123°5′; $\alpha = 0°$; $a_N = 15.15$ G), 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl[4a] (CNC = 125°4′; $\alpha = 15°8'$; $a_N = 16.05$ G), 2,2,6,6-tetramethylpiperidine-1-oxyl[4b] (CNC = 125°5′; $\alpha = 19°4$; $a_N = 16.30$ G), *cf.* R. Briere, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 3273 (1965); 2,2,5,5-tetramethyl-3-pyrrolidone-1-oxyl azine[3c] (CNC = 112°; $\alpha = 0°$; $a_N = 14.27$ G), *cf.* R. M. Dupeyre and A. Rassat, *J. Amer. Chem. Soc.*, **87**, 3771 (1965); 9-aza-bicyclo[3.3.1]nonan-3-one-1-oxyl (CNC = 114°2′; $\alpha = 30°1'$, $a_N = 17.55$ G), *cf.* R. M. Dupeyre and A. Rassat, *J. Amer. Chem. Soc.*, **88**, 3180 (1966).

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On Avoided Surface Crossings

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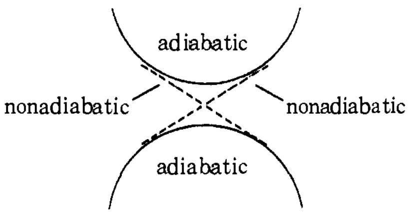
Abstract: A classification of avoided surface crossings relevant to organic chemistry is proposed. Four different types (A, B, C, and D) are defined. An "intermediate" Hamiltonian technique is introduced for describing appropriately the avoided-crossing region between a closed-shell surface and an open-shell surface. The gap size for avoided crossings near a symmetry-allowed crossing is shown to be proportional to the transition force between the two neighboring states.

Surface crossings, whether real or intended, are playing an increasingly important role in the interpretation of organic phenomena. It is well known that in Woodward–Hoffmann thermally forbidden reactions, there is an intended crossing between the ground-state surface and the surface for the doubly-excited state.[3] More recently the photochemical Norrish type II process has been shown to involve an intersection between the energy surface for excited reactant and that for ground reactant.[4] A similar surface crossing occurs in other major photochemical reactions.[4] Certain organic transients have two neighboring singlet surfaces with intersections and near-intersecting regions.[5] Our purpose here is not to deal with rigorously allowed intersections between electronic states. The theory of these crossings is well established.[6] Our intention is to bring to light the different types of "intended" or "avoided" crossings between states of the same spin multiplicity. In certain instances the avoided crossing occurs near a real crossing. In other cases the "intention" to cross is unknown to the real surfaces; the crossings are due to an approximate starting description of the wave functions for the two neighboring surfaces.

The first part of this paper contains a classification of the different types of avoided crossings which are known. In the second part of our work we introduce a method which allows for proper calculation of the neighboring surfaces in an avoided crossing region. Finally, in the third section, we demonstrate a simple law for the energy gap when a rigorously allowed crossing is destroyed concomitant to the destruction of a symmetry plane. The manner in which this gap varies with nuclear geometry is emphasized.

A Classification of Avoided Surface Crossings

A useful study of certain avoided crossings and of the appropriate terminology has been given by O'Malley.[7] The familiar distinction is made between stationary *adiabatic* states, which diagonalize the electronic Hamiltonian, and whose surfaces would be followed by slowly moving nuclei, and *nonadiabatic* (or diabatic) states for which the total electronic Hamiltonian is not diagonal. An avoided-crossing situation arises when the nonadiabatic surfaces intersect but when this intersection disappears by inclusion of the remaining off-diagonal terms



We have been able to distinguish between four types of avoided surface crossings. The first type (A) occurs *in the neighborhood of a true crossing of electronic states.* The other types (B, C, D) originate from "incorrect," nonadiabatic starting electronic wave functions, which are useful in that they are a good initial basis for discussing the "correct," adiabatic, surfaces. *In these cases a physical crossing never occurs.*

In the first case the previously *adiabatic* states and surfaces, which described correctly a physically correct intersection in one region of multidimensional space (C_s symmetry), become *nonadiabatic* when they are carried over into those regions of multidimensional space where the crossing is forbidden (C_1 symmetry). However, they again serve as a useful starting point for the study of the new, avoiding, adiabatic states in this region of space.

Type A. Neighborhood of a Symmetry-Allowed Crossing (Destruction of the Symmetry Element). The first type of avoided crossing is encountered for molecular geometries close to, but not identical with, a symmetrical geometry in which a crossing occurs rigorously between two electronic states. A common case will be the crossing between a symmetric A′ state and an antisymmetric A″ state for a molecular system with a plane of symmetry. Such interactions have been called "accidental" [6d] but are quite common. Examples of such crossings in organic chemistry include σ,π bitopic reactions[4b] (such as hydrogen abstraction by ketones), certain $\sigma(\sigma,\pi)$ tritopic reactions[4b] (coplanar α cleavage of hexadienones), etc. In the former family, one surface leads to a zwitterion, the other to a diradical; in the second family, the two surfaces lead to diradicals of different symmetry. If one or several nuclei are displaced slightly so as to destroy the symmetry plane, the crossing becomes forbidden since the adiabatic states must now have the same symmetry. Its intended character, however, shows up clearly for displacements which are not too large. Such a type A avoided crossing is illustrated in Figure 1.

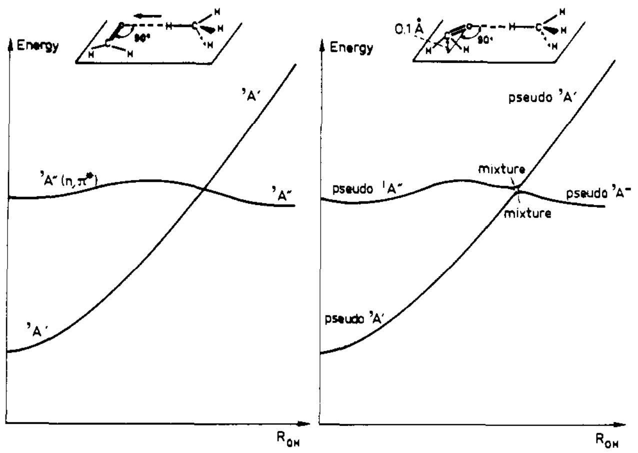


Figure 1. Type A avoided crossing. The left-hand figure shows the physical crossing between two states of different symmetry, while the right-hand side illustrates how a slight out-of-plane atomic displacement destroys the crossing.

It has already been emphasized[4] that the symmetry-allowed crossing is a property of the electronic states; it is not necessarily accompanied by any crossing at the molecular orbital level. In consequence, type A avoided crossings cannot be recognized by a molecular orbital description, or any other one-electron description of the molecule.

As will be done in each case, we will now characterize the avoided-crossing region by (a) the major electronic change occurring on either surface as it goes through the crossing region and (b) the term in the total electronic Hamiltonian operator which causes the avoided intersection. In the present case, the major electronic phenomenon shows up clearly by considering Figure 1. On the left-hand side, with the allowed crossing, the lowest surface has ^{1}A′ symmetry before the crossing and ^{1}A″ symmetry after the crossing. On the right-hand side, when the crossing is avoided, the previous symmetry notation is not rigorously valid, since the molecular symmetry plane has been destroyed. But, except right at the avoided crossing, state symmetries can still be easily recognized as pseudo-A′ or pseudo-A″ relative to the pseudo-symmetry plane. The ground surface has pseudo-A′ symmetry before the avoided crossing and pseudo-A″ symmetry right after the avoided crossing region. Thus this region is one of an abrupt state symmetry interchange. In a one-electron description of the state wave functions, one electron suddenly switches from a σ to a π orbital, or conversely. (In the hydrogen abstraction reaction the electronic configuration of ground reactant is $4\sigma,2\pi$ and that of excited reactant is $3\sigma,3\pi^4$).

It is an equally simple matter to determine the term in the total Hamiltonian which causes the change from an allowed crossing to an avoided crossing. We remember that in the perfectly symmetric molecular configuration the allowed crossing implies for the total electronic Hamiltonian

$$H = T + V_{\rm nn} + V_{\rm ne} + V_{\rm ee} \tag{1}$$

that the matrix element between states a and b vanishes[6]

$$\mathbf{H}_{\rm ab} = 0 \tag{2}$$

With the displacement of certain nuclei and concomitant destruction of the symmetry plane, the change in H is

$$\mathbf{H}' = \Delta(V_{\rm nn} + V_{\rm ne}) \tag{3}$$

This additional Hamiltonian operator can mix the wave functions for a and b. The detailed mechanism by which this mixing creates a gap between the two surfaces is well known. As we approach the region where a and b are nearly equi-energetic, the mixing which was small (second order) becomes large (first order), as required by perturbation theory. At a given point in this region, a and b interact *via* ΔH to form two new combinations (approximately a + b and a − b). One of these combinations has a lower energy than that of a or b, and the other has a higher energy. The gap between these two solutions is larger the closer a is to b. By plotting the solutions throughout the interaction region, one obtains two smooth curves. The lower of these links, a (<b), is on the left and b (<a) is on the right, making for a single surface. A similar, smooth behavior occurs for the higher surface. Hence the wave function describing a (previously ^{1}A′, say) can go continuously into that for b (previously ^{1}A″, say). In summary the avoided crossing arises from the *operator for change* (between symmetric and nonsymmetric situations) *in nuclear-nuclear and nuclear-electronic potential energy*. We will return to the effect of this operator and to the gap size in the third section.

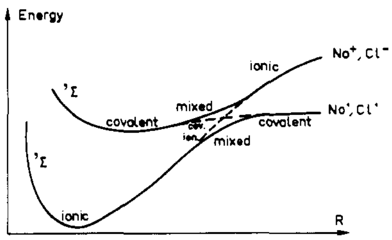


Figure 2. Type B avoided crossing. The figure shows the intended intersection (dashed lines) between the ionic and covalent surfaces for NaCl, as well as the "avoiding" adiabatic surfaces (full lines).

Type B. Avoided Crossing between an Ionic Configuration and a Covalent Configuration. The case of sodium chloride (NaCl) is probably the most famed type of avoided crossing.[8] It is illustrated in Figure 2. Let us first use a simple-minded model to describe the molecule at equilibrium. The ionic wave function for the bonding pair of electrons

$$\psi_{\rm ion} = \phi_{\rm Cl}(1)\phi_{\rm Cl}(2) \tag{4}$$

is a good approximation to the exact wave function of this highly polar molecule. Let us then plot the energy of $\psi_{\rm ion}$ as a function of distance: at large distances it correlates with the ion pair Na$^+$,Cl$^-$. At the same time the covalent function

$$\psi_{\rm cov} = \phi_{\rm Cl}(1)\phi_{\rm Na}(2) + \phi_{\rm Cl}(2)\phi_{\rm Na}(1) \tag{5}$$

which adequately describes an *excited* state of NaCl, correlates at infinity with the radical pair Na·,Cl·. Since the energy of the radical pair lies below that of the ion pair, the surfaces for the ionic configuration and for the covalent configuration intersect (dotted lines in the figure). The intersection occurs at a rather large internuclear distance (~10 Å).

The intersection observed here is a direct consequence of the relative crudeness of the theoretical model. If we lift the restriction that the wave function of a state be either purely covalent or purely ionic, the intersection disappears. Let us then allow $\psi_{\rm ion}$ and $\psi_{\rm cov}$ to mix in each state. At the critical internuclear distance where these two components are isoenergetic they will mix strongly, giving two solutions which are more accurate representations of the real states of the molecule. The lower solution joins smoothly onto the lower state for both shorter and longer bond lengths. The ground surface can then lead directly from an ionic molecule to a covalent dissociation, *via* a short region with mixed character.

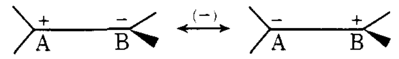
On the basis of our ionic-covalent model, we can speak of an avoided or intended crossing of the two surfaces near R = 10 Å. This case, like the two following ones, thus corresponds to an intersection which is allowed at some unsophisticated level of description, and which becomes forbidden at a more sophisticated level.

The avoided-crossing region is characterized by a spatial *electron jump*[9] from the chlorine atom to the sodium atom, as the wave function changes suddenly from (4) to (5). It is difficult to single out, in the total Hamiltonian, a term responsible for the mixing of covalent and ionic character. In practice both one-electron and two-electron terms in H will be effective. Possibly the best description is to say that, as the Na and Cl atoms move apart, the Coulombic attraction in the ion pair decreases so that *charge transfer* into a covalent diradical can occur. This allows the purely ionic wave function to convert smoothly into a covalent wave function.

Type B avoided crossings occur quite frequently in organic transients. One example exists in the rotation of singlet vinylmethylene to give an open cyclopropene diradical.[5] Another example is illustrated in Figure 3. Consider first the twisting of ethylene from 0 to 90° (Figure 3a). The ground state of ethylene leads to an orthogonal diradical D. The wave function for the ground state is mainly covalent at 0° and becomes purely covalent at 90°.

$$\psi_D = \phi_A(1)\phi_B(2) + \phi_B(1)\phi_A(2) \qquad (6)$$

The singly-excited π,π^* state leads, through twisting, to a high-energy "zwitterionic" state[10] which can be described as



The minus sign in parentheses indicates out-of-phase resonance between the two dipolar structures. The wave function of this excited state remains 100% ionic, throughout the entire twisting motion.[11]

$$\psi_{\pi,\pi^*} = \psi_Z = \phi_A(1)\phi_A(2) - \phi_B(1)\phi_B(2)$$

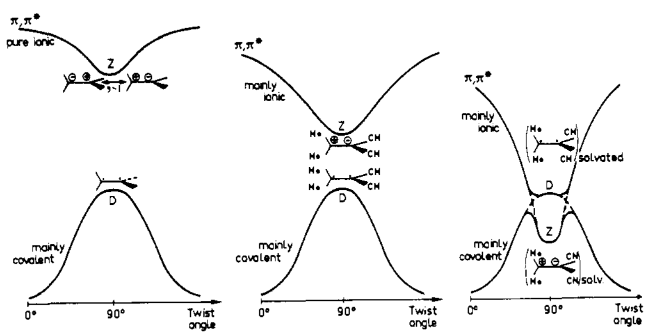
At 90° Z still lies more than 100 kcal/mol above D (Figure 3a). In a heteropolar olefin such as 1,1-dimethyl-2,2-dicyanoethylene (Figure 3b), this energy difference is significantly reduced.

Because of the heteropolar nature of the substituents, the ground state wave function, although still mainly covalent, has an increased ionic component while the excited state now has a small covalent component. The wave functions for D and Z remain respectively purely covalent and purely ionic.

Going one step further, we can deduce the form of the surfaces in a situation where Z lies *below* D. This should occur in extremely polar olefins, or by introducing the previous, moderately polar olefin in a highly polar solvent. The mainly ionic $\pi\pi^*$ state tends to correlate with Z, while the ground state tends to correlate with D. In this simple-minded picture, we obtain the crossing (dotted curves) indicated in Figure 3c, similar to that in NaCl. Again this crossing will be avoided; the ionic and covalent characters mix in the crossing region. The mixing is allowed since it is only at 90° that the ionic and covalent wave functions have different symmetries. The avoided crossing is reflected by a potential barrier on the ground surface and by a secondary minimum for Z. The surfaces of Figure 3 and their applications will be studied in detail elsewhere.[12]

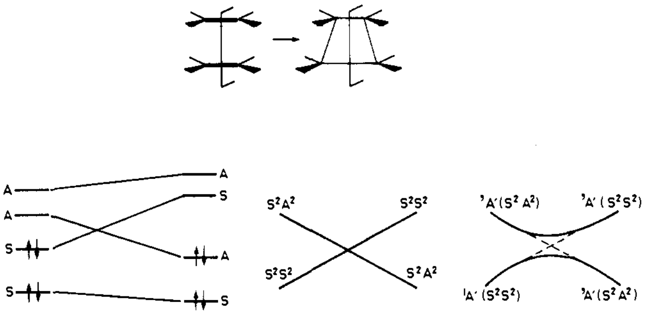
In principle avoided crossings related to type B could happen between any two valence-bond resonance structures which are close in energy and which interact weakly.

Finally certain avoided intersections belong both to family A and to family B.[13] In the Li + F_2 system, for instance, the allowed intersection for the isoceles triangle configuration (C_{2v} symmetry) occurs between a $^2A_1$, purely covalent, and a $^2B_2$, purely ionic, state. Near this geometry, therefore, there is an avoided crossing because of the lowering of symmetry (type A); this avoided crossing is also characterized by an electron-jump region (type B).



(a) ethylene (b) polar olefin in non-polar solvent (c) polar olefin in polar solvent

Figure 3. Type B avoided crossing in the twisting of unsymmetrical olefins in polar solvents: (a) the ground singlet and lowest excited singlet in the twisting of ethylene; (b) the same two states for 1,1-dimethyl-2,2-dicyanoethylene; (c) the same two states for 1,1-dimethyl-2,2-dicyanoethylene in a polar solvent. The intended intersections between ground surface and excited surface are shown in dashed lines and the adiabatic "avoiding" surfaces in full lines.



(a) Orbitals (b) Configurations (c) States

Figure 4. Type C avoided crossing for the 2s + 2s dimerization of ethylene: (a) the molecular orbital correlation diagram; (b) the intersection between ground and doubly-excited configurations; (c) the intended intersection between ground and doubly-excited states, when approximated by the one-electron configurations (dashed lines), and the "avoiding" adiabatic surfaces.

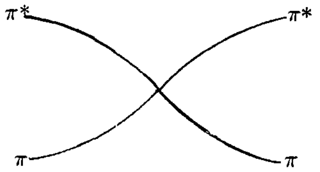
Type C. Avoided Crossing between Two Molecular Orbital Configurations at a Molecular Orbital Intersection. The type C avoided crossing is to molecular orbital theory what the type B crossing is to valence-bond theory. In the simplified picture in which electrons are ascribed to specific one-electron molecular orbitals, a symmetry-allowed crossing may occur between highest occupied MO and lowest unoccupied MO along some reaction coordinate. The most familiar case in organic chemistry is probably the symmetry-allowed orbital crossing in Woodward–Hoffmann thermally forbidden pericyclic reactions.[14] This is illustrated for the [2s + 2s] cycloaddition of two ethylene molecules in Figure 4a. In the pair of ethylene molecules, the highest occupied MO is S relative to the symmetry plane; in the product this MO has A symmetry. If we now plot the total energies of the *one-electron configurations* S^2S^2 and S^2A^2, we obtain the crossing in Figure 4b. At this level of approximation the ground-state surface intersects the potential surface for the doubly-excited state.

Again the description of the states as single configurations is incorrect in the region where the two configurations have nearly equal energies.[15] Explicit inclusion of the interelectronic repulsion operator, in the form of the instantaneous repulsion minus some averaged repulsion (which will have been included in the Hamiltonian serving to determine the molecular orbitals),[16] will mix the two configurations.

$$H_{12} = \Sigma \frac{1}{r_{ij}} - \overline{\Sigma \frac{1}{r_{ij}}} \qquad (7)$$

The lower surface, represented originally by S^2S^2, will mix in S^2A^2 character in the crossing region, and in doing so will go over smoothly to the lower, S^2A^2, surface of the product. The crossing is avoided, as first shown by Longuet-Higgins[3] (Figure 4c). One can think of the crossing as being allowed at the "one-electron" level but forbidden when electron correlation is included.[17]

The twisting of ethylene, which we have already considered in a different context, is also a case of type C avoided crossing. At 90° the bonding π and antibonding π^* one-electron self-consistent-field energies cross.

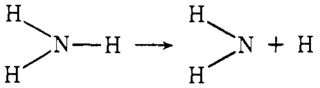


The configurations π^2 and π^{*2} also cross each other at 90°, where they show a cusp.[18] Configuration interaction leads to two well-separated states, as in Figure 4.

To summarize, type C avoided crossings occur between two states having the same total electronic symmetry (compare with type A avoided crossings). The essential characteristic of the avoided crossing region is a switch in the major configuration which composes either state. This accompanies the basic *orbital symmetry interchange.*

Type D. Avoided Crossing Due to a Weakly Avoided Molecular Orbital Intersection. The fourth type of avoided crossing is relatively rare. It occurs between the lowest excited state and a higher excited state in the coplanar dissociation of NH_3 to NH_2 + H[19] and in that of H_2O into OH + H. The interpretation of this type of avoided crossing owes much to the work of Horsley,[20] Mulliken,[21] and others. Let us illustrate the avoided crossing with the case of NH_3.

We consider first the correlation of the top occupied and lowest unoccupied orbitals of planar NH_3 in the decomposition.



Relative to the molecular symmetry plane, the lone pair orbital of ammonia has π symmetry and correlates simply with the pπ orbital of NH_2. There are also three crucial σ-type orbitals: the σ_{NH} bond orbital in the NH bond which is being stretched, the 3s Rydberg orbital on nitrogen, and the σ_{NH} antibonding bond orbital in the stretched NH bond. The correlation diagram for these three σ orbitals is at the heart of the avoided crossing phenomenon. The low, strongly bonding σ_{NH} orbital and the high, strongly antibonding σ_{NH}^* orbital can be considered to arise from the interaction of the σ_N lone pair orbital of NH_2 and the $1s_H$ hydrogenic orbital of H. In the products, σ_N lies below $1s_H$; therefore σ_{NH} correlates with σ_N while σ_{NH}^* descends rapidly and tends to correlate with $1s_H$. The diffuse $3s_N$ Rydberg orbital on nitrogen tends to correlate with itself. These tentative correlations imply a crossing between the 3s Rydberg orbital and the localized $\sigma_{NH}^*(\rightarrow 1s_H)$ orbital. However, since both molecular orbitals have the same symmetry and nonzero, although weak, overlap, their crossing is avoided. Any one-electron Hamiltonian, even of the simple extended Hückel type, will ensure that the two orbitals mix in the region where they are equi-energetic. The mixing region is relatively narrow, but suffices to cancel the orbital crossing which becomes weakly avoided (Figure 5a).

If we now plot (Figure 5b) the energies of the two electronic configurations arising from excitation of one lone-pair π electron to either $3s_N$ or σ_{NH}^*, the avoided crossing is carried over. After descending steeply as the hydrogen atom moves away from very short repulsive, internuclear NH distances, the lowest excited configuration (σ_{NH}^2, π, $3s_N$) tends to rise slowly toward the (σ_N^2, π, $3s_N$) configuration of products. Similarly, the second excited configuration (σ_{NH}^2, π, σ_{NH}^*) descends monotonically as it tends to correlate with the (σ_N^2, π, $1s_H$) configuration products. In the region of the orbitally-avoided crossing, the configurations start mixing and the energy surfaces avoid each other. The behavior is parallel to that of the $3s_N$ and σ_{NH}^* orbitals.

Contrary to type C avoidance, type D avoidance is simply carried through, one step further, from one-electron configurations to states, as shown in Figure 5c. The gap between the states is slightly larger than that between the configuration, since type C avoidance, due to the two-electron Hamiltonian (eq 7), will add onto the avoidance proper, due to the one-electron Hamiltonian, studied here. The correlation which we derive for the higher excited state to an ion pair differs from that of Herzberg.[19b] The minimum which we construct in Figure 5c for the second excited state is not observed spectroscopically.

The avoided crossing region is characterized by drastic changes in the character of the $3s_N$ orbital. From a highly diffuse Rydberg orbital it first borrows σ^* character and finally ends up as localized $1s_H$ orbital. The orbital-avoided-crossing region, or the state-avoided-crossing region, therefore correspond to fairly rapid *orbital contraction.*

An example of type D avoided crossing in organic chemistry occurs in ethylene, between the two lowest excited singlet states, in the early stages of its twisting.[11] For planar ethylene, the Rydberg $3p_y$ orbital lies below the π^* orbital, but rapidly the latter is stabilized by the twisting motion. Their crossing is weakly avoided because they have the same symmetry relative to the C_2 axis which is conserved during the twisting (Figure 6). The avoided-orbital crossing, and concomitant avoided-state crossing, occurs for a twist angle of 45°. Figure 4 of Peyerimhoff and Buenker's work[11] shows the behavior of the two lowest $^1B_1$ excited states, which is indeed very similar to Figure 5c. The avoided-crossing gap is no larger than 7 kcal/mol.

Summary

Our classification of avoided surface crossings of electronic states is summarized in Table I. For each type of crossing (A, B, C, D) we specify the general phenomenon responsible for the avoidance, the major characteristic of the avoided-crossing region, and the Hamiltonian terms which forbid the crossing.

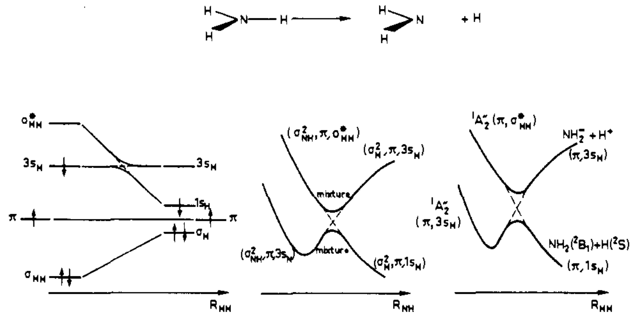
In certain systems, for instance the internal rotation in vinylmethylene,[5] an avoided crossing of type B can also be considered to belong to class A. This is because one family of class A crossings is that between a covalent, diradical like the A″ state and a zwitterionic A′ state. Then the class A avoided crossing has essentially the same characteristics as a class B avoided crossing, because the symmetry switch of one electron (class A) also happens to be a spatial jump from one atom to another (class B).

An "Intermediate Hamiltonian" Method for Calculating Avoided-Crossing Regions between Open and Closed Shells

The first and second types of crossing are frequently characterized by the fact that one of the two intersecting states is of *closed-shell* nature while the second one possesses an *open shell* with at least two odd electrons. Examples are closed-shell ionic Na^+,Cl^- *vs.* open-shell diradical Na·,Cl· (type B), or open-shell n,π^* excited singlet $^1A''$ *vs.*

Table I. Classification of Avoided Surface Crossings

Type	Origin	Characteristics of the avoided-crossing region	Hamiltonian responsible
A	Destruction of symmetry-allowed crossing	State symmetry interchange, symmetry switch of one electron	$\Delta(V_{\text{nn}} + V_{\text{ne}})$
B	Avoidance of crossing between ionic and covalent configurations	Spatial electron jump	Total H
C	Avoidance of two MO configurations at a molecular orbital crossing	Orbital symmetry interchange	H_{t2}
D	Avoided molecular orbital crossing	Orbital contraction	$H_{\text{l}}(+H_{\text{t2}})$



(a) Orbitals (b) Configurations (c) States

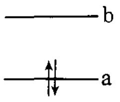
Figure 5. Type D avoided crossing for coplanar decomposition of NH_3: (a) orbital correlation diagram; (b) behavior of the first excited and second excited configurations (intended intersection in dashed lines, "avoiding" configurations in full lines); (c) behavior of the states, which parallels that of the corresponding configurations.

closed-shell ground singlet $^1A'$ in σ,π bitopic photochemical reactions.[4] The fundamentally different character of these two states leads to difficulties in the calculation of electronic potential energy surfaces in the region of the avoided crossing. We present here a simple method which appears to describe properly the relative behavior of the two surfaces in this region.

As an example, let us take the Norrish type II abstraction of a hydrogen atom of CH_4 by H_2CO (Figure 1). Let us first consider the manner in which the position of the crossing point between $^1A'$ ground state and (n,π^*) $^1A''$ excited state is obtained in the coplanar abstraction (Figure 1, left-hand side). A possible approach is to calculate both ground-state and excited-state energies, as a function of molecular geometry, from the molecular orbitals obtained in an SCF calculation of the ground configuration of the system. The Hartree-Fock operator for the orbitals of a closed-shell configuration is[22]

$$F = h + \sum_{j<a} (2J_j - K_j) + (2J_a - K_a) \qquad (8)$$

where the usual notation is employed and where the highest occupied and lowest unoccupied orbitals are labeled respectively a and b.



As is well known, operator 8 provides a good representation of the occupied orbitals, but a poor representation of the empty orbitals such as b. Consequently, the energy of the open-shell configuration built from these orbitals is too high. Thus the crossing of the two states is expected to occur too far along the reaction coordinate. This is illustrated in Figure 7 (point A) where the calculated curves[23] have been labeled 1c (closed) and 1o (open), respectively.

Alternatively, one may perform a SCF calculation on the open-shell configuration ab.

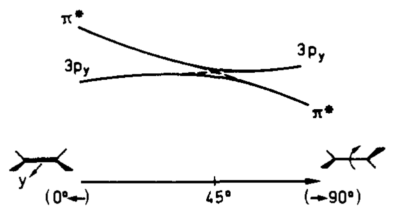


Figure 6.

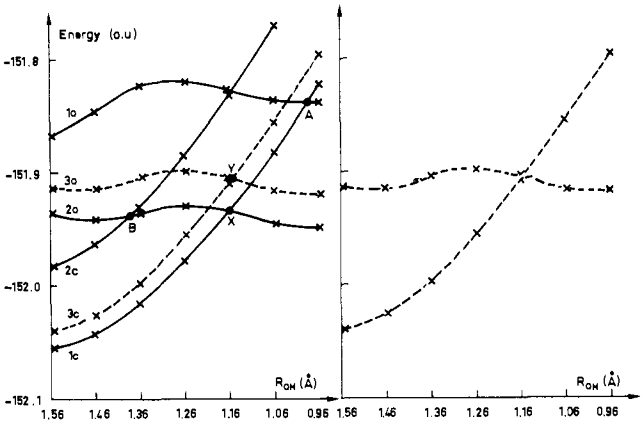
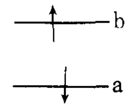


Figure 7. Application of the "intermediate" Hamiltonian method to the calculation of avoided crossings. The geometries are as in Figure 1: coplanar hydrogen abstraction by H_2CO from CH_4 on the left-hand side; the same with an out-of-plane displacement (0.1 Å) by carbonyl carbon atom on the right-hand side. 1, closed-shell Hamiltonian; 2, open-shell Hamiltonian; 3, intermediate Hamiltonian; o refers to the open-shell state and c to the closed-shell state.



For systems of the complexity envisaged here, a simple method is desirable for the SCF treatment of the open-shell problem. We use the single restricted open-shell Hamiltonian suggested by Nesbet[24]

$$F = h + \sum_{j<a} (2J_j - K_j) + (J_a - \tfrac{1}{2}K_a) + (J_b - \tfrac{1}{2}K_b) \qquad (9)$$

where all the molecular orbitals are eigenfunctions of the same operator. These molecular orbitals are good representations of the open-shell state but provide a poor representation, with too high an energy, of the closed-shell state. The resulting energy curves are labeled 2c and 2o in Figure 7. The surface crossing now occurs too soon (point B) along the reaction coordinate. We wish to emphasize that, although we have chosen the specific form in (9) for the open-shell Hamiltonian, this argument is general and does not depend on the particular form of the operator.

The *correct* crossing point X, as provided by our calculations, is of course the intersection between curve 1c, the best estimate of the closed-shell energy, and curve 2o, the best estimate of the open-shell energy.

Now let us assume that the carbonyl carbon atom is displaced slightly out of the molecular symmetry plane (Figure 1, right-hand side) in which case the crossing between ground surface and excited surface is avoided. We have seen that in the avoided-crossing region the electronic nature of the ground state switches progressively from $^1A'$, *i.e.*, closed-shell, to $^1A''$, *i.e.*, open-shell, and is a mixture in the vicinity of X. The proper quantum-mechanical description of such a situation requires a configuration interaction treatment between the closed-shell molecular orbital configuration and the open-shell molecular orbital configuration. A difficulty immediately arises in such a configuration interaction calculation because the best molecular orbitals used to build either configuration are eigenfunctions of different operators and are therefore not orthogonal. The calculation of the off-diagonal matrix element between the two configurations becomes an extremely arduous task, especially if one is calculating many points along the reaction coordinate. We could resort to using exclusively the Hamiltonians in (8) or (9), but, from what we have seen, these would inevitably lead to avoided-crossing regions at erroneous positions.

A simple solution to our dilemma is to introduce a *single* Hartree–Fock operator *intermediate* between (8) and (9). A single Hamiltonian avoids the nonorthogonality problem, and, if it treats both states with an equal bias, should lead to an avoided crossing in the proper region, *i.e.*, near X. Since (8) corresponds to the electronic configuration a^2 and (9) to the electronic configuration ab, an appropriate intermediate Hamiltonian should correspond to a potential which is the average of the two.

$$F = h + \sum_{j<\mathrm{a}} (2J_j - K_j) + {}^3\!/_2 (J_\mathrm{a} - {}^1\!/_2 K_\mathrm{a}) + {}^1\!/_2 (J_\mathrm{b} - {}^1\!/_2 K_\mathrm{b}) \quad (10)$$

This operator is that obtained, in the Nesbet approximation, from a function of the form

$$\psi = \frac{1}{\sqrt{2}} \left\{ |\ldots \mathrm{a}\bar{\mathrm{a}}| + \frac{1}{\sqrt{2}} (|\ldots \mathrm{a}\bar{\mathrm{b}}| - |\ldots \mathrm{b}\bar{\mathrm{a}}|) \right\} \quad (11)$$

i.e., an equally weighted linear combination of the closed-shell singlet configuration and of the open-shell triplet configuration. The use of the triplet multiplicity eliminates cross terms between the two configurations. This wave function represents an arbitrary state of mixed multiplicity and the molecular orbitals obtained from (10) will not even represent a true variational minimum for the trial function in (11) since the Nesbet approximation is employed.[24] This, however, causes no formal difficulty in the calculation, since the molecular orbitals obtained from (10) are simply used as the basis set for building determinantal functions which are eigenfunctions of spin, and since the SCF calculation is only a means for obtaining a particularly appropriate set of MO's for the problem at hand. The philosophy of this approach is similar to that previously employed by Roothaan in dealing with pairs of degenerate states,[25] and by Hinze in treating states of the same symmetry in diatomic molecules.[26,27]

From (10) the correct diagonal energy of the singlet open-shell configuration ^{1}ab is

$$E(^1\mathrm{ab}) = \sum_{j<\mathrm{a}} (\epsilon_j + h_j) + ({}^1\!/_4\epsilon_\mathrm{a} + {}^3\!/_4 h_\mathrm{a}) + ({}^3\!/_4\epsilon_\mathrm{b} + {}^1\!/_4 h_\mathrm{b}) - {}^3\!/_{16}(J_\mathrm{aa} + J_\mathrm{bb}) - {}^1\!/_4 J_\mathrm{ab} + {}^{13}\!/_8 K_\mathrm{ab} \quad (12)$$

while that of the closed-shell configuration $^1a^2$ is

$$E(^1\mathrm{a}^2) = E(^1\mathrm{ab}) + \epsilon_\mathrm{a} - \epsilon_\mathrm{b} + {}^1\!/_4(J_\mathrm{aa} + J_\mathrm{bb}) - {}^3\!/_2 K_\mathrm{ab} \quad (13)$$

where ϵ_j is the jth eigenvalue of the operator in (10).

Table II compares SCF energies (eq 8, 9, or 10) and the total closed-shell or open-shell energies obtained by the three methods. The upper part of the table gives the results for CH_2, while the lower part shows the energies for the coplanar hydrogen abstraction from methane by formaldehyde (Figure 1, left-hand side). In both cases the SCF energies for the intermediate Hamiltonian fall in between those for the closed and open Hamiltonians, as would be expected. Furthermore (last column of Table II), the energy *differences* between states calculated with the *single* operator in (10) compare well with those calculated using the appropriate Hamiltonian for each state.

The energies calculated from (10) for the two states in the coplanar hydrogen abstraction reaction are plotted, as 3c and 3o in Figure 6 (dotted lines). As predicted, for each state the energy falls in between that obtained from operators in (8) and (9), demonstrating the even-handed treatment of both states. More important still, the crossing point Y occurs at geometry essentially identical (R_{OH} = 1.16 Å) with our previous best crossing point X. We can now safely carry out a calculation for the noncoplanar reaction. The result for a 0.1 Å displaced carbonyl carbon atom is shown in Figure 6, right-hand side (see also Figure 1, right-hand side). The maximum and minimum typical of such an avoided crossing[28] show up at the appropriate geometry.

We have thus introduced a simple method for accurately describing certain type A[29] and all type B avoided surface crossings. The price which has to be paid for such a proper description of the avoided-crossing region is an absolute energy which, for both ground and excited states, is higher than obtained respectively from (8) or (9). However, the crucial feature, with respect to photochemical or radiationless processes which may involve these surfaces, is the *relative* energy at various geometries. By using a method which treats both states with equal bias, we can be confident that the relative positioning of the two surfaces is reasonably represented throughout.

Size of the Avoided-Crossing Gap (Class A) as a Function of Noncoplanarity

Let us consider the decay of a molecule from an excited surface to a ground surface at an avoided crossing. The exact avoiding surfaces are the *adiabatic* surfaces. The descent from one to another can be visualized as a situation in which the molecule remains on the intended-crossing sheet which links excited surface (on the left, say) to ground surface (on the right), *i.e.*, on the dotted lines (Figures 1 (right-hand side), 2, 3c, 4c, and 5c). The probability for decaying from one adiabatic surface to the other is the same as that for remaining on these *nonadiabatic*, intersecting surfaces. This probability P is extremely sensitive to the size of the energy gap g. The Landau–Zener classical expression for P is[30]

$$p = \exp[-\pi^2 g^2/(\hbar v \delta s)] \quad (14)$$

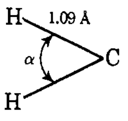
where v is the relative velocity of the dissociating moieties and δs is the difference in slopes, at the avoided crossing, between dotted curves. It is therefore extremely useful to know the exact thickness of the gap for use in (14) or in more sophisticated expressions[31] for transition probabilities between adiabatic potential energy surfaces.

Generally the gap size is

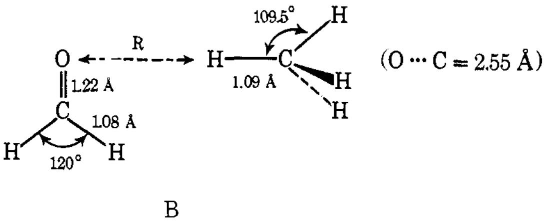
$$g = 2H_\mathrm{ab}' \quad (15)$$

where a and b are the two states which cross and H' (Table

Table II. Energies (au) Calculated by the Closed-Shell, Intermediate, and Open-Shell Hamiltonians[a]



A



B

	Closed-shell Hamiltonian (eq 8)		Open-shell Hamiltonian (eq 9)		Intermediate Hamiltonian (eq 10)		
α, deg	E_{SCF}	E_{closed} (eq 12)	E_{SCF}	E_{open} (eq 13)	E_{SCF}	E_{closed} (eq 12) E_{open} (eq 13)	Δ
				A			
105	−38.370	−38.370	−38.056	−38.306	−38.157	−38.369 −38.307	−0.002
120	−38.358	−38.358	−38.066	−38.324	−38.156	−38.358 −38.325	−0.001
135	−38.337	−38.337	−38.065	−38.330	−38.143	−38.336 −38.331	−0.002
				B			
R_{O-H}, Å							
1.56	−152.055	−152.055	−151.654	−151.937	−151.802	−152.040 −151.914	+0.008
1.46	−152.043	−152.043	−151.667	−151.943	−151.805	−152.027 −151.914	+0.013
1.36	−152.016	−152.016	−151.670	−151.937	−151.799	−151.998 −151.904	+0.015
1.26	−151.979	−151.979	−151.671	−151.931	−151.789	−151.957 −151.899	−0.010
1.16	−151.934	−151.934	−151.674	−151.936	−151.777	−151.910 −151.906	+0.006
1.06	−151.884	−151.884	−151.673	−151.947	−151.762	−151.866 −151.918	+0.011
0.96	−151.823	−151.823	−151.661	−151.949	−151.734	−151.795 −151.919	+0.002

[a] In the two examples considered the total energies are not affected by the 3 by 3 CI procedure. The quantity Δ(au) is the difference between ($E_{open} - E_{closed}$) calculated from the intermediate Hamiltonian and ($E_{open} - E_{closed}$) calculated from the appropriate Hamiltonians.

I) is that part of the Hamiltonian which mixes a and b, and creates the avoided crossing. In certain classes of avoided-crossing reactions, it is a simple matter to evaluate H_{ab}'. For class C avoided intersections, the matrix element of H_{12} between ground and doubly-excited configurations is an exchange integral.

$$g = 2K_{SA} \tag{16}$$

The exchange integral K_{SA}, between the two orbitals of different symmetry S and A, is generally small. It can be quite large (1 or 2 eV), however, if orbitals S and A are delocalized over the same set of atoms, as in antiaromatic transition states.[32] In class B avoided crossings, the gap is given by the matrix element of the total Hamiltonian between ionic wave function (see (4)) and covalent wave function (see (5)). It is essentially proportional to the *overlap* between the two atomic orbitals involved in the electron jump.[33] Accordingly, Grice and Herschbach have recently shown[9b] that the gap size is a decreasing exponential function of the crossing distance. We now concentrate on type A avoided crossings. We investigate how the gap size grows with the noncoplanarity of the system (Figure 1). In so doing, we will use a relatively new concept, that of a *transition force*, first introduced in 1963.[34]

Let us assume an initially coplanar system, for which two states, A′ and A″, cross each other as a function of some reaction coordinate which conserves the plane of symmetry. Let nucleus (charge Z_N), *originally in the symmetry plane*, be displaced algebraically by z in a direction **z** perpendicular to the symmetry plane, which is thereby destroyed. The change in Hamiltonian operator is given by eq 3. If the nuclear displacement along the z axis is assumed to be small, the change is nuclear–nuclear and nuclear–electronic potentials can be written as

$$\Delta V_{nn} + \Delta V_{ne} = z\left(\frac{\partial V_{nn}}{\partial z} + \frac{\partial V_{ne}}{\partial z}\right) = z\frac{\partial V}{\partial z} \tag{17}$$

where V is the *total* potential energy.[35] The matrix element of H' between the two states is then simply

$$H'_{A'A''} = z\left\langle {}^1A' \left| \frac{\partial V}{\partial z} \right| {}^1A'' \right\rangle = zF_{A'A''} \tag{18}$$

Thus eq 15, together with (18) for the matrix element of H' gives

$$g = 2zF_{A'A''} \tag{19}$$

The energy gap is equal to twice the nuclear displacement multiplied by the *transition force* $F_{A'A''}$ between the two states. Transition forces F_{ab} appear in the expression for the force constant of any state a. They measure the extent to which a nuclear displacement *mixes* this state with various states b.[34] It is therefore logical that the gap size should involve the transition force between the nearly-intersecting states.

If the wave functions for states A′ and A″, assumed to be singlets, are written out explicitly as

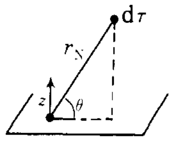
$$\begin{aligned} {}^1A' &= |a\bar{a}\ldots j\bar{j}k\bar{k}| \\ {}^1A'' &= \frac{1}{\sqrt{2}}(|a\bar{a}\ldots j\bar{j}k\bar{l}| + |a\bar{a}\ldots j\bar{j}l\bar{k}|) \end{aligned} \tag{20}$$

(a typical case would be k = σ, l = π or k = π, l = σ, as in the bitopic hydrogen abstraction reaction[4]) then

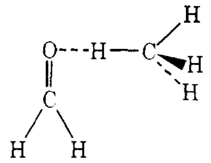
$$F_{\mathrm{A'A''}} = \sqrt{2}\left\langle \mathrm{k}\left|\frac{\partial V}{\partial \mathbf{z}}\right|\mathrm{l}\right\rangle \tag{21}$$

The matrix element of $\partial V/\partial \mathbf{z}$ between orbitals k and l can be easily reduced to a one-electron integral over the transition density ρ_{kl}

$$\left\langle \mathrm{k}\left|\frac{\partial V}{\partial \mathbf{z}}\right|\mathrm{l}\right\rangle = Z_{\mathrm{N}}\int \rho_{\mathrm{kl}}\frac{\cos\,\theta}{r_{\mathrm{N}}{}^{3}}\,\mathrm{d}\tau \tag{22}$$



as has been shown elsewhere.[34a] It is therefore possible to make a calculation of the gap if the molecular orbitals k and l are known and if the force integral in (22) can be evaluated.[36,37] However, quantum-mechanical calculations of force integrals are generally very sensitive to the density in the integrand, to the effective value chosen for Z, etc. We have preferred to measure directly the gap from the computed avoided surfaces. We considered a series of geometries (see Figure 1)



in which the carbonyl carbon atom is displaced by a varying exent z out of plane. The value of $F_{\mathrm{A'A''}} = g/2z$ is shown below

z, Å	g, au	$g/2z$, au
0.01	4.63×10^{-5}	2.30×10^{-3}
0.04	1.81×10^{-4}	2.26×10^{-3}
0.07	3.21×10^{-4}	2.29×10^{-3}
0.1	4.61×10^{-4}	2.30×10^{-3}
0.21	9.91×10^{-4}	2.36×10^{-3}

The proportionality of the gap to the out-of-plane displacement, predicted by formula 19, is remarkably obeyed. Hence the gap size, for type A avoided crossings, is a good measure of the *deviation of the molecular system from C_s symmetry*.[38]

Acknowledgment. The authors are extremely grateful to Professor T. Carrington for some pertinent remarks on the manuscript. They also thank Dr. Xavier Chapuisat, Dr. Danielle Grimbert, and Dr. John Horsley for helpful comments.

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Calculated Photoionization Cross-Sections and Angular Distributions for the Isoelectronic Series Ne, HF, H_2O, NH_3, and CH_4[1]

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Abstract: Photoionization cross-sections and angular distributions within the orthogonalized plane-wave approximation have been calculated for Ne and the ten-electron first-row hydrides HF, H_2O, NH_3, and CH_4. The calculations are appropriate for photoionization of randomly oriented molecules with an unpolarized photon beam. Three types of cross-sections are presented: (i) specific differential photoionization cross-sections for electrons emitted normal to the photon beam, $\sigma_\perp$, (ii) total differential photoionization cross-sections for electrons ejected normal to the photon beam, $\sigma_\perp^{\mathrm{tot}}$, and (iii) total photoionization cross-sections for electrons ejected in all directions, σ. Variations in computed cross-sections and asymmetry parameters β as a function of the kinetic energy of the photoelectrons for incident photon energies ranging from threshold to 1500 eV are discussed and possible interpretations are proposed. Relative experimental photoionization band intensities obtained with Ne I, He I, He II, and Mg Kα radiation sources and asymmetry parameters β obtained with He I radiation are compared with computed $\sigma_\perp$ and β values.

I. Introduction

The photoionization cross-sections of the ten-electron first-row hydrides CH_4, NH_3, H_2O, and HF are of fundamental importance in studies of atmospheric and astrophysical processes and in analysis of photoelectron spectral (PES) band intensities. Photoabsorption of vacuum ultraviolet solar radiation leading to photodissociation and photoionization plays a significant part in the heating and structure of the atmospheres. It is directly responsible for the ionosphere and contributes significantly to molecular dissociation and heating of the atmosphere above 100 km.[2] Since all gases have high photoabsorption cross-sections in the short wavelength end of the spectrum, it is expected that similar processes take place in planetary atmospheres other than that of the earth. CH_4, NH_3, and H_2O are common constituents of the atmospheres and although HF is not as common, traces of it have been observed in the atmosphere of Venus.[3] With regards to PES, it is possible to use the variation in differential photoionization cross-sections as a function of energy of the incident photons as a criterion for spectral assignments.[4] The ability to predict photoionization cross-sections is very important in PES, for spectral assignments should be consistent with regards to intensity as well as energy analysis of the bands.

In this paper we present the calculated differential photoionization cross-sections and angular distribution parameters for the ten-electron first-row hydrides and neon and compare these with the corresponding relevant experimental quantities. Three different types of cross-sections are presented. (1) The *specific differential photoionization cross-section* $(\mathrm{d}\sigma/\mathrm{d}\Omega)_j$ *is a measure of the number of electrons emitted from orbital j per unit time per unit solid angle* Ω. Since the most common experimental arrangement involves randomly oriented molecules and collection of photoelectrons through a slit centered normal to an incident unpolarized photon beam, we have calculated the corresponding averaged specific differential cross-section, henceforth referred to as $\sigma_\perp$. (2) The *total differential cross-section* $\sigma_\perp^{\mathrm{tot}}$ *has been calculated as the sum of the specific differential cross-sections for the experimental conditions described in case 1, i.e.* $\sigma_\perp^{\mathrm{tot}} = \sum_i \sigma_{\perp i}$ *where i represents a summation over all occupied orbitals.* (3) *The total specific cross-section* σ *is a measure of the number of electrons emitted from an orbital per unit time in all directions.* We have calculated the averaged σ corresponding to randomly oriented molecules and unpolarized incident photons. In order to observe the dependence of $\sigma_\perp$ and $\sigma_\perp^{\mathrm{tot}}$ on photon energy, calculations were performed for various photon energies between threshold and 1500 eV; plots of $\sigma_\perp$ and $\sigma_\perp^{\mathrm{tot}}$ *vs.* incident photon energy are presented for Ne, HF, H_2O, NH_3, and CH_4. These cross-sections are compared to relative experimental band intensities as obtained from Ne I, He I, He II, and Mg Kα radiation sources. The σ and the angular distribution parameter β are computed only for the four sources listed above. The calculated β values are compared to those obtained from experimental determinations using a He I radiation source.

The cross-sections and angular distributions are calculated in the plane-wave (PW) and orthogonalized plane-wave (OPW) approximations according to the theoretical equations derived by Ellison[5] and applied by Rabalais, *et al.*[6,7] Some of the most important elements of a cross-section cal-