

Vector correlations and polarization in molecular photofragmentation

J. Alberto BESWICK, *Université de Toulouse, F*

Photofragmentation processes in general produce anisotropic distributions of the products fragments' relative velocity and their angular momenta. These vector properties have received considerable experimental and theoretical attention as a mean to obtain detailed information on energetics and reaction mechanisms. The angular momentum polarization of the atomic or molecular fragments are particularly important in this context. The detailed study of the anisotropy of the fragments' angular momenta can provide crucial information on structure, symmetry, and dynamics in the continuum. They can give access to the relative phases of some transition matrix elements in addition to the amplitudes and they are extremely sensitive to interference effects when coherent excitation of several continua occurs. Electronic angular momentum polarization for instance, provides a direct probe of the motion of the electrons during the reaction as well as information on electronic structure, symmetries, and non-adiabatic couplings. The study of the product rotational angular momentum polarization provides on the other hand information about the bending and torsional forces acting during the reaction. The detailed information and understanding of these properties can provide means to control the production of polarized fragments to use in applications such as: spin-dependent effects in atomic, molecular, and surface physics. It is also worth noting that if the products are excited, the light emitted reflects the anisotropy of the fragments through its angular distribution and polarization.

The most detailed information on reaction dynamics is obtained if angular resolved polarization moments are measured (the so-called complete experiment), i.e., when the correlation between the fragments' relative velocity and the angular momentum is determined. In this talk, the quantum and semiclassical interpretation of experimental vector correlations in molecular photodissociation will be presented. Indeed, in many cases the fragments fluorescence polarization can be calculated by using the simple semiclassical treatment in terms of absorption and emitting oscillators. For the angular distributions of the fragments, it has been shown that when the rotational and electronic angular momentum and its projection along the body-fixed axis are well defined in the initial state, the quantum and quasiclassical expressions are identical for any initial polarization of the molecule prior to photolysis and for all values of angular momentum quantum numbers. These conclusions apply to preparation schemes employing optical excitation, static inhomogeneous and/or homogeneous electric and/or magnetic fields, as well as to molecules physisorbed on solids or clusters. This can be important for the interpretation of photofragment distributions when some other angular momenta are involved, such as electronic angular momentum, with and without nuclear spin, coupled to molecular rotation, asymmetric top rotational angular momentum, or internal vibrational angular momentum in polyatomics.

