Electronic Structure and Spectra of Acrylic Acid in the Vapor and Condensed Phases

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Near and vacuum UV absorption spectra of acrylic acid were measured at room temperature in the vapor phase and at 77 K in the condensed phase. From a comparative study of the observed spectra, a Rydberg excitation band was observed at 7.46 eV in addition to valence-shell transition bands. The estimated value of the quantum defect ($\delta=1.01$) indicates that the Rydberg orbital is 3s. A new modified CNDO-CI method applicable to planar molecules was developed and applied to acrylic acid to investigate the valence-shell transitions, the observed bands at ~5.0 and 6.71 eV being assigned to the transitions to the n-π^* and π-π^*, respectively.

Electronic absorption spectra of carboxylic acids have been studied extensively[1-3] in comparison with those of amides, acyl fluorides, and carbonyls. Concerning acetic acid, Barnes and Simpson[1] assigned the bands at 48000, 58000, 63000, and 68000 cm^{-1} to the transitions to n-π^*, n'-π^*, n-σ^*, and π-π^* states, respectively. On the other hand, from a comparison of the spectrum in the vapor phase with that in the condensed phase and also from the calculation of the electronic structure, Basch, Robin, and Kuebler[3] assigned the bands of trifluoroacetic acid observed near 48000, 62000, 68000, and 77000 cm^{-1} to the transitions to n-π^*, n-3s Rydberg, π-π^*, and n-3p Rydberg states, respectively, emphasizing the existence of Rydberg excitation bands in the vacuum ultraviolet (VUV) region.

Acrylic acid has the vinyl group conjugating with the carboxyl group. The conjugation may be expected to have some effect on both the valence-shell transition bands and the Rydberg excitation bands. According to our knowledge, the absorption spectrum of acrylic acid has scarcely been studied.[4] This is because analysis of the result may be complicated by the existence of the *s-cis-* and *s-trans*-isomers in the vapor phase at room temperature,[5] the formation of the dimer at higher pressure,[6] and the occurrence of thermal and photochemical reactions.[7]

In the present study, we have measured the near and vacuum UV absorption spectra of acrylic acid in the vapor and condensed phases, for the purpose of identifying the Rydberg excitation bands in addition to the valence-shell transition bands. Furthermore, to understand the electronic structure of acrylic acid, we have calculated the electronic structures of the *s-cis-* and *s-trans*-acrylic acids in monomeric form and also of the dimer by a new modified CNDO-CI method suitable for interpretation of electronic structures of planar molecules, σ- and π-orbitals being treated independently in estimating semi-empirical core resonance, Coulomb repulsion, and core potential integrals.

Experimental

Acrylic acid (Wako G. R. grade) was purified by vacuum distillation through a column filled with silica gel and diphosphorus pentaoxide immediately before use. Cyclohexane (Wako Spectro grade) was used without further purification.

Absorption spectra of the cyclohexane solution of acrylic acid were measured at room temperature with a Cary recording spectrophotometer model 14. Vapor-phase absorption spectra of acrylic acid at various pressures were measured at room temperature with a JASCO VUV-3 recording spectrophotometer,[8] a 10 cm cell being used. The vapor pressure of the sample was regulated with a cryogenic bath at various temperatures.

Near and vacuum UV absorption spectra in a condensed phase were measured at 77 K with a spectrophotometer constructed in our laboratory.[9] A thin film of pure acrylic acid was prepared by spraying the vapor onto a refrigerated CaF_2 window on a Dewar flask through a gas-inlet nozzle.

Theoretical

The modified CNDO-CI method (see Appendix) was applied to acrylic acid to investigate the valence-shell transitions. Since the monomeric *s-cis-* and *s-trans*-isomers and dimeric species of acrylic acid co-exist in the vapor phase,[5,6] calculations for all the species were performed by the use of the semi-empirical parameters listed in Table 1.

The geometry and molecular parameters for the monomeric and dimeric species were taken from the electron diffraction study by Ukaji.[10] The O–H bond length was assumed to be 0.96 and 1.00 Å for the monomer and dimer, respectively.

Results and Discussion

The absorption spectra measured with gaseous acrylic acid at various vapor pressures in the 43000—

TABLE 1. ONE-CENTER COULOMB REPULSION INTEGRAL ($\gamma_{\sigma_A\sigma_A}$ or $\gamma_{\pi_A\pi_A}$ (eV)) AND BONDING PARAMETER (β^0_A (eV)) FOR H, C, AND O ATOMS

	H	C		O		
		σ-AO	π-AO	σ-AO	π-AO	R-COOH[a]
γ	12.85	13.22	10.60	18.76	14.67	17.89
β^0_A	−12.0	−17.9	−12.9	−30.5	−19.8	−27.0

a) Values employed for both the σ- and π-AO's of O atom in the carboxyl group.

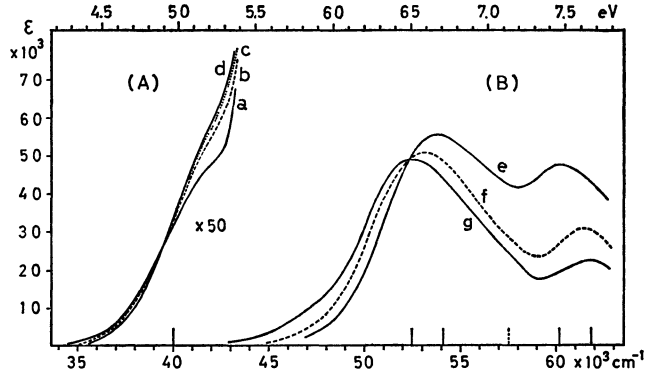

Fig. 1. Near and vacuum UV absorption spectra of acrylic acid measured at room temperature: (A) in cyclohexane (35000—43000 cm^{-1} region); (B) in the vapor phase (43000—63000 cm^{-1} region). The concentrations of acrylic acid are a, 8.9×10^{-4} M; b, 1.1×10^{-2} M; c, 2.7×10^{-2} M; d, 2.6×10^{-1} M; e, 2.3×10^{-6} M; f, 4.6×10^{-5} M; g 3.0×10^{-4} M.

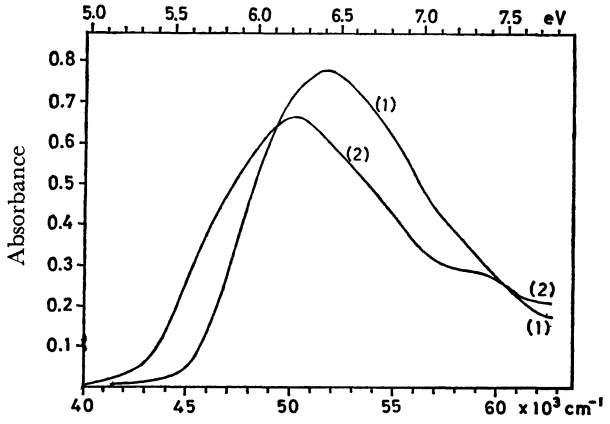

Fig. 2. Near and vacuum UV absorption spectrum observed at 77 K with a thin film of acrylic acid prepared (1) quickly (within one minute) and (2) slowly (for ten minutes).

63000 cm^{-1} region are shown in Fig. 1. This figure also shows the spectra measured for the cyclohexane solution with various concentrations of acrylic acid in the 35000—43000 cm^{-1} region. Spectral curves a and e in Fig. 1 are mainly due to the monomeric species, and curves d and g to the dimeric one. Since the *s-cis*- and *s-trans*-isomers of acrylic acid co-exist comparably,[5] we could only observe the spectrum for the mixture of both isomers. Table 2 gives transition energies and oscillator strengths calculated by the modified CNDO-CI method for the *s-cis*- and *s-trans*-isomers of acrylic acid.

From a comparison of the observed and theoretical values of the band intensity and position, the weak band near 40000 cm^{-1} (~5.0 eV) observed with the cyclohexane solution is safely ascribed to the first n-π^* transition. According to the concentration dependence of acrylic acid on the first n-π^* band (Fig. 1), the band shifts to higher frequencies by about 1000 cm^{-1} (0.12 eV) for the dimer. The result agrees well with the theoretical prediction (higher frequency shift of 0.13—0.14 eV by the dimer formation).

Let us turn to the VUV bands observed with acrylic acid. As is seen in curve e (Fig. 1), two absorption peaks appear at 54100 cm^{-1} (6.71 eV) and at 60200 cm^{-1} (7.46 eV) in the VUV absorption spectrum of gaseous acrylic acid. The band at 7.46 eV is very sensitive to the pressure of acrylic acid and decreases its intensity to a great extent with increasing pressure. This indicates that the upper state of the band is of the "big-orbit" nature. In order to check this point, we measured the VUV absorption spectrum in the condensed phase at 77 K. Actual measurements were made with thin films prepared by spraying gaseous acrylic acid on a cooled CaF_2 plate in a vacuum vessel; the result is shown in Fig. 2. Spectrum 1 was obtained for the sample prepared quickly (within one minute) and may conceivably correspond to that of anomalous solid; spectrum 2 was obtained for the sample prepared slowly (about ten minutes) and may correspond to that of the dimeric species in microcrystal. We can see that the 7.46 eV band observed with gaseous acrylic acid disappears almost completely in the condensed phase. This shows that the band is due to the transition to the upper state of "big-orbit" nature and can safely be assigned to the Rydberg transition.

The Rydberg excitation energy is expected to fit the following formula[3,11]

$$h\nu = I_p - (109737/(n-\delta)^2)$$

where $h\nu$ is the excitation energy (cm^{-1}), I_p is the ionization potential (cm^{-1}), and δ is the quantum defect which results from the penetration of Rydberg orbital into the core. By applying the equation to the observed band at 7.46 eV of acrylic acid, δ was determined to be 1.01, corresponding to $n=3$. This strongly suggests that the band is due to the transition to the 3s Rydberg orbital[11] as the first Rydberg band of CF_3COOH.[3]

The strong band at 6.71 eV in curve e (Fig. 1) is much less sensitive to the pressure of acrylic acid compared with that at 7.46 eV, although it shifts to lower frequencies with increasing pressure (by about 1600 cm^{-1} (0.20 eV)), and appears even in the condensed phase as strongly as in the vapor phase. Therefore, the band is interpreted to be a valence-shell transition band. From a comparison of the observed band position and intensity with the theoretical values given in Table 2, the 6.71 eV band can safely be assigned to the first π-π^* transition.

The spectrum of acrylic acid in the condensed phase (curve 2, Fig. 2) has a peak at 59500 cm^{-1} (7.38 eV). This may correspond to a band at 61800 cm^{-1} (7.66 eV) in the vapor-phase spectrum (curve g, Fig. 1). We interpret that the 7.66 eV band is different from the Rydberg transition band at 7.46 eV; the former is covered by the latter in the spectrum of low vapor pressure (curve e, Fig. 1). From the theoretical results (Table 2), the band at 7.66 eV in the vapor phase may tentatively be assigned to the transition to the second π-π^* state. Curves f and g (Fig. 1) show another weak band appearing as a shoulder at 57500 cm^{-1} (7.13 eV). This band may tentatively be as-

Table 2. Transition energies (ΔE (eV)) and oscillator strengths (f) observed and calculated for the monomeric and dimeric species of *s-trans*- and *s-cis*-acrylic acid

Assignment	Monomer						Dimer				
		s-cis-isomer		*s-trans*-isomer				*s-cis*-isomer		*s-trans*-isomer	
	ΔE_{obsd}[a]	ΔE_{calcd}	f_{calcd}	ΔE_{calcd}	f_{calcd}	main configuration	ΔE_{obsd}[a]	ΔE_{calcd}	f_{calcd}	ΔE_{calcd}	f_{calcd}
n-π^*	~5.0	3.91	0.000_3	3.84	0.000_6	14-15 (14-16)	~5.1	4.05[b]	0 0.000_9	3.97[b]	0 0.001
π-π^*	6.71	6.62	0.353	6.91	0.697	13-15	6.51	6.61 6.70	0.740 0	6.95 6.97	1.470 0
σ-π^*		6.91	0.002	6.92	0.000_7	11-15		6.74[b]	0 0.002	6.73[b]	0 0.000_8
n-π^*		7.73	0.007	7.57	0.004	14-16 10-15 14-15		7.65[b]	0 0.009	7.52[b]	0 0.006
π-π^*		8.27	0.268	8.12	0.014	12-15 (13-16)	7.66	8.03 8.18	0 0.650	7.86 7.97	0 0.029
π-σ^*		8.25	0.028	8.21	0.029	12-17 13-17 12-20		8.52[b]	0 0.050	8.49[b]	0.050 0
σ-π^*		8.89	0.000_6	8.78	0.005	10-15		8.72[b]	0 0.000	8.69[b]	0 0.005
n-σ^*		9.11	0.113	9.04	0.013	14-17 (13-16)		9.04 9.09	0.110 0	9.03 9.09	0.029 0

a) Observed values in the vapor phase. b) Degenerate levels.

signed to the weak σ-π^* or n-π^* transition.

Next, let us examine the nature of the valence-shell transition bands in detail. Figure 3 shows low-lying electron configurations (with in-plane transition moments) caused by valence-shell excitations and the energy levels of *s-trans*-acrylic acid evaluated by considering the configuration interaction. In this figure, *i-j* represents a singly excited configuration caused by the one-electron excitation from the *i*-th occupied orbital to the *j*-th vacant orbital. The shapes of orbitals 10 to 17 are also shown in Fig. 4. As is shown in Fig. 3, the 13-15 configuration of *s-trans*-acrylic acid contributes predominantly (87.8%) to the first allowed π-π^* state, and the 12-15 and 13-16 configurations contribute mainly (60.0% and 18.1%, respectively) to the second π-π^* state. From the shapes of orbitals 12, 13, 15, and 16 (Fig. 4), it is seen that the 6.71 eV band (*i.e.*, the first π-π^* band) is due to the π-π^* excitation within the vinyl group of acrylic

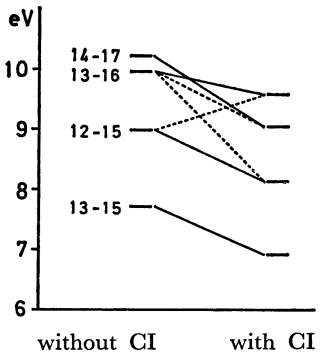

Fig. 3. Energy levels calculated with and without CI treatment for some lower π-π^* and n-σ^* excited states of *s-trans*-acrylic acid.

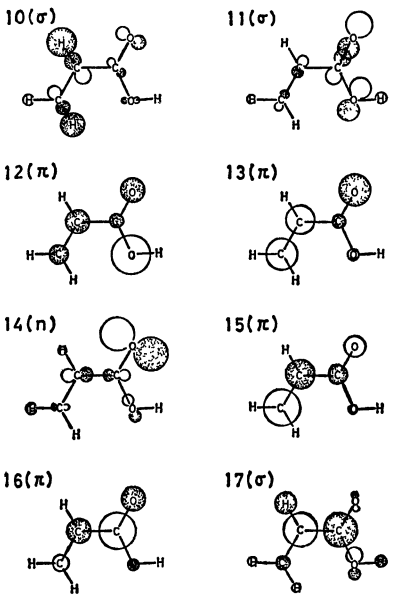

Fig. 4. Schematic shapes of some occupied and vacant MO's of *s-trans*-acrylic acid.

acid, and that the 7.66 eV band (*i.e.*, the second π-π^* band) is due to the intramolecular charge-transfer (from the carboxyl group to the vinyl group) excitation. The nature of the π-π^* transitions is different from that of formic or acetic acid.[2,3] The main configurations of other transitions are also listed in Table 2, and the characters of the transitions can easily be seen from the shapes of orbitals in Fig. 4. Essentially the same conclusion can be derived from the energy levels and wave functions calculated for *s-cis*-acrylic acid and for the dimer.

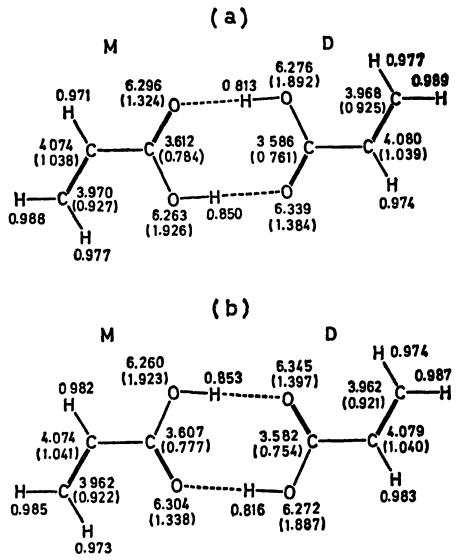

Fig. 5. The total and π- (in parentheses) electron densities calculated for monomeric and dimeric species of (a) *s-trans*-acrylic acid, and (b) *s-cis*-acrylic acid. The electron densities of the monomer and dimer are shown on the left-hand-side and right-hand-side molecules of the dimer, respectively.

Figure 5 shows electron densities for the ground states of monomeric and dimeric species of *s-cis*- and *s-trans*-acrylic acids. The dipole moment in the ground state was calculated to be 1.35 and 0.88 D for *s-trans*- and *s-cis*-acrylic acids, respectively.

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Appendix

Modified CNDO-CI Method Applicable to Planar Molecules. The original CNDO method by Pople, Santry, and Segal[12,13] and CNDO/S method by Bene and Jaffé[14] combined with configuration-interaction (CI) were modified to calculate the electronic structures of planar molecules.

a) Conditions for Transformation Invariance: Our guiding principle is to distinguish the σ- and π-electrons from each other in evaluating semi-empirically some kinds of integrals. Our consideration is restricted to only planar molecules. Let us fix the x-y plane as the molecular plane, and define the 2pz atomic orbital (AO) (designated as z_A) as π-orbital on atom A, π_A. Suppose that one of such operations within the molecular (x-y) plane as rotations about local axes and hybridization is designated by an orthogonal transformation matrix, **O**. In order to preserve invariance under these operations based on the assumption of zero differential overlap (ZDO) employed in the present procedure, the CNDO SCF procedure should satisfy the following transformation conditions between original atomic orbital basis functions, χ and new ones, $\mathbf{t}(=\mathbf{O}\chi)$, concerning core Hamiltonian matrix elements (H_{mn}) and Coulomb repulsion integrals ($(mn|ls)$).

$$H_{mn} = \sum_{\mu,\nu} O_{m\mu} O_{n\nu} H_{\mu\nu} \tag{1}$$

$$(mn|ls) = \sum_{\mu}\sum_{\nu}\sum_{\lambda}\sum_{\sigma} O_{m\mu} O_{n\nu} O_{l\lambda} O_{s\sigma} (\mu\nu|\lambda\sigma) \tag{2}$$

where Greek subscripts indicate the original basis functions, and Roman subscripts the new ones. From Eq. 1 the following relations are derived concerning the bonding parameters, $\beta^0_{\sigma_A}$, of the three σ-AO's on atom A and also concerning the core potential integrals, $(\sigma_A\sigma_A|V_B)$, between the σ_A orbitals and the core potential of atom B;

$$\beta^0_{\sigma_A} \equiv \beta^0_{s_A} = \beta^0_{x_A} = \beta^0_{y_A} \tag{3}$$

$$(\sigma_A\sigma_A|V_B) \equiv (s_As_A|V_B) = (x_Ax_A|V_B) = (y_Ay_A|V_B) \tag{4}$$

On the assumption of ZDO, Eq. 2 gives the following relations:
For the one-center Coulomb repulsion integrals;

$$\gamma_{\sigma_A\sigma_A} \equiv \gamma_{s_As_A} = \gamma_{x_Ax_A} = \gamma_{y_Ay_A} = \gamma_{s_Ax_A} = \gamma_{s_Ay_A} = \gamma_{x_Ay_A} \tag{5}$$

$$\gamma_{\sigma_A\pi_A} \equiv \gamma_{s_Az_A} = \gamma_{x_Az_A} = \gamma_{y_Az_A} \tag{6}$$

For the two-center Coulomb repulsion integrals;

$$(\sigma_A\sigma_A|\nu_B\nu_B) \equiv (s_As_A|\nu_B\nu_B) = (x_Ax_A|\nu_B\nu_B) = (y_Ay_A|\nu_B\nu_B) \tag{7}$$

where ν_B is a σ- or π-orbital on atom B. Equations 3—7 are concerned only with the σ-AO's. The corresponding integrals for π-AO, *i.e.*, $\beta^0_{z_A}$, $(z_Az_A|V_B)$, $\gamma_{z_Az_A}$, and $\gamma_{z_Az_B}$ can be determined separately from the values in Eqs. 3—7.

b) Parametrizations: On the basis of the above relationships, the one-center Coulomb repulsion integral, $\gamma_{\sigma_A\sigma_A}$ and $\gamma_{\pi_A\pi_A}$, were taken to be equal to the difference[15] between the ionization potential, I, and electron affinity, A, of an appropriate valence state.[16,17] Their values employed in the present paper are listed in Table 1. The $\gamma_{\sigma_A\pi_A}$ values and two-center Coulomb repulsion integrals between all the σ- and π-AO's were evaluated from the $\gamma_{\sigma_A\sigma_A}$ and $\gamma_{\pi_A\pi_A}$ values by the use of Klopman's equation,[18] Eqs. 6 and 7 being satisfied.

The core potential integral was evaluated for σ-AO by Eq. 8 and for π-AO by Eq. 9.

$$(\sigma_A\sigma_A|V_B) = Z_B \times (\sigma_A\sigma_A|\sigma_B\sigma_B) \tag{8}$$

$$(\pi_A\pi_A|V_B) = Z_B \times (\pi_A\pi_A|\sigma_B\sigma_B) \tag{9}$$

where Z_B is the core charge of atom B. The bonding parameters for σ- and π-AO's were assumed to be proportional to each valence state ionization potential for the carbon and oxygen atoms, whereas the value for the hydrogen atom, β^0_H was fixed to be -12.0 eV. From the best fit between observed and calculated transition energies, a proportionality constant was chosen to be 1.15 in the present calculation; the values are tabulated in Table 1.

Finally, $1/2(I+A)$ values necessary to evaluate one-center core matrix elements, $U_{\mu\mu}$, were adjusted semi-empirically to give a reasonable electron density for the formaldehyde molecule. Consequently, the lower values were found to be preferable for 2s and 2p orbitals of oxygen to the original values;[13] namely, 24.390 eV for the 2s AO, and 8.111 eV for the 2px, 2py, and 2pz AO's.

c) Hartree-Fock and CI Matrix Elements: According

to the present method, the Hartree-Fock matrix elements and the CI matrix elements for the singlet and triplet manifolds are modified from the original equations[13,19] and calculated by the use of the modified semi-empirical values determined above. In the CI treatment on the ZDO approximation, exchange integrals characteristic of the singlet manifold of the CI matrix elements between the n-π^*, σ-π^*, and π-σ^* configurations vanish and the singlet CI element coincides with the corresponding triplet one. Therefore, the calculated transition energies for the singlet and triplet manifolds of n-π^*, σ-π^*, or π-σ^* excited state are equal to each other and should be compared with the observed transition energies to the triplet states.

Results for Some Planar Molecules. The modified CNDO-CI method mentioned above was applied to such planar molecules as ethylene, formaldehyde, formic acid, *s-trans*-butadiene, *s-trans*-glyoxal, and *s-trans*-acrylaldehyde to investigate their electronic structures and to check the applicability of the method. The geometrical structures of these molecules were taken from the analysis of the rotation-vibration spectrum[20,21] and from the electron diffraction studies.[22,23]

a) Orbital Energies: Tables IA and IIA give orbital energies calculated by the present authors, together with experimental values obtained by photoelectron spectroscopy.[24,25] Except for *s-trans*-glyoxal the sequences of molecular orbitals calculated by the present authors are in accordance with those determined experimentally[24,25] and calculated by the other semi-empirical[26-28] and non-empirical[29-31] methods. In the case of *s-trans*-glyoxal, the calculated splitting between the two n-orbitals was nearly twice as large (3.45 eV) as the observed value[24] (~1.6 eV). Owing to this large calculated splitting, the experimental sequence[24] (n, n, π) was not predicted by the present calculation (n, π, n)

The experimental results[1,25] of formic acid concerning both the sequence of orbitals and transition energies were found to be well reproduced by the theoretical calculation when the β^0 (−27.0 eV) and γ value (17.89 eV) are commonly used for all the 2s and 2p AO's of the two oxygen atoms in the carboxyl group. On the basis of this fact, the calculations of formic acid listed in Tables IA and IIIA and of acrylic acid discussed before were performed by the use of the above β^0 and γ values.

b) Electron Densities: Figure IA shows the electron densities of ethylene, formaldehyde, formic acid, *s-trans*-butadiene, *s-trans*-glyoxal, and *s-trans*-acrylalde-

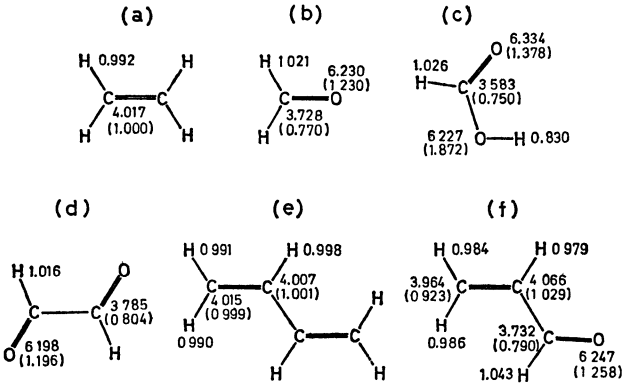

Fig. IA. The total and π- (in parentheses) electron densities of (a) ethylene, (b) formaldehyde, (c) formic acid, (d) *s-trans*-glyoxal, (e) *s-trans*-butadiene, and (f) *s-trans*-acrylaldehyde.

Table IA. Calculated orbital energies of ethylene, formaldehyde, and formic acid

C_2H_4			H_2CO			HCOOH		
Orbital	Energy (eV)	Ionization[a] potential (eV)	Orbital	Energy (eV)	Ionization[a] potential (eV)	Orbital	Energy (eV)	Ionization[b] potential (eV)
$b_{1u}(\pi)$	−13.15	10.51	$b_2(n)$	−13.17	10.88	n	−12.92	11.51
b_{1g}	−15.26	12.73	$b_1(\pi)$	−15.12	14.38	π	−13.29	12.50
a_g	−18.01	14.7	a_1	−18.57	16.0	σ	−15.37	14.78
b_{2u}	−23.76	15.82	b_2	−23.47	16.9	π	−18.64	15.76

a) Taken from Ref. 24. b) Taken from Ref. 25.

Table IIA. Calculated orbital energies of *s-trans*-butadiene, *s-trans*-glyoxal, and *s-trans*-acrylaldehyde

Butadiene			Glyoxal			Acrylaldehyde		
Orbital	Energy (eV)	Ionization[a] potential (eV)	Orbital	Energy (eV)	Ionization[a] potential (eV)	Orbital	Energy (eV)	Ionization[a] potential (eV)
$b_g(\pi)$	−11.49	9.07	$a_g(n)$	−12.06	10.6	n	−12.54	10.11
a_g	−14.23	11.4	$b_g(\pi)$	−14.37	14.03	π	−12.81	10.93
$a_u(\pi)$	−15.72	12.2	$b_u(n)$	−15.51	12.19	π	−16.59	13.7
a_g	−15.97		$a_u(\pi)$	−17.22	15.5	σ	−16.60	14.8
b_u	−16.89		a_g	−17.96	16.0	σ	−16.72	16.1
b_u	−21.19		b_u	−20.83	16.84	σ	−20.74	18.9

a) Taken from Ref. 24.

hyde. The C=O groups of formaldehyde, formic acid, glyoxal, and acrylaldehyde are fairly polarized. The dipole moments calculated by the present method for formaldehyde (2.25 D), formic acid (1.43 D), and acrylaldehyde (3.02 D) agree better with the experimental values (2.30, 1.4—1.7, 3.11 D, respectively)[32,33] than the theoretical values obtained by other authors.[13,26,34-38]

c) Transition Energies: Tables IIIA and IVA give some lower transition energies calculated for the planar molecules under consideration, together with the observed values. The result shows that the lowest singlet π-π^* transition energy of each molecule agrees satisfactorily with the observed value.[1,39-42]

The transition energies to the n-π^* state calculated for formaldehyde (3.19 eV) and acrylaldehyde (2.88 eV) agree well with the observed values to the triplet state (3.0 eV for both).[43,44] The calculated energy (1.87 eV) for the lowest n-π^* state of glyoxal is slightly lower than the observed triplet energy (2.38 eV).[45]

In the present calculation, the n-σ^* bands of formaldehyde, formic acid, glyoxal, and acrylaldehyde are predicted to appear at 9.46, 8.84, 8.43, and 9.16 eV, respectively, being 1—2 eV higher than the observed values assigned to the Rydberg or n-σ^* excited states.[1,40] Since the n-σ^* state of the molecules under consideration is expected to interact significantly with the Rydberg excited state, it is difficult to expect better agreement between the observed and calculated values of the n-σ^* transition energy in the present calculation in which the Rydberg 3s and 3p orbitals are disregarded.

Table IIIA. Singlet and triplet transition energies ($^1\Delta E$ and $^3\Delta E$ (eV)) and oscillator strength (f) calculated and observed for ethylene, formaldehyde, and formic acid

	Obsd		Calcd			
	$^3\Delta E$	$^1\Delta E$	$^3\Delta E$		$^1\Delta E$	f[a]
Ethylene						
π-π^*	4.6[b]	7.6[c]	5.48		7.66	0.470
σ-π^*				8.40		0
π-σ^*				9.53		0
σ-π^*				10.19		0
Formaldehyde						
n-π^*	3.0[d]	~4.3[e]		3.19		0
π-π^*	(4.2)[f]	7.94[e]	5.42		7.83	0.245
σ-π^*				8.03		0.016
n-σ^*		(7.10)[e]	8.73		9.46	0.037
Formic acid						
n-π^*		5.64[g]		4.54		0.000$_4$
π-π^*		8.3[h]	5.28		7.78	0.187
σ-π^*				7.68		0.008
n-σ^*		(7.5 or 8.7)[h]	8.46		8.84	0.009
π-σ^*				8.48		0.029

a) Calculated value for the singlet manifold. b) D. F. Evans, *J. Chem. Soc.*, **1960**, 1735. c) Taken from Ref. 41. d) Taken from Ref. 43. e) Taken from Ref. 40. f) Taken from Ref. 35. g) Taken from Ref. 3. h) Taken from Ref. 1.

Table IVA. Singlet and triplet transition energies ($^1\Delta E$ and $^3\Delta E$ (eV)) and oscillator strength (f) calculated and observed for *s-trans*-butadiene, *s-trans*-glyoxal, and *s-trans*-acrylaldehyde

	Obsd	Calcd		
	$^1\Delta E$	$^3\Delta E$	$^1\Delta E$	f[a]
s-trans-Butadiene				
π-π^*	6.0[b]	4.02	6.21	0.993
π-π^*	(7.2)[b]	5.82	8.02	0
σ-π^*		7.13		0
σ-π^*		8.38		0.002
σ-π^*		8.64		0
π-σ^*		8.66		0.001
π-σ^*		9.23		0
π-π^*		9.67	9.93	0
s-trans-Glyoxal				
n-π^*	2.72[c] (2.38)[d]	1.87		0
n-π^*	4.50[e]	3.44		0
π-π^*	7.2—7.6[f]	4.30	6.81	0.495
π-π^*		5.84	8.32	0
σ-π^*		7.14		0.017
n-π^*		7.47		0
n-σ^*	(6.0—6.7)[g]	7.49	8.43	0.069
σ-π^*		8.85		0
n-σ^*		8.94	9.58	0
s-trans-Acrylaldehyde				
n-π^*	3.76[g] (3.01—3.08)[h]	2.88		0
π-π^*	6.41[g]	4.20	6.55	0.733
π-π^*	(8.38 or 8.49)[g]	6.02	8.31	0.017
n-π^*		7.04		0
σ-π^*		7.46		0.007
n-σ^*	(7.08)[g]	8.47	9.16	0.026
σ-π^*		8.91		0.003
π-σ^*		9.31		0.004
π-π^*		9.79	10.11	0.019

a) Calculated value for the singlet manifold. b) Taken from Ref. 39. c) Taken from Ref. 45. d) Triplet transition energy taken from Ref. 45. e) H. L. McMurry, *J. Chem. Phys.*, **9**, 241 (1941). f) Taken from Ref. 42. g) Taken from Ref. 40. h) Triplet transition energy taken from Ref. 44.

In conclusion, the modified CNDO-CI method was found to be useful for the investigation of electronic structures of planar molecules, especially of lower excited π-π^* and n-π^* states.

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