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Ultraviolet Photodissociation Dynamics of 1-Pentyl Radical

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The ultraviolet (UV) photodissociation of jet-cooled 1-pentyl radical is investigated in the wavelength region of 236–254 nm using the high-\(n\) Rydberg-atom time-of-flight (HRTOF) technique. The H-atom photofragment yield spectrum of the 1-pentyl radical shows a broad UV absorption feature peaking near 245 nm, similar to the 2\(p\)_\(z\)-\(3s\) absorption bands of ethyl and \(n\)-propyl. The center-of-mass translational energy distribution, \(P(E_T)\), of the H+\(\text{C}_5\text{H}_{10}\) product channel is bimodal, with a slow peak at \(\sim 5\) kcal/mol and a fast peak at \(\sim 50\) kcal/mol. The fraction of the average translational energy release in the total available energy, \(\langle E_T \rangle\), is 0.30, with those of the slow and fast components being 0.13 and 0.58, respectively. The slow component has an isotropic product angular distribution, while the fast component is anisotropic with an anisotropy parameter \(\sim 0.4\). The bimodal translational energy and angular distributions of the H+\(\text{C}_5\text{H}_{10}\) products indicate two H-atom elimination channels in the photodissociation of 1-pentyl: (i) a direct, prompt dissociation from the electronic excited state and/or the repulsive part of the ground electronic state potential energy surface; and (ii) a unimolecular dissociation of internally hot radical in the ground electronic state after internal conversion from the electronic excited state.

Key words: Photodissociation, 1-Pentyl, Alkyl, Decomposition, Rydberg, Excited state

I. INTRODUCTION

Alkyl radicals are important intermediates in the oxidation processes of alkanes such as combustion. They can undergo extensive unimolecular reactions such as dissociation and isomerization and bimolecular reactions such as with oxygen [1, 2]; the dissociation of the alkyl radicals can influence the rate as well as the efficiency of combustion. Many studies have reported the dissociation mechanism of the alkyl radicals on the ground electronic state, while the studies on their excited states are relatively limited because of the short lifetime and the high reactivity. In this paper, we report our study on the photodissociation of the 1-pentyl radical in the UV region of 236 nm to 254 nm.

The dissociation and isomerization reactions of the 1-pentyl radical on the electronic ground state have been studied for decades experimentally [3–12] and theoretically [11, 13–18]. The allylic \(\text{C}–\text{C}\) bond cleavage to yield ethene (\(\text{C}_2\text{H}_4\)) and \(n\)-propyl radical (\(n\)-\(\text{C}_3\text{H}_7\)) product would be the main dissociation channel in the thermal decomposition of the 1-pentyl because of the low bond energy and dissociation energy barrier, and the \(n\)-propyl radical could further decompose to the ethene and methyl radical products [9, 10]. Miyoshi et al. observed isomerization of the 1-pentyl radical to the 2-pentyl radical via a 1,4 H-atom shift with a five-member ring transition state firstly, and in their Rice-Ramsperger-Kassel-Marcus (RRKM)/master-equation analyses estimated an energy barrier of this five-member ring isomerization lower than that of the \(\text{C}–\text{C}\) or \(\text{C}–\text{H}\) bond fission of 1-pentyl [10]. Unlike the three- or four-member ring isomerization that has an energy barrier close or higher than the \(\text{C}–\text{C}\) or \(\text{C}–\text{H}\) bond cleavage process [19, 20], the lower energy barrier of the 1,4 H-atom shift isomerization in 1-pentyl would be an important competing channel with the decomposition reactions. Jitariu et al.'s theoretical calculation of the 1,4 H-atom shift isomerization in the 1-pentyl radical [21] confirmed the result from Miyoshi et al. [10]. FIG. 1 shows the energy diagram and reaction pathways of the 1-pentyl radical based on the theoretical work by Jitariu et al. [21]. Manion et al. studied the thermal decomposition of 1-pentyl radical between 80 to 680 kPa and 833 to 1130 K by using the shock tube technique [11]. The product branching ratios of ethene and propene were determined to be in the range of 3 to 5 under the experimental conditions and the ethene product was dominant especially at higher temperature and pressure. The propene product was due to cleavage of the allylic \(\text{C}–\text{C}\) bond in the 2-pentyl radical, indicating that the competing isomerization channel is important in the decomposition of 1-pentyl radical. The ethene and propene products formed can be related to

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the concentration of the 1-pentyl and 2-pentyl radicals. The dissociation channels are shown below based on Jitarui et al.'s theoretical work [21]:

\[
\begin{align*}
1\text{-C}_5\text{H}_{11} & \rightarrow \text{H} + 1\text{-C}_5\text{H}_{10} & \Delta H_r;0 &= 35.0 \text{ kcal/mol} \\
& \rightarrow \text{H} + 2\text{-C}_5\text{H}_{10} & \Delta H_r;0 &= 33.0 \text{ kcal/mol} \\
& \rightarrow \text{C}_2\text{H}_4 + n\text{-C}_3\text{H}_7 & \Delta H_r;0 &= 28.8 \text{ kcal/mol} \\
& \rightarrow \text{CH}_3 + 1\text{-C}_4\text{H}_8 & \Delta H_r;0 &= 26.2 \text{ kcal/mol} \\
& \rightarrow \text{C}_2\text{H}_5 + C_3\text{H}_6 & \Delta H_r;0 &= 25.8 \text{ kcal/mol}
\end{align*}
\]

Based on the potential energy diagram, 1-pentyl radical could undergo cleavage of the C−H bond to produce the 1-pentene+H products or allylic C−C bond fission leading to the n-propyl+ethene products. A second dissociation pathway to the 1-pentene+H products is via isomerization of the 1-pentyl to 2-pentyl first, then followed by dissociation of the 2-pentyl radical. The isomerization of 1-pentyl to 2-pentyl has two pathways, 1,2 H-shift via a three-member ring transition state (energy barrier of 41.2 kcal/mol) and 1,4 H-shift with a five-member ring transition state (energy barrier of 23.4 kcal/mol), while the isomerization from 1-pentyl to 3-pentyl has one pathway via a four-member ring translation state (energy barrier of 40.5 kcal/mol), as shown in FIG. 1 [21]. Two dissociation pathways lead to the 2-pentene+H products: (i) isomerization of 1-pentyl to 2-pentyl then dissociation to 2-pentene+H, and (ii) isomerization of 1-pentyl to 3-pentyl followed by dissociation to 2-pentene+H. C_2H_5+C_3H_6 products could be formed from the dissociation of 2-pentyl radical after isomerization from 1-pentyl. The 1-pentyl could also isomerize to 3-pentyl then followed by unimolecular dissociation to produce CH_3+1-C_4H_8. The C–C bond scission of 2-pentyl and 3-pentyl product channels were confirmed by thermal decomposition studies with single-pulse shock tube technique [22].

The UV photodissociation dynamics investigation of 1-pentyl radical is limited, while there have been a few studies on other small n-alkyl radical such as ethyl [23–25], n-propyl [26, 27], and n-butyl [28, 29] radicals. The β-H atom elimination of ethyl and propyl radicals were confirmed by using partially deuterated precursors [24, 27]. The studies on the photodissociation of ethyl radical via 3s Rydberg state revealed bimodal product translational energy distribution and energy-dependence angular distribution of the H+ethene products and two dissociation pathways [24, 25]. At the 3s Rydberg excited state, the ethyl radical decays via a non-classical H-bridged structure producing a fast and anisotropic channel with the direct, prompt H-atom elimination and a slow and isotropic product channel from the unimolecular dissociation of the internally hot radical after the internal conversion to the ground electronic state [24, 25, 30]. The H-atom loss channels in the photodissociation of the n-propyl [27] and n-butyl [28] radicals via the 3s Rydberg state also have bimodal product translational energy distribution and angular distribution. The dissociation mechanism of the H-atom loss in the photodissociation of n-propyl and n-butyl radicals is proposed to be a direct, prompt dissociation coupling the Rydberg state and the repulsive part of the radical ground state surface with a large product translational energy release and anisotropic product angular distribution and a unimolecular dissociation of the internally excited radical on the ground electronic state after internal conversion with a small translational energy release and isotropic angular distribution.

This paper reports our recent study on the H-atom loss photodissociation dynamics of the jet-cooled 1-pentyl radical in the UV region of 236–254 nm. The H-atom photofragment yield (PFY) spectrum was obtained, revealing the UV absorption feature of the 1-pentyl radical for the first time. The product transla-
tional energy and angular distribution of the H+CD₃H₁₀ channel were obtained from the H-atom time-of-flight (TOF) spectra, and the photodissociation mechanism of the H-loss channel of the 1-pentyl radical was investigated.

II. EXPERIMENTS

The high-\(n\) Rydberg time-of-flight (HRTOF) technique was employed in this study, and the details of this technique and experimental setups have been described in previous publications [24, 27, 31]. The 1-pentyl radical molecular beam was formed by photolysis of 1-nitropentane precursor (Aldrich 97%) in He carrier gas, and was pumped by two-color resonant excitation radiation. The high-Rydberg state H atoms drifted with their nascent velocities in a microchannel plate (MCP) detector installed perpendicular to the molecular beam and the metastable H atoms were field-ionized in front of the detector and detected. The distance of the flight path was calibrated to be 37.06 cm by photodissociation of HBr at 236 nm with the spin-orbit splitting energy of Br\(\left(2P_{3/2}\right)\) and Br\(\left(2P_{1/2}\right)\) and the HBr bond dissociation energy. The ion signals were amplified by a fast preamplifier and averaged by a multichannel scaler to collect the H-atom product TOF spectra.

III. RESULTS

The H-atom TOF spectra of the photodissociation of the 1-pentyl radical were taken in the UV photolysis wavelength region of 236 nm to 254 nm with the polarization of the photolysis radiation parallel and perpendicular to the TOF axis. For background removal, the H-atom TOF spectra of the photodissociation of the 1-nitropentane precursor were also taken (with the 193-nm radical production photolysis laser off) in the UV photolysis wavelength region of 236 nm to 254 nm. The net H-atom TOF spectra were obtained after proper background subtraction (with the radical production photolysis laser on minus off). In FIG. 2, the open circles in FIG. 2 (a) and (b) show the net H-atom TOF spectra of the photodissociation of the 1-pentyl radical at 240 nm after proper background subtraction with the polarization of the photolysis parallel (\(\parallel\)) and perpendicular (\(\perp\)) to the TOF path. The power of the photolysis radiation was kept in the region of 1.2–2.4 mJ/pulse, and the H-atom signal had a linear dependence on the photolysis laser power. Both TOF spectra show a peak at \(\sim 17\) \(\mu\)s and the parallel spectrum has a stronger signal at the peak. In the longer flight time region, both spectra have an identical broad feature but with large noise.

The H-atom photofragment yield (PFY) spectrum of the 1-pentyl radical was obtained by integrating the net H-atom TOF spectra from photodissociation of 1-pentyl as a function of photolysis wavelength. All the integrated signals were normalized to that at 240 nm with the same photolysis power and laser shots. FIG. 3 shows the H-atom PFY spectrum of 1-pentyl in the region of 236–254 nm, with a broad feature peaking around 245 nm. There is no 1-pentyl UV absorption spectrum reported yet. Other primary alkyl radicals such as ethyl [32, 33] and \(n\)-propyl [27, 34] radicals show a strong absorption at \(\sim 245\) nm which are assigned to the 3s Rydberg state via the \(2P_{3/2}\) transition. As the \(\beta\) substitution by an alkyl group on the ethyl would not change the electronic state significantly because of the localized Rydberg excitation on the radical center [32, 33], the peak at 245 nm in the H-atom PFY spectrum of 1-pentyl could also be due to the \(2p_{3/2}\)→3s Rydberg state transition as well. The H-atom PFY spectrum of 1-pentyl can also be due to the \(2p_{3/2}\)→3s Rydberg state transition as well.
FIG. 3 H atom photofragment yield (PFY) spectrum of 1-pentyl radical as a function of the photolysis wavelength in the region of 236–254 nm. Open circles are the integrated HRTOF signals of the 1-pentyl radical by using the 1-nitropentane precursor. All the signals are normalized to the same laser shots and power. The error bars indicate the 95% confidence limit from multiple measurements.

atom PFY spectrum reveals the UV absorption features of the 1-pentyl radical for the first time.

The center-of-mass (CM) product translational energy distributions, $P(E_T)$'s, of the H+C$_5$H$_{10}$ product channel can be derived from the H-atom TOF spectra of the 1-pentyl radical. The CM translational energy of the products, $E_T$, is derived from the flight time of the H atom $t_H$ based on the following equation [27, 35–37]:

$$E_T = \left(1 + \frac{m_H}{m_{C_5H_{10}}} \right) E_H + \frac{m_H}{m_{C_5H_{10}}} E_{C_5H_{11}}$$

$$= \frac{1}{2} m_H \left[ \left(1 + \frac{m_H}{m_{C_5H_{10}}} \right) \left( \frac{L}{t_H} \right)^2 + \frac{m_H}{m_{C_5H_{10}}} E_{C_5H_{11}} \right]$$

(1)

where $E_H$ and $E_{C_5H_{11}}$ are the laboratory translational energy of the H-atom product and the parent 1-pentyl radical, $L$ is the length of flight. The second term is due to the parent 1-pentyl radical motion in the molecular beam which is perpendicular to the TOF axis, and it is much smaller compared to the first term and can be neglected. Using direct conversion from time to energy [27, 35–37], the product CM translational energy distributions of the H+C$_5$H$_{10}$ product channel at 240 nm photodissociation wavelength with parallel (||, $\theta=0^\circ$) and perpendicular ($\perp$, $\theta=90^\circ$) photolysis radiations are derived and shown in FIG. 4 (a) and (b) in the solid black lines. The $P(E_T)$ distributions can also be derived from modeling the H-atom TOF spectra in a forward-convolution procedure [38, 39]. In this modeling process, the H-atom product TOF spectrum is calculated by using a trial $P(E_T)$ distribution convoluted with the instrument and molecular beam functions. The calculated TOF spectrum is iteratively optimized by comparison with the experimental TOF spectrum and readjustment of the trial $P(E_T)$ distribution until an optimized $P(E_T)$ is reached. This forward-convolution method is helpful when the experimental TOF spectrum is noisy.

The forward-convolution fittings for the H-atom product TOF spectra at 240 nm are shown in the red curves in FIG. 2. The optimized $P(E_T)$ distributions used in the forward-convolution fitting are showed in red lines in FIG. 4 (a) and (b), and they have a good agreement with the $P(E_T)$ distributions from the direct conversion. The product CM translational energy and the photofragment angular distribution can be described in the equation shown below [40]:

$$P(E_T, \theta) = \left(\frac{1}{4\pi}\right) P(E_T) \left[1 + \beta P_2(\cos \theta)\right]$$

(2)

where $P(E_T)$ is the angle-integrated product translational energy distribution, $\beta$ is the anisotropy parameter ($-1 \leq \beta \leq 2$), $\theta$ is the angle between the electric vector of the linear polarized photolysis radiation and the recoiling velocity of the H-atom product, and $P_2(\cos \theta)$ is the second Legendre polynomial. At the parallel polarization,

$$P_{||}(E_T) = \left(\frac{1}{4\pi}\right) P(E_T) (1 + \beta)$$

(3)

and at the perpendicular polarization,

$$P_{\perp}(E_T) = \left(\frac{1}{4\pi}\right) P(E_T) \left(1 - \frac{1}{2} \beta\right)$$

(4)

FIG. 4 Center-of-mass product translational energy distributions, $P(E_T)$'s, of the H-atom product channel from the photodissociation of 1-pentyl radical at 240 nm with the linearly polarized photolysis radiation ($a$) parallel and ($b$) perpendicular to the TOF path and ($c$) the translational energy dependence anisotropy parameter $\beta(E_T)$. In (a) and (b), the $P(E_T)$ distributions are converted from the H-atom TOF spectra and are scaled with the same laser shots and power. The black lines are the $P(E_T)$'s and $\beta(E_T)$ from the direct conversion of the H-atom TOF spectra and the red curves are based on the forward-convolution fitting. The arrows indicate the maximum available energy for the H+1-pentene product channel at 240 nm.
By combing the $P_{||}(E_T)$ and $P_{\perp}(E_T)$ distributions from the direct conversion and from the forward-convolution process, the CM translational energy distributions at the magic angle ($\theta=54.7^\circ$), $P_{m}(E_T) = (1/4\pi)P(E_T)$, are calculated and shown in FIG. 5 in solid black line and solid red line, respectively. The $P_{m}(E_T)$ distribution is proportional to the angle-integrated product translational energy distribution $P(E_T)$. FIG. 4(c) shows the translational energy-dependent anisotropy parameter $\beta(E_T)$, which is calculated from the translational energy distributions with parallel and perpendicular polarization with

$$\beta(E_T) = 2 \times \frac{P_{||}(E_T) - P_{\perp}(E_T)}{P_{||}(E_T) + 2P_{\perp}(E_T)}$$

(5)

the black line is from the raw data and the red line is based on the forward-convolution distributions.

The CM product translational energy distributions with parallel and perpendicular polarization show two peaks, with the slow one at ~5 kcal/mol and the fast one at ~50 kcal/mol and extending to the maximum available energy of the H+1-pentene (CH$_2$CHCH$_2$CH$_2$CH$_3$) products channel (84.1 kcal/mol at 240 nm photolysis wavelength). The anisotropy parameter $\beta$ is about 0 (with large noise) when $E_T<40$ kcal/mol and increases to a maximum value of 0.4±0.1 at a large $E_T$ value of ~70 kcal/mol. The different $\beta$ values indicate at least two dissociation channels. In FIG. 5, two Rice-Ramsperger-Kassel (RRK)-type functions, $P(E_T) = A(E_T)^p(E_0-E_T)^q$ are used to deconvolute the $P_{m}(E_T)$ into a fast and slow components part [27]. $A$, $p$ and $q$ are variable parameters, and $E_0$ is 84.1 kcal/mol for the fast component and adjustable for the slow component [27]. The two fitted components (I for the fast one and II for the slow one) are shown in FIG. 5. Based on the fitting, the average translational energy release, $\langle E_T \rangle$, and the fraction of the average translational energy in the total available energy, $\langle f_T \rangle$, can be calculated for each component. For the fast channel (I), $\langle E_T \rangle$=48.7 kcal/mol and $\langle f_T \rangle$=0.58; and for the slow channel (II), $\langle E_T \rangle$=11.1 kcal/mol and $\langle f_T \rangle$=0.13, respectively. The overall $\langle f_T \rangle$ value of the H-loss product channel is 0.30. The integrated signals of component I and II give the branch ratio of the fast to slow component of ~0.6.

IV. DISCUSSION

The UV photodissociation dynamics of the jet-cooled 1-pentyl radical was investigated in the wavelength region of 236–254 nm for the first time. The H-atom product channels were observed from the H-atom TOF spectra. While there has been no UV absorption spectrum of the 1-pentyl radical reported before, the H-atom PFY spectrum showed a broad UV absorption feature peaking near 245 nm in the region of 236 to 254 nm for the first time. The UV absorption spectra of the ethyl and n-propyl radicals were observed with a peak at ~245 nm and the theoretical study assigned this peak to be the 3s Rydberg state via the $2p_z$–3s transition [27, 32–34]. The 1-pentyl PFY spectrum peak at ~245 nm would be assigned to the 3s Rydberg state via the $2p_z$–3s transition as well. Furthermore, similar to the photodissociation of other primary alkyl radicals via the 3s Rydberg state, the $P(E_T)$ distribution and $\beta(E_T)$ of the photodissociation of the 1-pentyl radical show a bimodal distribution (more discussion in the following). The fast component with a positive $\beta$ parameter and the slow component with an isotropic angular distribution indicate two distinct dissociation pathways in the photodissociation of the 1-pentyl radical. This photodissociation dynamics information is also consistent with the $2p_z$–3s Rydberg state excitation observed in the H-atom PFY spectrum of 1-pentyl in the region of 236 nm to 254 nm.

The CM translational energy distribution has a broad feature (the fast component) at ~50 kcal/mol and extends to the maximum available for the H+1-pentene product channel. The $\langle f_T \rangle$ value for this fast component is 0.58, supporting a non-statistical dissociation mechanism, and the $\beta$ value of 0.4 indicates that the dissociation time scale is shorter than one rotational period of the 1-pentyl radical (~10 ps). The dissociation mechanism for the fast component would be a direct, prompt dissociation of the electronic excited 1-pentyl radical on a repulsive potential energy surface to the ground state product probably via a conical inter-
section, coupling the 3s Rydberg state and the repulsive part of the ground state. The positive anisotropy parameter indicates that the velocity vector of the H-atom product is close to a parallel direction with respect to the \( \mathbf{p}_z \rightarrow 3s \) transition dipole moment. In going from ethyl to 1-pentyl, the \( \beta \)-substitution by an alkyl group would not change the Rydberg electronic transition of the primary alkyl radicals significantly, as the localized \( 2p_z \rightarrow 3s \) Rydberg excitation is mainly on the radical center [32, 33]. As in other \( n \)-alkyl radicals, the \( 2p_z \) orbital is perpendicular to the \( \alpha \)-CHH plane, and a \( \beta \)-CC bond or a \( \beta \)-CH bond is eclipsed to the \( 2p_z \) orbital to form two lowest energy conformers of the 1-pentyl radical, with the \( \beta \)-CH eclipsed conformer having a lower energy of about 0.1 kcal/mol [41]. The elimination of the eclipsed \( \beta \)-H atom would create another \( 2p_z \) orbital on the \( \beta \)-carbon which is parallel to the \( 2p_z \) orbital of the radical center and then form the \( \pi \) bond in the ground state of the 1-pentene product; the ejection of the \( \beta \)-H atom along the eclipsed CH bond will result in a positive anisotropy parameter, which is consistent with the experimental observation. The mechanism for the fast component would be the direct, prompt cleavage of the \( \beta \)-CH bond that is eclipsed to the \( 2p_z \) orbital of the 1-pentyl radical on a repulsive excited state surface and on a repulsive part of the ground state surface of 1-pentyl to produce the H atom and the ground state 1-pentene.

The anisotropy parameter \( \beta \) is around 0 for the slow component (II) with a small CM translational energy release (\( E_T < 40 \) kcal/mol), indicating another dissociation channel of the 1-pentyl radical to the H+\( C_5H_{10} \) products, and the dissociation time scale is longer than one rotation period of the 1-pentyl radical (\( \sim 10 \) ps). The \( P(E_T) \) distribution of the slow component peaks at \( \sim 5 \) kcal/mol with the average translational energy release (\( f_T \)) of \( \sim 0.13 \), showing a typical statistical energy distribution in the unimolecular dissociation. The slow component is consistent with unimolecular dissociation of the internally hot 1-pentyl radical on the ground electronic state after internal conversion from the electronic excited state. Based on the ground state potential energy diagram shown in FIG. 1, the pentyl system has multiple minima: 1-pentyl can isomerize to 2-pentyl via a 1,4 H-shift over the energy barrier of 23.4 kcal/mol or to 3-pentyl via a 1,3 H-shift over the energy barrier of 40.5 kcal/mol. The C–C bond fissions such as \( n\text{-}C_3H_7 + C_2H_4 \) have the lowest dissociation energy barriers, but our experimental technique could only detect the H-atom product channels. As the isomerization barrier of 1-pentyl to 2-pentyl is lower than the barriers of the \( \beta \) H atom eliminations to the H+1-pentene products from 1-pentyl and 2-pentyl, the H+1-pentene product channel could occur from both the 1-pentyl and 2-pentyl radicals. Among the H-atom loss product channels, the H+1-pentene product channel from the 1-pentyl radical has overall a low energy barrier and requires no additional isomerization step, and thus this pathway could be more likely. The peak of \( \sim 5 \) kcal/mol in the \( P(E_T) \) distribution is consistent with the 5 kcal/mol exit channel barrier of the unimolecular dissociation of 1-pentyl to the H+1-pentene products. The H-elimination of the 2-pentyl radical after the isomerization from the 1-pentyl radical could create H+1-pentene and H+2-pentene, and the unimolecular dissociation of the 3-pentyl radical to H+2-pentene should have a smaller probability due to the higher isomerization energy barrier from 1-pentyl radical.

V. CONCLUSION

The UV photodissociation of the 1-pentyl radical via the 3s Rydberg state was studied in the UV region of 236–254 nm. The H-loss channel was confirmed directly from the H-atom TOF spectra, and the H-atom photofragment yield spectrum revealed the UV absorption feature of the 1-pentyl radical for the first time. The H-atom product translational energy release and angular distribution have a bimodal distribution. The slow component peaks at \( \sim 5 \) kcal/mol and has an isotropic distribution, while the fast component peaks at \( \sim 50 \) kcal/mol and has an anisotropic angular distribution. The fraction of the average CM product translational energy release in the total available energy is about 0.30, and the branching ratio of the fast to the slow component is 0.6. The bimodal product translational energy distribution and angular distribution suggest two dissociation channels in the photodissociation of the 1-pentyl radical: (i) a direct, prompt H-atom elimination on the repulsive potential energy surface of the electronic excited state and/or the repulsive part of the ground electronic state; and (ii) a unimolecular dissociation of the hot 1-pentyl radical on the ground electronic state after the internal conversion from the excited state.

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