

A New Concept in Laser-Assisted Chemistry: The Electronic-Field Representation

Thomas F. George,* I. Harold Zimmerman, Jian-Min Yuan, John R. Laing, and Paul L. DeVries

Department of Chemistry, The University of Rochester, Rochester, New York 14627

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The interaction between states of radiation and matter has been of great interest to scientists for several hundred years. During much of that time, quantitative research has necessarily concentrated on macroscopic aspects of the matter-field interaction. The development of quantum theory, however, makes available a fundamental explanation of both microscopic and macroscopic interaction phenomena.

For most of the time since 1926 researchers have focused their attention on two kinds of particle-field models in which either the field represents a low-order perturbation on a simple particle system or vice versa.¹ The comparatively recent advent of the laser and of large-scale computing facilities has provided motive, means, and opportunity to study more complex interaction systems, including some which may be classified as lying between the two perturbation limits. Of immediate interest to us, for example, are systems that change dynamically with variation of some specified coordinate. While working on such problems, we have found it very helpful to introduce the idea of matter-field energy surfaces into our dynamical concept.²⁻⁷ In the course of this paper we shall attempt to describe what these surfaces are and to indicate the nature of their usefulness. That is, our aim is to show how various field-assisted chemical processes can be described in terms of mixed matter-field quantum states (with great emphasis on the electronic-field representation²⁻⁷) and their associated energies, which will generally be taken to vary as the particle configuration changes. We shall not discuss the complementary topic of collisional line broadening per se, but certainly our approach is applicable to this area, as it provides a conceptual framework for dynamical models of the broadening process.

The purpose behind the development of this dynamical particle-field representation may perhaps be more easily understood with the aid of Figure 1. Familiar methods for utilizing lasers in association with chemical processes (exemplified here by a reactive atom-diatom encounter) are suggested in the first two parts of the figure. We often think of using the laser

to state-select some particular one of the reactant species (Figure 1a) or to probe the reaction products (Figure 1b). Our current interest, however, is in using the laser to change the dynamics of the chemical process interactively, as suggested by Figure 1c.

There are several reasons for undertaking such an investigation. First, of course, is the fact that nature does not separate the two; molecules in a volume of gas undergoing irradiation do not stop colliding with one another. We should therefore like to have a more or less quantitative estimate of how severe the approximation is when we treat the two processes as independent. At high pressures, for example, it may be severe indeed. Of greater interest is the possibility that some particular transition between states of a reaction product might be accomplished more easily by illuminating the collision complex than by illuminating the isolated product directly. In such a case we might speak of collision-assisted laser-induced transitions. A particular instance where the effect would be very important is that in which an IR laser, incident on a reacting mixture, pumps a transition in the collision complex which correlates to a visible line in the product emission spectrum. We further note that the required matching of the field quantum with the particle-state transition energy is much less difficult during a collision than it is when the energy levels become fixed. We say that the collision acts to "tune" the separations between potential energy surfaces, and is thus able in many instances to induce resonance with the field quantum. Also of considerable interest is the possibility that apparent multiphoton absorptions are in some cases dynamically assisted single-photon steps occurring in rapid succession.^{8,9} We shall raise these points again as we proceed.

The Electronic-Field Representation

The presence of an intense, coherent radiation field complicates a molecular system in two ways: first, it distorts the electronic surfaces so that the properties

Thomas F. George is Professor of Chemistry at the University of Rochester. Following undergraduate studies at Gettysburg College, he went to Yale University for graduate work, and received his Ph.D. degree in 1970. He did postdoctoral research at Massachusetts Institute of Technology and at University of California, Berkeley, before joining the Rochester faculty. Dr. George's research centers on the theory of molecular rate processes, especially in the presence of external laser radiation.

I. Harold Zimmerman, who is a Research Associate at Rochester, received his Ph.D. degree from the University of Washington. Jian-Min Yuan and Paul L. DeVries are also Research Associates at Rochester. Dr. Yuan received his Ph.D. degree from the University of Chicago and had postdoctoral training at the University of Florida before coming to Rochester. Dr. DeVries received his Ph.D. degree from the University of Texas at Austin. John R. Laing, formerly a Postdoctoral Fellow at Rochester, is a Technical Specialist at the Xerox Corporation and received his Ph.D. degree from the University of Chicago.

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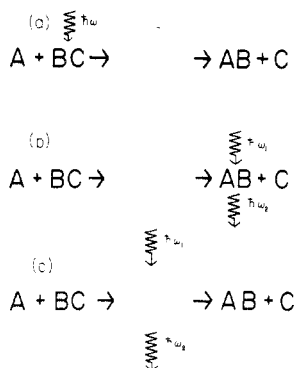


Figure 1. A representative illustration showing evolution toward the concept which motivates the present work. Interaction between the radiation field and a static chemical system is a familiar subject for research, leading to applications such as those shown in the first two lines of the figure. Laser selection of some initial reactant state, or the spectroscopic analysis of reaction products, is assumed to occur independently of any dynamical process. This view is often approximate, and during a molecular collision (for example) is generally incorrect. The present concept of electronic-field potential-energy surfaces has been developed to include processes such as that illustrated in the last line of the figure, where field-induced and dynamical effects must be treated together.

of the system are altered even if no electronic transitions occur; second, it shifts two electronic surfaces relative to one another by the field quantum $\hbar\omega$ whenever the corresponding electronic states are coupled via photon exchange with the field. As the field intensity increases and the molecular configuration varies, all electronic states tend to become coupled because of induced polarization effects. In this regime the original (electronic) labeling scheme breaks down completely and must be replaced by a scheme which treats electronic and photonic degrees of freedom more equitably. The result is the electronic-field representation. We shall see that it is also useful in many instances when field-induced polarization effects are negligible.

The simplest way to introduce the electronic-field representation is to begin with the idea of a "dressed molecule", of which the dressed atom¹⁰ is a special case. Consider a bound molecular system having time-independent energies W_1 and W_2 . A field of frequency $\omega = (W_2 - W_1)/\hbar$ is applied to the molecule. The extended system of molecule plus field now exhibits a set of pairwise degenerate energy levels W_{n1} and W_{n2} , $n = 0, 1, \dots$, given by $W_{n1} = W_1 + (n + 1)\hbar\omega$ and $W_{n2} = W_2 + n\hbar\omega$. Each pair is split by the coupling of the field to the molecular transition moment μ_{12} . Calling this coupling d for a given degeneracy pair and temporarily ignoring any other coupling we arrive at a two-state resonance approximation for the system, with Hamiltonian given by eq 1 (we subtract off the diagonal

$$H = \begin{pmatrix} W_1 + \hbar\omega & d \\ d & W_2 \end{pmatrix} \quad (1)$$

$n\hbar\omega$ term). This matrix has eigenvalues given by eq 2. By a similar procedure carried out for the next lower

$$E_2^{(\prime)} = 1/2 \{W_1 + W_2 + \hbar\omega\} \pm d \quad (2a)$$

$$= W_2 \pm d \quad (2b)$$

(10) C. Cohen-Tannoudji and S. Haroche, *J. Phys. (Paris)*, **30**, 153 (1969).

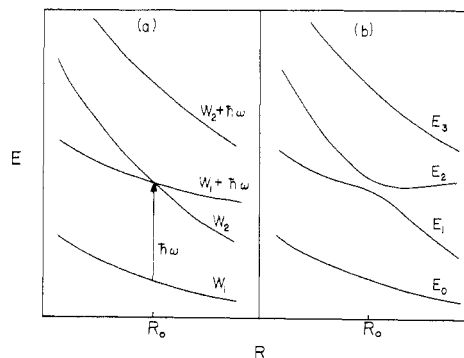


Figure 2. A sketch of two model nonreactive electronic surfaces W_1 and W_2 plus their shifted images $W_1 + \hbar\omega$ and $W_2 + \hbar\omega$ (a) and the electronic-field surfaces E_0, E_1, E_2 , and E_3 obtained from them (b). Since dynamic processes can couple the original electronic states independently of any field-induced effects, it is generally necessary to include all electronic surfaces for every photon shift. However, the limit of weak dynamical coupling makes it possible to ignore any but the two surfaces which cross. R_0 denotes the resonance transfer point in (a), which translates to the avoided crossing between E_1 and E_2 in (b).

value of n we may arrive at the energy levels given by eq 3. In this way we arrive at the energy levels for the

$$E_1^{(\prime)} = 1/2 \{W_1 + W_2 - \hbar\omega\} \pm d \quad (3a)$$

$$= W_1 \pm d \quad (3b)$$

dressed molecule.

The effect of the resonant laser field on the two-level molecule has been treated here according to the following prescription: (1) an extended molecule-plus-field system is introduced whose energy levels are pairwise degenerate as a result of the particular value chosen for ω ; (2) coupling between any but a degenerate level pair is ignored (the resonance approximation); (3) a new set of system energy levels is then obtained by diagonalizing each resulting 2×2 Hamiltonian. Within the validity of the resonance approximation, these new levels represent the allowed energy eigenvalues of the extended system.

The same prescription is used to derive the electronic-field representation, with certain adjustments.²⁻⁷ The most important modification is the introduction of coordinate dependence in the electronic energies and coupling terms. The electronic-field representation thus applies to a dynamic particle system, whereas the dressed-molecule approach assumes that the particle system is static. Using the new representation, we are able to treat many problems in the intense field limit that previously could be approached only if the field were weak. Most importantly to us, we can also investigate the effects of intense fields on molecular scattering systems.

A simple collision is depicted in Figure 2a, in which R is a generalized scattering coordinate and W_1 and W_2 are now a pair of electronically adiabatic surfaces. A field of frequency ω is superimposed on the scattering process. Again invoking the resonance approximation, we say that the principal effect of the field will be to cause transitions between W_2 and the shifted $W_1 + \hbar\omega$ surface, provided ω be chosen so as to cause these two curves to cross at some point R_0 . The location of R_0 will depend on the shapes of W_1 and W_2 as well as on ω . We should point out that the resonance condition is utilized here as a criterion as to which electronic surfaces are

likely to be important in the radiative transition.

The electronic states ϕ_1 and ϕ_2 associated with the surfaces W_1 and W_2 , respectively, are coupled by the kinetic energy operator as well as by the interaction between their coupling moments and the field. For this reason we not only include the two surfaces that come into resonance at R_0 but also the unshifted W_1 and the shifted $W_2 + \hbar\omega$ surfaces in Figure 2a. This addition represents a further departure from the procedure outlined for the dressed molecule, where no coupling existed in the absence of the field. However, if the dynamic coupling is weak, then we may approximate further and retain only the crossing surfaces $W_1 + \hbar\omega$ and W_2 together with the field-coupling d_{12} . The resulting Hamiltonian matrix may be diagonalized as before to yield the simplest possible set of electronic-field surfaces:

$$E_j = \frac{1}{2} \{ W_1 + W_2 + \hbar\omega + (-1)^j \sqrt{(W_2 - W_1 - \hbar\omega)^2 + 4d_{12}^2} \}, j = 1, 2 \quad (4)$$

We emphasize that, because of the coordinate dependences of W_1 , W_2 , and d_{12} , the electronic-field energies are not constant.

When it is not possible to ignore dynamically induced transitions, we have to consider the 4×4 Hamiltonian of eq 5, whose diagonal elements are the surfaces

$$H = \begin{pmatrix} W_1 & 0 & d_{11} & d_{12} \\ 0 & W_2 & d_{21} & d_{22} \\ d_{11}^* & d_{21}^* & W_1 + \hbar\omega & 0 \\ d_{12}^* & d_{22}^* & 0 & W_2 + \hbar\omega \end{pmatrix} \quad (5)$$

sketched in Figure 2a. Diagonalizing this matrix yields the electronic-field surfaces of Figure 2b. Note the presence of d_{11} and d_{22} in eq 5. These couple the adiabatic electronic states back to themselves, leading to exchange of a photon with the field without an accompanying transition between electronic states. If we ignore these terms (which we may not justify doing except on the grounds of convenience), then we have H' :

$$H' = \begin{pmatrix} W_1 & 0 & 0 & d_{12} \\ 0 & W_2 & d_{21} & 0 \\ 0 & d_{21}^* & W_1 + \omega & 0 \\ d_{12}^* & 0 & 0 & W_2 + \hbar\omega \end{pmatrix} \quad (6)$$

The 2×2 block in the center of the H' matrix is seen to be decoupled from the rest of the Hamiltonian and may be diagonalized to yield E_1 and E_2 just as given in eq 4; however, there is still the electronically nonadiabatic coupling to be taken into account. This added consideration keeps us from treating the reduced problem as the simple two-state system described earlier. Ignoring dynamical effects requires the additional assumption that they be negligible, as we have stated.

The electronic-field representation has been described and applied elsewhere, and we refer the interested reader to those papers for further detail.^{2,7} In the remainder of the present discussion we hope to show how this representation may serve to elucidate many features of the interaction between radiation and matter.

Bound Systems

We now discuss the effects exerted by an intense laser on a bound molecular system. By an intense field we shall mean a field sufficiently strong that its effects cannot be adequately described within the context of perturbation theory. In such cases we shall find it necessary to combine the idea of an electronic-field state representation with the techniques of ab initio determination of electronic-state functions and energies in molecules. This remark will be enlarged upon shortly. The following topics will then be of interest: (1) distortion of the molecular equilibrium configuration, (2) reorientation of the molecule, and (3) symmetry considerations. These same points will also require our attention when we discuss scattering systems later in this paper.

The coupling of different electronic states by the intense laser field leads to the absorption and emission of radiation. Of prime importance is the case where virtually all electronic states are coupled to one another by the field. For such a situation the original electronic labeling becomes useless as a means for describing the state of the system, and the whole task of defining energy levels and corresponding eigenfunctions has to be repeated. We therefore go to the electronic-field representation as extended to cover the present, more general situation.

Instead of just two electronic energy levels we assume that there are many, given as functions of the nuclear configuration which we specify by the generalized vector \mathbf{r} :

$$H_{e1}\phi_m(\mathbf{x},\mathbf{r}) = W_m(\mathbf{r})\phi_m(\mathbf{x},\mathbf{r}) \quad (7)$$

where \mathbf{x} is a notation intended to denote the collective coordinates of all electrons. The electronic-field state Φ_k is then given by the sum

$$\Phi_k(\mathbf{x},\mathbf{r}) = \sum_{mn} c_{kmn}(\mathbf{r})\phi_m(\mathbf{x},\mathbf{r})|n\rangle \quad (8)$$

and the extended Hamiltonian is

$$H = H_{e1} + H_{\text{rad}} + H_{\text{int}} \quad (9)$$

In eq 8, $|n\rangle$ is the n th number state of the Fokker-Planck representation for the field while in eq 9 H_{rad} is the free-field Hamiltonian for the laser beam and H_{int} represents the particle-field interaction. Various requirements can be made which serve effectively to limit the sums over m and n to specified ranges in eq 8, whereupon the coefficient functions c_{kmn} can be determined variationally. The procedure is very much analogous to that used in calculating ab initio energies and wave functions for the electronic problem alone. The addition of the field thus would seem to present no insurmountable barriers to the ab initio approach.

It is very likely that the equilibrium geometry of the molecule will change greatly in the presence of an intense field. That is, the lowest lying electronic-field surface $E_0(\mathbf{r})$ will generally have quite a different structure from that of $W_0(\mathbf{r})$. It should be possible to obtain some qualitative idea of what the new equilibrium configuration looks like for a given molecule (provided its dynamics are sufficiently well detailed) simply by noting where the field-shifted curves cross and how strong the coupling is at such points. Nuclear eigenstates consistent with E_0 should also be obtainable in some simple models, but it is not clear how relevant

to real systems such models might be. For example, it is common to think of the ground-state vibrational energy of a diatom as undergoing a uniform shift $\Delta_0\epsilon$ under the influence of a field:¹¹

$$\Delta_0\epsilon = \mu_0 \cdot \mathbf{E} + \mathbf{E} \cdot \bar{\alpha}_0 \cdot \mathbf{E} + \dots \quad (10)$$

Here, μ_0 and $\bar{\alpha}_0$ are the (linear) dipole moment vector and (constant) polarizability tensor, respectively. In reality, however, neither of these quantities has so simple a dependence on the nuclear configuration. Indeed, the expansion for $\Delta_0\epsilon$ becomes asymptotic as \mathbf{E} increases. Thus we cannot expect eq 10 to be even approximately valid for sufficiently strong fields. Not only is the surface shifted in the electronic-field limit, it is also distorted. Therefore the new nuclear eigenstates will not only be shifted in energy relative to the old, but will also be shifted relative to one another. We do not yet have a hand a simple way to model this aspect of the combined system, but with the aid of the electronic-field representation we are able to understand how it occurs.

If the photon frequency is much greater than the rotational frequency of a dipolar molecule, we should expect the rotational state to be largely unaffected by the presence or absence of the field. The successive torques applied to the dipole would come so rapidly as to average out to zero over a rotational period. In this limit the field has little chance of bringing about a net reorientation of the molecule. However, if the two frequencies are made to match for some rotational state J , and if the field is circularly polarized, then rather interesting effects might result. For example, we should expect the molecule to lock quickly into phase with the driving frequency, even though the chosen rotational level might be well away from that most populated in the absence of the field, simply because the strong field would override all competing influences. It is tempting to envision a host of molecules spread throughout some appreciable volume, all rotating in perfect phase with one another. If feasible, such a low-frequency laser might then be used to orient a target system and simultaneously to trigger the discharge of a second, higher energy laser, also polarized, in such a way that the triggered pulse would strike the target system just as the slave dipoles came into some optimally receptive alignment.

An intense, linearly polarized laser beam will define a preferred axis of quantization in its path. Spherical symmetry ceases to be possible under this circumstance, so that no electronic-field function Φ_k can correspond to an S state or to any other symmetrically filled atomic orbital. It is rather difficult to say anything further about the symmetry of the electronic-field states except in certain rather limited instances.

One such instance is the case in which a model two-level molecule interacts solely with the incident field. If the field dipole couples the two electronic states (call them A and B), then they must represent functions of mixed or opposed parity with respect to inversion of at least one of the coordinates in the interaction Hamiltonian H_{int} , which we write as

$$H_{\text{int}} = e \sum_i \mathbf{x}_i \cdot \mathbf{E} \quad (11)$$

in the electric dipole approximation. The sum is over all electrons. Only one electron will go from one orbital to another in our model, so that the two molecular orbitals that distinguish the two electronic states must have opposite parity. At the same time that the electronic transition occurs, a photon is exchanged with the field, so that the field states involved also have opposite parity in some sense. It is therefore evident that, for this model, we conserve a generalized system parity when a transition occurs; a symmetry rule is operating. Further, since we have limited ourselves to resonant energy exchange between the electronic and field modes of the system, we may write the electronic-field states as two-term sums:

$$\Phi_k(\mathbf{x}, \mathbf{r}) = c_{k1}(\mathbf{r})\phi_1(\mathbf{x}, \mathbf{r})|n+1\rangle + c_{k2}(\mathbf{r})\phi_2(\mathbf{x}, \mathbf{r})|n\rangle \quad (12)$$

where

$$c_{11} = c_{22} \quad (13a)$$

$$c_{21} = c_{12} \quad (13b)$$

The space symmetry of these functions is already seen to be mixed, even for so simple a case as that treated here. However, we can point to the fact that, since the exchange symmetry of the states is approximately conserved, the associated potential-energy surfaces E_1 and E_2 do not cross. This observation is still useful in the case of many electronic surfaces, provided the electric dipole matrix elements $\{\langle \phi_m | \mu | \phi_n \rangle\}$ are strong and the corresponding field-induced crossings between pairs $\{W_m + \hbar\omega, W_n\}$ are sufficiently isolated from all other such crossings.

This picture is also useful in helping to explain how multiphoton transitions might occur in molecules. If the nuclear motion is such as to create electronic transition resonances with the field at various accessible geometries, then photon exchange becomes highly favored there provided the nuclear motion may be treated as adiabatic. As the molecule becomes more excited, nuclear excursions become wider ranging. The chances of entering into configurations favoring interaction with the field therefore increase, leading to more rapid photon exchanges. In terms of the electronic-field surfaces, we would say that an increasing number of avoided crossings are to be expected as we approach the dissociation energy of the molecule. This view offers a dynamical explanation for the multiphoton dissociation of molecules.⁸ Some remarks may also be made regarding multiphoton processes that do not lead to dissociation. These are deferred to later in this paper.

Scattering Systems

In previous work²⁻⁵ we have utilized the electronic-field representation in connection with scattering problems.⁷ However, the model system treated there is sufficiently specialized that a more general discussion is called for. Part of that discussion has already been given previously in this paper. Now, we consider additional features of the representation that are specifically applicable to unbound systems.

Our original model system was characterized by two electronically adiabatic curves that decreased monotonically with increasing R , as in Figure 2a. The separation between the two curves likewise decreased monotonically as R grew. In this way we assured

(11) M. P. Bogaard and B. J. Orr, *MTP Int. Rev. Sci.: Phys. Chem., Ser. Two*, 2, 149 (1975).

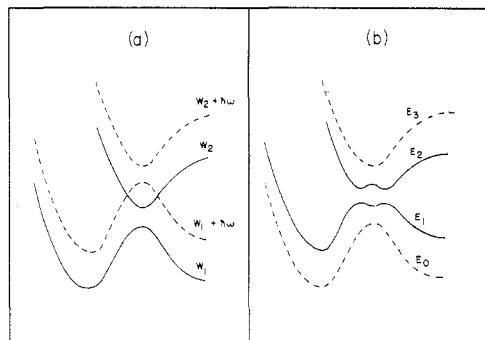


Figure 3. A sketch of two model nonreactive electronic surfaces W_1 and W_2 plus their shifted images $W_1 + \hbar\omega$ and $W_2 + \hbar\omega$ (a) and the resulting electronic-field surfaces E_0 , E_1 , E_2 , and E_3 obtained from them (b). This figure illustrates the utility of the electronic-field approach in clarifying the dynamical behavior of a more complicated scattering system undergoing irradiation.

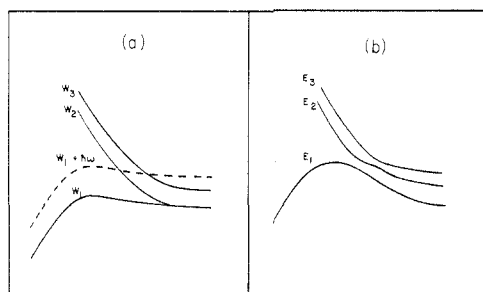


Figure 4. A sketch of three model electronic surfaces, one of which (W_1) is reactive, plus the shifted image $W_1 + \hbar\omega$ of the reactive surface (a). If the dynamical coupling of the corresponding electronic states is negligible, then the relevant electronic-field surfaces are those illustrated in (b). Here, E_1 correlates to W_2 asymptotically far to the right, E_2 similarly correlates to W_3 , and E_3 to $W_1 + \hbar\omega$. It is evident that the intense field can greatly inhibit reaction for this system when the initial electronic state corresponds to W_1 , while assisting reaction from W_2 and (to a lesser extent) W_3 .

ourselves of a single curve crossing when the field was added. Further, we noted that the intersection of the relatively shifted curves moved either inward or outward when we respectively increased or decreased the energy of the field quantum.

In reality, we expect a multitude of electronic surfaces to enter in, just as in the bound molecular case. These surfaces will hardly exhibit a generally monotonic behavior of any sort, and we can therefore anticipate instances when a given pair of them, shifted by the proper photon frequency, will exhibit more than one crossing. Instead of the relatively simple situation illustrated in Figure 2, we might then have something similar to Figure 3. The problem is still nonreactive, but the electronic field surfaces of Figure 3b are now much more structured than before.

Another complicating possibility is illustrated in Figure 4, where a shifted electronic surface crosses two other surfaces. In the particular example chosen, the surface W_1 is exothermic with respect to reaction while W_2 and W_3 are not. Should imposing the field couple the corresponding electronic states with sufficient strength, we would then expect the electronic-field representation to yield surfaces as depicted in Figure 4b. Comparing Figures 4a and 4b, we see that the field serves greatly to inhibit reaction starting from the right on the shifted $W_1 + \hbar\omega$ (E_3) surface, while enhancing the likelihood of reactions starting out on both W_2 and

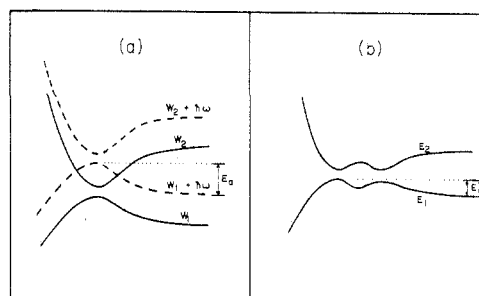


Figure 5. A sketch of two model electronic surfaces W_1 and W_2 plus their shifted images $W_1 + \hbar\omega$ and $W_2 + \hbar\omega$ (a). The lower member of each pair is reactive, but interaction with a field of suitable frequency can lead to loss of concertedness along the reaction coordinate as suggested by the well that appears on the lower electronic-field surface E_1 in (b) (E_0 and E_3 have been omitted for clarity).

W_3 (E_1 and E_2). It is obvious that reactivity from the ground electronic state Φ_1 is further damped for every additional surface crossed by $W_1 + \hbar\omega$, while reactivity from the intersected surfaces tends to increase. The field thus acts to lessen the distinction between what might otherwise be definitely reactive or nonreactive electronic states.

For the electronic surfaces sketched in Figure 5, we can even expect to see a concerted reaction become nonconcerted as the strong field is imposed. An exothermic process of activation energy E_a will probably retain about the same exothermicity in the presence of the field as it had before, but the activation energy will drop considerably for the example shown. The lessened barrier allows for more rapid tunneling in low-energy collisions, but the well in the lower electronic-field surface will trap the system and cause it to lose memory of its direction along the reaction path.

If a reaction can proceed along alternate pathways, the field can have yet another very important dynamical effect. Consider one reaction pathway to be represented by Figure 4 and another by Figure 5. From what we have seen, it is immediately obvious that a strong field of the right frequency will drastically alter the branching ratio for these two mechanisms. The effect is still likely to be important even for less starkly differing mechanisms, because reaction rates are sensitive to rather modest variations in the shape of the activation barrier. Even if only a single electronic surface is important in a particular reaction channel, the field can significantly alter its shape. If the molecular configuration at the transition state of a particular reaction channel has a large dipole moment or polarizability, it will be stabilized in the field and E_a will thus be lowered.¹² Also, if reactant and product species exhibit different permanent and induced dipoles, then we should expect the field to change the exothermicity of the reaction.

Symmetry rules^{13,14} with which to analyze chemical reaction dynamics (e.g., Woodward-Hoffmann rules) are based on the symmetry properties of the molecular configuration at the transition state.¹⁵ When a linearly polarized field is imposed on a reaction, the symmetry group that applies to the transition state will be of lower

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order than is true in the absence of the field unless the polarization vector happens to coincide with one of the symmetry axes of the activated complex. The symmetry rules that apply must therefore be based on the symmetry of the particle-plus-field system. This requirement may be relaxed when the field is a perturbation, but as the field intensity grows we can no longer take the electronic symmetry breaking to be small. What symmetry rules still apply must then be determined for each system under consideration.

Special Topics

Other field-induced effects are of interest and can be treated in our theory. We mention some of them here.

(a) Multiphoton Processes.^{7,8} For the most part, we have limited our discussion to cases in which only a single-photon process occurs. We now consider the possibility that two or more photons are exchanged with the field during a collision. Our attention is restricted to cases in which each photon exchange occurs independently of any other. For this class of problems, our approach is quickly applicable after a suitable (and simple) generalization.

For each additional photon exchange, an additional set of shifted electronic surfaces is included, with the magnitude of the shift equal to the number of field quanta involved. For example, in Figure 2a there was one set of shifted surfaces for the single-photon process. If a second photon is exchanged, then a further set of surfaces, shifted by two field quanta, is added. The resulting Hamiltonian matrix (including all relevant couplings) is then diagonalized to obtain the new electronic field representation. Subsequent treatment of the system dynamics then follows as usual. This approach should be useful when the number of exchanged photons remains small, but for large numbers of photons a different approach seems called for.

(b) Emission. In many cases, photon emission is as important as absorption in providing information about molecular structure. Even when structure per se is not of primary interest, a proper understanding of the emission process is desirable for its own sake.

When treating emission in the presence of an external field, it is usual to treat the emitter and the allowed modes of emission as comprising a system which the incident beam then perturbs.¹⁶ However, when the incident beam is very intense it seems reasonable to revise this approach. We pass first to the electronic-field representation, and then treat emission as a perturbation on the resulting system. Because we include dynamical motion on the electronic-field surfaces, we expect to ascertain which system configurations are most likely to emit. It should then be possible to determine the emission spectrum, at least for some simple models. This approach, presently under study in our laboratory,¹⁷ yields a problem very similar to that posed by Penning ionization¹⁸ when we pass to the limit of an emission continuum. [This approach can also be used to study chemiionization in an intense laser field.¹⁹] The emission peaks at a given configuration

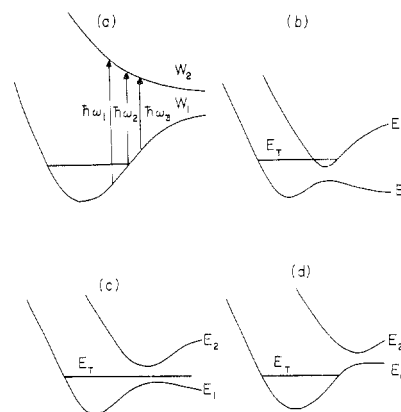


Figure 6. A sketch of two model electronic surfaces W_1 and W_2 together with the energy quanta of three candidate fields characterized by frequencies ω_1 , ω_2 , and ω_3 (a). The corresponding electronic-field surfaces are shown in (b), (c), and (d), respectively. For a given energy level E_T of the field-free system, frequencies that fall in the ω_2 class appear likely to maximize the probability for field-induced dissociation. This conclusion supports the Franck-Condon principle.

will center about those transitions between electronic states which leave the "instantaneous" translational energy invariant.

(c) Photodissociation. Unimolecular photodissociation in the intense laser field^{20,21} takes on many of the characteristics of type I predissociation²² in that the field-shifted lower surface crosses some number of unshifted upper ones. For a diatomic molecule characterized by one bound and one repulsive state, the corresponding field-free surfaces might resemble those sketched in Figure 6a as functions of the internuclear separation R . The horizontal line denotes the level of a vibrational state in the absence of the field and thus indicates the total energy of the field-free system.

We now consider what happens when a field of frequency ω_1 , ω_2 , or ω_3 is switched on. The magnitudes of the candidate field quanta are indicated in Figure 6a, and the resulting two-state electronic-field surfaces are sketched in Figures 6b, 6c, and 6d. The total energy is marked at E_T in each case.

In Figure 6b the field quantum $\hbar\omega_1$ is so great that E_T lies above the minimum of E_2 . Therefore the system will spend part of its time in the excited state well, and in fact can interact with the well at certain energies in such a way that the overall lifetime of the complex will tend toward an extreme maximum. Even away from such resonances, the excited-state well will tend to inhibit dissociation.

For our second candidate frequency, the field quantum $\hbar\omega_2$ shifts the lower surface in Figure 6a so as to cause the crossing to occur at the bound-state turning point. The resulting electronic-field surfaces are shown in Figure 6c. It is clear that the system is most likely to dissociate in this instance, especially if the field generates a strong coupling between the two original electronic states (the stronger the coupling, the greater the separation between E_1 and E_2 at the avoided intersection).

Finally, in Figure 6d we see the result when the field quantum $\hbar\omega_3$ leads to a crossing of the two surfaces at

(16) R. Loudon, "The Quantum Theory of Light", Oxford University Press, London, 1973, Chapter 8.

(17) K. S. Lam, I. H. Zimmerman, J. R. Laing, J. M. Yuan, and T. F. George, to be published.

(18) W. H. Miller, *J. Chem. Phys.*, **52**, 3563 (1970).

(19) J. C. Bellum, K. S. Lam, and T. F. George, to be published.

(20) R. N. Zare, *Mol. Photochem.*, **4**, 1 (1972).

(21) J. M. Yuan and T. F. George, *J. Chem. Phys.*, submitted.

(22) M. S. Child, *Mol. Spectrosc.*, **2**, 466 (1974).

a point outside the classically permissible range of R . The complex can be trapped behind the barrier on E_1 for a long time, again leading to a reduced rate of dissociation compared to the preceding example. Indeed, for $\hbar\omega_3$ sufficiently small there will be no dissociation, as the relative shift of the two surfaces need not bring the vibrational level of our example above the dissociation threshold.

This analysis of photodissociation based on electronic-field surfaces is consistent with the Franck-Condon principle, but it is not quantitative at the present stage. However, quantitative predictions are possible with the electronic-field approach, and we are presently testing it on some model systems. We note, for sufficiently weak coupling between two electronic states of a diatom such as those treated here, that the range of frequencies in the ω_2 class is rather narrow. It

is therefore possible that photodissociation of a diatom could exhibit some isotopic selectivity. That is, the vibrational levels of a diatom will shift as different isotopes are included, leading us to speculate that a laser of the proper frequency might excite one isotope to the "dissociation window" while raising others either too high or too low. We would not expect this mechanism to be extremely selective, but when used as the second stage of a laser isotope separation process it might prove useful nevertheless.

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Additions and Corrections

Volume 10, 1977

Geoffrey A. Ozin: Metal Atom Matrix Chemistry.
Correlation of Bonding with Chemisorbed Molecules.

Page 22. The following correction should be made in the caption to Figure 1: Change reference citation 1b to 6a.