Benchmark Measurements of H_3^+ Nonlinear Dynamics in Intense Ultrashort Laser Pulses

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(Received 27 April 2009; published 2 September 2009)

The H_3^+ ion is the simplest polyatomic molecule and is destined to play a central role in understanding such molecules in intense ultrashort laser pulses. We present the first measurements of the intense field dissociation and ionization of D_3^+ using coincidence three-dimensional momentum imaging. Our results show features that are a consequence of this molecule's unique equilateral triangular geometry, providing a fundamentally new system for theoretical development.

DOI: 10.1103/PhysRevLett.103.103004 PACS numbers: 33.80.Wz, 42.50.Hz

With electromagnetic fields comparable to a molecule's internal Coulomb fields, intense ultrashort laser pulses strongly affect molecular dynamics. Furthermore, these pulses are short enough to probe the molecular dynamics in time. As a result, ultrashort laser pulses have revolutionized molecular science, with broad applications including the control of molecular processes [1], generation of attosecond high-harmonic pulses [2], and time-resolved imaging of molecular reactions [3].

Our understanding of the response of atoms and molecules to strong laser fields has proceeded like essentially all studies of atoms and molecules—from simple systems to complex. In molecules, the first step in this chain of inquiry is the one-electron diatomic molecule H_2^+, and it has played a central role in developing our understanding of the behavior of molecules in intense laser fields [4]. H_2^+ has been most often produced by the laser itself from an H_2 target, since the experimentally challenging H_2^+ targets have only recently become available [5–7]. The behavior of the simplest two-electron diatomic molecule, H_2, has thus been studied experimentally in parallel with H_2^+.

As attention increasingly turns to polyatomic molecules in intense fields, it would again be useful to start with the simplest system: H_3^+. In contrast to H_2, neutral H_3 in its ground state is unstable; therefore the use of the more demanding H_3^+ ion-beam targets is essential. Unfortunately, H_3^+ ions have proven difficult to break with intense laser pulses, despite the efforts of many groups (see, for example, Ref. [8]).

Studies of triatomics certainly did not stop because of this failure and many other systems have been studied [4,9], despite being too complex to treat theoretically. These systems, however, have all had either linear or bent geometries. Thus, the fact that H_3^+ forms an equilateral triangle in its ground state [10] makes it especially interesting. In fact, its unique geometry has made H_3^+ a preferred test case for molecular structure calculations [11,12] as well as for exploring the stability of molecules under extreme conditions [13].

In addition to its benchmark status, H_3^+ is also the Universe's most abundantly produced polyatomic molecule. It plays a central role in interstellar chemistry [11,14–16] through its production in $H_2^+ + H_2 \rightarrow H_3^+ + H$ collisions and its destruction via dissociative recombination [17,18], $H_3^+ + e^- \rightarrow H_2 + H$ or $H + H + H$, and has been studied extensively (e.g., [19–23]).

Theoretically, studying H_3^+ in a strong field is a serious challenge. Even for the considerably simpler H_2^+ molecule, no calculations have yet been published that include *all* degrees of freedom. Only recently have calculations of few photon double ionization of H_2—with fixed nuclei—become available [24,25]. Double ionization of H_3^+, on the other hand, will tax theorists even if the nuclei are fixed due, in part, to its more complicated potential energy surface (PES) topology. And, if ionization is neglected, the quantum mechanical response of the nuclei to a strong field is also at the limit of theoretical abilities. Simplifying assumptions must thus be found, and experiment can provide the necessary guidance [26].

Taking the initial step in this process, we present here the first measurements of the breakup of D_3^+ in ultrashort intense laser pulses—recovering the full, correlated momentum distribution of all the nuclear fragments.

We have developed and employed a crossed-beam three-fragment coincidence three-dimensional momentum imaging technique that is an extension of our earlier work on diatomic molecules [7,27]. In brief, the fast moving neutral and ionic fragments, following interaction of the focused laser with the D_3^+ beam, are imaged and detected in coincidence using a time- and position-sensitive detector downstream from the interaction region. From the position and absolute time-of-flight information we retrieve the full 3D momenta of all fragments. Additionally, a weak static longitudinal electric field in the interaction region allows separation of fragments by their time of flight. Overall, this method provides detailed information about the interaction such as high resolution kinetic energy release (KER) and angular distributions. More important, in this specific case, is the efficient detection of all fragments and the coincidence nature of the measurement. This allows us to identify two- and three-body breakup of D_3^+ induced by 7 fs, 790 nm intense laser pulses. Details of our ion-beam imaging system [7] and Ti:sapphire laser setup [28] are provided elsewhere.

The choice of the D_3^+ isotopologue helps avoid problems caused by the HD^+ contaminant present in an H_3^+ beam. It is imperative to this work that the D_3^+ formed in our ion source is not vibrationally cold as this would make it more difficult to dissociate or ionize. Statistical calculations [29] for the formation reaction $D_2^+ + D_2 \rightarrow D_3^+ + D$ indicate a broad vibrational population peaking at D_3^+ ($v = 6$), ~1.95 eV above the minimum of the D_3^+ ground state PES.

Our two- and three-body breakup data of D_3^+ can be divided into three main reactions:
dissociation

$$\begin{aligned} D_3^+ + n\omega &\rightarrow D^+ + D_2 \\ &\rightarrow D_2^+ + D \\ &\rightarrow D^+ + D + D, \end{aligned}$$

single ionization

$$\begin{aligned} D_3^+ + n\omega &\rightarrow D^+ + D_2^+ + e^- \\ &\rightarrow D^+ + D^+ + D + e^-, \end{aligned}$$

and double ionization

$$D_3^+ + n\omega \rightarrow D^+ + D^+ + D^+ + 2e^-,$$

where $n\omega$ denotes the multiphoton interaction with the strong laser field. The relative importance of these channels varies rapidly with laser intensity, as shown in Fig. 1.

Figure 1 summarizes key information about the dynamics of D_3^+ fragmentation. For example, at lower intensities ($<2 \times 10^{15}$ W/cm^2) the breakup of D_3^+ is naturally dominated by dissociation as the intensity is insufficient to ionize. However, we find that two-body dissociation ($D^+ + D_2$ or $D + D_2^+$) is more probable than three-body dissociation ($D^+ + D + D$), in contrast to dissociative recombination studies [17,18], especially for vibrationally excited D_3^+ [17]. Likewise, for single ionization we find a similar competition between the $D^+ + D_2^+$ and $D^+ + D^+ + D$ channels where the two-body channel is dominant at low laser intensities, but the three-body channel becomes the strongest at higher intensity.

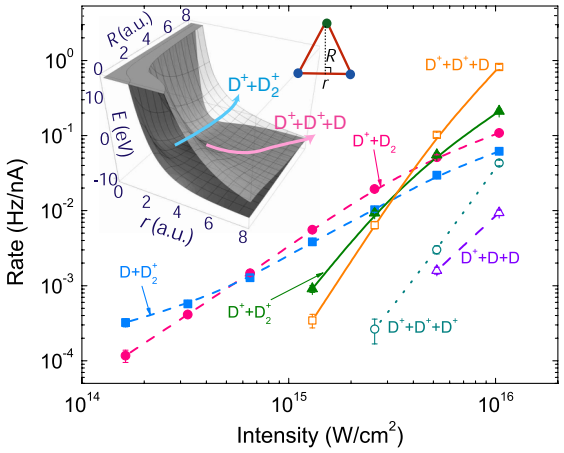

FIG. 1 (color online). Normalized rates for D_3^+ fragmentation channels as a function of laser intensity using 7 fs, 790 nm laser pulses. The rates have been normalized to the ion-beam current of ~5 nA. The error bars show the statistical error of the data. The inset shows cuts of the lowest two potential energy surfaces calculated for D_3^{2+}, where R and r are defined by the diagram.

We can develop a qualitative understanding of the relative importance of these channels from studying the PESs of D_3^+. As an example, in the inset of Fig. 1 we have calculated the lowest PESs of the one-electron D_3^{2+} molecule by solving the Born-Oppenheimer equation in three dimensions using B splines. One can identify a dissociation path leading to either $D^+ + D_2^+(1s\sigma_g)$ or $D^+ + D^+ + D$ on the ground state surface of the transient D_3^{2+}. The excited state, however, is repulsive along the internuclear coordinate r (see Fig. 1), thus preventing D_2^+ formation and leading only to the $D^+ + D^+ + D$ channel. As the laser intensity grows, the likelihood of ionization to the excited D_3^{2+} state increases. Since only $D^+ + D^+ + D$ occurs on the excited state, we expect this channel to eventually dominate over $D^+ + D_2^+$ at high enough intensities and observe this transition at 3.4×10^{15} W/cm^2 (see Fig. 1).

Because of the wealth of information in our measurements, a full discussion of all the breakup channels is outside the scope of this Letter. Instead, we highlight features of the three-body ionization channels as these are a direct consequence of the polyatomic nature of D_3^+.

We begin with double ionization of D_3^+ as this provides information about the ionization of the transient D_3^{2+} molecular ion created earlier in the laser pulse, in a similar way to studies of H_2^+ ionization using H_2 targets [30]. "Frozen" nuclei calculations by Bandrauk and Ruel [31], using the realistic equilateral triangle configuration of the parent H_3^+, predict an enhancement of H_3^{2+} ionization around $r \sim 7$ a.u., although this value may differ if nuclear motion is included. Nonetheless, at this critical r, a KER of about 12 eV is expected, if one neglects the kinetic energy gained earlier by the dissociating D_3^{2+}. This early energy gain is expected to be small on the transient D_3^{2+} ground state. The measured nuclear kinetic energy for 7 fs, 10^{16} W/cm^2 pulses, shown as a KER distribution in Fig. 2, is in clear disagreement with the theoretical prediction [31] as it peaks at much higher KER—around 25 eV—suggesting instead ionization at $r \sim 3.2$ a.u. It can be argued that the 7 fs laser pulses used may prevent stretching of the D_3^+ or the transient D_3^{2+} to $r = 7$ a.u. while the intensity is sufficiently high to ionize. Accordingly, we have repeated the measurements with 40 fs pulses, for which there is time for stretching, and the results show even less ionization around 12 eV (see Fig. 2). The measured KER distribution, therefore, favors direct ionization over enhanced ionization as the dominant mechanism leading to $D^+ + D^+ + D^+$. This assertion is further supported by the large difference in

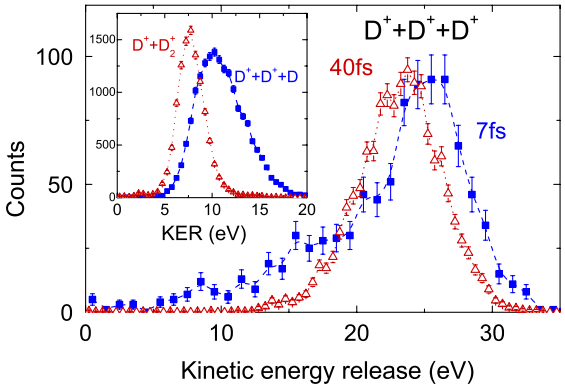

FIG. 2 (color online). The KER distribution for $D^+ + D^+ + D^+$ fragmentation following double ionization of D_3^+ using 7 fs pulses compared to 40 fs at 790 nm, 10^{16} W/cm^2. The inset shows the KER distribution for $D^+ + D_2^+$ and $D^+ + D^+ + D$ fragmentation following single ionization by the same 7 fs pulses. The error bars show the statistical error of the data.

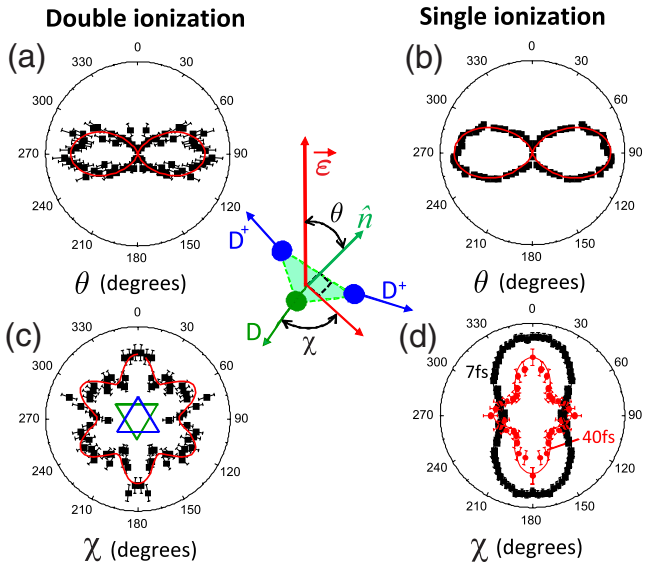

FIG. 3 (color online). (a),(b) The alignment θ of the normal vector to the molecular plane $\hat{n}$, relative to the laser polarization ε; see inset for definitions ($\theta > 180°$ is mirrored to complete the polar plot). (a) Double ionization and (b) single ionization, for 7 fs, 10^{16} W/cm^2 laser pulses. The fits to the data are $\sin^3\theta$ angular distributions. (c),(d) The orientation χ of the velocity vector of the D^+ and D fragments of double and single ionization, respectively, relative to the projection of the laser polarization within the molecular plane (for large fields within the molecular plane, i.e., $60° < \theta < 120°$). (c) Double ionization for 7 fs pulses, and (d) single ionization for 7 fs and 40 fs pulses. The error bars show the statistical error of the data.

KER between double and single ionization (see Fig. 2), as this sets a limit of a few eV on the maximum KER gain prior to the ionization of the second electron. Furthermore, the single ionization results are also approximately consistent with ionization at similar r to double ionization, obtaining a value of $r \sim 3.3$ a.u. for $D^+ + D_2^+$ and $r \sim 3.5$ a.u. for $D^+ + D^+ + D$ on the ground and excited PESs in Fig. 1 (inset), respectively.

One may still question whether the ionization of the second electron is induced directly by the laser field or by the electron-rescattering mechanism [32]. In electron rescattering, the first ionized electron is driven back by the laser field to inelastically scatter off the molecular ion left behind, causing double ionization. To test if rescattering is an important mechanism, we repeated the measurements using circularly polarized light, since this suppresses the rescattering mechanism by forcing the electron to miss the parent molecule [32]. The relative double ionization rate did not decrease, showing that rescattering plays no significant role in this process.

Arguably the most insightful information on D_3^+ breakup is provided by the alignment and orientation dependence of the molecular plane relative to the laser polarization (see definitions in Fig. 3). These are determined from the momenta vectors of the fragments measured in our 3D imaging scheme.

The *alignment* angle θ, between the normal vector of the molecular breakup plane and the laser polarization, is shown in Figs. 3(a) and 3(b) for three-body breakup in the double and single ionization channels, respectively. Both distributions peak at $\theta = 90°$ indicating that ionization is enhanced when the molecular plane is aligned with the laser polarization. Since the electrons in D_3^+ each occupy the same spatial molecular orbital composed roughly of hydrogenic $1s$ orbitals centered on each deuteron, the electron wave function is predominantly in the molecular plane. This fact, together with the tunnel ionization molecular Ammosov-Delone-Krainov (MO-ADK) model [33] prediction that the ionization rate is largest when the electron wave function with the largest extent is along the laser polarization, explains qualitatively the observed alignment peak at $\theta = 90°$. The degree of alignment shown in Figs. 3(a) and 3(b), however, is unexpectedly small when compared with the strong alignment observed for H_2^+ ionization ($\sim\sin^3\theta$ compared with $\sim\sin^{24}\theta$ for H_2^+ [34]). More surprising is the fact that both single and double ionization show the same degree of alignment ($\sim\sin^3\theta$)—an intriguing similarity that calls for future investigation.

The *orientation* angle χ is between the dissociation velocity of one fragment and the laser field projection within the molecular plane. The orientation distributions for the three-body channels, shown in Figs. 3(c) and 3(d) for single and double ionization, respectively, include only molecules aligned within $60° < \theta < 120°$, for which the field within the molecular plane is large enough to confidently define χ. In contrast to their similarity in alignment, double and single ionization differ significantly in their orientation dependence.

We observe a clear orientation preference for double ionization when a D^+ fragment is ejected along the laser polarization projection; see Fig. 3(c). Rather than the 120° separation one might expect starting from an equilateral

triangle, though, we measured peaks every 60°. This preference can be explained qualitatively by again invoking the MO-ADK model which predicts a higher tunneling ionization rate when the laser field points toward one of the deuterons because the electronic cloud extends further in that direction. Since the laser field oscillates along the polarization direction, the ionization rate will peak whenever one of the deuterons lies along the line defined by the polarization direction. For an equilateral triangle, this occurs once every 60°—first for a deuteron along the positive polarization direction, then along the negative polarization direction, and so on.

The orientation preference in single ionization is quite different as can be seen in Fig. 3(d) for both 7 and 40 fs pulses. Using 7 fs pulses, $D^+ + D^+ + D$ breakup favors the orientation for which the D fragment dissociates along the laser field within the molecular plane, $\chi = 0°$ and 180°. One may argue, using the MO-ADK model, that the reason for this preference is the same as for double ionization as the electron cloud of the dissociating $D_3{}^{2+}$ is stretched toward the D fragment. However, significant single ionization also occurs for $\chi = 90°$ and this contribution increases when using 40 fs pulses [see Fig. 3(d)]. This indicates that more complex dynamics are responsible for the orientation effect.

In closing, in a step towards understanding the dynamics of polyatomic molecules, we have reported first-of-their-kind measurements of $D_3{}^+$ fragmentation in intense ultrashort laser pulses. We anticipate that this work will motivate and direct future experimental efforts on the benchmark $H_3{}^+$ molecular system and its isotopologues under a wide variety of laser conditions. From a theory standpoint, extensive development of theoretical methods is needed to be able to treat even $H_3{}^+$, the simplest polyatomic molecule, under the extreme conditions of the ultrafast strong field produced by the laser. The importance of the present $H_3{}^+$ data is that it can be used to guide future theory. Insight from our results should aid in development of the appropriate approximations needed to perform calculations on $H_3{}^+$ and, ultimately, larger polyatomic molecules, while still capturing the essence of the physics involved in the processes.

We thank P. Q. Wang, M. Leonard, and E. Parke for their efforts in the early stages of this project. We also thank Z. Chang's group for providing the laser beams and C. W. Fehrenbach for his help with the ion beams. This work was supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy.

Note added.—Recently, research on the laser-induced dissociation of vibrationally cold D_3^+ by Alexander *et al.* [35] has appeared in the literature.

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