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The 3s versus 3p Rydberg state photodissociation dynamics of the ethyl radical

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The photodissociation dynamics of the ethyl radical following excitation into the 3s and 3p Rydberg states are revisited in a joint experimental and theoretical study. Two different methods to produce the ethyl radical, pyrolysis and *in situ* photolysis, are employed in order to modify the initial ro-vibrational energy distribution characterizing the ethyl radical beam. H-atom velocity map images following excitation of the radical at 243 nm and at 201 nm are presented and discussed along with *ab initio* potential energy curves focussing on the bridged C_{2v} geometry. The reported results show that the dynamics following excitation to the 3s Rydberg state is insensitive to the initial internal energy of the parent radical, in contrast to the dynamics on the 3p Rydberg state, which is strongly modified. The role of the bridged C_{2v} geometry on both photodynamics is highlighted and discussed.

1 Introduction

The role of radicals, and more specifically alkyl radicals, as crucial intermediates in photoinduced reactions in atmospheric and interstellar chemistry, has lead to a considerable interest on their photodynamics¹. Among them, the ethyl radical, one of the simplest alkyl radicals, constitutes a prototype for such studies and several theoretical and experimental investigations have been reported focusing in particular on its thermal decomposition^{2–6} and on its UV-VUV photoexcitation and further dissociation.^{7–15}

A first broad absorption band centered at ~ 245 nm and assigned to excitation to the 3s Rydberg state characterizes the absorption spectrum of the ethyl radical, while a second band centered at ~ 200 nm is attributed to the population of the 3p Rydberg state¹⁶. A first study on the photodissociation of the ethyl radical was carried out in the early 1990s by Koplitz and coworkers measuring the intensity of the Doppler profile of atomic hydrogen and deuterium from photoexcited ethyl and its isotopologues (i.e. CH_3CH_2 , CD_3CH_2 and CH_3CD_2) which were produced by *in*

situ photolysis of ethyl iodide, in a one-color experiment^{7,9}. Site-specific C-H bond cleavage from the methyl moiety (C_β) was then observed following excitation into the 3s Rydberg state at 248 nm while at 193 nm, a complete H-D isotope scrambling was found to mask any site-specific process. Investigations on the photodynamics on this 3p Rydberg state are indeed quite limited. In particular, Min *et al*¹⁰ reported and discussed the H-fragment averaged translational energy deduced from Doppler broadened fluorescence detection lines, following excitation at 205 nm. The fast H-atom loss observed was attributed to a curve crossing between the 3p excited state and a valence state, while complete H-D isotope scrambling was envisaged as hydrogen exchange on this 3p state. In the proposed picture, the latter state presents two minima separated by a small barrier which could be easily overcome by some vibrational excitation, the molecule going then back and forth above the two minima.

In contrast, the photodynamics on the 3s Rydberg state have received more recent attention. Pump-probe experiments involving H-atom Rydberg tagging time-of-flight spectroscopy¹² or velocity map imaging¹³ have been carried out employing two different methods to produce jet cooled ethyl radicals, either by photolysis of nitroethane or ethyl vinyl ether¹² or pyrolysis of *n*-propyl nitrite¹³. Two different contributions were observed in both experiments and attributed to different mechanisms. While a slow H-atom contribution was assigned to unimolecular dissociation on highly ro-vibrationally excited levels of the ground state, direct dissociation producing ethylene in its ground state was proposed to lead to a fast H-atom contribution. Several discrepancies exist, nevertheless, between the two experiments on the branch-

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ing ratio of the two processes and on the averaged translational energy $\langle E_T \rangle$ characterizing the fast H-atom loss^{12,13}. In agreement with theoretical studies including *ab initio* calculations of minimum energy pathways¹⁷ and direct *ab initio* molecular dynamics employing the trajectory surface hopping methodology¹⁴, the proposed dynamics involve an important modification of the geometry of the excited ethyl radical. A bridged C_{2v} structure is initially formed *i.e.*, one H-atom from the methyl moiety rotates being then located at 90° with respect to the C-C bond. In this C_{2v} geometry, the $3s$ state is adiabatically correlated to the formation of $H + C_2H_4$ in their respective ground states¹⁸. A conical intersection between the $3s$ state and the $\tilde{X}^2A'$ ground state governs then the dissociation. Fast H-atoms are produced by direct dissociation while some population goes into the ground state and slowly dissociates, giving rise to the slow contribution. A disagreement still exists, however, concerning the unimolecular dissociation leading to the slow H atoms^{14,15}. Finally, Matsugi¹⁹ performed a classical trajectory study revealing in particular the existence of a minor roaming pathway in ground state ethyl leading to $C_2H_3 + H_2$ followed by secondary dissociation of C_2H_3 into $C_2H_2 + H$.

Fig. 1 Scheme of the experimental procedure. A first nanosecond laser pulse centered at ~ 243.1 nm or at ~ 201 nm is used to excite the ethyl radicals into the $3s$ or $3p$ Rydberg states. The $H(2s^2S)$ atoms following dissociation are detected using a (2+1) resonance enhanced multiphoton ionization (REMPI) scheme at ~ 243.1 nm. Ethyl radicals are produced either by pyrolysis, *i.e.* vibrationally cold, or by *in situ* photolysis of ethyl iodide, *i.e.* with an internal energy distribution as indicated in the figure: $\langle E_{int} \rangle = 0.64$ eV²⁰ or $\langle E_{int} \rangle = 1.27$ eV²¹, respectively (See text).

We have recently investigated the photodynamics following excitation of the ethyl radical in the $3p$ Rydberg state by means of a pump-probe scheme and velocity map imaging²². A novel mechanism for site-specific H-atom elimination, leading to $CH_3CH + H$, was reported and discussed with the aid of *ab initio* calculations, including potential energy curves and non-adiabatic coupling matrix elements. This prompt H-atom elimination was indeed accessed by an initial internal energy content into the radical. In the present study, we aim at a deeper understanding of the pho-

todynamics of the ethyl radical by focusing on two main aspects: on one hand, the effect of the initial internal excitation of the ethyl radicals depending on the method chosen to produce them and, on the other hand, the H-D isotope scrambling and the role of the C_{2v} bridged structure.

A scheme of the experimental procedure employed in the present work is presented in Figure 1. Ethyl radicals are produced using two different methods: either pyrolysis of *n*-propyl nitrite as in Ref.¹³, or by *in-situ* photolysis of ethyl iodide. While the former produces vibrationally cold radicals, the latter forms radicals with a non-negligible internal energy depending on the photolysis process. Two different excitation wavelengths have been employed: 243.1 nm and 201.2 nm, in order to populate the $3s$ and $3p$ Rydberg state, respectively, while the produced H-atom fragments are then detected employing a (2+1) resonance enhance multiphoton ionization (REMPI) scheme at 243.1 nm. The experimental findings are complemented by *ab initio* calculations, including potential energy curves from the C_{2v} symmetry. The experimental and theoretical methodologies are briefly described in next section while the results are presented in Sections 3 and 4 and discussed jointly in Section 5. Section 6 is dedicated to summarize the most important conclusions of this work.

2 Methods

2.1 Experimental

The main characteristics of the experimental setup have been already described in detail^{23,24} and only a brief summary will be reported here. Ethyl radicals are produced employing two different methods: either pyrolysis or *in situ* photolysis. For the former, the precursor, *n*-propyl nitrite, was seeded in helium (10%, 1 atm backing pressure) and expanded into vacuum using a pulsed nozzle (General Valve Series 9, 0.5 mm orifice) with a heated SiC tube mounted at the exit in order to produce ethyl radicals by flash pyrolysis^{25,26}. Otherwise, ethyl iodide is employed as a precursor for photolysis, similarly seeded in Helium (10%, 1 atm backing pressure) and expanded into vacuum using the pulsed nozzle. The gas pulse passes then, in both cases, through a skimmer (Beam Dynamics, Standard Model 2, 0.5 mm diameter orifice) and reaches the ionization chamber. This implies that the ethyl radicals produced by pyrolysis are jet cooled – although characterized by a considerable rotational temperature – whereas those produced by *in situ* photolysis of the precursor in the interaction region are significantly rovibrationally excited, the internal energy of the radical being characterized by the energy release of the photodissociation process of the precursor molecule. One-color experiments at 243.1 nm were performed employing a Nd:YAG (Quanta Ray Pro 190) pumped frequency doubled dye laser. In the case of *in situ* photolysis, one-photon absorption of this laser produces firstly ethyl radicals while, in any case, this pulse laser will lead to one-photon excitation above the $3s$ Rydberg state and dissociation of ethyl radicals. The H atoms produced are detected then by the (2 + 1) REMPI scheme at 243.1 nm using the $2s(^2S_{1/2}) \leftarrow 1s(^2S_{1/2})$ transition. **The probe laser frequency was scanned over the Doppler profile in the resonant transition frequency in order to ionize all photofragment velocities.**

In the two-color experiments, 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), producing radiation around 201 nm (0.15 mJ/pulse). Similarly, this laser is employed for *in situ* photolysis of ethyl iodide forming ethyl radicals, while in all cases it is also used as a pump laser for excitation of the radicals above the $3p$ Rydberg state. In the case of *in situ* photolysis, this pump wavelength is tuned at 201.2 nm, so that the 0_0^0 origin of the B -band of ethyl iodide is excited²¹ ensuring a maximal formation of ethyl radicals. The produced $H(^2S)$ atoms are similarly ionized 10 ns later using the (2 + 1) REMPI scheme at 243.1 nm (probe wavelength), which is produced as described above.

We remark that photolysis of ethyl iodide at 201.2 nm produces ethyl radicals with a characteristic internal energy of about 1.27 eV²¹. In contrast, ethyl radicals characterized by a 0.64 eV ro-vibrational energy are produced by photolysis at 243 nm, in agreement with previous investigations²⁰ and according to our recorded velocity map images of ethyl radical from the ethyl iodide photolysis.

The generated H^+ ions are accelerated by a 6 kV voltage applied to the repeller plate and pass through a field-free time-of-flight (TOF) region (45 mm) before hitting the impedance matched microchannel plates (Chevron configuration, 40 mm diameter) of our velocity map imaging (VMI) apparatus set in the single-field configuration²⁷. 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.

The velocity map H^+ images are quadrant symmetrised and Abel inverted using the Hankel transform, prior to extracting the translational energy and angular distributions. Independent velocity-radius calibration of the apparatus is done by measuring resonantly ionized $CH_3(v = 0)$ fragments produced after the photodissociation of CH_3I at 333.45 nm (one color pump-probe experiment) at different repeller potentials, taking advantage of the well known kinetic energy release of the $I(^2P_{3/2})$ yielding channel at this photolysis wavelength.

2.2 Theoretical

Two sets of potential energy curves (PECs) have been computed in order to explore the reported fragmentation mechanism for the dissociation of the $3s$ Rydberg state, which involves a migration to the bridge geometry of C_2H_5 (C_{2v}) prior to H-atom elimination^{12,13,17}. To visualize the H-atom migration, the Jacobi coordinates shown in Figure 2(top, C_s geometry) were employed, and for each of the Jacobi angles, θ , which have been considered between 10° and 90° , the other coordinates were optimized at CASPT2 level for the ground state. The optimized geometries were then employed to perform MRCI calculations including the excited electronic states to build the associated PECs and see their evolution along the θ coordinate. The values for angles between 90° and 170° are then obtained by symmetry. The equilibrium

C_{2v} geometry is obtained for the Jacobi angle of 90° , as observed in Fig. 2(bottom). The PECs leading to H-atom elimination were computed keeping frozen all the coordinates but R , thus maintaining the C_{2v} geometry.

To keep the homogeneity of the vertical excitations compared to our previous work²², the same level of calculation and procedure were repeated. More specifically, state-averaged complete active space self-consistent field (SA-CASSCF) calculations have been performed with an active space consisting of 13 electrons in 10 orbitals, the two first orbitals being kept closed. CASSCF references and orbitals were then used for an internally contracted multi-reference configuration interaction (MRCI) treatment using the MOLPRO package²⁸. Due to a convergence problem in the excited states, the Davidson correction was not applied to the MRCI energies. In order to ensure homogeneity in all calculations, including our previous work²² and in particular to employ the same active orbitals, all *ab initio* calculations (for both the C_s and C_{2v} geometries) were performed using the C_1 group of symmetry, assuming the additional cost of the calculations and a limitation on the number of electronic states that can be calculated.

Fig. 2 Schemes of the Jacobi coordinates, R and θ , associated to the H-atom migration (top) and to the C_{2v} geometry used for the H-atom elimination (bottom).

3 Experimental results

3.1 One-color experiments: photodissociation from the $3s$ Rydberg state at 243 nm

The photodynamics of the ethyl radicals in the $3s$ Rydberg state have been revisited. Ethyl radicals produced either by pyrolysis or by photolysis are photoexcited at 243.1 nm in a one-color experiment, where the hydrogen atoms from its photodissociation are detected by (2+1) REMPI. The H-atom images along with the corresponding translational energy distributions (TED) derived from the angular integration of the images are depicted in Figure 3. As it can be seen, in both cases – pyrolysis or photolysis – two contributions can be observed: an isotropic blot in the center of the image, leading to a Boltzmann-type distribution in the TED, and a broad contribution at higher radius, slightly observed in the images, corresponding to a broad Gaussian-type peak in the TED. The TEDs have been accordingly fitted by employing a Gaussian function for the broad contribution at higher energies and Eq. (1)

for the Boltzmann-type contribution at lower energies:

$$I(E_T) = AE_T^i(1 - E_T)^j \quad (1)$$

where E_T is the translational energy and A , i and j are fitting parameters that do not contain physical meaning.

Fig. 3 H-atom velocity map image along with the corresponding translational energy distribution (TED), from photodissociation of ethyl radicals produced by pyrolysis (a) or *in situ* photolysis (b), photoexcited at 243.1 nm. Black line: experimental data; red line: Gaussian function; blue line: fit to Eq. (1); magenta line: overall fit (see the text for details). Vertical bars indicate the maximum available energy for the different possible dissociation channels: solid line corresponds to the $\text{H} + \text{C}_2\text{H}_2(\tilde{\text{X}}^1\text{A}_g)$ channel and dashed line correspond to the $\text{H} + \text{C}_2\text{H}_2(\tilde{\text{A}}^3\text{B}_{1u})$ channel (considering D_{2h} symmetry). In the case of photolysis, an internal energy of the parent molecule $\langle E_{\text{int}} \rangle = 0.64$ eV²⁰ is considered for the calculation of the maximum available energy.

As observed in Figure 3, a similar relative intensity between the two contributions is observed in both cases. Although the ro-vibrational energy (0.64 eV) characterizing ethyl radicals produced by photolysis in this case is lower than the initial internal energy of ethyl following photolysis of the same precursor at ~ 201 nm, it would be expected to be enough to modify the photodynamics. Strikingly, the internal energy content provided to the ethyl radicals produced by photolysis in comparison with pyrolysis, **does** not have any effect on the photodynamics taking place. We can assume that in both cases, ethyl radicals are excited within the 3s Rydberg state. The internal energy provided by *in situ* pho-

tolysis would energetically allow to access the 3p Rydberg state of the ethyl radical, but only in lower rovibrational levels. This scenario is improbable because the photolysis of $\text{C}_2\text{H}_5\text{I}$ produces a rovibrationally excited ethyl radical, which is rather unlikely to be excited in low rovibrational levels of an excited electronic state by one photon absorption

The TEDs obtained in the present investigation are compared in Figure 4 to those previously reported on the photodissociation of jet cooled ethyl radicals at slightly different excitation wavelengths by Zhang and co-workers¹² and Fischer and co-workers¹³. While the former employed the H-atom Rydberg tagging technique for detection of the H atoms, the latter performed a similar imaging experiment where the jet cooled ethyl radicals were produced by pyrolysis of *n*-propyl nitrite, like in the present work, and the H-atoms were detected by (1+1') REMPI via the 1s-2p transition at 121.6 nm (Lyman- α).

The relative intensity of the fast broad contribution with respect to the slow component at small translational energies as well as the translational energy $\langle E_T \rangle$ at the maximum of intensity of this fast contribution are strikingly different depending on the experiment. While Zhang and co-workers¹² estimated a fast contribution characterized by $\langle E_T \rangle = 2.6$ eV and by a similar intensity with respect to the slow component, Fischer and co-workers reported a $\langle E_T \rangle = 1.8$ eV and a much lower yield. The differences observed between the present results characterized by $\langle E_T \rangle = 1.97$ -2.06 eV (depending on the method used for the production of the ethyl radical, pyrolysis or photolysis), and those from Zhang and co-workers¹² could indeed be attributed to the different detection and experimental technique, **where the H-atom Rydberg tagging might lead to a particularly efficient detection of the fast channel in spite of the slow contribution**. In contrast, the slightly higher $\langle E_T \rangle$ and minor yield of the fast component in the present investigation compared to those obtained by Fischer and co-workers¹³ might seem rather **unexpected although it could be due to the different REMPI schemes employed leading to a different detection efficiency and sensitivity**. The discrepancies between the various experiments will be discussed in Section 5 in terms of the role of the excitation wavelength on the reaction pathways although it is necessary to keep in mind the possible effect of the different experimental methods mentioned here. Moreover, the anisotropy parameter β obtained in the present work for the fast channel of the H-atom elimination from ethyl radicals produced by pyrolysis is $\beta = 0.40 \pm 0.05$, which is comparable to the β values reported by Zhang and co-workers ($\beta = 0.50$) and Fischer and co-workers ($\beta = 0.45$).

3.2 Two-color experiments: photodissociation from the 3p Rydberg state at 201 nm

Two-color experiments have been performed where a first pump pulse at around 201.2 nm is employed to excite the ethyl radicals produced to the 3p Rydberg state, while the H-atom fragments are detected by (2+1) REMPI at 243.1 nm. Similarly to Figure 3, the H-atom images along with the TEDs are depicted in Figure 5 for ethyl radicals produced either by pyrolysis (top) or by photolysis (bottom). In strong contrast to what is observed

Fig. 4 Translational energy distribution (TED) of H-atoms from the photodissociation of ethyl radicals photoexcited into the 3s Rydberg state, obtained in the present work at ~ 243 nm (black and red curves), compared to the ones previously reported by Zhang and co-workers (green curve, adapted from Ref.¹²) and Fischer and co-workers (blue curve, adapted from Ref.¹³).

for the 3s-Rydberg state excitation, the differences between both methods to produce ethyl radicals are now striking. While a blot dominates the image leading to a Boltzman-type distribution when ethyl radicals are produced by pyrolysis, photoexcitation of vibrationally-hot ethyl radicals as formed by *in situ* photolysis, leads to a pronounced second contribution: an isotropic ring at higher radius, yielding a sharp Gaussian peak in the TED²². Besides, the Boltzmann-type distributions differ: in Figure 5(a), the slow component presents a maximum of intensity at threshold energies, while in Figure 5(b), its maximum is around $\langle E_T \rangle = 0.5$ eV and it is characterized by a larger full width at half maximum (FWHM). For slow reactions characterized by a long reaction time, the available energy is usually redistributed among different internal degrees of freedom. In the case of ethyl radicals formed by *in situ* photolysis, where the radicals have a higher initial ro-vibrational energy, this intramolecular vibrational redistribution (IVR) can then lead to broader Boltzmann distributions.

Although the distribution in Figure 5(b) is in good agreement with our previous study²², some differences on the shape of this slow contribution and on the relative intensity of the two peaks can be observed. It can be attributed to the different REMPI schemes employed, the (3+1) REMPI used in Ref.²² allowing a great energy resolution in spite of a lower intensity.

The available energy for dissociation, E_{av} , can be derived according to

$$E_{av} = h\nu + E_{int}(\text{parent}) - D_0 \quad (2)$$

where $h\nu$ is the photon energy, $E_{int}(\text{parent})$ is the ethyl initial internal energy, and D_0 is the dissociation energy.

The narrow peak in the TED shown in Figure 5(b) is attributed to the $H(^2S) + CH_3CH(1^1A'')$ channel, which is characterized by $D_0 = 5.91$ eV, according to our calculations²². The vertical

Fig. 5 H-atom velocity map image along with the corresponding translational energy distribution (TED), from photodissociation of ethyl radicals produced by pyrolysis (a) or *in situ* photolysis (b), photoexcited at 201.2 nm. Vertical bars indicate the maximum available energy for the three first C_α dissociation limits, i.e. $H(^2S) + CH_3CH(\bar{X}^3A'')$ (blue), $H(^2S) + CH_3CH(1^1A')$ (brown) and $H(^2S) + CH_3CH(1^1A'')$ (orange). In the case of photolysis, an internal energy of the parent molecule $\langle E_{int} \rangle = 1.27$ eV²¹ is considered for the calculation of the maximum available energy.

bar in Figure 5(b) represents the corresponding E_{av} of this dissociation channel. As previously found in Ref.²², this is a C_α site-specific channel (i.e. H-atom elimination from the methylene moiety of the ethyl radical) that occurs after excitation of internally hot ethyl radicals through a fast non-adiabatic crossing to a valence bound state followed by dissociation through a conical intersection. A remarkably effective promoting vibrational mode may induce a high selectivity at the conical intersection leading to this prompt channel and preventing the IVR to be reflected in the measured image.²²

4 Theoretical results

Ab initio calculations, including potential energy curves (PECs) of the ground and excited states of the ethyl radical have been performed in order to explore the reaction pathways following excitation into the 3s and 3p Rydberg states. An interesting fact arising from the calculations is that only the $3p_z$ Rydberg state is found within the six first electronic states while the $3p_x$ and $3p_y$ states would likely lie at higher energies, not reached in the

present experiments. Following a detailed analysis of the character of the electronic wavefunctions, the six electronic states were identified as the ground state, the $3s$, the $3p_z$ and three valence states, in agreement with our previous work²². Hence, the $3p_z$ Rydberg state is referred here as $3p$ for simplicity. Further calculations of higher excited states on the Franck Condon region could be of potential interest to deeply understand the strong non-degeneracy of the $3p$ Rydberg manifold and its effect on the photodynamics.

In our recent work,²² the PECs as a function of the C-H distance leading to the CH_3CH (carbene) + H and C_2H_4 (ethylene) + H dissociation channels were presented and discussed. Based on these results, the reported site-selective prompt dissociation channel following excitation in the $3p$ Rydberg state was attributed to a fast non-adiabatic crossing to a valence bound state followed by dissociation through a conical intersection. In contrast, no direct dissociation channel leading to the ethylene co-fragment was observed.

The calculations presented in the present work aim at unraveling the role of the bridged C_{2v} structure in the photodynamics following excitation into both the $3s$ and $3p$ Rydberg states of the ethyl radical.

Fig. 6 Computed potential energy curves as a function of θ angle (see the text for more details). Black: ground state. Red: $3s$ Rydberg state. Blue: $3p$ Rydberg state. Yellow and green: valence states.

The potential energy curves as a function of the θ Jacobi angle are depicted in Figure 6, while the PECs as a function of the R C-H distance for the bridged C_{2v} structure are displayed in Figure 7. As can be seen in Figure 6, the ground state presents two minima at around $\theta \approx 40^\circ$ and $\approx 160^\circ$ corresponding to the two C_s equilibrium geometries of the ethyl radical – the H-atom bound to each C atom. A maximum is found at $\theta = 90^\circ$, which represents the bridged C_{2v} structure. In contrast, the PECs corresponding to the $3s$ and $3p$ Rydberg states slightly decrease in energy as a function of the Jacobi angle θ , presenting a minimum in the C_{2v} geometry ($\theta = 90^\circ$). The formation of the bridged C_{2v} structure following excitation to the $3s$ and $3p$ Rydberg states is therefore

Fig. 7 Computed potential energy curves as a function of C-H distance from an initial bridged C_{2v} structure of the ethyl radical (see the text for more details). Black: ground state. Red: $3s$ Rydberg state. Blue: $3p$ Rydberg state.

favorable. The PECs of the upper valence states are, in contrast, similar to the ground state.

As observed in Figure 7, a repulsive PEC characterizes the H-atom elimination dynamics on the $3s$ Rydberg state from a bridged C_{2v} geometry, similarly to the early result from Ref.¹⁸. In agreement with latter studies, this state will undergo direct dissociation mediated by the conical intersection with the ground state, observed at $R_{\text{C-H}} \approx 1.5$ Å. Fast H-atom may then be produced by direct dissociation, while some population may go into the well of the ground state. In the latter case, the energy would be redistributed in the different modes and the ethyl will end up dissociating slowly due to the excess of energy.

In Figure 7, the $3p$ Rydberg state presents, in contrast, a stable minimum in C_{2v} at $R_{\text{C-H}} \approx 1.25$ Å, and thus it cannot undergo direct dissociation. The H-atom would more likely follow the migration to the other C atom. Due to the excess of energy, the ethyl radical can then oscillate between the two C_s geometries producing repeated H-atom exchange until the system relaxes via internal conversion to the lower $3s$ Rydberg state.

5 Discussion

The main findings arising from this work are summarized in Figure 8, where an energy level diagram obtained according to the present theoretical calculations, in particular those shown in Figures 6 and 7, and the calculations presented in Ref.²², is displayed including the first excited electronic states and the different geometries involved in the ethyl radical photodynamics, considering a final dissociation into channels $\text{CH}_2\text{CH}_2 + \text{H}$ and $\text{CH}_3\text{CH} + \text{H}$.

Photoexcitation into the $3s$ Rydberg state favors an initial rotation of one H-atom from the methyl moiety, being then located at a Jacobi angle $\theta = 90^\circ$. In this bridged C_{2v} geometry, the radical undergoes direct dissociation, governed by a conical intersection between the $3s$ and the ground state. A part of the population goes then into highly ro-vibrationally excited levels of the ground

Fig. 8 Energy level diagram based on the *ab initio* calculations presented in this work and those of Ref.²². The first electronic states (ground state, $3s$ and $3p$ Rydberg states, and two valence excited states) are included as well as reaction pathways into two main H-atom dissociation channels: $\text{CH}_2\text{CH}_2 + \text{H}$ and $\text{CH}_3\text{CH} + \text{H}$. Relevant symmetry groups and geometries are also included. Double cones represent conical intersections and circles represent avoided crossings. The initial internal energy $\langle E_{\text{int}} \rangle$ of the ethyl radical arising from the *in situ* photolysis of the precursor used in some of the experiments is also indicated. Red arrows illustrate the dissociation pathways following excitation into the $3s$ Rydberg state, while blue arrows show the dissociation pathways following excitation into the $3p$ Rydberg state.

state (pathway labelled 1a in Fig. 8), leading to slow unimolecular dissociation as reflected by the Boltzmann type distribution observed in the TED (see Figure 3). The other part of the population will directly dissociate into ethylene in its ground state (labelled 1b in Fig. 8), leading to fast dissociation as reflected by the shifted Gaussian contribution observed in the TED (see Figure 3). The favorable initial formation of the bridged C_{2v} geometry and the repulsive shape of the $3s$ Rydberg state as shown in Fig. 7 explain the site-specific dissociation into the $\text{H} + \text{CH}_2\text{CH}_2$ channel previously reported^{7,8}. The photodissociation into $\text{CH}_3\text{CH} + \text{H}$ is, in addition, energetically inaccessible, as seen in Fig. 8.

Besides the possible effect discussed in Section 3.1 of the different experimental techniques used, the discrepancies observed between previous experiments performed by the Zhang¹² and Fischer¹³ groups concerning, in particular, the branching ratio between both reaction channels could have been attributed to the initial energy characterizing the ethyl radical produced. Taking into account our calculations and proposed reaction pathways, the branching ratio between the two channels, slow and fast H-atom elimination, can only reflect the role of the conical intersection. The transfer of population at conical intersections has previously been shown to be somewhat selective regarding vibrational or rotational motion, especially those which involves a breakdown of symmetry. This has been previously reported and extensively discussed in photodissociation of *e.g.* alkyl halides

molecules, for instance, in Ref.²⁹.

The present experiments show, however, that for photodissociation of the ethyl radical in the $3s$ Rydberg state, the same results have been obtained employing pyrolysis, and thus vibrationally cold ethyl radicals, or *in situ* photolysis, *i.e.* ethyl radicals characterized by an initial internal energy of 0.64 eV. According to the results depicted in Fig. 3, the yield into the two channels cannot be directly related to the initial ro-vibrational excitation of the ethyl radical, but rather to the photon energy. A lower excitation energy would seem to enhance the probability to produce the fast H-atom channel at the conical intersection. A detailed study as a function of the excitation energy might be interesting in this sense. On the other hand, it is also interesting that the $\langle E_T \rangle$ and the FWHM characterizing the slow unimolecular channel in Fig. 3 are similar for the two methods used to produce the ethyl radicals (pyrolysis or photolysis). An intramolecular vibrational energy redistribution (IVR) of the added 0.64 eV of internal energy of ethyl from photolysis should have been reflected in the TED. However, the conical intersection mediating the $3s$ Rydberg state dissociation seems to have a major role in the distribution of the available energy.

The dynamics following photoexcitation into the $3p$ Rydberg state is, in contrast, very sensitive to the initial internal energy of the ethyl radical. A single Boltzmann-type contribution is observed in Fig. 5(a) following excitation of vibrationally cold ethyl

radicals at 201 nm, that can be attributed to internal conversion to lower states, in particular the $3s$ Rydberg state, and further slow unimolecular dissociation. On the other hand, two different dissociation channels are observed for ethyl radicals produced by *in situ* photolysis, *i.e.* the initial ro-vibrational internal energy gives access to a richer photodynamics. A prompt site-specific C_α H-atom elimination into $\text{CH}_3\text{CH} + \text{H}$ (labelled 2b in Fig. 8) is accessed through a fast non-adiabatic crossing to a valence bound state followed by dissociation via a conical intersection²². A particularly effective vibrational promoting mode plays a remarkable role in this photodissociation pathway²² characterized by a narrow peak in the measured TED.

In addition, as depicted in Fig. 8, several avoided crossings exist and are found in the adiabatic representation of the partially explored potential energy curves of the $3p$ Rydberg state and the two valence states, which also show avoided crossings with the $3s$ Rydberg state. These regions of avoided crossings, which are associated to rather strong couplings between the different electronic states and allow efficient population transfer between them, are accessible by means of the internal energy characterizing the ethyl radical. Since several avoided crossings exist, several routes of relaxation can occur and compete, which may lead to an effective randomization of the internal energy, as indicated by the arrow labelled 2a in Fig. 8. The initial population can thus relax and slowly dissociate, either through the $3s$ Rydberg state or through the formation of $\text{CH}_3\text{CH}(\tilde{A}^1A')$. The larger FWHM and higher energy position of the maximum of the Boltzmann-type component of the TED compared to that shown in Fig. 3(a) for photodissociation in the $3s$ Rydberg state, reflects the IVR. A more effective IVR is expected following pathway 2a, taking into account the initial internal energy of 1.27 eV.

The role of the bridged C_{2v} geometry in the complete H/D-atom scrambling reported in the literature⁷ is particularly interesting. The results in Fig. 6 demonstrate the favourable initial formation of this C_{2v} geometry also following excitation in the $3p$ Rydberg state. This state is, however, completely stable in C_{2v} and could only dissociate through internal conversion to lower states, being then a slow dissociation. The radical would therefore likely go back and forth between the C_{2v} and C_s symmetries, inducing a complete H/D-atom scrambling. The internal energy provided in our experiment to the radical permits nevertheless a favorable pathway for prompt site-selective dissociation.

6 Conclusions

The photodissociation dynamics of the ethyl radical following excitation into the $3s$ and $3p$ Rydberg states are revisited in a joint experimental and theoretical study. Two different methods to produce the ethyl radical, pyrolysis and *in situ* photolysis, are employed in order to modify the initial ro-vibrational energy distribution characterizing the ethyl radical beam. H-atom velocity map images have been recorded following excitation of the radical at 243 and 201 nm and employing a (2+1) REMPI scheme to detect H-atoms. The experimental results are presented and discussed along with *ab initio* potential energy curves, computed as a function of the θ Jacobi angle characterizing the change of geometry of the radical from C_s to a bridged C_{2v} geometry as well

as as a function of the R_{C-H} distance within the C_{2v} symmetry. The reported results show that the dynamics following excitation in the $3s$ Rydberg state are insensitive to the initial internal energy of the parent radical, in contrast to the dynamics on the $3p$ state, which are strongly modified. The role of the bridged C_{2v} geometry on both photodynamics has been highlighted and discussed. While the $3s$ Rydberg state undergoes direct dissociation mediated by a conical intersection, the $3p$ Rydberg state is completely stable in C_{2v} symmetry and can go back and forth between the C_{2v} and the C_s geometries, leading to an important H/D-atom scrambling.

Conflicts of interest

There are no conflicts to declare.

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