Vector Correlations in Molecular Photodissociation: Femtosecond Stereodynamics

Oleg S. Vasyutinskii

Ioffe Institute, Polytekhnicheskaya 26, 194021 St.Petersburg, Russia
e-mail: osv@pms.ioffe.ru

As was realized many years ago, angular momentum correlations play a significant role in molecular photodissociation. Molecular interactions always occur through anisotropic

forces and give rise to anisotropic angular momentum distributions which may have relation to approach direction, scattering direction, photon polarization, etc [1].

The lecture reports the results of experimental and theoretical study of time-resolved vector correlations in the femtosecond photolysis of polyatomic molecules by predissociation and direct dissociation mechanisms [2]. Experimentally, the photolysis of methyl iodide (CH3I) via the B-band at 201.2 nm has been studied [3]. Time-dependent anisotropy parameters βi has been determined from fragment angular distributions using the pump-probe technique coupled with the velocity map imaging detection of the dissociation products CH3(v=0) and I*(2P1/2). The results obtained were theoretically interpreted with a quantum mechanical quasiclassical theory which took into account the alignment of CH3 photofragments orbital momentum, nonadiabatic interaction between the 3R1 and 3A1(E) excited states, excited state symmetries, the parent molecule rotation during dissociation, and the CH3 fragment rotation after the bond break. The time-dependent vector correlations were described by a set of the anisotropy transforming coefficients $\boldsymbol{c}^{K}_{K_d q}$ [4,5].

The results obtained demonstrate an important role of the molecular orbital angular momentum alignment and molecular rotation on the time-dependent photolysis. Comparison between the photolysis via the predissociative 3R1 and direct dissociative 3A1(E) excited states showed the profound role of the predissociation mechanism. The 3R1 and 3A1(E) excited state lifetimes, anisotropy transforming coefficients, parent molecule beam temperature, and molecular rotation angles were determined from the experimental data.

References

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