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Doppler-free ion imaging of hydrogen molecules produced in bimolecular reactions

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Abstract

We report on the use of two-color Doppler-free $[(1+1')+1/1']$ resonance enhanced multiphoton ionization (REMPI) for three-dimensional imaging of state-selected product molecules from bimolecular reactions. We demonstrate the viability of this method by measuring differential cross sections for the reaction $H + D_2 \rightarrow D + HD(v'=1, j'=1,5,8)$ at 1.7 eV collision energy. We achieve higher resolution allowing us to observe oscillations that were not resolved by previous experiments; these oscillations agree closely with quantum mechanical calculations.

1. Introduction

Ion imaging has rapidly become a robust and powerful technique for investigating the dynamics of dissociation processes and bimolecular reactions [1,2]. Most ion imaging experiments use a charge coupled device camera to measure either a projection or a slice of the Newton sphere of nascent reaction products. If an inherently fast position-sensitive detector such as a delay line anode [3] is used, the complete three-dimensional (3D) velocity distribution of products may be measured directly [4–6]. We recently built such an instrument and calibrated it using Doppler-free imaging of H (D) atoms from HBr (DBr) photolysis [7]. In this Letter, we apply a similar technique to $HD(v', j')$ molecules produced in the $H + D_2$ exchange reaction and demonstrate the first use of Doppler-free ionization to obtain complete 3D images of state-selected bimolecular reaction products.

State-specific imaging of molecular hydrogen is of particular interest because hydrogen abstraction and exchange reactions are found ubiquitously in nature, and the $H + H_2$ reaction and its isotopic variants have been a crucial benchmark system for theoretical advances in gas-phase reaction dynamics [8]. Resonance enhanced multiphoton ionization (REMPI) is commonly used to convert neutral reaction products in a specific rovibrational level into cations that can be imaged. Doppler broadening can be a significant impediment to laser-based detection of these fast-moving products. This broadening can be overcome for two-photon-resonant detection schemes by splitting the laser beam into two counterpropagating beams; absorption of one photon from each beam leads to cancellation of the Doppler shift. It was recognized early on that this technique could be used for high-resolution spectroscopy [9], and the first Doppler-free two-photon absorption experiments were reported in 1974 nearly simultaneously by several research groups [10–12]. The technique has since been used with great success to measure rotationally resolved spectra of complex molecules [13].

In addition to the high resolution of Doppler-free spectroscopy, another advantage is increased sensitivity: all molecules meet the resonance condition at the same frequency regardless of their velocities parallel to the probe laser propagation axis. Vrakking et al. [14] demonstrated ultra sensitive detection of static H_2 using Doppler-free $[2+1]$ REMPI with a position-sensitive detector in 1992, but it is only recently that Doppler-free techniques have

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been applied to ion imaging of unimolecular chemical reactions [7,15–18]. These experiments focused on the detection of H and D atom photofragments, in part owing to their large two-photon absorption cross sections as well as the substantial Doppler broadening resulting from their high speeds. Doppler-free ionization can enhance the H-atom signal by more than an order of magnitude [15]. This fact allows for lower laser power, which in turn decreases the nonresonantly ionized background and reduces the space charge effects that often limit the resolution of ion imaging experiments. These advantages become even more important for studying the products of bimolecular reactions. Bimolecular reactions yield inherently lower signals than photodissociation processes, and diatomic or polyatomic products may be distributed over many quantum states, which greatly increases the difficulty of state-specific detection. A potential problem with Doppler-free detection is that two photons may be absorbed from the same laser beam, giving rise to a Doppler-shifted background superimposed on the Doppler-free signal. This background may be reduced or eliminated by several different approaches [15,16]. One such approach is to use counterpropagating laser beams of different colors so that the resonant transition cannot be achieved with two photons from the same beam. In the work described here, we have used this approach to demonstrate a new method for imaging molecular hydrogen via two-color Doppler-free $[(1+1') + 1/1']$ REMPI.

2. Experimental method

Only the details pertinent to the present work will be described here because the experimental setup is similar to that previously described [7]. A mixture of 1% HBr (Matheson, research grade) in D_2 (Cambridge Isotope Laboratories, 99.9% isotopic purity) with a typical backing pressure of 1.3 bar is supersonically expanded into a vacuum chamber through a pulsed valve (General Valve Corporation, Series 900 pulsed solenoid valve, conical body, 0.5 mm orifice, Kel-F poppet). Two vertically polarized counterpropagating laser beams tunable between 209 and 212 nm (180 μJ/pulse, 5 ns width, 10 Hz) are overlapped spatially and temporally in the molecular beam. The laser beams are generated by frequency tripling the output of two dye lasers (Quanta-Ray PDL-1, Lambda Physik LPD 3000), each pumped by the second harmonic of a Nd:YAG laser (Quanta-Ray DCR-3, GCR-4). The tripled light is separated by dichroic mirrors and each beam is then expanded by a 1:3 Galilean telescope and focused onto the molecular beam by a lens (nominal $f = 60$ cm in one case, 50 cm in the other). The combined pulses of light from both lasers first photolyze HBr to produce fast-moving H atoms that react with D_2 and then ionize the nascent HD(v',j') products via the two-photon $E,F\ {}^1\Sigma_g^+ - X^1\Sigma_g^+$ (0,1) REMPI transitions. One laser is detuned from the line center by 8 cm^{-1} to the blue, and the other laser is detuned to the red by the same amount so that the two-photon resonant transition can only be driven by the absorption of one photon from each laser beam. A third photon from either laser beam ionizes the excited molecule. These ions are formed in the extraction region of a Wiley-McLaren time-of-flight mass spectrometer. Extraction and acceleration voltages of −15 and −60 V, respectively, accelerate the ions toward the time- and position-sensitive detector whose output can be analyzed to yield the 3D velocity of each particle.

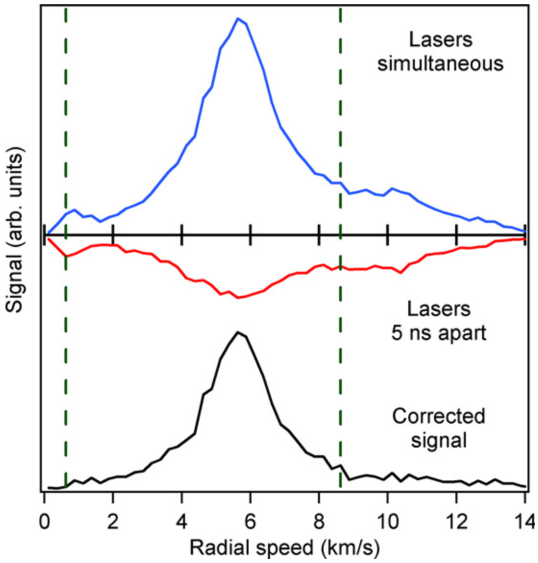

Fig. 1. Measured speed distribution with background subtraction for HD$(v' = 1, j' = 8)$. The region between the dashed lines corresponds to the range of allowed speeds for reaction with fast-channel H atoms (see Table 1).

Useful images can be obtained from fewer than 1000 events, but typically ∼5000 events are required to produce a differential cross section (DCS) with reasonable statistical error. Count rates are kept below one event/s to avoid distortion of the image by space charge, which can be identified in extreme cases by a dark channel running through the center of the image where excess Br^+ and HBr^+ ions in the laser path have repelled the HD^+ ions and depleted the signal. We combine from 3 to 6 images taken on at least two different days and use the standard deviation of the mean to estimate the error. The two-color Doppler-free detection scheme eliminates any possible Doppler-shifted background from our images, but nonresonant background ionization is still observed. By alternating on a shot-to-shot basis between firing the lasers simultaneously and offset by 5 ns, the background from both lasers can be subtracted (Fig. 1).

3. Results and discussion

3.1. Differential cross sections for the reaction H + D_2

We use the *photoloc* technique (photoinitiated reaction analyzed by the law of cosines) [19] to map the observed laboratory product speeds $|v_i|$ to unique scattering angles