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

Formation of highly excited iodine atoms from multiphoton excitation of CH_3I

Kristján Matthíasson[1#], Greta Koumarianou[2#] , Meng-Xu Jiang [1#], Pavle Glodic [2#]
Peter C. Samartzis[2*] and Ágúst Kvaran[1*]

1. *Science Institute, University of Iceland, Dunhagi 3, 107 Reykjavík, Iceland.*
2. *Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, Vassilika Vouton, 71110 Heraklion, Greece.*

Supplementary material

Content: pages:

Fig. S1: I^+ ion REMPI Spectra..... 1

Fig. S2: Non-resonance mass spectra at 69 384 cm^{-1} and 69 539 cm^{-1}. .....…... 2

Fig. S3 (a – c): Photoelectron KERs…… 3 – 5

Fig. S4 (a - h): Angular distributions for CH_3^+ images…… 6 – 9

Fig. S5 (a - h): Angular distributions for I^+ images……. 10 – 13

Table S1: Anisotropy parameters for CH_3^+ images ……. 14

Table S2: Anisotropy parameters for I^+ images …… 15

Fig. S1

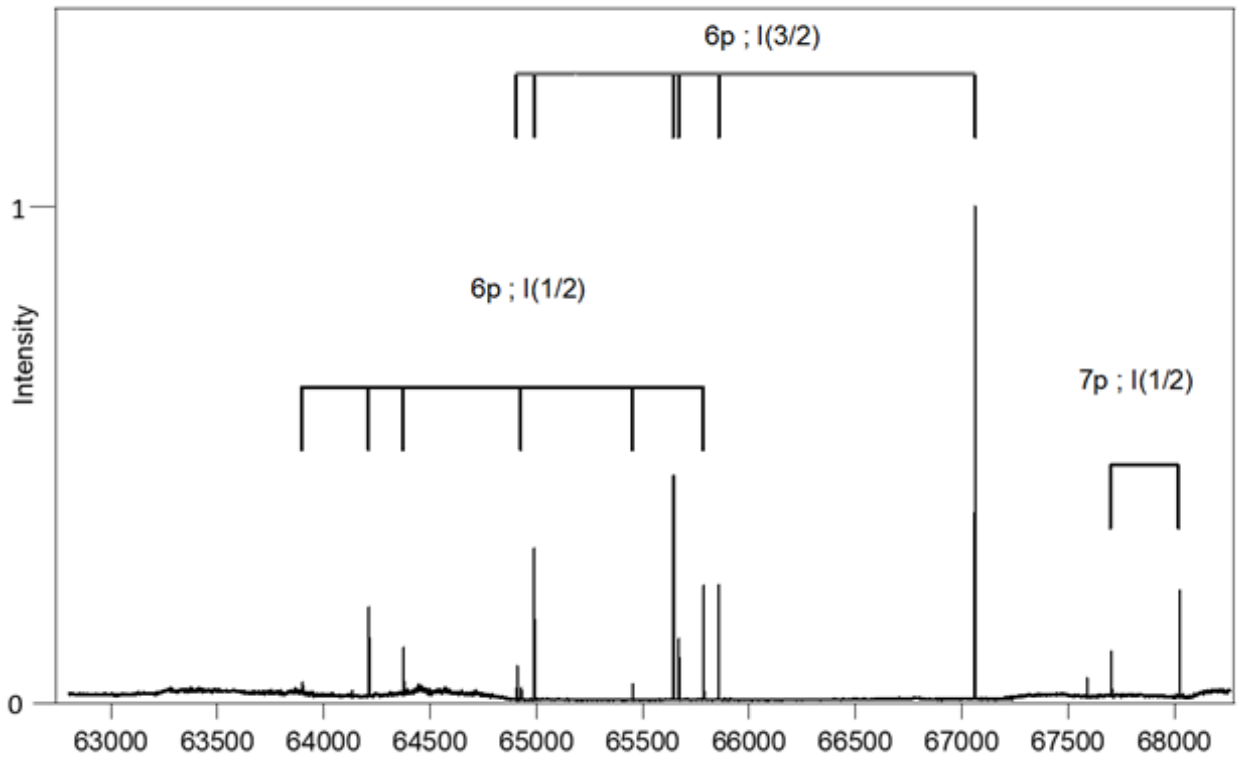

Fig. S1: *Figure shows REMPI spectra for I^+ ion in the energy region of 65 000 cm^{-1} to 70 000 cm^1. Grid shows iodine atomic lines according to NIST. Atomic lines originate from either iodine atoms in the ground (I(3/2)) or the spin-orbit excited (I(1/2)) state.*

Fig. S2

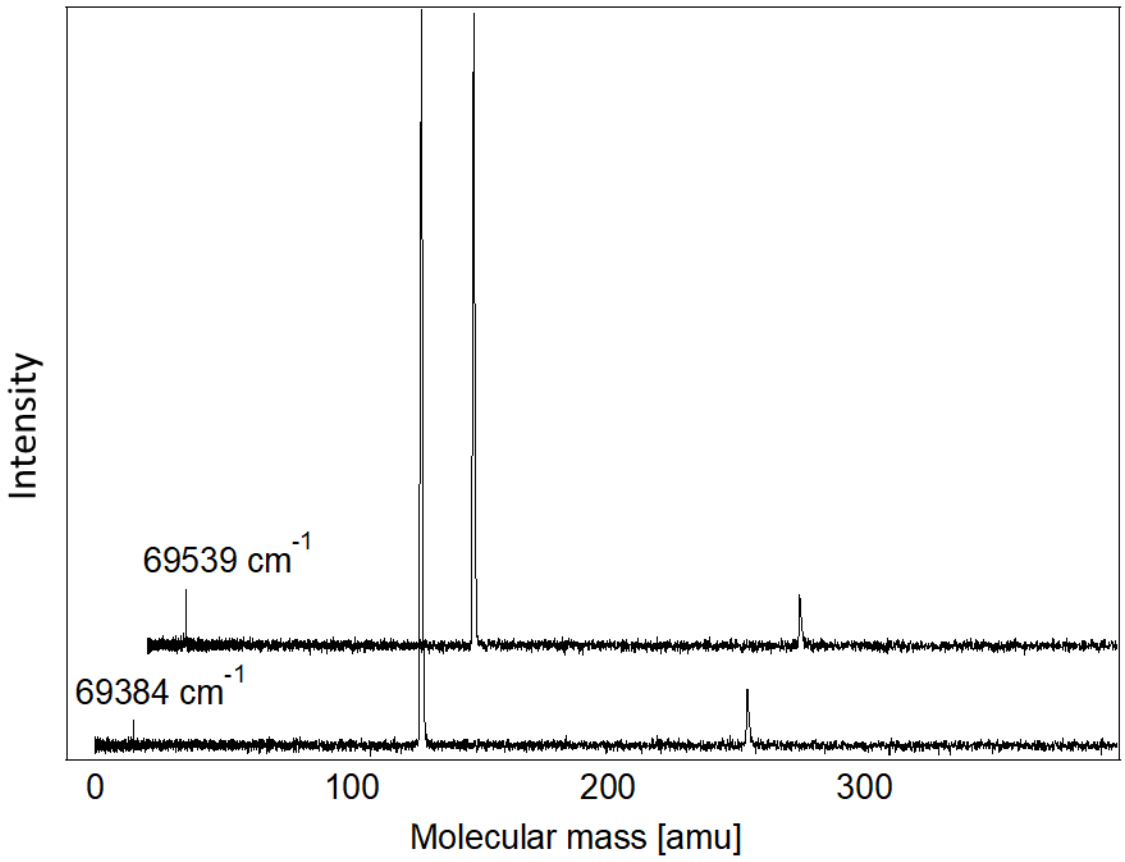

Fig. S2*: Figure shows mass spectra at non-resonant frequencies of 69 384 cm^{-1} and 69 539 cm^{-1}. CH_3^+, I^+ and I_2^+ mass peaks are observed due to non-resonance excitation and ionization.*

Fig. S3

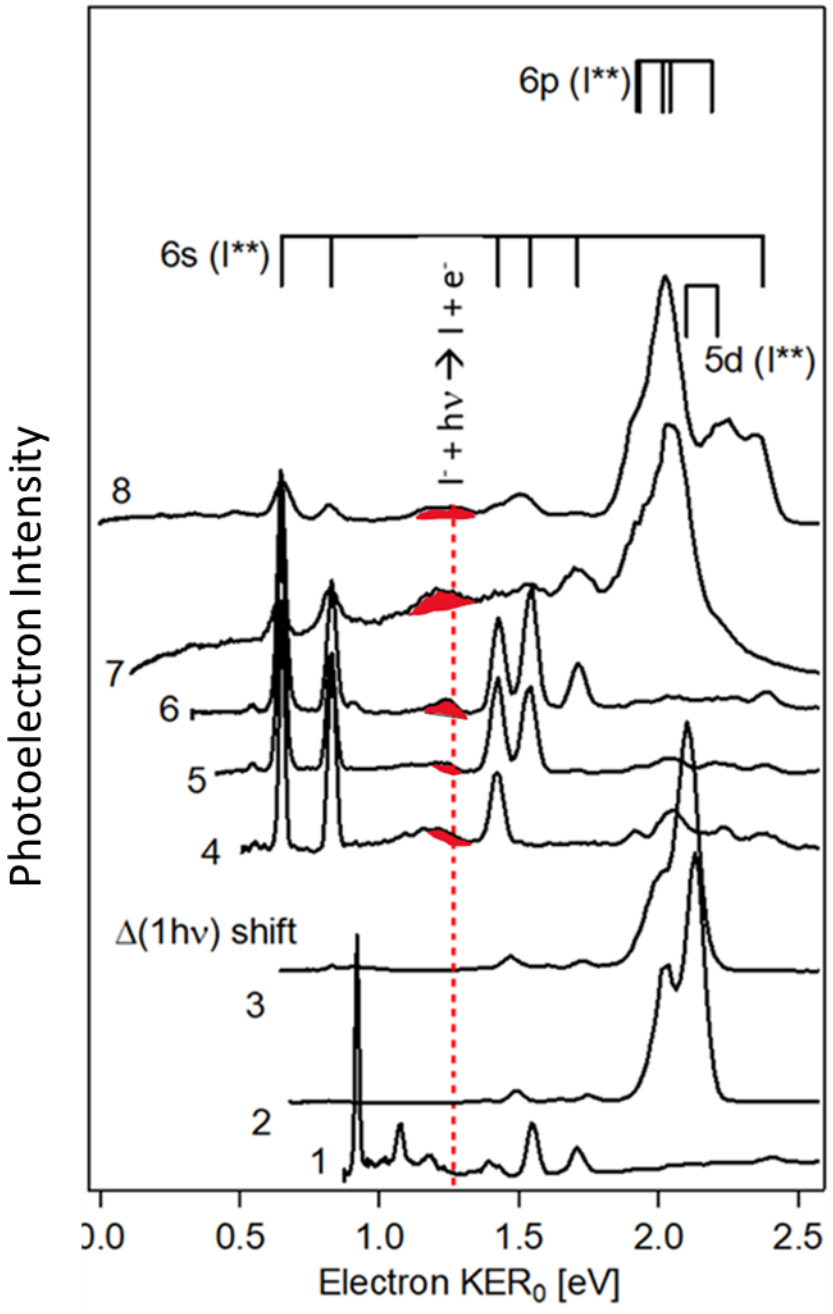

Fig. S3a*: Photoelectron KERs derived from images no. 1 – 8 (see paper main text) shifted by a one-photon energy difference (Δ(1hν) = /1hν$_i$ - 1hν$_0$/) with respect to the spectrum for the highest energy excitation (i.e. reference spectrum, no. 8). Common energy thresholds (energy maxima) for one-photon ionization of Rydberg iodine atoms (I**) are indicated by sticks above the KERs. The threshold for electron ejection of I^- is indicated by a red broken line and the corresponding peaks(shoulders) are highlighted in red. The spectra are normalized to the strongest peak in each spectrum.*

Fig. S3

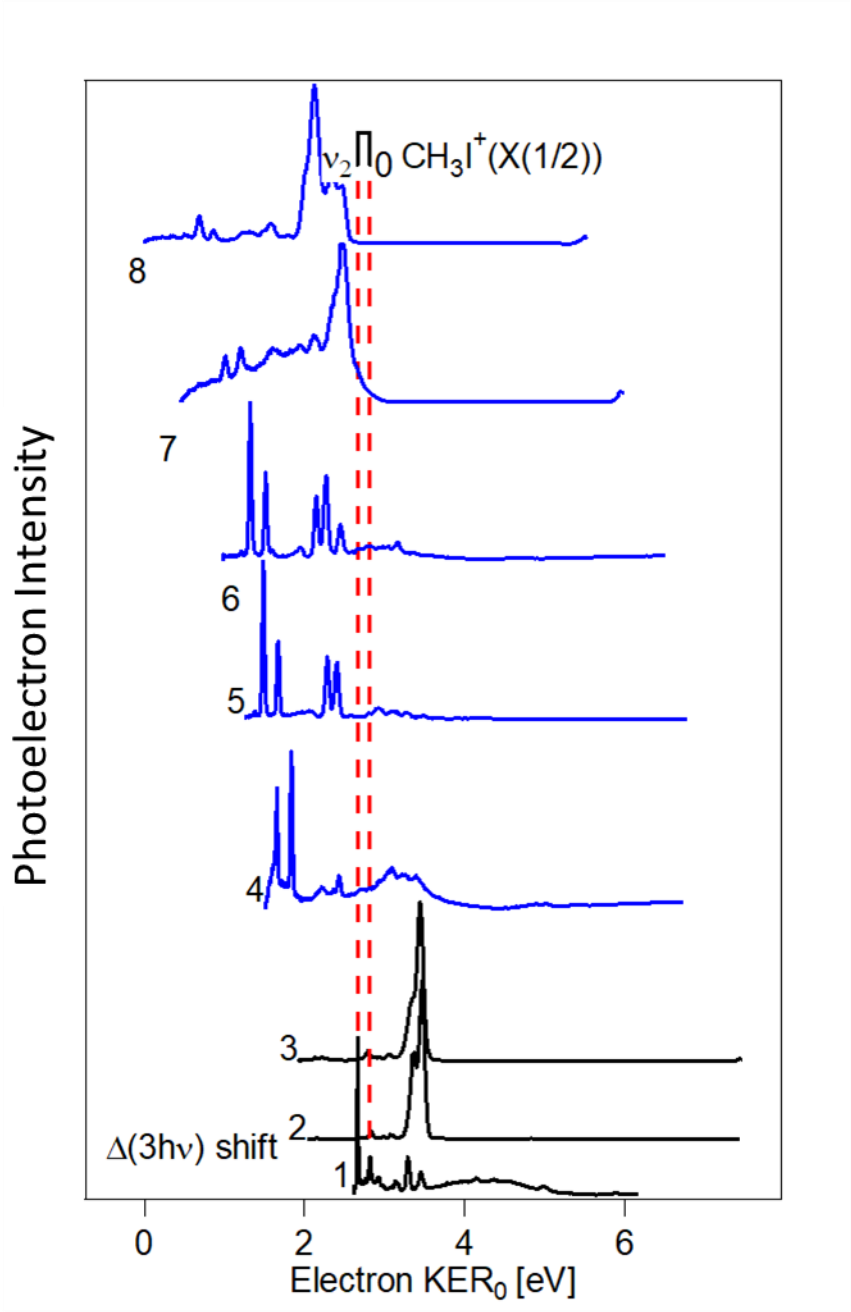

***Fig. S3b**: Photoelectron KERs derived from images 1 – 8 (see paper main text) shifted by a three-photon energy difference ($\Delta(3h\nu) = |3h\nu_i - 3h\nu_0|$) with respect to the spectrum for the highest energy excitation (i.e. reference spectrum, no. 8). Common energy thresholds (energy maxima) for autoionization of superexcited CH_3I ($CH_3I^{\#}$) are indicated by sticks above the KERs. The spectra are plotted as a function of the electron KER for the reference spectra (KER_0). The spectra are normalized to the strongest peak in each spectrum.*

Fig. S3

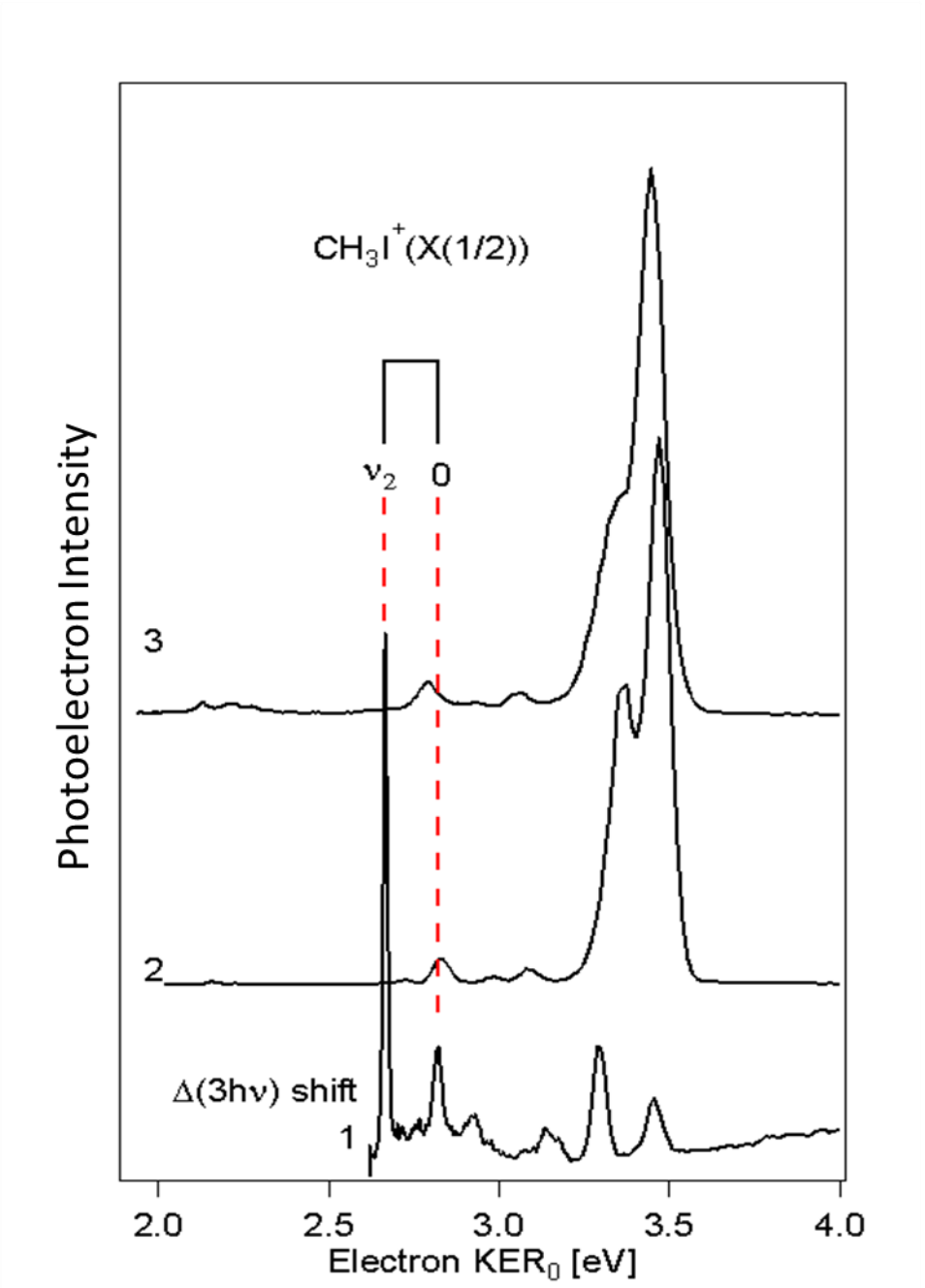

***Fig. S3c**: Photoelectron KERs derived from images 1 – 3 (see paper main text) shifted by a three-photon energy difference ($\Delta(3h\nu) = |3h\nu_i - 3h\nu_0|$) with respect to the spectrum for the highest energy excitation recorded (i.e. reference spectrum, no. 8). Common energy thresholds (energy maxima) for autoionization of superexcited CH_3I ($CH_3I^{\#}$) are indicated by sticks above the KERs. The spectra are plotted as a function of the electron KER for the reference spectra (KER_0). The spectra are normalized to the strongest peak in each spectrum.*

Fig. S4.

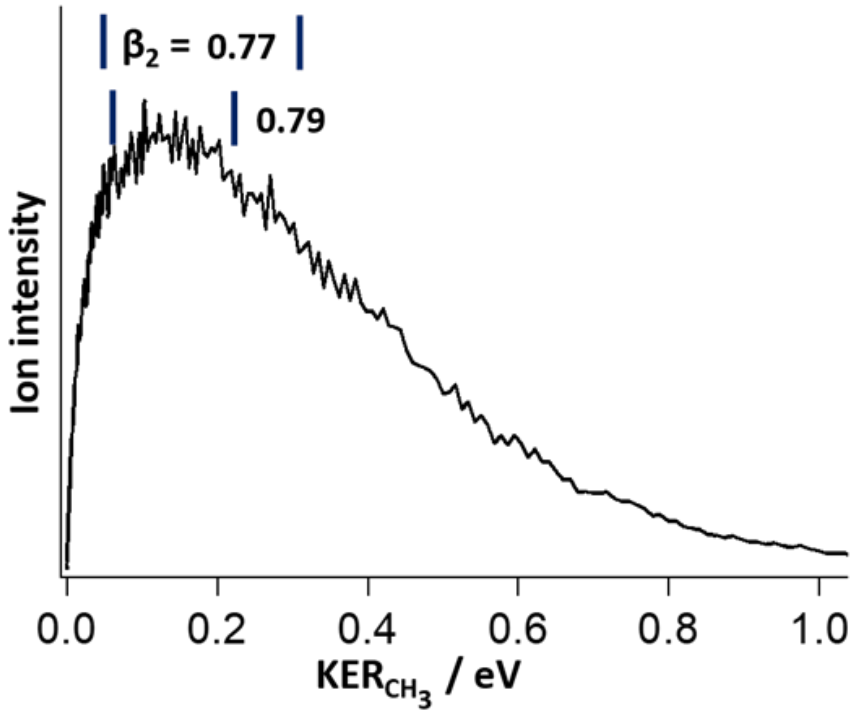

Fig. S4-a: *CH_3^+ KER spectrum and anisotropy, β_2 values. 2hν = 55700 cm^{-1}.*

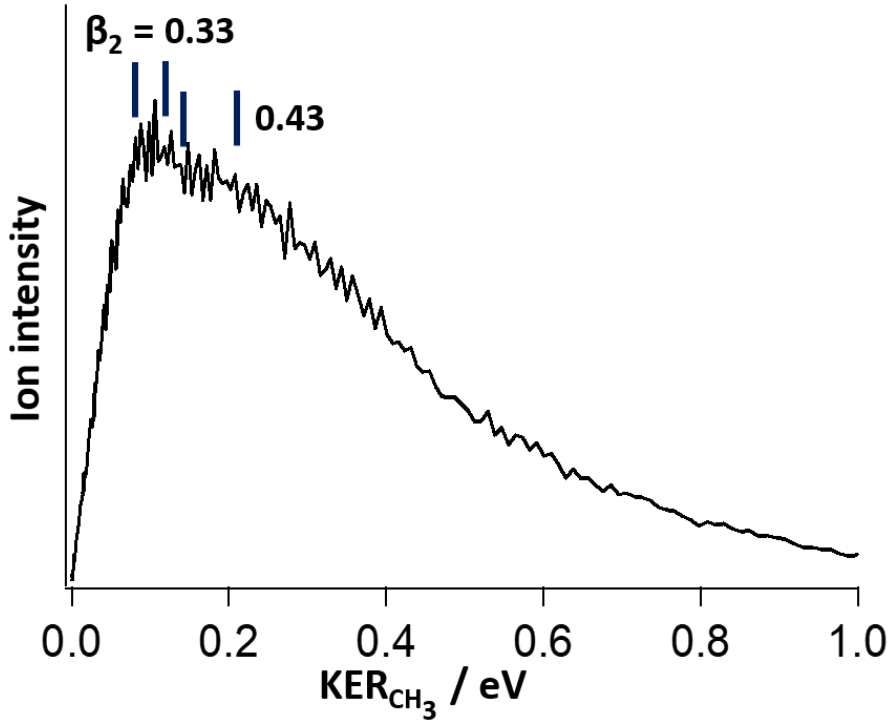

Fig. S4-b: *CH_3^+ KER spectrum and anisotropy, β_2 values. 2hν = 58926 cm^{-1}.*

Fig. S4.

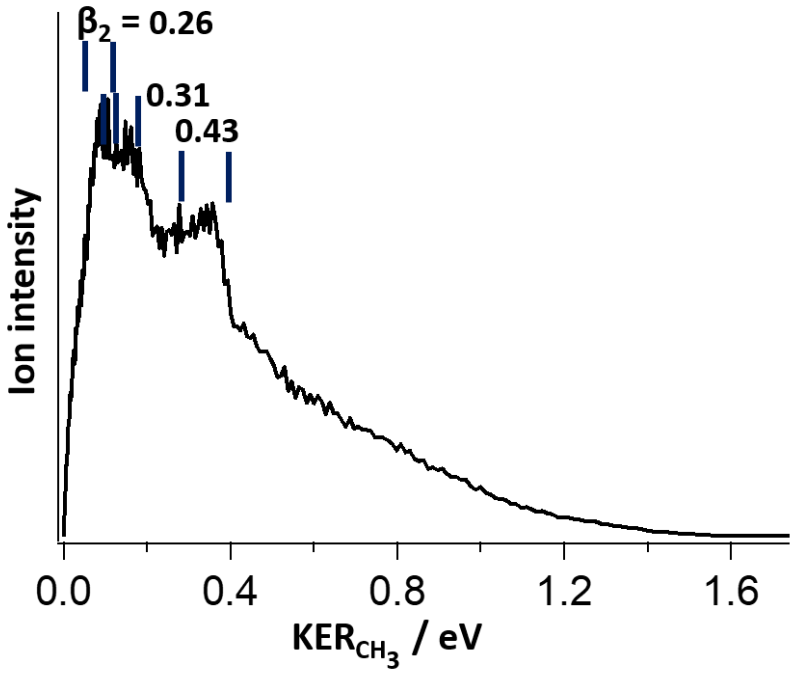

Fig. S4-c: *CH_3^+ KER spectrum and anisotropy, β_2 values. 2hν = 59362 cm^{-1}.*

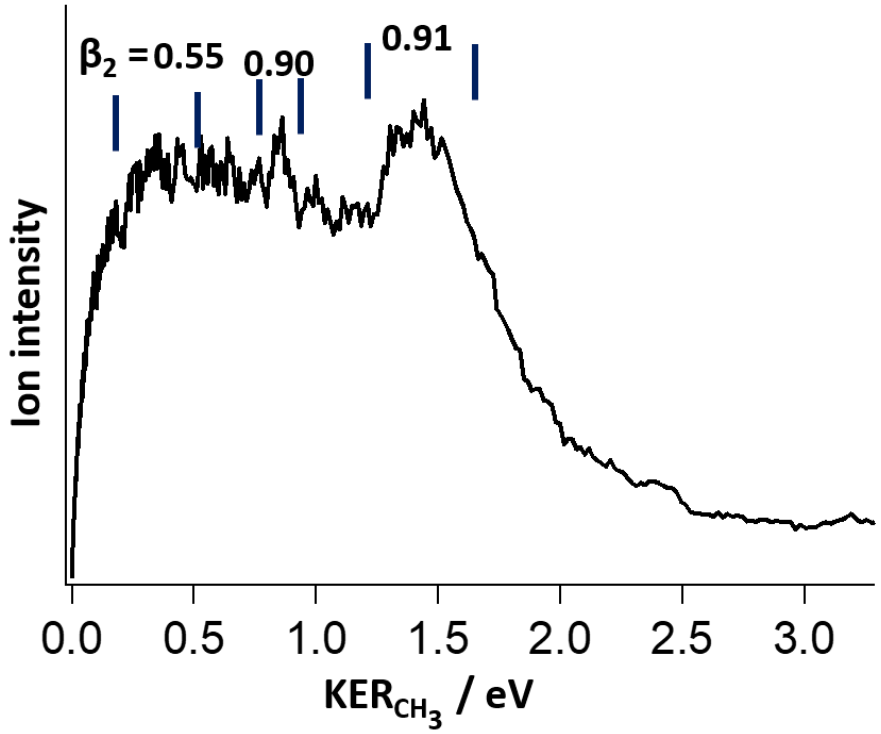

Fig. S4-d: *CH_3^+ KER spectrum and anisotropy, β_2 values. 2hν = 61632 cm^{-1}.*

Fig. S4.

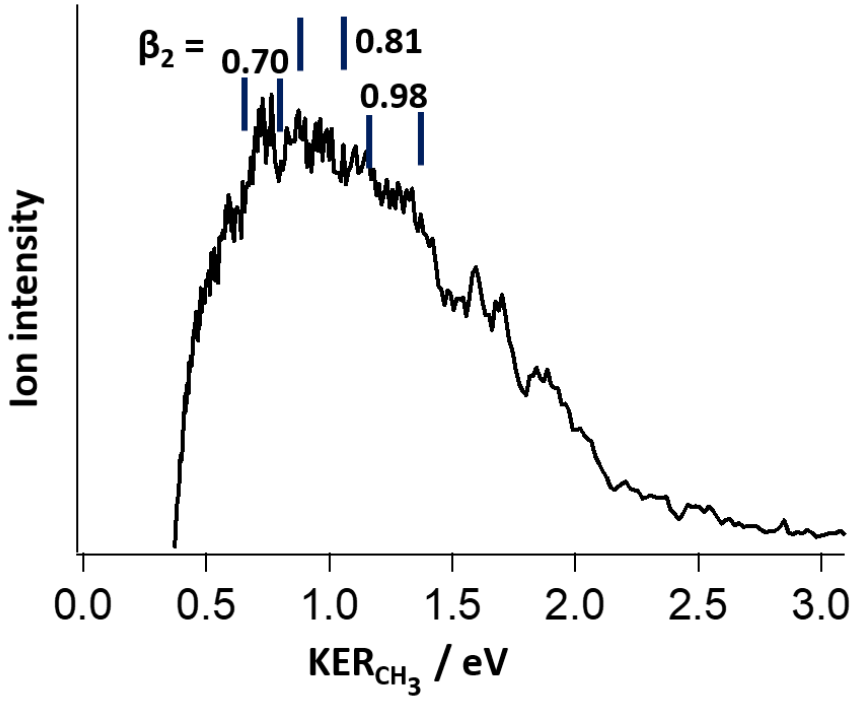

Fig. S4-e: *CH_3^+ KER spectrum and anisotropy, β_2 values. 2hν = 63067 cm^{-1}.*

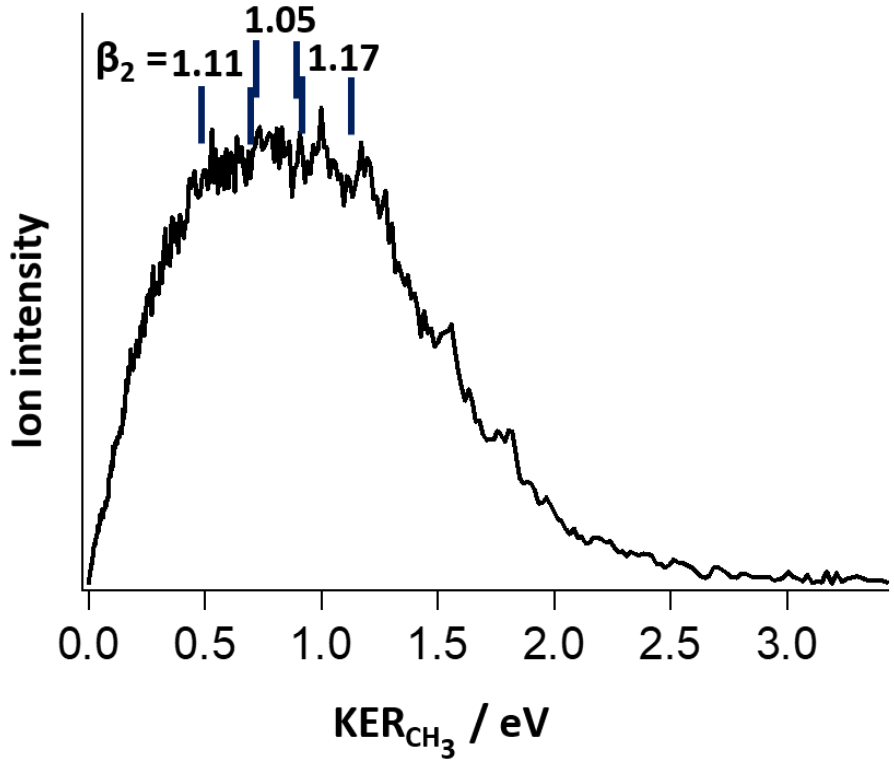

Fig. S4-f: *CH_3^+ KER spectrum and anisotropy, β_2 values. 2hν = 64484 cm^{-1}.*

Fig. S4.

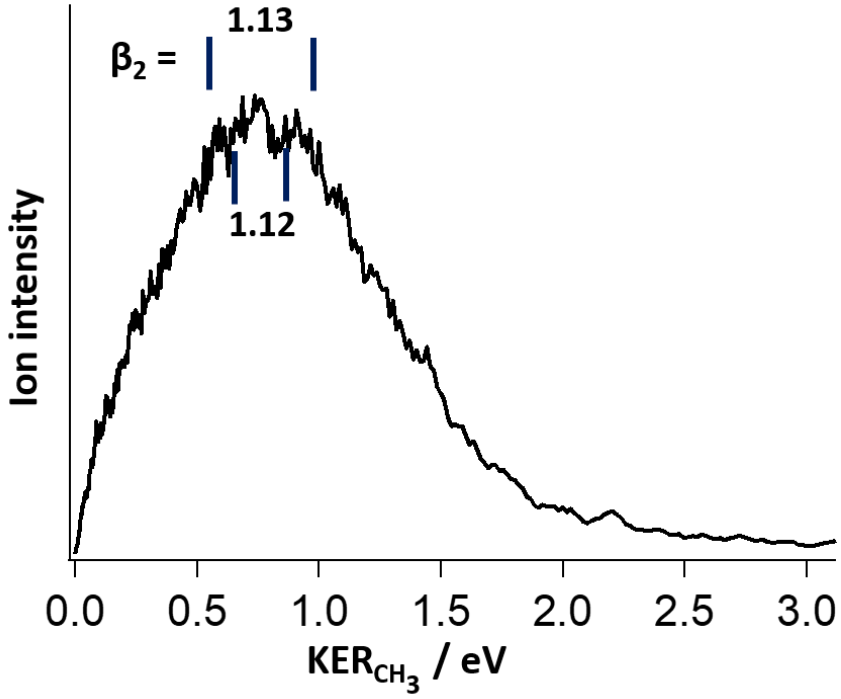

Fig. S4-g: *CH_3^+ KER spectrum and anisotropy, β_2 values. $2h\nu$ = 67984 cm^{-1}.*

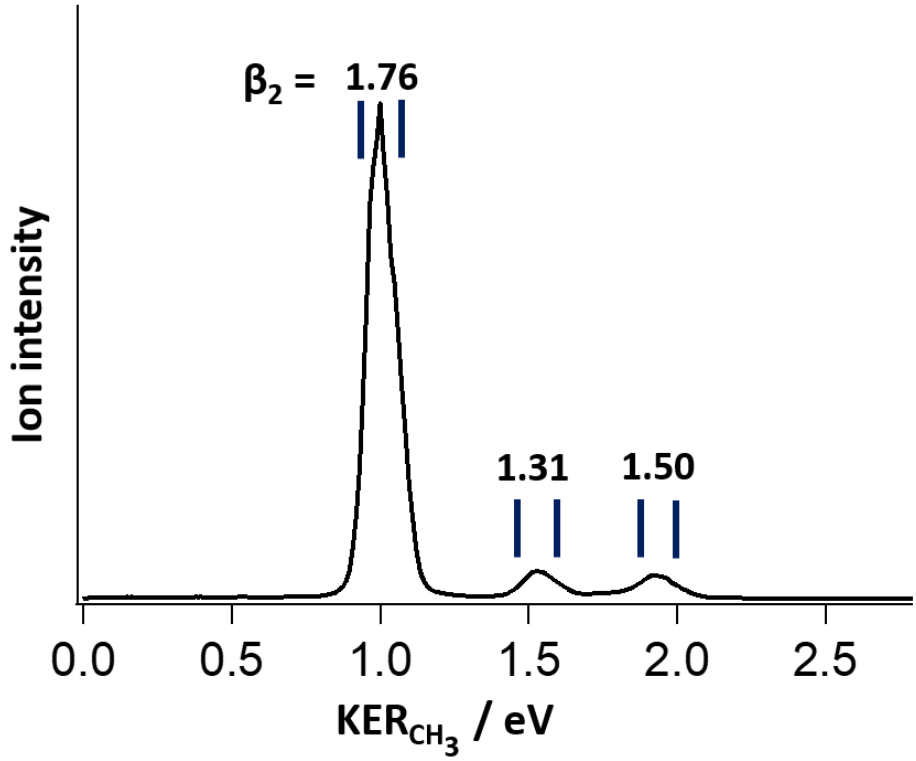

Fig. S4-h: *CH_3^+ KER spectrum and anisotropy, β_2 values. $2h\nu$ = 69783 cm^{-1}.*

Fig. S5.

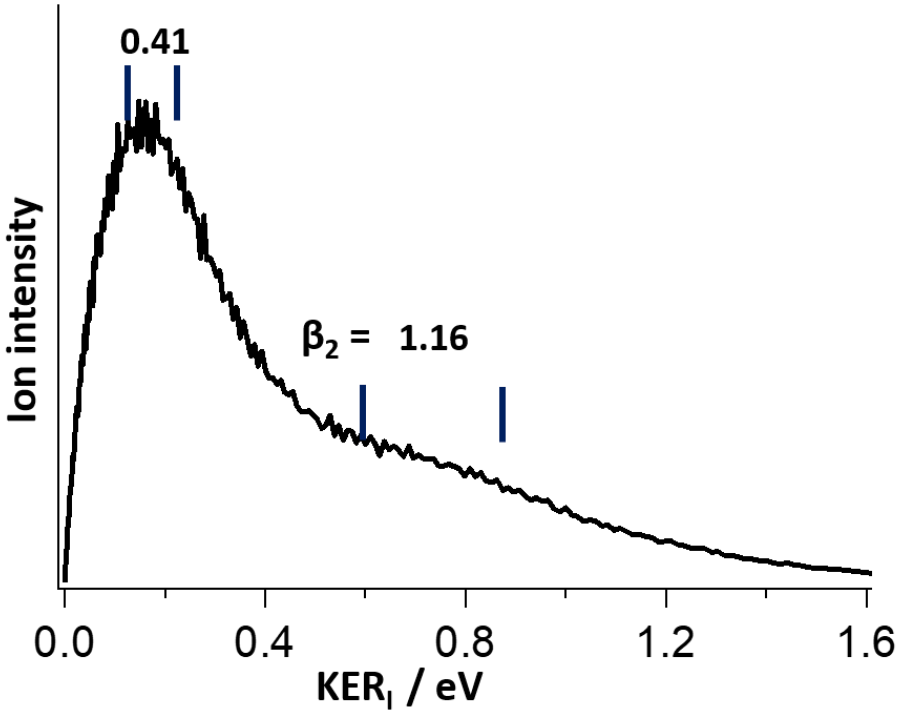

Fig. S5-a: *I^+ KER spectrum and anisotropic β_2 values. 2hv = 55700 cm^{-1}.*

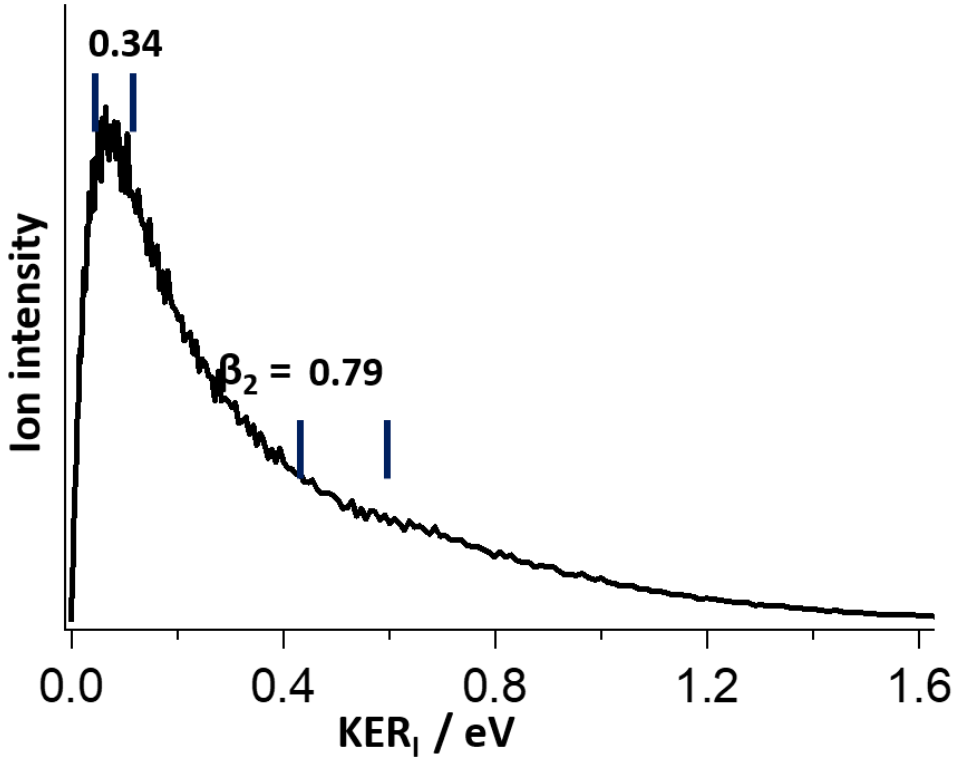

Fig. S5-b: *I^+ KER spectrum and anisotropic β_2 values. 2hv = 58926 cm^{-1}.*

Fig. S5.

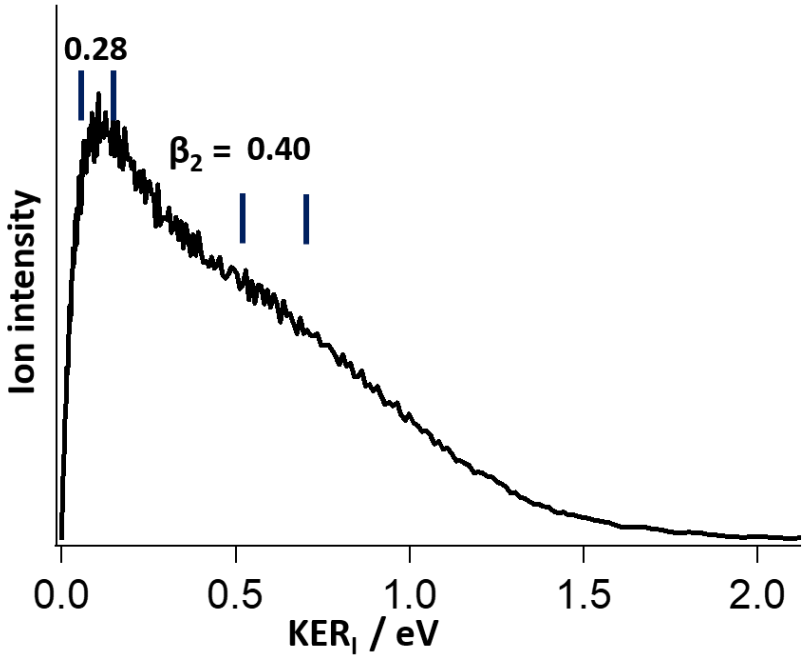

Fig. S5-c: *I^+ KER spectrum and anisotropic β_2 values. 2hν = 59362 cm^{-1}.*

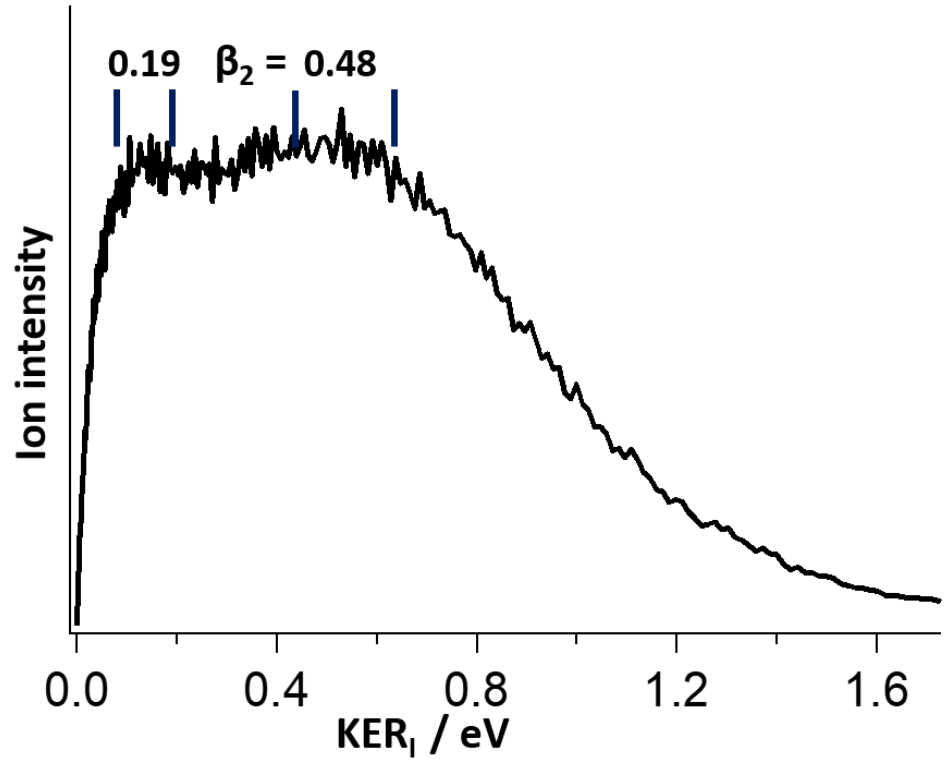

Fig. S5-d: *I^+ KER spectrum and anisotropic β_2 values. 2hν = 61632 cm^{-1}.*

Fig. S5.

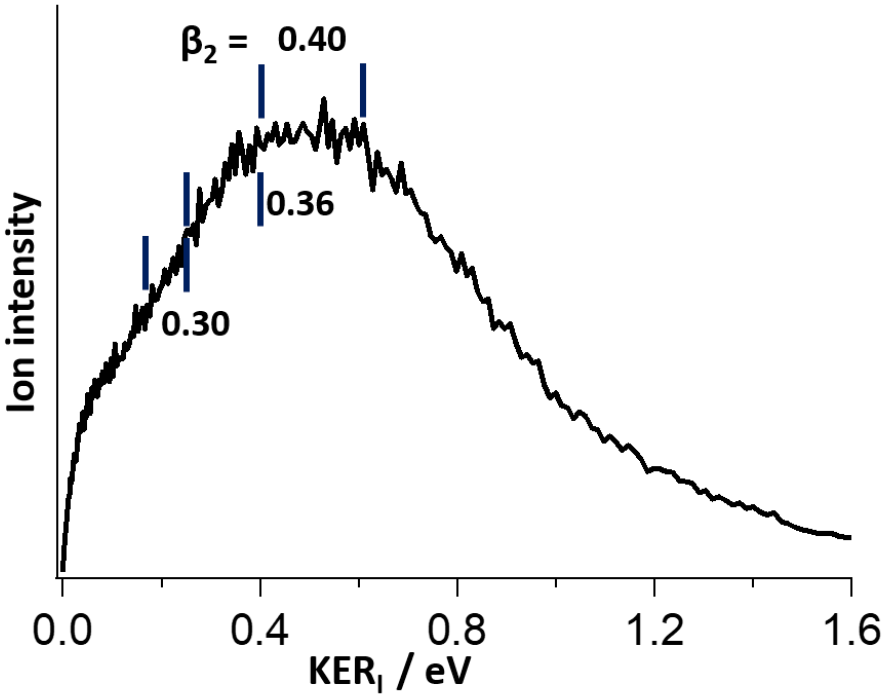

Fig. S5-e: *I^+ KER spectrum and anisotropic β_2 values. 2hv = 63067 cm^{-1}.*

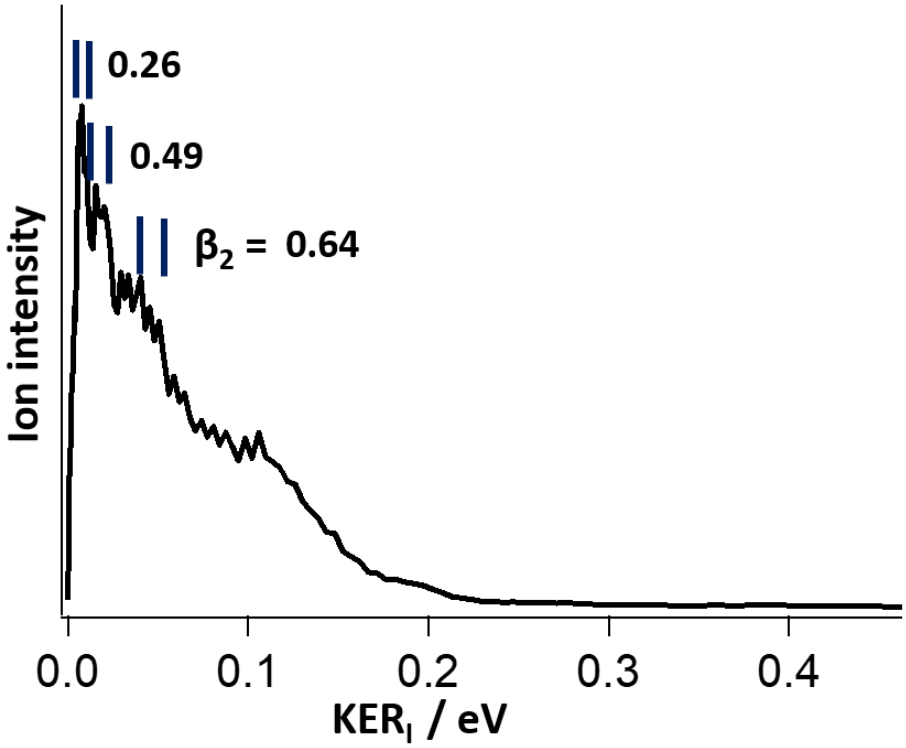

Fig. S5-f: *I^+ KER spectrum and anisotropic β_2 values. 2hv = 64484 cm^{-1}.*

Fig. S5.

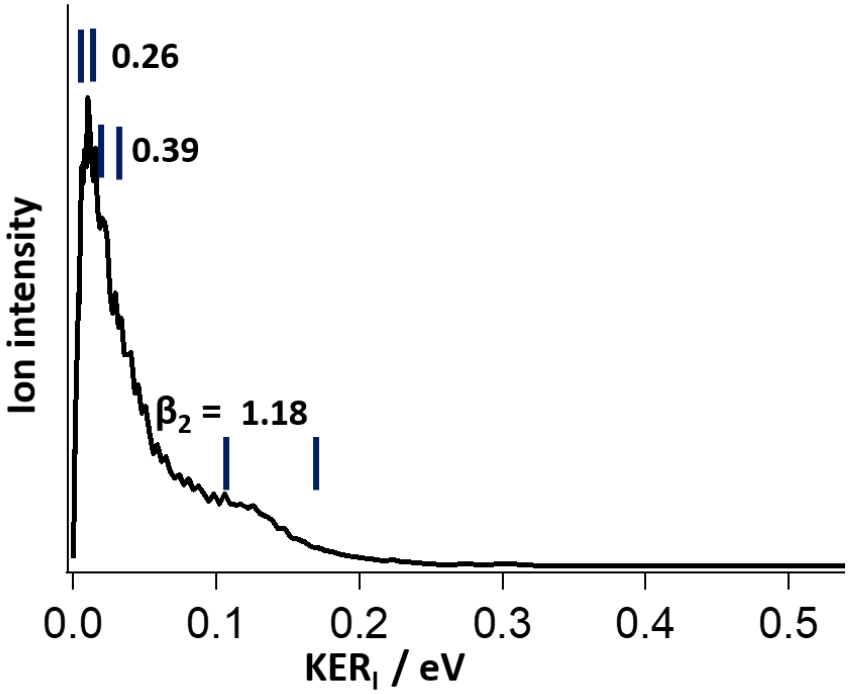

Fig. S5-g: *I^+ KER spectrum and anisotropic β_2 values. 2hν = 67984 cm^{-1}.*

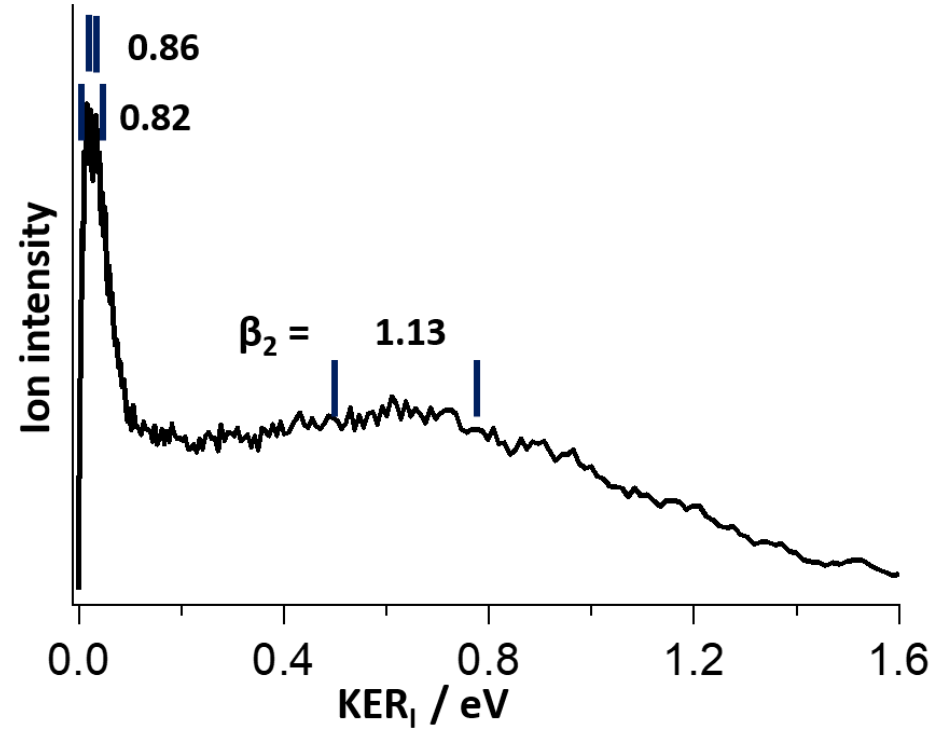

Fig. S5-h: *I^+ KER spectrum and anisotropic β_2 values. 2hν = 69783 cm^{-1}.*

Table.S1: *Anisotropy parameters (β) from figures S4a-h (CH_3^+ images / KERs) and major fragmentation channels (see paper main text).*

Figure	$2h\nu$ /cm^{-1}	KER / eV	Major Channels	β_2	Δ	β_4	Δ	β_6	Δ
S3-a	55700	0.05−0.22	3c,4	0.77	±0.01	−0.08	±0.1	−0.01	±0.01
		0.03−0.34		0.79	±0.01	−0.08	±0.1	−0.01	±0.01
S3-b	58926	0.07−0.11	3c,4	0.33	±0.01	0.07	±0.01	−0.05	±0.01
		0.13−0.23		0.43	±0.01	−0.06	±0.01	−0.04	±0.01
S3-c	59362	0.07−0.11	3c,4	0.26	±0.01	0.05	±0.01	−0.07	±0.02
		0.13−0.18		0.31	±0.01	−0.06	±0.01	0.01	±0.01
		0.28−0.38		0.43	±0.02	−0.07	±0.02	−0.08	±0.02
S3-d	61632	0.22−0.50	3b	0.55	±0.04	0.1	±0.05	−0.07	±0.05
		0.79−0.95		0.90	±0.06	0.04	±0.07	−0.18	±0.07
		1.13−1.69		0.91	±0.12	0.08	±0.13	−0.42	±0.14
S3-e	63067	90−110	3b	0.70	±0.05	−0.09	±0.05	−0.12	±0.06
		120−140		0.81	±0.06	−0.13	±0.07	−0.15	±0.07
		150−170		0.98	±0.09	−0.22	±0.10	−0.14	±0.10
S3-f	64484	120−140	3b	1.11	±0.06	−0.03	±0.05	−0.18	±0.06
		140−160		1.05	±0.09	−0.09	±0.09	−0.08	±0.10
		160−180		1.17	±0.08	−0.02	±0.08	−0.11	±0.09
S3-g	67984	140−160	3b	1.13	±0.02	−0.13	±0.04	0.01	±0.05
		130−170		1.12	±0.02	−0.19	±0.02	−0.00	±0.03
S3-h	69783	0.93−1.03	1	1.76	±0.06	−0.08	±0.05	0.04	±0.05
		1.43−1.55		1.31	±0.23	−0.35	±0.22	−0.16	±0.23
		1.82−1.95		1.50	±0.11	−0.18	±0.10	−0.23	±0.120

Table.S2: *Anisotropy parameters (β) from figures S5a-h (I^+ images / KERs) and major fragmentation channels (see paper main text).*

Figure	$2h\nu$ /cm^{-1}	KER / eV	Major Channels	β_2	Δ	β_4	Δ	β_6	Δ
S5-a	55700	0.014−0.032	3c,4	0.86	±0.01	−0.07	±0.01	−0.03	±0.01
		0.007−0.030		0.82	±0.01	−0.11	±0.01	−0.03	±0.01
		0.504−0.788		1.13	±0.03	0.03	±0.04	0.00	±0.04
S5-b	58926	0.007−0.014	3c,4	0.26	±0.02	−0.02	±0.00	−0.01	±0.00
		0.014−0.027		0.39	±0.01	−0.06	±0.01	0.00	±0.01
		0.106−0.148		1.18	±0.06	−0.20	±0.10	0.21	±0.10
S5-c	59362	0.005−0.011	3c,4	0.26	±0.00	−0.05	±0.00	−0.00	±0.00
		0.014−0.024		0.49	±0.01	−0.06	±0.01	0.03	±0.01
		0.040−0.051		0.64	±0.02	−0.12	±0.02	0.09	±0.02
S5-d	61632	0.172−0.284	3b	0.30	±0.01	0.00	±0.01	0.01	±0.01
		0.284−0.424		0.36	±0.01	0.00	±0.02	0.01	±0.02
		0.424−0.592		0.40	±0.01	0.05	±0.02	0.02	±0.02
S5-e	63067	0.059−0.197	3b	0.19	±0.01	0.03	±0.01	0.02	±0.01
		0.424−0.592		0.48	±0.01	0.02	±0.02	−0.01	±0.02
S5-f	64484	0.065−0.130	3b	0.28	±0.00	0.01	±0.01	−0.01	±0.01
		0.504−0.686		0.40	±0.01	-0.01	±0.01	0.02	±0.01
S5-g	67984	0.043−0.106	3b	0.34	±0.00	0.03	±0.00	−0.01	±0.00
		0.424−0.592		0.79	±0.02	0.11	±0.02	−0.01	±0.02
S5-h	69783	0.139−0.187	1	0.41	±0.00	0.02	±0.00	0.00	±0.00
		0.592−0.788		1.16	±0.01	0.09	±0.01	0.00	±0.01