

CNDO TREATMENTS ON ELECTRONIC SPECTRA
OF SMALL MOLECULES

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The modified CNDO method of Del Bene and Jaffé is employed to interpret electronic spectra of 22 small molecules containing 3–6 atoms. The limits of this method in predicting ground state properties are briefly discussed.

This paper concerns the application of the CNDO method to the electronic spectra of small closed shell molecules. By small molecules we imply systems consisting of 3–6 atoms. It might be assumed that systems of this size belong to the domain of *ab initio* calculations, however, the situation here is not so clear-cut. First, the present state of nonempirical calculations in interpreting electronic spectra is not so satisfactory that the semiempirical studies should cease to be topical and, second, the computational costs associated with accurate nonempirical calculations on larger than triatomic systems are still considerable. The stimulus for the present study arose from the finding that the modified CNDO method of Del Bene and Jaffé¹ (subsequently referred to as DBJ), developed for interpreting electronic spectra of medium-sized molecules with π and nonbonding orbitals, also gives satisfactory results for small radicals^{2,3}. Here we have attempted a similar study on small closed shell molecules. Except for formaldehyde, we have selected molecules which either have not yet been studied at all by semiempirical all-valence electron methods or were studied by other than the DBJ method. The latter are HCN (ref.⁴), CO₂ (ref.⁴), HCF (refs.^{4,5}), HNO (ref.⁵), HFCO (ref.⁵), propynal⁵, NH₃ (ref.⁶), H₂O (refs.^{7,8}), and CH₃NO (ref.⁹).

The results of calculations reported in the literature^{1,10–14} clearly demonstrate that the configuration interaction treatment based on the ground state molecular orbitals given by the standard CNDO/2 or INDO methods does not provide reasonable transition energies. This has led several authors to modifications in the CNDO/2 computational scheme, from which the DBJ version has become the most popular (for DBJ treatments on small molecules see refs.^{15–17}). Segal⁵ attempted to arrive at reasonable transition energies within the INDO formalism and usual parameter set by means of a new variational procedure for calculating excited state wave functions. His procedure, which is similar to the "second method" of Huzinaga¹⁸ or to the OCBSE method¹⁹ gave very good $\sigma \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$, and $\sigma \rightarrow \sigma^*$ transition energies but unsatisfactory results for $\pi \rightarrow \pi^*$ transitions. In our opinion, a modi-

fication in the CNDO/2 scheme is inevitable, because any refined CI or variational treatment cannot overcome the trouble given by the CNDO/2 SCF method — an unrealistic ordering of MO's (e.g. with benzene the predicted highest occupied MO is of the σ type). Concerning the other studies related to this topic let us mention that Salahub and Sandorfy^{6,20-22} have reported calculations using an extended basis set which permits the analysis of Rydberg transitions and the inclusion of doubly excited states is found⁷ to have very little effect on the calculated spectral data.

CALCULATIONS

The CNDO version of Del Bene and Jaffé¹ was followed closely except for the two centre repulsion integrals which were evaluated by the Mataga and Nishimoto formula rather than by means of the Pariser and Parr approximation. On plotting the CNDO/2 parameters for hydrogen, carbon, nitrogen, and oxygen against the parameters suggested by Del Bene and Jaffé, we chose tentatively the following parameters for fluorine: $\gamma_{FF} = 13.9$ eV and $\beta_F^0 = -55$. In the configuration interaction treatment we have considered all singly excited states corresponding formally to electron promotions from the six highest occupied molecular orbitals to the six lowest unoccupied molecular orbitals. With smaller systems having less than six occupied or unoccupied MO's the CI basis set was truncated according to the MO's available. The energies of the doubly excited states for methylene and ozone were calculated by means of the formula²³

$$E(i \rightarrow k, i \rightarrow k) = 2F_{kk} - 2F_{ii} - 4J_{ik} + 2K_{ik} + J_{ii} + J_{kk}, \quad (1)$$

where all the symbols have conventional meanings.

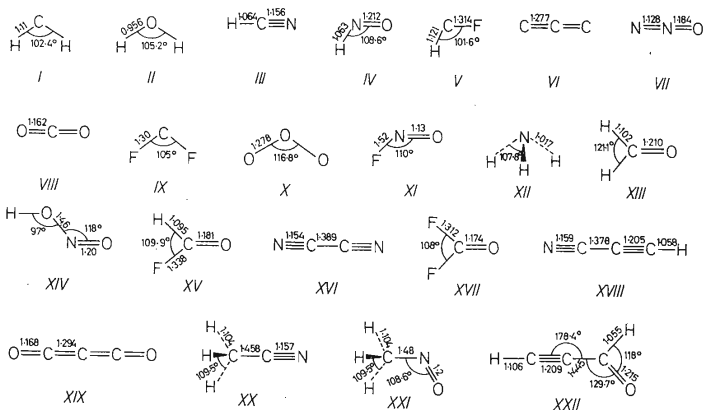
Compounds Studied

The twenty-two molecules studied are presented in Scheme 1. The molecular geometries assumed in calculations (Scheme 1) have been taken from ref.²⁴ except for *IX*²⁵ and *XIX*²⁶. The geometries adopted for *XXI* and in part for *XIV* and *XXII* were inferred from similar molecules.

RESULTS AND DISCUSSION

Ground state properties. The computational scheme¹ employed here was developed to reproduce solely the transition energies and therefore the predicted ground state properties are less reliable than the results given by other methods e.g. by CNDO/2 or MINDO/2. Nevertheless, it is useful to see to which degree the ground state properties are amenable to this treatment. The introduction of empirical electronic repulsion integrals destroys the balance between attractive and repulsive forces so that the method as such cannot be used for geometrical predictions. Most probably a composite function for the core-core repulsions, similar to that in the MINDO method²⁷, should be employed here because reasonable equilibrium geometries are not obtained either by the point charge approximation or by setting the core-core repulsions equal to electron-electron repulsions.

The method of Del Bene and Jaffé reproduces first ionization potentials within an error of ± 1 eV^{15,28}. The data for systems *I*–*XXII*, calculated by means of the



SCHEME 1

Koopmans theorem, are seen, in Table I and Fig. 1, to be of comparable accuracy. Extremely low electron affinities for water and ammonia are due to the fact that the theory predicts the electron uptake to be in an antibonding σ^* orbital. The electronic spectra, however, strongly suggest that there are several Rydberg atomic orbitals which lie below the σ^* orbitals. For this reason the electron affinity for water was omitted in the plot in Fig. 1. Also the third ionization potentials observed for ozone and acetonitrile were omitted because they have no predicted counterparts. This is probably due to the fact that on exploiting Koopmans theorem one cannot arrive at all possible excited states of the respective cation radical. Probably also the higher ionization potentials observed for H_2O at 18.3 eV and for HCN at 19.06 eV are not accounted for by Koopmans theorem and are therefore drastically overestimated by the theory. Dipole moments given by the DBJ method are generally not as good as those obtained from the original CNDO/2 method, however, they are not unreasonable^{15,17}. This also applies with systems II, III, VII, X–XIII, XV, XVIII, XX, and XXII for which experimental data are available^{30,33}: with CNDO/2 calculations the average error is 0.47 D, while with the DBJ calculations it is 0.50 D.

Electronic spectra. Calculated and observed data are summarized in Table II. The electronic spectrum of the bent methylene (I) having a 1A_1 ground state was recorded in the flash photolysis of diazo methane²⁴. The theory reproduces well a fairly strong S_0-S_1 band in the visible and near infrared but does not interpret a very weak band in the near ultraviolet region. The *ab initio* calculations^{34–36}

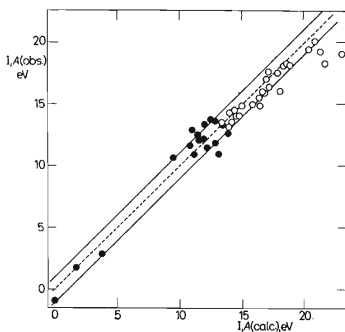


FIG. 1

Plot of the Calculated Ionization Potentials and Electron Affinities against the Experimental Data

Unit slope is indicated by the dashed line, range of ± 1 eV errors by solid lines; ● first ionization potentials and electron affinities, ○ higher ionization potentials.

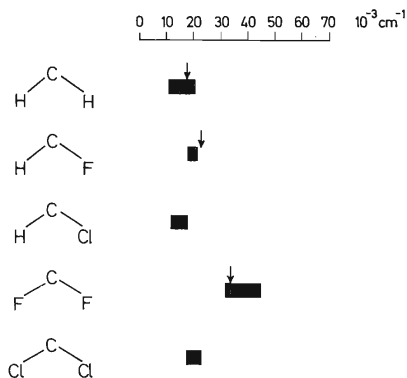


FIG. 2

Localization of the Observed Long-Wavelength Absorption Bands of Methylene and of Its Halogen Derivatives

First DBJ transitions are indicated by arrows.

give the same picture, however Chu and collaborators³⁶ have demonstrated the presence of the next low-lying state, ${}^1A_1^*$, which is due to the two-fold electron promotion ($\varphi_3 \rightarrow \varphi_4$) from the lone-pair sp^2 hybrid orbital to the p -type lone-pair orbital perpendicular to the molecular plane. The ${}^1A_1^*$ state has been predicted to be only 1.92 eV ($15\,500\text{ cm}^{-1}$) above the 1A_1 ground state and from Fig. 1 in ref.³⁶ we have estimated the vertical ${}^1A_1^* \leftarrow {}^1A_1$ transition energy as $\sim 38\,300\text{ cm}^{-1}$. As the DBJ SCF excitation energy given by Eq. (I) is very close to this value ($40\,700\text{ cm}^{-1}$), the ${}^1A_1^* \leftarrow {}^1A_1$ assignment affords a plausible interpretation of the absorption observed at $27\,600\text{--}30\,300\text{ cm}^{-1}$. Fluorine substitution (in *V* and *IX*) is associated with the hypsochromic shift of the first absorption band which is reproduced well by the theory (Fig. 2). Also with chloro derivatives a long-wavelength tail of the first band is shifted but the observed blue shift is less remarkable. The analysis of the observed spectrum of water (*II*) led to the assignment of a series of Rydberg transitions²⁴. Even the first transition, $\tilde{A} \leftarrow \tilde{X}$, observed in the 145–186 nm region was assigned to a Rydberg transition with the upper state $\dots (1b_2)^2 (3a_1)^2 (1b_1) (3sa_1)$ configuration²⁴. The first two transitions, $\tilde{R} \leftarrow \tilde{X}$ and $\tilde{S} \leftarrow \tilde{X}$, where Herzberg presents no electron configurations, are located at $116\,800$ and $125\,800\text{ cm}^{-1}$, respectively. The two energy lowest DBJ transition energies correspond to the $114\,800$ and $121\,700\text{ cm}^{-1}$ wavelengths, however the agreement is probably fortuitous because there is some experimental evidence that these bands are also probably due to Rydberg transitions. The predicted electronic transitions are due to pure $\varphi_4 \rightarrow \varphi_5$ and $\varphi_4 \rightarrow \varphi_6$ electron promotions, φ_4 being localized in the oxygen $2p_z$ AO. With cyano compounds, hydrogen cyanide (*III*), dicyanogen (*XVI*), cyanoacetylene (*XVIII*), and acetonitrile (*XX*) the theory fails to reproduce the longest-wavelength bands, the predicted transition energies being drastically underestimated. Hyponitrous acid, HNO (*IV*), is an unstable molecule with a life time of about 0.1 s^{24} . The wavelength predicted for the first band, $12\,100\text{ cm}^{-1}$, is shifted somewhat bathochromically with respect to the absorption observed at $13\,000\text{--}18\,200\text{ cm}^{-1}$. The emission band is located at $10\,400\text{--}16\,700\text{ cm}^{-1}$. The first two theoretical excited states are due to rather pure $\varphi_6 \rightarrow \varphi_7$ and $\varphi_4 \rightarrow \varphi_7$ transitions, φ_4 , φ_6 , and φ_7 being a bonding σ orbital of the N—O bond, a nonbonding orbital almost localized on the oxygen, and the antibonding π^* orbital, respectively. The theory interprets well the hypsochromic shift observed for the first band on going from *IV* to its fluoro and hydroxy derivatives (*XI*, *XIV*), however, the transition energies in *XI* and *XIV* are also underestimated. The respective electronic transition in *XI* is of the $n \rightarrow \pi^*$ type ($\varphi_9 \rightarrow \varphi_{10}$). In the upper state of the next transition in *XI* two configurations dominate: $\varphi_7 \rightarrow \varphi_{10}$ (61%) and $\varphi_5 \rightarrow \varphi_{10}$ (37%). The pertinent orbitals can be characterized as follows: φ_5 is a bonding σ orbital, φ_7 is a nonbonding fluorine orbital, and φ_{10} is an antibonding π^* orbital localized on the NO bond. On going from *IV* to its methyl derivative *XXI*, the first observed band is shifted very little. This is in agreement with the calculations which predict very small changes in several of the lowest energy electro-

TABLE I
Ionization Potentials (IP) and Electron Affinities (EA)

Compound	IP (calc. ^a), eV	IP (obs. ^b), eV	EA (calc. ^a), eV
CH ₂	12.92, 16.06, 26.91	11.82 ^c	-0.05 (-0.95) ^{c,d}
H ₂ O	13.93, 16.52, 21.84, 42.87	12.61, ~14.8, ~18.3	-9.82 (~0.9) ^{c,d,e}
HCN	12.84(2), 14.78, 23.11, 35.74	13.60 ^f , ~14 ^f , ~19.06 ^f	-0.71
HNO	11.35, 14.62, 17.41, 20.13, 26.21		0.99
HCF	12.28, 17.29, 17.37, 19.92, 24.70		0.10
C ₃	11.55(2), 12.46, 15.49, 24.87	12.1 ^g	1.77(2) (1.8) ^{c,d}
N ₂ O	11.08(2), 17.22, 18.63(2), 20.93	12.89, 16.38, 18.23, 20.11	0.90(2)
CO ₂	12.50(2), 17.15, 18.40(2), 20.51	13.78, ~17.6, 18.08, 19.40	-0.38(2)
CF ₂	13.42, 15.87, 16.48, 18.66, 19.67	13.30 ^c	0.21
O ₃	11.40, 13.30, 13.48, 19.40, 21.37	12.52, 13.5, ~17, 19.3	3.73 (2.89) ^{c,d}
NOF	12.79, 15.40, 15.80, 17.80, 19.07		1.25
NH ₃	13.12, 18.12(2), 36.39	10.85, ~16	-6.58
CH ₂ O	11.18, 13.96, 16.71, 20.41, 24.99	10.88, ~14.3, ~15.95	-0.18
HONO	12.36, 13.19, 15.66, 15.75, 18.44		1.84
CHFO	12.22, 13.71, 15.35, 18.32, 18.34	11.4 ^c	-0.02
C ₂ N ₂	11.99(2), 14.36, 14.98(2), 16.42, 25.88	13.36, 14.49, 14.86, 15.47	0.89(2)
F ₂ CO	13.24, 13.60, 16.28, 16.45, 17.10		0.27
HC≡C-CN	10.84(2), 14.17(2), 14.47, 18.90, 25.25	11.60, 13.54, 14.03, ~18.1	0.52(2)
C ₃ O ₂	9.45(2), 15.87(2), 16.88, 17.14(2), 18.52	10.60, ~14.9, ~15.9, ~17	1.13(2)
CH ₃ CN	11.86(2), 13.91, 17.93(2), 19.27	12.21, 13.14, ~16.2, ~17.5	-1.09(2)
CH ₃ NO	10.65, 13.40, 14.85, 18.21, 18.44		0.57
HC≡C-CHO	11.03, 11.16, 11.37, 14.80, 16.66		0.60

^a Orbital degeneracies are given in parentheses. ^b These are vertical ionization potentials taken from ref.²⁹ unless otherwise noted. ^c Taken from ref.³⁰ EA (obsd.), eV. ^e The observed electron affinity is most likely due to an electron uptake to a Rydberg orbital, cf. text. ^f Taken from ref.³¹. ^g Ref.³².

TABLE II
Calculated and Observed Electronic Spectral Data^a

Compound	$\tilde{\nu}_1$	$\log f_1$	Assignment	$\tilde{\nu}_2$	$\log f_2$	Assignment	$\tilde{\nu}_3$	$\log f_3$	Assignment
CH ₂	calc. 19.3	-1.59	$^1B_1 \leftarrow ^1A_1$	40.7 ^b		$^1A_1 \leftarrow ^1A_1$	59.06	forbidden	$^1A_2 \leftarrow ^1A_1$
	obs. 11.1-20.0			27.6-30.3			69.5		
H ₂ O	calc.		Rydberg transitions	114.8	forbidden	$^1A_2 \leftarrow ^1A_1$			
	obs.								
HCN	calc. 38.6	forbidden	$^1\Delta \leftarrow ^1\Sigma^+$	56.4	-1.44	$^1\Pi \leftarrow ^1\Sigma^+$	77.6	-1.41	$^1\Pi \leftarrow ^1\Sigma^+$
	obs. 52.2-62.5			64.5-74					
HNO	calc. 12.1	-3.10	$^1A'' \leftarrow ^1A'$	57.7	-2.67	$^1A'' \leftarrow ^1A'$	76.7	-0.30	$^1A' \leftarrow ^1A'$
	obs. 13.0-18.2								
HCF	calc. 22.9	-1.66	$^1A'' \leftarrow ^1A'$	74.3	-1.50	$^1A'' \leftarrow ^1A'$	84.6	-0.67	$^1A' \leftarrow ^1A'$
	obs. 16.7-22.2								
C ₃	calc. 23.9	-1.47	$^1\Pi_u \leftarrow ^1\Sigma_g^+$	26.9	forbidden	$^1\Delta_u \leftarrow ^1\Sigma_g^+$	39.2	forbidden	$^1\Pi_g \leftarrow ^1\Sigma_g^+$
	obs. 22.4-29.4								
N ₂ O	calc. 23.0	forbidden	$^1\Delta \leftarrow ^1\Sigma^+$	67.6	-1.66	$^1\Pi \leftarrow ^1\Sigma^+$	79.9	forbidden	$^1\Delta \leftarrow ^1\Sigma^+$
	obs. 38.5 ^c			65-71			74-81.4		
CO ₂ ^d	calc. 46.9	forbidden	$^1\Delta_u \leftarrow ^1\Sigma_g^+$	82.5	forbidden	$^1\Pi_g \leftarrow ^1\Sigma_g^+$	88.0	forbidden	$^1\Delta_g \leftarrow ^1\Sigma_g^+$
	obs. 46.0			72.0-82.0			85.5-88.5		
CF ₂	calc. 32.4	-1.39	$^1B_1 \leftarrow ^1A_1$	74.6	forbidden	$^1A_2 \leftarrow ^1A_1$	88.6	-0.76	$^1B_2 \leftarrow ^1A_1$
	obs. 30.8-45.5								
O ₃ ^e	calc. 14.4	forbidden	$^1A_2 \leftarrow ^1A_1$	14.9	-3.73	$^1B_1 \leftarrow ^1A_1$	25.6 ^b ; 36.8 ^b		$^1A_1 \leftarrow ^1A_1$
	obs. 10.0-14.3			16.4-18.2			26.8-33.3		
NOF	calc. 23.3	-2.76	$^1A'' \leftarrow ^1A'$	58.5	-2.92	$^1A'' \leftarrow ^1A'$	77.6	-0.97	$^1A' \leftarrow ^1A'$
	obs. 29.8-38.5								
NH ₃	calc.			87.5	-1.72	$^1A_1 \leftarrow ^1A_1$			
	obs.		Rydberg transitions						

CH ₂ O	calc. 25.6 obs. 28.3—43.5	forbidden	$^1A_2 \leftarrow ^1A_1$	67.2	-2.04	$^1B_1 \leftarrow ^1A_1$	74.4	-1.20	$^1B_2 \leftarrow ^1A_1$
HONO	calc. 16.3 obs. 26.0—31.7	-2.88	$^1A'' \leftarrow ^1A'$	50.9	-3.13	$^1A'' \leftarrow ^1A'$	57.8	-0.63	$^1A' \leftarrow ^1A'$
CHFO	calc. 33.3 obs. 37.0—50.0	-3.59	$^1A'' \leftarrow ^1A'$	66.4	-2.08	$^1A'' \leftarrow ^1A'$	77.0	-0.39	$^1A' \leftarrow ^1A'$
C ₂ N ₂	calc. 31.6 obs. 44.2—55.0	forbidden	$^1\Delta_u \leftarrow ^1\Sigma_g^+$	43.3 59.5—69.0	forbidden	$^1\Delta_g \leftarrow ^1\Sigma_g^+$	57.1	-1.73	$^1\Pi_u \leftarrow ^1\Sigma_g^+$
F ₂ CO	calc. 39.4 obs. 48.4—55.6	forbidden	$^1A_2 \leftarrow ^1A_1$	74.6	-2.11	$^1B_1 \leftarrow ^1A_1$	75.3	-0.296	$^1A_1 \leftarrow ^1A_1$
HCCCN	calc. 26.9 obs. 36.8—43.5	forbidden	$^1\Delta \leftarrow ^1\Sigma^+$	40.1 43.5—47.6	forbidden	$^1\Delta \leftarrow ^1\Sigma^+$	53.9	-1.585	$^1\Pi \leftarrow ^1\Sigma^+$
C ₃ O ₂	calc. 23.6 obs. 30.3—41.7	forbidden	$^1\Delta_u \leftarrow ^1\Sigma_g^+$	38.7	forbidden	$^1\Delta_g \leftarrow ^1\Sigma_g^+$	47.1	-1.83	$^1\Pi_u \leftarrow ^1\Sigma_g^+$
CH ₃ CN	calc. 37.3 obs. 52.5—62.5	forbidden	$^1A_1, ^1E \leftarrow ^1A_1$	57.0	-1.81	$^1E \leftarrow ^1A_1$	77.9	-1.53	$^1E \leftarrow ^1A_1$
CH ₃ NO	calc. 11.9 obs. 14.1—16.9	-3.21		57.8	-3.59		74.5	-0.30	
HCCCHO	calc. 24.9 obs. 26.1—33.3	forbidden	$^1A'' \leftarrow ^1A'$	28.7	forbidden	$^1A'' \leftarrow ^1A'$	32.4 38.9—46.5	-2.23	$^1A' \leftarrow ^1A'$

$^a \tilde{\nu}$ and f stand for wavenumbers (10^{-3} cm^{-1}) and oscillator strengths, respectively; experimental data are taken from ref.²⁴, ^b SCF excitation energy; the upper state is a doubly excited state (see text). ^c Maximum of intensity of a very weak continuum starting at $32\,600 \text{ cm}^{-1}$. ^d $\tilde{\nu}_4$ calc. 94.0, obs. 89; assignment $^1\Sigma_u^+ \rightarrow ^1\Sigma_g^+$. ^e $\tilde{\nu}_4$ calc. 44.1, obs. 33.3—45.5, $\log f_4$ (calc.) — 0.15, assignment $^1B_2 \leftarrow ^1A_1$.

nic transitions in *IV* upon methyl substitution. With the C_3 molecule (*VI*), the theory predicts two electronic transitions (at 23870 and 26950 cm^{-1}) in the region of the observed band (24400–29400 cm^{-1}). Absorption of nitrous oxide (*VII*) in the near ultraviolet is not well understood. In that region several very weak continua have been observed, the longest-wavelength of which starts at 32600 cm^{-1} . In spite of the uncertain nature of this absorption, the predicted transition energy is drastically underestimated. Also our ${}^1\Delta \leftarrow {}^1\Sigma^+$ assignment is in disagreement with the ${}^1\Sigma^+ \leftarrow \leftarrow {}^1\Sigma^+$ assignment of Herzberg. The next two transition energies are interpreted well. With the isoelectronic carbon dioxide (*VIII*), the theory reproduces remarkably well the absorption in the whole region of the observed spectrum. Good overall agreement is also found for ozone (*X*). The three interpreted bands can be assigned to almost pure $\varphi_8 \rightarrow \varphi_{10}(n \rightarrow \pi^*)$, $\varphi_7 \rightarrow \varphi_{10}(n \rightarrow \pi^*)$, and $\varphi_9 \rightarrow \varphi_{10}$ (nonbonding $\pi \rightarrow \pi^*$) electron promotions. The recent *ab initio* calculations³⁷ give the same picture and assign the band at 26800–33300 cm^{-1} to a two-electron ${}^1A_1 \leftarrow {}^1A_1$ transition with the upper state containing 6 π electrons. The DBJ computational scheme gives the same result but predicts two two-electron $n \rightarrow \pi^*$ transitions in that region. All observed bands of ammonia (*XII*) were assigned to Rydberg transitions. The theory predicts the first valence-shell transition at 87500 cm^{-1} . On going from formaldehyde (*XIII*) to its mono (*XV*) and difluoro (*XVII*) derivatives, the theory reproduces the observed blue shift of the first band, the agreement being fair when judged semiquantitatively. For formaldehyde the calculation predicts a $\pi \rightarrow \pi^*$ transition at 82200 cm^{-1} . The *ab initio* calculations^{38–41} predict the 1A_1 ($\pi \rightarrow \pi^*$) state to lie above the 2B_2 ionization limit (10.88 eV, *i.e.* 87800 cm^{-1}). The theory reproduces well the location and the transition moment direction (perpendicular to the molecular plane) for the first band of propynal (*XXII*) while it underestimates the transition energy for the second observed band. The predicted first transition energy in carbon suboxide (*XIX*) is also underestimated.

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