J. Am. Chem. Soc. **1988**, *110*, 5977–5981

applications can be given. Molecular orbitals of the molecule in its ground-state minimum geometry having a point group G are calculated. Subsequently, the efficiency factors f_λ of section 5 are determined by means of eq 14 for any irreducible representation Γ_λ of G. If for particular Γ_λ large values of f_λ are obtained, those Γ_λ are considered to be symmetry species of the relaxation pathway. In order to find which nuclear motions constitute the pathway, contour plots of ρ_λ^{00} as defined by eq 16 are inspected. By using the criterion for nuclear motions as contained in Figure 1, the form of these plots near the various atoms should indicate molecular geometry changes which make up the energetically favorable relaxation pathway.

8. Discussion

In the previous sections relaxation pathways were considered which lead from the point on the first excited-state surface with ground-state geometry to the excited-state equilibrium geometry. A two-step scheme has been suggested where in the first step the pathway symmetry Γ_λ is determined by means of the efficiency factors f_λ. In the second step, the favorable relaxation pathway is selected from the manifold of pathways transforming as Γ_λ by inspecting plots of the overlap function ρ_λ^{00}. In this section we relate the procedure to previous work, and an attempt is made to identify its limitations. Central to the scheme is the idea that along the pathway the energy lowering is large provided that a large number of higher lying excited states is available to interact with the first excited state. This concept uses the accepted experience that the energy lowering is significant when the dimension of the basis set into which a wave function is expanded is large.[35] The extension to many excited states also holds for the overlap function ρ_λ^{00} which results from the transition densities between the first excited-state wave function and the members of the basis set consisting of wave functions of all higher excited states appropriate for interaction. In addition ρ_λ^{00} contains, in an approximate way, the energy difference between the interacting states. Therefore, the suggested criterion is more general than the original Bader–Pearson concept, where only the most important member in the basis set is used, namely the wave function for the state located above the considered state. Important is the assumption that the first excited state is well approximated by one singlet wave function characterized by the HOMO–LUMO excitation. Implicit in this is that the CI expansion of that state is dominated by the HOMO–LUMO configuration constructed from the SCF ground-state orbitals. This assumption may fail when the first excited state is totally symmetric. In this case the ground-state configuration enters significantly into the CI expansion for the first excited state. Therefore, we conclude the suggested procedure should be more reliable for nontotally symmetric than for totally symmetric first excited states.

Acknowledgment. Many valuable comments and suggestions of Drs. H. Kupka, F. Mark, and G. Olbrich are gratefully appreciated. Many stimulating discussions with Prof. E. A. Halevi are acknowledged.

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(35) The relation between an increase of a basis set and the resulting energy lowering is a consequence of the theorem of Hylleraas and Undheim (Hylleraas, E. A.; Undheim, B. *Z. Physik* **1930**, *65*, 759) and MacDonald (Mac Donald, J. K. L. *Phys. Rev.* **1933**, *43*, 830).

A Symmetry-Based Procedure for the Determination of Molecular Geometry Changes Following Electronic Excitation. 2. Relaxation Pathways for the Excited States of Ethylene, Acetone, Butadiene, and Methylenimine

V. Bachler

Contribution from the Max-Planck-Institut für Strahlenchemie, Stiftstrasse 34-36, D-4330 Mülheim a.d. Ruhr, Federal Republic of Germany. *Received June 29, 1987*

Abstract: A qualitative symmetry-based procedure, which permits a determination of probable geometry changes of a molecule occurring after electronic excitation, is demonstrated by determining the known geometry changes for ethylene, acetone, *trans*-butadiene, and methylenimine. The results are compared with published calculations and experiments.

1. Introduction

In the preceding paper in this issue,[1] a qualitative procedure was proposed for determining molecular geometry changes following electronic excitation. According to the Frank–Condon principle, vertical excitation produces an excited state of a molecule where the ground-state geometry is still retained. After excitation, the geometry rearranges on the excited-state surface along a relaxation pathway which leads to the excited-state minimum geometry. Such a pathway can be described by a superposition of geometry changes along the various symmetry coordinates, S_λ, transforming as the irreducible representations, Γ_λ, of the ground-state point group, G.[1] In order to determine which Γ_λ are symmetries for the relaxation pathway, the efficiency factors f_λ were proposed.[1]

$$f_\lambda = \sum_{i=l+1}^{\text{unocc}} \mu \frac{1}{\epsilon_i^{00} - \epsilon_l^{00}} + \sum_{i=1}^{\text{occ}-1} \nu \frac{1}{\epsilon_h^{00} - \epsilon_i^{00}} \qquad (1)$$

The quantities ϵ_l^{00} and ϵ_h^{00} are the energies of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), respectively. They are calculated at the ground-state geometry which is indicated by the superscript 00. In the first term of eq 1, i ranges over unoccupied molecular orbitals located above the LUMO. In addition the summation is restricted to orbitals which have the proper symmetry, Γ_μ, to interact with the LUMO when the pathway is of Γ_λ symmetry. In the second term of eq 1, i runs over orbitals having lower energy than the HOMO. The sum comprises only those orbitals which belong to the symmetry species, Γ_ν, being appropriate for an interaction with the HOMO when the pathway transforms as Γ_λ. The form of eq 1 shows that f_λ is large provided many orbitals of proper symmetry are present and are energetically close to the

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(1) Bachler, V.; Polansky, O. E., preceding paper in this issue.

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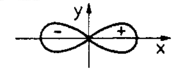
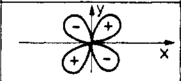
Scheme I. Two Important Forms of the Overlap Function $\rho_\lambda{}^{00}$ Near an Atom A Located at the Origin of the Coordinate Systems[a]

ρ_λ^{00} near A	result
	favourable **(a)**
	unfavourable **(f)**

[a] Type (a) favors a motion of the atom; type (f) is unfavorable.

frontier orbitals. In the preceding paper it was shown that eq 1 can be used to calculate the f_λ value for any irreducible representation, Γ_λ, of G. Those Γ_λ for which large values are obtained are considered as symmetries for a relaxation pathway. Further, it was proposed that after finding the relevant Γ_λ, the pathway could be more closely specified by inspecting the form of the overlap function $\rho_\lambda{}^{00}$ given by[1]

$$\rho_\lambda{}^{00} = \sum_{i=l+1}^{\mathrm{unocc}} \mu \frac{\varphi_i{}^{00}\varphi_l{}^{00}}{(\epsilon_i{}^{00} - \epsilon_l{}^{00})^{1/2}} - \sum_{i=1}^{\mathrm{occ}-1} \nu \frac{\varphi_h{}^{00}\varphi_i{}^{00}}{(\epsilon_h{}^{00} - \epsilon_i{}^{00})^{1/2}} \qquad (2)$$

Here, $\varphi_h{}^{00}$ and $\varphi_l{}^{00}$ are the HOMO and LUMO, respectively, and the index i runs over the same set of orbitals as in eq 1. For the applications below, the forms (a) and (f) of $\rho_\lambda{}^{00}$ of the preceding paper in this issue are important. The relevant conclusions are repeated in Scheme I. Consider an atom located in Scheme I at the origin of the coordinate system. If the form of $\rho_\lambda{}^{00}$ is like case (a), the atom should move along the x-axis. However, forms like case (f) indicate that the position of the atom should remain unchanged. Inspection of $\rho_\lambda{}^{00}$ near all atoms by means of Scheme I leads to a qualitative identification of the relaxation pathway. In the following sections we refer to the cases (a) and (f) without explicitly mentioning that Scheme I and the conclusions contained therein are used.

The purpose of this paper is to illustrate how the efficiency factors, f_λ, supplemented by the overlap functions, $\rho_\lambda{}^{00}$, can be used for a qualitative identification of the relaxation pathways. Molecules are treated for which detailed calculations and/or experiments are available in the literature, and it is shown how they agree with the qualitative results.

2. Ethylene in the π–π^* State

Potential energy surfaces for ground and many excited states of ethylene have been calculated by accurate quantum chemical methods.[2] These calculations provide a sound basis for testing the proposed qualitative procedure. The ground-state D_{2h} equilibrium geometry was adopted, and molecular orbitals and their energies were calculated by using the 4-31G basis set.[3] Ethylene was assumed to be electronically excited to the π–π^* B_{3u} state. Following this excitation, the D_{2h} geometry changes along a pathway on the π–π^* surface which is considered as a linear combination of various symmetry coordinates being symmetry adapted in D_{2h}. Our aim is to determine those symmetry coordinates which constitute the relaxation pathway.

Firstly, we calculate the f_λ for those Γ_λ of D_{2h} which are irreducible representations of ethylene vibrations. The symmetries of vibrations are listed in the first column of Table I and in the second column, the symmetries of LUMO and HOMO of ethylene are given. The third column contains molecular orbitals which interact with the LUMO and HOMO, respectively, when a geometry distortion of Γ_λ symmetry occurs. The f_λ values, given in the fourth column, indicate that all in-plane a_g, b_{1g}, b_{2u}, and b_{3u} modes of ethylene are ineffective because either f_λ is small or orbitals with proper symmetry for interaction are absent. The large f_λ values indicate that only the three out-of-plane modes a_u, b_{1u}, and b_{2g} will be favorable directions for a relaxation pathway.

Table I. Ethylene in Its First π–π^* State[a]

Γ_λ	MO	interacting with MO	f_λ
a_g	$1b_{2g}$	$2b_{2g}$	1.261
a_u	$1b_{2g}$	$2b_{2u}$ $3b_{2u}$ $4b_{2u}$	18.143
	$1b_{1u}$	$1b_{1g}$	
b_{1g}			
b_{1u}	$1b_{2g}$	$4b_{3u}$ $5b_{3u}$ $6b_{3u}$ $7b_{3u}$ $8b_{3u}$	19.617
	$1b_{1u}$	$3a_g$ $2a_g$	
b_{2g}	$1b_{2g}$	$4a_g$ $5a_g$ $6a_g$ $7a_g$	17.807
	$1b_{1u}$	$2b_{3u}$	
b_{2u}			
b_{3u}	$1b_{2g}$	$2b_{1u}$	1.429

[a] The symmetries of distortions, Γ_λ, the interacting orbitals, and the corresponding efficiency factors f_λ are given. Ethylene relaxes along a_u, b_{1u}, and b_{2g} out-of-plane coordinates.

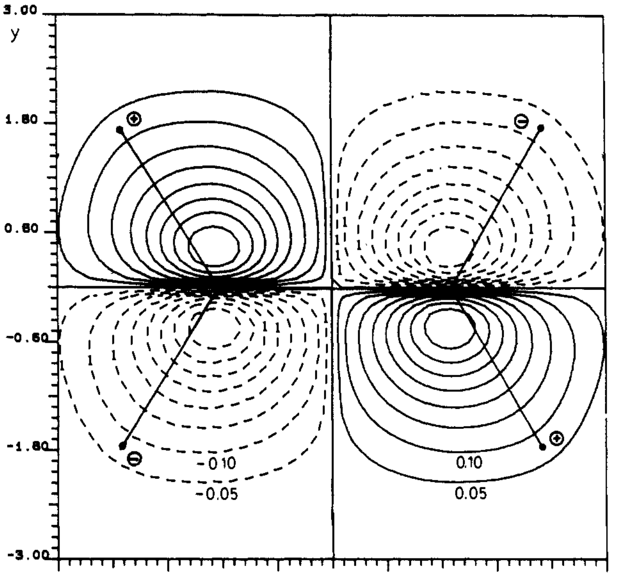


Figure 1. Contour lines of $\rho_{a_u}{}^{00}$ for ethylene in a plane parallel to the molecular x,y-plane and intersecting the z-axis at z = 0.5 au. The projection of the molecular skeleton onto the plane and the resulting twist about the double bond are also shown.

Secondly, we inspect the form of the overlap functions for the relevant symmetries. Our objective is to specify the relaxation pathway in more detail. For the a_u symmetry coordinate, contour lines of $\rho_{a_u}{}^{00}$ are depicted in Figure 1 in a plane which is parallel to the molecular x,y-plane; the drawing plane intersects the z-axis at a value of 0.5 au. The projection of the molecular skeleton onto that plane is also depicted. Continuous and dashed lines in Figure 1 designate positive and negative functional values, respectively. An equivalent drawing could be made for a plane which is also parallel to the molecular x,y-plane but intersecting the z-axis at −0.5 au. Because $\rho_{a_u}{}^{00}$ is antisymmetric with respect to the molecular plane, positive (negative) functional values would appear in such a drawing in regions where in Figure 1 negative (positive) values are present. By using this antisymmetric property, we realize that the unfavorable case (f) holds for the form of $\rho_{a_u}{}^{00}$ near the carbon atoms, and their position should remain unchanged. For the hydrogen atoms, however, the favorable case (a) is valid. Moreover, regions with positive and negative values of $\rho_{a_u}{}^{00}$ are arranged in space in a way that the well-known twist about the double bond is indicated.

The f_λ values of Table I also show that a pathway transforming as a reducible representation Γ containing b_{1u} and b_{2g} symmetry coordinates should be favorable. In Figure 2, contour lines for the overlap function, $\rho_\Gamma{}^{00}$, are depicted by using the same plane as for Figure 1. Because $\rho_\Gamma{}^{00}$ is antisymmetric with respect to the molecular x,y-plane, the favorable case (a) holds for the right

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(2) For a review, see: Mulliken, R. S.; Ermler, W. C. *Polyatomic Molecules*; Academic Press: 1981; p 223.

(3) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1970**, *54*, 724.

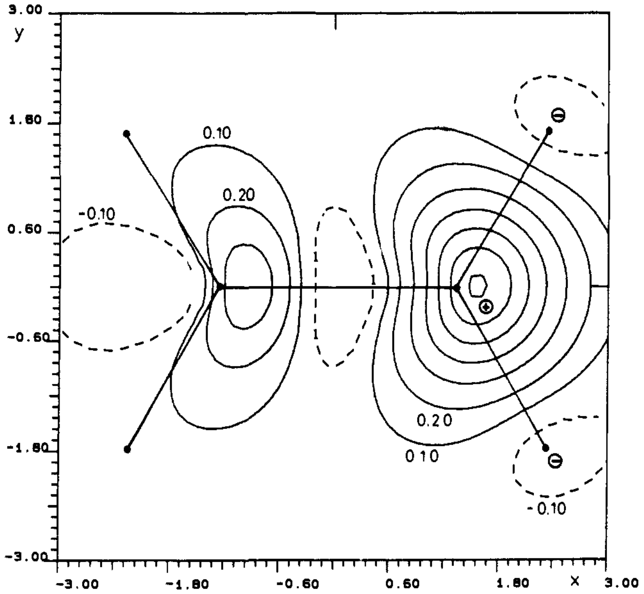

Figure 2. Contour lines for a superposition of $\rho_{b_{1u}}^{00}$ and $\rho_{b_{2g}}^{00}$ for ethylene in the same plane as in Figure 1. The projection of the molecular skeleton onto the plane and the resulting pyramidalization of one carbon atom are indicated.

carbon atom of Figure 2 and the attached hydrogen atoms. The left carbon atom in Figure 2, however, should remain unmoved because the unfavorable case (f) holds. The high functional values near the right carbon atom, and the location of positive and negative values in space, indicate that a favorable pathway involves the pyramidalization of only one carbon atom in ethylene (see Figure 2). If the energy of the perpendicular D_{2d} S_1 state of ethylene is calculated by using natural S_1 orbitals in the CI treatment, a further energy decrease of ≈10 kcal is derived when one carbon atom is pyramidalized by 40°.[4] Such a pyramidalization causes a significant charge separation in the first excited state of ethylene. This is known as the sudden polarization effect,[5] and its importance in various conjugated polyenes has been pointed out. Its impact on the process of vision has also been discussed.[6] Thus, our qualitative results, based on the efficiency factors and the form of the overlap functions alone, are corroborated by the results of extensive computations in the literature.

3. Acetone in the n–π* State

Aliphatic ketones undergo a large variety of photoreactions in the liquid[7] as well as in the gas phase.[8] Since acetone is the simplest of these, much effort has been directed to determining its geometry changes following electronic excitation. Here, we apply the qualitative procedure of the preceding paper in this issue to investigate how the ground-state geometry of acetone is modified after it has been vertically excited into its A_2 n–π* electronic state.

Molecular orbitals and their energies were calculated for the C_{2v} ground-state equilibrium geometry by using the 4-31G basis set.[3] In acetone all Γ_λ of the C_{2v} group are symmetry species for vibrations. For all Γ_λ the f_λ are given in Table II. A linear combination of the symmetric (a_1) and asymmetric (b_1) carbon–carbon stretching coordinates is incorporated into the pathway for the α-cleavage which is observed experimentally.[7,8] The smallness of the f_{a_1} and f_{b_1} values found in this work, however, as compared to the other f_λ values (see Table II), shows that the excited-state geometry is not reached along a pathway containing the symmetry coordinates which are important for the α-cleavage.

Table II. Acetone in Its First n–π* State[a]

Γ_λ	MO	interacting with MO	f_λ
a_1	$3b_2$	$4b_2$ $5b_2$ $6b_2$ $8b_2$	23.144
	$5b_1$	$4b_1$ $3b_1$ $2b_1$	
a_2	$3b_2$	$6b_1$ $7b_1$ $8b_1$ $9b_1$ $10b_1$ $11b_1$ $12b_1$ $13b_1$ $14b_1$ $15b_1$	43.605
	$5b_1$	$2b_2$ $1b_2$	
b_1	$3b_2$	$2a_2$ $3a_2$ $4a_2$	24.956
	$5b_1$	$8a_1$ $7a_1$ $6a_1$ $5a_1$ $4a_1$	
b_2	$3b_2$	$9a_1$ $10a_1$ $11a_1$ $12a_1$ $13a_1$ $14a_1$ $15a_1$ $16a_1$ $17a_1$ $18a_1$ $19a_1$ $20a_1$ $21a_1$	40.313
	$5b_1$	$1a_2$	

[a] The symmetries of distortion, Γ_λ, the interacting orbitals and the corresponding efficiency factors f_λ are given. Symmetry arguments alone favor the a_2- and b_2-coordinates as the relaxation pathway.

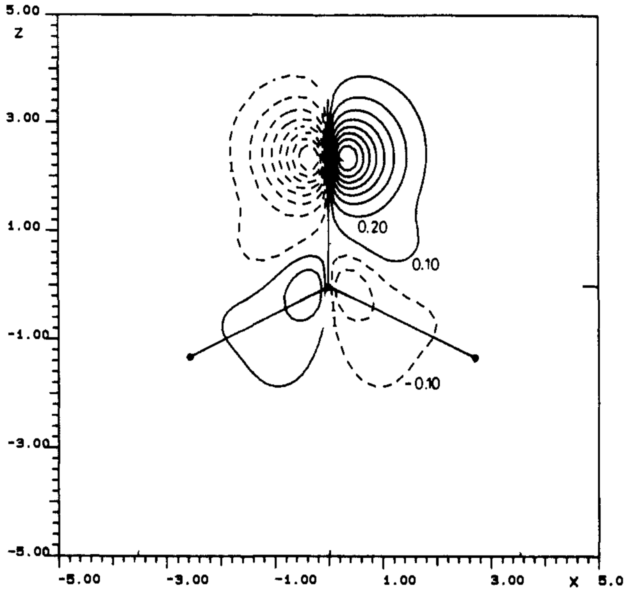

Figure 3. Contour lines of $\rho_{a_2}^{00}$ of acetone in the n–π* state. The plane is parallel the molecular x,z-plane and intersects the y-axis at y = 0.5 au. The projection of the nuclear framework onto the plane is indicated.

For Γ_{a_2} a large f_{a_2} value is derived (see Table II) which is consistent with the concept that for a favorable pathway a large number of orbitals should interact (see Table II). The a_2 symmetry coordinates of acetone can only be made up of motions of the hydrogen atoms of the methyl groups. If they are an efficient relaxation pathway, the overlap function $\rho_{a_2}^{00}$ should have large functional values near the hydrogen atoms. A contour plot of $\rho_{a_2}^{00}$ is given in Figure 3 for a plane which is parallel to the molecular x,z-plane, and it intersects the y-axis at y = 0.5 au. The methyl groups are surrounded only by low functional values of $\rho_{a_2}^{00}$ (see Figure 3). Thus, in spite of the large f_{a_2}, the form of the overlap function is unfavorable for an a_2 motion of the methyl–hydrogen atoms. Near the atoms of the carbonyl group high functional values of $\rho_{a_2}^{00}$ are observed (see Figure 3). However, $\rho_{a_2}^{00}$ is antisymmetric with respect to the molecular x,z-plane, and therefore for these atoms the unfavorable case (f) holds (see Figure 3). Consequently, an a_2 relaxation pathway on the n–π* energy surface should be of minor importance.

The magnitude of the f_λ values in Table II suggests that the b_2 out-of-plane symmetry could be a symmetry for a relaxation pathway. For this symmetry species, a large number of orbitals is available for interaction (see Table II). Contour lines of the overlap function $\rho_{b_2}^{00}$ are given in Figure 4. Again, a drawing

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(4) Buenker, R. J.; Bonacic-Koutecky, V.; Pogliani, L. *J. Chem. Phys.* **1980**, *73*, 1836, Figure 8.

(5) Berthier, G. In *Quantum Theory of Chemical Reactions*; Daudel, R., et al., Eds.; Reidel: Dordrecht, 1981; Vol. II, p 285.

(6) Salem, L. *Acc. Chem. Res.* **1979**, *12*, 87.

(7) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin: Menlo Park, CA, 1978; p 528.

(8) Lee, E. K. C.; Lewis, R. S. *Adv. Photochem.* **1980**, *12*, 1.

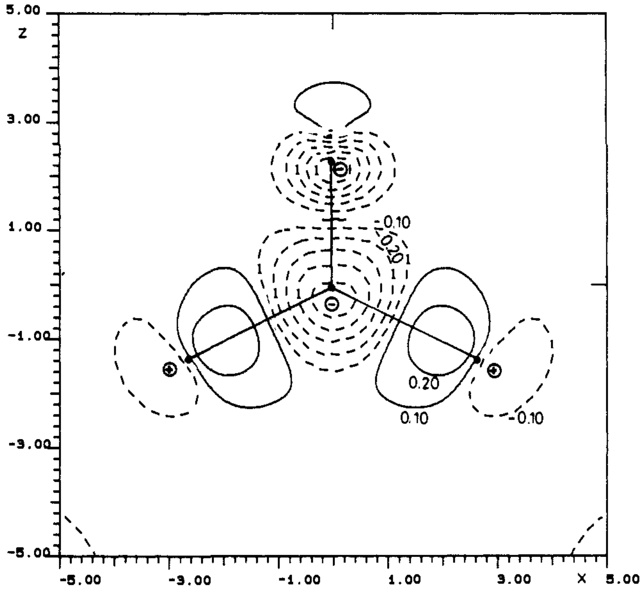

Figure 4. Contour lines of $\rho_{b_2}{}^{00}$ of acetone in the n-π^* state. The plane used is parallel to the molecular x,z-plane and intersects the y-axis at $y = 0.5$ au. The pyramidalization at the carbonyl carbon atom is indicated.

plane parallel to the molecular x,z-plane is used which intersects the y-axis at $y = 0.5$ au. Because $\rho_{b_2}{}^{00}$ is antisymmetric with respect to the molecular plane, the favorable case (a) holds for the atoms of the carbonyl group. Moreover, the carbon atoms of the methyl groups are situated in regions where the favorable case (a) is likely to operate (see Figure 4). Positive and negative values are located in space in such a way that pyramidalization of the carbonyl carbon atom is indicated (see Figure 4). For formaldehyde such a pyramidalization has been found experimentally[9] and by extensive calculations.[10] In S_1 acetone the experimental out-of-plane angle turned out to be 28°.[11] By using the optical detection of magnetic resonance (ODMR) technique, Gehrtz et al. determined a value of ≈38° for acetone in the T_1 state.[12] Our qualitative result is also supported by the recent experiments of Baba et al.[13a,14a] By using the supersonic jet expansion technique, they obtained vibrationally resolved fluorescence excitation spectra from the n-π^* state. The out-of-plane wagging and methyl internal rotations of the methyl groups turned out to be the dominant motions stabilizing the n-π^* state of acetone.[13b,14b]

The above analysis showed that the f_λ and the forms of the corresponding $\rho_\lambda{}^{00}$ together constitute an appropriate tool for selecting energetically favorable directions on the first excited-state surface.

4. *trans*-Butadiene in the π-π^* State

Polyene photochemistry is relevant for the process of vision,[6] and of central importance to an understanding of it is how the electronic excitation energy in polyenes is transformed into nuclear motions. A detailed knowledge of the forms of the excited state potential energy surfaces of polyenes is therefore desirable. In the subsequent analysis the qualitative procedure proposed in the preceding paper in this issue is applied to *trans*-butadiene, the first member of the polyene series.

Molecular orbitals for *trans*-butadiene in its C_{2h} ground-state equilibrium geometry were calculated by using the 4-31G basis set.[3] We assume that *trans*-butadiene is vertically excited into its π-π^* B_u state. The f_λ were calculated for all Γ_λ of C_{2h}. The numerical values recorded in Table III show that a relaxation pathway should be described by b_g and a_u symmetry coordinates (see Table III). Thus, the pathway should transform as a reducible representation Γ containing the two irreducible representations Γ_{b_g} and Γ_{a_u}. All b_g and a_u symmetry coordinates of *trans*-butadiene are out-of-plane, but by using only the efficiency factors we are unable to determine which out-of-plane motion lowers the energy the most. Here, we supplement our analysis by inspecting the form of the overlap functions $\rho_\Gamma{}^{00}$ for the reducible representation Γ.

Table III. *trans*-Butadiene in Its First π-π^* State[a]

Γ_λ	MO	interacting with MO	f_λ
a_g	$2a_u$	$3a_u$ $4a_u$	2.521
b_g	$2a_u$	$7b_u$ $8b_u$ $9b_u$ $10b_u$ $11b_u$ $12b_u$ $13b_u$ $14b_u$ $15b_u$ $16b_u$ $17b_u$ $18b_u$ $19b_u$ $20b_u$	49.605
	$1b_g$	$7a_g$ $6a_g$ $5a_g$ $4a_g$ $3a_g$	
a_u	$2a_u$	$8a_g$ $9a_g$ $10a_g$ $11a_g$ $12a_g$ $13a_g$ $14a_g$ $15a_g$ $16a_g$ $17a_g$ $18a_g$ $19a_g$ $20a_g$	39.166
	$1b_g$	$6b_u$ $5b_u$ $4b_u$ $3b_u$	
b_u	$2a_u$	$2b_g$ $3b_g$ $4b_g$	18.295
	$1b_g$	$1a_u$	

[a] The symmetries of distortions, Γ_λ, the interacting orbitals, and the corresponding efficiency factors f_λ are given. *trans*-Butadiene relaxes along b_g and a_u out-of-plane coordinates.

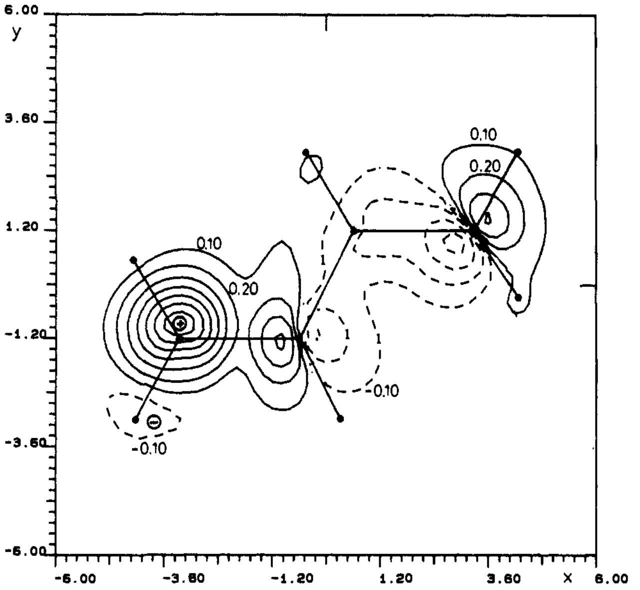

Figure 5. Contour lines of a superposition of $\rho_{b_g}{}^{00}$ and $\rho_{a_u}{}^{00}$ for *trans*-butadiene in the B_u π-π^* state. The plane shown is parallel to the molecular plane and intersects the z-axis at $z = 0.5$ au. The induced nuclear motions are indicated.

Contour lines for $\rho_\Gamma{}^{00}$ are depicted in Figure 5 in a plane being parallel to the molecular x,y-plane and which intersects the z-axis at $z = 0.5$ au. The projection of the molecular skeleton onto the plane of drawing is also indicated. By inspection of Figure 5, we can see that the left most carbon atom in Figure 5 is surrounded by high functional values. Taking into account that $\rho_\Gamma{}^{00}$ is antisymmetric with respect to the molecular plane, we observe that the favorable case (a) holds for that carbon atom. All other carbon atoms are located in spatial regions where either low functional values are present or where the unfavorable case (f) obtains. Thus, the form of $\rho_\Gamma{}^{00}$ indicates that after an excitation into the π-π^*

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(9) Jones, V. T.; Coon, J. B. *J. Mol. Spectrosc.* **1969**, *31*, 137.

(10) Buenker, R. J.; Peyerimhoff, S. D. *J. Chem. Phys.* **1970**, *53*, 1368. Baba, M.; Nagashima, U.; Hanazaki, I. *Chem. Phys.* **1985**, *93*, 425.

(11) Swalen, J. D.; Costain, C. C. *J. Chem. Phys.* **1959**, *31*, 1562.

(12) Gehrtz, M.; Bräuchle, C.; Voitländer, J. *Mol. Phys.* **1984**, *53*, 769.

(13) (a) Baba, M.; Hanazaki, I. *Chem. Phys. Lett.* **1983**, *103*, 93. (b) See ref 13a, Figure 2 and corresponding text.

(14) (a) Baba, M.; Hanazaki, I.; Nagashima, U. *J. Chem. Phys.* **1985**, *82*, 3938. (b) See ref 14a, Figure 6 and corresponding text.

Table IV. Methylenimine in Its First n–π^* State[a]

Γ_λ	MO	interacting with MO	f_λ
a′	2a″	3a″ 4a″	14.335
	7a′	6a′ 5a′ 4a′	
a″	2a″	8a′ 9a′ 10a′ 11a′ 12a′ 13a′ 14a′ 15a′ 16a′ 17a′ 18a′ 19a′ 20a′	64.344
	7a′	1a″	

[a] The symmetries Γ_λ of distortions, the interacting orbitals, and the corresponding efficiency factors f_λ are given. Methyleneimine relaxes along a″ out-of-plane coordinates.

state, a significant pyramidalization of one terminal carbon atom occurs. The form of ρ_Γ^{00} near the hydrogen atoms bonded to that carbon atom also supports the deduction that pyramidalization occurs. Such a pyramidalization decouples one methylene group from the remaining allylic π-electron system, and the methylene group can then rotate about the remaining σ-bond. A rotation without pyramidalization is the classic prediction of Hoffmann,[15] which has been confirmed by the extensive calculations of Bonacic-Koutecky et al.[16] Aoyagi et al. performed a full geometry optimization for the A_g and B_u excited states of *trans*-butadiene by using the MCSCF procedure in the complete active space.[17] The optimized geometries for the singlet excited B_u state, located above the singlet excited A_g state, show for the first time a local minimum at a planar geometry.[17] However, a minimum with lower energy has been found where on terminal methylene group is rotated, and in this case it is also strongly pyramidalized by a flapping angle of 82°.[17] Thus, our qualitative results are substantiated by extensive calculations.

5. Methylenimine

Methylenimine is the simplest of Schiff bases which show a wide range of ground-state and excited-state chemistry.[18] One aspect of the n–π^* photochemistry of substituted imines is the photochemical syn–anti isomerization about the carbon–nitrogen double bond.[19] The isomerization pathway can be considered as a motion of the substituent at the nitrogen, and it can be in-plane (inversion) and/or out-of-plane (twisting). As a model compound for the syn–anti isomerization, methylenimine is investigated below. Our intention is to find the pathway along which methylenimine modifies its ground-state geometry after an excitation into the n–π^* state.

An energy-minimized geometry of methylenimine[20] was used; the molecular orbitals and their energies were calculated by using the 4-31G basis set.[3] Methylenimine is considered to be excited into its n–π^* A″-state. The f_λ for the two irreducible representations a′ and a″ and the corresponding interacting molecular orbitals are recorded in Table IV. The numerical values indicate that the first excited A″ state should be stabilized by an a″ out-of-plane relaxation pathway (see Table IV). In order to determine which out-of-plane motion is efficient, we inspect the form of $\rho_{a''}^{00}$. Contour lines for $\rho_{a''}^{00}$ are given in Figure 6, by means of a plane being parallel to the molecular x,y-plane and which intersects the z-axis at 0.5 au. Because $\rho_{a''}^{00}$ is antisymmetric with respect to the molecular plane, we see that for the carbon and nitrogen atom the unfavorable case (f) operates. Consequently, motions of these atoms are not involved in the relaxation pathway. However, for all three hydrogen atoms, the favorable case (a) holds. Regions with positive and negative values of $\rho_{a''}^{00}$ are located in space such that an out-of-plane rotation about the carbon–nitrogen double bond is indicated. This qualitative result is substantiated by results of Bonacic-Koutecky et al.,[21] who calculated S_1 and T_1 potential energy surfaces as a function of the CNH in- and out-of-plane angles. The low-energy pathway on both surfaces involves primarily changing the out-of-plane angle;[21] the in-plane angle remains almost unchanged.[21] A rigorous dynamical treatment of this photoisomerization has been performed by Russegger,[22] who shows that the out-of-plane motion on the T_1 surface is the large amplitude motion along which the isomerization is driven, at least on the T_1 surface. This surface touches the ground-state potential energy surface, and the isomerization is completed on the latter where the in-plane motion becomes effective.[22] This is beyond the scope of our analysis, however.

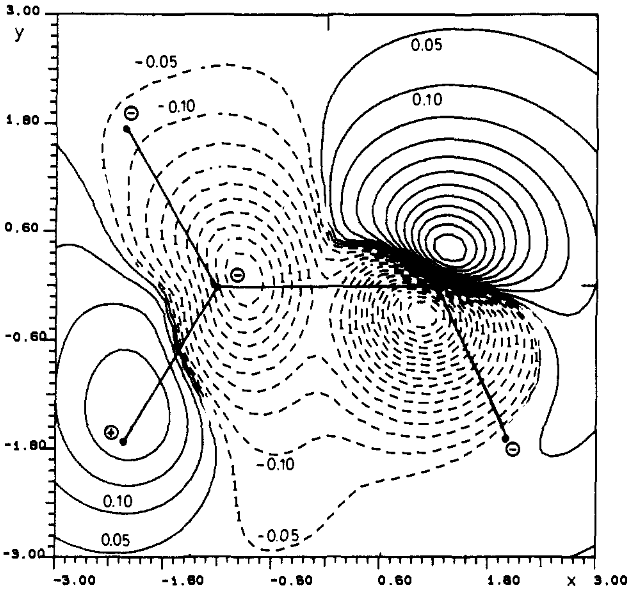

Figure 6. Contour lines of $\rho_{a''}^{00}$ for methylenimine in the A″ n–π^* state. The plane shown is parallel to the molecular plane and intersects the z-axis at z = 0.5 au. The resulting rotation about the double bond is indicated.

The substantiation of our qualitative results by previous extensive calculations supports our proposal that the symmetry-based procedure given in the preceding paper is a qualitative tool to find relaxation pathways on the first excited state potential energy surface.

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Registry No. ethylene, 74-85-1; acetone, 67-64-1; 1,3-butadiene, 106-99-0; methylenimine, 2053-29-4.

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(15) Hoffmann, R. *Tetrahedron* **1966**, *22*, 521, Figure 5.

(16) Bonacic-Koutecky, V.; Persico, M.; Döhnert, D.; Sevin, A. *J. Am. Chem. Soc.* **1982**, *104*, 6900.

(17) Aoyagi, M.; Osamura, Y.; Iwata, S. *J. Chem. Phys.* **1985**, *83*, 1140, in particular Figure 3 and Table I.

(18) *The Chemistry of the Carbon–Nitrogen Double Bond*; Patai, S., Ed.; Interscience Publishers: New York, 1970.

(19) See Wettermark, G. *Photochemistry of the Carbon–Nitrogen Double Bond*; in ref 18, p 565.

(20) See ref 21, Table I.

(21) Bonacic-Koutecky, V.; Michl, J. *Theor. Chim. Acta* **1985**, *68*, 45.

(22) Russegger, P. *Chem. Phys.* **1978**, *34*, 329.