THE JOURNAL OF CHEMICAL PHYSICS **127**, 131101 (2007)

Molecular fragmentation driven by ultrafast dynamic ionic resonances

Brett J. Pearson,[a] Sarah R. Nichols, and Thomas Weinacht[b]
Department of Physics, Stony Brook University, Stony Brook, New York 11794, USA

(Received 29 June 2007; accepted 6 September 2007; published online 2 October 2007)

The authors time resolve molecular motion in bound state, ionic potentials that leads to bond cleavage during the interaction with intense, ultrafast laser fields. Resonances in molecular ions play an important role in dissociative ionization with ultrafast laser fields, and the authors demonstrate how these resonances evolve in time to produce dissociation after initial strong-field ionization. Exploiting such dynamic resonances offers the possibility of controlled bond breaking and characterizing time-dependent molecular structure. © *2007 American Institute of Physics*.
[DOI: 10.1063/1.2790419]

Interest in laser selective chemistry[1,2] and molecular imaging[3–7] has driven many advances in our understanding of the interaction of molecules with intense, ultrafast laser fields. Developments in ultrafast laser technology have permitted the generation of shorter pulses and greater control over them, benefiting the study of strong-field, molecular photofragmentation. The field is especially rich, as it involves both resonant and off-resonant electronic transitions, vibrational wave packets, and multiple, interfering pathways to fragment dissociation. Different models have been proposed to explain the observed photoionization and fragmentation patterns in ion time-of-flight mass spectra for various molecular families (for example, see Refs. 8–15).

For femtosecond laser pulses with peak intensities where the Keldysh parameter, $\gamma = \omega_{\text{laser}}/\omega_{\text{tunneling}}$, is less than 1, tunnel ionization takes place rapidly, leading to substantial ionization on the rising edge of the pulse.[10,16] Therefore, resonances in the ionic spectrum can have an important effect on the outcome of the laser-molecule interaction. Ionic resonances in the near infrared are common in small polyatomic molecules with many electrons[11] as a result of the low cost in energy associated with moving the electron hole left by ionization around the molecule. Furthermore, since the equilibrium geometry of the ion is generally different than that of the neutral molecule, ionization can produce large amplitude vibrational motion in the ion that leads to inherently dynamic resonances.[17] Thus one expects that ionic resonances in the infrared are common, dynamic, and important for understanding the dissociation of small polyatomic molecules in intense ultrafast laser fields.[15]

Recent studies have examined the role that ionic resonances play in the fragmentation process.[14,18–20] Specifically, it has been suggested that single-photon resonances in the molecular ion provide efficient pathways to multiple fragmentation channels.[11,14,18] Other studies have found molecular systems that appear to show little or no fragmentation despite having single-photon absorptions from the ionic ground state.[19] Although the static absorption spectrum of the ion may be useful in cases where the neutral and ionic equilibrium geometries are similar, when they are substantially different, wave packet motion in the ionic state can lead to dynamic resonances that must be taken into account to understand the fragmentation pattern. In this work we time resolve ionic resonances in a family of molecules (halogenated methanes) and find that the resonances are dynamic and have temporally delayed onsets.

Figure 1 shows a cartoon picture of one dimensional potential energy surfaces (PESs) relevant to ionization followed by dissociation in a small, polyatomic molecule such as the type considered in this paper. The x axis describes the atomic separation between the two atoms originally bound in the neutral molecule (e.g., CH_2X-Y separation in a halomethane CH_2XY, where $X,Y \in \{F,Cl,Br,I\}$). The lowest state in Fig. 1 corresponds to the neutral ground state of the molecule, while the intermediate state is the ground ionic PES. The highest state represents a dissociative ionic state (or a bound state coupled to dissociative states) whose separation from the ground ionic state for particular bond lengths is resonant in the near infrared ($\sim$1.5 eV). If a wave packet on the ground ionic state passes through a single-photon resonance with the excited state, population in the ground ionic state may be transferred efficiently, leading to fragmentation.

We begin with pulses from an amplified titanium:sapphire laser system that are subsequently split in a Mach-Zehnder interferometer (for a more detailed description of the experimental apparatus see Ref. 21). One arm of the interferometer contains a pulse shaper with a computer-controlled acousto-optic modulator (AOM) as the shaping element.[22] This configuration permits two-pulse experiments where a probe pulse measures the dynamics initiated by the pump pulse. The AOM has complete control over either the pump or probe pulse (pulse energy, pulse duration, and relative time delay). The two pulses are focused and intersect in an effusive molecular beam inside a vacuum chamber equipped with a time-of-flight mass spectrometer (TOFMS) that resolves the different fragment ions. Peak pump pulse intensities are approximately 1.7×10^{14} W/cm^2.

We choose the halomethane family of molecules since they have been studied extensively (partly due to their im-

---

[a] Present address: Department of Physics and Astronomy, Dickinson College, Carlisle, Pennsylvania 17013, USA

[b] Electronic mail: tweinacht@sunysb.edu

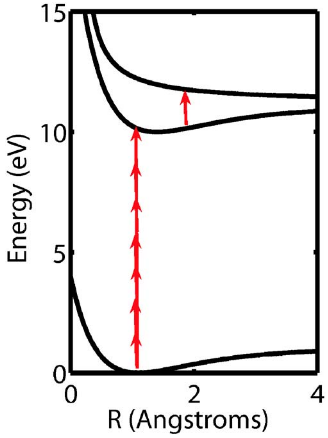

FIG. 1. (Color online) Model potential energy surfaces showing an ionic resonance along one bond coordinate in a polyatomic molecule. Population in the lower bound ionic state is transferred into a higher-lying dissociative state through a single-photon transition initiated at the appropriate time by the probe pulse.

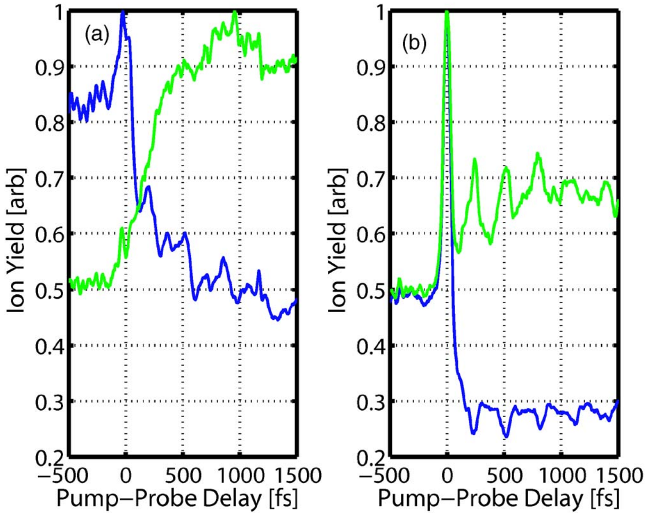

FIG. 2. (Color online) (a) Ion signal as a function of pump-probe delay for CH_2BrI^+ (blue, dark) and CH_2I^+ (green, light) in the parent molecule CH_2BrI. (b) Similar data for $CH_2I_2^+$ (blue, dark) and CH_2I^+ (green, light) in the molecule CH_2I_2. All curves are individually normalized.

portance in atmospheric chemistry[23]), and they clearly illustrate the importance of dynamic ionic resonances in dissociative ionization. Furthermore, halomethanes, especially those of the form CH_2XY, have been examined as prototypical molecules for studying and controlling unimolecular dissociation reactions (for examples in CH_2BrI and CH_2I_2, see Refs. 21 and 23–35). The temporal dynamics of the ionic resonance discussed above can be directly resolved for the molecule CH_2BrI, as shown in Fig. 2. Figure 2(a) plots the CH_2BrI^+ and CH_2I^+ signals as a function of delay time between two 35 fs laser pulses. The "pump" pulse, with an intensity of approximately 1.7×10^{14} W/cm^2, arrives first, ionizing the molecule. The "probe" pulse ($\sim 6.6\times 10^{13}$ W/cm^2) follows, after which we collect molecular ions in the TOFMS. The probe pulse alone produces negligible independent ion signal. The intensities are calibrated following the procedure described in Ref. 36. As the delay between the pump and probe pulses increases, the parent ion signal drops while the fragment CH_2I^+ signal increases. This turn-on is a crucial property of the ionic resonance, as the resonance will not be observed with a single, ultrashort pulse. Only after the wave packet has propagated on the PES can the probe pulse transfer the population from the bound PES leading to CH_2BrI^+ to a dissociative PES leading to CH_2I^+ (we find that other fragments in this molecule show similar behavior). Based on this picture, one expects increased fragmentation for longer pulses, since the wave packet in the ionic state will begin to pass through the resonance during the pulse. Increasing fragmentation as a function of laser chirp for a fixed pulse energy has been observed in several experiments.[21,37,38]

Careful examination of the data in Fig. 2(a) suggests oscillatory wave packet behavior underlying the ionic resonance. Although the general trend for the parent ion signal is downward, any modulation in the signal would indicate that the transition probability is modified as the wave packet on the ground ionic state oscillates within the potential well. Dispersion of the wave packet on what is actually a multidimensional surface will tend to wash out any modulations, and we find an example of much clearer oscillations in a different halomethane. Figure 2(b) shows the parent ion ($CH_2I_2^+$) and CH_2I^+ signals as a function of pump-probe delay in CH_2I_2. Although the initial "turn-on time" (roughly the time for the signal to go from 10% to 90% of the maximum signal level) of the resonance is much faster in this molecule, the probability of population transfer continues to be modulated as the wave packet in the bound PES oscillates back and forth without suffering substantial dispersion. The large peak in both ions at zero delay time is due to optical interference between the pump and probe pulses. The modulations in the $CH_2I_2^+$ and CH_2I^+ signals are the same frequency (approximately 111 cm^{-1} or 3.45 THz) but π out of phase. This frequency is close to the observed value for the neutral ground state I–C–I scissors mode (127 cm^{-1}) (Ref. 39) and even closer to the value for the ionic ground state I–C–I scissors mode (113 cm^{-1}).[40] We suspect that I–C–I scissors motion in the molecular ion plays a role in the fragment modulation.[41] We are currently performing detailed calculations of the ionic PESs to determine exactly what motion gives rise to the observed modulations.

We have found these types of resonances to be quite general among members of the halomethane family that have a stable parent ion. For example, CH_2ClI, CH_2Br_2, and CH_2BrCl also show single-photon resonances out of the parent ion state with a range of turn-on times from less than 100 fs to over 400 fs (in the current configuration, we are unable to reach shorter time delays than 50 fs due to optical interference between the pump and probe pulses). As described above, if the turn-on time is short compared to the pump pulse duration, the initial ionization and resultant excitation of the ion can proceed within a single pulse, leaving little, if any, parent ion.[18]

To confirm that our observations are a consequence of single-photon ionic resonances, we measure the yield of ion fragments versus the intensity of the probe laser pulse. Figure 3 shows data from the molecule CH_2BrI, where an un-

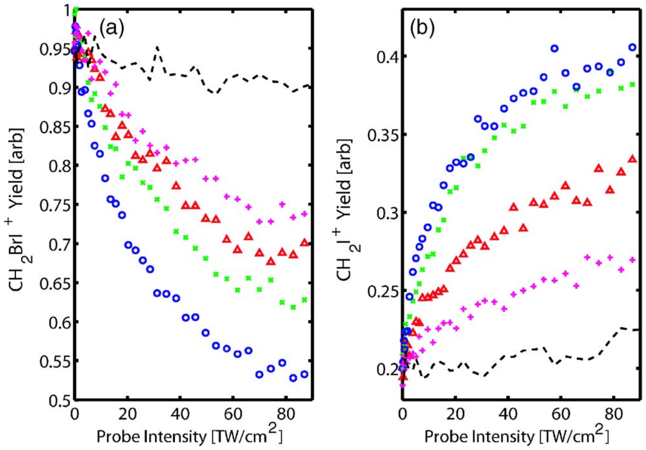

FIG. 3. (Color online) (a) Parent (CH_2BrI^+) ion signal as a function of probe pulse intensity for pump-probe time delays of 50 fs (pink pluses), 200 fs (red triangles), 500 fs (green crosses), and 1000 fs (blue circles). Also shown is the ion signal for the reverse pulse ordering with a pump-probe delay of −200 fs (black dashed). (b) Similar plots for the partner fragment CH_2I^+. All curves are normalized to the same value. When the background from the pump pulse is subtracted, the plots for CH_2I^+ at 1000 fs show a log-log slope of about 1 ± 0.1, indicating their single-photon origin.

shaped pump pulse (35 fs, $\sim 1.7 \times 10^{14}$ W/cm^2) with fixed energy ionizes the molecule. This pulse is followed in time by a probe pulse (35 fs) whose intensity is scanned. The five different curves correspond to different pump-probe time delays. Panel (a) shows the parent ion (CH_2BrI^+) signal as a function of probe pulse energy, while panel (b) shows one of the dissociative fragments (CH_2I^+).

At short time delays (50 fs), the parent ion signal decreases moderately with increasing probe pulse intensity, while the CH_2I^+ fragment (as well as other fragments not shown) shows a corresponding increase. As the time delay between pulses is increased, the decrease in the parent ion with intensity becomes much more dramatic, in agreement with Fig. 2, which showed that the ionic resonance between the bound and dissociative PESs turns on over a few hundred femtoseconds. At short time delays, only some of the wave packet initially launched on the bound PES has reached fragment separations where the excited dissociative state is in resonance with the parent ion. In fact, in the limit of zero (a single pulse) and negative time delays, the transfer efficiency is quite low since the excited state is effectively nonresonant at this fragment separation. Only after an appreciable time delay does the ionic resonance turn on. This is shown explicitly by the dashed curve in Figs. 3(a) and 3(b), which plots the ion yield as a function of probe intensity at a time delay of −200 fs (with the probe preceding the pump pulse). Here there is relatively little population transfer between states, as the resonance has not yet turned on.

It is important to note that the (negative) slope of the parent ion signal is nonzero even at zero probe pulse energy (see Fig. 3(a), especially the curve at 1000 fs delay), confirming that the ionic transition initiated by the probe pulse is truly a single-photon process. This behavior is matched by the initial positive linear slope in the CH_2I^+ fragment ion. The saturation of the signal and the large changes in the fragment yields both attest to the strong coupling of the two states. The fragments saturate before complete depletion of the population due to a variety of factors, both technical and fundamental. Of technical importance is the imperfect spatial overlap between the pump and probe pulses, which cross in the focus and are not perfectly mode matched. Fundamentally, there is also incomplete temporal overlap of the wave packet on the ionic PES and the probe pulse. In measurements where we scanned the duration of the probe pulse at a fixed time delay (200 fs), we found that the CH_2I^+ yield increased and the parent ion decreased with increasing probe pulse duration. These results are consistent with the probe pulse strongly coupling the two states and being most effective when it matches the temporal duration of the wave packet passing through the resonance.[42]

The measurements shown in Figs. 2 and 3 suggest that one could use dynamic ionic resonances to control dissociation. We have performed feedback control experiments in CH_2BrI that indicate that it is possible to enhance the formation of CH_2I^+ at the expense of parent ion by shaping the laser pulse. Yields in the control experiments are consistent with the pump-probe results shown here, and the optimal pulses discovered by the learning algorithm contained multiple pulses with separations of a few hundred femtosecond (similar to the pump-probe experiment).

We have shown how dynamic resonances in ionic potentials play an important role in the fragmentation of molecules exposed to intense ultrafast laser pulses. These resonances can be used to influence bond breaking and characterize changes in the time-dependent molecular structure. In order to give a more detailed explanation the observed behavior, we believe that PESs of at least two dimensions are required. However, the detailed exploration of the various fragment yields versus pump-probe delay and their interpretation in terms of wave packet evolution on multidimensional PESs is beyond the scope of this paper and will be the subject of a forthcoming publication.

We gratefully acknowledge support from the National Science Foundation under Award No. 0555214. S.R.N. gratefully acknowledges the support of a Stony Brook University Graduate Council Fellowship.

[1] R. N. Zare, Science **279**, 1875 (1998).
[2] T. Brixner and G. Gerber, ChemPhysChem **4**, 418 (2003).
[3] E. Skovsen, H. Stapelfeldt, S. Juhl, and K. Mølmer, Phys. Rev. Lett. **91**, 090406 (2003).
[4] S. Gräfe, D. Scheidel, V. Engel, N. E. Henriksen, and K. B. Møller, J. Phys. Chem. A **108**, 8954 (2004).
[5] J. Itatani, J. Levesque, D. Zeidler, H. Niikura, H. Pépin, J. C. Kieffer, P. B. Corkum, and D. M. Villeneuve, Nature (London) **432**, 867 (2004).
[6] I. Ben-Itzhak, P. Q. Wang, J. F. Xia, A. M. Sayler, M. A. Smith, K. D. Carnes, and B. D. Esry, Phys. Rev. Lett. **95**, 073002 (2005).
[7] K. Ohmori, H. Katsuki, H. Chiba, M. Honda, Y. Hagihara, K. Fujiwara, Y. Sato, and K. Ueda, Phys. Rev. Lett. **96**, 093002 (2006).
[8] T. Seideman, M. Y. Ivanov, and P. B. Corkum, Phys. Rev. Lett. **75**, 2819 (1995).
[9] M. J. DeWitt and R. J. Levis, J. Chem. Phys. **108**, 7045 (1998).
[10] R. J. Levis and M. J. DeWitt, J. Phys. Chem. A **103**, 6493 (1999).
[11] W. Fuß, W. E. Schmid, and S. A. Trushin, J. Chem. Phys. **112**, 8347 (2000).
[12] M. Lezius, V. Blanchet, D. M. Rayner, D. M. Villeneuve, A. Stolow, and M. Y. Ivanov, Phys. Rev. Lett. **86**, 51 (2001).
[13] M. Lezius, V. Blanchet, M. Y. Ivanov, and A. Stolow, J. Chem. Phys. **117**, 1575 (2002).

[14] S. A. Trushin, W. Fuß, and W. E. Schmid, J. Phys. B **37**, 3987 (2004).
[15] S. Smith, A. Markevitch, D. Romanov, X. Li, R. Levis, and H. Schlegel, J. Phys. Chem. A **108**, 11063 (2004).
[16] L. V. Keldysh, Sov. Phys. JETP **20**, 1307 (1965).
[17] D. Cardoza, B. J. Pearson, and T. Weinacht, J. Chem. Phys. **126**, 084308 (2007).
[18] H. Harada, S. Shimizu, T. Yatsuhashi, S. Sakabe, Y. Izawa, and N. Nakashima, Chem. Phys. Lett. **342**, 563 (2001).
[19] L. Robson, K. W. D. Ledingham, A. D. Tasker, P. McKenna, T. McCanny, C. Kosmidis, D. A. Jaroszynski, D. R. Jones, R. C. Issac, and S. Jamieson, Chem. Phys. Lett. **360**, 382 (2002).
[20] H. Harada, M. Tanaka, M. Murakami, S. Shimizu, T. Yatsuhashi, N. Nakashima, S. Sakabe, Y. Izawa, S. Tojo, and T. Majima, J. Phys. Chem. A **107**, 6580 (2003).
[21] F. Langhojer, D. Cardoza, M. Baertschy, and T. Weinacht, J. Chem. Phys. **122**, 014102 (2005).
[22] M. A. Dugan, J. X. Tull, and W. S. Warren, J. Opt. Soc. Am. B **14**, 2348 (1997).
[23] J. C. Mössinger, D. E. Shallcross, and R. A. Cox, J. Chem. Soc., Faraday Trans. **94**, 1391 (1998).
[24] M. Kawasaki, S. J. Lee, and R. Bersohn, J. Chem. Phys. **63**, 809 (1975).
[25] L. J. Butler, E. J. Hintsa, S. F. Shane, and Y. T. Lee, J. Chem. Phys. **86**, 2051 (1987).
[26] S. J. Lee and R. Bersohn, J. Phys. Chem. **86**, 728 (1982).
[27] T. Takayanagi and A. Yokoyama, Bull. Chem. Soc. Jpn. **68**, 2225 (1995).
[28] J. C. Williamson, J. Cao, H. Ihee, H. Frey, and A. H. Zewail, Nature (London) **386**, 159 (1997).
[29] I. Pastirk, E. J. Brown, Q. Zhang, and M. Dantus, J. Chem. Phys. **108**, 4375 (1998).
[30] X. Zheng and D. L. Phillips, J. Chem. Phys. **113**, 3194 (2000).
[31] D. Bingemann, A. M. King, and F. F. Crim, J. Chem. Phys. **113**, 5018 (2000).
[32] D. G. Abrashkevich, M. Shapiro, and P. Brumer, J. Chem. Phys. **116**, 5584 (2002).
[33] A. Tarnovsky, M. Wall, M. Gustafsson, N. Lascoux, V. Sundstrom, and E. Akesson, J. Phys. Chem. A **106**, 5999 (2002).
[34] D. Cardoza, C. Trallero-Herrero, F. Langhojer, H. Rabitz, and T. Weinacht, J. Chem. Phys. **122**, 124306 (2005).
[35] J. Davidsson, J. Poulsen, M. Cammarata, P. Georgiou, R. Wouts, G. Katona, F. Jacobson, A. Plech, M. Wulff, G. Nyman *et al.*, Phys. Rev. Lett. **94**, 245503 (2005).
[36] S. M. Hankin, D. M. Villeneuve, P. B. Corkum, and D. M. Rayner, Phys. Rev. A **64**, 013405 (2001).
[37] R. Itakura, K. Yamanouchi, T. Tanabe, T. Okamoto, and F. Kannari, J. Chem. Phys. **119**, 4179 (2003).
[38] V. V. Lozovoy, T. C. Gunaratne, J. C. Shane, and M. Dantus, ChemPhysChem **7**, 2471 (2006).
[39] M. M. Heckscher, L. Sheps, D. Bingemann, and F. F. Crim, J. Chem. Phys. **117**, 8917 (2002).
[40] X. Zheng and D. L. Phillips, J. Phys. Chem. A **104**, 6880 (2000).
[41] D. Geissler, B. J. Pearson, and T. C. Weinacht, J. Chem. Phys. (to be published).
[42] D. Cardoza, B. J. Pearson, M. Baertschy, and T. Weinacht, J. Photochem. Photobiol., A **180**, 277 (2006).