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FEATURE ARTICLE

Nonstationary Electronic States and Site-Selective Reactivity

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An efficient route to the site-selective reactivity of electronically excited states of multicentered molecules is discussed. In the first stage the migration of the electronic excitation occurs. This can operate over an extensive range without extensive draining of energy into the nuclear frame. Only in a second stage, once the optimal site has been reached, does the excess energy become available for bond breaking or isomerization at the new, optimal, site. This two-stage mechanism, where electronic excitation (or the charge) is the scout, avoids the pitfall of conventional large molecule kinetics. (In that view, known as the quasi equilibrium theory, the electronic excitation is first converted to nuclear modes. But then there are so many available vibrational states that the probability for the excitation energy to become localized at the necessary site is too small and the resulting reaction rate is too slow.) By confining the site search to the electronic manifold, it becomes a highly efficient process. The recent novel experiments of Weinkauf et al. on (positive) charge migration and dissociation of peptide ions are suggested as an example of the considerations above where there is a facile migration of the positive charge followed by reactivity at the selected site. The peptide is modeled as beads on a chain. Interbead and intrabead coupling are discussed in terms of adiabatic and diabatic states. We find a multistep mechanism (unlike superexchange): a charge-directed reactivity (CDR) model. Such efficient ranging could also take place in other chain structures and suggests that there will be examples where electronic processes set the time scale for the chemical change.

I. Introduction

We discuss two central questions that arise in understanding the reactivity of excited large, multicentered molecules and propose a new mechanism that addresses both issues together. The first question is how does the energy needed to, say, break a bond, become localized if initially it is distributed over the very many degrees of freedom of the large molecule? The other is how is the site of reactivity selected, particularly in a molecule with several possible such sites. Our proposal is that reactivity follows charge (or, in general, electronic excitation), and the purpose of this paper is to explain the concept of electronic excitation (or, specifically, the charge) as a scout and why it answers the questions raised above, to show how this mechanism differs from the conventional approach, and to provide an overview of the experimental and theoretical considerations that led us to this proposal and to its limitations. Occasionally we also comment on the possible directions for additional applications and for further development of the main ideas.

We will specifically discuss the recent experiments of Weinkauf et al.[1,2] In the background is the following earlier experimental observation: Ions of small and intermediate sized peptides, which contain a relatively low excess energy (corresponding to the absorption by the ion of one or two visible photons), do dissociate at a measurable rate.[3−6] The dissociation occurs at one or more sites which are known to be peptide bonds of low dissociation threshold.[3,7]

From an RRKM point of view, the result that peptides with comparatively low excess energy do dissociate at a measurable rate is surprising.[4] Even small peptides are large enough that the excess energy is distributed over very many degrees of freedom. The density of vibrational states, $\propto E^{s-1}$ (crude RRK estimate) increases so fast with the energy E or with the number s of vibrational modes that the localization of a finite fraction, E_0, of E in the bond to be broken is of very small measure, viz., $((E - E_0)/E)^{s-1} = (1 - E_0/E)^{s-1} \approx \exp(-E_0/(E/s - 1))$. A peptide such as Leu-Leu-Leu-Leu-Trp with five amino acid residues already has $s \approx 300$ so that with low excess energy the ion is not expected to dissociate in a mass spectrometer. More quantitative estimates of the density of states[8] confirm this conclusion.

Insofar that repeated experiments verify that positively charged peptide ions, which are initially not hot, do fragment when their energy content is not much above the threshold value, E_0, requires that an explanation be provided. (Examples, as shown in Figure 1, include $(Leu)_4$-Trp,the hexapeptide shown in Figure 2, and even larger structures.[3])

Figure 1 adds another, and equally challenging, part to the puzzle: It is demonstrated by Weinkauf et al. that the peptide ions can dissociate at a site far away from the initial ionization

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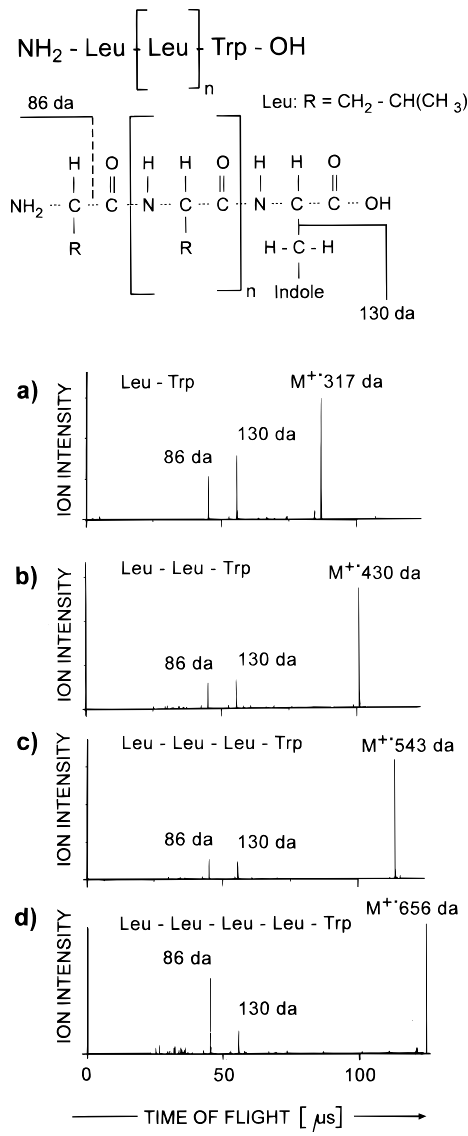

Figure 1. The mass of 86 Da is the fragmentation at the N-terminal (departure of the leftmost leucine as a positive ion, i.e., $H_2{-}N^+{=}CH{-}R_{leu}$ loss, $R_{leu} \equiv CH_2{-}CH(CH_3)_2$). The mass of 130 Da is the fragmentation to a positively charged chromophore ion (R_{trp}^+ loss, $R_{trp}^+ \equiv CH_2{-}\text{indole}^+$). In these experiments the UV laser intensity is 5×10^6 W/cm^2, and the experimental parameters have been kept constant to within experimental error, for all four cases shown. That even for the smallest peptide, case a, there are only two fragmentation channels indicates that the internal energy cannot be too high. It is estimated that one UV photon of 4.5 eV is absorbed by the peptide cation, cf. Figure 3. The N-terminal fragmentation channel, where the leftmost fragment departs as an ion, requires charge migration, yet its yield increases with peptide length. See Figure 2 for the case where the N-terminal channel is the dominant fragmentation mode.

which is localized at the aromatic chromophore. Moreover, the departing ion is such that charge has necessarily moved from the chromophore, which is at one end of the peptide, to the N-terminus at the other end. These experiments, which demonstrate site-selective reactivity, are discussed in section II.

We emphasize that we are considering positively charged peptide ions formed by ionization of the closed shell neutrals (i.e., odd electron systems). These ions are unlike the even electron systems used in those experiments where charged biomolecules are formed by attaching a closed shell ion to the neutral, e.g., protonated molecules.

The first issue we thus need to address is how does the large molecule manage to overcome the high entropic barrier to dissociation; how, despite the low entropy of the transition state,

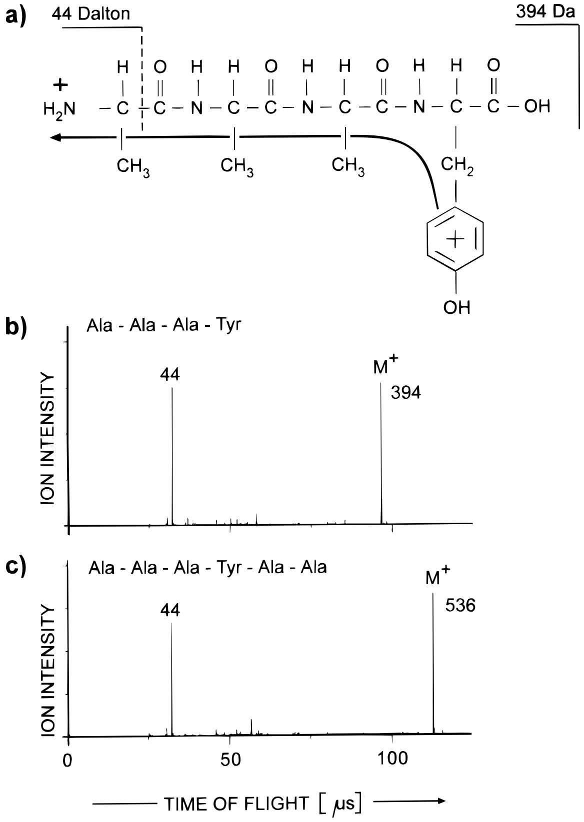

Figure 2. Same as Figure 1 but for the peptides (Ala)$_3$-Tyr (b), and (Ala)$_3$-Tyr-(Ala)$_2$ (c). Here the mass spectrum is primarily either that of the parent ion or, at mass 44 Da, due to the loss of the leftmost alanine as a positive ion (a), drawn for the smaller peptide (Ala)$_3$-Tyr. For either peptide, whether the chromophore is on the right or in the middle, the dissociation channel is the loss of a positive ion from the N-terminal on the left. Note that (Ala)$_3$-Tyr-(Ala)$_2$ is a hexapeptide, yet it undergoes facile dissociation.

where the energy is localized, the system manages to reach it from the state of much higher entropy where the energy is spread over many degrees of freedom. Clearly the solution that we will favor is that the very description above contains a logical shortcoming. Yet the assumption that the bottleneck to dissociation is a region of low entropy seems inevitable. It does take energy to break a bond, and once localized in the bond to be broken, this energy is not available for distribution among the entire manifold of vibrational modes. If at the transition state the balance of the energy, $E - E_0$, is not uniformly distributed, then the entropy of the transition state is even lower, which only makes matters worse. The only way out that we could see[4] is that the assumption that, to begin with, the entire available excess energy E is distributed over all the vibrational degrees of freedom is at fault. This key assumption of the conventional approach to unimolecular dissociation must be modified.

The proposal that the excess energy is not spread among the many vibrational modes does however raise two immediate questions. (i) If the energy is not distributed among all the vibrations, then where is it? and (ii) How does it ultimately get to the vibration and, in particular, how does it get to the site where dissociation occurs? The purpose of this paper is to discuss these two questions and to propose possible answers on the basis of the recent series of experiments of Weinkauf et al.[1,2]

Implicit in the above questions are two notions that would be worth understanding also within the more general context of reactivity of molecules. One is the notion of site selectivity, and the other is the quiescent period until that site is selected. If one can identify what is involved, it might be possible to apply it to other ionic systems[7,9−11] and to photoselective processes[12] in large systems in general.

There are more global considerations which suggest that the questions we address are worthwhile. The essence of the first problem is that there is a process with a seemingly very high entropy barrier, and yet this process is observed to take place. In other words, the system does find a way to avoid the high entropy barrier. We show here that the system manages to reach the same final state but by a completely different route. There are other examples with a similar characteristic, namely, that a seemingly very improbable process does occur. Possibly, our understanding of the present class of examples may help in seeking a solution for other classes (the most familiar example of which is probably the "Levinthal paradox" in the kinetics of protein folding. See ref 13 for a recent perspective) and eventually provide a more global view.

The alternative route for avoiding the entropy barrier in the conventional approach is the here proposed mechanism for electronic control of reactivity without concomitant nuclear relaxation. This gives rise to another possible generalization. It suggests that it might be of interest to think prior to nuclear motion as setting the time scale for chemistry: that there may be an electronic time scale which, as in the Weinkauf examples, determines site selectivity, prior to the onset of the rearrangement of the nuclear skeleton, a rearrangement which ultimately appears as the chemical change.

Section II discusses the system and begins to explore the notion of charge localization. We discuss first the Weinkauf et al. experiments[1,2,14] and then a simple model of a peptide as beads along a chain. This model, as presented in sections II−IV, does not do full justice to the degree of detail that can be extracted by the experiments, and we refer to a forthcoming review[15] for a more refined discussion of the energetics. Three kinds of nonstationary electronic states are discussed in section III. One is the usual Born−Oppenheimer (or adiabatic) kind of electronic states. These are nonstationary due to the motion of the nuclei. The second kind is the diabatic basis where states are nonstationary due to electronic coupling. For the present application we propose a third basis, which is a mixed version. This special version is nonstationary due to interbead electronic coupling and is also nonstationary due to intra-bead nuclear motion. Section IV is a qualitative discussion of the anticipated theory presented in section V. In section VI we discuss a more general case where the charge migrates back and forth between the different beads. An extreme limit of this case is a random motion of the charge along the chain. In terms of the interconversion of electronic and vibrational energy, we have the limit of section V where to begin with charge migration occurs with little draining of energy into the nuclear modes. Only after this ranging does reactivity occur. The opposite limit is the fast relaxation of the electronic energy as in the quasi equilibrium theory,[16−18] where the nuclear modes act as a sink. Intermediate between the two extremes is the ongoing exchange between the two sets of modes, a limit whose one familiar manifestation is "inverse electronic relaxation".[12] Section VII provides concluding remarks.

II. Peptide Ions in the Gas Phase

The new experiments of Weinkauf et al.[1,2] shed additional and specific light on the problem of site-selective reactivity. In particular, these experiments suggest an alternative, electronic, mechanism. This is due to the presence of a (positive) charge and hence to a highly efficient charge transfer in the peptide ion which is excited above a (low) threshold energy. Reactivity then follows the location of this charge (≡hole). In other words, the dissociation is slower than the charge migration and is governed by it, hence a charge directed reactivity (CDR) model. This separation of time scales will be shown to be a key ingredient in overcoming the entropy barrier to dissociation in the conventional approach, which arises from the assumption that energy randomization among the vibrations precedes dissociation. It is also this separation that introduces an electronic time scale which precedes nuclear rearrangement.

The experiments are performed on cooled small and intermediate sized tailor-made peptides in the gas phase. These can be ionized site selectively by using peptides with an aromatic chromophore (say, tyrosine or tryptophan) at one end. Without further photoexcitation the ion is stable. Photodissociation can be induced by a further resonant UV absorption of the aromatic chromophore. Weinkauf et al. have extensively studied the localization of the initial charge, including by time-resolved experiments.[14] They have furthermore presented extensive evidence for the photoactivation of the charge migration. Their work is reviewed in ref 15.

Weinkauf et al. have interpreted their observations in terms of an initially localized charge on the chromophore followed by charge migration along the peptide backbone, like a beaded chain. At threshold, this migration and its final point of arrival have been shown to be strongly dependent on the sequence of the peptide. The process can be terminated by the presence of a suitable amino acid along the skeleton of the peptide. This shows a strong near-neighbor coupling and only a weak long-range coupling. By the experimental evidence, the charge migration is fast as compared to the nuclear deformation of the peptide. Therefore the reactivity will follow the charge, both in time and in terms of its spatial location. Typical experimental results are shown in Figures 1 and 2.

Figure 1 shows the UV ionization/UV dissociation mass spectra of the series of peptides $(\mathrm{Leu})_n$-Trp, $n = 1-4$. We write the sequence of amino acids in the peptide in the conventional order so that the NH_2 group is attached at the left ("the N terminus") and the OH group is on the right. Two competing fragmentation channels are found: a chromophore channel, where the charge stays at the chromophore, and an N-terminal channel, where dissociation occurs at the other end of the peptide, with the charge at the N-terminus. The N-terminus dissociation channel dominates for the same experiment carried out for the peptides $(\mathrm{Ala})_3$-Tyr and $(\mathrm{Ala})_3$-Tyr-$(\mathrm{Ala})_2$, as shown in Figure 2.

The N-terminal channel provides direct evidence that the charge has moved across the peptide, from the chromophore to the N-terminus at the left end. Note that for the peptides $(\mathrm{Leu})_n$-Trp and $(\mathrm{Ala})_3$-Tyr the chromophore is at the other end from the N-terminal, while for $(\mathrm{Ala})_3$-Tyr-$(\mathrm{Ala})_2$ the chromophore is in the middle.

Other relevant experiments include those of Chattoraj et al.[19] on charge migration in bichromophoric molecules and, more in general, excitation transfer in bichromophoric systems[20] and under solvent-free conditions.[21] Here however we are specifically concerned with the notion that reactivity follows charge, namely, that the system can achieve site selectivity by using the charge as a scout, thereby avoiding the high entropic cost of searching for the weak bond in the vibrational energy landscape.

That the site search process does not involve extensive nuclear relaxation also explains why it is not sensitive to the very many possible conformations of the peptides. It is of course these many states (see the low-frequency peak in Figure 1 of ref 5) that make the problem that once the energy is delocalized over the many vibrational modes, there arises an entropy bottleneck for energy relocalization in the bond to be broken.

Toward the interpretation of charge migration, Weinkauf et al. suggested a zero-order picture of the peptide as a chain of beads, each bead with its own ionization potential. Specifically, the peptide is a stringlike structure, having functional groups of low IP separated by saturated carbon bridges. The local energetics are assumed to be similar to their smaller analogues as determined by He I photoelectron spectra. The correlation between charge transfer and local electronic properties could be demonstrated by experiments on specially designed peptides. These, as well as studies of the energetic threshold to charge transfer from the aromatic chromophore are reviewed elsewhere.[15] Here we just note that all these studies provide strong evidence of through bond multistep charge migration.

The aim of this paper is to set up a description of charge-driven reactivity. To do so, we consider a model system of beads along a string, where, initially, the charge is localized at one end. We will, of course, have to consider the role of the nuclear degrees of freedom, and we shall do so below. We shall also have to recognize that the beads are not structureless. Before bringing all these essential complexities in, we consider a simplistic and purely electronic situation.

For a stringlike structure, at the crudest, tight binding, approximation, the electronic Hamiltonian matrix for, say, A-A-A-T will look like

$$H = \begin{pmatrix} IP_A & \beta_{AA} & & \\ \beta_{AA} & IP_A & \beta_{AA} & \\ & \beta_{AA} & IP_A & \beta_{AT} \\ & & \beta_{TA} & IP_T \end{pmatrix} \qquad (2.1)$$

where the diagonal elements are the site ionization potentials and the off-diagonal elements are the near-neighboring site-transfer integrals, $\beta_{TA} = \beta_{AT}$. Say $IP_T < IP_A$. To see that there is an eigenvalue corresponding to an ionization potential a shade lower than IP_T, with an eigenvector localized at the T end, one can, for example, proceed by first introducing molecular orbitals just for the A part. Then the partly diagonalized Hamiltonian takes the form

$$H = \begin{pmatrix} IP_A + \sqrt{2}\beta_{AA} & & \beta & \\ & IP_A & & \\ \beta^T & & IP_A - \sqrt{2}\beta_{AA} & \\ & & & IP_T \end{pmatrix} \qquad (2.2)$$

where β is a row vector, $\beta\cdot\beta^T = \beta_{TA}^2$, and the three eigenvalues obtained for the A part by itself are IP_A, $IP_A \pm \beta_{AA}\sqrt{2}$. Because the ionization potential of T is lower than that of A, cf. Figure 3, the secular equation for the full Hamiltonian, $\det(H - E) = 0$, has three higher roots where the eigenvectors are localized on the A sites, and one eigenvector is preferentially localized on T site; the corresponding eigenvalue is even lower than the local IP. The other three eigenvalues are banded about the ionization potential of A. In this way, the local electronic structure of bifunctional molecules as found in He I photoelectron spectra[22] can be understood. The extent of localization depends on the ratio of the two β's in (2.1). In other words, when one diagonal element is lower, the eigenstates of the tight binding Hamiltonian manifest clear localization. It is therefore not unreasonable to imagine a fully localized zero-order basis, where each basis state is representing a "bead" in the chain of amino acids that is the peptide. Such a basis is introduced in section III.

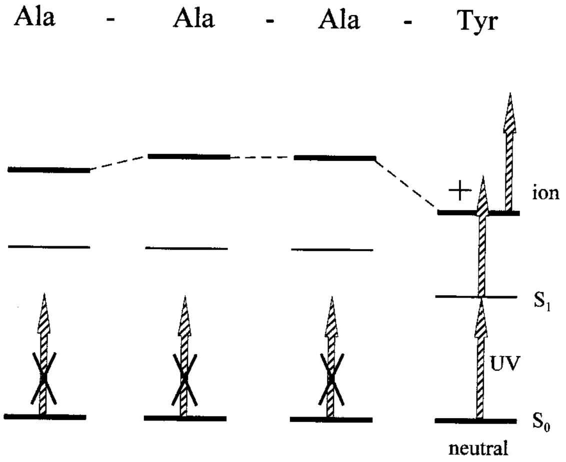

Figure 3. Schematic zero-order energy levels for the peptide Ala-Ala-Ala-Tyr, cf. Figure 2 and eq 2.1, and the principle of the excitation scheme leading to a localized ionization.[1,2] The aromatic chromophore (Tyr) is ionized by a resonant UV two-photon scheme via its S_1 intermediate. The S_1 state of Alanine lies higher and is not accessed by the UV photon. The ion is estimated to absorb one more UV photon, and hence its total energy is not much above the threshold dissociation energy E_0. Following the convention of Weinkauf et al.,[1,2] the ionization potential is shown as the energy that is added to the ground state. One often uses a different representation in which the ionization threshold is taken as the zero of energy. In such a representation, bound levels have negative energies and a state of lower IP is nearer to the zero.

Even in zero order, the picture for a real peptide is a shade more complex due to at least two considerations. First, the beads have internal structure and so can have excited electronic states. Such states may be particularly important in the chromophore.[2] The formalism discussed in section V can allow for the possibility of more than one electronic state per bead. The second point is that, because of the lone pair of the N atom, the charge can be localized at the N-terminus, which is on the left end, as shown for $(\text{Ala})_3$-Tyr in Figure 2. In other words, and as mentioned before, a zero-order picture of the excited peptide ion, Figure 3, is that of nearly degenerate functional groups of low IP spaced by carbon bridges, with local electronic coupling.

The localization of the eigenstates of the tight binding Hamiltonian is equally seen when one thinks in terms of a free electron model.[23] The usually flat potential bottom of the well wherein the charge moves has, for the present view, a well at the T end. If that additional well is deep enough, the ground state will be localized in this well region and the lowest excited states will (by orthogonality) avoid the well region.

The simple considerations above can of course be done in a much more elegant fashion. There is indeed an extremely rich literature on electronic transport and localization in disordered linear arrays in both the quantal[6,24−26] and the hopping[27] limits. (For an elementary introduction see chapter 13 of ref 28. For an analytical solution of the equations of motion see ref 29.) In the more recent literature there is also very extensive discussions on the coupling of the electronic and the lattice motions (See refs 30−35 and references therein). In this paper we are discussing the migration of a positive charge. Reference should also be made to the rich literature on electron transfer,[36] where questions of the coupling for nonadiabatic electron transfer have received much attention.[37−47]

The localization discussed above, due to a site with different diagonal elements than its neighbors, is also familiar in another context, viz., that of characteristic functional group frequencies in the infrared vibrational spectra of large polyatomic molecules.[48] The most familiar are the high-frequency modes such as CH or OH, whose absorption stands apart even though the normal modes of molecules are, in principle, delocalized. This has been addressed very early on[49] with the conclusion that there will indeed be localized vibrations with characteristic frequencies, which are a shade, but not much, shifted by the rest of the molecular frame. The physics is different, but the mathematics of the normal vibrations and of the tight binding approximation for the electronic states is isomorphous. We shall not follow this detailed line of development but rather ask, in the following section, for a more molecular description: Can one identify the nature of the nonstationary electronic states that play a part in steering the reactivity?

III. Nonstationary Electronic States

Electronic states, localized on particular beads along the peptide string, are clearly nonstationary, as witnessed by the charge migration. Isn't one better off using the familiar stationary delocalized states? This question is based, however, on an implicit assumption, an assumption which is by no means obviously valid.

The electronic states that are produced by the usual quantum chemical methodologies *are not stationary*. To be sure, the ground state of molecules is typically, to a very good approximation, stationary. (We are assuming the absence of external fields.) But the usual excited states of large molecules are not stationary, and much current experimental work using ultrafast pump−probe techniques is aimed at elucidating the nature of their dynamics.[50−54]

The Born−Oppenheimer states of quantum chemistry do diagonalize a Hamiltonian, but it is not the full Hamiltonian. The states of quantum chemistry are stationary only when the nuclei are clamped. When the nuclei are allowed to move, the electronic states can be coupled by the, so-called, nonadiabatic or non-Born−Oppenheimer terms. This coupling is important only when the gap between two electronic states is small and therefore the ground electronic state is typically not so perturbed. Already in 1937 Teller[55] pointed out that excited electronic states of polyatomic molecules not only can get near but can outright cross, in a conical fashion. The importance of such conical intersections is a subject of much current research.[56−63]

When the motion of the nuclei is allowed, as one must do in any discussion of dissociation, then the familiar excited states are not stationary,[64] with several examples already recorded of transfer times between different states which are comparable to vibrational periods.

The peptides under discussion not only are not in their ground state but contain a substantial excitation (one or more visible photons) beyond the minimal electronic energy needed to form the ion.

There is an alternative set of electronic states, a set that is stationary under the motion of the nuclei. This is the so-called "diabatic states". There is not a very simple definition of what a diabatic state is. It is easier to define it by what it is not: It is not varying substantially when the nuclei move. That is why it is stationary under this perturbation. On the other hand, the diabatic states do *not* diagonalize the electronic Hamiltonian. There is a finite electronic coupling between different diabatic states. The transfer integral β in eq (2.1) is an example of such a coupling.

Like their Born−Oppenheimer counterparts, the coupling between diabatic states is effective only if they are energetically close, which, as discussed in section II, is the typical situation in the peptide ions. The transfer matrix element is not, by itself, enough. One needs to be able to bridge the electronic energy gap. Unlike their Born−Oppenheimer counterparts, the diabatic states are resilient to the nuclear motion. This motion is, however, relevant if it brings the system to a configuration where the effective coupling between the diabatic states is large. (See ref 62 for a recent example where the system gets in and out of effective coupling.)

In the next section we show how to blend the two pictures.

IV. Charge Migration and Site-Selective Reactivity in Peptide Ions

Section III discussed two types of electronic states, adiabatic, which are nonstationary due to the motion of the nuclei, and the diabatic states, which are nonstationary due to electronic coupling. The purpose of this section is to propose a picture of charge migration and reactivity in peptide ions which involves an alternative, hybrid type of states.

Specifically we propose to marry the two pictures: Each bead is coupled to its neighboring beads by electronic terms, but each bead, by itself, is described by adiabatic states. That is, we use the basis made up of the adiabatic states of the individual beads. As far as any particular bead along the peptide is concerned, the basis is locally adiabatic and so is adjusted to the local electronic conditions. It is also coupled to its local nuclear configuration. But as far as the interbead situation is concerned, this is a diabatic basis.

It is well-known that reactivity is at the site where the positive charge is. In an RRKM-like framework, where the energy is first made available to the vibrations[16−18] (but see part II of ref 11), this is interpreted as dissociation occurring at the weakest bond. The low probability of localizing the necessary excess vibrational energy at that bond is sometimes overlooked. We all recognize that this probability is higher the lower the threshold energy for bond breaking is. What is overlooked is the exponential decrease of this probability with the size (=number of atoms) of the molecule, or in zero order, the probability scales exponentially ($E_0/(s - 1)$), cf. section I. In the present view, larger systems can avoid this entropic barrier if reactivity follows the charge. Initially, whatever delay there is, it is primarily due to charge migration to the optimal site. Only then does nuclear rearrangement set in. If energy is first made available to the vibration, bond breaking is due to a rare event where the necessary vibrational energy becomes localized in the optimal site (=the site of low E_0). An alternative is to first select the site by electronic considerations.

Charge migration is between the beads and is determined by their individual properties. This has already been tested by Weinkauf et al. using specially synthesized peptides with single-site substitution.[1,2] The important point about the diabatic description of the process of charge migration is that it makes the process not strongly coupled to the vibrations. In other words, the strength of the electronic coupling is clearly dependent on the distance between the beads; therefore, charge migration will be influenced when there is motion of the nuclei, but during the coupling, the molecule will not irreversibly lose energy to the nuclear motion. The peptide can avoid any large-scale excitation of the vibrations until the charge has migrated to the site where the dissociation will take place. This is an important attribute for the survival of reactivity until the optimal site is selected.

The charge is used by the peptide as a scout for locating the site where reactive changes are to occur. This site need not be at the other end of the peptide nor need it be unique. There can be more than one site along a given chain, and the charge needs to explore site after site. As such, the multistep charge migration mechanism we discuss here differs from the McConnel superexchange route.[20,33,65] We have a single "donor" of charge, which is the chromophore, where the hole was initially localized, but there is no unique "acceptor", e.g., Figure 1. Moreover, there can be a number of (possibly, many) steps between the donor and the ultimate acceptor.

The local nature of the reactive event, at a bond not necessarily near the site of the initial excitation, is an essential ingredient of the model. The other essential idea is the essentially dissipation-free migration of the hole. This need not be the rule, but, as we show in section V, it can be the case. Of course, the charge transfer is dominated by Franck−Condon considerations. But when we speak of such terms as charge migration, we are using a time dependent picture. What is then needed is to be able to show that the time dependent solution of the Schroedinger equation admits a possible solution where the charge migrates in a dissipation-free manner. The very fact that one can experimentally observe and theoretically discuss and compute (e.g., ref 36) alternative scenarios, where the coupling to the vibrations is dissipative, shows that a nondissipative route is not the invariable rule. The common hypothesis in mass spectrometry that the relaxation of the electronic energy to vibrational excitation is the first and fastest process requires that we show that a nondissipative migration of charge is not impossible. We do this in section V and return to a critique of the model in section VI.

V. Concerted Charge Migration Dynamics

Martinez et al.[61,62,66−69] have presented a quantum mechanical formalism for dynamics on several electronic states. Their approach lends itself to be used with either a diabatic or an adiabatic basis but is equally suitable for the present point of view, which uses a basis of mixed character, interbead diabatic states and intrabead adiabatic ones. The purpose of this section is to adapt the general methodology to the specific problem at hand. In particular we discuss how the mixed electronic basis is used and also how the computational approach applies the very same strategy as we suggest is also used by nature in the process of concerted charge migration. In the computational approach this is done because of considerations of numerical efficiency, but this is not unlike the need to avoid an entropic barrier. Specifically, we will point out how the computational approach uses the Franck−Condon overlap criterion for deciding on the effectiveness of the coupling between electronic and nuclear modes. In section VI below we argue however that the concerted case is a special one and that in general the theoretical picture admits also of a more general situation where the charge flow is not necessarily unidirectional and/or dissipation free.

A. The Total Wave Function. In the formalism of Martinez et al., the total time dependent wave function of the system is expanded as a weighted sum over electronic states. Each component in the sum is a product of an electronic and a (time dependent) nuclear wave function.

$$\Psi = \sum_i C_i(t)\, \phi_i(r;R)\, \chi_i(R;t) \tag{5.1}$$

where r and R stand for the electronic and nuclear coordinates and hence are multidimensional variables. The electronic wave functions are allowed to depend parametrically on the nuclear coordinates, and in the present approach this comes about as follows. The electronic state index i represents a state where the hole is localized on the ith bead in the chain. In other words, the electronic state $\phi_i(r;R)$ is a product state of the local wave functions, φ_j, of each bead with the wave function of the ith bead being different in that it corresponds to the ionized state of the bead, i.e., to a hole being present on the ith bead.

$$\phi_i(r;R) = \varphi_i^+ \prod_{i' \neq i} \varphi_i{}' \tag{5.2}$$

The electronic states φ_j localized on the beads are adiabatic, and this leads to their dependence on the nuclear coordinates of the jth bead, due to the usual electronic part of the total Hamiltonian being parametrized by the positions of nuclei. On the other hand, the electronic wave functions (5.2) are a diabatic basis as far as the interbead dynamics are concerned. The dynamical equations of motion as derived below assume that the matrix elements of the *total* Hamiltonian in the electronic basis are a given input. Hence the mixed character of the wave function has implications for the explicit evaluation of the coupling matrix elements but does not require special handling otherwise. In the spirit of the tight binding (or Hückel) approximation, the wave functions of electronic states of even neighboring beads are taken to be orthogonal over the electronic coordinates,

$$\int \mathrm{d}r \varphi_j^*(r;R)\, \varphi_i(r;R) = \delta_{i,j} \tag{5.3}$$

but this is not essential and can be avoided. If we forget the internal structure of the beads and use the language of tight binding, then what we are discussing is a tight binding approximation for the hole. In the ith basis state, the hole is on the ith bead and all other beads are "empty" (that is, they have their full complement of electrons).

The (complex) amplitudes C_i determine the population (i.e., $|C_i|^2$) and the degree of coherence of the different electronic states. The initial conditions in the Weinkauf experiment specifies that the chromophore is ionized at $t = 0$ and all other beads are in their neutral state. So only one particular electronic state is initially occupied. The subsequent evolution is determined by the equations of motion to be discussed below.

B. The Nuclear Wave Functions. The time dependent nuclear wave function for the ith electronic state is represented in a manner corresponding to that of the electronic state itself: a linear combination of wave functions, each term being a product of a time dependent traveling wave function representing the interbead motion and nuclear basis states for each bead.

$$\chi_i(R;t) = \sum_j \mathrm{d}_{i,j}(t)\, \chi_j^i(R;\bar{R}_j^i(t), \bar{P}_j^i(t), \gamma_j^i(t), \alpha_j^i(t)) \prod_{\text{beads}} \chi_{\text{bead}} \tag{5.4}$$

If there is no observed fragmentation of individual amino acids, the nuclear basis functions for the beads themselves, χ_{bead}, can be considered to be well described by the Born−Oppenheimer approximation.

In principle each term in (5.4) can be sufficient to describe the nuclear motion in a given electronic state. However, in the application to the experiments of Weinkauf et al.,[1,2] we want to have the interpretation that the wave function describes a nondissipative, classical-like motion of the nuclei. We therefore take each time dependent basis state as centered about a classical trajectory which is determined by the potential of the ith electronic state. Equations of motion for this purpose are given in the papers of Martinez et al., including[69] the multidimensional case. This means that there will be two types of coupling terms that affect the nuclear motion:

(i) The interstate coupling due to the migration of the charge. These are the terms that we are definitely interested in. We need to show that charge can migrate without an extensive distortion of the nuclear frame.

(ii) The intrastate coupling terms. These arise between different terms of (5.4), i.e., nuclear wave functions that belong to the same electronic state and describe quantum corrections to the classical motion on a given electronic state.

Martinez et al. have provided equations of motion including the intrastate coupling (the so-called, full multiple spawning, or the FMS procedure). Must we here retain the intrastate coupling? The answer is "not really". If the final dissociation is "direct" in the sense that the energy is localized in the bond to be broken, which then promptly breaks, the answer is clearly no. If the final dissociation is delayed and more RRKM-like, with energy being first delocalized over several modes and only later localizing, the answer can still be no. The reason is that a classical trajectory can manifest a delayed dissociation and therefore so can the nuclear basis state localized about it.

For the reason discussed above we will, toward the end of this section, retain only one nuclear wave function per electronic state. This assumption will be further examined in section VI. We emphasize that the nuclear state that we do retain is a nonstationary state and that it evolves in time in a prescribed manner, i.e., by following a classical trajectory about which it is centered. It is because of this evolution that one nuclear state may be sufficient. It is because it is one state that the evolution is coherent and dissipation free.

C. The Equations of Motion. The time dependence of the total wave function requires solving for the time evolution of the coefficients $D_{\mathrm{i}}^{\mathrm{j}} \equiv C_i d_{i,j}$, which are the quantal amplitudes for being in the nuclear basis state j on the electronic state i at time t. Note that the number of these coefficients equals the number of electronic states that are included (i.e., by the range of the index i, which is the number of beads and equals the number of amino acids in the peptide) because we retain only one nuclear basis state per electronic state. Note also that the number of coupled equations is not dependent on the number, s, of nuclear degrees of freedom. To conclude, the number of coupled equations of motion is just as in the tight binding approximation, i.e., one equation per electronic state (=per bead).

A set of coupled equations of motion for the coefficients is obtained by taking the scalar product of the time dependent Schroedinger equation for the total wave function on each nuclear basis state. This prescription ("Dirac's variation of constants") is variational in nature. The resulting equation of motion is

$$\mathrm{d}D_j^i/\mathrm{d}t = -i[(\mathbf{H}_{i,i} - i\dot{\mathbf{S}}_{i,i})_{j,j}D_j^i] - i\sum_{i'\neq i}\sum_k(\mathbf{H}_{i,i'})_{j,k}D_k^{i'} \tag{5.5}$$

The equation is written so as to distinguish the intrastate ($i = i'$) and interstate ($i \neq i'$) terms. The matrices **H** and **S** are defined by integration first over the electronic coordinates only; for example,

$$H_{i,i'} \equiv \int \mathrm{d}r\phi_{i'}^*(r;R)\; H\phi_i(r;R) \tag{5.6}$$

The orthonormality, (5.3), of the electronic states means that **S** acts as the identity matrix, but **H** is an operator. Equation 5.5 requires as input the matrix elements of the **H** and **S** matrices in the nuclear basis states. The intrastate ($i = i'$) coupling in the equation of motion is due both to the Hamiltonian matrix elements

$$(\mathbf{H}_{i,i})_{j,j} = \langle\chi_j^i|H_{i,i}|\chi_j^i\rangle \tag{5.7}$$

and (because χ is not real but carries a phase) to the time dependence of the overlap

$$(\dot{\mathbf{S}}_{i,i})_{j,j} \equiv \langle\chi_j^i|\partial\chi_j^i/\partial t\rangle \tag{5.8}$$

The interstate coupling is similar to (5.7) except that it is defined by the elements of the Hamiltonian that are off diagonal in the electronic-state index:

$$(\mathbf{H}_{i,i'})_{j,k} = \langle\chi_j^i|H_{i,i'}|\chi_k^{i'}\rangle \tag{5.9}$$

There is no overlap term because the overlap is diagonal in the electronic-state index.

The equations of motion (5.5) are analogous to the MIS method of Martinez et al. They are not exact because of the neglect of intrastate coupling. The important point for subsection D below is that the interstate coupling terms (5.9) are localized. To see this, let us take the Born–Oppenheimer separation to be valid for the amino acids themselves. Then the nuclear kinetic energy term commutes with the electronic basis because it is a diabatic basis as far as the interbead motion is concerned. In this approximation, the interstate coupling, (5.9), is replaced by

$$\begin{aligned}(\mathbf{H}_{i,i'})_{j,k} &= \langle\chi_j^i|H_{i,i'}|\chi_k^{i'}\rangle \\ &= \langle\chi_i^j|E_{i,i'}(R)|\chi_k^{i'}\rangle + \langle\chi_i^j|T|\chi_k^{i'}\rangle\delta_{i,i'}\end{aligned} \tag{5.10}$$

with $E_{i,i'}(R)$, $i \neq i'$, being the potential coupling between different sites (that is, it is the analogue of β of eq (3.1)). In other words, we expect that only such states i' are coupled to the state i, which are the states on the beads to its left and right, respectively.

D. Spawning. Spawning, as an essential ingredient in the approach of Martinez et al., has been extensively discussed. Our purpose here is to draw an analogy between spawning as a numerical device and the physics of the charge migration, with special reference to the Franck–Condon principle.

First note that, necessarily, the equation of motion is solved by propagating in finite time steps. On the other hand, in describing an initially localized hole, cf. section II, the initial wave function is confined to a particular electronic state (=the hole being localized on a particular bead) and, in the present model, to a particular nuclear basis function. After some time steps, due to interbead coupling, the total wave function must develop a presence on other beads (=on other electronic states; that is, the hole migrates). This is brought about by the spawning procedure as follows. A necessary condition for spawning is that the effective interstate (=interbead) coupling reaches a threshold value (preassigned and determined by numerical convergence requirements). If the other electronic state is empty, then this is also a sufficient condition, and a new nuclear basis state, on the so far unoccupied electronic state, is added to the total wave function. The point is that by the Franck–Condon principle (which is expressed via a saddle point procedure[70]) this new nuclear state is taken to be localized at the same location as the nuclear state on the already occupied electronic state. We refer to the literature for an efficient way to build such a state.

The special way of preparing a basis set of nuclear states ensures that every spawn is into a nuclear state of maximal overlap. In the full method of Martinez et al. one can spawn at every time step. The simple physical model discussed in this paper is that we spawn only once. That there is only one spawn is an approximation, but (i) it is an approximation which is made in the spirit of the Franck–Condon principle because that one spawning is into a (nonstationary) nuclear basis state of maximal overlap with the nuclear state which originated the transfer. (ii) It is less approximate then it sounds. In simple physical examples that were so far examined in detail this is not an unreasonable approximation. Indeed, this is just what is assumed in the original approach of Landau and Zener and of Teller[55,71,72] and also in the weak coupling limit.[12,73] (iii) It can always be improved upon by allowing multiple spawns. See also section VI. What one achieves by this approximation is that there is no premature draining of energy. The charge migrates from bead to bead without undue energy exchange between vibration and electronic degrees of freedom. If the site reached is optimal, the nuclear dynamics will follow the classical trajectory to a separating of products. If the site is not optimal, a spawning into the next electronic state will occur; that is, the charge will migrate to the next bead.

E. Discussion. The series of considerations as detailed above show that the physical picture suggested by the experiments of Weinkauf et al. can be derived by a sequence of well-defined approximations to the exact dynamics. Specifically, charge can migrate along the beads that make up the peptide without a concomitant draining of the energy to the nuclear degrees of freedom. Dissociation of the peptide can take place between any two beads if enough energy is available. The reason is that there is one nuclear wave function for each electronic state and each electronic state corresponds to the charge being localized on a different bead. For dissociation to take place, the classical trajectory which “guides” the nuclear wave function must be able to have enough energy so that it can reach the separated products (with the charge localized on that fragment as corresponding to the relevant electronic state. We reiterate: each electronic state corresponds to the charge being localized on a different bead). Whether the dissociation is direct or not depends on the nature of the classical trajectory, and this cannot be specified in general. What is clear is that the charge guides the dissociation and that the site of reactivity can be any local minimum in energy along the chain, where enough energy is available. The site of the initial excitation is not relevant to the nuclear dynamics when dissociation takes place. Reactivity is determined by the electronic state at the site where bond breaking is to occur. This local character of the reactivity is a direct result of the nature of the electronic states employed in the description. They are states of localized charge and are nonstationary; hence, they can manifest charge migration. But the states are not stationary due to electronic coupling, cf. eq (5.9) and (5.10), rather than due to the non stationarity of the more familiar global Born−Oppenheimer states.

VI. Charge Migration Dynamics in the General Case

The discussion in section V led to a picture of a directed charge migration along the peptide chain without any back transfer or dissipation of energy in the nuclear modes. It is important to emphasize that this is not the most general case which is consistent with the nature of the electronic states that were used. Rather, the equations of motion (5.10) do allow for a different behavior, as will be discussed in this section.

Up to and including (5.10), the discussion in section V rested on two assumptions. One was the choice of an electronic basis state, of mixed character, where, for different electronic states, the charge is localized on different sites. In principle, if one uses the full (FMS[61,68,69]) procedure, then this is not an approximation. As long as the basis set is complete, it need not be physically realistic. The exact treatment of the inter- and intrabead coupling can correct for any deficiency of the zero-order electronic basis. But we are not handling the coupling exactly in (5.10), so the choice of electronic basis is important. The other assumption invoked in deriving (5.10) is the neglect of intrabead coupling. That is numerically important but not likely to change the essential physics. The important approximations in section V begin after eq (5.10).

The first special approximation is the assumption of just one nuclear basis state per electronic state. Mathematically, this is the approximation of retaining just one term in eq (5.4). This is not unphysical because that one term does have the flexibility to allow dissociation, either direct or delayed. Specifically, because the nuclear wave function tracks an exact classical trajectory, it can describe intramolecular vibrational relaxation (IVR) and hence a delayed dissociation.

The essential special assumption here is that of allowing just one spawning event into or out of a given electronic state. This is quite reasonable in a direct dissociation but need not be the case in a long living species. In principle, spawning can occur many times into/out of a given electronic state, so much so that we have seen an example[62] where the transitions into and out of occurred so frequently that the population in a given (diabatic, as here) electronic state could be described as undergoing a random walk with an absorbing boundary. (The long time boundary is absorbing because ultimately the molecule did dissociate just as in the present problem.)

The general case then is when the hole proceeds in a zigzag fashion, moving to the right and left between the beads of the chain. When it does so, there can also be a defacto dissipation of energy into the nuclear frame because subsequent spawnings need not be into the same nuclear state and, in general, they will not be. If one thinks in terms of “conduction” of the positive charge, this is the case when there are many scatterers so that the conduction is “ohmic” and not dissipation free. Such losses will also imply that a higher energy is needed to transport the charge across the chain.

A quantitative characterization of the properties of the system that determine which dynamical limit (rapid dissipation or dissipation-free ranging with subsequent dissipation) is more appropriate requires, of course, the explicit evaluation of the matrix elements of the Hamiltonian. Clearly, a system built from subunits of beads where the interbead electronic coupling is weaker than the intrabead coupling favors the mechanism we discussed. The beadlike model for the peptide is a special case of such a hierarchical structure. It should however be recognized that, in general, the equations of motion admit either behavior as a possible limit with the general case being intermediate, with energy moving back and forth between the electronic and vibrational modes.

VII. Concluding Remarks

We propose a model where the charge scouts for the site of reactivity without energy dissipation. The model was discussed with special reference to the experimental observations of Weinkauf et al. on the dissociation of selectively excited peptide ions and to the theoretical framework of Martinez et al. The model makes electronic considerations that set both the time and the place where chemistry can begin to take place. This avoids the problem of the conventional approach, where energy is first dissipated into the sea of possible vibrational states, which requires that the energy localization, necessary to overcome a barrier, occurs by a rare fluctuation. In the proposed point of view, reactivity does not germinate until the charge-selected site is reached.

The design and interpretation of the experiments and the accompanying theory are made possible by adopting a nonstationary point of view. Femtosecond and nanosecond time-resolved experiments have identified that the site of initial optical excitation is localized. Dissociation is observed to occur also at another site, not directly related to the site of excitation. We consider that the dissipation free migration of the charge performs the function of locating the site of reactivity. This ranging by an electronic process provides a time scale faster than the subsequent nuclear motion that is required for chemistry.

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