Time and frequency dynamics of photodissociation in sodium iodide

A.B. Alekseyev[1], R.J. Buenker[1], N. Balakrishnan,
H.R. Sadeghpour, S.T. Cornett[2], and M.J. Cavagnero[2]

Harvard-Smithsonian Center for Astrophysics, 60 Garden St., Cambridge, MA 02138, USA
E-mail: hsadeghpour@cfa.harvard.edu
[1] *Fachbereich 9–Theoretische Chemie, Bergische Universität–Gesamthochschule Wuppertal, D-42097 Wuppertal, Germany*
[2] *Department of Physics and Astronomy, The University of Kentucky Lexington, KY 40506-0055*

Ab initio configuration interaction calculations of the electronic binding energies, spin-orbit coupling matrix elements and transition dipole moments of NaI are presented and used to construct adiabatic and diabatic representations of the 0^+ molecular states relevant to photodissociation. The dynamics of photopredissociation is elucidated by multichannel time-dependent wavepacket propagation in the diabatic representation. Results of femtosecond pump-probe experiments are analyzed and specific features of the observed signals are ascribed to spatial and temporal characteristics of the wavepacket. In particular, the rate of decay of the electronically excited component of the wavepacket is found to be in close agreement with observations of the excited state population. Partial photoabsorption cross sections for the production of iodine atoms in the ground ($^2P_{3/2}$) and excited ($^2P_{1/2}$) spin-orbit states are found to peak at excitation wavelengths of 322 and 263 nm, respectively, in accord with experimental data.