

Phase dependence of OD^+ , HOD^+ , and H_3^+ ions released from the deuterated dication of methanol under $\omega/2\omega$ laser field irradiation



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ABSTRACT

Multielectron dissociative ionization of gas phase deuterated methanol (CH_3OD) molecules under the irradiation of a 30 fs asymmetric two color ($\omega/2\omega$) laser field is studied by means of time-of-flight mass spectrometry. The dependence on phase φ between the two laser beams of OD^+ , HOD^+ , H_3^+ fragment ions released from the dissociation of the dication has been investigated. Based on the phase dependence and the recorded angular distributions, it is proposed that the OD^+ , HOD^+ ions can be ejected from fast and slow dissociation processes. The fast dissociation process is attributed to fragmentation from singlet states. The possibility that the slow dissociation process involves a long-lived metastable state and/or dissociation from triplet states is also discussed. The dependence of the H_3^+ ion on phase φ reveals the existence of two different, as far as the time scale is concerned, stages in its production.

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1. Introduction

In the past few decades, the dynamics of molecules under the irradiation of an intense laser field have been a subject of extensive study, both theoretically and experimentally. Recently, laser fields with asymmetric profiles are utilized, in order to shed more light into the ionization/dissociation processes. Various techniques have been proposed and applied experimentally. The most common among them are those employing phased tagged few-cycle-laser-pulses [1–4]. Few-cycle-pulses exhibit an intrinsic asymmetry related to the phase φ of the pulse envelope. Another phase control technique is the two-color scheme, first introduced by Brumer and Shapiro [5–7]. When the two colors is the combination of even and odd harmonics ($\omega/2\omega$ scheme), the resultant superimposed electric field, exhibits directionality that can be altered simply by adjusting the relative phase φ between the two colors [8–13]. Pronounced asymmetries have been recorded in the ejection direction of the fragments that can be controlled by adjusting the phase φ . Both methods have led to important conclusions about the orientation dependent ionization rate of small molecules [13–15], the preferential direction of the produced fragments/electrons [16–19], and the coupled electron-nuclear dynamics [20,22]. Our group has demonstrated the ability of an asymmetric laser field to distinguish between different routes that result on fragments with the

same features (kinetic energy, mass/charge) based on their different dependence on the shape of laser field, i.e. the phase φ . Specifically using nitrous oxide as a molecular target under two-color irradiation it was shown that all the recorded fragments present a dependence over φ which can be interpreted in the context of selective ionization/dissociation of oriented molecules [16]. However, fragments that result from a specific dissociation procedure of the doubly charged parent molecule exhibit a peculiar dependence on the phase which corresponds to a superposition of two sinusoidal functions having a frequency ratio of two. The experimental findings were attributed to the contribution of fast and slow dissociation procedures that result to the same species. The fast dissociation process follows the electric field's direction while the slow one the intensity maxima [23].

Furthermore, more recently, we have studied the H-migration in the methanol case. By utilizing an $\omega/2\omega$ asymmetric laser field we were able to distinguish the most probable site of the molecular skeleton where the H-migrates from [24].

In this work, partially deuterated methanol molecules (CH_3OD) have been studied under the irradiation of a two-color laser field. As in the case of nitrous oxide molecules, fragments with the characteristic two frequency component have been observed. For the CH_3OD case, however, more than one fragments, exhibit this peculiar behavior, namely H_3^+ , OD^+ and HOD^+ ions which are released from the dication. A recent theoretical study on methanol molecule concludes that fragments of the dication may originate either from a singlet or a triplet state [25]. From the presented simulations of the molecular structure in the triplet and singlet dication ground

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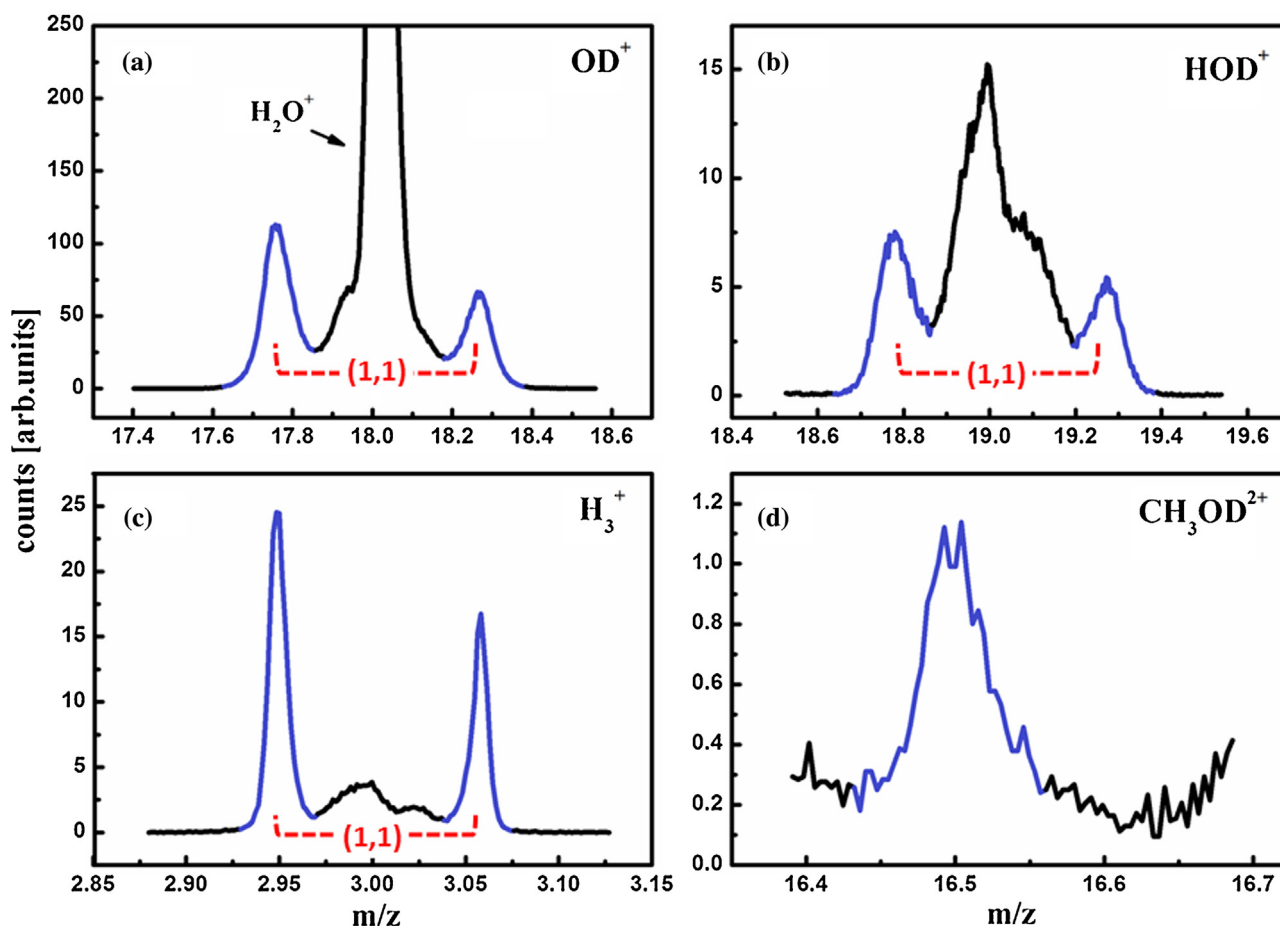


Fig. 1. Time-of-flight mass spectra peak profiles of (a) OD^+ , (b) HOD^+ , (c) H_3^+ fragments and (d) $\text{CH}_3\text{OD}^{2+}$ of CH_3OD under the irradiation of $\omega/2\omega$ laser field. The red-dotted lines point fragments that resulted from the dissociation of the doubly charged parent molecule $\text{CH}_3\text{OD}^{2+}$ with non-zero kinetic energy. The blue lines in each graph indicate the integration region.

states is expected that the OD^+ fragments should be ejected with almost the same kinetic energies implying that these fragments cannot be clearly distinguished as individual peaks in a time-of-flight spectrum. The same is valid for the HOD^+ ions too. Based on our previous work, in this paper we attempt to explore if the $\omega/2\omega$ technique can be used in order to distinguish between fragments originating from different precursor states. Moreover, in the same context, the angular distribution of H_3^+ will be examined in order to clarify if the reported ‘almost isotropic’ shape [26,27] is the result of the contribution of a ‘slow’ and a ‘fast’ dissociation channel.

2. Experimental setup

The experimental setup has been described elsewhere and only a brief description will be given here [21]. Methanol molecules (CH_3OD) have been studied under the irradiation of a two color $\omega/2\omega$ laser field by means of time-of-flight (ToF) mass spectrometry. The two color laser field is produced by the combination of the fundamental laser frequency of a Ti:Sapphire laser system, centered at 800 nm (30 fs duration, 5 mJ/pulse, 1 kHz repetition rate) and its second harmonic produced by a 200 μm thick BBO crystal. Both beams are co-propagating but are not temporally overlapped. Two calcite crystals of thickness 2.4 mm and 1.6 mm properly orientated are inserted into their common path to achieve time overlap and control over the phase φ , respectively. A dual waveplate (λ at 800 nm and $\lambda/2$ at 400 nm) ensures that the beams have the same polarization. Just before the entrance in the ToF interaction region, another waveplate ($\lambda/2$ at 800 and 400 nm) is introduced

for recording the angular distributions, along with an iris for intensity adjustments. Both beams are focused by a spherical mirror of 20 cm focal length. The data presented in this paper are recorded for intensities $I_\omega = 4.4 \times 10^{14} \text{ W/cm}^2$ and $I_{2\omega} = 1.6 \times 10^{14} \text{ W/cm}^2$ unless otherwise stated. The methanol molecules are introduced into the ToF interaction chamber effusively. The ion fragments resulting from the interaction of the asymmetric $\omega/2\omega$ field with the CH_3OD molecules are extracted by a weak electric field (144.4 V/cm), while the ionic signal is 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 phase φ of the $\omega/2\omega$ laser field was calibrated by making additional measurements on carbon monoxide (CO) and by comparing them with published data [13]. We define the relative phase difference as $\varphi = 0$ ($\varphi = \pi$) when the electric field’s maxima point towards (away from) the detector.

3. Results and discussion

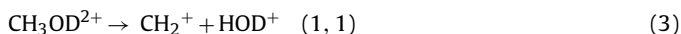
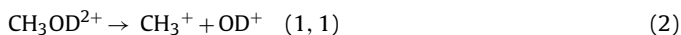
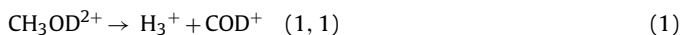
In Fig. 1 the ToF spectra of some photofragments produced by the dissociative ionization of methanol molecules (CH_3OD) under the irradiation of $\omega/2\omega$ laser field (Fig. 1(a)–(c)) is depicted. The fragment ions exhibit a complex peak profile in the ToF spectrum made up by three components at least. The central components arise from fragments released with small or zero kinetic energy, while the peak components at both sides consist of ions with the same m/z ratio produced with significant kinetic energy. Those initially ejected towards the detector result in the forward peak

component recorded at shorter time of flight, while the ions ejected to the opposite direction give rise to the other backward component arriving later at the detector after their trajectory is reversed by the extracting field. The time spacing between the forward and backward component enables the estimation for the kinetic energy of the specific fragment. Moreover, the single peak presented in Fig. 1(d), recorded at $m/z = 16.5$, is assigned to the $\text{CH}_3\text{OD}^{2+}$ dication. It should be noted that in the case of CH_3OH (data not presented here) it is difficult to distinguish the dication because it overlaps with the strong O^+ ion signal.

Based on the momentum conservation principle, we were able to assign fragments that originate from the same charged state.

This study is focused on fragments that result from the doubly charged methanol via “two-body fragmentation”. This type of channels are commonly described in the literature by the notation (n,p) , where the integers n,p stand for the charge multiplicity of each fragment.

The photodissociation processes of interest are:



In Fig. 1 the expanded views of the fragments of interest are given.

An ultrashort laser field interacts more strongly with those molecules that have their electron cloud already orientated towards the field direction [28]. Due to its asymmetric profile, the $\omega/2\omega$ laser field, employed in this work, can also distinguish between the “head-to-tail” order of the molecular ensemble, i.e. the molecules that interact more strongly with an asymmetric field are those with the maxima of the electron cloud distribution in a direction opposite to the field’s (selective ionization of oriented molecules) [16,17]. Consequently, the forward/backward components of all fragments exhibit dependence over the $\omega/2\omega$ electric field profile, best described by the phase φ between the ω and 2ω colors.

In order to visualize the dependence over the phase φ , the integrated signal of each component is obtained and the contrast (beta parameter, β) between forward and backward components is introduced:

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

where Y_f and Y_b stands for the yield of forward and backward integrated signal, respectively. The beta parameter, in most cases, is fitted with a sinusoidal which oscillates with the same frequency as the direction of the asymmetric laser field. Various conclusions can be drawn by a beta parameter plot, e.g. the site of the molecule from which each fragment is preferentially ejected [24]. More specifically, fragments that reached their maximum value at $\varphi=0$ are released towards the detector, whilst their partner fragments, as appeared in Eqs. (1)–(3), reached maximum value at $\varphi=\pi$. In Fig. 2 the beta parameter plots of H_3^+ , OD^+ and HOD^+ , are summarized. Obviously, the beta parameter plots of these fragments are slightly out of phase with each other, meaning that the additional excitation steps leading to the fragmentation channels (1)–(3), exhibit different dependence over the phase φ [29,30]. In the same graph the beta parameter plots of CH_3^+ , CH_2^+ , partner ions of the OD^+ , HOD^+ ions respectively, are given. As it can be seen, the beta parameter plots of $\text{OD}^+-\text{CH}_3^+$ and $\text{HOD}^+-\text{CH}_2^+$, are out of phase with each other. Such a behavior is a signature of the selective ionization of oriented molecules. The beta parameter plot of the COD^+ fragment, partner of the H_3^+ ion, is not presented. Due to its large mass in comparison with the H_3^+ ion, this fragment acquires a small amount of the total released kinetic energy. As a result, a broad peak appears in

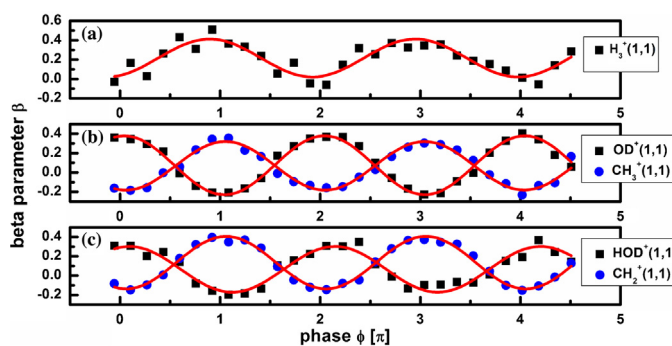


Fig. 2. Beta parameter plots of (a) H_3^+ , (b) OD^+ , CH_3^+ and (c) HOD^+ , CH_2^+ from CH_3OD methanol recorded for intensities $I_{\omega} = 3.8 \times 10^{14} \text{ W/cm}^2$ and $I_{2\omega} = 2.0 \times 10^{14} \text{ W/cm}^2$. The experimental data are denoted by black squares and blue circles, while the red line is a sinusoidal fitting. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the mass spectrum with no clear forward/backward components, making it difficult to derive a beta parameter plot.

While the beta parameter describes well the dependence over φ , it can also hide information which is apparent in the integrated signal. Indeed, by inspecting the integrated signal of the H_3^+ , OD^+ , HOD^+ fragments (Fig. 3), a smaller sinusoidal contribution corresponding to a double frequency 2ω is observed more or less clearly in all three fragments. Typically, dependence on 2ω is expected for the integrated signal of the dication which follows the maxima of the electric field [14] and this is experimentally confirmed as depicted in Fig. 3(g). The existence of both frequencies have been verified by Fourier-transforming the integrated signal of each fragment and the contribution of the double frequency component, 2ω , is found to be largest for the H_3^+ ion followed by the HOD^+ and OD^+ .

Such a pattern is not common in experiments employing asymmetric laser fields. A similar pattern has been recorded by our group, for nitrous oxide molecule (N_2O) under the irradiation of the $\omega/2\omega$ laser field. In that case, NO^+ and N^+ fragments, resulting through the photodissociation process of the doubly charged molecule ($\text{N}_2\text{O}^{2+} \rightarrow \text{NO}^+ + \text{N}^+$), exhibit the same peculiar 2ω dependence over the phase φ [23]. However, in the N_2O case no other fragments exhibit similar behavior contrary to the methanol molecule where at least three fragments present such dependence.

Following the interpretation given for the N_2O molecule, the existence of two routes, a fast and a slow one, resulting in the same species may be apparent.

It is well known that during the interaction of strong laser pulses with molecules the potential energy surfaces (PES) are modified (dressed states). The elongation of the molecular bonds in dressed states could lead to fast dissociation, especially for one of the three equivalent C–H bonds, a procedure that is called field assisted dissociation (FAD) [31]. A rough estimation based on the data available in the literature (Fig. 4 in Ref. 31) leads to the conclusion that, for the pulse duration and the laser intensity used in the present work, no other bond dissociation is expected from the dressed states. Of course, all the molecular bonds are elongated which facilitates the photon absorption leading in enhanced multiple ionization rate. After the end of the laser pulse, intramolecular processes are taking place within the zero field PES. The excess electronic energy absorbed is transformed to nuclear energy (vibrational/rotational) within an interval of few fs (for vibronic relaxation) resulting in multiply charged ‘hot ions’ that easily fragment to lighter ones.

The time difference between the ion released via FAD and from internal (vibronic) relaxation is expected to be in the order of tens of fs (i.e. very small compared to the rotational molecular period) and therefore their discrimination cannot be based on the angular distribution measurements. Another probable route for the

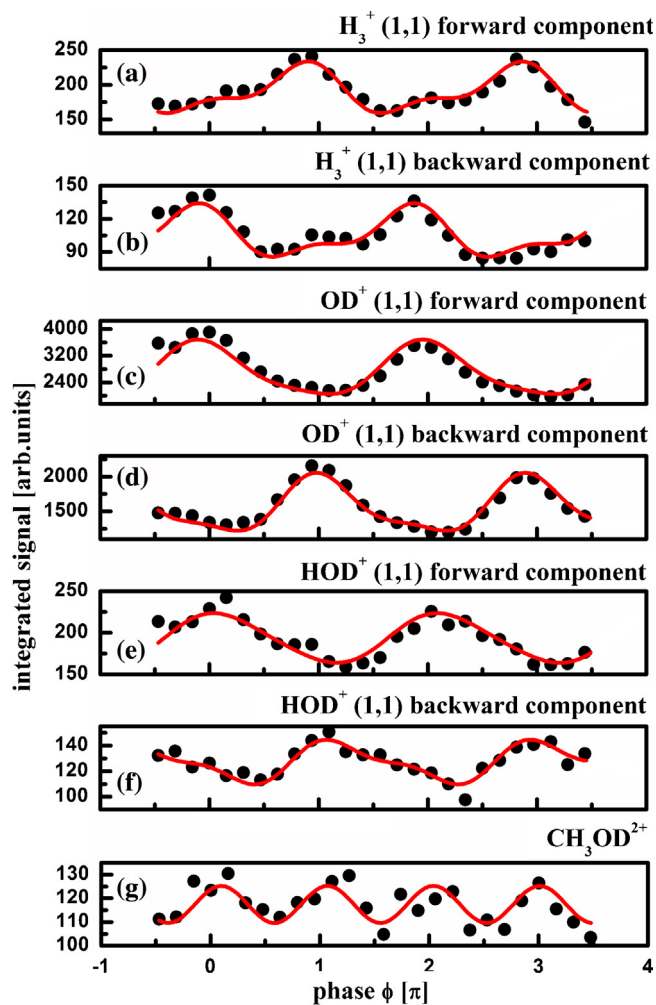


Fig. 3. (a)–(f) The integrated signal of H_3^+ , OD^+ , and HOD^+ ions from CH_3OD methanol (forward and backward component) as a function of the phase φ . The fitting function (red line) is the sum of two sinusoidal with frequency ratio two. (g) The integrated signal of the dication $\text{CH}_3\text{OD}^{2+}$. The red line is a sinusoidal fitting. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

molecular relaxation is that via intersystem crossing leading to triplet molecular states. The latter non-radiative processes are typically slower than the rotational molecular period. The existence of a long-lived metastable state is also a possibility that cannot be excluded. The released fragment ions from triplet or metastable states are expected to have an isotropic angular distribution.

In the following sections the above mentioned methanol fragments are discussed separately.

• OD^+ and HOD^+ fragments

Recently, Thapa et al. [25] have studied theoretically the dynamics of the photo-ionization and dissociation of the methanol molecular ions formed in the presence of a strong laser field. Although the calculations were focused mainly on methanol monocation, results are also addressed for neutral and doubly charged species. According to their calculations the dissociation can proceed either on singlet or triplet state of the dication and for both states the fragmentation dynamics along with the relative enthalpies were summarized. Various channels with typical fragments as H^+ , H_2^+ , OH^+ and HOH^+ , originating from the triplet or the singlet state of the doubly charged methanol, are discussed.

Although we have studied a deuterated derivative of methanol, we may attempt to compare our experimental values with those

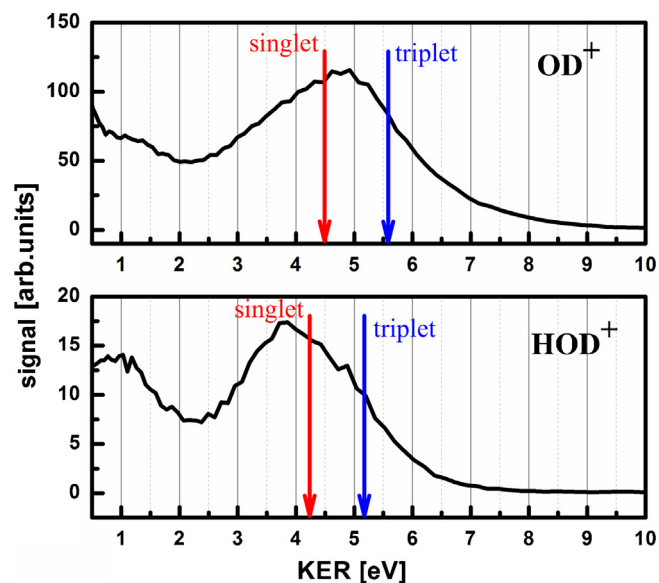


Fig. 4. Kinetic energy mass spectra of (a) OD^+ and (b) HOD^+ fragment ions. The red/blue arrows point the kinetic energy release calculated in [25] for the singlet/triplet states respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

reported theoretically, because both methanol and its deuterated derivative exhibit similar electronic structure and, therefore no significant differences should be expected in the ionization process. As reported by Thapa et al. for both OH^+ and HOH^+ ions the difference in kinetic energy release between those originating from the triplet or the singlet state is about 1 eV. Specifically, according to their calculations OH^+ (HOH^+) resulting from the singlet state should be produced with almost 4.5 eV (4.2 eV) kinetic energy release while for the fragments originating from the triplet state the corresponding value is 5.6 eV (5.2 eV). This energy difference is not enough to lead in well separated mass spectra features for OD^+ and HOD^+ fragments ejected from the singlet or the triplet state. This fact is obvious in the ToF spectrum of OD^+ and HOD^+ fragment in which the horizontal time axis has been transformed in kinetic energy (Fig. 4).

As discussed above the dissociation from dressed and singlet states is very fast when compared with the rotational period of the parent molecule. Thus, the ejected fragments will preserve the selectivity that is imprinted in the ionization process, i.e. they should exhibit directionality. The signal dependence on φ will be a sinusoidal function that follows the direction of the laser field (ω). Therefore, the main contribution in the integrated signal (Fig. 3) is attributed to dissociation from dressed and/or singlet states. On the other hand, molecular relaxation via intersystem crossing is leading to a triplet state which implies that the precursor lives long enough and as a result, loses the initial selectivity. The dependence on phase φ will now follow the intensity maxima and, consequently, the resultant fragments will exhibit a sinusoidal dependence with the double frequency (2ω). From this approach it is reasonable to conclude that in Fig. 3 the smaller contribution arises from ions KER prepared in a triplet or a metastable state.

If the above mentioned interpretation is valid, the angular distributions of these fragments, for a constant phase φ , should also reveal some specific features. Fragments that are prepared in a dressed/singlet state should exhibit anisotropic angular distributions, while those prepared in a triplet/metastable state should yield isotropic angular distributions. In Fig. 5 the normalized angular distributions of OD^+ , HOD^+ , H_3^+ are given. Even though, their angular distributions are anisotropic, none of them reaches

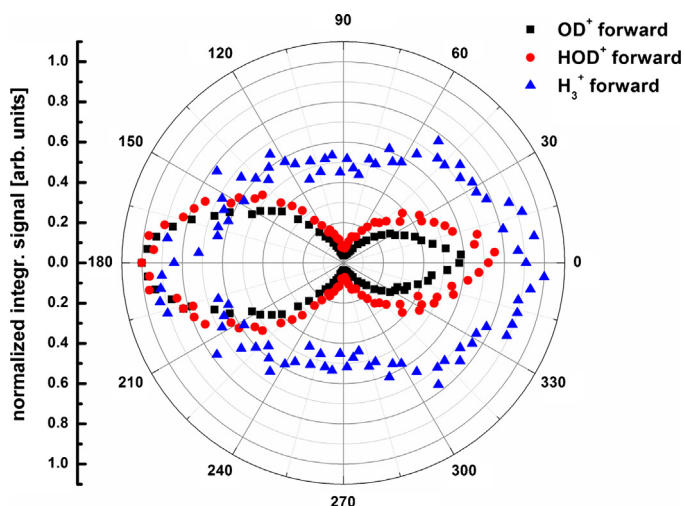


Fig. 5. The normalized angular distributions of H_3^+ , OD^+ , and HOD^+ ions recorded for a constant phase $\varphi = \pi$.

zero when the laser polarization is vertical to the ToF axis (90°), implying that a smaller isotropic contribution is also apparent. The OD^+ fragment is the most anisotropic followed by the HOD^+ (and H_3^+ fragment). This observation is in accordance with the plots of Fig. 3, where the smaller contribution with the double frequency (2ω) is also smaller for the OD^+ fragment, followed by the HOD^+ and H_3^+ fragment.

• H_3^+ fragment

For the H_3^+ fragment the 2ω signal (Fig. 3(a) and (b)) as well as the anisotropic angular distribution with the isotropic component (Fig. 5) have also been recorded.

The angular distributions of H_3^+ fragment resulting from organic molecules under irradiation with (in most cases) a single color laser field, has been found to be almost isotropic. This observation has led to the conclusion that the production of H_3^+ fragment is a slow procedure with a lifetime comparable to the rotational period of the parent molecule. The existence of a quasi-bound transition state in the potential energy surface of the doubly charged parent molecule has also been confirmed [26,32]. The existence of such a barrier in the direction of the H_3^+ production channel has been considered to be responsible for the experimentally almost isotropic angular distributions. However, a study on different laser intensities on CH_3Cl molecule and the dependence of the angular distribution of H_3^+ fragment as a function of the intensity concludes that the angular distribution of H_3^+ fragment becomes more anisotropic as the laser intensity is increased [33]. The interpretation that was given is that the stronger electric field affects the potential energy surface of the doubly charged parent molecule.

Nevertheless, the recorded angular distribution of H_3^+ fragment utilizing a ToF mass spectrometer are found to be anisotropic (Fig. 5), i.e. different from that reported by previous publications. This discrepancy should be elucidated. The latter can be based on two experimental findings which are beyond any doubt. Firstly the ω and 2ω dependence of the integrated signal and secondly the fact that the signal is not zero when vertical to the ToF axis laser polarization is applied. These two findings imply that two different mechanisms – one fast and one slow as compared to the molecular rotational period – contribute to its formation. Since in the theoretical work of Thapa et al. there is no prediction for the H_3^+ formation from singlet/triplet states, other channels leading to a fast and a slow H_3^+ production should be involved.

Nakai et al. [27] in their work concerning the H_3^+ production from methanol have concluded that a “long-lived neutral molecular hydrogen” appears as transient moiety in the doubly charged methanol molecule. The molecular hydrogen stays close to the parent molecule due to van der Waals forces, and then along with another hydrogen atom from the parent molecule they formed the H_3^+ ion. The calculated charge of the H_2 molecule as a function of time is also given in that work. They found that the charge is oscillating between the H_2 and the rest of the molecule. In Fig. 5 of their paper it is clear that H_2 molecule can gain its charge via a very fast procedure (completed within an interval of ~ 75 fs). After this interval and for a period of about ~ 150 fs the charge of molecular hydrogen has a mean value of zero. Finally the mean charge of H_2 is once again larger than zero.

Based on that description the fast channel may take place in the first ~ 75 fs when the H_2^+ moiety appears and attaches a neutral hydrogen atom from the rest of the molecule. In the same perspective, the slow H_3^+ production channel may take place for $t > 225$ fs when the H_2 molecule acquires once more charge, and subsequently attaches a neutral hydrogen atom to form H_3^+ . Both H_3^+ production channels result in fragments with the same m/z value and kinetic energy, and thus makes it impossible to distinguish them simply by inspecting the ToF spectrum.

As far as the discrepancy between the recorded angular distribution and that reported in the literature is concerned, we would like to mention that a ToF spectrum is just a one dimensional curve produced by the integration of the three dimensional Coulomb explosion signal within the limits of the ToF-MS spectrometer detection cone, which is parallel to the ToF axis. The detection efficiency is a function of the polar angle θ between the ejection direction of the fragments and the ToF axis. In order to make a quantitative comparison the ToF acceptance angle has been estimated by using the Simion 8.0 simulation software. For H_3^+ fragment ions ejected towards the detector (forward component) with kinetic energies similar to the experimentally recorded ones (3.5 ± 0.4 eV), the acceptance angle values is estimated to be 5° .

By analyzing the angular distributions, recorded for a constant phase φ , it is possible to reach a rough estimation of the fast/slow channels ratio. The angular distributions of Fig. 5 can be fitted by the function $Y_{ang} = d + \alpha \cdot (\cos \theta)^n$, where the d parameter describes the isotropic component, the α parameter the maximum value along the ToF axis, and θ is the polar angle. The results of the fitting procedure suggests a value of 2 for the n parameter for all three distributions and the total integrated volume for the anisotropic and isotropic component can be calculated by the formula:

$$V_{anis} = \int_0^{2\pi} d\phi \int_0^\theta \sin \theta d\theta \int_0^{a \cos^n \theta} r^2 dr \quad \text{and}$$

$$V_{isot} = \int_0^{2\pi} d\phi \int_0^\theta \sin \theta d\theta \int_0^{a-d} r^2 dr.$$

Following straight forward mathematics the ratio is obtained:

$$\frac{V_{anis}}{V_{isot}} = \frac{(a-d)^3}{7d^3} \cdot \frac{(1 - \cos^7 \theta)}{(1 - \cos \theta)}.$$

By setting $\theta = 90^\circ$ (in order to account only for the forward component) and for the H_3^+ ion, the above mentioned ratio takes the value $V_{anis}/V_{isot} = 0.04$, implying that the anisotropic component is actually smaller than the isotropic one in agreement with the already published data. At that point someone may wonder if this approach is applicable for the OD^+ and HOD^+ fragments too. In principle there is no problem and the analysis approach could be used for the determination of the population ratio between

molecules that fragment via dressed/singlet states with respect to those dissociating from the triplet or metastable states. However, due to their small isotropic component, which lies within the limits of experimental error, any estimation of this ratio is unsafe, although it is clear that the vast majority of the fragments are produced in the dressed and singlet states.

4. Conclusions

We have studied the fragmentation dynamics of methanol (CH_3OD) under the irradiation of an intense two-color $\omega/2\omega$ laser field. The resultant H_3^+ , OD^+ , HOD^+ fragments originating from the doubly charged parent molecule exhibit strong phase dependence. The variation of the integrated signal of each fragment with a frequency that follows the asymmetric's field direction (ω), indicates that a faster dissociation channel than the molecular rotation period is involved. However, in part, the integrated signal is found to follow the intensity maxima (2ω). These ions are expected to be released from long lived precursors. The angular distributions of the ejected fragments are in agreement with this approach. We attributed the fast dissociation processes, leading to OD^+ and HOD^+ ejection to dissociation taking place in singlet states, while the slower ones are assigned to fragmentation within the triplet and/or metastable states. For the H_3^+ ion, the dependence of the integrated signal on phase φ exhibits two sinusoidal components too (ω and 2ω). The interpretation of this dependence is attributed to two different (with respect to the timescale) processes leading in its formation and could be thought as an experimental confirmation of that proposed previously [27]. Although, the angular dependence recorded with a ToF-MS spectrometer with a high angular resolution stresses the contribution of the anisotropic component over the isotropic one, simple calculations, taking into account the acceptance angle of the spectrometer and the kinetic energy of the fragments, suggest that the isotropic fragmentation is clearly the dominant process. This in fact is in accordance with previous reports on the ejection of H_3^+ from methanol where it is described as almost isotropic.

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