

# Production of excited iodine and the control of I\*/I branching ratio in the photodissociation of NaI

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## Abstract

Control of the outcome of a chemical reaction has long been the cherished goal of chemists. The advent of femtosecond laser pulses has revolutionized this idea and femtochemistry has become a major area of research in which realtime dynamics of chemical reactions can be probed, understood and possibly controlled. In the simplest case of the photodissociation of a molecule, a femtosecond laser pulse initiates the process and a subsequent ‘probe’ laser pulse interrogates the dissociating molecular species. The alkali metal halides, especially NaI has served as a prototype for such investigations for over a decade. In the case of NaI, the dissociation yields either neutral Na + I atoms or Na<sup>+</sup> and I<sup>-</sup> ionic species. However, all theoretical approaches so far have considered the production of Na+I products in the ground state. The spin-orbit interaction in iodine is large and results in a splitting of about 0.95 eV between the ground  $^2P_{3/2}$  and the excited  $^2P_{1/2}$  states. The asymptote of the Na+I( $^2P_{1/2}$ ) channel lie below the ionic dissociation threshold and the corresponding potential curve has not been calculated before. Here we present explicit ab initio calculations of the adiabatic potential energy curves, transition dipole matrix elements and spin-orbit coupling matrix elements in NaI, and investigate the photodissociation dynamics on the computed electronic states using a time-dependent wave packet description. The possibility of two-photon coherent control to influence the branching ratio between the ground and excited states of iodine is also explored.