

Electronic Transitions in Hydrogen Bonded Dimers of Carboxylic Acids in the Vapour Phase: An Electron Energy Loss Spectroscopic Study†

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An electron energy loss spectroscopic study of the formic acid dimer has shown bands centred around 7.2, 8.5, 9.8, and 11.1 eV, of which the first and the third bands are assigned to $n-\pi^*$ transitions and the other two to $\pi-\pi^*$ transitions; similar transitions are found in the acetic acid dimer.

Cyclic dimers of carboxylic acids constitute one of the most important hydrogen bonded systems. These dimers, associated with relatively high hydrogen bond energies¹ (~ 60 kJ mol⁻¹), have been investigated in detail by means of quantum theory and vibrational spectroscopy.^{2,3} Orbital energies of the dimers of simple carboxylic acids such as formic acid have been determined from u.v. photoelectron spectroscopy.⁴ The dimer shows considerable interaction between the states of σ symmetry, giving rise to a fairly large splitting of the n level in the dimer. In spite of these extensive investigations, electronic transitions of these dimers have not been characterized hitherto.⁵ We would expect the dimers to exhibit electronic transitions in the vacuum u.v. region, but the only previously reported experimental study we are aware of, is a preliminary u.v. spectroscopic study by Barnes and Simpson.⁶ There have been a few theoretical calculations of the electronic spectra of the dimers of formic acid^{7,8} but the predictions differ widely. We have investigated the electronic spectra of the dimers of formic and acetic acids in vapour phase by means of electron energy loss spectroscopy (EELS) which is ideally suited to probe electronic transitions in the vacuum u.v. region. With the aid of MO calculations we have made assignments of the observed transitions of the dimer for the first time. We report the essential results in this communication in view of the wide chemical interest in this system.

In order to obtain molecular electron energy loss spectra, we built a spectrometer consisting of a hemispherical electron

monochromator, a collision chamber, a hemispherical electron energy analyser, and a channeltron electron multiplier.⁹ Since enhanced pressure, rather than reduced temperature, better serves the purpose of increasing the dimer population,

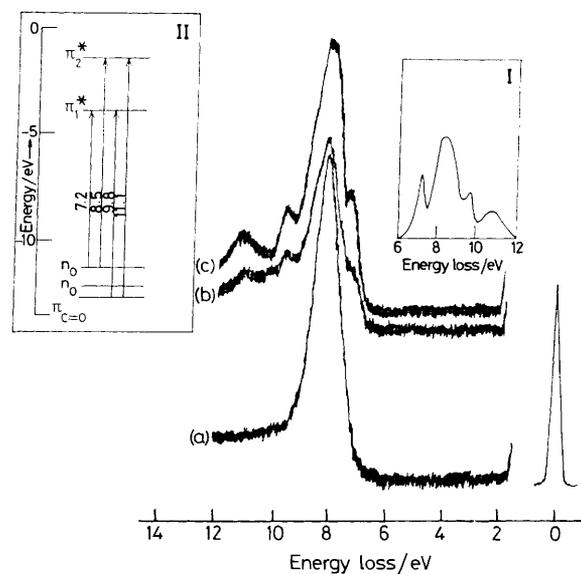


Figure 1. Electron energy loss spectra of formic acid in the vapour phase: (a) essentially due to monomer; (b) and (c) at higher pressures with increasing dimer content. Inset I is the spectrum of the pure dimer and inset II is the energy level scheme.

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we have used an effusive nozzle (0.4 mm diam.). An electron beam of 45 V [300 meV full width at half maximum (FWHM)] was employed.

Monomeric formic acid shows an intense EELS feature around 8.1 eV (153 nm) due to the π - π^* transition.^{6,10} With increase in pressure, we see the emergence of new bands peaking at 7.2, 9.8, and 11.1 eV (172, 126, and 112 nm), besides an intense feature around 8.3 eV (149 nm) close to that of the monomer (Figure 1). On eliminating the features due to the monomer, we were able to get the spectrum of the pure dimer shown in inset I of Figure 1. U.v. spectroscopic measurements⁶ have shown the presence of a band around 7.5 eV due to the dimer and a broad, intense feature centred around 8.5 eV. The first three HOMOs of the formic acid dimer are at 11.3 ($n_1C=O$, b_u), 12.0 ($n_2C=O$, a_g), and 12.6 eV (π , a_u/b_g) as found from He I photoelectron spectra.^{4,11} We assign the 7.2 and 8.5 eV bands to the two n_1 - π^* transitions from the n ($C=O$) level at 11.3 eV to the two π^* states; the 9.8 and 11.1 eV bands are then due to the two π - π^* transitions from the π level at 12.6 eV (see inset II of Figure 1). The 8.5 eV band is somewhat broad and could possibly have another band due to the n_2 - π^* transition under the envelope. Our calculations on the ground and excited states of the dimer at the MP2/3-21G level predict the first n - π^* transition at 6.6 eV.

Our observations and assignments of the electronic spectra of the formic acid dimer differ from the predictions of Iwata and Morokuma⁷ based on the two configuration electron-hole pair (TCHEP) formalism that the n - π^* transitions of the dimer should occur at 5.7 and 6.3 eV and a π - π^* transition at 5.1 eV. The two transitions predicted by Lipinski and Sokalski⁸ based

on INDO calculations (n - π^* 8.3 eV, π - π^* 9.4 eV) are in agreement with the present study.

The first two lone pair orbital energies of the acetic acid dimer are around 10.6, 11.2 eV and the π level is at 12.1 eV.¹¹ Our EELS measurements on this dimer clearly show transitions around 7.1 and 9.0 eV which can be assigned to n - π^* and π - π^* excitations respectively.

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