Supplementary Information

Structural dynamics effects on the ultrafast chemical bond cleavage of a photodissociation reaction

M. E. Corrales, V. Loriot, G. Balerdi, J. González-Vázquez, R. de Nalda, L. Bañares and A. H. Zewail

I. Transients measured for the photodissociation channel yielding CH_3+I*($^2P_{1/2}$).

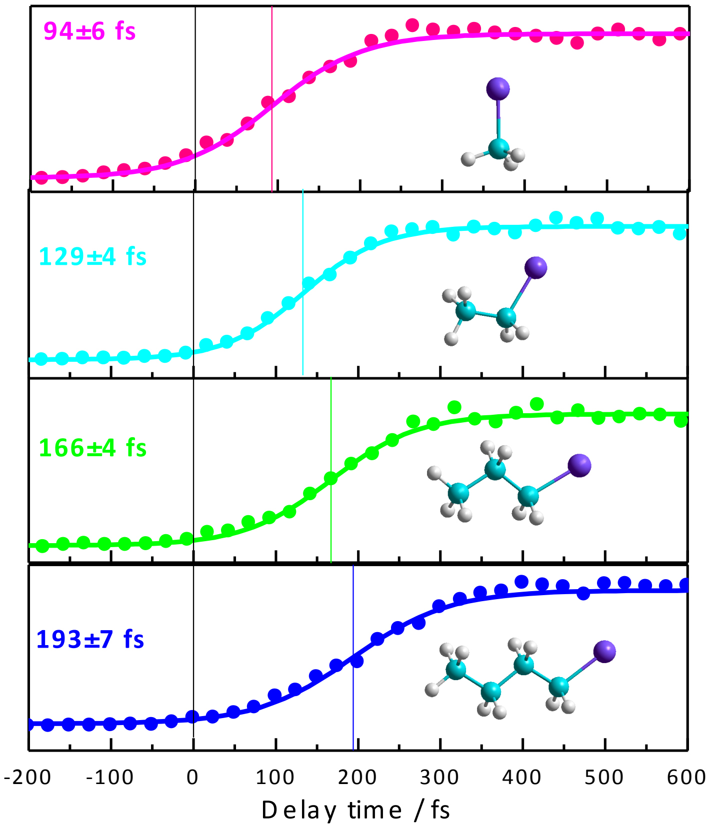

Figure SI-1. Transients measured for the series of linear alkyl iodide molecules for the channel of the reaction yielding spin-orbit excited iodine $^2P_{3/2}$ atoms. The reaction (clocking) times are referred to the time zero found *in situ* by measuring the 1+1' ionization signal in Xe. Time zero is indicated in each panel by means of a vertical dashed line. The reaction time is defined as the time between time zero and the time corresponding to the middle of the rise of the transient (indicated by vertical lines in each panel). The reaction times obtained as a mean value of several measurements along with the error bar reflecting the standard deviation are indicated in each panel.

II. Potential energy curves calculated at the CASPT2 level of theory for the different alkyl iodides studied in this work.

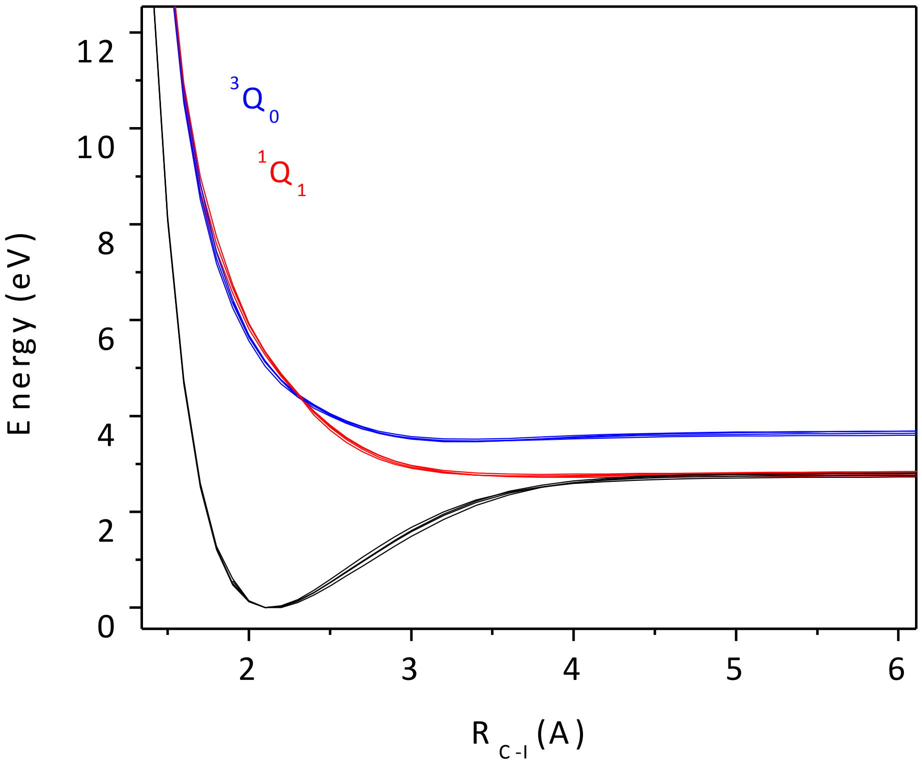

Figure SI-2. Potential energy curves calculated at the CASPT2 (see Methodology section) level of theory for CH_3I, C_2H_5I, *n*-C_3H_5I, *n*-C_4H_9I, *i*-C_3H_5I and *n*-C_4H_9I. In all cases, at each C-I distance the geometry of the molecule in the ground state is optimized befoge energy calculation. As can be seen, the shape of the different potential energy curves and the location of the $^3Q_0/^1Q_1$ conical intersection are very similar for all linear and branched alkyl iodides studied in this work.

III. Movies of specific on-the-fly trajectories for all the molecules in both the linear and branched series.

Included as avi files.