidence is that isolated DCl does not spontaneously dissociate on a cold ice surface.[24] However, there may be some evidence that clustered HCl can dissolve in ice particles.[25]

A similar series of studies have addressed the issue of ionization of salt molecules by small water clusters and on surfaces. Peslherbe et al. found that NaI exists as contact ion pairs, even in fairly large ion clusters.[26] Petersen and Gordon[27] found the same to be true for NaCl. In contrast, Jungwirth found that as few as six water molecules are sufficient to cause the Na$^+$ and Cl$^-$ ions produced by the solvation of NaCl to separate to far ends of the cluster.[28] Of course, these studies involve somewhat different conditions and assumptions. However, they illustrate that our understanding of ion pair formation in small clusters is still in the nascent stage. This reinforces our desire to further develop and test our method for handling the extreme anharmonicity associated with such processes.

The main objective of our present study is to compute the *anharmonic* vibrational spectra of (HCl)$_n$(NH$_3$)$_n$ and (HCl)$_n$-(H$_2$O)$_n$ clusters using ab initio potential energy surfaces. Recently, we have developed an algorithm that combines anharmonic vibrational spectroscopy with direct calculation of ab initio potentials.[2] The method accounts for anharmonicities and couplings between vibrational modes using the Correlation-Corrected Vibrational Self-Consistent Field (CC-VSCF) approach[29] and, therefore, provides a superior alternative to the existing techniques based on scaling the harmonic vibrational frequencies. This method was applied to a number of hydrogen-bonded systems[3] using the potentials obtained at the MP2/TZP level of ab initio theory and was shown to provide reasonably accurate anharmonic frequencies (with typical deviations from experimental values of the order of 30−50 cm^{-1}). In the present study, we apply this direct ab initio CC-VSCF method to obtain anharmonic vibrational spectra of hydrogen-bonded and ionic clusters of ammonia/hydrogen chloride and water/hydrogen chloride. The calculated vibrational spectra can assist possible experimental identification of such clusters in the future.

Methodology

All ab initio calculations of the hydrogen-bonded and charge-separated complexes of HCl with H$_2$O and NH$_3$ are performed using the second-order Møller−Plesset (MP2) level of electronic structure theory[30] within the electronic structure package GAMESS.[31] The equilibrium geometries of the complexes are optimized using analytic gradients. Second derivative (Hessian) matrices are calculated numerically using double differencing of analytic gradients. Several basis sets are used to obtain equilibrium structures and to estimate binding energies of smaller (1:1) complexes: Dunning-Hay double-ζ + polarization (DZP),[32] Dunning's triple-ζ + polarization (TZP),[33] TZP with diffuse functions (TZ++P), and augmented correlation-consistent valence triple-ζ (aug-cc-pVTZ).[34] The DZP basis set is found to somewhat overestimate lengths of hydrogen bonds (by about 0.05−0.07 Å) and underestimate elongation of H−Cl distances due to hydrogen bonding (by about 0.01−0.02 Å). On the other hand, the TZP basis set is found to predict equilibrium geometries and harmonic frequencies of small complexes well (compared with the larger correlation-consistent
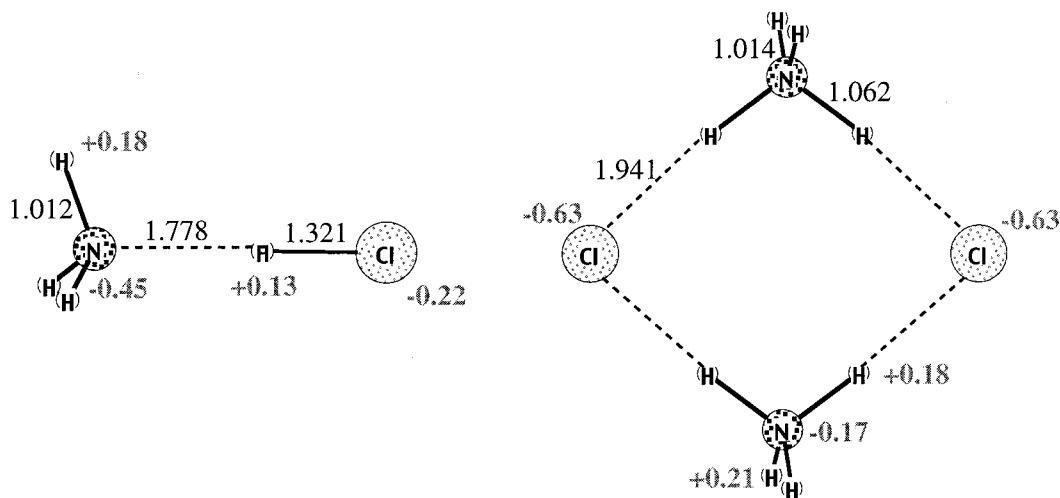
(HCl)$_n$(NH$_3$)$_n$ and (HCl)$_n$(H$_2$O)$_n$ Clusters

J. Phys. Chem. A, Vol. 105, No. 36, 2001 **8325**

Figure 1. Equilibrium structures (angs.) and partial charges of hydrogen-bonded and ionic complexes of NH$_3$ and HCl, obtained at the MP2/TZP level of ab initio theory.

triple-ζ set), and this basis set is chosen to study larger (2:2 and 4:4) complexes. The TZP basis set is also used in this study to obtain potential energy values for anharmonic vibrational frequency calculations.

Anharmonic vibrational frequencies are obtained using Vibrational Self-Consistent Field (VSCF) method[35,36] and its Correlation-Corrected (CC-VSCF) extension via second-order perturbation theory.[29] The calculations are performed using the combined ab initio/VSCF approach described in detail previously[2] and implemented in the electronic structure package GAMESS.[31] This method employs a grid over a region of the space of normal coordinates, which covers the domain of nuclear configurations relevant to the vibrational states computed. The potential energy values are computed for these grid points directly from the ab initio program.

The VSCF method is based on a separability approximation,[35,36] that reduces the problem of solving the N-dimensional vibrational Schrödinger equation for the N-mode system to solving N single-mode VSCF equations of the form:

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial Q_j^2} + \bar{V}_j^{(n_j)}(Q_j)\right]\psi_j^{(n_j)} = \epsilon_n \psi_j^{(n_j)} \quad (1)$$

where $\bar{V}_j^{(n_j)}(Q_j)$ is the effective VSCF potential for mode Q_j:

$$\bar{V}_j^{(n_j)}(Q_j) = \langle \prod_{l\neq j}^{N} \psi_l^{(n_j)}(Q_l)|V(Q_1,...,Q_N)|\prod_{l\neq j}^{N} \psi_l^{(n_l)}(Q_l)\rangle \quad (2)$$

$V(Q_1,...,Q_N)$ is the full potential of the system. The total vibrational state of the system in this approximation is given by $\Psi = \prod_{j}^{N}\psi_j^{(n_j)}(Q_j)$.

Equations 1 and 2 are solved self-consistently. The resulting solutions are further corrected for correlation effects between the vibrational modes using second-order perturbation theory (CC-VSCF).[29]

The following approximation for the potential is used:[29] the potential of the system is represented by the sum of separable (single-mode) terms and pair coupling terms, neglecting interactions of triples of normal modes and higher-order interactions

$$V(Q_1,...,Q_N) = \sum_{j}^{N} V_j^{diag}(Q_j) + \sum_{i}^{N-1}\sum_{j>i}^{N} V_{ij}^{coup}(Q_i,Q_j) \quad (3)$$

Experience from previous applications to other hydrogen-bonded systems supports the validity of this approximation, though in principle it must be tested carefully for each new system.[3] "Diagonal" (single-mode) terms $V_j^{diag}(Q_j) = V(0,...,Q_j,...,0)$ and the pairwise mode−mode coupling terms $V_{ij}^{coup}(Q_i,Q_j) = V(0,...,Q_i,...,Q_j,...,0) - V^{diag}(Q_i) - V^{diag}(Q_j)$ are calculated directly from the ab initio program on 8-point grids along each normal coordinate, and on 8 × 8 square grids for each pair of normal coordinates. This requires computation of 8*N + 64*$N(N - 1)/2$ points on the potential energy surface of each molecular system with N normal modes. The calculated ab initio potentials are interpolated into 16 and 16 × 16 point grids and used for numerical solution of the one-dimensional VSCF equations (employing the collocation method of Yang and Peet[37]). This technique was shown to work reasonably well for water clusters and other hydrogen-bonded systems studied previously, and to predict anharmonic frequencies for the highest frequency stretching vibrations with the accuracy of 30−50 cm^{-1} compared with experiment.[3]

In addition to anharmonic vibrational frequencies, the anharmonic IR intensities are calculated using the ab initio dipole moments computed along the normal coordinates Q_i:

$$I_i = \frac{8\pi^3 N_A}{3hc}\omega_i|\langle\psi_i^{(0)}(Q_i)|\vec{\mu}(Q_i)|\psi_i^{(m)}(Q_i)\rangle|^2 \quad (4)$$

where ω_i is the VSCF vibrational frequency for the normal mode i, and $\psi_i^{(0)}$ and $\psi_i^{(m)}$ are VSCF wave functions for the ground and the mth excited vibrational states.

Results and Discussion

(HCl)·(NH$_3$) Complex. Equilibrium geometries of the 1:1 and 2:2 complexes of HCl and NH$_3$ molecules, obtained at the MP2/TZP level of ab initio theory, are shown in Figure 1. Also shown are partial charges, obtained using the Löwdin population analysis.[38] The dissociation energies (D_e) of these complexes, estimated at the MP2 level with different basis sets, including the effects of the basis set superposition error (BSSE), are presented in Table 1. The bond lengths shown in Figure 1 and the dissociation energies presented in Table 1 are in good agreement with those calculated by Tao at the MP2/6-311++G-(2d,p) level of theory.[6]

Both Tao's and our calculations predict that the 1:1 complex has a hydrogen-bonded structure with a rather strong hydrogen

8326 *J. Phys. Chem. A, Vol. 105, No. 36, 2001*

Chaban et al.

TABLE 1: Binding Energies (kcal/mol) for Complexes of NH₃ with HCl, Calculated at the MP2 Level of ab Initio Theory with Different Basis Sets

system	basis set	D_e, kcal/mol
NH₃·HCl	DZP	9.4
	TZP	9.7
	TZP+bsse[a]	7.6
	TZ++P	9.9
	TZ++P + bsse	7.5
	aug-cc-pVTZ	9.2
	aug-cc-pVTZ + bsse	8.5
(NH₃)₂·(HCl)₂	DZP	33.9
	TZP	43.4

[a] Basis set superposition error correction.

TABLE 2: Vibrational Frequencies (cm⁻¹) and IR Intensities (km/mol) of Fundamental Excitations for HCl---NH₃ Complex and NH₃ and HCl Molecules (MP2/TZP level of theory)

	HCl---NH₃ complex			NH₃ + HCl				
	frequencies			frequencies				
mode	harm	CC-VSCF	intens.	harm	CC-VSCF	exp.	intens.	interpretation
1	3681	3463	16	3713	3512	3444	4	NH stretch
2	3681	3448	16	3713	3467	3444	4	NH stretch
3	3533	3336	0	3553	3392	3337	0	NH stretch
4	2403	2113	1692	3049	2949	2991	28	HCl stretch
5	1676	1613	30	1689	1627	1627	26	NH₃ bend
6	1676	1621	30	1689	1625	1627	26	NH₃ bend
7	1170	1154	166	1055	899	950	214	NH₃ umbrella
8	798	818	71					
9	798	818	71					
10	230	437	15					
11	230	432	15					
12	189	176	23					

TABLE 3: CC-VSCF Vibrational Frequencies (cm⁻¹) and IR Intensities (km/mol) of the First Overtone Excitations for HCl-- -NH₃ Complex and Isolated NH₃ and HCl Molecules (MP2/TZP level of ab initio theory)

	HCl- - -NH₃ complex		NH₃ + HCl		
mode	freq	intens.	freq	intens.	interpretation
1	7019	0	6883	0	NH stretch
2	6997	0	6738	0	NH stretch
3	6658	0	6711	0	NH stretch
4	3900	66	5799	1	HCl stretch
5	3221	0	3246	0	NH₃ bend
6	3241	0	3249	0	NH₃ bend
7	2192	0	1585	11	NH₃ umbrella
8	1659	2			
9	1659	2			
10	1002	0			
11	982	0			
12	340	2			

bond. Its bond distance is found to be $R = 1.78$ Å at the MP2/TZP level of ab initio theory used in this paper. A calculation with a larger, aug-cc-pVTZ, basis set predicts a somewhat shorter value, $R = 1.74$ Å. The N−Cl distance obtained at the MP2/TZP level is 3.10 Å, which is in a good agreement with the experimental value of 3.14 Å for R_0(N−Cl).[39] The H−Cl distance in this structure is elongated by about 0.045 Å compared with the isolated H−Cl molecule, while N−H distances are less perturbed and are closer to those in isolated NH₃ (1.012 vs 1.009 Å). As follows from the calculated partial charges, the HCl component in this complex has substantially larger ionic character than the isolated HCl. It will be shown further that these electronic structure features have a strong effect on the vibrational spectrum of this complex. The dissociation energy (D_e) of the 1:1 complex predicted by the highest level calculation employed in this study (MP2/aug-cc-pVTZ corrected for BSSE) is 8.5 kcal/mol, an energy corresponding to a very strong hydrogen bond.

The calculated vibrational frequencies and infrared intensities for fundamental excitations of the 1:1 H₃N···HCl complex are presented in Table 2, along with the data for the isolated HCl and NH₃ molecules presented for comparison. The first two columns of Table 2 list harmonic and anharmonic (CC-VSCF) frequencies, and the third column represents IR intensities calculated using VSCF wave functions. The same information is given for the isolated HCl and NH₃ fragments, along with the experimental frequencies. It can be seen from Table 2 that the stretching and bending frequencies of the NH₃ molecule do not change very much upon the complexation with HCl. On the other hand, the frequency of the H−Cl stretch decreases drastically (by more than 800 cm⁻¹) upon the formation of the

complex (from 2949 down to 2113 cm⁻¹). This drastic change is already noticeable at the harmonic level (where the frequency decreases by about 600 cm⁻¹), but it is considerably enhanced when anharmonic effects are included. This is due to the much higher anharmonicity of the elongated H−Cl bond in the hydrogen-bonded complex as compared to the isolated HCl molecule. The intensity of this transition also increases dramatically, from 28 km/mol in the isolated HCl to 1692 km/mol in the complex. Given that the fundamental frequencies are so anharmonic, it seems likely that the overtone transitions could also have a reasonable intensity. Indeed, the first overtone frequency for the H−Cl stretch in the H₃N···HCl complex is estimated to be around 3900 cm⁻¹, and its intensity is found to be quite high, 66 km/mol. A list of the overtone frequencies and intensities is given in Table 3.

The structural results obtained for the H₃N···HCl complex are in good agreement with previous studies; it is the calculated anharmonicities that break new ground. The anharmonic effects are dramatic, especially for the H−Cl stretching motion. Del Bene and Jordan[4] have previously estimated the anharmonic effects for the 1:1 (HCl)·(NH₃) by solving for the vibrational states on a reduced dimensionality potential surface, and obtained even larger estimates for the anharmonicity than reported here. In their calculations, the fundamental frequency for the H−Cl stretch of H₃N···HCl reduces from the harmonic value of 2541 cm⁻¹ to 2278 cm⁻¹ in the one-dimensional approximation and to 1869 cm⁻¹ in the two-dimensional approximation.[4] Our calculated value (2113 cm⁻¹) is between these two values. Clearly this molecule, which is very close to the borderline between hydrogen-bonded and ionic structures, presents a severe test of the theory.

Similarly divergent results are obtained in matrix isolation spectroscopy. Ault and Pimentel[11] assigned the H−Cl stretch for the 1:1 (HCl)·(NH₃) complex to a transition at 705 cm⁻¹ in a nitrogen matrix, and speculated that the overtone occurs at 1438 cm⁻¹. Barnes et al.[12] reviewed these assignments and concurred with only slight correction of the frequencies. It seems very unlikely to us, however, that the overtone of such an anharmonic transition would lie so close to twice the fundamental frequency. Barnes assigns the H−Cl stretch to 1371 cm⁻¹ in an Ar matrix. Thus the bonding is found to be extremely sensitive to the matrix environment. This conclusion was recently reaffirmed by Andrews et al.[13] who measured the spectrum in a neon matrix (where matrix effects are expected to be far smaller than in argon due to the much smaller polarizability of neon) and found the H−Cl stretch to be at 2084 cm⁻¹. Making an analogy to the matrix dependence of the H−F

(HCl)$_n$(NH$_3$)$_n$ and (HCl)$_n$(H$_2$O)$_n$ Clusters

J. Phys. Chem. A, Vol. 105, No. 36, 2001 **8327**

TABLE 4: Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) for (HCl)$_2$-(NH$_3$)$_2$ Complex (MP2/TZP level of ab initio theory)

	frequencies			
mode	harm	CC−VSCF	intensities	interpretation
1	3660	3456	125	free asym NH stretch
2	3660	3456	2	free asym NH stretch
3	3573	3333	0	free sym NH stretch
4	3572	3377	176	free sym NH stretch
5	2820	2408	0	bonded sym NH stretch
6	2804	2466	3717	bonded asym NH stretch
7	2781	2469	2691	bonded sym NH stretch
8	2622	2162	0	bonded asym NH stretch
9	1749	1688	0	
10	1720	1668	0	
11	1718	1666	27	
12	1717	1665	0	
13	1588	1554	125	
14	1573	1538	0	
15	1537	1507	0	
16	1511	1482	258	
17	1432	1395	46	
18	1410	1372	0	
19	502	592	34	
20	444	550	0	
21	304	430	0	
22	299	305	0	N−N, Cl−Cl stretch
23	295	304	228	N−Cl stretch
24	292	296	196	N−Cl stretch
25	289	422	0	
26	223	364	1	
27	222	214	0	
28	217	364	0	
29	90	89	0	Cl−Cl, N−N stretch
30	63	108	70	

stretch in H$_3$N···HF complex, they postulate that the gas-phase value of the H−Cl stretching frequency of H$_3$N···HCl is at about 2200 cm^{-1}, in good accord with our calculated value, but much higher than the two-dimensional value of Del Bene and Jordan.[4]

Barnes et al.[12] assign the E-type NH$_3$ rock mode to a frequency of 733 cm^{-1} in Ar, and Andrews et al. assign this mode to 709 cm^{-1} in Ne. These are in reasonable accord with our calculated value: 818 cm^{-1}. Also, the calculated and measured frequencies for the E-type NH$_3$ stretches are quite close; 3450 cm^{-1} calculated versus 3420 cm^{-1} measured in the argon matrix. In addition, our calculated frequency for the NH$_3$ umbrella motion indicates a significant increase over the free molecule value, in agreement with the matrix results. Given the significant uncertainty in the gas-phase values for the vibrational frequencies of H$_3$N···HCl, a gas-phase search for the spectrum will be quite difficult. For initial identification of the gas-phase dimer, the NH$_3$ stretching transitions are good candidates. There is a small frequency shift and the transitions are predicted to be significantly more intense than those in free ammonia.

(HCl)$_2$·(NH$_3$)$_2$ Complex. It was shown by Tao[6] that in contrast with 1:1 complex, the 2:2 and 4:4 complexes of HCl and NH$_3$ have ionic (NH$_4$$^+Cl^-$) rather than hydrogen-bonded structures. Our MP2/TZP calculations confirm the ionic structure for the 2:2 complex (see Figure 1). Löwdin population analysis gives partial charges of −0.63 on Cl atoms. Each NH$_4$$^+$ fragment has two free N−H bonds, whose bond lengths are close to those of the N−H bonds in the 1:1 hydrogen-bonded structure and in the free NH$_3$ molecule, and two N−H bonds that point toward Cl$^-$ ions and are elongated by about 0.05 Å. The dissociation energy (D_e) of the 2:2 ionic complex with respect to 2NH$_3$ + 2HCl is estimated to be about 43 kcal/mol at the MP2/TZP level of theory (Table 1). The calculated harmonic and CC-VSCF vibrational frequencies for the 2:2 ionic structure are listed in
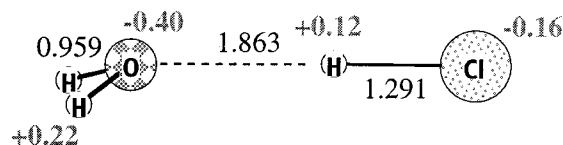
Figure 2. Equilibrium structure (angs.) and partial charges of the hydrogen-bonded complex of HCl with H$_2$O, obtained at the MP2/TZP level of ab initio theory.

TABLE 5: Binding Energies (kcal/mol) for Complexes of H$_2$O with HCl, Calculated at the MP2 Level of ab Initio Theory with Different Basis Sets

system	basis set	D_e, kcal/mol
H$_2$O·HCl	DZP	6.4
	TZP	6.6
	TZP + bsse[a]	5.4
	aug-cc-pVTZ	4.5
	aug-cc-pVTZ + bsse	4.0
(H$_2$O)$_2$·(HCl)$_2$		
hydrogen-bonded	TZP	22.7
ionic	TZP	15.8
(H$_2$O)$_4$·(HCl)$_4$		
hydrogen-bonded	TZP	55.7
ionic	TZP	72.0

[a] Basis set superposition error correction.

Table 4. It can be seen from Table 4 that the four highest frequencies, which correspond to free N−H stretches, are only slightly (10 to 50 cm^{-1}) lower than those of the free NH$_3$ molecule. On the other hand, the next four stretching frequencies, corresponding to elongated N−H bonds, are red shifted to a very large extent (by 1000−1300 cm^{-1}) compared with the frequencies of the isolated NH$_3$. Two of these stretching vibrations, located at about 2460−2470 cm^{-1}, have very high intensities. These excitations (or the corresponding overtones, which are calculated to be in the region of 4850−4900 cm^{-1}) are good candidates for experimental observation. While it is not trivial to produce such tetramers, it may be possible by using liquid helium nano-droplet technology.

(HCl)·(H$_2$O) Complex. Similar to the 1:1 complex of (HCl)·(NH$_3$), the (HCl)·(H$_2$O) complex also has a hydrogen-bonded structure as shown in Figure 2. However, the hydrogen bond from HCl to H$_2$O is weaker than that to NH$_3$ reflecting the smaller proton affinity of water compared to ammonia. The length of the O···H hydrogen bond is 1.86 Å at the MP2/TZP level, with little change upon increasing the basis set to aug-cc-pVTZ. This is longer than the hydrogen bond in the ammonia complex (1.78 Å) and is shorter than the O···H hydrogen bond in the water dimer (1.92 Å).[3] The dissociation energy (D_e) of the H$_2$O···HCl complex is about 4 kcal/mol at the highest level of theory used here (see Table 5). This is about half of the dissociation energy of the NH$_3$···HCl complex. The H−Cl bond is not elongated to the same extent as in the complex with ammonia, but is about 0.015 Å longer than in the isolated H−Cl molecule. This is also reflected in the vibrational spectrum. The H−Cl stretch in H$_2$O···HCl is red shifted by about 200 cm^{-1} from the H−Cl frequency of the isolated HCl and its intensity is enhanced by more than a factor of 20! The H−Cl fundamental frequency for this complex is predicted to be around 2700 cm^{-1}. All calculated fundamental vibrational frequencies for H$_2$O···HCl complex are given in Table 6. In contrast to the NH$_3$···HCl complex, overtone excitations for H$_2$O···HCl, listed in Table 7, are predicted to have very low intensities.

(HCl)$_2$·(H$_2$O)$_2$ Complexes. The situation is much more interesting in the 2:2 complex (HCl)$_2$·(H$_2$O)$_2$. Here, both hydrogen-bonded and ionic structures are found to be minima on the potential energy surface at the MP2/TZP level of theory.

TABLE 6: Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) of Fundamental Excitations for HCl---H$_2$O Complex and H$_2$O and HCl Molecules (MP2/TZP level of theory)

| | HCl---H$_2$O complex | | | H$_2$O + HCl | | | | |
| | frequencies | | | frequencies | | | | |
mode	harm	CC-VSCF	intensities	harm	CC-VSCF	exp.	intensities	interpretation
1	4004	3762	86	4015	3797	3756	49	OH stretch
2	3871	3647	20	3877	3691	3652	5	OH stretch
3	2836	2709	625	3049	2949	2991	28	HCl stretch
4	1621	1561	73	1603	1547	1595	77	H$_2$O bend
5	607	673	94					
6	446	579	111					
7	179	407	169					
8	173	460	13					
9	155	324	85					

TABLE 7: CC-VSCF Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) of the First Overtone Excitations for HCl---H$_2$O Complex and H$_2$O and HCl Molecules MP2/TZP Level of ab Initio Theory)

| | HCl---H$_2$O complex | | H$_2$O + HCl | | | |
| | | | frequencies | | | |
mode	frequencies	intensities	CC-VSCF	exp.	intensities	interpretation
1	7692	0	7472	7445	0	OH stretch
2	7217	2	7303	7202	1	OH stretch
3	5216	0	5799		1	HCl stretch
4	3107	1	3081	3152	2	H$_2$O bend
5	1373	1				
6	1263	0				
7	1046	1				
8	911	1				
9	715	0				

Their equilibrium geometries are shown in Figure 3. The hydrogen-bonded structure has two very strong Cl−H···OH$_2$ hydrogen bonds. The H−Cl bonds participating in this hydrogen bonding are elongated by about 0.036 Å, as compared with the free H−Cl distance. This elongation is much larger than in the 1:1 complex and the hydrogen bonds are much stronger. The hydrogen-bonded structure also has two HOH···ClH hydrogen bonds, but these are over 0.6 Å longer than the strong Cl−H···OH$_2$ hydrogen bonds. Even taking the larger radius of the Cl atom into account, the HOH···ClH bonds are clearly relatively weak. Between the two strong hydrogen bonds and the two weak ones, the overall hydrogen bonding energy is not quite 4 times that of the 1:1 complex. It can be seen from Figure

3 that the ionic structure is more compact than the hydrogen-bonded one. It has substantial partial charges (about −0.5) on the Cl atoms. Each H$_3$O$^+$ fragment in this structure has two very elongated O−H bonds that point toward the Cl ions.

The calculated harmonic and CC-VSCF corrected vibrational frequencies of the hydrogen-bonded and ionic structures are listed in Table 8. The most noticeable feature of the vibrational spectrum of the hydrogen-bonded structure is one of the H−Cl stretches that has very high intensity. Its anharmonic frequency is calculated to be 2296 cm^{-1}, much lower than the H−Cl stretching frequency of the 1:1 H$_2$O···HCl complex and closer to the 2113 cm^{-1} frequency of the 1:1 (HCl)·(NH$_3$). The intensity of the H−Cl stretch in the (HCl)$_2$·(H$_2$O)$_2$ complex is
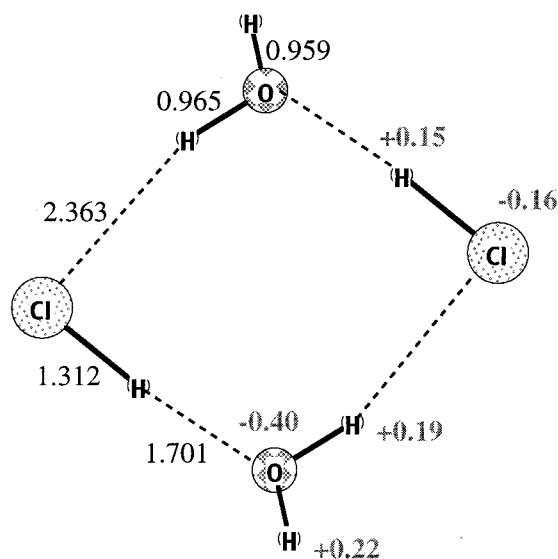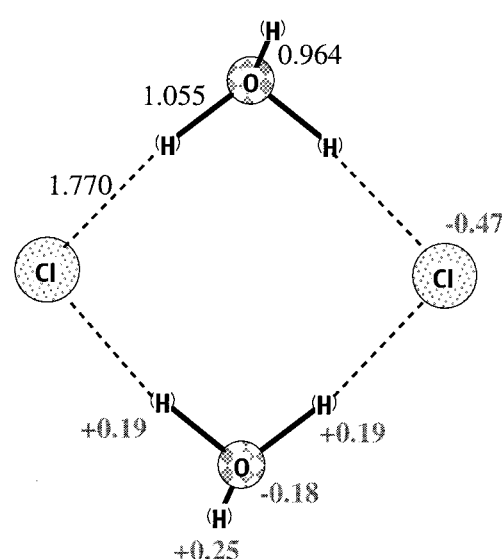

Figure 3. Equilibrium structures (angs.) and partial charges of the hydrogen-bonded and ionic compexes of 2HCl with 2H$_2$O (MP2/TZP level of theory).

(HCl)$_n$(NH$_3$)$_n$ and (HCl)$_n$(H$_2$O)$_n$ Clusters

J. Phys. Chem. A, Vol. 105, No. 36, 2001 **8329**

TABLE 8: Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) for Hydrogen-Bonded and Charge-Separated (HCl)$_2$−(H$_2$O)$_2$ Complexes (MP2/TZP level of ab initio theory)

| | hydrogen-bonded | | | | ionic | | | |
| | frequencies | | | | frequencies | | | |
mode	harm	CC-VSCF	intensities	intrepretation	harm	CC-VSCF	intensities	interpretation
1	3963	3673	305	asym OH str	3869	3603	1	free OH str
2	3963	3688	4	asym OH str	3868	3548	298	free OH str
3	3787	3478	476	sym OH str	2466	2036	0	bonded sym OH str
4	3780	3498	0	sym OH str	2388	2095	4439	bonded sym OH str
5	2568	2296	2163	HCl str	2315	2007	6552	bonded as OH str
6	2526	2237	0	HCl str	1881	1431	0	bonded as OH str
7	1644	1597	0	H$_2$O bend	1729	1593	0	HOH bend
8	1640	1596	76	H$_2$O bend	1656	1522	140	HOH bend
9	852	845	0		1598	1487	77	HOH bend
10	778	774	206		1527	1330	0	HOH bend
11	609	654	262		1237	1153	1	H$_3$O$^+$ umbrella
12	588	634	0		1231	1157	513	H$_3$O$^+$ umbrella
13	500	603	184		852	882	9	
14	447	591	0		737	767	0	
15	340	473	118		498	516	47	
16	318	437	0		495	512	0	
17	215	261	70	Cl−O str	391	429	0	
18	206	279	0	Cl−O str	386	415	160	
19	177	375	0		362	381	0	Cl−Cl, O−O str
20	172	382	155		358	388	239	Cl−O str
21	133	143	18	Cl−O str	354	372	158	Cl−O str
22	119	114	0	Cl−O str	138	82	0	Cl−O str
23	51	67	0	Cl−Cl, O−O str	104	100	0	Cl−Cl, O−O str
24	19	14	0	out of plane	53	71	29	out of plane
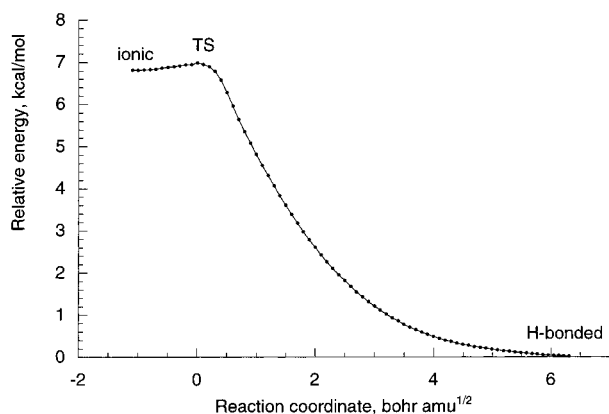
Figure 4. Reaction path for rearrangement between ionic and hydrogen-bonded structures of (HCl)$_2$−(H$_2$O)$_2$ complex.

calculated to be 70 times that of free HCl. There are also two O−H stretches that have rather high intensities and thus may be observable. Their calculated anharmonic frequencies are 3673 and 3478 cm^{-1}. The vibrational spectrum of the ionic structure also has many interesting features. Calculations predict several frequencies with high intensities: one of the two free O−H stretches at about 3550 cm^{-1} and two out of four bonded O−H stretches at about 2100 and 2000 cm^{-1}.

At the MP2/TZP level, the hydrogen-bonded isomer of (HCl)$_2$·(H$_2$O)$_2$ is bound by about 23 kcal/mol with respect to the 2H$_2$O + 2HCl limit, and the ionic isomer is 6.9 kcal/mol higher in energy than the hydrogen-bonded one (Table 5). The minimum energy reaction path is computed for the rearrangement between the ionic and the H-bonded isomers using the intrinsic reaction coordinate (IRC) method[40] with the second-order Gonzalez-Schlegel algorithm[41] and a step size of 0.1 amu$^{1/2}$·bohr. This reaction path is shown in Figure 4. The minimum corresponding to the ionic form is very shallow, and the barrier between the two isomers is very low (less than 1 kcal/mol). Therefore, the ionic isomer is hardly stable in the

gas phase. However, the ionic configuration should have a significant effect on the vibrational level structure, and it may be possible to design time-domain experiments in which the configurations pertinent to the ionic form will be accessed in the dynamics. In addition, similar to the 1:1 complex of HCl with NH$_3$, the ionic structure of (HCl)$_2$·(H$_2$O)$_2$ may become more stable than the hydrogen-bonded one in the environment of rare gas matrices with high polarizabilities (i.e., Ar or Kr).

Because of the large red shift of the H−Cl frequency in the hydrogen-bonded (HCl)$_2$·(H$_2$O)$_2$ complex, its experimental measurement may be challenging. Again, it may be that the O−H stretching motions of the nonbonded water modes can be used to locate and identify the molecule since they are reasonably strong and show a significant shift from the frequencies of free water. If the spectrum of the molecule could be obtained and assigned, it would be especially exciting since the complex is so close in energy to the hydrogen-bonded to ionic-isomerization threshold.

(HCl)$_4$·(H$_2$O)$_4$ Complexes. Cubic hydrogen-bonded and ionic structures of the 4:4 complex of HCl and H$_2$O are shown in Figure 5. For this complex, the ionic isomer is almost 16 kcal/mol more stable than the hydrogen-bonded one. The binding energy of the ionic structure is 72 kcal/mol at the MP2/TZP level, well over four times that of the 2:2 ionic structure. The ionic structure has four equivalent H$_3$O$^+$ fragments with all three O−H bonds pointing toward Cl$^-$ ions. Although the hydrogen-bonded isomer is less stable than the ionic one, it is still considerably stabilized relative to the 1:1 and 2:2 complexes since there are now no "dangling" hydrogen bonds. The ClH···OH$_2$ hydrogen bonds are extremely short, only 1.58 Å, compared to 1.70 Å in the 2:2 complex and 1.86 Å in the 1:1 complex. The H−Cl bonds are about 0.06 Å longer than in the isolated H−Cl molecule. The hydrogen bonding energy, about 56 kcal/mol (MP2/TZP level of theory), is 2.5 times that of the 2:2 complex and 8 times that of the dimer.

Although we have not estimated the height of the barrier between the ionic and hydrogen-bonded isomers of the 4:4
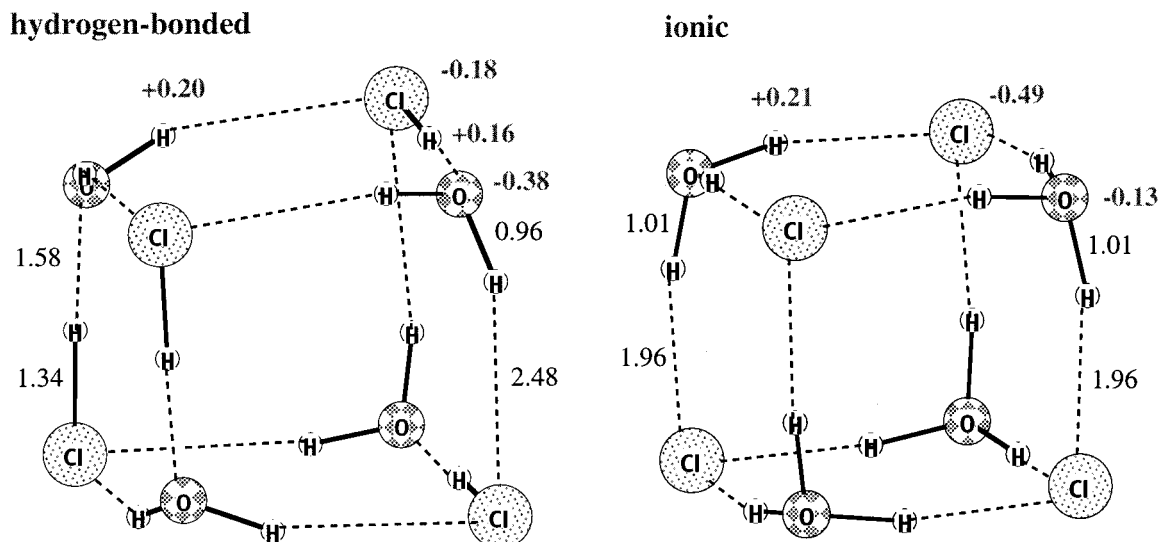
hydrogen-bonded

ionic

Figure 5. Equilibrium bond lengths (angs.) and partial charges of the hydrogen-bonded and ionic compexes of 4HCl with 4H$_2$O (MP2/TZP level of theory).

TABLE 9: Highest (>1000 cm^{-1}) Harmonic Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) for Hydrogen-Bonded and Charge-Separated (HCl)$_4$-(H$_2$O)$_4$ Complexes (MP2/TZP level of ab initio theory)

	hydrogen-bonded			ionic		
mode	harm. freq.	intens.	intrepretation	harm. freq.	intens.	interpretation
1	3895	648	asym OH str	3140	0	sym OH str
2	3889	387	asym OH str	3125	181	asym OH str
3	3889	310	asym OH str	3124	163	aym OH str
4	3882	2	asym OH str	3123	171	sym OH str
5	3784	145	sym OH str	3100	5537	bonded OH str
6	3784	147	sym OH str	3097	5541	bonded OH str
7	3782	8	sym OH str	3097	5562	bonded OH str
8	3781	260	sym OH str	2889	0	bonded OH str
9	2233	3627	HCl str	2889	0	asym OH str
10	2233	3919	HCl str	2888	0	asym OH str
11	2183	64	HCl str	2885	0	asym OH str
12	2140	11	HCl str	2885	0	asym OH str
13	1666	62	H$_2$O bend	1755	0	HOH bend
14	1651	34	H$_2$O bend	1755	0	HOH bend
15	1651	39	H$_2$O bend	1740	99	HOH bend
16	1648	1	H$_2$O bend	1740	98	HOH bend
17				1740	97	HOH bend
18				1697	0	HOH bend
19				1697	0	HOH bend
20				1697	0	HOH bend
21				1381	0	H$_3$O$^+$ umbrella
22				1315	749	H$_3$O$^+$ umbrella
23				1314	744	H$_3$O$^+$ umbrella
24				1313	745	H$_3$O$^+$ umbrella

complex, we believe that both structures are stable and it is possible to isolate each of them experimentally. To help identify the species, we have calculated harmonic vibrational frequencies for both isomers. The harmonic frequencies above 1000 cm^{-1}, as well as the corresponding harmonic intensities, are listed in Table 9. The hydrogen-bonded structure has two very intense H−Cl stretches at about 2200 cm^{-1} (harmonic values). These vibrations can be expected to be even more anharmonic than the H−Cl stretching vibrations of smaller, 2:2 and 1:1 complexes. CC-VSCF calculations for such a large (20 atom) system are computationally very demanding due to the large number of required potential surface points. Therefore, we estimate the anharmonic effects based on the CC-VSCF results for smaller complexes. Assuming that the anharmonic effects on the H−Cl

stretches of the 4:4 complex are about 300 cm^{-1} (only slightly larger than for the 2:2 complex), we obtain an estimated H−Cl stretching frequency of approximately 1900 cm^{-1}. Similar assumptions suggest that the four higher frequency O−H stretches should be located around 3620 cm^{-1}, while the four intermediate ones should appear around 3470 cm^{-1}.

The O−H stretches of the 4:4 ionic structure display quite a different pattern from that of the 2:2 ionic complex: both the highest and the lowest frequency stretches disappear. This is due to the fact that all of the O−H bonds in the 4:4 complex are equivalent. They are elongated compared with the free O−H distances, but not to the same extent as the bonded O−H stretches in the 2:2 ionic complex. Consequently, all the O−H stretch vibrational frequencies of the 4:4 ionic complex (that have non-zero intensities) are located in the region of 3100 cm^{-1} in the harmonic approximation, and probably shift to about 2800 cm^{-1} when anharmonicity is included. This is intermediate between the free O−H stretches (3600−3700 cm^{-1}) and the extremely elongated O−H stretches of the 2:2 complex (2000−2100 cm^{-1}). These 2800 cm^{-1} frequencies can serve as a fingerprint of the (HCl)$_4$·(H$_2$O)$_4$ ionic structure for experimental identification.

Whereas the (HCl)·(NH$_3$) complex is found to switch to the ionic form for the 2:2 combination, that of (HCl)·(H$_2$O) becomes ionic for the 4:4 combination. Since the ionic isomer is calculated to be about 16 kcal/mol more stable than the hydrogen-bonded one, the vibrational motions may be well behaved enough that the anharmonic frequencies estimated here are reasonable approximations to the true frequencies. The highly symmetric, near cubic, structure of the ionic complex results in a rather simple predicted OH stretch spectrum with an extremely intense peak at 3100 cm^{-1} in the harmonic approximation, which we expect to shift to about 2800 cm^{-1} when anharmonicity is included. As synthetic techniques for mixed clusters improve, the observation of this species will be especially exciting.

Although the main focus of this paper has been the infrared spectroscopy of two classes of extremely anharmonic molecules, we comment here on the topic of dissociative ionization of hydrogen halides at ice surfaces. This topic has been the subject of intense theoretical analysis, most of which has been directed at the question: "How many water molecules are necessary to

$(HCl)_n(NH_3)_n$ and $(HCl)_n(H_2O)_n$ Clusters

J. Phys. Chem. A, Vol. 105, No. 36, 2001 **8331**

dissociate a hydrogen halide?" This is a topic of fundamental interest that may have significant implications for atmospheric chemistry. To this end we wish to draw attention to the significant cooperative effect of ionizing two hydrogen halide molecules. Already for the $(HCl)_2 \cdot (H_2O)_2$ complex the hydrogen-bonded structure is only 7 kcal/mol more stable than the ionic one. This barrier is small enough that it could be surmounted, for instance, by a single quantum of O−H stretch excitation. It is likely that additional water molecules could further reduce the barrier. Adding both water and hydrogen chloride molecules achieves a very stable ionic structure at the 4:4 complex. So, the answer to the question of how many water molecules are necessary to dissociate hydrogen chloride will certainly depend on whether the hydrogen chloride molecules are isolated from each other, or whether they are able to migrate toward each other on the ice surface.

Conclusions

In this study, ab initio MP2/TZP potential energy surfaces are employed to compute geometrical structures and anharmonic vibrational spectra for the $(HCl)_n(NH_3)_n$ ($n = 1,2$) and $(HCl)_n$-$(H_2O)_n$ ($n = 1,2,4$) complexes. For the complexes with $n = 1$ and $n = 2$, the correlation-corrected vibrational SCF (CC-VSCF) method is used which explicitly includes anharmonicity and coupling between different normal modes in the calculated vibrational frequencies. Anharmonic effects in these systems are found to be very large, and their incorporation to be crucial for prediction of reliable vibrational spectra.

Although 1:1 HCl·NH₃ and HCl·H₂O complexes are found to have traditional hydrogen-bonded structures (in agreement with previous studies), the H−Cl fragments of these complexes have much longer bond distances and higher ionic character than the isolated H−Cl molecule. This results in a very significant red shift of the H−Cl stretching frequency in these complexes accompanied by a dramatic increase of its infrared intensity. The red shift is extremely large in the HCl·NH₃ complex (840 cm⁻¹). Our calculated anharmonic value for the H−Cl stretching frequency of this complex is 2113 cm⁻¹, which is between the value measured by Andrews et al.[13] in a Ne matrix (2084 cm⁻¹) and their estimated gas-phase value of about 2200 cm⁻¹. Observation of this mode in the gas phase would be especially interesting. However, observation of the H−Cl stretch in the 1:1 HCl·H₂O complex may be easier since the red shift is more modest, 240 cm⁻¹, while still yielding a considerable increase in intensity. Our predicted anharmonic value for the H−Cl stretch in the HCl·H₂O is about 2700 cm⁻¹.

The transition from hydrogen-bonded to ionic structure is found to take place at $n = 2$ for complexes of HCl with ammonia and at $n = 4$ for complexes with water. However, in the 1:1 HCl/ammonia and the 2:2 HCl/water complexes, the ionic structures are already close in energy to the (more stable) hydrogen-bonded ones. These ionic structures are not stable for the gas phase complexes, but may become more stable in matrix environments with high polarization effects. This explains the extreme sensitivity of the experimentally measured spectra of the HCl·NH₃ complex to the matrix environment. In the absence of true gas-phase spectra, it would be very advantageous to obtain spectra in helium nano-droplets to minimize the matrix shifts on the spectra. Just as the experimental data is very sensitive to environment, the theoretical values are extremely sensitive to the calculated potential. A method such as direct CC-VSCF (that calculates anharmonic vibrational frequencies for ab initio potential surfaces) is essential for the systems studied here since empirical force fields, in general, do not describe the transition from hydrogen to ionic bonding correctly.

We note with special interest the $(HCl)_2(H_2O)_2$ case: the hydrogen-bonded form is energetically more stable, but infrared excitation of an O−H or H−Cl stretching frequency should suffice for the cluster to access configurations corresponding to the ionic form. This suggests the possibility of using time-domain spectroscopy to observe the dynamics of ion formation in this system.

For the ionic structures that result for $(HCl)_2 \cdot (NH_3)_2$ and $(HCl)_4(H_2O)_4$ complexes, extremely intense transitions appear in regions very different from those of free HCl, NH₃, and H₂O molecules, and from those of the hydrogen-bonded complexes. For the $(HCl)_2 \cdot (NH_3)_2$ complex these are predicted to occur at about 2470 cm⁻¹ while for the $(HCl)_4(H_2O)_4$ complex they occur in the region of 2800 cm⁻¹. Therefore, these ionic complexes are quite promising candidates for an experimental search.

Finally, we note that the cooperative effects in the "solvation" of hydrogen halides are extremely important. Thus, while four water molecules may not be sufficient to ionize a single hydrogen chloride molecule, the same four water molecules can easily ionize four hydrogen chloride molecules.

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