



## VIBRONIC COUPLING IN IONIZED ORGANIC MOLECULES: STRUCTURAL DISTORTIONS AND CHEMICAL REACTIONS

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Ionized organic molecules (radical cations, RC) are prone to undergo vibronic coupling whenever there is a relatively small energy gap ( $< 2$  eV) between their ground and excited states. The force constant for the symmetry-allowed vibrational mode that couples these states is lowered by the vibronic interaction so that the RC can distort more easily along this specific mode. This pseudo-Jahn-Teller effect can result either in a permanent structural distortion of the RC relative to the symmetry of the parent neutral molecule or to an energetically favored pathway for a facile chemical rearrangement along this predictable reaction coordinate. Recent work has provided examples of both of these dramatic consequences of vibronic coupling. Thus, in the first class, dynamic ESR studies have shown that ionized bicyclo[2.2.2]oct-2-ene undergoes a structural distortion from the  $C_{2v}$  point group of the neutral parent molecule by twisting at the olefinic  $\pi$  bond to the lower  $C_2$  symmetry in the RC (*Chem. Eur. J.* **2002**, *8*, 1074). These experiments clearly revealed a double minimum in the potential energy surface along the  $a_2$  torsional mode. This is in accord with the coupling of the  ${}^2B_1$  and  ${}^2B_2$  Born-Oppenheimer states in  $C_{2v}$  symmetry, this mixing of the  ${}^2B_1$   $\pi$ -ionized ground state and the  ${}^2B_2$   $\sigma$ -ionized excited state being facilitated by the low ( $\sim 1.0$  eV) gap between these states, as estimated from photoelectron spectroscopy. Turning to the second class of RC where unimolecular rearrangement reactions are promoted by vibronic interaction, several cases have emerged where the rearrangement would not be expected if it were based only on the ground-state properties of the RC. It was found (*Chem. Phys. Lett.* **1988**, *143*, 521) that the ethylene oxide RC undergoes C-C ring opening to the oxallyl species despite the fact that the ground state corresponds to ionization from the *nonbonding* oxygen  $\pi$  lone-pair orbital. The reaction develops excited-state character as a result of the vibronic mixing so that the activation barrier to ring opening is lowered. We will discuss the unusual rearrangements of the bicyclo[1.1.1]pentane and [1.1.1]propellane RC from a similar perspective, emphasis being placed on the decisive role of symmetry in predicting the course of these rearrangements. We illustrate how this approach can reconcile conflicting considerations on some of the „unexpected” reaction pathways followed by highly strained organic RC.