Calculation of Some Electronic Excited States of Formaldehyde

Remarks on the $\pi \to \pi^*$ Transition

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The optimized MO's of several excited states of formaldehyde have been calculated by means of a large basis set of modified Gaussian functions; particular attention has been paid to the $\pi \to \pi^*$ transition. The total energy of the various states has been obtained as the sum of the SCF and correlation energies; the last one has been calculated as a functional of the electronic density. The calculated values for the transition energies are in good agreement with the experiment. A strong interaction of the $\pi \to \pi^*$ state with the continuum is evidentiated; this fact can justify the absence of the $\pi \to \pi^*$ band in the absorption spectrum.

Key words: Excited states of formaldehyde, MO's of – Formaldehyde, $\pi \to \pi^*$ transition

1. Introduction

The absorption spectrum of formaldehyde shows, in the range 57000 to 85000 cm^{-1}, many peaks ascribed to the $2b_2 \to na_1$ ($^1B_2$), $2b_2 \to nb_2$ ($^1A_1$), $2b_2 \to nb_1$ ($^1A_2$), $5a_1 \to nb_1$ ($^1B_1$) transitions. No band due to $\pi \to \pi^*$ ($^1A_1$) transition is reported. Many theoretical calculations suggest that the excitation energy of this transition lies between 9.9 and 11.71 eV (cf. Table 1). Since this value is close to the ionization threshold value of 10.88 eV for the $2b_2 \to nb_2$ ($^1A_1$) transition, it seems reasonable to assume an autoionization process because of the interaction of the $\pi \to \pi^*$ state with some $2b_2 \to nb_2$ and the continuum. This means that the $\pi \to \pi^*$ state is not a true molecular eigenstate; therefore its absorption curve is too large to be observed.

The excited states of this molecule were calculated by several authors employing the CI treatment [4–9], by McKoy using the equations of motion method [10],

Table 1. Ground state (a.u.) and vertical transition (eV) energies from various calculations

		Ref. [4]	Ref. [5]	Ref. [6]	Ref. [7]	Ref. [8]	Ref. [9]	Ref. [10]	Ref. [11]	Pres. Work	Exp. [1]
Ground	SCF	−113.8094	−113.8129	−113.8097	−113.8563	−113.8911	−113.8951	—	−113.8290	−113.9086	−114.562
	SCF+CI	—	—	−113.9073	−113.9839	−114.201	—	—	−113.9409	−114.4493[a]	
$^1A_1(\pi \to \pi^*)$		11.72	11.41	11.31	9.90	11.2	10.62	10.10	10.77	10.82	—[b]
$^3A_1(\pi \to \pi^*)$		4.99	5.69	5.66	—	—	5.70	5.29	5.95	5.96	6.0[c]
$^1B_2(2b_2 \to 6a_1)$		—	7.38	7.48	—	—	7.45	7.28	—	7.14	7.10
$^1B_2(2b_2 \to 7a_1)$		—	8.39	—	—	—	—	8.12	—	8.02	8.14
$^1B_2(2b_2 \to 8a_1)$		—	—	—	—	—	—	—	—	8.96	9.24
$^1B_2(2b_2 \to 9a_1)$		—	—	—	—	—	—	9.55	—	9.30	9.62

[a] SCF+correlation energy (see text).
[b] Harding and Goddard III [11] reported the experimental value of the $\pi \to \pi^*$ transition energy as 10.5 eV. This value they themselves considered as not a very reliable one.
[c] Chutjian, H., Ref. [2].

and lastly by Harding *et al.* using generalized valence bond and CI wavefunctions [11]. The accuracy of the results obtained by the CI method is difficult to estimate: in fact it is impossible to quote exactly the percentage of the correlation energy in the ground and in the excited states. This percentage is anyway quite low, and lies in the range from 10% to 40% [8].

We have recently found a method which allows the distinct calculation of both the SCF and correlation energies for the different states [15]. This method takes into account the open shell problems and the orthogonality constraints with respect to the underlying states. The correlation energy is calculated by integrating an electronic density functional [16]. Using this technique, we have calculated the energy of some of the $2b_2 \to na_1$ states for which the experimental data are available, so that a direct comparison can be made to judge the accuracy of the method and of our basis set. Afterwards, we have calculated the energy of the $\pi \to \pi^*$ state and of the $^2B_2$ ion. The calculations are carried out at fixed geometric parameters, thus considering only vertical transitions. The excitation energies obtained for the $2b_2 \to na_1$ transitions agree well with the experimental values (the magnitude of error is <0.3 eV); this leads us to think that the result for the $\pi \to \pi^*$ transition (10.82 eV) is also equally good. This suggests that we are not dealing with a stationary state and that there is an autoionization process.

2. Basis Functions

A set of modified Gaussian basis functions, [17, 18] centred on the various atoms, has been employed. This set has been completed by some very expanded s, p and d functions on the centre of negative charges of the $^2B_1$ ion. Geometrical parameters are the following [3]:

$R_{CO} = 2.2864$ a.u., $R_{CH} = 2.1164$ a.u.
$\widehat{HCH} = 118°$, $R_{CX} = 1.048$ a.u.

where R_{CX} is the distance of the centroid from the carbon.

Orbital exponents for the functions centred on the atoms do not offer any difficulties: they are those needed for describing the ground state. We got them from Huzinaga's tables [19, 20] which concern isolated atoms, but are well suited for the valence orbitals of molecules also [12]. Regarding orbital exponents of the Rydberg levels, the analysis illustrated by Fig. 1 has been made. It is evident that a description of the $6a_1$ orbital (referred to as $3s$ Rydberg) needs functions with orbital exponents between 0.03 and 0.001 while the $7a_1$ orbital ($3p$ Rydberg) needs orbital exponents between 0.032 and 0.008.

We think that a similar analysis of the basis functions is very useful because no device or refining of the theory shall give correct results if the basis employed is not composed of suited functions. In Table 2 are reported orbital exponents of the functions we have employed.

Table 2. Basis functions

Centre	Type	Orbital exponent
C	s	(16067.118, 2365.8824, 542.29752, 148.23131)[a], (46.007872, 15.853338, 5.8801611)[b], 4.1833454, 2.2821385, 0.6169005, 0.2742436, 0.1339569, 0.0615619 (42.0201, 8.90332, 2.57917)[c], 0.89487, 0.338303, 0.13761, 0.055645
	p_x, p_y, p_z d_{z^2}, d_{xz}, d_{yz}	1.5, 0.5
O	s	(30518.035, 4547.8916, 1044.4654, 284.96896)[d], (91.606655, 30.986724, 11.579711)[e], 8.7266833, 4.4835041, 1.164619, 0.5064046, 0.2481748, 0.1228019 (78.603, 17.5167, 5.54421)[f], 2.05152, 0.794239, 0.305583, 0.112384
	p_x, p_y, p_z d_{z^2}, d_{xz}, d_{yz}	1.5, 0.5
H	s	(18.61, 4.239, 0.6577)[g], 0.1483 1.0
	p_x, p_y, p_z	
C–O	s	0.03, 0.014, 0.006, 0.0028, 0.0013, 0.0006, 0.0002
	p_x, p_z	0.032, 0.016, 0.008
	d_{xz}	0.032, 0.016, 0.008

[a] Contracted; coefficients 0.00488113, 0.03666171, 0.19235652, 0.83226855.
[b] Contracted; coefficients 0.1405424, 0.33170913, 0.44811123.
[c] Contracted; coefficients 0.00972229, 0.07475669, 0.30378031.
[d] Contracted; coefficients 0.00596971, 0.03377769, 0.21239072, 0.81642901.
[e] Contracted; coefficients 0.12837, 0.31878733, 0.44575201.
[f] Contracted; coefficients 0.0116459, 0.08317463, 0.30401735.
[g] Contracted; coefficients 0.023, 0.193, 1.

Table 3. SCF, correlation and total energy of some states of the series $2b_2 \rightarrow na_1(^1B_2)$

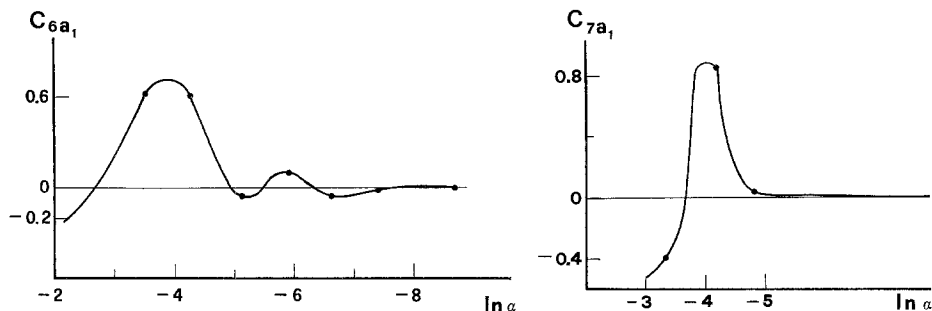| State	Excitation	E_{SCF}(a.u.)	E_c(a.u.)	E_{tot}(a.u.)	ΔE_{SCF}(eV)	ΔE_{tot}(eV)	ΔE_{exp}(eV)
$^1A_1$	Ground State	−113.9086	−0.5407	−114.4493	—	—	—
$^1B_2$	$2b_2 \rightarrow 6a_1$	−113.6722	−0.5146	−114.1868	6.43	7.14	7.10
$^1B_2$	$2b_2 \rightarrow 7a_1$	−113.6436	−0.5110	−114.1546	7.21	8.02	8.14
$^1B_2$	$2b_2 \rightarrow 8a_1$	−113.6099	−0.5099	−114.1198	8.13	8.96	9.24
$^1B_2$	$2b_2 \rightarrow 9a_1$	−113.5979	−0.5094	−114.1073	8.45	9.30	9.62
$^2B_2$	Ion	−113.5530	−0.5050	−114.0580	9.67	10.65	10.88

Fig. 1. Behaviour of coefficients as a function of $\ln\alpha$ (α = orbital exponent). The points denote the values corresponding to the α's of our basis set. a) $6a_1$ orbital; b) $7a_1$ orbital

3. Rydberg Series $2b_2 \to na_1$

The first four terms of this series have been calculated. The wavefunction which has been optimized in every case corresponds to an occupation of the type:

$$(1a_1')^2 (2a_1')^2 (3a_1')^2 (4a_1')^2 (1b_2')^2 (5a_1')^2 (1b_1')^2 (2b_2')(na_1')$$

The two determinants which are obtained by interchanging the spin functions of the last two monooccupied orbitals have been combined to give singlet and triplet states. The apex in the orbitals means that they are changed when compared with the underlying states, while the orthogonality condition is assured by the last singly occupied orbital. When the SCF functions of the states have been obtained, a calculation of the correlation energy has been carried out, as shown in previous papers [16, 21].

The analysis of the na_1 MO's shows that the $6a_1$ and $8a_1$ orbitals are substantially formed by s-type functions; they have $\langle r^2 \rangle$ values respectively of 49.34 and 204.07 (a.u.)^2. Therefore they are referred to as Rydberg $3s$ and $4s$ in the Mulliken notation [22]. Analogously the $7a_1$ and $9a_1$ orbitals, principally built up by expanded p functions, have $\langle r^2 \rangle$ values of 60.62 and 210.19 (a.u.)^2; therefore they can be assimilated to Rydberg $3p$ and $4p$. The next orbital, corresponding to the Rydberg $4d_\sigma$, does not appear in our series because there are no suitable functions in the basis set. The values of SCF and correlation energies of the various states are reported in Table 3.

4. $\pi \to \pi^*$ Transition

By minimizing the energy corresponding to the state represented by the function

$$\Psi = \mathrm{Core}\{\pi(n-1)\bar{\pi}^*(n) + \pi^*(n-1)\bar{\pi}(n)\} \tag{1}$$

we obtain an SCF energy of -113.5379 a.u. and a correlation energy of -0.510 a.u. The SCF wavefunction does not show evidence of a strong Rydberg character, differently from the ethylene $\pi \to \pi^*$ singlet state [21]. But also in this case we doubt whether it furnishes the correct value of electron density. In fact, the SCF energy of (1) shows a very small variation in a large range of Rydberg character percentage of the π^* orbital, while the variation of the correlation energy is quite

large. In order to overcome this difficulty, we have divided the $2b_1$ (π^*) orbital into two parts:

$$2b_1 = \sin\theta b_v + \cos\theta(b_r - Sb_v)(1 - S^2)^{-1/2};$$

$$S = \langle b_r | b_v \rangle$$

b_r is the Rydberg part of the $2b_1$ orbital; its remaining part, b_v, has substantially a valence character. The resulting wavefunction can be written as:

$$\Psi = \sin\theta\psi_v + \cos\theta\psi_r$$

The variations of $\langle \Psi\mathscr{H}\Psi \rangle$, correlation energy, total energy and $\langle \pi^* | x^2 | \pi^* \rangle$ as a function of $\cos^2\theta$ are reported in Figs. 2–5.

The minimum of the total energy so obtained is -114.0516 a.u.[1]. It corresponds to a Rydberg character of about 15%, with $\langle \pi^* | x^2 | \pi^* \rangle = 23.2$ (a.u.)^2.
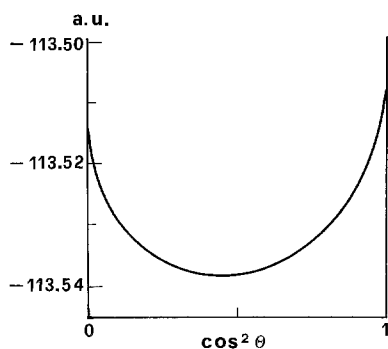

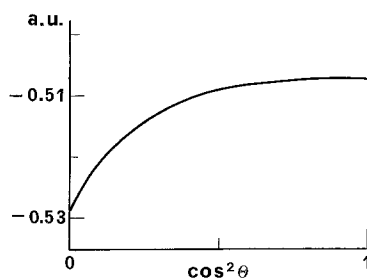**Fig. 2.** SCF energy of the $\pi \to \pi^*$ state versus $\cos^2\theta$ (fraction of Rydberg character)

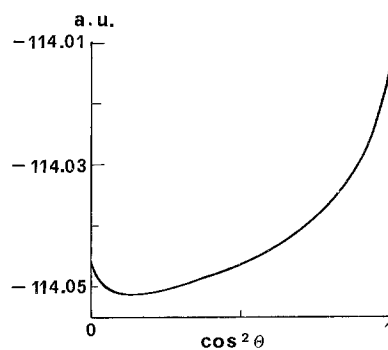**Fig. 3.** Correlation energy of the $\pi \to \pi^*$ state versus $\cos^2\theta$

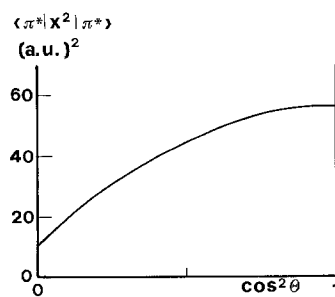**Fig. 4.** Total energy of the $\pi \to \pi^*$ state versus $\cos^2\theta$

Fig. 5. $\langle \pi^* | x^2 | \pi^* \rangle$ value versus $\cos^2\theta$

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[1]   The research of this minimum is justified by the fact that our calculation follows this scheme:

a) The wavefunction is written as the product of an Hartree–Fock type wavefunction, Ψ, and a suited correlation function, Φ, such that $|\Psi\Phi|^2 = 1$

b) Starting from the formula $E = \langle \Psi\Phi|\mathscr{H}|\Psi\Phi \rangle$ and introducing some approximations, one obtains:

$$E \simeq \langle \Psi|\mathscr{H}|\Psi \rangle + E_c = E_0 + E_c$$

where E_c is given by the formula (19) of Ref. [16] or by its generalization in Ref. [21].

From our calculations the $\pi \to \pi^*$ transition occurs at 10.82 eV while the $^2B_2$ ionization energy is 10.65 eV. We think that the most significant quantity is the relative position of these two energies rather than their absolute values. This statement is based on the fact that the same method is followed for the calculation of both the above mentioned state and the ground state; thus the same error has been introduced in the calculation of both the SCF and the correlation energies for all the three states. This cannot be said for certain for the calculations worked out by the CI method. Every configuration brings, indeed, a very specific contribution to the correlation energy (radial, angular, etc.) and the amount of this contribution can be different in the various states. The percentage of the correlation energy obtained by the CI method is hardly greater than 40%. This low percentage is, in principle, not a sufficient reason to conclude that the results have a low reliability. The fundamental problem, indeed, is to evaluate accurately the correlation energy of the outer electrons which are liable for the greatest variations of the charge density in the transitions; to disregard the correlation energy of the inner shell electrons should not be important in these cases. An accurate analysis of these problems is however extremely difficult because it implies a detailed knowledge of the employed configurations, considering both their structure and the basis functions which mostly contribute to the involved molecular orbitals. The above mentioned difficulties do not appear in our method, by which it is possible to obtain at least 95% of the correlation energy.

Going back to the calculated values, we think that the maximum absolute error is not greater than 0.3 eV, while the relative error is still lower. We conclude that the energy of the $\pi \to \pi^*$ state should lie at a value of 0.2 eV above the $^2B_2$ ion energy. This result is in a good agreement with the values given by Refs. [5], [6], [8]. Therefore, it is reasonable to think that $\pi \to \pi^*$ state is not a true eigenstate of the system, but is an autoionizing one, which should be described as a combination (with time-dependent coefficients) of the $\pi \to \pi^*$ ($^1A_1$) wavefunction and some others of the $2b_2 \to nb_2$ series and the continuum.

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