

# ROAMING MECHANISM IN PHOTODISSOCIATION OF NITROBENZENE

The roaming mechanism has gained some traction as a recognizable model.<sup>1,2</sup> This mechanism involves typically the near complete dissociation of a molecule into two radical fragments. But before they can completely separate they form a loose complex on a flat potential energy surface. The two fragments can then wander about each other (the “roaming” part of the mechanism), eventually finding an alternative exit channel. The first example was the dissociation of formaldehyde which forms the complex  $\text{H} + \text{CHO}$ .<sup>3</sup> The hydrogen atom roams over to the other side of the HCO fragment and then abstracts the second hydrogen atom to form  $\text{H}_2$  and CO – with the unusual signature of a hot  $\text{H}_2$  molecule and CO in low rotational/vibrational states.

The photodissociation of nitrobenzene is now suggested to also follow a roaming pathway.<sup>4</sup> Bimodal distribution is found for the NO product channel. There is a slow component with low J and a fast component with high J. This suggests two different operating mechanisms for dissociation.

G2M(CC1)/UB3LYP/6-311+G(3df,2p) computations provide the two mechanisms. Near dissociation to phenyl radical and  $\text{NO}_2$  can lead to a roaming process that eventually leads to recombination to form phenyl nitrite, which can then dissociate to the slow NO product. The fast NO product is suggested to come from rearrangement of nitrobenzene to phenylnitrite on the triplet surface, again eventually leading to loss of NO, but with high rotational excitation.

Source: <http://comporgchem.com/blog/?p=2038>