Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Subpicosecond HI Elimination in the 266 nm Photodissociation of Branched Iodoalkanes

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Supplementary Information

i) Determination of the Anisotropy Parameters (β) for the different photodissociation channels, and their respective error limits

The most sensitive measurement of the anisotropy parameter (β) is obtained by comparing the integrated experimental signal intensities for the forward peak of the time-of-flight (TOF) spectra at the polarization angles where the signal intensities are the maximum and minimum, respectively. The integrated signal intensities were normalized with the maximum set to 1.0. The normalized minimum signal intensity is used to determine the correct β value for a particular photodissociation channel. In our experiments, the uncertainty in the integrated signal intensities was measured to be +/- 10%, while the uncertainty in the polarization angle was +/- 2°. Taking these into account, the value of β and its associated uncertainty for each photodissociation channel were determined by comparing the measured normalized minimum integrated signal to calculated polarization angular distributions using various input values of β.

The results of the experimentally obtained β values, and their respective error limits analysis, for the different channels are the following:

1) For 1-C_3H_7I, β for the I* + C_3H_7 channel was 1.84 (+0.02/-0.03). See Fig. S1.

2) For 2-C_3H_7I, β for the I + stable C_3H_7 channel was 1.90 (+0.03/-0.04). See Fig. S2.

3) For 2-C_3H_7I, β for the HI + C_3H_6 channel was 1.94 (+0.04/-0.06). See Fig. S3.

4) For 1-C_3H_7I, β for the I + C_3H_7 channel was 1.76 (+0.03/-0.02). See Fig. S7.

5) For 2-C_3H_7I, β for the I* + C_3H_7 channel was 1.94 (+0.02/-0.01). See Fig. S9.

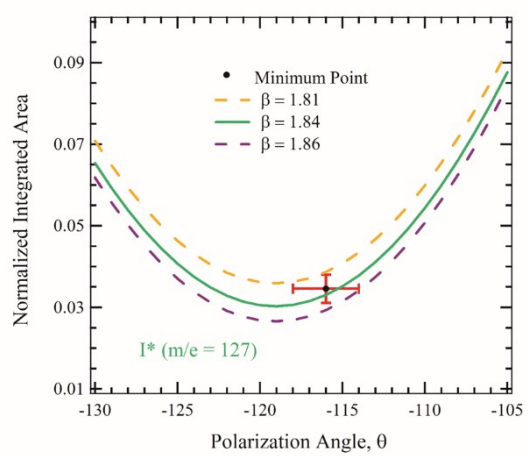

Fig. S1: *Normalized integrated polarization angular distributions, at lab angle of 10°, for I* + C_3H_7 from 1-C_3H_7I photodissociation: the black dot corresponds to the experimentally obtained minimum integrated signal intensity; the error bars are shown in red; the dashed orange line corresponds to the calculated distribution for β = 1.81; the solid green line for β = 1.84; the dashed purple line for β = 1.86. Minimum θ_{pol} was -116° (+/- 2°), and β = 1.84 (+0.02/-0.03). The P(E) is depicted in Fig. 3 of the main article. See Figs. 4 and 5 in the main article for reference.*

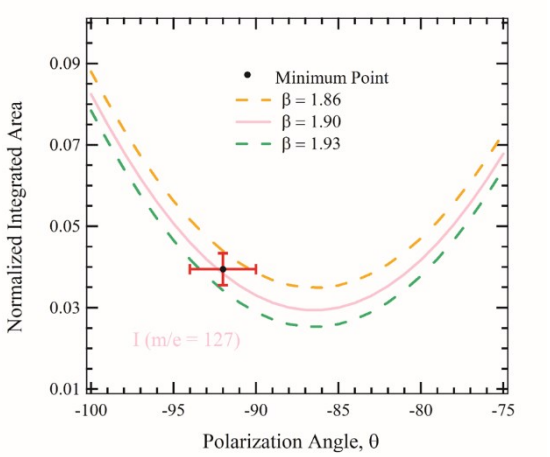

Fig. S2: *Normalized integrated polarization angular distributions, at lab angle of 10°, for I + stable C_3H_7 from 2-C_3H_7I photodissociation: the dashed orange line corresponds to calculated distribution for β = 1.86; the solid pink line corresponds to β = 1.90; the dashed green line corresponds to β = 1.93. Minimum θ_{pol} was at -92° (+/- 2°), and β = 1.90 (+0.03/-0.04). The P(E) is depicted in Fig. 8 of the main article. See Figs. 9 and 10 of the main article for reference.*

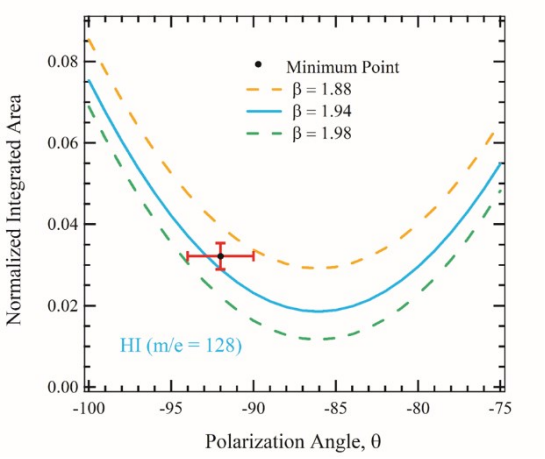

Fig. S3: *Normalized integrated polarization angular distributions, at lab angle of 10°, for HI + C_3H_6 from 2-C_3H_7I photodissociation: the dashed orange line corresponds to the calculated fit for β = 1.88; the solid blue line corresponds to β = 1.94; the dashed green line corresponds to β = 1.98. Minimum θ_{pol} was obtained at -92° (+/- 2°), and β was measured to be 1.94 (+0.04/-0.06), respectively. The P(E) for the calculated fits is depicted in Fig. 8 of the main article. See Figs. 12 and 13 of the main article for reference.*

ii) Relationship between excited state lifetime (τ), anisotropy parameter (β), and rotational temperature (T)

For a pure parallel transition, in the axial recoil limit, the anisotropy parameter, β = 2.0 if dissociation is much faster than the timescale for parent rotation. A reduction in β from the limiting value of 2.0 occurs when the excited state lifetime (τ) is sufficiently long to allow some parent rotation prior to product formation. Yang and Bersohn, (*J. Chem. Phys.*, 1974, **61**, 4400-4406) derived a relationship between β and τ for an ensemble of parent molecules characterized by a rotational temperature T using a pseudodiatomic model as a first order approximation for polyatomic molecules:

$$\beta = \frac{1}{2}(1 + 3\gamma e^{\gamma} \int_{\gamma}^{\infty} \frac{e^{-v}}{v} dv) \qquad (1)$$

where

$$\gamma = \frac{I}{8kT\tau^2} \qquad (2)$$

Here, I is the moment of inertia in the parent molecule relevant for product formation, k is the Boltzmann constant, T is the rotational temperature of the parent molecules, and τ is the lifetime of the parent molecules prior to dissociation. For the HI + C_3H_6 channel from photodissociation of 2-C_3H_7I, we calculated the expected values of τ for various values of β and rotational temperatures, T. We used I = 3.38 x 10^{-45} kg m^2 for HI elimination, which is taken to be the same as for C-I bond fission. The results are tabulated below and are plotted as Fig. S4.

T (K)	β	τ (picoseconds)
10	1.88	0.535
10	**1.94**	**0.365**
10	1.98	0.205
5	1.88	0.760
5	**1.94**	**0.515**
5	1.98	0.290
2	1.88	1.200
2	**1.94**	**0.810**
2	1.98	0.455

Using β = 1.94, dissociation timescales of τ ranges from 0.365 to 0.810 ps for T ranging from 10 K to 2 K. As noted in the article, however, since we used the warmer early part of the pulsed beam, temperatures are not expected to be as low as 2 K.

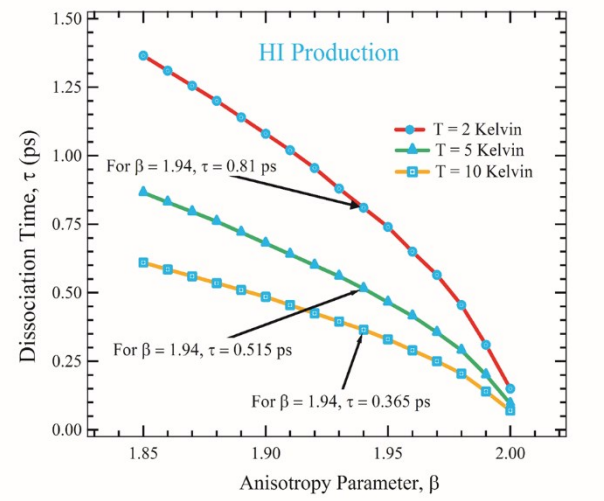

Fig. S4: *Plot of dissociation time (τ) vs. anisotropy parameter (β) for 2-C_3H_7I, assuming different rotational temperatures (T). For T = 2 K and β = 1.94, the calculated dissociation time is 0.81 ps; for T = 5 K and β = 1.94, the calculated dissociation time is 0.515 ps; for T = 10 K and β = 1.94, the calculated dissociation time is 0.365 ps.*

iii) Polarization TOFs and determination of β for the I ($^2P_{3/2}$) + C_3H_7 channel from 1-C_3H_7I photodissociation

The anisotropy parameter for the minor I ($^2P_{3/2}$) + C_3H_7 channel was found to be β = 1.76 (+0.03/-0.02) on the basis of experimental data shown in Figs. S6 and S7.

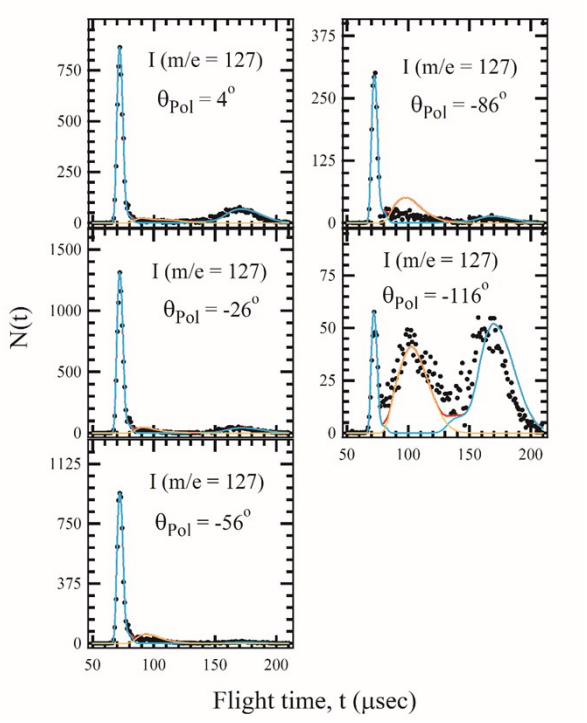

Fig. S5: *Time-of-flight spectra for I($^2P_{3/2}$) from 1-C_3H_7I photodissociation, at indicated polarization angles. The blue lines are the calculated TOFs for the I + C_3H_7 channel; the orange lines are the calculated TOFs for the 1-C_3H_7I cluster photodissociation channel. The red lines correspond to the calculated overall TOFs. The laboratory angle was 10°. The relevant P(E)s are depicted in Figs. 3 and 6 of the main article.*

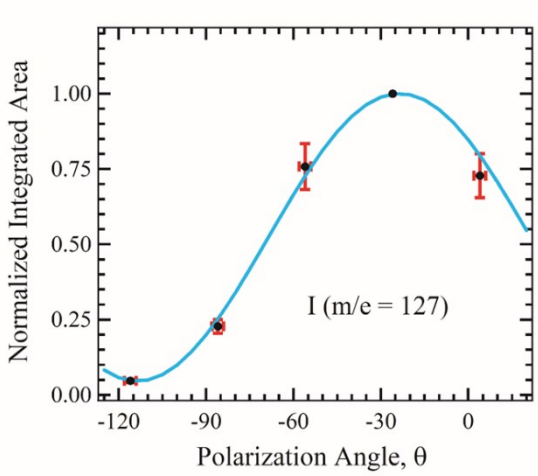

Fig. S6: *Integrated polarization angular distributions, at lab angle of 10°, for I($^2P_{3/2}$) + C_3H_7 from 1-C_3H_7I photodissociation: the blue line corresponds to the calculated distribution. See Fig. S5 for reference.*

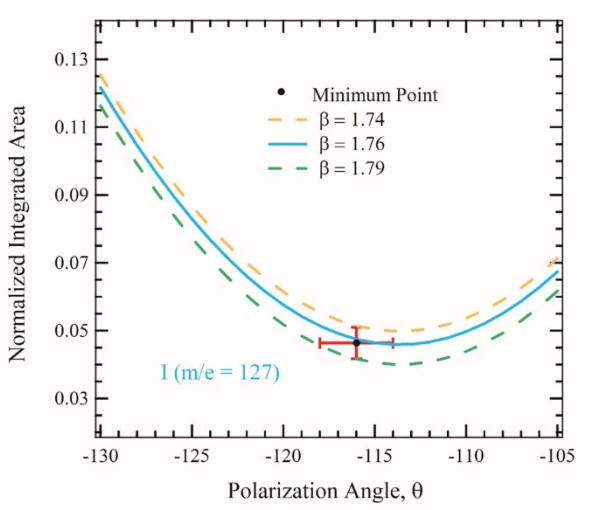

Fig. S7: *Normalized integrated polarization angular distributions, at lab angle of 10°, for $I(^2P_{3/2})$ + C_3H_7 from 1-C_3H_7I photodissociation: the dashed orange line corresponds to β = 1.74; the solid blue line corresponds to calculation with β = 1.76; the dashed green line corresponds to β = 1.79, respectively. Minimum θ_{pol} was obtained at -116° (+/- 2°), and β = 1.76 (+0.03/-0.02). See Figs. S5 and S6 for reference.*

iv) Polarization TOFs and determination of β for the I* ($^2P_{1/2}$) + C_3H_7 channel from 2-C_3H_7I photodissociation

I* ($^2P_{1/2}$) + C_3H_7 is the minor channel (15%) in the photodissociation of 2-C_3H_7I. The TOF spectra for various polarization angles, are shown in Fig. S8, recorded at a lab angle of 10°.

For this channel, β = 1.94 (+0.02/-0.01) (see Fig. S9).

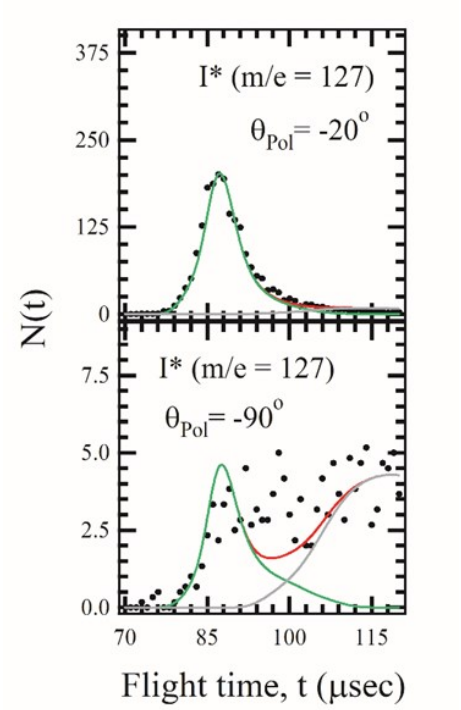

Fig. S8: *Time-of-flight spectra for I*($^2P_{1/2}$) from 2-C_3H_7I photodissociation, at indicated polarization angles. The green lines are calculated TOFs for the I* + C_3H_7 channel; the gray lines are calculated TOF for the 2-C_3H_7I cluster photodissociation channel. Lab angle was 10°. The relevant P(E)s are depicted in Figs. 8 and 6 of the main article.*

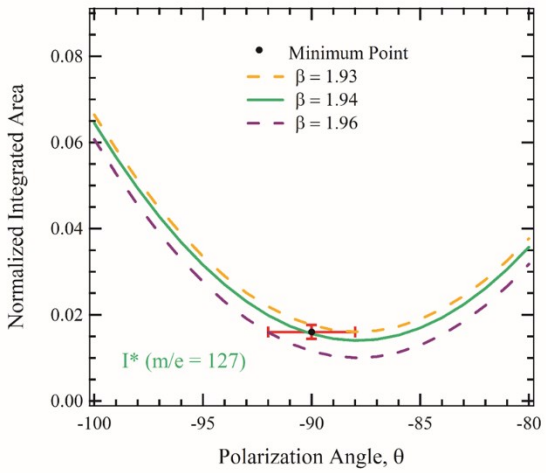

Fig. S9: *Integrated polarization angular distributions, at lab angle of 10°, for I* + C_3H_7 from 2-C_3H_7I photodissociation: the dashed orange line is for β = 1.93; the solid green line is for β = 1.94; the dashed purple line is for β = 1.96. Minimum θ_{pol} was obtained at -90° (+/- 2°), and β = 1.94 (+0.02/-0.01). See Fig. S8 for reference.*