THEORETICAL ANALYSIS OF THE SPECTROSCOPIC PARAMETERS OF THE FORMALDEHYDE MOLECULE

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The results of calculations are presented of certain spectroscopic characteristics of the formaldehyde molecule including the transition probabilities and the oscillator strengths of the dipole transitions in the vacuum UV range of molecular spectrum improving the theoretical and experimental data obtained previously. The calculations were based on the method of the motion equations taking account of the most important correlation effects using a scheme which was proposed and checked previously. These results (some of them were first obtained) can be useful in a wide variety of applications including the atmospheric optics.

Introduction. Formaldehyde as gaseous impurity is present in the Earth's atmosphere as well as in the atmospheres of other planets. Considerable interest in studying its spectroscopic characteristics was stimulated when formaldehyde was recently discovered in the interstellar dust clusters.[1] Also of interest are certain extraordinary characteristics of the molecular spectrum of formaldehyde and the parameters of this spectrum in the vacuum UV range.[2-13] It is well known that studies of the photochemical reactions of carbonyl compounds including the mechanisms of such reactions are intimately related to the problem of calculating and studying the nature of the excited states of the organic molecules, in particular of the molecule of formaldehyde.[10] Actually, formaldehyde is an important prototype in studying the salient features of the carbonyl compounds and polyatomic molecules in general.[10,14] Although the molecule of formaldehyde has already been studied in quite a few papers (see Ref. 1–14), its certain spectroscopic parameters have not yet been confirmed reliably till now, while other parameters have been obtained only theoretically and, unfortunately, have not yet been checked experimentally. First of all we mean the oscillator strengths of a large number of transitions. As for the Rydberg series, the intensity distributions appears to be extraordinary.[12,13] Another characteristic of this spectrum is the lack of any band which could be associated with the $\pi \to \pi^*$–valence transition. Our results show that a transition exists to the state $^1A_1(\pi, \pi^*)$ at a wavelength of 1265 Å with oscillator strength $f = 0.08$. This state is strongly affected by the interaction between the adjacent states $^1A_1(2b_2npb_2)$ and the π^*–valence state (for more details see Ref. 2). Considerable attention is now devoted to the nonplanar excited states $^1A_2$ and $^3A_2$ of formaldehyde. Among their interesting salient features is the change in the nonplanar structure accompanying the excitation of the molecule to its singlet or triplet $^{1,3}A_2$ states.[14] The states $^1A_2$ and $^3A_2$ of formaldehyde molecule were considered previously in detail in connection with the most important question: whether the spin–polarization effects may lead to virtual violation of the well–known Hund rule. Thus, it was demonstrated that the spin–polarization effects were almost identical in both states, so that practically they did not affect the energy of splitting.[10] Among the latest important studies devoted to H_2CO is Ref. 14, which presents the results of calculation of several states in the approximation of configurational interaction, in particular, $^1A_2$ and $^3A_2$, which arise in formaldehyde as a result of the low–lying n–π^* excitation.

This paper presents the results of calculation of several spectroscopic parameters, namely, the oscillator strengths of the dipole transitions in the vacuum UV range of molecular spectrum of formaldehyde, which improve the previously obtained experimental and theoretical data, in particular, new values have been obtained of the oscillator strengths of the transitions to the states $^1A_1(\pi$–$\pi^*)$ and $^1B_1(\sigma$–$\pi^*)$. Calculations were performed on the basis of the method of the motion equations,[2,5,16] taking effective account of the most important polarization effects, including the effects determined by the so–called $2p$–$2h$ (two particles–two holes) interactions. In contrast, e.g., to Ref. 2, these effects have been accounted for following a scheme proposed and checked in Refs. 17–20. The choice of this calculaitonal method is explained below.

The calculational scheme. The problems of calculating various spectroscopic characteristics of a molecule, in particular, the intensities of the bands in the photoelectronic spectra, which are known to be determined by the corresponding photoionization cross sections, the oscillator strengths, the intensities of transitions between the states of different multiplicity, and the intercombinative and the Rydberg electronic transitions, etc, are up–to–date and quite complicated problems.[21] Until recently most of the studies of the electronic transitions in molecules had been mainly devoted to the transitions within the valence shell, while the Rydberg transitions were not considered in sufficient detail, due to a number of the well–known reasons. As a rule, such transitions take place in the vacuum UV range and cannot be adequately described on the basis of traditional *a priori* calculational methods using the virtual orbital bases. One of the first studies of the Rydberg transitions (aliphatic hydrocarbons were considered) yielded acceptable calculated results by expanding the orbital basis due to the shell with $n = 2$ for hydrogen and the shell with $n = 3$ for carbon. However, such an expansion of the basis demanded a considerable expense of computer time.[21] Meanwhile, to analyze more terms in the Rydberg series, the basic set must be expanded due to outermost shells, so that the nonempirical calculations become more and more difficult and cumbersome while the empirical evaluations of the integrals used in the semiempirical techniques appeared to be rather problematic.[3,21] In such a situation an alternative is apparently seen in the method of the motion

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equations, proposed in Refs. 2, 15, and 16, which makes it possible to calculate the transition momenta, the probabilities, the oscillator strengths, etc., directly, avoiding the problems associated with routine calculations (with some prescribed accuracy) of the wave functions and total energies of the molecular states. As to the application, the method has been successfully employed to calculate various spectroscopic characteristics of both the inorganic (e.g., N_2, CO, etc.) and organic (e.g., C_6H_6, etc.) molecules.[15,16] Recently it was not widely used probably because the characteristics of molecules, which could be calculated, were limited in number. However, the interest in the method has increased again, since it has been successfully used to calculate the oscillator strengths of heavy atoms as well as to describe a very important and fine effect of the parity nonconservation in atoms.[22] As shown previously,[15,16] to obtain an acceptable accuracy, rather limited orbital basis could be used, however, it results in the need to consider accurately such important correlation effects as the "continuum pressure", the energy dependence of the potential of the self–matched field, and the effects associated with taking account of the so–called $2p$–$2h$ interactions (two particles–two holes).[23-26] Accounting for these effects by the standard methods (in the framework of the perturbation theory) drastically complicates the problem.[17,27] To take into account the above–mentioned effects an efficient procedure was developed in Refs. 17–20, on the basis of the formalism of the density functional using the corresponding energy–dependent exchange–correlation pseudopotentials. Their use in the scheme of the motion equations makes it possible adequately to take into account, for example, the $2p$–$2h$ interactions (see below) without increasing the volume of calculations and with acceptable accuracy of the obtained results. Such a modified approach has already been used for test computations of the spectrum of the excited states of the benzene molecule, for preliminary consideration of formaldehyde, and for other studies. It appeared to be quite effective,[28] from the viewpoint of its economic efficiency and accuracy of calculations and comparison with the available reliable experimental data.[13] Now we shall briefly consider the significant points of the method. According to Ref. 2, the operator producing the excited state $|\lambda>$ of the molecule with the ground state $|0>$, i.e. $|\lambda> = Q_\lambda^+ |0>$, is an exact solution of the motion equation

$$<0| [\delta Q_\lambda, H, Q_\lambda^+] |0> = \omega_\lambda <0| [\delta Q_\lambda, Q_\lambda^+] |0> , \tag{1}$$

where ω_λ is the transition frequency, the amplitudes Q_λ^+ are the coefficient of the matrix of the transition $|0> \to |\lambda>$, and the binary commutator is defined by the relation $2[A, H, B] = [A, [H, B]] + [[A, H], B]$. Taking account for the excitations of the type "one particle–one hole" ($1p$–$1h$) in Q_λ^+, Eq. (1) may be reduced to a matrix equation for the amplitudes $\{Y_{m\gamma}\}$ and $\{Z_{m\gamma}\}$

$$\begin{bmatrix} A & B \\ -B^* & A^* \end{bmatrix} \begin{bmatrix} Y(1) \\ Z(1) \end{bmatrix} = \mathrm{w_k} \begin{bmatrix} D & 0 \\ 0 & D \end{bmatrix} \begin{bmatrix} Y(1) \\ Z(1) \end{bmatrix} , \tag{2}$$

(the coefficients of matrices A, B, and D were described in detail in Refs. 2 and 16). These amplitudes determine the moment of transition $M_{0\lambda}$:

$$M_{0\mathrm{k}} = \sqrt{2} \sum_{m_\gamma} [Y^*_{m\gamma}(1)\, M_{m\gamma} + Z^*_{m\gamma}(1)\, M_{m\gamma}] , \tag{3}$$

and the oscillator strength corresponding to the transition $|0> - |\lambda>$

$$f_{0\lambda} = \frac{2}{3} G\omega_\lambda M^2_{0\lambda} , \tag{4}$$

Here G is the degeneration factor and $M_{m\gamma}$ is the particle–hole coefficient M of the matrix. An acceptable accuracy is obtained in the framework of the method for a limited orbital basis, because the above mentioned correlation effects, in particular, the $2p$–$2h$ interactions, are considered adequately. An account of the $2p$–$2h$ coefficients in Q_λ^+ is equivalent to renormalization of the matrices in Eq. (2) to ω; according to Refs. 17–20 it results in a weight coefficient $a(r) = [1 - \Sigma(r)]^{-1}$ entering into the matrix coefficients. Here

$$\Sigma(r) = -0.254[0.328\rho^{1/3}(r) + 0.204\rho^{1/3}(r) / (1 + 18.376\rho^{1/3}(r)] \tag{5}$$

(ρ is the electron density). In order to simplify the calculations without loss of accuracy, the coefficient $a(r)$ may be replaced by $a(0)$, in accordance with the procedure, which is well known and strictly founded in the theory of the atomic photoeffect and is based on the approximation of random phases with exchange.[29] Below we present some results of calculations of the oscillator strengths corresponding to the important electronic dipole transitions in the formaldehyde molecule.

Calculated results. The electronic configuration of the formaldehyde molecule in the ground state has the form

$$1a_1^2\, 2a_1^2\, 3a_1^2\, 4a_1^2\, 1b_2^2\, 5a_1^2\, 1b_1^2\, 3b_2^2 .$$

The geometry of the molecule we choose for our calculations corresponds to the generally accepted experimental geometry of the ground state.[12] In our calculations we employed the $[3s\,2p/1s]$ valence basis of the Gaussian (contracted) functions to which the diffuse Gaussian basis functions were added (see Ref. 2 for the details of this choice and for a comprehensive description of this basis). We only note here that the sought–after basis makes it possible adequately to describe the transitions in the molecule valence shell and as well as the transitions to the first terms of the Rydberg series. The presence of the Rydberg components in the basis is explained by the fact that it is impossible adequately to describe both the valence and the Rydberg configurations responsible for certain spectral characteristics of formaldehyde. Table I shows the calculated values of the oscillator strengths of the considered dipole transitions along with analogous data borrowed from Ref. 2 for comparison as well as with the recommended experimental values.[2,12–14] The calculated value of the oscillator strength corresponding to the ${}^1A_1 \to {}^1B_1(\sigma \to \pi^*)$ transition agrees fairly well with the value calculated in Ref. 2, and corresponds to the weak absorption at 1340–1430 Å (8.7–9.4 eV). This is the only transition in the valence shell existing in the spectrum at wavelengths below 2000 Å. The most extraordinary characteristic of the spectrum of formaldehyde is the transition to ${}^1A_1(\pi$–$\pi^*)$ which is experimentally observed neither in the electronic diffusion nor in the absorption spectra. The value of f we recommend for this transition is slightly less than the corresponding value given in Ref. 2. Note that the indicated state corresponds to the states of the valence type with certain Rydberg features because of interaction with the adjacent Rydberg states. The ${}^1B_2(2b_2 3pa_1)$ and ${}^1B_2(2b_2 4pa_1)$ states should be mentioned among the Rydberg transitions: the oscillator strengths corresponding to the transitions to these states agree fairly well with the experimental data. Similarly the ${}^1A_1(n$–$3pb_2)$ state: the efficient account of the interaction with the

$^1A_1(2\,b_2nd\,b_2)$ states allows us to obtain $f = 0.038$ (the corresponding experimental value is $f^{\text{exp}}= 0.017$). The value f^{exp} corresponding to the transition to the state $^1A_1(2\,b_24\,pb_2)$ is not available, and we recommend $f = 0.003$. As for the transitions to the Rydberg states, which converge to the second ionization potential, namely, the states $^1B_1(\pi\text{–}3\,s)$ and $^1B_1(\pi\text{–}3\,pa_1)$, the values of the oscillator strengths obtained for them are somewhat less than those recommended in Ref. 2 and they appear to be more accurate. Table II contains the data on excitation energies for the considered states obtained by various methods such as the multiconfiguration approximation, the present method, the method of the motion equations[2,4,16] (with an account of the electron–hole effects following the technique described in Ref. 2) as well as the experimental values taken from Refs. 7 and 10–14. As can be seen from Table II, the wavelengths of the transitions considered in the present paper agree fairly well with experimental values. The values of the transition energies for the first five transitions are more accurate than the corresponding calculated values taken from Refs. 2 and 4. It should be noted that because of the rather limited possibilities to take into account the additional configurations, the transition energies calculated in the multiconfiguration approximation[4] and given in Table II are in a somewhat worse agreement with the experiment, than, say, the presently obtained values. Recent calculation based on the method of superposed configurations[14] permitted one to calculate the energies of splitting for the state $^{1,3}A_2(n\text{–}\pi*)$ (singlet–triplet splitting), to account accurately enough for the configuration interaction, and to reproduce the experimental value of this energy to an accuracy $\delta \simeq 0.001$ a.u., namely, $\Delta E = 0.012$ a.u. (corresponding experimental value is $\Delta E = 0.011$ a.u.). For comparison, we also give the energies of splitting calculated in Ref. 2: $\Delta E = 0.021$ a.u., and those obtained in the present study: $\Delta E = 0.019$ a.u. One of the reasons for such situation lies in the different manner in which the correlation effects influence the singlet and the triplet terms. As our calculations show, it appears to be extremely important to take account of the correlation effects, particularly, the energy dependence of the potential of the self–matched field associated with the so–called $2p$––$2h$ interactions (see above), for accurate calculation of the transition wavelengths. Accounting for the $2p$–$2h$ effects improves the agreement between the calculated and experimental transition energies by 15–30%. According to Ref. 4, since the oscillator strength is proportional to the transition frequency and, in addition, the effects associated with the $2p$–$2h$ interactions lead to a re–normalization of the partially hole matrix coefficient, an account of the correlation effects (the formalism of the method of the motion equations deals with the partially hole correlations) appears to be very important for obtaining the calculated oscillator strengths of the transitions which agree very well with experimental values. Accounting for the sought–after correlation effects improves the agreement between the calculated and experimental values of the oscillator strengths by approximately 10–25% (in particular, for the experimentally investigated transitions). Although the agreement between the calculated oscillator strength and the corresponding experimental value is very good (in particular, for the $^1B_2\,n-3\,pa_1$ and $^1B_2\,n-4\,pa_1$ transitions) for several transitions, e.g. , for the $^1B_2\,n-3\,s$ and $^1A_1\,n-3\,pb_2$ transitions, the values of f calculated in our paper agree worse with the experimental data. One of the factors of this circumstance is connected with the procedure one uses to take into account the $2p$–$2h$ coefficients in the transition matrix Q_λ. The point is that the coefficient $a(r)$ given by Eq. (5) should be present in exact calculations of the matrix coefficients. It is replaced by the value $a(0)$ in our calculations performed according to the well–known procedure based on the theory of the atomic photoeffect (see above). Note in conclusion that the authors of Ref. 14 calculated the energy differences ΔE between the singlet and the triplet $^{1,3}A_2(n\pi*)$ states of H_2CO in the approximation of configurational interaction, as well as various contributions to ΔE (the energies of electron–nucleus and electron–electron interactions, etc.) as functions of the distance between the nuclei of carbon and oxygen (R_{CO}). Not going into any details of the behavior of sought–after contributions ΔE, we only comment here that the dependence $\Delta E(R_{\text{CO}})$ calculated by our method, practically completely coincides with $\Delta E(R_{\text{CO}})$ taken from Ref. 14 (see also Ref. 30), and only has worse accuracy (see the results for ΔE, given above).

TABLE I. Oscillator strengths of dipole transitions in the formaldehyde molecule.

State	Transition	f Ref. 2	F (our results)	f^{exp} Refs. 2,12, and 13
$^1A_1$	π–π*	0.10	0.08	–
$^1B_1$	σ–π*	0.002	0.0016	–
$^1B_2$	n–$3s$	0.020	0.017	0.028
$^1B_1$	π–$3s$	0.060	0.046	–
$^1B_1$	π–$3pa_1$	0.020	0.017	–
$^1B_2$	n–$3pa_1$	0.040	0.034	0.032
$^1A_1$	n–$3pb_2$	0.050	0.038	0.017
$^1A_1$	n–$4pb_2$	0.004	0.003	–
$^1B_2$	n–$4pa_1$	0.040	0.034	0.032

TABLE II. Excitation energies (vertical) in the formaldehyde molecule (see text).

State	Transition	ΔE Ref. 2	ΔE Ref. 4	ΔE (our results)	ΔE^{exp} Refs. 7,10, and 14
$^1A_1$	π–π^*	10.10	9.90	9.80	–
$^1B_1$	σ–π^*	9.19	9.03	9.01	9.00
$^1B_2$	n–$3s$	7.28	7.38	7.13	7.08
$^1B_1$	π–$3s$	11.20	–	10.98	–
$^1B_1$	π–$3pa_1$	12.20	–	11.96	–
$^1B_2$	n–$3pa_1$	8.12	8.39	7.96	8.14
$^1A_1$	n–$3pb_2$	8.15	8.11	7.90	7.97
$^1A_1$	n–$4pb_2$	9.40	–	9.21	9.58
$^1B_2$	n–$4pa_1$	9.55	–	9.42	9.63

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