An observation concerning electronically excited retinal

(dipole/electron transfer/oxidation/energy)

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ABSTRACT   The observation of Mathies and Stryer of highly polar excited electronic states of *all-trans*-retinal, its unprotonated Schiff base, a salt of the protonated Schiff base, and 11-*cis*-retinal leads us to propose a possible consequence of the existence of such species. The highly polar excited molecule may have sufficient potential to oxidize its surroundings, thus achieving a transfer of one electron. Experimental evidence is combined with crude model calculations to support the possible role of these excited states as electron transfer agents.

Recently Mathies and Stryer reported experimental evidence (1) which demonstrates that *all-trans*-retinal, its unprotonated Schiff base with *n*-butylamine, the Cl^- salt of this protonated Schiff base, and 11-*cis*-retinal all undergo large changes in dipole moment [$\Delta\mu$ about 10–16 debyes (D; 1 D = 3.338×10^{-30} m · C)] when they are vertically photochemically excited to their lowest energy ($\pi \rightarrow \pi^*$) singlet states. Salem (2) has discussed the so-called sudden polarization of charge density in the electronically excited 11-*cis*-12-*s*-*cis*-nonatetraenylidene-methyliminium ion, which he uses as a reasonable model of the chromophoric part of rhodopsin. His theoretical calculations predict that the dipole moment of this model compound should change by 35–40 D as the molecule is excited and twisted about its 11–12 bond. Fröhlich (3) has given an excellent discussion of the possible physical and chemical consequences of having such highly polar species present as biological intermediates in the visual process. The authors of refs. 1 and 2 have speculated about the role of polar excited states as energy storage areas and as potential driving forces for subsequent molecular and/or surrounding rearrangements. It has also been pointed out that the effects of surrounding counter ions (or other fixed charges), oriented dipoles, or polarizable groups on the protein could, by stabilizing the polar state, have large effects on the position of the $\pi \rightarrow \pi^*$ absorption of the retinal (1). However, there is one possibility which seems to have been overlooked by these authors and which may be an especially likely event in condensed-phase systems that (suddenly) contain molecules with very large dipole moments.

We have recently shown (4–6) that (small) highly polar molecules (e.g., LiH, LiF, LiCl, BeO, NaH) can attach external electrons to their electropositive ends to form stable anions. Earlier model calculations in which the polar molecule was replaced either by a point dipole (7, 8) or by a fixed finite dipole (9–14), two charges ($\pm q$) separated by a fixed distance (R), showed stable anion states for electrons moving in these model potential fields whenever the dipole moment exceeded 1.625 D. Because both of these dipole models neglect the presence of atomic core electrons, the value of the critical dipole moment (1.625 D) and the resulting electron binding energies cannot

be trusted, even in a qualitative sense for most electron–polar molecule systems. The point dipole approximation gives infinite binding for dipole moments greater than 1.625 D (7, 8). The fixed finite dipole's (FFD) lowest energy state correlates, for large separation of the two charges, with the 1*s* hydrogenic state of an electron moving about a $+q$ charge. Excited states of this model correlate with higher (2*s*, 2*p*, etc.) hydrogenic states. Our *ab initio* studies of electrons binding to polar molecules demonstrate (4–6) that the ground state of the FFD overestimates the electron binding energy for the molecules in the above list. This is due to the fact that, in these polar molecules, the 1*s* orbital of the electropositive atom is already doubly occupied; the "extra" electron must go into a 2*s* or 2*p*-like orbital (for Na^+X^- compounds it goes into the 3*s*- or 3*p*-like orbital) whose binding energy is considerably less. Our work also demonstrated that the energy of the 2*s* state of the FFD (3*s* for Na^+X^- compounds) underestimates the electron binding energy. This state has too small a binding energy because the FFD model does not allow for the penetration of the "2*s*" (or "3*s*") orbital into the occupied $1s^2$ (or $1s^2 2s^2 2p^6$) core. Thus, it appears that neither the lowest energy state nor the excited states of the FFD are useful for giving accurate predictions of electron binding energies. However, they can be useful for providing crude upper (ground state of FFD) and lower (appropriate excited state) bounds to these binding energies. It is our intention to demonstrate that the retinal compounds studied in ref. 1 are capable of attaching an electron with a binding energy that is sufficiently large to make the detachment of this electron from the retinal's surroundings a not unlikely event.

Because of the large separation (2) (>6 Å) between the positive and negative charge in the excited states of the above retinal compounds, the FFD model's energy levels can be accurately approximated by the appropriate hydrogenic energy levels.[†] The theoretical calculations of Salem (2) predict that the magnitude of the charge migration accompanying excitation and twist around the 11–12 bond in his model compound is 0.94 e^-. The experimental results of Mathies and Stryer (1), which give (vertical) dipole moment changes of the order of 10–15 D over a distance[‡] of $\approx$ 7 Å, can be used to compute a charge migration of 0.30–0.45 e^-. The 1*s* and 2*s*, 2*p* hydrogenic orbital energies for q = 0.30–0.90, which should give upper and

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Abbreviations: D, debye; FFD, fixed finite dipole.

[†] For the positively charged carbon atoms in excited retinal, it is appropriate to use the FFD 2*s* (or 2*p*) energy level because the 1*s* orbital is doubly occupied.

[‡] The authors of ref. 1 state that the positive charge in the excited states of the retinal compounds studied resides in the cyclohexene ring. However, Salem (15) points out that this ring is not in conjugation with the 7–16 network and refers to x-ray structural data to support this statement. Therefore, we have based our calculations on Salem's assumption that the positive charge resides primarily on the C_7–C_{11} atoms, with an average charge separation distance of 6.8 Å. This average charge separation takes into account charge delocalization throughout the C_7–C_{11} region of space.

lower bounds to the binding energy to the positive carbon center in excited retinal, are $E_{1s} = 28-254$ kcal/mol and $E_{2s,2p} = 7-64$ kcal/mol, respectively (1 kcal = 4.184 kJ). Thus, if the surroundings of the excited retinal molecule contain, in the neighborhood of the molecule's positive center, a functional group whose ionization potential is less than 100 kcal/mol (4.3 eV), it is possible that the excited (and perhaps twisted) retinal could cause an electron to be detached from the surroundings and attached to itself, thereby achieving a net charge movement in the retinal–surroundings system. Before photon absorption, the positive charge is primarily on the end atom with a counter anion nearby. After absorption, twist, *and* electron transfer, the positive charge is in the retinal's surroundings. It is this (possible) process of photon absorption to create a highly polar species followed by combined oxidation of the surroundings and reduction of the retinal that has thus far been neglected in discussion of the consequences of the polar nature of the excited retinal molecules. By no means have we presented any new information here to argue in favor of the occurrence of this sequence of reactive events. We only intended to demonstrate, using experimental evidence plus crude model calculations that, our experience shows, give upper and lower bounds to electron binding energies, that the electron transfer step described above is a possibility to consider if the ionization potential of a nearby surrounding molecule is lower than the electron binding energy of the excited retinal. Experiments exploring the interplay between the absorption of light by model chromophores and the oxidation potential of the surroundings or solvent would likely shed light on this question. One primary objective of this brief note is to stimulate researchers in this area to carry out such experiments.

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