

ELECTRONIC TRANSITIONS OF HYDROGEN BONDED COMPLEXES: AN ELECTRON ENERGY LOSS SPECTROSCOPIC STUDY*

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ABSTRACT

Electronic spectra of hydrogen bonded complexes have been studied by electron energy loss spectroscopy and assignments made based on experimental orbital energies from HeI photoelectron spectra and molecular orbital calculations. Electronic transitions of diethyl ether-HCl and SO₂·HCl complexes show small shifts from those of HCl and the free electron donor, as expected of weakly interacting systems. Electronic spectra of the dimers of formic and acetic acids are markedly different from those of the monomers. Dimers show characteristic n→π* and π→π* transitions in the 7-11 eV region.

INTRODUCTION

Hydrogen bonding probably constitutes the most important class of intermolecular interactions with wide implications in chemistry and biology. There has been much effort in the study of intermolecular hydrogen bonded complexes by a variety of spectroscopic techniques, especially vibrational spectroscopy. In recent years, a few workers have employed ultraviolet photoelectron spectroscopy (UVPES) employing HeI radiation to obtain orbital energies of hydrogen bonded complexes. Special mention must be made in this context of the study of the dimethyl ether-hydrogen chloride complex [1] and the dimers of formic and acetic acids [2]. Information on the electronic transitions of hydrogen bonded complexes is however limited, primarily because many of the transitions are in the vacuum ultraviolet (UV) region. We have attempted to investigate the electronic transitions in a few hydrogen bonded complexes by means of electron energy loss spectroscopy (EELS) which readily provides information on the electronic transitions in the vacuum UV region. A knowl-

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edge of the electronic transitions along with the data on orbital energies obtained from UVPES has enabled us to understand the electronic structure of the hydrogen bonded systems. The systems examined are $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{HCl}$, $\text{SO}_2\cdot\text{HCl}$ and the dimers of formic and acetic acids, the carboxylic acid dimers being archetypal examples of strong hydrogen bonds of considerable chemical interest.

EXPERIMENTAL AND COMPUTATIONAL DETAILS

Ultraviolet photoelectron spectra were recorded with a laboratory-built spectrometer [3] consisting of a HeI lamp, a 3 mm diameter collision chamber and a channeltron electron multiplier. Differential pumping allowed for operation of the HeI lamp at 1.5 torr, a sample pressure of 0.1–0.5 torr and a pressure of 5×10^{-5} torr in the rest of the spectrometer. The resolution of the spectrometer was 80 meV FWHM at 19.7 eV. $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{HCl}$ and $\text{SO}_2\cdot\text{HCl}$ were prepared in a vacuum line by co-condensation of the donor with a small excess of HCl at 77 K in a glass ampoule fitted with a teflon tap. Samples of these mixtures were gently warmed to room temperature and admitted to the spectrometer by means of a needle valve. The initial spectra contained new features due to the complexes besides features of the excess components which then got pumped away to essentially give the spectra of the complexes. Any features due to the free donor or acceptor remaining in the spectra were removed by an interactive computer program. The stripping procedure was similar to that described in ref. 1. The spectra of the 1:1 complexes thus obtained were identical whether the initial composition had excess donor or acceptor.

Electron energy loss spectra were recorded with a laboratory-built spectrometer [4] consisting of a hemispherical electron monochromator (125 mm mean diameter), a collision chamber, a hemispherical electron energy analyzer (140 mm mean diameter), and a channeltron electron multiplier. By means of differential pumping, a sample pressure of 5×10^{-4} torr could be produced in the collision chamber while the rest of the spectrometer remained at 2×10^{-6} torr. An electron beam of 45 V with 300 meV FWHM was employed in the present study.

In the case of the dimers of formic and acetic acids an effusive nozzle of 0.4 mm diameter was used at various stagnation pressures. The present design did not allow us to determine the exact stagnation pressure. The local gas pressure in the collision chamber was controlled by positioning the differential pumping inlet directly opposite the nozzle.

Hartree–Fock energies of the complexes were computed in the framework of the SCF-LCAO-MO method using the GAUSSIAN 86 program [5]. The split valence 3-21G basis set was used in all the computations except for $\text{SO}_2\cdot\text{HCl}$; where in addition to 3-21G, a 6-31G* basis was also used. Monomer geometries were fully optimized and used as input for the calculations on the complexes.

RESULTS AND DISCUSSION

Diethyl ether-hydrogen chloride

The HeI spectrum of the complex between dimethyl ether and HCl has been reported by Carnovale et al. [1] who found some shifts in the ionization energies (IE) of the donor and acceptor due to hydrogen bonding. In Fig. 1 we show the HeI spectrum of a mixture of $(C_2H_5)_2O$ and HCl. In the same figure, we have also shown the HeI spectra of $(C_2H_5)_2O$ and HCl. The spectrum of $(C_2H_5)_2O$ shows the characteristic band due to n_O orbital ionization at 9.6 eV. The band at 11.1 eV is due to n_O and the features in the 11.9–16.3 eV region have contributions from the σ_{CC} , π_{CH_3} , π_{CH_2} and σ_{CO} orbital ionizations. The spectrum of HCl shows bands at 12.8 and 16.2 eV due to π_{Cl} and σ_{HCl} ionizations respectively. Visual comparison of the spectra of the mixture and the free components reveals interesting features. The first band has a shoulder at the

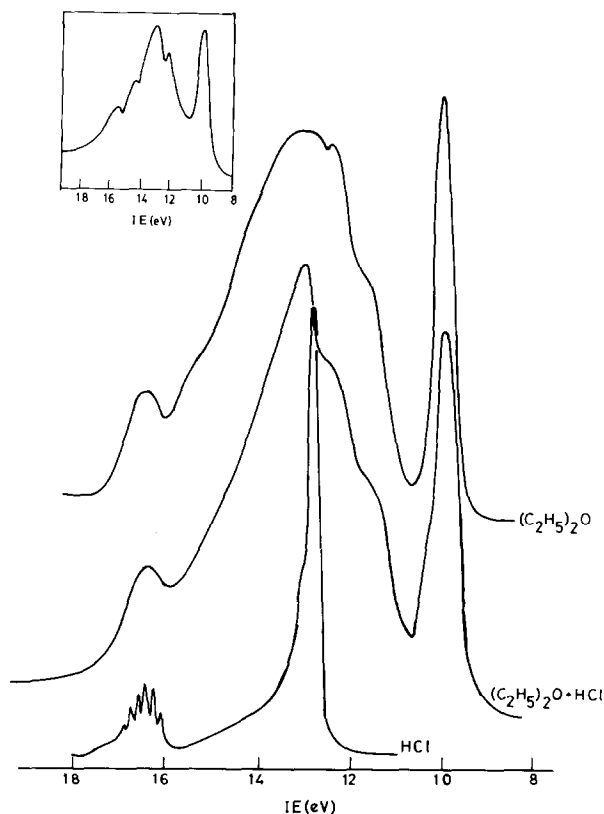


Fig. 1. HeI spectra of $(C_2H_5)_2O$, HCl and a mixture of $(C_2H_5)_2O$ and HCl. The spectrum of the pure heterodimer obtained after stripping is shown in the inset.

higher IE side, and there is no feature where HCl has characteristic bands. We have obtained the spectrum of the pure 1:1 heterodimer by the spectrum stripping procedure (see the inset of Fig. 1).

There is considerable similarity between the HeI spectra of the HCl complexes of dimethyl ether and diethyl ether. We have listed the experimentally observed IEs in Table 1 along with the orbital assignments based on MO calculations. In the calculations, ether and HCl were fixed at their optimized geometries and the angle between the COC plane and the O \cdots H bond (α), the O \cdots H distance and the OHCl angle were varied. In the optimized geometry of the complex the α and OHCl angles were 140.03° and 175.52° with an O \cdots H distance of 1.61 Å. The calculated O \cdots H distance in the dimethyl ether-HCl complex was 1.54 Å by keeping a linear OHCl arrangement [1]. The experimental O \cdots Cl distance in the case of H₂O \cdots HCl heterodimer [6] is 3.21 Å assuming a linear OHCl arrangement. Taking an H-Cl distance of 1.27 Å [7], the O \cdots H bond length works out to be 1.94 Å, which is considerably longer than the calculated value in the ether-HCl complexes. The experimental O \cdots H distance in the methanol-HCl complex [8] is also close to 1.9 Å, assuming a linear hydrogen bond. According to the present calculation, a linear OHCl arrangement may not be the most stable one, although the deviation from linearity is rather small. The computed dissociation energy (30 kJ mol⁻¹) found by us is, however, close to the experimental value (31 kJ mol⁻¹) obtained for the dimethyl ether-HCl complex [9].

As in the case of dimethyl ether-HCl complex, the eigenvalues of the diethyl ether-HCl complex are also sensitive to the O \cdots H bond length. At the optimized geometry, the highest occupied molecular orbital (HOMO) is one of the nearly degenerate π_{Cl} orbitals. An examination of the HeI spectrum shows on the other hand, that the first band is associated with n_{O} ionization. While at shorter O \cdots H distances (1.50–1.60 Å) π_{Cl} is the HOMO, at longer O \cdots H distances (1.85–1.95 Å) n_{O} becomes the uppermost occupied orbital. Since a

TABLE 1

Occupied orbital energies and assignments of diethyl ether-hydrogen chloride complex

IE _v (eV)	Calculated MOs		
	- ϵ (eV) 3-21G	Character	MO
9.8	11.47	n_{O}	19a'
12.0	12.00, 12.01	π_{Cl}	18a', 11a''
13.5	13.04, 13.45, 14.27	$n_{\text{O}}, \pi_{\text{CH}_3}$	17a', 10a'', 9a''
14.3	14.54, 14.69, 15, 29	$\sigma_{\text{CC}}, \pi_{\text{CH}_3}$	8a'', 16a', 15a'
15.6	15.89	σ_{HCl}	14a'

shorter O \cdots H distance would not be consistent with the experimental spectrum, we have used a distance of 1.90 Å for the final calculation keeping all other values the same as the optimized geometry. This O \cdots H distance is also close to the experimental value found in the complexes of HCl with H₂O and CH₃OH discussed above. Assignments based on such a calculation (Table 1) show that the π_{Cl} and σ_{HCl} ionization energies are lowered by 0.8 and 0.6 eV on hydrogen bond formation; the n_{O} ionization is increased by 0.2 eV. The shifts are lower than those found in the dimethyl ether-HCl complex [1]. The direction of the shifts can be understood on the basis of the transfer of electron density from ether to HCl.

Electron energy loss spectra of diethyl ether, HCl and that of the heterodimer are shown in Fig. 2. The EEL spectrum of diethyl ether has been reported earlier [4]. The features at 6.6 and 7.0 eV are assigned to $n \rightarrow \sigma^*$ transitions and the band at 8.6 eV is due to $\sigma \rightarrow \sigma^*$ excitation. The EEL spectrum of HCl shows bands at 7.5, 9.3, 9.8, 10.9, 12.1 and 13.7 eV. All the bands are observed in the optical studies [10] except the last one which is assigned to the $\sigma_{\text{HCl}} \rightarrow 4p_{\sigma}$ transition. The EEL spectrum of the complex exhibits bands at 6.3, 7.2, 8.4, 9.2, 10.8 and 12.2 eV. We see that the electronic transitions of ether undergo measurable shifts due to complex formation. The transitions of the ether moiety show a shift of 0.2–0.3 eV to lower energies. The transitions of HCl are not affected to a significant extent. The transition energies and assignments are listed in Table 2.

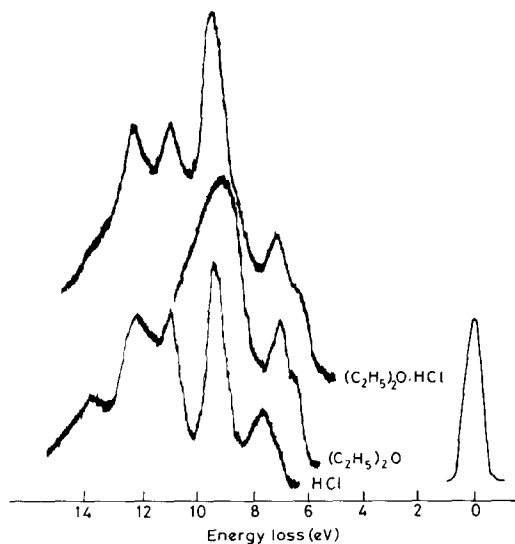


Fig. 2. Electron energy loss spectra of $(\text{C}_2\text{H}_5)_2\text{O}$, HCl and $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{HCl}$.

TABLE 2

Electronic transitions of diethyl ether-hydrogen chloride heterodimer

Transition energy (eV)	Shift from free HCl or ether values (eV)	Assignment
6.3 (6.6) ^b	-0.3	$n \rightarrow \sigma^*$ (ether)
7.2 (7.5) ^a	-0.3	$n \rightarrow \sigma^*$ (HCl)
8.4 (8.6) ^b	-0.2	$\sigma \rightarrow \sigma^*$ (ether)
9.2 (9.8) ^a	-0.4	$n \rightarrow 4p_\sigma$ (HCl)
10.8 (10.9) ^a	-0.1	$n \rightarrow 4d_\sigma$ (HCl)
12.2 (12.1) ^a	-0.1	$\sigma \rightarrow \sigma^*$ (HCl)

^aValue in parentheses is that of free HCl. ^bValue in parentheses is that of ether.

$SO_2 \cdot HCl$

This complex has been characterized recently by microwave spectroscopy [11]. The optimized structural parameters obtained from MO calculations on this complex (carried out with 3-21G and 6-31G* basis sets) are comparable to the experimental values [11]. The dissociation energy of the complex is 31.1 kJ mol⁻¹ and 9.0 kJ mol⁻¹ from 3-21G and 6-31G* calculations respectively. The HeI spectrum of this complex has been investigated recently in this laboratory [12] and shows features at 12.3, 12.6, 13.0, 13.4 and 14.5 eV due to n_{Cl} , $n_S(n_O)$, n_O , n_O and σ_{HCl} orbital ionizations respectively.

EEL spectra of SO_2 and the $SO_2 \cdot HCl$ complex are shown in Fig. 3. The EEL spectrum of SO_2 obtained by us is in agreement to that in the literature [13]. The complex shows slight shifts in the transition energies compared to free SO_2 and HCl. The SO_2 transition energies are decreased by around 0.2 eV while that of HCl is increased by 0.2–0.3 eV. This is mainly due to the destabilization or upward shift of the unoccupied orbitals of HCl. The observed transition energies and the shifts along with the assignments are listed in Table 3.

EELS of the dimers of formic and acetic acids

Dimers of formic and acetic acids have been studied by HeI spectroscopy by a number of workers [2, 14, 15]. Even though MO calculations on the electronic transitions of the dimers have been reported [16,17], the only experimental investigation of which we are aware is a preliminary study reported by Barnes and Simpson [18] some years ago. The EEL spectrum of monomeric formic acid shows only one transition at 8.1 eV assigned to the $\pi \rightarrow \pi^*$ excitation of the carbonyl group and the other transitions ($n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$) are not seen, unlike the optical spectrum [19].

We have studied the EEL spectra of formic acid at various nozzle pressures

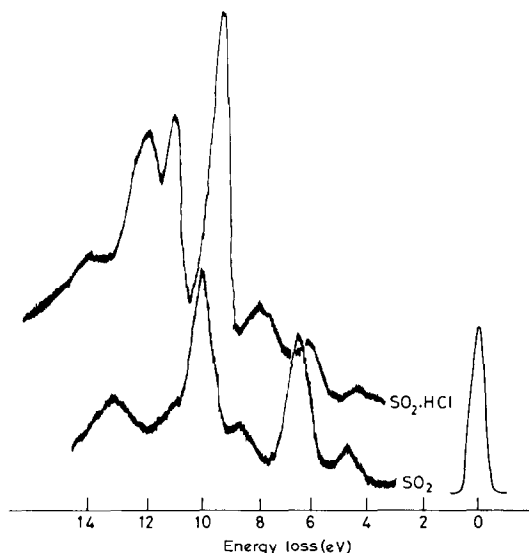


Fig. 3. Electron energy loss spectra of SO_2 and $\text{SO}_2 \cdot \text{HCl}$.

TABLE 3

Electronic transitions of $\text{SO}_2 \cdot \text{HCl}$

Transition energy (eV)	Shift from free HCl or SO_2 values (eV)	Assignment
4.2 (4.6) ^b	-0.4	$\pi_{\text{SO}} \rightarrow \pi_{\text{SO}}^*(\text{SO}_2)$
6.0 (6.4) ^b	-0.4	$\pi_{\text{SO}} \rightarrow \pi_{\text{SO}}^*(\text{SO}_2)$
7.5 (8.6) ^b	-1.1	$\pi_{\text{SO}} \rightarrow \pi_{\text{SO}}^*(\text{SO}_2)$
7.9 (7.5) ^a	+0.4	$n \rightarrow \sigma^*(\text{HCl})$
9.5 (9.8) ^a	+0.3	$n \rightarrow 4p_\sigma(\text{HCl})$
11.1 (10.9) ^a	+0.2	$n \rightarrow 4d_\sigma(\text{HCl})$
12.1 (12.1) ^a	0.0	$\sigma \rightarrow \sigma^*(\text{HCl})$
14.0 (13.7) ^a	+0.3	$\sigma \rightarrow 4p_\sigma(\text{HCl})$

^aValue in parentheses is that of free HCl. ^bValue in parentheses is that of SO_2 .

at room temperature. Spectra of formic acid at various pressures are given in Fig. 4. At low pressures, only the monomer is observed. On increasing the pressure, three new features become prominent, at 7.2, 9.8 and 11.1 eV. The preliminary study of Barnes and Simpson [18] showed the first dimer band is at 7.5 eV close to the first EEL feature. We have carried out a simple decomposition of the EEL spectrum obtained at highest pressure composed of features of both monomer and the dimer to five gaussians assuming that the band at 8.1 eV is

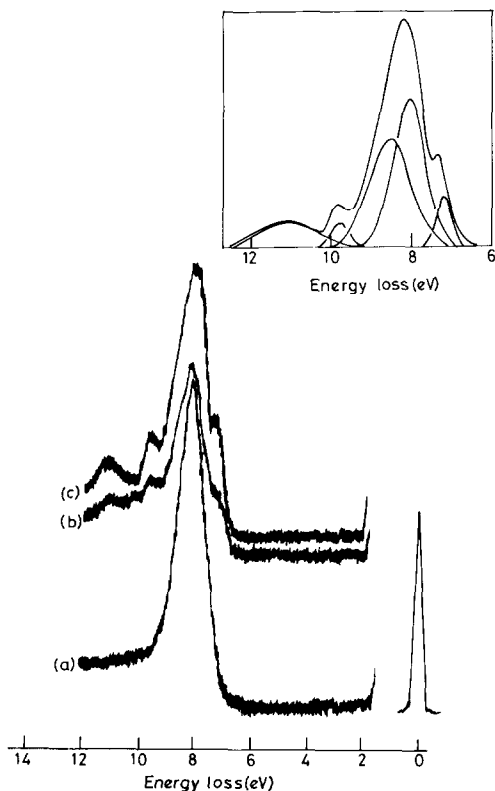


Fig. 4. Electron energy loss spectra of formic acid at various pressures, (a) to (c) in order of increasing pressure. The decomposed spectrum is shown in the inset.

due to the monomer. Spectral decomposition was carried out after background subtraction and the decomposed spectrum is shown in the inset of Fig. 4.

We have carried out calculations at the MP2/3-21G level on the first two excited states of the formic acid dimer in order to make spectral assignments. Full geometry optimization with C_{2h} symmetry was carried out for the excited and ground states at the 3-21G level. The first three MOs of formic acid dimer are at 11.3 ($n_{O,C=O}$), 12.0 ($n_{O,C=O}$) and 12.6 ($\pi_{C=O}$) eV as found from the HeI spectrum [14]. On the basis of our calculations and the optical spectrum [18], we assign the first two transitions to the two $n \rightarrow \pi^*$ excitations. The bands at 9.8 and 11.3 eV are assigned to the $\pi \rightarrow \pi^*$ excitations. The 8.5 eV band is rather broad and could have another $n \rightarrow \pi^*$ band in the envelope. The assignments along with the computed transition energies are listed in Table 4. Based on these assignments and data from the HeI spectrum, the partial molecular orbital diagram shown in Fig. 5 has been constructed. Our observations differ from the predictions of Iwata and Morokuma [16] based on TCHEP formalism which propose two $n \rightarrow \pi^*$ transitions at 5.7 and 6.3 eV and one $\pi \rightarrow \pi^*$ tran-

TABLE 4

Electronic transitions of formic acid dimer

Transition energy (eV)	MP2/3-21G	Optical (eV)	Assignment
7.2	6.22 ^a (6.55) ^b	7.4	$n_O \rightarrow \pi_1^*$
8.5	10.84 ^a (11.22) ^b	8.1	$n_O \rightarrow \pi_2^*$
9.8			$\pi \rightarrow \pi_1^*$
11.3			$\pi \rightarrow \pi_2^*$

^aTriplet state. ^bSinglet state.

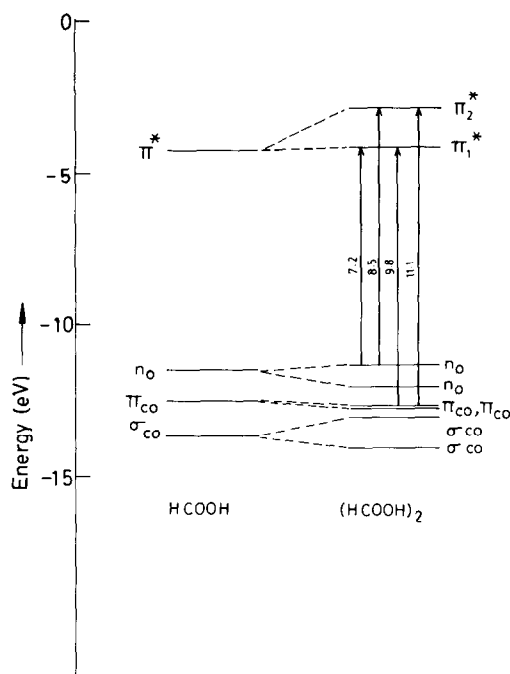


Fig. 5. Partial energy level scheme of formic acid dimer.

sition at 5.1 eV. The assignments are in agreement with the INDO calculations of Lipinski and Sokalski [17].

The EEL spectrum of acetic acid monomer has been reported earlier [4]. The bands at 8.0 and 9.8 eV are assigned to $n \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ transitions. EEL spectra of acetic acid observed at various pressures are shown in Fig. 6. On increasing the nozzle pressure, two distinct features appear at 7.1 and 9.0 eV. The optical spectrum reported by Barnes and Simpson [18] has the first band at 7.4 eV. This, along with the expected similarity to the spectrum of formic acid dimer, suggest significant dimer contribution in the spectrum. By analogy

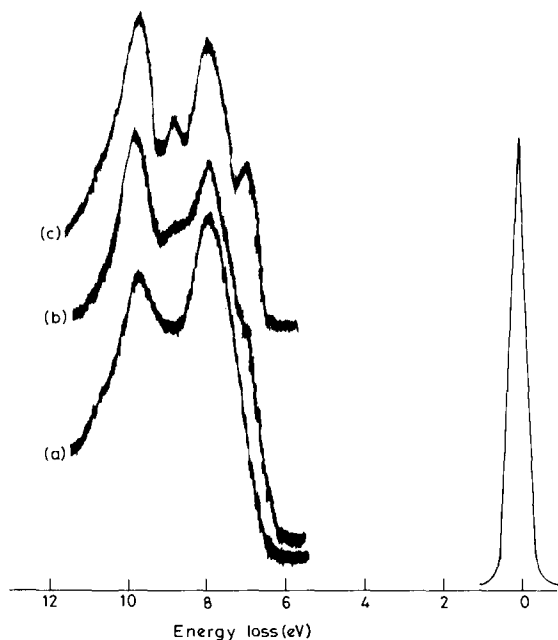


Fig. 6. Electron energy loss spectra of acetic acid at different pressures, (a) to (c) in order of increasing pressure.

with the formic acid dimer, the bands of acetic acid dimer at 7.1 and 9.0 eV are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. We are, however, not sure of the presence of any dimer transitions under the intense bands at 8.0 and 9.8 eV.

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