Retaining of optically-induced coherency in rotation of photofragments under collisionless conditions and in noisy environments.

M. Gelin.

After the photolysis of parent molecules, the incipient photoproducts are produced with a non-equilibrium distribution over their angular momenta. This non-equilibrium distribution is subsequently relaxed due to collisions of photofragments with buffer species. So, the natural question arises: "Whether is it possible to extract information about the phofragmentation dynamics by monitoring the photoproduct anisotropy decay, or a few collisions are enough to maintain an equilibrium distribution so that the observed data reflect orientational relaxation under equilibrium conditions?"

First, we consider a classical mechanic theory of the rotational and orienational relaxation of photofragments in various collisional environments [1]. Our main finding are summarized as follows. The photofragment ensemble retains substantial memory about its initial non-equilibrium distribution. This allows one to know about features of the photofragmentation dynamics, and also to get information on the efficiency of the angular momentum change due to collisions of fragments with buffer species. These conclusions are valid not only for the short time behavior for the anisotropy, but also for its long time decay.

Second, we concentrate on rotational quantum effects in the ensemble of photofragments [2]. We start from the consideration of rotational recurrences (RRs) under collision free conditions. We demonstrate that the process of the photofragmentation does not change the period of RRs, but affects significantly the RR width and shape. Namely, if the main source of the rotational excitation of fragments is due to the parent molecule rotation, the rotational transients broaden significantly as compared with the case of "free" photofragments. If the main source of the rotational excitation of fragments is due to the torque originating from the rupture of chemical bonds of the parent molecule, the RRs exhibit a kind of "fine structure", with the period of oscillations inversely proportional to the acquired angular momentum. Finally we touch upon the influence of encounters on the RR behavior. We demonstrate that collisions give rise to the phenomenon of the RR temporal diffusion, i.e. the graduate change of the form of RRs at different time intervals. This is a direct manifestation of the relaxation of the photofragment ensemble to equilibrium.

[1] A.P. Blokhin, M.F. Gelin. Chem. Phys. 252 (2000) 323.
[2] A.P. Blokhin, M.F. Gelin. Optics and Spectroscopy 88 (2000) 729.