November, 1979] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (11), 3223—3225 (1979) 3223

Photoelectron Spectra of Hydrogen-bonded Complexes

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(Received April 26, 1979)

The photoelectron spectra of typical hydrogen-bonded complexes, CF_3COOH–$(C_2H_5)_2NCH_3$, CF_3COOH–$(n\text{-}C_3H_7)_3N$, CF_3CF_2COOH–$(C_2H_5)_2NCH_3$, and CF_3CF_2COOH–$(n\text{-}C_3H_7)_3N$ were observed in the gas phase. It was found that the nonbonding orbital of the proton acceptor is stabilized significantly by hydrogen-bond formation while the three higher occupied orbitals of the proton donor are destabilized. The large orbital energy changes due to hydrogen-bond formation strongly support the charge-transfer model for the hydrogen bond.

Photoelectron spectroscopy is expected to give effective informations concerning the electronic structure of hydrogen-bonded systems and also concerning the nature of hydrogen bond. This is because the photoelectron spectrum of the hydrogen-bonded complex gives the orbital energy shifts due to hydrogen-bond formation within the limitation of Koopmans' theorem.

In a previous paper,[1)] we reported the photoelectron spectra of some electron donor-acceptor complexes in the gas phase, and found that this technique was quite effective for the study of the intermolecular interaction. In this paper, in order to clarify the nature of hydrogen bond, we have studied the He I photoelectron spectra of hydrogen-bonded complexes between carboxylic acids as proton donors and alkylamines as proton acceptors in the gas phase. In actuality, *N*,*N*-diethylmethylamine and tripropylamine are taken as proton acceptors, and trifluoroacetic acid and pentafluoropropionic acid as proton donors.

Experimental

N,*N*-Diethylmethylamine (DEMA) and tripropylamine (TPA) were purified by distillation. Commercially available trifluoroacetic acid (TFAA) and pentafluoropropionic acid (PFPA) were used without further purification. Purity of the amines and the carboxylic acids was checked by NMR spectroscopy. An aliphatic amine and a carboxylic acid were introduced through needle valves into a 5-liter gas reservoir and were mixed with each other. The nonexistence of chemical products except for hydrogen-bonded complexes in the mixtures was checked by NMR spectroscopy for the liquid phase. The mixed gas was introduced into the ionization chamber of a photoelectron spectrometer, the details of which were described in a previous paper.[2)] The photoelectron spectra of the hydrogen-bonded complexes and their component molecules were measured at room temperature, the He I resonance line being used as the excitation source. At the initial stage of the measurement of the mixed gases, the bands of the free amines added in slight excess appear strongly in addition to those of the hydrogen-bonded complexes. The bands of the free amines, however, rapidly decreased in intensity, and the spectra turned out to be composed almost completely of the bands of the hydrogen-bonded complexes.

Results and Discussion

The photoelectron spectra of hydrogen-bonded systems such as TFAA–DEMA, PFPA–DEMA, TFAA–TPA, and PFPA–TPA are shown in Fig. 1, together with those of component molecules. The measurements were performed with very high sensitivity for the hydrogen-bonded complexes because of their low vapour pressure. This is the reason why the signal of only a trace of water appears in the spectra of the complexes. The vertical ionization potentials (I_v) of the hydrogen-bonded complexes and the component molecules are summarized in Table 1.

Thomas[3)] has assigned the first band of TFAA to the nonbonding (n) orbital mainly localized on the oxygen atom of the carbonyl group, the second band to a π orbital, and the third band to a σ orbital which is denoted by n′ hereafter. The shapes of the higher occupied molecular orbitals of TFAA obtained by the CNDO/2 calculation are schematically shown in Fig.

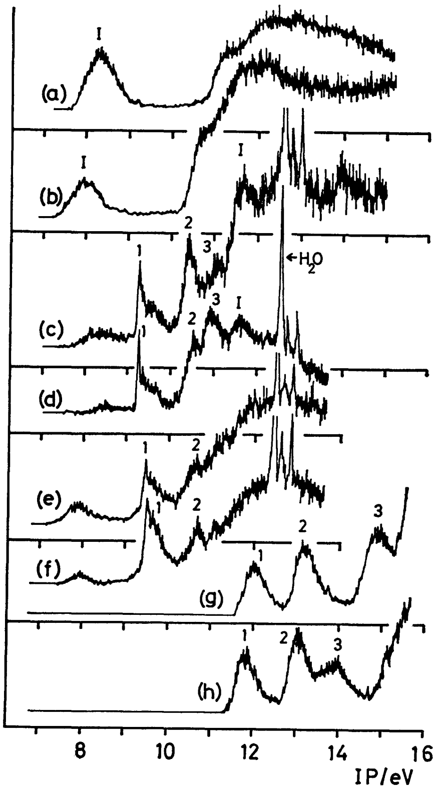

Fig. 1. Photoelectron spectra of hydrogen-bonded complexes and their component molecules: curve (a), DEMA; curve (b), TPA; curve (c), TFAA–DEMA complex; curve (d), PFPA–DEMA complex; curve (e), TFAA–TPA complex; curve (f), PFPA–TPA complex; curve (g), TFAA; curve (h), PFPA.

TABLE 1. VERTICAL IONIZATION POTENTIALS, $I_V(J)$, OF HYDROGEN-BONDED COMPLEXES AND THEIR COMPONENT MOLECULES

Species	$I_V(J)$/eV			
$J^{a)}$	1	2	3	I
TFAA	12.00	13.16	14.83	
PFPA	11.94	13.09	14.04	
DEMA				8.32
TPA				7.94
TFAA-DEMA	9.26	10.41	11.23	11.64
PFPA-DEMA	9.24	10.38	10.94	11.63
TFAA-TPA	9.53	10.71		
PFPA-TPA	9.49	10.67		

a) J shows the numbering of the photoelectron spectral band given in Fig. 1 from which the vertical ionization potential in this table was obtained.

TABLE 2. PHOTOELECTRON SPECTRAL BAND SHIFTS, $\Delta I_V(J)$, DUE TO HYDROGEN-BOND FORMATION

Species	$\Delta I_V(J)$/eV			
	Carboxylic acid			Amine
$J^{a)}$	1(n)	2(π)	3(n′)	I(n)
TFAA-DEMA	−2.74	−2.75	−3.60	3.32
PFPA-DEMA	−2.70	−2.71	−3.10	3.31
TFAA-TPA	−2.47	−2.45		
PFPA-TPA	−2.45	−2.42		

a) See the footnote a) for Table 1.

2. The ordering of the first three bands of PFPA may safely be regarded to be the same as in the case of TFAA judging from the band shapes and positions. The first band of the alkylamine is assigned to the nonbonding orbital localized on the nitrogen atom.

Let us turn to amine–carboxylic acid systems. As is seen in Fig. 1 which shows the photoelectron spectra of the TFAA–DEMA, PFPA–DEMA, TFAA–TPA, and PFPA–TPA systems, each of the amine–carboxylic acid systems has several bands pertinent to the corresponding hydrogen-bonded complex, in addition to the band around 8 eV due to the corresponding free amine added in excess. The bands due to the complex are numbered as shown in Fig. 1. The energy separation between bands 1 and 2 of the hydrogen-bonded complex is nearly equal to that of the free carboxylic acid. This means that bands 1 and 2 of the hydrogen-bonded complex correspond to bands 1 and 2 of the carboxylic acid, respectively. The CNDO/2 calculations made for the TFAA–DEMA system taken as an example show that the energy separation is almost unaffected by hydrogen-bond formation (1.51 eV for the free acid; 1.49 eV for the weak complex with the N–H distance of 1.6 Å; 1.42 eV for the strong complex with the distance of 1.2 Å). This is consistent with the present assignment. According to this assignment, the shifts of bands 1 and 2 due to hydrogen-bond formation amount to 2.70—2.75 eV for the systems containing DEMA and to 2.42—2.47 eV for the systems containing TPA (see Table 2).

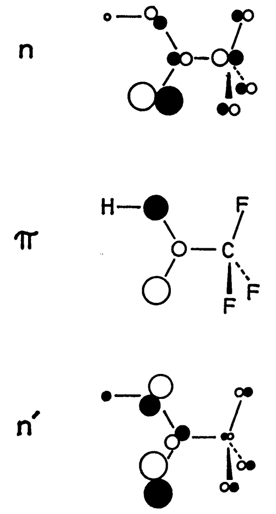

Fig. 2. Schematic representation of the higher occupied molecular orbitals of trifluoroacetic acid.

Another possible assignment of bands 1 and 2 of the hydrogen-bonded complexes is to assign one of them to the n orbital of the amine and the other band to the n orbital of the carboxylic acid. This assignment, however, may lead to unreasonable band shifts. Let us consider, as an example, the case in which bands 1 and 2 are assigned to the n orbitals of the amine and the carboxylic acid, respectively. The shift of the amine band due to complex formation with TFAA is 0.94 eV for DEMA and 1.59 eV for TPA. This apparently indicates that TPA is stronger as proton acceptor than DEMA. On the other hand, the shift of the carboxylic acid band due to complex formation with the amine is 1.59 eV for DEMA and 1.29 eV for TPA. This seems to show that TPA is weaker as proton acceptor than DEMA. From the above consideration, the assignment of either of bands 1 and 2 to the n orbital of the amine is unacceptable.

Judging from the orbital shape of the carboxylic acid shown in Fig. 2, the shift due to hydrogen-bond formation is larger for band 3 (n′ band) than for band 1 (n band). Therefore, it is expected that band 3 of PFPA at 14.04 eV appears below 11.34 eV for the PFPA–DEMA hydrogen-bonded system. Thus, the third and fourth bands of the system are assigned to the shifted bands of the third band of PFPA and of band I of DEMA, respectively. From an analogy with the PFPA–DEMA system, the third and fourth bands of the TFAA–DEMA system are tentatively correlated with band 3 of TFAA and band I of DEMA, respectively. In the TFAA–TPA and PFPA–TPA complexes, bands 3 and I are covered with a background band and their exact positions can not be decided.

The band shifts due to hydrogen-bond formation are summarized in Table 2. We can see that the n bands of the proton acceptors (amines) shift towards the higher-IP region by hydrogen-bond formation while the n bands, π bands, and n′ bands of the proton donors (carboxylic acids) shift towards the lower-IP region. These tendencies can well be explained by the contribution of the dative structure (–COO$^-$···

$\mathrm{H{-}N^{+}}\!\!<\!\!\!-$) as is expected from the charge-transfer mechanism⁴⁾ of hydrogen-bond formation. The large energy shifts of the bands of the component molecules due to hydrogen-bond formation indicate that the contribution of the dative structure to these hydrogen-bonded complexes is quite significant.

The n, π, and n′ bands of the proton donor and the n band of the proton acceptor shift a little more in the system containing TFAA as the proton donor than in the system containing PFPA. This suggests that TFAA is slightly stronger as the proton donor than PFPA. Concerning proton acceptors, the band shift due to hydrogen-bond formation is less in the system containing TPA. This is reverse to the order of the proton-accepting ability expected from their ionization potentials. This contradiction may be explained in terms of the steric hindrance effect.

References

1) C. Utsunomiya, T. Kobayashi, and S. Nagakura, *Chem. Phys. Lett.*, **39**, 245 (1976).

2) T. Kobayashi, K. Yokota, and S. Nagakura, *J. Electron Spectrosc.*, **2**, 449 (1973).

3) R. K. Thomas, *Proc. R. Soc. London, Ser. A*, **331**, 249 (1972).

4) R. S. Mulliken and W. B. Person, "Molecular Complexes," Wiley-Interscience, New York (1969).