

An Ultraviolet Photoelectron Spectroscopic Study of the Hydrogen Bonded Dimers of Methanol, Ethanol, and Dimethylamine in the Vapor Phase

Hydrogen bonded dimers of a few molecules have been studied in the free state by vibration spectroscopy and cognate techniques, particularly in relation to their structure and thermodynamic properties (1, 2). Alcohol dimers cannot be examined in the vapor phase as readily as the dimers of carboxylic acids because of the small fraction of the associated species and low association enthalpies. Vital information related to

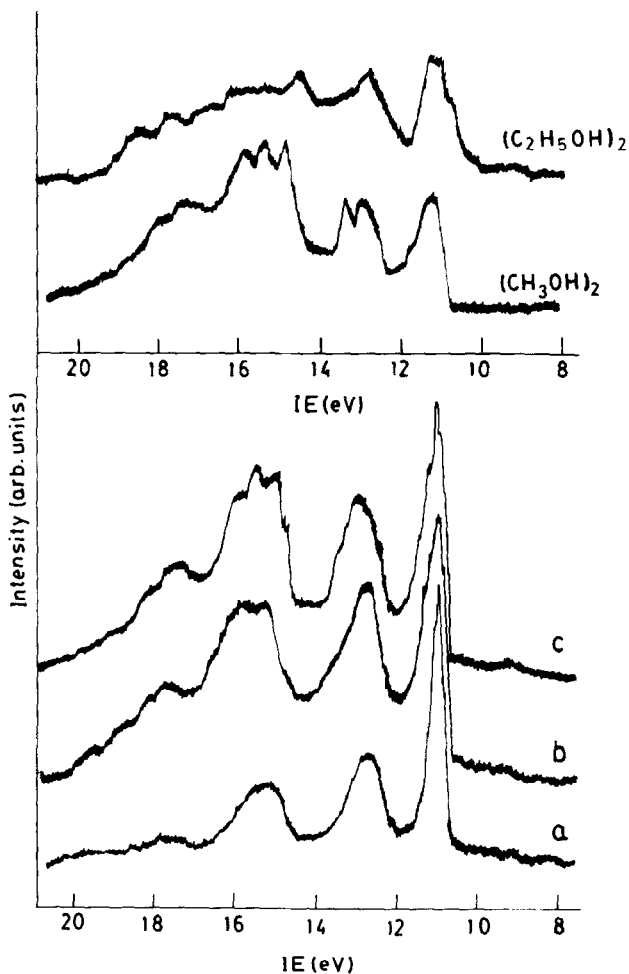


FIG. 1. HeI photoelectron spectra of methanol at various stagnation pressures. The stagnation pressure increases from a to c. Spectra of the dimers of methanol and ethanol obtained after stripping are also shown.

the electronic structures of homodimeric hydrogen bonded species by means of ultraviolet photoelectron spectroscopy (UVPES) is therefore essentially limited to carboxylic acids (3, 4). In order to obtain higher concentrations of alcohol dimers for UVPES investigations, it becomes necessary to have molecular beams generated through an appropriate jet (5, 6). In the present study, we have investigated the electron states of the dimers of methanol and ethanol by employing an indigenously built molecular-beam photoelectron spectrometer (7). More importantly, we have studied, for the first time, the vapor phase UVPE spectrum of the hydrogen bonded dimer of dimethylamine with a N-H...N bond and made assignments based on ab initio molecular orbital (MO) calculations. Unlike the alcohol dimers there is little or no information in the literature on amine dimers in the free state (1).

HeI UV photoelectron spectra were recorded at several stagnation pressures with a double chamber spectrometer equipped with a 0.1-mm nozzle. The resolution of the instrument was 50 meV at 15.9 eV ionization energy (IE). In Fig. 1, we show the spectra of methanol at different stagnation pressures (10–20 mbar). As the pressure increases, the spectrum becomes more complex and additional features develop on all of the bands. These additional features are due to the dimer, which is the predominant species, rather than higher clusters, in such nozzle expansions (8). The spectrum of the pure dimer obtained after spectrum stripping is also shown in Fig. 1. It was ensured that the observed features were intrinsic by carrying out measurements under different conditions. In Table I we list the experimental IEs along with the orbital energies of the linear methanol dimer obtained from SCF/3-21G calculations (9) which made use of the optimized monomer geometry. The agreement between the two is good.

The first two bands (11.2 and 11.9 eV) in the UVPE spectrum of the methanol dimer arise from the nonbonding oxygen orbitals of the donor moiety in the dimer; these are followed by the corresponding orbitals of the acceptor moiety giving bands at 13.0 and 13.4 eV. The nonbonding orbitals give rise to bands at 10.9 and 12.7 eV in the case of the monomer. The bands at 14.9 and 15.4 eV are due to ionizations of the C–O and C–H bonding orbitals of the donor. We suspect that the first vertical IE of methanol dimer reported at 10.4 eV by Tomoda and Kimura (6) may be due to HeI_β ionization of the \bar{n}_0 orbital of the monomer. This explains why the adiabatic IE (9.8 eV) obtained by these workers is lower than the appearance potential (10.3 eV) obtained from the photoionization (PI) study (10). We obtain an adiabatic IE of 10.7 eV which gives a more acceptable value for the dissociation energy (0.3 eV) for the ground state molecular ion, in agreement with the PI study.

TABLE I
Occupied Orbital Energies of Dimers of CH₃OH and C₂H₅OH

$I_V^{(a)}$ (eV)		
(CH ₃ OH) ₂	(C ₂ H ₅ OH) ₂	- $\epsilon^{(b)}$
11.2	10.7	10.7
11.9	11.2	11.9
13.0	12.8	12.8
13.4	-	14.0
14.9	14.4	14.9
15.4	-	15.7

(a) Vertical ionization energy.

(b) Calculated orbital energies for the linear dimer.

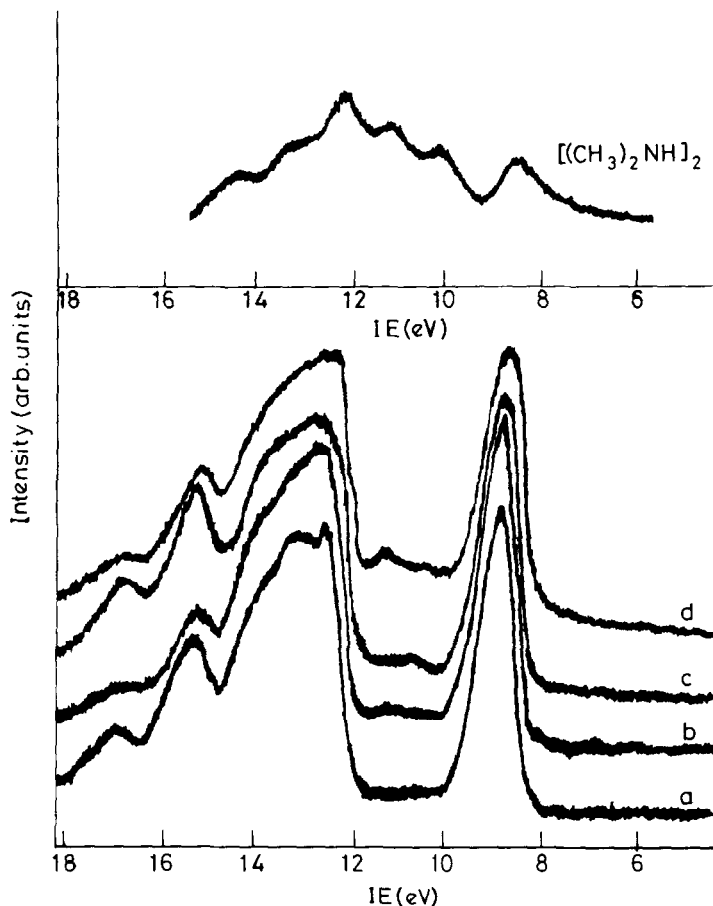


FIG. 2. HeI photoelectron spectra of dimethylamine at different stagnation pressures. The stagnation pressure increases from a to d. The spectrum of the pure dimer obtained after stripping is also shown.

We have also studied the UVPE spectrum of ethanol at different stagnation pressures. We have shown the spectrum of the pure dimer obtained after spectrum stripping in Fig. 1. The spectrum is comparable to that of methanol dimer suggesting similar ionizations. We list the vertical IEs in Table I.

The N-H...N hydrogen bond in dimethylamine is considerably weaker than the O-H...O hydrogen bond in the dimers of alcohols as revealed by SCF/3-21G calculations. We have, however, been able to obtain the UVPE spectrum of the dimethylamine dimer (Fig. 2) by recording spectra at different stagnation pressures (10–20 mbar). We see that as the stagnation pressure increases, two well defined features appear in the 10–12 eV region. Along with the appearance of these new bands, the monomer bands undergo broadening. These changes are clearly due to the formation of the dimer. The spectrum of the dimer obtained after spectrum stripping is also shown in Fig. 2.

We have assigned the features of the amine dimer on the basis of MO calculations. The calculations give an N...H distance of 2.20 Å, which is larger than the O...H distance in the methanol dimer (1.81 Å). The optimized geometry gave a nearly linear hydrogen bond not very different from that in methanol dimer. In Table II we list the calculated orbital energies of the dimethylamine dimer along with the assignments. The lone pair IEs undergo an average shift of ~1 eV in the dimer compared to the monomer (9.0 eV). The data in Table II constitute the first characterization of the electron states of an amine dimer.

TABLE II
Occupied Orbital Energies and Assignments of the (CH₃)₂NH Dimer

I _v (eV)	-ε	Character	MO
8.3	8.7	n _N	16a'
10.0	9.9	n _N	15a'
11.1	13.1	σ _{CN}	10a"
	13.3	σ _{CN}	14a'
12.0	13.9	σ _{CN}	9a"
	14.1	σ _{CN}	13a'
13.3	14.2	π _{CH3}	8a"
14.7	15.0	π _{CH3}	7a"

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