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Imaging the elusive C-C bond dissociation channel of photoexcited ethyl radical

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ABSTRACT

The C-C bond dissociation channel of the ethyl ($\text{CH}_3\text{--CH}_2$) radical is investigated at 197.4, 199.98 and 201 nm by velocity map imaging and resonance enhanced multiphoton ionization (REMPI) detection of the produced CH_3 fragments. On the light of high level *ab initio* calculations performed in this work, up to four dissociation pathways are identified leading, respectively, to ground state CH_3 radicals in correlation with CH_2 fragments in the first four electronic states. The major pathway is associated to threshold dissociation over an exit barrier located at the point of a conical intersection between the initially populated $3p_{A'}$ state and a dissociative valence state. As discussed in the text, the concomitance of both features opens the narrow window in which C-C bond dissociation occurs for ethyl and, presumably, for other similar alkyl radicals.

1. Introduction

In a recent series of publications, the photoinduced hydrogen-atom elimination in the ethyl ($\text{CH}_3\text{--CH}_2$) radical has been exhaustively investigated by our group using a combination of resonance enhanced multiphoton ionization (REMPI) and velocity map imaging detection of the produced hydrogen atoms.[1–4] Relevant to the study is the technique employed for the generation of the ethyl radicals, namely, *in situ* generation of radicals by photodissociation of a precursor, ethyl iodide in the present case. The initial deposit of internal energy made in the hot ethyl radicals, by partitioning the precursor's available energy between the different degrees of freedom of the products (ethyl radicals and iodine atoms), has proved to play a critical role in the subsequent photo-decomposition process of the radical.[1] Several dissociation channels were thoroughly described in those works, revealing a rich excited state dynamics. The studies, which covered a large excitation region ranging from 243 to 193 nm, allowed us to

divide the photodissociation of the ethyl radical in three dynamical regions, possessing each one of them its own particularities. At 243 nm (around the center of the *A* band), the ethyl radical is taken to the Rydberg $3s$ state, where a conical intersection mediates in the otherwise rather direct dissociation process. The role of the internal energy inherited in the generation process, irrelevant at 243 nm, changes at 201 nm – corresponding to the maximum absorption of the *B* band – where excitation at the Rydberg $3p_{A'}$ occurs. The excess of energy provided in the photolysis of the precursor enables the access to an intricate region of the potential energy landscape, characterized by numerous non-adiabatic crossings between the different curves. An undetected and unpredicted C-H fast dissociation pathway was found [1]. The particularity of the new dissociation pathway lays in the specificity of the dissociation site, anchored in the $C_\alpha H_2$ moiety. Finally, at 193 nm, new fast C-H site-specific dissociation channels, bound either to the $C_\alpha H_2$ or to the $C_\beta H_3$ moieties concur and compete with the persistent low energy decomposition pathways [4]. Slow C-H bond dissociation through internal redistribution of the available energy associated to both sites completes the photodissociation picture in the three dynamical regions. Quantification of the statistical contribution to the total H-atom signal was made by the use of different ethyl isotopologues.

The natural next step in the characterization of the ethyl radical photodynamics is the study of the C-C bond scission. To the best of our knowledge, the tert-butyl radical[5–7] and the cyclohexyl radical[8] are the only alkyl radicals for which the CH_3 -loss channel has been described. Negru *et al.*[7] found for tert-butyl that the translational energy release of produced CH_3 matched that of the CH_3 -coproduct, the dimethylcarbene. Such correspondence points to a direct dissociation along the coordinate connecting the *t*-butyl $3p$ state with the 1A ground state of dimethylcarbene. The proposed picture involves, therefore, excitation to the $3p$ -state followed by a rapid curve crossing to a valence state, which leads in turn to a direct C-C bond fission. At extended C-C bond lengths, however, the valence state intersects the ground potential energy surface, where the intramolecular vibrational energy redistribution (IVR) favors statistical dissociation through the C-H bond. More recently, the photodissociation of cyclohexyl radicals was found to yield CH_3 in correlation with 1,3-pentadiene with a branching ratio of around 1%. [8] A slow translation energy distribution was reported and assigned to a statistical dissociation over exit barriers, this channel requiring a ring-opening and several internal H-atom abstractions prior to dissociation.

In this work, the C-C decomposition of photoexcited ethyl radical is studied through detection of ground state methyl radicals, in a similar fashion to that employed for the C-H bond dissociation in our precedent works. The original idea was to carry out a complete study of the C-C channel, identifying all the dynamical regions and processes leading to CH_3 and CH_2 products. The description of the experiments carried out, and the theoretical calculations performed to rationalize the results constitute the body of the present work.

2. Experimental and theoretical details

2.1. Experiment

The main characteristics of the experimental setup have been already described in detail[9, 10] and only a brief summary will be reported here. Ethyl iodide, employed as precursor of hot ethyl radicals, is seeded in helium (10%, 1 atm backing pressure)

and expanded into vacuum using a pulsed nozzle (General Valve Series 9, 0.5 mm orifice). The gas pulse passes through a skimmer (Beam Dynamics, Standard Model 2, 0.5 mm diameter orifice) and reaches the ionization chamber. A sum-frequency mixing nonlinear crystal is used to combine the fundamental and the second harmonic radiation of a Nd:YAG (Quanta Ray Pro 230) pumped frequency doubled dye laser (Sirah Cobra-Stretch). The radiation produced, between 197.4 (the shortest wavelength we can get in this experimental setup; 10 μ J/pulse) and 201 nm (0.15 mJ/pulse) is employed for *in situ* photolysis of the ethyl iodide precursor forming radicals with a substantial internal energy. The same radiation is used as well for excitation of the radicals into the $3p_{A'}$ Rydberg state.

The probe laser is the output of a tunable doubled Nd:YAG (Quanta Ray Pro 230) pumped dye laser (Sirah Cobra-Stretch). CH_3 fragments in the ground vibrational state ($\nu=0$) are detected via a 2+1 REMPI process on the Q branch of the $3p_z$ ($^2A_2'' \leftarrow \tilde{X}^2A_2''$) transition at 333.45 nm. The generated CH_3^+ ions are accelerated by a 6 kV high voltage applied to the repeller plate and pass through a field-free time-of-flight (TOF) region (45 cm) before hitting the impedance matched microchannel plates (Chevron configuration, 40 mm diameter) of our velocity map imaging (VMI) apparatus set in the single-field configuration[11]. The resulting electron avalanche strikes a phosphor screen (P47), thereby creating the ion image, which is recorded by a CCD camera (SONY 1024 x 768 pixel) controlled using National Instrument (NI) LabView 7.1 and IMAQ VISION software.

2.2. Theory

The potential energy curves (PECs) of the different electronic states of the ethyl radical were obtained using state-averaged complete active space self-consistent field (SA-CASSCF) calculations[12] followed by the internally contracted multi-reference configuration interaction (MRCI) treatment,[13] available in the MOLPRO package [14]. For this system, it was found that Davidson correction becomes unstable for the excited states probably due to strong couplings between them. Therefore, no correction to the size inconsistency of MRCI was included. The active space used for these calculations consists of 13 electrons in 10 orbitals, the two first orbitals being kept closed (those associated to the $1s$ orbitals of the two carbon atoms). The two closed orbitals at CASSCF level were considered as core orbitals in the MRCI treatment. Calculations were performed within the C_s symmetry group and four states of A' symmetry and four states of A'' symmetry were included in the state-average. For all the calculations, the aug-cc-pVTC basis set of Dunning[15] was used for C and H atoms.

The ethyl radical is composed of 7 atoms and thus possesses 15 degrees of freedom. The purpose of the calculations is to obtain a simple (one dimensional) representation of the energetics of the electronic states involved as a function of R_{CC} , the distance between the CH_3 and CH_2 moieties. A partial relaxation of the ground state of the system has been performed at CASPT2 level at each R_{CC} distance between 0.6 and 5 Å. This presents the advantage to match the dissociation energy of the ground state, always keeping in mind that the calculated path is not necessarily the most favorable for the excited states. The MRCI calculations of the excited states were then performed at the obtained ground state geometries, where the four first states of A' symmetry and the three first states of A'' symmetry were calculated.

The diabaticization was carried out using the model presented in Refs.[16, 17]. This method consists of estimating geometrically the mixing angles between the different

states along the reaction coordinate that allow to pass from the adiabatic to the diabatic representations. The non-adiabatic coupling matrix elements (NACMEs) between the different states are then obtained as the derivative of the corresponding mixing angle as a function of the chosen coordinate, in this case, the C-C bond.

3. Results

3.1. *Experimental results*

Figure 1 depicts the main results of the present work. Methyl (CH_3) fragments were generated in the photodissociation of internally excited ethyl radicals at 197.4, 199.98 and 201 nm, and those produced in the vibrational ground state, $\text{CH}_3(\nu=0)$, were resonantly ionized giving rise to the images shown in the figure. The three images share little in common, which suggests significant changes in the decomposition dynamics through the C-C bond fission in this rather small interval of excitation wavelengths studied.

At 197.4 nm (the shortest excitation wavelength experimentally available in this work), the reconstructed velocity map image consists of two features, a broad low-recoiled isotropic ring and a central contribution. In the 199.98 nm reconstructed image, the same features can be identified although the inner radius of the ring – whose intensity has dropped noticeably with respect to the previous excitation wavelength – displays the shape of a quasi-full circle. The outer radius of the ring, which accounts for the maximum recoil of the contribution, does not show significant variations, however. At 201 nm the situation changes abruptly and the reconstructed image consists of an intense broad feature at the center of the image surrounded by a faint isotropic contribution. Significantly, the overall size (in pixels) of the three images is roughly the same.

The translational energy distributions (TEDs), obtained from angular integration of the images, add information about the number and the importance of the different contributions. At 197.4 nm, the central part of the image appears in the TED as a shoulder of a larger peak – the homologous counterpart of the ring in the image – centered at ~ 0.5 eV, which seems to be endowed with a large tail at the high-energy side spreading up to ~ 2.4 eV. In a first impression, however, the tail might belong to the low energy contribution – the shoulder – conforming, therefore, a Boltzman-like distribution on which the Gaussian peak rests. In order to clarify the number and nature of the contributions in the 197.4 nm distribution, CH_3 images at two laser pump energies were taken. The results, also shown in Figure 1 were unquestionably clarifying. The peak and the tail, not affected by the pump energy, are not connected to the low-energy contribution; on the other hand, the dependence shown by the shoulder indicates a near-zero recoil, fourth contribution of multiphoton nature. The multiphoton regime was easily characterized within the 10 μJ energy range of the excitation laser. At energies somewhat below 10 μJ , the three components displayed in the pink curve of Figure 1c were recovered. At energies slightly above 10 μJ , the increase of the low-energy part (Figure 1c, purple curve) denounces the multiphoton character of the contribution, a highly non-linear process.

As the excitation energy is decreased (longer excitation wavelengths), the overall intensity of the TEDs becomes weaker, due mostly to the decrease of the ring intensity. In addition, at 199.98 nm, the full-width-at-half-maximum (FWHM) of the peak increases from 0.5 to 0.7 eV and the shoulder, barely visible in the TED, is mostly

Figure 1. Abel-inverted images (insets) and the corresponding translational energy distributions (TEDs) obtained after angular integration of the images, of methyl fragments produced in the photodissociation of ethyl radicals at 197.4 nm (top), 199.98 nm (middle) and 201 nm (bottom) nm. Ground state $\text{CH}_3(\nu=0)$ fragments were detected using a (2 + 1) REMPI scheme at 333.45 nm. At 197.4 nm excitation wavelength, images were taken at two slightly different pump laser energies to display the differences between the "low" energy (pink curve) and "high" energy (purple curve) regimes, although only the "low" energy image is shown. The corresponding translational energy distributions (TEDs) obtained after angular integration of the images are shown as well.

overlapped with the main contribution. At 201 nm, the TED shows no evidence of the peak and the TED consists of a single contribution, peaking at zero energies, and a tail, which drops to zero at ~ 3 eV. It is relevant to mention that the pump energy had to be increased to the multiphoton regime to be able to record any signal at 201 nm.

3.2. Theoretical results

The top panel of Figure 2 represents the adiabatic potential energy curves (PECs) computed as a function of the C-C bond distance leading to the $\text{CH}_3 + \text{CH}_2$ dissociation limit. In order to shed light on the intrinsic character of the electronic wavefunctions of the excited states and to estimate the intensities of the couplings between them, the adiabatic PECs have been diabaticized following the scheme presented in Refs. [10] and [17]. The non-adiabatic coupling matrix elements (NACMEs) associated with the kinetic (derivative) couplings are depicted in Figure 3. The result of the diabaticization is presented in the bottom panel of Figure 2.

Figure 2. Adiabatic (top) and diabatic (bottom) potential energy curves as a function of the C–C distance. The magenta line represents the ground state; black, red and gray lines represent the $3s$, $3p_{A'}$ and $3p_{A''}$ Rydberg states, respectively. Green, blue and purple lines represent valence states in increasing Franck-Condon energy, *i.e.* V_b , V_{d1} and V_{d2} , respectively. The orange circles depicted in the bottom panel represent the three conical intersections found between the indicated excited states.

The first three excited states, the $3s$, $3p_{A'}$ and $3p_{A''}$ Rydberg states (black, red and grey curves) present a bound shape without exit barrier. At higher energies, two valence states, V_b (green) and V_{d1} (blue) in the Franck-Condon region, and an additional valence state V_{d2} , at longer C–C distances, complete the picture.

Four dissociation limits are obtained from the calculations, all of them correlating to CH_3 in the electronic ground state, $\tilde{X}^2A_2''$, and to different electronic states of the CH_2 product. Dissociation of ethyl radicals in the ground state correlates with ground state $\text{CH}_2 \tilde{X}^3B_1$ product radicals; CH_2 radicals in the excited $\tilde{a}^1A_1$, $\tilde{b}^1B_1$ and $\tilde{c}^1A_1$ electronic states correlate to the V_{d1} , V_{d2} and V_b valence states, respectively. As in the case of the C–H dissociation channel, excitation above 200 nm takes place to the Rydberg $3p_{A'}$ state and, therefore, any dissociation leading to CH_3 and CH_2 products must happen through non-adiabatic curve crossings, conical intersections or internal relaxation to lower levels of the ethyl radical.

It is also worth to mention that performing the calculations within the C_s symmetry allows us to characterize the $3p_{A''}$ Rydberg state that could not be included in the previous works exploring the H-atom dissociation channels, where no symmetry was

Figure 3. Non-adiabatic coupling matrix elements (NACMEs) associated with the kinetics couplings, obtained from the diabaticization procedure. The narrow NACMES $V_{d1}-V_b$ (magenta), $3p_{A'}-V_b$ (blue) and $3s-V_{d1}$ (black), correspond to the conical intersections represented by the orange circles in Figure 2.

considered for reason of homogeneity (the orbitals included in the active spaces using C_s symmetry are not identical when treating the dissociation from C_α and C_β). This Rydberg state remains however uncoupled with the other states below 8 eV, and should decay by internal conversion as it is not coupled to any dissociative state energetically available in the experiment.

4. Discussion

As in previous works, to quantify the magnitude of the different contributions in the images and TEDs, a deconvolution analysis of the distribution profiles shown in Figure 1 was performed. On the basis of the TED measured at the excitation wavelength of 197.4 nm, a tentative 3-Gaussian functions deconvolution procedure was carried out for the TEDs measured at the three excitation wavelengths studied. One cropped Gaussian function was set for the low-energy contribution (accounting for both the single-photon and the multiphoton contributions); a rather narrow Gaussian function was set at ~ 0.5 eV to reflect the main peak in the distributions, and the tail was described by a wider Gaussian function, centered at the high energy side of the main peak. The results of the deconvolution analysis, represented in Figure 4, are mostly clarifying. The main outcome is that the three TEDs are well reproduced by the three Gaussian functions used, or, in other words, that the three contributions identified for the TED at 197.4 nm are conforming the distributions at 199.98 nm and, more surprisingly, at 201 nm.

To rationalize the three contributions mentioned above, energy references for the possible dissociation limits are required. The references, represented in Figure 4 by vertical bars, denote the available energy, E_{av} , for each photodissociation channel that can be derived according to:

$$E_{av}(\text{CH}_3) = h\nu + E_{\text{int}}(\text{C}_2\text{H}_5) - D_0 - E_{\text{int}}(\text{CH}_2) \quad (1)$$

where $h\nu$ is the photon energy, $E_{\text{int}}(\text{C}_2\text{H}_5)$ is the internal energy of the ethyl radical produced by *in situ* photolysis of the precursor, ethyl iodide; the term $E_{\text{int}}(\text{CH}_2)$ includes the rovibrational and electronic energy of the CH_2 co-product, and D_0 is the C-C bond dissociation energy, which is estimated to be 4.25 eV, based on the enthalpies of formation[18]. The asymptotic values for the different dissociation channels associated with several electronic states of the CH_2 product – included in $E_{\text{int}}(\text{CH}_2)$ –, obtained from Ref. [19], are summarized in Table 1 and compared to the dissociation limits obtained from the theoretical calculations described in the previous sections. A rather good agreement is observed, especially for the formation of methylene in its ground state and in the $\tilde{b}^1B_1$ state.

Table 1. Asymptotic energies (in eV) characterizing the different dissociation channels leading to $\text{CH}_3(\tilde{X}^2A'_2)$ in correlation with CH_2 in several electronic states, in terms of the sum of the dissociation energy D_0 and the corresponding electronic energy of the CH_2 co-product. Experimental values from Ref. [19] are compared with the theoretical calculations from the present work.

CH_2 electronic state	Experiment [19]	Theory [present work]
X^3B_1	4.25	4.31
$\tilde{a}^1A_1$	4.64	5.15
$\tilde{b}^1B_1$	5.67	5.80
$\tilde{c}^1A_1$	6.81	7.40

To the best of our knowledge there is no data regarding the energetics of the photodissociation of ethyl iodide at 197.4 nm, but the process at 199.98 nm and 201 nm have been recently studied in our group, precisely at the excitation wavelengths 201.19 nm [20, 21] and 200.08 nm [21] with nanosecond [20] and femtosecond [21] lasers. In particular, the photodissociation of ethyl iodide at 201.19 nm produces ethyl radicals in correlation with iodine atoms in both spin-orbit states, $\text{I}(^2P_{3/2})$ and $\text{I}^*(^2P_{1/2})$ [20] (no $\text{I}(^2P_{3/2})$ was observed in the femtosecond experiments reported in Ref. [21] due to the quantum yield for production of I^* , Φ^* , close to one). The fractions of the available energy channeled into internal degrees of freedom of the products for the $\text{C}_2\text{H}_5 + \text{I}$ and $\text{C}_2\text{H}_5 + \text{I}^*$ channels, f_{int} , are 0.68 and 0.44, respectively, although in the latter case, the corresponding broad distribution ranges from 0.33 to 0.61 [20].

Assuming similar f_{int} values for the three excitation wavelengths studied in this work, three dissociation limits can be established for $E_{\text{int}}(\text{C}_2\text{H}_5)$, considering only ethyl fragments produced in correlation with spin-orbit excited iodine atoms. A higher limit, $E_{\text{int}}^{\text{max}}(\text{C}_2\text{H}_5)$, derives from $f_{\text{int}}=0.61$, a lower limit, $E_{\text{int}}^{\text{min}}(\text{C}_2\text{H}_5)$, corresponds to $f_{\text{int}}=0.33$, and the most probable limit, $E_{\text{int}}^{\text{mp}}(\text{C}_2\text{H}_5)$, derives from $f_{\text{int}}=0.44$. The values of $E_{\text{int}}^{\text{min}}(\text{C}_2\text{H}_5)$, $E_{\text{int}}^{\text{max}}(\text{C}_2\text{H}_5)$ and $E_{\text{int}}^{\text{mp}}(\text{C}_2\text{H}_5)$ as well as the subsequent estimations of the maximum, minimum and most probable values for the available energy of each dissociation channel, $E_{\text{av}}^{\text{min}}$, $E_{\text{av}}^{\text{max}}$ and $E_{\text{av}}^{\text{mp}}$, are gathered in Table 2. Notice that the experimental values of D_0 and $E_{\text{int}}(\text{CH}_2)$ from Table 1 have been employed to derive these available energies.

As observed in Table 2, for a given dissociation channel, the values obtained at each excitation wavelength vary significantly depending on the f_{int} considered for the precursor photolysis step. Therefore, some shift and/or broadening can be expected

Table 2. Internal energy characterizing the ethyl radicals produced by photolysis *in situ* of ethyl iodide, $E_{\text{int}}(\text{C}_2\text{H}_5)$, and corresponding available energy, E_{av} , for the subsequent photoinduced dissociation into $\text{CH}_3(\tilde{X}^2A_2')$ in correlation with CH_2 in several electronic states, for the three excitation wavelengths (λ_{exc}) employed. Regarding the precursor photolysis step, three scenarios are considered: a minimum value of $f_{\text{int}} = 0.33$ (min), a maximum value of $f_{\text{int}} = 0.61$ (max) and the most probable value of $f_{\text{int}} = 0.44$ (mp) (see the text for more details).

λ_{exc}	201 nm			199.98 nm			197.4 nm		
$E_{\text{int}}(\text{C}_2\text{H}_5)$	min	max	mp	min	max	mp	min	max	mp
	0.93	1.72	1.24	0.94	1.74	1.26	0.97	1.79	1.29
E_{av}	min	max	mp	min	max	mp	min	max	mp
X^3B_1	2.84	3.63	3.15	2.89	3.69	3.21	3.00	3.82	3.32
$\tilde{a}^1A_1$	2.45	3.23	2.76	2.50	3.30	2.82	2.61	3.43	2.93
$\tilde{b}^1B_1$	1.42	2.21	1.73	1.47	2.27	1.79	1.58	2.40	1.90
$\tilde{c}^1A_1$	0.28	1.07	0.59	0.33	1.14	0.65	0.44	1.26	0.76

when assigning a contribution in the TED to any dissociation channel based on the corresponding E_{av} .

In Figure 4 the references for the available energy obtained as described above are plotted on top of the result of the deconvolution process for the three translational energy distributions. For simplicity, only three references have been included in each plot: the $E_{\text{av}}^{\text{mp}}$ for the three asymptotes producing $\text{CH}_2(\tilde{c}^1A_1)$, $\text{CH}_2(\tilde{a}^1A_1)$ and $\text{CH}_2(\tilde{b}^1B_1)$.

The structure of the distributions – taking into account the information provided by the deconvolution – and the dependence on the excitation wavelength, resembles a particular, well described situation occurring in photodissociation dynamics; namely, dissociation at the threshold of an exit barrier. For instance, in an earlier VMI work on the photodissociation of acetaldehyde (CH_3CHO), the radical channel ($\text{CH}_3 + \text{HCO}$) was studied between 315 and 325 nm through detection of both the CH_3 and HCO fragments.[22] Three dynamical regions were characterized: at dissociation wavelengths below 319 nm, the product images consisted of a well defined ring, coherent with a fast direct dissociation on a repulsive surface (the triplet T_1); at dissociation wavelengths above 319 nm, Boltzmann shape of the translational energy distributions indicated an intersystem crossing (ISC) relaxation mechanism, where dissociation occurs on the ground state (S_0). Those results confirmed the existence of an exit barrier on the triplet T_1 potential energy surface (PES). More importantly, at 319 nm, at the exact energy of the triplet barrier, the CH_3 translational energy distribution showed a mixed nature. The peak associated to the fast dissociation process was still present, although the amplitude was reduced by several orders of magnitude. The fast component was rationalized by a mechanism that does occur above the exit barrier of the T_1 PES, but which initially does not have enough available energy to cross it. Contribution from vibrationally excited parent molecules present in a small amount in the molecular beam, is enough to reach the excited state with enough energy to surmount the barrier. Those molecules who fail to cross the barrier contribute to the slow component attributed to ISC to the ground state. In those experiments, a third contribution was detected: the aforementioned slow and fast features seated on a broad structureless signal extending up to energies well above the available energy, but no assignment to this contribution was made [22].

The described picture of the photodissociation of acetaldehyde at 319 nm, at the exact excitation energy corresponding to an exit barrier, resembles extraordinarily the present case, with similar prototypical contributions. The theoretical calculations presented in Figure 2b allows us to infer the underlying dissociation dynamics and to

Figure 4. Deconvolution analysis of the TEDs represented in Figure 1. The distributions were decomposed using Gaussian functions accounting for the three main features distinguishable at the excitation wavelength 197.4 nm. Vertical bars indicate the available energy, E_{av}^{mp} , for the photodissociation of the ethyl radicals into $\text{CH}_3(\tilde{X}^2A_2'')$ and CH_2 in the first three excited electronic states, $\tilde{a}^1A_1$, $\tilde{b}^1B_1$ and $\tilde{c}^1A_1$, from ethyl radicals characterized by the most probable internal energy $E_{int}^{mp}(\text{C}_2\text{H}_5)$ (see the text for more details).

identify the possible exit barrier involved. At 201 nm excitation wavelength, and taking into account the internal energy inherited in the photodissociation of the precursor, the ethyl radicals possess ~ 7.8 eV, enough to reach the conical intersection between the Rydberg $3p_{A'}$ and the valence V_b states. Although the present theoretical model is a 1D calculation along the C-C internuclear distance with geometry optimization in the ground electronic state, such conical intersection is located roughly at the top of the exit barrier which characterizes the V_b state. Therefore, excitation in the vicinity of the conical intersection can induce dissociation through the exit barrier into $\text{CH}_3(\tilde{X}^2A_2)$ and $\text{CH}_2(\tilde{c}^1A_1)$ fragments, whose yield increases with increasing excitation energy.

The fate of those radicals who fail in reaching the conical intersection and overcome the exit barrier, may be responsible for the other two contributions observed in the TEDs. Indeed, a fraction could relax to the ground state by internal conversion, generating the slow contribution in the TEDs. More interestingly, the remainder fraction of radicals who do not succeed in passing the barrier could predissociate through the V_{d1} state, resulting in methyl fragments in correlation with CH_2 in the first excited state, $\tilde{a}^1A_1$, giving rise to the higher energy, low intensity and broad component in the TEDs.

The energy references plotted in Figure 4 confirm and strengthen the former assignment. The rising slope of the central contribution is reasonably located close to $E_{\text{av}}^{\text{mp}}$ and in any case between the $E_{\text{av}}^{\text{min}}$ and $E_{\text{av}}^{\text{max}}$ values for the $\text{CH}_2(\tilde{c}^1A_1)$ asymptote. From the values gathered in Table 2 and taking into account, in particular, $E_{\text{av}}^{\text{mp}}$ for the lowest electronic states of the CH_2 fragment, the high-energy contribution can be safely assigned to the $\text{CH}_3 + \text{CH}_2(\tilde{a}^1B_1)$ channel.

5. CONCLUSIONS

The C-C bond dissociation of the ethyl radical is studied through velocity map imaging and REMPI detection of the produced CH_3 radicals and the experimental results are rationalized in terms of high level *ab initio* calculations of one-dimension potential energy curves along the C-C coordinate. Excitation at ~ 201 nm leads the ethyl radical to a conical intersection between the Rydberg $3p_{A'}$ and the valence V_b states, at the threshold of an exit barrier. As such, direct population of the valence state above the barrier occurs, enabling a major fast dissociation channel, correlating with ground state $\text{CH}_3(\tilde{X}^2A_2)$ radicals and CH_2 radicals in the $\tilde{c}^1A_1$ excited state. Population transfer to the valence V_b state enables two additional minor, fast and slow dissociation channels, leading to $\text{CH}_2(\tilde{a}^1A_1)$ radicals in correlation with CH_3 ground state fragments, and to ground state CH_2 by internal conversion, respectively.

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