

# Supporting Information: Photoisomerization of Vibrationally Hot Tetramethylethylene Produced by Ultrafast Internal Conversion from the Excited State

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**Photoelectron spectra of the reactant and two possible products:** We measured the photoelectron spectra of the reactant (R; TME) and two possible products (P1, 2,3-DM-1-B; P2, 3,3-DM-1-B) using the 90-nm pulse. The measured photoionization signal intensity is proportional to sample density in a molecular beam. We assumed that the sample density was proportional to its vapor pressure if the molecular beam was formed by expanding a sample gas from a nozzle without the carrier gas. Vapor Pressure  $p$  at temperature  $T$  is given by the Antoine equation:

$$\log_{10} p = A - \frac{B}{C + T} \quad (\text{S1})$$

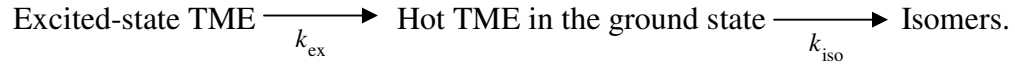
Table S1 shows reported Antoine coefficients for the three compounds.<sup>S1</sup> Thus the relative photoionization cross sections of the three molecules were estimated from the observed photoionization signal intensities and the vapor pressures of these compounds.

Name	A	B	C
TME	6.88803	1197.5694	225.653
2,3-DM-1-B	6.99600	1225.8374	242.271
3,3-DM-1-B	6.91649	1115.9799	235.289

**Table S1.** Antoine coefficients for TME, 2,3-DM-1-B, and 3,3-DM-1-B.

(S1) Yaws, C. *The Yaws Handbook of Vapor Pressure: Antoine coefficients*; Elsevier: Oxford, U.K.; 2015.

**Derivation of Equation (1):** We considered the following two-step reaction:



The electronic populations of TME in the excited-state  $P_{\text{ex}}(t)$  and in the vibrationally hot ground state  $P_{\text{hot}}(t)$  are respectively described as

$$P_{\text{ex}}(t) = P_{\text{ex}}^0 \exp(-k_{\text{ex}}t) \quad (\text{S2})$$

$$P_{\text{hot}}(t) = P_{\text{ex}}^0 \frac{k_{\text{ex}} \{ \exp(-k_{\text{ex}}t) - \exp(-k_{\text{iso}}t) \}}{k_{\text{iso}} - k_{\text{ex}}} \quad (\text{S3})$$

where  $k_{\text{ex}}$  and  $k_{\text{iso}}$  are the rate constants, and  $P_{\text{ex}}^0$  represents the excited state population at  $t = 0$ . The electronic population of the isomers  $P_{\text{iso}}(t)$  is given by

$$P_{\text{iso}}(t) = P_{\text{ex}}^0 - P_{\text{ex}}(t) - P_{\text{hot}}(t). \quad (\text{S4})$$

The excited state lifetime  $\tau_{\text{ex}} = (k_{\text{ex}})^{-1}$  was fixed to be 2.6 ps [Fig. 1(b)], while the unimolecular reaction of vibrationally hot TME was not completed within the delay time range of this study [Fig. 5]. Thus  $k_{\text{iso}} \ll k_{\text{ex}}$  and  $k_{\text{iso}}t \sim 0$  hold, and Equations (S3) and (S4) become

$$P_{\text{hot}}(t) = P_{\text{ex}}^0 \{1 - \exp(-k_{\text{ex}}t)\} \quad (\text{S5})$$

and

$$P_{\text{iso}}(t) = P_{\text{ex}}^0 \frac{k_{\text{iso}}}{k_{\text{ex}}} \{k_{\text{ex}}t + \exp(-k_{\text{ex}}t) - 1\}, \quad (\text{S6})$$

respectively. The first, second, and last terms in Equation (1) respectively correspond to the contributions from  $P_{\text{ex}}(t)$ ,  $P_{\text{iso}}(t)$ , and  $P_{\text{hot}}(t)$ . However, the contribution of  $P_{\text{hot}}(t)$  to the PKE spectrum was small, and the variation in the PKE spectrum due to vibrational excitation was represented by the last constant term.