

which is 1.260,²⁵ 1.260,¹⁷ 1.277,¹⁸ and 1.283 Å,⁵ respectively, for the above four complexes. Key band assignments are given in Tables IV and V.

Conclusion

Raman spectra of Os₂(O₂CCH₃)₄Cl₂ taken at resonance with the axially polarized 383-nm band ($\pi(\text{Cl}) \rightarrow \pi^*(\text{Os}_2)$)⁶ are characterized by long progressions in which the (axial) mode, ν_1 , $\nu(\text{OsOs})$ at 229 cm⁻¹ acts as the progression-forming mode. This behavior, which is characteristic of A-term resonance Raman scattering of a_{1g} modes,²⁶ implies that the structural change

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consequent upon excitation to the resonant $\pi^*(\text{Os}_2)$ electronic state is substantial and principally along the Os-Os coordinate. The wavenumber of ν_1 is only slightly greater than that ($\sim 220 \text{ cm}^{-1}$)⁶ detected as structure to the long wavelength electronic bands of the complex, such as that ($\delta \rightarrow \delta^*$) at ca. 850 nm; clearly, the progression-forming mode in the electronic bands is likewise ν -(OsOs), although the small ground-state to excited-state wavenumber change for ν_1 in these bands implies that, for such excited states, only very small changes occur to the osmium-osmium bond length.

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A Symmetry-Based Procedure for the Determination of Molecular Geometry Changes Following Electronic Excitation.

1. Outline of the Qualitative Method

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Abstract: An extension of the Bader-Pearson concept to nondegenerate first excited states is presented which permits a qualitative determination of the relaxation pathway along which the molecular geometry changes following electronic excitation. A symmetry criterion for the relaxation pathway has been developed, according to which the most favored path is that which permits coupling of the first excited state with a large number of higher excited states close to the first excited state. Excited-state geometries of low symmetry are treated in a novel way by considering the pathway symmetry as a superposition of two different irreducible representations; numerical quantities are suggested for estimating the likelihood of particular representations to occur in the superposition. After determining the relevant symmetry species, the pathway is specified in greater detail by inspection of plots of the overlap function between interacting orbitals, and a procedure for using such plots is described.

1. Introduction

Photochemical and spectroscopic properties of electronically excited molecules are frequently rationalized by referring to the form of the excited state potential energy surface. A photochemical reaction starts along that direction on the excited-state surface which leads to the smallest energy increase or even an energy minimum. Provided the pathway for an energy decrease is identical with a normal mode, a long vibrational progression in that mode may be observed in highly resolved electronic spectra.

Large scale configuration interaction methods proved to be reliable for the calculation of excited state potential energy surfaces.¹ The computational effort, however, would be diminished if a qualitative procedure were available predicting directions on the surface which are energetically favorable. Such a scheme would also be of use for the interpretation of large scale ab initio results, where a qualitative explanation of reliable results is often obscured by a maze of numbers. For ground-state surfaces the Bader-Pearson concept²⁻⁴ relates explicitly the symmetry of the total wave function and the symmetry of reaction pathways. The essence of this concept is that the direction of a particular nuclear motion is energetically favorable if the electronic charge density

can follow the motion easily. This simple concept led to a comprehensive rationalization of ground-state chemistry.³ It has recently been incorporated by Bader into his theory of chemical reactivity which is based on a spatial partitioning of the electronic charge density.⁵

Few attempts have been made to apply the Bader-Pearson concept to electronically excited-state surfaces. A general rule for predicting the geometry of electronically excited molecules has been derived,⁶ but for conjugated molecules it had to be extended.⁷ Devaquet generalized the Bader-Pearson concept to first excited states⁸ and applied it to a variety of electronically excited molecules.^{8,9} However, in several instances it seemed difficult to discriminate between alternative directions for relaxation pathways. Nakajima analyzed carbon-carbon bond length changes of conjugated molecules following electronic excitation.⁷ The bond length changes are correctly predicted, but molecular orbitals for σ -electrons are not explicitly considered. This restriction limits the procedure to nuclear motions in which planarity is retained. Bond length changes following electronic excitation can also be deduced from the ΔP -matrix as suggested by Zimmerman.¹⁰ This matrix is defined as the difference be-

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tween the bond order matrix for the excited state and that for the ground state. The primary assumption is that bond length changes of a bond $r-t$ are related to the corresponding matrix elements ΔP_{rt} . A negative ΔP_{rt} indicates that in the excited state the bond should be weakened; a positive number implies bond tightening¹⁰. In addition, a partitioning of the analytic expression for the excitation energy ΔE led to energy increments ΔE_{rt} which refer to a bond.¹¹ The quantities ΔP_{rt} and ΔE_{rt} have been used to identify those parts of a molecule which carry the electronic excitation energy.¹¹ They are useful for a neat rationalization of a broad range of photochemistry and a detailed analysis of the di- π -methane rearrangement has been performed.¹² Recently, Morrison et al. applied difference density plots between the first excited state and the ground state to visualize electron density changes accompanying the excitation process.¹³ The plots indicated well the bond strength changes which followed the excitation process.¹³ These plots could be applied for a qualitative prediction of excited-state geometries. One could use the ground-state geometry for calculating the difference density distribution. This choice is suggested by the expectation that such difference density distributions contain information about how the excited state geometry differs from that of the ground state. Difference density distributions calculated at the ground-state geometry transform totally symmetric in the ground-state point group. Therefore, their use is only appropriate for excited-state geometries which might be different from that of the ground state, but where the ground-state point group is retained. Many excited states, however, have a geometry with lower symmetry, where the ground-state point group is not preserved. It is this symmetry lowering which can be treated by means of the Bader-Pearson concept.

In this paper we extend the Bader-Pearson concept to nuclear motions on the first excited state potential energy surface more rigorously than has been done previously. In the subsequent paper applications are presented which demonstrate that this procedure is a valuable qualitative tool.

2. Theoretical Background

Consider a molecule in its ground-state equilibrium geometry having a point group G . A vertical electronic excitation to the first excited state leads to a point on its surface where the ground-state point group G is still retained.¹⁴ Afterwards, in a time interval of about 10^{-12} s,¹⁵ the nuclear framework rearranges along a relaxation pathway which leads to the excited-state minimum geometry. By analogy with the procedure of Rodger and Schipper,¹⁶ any geometry change in that direction can be represented as a linear combination of symmetry coordinates, S_i , which form a complete set, and are symmetry adapted in G . Our objective was to design a qualitative procedure to determine which S_i dominate such a superposition. Devaquet assumed implicitly that only one S_i is important and that this S_i is the relaxation pathway.⁸ However, the more general case is that a geometry change is a superposition of various S_i transforming as different symmetry species. An example is the $\pi-\pi^*$ excited-state geometry of *trans*-butadiene which is reached by lowering the C_{2h} ground-state symmetry along a rotation of only one methylene group. Such a rotation is a superposition of b_g and a_u symmetry coordinates, and here the relaxation pathway transforms as a

reducible representation in C_{2h} . In order to have access to these low-symmetry cases we assume that the excited-state minimum geometry is reached by a distortion along two symmetry coordinates, S_i and S_j , transforming as the irreducible representations Γ_{S_i} and Γ_{S_j} , respectively, of G . If Γ_{S_i} and Γ_{S_j} are different, this scheme includes pathways transforming as a reducible representation of G , as in the case of *trans*-butadiene.

After stating the symmetry features of our model, we are interested in the energy change arising from a geometry distortion along S_i and S_j . We assume that the electronic Schrodinger equation at the ground-state geometry, designated by (0,0), can be solved for all electronic states k

$$H(0,0) \phi_k(0,0) = E_k(0,0) \phi_k(0,0) \quad (1)$$

The electronic Hamiltonian $H(\Delta S_i, \Delta S_j)$ corresponding to the distorted geometry can be expanded into a Taylor series about the ground-state molecular geometry

$$\begin{aligned} H(\Delta S_i, \Delta S_j) = & H(0,0) + \left(\frac{\partial H}{\partial S_i} \right)_{00} \Delta S_i + \left(\frac{\partial H}{\partial S_j} \right)_{00} \Delta S_j + \frac{1}{2} \left(\frac{\partial^2 H}{\partial S_i^2} \right)_{00} \Delta S_i^2 + \\ & \left(\frac{\partial^2 H}{\partial S_i \partial S_j} \right)_{00} \Delta S_i \Delta S_j + \frac{1}{2} \left(\frac{\partial^2 H}{\partial S_j^2} \right)_{00} \Delta S_j^2 + \dots \equiv H^{00} + \\ & H^{10} \Delta S_i + H^{01} \Delta S_j + \frac{1}{2} H^{20} \Delta S_i^2 + H^{11} \Delta S_i \Delta S_j + \frac{1}{2} H^{02} \Delta S_j^2 \quad (2) \end{aligned}$$

Here, the derivatives of the Hamiltonian with respect to S_i and S_j are denoted by the symbol H^{mn} ; a particular H^{mn} is defined by its corresponding term in the expansion (2). The wave functions and energies of the new geometry can also be expanded into a Taylor series. If we assume the first excited state is nondegenerate and that the derivatives of the first excited state wave function with respect to S_i and S_j can be represented with sufficient accuracy by a linear combination of n functions $\phi_k(0,0)$ ($k = 0, 1, \dots, n-1$), nondegenerate double perturbation theory can be applied.¹⁷ Here, we give only the final expression for the energy at point $(\Delta S_i, \Delta S_j)$ on the first excited state surface; the formula is valid up to second order in the distortions ΔS_i and ΔS_j

$$\begin{aligned} E_1(\Delta S_i, \Delta S_j) = & E_1^{00} + \langle 1^{00} | H^{10} | 1^{00} \rangle \Delta S_i + \langle 1^{00} | H^{01} | 1^{00} \rangle \Delta S_j + \\ & \frac{1}{2} \{ \langle 1^{00} | H^{20} | 1^{00} \rangle \Delta S_i^2 + \langle 1^{00} | H^{02} | 1^{00} \rangle \Delta S_j^2 \} + \\ & \langle 1^{00} | H^{11} | 1^{00} \rangle \Delta S_i \Delta S_j + \frac{1}{2} \sum_{k=0}^n \frac{\langle 1^{00} | H^{10} | k^{00} \rangle^2}{E_1^{00} - E_k^{00}} \Delta S_i^2 + \\ & \frac{1}{2} \sum_{k=0}^n \frac{\langle 1^{00} | H^{01} | k^{00} \rangle^2}{E_1^{00} - E_k^{00}} \Delta S_j^2 + \\ & \sum_{k=0}^n \frac{\langle 1^{00} | H^{10} | k^{00} \rangle \langle k^{00} | H^{01} | 1^{00} \rangle}{E_1^{00} - E_k^{00}} \Delta S_i \Delta S_j \quad (3) \end{aligned}$$

The primes attached to the summation signs mean that the contribution for $k = 1$ is to be omitted. Equation 3 can also be derived, without using perturbation theory, by forming first- and second-order derivatives of the first excited state energy with respect to S_i and S_j , taken at the ground-state geometry.¹⁸

3. Symmetry Analysis and Preferred Geometry Relaxations

In the previous section we showed that the energy of a molecule, after vertical excitation involving a change of geometry along the symmetry coordinates S_i and S_j , is given by eq 3. Here, we apply symmetry arguments which lead to a simple rule for excited-state surfaces and to an assessment of the validity of the second-order approximation used in eq 3.

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The superscripts m and n of the operators H^{mn} in (3) designate the m th and n th derivative of the electronic Hamiltonian with respect to S_i and S_j , respectively, taken at the ground-state geometry with point group G . The operators H^{10} in (3a) and H^{01} in (3b) transform as Γ_{S_i} and Γ_{S_j} , respectively, which are the irreducible representations of the symmetry coordinates S_i and S_j . Because the first excited state is assumed to transform as a nondegenerate irreducible representation $\Gamma_{1\infty}$ of G , (3a) and (3b) vanish in the case where Γ_{S_i} and Γ_{S_j} are nontotally symmetric.¹⁹ The contributions (3a) and (3b) are the first derivatives of the energy with respect to S_i and S_j ,²⁰ respectively. Using the above symmetry argument and the meaning of (3a) and (3b), a simple but general rule for the surface of a nondegenerate first excited state holds:²¹ the potential energy surface, represented as a function of two nontotally symmetric nuclear distortions S_i and S_j , has a minimum, a maximum, or a saddle point, located at the ground-state geometry. The special case for a distortion along one S_i is known for many molecules, and we mention two prominent examples: the first excited $n-\pi^*$ state surface of formaldehyde has a maximum at the planar minimal C_{2v} ground-state geometry when this surface is plotted as a function of the nontotally symmetric pyramidalization coordinate,²² and the $\pi-\pi^*$ state energy surface of ethylene has a maximum at the planar D_{2h} ground-state geometry when it is represented as a function of the nontotally symmetric twisting motion.²³ Another consequence of the symmetry rule for (3a) and (3b) is that photodissociations on excited-state surfaces, having at any point of the pathway a nonvanishing derivative with respect to the pathway coordinate, should not proceed along nontotally symmetric coordinates of the ground-state point group.

The contributions (3c), (3d), (3e) refer to motions of the nuclei in the unrelaxed charge distribution²⁴ of the first excited state. Consequently, they inhibit a geometry change toward the first excited-state minimum. The second-order contributions which favor a geometry change are the terms (3f), (3g), and (3h). The derivation using double perturbation theory¹⁷ shows that they describe electronic relaxations²⁴ and that they are energy lowering. Only those members of the sums in (3f), (3g), and (3h) can contribute for which the triple direct products $\Gamma_{1\infty} \times \Gamma_{S_i} \times \Gamma_{k\infty}$ and/or $\Gamma_{1\infty} \times \Gamma_{S_j} \times \Gamma_{k\infty}$ contain the totally symmetric representation. Because G is assumed to have only nondegenerate representations, a coupling of S_i and S_j in (3h) occurs only when Γ_{S_i} and Γ_{S_j} are identical. This case is important, because for one irreducible representation various symmetry coordinates might exist.

In many instances the geometry change following vertical excitation leads to a symmetry lowering. From the analysis of Rodger and Schipper such a symmetry decrease can only occur along nontotally symmetric S_i and/or S_j .²⁵ Because we assume that the first excited state is nondegenerate by symmetry, the only terms which can induce an energy lowering symmetry decrease are the second-order contributions (3f–h). If the symmetry lowering pathway is entered, we could employ the continuity principle of Rodger and Schipper¹⁶ to repeat the symmetry analysis at the new geometry with lower point group symmetry. This would lead to nonvanishing first-order terms (3a) and/or (3b) because the formerly induced relaxation pathway would be totally symmetric in the smaller group. If we apply Pearson's rule that a pathway is totally symmetric in the retained group,²⁶ we conclude that the smaller group is retained, because now the first-order terms (3a) and (3b) outweigh the second-order terms. The symmetry lowering is induced at a stationary point¹⁶ by the second-order terms

(3f–h), but it is preserved along the path by the first-order contributions (3a) and (3b). These considerations suggest that in spite of eq 3 being based on a second-order approximation, it should also be valid for larger steps along the relaxation pathway.

4. Selecting the Preferred Relaxation Pathway

In this section we apply eq 3 to design a qualitative procedure for determining the pathway along which the molecular geometry relaxes on the first excited state potential energy surface after vertical electronic excitation. In accordance with the Bader–Pearson concept,^{2–4} our criterion for a relaxation path is that the energy lowering parts of (3f–h) should be large. Here, we illustrate how this criterion can be used.

Consider a relaxation pathway composed of two symmetry coordinates S_i and S_j . In many instances all three relaxation terms (3f–h) are important, and we need to be able to collect (3f–h) into one compact expression. This is achieved by defining a new operator O_λ^1 , the sum of H^{10} and H^{01}

$$O_\lambda^1 = H^{10} + H^{01} \quad (4)$$

Depending on the symmetry of S_i and S_j , O_λ^1 transforms either as an irreducible or as a reducible representation Γ_λ of G . Because O_λ^1 is a multiplicative operator, all energy-lowering contributions of (3f–h) can be collected in one term, R_λ , called the relaxation term, which also contains a possible coupling between S_i and S_j

$$R_\lambda = -\frac{1}{2} \sum_{k=2}^{n_\lambda} \frac{\langle 1^{00} | O_\lambda^1 | k^{00} \rangle^2}{E_k^{00} - E_1^{00}} \quad (5)$$

The sum ranges only over those states above the first excited state which have the proper symmetry, such that for any k the direct product $\Gamma_{1\infty} \times \Gamma_\lambda \times \Gamma_{k\infty}$ contains the totally symmetric representation. There are n_λ states meeting this requirement. If R_λ is approximated by the first member of the sum in eq 5 ($k=2$), we arrive at the assumptions of Devaquet: A molecule in its first excited state relaxes along the pathway which has the proper symmetry to permit a coupling between the first and second excited state.⁸ Such a strong coupling is also the basis for the proximity effect on relaxation pathways and spectroscopic properties of heterocyclic compounds as recently discussed by Lim.²⁷ On the basis of eq 5, Devaquet's assumption⁸ is easily recognized as a special case of two more general conditions for a relaxation pathway: (i) The symmetry Γ_λ of a relaxation pathway should be appropriate for a large number of higher excited states to interact with the first excited state. In addition, they should be energetically close to the first excited state.

However, knowing only Γ_λ for the pathway is insufficient because various nuclear motions all transforming as Γ_λ can be present. In order to select the relaxation pathway from the variety of paths, the following condition is suggested. (ii) From the manifold of pathways transforming as Γ_λ , the relaxation pathway is that for which the corresponding operator O_λ^1 leads to a large relaxation term R_λ .

Our intention was to develop a qualitative procedure, which employs these two conditions (i) and (ii). For this purpose it is desirable to have R_λ in a form where the coupling with all higher excited states is contained in one integral. This is achieved by using the elementary inequality between n real numbers²⁸

$$\frac{(a_1 + a_2 + \dots + a_n)^2}{n} \leq (a_1^2 + a_2^2 + \dots + a_n^2) \quad (6)$$

If we define a_k as

$$a_k = \frac{\langle 1^{00} | O_\lambda^1 | k^{00} \rangle}{(E_k^{00} - E_1^{00})^{1/2}} \quad (7)$$

the multiplicative property of O_λ^1 and the left-hand side of (6)

(19) See ref 16, in particular theorem 1 on p 335 for the case (ii).

(20) See ref 3, p 14.

(21) For ions of molecules this rule is contained in Figure 12 of p 477 of ref 3; for electronic excitations, see: Clark, R. J. H.; Stewart, B. *Struct. and Bonding* **1979**, *36*, 1, in particular p 14.

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lead to an approximate relaxation term

$$\tilde{R}_\lambda = -\frac{1}{2n_\lambda} \left[\sum_{k=2}^{n_\lambda} \frac{\langle 1^{00} | O_\lambda^1 | k^{00} \rangle}{(E_k^{00} - E_1^{00})^{1/2}} \right]^2 - \frac{1}{2n_\lambda} \left[\int O_\lambda^1 \phi_1^{00} \psi_\lambda^{00} d\tau \right]^2 \quad (8)$$

Here the function ψ_λ^{00} is defined as

$$\psi_\lambda^{00} = \sum_{k=2}^{n_\lambda} \frac{\phi_k^{00}}{k^{00}(E_k^{00} - E_1^{00})^{1/2}} \quad (9)$$

and the sums in (8) and (9) run over the same n_λ excited states as in eq 5. ψ_λ^{00} resembles a perturbed first-order wave function.²⁹ The derivative of the first excited state wave function with respect to the distortion is constructed as a superposition of all unperturbed ϕ_k^{00} . The weight of a particular ϕ_k^{00} in the superposition is regulated by the energetic distance to the first excited state. Inequality (6) shows that the absolute value of \tilde{R}_λ is a lower bound to the absolute value of the exact relaxation term, R_λ

$$|\tilde{R}_\lambda| \leq |R_\lambda| \quad (10)$$

Despite the fact that \tilde{R}_λ is only an approximation to R_λ it has the advantage that the interaction of the first excited state with all higher states is contained in only one integral (see eq 8). This fact makes \tilde{R}_λ an appropriate starting point for the design of a qualitative method based on the conditions (i) and (ii).

4.1 Implementing Condition (i). \tilde{R}_λ can be used to derive a simple quantity which permits us to assess how condition (i) holds for a pathway symmetry, Γ_λ . If we assume the various Γ_λ have comparable product functions $O_\lambda^1 \phi_1^{00}$ (see eq 8), the integration in (8) leads to a large \tilde{R}_λ , provided the absolute functional values of ψ_λ^{00} are large at many points in space. This property of ψ_λ^{00} should lead to a large norm of ψ_λ^{00} which is given by the integral

$$\int \psi_\lambda^{00} \psi_\lambda^{00} d\tau = \sum_{k=2}^{n_\lambda} \frac{1}{(E_k^{00} - E_1^{00})} = f_\lambda \quad (11)$$

where the orthonormality of the ϕ_k^{00} has been used. For a particular Γ_λ , condition (i) is favorable provided for that Γ_λ a large number of higher excited states with proper symmetry is close to the first excited state. Such a situation would be indicated by a large value of f_λ , and we call f_λ the efficiency factor for the representation Γ_λ . Thus, the likelihood of a given Γ_λ to be an important symmetry species for a relaxation pathway can be determined by using numerical f_λ values.

4.2 Implementing Condition (ii). In order to determine how condition (ii) holds for a pathway symmetry Γ_λ , we define a function ρ_λ^{00} as

$$\rho_\lambda^{00} = \sum_{k=2}^{n_\lambda} \frac{\phi_1^{00} \phi_k^{00}}{(E_k^{00} - E_1^{00})^{1/2}} = \phi_1^{00} \psi_\lambda^{00} \quad (12)$$

which contains products between many electron functions of the first excited state ϕ_1^{00} and the wave functions ϕ_k^{00} of all interacting higher excited states weighted by their energy difference. Using this ρ_λ^{00} , \tilde{R}_λ is given by

$$\tilde{R}_\lambda = -\frac{1}{2n_\lambda} \left[\int O_\lambda^1 \rho_\lambda^{00} d\tau \right]^2 \quad (13)$$

It is important to realize that in eq 13 only one ρ_λ^{00} exists for a particular pathway symmetry Γ_λ , whereas a manifold of pathways and operators, O_λ^1 , all transforming as Γ_λ , might exist. Consequently, the unique form of ρ_λ^{00} can be used to select the relaxation pathway from the manifold of available paths. Condition (ii) provides the key to the procedure to be followed: A pathway is energetically favorable provided it corresponds to an O_λ^1 giving rise to a large \tilde{R}_λ . This condition implies that the form of the operator function O_λ^1 should match the given form of ρ_λ^{00} such

that the integrand $O_\lambda^1 \rho_\lambda^{00}$ (see eq 13) has large functional values of the same sign at many points in space. In section 6 this matching condition is used to derive a qualitative criterion which allows the form of ρ_λ^{00} to be used for the detection of the relaxation pathway.

Thus, the procedure comprises two successive stages: in a first, the symmetry species, Γ_λ , having the largest f_λ value is determined, and Γ_λ is assumed to be the symmetry species of the pathway; in a second, ρ_λ^{00} is used to select from the Γ_λ manifold of paths the favorable relaxation pathway.

5. Relaxation Pathways and Interacting Molecular Orbitals

As a qualitative tool to determine the symmetry Γ_λ of a relaxation pathway, the efficiency factors f_λ were introduced in section 4. In addition the function ρ_λ^{00} was suggested as a device to specify the relaxation pathway. In this section we formulate these quantities in terms of molecular orbitals and show how they are related to the concept of interacting orbitals.

Equations 11 and 12 for f_λ and ρ_λ^{00} , respectively, were derived by assuming that ϕ_1^{00} and all ϕ_k^{00} are eigenfunctions of the electronic Hamiltonian for the ground-state geometry. Because we are interested in a qualitative procedure, we consider ϕ_1^{00} and all ϕ_k^{00} to be approximated by one singlet determinantal wave function³⁰ composed of SCF molecular orbitals, $\{\varphi^{00}\}$, calculated at the ground-state geometry. Moreover, we assume that the first excited state wave function ϕ_1^{00} is characterized by the HOMO-LUMO excitation $h-l$. In addition, only interactions of the first excited state with higher excited states are accounted for whose wave functions ϕ_k^{00} refer to single excitations $h'-l'$. Here, h' and l' designate all occupied and unoccupied orbitals, respectively, which are different from the frontier orbitals. A further simplification arises from the fact that the operator O_λ^1 is a one-electron operator: only these parts of the electronic Hamiltonian depend explicitly on the nuclear coordinates. By using Slater's rules for expectation values over determinantal wave functions,³¹ we realize that the integrals $\langle 1^{00} | O_\lambda^1 | k^{00} \rangle$ of eq 8 are nonvanishing provided two conditions hold, namely, $h' = h$ but $l' \neq l$ and $l' = l$ but $h' \neq h$.⁷ The qualitative character of the proposed scheme implies that the eigenvalues E_1^{00} and E_k^{00} in eq 9 can be approximated by the corresponding expectation values.³⁰ When we also neglect all two-electron integrals over molecular orbitals, the efficiency factor f_λ is now given by

$$f_\lambda = \sum_{i=l+1}^{\text{unocc}} \mu \frac{1}{\epsilon_i^{00} - \epsilon_l^{00}} + \sum_{i=1}^{\text{occ}-1} \nu \frac{1}{\epsilon_h^{00} - \epsilon_i^{00}} \quad (14)$$

Here, ϵ_h^{00} and ϵ_l^{00} are the energies of the HOMO and LUMO, respectively. In the first part of (14) the index i runs over all unoccupied orbitals of symmetry species Γ_μ interacting with the LUMO. Γ_μ is fixed by the condition that the triple direct product $\Gamma_l \times \Gamma_\lambda \times \Gamma_\mu$ contains the totally symmetric representation. In the last term of (14) i ranges over all occupied orbitals of symmetry species Γ_ν which interact with the HOMO. Γ_ν is given by the requirement of containing the totally symmetric representation in the triple direct product $\Gamma_h \times \Gamma_\lambda \times \Gamma_\nu$. Now, condition (i) of section 4 for a pathway symmetry Γ_λ is recognized as a condition at the MO level. A Γ_λ is favorable provided that for Γ_λ a large number of unoccupied and occupied orbitals have the proper symmetry to interact with the LUMO and HOMO, respectively. In addition they should have small energy spacings with respect to the frontier orbitals. Such a favorable situation is indicated by a large f_λ value. In order to employ condition (ii) of section 4 at the MO level, \tilde{R}_λ is formulated as

$$\tilde{R}_\lambda = -\frac{1}{2n_\lambda} \left[\sum_{i=l+1}^{\text{unocc}} \mu \frac{\langle \varphi_i^{00} | O_\lambda^1 | \varphi_l^{00} \rangle}{(\epsilon_i^{00} - \epsilon_l^{00})^{1/2}} - \sum_{i=1}^{\text{occ}-1} \nu \frac{\langle \varphi_h^{00} | O_\lambda^1 | \varphi_i^{00} \rangle}{(\epsilon_h^{00} - \epsilon_i^{00})^{1/2}} \right]^2 - \frac{1}{2n_\lambda} \left[\int O_\lambda^1 \rho_\lambda^{00} d\tau \right]^2 \quad (15)$$

(30) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69, eq 66.

(29) See, for example: Eyring, H.; Walter, J.; Kimball, G. E.; *Quantum Chemistry*; Wiley: New York, 1964; eq 7.31.

(31) Slater, J. C. *Quantum Theory of Molecules and Solids*; McGraw-Hill: New York, 1963; Vol. 1, p 285.

The HOMO and LUMO are designated by $|\varphi_h^{00}\rangle$ and $|\varphi_l^{00}\rangle$, respectively; the sums run over the same set of molecular orbitals as in (14). The function ρ_λ^{00} appearing in (15) is now given as

$$\rho_\lambda^{00} = \sum_{i=l+1}^{\text{unocc}} \mu \frac{\varphi_i^{00} \varphi_l^{00}}{(\epsilon_i^{00} - \epsilon_l^{00})^{1/2}} - \sum_{i=1}^{\text{occ}-1} \nu \frac{\varphi_h^{00} \varphi_i^{00}}{(\epsilon_h^{00} - \epsilon_i^{00})^{1/2}} \quad (16)$$

Equation 15 shows that \tilde{R}_λ arises from orbital interactions mediated by the operator O_λ^1 . Thus, we have related the determination of a favorable relaxation pathway to orbital interactions, a concept which can be widely used for the rationalization of a broad range of chemistry.³² \tilde{R}_λ is also the square of an integral over the function $O_\lambda^1 \rho_\lambda^{00}$ (see eq 15). Here, ρ_λ^{00} is defined by (16), and it contains a sum of products of orbitals weighted by their energy difference. We call ρ_λ^{00} the overlap function for the pathway symmetry Γ_λ . It is conceptually related to the transition density used for ground-state surfaces by Bader⁵ and for excited states by Devaquet⁸ and Nakajima.⁷ However, ρ_λ^{00} is more general because it contains all orbitals appropriate for interaction and their energy. Thus, the energetic criterion, used previously^{2-4,8} to focus on the state located above the considered state, is extended, and it is incorporated at the MO level into ρ_λ^{00} (see eq 16). Due to the arbitrary phase factors of molecular orbitals, however, which can be plus or minus one, ρ_λ^{00} is still undefined because the signs of the products in the sums of eq 16 are arbitrary. In order to define ρ_λ^{00} unambiguously and to make \tilde{R}_λ large, we select in all subsequent applications the phase factors such that the norm of ρ_λ^{00} has its maximal value.

On the basis of the outline above, the following procedure for finding relaxation pathways is suggested: an SCF calculation for the molecule at its ground-state geometry having the point group G is performed. For any irreducible representation Γ_λ of G , efficiency factors f_λ are calculated by means of (14). If for one or several Γ_λ large values are derived, (16) is used to produce contour plots of the overlap function ρ_λ^{00} . In the next section a recipe is given as to how these plots can be qualitatively applied to find the relaxation pathway.

6. Form of the Overlap Function and Preferred Relaxation Pathways

In section 5 the efficiency factors f_λ and the overlap function ρ_λ^{00} for a representation Γ_λ were given at the MO level. A favorable Γ_λ for a relaxation pathway should be indicated by a large f_λ value. However, the symmetry alone does not specify the pathway, because for one Γ_λ a variety of nuclear motions all transforming as Γ_λ might exist. In order to find the relaxation pathway we use the fact that it is characterized by an efficient operator O_λ^1 which matches the overall form of ρ_λ^{00} such that the integration, giving \tilde{R}_λ (see eq 15), leads to a large value. In the following, we use this matching condition to find a recipe for using the form of ρ_λ^{00} to identify the relaxation pathway.

Consider a molecule of N atoms. At any atomic ground-state position of an atom we can fix a local coordinate system whose axes are parallel to the space fixed coordinate system. Changes of the atomic positions along the various axes of the local coordinate systems form a set of cartesian vectors from which symmetry coordinates S_i are constructed. The operator O_λ^1 is composed of the operators H^{10} and H^{01} (see eq 4), and H^{10} is given by

$$H^{10} = \left[\left(\frac{\partial H}{\partial x_A} \right) \left(\frac{\partial x_A}{\partial S_i} \right) + \left(\frac{\partial H}{\partial y_A} \right) \left(\frac{\partial y_A}{\partial S_i} \right) + \left(\frac{\partial H}{\partial z_A} \right) \left(\frac{\partial z_A}{\partial S_i} \right) + \dots \left(\frac{\partial H}{\partial z_N} \right) \left(\frac{\partial z_N}{\partial S_i} \right) \right]_{00} \quad (17)$$

where the chain rule for composite functions³³ has been applied.

(32) Albright, T. A.; Burdett, J. K.; Whangbo, M. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

(33) See, for example: Spiegel, M. R. *Advanced Calculus*; McGraw Hill: New York, 1963; p 106.

$\left(\frac{\partial H}{\partial x_A} \right)_{00}$	ρ_λ^{00} near A	$\rho_\lambda^{00} \left(\frac{\partial H}{\partial x_A} \right)_{00}$	result
			favourable (a)
			favourable (b)
			favourable (c)
			unfavourable (d)
			unfavourable (e)
			unfavourable (f)

Figure 1. Relations between the form of the operator function for a motion of atom A along the x -axis and the form of the overlap function ρ_λ^{00} making that motion favorable or unfavorable.

The expression for H^{01} is derived from (17) by writing j instead of i . Inspection of (17) indicates that H^{10} is a sum of operators for the forces acting on the atoms along the local coordinate axes. Any operator is multiplied by a factor which is an element of the matrix transforming from the set of symmetry coordinates $\{S_i\}$ to the local cartesian coordinates. These factors guarantee that H^{10} is symmetry adapted. The force operator for the force acting on atom A along the x_A -axis is given by³⁴

$$\left(\frac{\partial H}{\partial x_A} \right)_{00} = -\frac{N_A x_1}{r_1^3} \quad (18)$$

Here, r_1 is the distance of the electron from the origin of the local coordinate system for atom A, and x_1 is the x -coordinate of the electron position. N_A is the nuclear charge of atom A. The operators for the forces along y_A and z_A are derived by writing y_1 or z_1 , respectively, instead of x_1 in (18). We realize that all force operators in (17) transform as the local cartesian axis. The operator $(\partial H / \partial x_A)_{00}$ decreases fast when r_1 increases (see eq 18) indicating that for a significant contribution of atom A to the integral in (15), the form of ρ_λ^{00} near A is important. In Figure 1 various possible forms of the overlap density function ρ_λ^{00} in the x, y -plane of the local coordinate system are schematically depicted. In addition, regions of $(\partial H / \partial x_A)_{00}$ with positive and negative functional values are symbolically indicated. The resulting positive and negative areas of the integrand $(\partial H / \partial x_A)_{00} \rho_\lambda^{00}$ are also given (see Figure 1). If ρ_λ^{00} near atom A has the form of type (a), (b), or (c) not only in the x, y -plane but also in all planes being parallel to the x, y -plane, a large integral over $(\partial H / \partial x_A)_{00} \rho_\lambda^{00}$ is derived. This is because the integrand is either positive or only at a few points in space, zero. Consequently, such forms of ρ_λ^{00} near A favor the motion of atom A along the x -axis. If, however, ρ_λ^{00} near atom A has the forms (d), (e), or (f), the position of atom A should remain unchanged. This is due to the fact that integration over $(\partial H / \partial x_A)_{00} \rho_\lambda^{00}$ leads to a small integral, because any positive functional value of the integrand is matched by a corresponding negative value (see Figure 1). The overlap function ρ_λ^{00} extends over all regions of the molecule and transforms as Γ_λ . Therefore, inspection of ρ_λ^{00} and analysis of the forms near all atoms by means of Figure 1 should indicate the most effective relaxation pathway with symmetry Γ_λ .

7. A Scheme for the Determination of Relaxation Pathways

In the previous sections, the efficiency factors f_λ and the overlap function ρ_λ^{00} were introduced as a tool to determine qualitatively molecular geometry changes following electronic excitation. After formulating f_λ and ρ_λ^{00} at the MO level a complete scheme for

(34) Nakatsuji, H.; Koga, T. In *The Force Concept in Chemistry*, Deb, B. M., Ed.; Van Nostrand: New York, 1981; Chapter 3, p 137.

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.

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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

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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

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

The quantities ϵ_i^{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

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