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

Supporting Information

Vibration Mediated Photodissociation Dynamics of CH_3SH: Manipulation of the Dynamic Energy Disposal into Products

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Figure S1. 1- and 2-color H^+ PHOFEX of photodissociation of CH_3SH and TKER distributions

Figure S2. 3-color IR+UVs H^+ PHOFEX of photodissociation of CH_3SH

Figure S3. Power (or IR mode) dependent TKER distributions of UVs and IR+UVs of photodissociation of CH_3SH

Table S1. Fitting-parameters for TKER distributions in the Figure 1.

Table S2. Average TKER distributions and kinetic energy fractions in the Figure 1.

Figure S4. TKER distributions of photodissociation of CH_3SH in various set of IR (v_3, v_2, v_1/v_9) + UVs (216-226 nm plus 263-278 nm)

Figure S5. Energy correlation plot for the photodissociation of MeSH (CH_3SH).

Figure S6. De-convolution of Figure 1 (c) and (e).

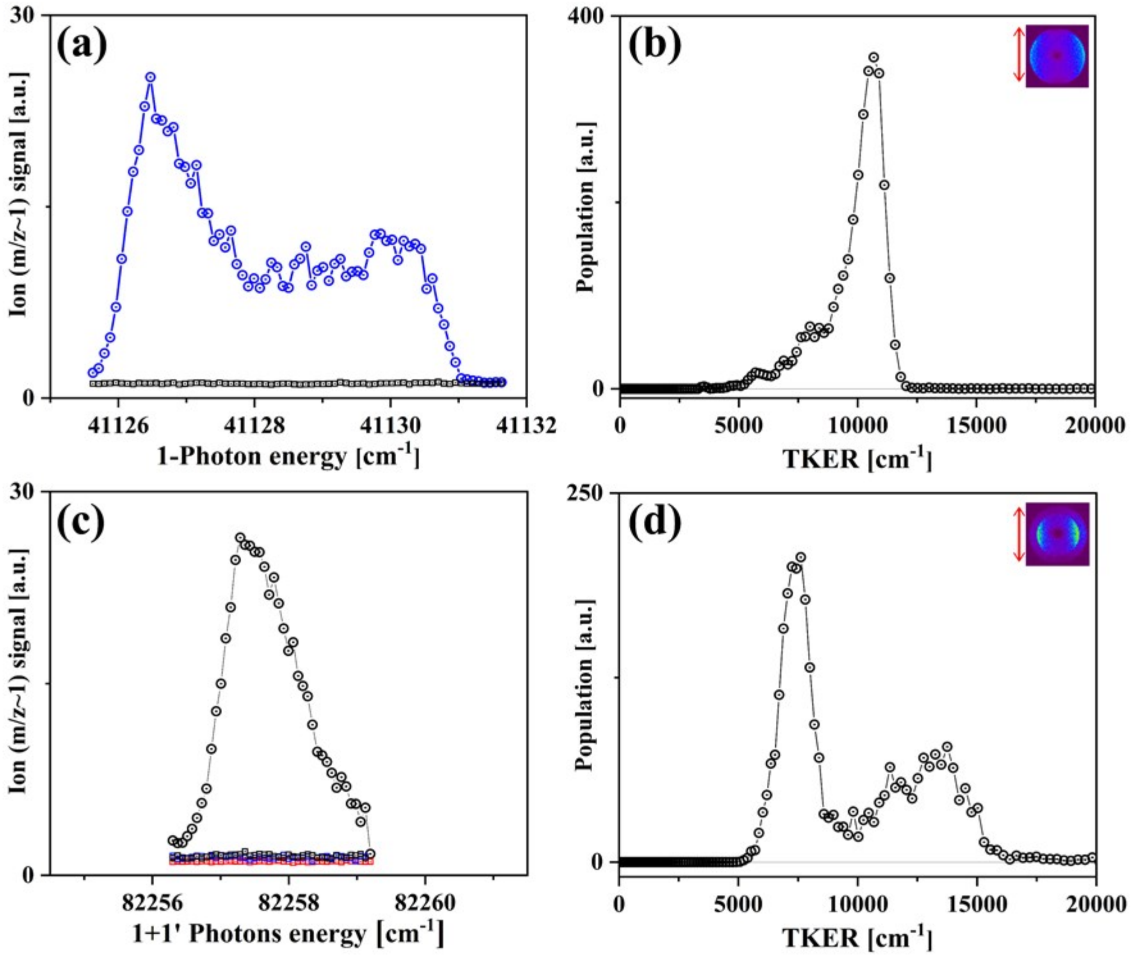

Figure S1. H^+ photofragment excitation (PHOFEX) spectra (a and c) and corresponding velocity map ion imaging (VMI) for the H^+ ions (b and d) following photodissociations of methyl mercaptan (CH_3SH). (a) Doppler scan for the photoexcitation of H atom *via* 2s-1s state is done by 2+1 REMPI. Blue circle: nozzle-on, black rectangle: nozzle-off ion intensities. (b) Total kinetic energy release (TKER) distribution after photodissociation of CH_3SH ~243.1 nm laser beam. Inset is raw image of H^+ and the laser polarization axis is shown as red arrow. (c) Doppler scanned H^+ PHOFEX spectrum using two color laser beams (224 + 266 nm). Black circle: normal signal, black rectangle: nozzle-off signal, red rectangle: 266 nm, blue rectangle: 224 nm. (d) TKER distribution after photodissociation of CH_3SH using 224 nm and 266 nm laser beams.

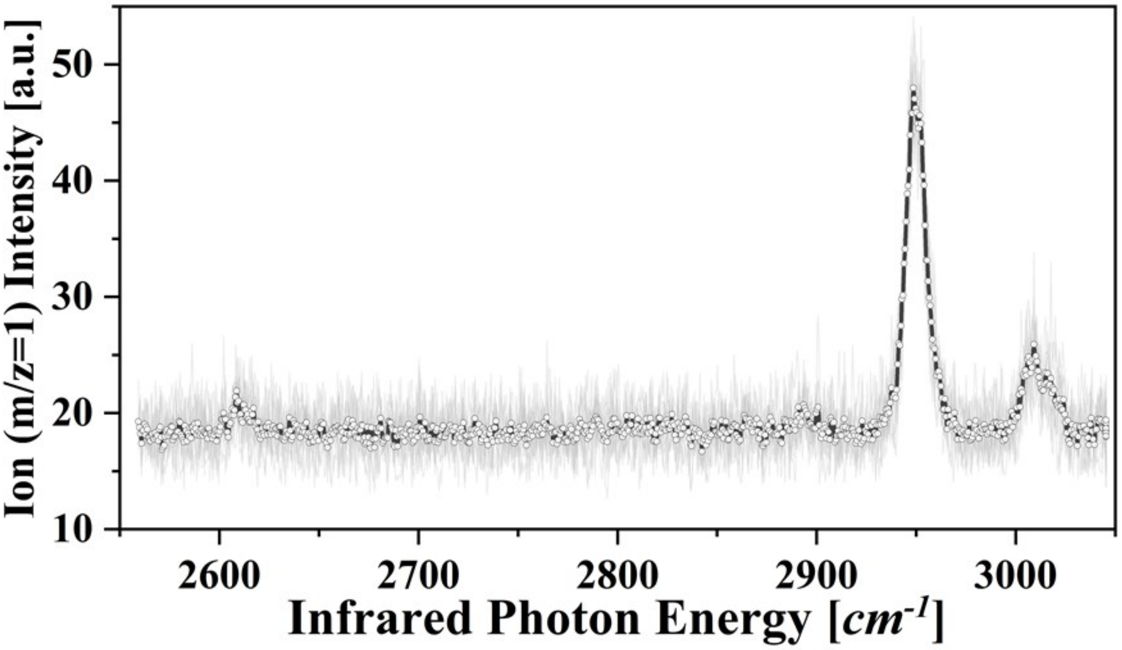

Figure S2. IR+UV (224 + 266 nm) H^+ PHOFEX spectra. IR laser was introduced 5 ns before two simultaneously counter-propagated UVs. Dark-gray line with circles is average PHOFEX spectrum. Overlapped light-gray lines are single experiments, respectively. Tangible three peaks are assigned as ν_3 (2608), ν_2 (2951), and ν_1/ν_9 (3007) as recent IR+VUV study, respectively.[S1]

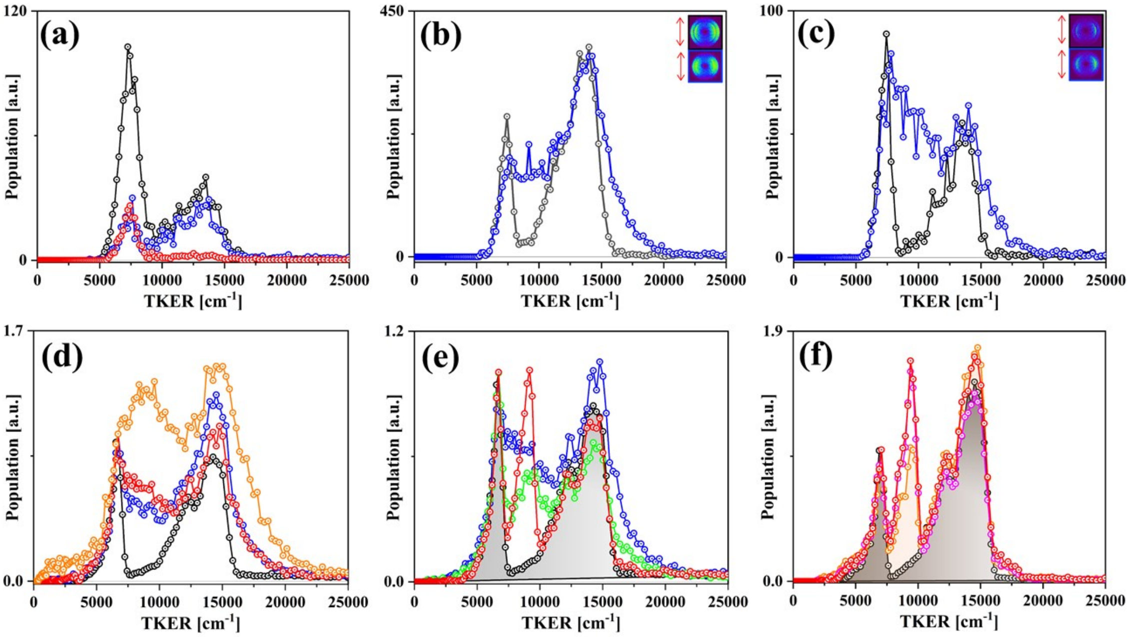

Figure S3. Total kinetic energy release distributions of reduced Doppler double-pump photodissociation of MeSH (CH_3SH) following H^+ velocity map ion imaging (VMI) experiments. (a)-(c) 224 + 266 nm UV laser beams, (d)-(e) 220 + 271 nm UVs, and (f) 221 + 270 nm UVs, respectively. IR (v_2)-UVs (blue) and UVs (black) are shown. Inset shows lasers (IR, UVs) polarization (red arrow) and raw 2D images (upper: UVs, lower: IR (v_2)+UVs) for (b) and (c), respectively. (d) 200 μJ (blue), 400 μJ (red), and 1000 μJ (orange) of v_2 vibration mediated TKER distributions are shown. For the same UVs as (d), the mode-dependent vibration mediated TKER distributions are in (e). 300 μJ (red), 400 μJ (blue), and 400 μJ (green) for v_3 (S-H stretch), v_2, and v_1/v_9 (C-H_3/C-H_2 anti-symmetric stretch) vibration mediated TKER distributions are shown with that by UVs without IR (gray shaded black circles.). With 221 and 270 nm UVs, (f) orange (800 μJ), pink (1700 μJ), and red (2200 μJ) of v_3 mediated TKER distributions.

Table S1. Fitting-parameters for total kinetic energy release (TKER, kcal/mol) in Figure 1. Each dynamic component is de-convoluted as one gaussian function. (i.e. $\frac{A}{W\sqrt{\pi/2}}e^{-2(\frac{x-a}{W})^2}$ where $\boldsymbol{A}$ is amplitude, $\boldsymbol{W}$ is width, $\boldsymbol{a}$ is a center, and $\boldsymbol{x}$ is dependent variable (TKER).)

$CH_3S\cdot$ ν_3(S-C stretch) quanta	**Spin-orbit symmetry**	**268.844 nm**			**IR (CH_3S-H stretch, ν_3, 2607.5 cm^{-1}) + 268.844 nm**			**IR (C-H_3SH symmetric stretch, ν_2, 2950.9 cm^{-1}) + 268.844 nm**			**IR (overlapped C-H_3SH asymmetric stretches, ν_1/ν_9, 3006.7 cm^{-1}) + 268.844 nm**		
		Area	**Center**	**Width**	**Area**	**Center**	**Width**	**Area**	**Center**	**Width**	**Area**	**Center**	**Width**
0	**$E_{3/2}$**	**1.620**	**20.250**	**1.8**	**1.710**	**27.450**	**1.8**	**0.410**	**28.737**	**1.85**	**0.163**	**28.897**	**1.85**
1		**0.470**	**18.171**	**1.8**	**1.100**	**25.571**	**1.8**	**0.450**	**26.658**	**1.85**	**0.169**	**26.818**	**1.85**
2		**0.160**	**16.092**	**1.8**	**0.630**	**23.492**	**1.8**	**0.650**	**24.579**	**1.85**	**0.140**	**24.739**	**1.85**
3		**0.100**	**14.013**	**1.8**				**0.770**	**22.500**	**1.85**	**0.080**	**22.660**	**1.85**
0	**$E_{1/2}$**	**0.729**	**19.509**	**1.8**	**0.770**	**26.909**	**1.8**	**0.185**	**27.996**	**1.85**	**0.073**	**28.156**	**1.85**
1		**0.212**	**17.430**	**1.8**	**0.495**	**24.830**	**1.8**	**0.203**	**25.917**	**1.85**	**0.076**	**26.077**	**1.85**
2		**0.072**	**15.351**	**1.8**	**0.284**	**22.751**	**1.8**	**0.293**	**23.838**	**1.85**	**0.063**	**23.998**	**1.85**
3		**0.045**	**13.272**	**1.8**				**0.347**	**21.759**	**1.85**	**0.036**	**21.919**	**1.85**

Unit [kcal/mol]

Table S2. Average TKER (kcal/mol) and percentages of energy fraction into kinetic energy for Figure 1. Assumption that the all available energies are released as kinetic energy by the photo-excitation of CH_3SH using 268.844 nm allows us to set the reference (dynamics through UV-alone) and to quantify the aforementioned percentages of degrees of TKER for available energy from IR+UV experiment.

For all $CH_3S\cdot$ ν_3(S-C stretch) quanta (0, 1, 2, and 3)	**268.844 nm**	**IR (CH_3S-H stretch, ν_3, 2607.5 cm^{-1}) + 268.844 nm**	**IR (C-H_3SH symmetric stretch, ν_2, 2950.9 cm^{-1}) + 268.844 nm**	**IR (overlapped C-H_3SH asymmetric stretches, ν_1/ν_9, 3006.7 cm^{-1}) + 268.844 nm**
$\langle E_{k,\,S=3/2}\rangle$ [kcal/mol]	**19.264**	**26.008**	**25.035**	**26.302**
$\langle E_{k,\,S=3/2}\rangle/\langle E_{Total\ available}\rangle$ [%]	**100**	**97.3**	**90.4**	**94.4**
$\langle E_{k,\,S=1/2}\rangle$ [kcal/mol]	**18.523**	**25.267**	**24.294**	**25.561**
$\langle E_{k,\,S=1/2}\rangle/\langle E_{Total\ available}\rangle$ [%]	**100**	**97.3**	**90.1**	**94.3**

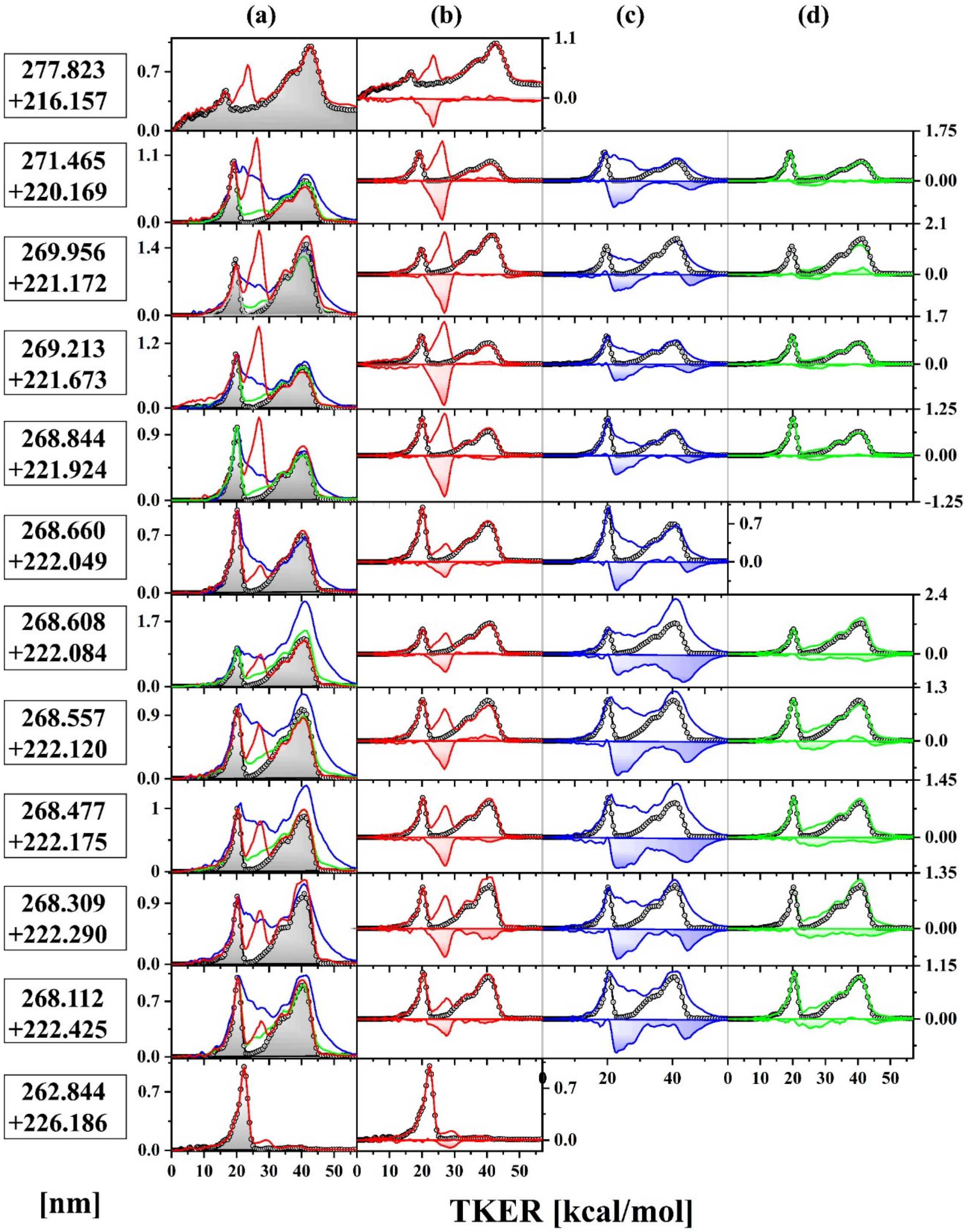

Figure S4. Total kinetic energy release (TKER) distributions of reduced Doppler double-pump photodissociation dynamics of CH_3SH using various combinations of two UVs following IR pre-excitations. Left boxes label the following TKER distributions. Black (or filled black): UVs, red: $1v_3$+ UVs, blue: $1v_2$+UVs, green: $1v_1/v_9$+ UVs. Filled color implies the experimental difference population between $IR_{off} - IR_{on}$. (a) total overlapped TKER distributions, (b) S-H stretch mediated one, (c) C-H_3 symmetric stretch mediated one, and (d) overlapped C-H_3 antisymmetric and antisymmetric C-H_2 stretches mediated TKER distributions, respectively. Abscissa is TKER [kcal/mol] and ordinate is normalized population [a.u.]. Top (278+216 nm) and bottom (263+226 nm) experiment used loose focusing (20 cm) of one UV (e.g. 216 nm) beam and low power IR (0.3 mJ/pulse for 2608 cm^{-1}, 1 mJ for 3007 cm^{-1}, and 2 mJ for 2951 cm^{-1}) which has linearly parallel polarization to detection plate. Whereas, rests of experiments used tight focusing UVs (15 cm) and high-power IR (1.5 mJ/pulse for 2608 cm^{-1} except 1.7 mJ for (269.95+221.17 nm), 2 mJ for both 2951 cm^{-1} and 3007 cm^{-1}, respectively) which has linearly orthogonal polarization to detection plate. Experimental data were 3-point smoothed.

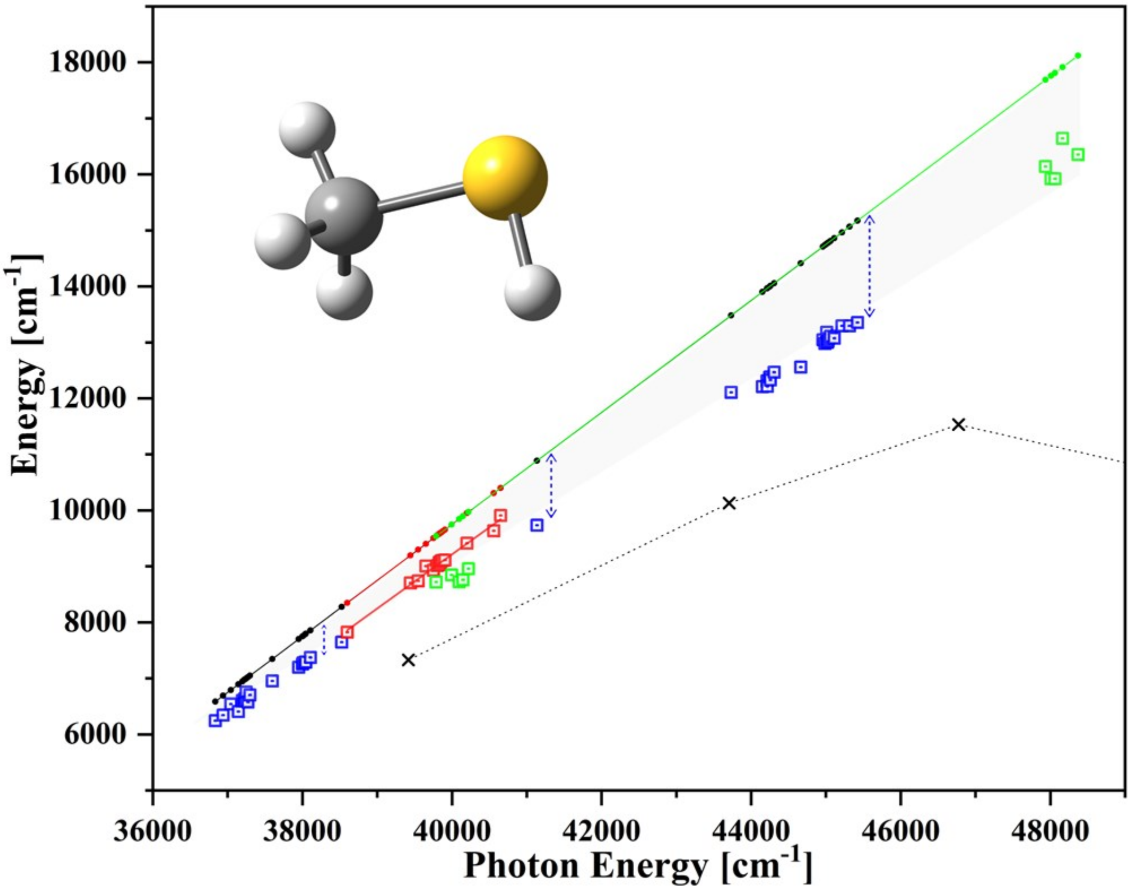

Figure S5. Energy correlation plot for the photodissociation of MeSH (CH_3SH). Inset shows the optimized ground-state CH_3SH structure calculated by Gaussian 09 (DFT B3LYP/6-31G(d,p)).[S2] Circles indicate expected maximum kinetic energy release, i.e. available energy ($E_{avl} = E_{photon(s)}-D_0$ (30 250) cm^{-1}) for each photon energy.[S3] Rectangle is for the average TKER (total kinetic energy release) (i.e. $<E_{TKER}>$) following the corresponding photon-energies for photo-excitations. Black/blue: UV only, red: IR (S-H stretch) + UV, green: IR ($C-H_3$ symmetric stretch) + UV, respectively. Filled light-gray area with dash-arrows show difference between expected $<E_{TKER}>$ and the experiments. x mark indicates the previous experimental reference at 300K.[S4]

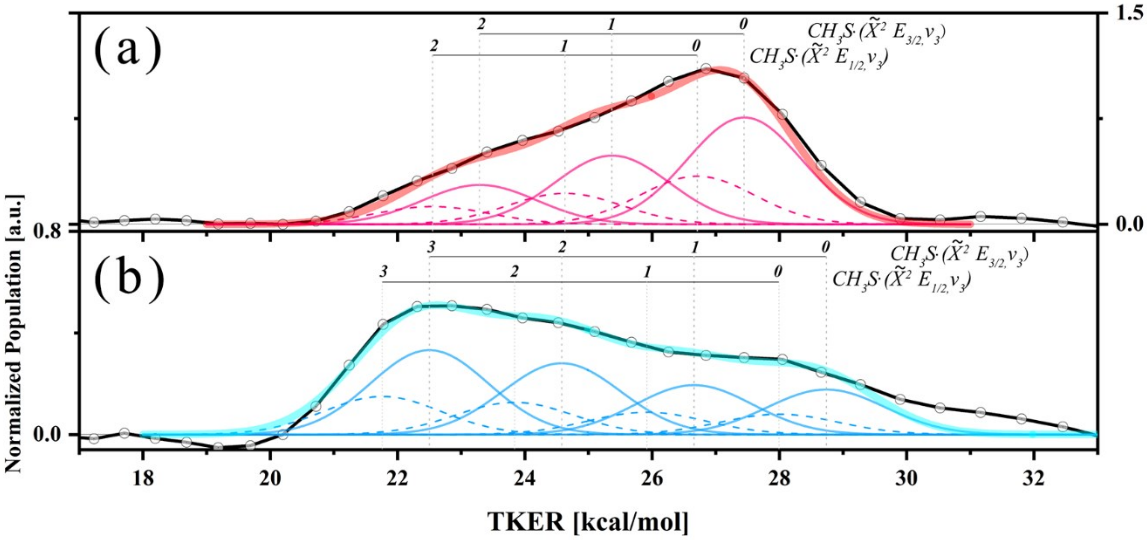

Figure S6. Deconvolution of the Figure 1 (c) and (e). (a) and (b) are reproduced TKER distributions from Figure 1 (c) and (e), respectively. To illustrate the de-convolutions of $CH_3S\cdot$ ($\tilde{X}^2\ E_{\Omega}$, v_3) components, tie-bars are drawn. v_3=0,1,2,3 are progressed. Each colored solid-line is gaussian-function for each $CH_3S\cdot$ ($\tilde{X}^2\ E_{3/2}$, v_3) component and each dashed-line is gaussian-function for each $CH_3S\cdot$ ($\tilde{X}^2\ E_{1/2}$, v_3) component. The population of $E_{1/2}$:$E_{3/2}$ is assumed to be 0.45 and The S-H dissociation energy of 30 250 ± 100 cm^{-1} has been used for the simulation.[S3] Each center of the gaussian-function is $<E_{TKER}>$ for each component (Table S1). Sum of all same spin symmetry components is then averaged by the populations ($<E_{k,\ S=1/2\ or\ 3/2}>$ in Table S2). $<E_{Total\ available}>$ is estimated TKER that sum of input IR photon energy and measured $<E_{TKER}>$ by 268.844 nm. $<E_{k,\ S=1/2\ or\ 3/2}>/<E_{Total\ available}>$ are then calculated for the IR+(268.844+221.924 nm) experiment case. In Figure S5, whereas, $<E_{TKER}>$ = ($\frac{Sum\ of\ (population * corresponding\ TKER)}{Sum\ of\ populations}$) which is experimentally determined and spin-orbit branches were not considered.

Supporting References

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