Vibrationally Induced Stabilization of Vertically Excited States

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Abstract: This paper examines the vibrationally induced stabilization of the lowest singlet and triplet *vertically* excited states of a molecule. It is qualitatively shown that one nuclear motion (sometimes two) will lead to a particularly favorable (at least initially) stabilizing path. This motion, energetically favored over the other possible motions of the excited species, is selected on symmetry, geometric, and energetic grounds and it determines the shape of the stabilized excited state as well as its photochemical behavior.

It is well known that the excited $\pi\pi^*$ triplet state of ethylene is 90° twisted around the C–C bond[2a] and that the $n\pi^*$ triplet state of formaldehyde is pyramidal.[2b] In both cases the planar vertically excited states have been stabilized by geometrical transformations, some being very pronounced (twisting or bending of the CH_2 groups and shortening of the CC and CO bonds) and some others being less apparent (increase of the CH_2 angles, for example). The problem then arises of selecting the most "efficient" stabilizing motions. They will determine (roughly) the shape of the stabilized excited species and its photochemical behavior. Indeed these relaxation processes are usually much more rapid (relaxation time $\sim 10^{-12}$ sec) than the collision ones (collision time $\sim 10^{-10}$ sec) and the excited state reacts after having reached the absolute (or at least a secondary) minimum of its potential energy surface. In this paper we put forth the rules which govern the selection of the most rapidly stabilizing motions and illustrate them with some very simple examples.

I. Selection Rules for the Stabilizing Vibrations. The present investigation is based on the Herzberg–Teller approach in which the Hamiltonian of the system is expanded in powers of normal (or symmetry) coordinates about the equilibrium nuclear configuration of the ground state. Such a framework has been extensively used as the starting point in all studies of the vibrationally induced perturbations in molecular *ground-state* electronic distributions.[3] In the case of *excited state* structures this development was implied in the empirical rule given by Pearson:[4] "the first excited state of a molecule containing n electrons should belong to the same point group as the ground state of a similar molecule having $n + 1$ or $n + 2$ electrons. The extra one or two electrons are assumed to be in that molecular orbital which becomes occupied in the excited state." This rule was in fact given in 1953 by Walsh[5] whose reasoning was based on the behavior of the vacating and filling MO's when nuclear positions are changed. Even though this rule appears to work quite well it is worthwhile to further detail the method in order to gain more insight into the particular vibrations involved in the stabilization process.

Before considering the mathematical formalism two points have to be clarified. In the first place[6] the molecular orbital $\varphi_j = |j\rangle$ for the excited state derived from the transition $i \rightarrow j$ is considered here to be a virtual orbital from the ground-state calculation. In other words $|j\rangle$ is the solution of an Hamiltonian whose field terms are due to all N electrons.

$$(h + 2J_c - K_c + 2J_i - K_i)|j\rangle = \epsilon_j|j\rangle \qquad (1)$$

(In this equation J_c and K_c are the Coulomb and exchange operators for the closed shell of $N - 2$ electrons.) However the appropriate field for the excited state orbital $|j\rangle$ contains only interactions with $N - 1$ electrons. The simplest possible way to take this into account is to choose $|j\rangle$ to be solution of

$$(h + 2J_c - K_c + J_i \pm K_i)|j\rangle = \epsilon_j'|j\rangle \qquad (2)$$

where (+) and (−) are for the singlet and triplet state, respectively, and where the orbitals in J_c and K_c and J_i, and K_i are assumed to have their ground-state forms. This is called the frozen core[7] or IVO[8] approximation and corresponds to variationally adjusting the orbital $|j\rangle$ in the open-shell Hartree–Fock wave function for the excited state. This first comment has in fact nothing to do with the basic equations we are going to derive but must be borne in mind in some qualitative (for example, in the case of the $\pi \rightarrow \pi^*$ singlet state of ethylene) and in *all* quantitative applications of our results. The second point is that the molecular geometrical transformations are expressed in terms of the symmetry coordinates S rather than in terms of the normal vibrational coordinates Q. The S-type coordinates depend only on the symmetry properties of the molecule and (due to the Franck–Condon principle) are the same for the ground state and the vertical excited states. The Q-type coordinates depend on the actual potential energy function (or force field), which changes in the excitation process. The nuclear coordinate-depending part of the total hamiltonian $\mathcal{H}$ is written as

$$H = V_{NN} + V_{Ne} = \sum_{NN'} \frac{Z_N Z_{N'} e^2}{R_{NN'}} - \sum_N \sum_i \frac{Z_N e^2}{R_{Ni}} \qquad (3)$$

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(2) (a) A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **63**, 639 (1969); (b) G. W. Robinson and V. E. Di Giorgio, *Can. J. Chem.*, **36**, 31 (1958).

(3) (a) R. F. W. Bader, *ibid.*, 40, 1164 (1962); (b) R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 4947 (1969); *Accounts Chem. Res.*, **4**, 152 (1971); (c) L. Salem, *Chem. Phys. Lett.*, **3**, 99 (1969); (d) J. Burdett, *J. Chem. Phys.*, **52**, 2983 (1970); *Appl. Spectrosc., Rev.*, **4**, 43 (1970).

(4) R. G. Pearson, *Chem. Phys. Lett.*, **10**, 31 (1971).

(5) A. D. Walsh, *J. Chem. Soc.*, 2325 (1953).

(6) The author is very indebted to one of the referees for this helpful comment.

(7) H. Lefebvre-Brion, C. Moser, and R. Nesbet, *J. Mol. Spectrosc.*, **13**, 418 (1964).

(8) W. J. Hunt and W. A. Goddard III, *Chem. Phys. Lett.*, **3**, 414 (1969).

The first term (nuclear repulsion term) does not depend on the electronic coordinates. The second one (nuclear–electron attraction term) may be written as the sum of monoelectronic operators $\nu(i)$,

$$V_{\mathrm{Ne}} = \sum_i \left\{ \sum_{\mathrm{N}} \frac{Z_{\mathrm{N}} e^2}{R_{\mathrm{N}i}} \right\} = \sum_i \nu(i) \tag{4}$$

We want to find out how the energy E_{N} varies in the vicinity of the ground-state equilibrium geometry if a ground-state molecule (normalized ground-state wave function $|0\rangle$, energy E_0) is promoted to an excited state (normalized wave function $|n\rangle$, energy E_n). The first derivative of the eigenstate energy E_n with respect to a slight change S in the ith symmetry coordinate under adiabatic or quasistatic conditions (*i.e.*, the slope P_n of the curve $E_n(S)$) is given by[9]

$$P_n = \frac{\partial E_n}{\partial S} = \left\langle n \left| \frac{\partial \mathcal{H}}{\partial S} \right| n \right\rangle = \frac{\partial V_{\mathrm{NN}}}{\partial S} + \left\langle n \left| \frac{\partial V_{\mathrm{Ne}}}{\partial S} \right| n \right\rangle \tag{5}$$

Prior to further developments one has to remember that eq 5 is only true if[6]

$$\langle \delta n | \mathcal{H} - E_n | n \rangle + \langle n | \mathcal{H} - E_n | \delta n \rangle = 0 \tag{6}$$

(This may be easily shown by differentiating the eigenvalue equation $(\mathcal{H} - E_n)|n\rangle = 0$.) More precisely (6) is true if (a) $|n\rangle$ is the exact solution of the eigenvalue equation or (b) $|n\rangle$ is determined variationally. For the frozen core or virtual orbital wave functions this condition is not satisfied (although it would be for the Hartree–Fock wave function for the excited state). Therefore eq 5 (and so the following equations) is only an approximation even though this approximation is probably a reasonable one.

An expression similar to (5) may be written for the first derivative of the ground state energy E_0. The ground state $|0\rangle$ being stable in its equilibrium geometry, the energy E_0 is a minimum with respect to small relative displacements of the nuclei

$$P_0 = \frac{\partial E_0}{\partial S} = \left\langle 0 \left| \frac{\partial \mathcal{H}}{\partial S} \right| 0 \right\rangle = \frac{\partial V_{\mathrm{NN}}}{\partial S} + \left\langle 0 \left| \frac{\partial V_{\mathrm{Ne}}}{\partial S} \right| 0 \right\rangle = 0 \tag{7}$$

Therefore eq 3 may be more symmetrically rewritten as

$$P_n = \left\langle n \left| \frac{\partial V_{\mathrm{Ne}}}{\partial S} \right| n \right\rangle - \left\langle 0 \left| \frac{\partial V_{\mathrm{Ne}}}{\partial S} \right| 0 \right\rangle \tag{8}$$

The Hamiltonian $\mathcal{H}$ being invariant under all symmetry operations of the molecule, $\partial V_{\mathrm{Ne}}/\partial S$ and S have the same symmetry. If S belongs to the totally symmetric irreducible representation of the point group of the molecule $\partial E_n/\partial S$ is generally different from zero. If S belongs to a nontotally symmetric representation, the two integrals in (8) are identical, equal to zero. For example, the SCF *ab initio* potential energy surfaces of the $n\pi^*$ and $\pi\pi^*$ triplet excited states of acrolein show that $\partial E_{n\pi^*}/\partial S$ and $\partial E_{\pi\pi^*}/\partial S$ vanish when S is the nontotally symmetric twist of the CH_2 terminal group whereas these first derivatives have different finite values when S is the totally symmetric relaxation of the skeletal bonds.[10] Then the important fact is that the primary stabilizing motions of the Franck–Condon vertically excited states are totally symmetric ones, the nontotally symmetric ones being inefficient. In relation to this rule it is worthy of note that in photoelectron spectroscopy only totally symmetrical vibrations are detected in the fine structure of the bands. Using now the fact that V_{Ne} is the sum of monoelectronic operators $\nu(i)$, the formulas 5–8 may be expressed in terms of the ground-state molecular orbitals.[11] The closed shell ground-state wave function $|0\rangle$ may be written as

$$|0\rangle = |1\bar{1} \ldots p\bar{p} \ldots n\bar{n}|$$

then

$$P_0 = \frac{\partial E_0}{\partial S} = \frac{\partial V_{\mathrm{NN}}}{\partial S} + 2 \sum_{p=1}^{n} \left\langle p \left| \frac{\partial \nu}{\partial S} \right| p \right\rangle = 0 \tag{9}$$

Similar developments may be carried out over various excited states $|n\rangle$ giving, after being combined with (9), the slopes at the origin of the curves $E_n(S)$

$|n\rangle$ = singly excited state $i \to j$

$$P_{i\to j} = \left\langle j \left| \frac{\partial \nu}{\partial S} \right| j \right\rangle - \left\langle i \left| \frac{\partial \nu}{\partial S} \right| i \right\rangle \tag{10}$$

Doubly excited state $i\bar{i} \to j\bar{j}$

$$P_{i\bar{i}\to j\bar{j}} = 2\left(\left\langle j \left| \frac{\partial \nu}{\partial S} \right| j \right\rangle - \left\langle i \left| \frac{\partial \nu}{\partial S} \right| i \right\rangle \right) \tag{11}$$

Cation $i \to j = \infty$

$$P_{i\to\infty} = -\langle i | \partial\nu/\partial S | i \rangle \tag{12}$$

Anion $i = \infty \to j$

$$P_{\infty\to j} = \langle j | \partial\nu/\partial S | j \rangle \tag{13}$$

Let us return briefly to photoelectron spectroscopy. It is well known that among all possible totally symmetric vibrations, only a few appear in the fine structure. For instance, the structure of the $1a_2 \to \infty$ ionization band of furan shows only three totally symmetrical vibrations among eight possibilities.[12] Formula 12 would be a useful (even though approximate) starting point in selecting these active vibrations in view of the fact that the slope of the curve $E_n(S)$ strongly depends on the molecular orbital which loses the ionized electron. From the formulas 10–13 some simple relations may be obtained between the slopes of the various curves $E_n(S)$ dealing with the same pair of MO's (i occupied and j unoccupied).

$$P_{i\bar{i}\to j\bar{j}} \text{ (doubly excited state)} = 2P_{i\to j} \text{ (corresponding singly excited state)} \tag{14}$$

$$P_{i\to\infty} \text{ (cation)} + P_{\infty\to j} \text{ (anion)} = P_{i\to j} \text{ (corresponding singly excited state)} \tag{15}$$

The only approximation[13] in these relations is that the matrix elements of $\partial\nu/\partial S$ between the wave functions of the free incoming or leaving electron (in (10) and

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(9) W. B. Brown, *Proc. Cambridge Phil. Soc.*, **54**, 251 (1958).

(10) (a) A. Devaquet and L. Salem, *Can. J. Chem.*, **49**, 975 (1971); (b) A. Devaquet, *J. Amer. Chem. Soc.*, **94**, 5160 (1972).

(11) L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1966, p 529.

(12) P. J. Derrick, L. Asbrink, O. Edgvis, B. Ö. Jonsson, and E. Lindholm, *Int. J. Mass Spectrom. Ion Phys.*, **6**, 161 (1971).

(13) In the case of the anion the virtual orbitals are already frozen core approximations to the "extra orbital." Such negative ions tend to be quite diffuse and, in the frozen core approximation, they often are not even bound.[14] Then due to the large difference between $|j\rangle$ (negative ion) a large, diffuse orbital and $|j\rangle$ (excited state) a compact, valence orbital in many cases, the relation (15) is of only marginal validity.[6]

(14) T. H. Dunning, W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, 4, 147 (1969).

(9)) have been neglected due to the entirely different spatial localizations of the various parts of these integrals. Moreover these relations are valid only because the ith symmetrical displacement S is the same for the four considered excited states, depending only on the molecular geometry which remains unchanged in the different vertical excitation processes. That would not be the case if S were replaced by some normal vibrations Q, which changes with each excited state. At best these relations might be approximately valid when these changes in the normal vibrations in the four considered configurations are sufficiently small.

The nontotally symmetric motions which were inefficient in the study of the slope P_n will play the major role in the study of the curvature of the curve $E_n(S)$ near the origin. This curvature $q_n = \partial^2 E_n/\partial S^2$ is given by[9]

$$q_n = \frac{\partial^2 E_n}{\partial S^2} = \left\langle n\left|\frac{\partial^2 H}{\partial S^2}\right|n\right\rangle - 2\sum_{k\neq n}|\langle n|\partial H/\partial S|k\rangle|^2/(E_k - E_n) \quad (16)$$

where the sum over $|k\rangle$ includes all states having the same multiplicity as $|n\rangle$. The first term in (16) represents "the energy change due to the nuclear motion within a fixed electronic density"[3c] and corresponds mathematically to the classical force constant, with the restriction that it is not defined in a region of minimum energy. Following Salem,[3c] the second term in (16) can be defined as the "relaxability" of the molecule along the coordinate S; *i.e.*, it represents the "energy change due to the rearrangement of the electronic density induced by the nuclear displacement."[15] The first "classical" term generally does not vanish: $\partial^2 H/\partial S^2$ as well as the square of the excited state wave function $|n\rangle$ belong to the totally symmetric irreducible representation of the molecular point group. In the particular case of the ground state $|0\rangle$ this term would be the classical force constant k_0

$$k_0 = \frac{\partial^2 V_{\mathrm{NN}}}{\partial S^2} + 2\sum_{p=1}^{n}\left\langle p\left|\frac{\partial^2 \nu}{\partial S^2}\right|p\right\rangle \quad (17)$$

In the case of the singlet excited state $i \rightarrow j$ this term is written as

$$k_n = \frac{\partial^2 V_{\mathrm{NN}}}{\partial S^2} + 2\sum_{p=1}^{n}\left\langle p\left|\frac{\partial^2 \nu}{\partial S^2}\right|p\right\rangle - \left\langle i\left|\frac{\partial^2 \nu}{\partial S^2}\right|i\right\rangle + \left\langle j\left|\frac{\partial^2 \nu}{\partial S^2}\right|j\right\rangle \quad (18)$$

and then may be easily expressed as the ground-state force constant corrected by two terms depending on the particular excitation process defining $|n\rangle$

$$k_n = k_0 + \left\langle j\left|\frac{\partial^2 \nu}{\partial S^2}\right|j\right\rangle - \left\langle i\left|\frac{\partial^2 \nu}{\partial S^2}\right|i\right\rangle \quad (19)$$

Relations of the same type as (15) and (16) are readily derived for the k's (with the restriction pointed out in footnote 13)

$$k_{i\bar{i}\rightarrow j\bar{j}}\ (\text{doubly excited state}) = 2k_{i\rightarrow j}(\text{corresponding excited singlet}) - k_0 \quad (20)$$

$$k_{i\rightarrow\infty}(\text{cation}) + k_{\infty\rightarrow j}(\text{anion}) = k_{i\rightarrow j} - k_0 \quad (21)$$

We now focus our attention on the relaxability term. The more negative this term, the more efficient will be the stabilization process, even though it appears already that the ground state $|0\rangle$ is going to give a positive contribution ($E_0 - E_n < 0$). The problem is then to select the pair excited state $|k\rangle$ — vibration S which gives the most important negative contribution and therefore the best approximation of the relaxability. At first view the important factors to be considered are energetic (related to the energy difference which appears in the denominator) and geometric factors (related to the matrix elements of the numerator), the latter being further divided into symmetry and "spatial localization" properties. Before any discussion of these factors it is necessary to calculate the matrix elements $\langle n|\partial H/\partial S|k\rangle$, limiting ourselves to the case where $|n\rangle$ is the lowest excited singlet state $i \rightarrow j$.

$$|n\rangle = \frac{1}{\sqrt{2}}\{|\ldots i\bar{j}| + |\ldots j\bar{i}|\} \quad (22)$$

(a) If $|k\rangle$ is a closed shell wave function (ground or doubly excited states) the only nonzero matrix elements arise when $|k\rangle$ is the ground state $|0\rangle$ or the "corresponding" doubly excited state $|k\rangle = i\bar{i} \rightarrow j\bar{j}$. In both cases the numerators are identical.

$$\left|\left\langle 0\left|\frac{\partial H}{\partial S}\right|n\right\rangle\right|^2 = \left|\left\langle k_{i\bar{i}\rightarrow j\bar{j}}\left|\frac{\partial H}{\partial S}\right|n\right\rangle\right|^2 = \left|\left\langle i\left|\frac{\partial \nu}{\partial S}\right|j\right\rangle\right|^2 \quad (23)$$

The denominators of these two terms have opposite signs (the energy difference $|E_{i\bar{i}\rightarrow j\bar{j}} - E_n|$ being generally smaller than $|E_n - E_0|$). The positive "destabilizing" contribution of the ground state is then roughly cancelled by the negative contribution of the corresponding doubly excited state (roughly because the net contribution of these two terms is often negative).

(b) If $|k\rangle$ is a singlet state resulting from the promotion of an electron from the kth occupied to the lth unoccupied MO

$$|k\rangle = \frac{1}{\sqrt{2}}\{|\ldots i\bar{i}\ k\bar{l}| + |\ldots i\bar{i}\ l\bar{k}|\} \quad (24)$$

then a typical term in the matrix element $\langle n|\partial H/\partial S|k\rangle$ is for example

$$\langle|\ldots i\bar{j}\ k\bar{k}||\partial H/\partial S||\ldots i\bar{i}\ k\bar{l}|\rangle \quad (25)$$

Because of the monoelectronic nature of the operator $\partial H/\partial S$, three cases occur:[11] if $i \neq k$ and $j \neq l$, the matrix element (25) vanishes; if $i \neq k$ and $j = l$, the absolute value of (25) is given by $|\langle i|\partial\nu/\partial S|k\rangle|$; if $i = k$ and $j \neq l$, the absolute value is now given by $|\langle j|\partial\nu/\partial S|l\rangle|$. Then the behavior of the relaxability of the lowest singlet excited state $i \rightarrow j$ is governed by two factors. The first is that the destabilizing contribution of the ground state is quasicancelled by the negative contribution of the corresponding doubly excited state. The second is that the sum over the singly excited states reduces to the particular ones where the electron leaves the ith MO (going up to anyone of the ground state empty MO's) or reaches the jth MO (starting from anyone of the ground state occupied MO's). Among all these particular excited states the selection of the most stabilizing vibrations is based on the magnitude of the matrix element $\langle i|\partial\nu/\partial S|k\rangle$ or $\langle j|\partial\nu/\partial S|l\rangle$ and of the energy difference $E_k -$

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(15) (a) L. Salem, *J. Chem. Phys.*, **38**, 1227 (1963); (b) R. F. W. Bader and A. D. Brandrauk, *ibid.*, **49**, 1666 (1968).

E_n. Obviously the comparison is restricted to vibrational modes involving the same types of internal valency coordinates:[3c] for example, the rules may indicate the best twisting vibration among all possible twisting vibrations but do not afford the comparison of the "best" twisting and stretching vibrations.

(1) The first selection rule is based on symmetry grounds. The numerators are nonzero if the direct product x of the irreducible representations to which i and k (or j and l) belong does contain the irreducible representation to which S belongs. If, as usual, Γ represents these irreducible representations of the point group of the molecule, the above is expressed by

$$\Gamma(i) \times \Gamma(k) \subset \Gamma(S)$$

and/or

$$\Gamma(j) \times \Gamma(l) \subset \Gamma(S) \tag{26}$$

It appears already that the more sophisticated the point group of the molecule, the more precise will be the selection of the vibrations giving a nonzero contribution to the relaxability.

(2) The second selection rule is based on the respective spatial localizations of the molecular motion S and of the transition densities P_{ik} or P_{jl}. Even if a matrix element does not vanish under (26) its magnitude may be very small if the transition density is localized in regions near nuclei which are not involved in the motion. Roughly speaking, the second rule is that the transition density P_{ik} (or P_{jl}) and the nuclei involved in the vibration S must be localized in the same region of the molecule in order to be sufficiently overlapping and then give a significant matrix element in the numerator of (16).

(3) Finally, the third (energetic) selection rule takes into account the denominator $E_k - E_n$ and is the analog of Bader's condition.[3a,16] Among all possible excited singlet states lying above (in terms of vertical excitation energies) the lowest one and obeying the two aforementioned conditions, the one which determines the symmetry of the S motion is the lowest. It must be pointed out that the energy difference $E_k - E_n$ plays another important role in the third derivative of the energy E_n with respect to S (in what would correspond to the anharmonic constant at the equilibrium configuration in the case of the ground state).

$$\begin{aligned}\frac{\partial^3 E_n}{\partial S^3} &= \left\langle n \left| \frac{\partial^3 H}{\partial S^3} \right| n \right\rangle + \\ &4\sum_{k \neq n} \sum_{m \neq k} \frac{\left\langle n \left| \frac{\partial H}{\partial S} \right| k \right\rangle \left\langle k \left| \frac{\partial H}{\partial S} \right| m \right\rangle \left\langle m \left| \frac{\partial H}{\partial S} \right| n \right\rangle}{(E_k - E_n)(E_m - E_k)} + \\ &4\sum_{k \neq n} \sum_{m \neq n} \frac{\left\langle n \left| \frac{\partial H}{\partial S} \right| k \right\rangle \left\langle k \left| \frac{\partial H}{\partial S} \right| m \right\rangle \left\langle m \left| \frac{\partial H}{\partial S} \right| n \right\rangle}{(E_k - E_n)(E_m - E_n)} - \\ &6\sum_{k \neq n} \frac{\left\langle n \left| \frac{\partial H}{\partial S} \right| k \right\rangle \left\langle k \left| \frac{\partial^2 H}{\partial S^2} \right| n \right\rangle}{E_k - E_n} + \\ &2\sum_{k \neq n} \frac{\partial}{\partial S}(E_k - E_n) \frac{\left| \left\langle n \left| \frac{\partial H}{\partial S} \right| k \right\rangle \right|^2}{(E_k - E_n)^2}\end{aligned} \tag{27}$$

The first term in (27) would correspond to the classical anharmonicity in the ground state case while the other ones result from the rearrangements of the charge density.

Let us suppose for simplicity that the point group of the molecule does not contain degenerate irreducible representations and consider a nontotally symmetric mode S such that the first selection rule (expressed in terms of states) holds.

$$\Gamma(n) \times \Gamma(k) \subset \Gamma(S) \tag{28}$$

Then the only nonvanishing term in (27) is the last one. For instance in the second term of (27) the first factor is nonzero (28). The second one does not vanish if, in addition, we have

$$\Gamma(k) \times \Gamma(m) \subset \Gamma(S) \tag{29}$$

but the two simultaneous relations 28 and 29 require that the wave functions $|n\rangle$ and $|m\rangle$ belong to the same irreducible representation. The third factor then vanishes, $\partial H/\partial S$ being not totally symmetric. Using the selection rule, the sum over $|k\rangle$ in the last term of (27) generally reduces to a single term

$$\frac{\partial^3 E_n}{\partial S^3} = 2\frac{\partial}{\partial S}(E_k - E_n)\frac{\left| \left\langle n \left| \frac{\partial H}{\partial S} \right| k \right\rangle \right|^2}{(E_k - E_n)^2} \tag{30}$$

If S is a stabilizing vibration for the excited state $|n\rangle$ (and therefore a destabilizing one for $|k\rangle$) then $E_k - E_n$ increases with S. The anharmonicity is positive and the curvature, initially negative, may vanish and become positive, a minimum appearing in the curve $E_n(S)$.

To conclude this study of the selection rules, it should be emphasized that *all* these conditions must be satisfied for reasonable predictions to be made, as will be seen in the following simple examples dealing with molecules whose excited state behavior is already known. In addition, these rules may be also applied in the case where $|n\rangle$ is a triplet state. However, one has always to remember that the virtual orbitals are not very well adapted to quantitative evaluation of the matrix elements. The molecular orbital $|j\rangle$ will be different for the singlet and triplet states arising from the *same* orbital excitation $i \rightarrow j$. This difference is related to the term $K_i|j\rangle$ in (2). If the orbitals $|i\rangle$ and $|j\rangle$ are concentrated in the same region of space then this term is expected to be large and the singlet and triplet orbitals should be considerably different. This problem has been studied by various authors for ethylene and formaldehyde.[14,17,18] They conclude that there is a marked difference between singlet and triplet π^* orbitals derived from $\pi \rightarrow \pi^*$ excitations but only slight differences in those obtained from $\sigma \rightarrow \pi^*$, n $\rightarrow \pi^*$, and $\pi \rightarrow \pi^*$ (triplet) excitations.

II. Application of the Selection Rules in the Case of Single Conjugated Molecules. The first example (formaldehyde) has been chosen to clarify the use of the first and third selection rules. Consider for instance the nπ^* vertically singlet excited state ($^1A_2$) (point group C_{2v}). The sequence of the singlet excited states

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(16) R. F. W. Bader, *Mol. Phys.*, **3**, 137 (1960).

(17) R. Buenker, S. Peyerimhoff, and W. Kammer, *J. Chem. Phys.*, **55**, 814 (1971).

(18) J. L. Whitten and M. Hackmeyer, *ibid.*, **51**, 5584 (1969).

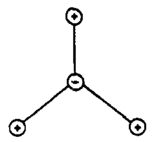

Figure 1. B_2 type normal vibration of formaldehyde.

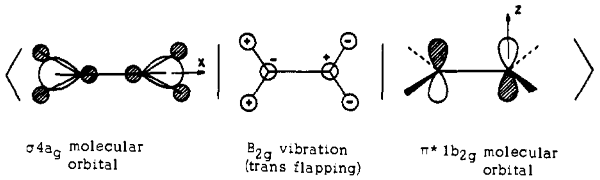

Figure 2. Representation of the matrix element $\langle 4a_g | \partial v/\partial S | \pi^* \rangle$ when S is the B_{2g} vibration of ethylene.

is experimentally known to be[2,19]

$\|n\rangle$:	$n(2b_2) \longrightarrow \pi^*(2b_1)$	$^1A_2$	4.3 eV
$\|k\rangle$:	$\sigma(5a_1) \longrightarrow \pi^*(2b_1)$	$^1B_1$	7.1 eV
	$\pi(1b_1) \longrightarrow \pi^*(2b_1)$	$^1A_1$	8.0 eV
	$n(2b_2) \longrightarrow \sigma^*(6a_1)$	$^1B_2$	10 eV

The symmetries of the associated motions are given (using (26)) by

Excited state	Direct product	Energy dif $E_k - E_n$
$^1B_1$	$5a_1 \times 2b_2 \longrightarrow B_2$	2.8 eV
$^1A_1$	$2b_2 \times 1b_1 \longrightarrow A_2$	3.7 eV
$^1B_2$	$6a_1 \times 2b_1 \longrightarrow B_1$	5.7 eV

First of all the A_2-type motion corresponds to a rotation of the whole molecule and does not stabilize the excited species. The B_1 motion corresponds to in-plane displacements of the nuclei (see for example the B_1 normal vibration of an XYZ_2 molecule[20]). There is then only a small coupling between these in-plane vibrations and the in-plane (σ) → out-of-plane (π) electronic transition density. The small magnitude of the numerator's matrix element and the relatively important denominator's energy difference both provide a poorly efficient relaxability. The stabilization process appears then to follow a B_2-type vibration. This vibration[20] is represented below (motions perpendicular to the plane of the paper being as usual indicated by + or − signs in the circle representing the particular nuclei, Figure 1). Such a motion is well adapted to couple the $\sigma \rightarrow \pi$ transition density and moreover corresponds to the smallest energetic gap $E_k - E_n$. Due to this vibration the singlet (and also the triplet) $n\pi^*$ of formaldehyde acquires a pyramidal structure, the out-of-plane angle being 31° (35° for the triplet state).

The second example (ethylene molecule, D_{2h} point group) will mainly be used to further improve the "spatial localization" selection rule. Let us first consider the *lowest* triplet state $^3|n\rangle = {}^3B_{3u}$. Its calculated transition energy (4.25 eV)[17] is in good agreement with experiment (4.6 eV)[21] It is predominantly a *valence* excited state. As shown in Table I three nontotally symmetric motions may stabilize this vertically excited state: (a) a B_{2g} motion (trans flapping ν_8 vibration) which couples the $^3B_{3u}$ state with two $^3B_{3u}$ triplets; (b) a B_{1u} motion (cis flapping ν_7 vibration) which couples the $^3B_{3u}$ state with two $^3B_{2g}$ states; and finally (c) an A_u twisting motion ν_4 due to the coupling between $^3B_{3u}$ and $^3B_{3g}$ states. In addition, Table I gives the principal quantum number n of the upper molecular orbital of each excited states. It is seen that, in terms of matrix elements between *molecular orbitals*, five of the six couplings involve the overlap of the $1b_{2g}$ ($n = 2$) compact, valence MO of the $^3B_{3u}$ state with the large and diffuse molecular orbitals ($n = 3$) of the $^3|k\rangle$ states. Such matrix elements are expected to be small and so are the corresponding cis or trans flapping deformations. (In addition, it is not possible, without quantitative calculations, to decide which one of the two flapping motions is here predominant.) As an example the matrix element corresponding to the coupling between $^3B_{3u}$ and $^3B_{1u}$ states (*via* a B_{2g} vibration) is schematically represented by the Figure 2. This trans flapping motion couples remarkably well with the two MO's. For instance on the left half-part of the molecule it decreases the CH antibonding interactions in $4a_g$ and increases the bonding ones between the hydrogen 1s atomic orbitals, the positive lobe of the carbon sp_2 orbital (σ $4a_g$ MO) and the positive lobe of the $2p_z$ atomic orbital (π^* $1b_{2g}$ MO). On the other hand the coupling between the $^3B_{3u}$ and the second $^3B_{3g}(1b_{1g} \rightarrow 1b_{2g})$ states involves a matrix element between two valence orbitals ($1b_{1u}$ and $1b_{1g}$, respectively). Such a matrix element (schematically represented by Figure 3) is expected to be bigger than the preceding ones and, even though the energy denominator is also bigger (5.27 eV), the twist will be the most efficiently stabilizing motion. (Moreover, additional A_u coupling is provided by the lowest $^3B_{3g}(1b_{1u} \rightarrow 2b_{2u})$ state.) There is therefore little difficulty in

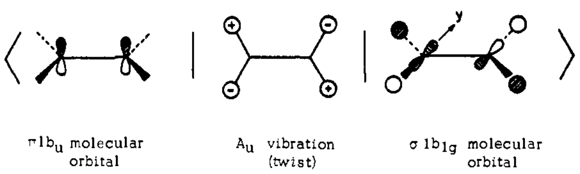

Figure 3. Representation of the matrix element $\langle 1b_u | \partial v/\partial S | 1b_{1g} \rangle$ when S is the A_u vibration of ethylene.

Table I. Nature of the Vibrations which Couple the $^3B_{3u}(1b_{1u} \rightarrow 1b_{2g})$ State of Ethylene ($^3|n\rangle$ State) with the Neighboring Triplet Excited States ($^3|k\rangle$)[a]

$^3\|k\rangle$ states	n	$E_k - E_n$, eV	$\Gamma(S)$	Nature of the vibration S
$B_{3u}(1b_{1u} \rightarrow 2b_{2g})$	3	5.28	A_g	ν_1
$B_{3g}(1b_{1g} \rightarrow 1b_{2g})$	2	5.27	A_u	ν_4 twisting
$B_{2g}(1b_{1u} \rightarrow 4b_{3u})$	3	5.04	B_{1u}	ν_7 cis flapping
$A_u(1b_{1u} \rightarrow 2b_{1g})$	3	4.18	B_{3g}	
$B_{1u}(1b_{1u} \rightarrow 5a_g)$	3	4.12	B_{2g}	ν_8 trans flapping
$A_g(1b_{1u} \rightarrow 2b_{1u})$	3	3.48	B_{3u}	ν_{11} or ν_{12}
$B_{2g}(1b_{1u} \rightarrow 3b_{3u})$	3	3.24	B_{1u}	ν_7 cis flapping
$B_{2g}(1b_{1u} \rightarrow 2b_{2u})$	3	3.22	A_u	ν_4 twisting
$B_{1u}(1b_{1u} \rightarrow 4a_g)$	3	2.54	B_{2g}	ν_8 trans flapping

[a] The number n is the appropriate principal quantum number of the upper orbital for the $^3|k\rangle$ excited state. (In the case of the $^3B_{3u}$ state $n = 2$.) The values of the various vertical transition energies (E_k, E_n) are those *calculated* by Buenker, *et al.*[17] The S vibrations are numbered according to Herzberg, ref 20, p 107.

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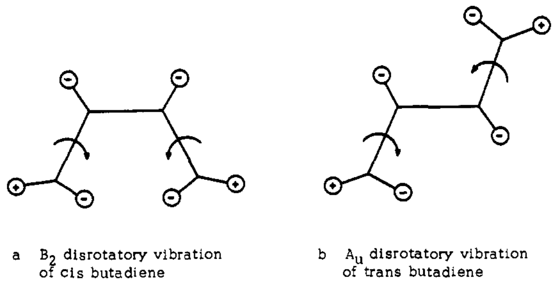
a B_2 disrotatory vibration of cis butadiene

b A_u disrotatory vibration of trans butadiene

Figure 4. Disrotatory vibrations of *cis*- and *trans*-butadiene.

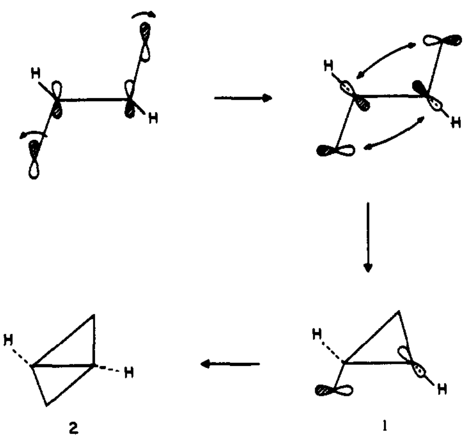

Figure 5. Disrotatory closure of *trans*-butadiene giving bicyclo-[1.1.0]butane (2).

Table II. Nature of the Vibrations which Couple the $^1B_{3u}$ State of Ethylene ($^1|n\rangle$ State) with the Neighboring Singlet Excited States ($^1|k\rangle$)[a]

$^1\|k\rangle$ states	n	$E_k - E_n$, eV	$\Gamma(S)$	Nature of the vibration S
$B_{3u}(1b_{1u} \rightarrow 2b_{2g})$	2	+2.41	A_g	ν_1
$B_{3g}(1b_{1g} \rightarrow 1b_{2g})$	2	+1.56	A_u	ν_4 twisting
$B_{2g}(1b_{1u} \rightarrow 4b_{3u})$	3	+1.0	B_{1u}	ν_7 cis flapping
$A_u(1b_{1u} \rightarrow 2b_{1g})$	3	+0.12	B_{3g}	
$B_{1u}(1b_{1u} \rightarrow 5a_g)$	3	+0.12	B_{2g}	ν_8 trans flapping
$A_g(1b_{1u} \rightarrow 2b_{1u})$	3	−0.29	B_{3u}	ν_{11} or ν_{12}
$B_{2g}(1b_{1u} \rightarrow 3b_{3u})$	3	−0.77	B_{1u}	ν_7 cis flapping
$B_{3g}(1b_{1u} \rightarrow 2b_{2u})$	3	−0.83	A_u	ν_4 twisting
$B_{1u}(1b_{1u} \rightarrow 4a_g)$	3	−1.38	B_{2g}	ν_8 trans flapping

[a] The number n is the appropriate principal quantum number of the upper orbital for the $^1|k\rangle$ excited state. (In the case of the $^1B_{3u}$ state $n = 3$.) The values of the various vertical transition energies (E_k, E_n) are those *calculated* by Buenker, *et al.*[17] The S vibrations are numbered according to Herzberg, ref 20, p 107.

accepting Mulliken's hypothesis that the equilibrium structure of the molecule in this $^3B_{3u}(T)$ state has an antiplanar arrangement of hydrogen atoms.[22] Walsh has suggested that a pyramidal arrangement of the bonds around each carbon atom would correspond to the excited orbital's acquiring some s character which would stabilize the orbital. (He also suggested that each carbon atom would be slightly out of the mirror plane bisecting the HCH angle of the other CH_2 group.)[5] Theoretical calculations[23] indicate that in the first excited triplet state the conformation of the ethylene involves both a twisting and a flapping motion of the CH_2 groups. Rules summarizing the excited states which are important for enhancing various nuclear motions in the ground state already have been formulated by Salem.[24] In the present case the only excited states $|k\rangle$ interacting with a given excited state $|n\rangle = i \rightarrow j$ (interacting in the sense that the matrix element $\langle n|\partial H/\partial S|k\rangle$ is nonzero) are of the two types $i \rightarrow l$ or $k \rightarrow j$. The simple ethylene case enables us to predict that if the pair (jl) is of σ (CH antibonding, CH_2 bonding)–π^*-type, the associated motion is a flapping, and that if the pair (ik) is of σ(CH bonding, CH_2 antibonding)–π-type, the associated motion is a twist of the CH_2 terminal group.

Let us now consider the corresponding $^1B_{3u}$ singlet state which is the lowest $\pi \rightarrow \pi^*$ state but not the lowest singlet state. Its vertical excitation energy is calculated to be 8.32 eV and the eventual correlation of this state with the V state of ethylene (at 7.6 eV) is carefully discussed by Buenker, *et al.*[17] For our own purpose it has simply to be recalled that this state has a diffuse character but that its charge density contours emphasize that it should not be associated with a *pure* Rydberg state. Both lower and higher energy singlet states have to be taken into account in our study and, as shown in Table II, the following qualitative conclusions may be drawn. (a) The cis flapping motion determines two couplings; the first one, between $^1B_{3u}$ and $^1B_{2g}$ ($1b_{1u} \rightarrow 3b_{3u}$), destabilizes the vertical excited $^1B_{3u}$ state ($E_k - E_n < 0$); the second one, between $^1B_{3u}$ and $^1B_{3g}$ ($1b_{1u} \rightarrow 4b_{3u}$), stabilizes the vertical $^1B_{3u}$ state ($E_k - E_n > 0$). The two contributions roughly cancel. They certainly both correspond to small matrix elements ($\langle 1b_{2g}|\partial v/\partial S|3b_{3u}\rangle$ and $\langle 1b_{2g}|\partial v/\partial S|4b_{3u}\rangle$, respectively) involving diffuse MO's ($n = 3$), and the denominators have similar magnitudes but opposite signs. (b) The stabilizing trans flapping motion which corresponds to a denominator of 0.12 eV appears to be more efficient than the destabilizing one (energy denominator −1.38 eV). Therefore such a deformation might be expected to be present in the relaxed configuration. (c) The predominant A_u twisting motion is also stabilizing. The A_u vibration couples the $^1B_{3u}$ state, a predominantly (but not true) Rydberg state ($n = 3$) with the first *valence* singlet state $^1B_{3g}$ ($n = 2$). During the twist the $^1B_{3u}$ state is stabilized and acquires more and more valence character by vibronic mixing with the $^1B_{3g}$ state. Thus the diffuse singlet for the planar geometry correlates with a singlet possessing a great amount of valence character in antiplanar geometry (though certainly much less than the corresponding triplet in the antiplanar geometry).[17]

The aforementioned selection rules being mainly based on the symmetry and on the spatial localization of molecular orbitals, it is not surprising that they are strongly related to the Woodward–Hoffmann rules. The final example dealing with the $^1\pi \rightarrow \pi^*$ excited states of *cis*- and *trans*-butadiene illustrates this fact. Theoretical calculations[25] have shown that the lowest singlet excited state of *cis*- and *trans*-butadiene is not the $\pi_2 \rightarrow \pi_3^*$ state (respectively $^1B_2$ and ^1B_u) but rather the mixed ($\pi_2 \rightarrow \pi_4^* + \pi_1 \rightarrow \pi_3^*$) state (respectively $^1A_1$ and ^1A_g). The excited singlet states are given in Chart I.

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Chart I

	cis-Butadiene			*trans*-Butadiene	
$\|k\rangle =$	$^1B_1$	-154.390 au	$\|k\rangle =$	^1A_u	-154.395 au
	$^1B_2$	-154.421 au		^1B_u	-154.397 au
$\|n\rangle =$	$^1A_1$	-154.489 au	$\|n\rangle =$	^1A_g	-154.569 au
$\|o\rangle =$	$^1A_1$	-154.766 au	$\|o\rangle =$	^1A_g	-154.722 au

In order to relate the selection rules to the conrotatory and disrotatory Woodward–Hoffmann displacements we focus our attention on the possible twist of the CH_2 terminal groups.

In the case of *cis*-butadiene the symmetries of the vibrations associated with the $^1B_1$ and $^1B_2$ excited states are respectively B_1 and B_2. The B_1 vibration does not provide any twist of the CH_2 groups whereas the B_2 one displays a disrotatory behavior (Figure 4a). This photochemical disrotatory motion is in accord with the Woodward–Hoffmann rules and produces cyclobutene.

In the *trans*-butadiene case the vibrational symmetries associated with the ^1B_u and ^1A_u excited states are respectively B_u and A_u. Here again B_u does not involve any twisting motion whereas the A_u vibration is a disrotatory one (including also the in-phase out-of-plane motion of the central hydrogen atoms (Figure 4b). These two motions distort the highest occupied MO in such a way that the increased overlaps (arrows in Figure 5) lead to the formation of bicyclo[1.1.0]butane (**2**).

This reaction may be a slow concerted one or a two-step reaction involving the intermediate **1**.[26]

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Pattern Recognition.[1] A Powerful Approach to Interpreting Chemical Data

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Abstract: Pattern recognition is a newly developing branch of artificial intelligence that shows a great deal of promise in providing a generalized approach to solutions of a large class of data analysis problems in experimental chemistry. A general statement of the problem is: can an obscure property of a collection of objects (elements, compounds, mixtures, etc.) be detected and/or predicted using indirect measurements made on the objects? One particular method within the realm of pattern recognition, the learning machine, has been successfully applied to spectroscopic data for direct detection of molecular structural units. This paper introduces pattern recognition in a much broader scope. Using a synthetic data base and a data base of chemical interest, the major approaches within pattern recognition are examined. One method representing each approach is applied to the two fundamentally different data sets, first to compare the results, but also to illustrate the far-reaching problem solving capability.

A large amount of experimental science deals with predicting properties of objects which are not directly measurable. In chemistry, the objects range from pure elements or compounds to complicated industrial and natural products. The properties can be fundamental, such as atomic or molecular structure, or less fundamental, such as reactivity, permeability, absorptivity, etc. All too often, these properties are not directly measurable and must be found using experimental measurements which are known to be related, in some way, to the sought-for property. In some cases a theoretical relationship between measurements and the property is used. A few simple but common examples serve to clarify this point. Emission spectrometry does not provide a direct measure of atomic composition (few methods do) but rather a measure of the wavelengths of light emitted when a sample is "pumped" with energy. The mathematics of atomic theory provide the connection between combinations of various wavelengths and the structure of atoms. Along the same lines, nmr spectrometry does not provide a direct measure of molecular structure but rather a measure of how isotopes are perturbed under various experimental conditions. Group theory provides the connection between nmr parameters and molecular structure.

To proceed, let us consider a less fundamental property of chemical compounds, reactivity. We will assume that one is faced with the problem of predicting the reactivity within a very large number of samples (compounds or mixtures of compounds). There are three methods of determining whether or not two compounds will react in a prescribed manner. The first and most obvious is the direct determination method consisting of adding one to the other under the desired conditions of temperature and pressure. The next method, herein called the theoretical method, is to study bonding possibilities of the molecules taking into consideration such things as orbital symmetry, steric hindrance, etc. Although these two methods are the most desirable, they may not be feasible. Direct methods may be prohibitively expensive, time con-

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