PHOTODISSOCIATION DYNAMICS OF GAS-PHASE SMALL MOLECULES

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1. INTRODUCTION

Any detailed discussion of the vacuum ultraviolet (VUV) photophysics of simple polyatomic molecules must involve consideration of the strong inter-relation between photochemistry and spectroscopy. The present paper concentrates largely on just one photophysical aspect -- photodissociation (i.e., molecular fragmentation as a result of photon absorption) -- since this represents one of the more probable, more interesting and, indeed, more studied consequences of the interaction of VUV photons with gas-phase small molecules. Thus, in the specific examples considered below, neither fluorescence nor photoionization significantly compete with photodissociation as the dominant decay process from the parent-molecule excited states prepared by photon absorption.

Traditionally, photodissociation has been represented most simply in terms of the process

\[ AB + h\nu \rightarrow A + B \, . \]

While there was a time, not so long ago, when the limit of a photochemist's aspiration involved merely the identification of the product fragments A and B, the combined efforts of present-day experiment and theory now render possible a fairly complete picture of the detailed dynamical aspects of the dissociation. In general, the absorbed VUV photon will carry energy \( h\nu \) which is greater than that required to break the A-B bond, \( D_0^a(A-B) \); often, in fact, the excess energy will be sufficient to allow formation of one (or even both) of the fragments in electronically excited

states, which may then spontaneously fluoresce. In pre-laser days, the observation of this photofragment fluorescence represented the only possible route to a study of photodissociation dynamics under anything even approaching collision-free conditions. This explains, in part at least, the traditional emphasis placed on studies of small molecule photodissociation as a result of VUV (rather than less energetic near-UV or even visible) photoexcitation. Important photochemical and spectroscopic information may be derived from measurements of the branching ratios for the various energetically allowed decomposition pathways which follow photon absorption; studies of this kind provide a useful point of entry into a survey of the VUV photophysics of a few selected gas-phase small molecules.

Having characterized some, or preferably all, of the fragmentation channels, further insight into the dynamics of any particular dissociation process requires completion of the detailed energy balance between reactants (parent molecule plus the photon) and the resulting photofragments. Overall energy conservation requires that the excess energy be partitioned into relative translational motion of the recoiling fragments and/or into their respective internal quantum states: That is,

\[ E_{\text{int}}^{AB} + h\nu = E_{\text{int}}^{A} + E_{\text{int}}^{B} + \frac{P_{AB}^2}{2\mu_{AB}} + D_o(A-B) \]

where the relative translational energy of the products is expressed in terms of the relative linear momentum \( \mathbf{P} \). Angular momentum conservation can influence the pattern of energy disposal through the requirement that

\[ J_{\text{AB}*} = J_A + J_B + \mathbf{L} \]

where \( J_{\text{AB}^*} \), \( J_A \) and \( J_B \) are rotational angular momenta of the photoexcited molecule and the resulting photofragments, respectively; and where \( \mathbf{L} \) is the relative orbital angular momentum of the recoiling fragments. As we proceed, the importance of angular momentum conservation in constraining the partitioning of excess energy amongst the various product degrees of freedom will become increasingly apparent.

Product-state detection methods are now sufficiently advanced as to enable precise determination of the primary energy disposal pathways in a number of photodissociations. For example, translational energy disposal may be derived through measurement of the fragment velocity distributions using molecular beams and time-of-flight methods. Internal vibrational, and even rotational, state distributions have been obtained by monitoring and ana-