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Electron states of the HCl dimer

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The He I photoelectron spectrum of HCl dimer has been recorded and the observed ionizations at 12.3, 13.6, 15.1 and 17.0 eV have been assigned to different orbitals on the basis of molecular orbital calculations. The observed first adiabatic IE (11.9 eV) agree well with the value of 11.91 eV from a photoionization study of the dimer. The two HCl units in the dimer are nonequivalent and there is significant interaction between the σ orbitals. Both the calculations and the experiment show that the geometry undergoes considerable distortion on ionization.

INTRODUCTION

Dimers of hydrogen halides constitute the simplest class of hydrogen bonded systems. These dimers have been investigated by rotational-vibrational spectroscopy in the free state as well as in rare gas matrices.¹⁻⁵ A majority of these studies pertain to the HF dimer. A high resolution study of the HCl dimer⁴ suggests an orthogonal structure with rapid tunneling between the equivalent forms. The zero-point center-of-mass separation of the constituents is 3.797 Å calculated from the rotational constants. Based on absolute infrared intensities,⁵ the zero-point dissociation energy of the HCl dimer is estimated to be rather small (5.2 kJ mol⁻¹).

According to the electrostatic model,⁶ the monomer units are nearly orthogonal in the dimer. Molecular orbital (MO) calculations⁷⁻¹¹ predict a nearly linear hydrogen bond geometry for the HCl dimer, different from that predicted by the electrostatic model. Expansion of the basis sets does not result in any significant change in the dimer structure and higher order correlation terms do not affect the hydrogen bond energy substantially.⁷ MO calculations at the self-consistent-field (SCF) level using core pseudopotentials and polarized split-valence basis sets give equilibrium geometries which support the electrostatic model.¹¹ An analysis of the spectroscopic properties and charge densities, however, shows that charge-transfer effects are important.

In spite of all the various studies mentioned above, the experimental electronic structure of the hydrogen halide dimers has not been explored hitherto. We have employed ultraviolet photoelectron spectroscopy (UVPEs) to investigate the HCl dimer, making use of a molecular beam sample inlet to obtain a high concentration of the dimer species. It is to be noted that photoelectron spectroscopy has been employed recently to study the electron states of van der Waals molecules.¹²⁻¹⁴ These studies have revealed that the ionic states of van der Waals molecules are generally strongly bound, contrary to expectation. In most of the systems, the ionic state potential minimum is far removed from the Franck-Condon region and the structures undergo large distortions on ionization. In water dimer, for example,¹⁵ the

ground ionic state potential minimum corresponds to that of a complex between H₃O⁺ and OH. In the present study, the observed ionization energies (IEs) of the HCl dimer have been assigned to the different orbitals based on SCF/16-31G* molecular orbital calculations. The study supports the nonequivalence of the two HCl units in the dimer⁸ and indicates considerable interaction between the σ orbitals.

EXPERIMENTAL

The photoelectron spectrum was measured with a double chamber photoelectron spectrometer¹⁶ fabricated in the laboratory for the study of weak molecular interactions. HCl gas subjected to repeated freeze-pump-thaw cycles was collected in glass bulbs at about one atmosphere pressure. The bulbs were connected to the spectrometer through a variable leak valve. A high pressure pirani gauge monitors the stagnation pressure behind the nozzle. Glass nozzles of two different diameters (0.15 and 0.10 mm) were used in the experiment. The UVPE spectrum was studied in the 10-20 torr stagnation pressure range. The HCl monomer spectrum was obtained at the lowest stagnation pressure. The spectrometer resolution was 50 meV for 5.3 eV kinetic energy electrons. Each spectrum consisted of 1000 data points acquired by a personal computer.

MO calculations were carried out at the 6-31G* level using the GAUSSIAN 86 system of programs.¹⁷ The 6-31G* basis set is generally satisfactory in predicting geometries, dipole moments, and interaction energies of van der Waals systems.¹⁸ In our calculations, the geometries of both the dimer and the monomer were fully optimized. For the dimer, we have considered the C_s structure since both the experimental and the theoretical studies point toward this conclusion.⁷

RESULTS AND DISCUSSION

In Fig. 1 we show the He I photoelectron spectra of HCl at different stagnation pressures. The figure shows the pressure dependence of the spectrum in the 10-15 torr range. The spectrum marked (a) is due to the monomer which shows two bands with vertical IEs of 12.75 and 16.25 eV due to the ²Π and ²Σ states, respectively.¹⁹ With increase in the stagnation pressure, we see the emergence of four new features shown by arrows in the figure. The vertical IEs corresponding to these features are 12.3, 13.6, 15.1, and 17.3 eV

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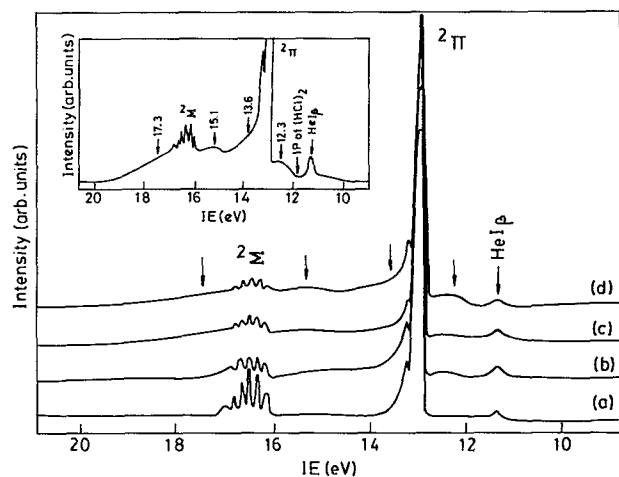


FIG. 1. HeI PE spectrum of HCl at different stagnation pressures. The nozzle stagnation pressures are (a) 10 torr, (b) 11 torr, (c) 12 torr, and (d) 13 torr. The new features are indicated by arrows. Note the HeI β feature. Each spectrum is normalized with respect to the 2π peak which is of ~ 3000 c/s. The inset shows an expanded spectrum of the monomer/dimer mixture. The spectrum is truncated for clarity.

and the adiabatic IE of the first feature is 11.9 eV. It is known in the case of van der Waals molecules that there is a limiting stagnation pressure below in which only dimers are formed.²⁰ When the stagnation pressure was increased above 17 torr, we observed that the peak maxima corresponding to the new features shift to still lower IEs showing the formation of heavier clusters. Below this pressure, an increase in the nozzle stagnation pressure only increased the intensity of the four features mentioned earlier. We believe that these four features are due to the HCl dimer. Furthermore, the adiabatic IE (11.9 eV) of the first peak in the spectrum is remarkably close to the adiabatic IE of (HCl) $_2$ obtained from the photoionization study²¹ (11.91 eV), thereby suggesting that we are dealing with the dimeric species. From the band intensities of the monomer and the dimer, the concentration of the dimer calculated²² in the nozzle expansion is $\sim 2\%$.

The orbital energies from the MO calculations are generally correlated to the observed IEs from the UVPE spectrum on the basis of Koopmans' approximation.²³ In the case of π orbitals, the enhanced relaxation effects generally play an important role in deciding the IE shift accompanying dimerization.²⁴ In the case of other orbitals, experimental IE shifts between the free components and the complexes are dominated by electrostatic effects and Koopmans' approximation generally holds good.²⁵

We have computed the orbital energies at the SCF/6-31G* level for the neutral HCl dimer. We have also carried out calculations for the ground and first excited states of the dimer ion. The optimized geometries for the neutral ground state and the first two ionic states are given in Fig. 2. The optimized neutral dimer structure is one in which the monomers are nearly orthogonal with a hydrogen bond length of 2.90 Å. In the $2A''$ state, the geometry resembles that of the

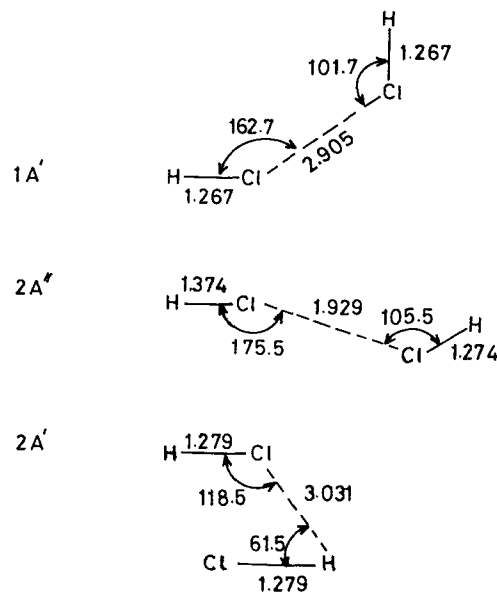


FIG. 2. Predicted geometries of the various states of the HCl dimer.

ground state, but the hydrogen bond length is shorter (1.93 Å). In the $2A'$ state, the structure undergoes considerable distortion and the optimized geometry is nearly rectangular. The hydrogen bond length is 3.03 Å in the $2A'$ state, greater than the neutral state value by 0.13 Å; we do not see any evidence for proton transfer unlike in the case of H $_2$ O dimer ion.¹⁵

The 6-31G* MO calculations give a binding energy of 4.6 kJ mol $^{-1}$ for the HCl dimer and it reduces to 3.8 kJ mol $^{-1}$ when zero-point contribution is included.⁷ This value may be compared with the experimental zero-point dissociation energy of 5.2 kJ mol $^{-1}$ deduced from absolute infrared intensities.⁵

The first observed ionization at 12.3 eV is clearly due to the chlorine lone pair of HCl dimer. The calculated orbital energy for the highest occupied $4a''$ orbital (chlorine lone pair) is 12.71 eV and the next lone pair MO ($14a'$) has an energy of 12.77 eV. Our Δ SCF calculations give vertical ionization energies of 11.38 and 12.33 eV for the $2A''$ and $2A'$ states, respectively. While the vertical IEs are separated by 1 eV, the adiabatic IEs are close (11.12 and 10.90 eV, respectively, for the two states). The calculations show a crossover between the two states near the potential minimum. We assign the first photoelectron feature to these closely lying states. Although the difference in the vertical IEs of the monomer and the dimer is small (0.45 eV), the difference between the adiabatic IEs is large (0.85 eV) showing that the structure undergoes a significant distortion on ionization in agreement with the calculations.

The next ionization (at 13.6 eV) is from the nonbonding chlorine lone pairs of the proton acceptor. Koopmans' IEs for these orbitals are 13.37 and 13.41 eV. In the experiment, we observe only one feature corresponding to this ionization at 13.6 eV. The Koopmans' IE for the nonbonding chlorine lone pair of the monomer is 12.93 eV. The theoretical shifts

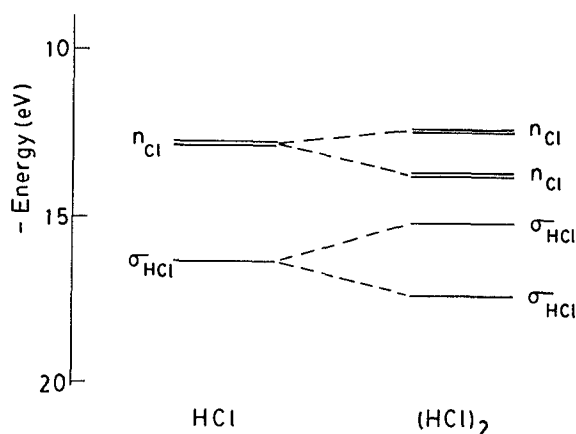
TABLE I. Experimental IEs from HeI PES, theoretical orbital energies, and assignments of the HCl dimer.

Vertical IE (eV)	SCF/6-31G*		
	$-\epsilon$ (eV)	Character	MO
12.3	12.71, 12.77	n_{Cl}	$4a''$, $14a'$
13.6	13.37, 13.41	n_{Cl}	$3a''$, $13a'$
15.1	16.92	σ_{HCl}	$12a'$
17.3	17.55	σ_{HCl}	$11a'$

for the dimer from the free monomer value are -0.17 and $+0.44$ eV, respectively, for the two nonbonding levels. This shift arises from a charge-transfer of $0.005 e$ from the proton acceptor to the donor on dimerization. The importance of charge transfer in determining the properties of the dimer has also been pointed out by Hannachi and Silvi.¹¹ Assuming Koopmans' approximation to hold, the experimental shifts of the lone pair orbitals in the dimer are -0.45 and $+0.85$ eV, respectively. The apparent large shift of the second band suggests that there may be vibrational excitations accompanying this ionization.

The last two ionizations at 15.1 and 17.3 eV are from the σ_{HCl} orbitals. The Koopmans' IEs are 16.92 and 17.55 eV for these levels. Theoretical splitting of the σ levels is 0.63 eV and the shifts from the free monomer value are -0.18 and $+0.45$ eV. In Table I we list the observed IEs along with the calculated orbital energies and assignments. We see that the σ orbital undergoes a shift of ~ 1.1 eV on dimerization. The character of the orbitals described in Table I is on the basis of the linear combination of atomic orbital (LCAO) coefficients. The coefficients show that there is negligible mixing of the monomer orbitals on complexation. The photoelectron spectrum of HCl dimer assigned in Table I is thus in accordance with the structure showing considerable interaction between the σ orbitals, but marginal interaction between the orbitals of π symmetry. The MO level scheme for the HCl dimer based on our data is shown in Fig. 3. The diagram reflects the donor-acceptor picture of hydrogen bonding. Based on the present study, we are not able to comment on the nature of bonding in the molecular ion *vis a vis* the neutral dimer (ion-dipole vs dipole-dipole, etc.).

Taking the ground state dissociation energy of the dimer and the adiabatic IE of monomeric HCl, the dissociation energy for the ${}^2A'$ state is estimated to be 0.5 eV. The estimated dissociation energy is only a lower estimate since the adiabatic IE may not correspond to the minimum of the potential surface in such weakly interacting systems. It was not possible to deduce the adiabatic IEs of the other states due to the overlapping monomer features.

FIG. 3. Molecular orbital scheme of the HCl dimer showing significant interaction between the orbitals of σ symmetry.

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