

Vector Correlations in Molecular Photodissociation: Production of Spin-Polarized H-Atoms and Femtosecond Stereodynamics

O. S. Vasyutinskii*

I. Ioffe Institute, 26 Polytechnicheskaya, 194021 St.Petersburg, Russia

The talk presents recent achievements in the rapidly growing field of angular momentum polarization in reactive collisions and molecular photodissociation. The outstanding role of angular momentum in chemical reactions has been realized many years ago. Molecules always interact with each other by anisotropic forces, giving rise to anisotropic angular momentum distributions which may have relation to approach direction, scattering direction, photon polarization, etc [1].

Although the production of spin-polarized hydrogen atoms in molecular photodissociation by circularly polarized photolysis laser was considered theoretically more than thirty years ago [2], it has been directly experimentally observed only recently, by detection of the polarized fluorescence in the H atoms excited by circularly polarized Lyman-alpha radiation [3]. More recently, a new and more practically convenient experimental techniques have been realized [4-6] allowing for direct measurement of the velocity dependence of hydrogen atom spin polarization with high resolution and sensitivity. The strategy was a two-color high-n Rydberg excitation of hydrogen atoms by a linearly polarized Lyman- α laser and a circularly polarized UV tagging laser combined either with Rydberg time-of-flight approach, or with slice imaging, followed in both cases by a pulsed-field ionization. The techniques allow for experimental determination of all three anisotropy parameters α_1 , γ_1 , and γ'_1 [1] which contain important information on the photodissociation dynamics (excited state symmetry, nonadiabatic and long-range interactions, quantum mechanical scattering phase shifts, etc.). The techniques were realized in photodissociation of HCl, HBr, and DBr molecules and can be used for production of dense highly polarized atomic and nuclear targets and beams for high-energy collision and surface scattering experiments. Moreover, the method can be applied for the study of dissociation of polyatomic molecules and reactive scattering and promises a wealth of new detail concerning these elementary processes.

The talk also presents 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. Experimentally, the photolysis of methyl iodide (CH₃I) by linearly polarized laser beam via the B-band at 201.2 nm has been studied [7-8]. Time-dependent anisotropy parameters β 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*($^2P_{1/2}$). 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 3R_1 and $^3A_1(E)$ 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 anisotropy parameters [1]. 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 3R_1 and direct dissociative $^3A_1(E)$ excited states showed the profound role of the predissociation mechanism. The 3R_1 and $^3A_1(E)$ 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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*Corresponding author: osv@pms.ioffe.ru