

Quantum-chemical study of the properties of the excited states of organic molecules

I. A survey of quantum-chemical methods and semiempirical calculation of photodissociation of ketene

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Individual methods for quantum-chemical calculation of electron-excited states are analyzed at the SCF level (approximation of the ground state molecular orbitals — GSMO, approximation of improved GSMO and direct SCF calculation of excited states) and by means of configuration interaction.

The method of electron-hole potential and the Nesbet's method with the limited configuration interaction containing selected biexcited configurations is applied to calculation of the potential curves of photodecomposition of a ketene molecule and to the computation of the geometry of formaldehyde in $^{1,3}(n, \pi^*)$ states.

Applications illustrate the suitability of the use of the methods (within semiempirical parametrizations) for interpretation of the properties of electron-excited organic molecules including photochemical reactions.

Анализируются квантовохимические SCF методы (в приближении молекулярных орбиталей основного состояния — GSMO, в приближении улучшенных GSMO и прямой SCF метод для возбужденных состояний) и метод конфигурационного взаимодействия для расчета электронно-возбужденных состояний.

Метод электрон-дырка потенциала и метод Несбета дополнен взаимодействием ограниченного количества конфигураций, содержащих выбранные двухкратновозбужденные конфигурации, были применены для расчета потенциальных кривых фоторазложения молекулы кетена и для расчета геометрии формальдегида в $^{1,3}(n, \pi^*)$ состояниях.

Расчеты показали пригодность полуэмпирических методов для интерпретации свойств электронно-возбужденных органических молекул включая фотохимические реакции.

Quantum-chemical calculations of the wavefunction of the excited state in the method of molecular orbitals

For approximate description of the ground state of molecules with closed electron shells the Slater determinant type wavefunction constructed from molecular orbitals (MO) obtained by the Hartree—Fock method is usually employed. Such a type of wavefunction reproduces well many observable quantities, especially geometry, dipole moments, polarizability, heats of formation, etc. The choice of the approximate shape of the wavefunction and the method for calculation of MO's and the proper overall wavefunction is more complicated for the excited states in relation to the ground state. The configuration interaction (CI) is the most general method for calculating the properties of the excited states. Since there are many possible configurations* and the convergence of CI expansion is slow, calculations including all possible configurations are practically not feasible. That is why both nonempirical — *ab initio* and semiempirical calculations have to be simplified. We have in mind simplifications of the way of obtaining MO's for an excited state and the choice of configurations for CI expansion. The consistency of calculations of both ground state and excited states wavefunctions is usually required. For instance, the energy difference between the exact and approximate values of the total energy for different states should be constant, the wavefunctions of the individual states should be mutually orthogonal, etc.

SCF methods

The SCF methods for calculating excited states have been developed with the aim to describe vertical excited states which would be consistent with the measured Franck—Condon excitation energies.

Three groups of methods can be distinguished [1] according to the way of consideration of the interaction between the closed shell and open shell electrons:

a) Approximation of virtual orbitals (VO) called also GSMO method. Excited states are described by MO's obtained from the SCF solution of the ground state.

b) Approximation of improved virtual orbitals called also IGSMO method. MO's of the ground state are improved by taking account of the physical consequences of electron excitation, *i.e.* formation of the electron hole in completely occupied MO's in the ground state and the presence of the excited electron in virtual, earlier unoccupied orbitals.

* The number of configurations for the systems with n electrons and N functions of the basis AO grows as n^N , and for CI with biexcited configurations it grows as N^5 .

c) Direct SCF calculation of the excited state wavefunction — ESMO method (Excited State MO). One-electron Hamiltonian of Hartree—Fock (HF) type is constructed for the excited state generating the respective MO's. A shortcoming of this approach is also that the overall wavefunction constructed from these orbitals is generally not orthogonal with respect to the ground state wavefunction constructed *e.g.* from the SCF solution for the ground state.

GSMO approximation

Molecular orbitals, which are eigenfunctions of one-electron HF operator for the ground state, can be used for constructing excited state wavefunctions in the form of one Slater determinant or a linear combination of several Slater determinants. Virtual orbitals describe distribution of the hypothetical electron in the field of all, *i.e.* N electrons in the ground state but the real excited electron lies in the field of only $N - 1$ electrons. When using extended AO bases (no such shortcoming of VO's occurs in the minimal bases without diffuse AO's) it leads to extreme diffusion of VO's.

Use of this approximation may lead to qualitatively incorrect conclusions, *i.e.* in determination of the geometry of molecules in the excited states.

IGSMO approximation

One of the characteristic properties of the SCF wavefunction of the ground state in the form of Slater determinant is its invariance with respect to unitary transformation of occupied or virtual orbitals. This allows transformation of virtual or occupied orbitals so as to minimize the energy of the excited state keeping the wavefunction of the ground state unchanged. *Huzinaga* [2, 3] showed that by using an arbitrary one-electron Hermitian operator $\hat{\Omega}$ and projection operator \hat{P} belonging to the subspace of occupied MO's

$$\hat{P} = \sum_i^{\text{occ}} |\varphi_i\rangle \langle \varphi_i| \quad (1)$$

an operator \hat{F}' can be formed according to the relation

$$\hat{F}' = \hat{F} + \hat{V} = \hat{F} + (1 - \hat{P})\hat{\Omega}(1 - \hat{P}) \quad (2)$$

where \hat{F} is the HF operator for the ground state. The operator \hat{F}' does not modify the spectrum of occupied orbitals but allows manipulation with virtual orbitals. If we *e.g.* choose

$$\hat{\Omega} = -\hat{J}_i + \hat{K}_i \pm \hat{K}_i \quad (3)$$

the potential $\hat{\Omega}$ represents formation of a hole in the i -th MO, from which an electron is excited, the plus sign and the minus sign show whether the excited electron spin has changed or not.

The "electron-hole potential" method of *Morokuma and Iwata* [4] is based on similar ideas. The space defined by HF MO's $\{\psi_i\}$ obtained for the ground state is divided into two subspaces corresponding to occupied (D) and virtual (V) orbitals. New MO's for the excited state are then chosen so as to minimize the energy of the excited singlet and triplet states described by one-configuration wavefunction ${}^{1,3}\Phi_{(m\rightarrow k)}$. The new MO's $\{\varphi\}$ are required to be formed from HF MO's $\{\psi\}$ by unitary transformations

$$\varphi_m = \sum_j^D a_{mj} \psi_j; \quad \varphi_k = \sum_j^V b_{kj} \psi_j \quad (4)$$

Moreover, the condition of orthogonality of orbitals is retained. The condition for the minimum of the total energy then leads to the coupled secular equations. Their iterative solution gives new orbitals $\{\varphi_i\}$

$$\begin{aligned} (\hat{F} + \hat{J}_k - \hat{K}_k \mp \hat{K}_k) \varphi_i &= \lambda_i \varphi_i & i \in D \\ (\hat{F} - \hat{J}_m + \hat{K}_m \pm \hat{K}_m) \varphi_l &= \gamma_l \varphi_l & l \in V \end{aligned} \quad (5)$$

The EHP method is thus unambiguously defined, *i.e.* it does not depend on either adjustable parameters or the choice of configurations and is applicable to the excited states of arbitrary symmetry. The wavefunction of the excited ${}^s\Phi_{(m\rightarrow k)}$ state obtained by the EHP method shows some remarkable properties. It retains its orthogonality with respect to the wavefunction of the ground state, and the Brillouin theorem is valid not only for the ground state but also for singly excited configurations.

Apart from the one-configurational EHP method, the authors [2, 3] also derived two-configurational and multiconfigurational versions [2, 3] recommended for cases where the corresponding excited state cannot be adequately described by one-configuration function.

ESMO methods

In search for HF operators for the open-shell systems in spin restricted (RHF) formalism a general form of HF equations is achieved

$$\hat{F}_i |\varphi_i\rangle = \sum_j |\varphi_j\rangle \theta_{ji} \quad (6)$$

Operators \hat{F}_i can be the same for individual groups of orbitals (*e.g.* for closed shells) and invariant with respect to unitary transformation of these orbitals. But unitary transformation cannot remove nondiagonal elements θ_{ji} connecting closed

and open-shell orbitals. For series of open-shell systems *Roothaan* [5] derived HF equations in the form of pseudoeigenvalue problem

$$[\hat{h} + 2\hat{J}_T - \hat{K}_T + 2\alpha(\hat{L}_T - \hat{J}_O) - \beta(\hat{M}_T - \hat{K}_O)]\varphi_i = \varepsilon_i\varphi_i \quad (7)$$

(For explanation of symbols see Ref. [5].)

Application of the *Roothaan's* method is confined to special open shell cases [5], e.g. to the lowest triplets of certain symmetry. *Huzinaga* [6] extended this scheme to electron configurations consisting of two open shells of different or the same symmetry.

Birss and *Fraga* [7] proposed an SCF theory for the open-shell systems applicable to arbitrary configurations without restriction of the number or symmetry of open shells. *Huzinaga* [8] and *Caballol et al.* [9] proposed generalized Fock operators which have some technical (e.g. SCF convergence) or conceptual advantages. The generalized forms of the Fock operators have been analyzed [10] from the view-point of the generalized Brillouin theorem [11].

Methods with generalized SCF operator [10] have not found application in practical calculations. Nesbet's formalism has been used more often, especially for solving photochemical problems. Its main advantage is the simplicity and quickness although the resulting MO's are not optimal in view of the variation principle.

Nesbet's method

MO's of the one-configuration singlet and triplet wavefunctions in $^{1,3}\psi_{(a\rightarrow b)}$ are generated by the HF operator

$$\hat{F} = \hat{h} + \sum_j (2\hat{J}_j - \hat{K}_j) + \left(\hat{J}_a - \frac{1}{2}\hat{K}_a\right) + \left(\hat{J}_b - \frac{1}{2}\hat{K}_b\right) \quad (8)$$

where j runs over doubly occupied orbitals; a and b are the indices of singly occupied orbitals. MO's obtained as eigenvalues of the HF operator represent well the respective excited state although the operator is not obtained by variational procedure and the respective wavefunction with MO's generated by the operator (8) does not yield minimum energy.

The method with the effective HF operator* is popular in calculations of potential hypersurfaces of the excited states especially because of its simplicity and quickness. Its application is usually followed by limited configuration interaction.

* The effective operator in the form (8) is equivalent to the operator of the generalized "half electron" method [12].

Configuration interaction

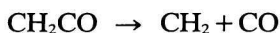
The one-configuration wavefunction in the form of Slater determinant is not capable of describing correlation of electrons mainly between electrons with opposite spins occupying the same MO. Despite this, such description is often sufficient, especially in the study of the properties of molecules in the vicinity of equilibrium geometries or in studying phenomena where no great changes occur in the number and character of bonds in the system.

But the HF model often fails as a result of degenerations or small energy difference in the states depicted by various Slater determinants. Such situations arise in calculations of energy surfaces in the ground and excited states. Therefore description of energy hypersurfaces necessitates consideration of the wavefunction obtained by configuration interaction method or by the method of multiconfiguration SCF. The choice of configurations for CI can be specific for individual cases and should be based on the analysis of orbital and state correlation diagrams.

Calculations of photodissociation of ketene and geometry of formaldehyde in $^{1,3}(n, \pi^)$ states*

We used the Nesbet's HF operator together with limited CI for description of the photodissociation of ketene (H_2CCO). The CCO group is linear in the ground state and the symmetry of a molecule is C_{2v} . The electron configuration of the ground state is $(1a_1)^2 (2a_1)^2 (3a_1)^2 (1b_1)^2 (4a_1)^2 (1b_2)^2 (2b_1)^2 (2b_2)^2$ (only valence orbitals are considered).

Figs. 1—3 show orbital and state correlation diagrams for the dissociation



in C_{2v} symmetry.

The electronic configuration of the ground state of ketene when the occupation of orbitals remains unchanged correlates with higher excited singlet state of methylene 2^1A_1 . Interaction with biexcited configuration... $(4a_1)^2 (2b_1)^2 (5a_1)^2$ leads to avoided crossing (A, Fig. 2) so that the ground state correlates with the lowest methylene singlet $1A_1$. The correlation diagrams in Figs. 2 and 3 indicate that none of the lowest excited states of ketene correlates with the ground state of the product, *i.e.* $\text{CO} (^1\Sigma^+)$, $\text{CH}_2 (^3B_2)$; *i.e.* dissociation along the reaction path is in the C_{2v} symmetry forbidden.

The situation changes remarkably if the C_{2v} symmetry is changed by bending the CCO group in the plane of the molecule (corresponding to the change of geometry by excitation to the state $^{1,3}B_2$). The symmetry lowers to the type C_s . In this geometry the symmetry of orbitals a_1 and b_1 changes to the symmetry a' (C_s) (σ

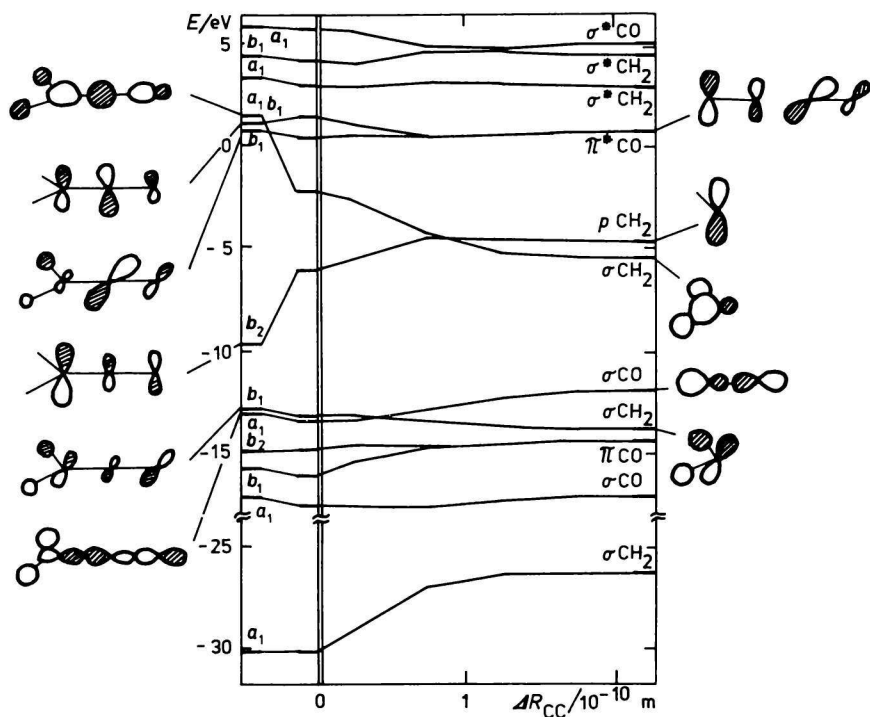


Fig. 1. SCF MINDO/2 molecular orbitals correlation diagram for dissociation of linear ketene $\text{CH}_2\text{CO} \rightarrow \text{CH}_2 + \text{CO}$ in ${}^1,{}^3B_2$ states.

(Molecular orbital energies on the left correspond to SCF energies in the ground 1A_1 state.)

orbitals symmetrical with respect to the plane of the molecule) and the symmetry of orbitals b_2 changes to the symmetry a'' (π orbitals asymmetrical with respect to the plane of the molecule). The lowest excited state is then triplet ${}^3A''$, which correlates directly with the CO (${}^1A'$, ${}^1\Sigma^+$) and CH_2 (${}^3A''$, 3B_2) products; this shows that direct adiabatic pathway from reactants to products along the hypersurface of the lowest excited state is possible.

Figs. 4—7 show the results of the calculation of energies for individual states along reaction pathways as have been described above. The points denote values obtained by the SCF method (with the effective HF operator of Nesbet type) followed by CI including the configuration of the ground state with doubly occupied lowest orbitals, then four paired biexcited configurations and 20 configurations singly excited with respect to the ground state configuration. The respective effective HF operator was constructed for the configuration B_2 in C_{2v} symmetry and A'' in C_s symmetry. The semiempirical MINDO/2 method parametrized on heats of formation was applied [13].

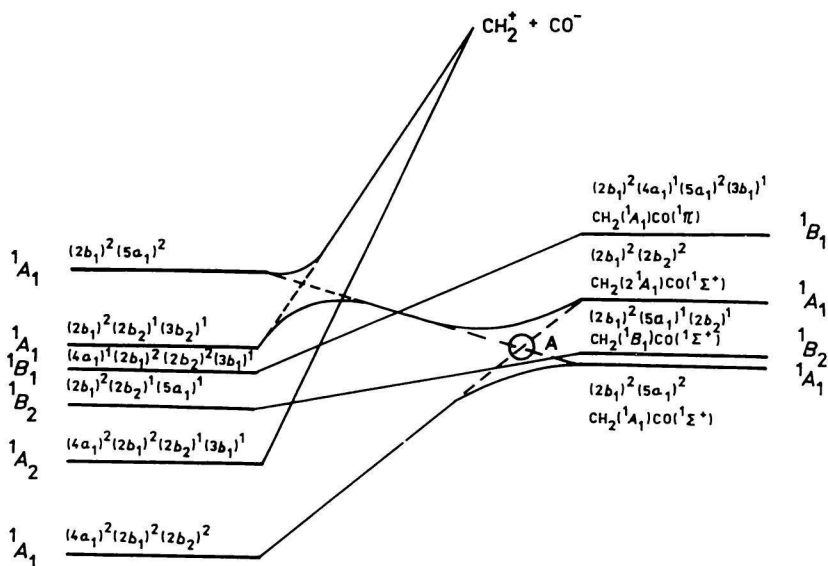


Fig. 2. State correlation diagram for dissociation of ketene (schematically).
Singlet states.

Dissociation curves for the ketene dissociation in C_{2v} symmetry are in Figs. 4 and 5. Some experimental data and results of other calculations for this reaction can be used for judging the reliability of the calculated curves. Table 1 contains data for ΔH_m^0 of the decomposition of ketene and data for molar energy differences of the three lowest methylene states. The MINDO/2 method yields values closer to the experiment than data of accessible *ab initio* calculations. If the course of dissociation curves is compared e.g. with the MC SCF results [14] in the basis of 36 contracted GF (i.e. basis DZ + diffuse *s* function for C atoms), we find a surprising accord of the shape of curves for one 1A_1 state. The curve has characteristic shape with the maximum value of 519 kJ mol^{-1} at $\Delta R_{CC} = 1 \times 10^{-10} \text{ m}$, MC SCF calculation gives at the same distance the maximum of 486 kJ mol^{-1} . The dissociation limit of 507 kJ mol^{-1} (Fig. 4) is higher than MC SCF value of 363 kJ mol^{-1} . The experimental value calculated from the data in Table 1 is 435 kJ mol^{-1} . The curves for $^{1,3}A_2$ states show the same course as those obtained by MC SCF calculation. They represent bound states in C_{2v} symmetry, as has been shown in the analysis of correlation diagrams. The initial configuration for SCF calculation was that of B_2 state (see above). According to MC SCF [14] and SCF CI [15] calculations the configuration ought to show repulsion course for singlet and triplet states. Because of the low value of the energy of $^{1,3}B_2$ state in MINDO/2 parametrization, the shape of the curve is distorted.

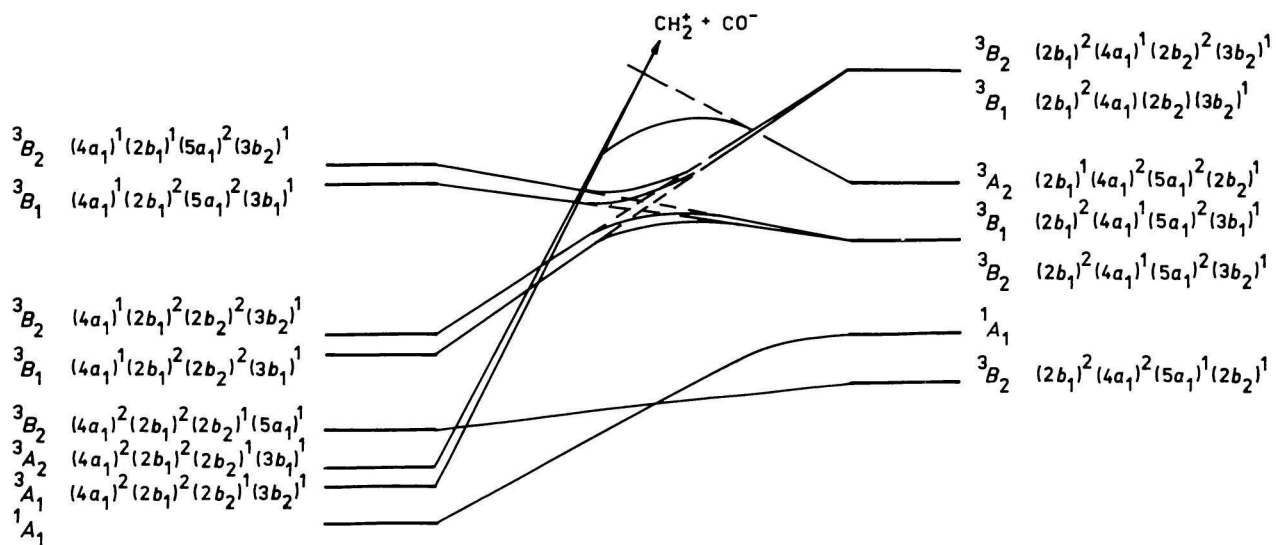


Fig. 3. State correlation diagram for dissociation of ketene (schematically).
Triplet states.

Figs. 6 and 7 show results of the curves for dissociation of the bent ketene. The angle O—C—C (145°) was kept constant in this dissociation. The value of 145° was obtained by optimizing the OCC angle of ketene in $^1A''$ state in MINDO/2 parametrization. Yamabe and Morokuma have examined [16] the bent dissociation path of ketene in minimal STO-3G basis by one-configuration generalized HF method. They showed that by optimization of the C—C—O angle during dissociation the angle changes very little.

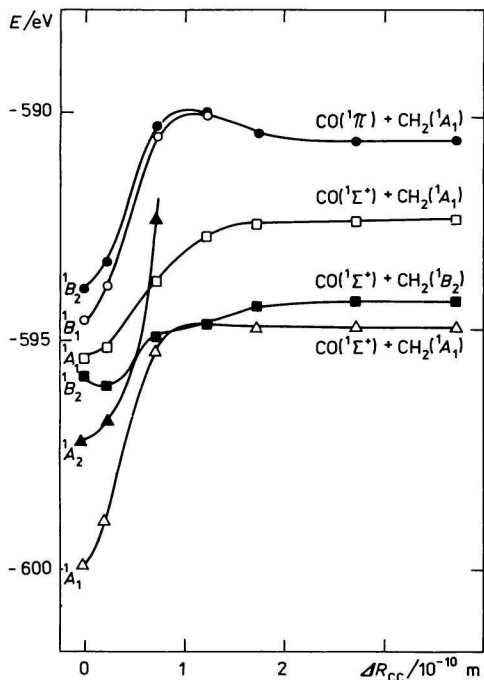


Fig. 4. Dissociation of ketene
 $\text{CH}_2\text{CO} \rightarrow \text{CH}_2 + \text{CO}$ in the C_{2v} and
 C_s symmetries (CI calculation — for
 details see the text).
 Singlet C_{2v} states.

The curves calculated for $^{1,3}A'$ show smooth course with an activation barrier of 264 kJ mol^{-1} for $^3A''$ and 373 kJ mol^{-1} for $^1A''$. The shallow minima at the beginning of dissociation correspond to the extension of equilibrium distance R_{CC} in the excited state as compared with the ground state. The curve of the $^1A''$ state calculated by us is very similar to that reported by the authors [16]. The activation barrier in the STO-3G basis is 328 kJ mol^{-1} for the singlet and 138 kJ mol^{-1} for the triplet. In contrast to our calculation the dissociation curve for the triplet passes through the maximum at $\Delta R_{\text{CC}} \approx 1 \times 10^{-10} \text{ m}$.

Changes in the character of the lowest states during dissociation are expressed by variations in calculated contributions of the main components of CI wavefunction

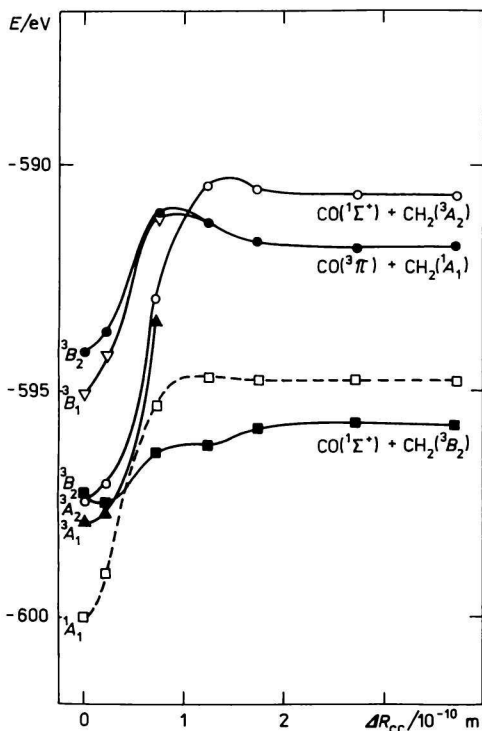


Fig. 5. Dissociation of ketene $\text{CH}_2\text{CO} \rightarrow \text{CH}_2 + \text{CO}$ in the C_{2v} and C_s symmetries (CI calculation — for details see the text). Triplet C_{2v} states.

along reaction pathway (C_s symmetry). Table 2 contains a choice of configurations contributing most in CI expansions for the two lowest singlet states $^1A'$ and $^1A''$. Table 3 shows expansion coefficients of the wavefunction for the configurations in Table 2. As mentioned above, the ground state $^1A'$ with the dominant configuration *I* changes gradually to the state with the dominating configuration *II*. In the region, where R_{CC} is $1.5\text{--}2 \times 10^{-10}$ m, i.e. in the ascending part of the dissociation curve, also the singly excited configuration *V* remarkably contributes and causes the disappearance of the barrier on the curve (Fig. 6). The singly excited configuration *III* evidently dominates in the state $^1A''$ (similarly to $^3A''$) along reaction pathway; its coefficient does not fall below 0.93. The SCF wavefunction obtained by effective HF operator describes well this state.

Photolytic decomposition of ketene at greater wavelengths ($\lambda > 360$ nm) probably starts from the state 1A_2 which is most populated during absorption. This state of ketene can pass to 3A_2 or 3A_1 by radiationless intersystem crossing. Adiabatic dissociation from these states is not possible. At relatively small variations of the distance ΔR_{CC} these states cross the $^{1,3}B_2$ states. But the transition from the A_2 state to B_2 requires substantial changes in electron distribution. If, however, the C—C—O group loses its linear character and bends in the molecular plane, so that

the symmetry decreases to C_s , both A_2 and B_2 states change to the A'' symmetry and start to interact. Their crossing becomes avoided and the triplet $^3A''$ is able to pass adiabatically along its own hypersurface to the products in the ground state, i.e. CO ($^1\Sigma^+$) and CH₂ (3B_2). Under these conditions the singlet $^1A''$ correlates with the products CO ($^1\Sigma^+$) and CH₂ (1B_2).

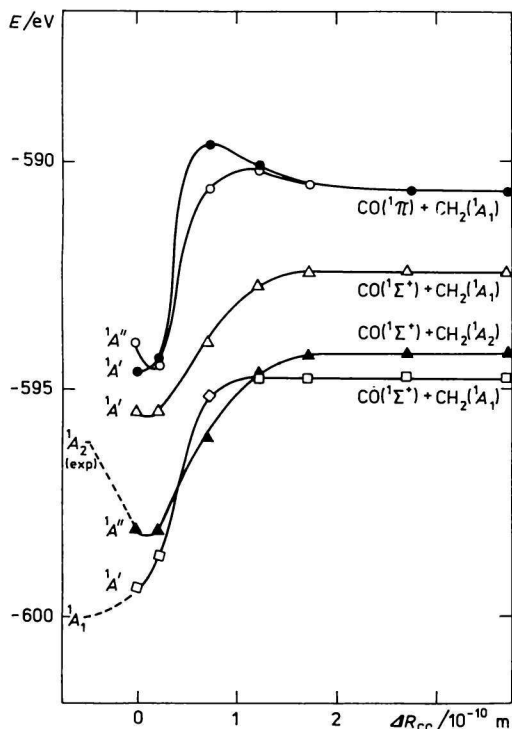


Fig. 6. Dissociation of ketene $\text{CH}_2\text{CO} \rightarrow \text{CH}_2 + \text{CO}$ in the C_{2v} and C_s symmetries (CI calculation — for details see the text). Singlet C_s states.

Table 1

Experimental and calculated data for ketene (ΔH_m^0) and methylene (ΔE)

	Exp ^a	MINDO/2 ^b	SCF CI ^c ab initio (C_s)	MC SCF ^c ab initio (C_{2v})
ΔH_m^0 /(kJ mol ⁻¹)	338.4	422.0	112.9	270.2
ΔE ($^3B_2 \rightarrow ^1A_1$)/(kJ mol ⁻¹)	95.5 ^d	94.6	137.0	92.6
ΔE ($^1A_1 \rightarrow ^1B_2$)/(kJ mol ⁻¹)	84.9	55.0	65.6	97.5

a) Ref. [15]; b) this paper; c) Ref. [14]; d) The value experimentally not precisely known; in [17] it is 101.3 kJ mol⁻¹, in [18] 5.8 kJ mol⁻¹.

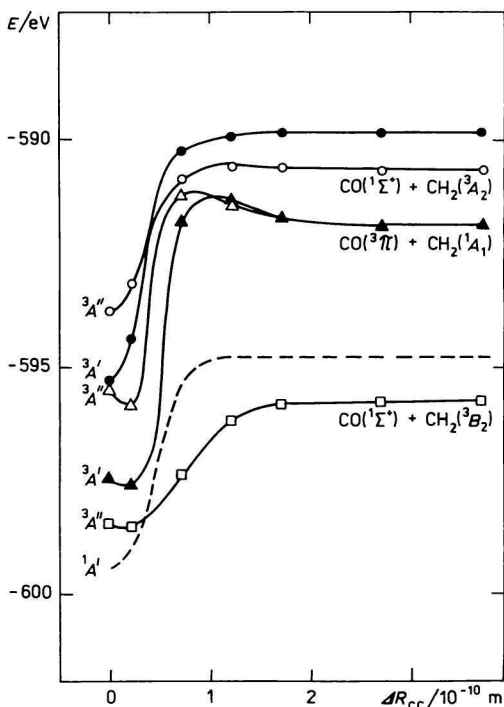


Fig. 7. Dissociation of ketene $\text{CH}_2\text{CO} \rightarrow \text{CH}_2 + \text{CO}$ in the C_{2v} and C_v symmetries (CI calculation — for details see the text).
Triplet C_v states.

There are three ways of photochemical decomposition of ketene; the most appropriate from the energetical point of view is the decomposition into 3B_2 (CH_2) and ${}^1\Sigma^+$ (CO). The first excited singlet 1A_2 passes probably by bending to the ${}^1A''$ state and dissociates along its own hypersurface to products $\text{CO} ({}^1\Sigma^+)$ and $\text{CH}_2 ({}^1B_2)$; it can also pass to the surface ${}^1A'$ by collisional deactivation especially in the domain where the hypersurfaces ${}^1A''$ and ${}^1A'$ intersect. The source of methylene in the triplet state 3B_2 is probably the ${}^3A''$ state of ketene which is formed by the intersystem crossing from the singlet ${}^1A''$ state.

Table 2

Occupation of MO's for individual configurations of ketene in C_v symmetry

MO	$1a''$	$5a'$	$6a'$	$2a''$	$7a'$	$8a'$	$3a''$
I	2	2	2	2			
II	2	2	2		2		
III	2	2	2	1	1		
IV	2	2	2	1		1	
V	2	2	2	1			1
VI	1	2	2	2	1		
VII	2	2	1	1	2		

Table 3

CI coefficients of the two lowest singlet states

State	Configuration	$R_{CC}/10^{-10}$ m				
		1.315	1.5	2.0	3.0	5.0
'A'	I	-0.9611	-0.9059	-0.7380	-0.3630	-0.3587
	II	0.0900	0.1628	0.6455	0.9291	0.9310
	V	0.2584	0.3778	0.1754	0.0200	0.0000
'A''	III	0.9731	0.9630	0.9343	0.9949	1.0000
	IV	-0.1640	-0.2311	-0.1074	-0.0200	—
	VI	0.1573	0.1282	0.1102	0.0060	—
	VII	—	—	-0.3183	0.1000	—

Table 4

Comparison of experimental and theoretical values for geometrical parameters of formaldehyde

Molecule (Symmetry)	Optimized parameter	State	EHP INDO	VO ^b INDO	exp	CNDO ^d CI	exp ^f Ground state
H ₂ CO (C _v)	α^c	¹ A'(n→π*)	32°	0°	31° ^c	31°	
		³ A'(n→π*)	37°	0°	35.6° ^f		0°
		³ A'(π→π*)	28°	—	—		
	$(R_{CO}/10^{-10}$ m) ^a	¹ A''(n→π*)	1.280	1.280	1.323° ^c	1.280	
³ A'(n→π*)		1.280	1.280	1.291° ^f		1.21	
³ A'(π→π*)		1.380	—	—			

a) Bond lengths; b) obtained from MO's of the ground state; c) experimental values from Ref. [20]; d) CNDO CI results [19]; e) the out-of-plane angle of CO group; f) data from Ref. [21].

Calculation of geometry of formaldehyde in excited states

The calculation of the geometry of formaldehyde in the excited states can be used as an example of the possibilities of the application of the EHP method. Calculations were done in the INDO parametrization. Geometry was optimized by quadratic minimization of individual geometrical parameters.

Formaldehyde, planar in its ground state, assumes a pyramidal shape in the excited state. The CO bond elongates at the same time. But in GSMO approxima-

tion the excited state (singlet or triplet) retains the planar structure. The minimum of the energy for the pyramidal form is reached on incorporating CI, out-of-plane angle in the $^1A''$ state is 31° [19].

The application of the EHP method leads to the expected change of the angle consistently with experiment. The $^1A''$ state (Table 4) has minimum at 32° and the $^3A''$ triplet at 37° . The experimental values are 31° and 35.6° , respectively. The out-of-plane angle for the $^3A'$ state corresponding to $\pi \rightarrow \pi^*$ excitation is 28° . There is no comparable value for this state available because $\pi \rightarrow \pi^*$ transition is not observed in the spectrum of formaldehyde. The CO bond lengthens in the singlet and triplet $^1,^3A''$ states to 1.280×10^{-10} m even in GSMO approximation. Neither the EHP method nor CI change the result.

Conclusion

After analysis of SCF methods for excited states we chose two methods: the EHP method and the Nesbet's method with limited CI. They were applied in semiempirical parametrizations to calculation of photochemical dissociation of ketene (Nesbet's method and MINDO/2) and to computation of the geometry of formaldehyde in the excited states (EHP, INDO). Applications illustrated the suitability of the use of these methods for interpretation of the properties of organic molecules in electronic excited states.

Other calculations using the described methods will be the subject of subsequent papers.

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