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Study of HCl Clusters in Helium Nanodroplets: Experiments and ab Initio Calculations as Stepping Stones from Gas Phase to Bulk[†]

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Presented here are the results of the joint theoretical and infrared laser spectroscopic study of the hydrogen chloride monomer and clusters, $(HCl)_n$ ($n = 1-6$), isolated in helium nanodroplets. The H−Cl stretching bands of the dimers and trimers show a large increase in the band intensity as well as low frequency shift with respect to that in a single HCl molecule. The average frequency of the bands for clusters larger than trimers remains approximately constant, which correlates well with the onset of the folded cyclic structure and the full development of the hydrogen bonding in larger clusters. The structure of the clusters was found to be cyclic planar for trimers, slightly twisted square planar for tetramers, envelope-like for pentamers, and folded pseudobipyramidal for hexamers. This change in structure upon an increase of the cluster size can be seen as an early stage of the structural transition to the HCl solid, which consists of zigzag chains of HCl molecules. Spectra of large clusters of about 500 molecules consist of a single band, which encompasses the same frequency range of trimers through hexamers.

1. Introduction

Hydrogen chloride (HCl) is a simple textbook example of a hydrogen-bonding molecule. The HCl dimer is found to be a very floppy and weakly bound complex having dissociation energy of about $D_0 = 5.25$ kJ/mol.[1] The vibrationally averaged structure of the dimer is L-shape planar with an external angle (H···Cl−H) of about 95°.[2−4] Small HCl clusters up to tetramers have been studied via spectroscopy in gas phase,[5−10] liquid,[11] matrix,[12−15] and large Ar clusters[16] as well as by theoretical calculations.[2,17−21] It is well-established that the most stable structures of the HCl trimer and tetramer are cyclic.[3,7,10,20] However, much less is known on the structures of larger HCl clusters. The central questions of this work are how the planar cyclic structure, a characteristic for small clusters, transforms into the three-dimensional structure for larger clusters and whether or not the cyclic structure prevails in larger clusters or is replaced by a branched one where the chlorine atoms serve as double acceptors.

In this paper, we report the results of a joint theoretical and infrared laser spectroscopic study of the hydrogen chloride clusters formed in helium nanodroplets.[22−25] The H−Cl stretching bands of the dimers, trimers, and tetramers show a large increase in the infrared intensity and low-frequency shift with respect to that in a single HCl molecule. The average frequency of the bands for clusters of $\langle n \rangle = 4-500$ remains approximately constant at about 2770 cm^{-1}, which correlates well with the onset of the folded cyclic structure and with the full development of hydrogen bonding in larger clusters. We have identified absorption bands of clusters up to hexamers. Both calculations and experiments indicate that pentamers have an envelope-like structure, whereas a folded chain geometry resembling a bipyramid is identified for hexamers.

2. Experimental Technique

The helium nanodroplet technique has been described in detail elsewhere.[22−25] This method provides an ultimate matrix for formation and high-resolution spectroscopy of molecular clusters. The superfluid state of the droplets contributes to the observation of free molecular rotation and extremely narrow rovibrational spectral lines of the embedded species.[23,26,27] Moreover, molecules embedded independently recombine to form clusters in the interior of the droplets. The helium droplet isolation technique provides fine control over the size of the clusters, whereby the average number of molecules in the clusters is directly proportional to the pick-up pressure. It is well-known that the matrix shift of the vibrational frequencies of the molecules and molecular complexes in helium droplets is very small and is usually about or less than 0.02% of the vibrational frequency.[26−29]

In this work, helium nanodroplets having an average size of about 4×10^3, 1.6×10^4, and 2.5×10^6 atoms are formed by supersonic expansion of high-purity helium (99.9999%) gas at the source pressure of $P_0 = 20$ bar into vacuum through a 5 μm nozzle at a temperature of $T_0 = 15$, 11, and 9 K, respectively. The droplet beam passes through a 1.5 mm diameter skimmer and captures the HCl molecules in a 12 cm long pick-up chamber. The spectra were obtained by using an infrared pulsed laser (Laser Vision, 7 ns duration, 20 Hz repetition rate, 1 mJ pulse energy) having a line width of about 1 and 0.08 cm^{-1} with the injector seeder of the pump Nd:YAG laser (Continuum Powerlite 8020) off and on, respectively. The laser beam is aligned antiparallel to the helium nanodroplet beam in order to maximize the interaction length. The absorption of a laser photon by encapsulated HCl clusters is followed by energy transfer to the host droplets and subsequent evaporation

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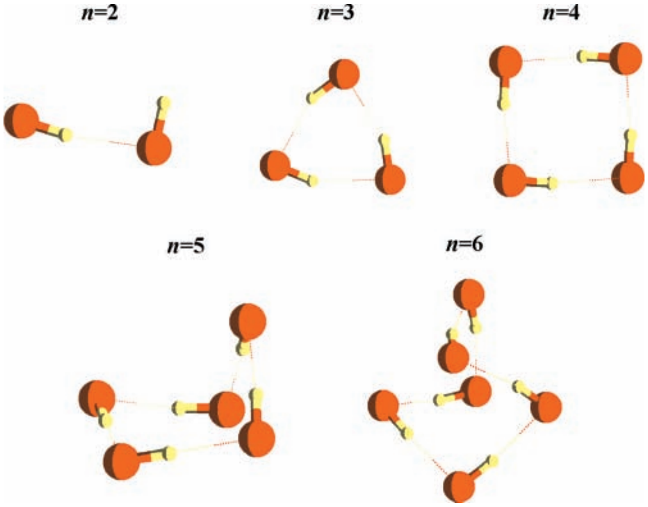

Figure 1. Global minimum structures of $(HCl)_n$ ($n = 2-6$) clusters calculated at the MP2 level with an 6-311++G(3df,3pd) basis set using Gaussian 03.

of several hundred helium atoms. The total flux of the droplet beam is detected by a quadrupole mass filter, which is adjusted to transmit all masses larger than 6 u. The resonant vibrational absorption leads to a transient decrease of the mass spectrometer signal.

3. Results

3.1. Ab Initio Calculations. In spite of the numerous previous theoretical calculations of the structures and vibrational frequencies of small HCl clusters,[2,17−20] there have been very few studies of large HCl clusters beyond the pentamer.[3] Therefore, we have carried out calculations of the structures and vibrational frequencies of HCl clusters up to hexamer using the Møller−Plesset perturbation theory at the second-order (MP2) level. The geometries of all molecules have been fully optimized with the Dunning's correlation consistent polarized valence double-ζ basis set augmented with diffuse functions (aug-cc-pVDZ) basis set, the Pople's triple-ζ basis set (6-311++G**) with *p* polarization functions on hydrogen and *d* polarization functions on all other atoms plus diffuse functions, and the 6-311++G-(3df,3pd) basis set using Gaussian 03.[30] The local minimum structures are verified by observing that no negative vibrational frequencies were obtained with the optimized structures. Figure 1 shows the global minimum geometries of the $(HCl)_n$ ($n = 2-6$) clusters, which are found to be cyclic. We have found that the structure of the tetramer is twisted cyclic. The pentamer is also cyclic with one HCl molecule sitting almost upright with respect to the tetramer ring. The structure of the hexamer resembles a bipyramid. The results, including structures, frequencies, and infrared intensities from the ab initio calculations are presented in the Supporting Information in Figure S1 and in Tables S1−S5.

The structures and relative energies of local minimum isomers of HCl pentamer and hexamer are presented in the Supporting Information (see Figure S2). Some of the low-lying isomers have energies of only few kilojoules per mole higher than that for the global minimum isomers in Figure 1. This small energy difference may be comparable with the error of the calculations. Therefore, calculations alone are not sufficient to determine the isomers of clusters occurring in He droplets. However, as will be discussed in section 4.3 the observed spectra strongly support predominant formation of the global minimum isomers in He droplets.

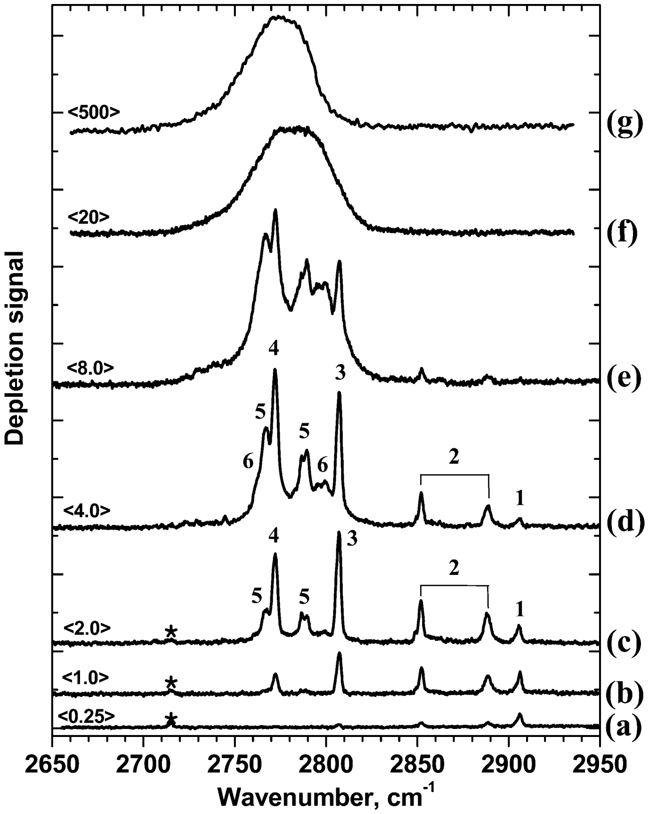

Figure 2. Spectra of HCl molecules and clusters in He droplets of 4000 atoms measured at different pressures of HCl in the pick-up cell: (a) 2.1×10^{-6}, (b) 8.5×10^{-6}, (c) 1.7×10^{-5}, (d) 3.4×10^{-5}, (e) 6.8×10^{-5}, (f) 4.7×10^{-5}, and (g) 1.0×10^{-4} mbar. The numbers in brackets show the average number of molecules captured by the He droplets. The band marked with an asterisk is assigned to H_2O-HCl complexes. The upper spectra (f) and (g) with $\langle n \rangle = 20$ and $\langle n \rangle = 500$ have been measured in larger He droplets of 1.6×10^4 and 2.5×10^6 atoms, respectively.

3.2. Spectra of $(HCl)_n$ in He Droplets. Figure 2 shows the spectra of HCl clusters as measured at different pressures of HCl in the pick-up cell and in He droplets of different average size. The numbers in brackets show the average number of HCl molecules captured by the helium nanodroplets, which is proportional to the pick-up pressure and droplets' capture cross section. The proportionality coefficient in small droplets of about 4000 He atoms has been obtained by fitting the intensity of the cluster bands as a function of pick-up pressure to Poisson functions (see Figure S3 in the Supporting Information). In the case of larger droplets the numbers are estimated assuming geometrical capture cross section. At the lowest HCl pick-up pressure, $\langle n \rangle = 0.25$, the R(0) line of the monomer at 2905.4 cm^{-1} and free (υ_1) and bonded (υ_2) bands of HCl dimer at 2888.0 and 2851.9 cm^{-1}, respectively, are seen in the spectrum. An additional weak band at 2715.0 cm^{-1}, marked with an asterisk, is assigned to the H_2O-HCl complexes. Water molecules are captured from the rest gas in spite of the low residual pressure in the vacuum chambers of less than 10^{-7} mbar.

At higher pick-up pressure, the bands due to trimer through hexamer appear in the spectra at lower frequency. We were not able to identify free H−Cl stretches for the trimer and larger clusters, which indicates that these clusters have a cyclic structure, in agreement with the results of ab initio calculations. The frequencies of the observed bands of small clusters are listed in Table 1 which also contains the measured intensities of dimers, trimers, and tetramers obtained from the spectra as

TABLE 1: Frequency of $(HCl)_n$ ($n = 1-6$) Clusters in He Droplets and in the Gas Phase[a]

	this work, in He			
$(HCl)_n$ n	frequency[b]	relative IR intensity[c]	nozzle beam	ragout jet[d]
1[e]	2905.4	1	2906.2[f]	
2, ν_1[g]	2888.0	2.5	2890.8[h]	2890.0
2, ν_2[i]	2851.9	2.5	2857.2[h]	2856.9
3	2807.7	11	2809.8[j]	2809.7
4	2772.3	22	2774−2778[j]	2776.6
5	2786.4			
5	2789.6			2791.6?
5	2767.6			2770.5?
6	2800.1			
6	2795.4			
6	2762			

[a] The frequencies are in wavenumbers (cm^{-1}). The gas-phase frequencies are for $H^{35}Cl$ molecules and corresponding clusters. [b] Error limits are ±0.2 cm^{-1}. [c] The infrared intensity relative to that of the fundamental band in free HCl molecules of 25 km/mol (refs 51 and 52). The error limits are estimated to be 20%, 30%, and 40% for the dimers, trimers, and tetramers, respectively. [d] From ref 9. [e] R(0) line. [f] From ref 34. [g] $K' = 1 \leftarrow K'' = 0$ sub-band. [h] From ref 5. [i] $K' = 0 \leftarrow K'' = 0$ sub-band. [j] From ref 10.

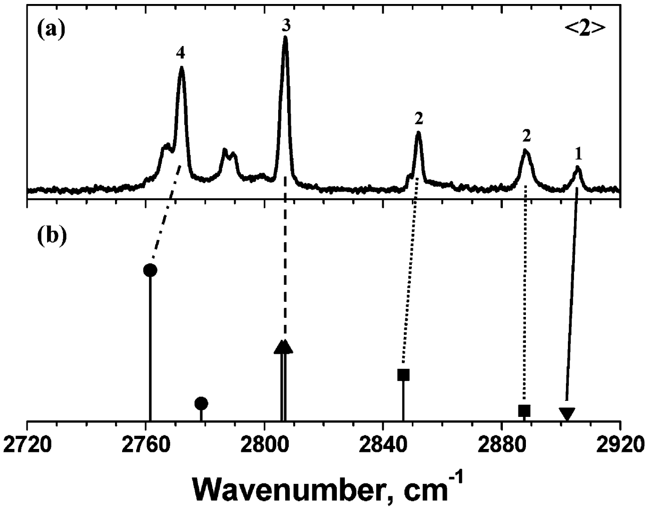

Figure 3. (a) Spectrum of $(HCl)_n$ clusters in He droplets for the average cluster size of $\langle n \rangle = 2$. (b) The scaled ab initio frequencies for the monomers, dimers, trimers, and tetramers are shown by down triangle, square, triangle, and circle, respectively.

described in details elsewhere.[31] The spectra of very large $(HCl)_n$ clusters of about $\langle n \rangle = 20$ and $\langle n \rangle = 500$ in Figure 2, parts f and g, have a broad structureless band around 2780 and 2775 cm^{-1}, respectively, with a full width at half-maximum (fwhm) of about 30 cm^{-1}. The broad band is a convolution of the spectra due to the bonded H−Cl stretching vibration in clusters of different sizes according to Poisson distribution, which cannot be resolved.

Figure 3a shows the measured IR spectrum of the HCl clusters having average size of $\langle n \rangle = 2$ solvated in helium nanodroplets. According to the Poison pick-up statistics,[23,24,31] the droplets have an appreciable population of clusters of up to tetramers. The most intense peak in the spectrum at 2807.7 cm^{-1} is assigned to the cyclic trimer based on the pick-up cell pressure dependence experiments (see Figure S3 in the Supporting Information). It is also in good agreement with results of previous experiments in the gas phase,[5,9,10,32,33] which are listed in Table 1. Similarly, the strong peak at 2772.3 cm^{-1} is assigned to the cyclic tetramers. Figure 3b shows the calculated spectra for the clusters up to tetramer [monomer (down triangle), dimer (square), trimer (triangle), and tetramer (circle)]. It is seen that the scaled (0.960 in order to account for anharmonicity) calculated frequencies are in good agreement with the experimental results.

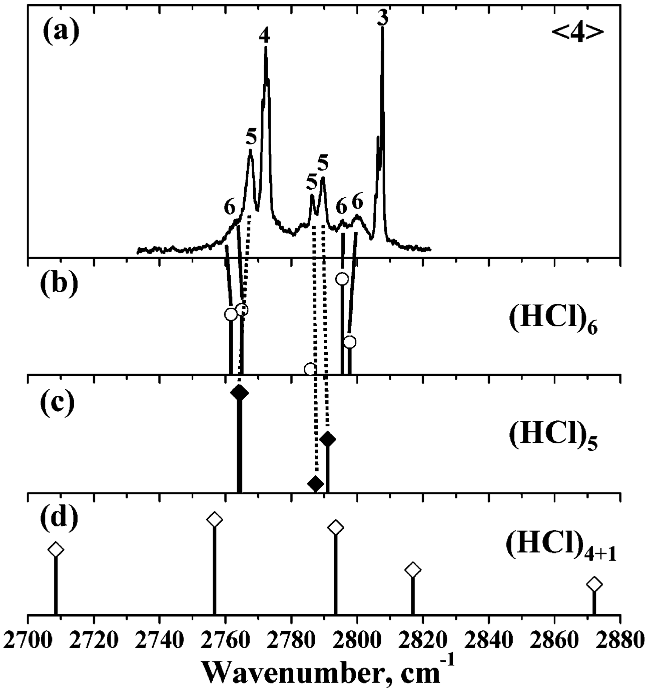

Figure 4. (a) High-resolution ($\delta\nu = 0.08$ cm^{-1}) spectrum of $(HCl)_n$ clusters in He droplets; $\langle n \rangle = 4$. The stick spectra are the results of calculations for the cyclic hexamers (b) and pentamers (c) using the MP2/aug-cc-pVDZ level of theory. Panel d shows the spectrum of the tail (4 + 1) isomer of the pentamer calculated with the same basis set.

A higher resolution spectrum of the clusters having an average number of four HCl molecules is shown in Figure 4a. The pick-up pressure dependence experiments were used to assign the experimental vibrational bands of pentamers and hexamers indicated in Figure 4. The relative intensities of the hexamer bands are smaller as compared to pentamer bands due to a factor of two-thirds smaller abundance of the former in the droplets at the used experimental conditions. The results of the ab initio calculations for the cyclic pentamer and hexamer of HCl clusters are shown in Figure 4, parts c and b, respectively. Finally, the spectrum in Figure 4a also has a contribution from larger clusters of $n > 6$, which are responsible for the broad underlying band having a width of about 20 cm^{-1} (fwhm). This band is more obvious in the spectra of larger clusters in Figure 2e−g.

4. Discussion

4.1. Monomer. We have assigned the 2905.4 cm^{-1} peak to the R(0) rovibrational line of the single HCl molecules. The R(0) line is shifted toward lower frequency by about 0.9 cm^{-1} as compared to the gas-phase value of 2906.25 cm^{-1}.[34] A somewhat larger shift of 2.2 cm^{-1} has been previously observed in the case of HF molecules in He droplets.[35,36] Because the rotational constants of the light molecules in He droplets were found to be very similar to those in the gas phase,[31,35,37−40] the measured shift should be very similar to that of the vibrational band origin in He droplets, which can be estimated to be at 2885.3 cm^{-1} by using the rotational constant of the free HCl molecules of 10.14 cm^{-1}.[34]

It is known that the relaxation time of the vibrationally excited HF molecules is much longer than the flight time of the droplets. Based on the similarity with HF molecules, we expected a similar long relaxation time of the vibrationally excited HCl. In order to estimate the lifetime, we have compared the time-resolved depletion signal originating from the laser excitation of monomers and trimers, in which the latter are expected to have a short relaxation time. From the ratio of the two signals, the lifetime of the vibrationally excited HCl molecules was estimated to be about 0.6 ms. This time, although long, is shorter than the time of flight of the molecules from the pick-up cell to the mass spectrometer of about 3 ms. Therefore, most of the excited molecules have sufficient time to relax, and on average only an estimated 10% of the molecules remain in the vibrationally excited state upon reaching of the detector. Thus, the relaxation time of the HCl is shorter than that in HF, which correlates well with about 1000 cm^{-1} smaller vibrational quantum in the former.

4.2. Dimer. The frequencies of the two dimer bands are in good agreement with the previous measurements in the gas phase, see Table 1. $(HCl)_2$ is a prolate nearly symmetric top, having rotational constants of $A = 11.0$ cm^{-1}, $(B + C)/2 = 0.065$ cm^{-1}.[5,41] The band at 2888.0 cm^{-1} is assigned to the free H−Cl stretch mode (ν_1), which is predominantly a perpendicular band. Thus, the observed transition in He droplets at $T = 0.38$ K should be assigned to the $K' = 1 \leftarrow K'' = 0$ sub-band. The measured frequency compares well with that of the $K' = 1 \leftarrow K'' = 0$ sub-band in the gas phase at 2890.8 cm^{-1}.[5] The band at 2851.9 cm^{-1} is assigned to the bonded H−Cl stretching vibration (ν_2), which is a predominantly parallel band. The free (ν_1) and bonded (υ_2) H−Cl stretching bands of the dimers in He droplets are shifted toward lower frequency by ∼3 and ∼5 cm^{-1}, respectively, as compared to corresponding bands in the gas phase.

The frequency difference between the υ_1 and υ_2 stretches of 36 cm^{-1} is very close to the calculated value of 40 cm^{-1}. However, calculations, which were done in this work at geometry close to equilibrium, gave an intensity ratio for the υ_2 and υ_1 bands of about 4:1, i.e., showing a large expected increase in the intensity of the bonded stretch. On the other hand, the experimental results indicate the integrated intensity ratio of the bands to be close to 1:1. Each of the bands is enhanced by about a factor of 2.5 with respect to the monomer band as shown in Table 1. This large discrepancy between the results of calculations and experiment could be attributed to the intensity sharing due to the extensive mixing of the υ_2 and υ_1 states in the cause of the rapid interchange tunneling in the HCl dimers.[5] Higher resolution spectra of the monomer and dimer as well as the magnitude of the interchange-tunneling splitting of the $(HCl)_2$ in helium droplets will be discussed elsewhere.[42]

4.3. $(HCl)_n$, $n = 3-6$, Clusters. We begin this discussion by reviewing a number of related results from the previous helium nanodroplet studies of other H-bonded linear molecules, such as HCN[24,43] and HF.[24,44] $(HCN)_n$ clusters obtained in He droplets were found to grow as a linear chain up to $n = 7$ subunits long. The formation mechanism includes the guidance of the incoming molecules by the electric field of the previously formed cluster and the stabilization of the cluster in a linear configuration which corresponds to a local potential energy minimum. The size of the linear clusters was assumed to be limited by the size of the host He droplet. On the other hand, $(HF)_n$ complexes in He droplets are cyclic up to $n = 4$, whereas the spectrum of $(HF)_5$ was assigned to a cyclic tetramer with an additional molecule in the tail arrangement.[24,44] The preference of the cyclic structure is related to a large quadrupole moment of the HF molecules. Another factor is the large rotational constant of the HF molecules, which must facilitate the attainment of the global minimum structure via tunneling. In particular, the tunneling is presumably responsible for the insertion of the fourth HF molecule into the preformed cyclic trimer. Observation of the branched $(HF)_5$ complexes in He droplets shows that the fifth dangling HF molecule cannot overcome the insertion barrier into the cyclic tetramer which has almost twice larger total binding energy than that of the cyclic trimer due to a smaller ring strain.[3,35] In contrast, calculations predict that the global minimum structures are cyclic for $(HF)_n$ ($n = 3-10$).[3]

The binding in $(HCl)_2$ of 5.25 kJ/mol is more than a factor of 2 weaker than that in $(HF)_2$ of about 12.4 kJ/mol.[1,45,46] An even larger difference is found in the B3LYP/auc-cc-pVDZ calculations of binding energy of tetramers of HCl and HF of 20.8 and 91.5 kJ/mol,[3] respectively. Therefore, the HCl dimers are much floppier than HF dimers,[2,4,5,19,47] and the HCl molecules in clusters must experience a larger amplitude motion as compared to their HF counterpartners.[5] This is consistent with the results of this work that an incoming HCl molecule is able to insert itself into the larger preformed cyclic clusters at the low temperature of He droplets to form larger cyclic complexes, at least up to hexamer. The single absorption line in the spectra of trimers and tetramers suggests a nearly planar ring structures in agreement with calculations. Splitting of the lines in the pentamers and hexamers spectra is consistent with nonplanar geometry. The comparison of the measured and calculated band patterns shows that pentamers and hexamers have envelope and bipyramidal structures, respectively. Figure 4d shows the stick spectrum of a branched pentamer, which has an HCl molecule attached to the cyclic tetramer, $(HCl)_{4+1}$. It is seen that the band pattern in the panel d of Figure 4 is very different from the observed experimental spectrum (Figure 4a). Therefore, the HCl pentamer formed in helium droplets should be assigned to a cyclic isomer, which has been calculated to be a global minimum structure. The calculated spectra of the low-energy isomers of hexamer are compared with the experimental spectrum in the Supporting Information (see Figure S4 in the Supporting Information). This comparison supports our assignment of the hexamer to a cyclic bipyramidal structure as shown in Figure 1.

Figure 5 shows frequency shift, $\Delta\upsilon$, of the average frequency of the cluster bands with respect to the band origin of the monomer, which was obtained in experiment and calculations. The last are unscaled harmonic frequencies.

The measured infrared intensities of the clusters are shown in Table 1. The overall infrared intensity for dimers increases about a factor of 5 with respect to single HCl molecules, which is consistent with the formation of the hydrogen bond. In trimers, in spite of the presence of three hydrogen bonds, the infrared intensity increases only by a factor of about 2 as compared to dimers, which is probably related to the strained structure of the trimer. Finally, in tetramers, the intensity is a factor of about 4 larger than in dimers, which correlates well with the four hydrogen bonds and an approximate 90° angle between HCl molecules in tetramer as seen in the crystals.[48,49] With respect to the monomer, the infrared intensity per hydrogen bond increases in the tetramer by about a factor of 5. In comparison, in HCl crystal[50] the transition dipole moment per molecule has been found to be about 190 km/mol (with dielectric correction), which is a factor of about 7.5 larger than that in the gas phase of about 25 km/mol.[51,52]

4.4. Large $(HCl)_n$ Clusters. We observed that the structure of hexamers closely resembles a bipyramidal geometry for the

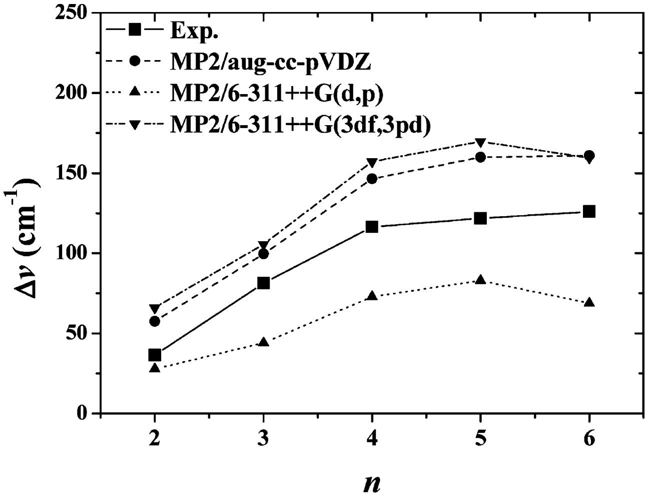

Figure 5. Average frequency shift of the bonded HCl vibration with respect to the band origin of the single HCl molecules vs cluster size *n*. The squares with the solid line are the experimental results of this work. Filled circles, up triangles, and down triangles are results of the MP2 level of theory with aug-cc-pVDZ, 6-311++G(d,p), and 6-311++G(3df,3pd) basis sets.

minimal energy configuration with only singly hydrogen-bonded atoms and close packing. It would be interesting to see if this trend continues in larger clusters. The spectra for larger clusters of $\langle n \rangle = 20$ and $\langle n \rangle = 500$ are shown in Figure 2, parts f and g, respectively. The spectra of large clusters are structureless rather symmetric bands having frequency (bandwidth) of 2780-(30) and 2775(30) cm^{-1}, respectively. It is remarkable that band centers of the large clusters are very close to the average frequency of pentamers and hexamers of 2777 and 2781 cm^{-1}, respectively. About 5 cm^{-1} smaller frequency in $\langle n \rangle = 500$, as compared to $\langle n \rangle = 20$, is probably a finite size effect. Moreover, the band breadth correlates nicely with the spread of the bands in pentamers and hexamers of about 30 cm^{-1}. The spectra of the large clusters in Figure 2, parts f and g, show no free H−Cl stretching bands at around 2886 cm^{-1}. This is consistent with the two different structures of the cluster. One is the branched structure, in which all HCl molecules on the surface of the clusters are hydrogen bonded to the chlorine atoms of the inner HCl clusters. In such a cluster, the hexamers provide the most efficient hydrogen-bonding sites (chlorine pointing out) for additional approaching HCl molecules, which makes the Cl atoms of the molecules in the ring function as double acceptors. The vibrational frequency of the double-acceptor HCl molecules in pentamers and hexamers is expected to be about 2709 and 2707 cm^{-1} and of the donor tail molecules about 2872 and 2858 cm^{-1}, respectively, as suggested by results of the calculations for the 4 + 1 and 5 + 1 clusters in Figure 4d and Figure S4d in the Supporting Information, respectively. The large spread of the absorption bands in the branched clusters is in disagreement with rather narrow measured band in large clusters of about 30 cm^{-1}. Another structure, which is in agreement with the present observations, is the folded cyclic structure that extends to much larger clusters. X-ray diffraction studies show that the HCl crystal structure is face-centered orthorhombic with respect to the chlorine atoms, having planar zigzag chains with the HCl molecules each serving as a single hydrogen-bond donor and acceptor with angles between the molecular axis of about 90°.[48,49] Figure 1 shows that the similar structure, but folded, is found for the tetramers, pentamers, and hexamers. Therefore, we can speculate that the singly connected hydrogen-bonded cyclic structure may proliferate to larger HCl clusters.

The spectrum of the large clusters deviates from the spectra in HCl low-temperature crystals.[50,53] The latter have two bands at 2708 and 2749 cm^{-1} ($\delta\nu \sim 20$ cm^{-1}), which were assigned to the Davidov-type doublet due to exciton interaction between the molecules arranged in parallel zigzag chains.[54] The parallel zigzag chain pattern is not expected to be found in clusters, because such structures are energetically unfavorable due to the large number of unsaturated H-bonds on the surface. The spectrum of large clusters resembles that of a metastable low-temperature phase or a high-temperature disordered phase having absorption bands centered around $\nu = 2780$ and $\nu = 2768$ cm^{-1}, respectively.[53,55]

5. Conclusion

In this work we report the infrared spectra of the HCl clusters in He droplets. Structure and spectra of clusters up to hexamer have also been calculated at the MP2 level with various basis sets. We obtained that clusters up to hexamer formed in helium nanodroplets have cyclic structure which corresponds to the global energy minimum. This finding indicates that an incoming HCl molecule is able to insert into the preformed cyclic clusters at an extremely low temperature of $T = 0.38$ K. The results indicate a nonplanar twisted structure for tetramers, an envelope-like structure for pentamers, and a pseudobipyramid for hexamers. The absence of the bands due to free H−Cl stretches in the spectrum of large $(HCl)_n$ clusters ($n > 20$) is consistent with either branched structures with the surface HCl molecules oriented with the hydrogen atoms toward the cluster center or a cluster consisted of a folded chain of HCl molecules.

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Supporting Information Available: Figures of the $(HCl)_n$ ($n = 4-6$) clusters calculated at the MP2 level, pick-up pressure dependence of the intensity of several observed bands, and tables of the results of the $(HCl)_n$ ($n = 4-6$) clusters from MP2 calculations with various basis sets [aug-cc-pVDZ, 6-311++G-(d,p), and 6-311++G(3df,3pd)]. This material is available free of charge via the Internet at http://pubs.acs.org.

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