



Hydrogen migration in methanol studied under asymmetric fs laser irradiation



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ABSTRACT

Hydrogen migration processes in deuterated methanol (CH_3OD) under the irradiation of ultrashort (30 fs) two color (400/800 nm) laser field have been investigated by means of time-of-flight mass spectrometry. The utilization of an asymmetric $\omega/2\omega$ laser field contributes to a better understanding of hydrogen migration processes. Based on the comparative study of the asymmetry dependence and the angular distributions of the H_2D^+ , HOD^+ and H_2OD^+ fragment ions, whose formation requires hydrogen migration, it was feasible to distinguish the most probable site of the molecular skeleton where the hydrogen migrates from.

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1. Introduction

Hydrocarbon molecules under strong laser fields exhibit quick skeletal deformation/isomerization. The isomerization process has been reported to proceed very fast in the scale of tens of femtoseconds [1]. This skeletal deformation requires the fast migration of hydrogen atoms/protons over the molecule. Such hydrogen migrating processes have been reported on various molecules, i.e. methanol, ethanol, propanol, butadiene, acetylene, benzene etc. [1–8]. The hydrogen migration process has attracted a lot of interest, because the knowledge of the mechanism at play can be used in future years to control chemical bond breaking.

Methanol (CH_3OH) is one of the simplest molecules that exhibits hydrogen migrating channels. Signature fragments ejected after Coulomb explosion of multiply charged molecular ions, manifesting the existence of such pathways, are the H_3^+ , H_2O^+ and H_3O^+ ions. While the latter two ions are definitely products of hydrogen migrating process, the H_3^+ formation could also proceed through a channel where hydrogen migration is not required. Different techniques have been applied in order to clarify the migrating process from methanol like for example electron impact [9] or photodissociation [1–8]. The majority of the photodissociation studies were performed by using fs single color laser pulses. Therefore, the investigation of hydrogen migration processes was based mainly on the influence of laser parameters, i.e. the intensity, the pulse duration and the polarization of the laser beam. In the present work, the hydrogen migration processes in methanol are studied, for the first time, under the irradiation of a strong ultrashort

two color ($\omega/2\omega$) laser field [10–13]. A two color laser field exhibits an asymmetric profile that can be used for selective ionization of oriented molecules, with respect to the laser polarization axis. Since methanol can be thought as a ‘linear’ polyatomic molecule [14] its selective ionization studies are of interest *per se*. Moreover, the asymmetric irradiation offers an extra experimental parameter i.e. the phase φ between the two colors which probably could be utilized in order to shed more light in the hydrogen migration process. Thus, we would like to explore if this technique allows us to draw some conclusions for the so far unanswered question about the specific position in the molecular skeleton of the hydrogen atoms that migrate resulting in the formation of the above mentioned fragment ions. Moreover, the angular distribution of the ions ejected under asymmetric laser irradiation is expected to offer the ability for an estimation of the lifetime of transient species (precursors) involved.

The present study is focused on the directional ejection of fragment ions of the doubly charged methanol molecule. In order to identify fragments resulting from the hydrogen migration, it is necessary to tag the hydrogen atoms that originate from the carbon site of the molecule and those that originate from the oxygen one. The simplest way to achieve this is to study the deuterium substituted methanol, in which the hydrogen in the hydroxyl group has been substituted by deuterium atom (CH_3OD). Thus, albeit CH_3OH has also been studied, the data presented in this work are those recorded for the CH_3OD molecule.

2. Experimental setup

The experimental setup has been described elsewhere [15] and only a brief description will be given here. We have studied

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methanol under two color $\omega/2\omega$ laser field by means of time-of-flight (TOF) mass spectrometry. The $\omega/2\omega$ laser field can be mathematically described by the equation:

$$\vec{E}(t) = \vec{E}_0(t)[\cos(\omega t) + \gamma \cos(2\omega t + \varphi)],$$

where $\vec{E}_0(t)$ is the pulse envelope, γ the relative electric field strengths and φ the phase difference between the two-colors. Experimentally, the asymmetric laser field is utilized by mixing the 800 nm fundamental laser frequency of a Ti:Sapphire laser system (30 fs duration, 5 mJ/pulse, 1 kHz repetition rate) with its second harmonic (at 400 nm) produced in a 200 μm thick BBO crystal. After the BBO crystal both the ω and 2ω laser fields are linearly polarized with perpendicular polarization. Therefore, a dual waveplate (λ at 800 nm and $\lambda/2$ at 400 nm) is introduced into their common path to ensure that they are both polarized parallel to the TOF mass spectrometer axis.

Although the two color pulses are spatially overlapped they arrive in the interaction region with a temporal lag due to the difference in their group velocities. This time difference can be compensated by inserting two calcite crystals properly oriented in their common path. The first calcite crystal makes coarse adjustments to the time delay while the second fine tunes the temporal overlap, providing at the same time a control for the phase φ of the $\omega/2\omega$ field. Additionally, a dual waveplate ($\lambda/2$ at 800 nm and 400 nm) was also employed so as to adjust the angle between the linear polarized $\omega/2\omega$ field and the time-of-flight axis. Both of the 800 and 400 nm laser fields are focused by a spherical mirror of 20 cm focal length in the interaction region of a home-made TOF mass spectrometer. We controlled the total intensity of the $\omega/2\omega$ field by adjusting the diameter of an iris that was placed just before the entrance window of the time of flight. The maximum intensity achieved in the interaction region was $I_\omega \approx 2.8 \times 10^{15} \text{ W/cm}^2$ and $I_{2\omega} \approx 1.5 \times 10^{15} \text{ W/cm}^2$ (the pulse duration of the 2ω beam is estimated to be ~ 40 fs in the interaction region). However, the majority of the experimental data were recorded at $I_\omega \approx 4.4 \times 10^{14} \text{ W/cm}^2$ and $I_{2\omega} \approx 1.6 \times 10^{14} \text{ W/cm}^2$ which corresponds to an electric field strength ratio of $\gamma \sim 0.6$, unless otherwise stated. The methanol molecules are introduced into the time of flight interaction chamber effusively. The ion fragments were extracted by a weak electric field (144.4 V/cm) to ensure higher kinetic energy resolution. The ionic signal resulting from the interaction of the asymmetric $\omega/2\omega$ field with the CH_3OD molecules was detected by a chevron type micro-channel detector and recorded by an Ultrafast Multiscaler card (FASTComTec, Model TOF P7888) which has a 1 ns time resolution. The $\omega/2\omega$ laser field reaches its maximum asymmetry twice in a 2π period, when the relative phase between the two colors is $\varphi = 0$ or $\varphi = \pi$, and with a reverse direction. We define the relative phase difference as $\varphi = 0$ when the electric field point towards the detector and $\varphi = \pi$ when the electric field maxima point away from the detector. We were able to calibrate the phase of the $\omega/2\omega$ laser field, by making additional measurements on CO and comparing them with published data [16,17].

3. Results and discussion

A typical time of flight mass spectrum of methanol under the $\omega/2\omega$ laser field irradiation is depicted in Figure 1(a). All the mass spectra features that correspond to fragment ions ejected from multiply charged precursors exhibit the characteristic complex peak profile consisting of at least two components. The forward peak components (those that are recorded at earlier arrival times) correspond to ions that are released towards the detector, while those that arrive at later times (backward peaks) are initially ejected away from the detector before being reversed by the extracting field. The time spacing between the forward and

backward peak components can be utilized in order to estimate the kinetic energy of each fragment.

In a symmetric single color field the forward and backward peaks of a specific fragment are expected to be equal, in the ideal situation where the detection efficiency is not reduced for the backward ejected ions. In the context of the MO-ADK molecular ionization model it is well established that molecules which interact more effectively with a linearly polarized ultrashort laser field are those that have their electron cloud already oriented towards the field. In other words, the ionization rate is angular depended [18]. A symmetric laser field that interacts with molecules exhibiting an asymmetric HOMO, cannot 'distinguish' between those molecules that point toward the detector or away from it, and that is the reason for the almost equal forward and backward peaks in a time of flight spectrum. However, this is no longer valid for a laser field with an asymmetric profile, like that employed in the present work. An asymmetric field can 'distinguish' between these orientations and the forward/backward peak components of the mass spectra will exhibit dependence over the asymmetric profile (selective ionization of oriented molecules). This selectivity can be utilized to map, in first approximation, the HOMO of asymmetric molecules [19], although directional asymmetries have also been recorded for molecules with a symmetric HOMO, e.g. H_2 and N_2 [13,20–22], under asymmetric laser field irradiation. The recorded asymmetries in this case, were ascribed to coupled electron-nuclear dynamics, i.e. the oscillating asymmetric laser field drives the electrons of the dissociative molecule back and forth and as the internuclear distance increases the inner barrier rises resulting in electron localization. This results in a preferential ejection of the fragments. Recently, Miura et al. performed experiments on acetylene (C_2D_2) under the irradiation of an intense few-cycle-pulse. The recorded asymmetry on the directional emission of the D^+ fragments was attributed to the laser-assisted C–D bond weakening [23].

A well-established parameter used to visualize the dependence over the asymmetric laser profile, is the beta parameter that is defined as:

$$\beta = \frac{Y_f - Y_b}{Y_f + Y_b}$$

where Y_f , Y_b stands for the yield of forward and backward integrated signal respectively [13]. Since the asymmetry profile of the laser field is adjusted by the relative phase φ , β will be a function of φ .

All fragments exhibit dependence over the phase φ , but as stated above, this work is focused on the hydrogen migration processes and therefore, the following discussion is limited to fragments released from the doubly charged parent ion. The identification of the different fragmentation channels is based on momentum conservation principle arguments and their dependence on the phase φ of the laser field.

In Figure 1(b)–(f), the parts of the mass spectra regions that corresponds to the fragment ions of interest are shown expanded. All fragments exhibit a triplet pattern mass spectrum, i.e. a central peak corresponding to fragments with small or zero kinetic energy, and two side peaks on both sides of the central peak. The central peaks are ascribed to fragments produced by the singly charged methanol. For OD^+ ion ($m/z = 18$) the central peak exhibits strong contribution from background water vapor. As far as the discrimination of H_3^+ and the HD^+ ions is concerned (both ions corresponds to the same $m/z = 3$) this is based on their different kinetic energy and on the close resemblance observed for the beta plots and the angular distributions of the CH_3OD fragment ion at $m/z = 3$ and the H_3^+ ionic fragment of CH_3OH recorded at similar laser irradiation conditions (data not presented here). Similarly, the mass spectra feature corresponding to $m/z = 4$ can be safely attributed to

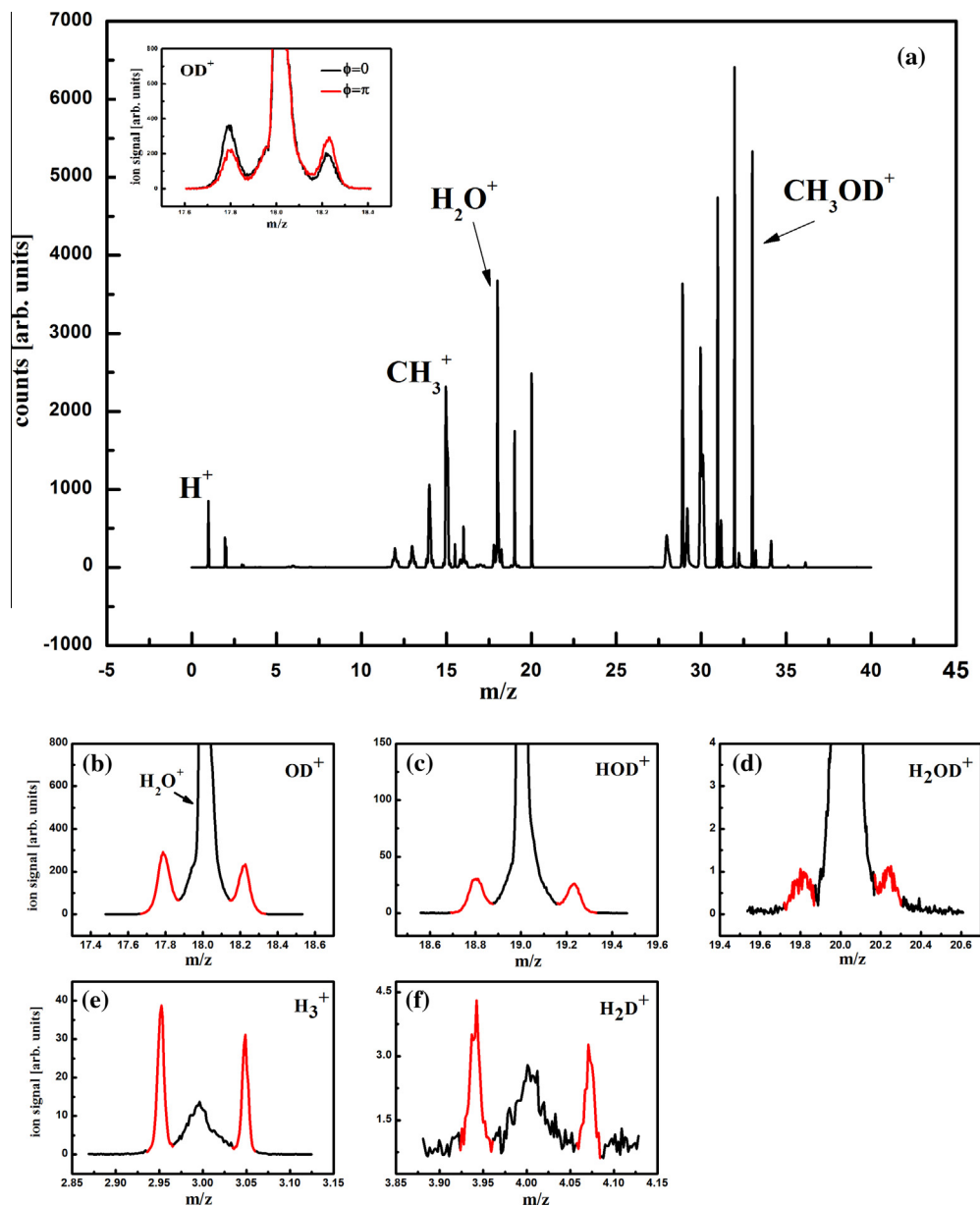


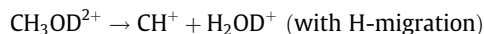
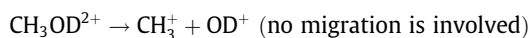
Figure 1. (a) A typical TOF mass spectrum of methanol under irradiation of a two color $\omega/2\omega$ laser field. In the insert the dependence on φ of the OD^+ is depicted. (b)–(f) The TOF spectrum in the region of the OD^+ , HOD^+ , H_2OD^+ , H_3^+ and H_2D^+ fragments is presented while the integration areas are indicated by red color. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

H_2D^+ at laser intensities up to $6 \times 10^{14} \text{ W/cm}^2$, which are lower than the threshold intensity for C^{3+} fragment ion.

For methodological reasons the following discussion related to $[\text{CH}_3\text{OD}^{2+}]$ fragmentation is presented in two separate sections. The first one concerns dissociation channels involving the break-up of a carbon–oxygen bond, while the second section refers to carbon–hydrogen bond break up and the formation of molecular hydrogen ions.

- *Fragments released following the carbon–oxygen bond breaking*

The possible two- body dissociation channels for the doubly charged parent ion are:



In Figure 2(a)–(c) the beta parameter plots of OD^+ , HOD^+ and H_2OD^+ respectively are depicted. Obviously, all three fragments exhibit a dependence on φ . The OD^+ fragment exhibits a strong dependence on φ reflecting the selective ionization of oriented molecules with the laser polarization axis i.e. the doubly charged precursor ions are produced more efficiently when the asymmetric laser field points along the carbon–oxygen direction. Moreover, it is evident that the two other fragments HOD^+ and H_2OD^+ , where a migrating process of one or two hydrogens is involved, exhibit φ dependence also, even though the latter seems to weaken as extra hydrogen migrates. In other words the migrating channels still hold the selectivity that has been imprinted in the ionization process [24]. This is conceivable only if the H-migration as well as the dissociation is fast enough, with respect to the rotational period of the parent molecule. Otherwise, it is expected that the

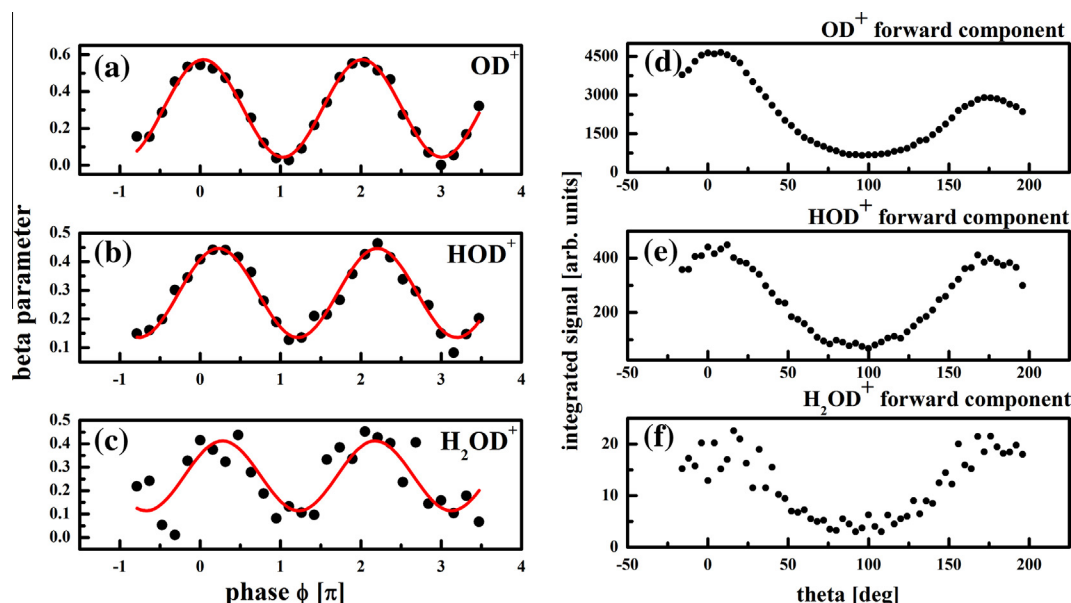


Figure 2. (a)–(c) Beta parameter asymmetry plots of the fragments OD^+ , HOD^+ , H_2OD^+ respectively. The experimental data are denoted by black circles, while the solid red line is a sinusoidal fitting. (d)–(f) The angular distributions of the forward peak components of the fragments OD^+ , HOD^+ and H_2OD^+ respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

angular distribution of fragment ions (Figure 2(d)–(e)) should be closer to an isotropic one.

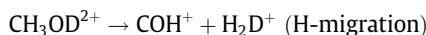
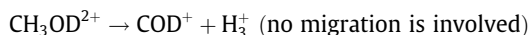
Although the fragments present a sinusoidal dependence on ϕ with the same frequency, those requiring H-migration are slightly out of phase with respect to that of OD^+ ion, reaching their maximum value in the beta parameter plots at $\phi = 0.7$ rad ($\sim 40^\circ$).

These phase shifts are not easily explainable. Recently, phase shifts have been reported [25] in experiments where phase-tagged few-cycle-pulses were used, and they have been attributed to the phase dependence of the subsequent double ionization process involved (rescattering). The reported phase shifts were impressive (about 125°), although theoretically it was expected to be even larger (more than 165°). Obviously, in our case the phase shifts are much smaller (by a factor of three) and the observed shifts cannot be attributed to rescattering ionization. Recently, Miura et al. [23] have shown that for the asymmetric dissociation channel of C_2D_2 ($\text{C}_2\text{D}_2^{2+} \rightarrow \text{C}_2\text{D}^+ + \text{D}^+$) the fragmentation to D^+ depends on the phase of the laser field i.e. under certain experimental conditions, molecular fragmentation exhibits dependence on phase.

As stated above, in the present experiments the fragmentation is taking place within selectively ionized oriented molecules and since the ionization rate is phase dependent, reaching its maximum value when the electric field is more asymmetric (at $\phi = 0$ and $\phi = \pi$), it is reasonable to assume that when the dissociation is fast (Coulomb explosion), the released fragments will reveal a concert dependence on phase. However, when additional steps are involved in the fragment formation, it is not straight forward that the phase ϕ dependence will remain unaffected. Thus, it is plausible that the recorded phase shifts of the fragments originate from the superposition of the ϕ dependence of the ionization and the dissociation processes involved. This implies that the HOD^+ and H_2OD^+ phase shifts can be attributed to the fact that, beyond the initial ionization, molecular dissociation could be affected by the shape of the laser field too.

- *Fragments released without carbon–oxygen bond breaking*

This category includes the following dissociation channels:



In Figure 3 the beta parameter plots and angular distributions of the associated fragments are depicted. For reasons of comparison, in the same figure, the associated plots of CH_3^+ fragment ion are given (Figure 3(a) and (d)). The H_3^+ fragment (Figure 3(b)) exhibits strong ϕ dependence while its angular distribution undoubtedly has an anisotropic component with its maximum lying in the direction of the laser field. Note that its maximum value is achieved for $\phi = \pi$. Once again, the anisotropic component of the angular distribution can be thought of as a signature of a dissociation process which is faster than the rotational period. The maximum of the H_3^+ and H_2D^+ ions in the ϕ dependence plot is found to be shifted with respect to that of CH_3^+ (Figure 3(a)–(c)). It is reasonable to assume that the interpretation presented above for the case of HOD^+ and H_2OD^+ ions could be valid for this case too.

Recently, Nakai et al. have investigated by first-principle molecular dynamics simulation the formation of the trihydrogen ion from CD_3OH methanol [26]. Specifically, they assumed an ensemble of methanol molecules in room temperature, prepared in the $\text{CD}_3\text{OH}^{2+}$ ground state by instantaneous ionization. Starting from these initial conditions, they studied the time evolution of the ensemble, and particularly the nuclear dynamics that lead to the formation of D_3^+ and HD_2^+ . They concluded that the release of trihydrogen ion from methanol (with or without hydrogen migration) requires, as an intermediate step, the formation of neutral molecular deuterium (D_2) that remains enough time close to the parent molecule due to van der Waals forces. In a second step, the trideuteron ion can be formed after a proton removal from the carbon site (no migrating pathway) or from the oxygen site of the molecule (migrating pathway). Furthermore, Thapa and Schlegel [27] have performed extensive calculations on methanol's dissociation and they have found that H_2 can be formed from the singlet state of molecular dication ($\text{CH}_3\text{OH}^{2+} \rightarrow \text{HCOH}^{2+} + \text{H}_2$), while the crossing to a lower energy surface (-26 kcal/mol) leads to H_2^+ creation. Moreover, they found that a more exothermic (-79 kcal/mol) process leading to H_2^+ can take place in the triplet state of the dication via a stepwise pathway where the initial dissociation to H^+ is followed by H abstraction.

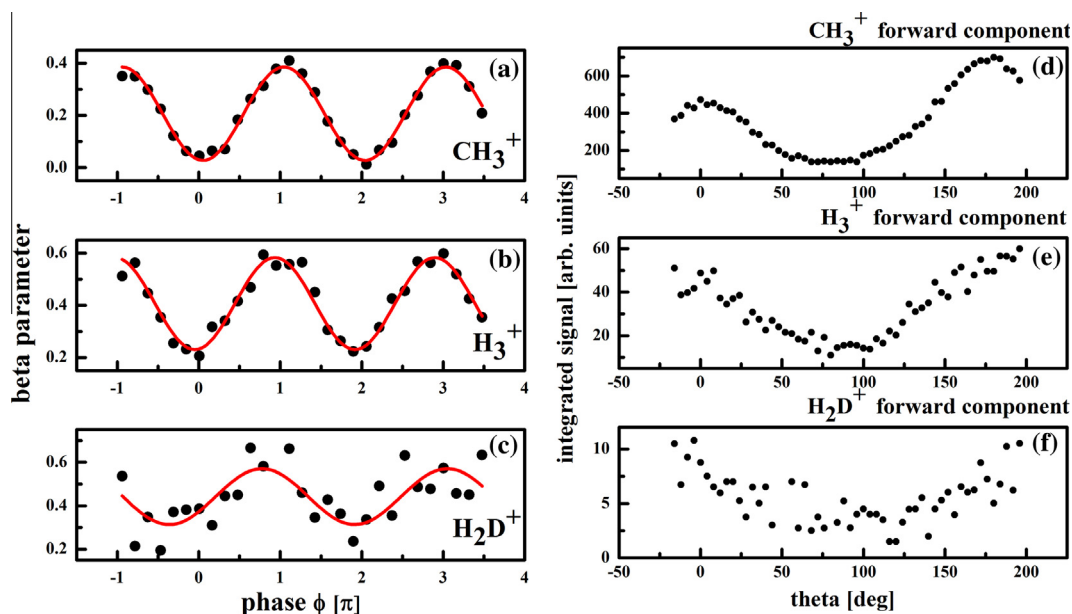


Figure 3. (a)–(c) Beta parameter asymmetry plots of the fragments CH_3^+ , H_3^+ , H_2D^+ respectively. The experimental data are denoted by black circles, while the solid red line is a sinusoidal fitting. (d)–(f) The angular distributions of the forward time-of-flight components of the fragments CH_3^+ , H_3^+ , H_2D^+ respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In the present work a different isotopomer of methanol is studied. However, the electronic structure of the isotopomers is identical, and no significant differences should be expected in the ionization process [28].

The lifetime of the precursor state of the doubly charged methanol, resulting in H_3^+ and H_2D^+ , has been estimated to be comparable to the rotational period of the parent molecule [2,29,30]. This slow dissociation procedure results in fragments with broader angular distributions compared to those involving C–O bond break-up. However, from the present work it is evident that H_3^+ and H_2D^+ ions exhibit a strong anisotropic component in their angular distributions which is understandable only if the dissociation process is completed in a time interval smaller than the rotational period of the parent molecule.

The interpretation of the observed dependence on φ parameter for the H_3^+ ions (maximum at $\varphi \sim \pi$, Figure 3(b)) is easily conceivable i.e. the H_2 formation is followed by a proton removal from the C-site of the molecule resulting in the H_3^+ production, which is sequentially ejected in the direction of the carbon site of the oriented molecule. This implies that H_3^+ and the CH_3^+ are expected to present a maximum at similar φ phase values of the asymmetric field which is in agreement with our results.

As far as the H_2D^+ is concerned, there is a question about its formation. The above mentioned theoretical work assumes that the created molecular hydrogen has the ability to migrate also to the oxygen site of the molecule where, after the deuterium abstraction, the H_2D^+ can be produced. Alternatively, the H_2D^+ could be formed simply after a D-migration to the carbon site of the molecule where it could interact with the already formed H_2 .

The recorded dependence on φ of the H_2D^+ ions is found to be in phase with H_3^+ , thus our experimental data support that this ion is preferentially ejected from the carbon site rather than the oxygen one, which implies that D-migration is the most probable mechanism involved in the H_2D^+ creation.

Nevertheless, the ability for the H_2 ‘roaming’ towards the other side of the C–O bond cannot be excluded. Therefore, the creation of the H_2D^+ ions via the two above mentioned processes involving migration of a molecular (H_2) or an atomic (D) hydrogen migration at opposite directions may be both at play. However, our

experimental results support that the probability for these routes to occur is not the same. We conclude that it is more probable for the deuterium atom to migrate towards the CH_3 -moiety of methanol otherwise no φ dependence could be recorded.

4. Conclusions

The selective ionization of oriented methanol (CH_3OH and CH_3OD) in gas phase has been achieved by utilizing an asymmetric 30 fs two color laser field. The fragmentation of the doubly charged parent molecular ion as a function of the phase φ of the $\omega/2\omega$ laser field reveals that all fragments exhibit directionality that can be altered by the phase, which manifests the selective ionization of oriented molecules. This work focuses on the hydrogen migration processes and since its investigation is facilitated in the CH_3OD case, the data presented here are restricted to this molecule.

It is found that oxygen containing fragments present a maximum in their beta parameter asymmetry plots at $\varphi = 0$, while CH_x^+ ($x = 1-3$) at $\varphi = \pi$. Thus, this kind of plots can be used for the elucidation of the most probable direction the fragments are ejected to i.e. to discriminate if the fragments are ejected from the C- or the O-site of the molecule. In agreement with this statement, the H_3^+ ions present a maximum at $\varphi \sim \pi$ since, for the CH_3OD case, no H-migration is needed for H_3^+ formation which implies that the ion is produced at the carbon site of the molecule.

On the other hand, for the H_2D^+ ion formation it is concluded that the most probable pathway is that involving D-migration since it reveals almost the same dependence on φ as that of CH_x^+ and H_3^+ ions. Obviously, the other probable pathway where a roaming of a H_2 molecule is assumed from the carbon to the oxygen site of the molecule, cannot be excluded. Nevertheless, the recorded data imply that among these two possible routes, the most probable is the D-migration one, otherwise no φ dependence should be observed.

Finally, from the anisotropic component of the angular distributions of the H_3^+ and H_2D^+ ions it is concluded that the procedure leading to these ions creation is faster than the rotational period of the molecule.

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