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

Noah T. Goldberg, Konrad Koszinowski, Andrew E. Pomerantz [1], Richard N. Zare [*]

Department of Chemistry, Stanford University, Stanford, CA 94305-5080, USA

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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.

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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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[*] Corresponding author. Fax: +1 650 725 0259.
E-mail address: zare@stanford.edu (R.N. Zare).
[1] Present address: Schlumberger-Doll Research, 36 Old Quarry Rd, Ridgefield, CT 06877.

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
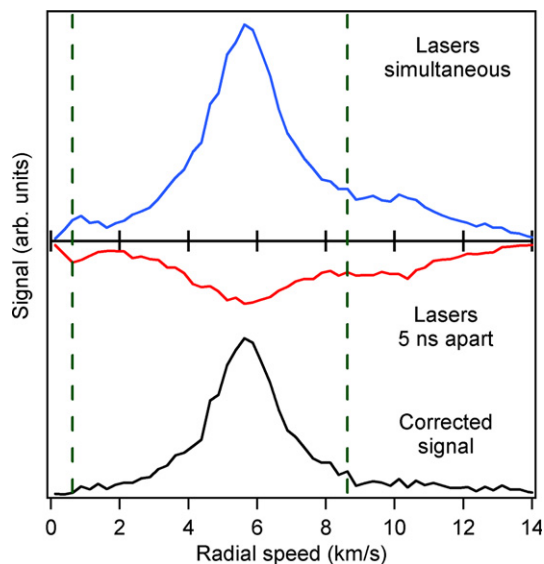

Fig. 1. Measured speed distribution with background subtraction for $HD(v' = 1, j' = 8)$. The region between the dashed lines corresponds to the range of allowed speeds for reaction with fast-channel H atoms (see Table 1).

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.

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

θ_i in the center-of-mass frame (Fig. 2). This approach has three requirements. First, the center-of-mass speed $|u_{CM}|$ must be sharply defined, which we achieve by cooling the molecular beam and by using a narrow photolysis wavelength. Second, the internal energies of the products must be known in order to calculate $|u_{prod}|$, which we achieve by ionizing only a specific rovibrational state. Finally, the distribution of laboratory speeds $|v_i|$ must be accurately determined, which we achieve by using a fast detector that can measure the 3D velocity of each ion. The angular resolution of this technique is best when $|u_{CM}|$ and $|u_{prod}|$ are similar, so that the range of laboratory speeds is maximized. The allowed range of laboratory speeds is determined by the energetics and kinematics of the system; these parameters are summarized in Table 1. The average rotational energies of the HBr and D_2 reactants in the molecular beam (0.016 and 0.023 eV, respectively) are included in the analysis and contribute about 100 m/s to the observed speeds. In Fig. 3 we compare the DCSs measured in the present experiment to previous experimental work and quantum mechanical calculations on the BKMP2 potential energy surface [20]. The calculated DCSs were convolved with a Gaussian of the same width as the photoionization recoil of the REMPI detection scheme, and all other sources of blurring were neglected. All three sets of data were normalized to the same integral cross sec-
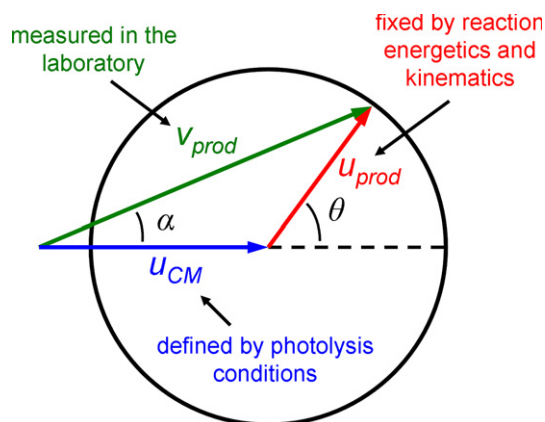

Fig. 3. Differential cross sections $I(\theta)$ weighted by $\sin \theta$ for $H + D_2 \rightarrow D + HD(v' = 1, j')$. The scattering angle is defined so that 0° corresponds to forward scattering relative to the incident H-atom direction. The results of the present work (with 1σ error bars) are normalized to the same integral cross section as the quantum mechanical calculations (solid line) and experimental results (filled triangles) from Ref. [20].

Fig. 2. Collapsed Newton diagram illustrating the *photoloc* technique. Measurement of the laboratory product speed $|v_{prod}|$ uniquely determines the triangle spanned by the center-of-mass velocity u_{CM} and the center-of-mass product velocity u_{prod}, and thus permits straightforward calculation of the center-of-mass scattering angle θ from the law of cosines.

tion. We find near-perfect agreement with the previous experiment (error bars are omitted for clarity) for all three HD product states. The resolution of the present experiment is superior to that of the old experiment and succeeds in qualitatively matching several oscillations in the quantum mechanical calculations that were previously unresolved. In particular, we observe evidence of two separate backward-scattering maxima for $HD(v' = 1, j' = 1)$ instead of a single peak, and for $HD(v' = 1, j' = 5,8)$ we see shoul-

Table 1
Summary of experimental and theoretical parameters for the reaction $H + D_2 \rightarrow D + HD(v' = 1, j')$

HD(j')	Collision energy (eV)			Allowed laboratory speed range (m/s)[a]	
	Experiment[a]		QM calculation		
	Fast	Slow		Fast	Slow
1	1.73	1.37	1.70	1577–9721	1146–8401
5	1.71	1.35	1.70	1211–9304	706–7903
8	1.67	1.31	1.64	616–8614	55–7035

[a] Photolysis of HBr proceeds by two different channels, each of which deposits a different amount of translational energy in the H atom reactant.
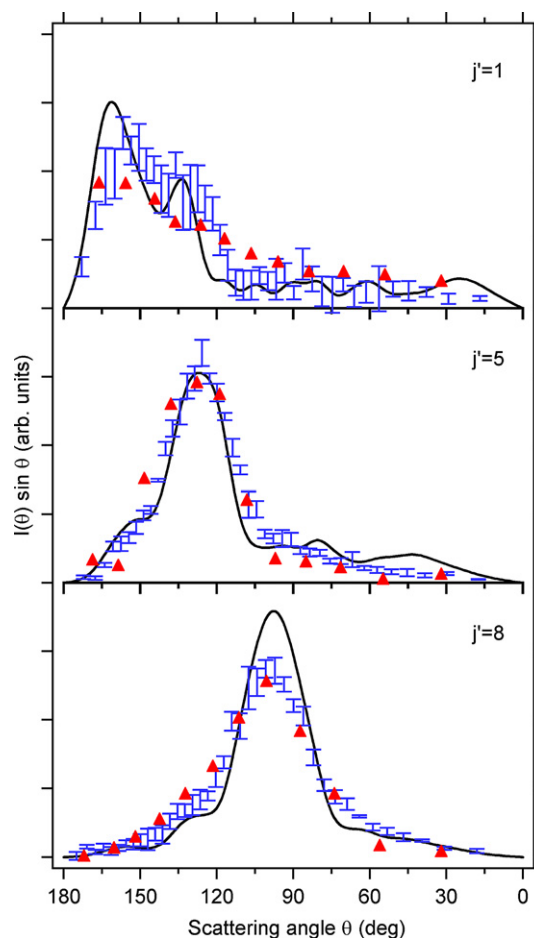
ders at 160° and 130°, respectively, that were previously unresolved from the main peak.

In previous experiments on the photolysis of HBr, we found that our velocity resolution was limited by the 420 m/s photoionization recoil of the [2 + 1] REMPI scheme for atomic hydrogen [7]. In the present experiment, the photoionization recoil varies from 157 m/s for $HD(v' = 1, j' = 1)$ to 165 m/s for $HD(v' = 1, j' = 8)$. Empirically, we find that using a bin width of 200 m/s (40 distinct scattering angles compared with 12 angular bins measured in the previous experiment [20]) maximizes the number of features that can be resolved, suggesting that the recoil is the dominant source of blurring. This finding is important because, for sharp forward scattering, even large peaks in the DCS may be too narrow in velocity space to escape being blurred into the baseline noise. It is therefore crucial to ensure that instrumental blurring is minimized.

Photolysis of HBr yields both ground-state Br and spin-orbit-excited Br*. The H atom receives different amounts of kinetic energy from each channel, so we obtain two populations at different speeds that we refer to as 'fast' and 'slow' H atoms, respectively. The allowed range of HD product speeds from the two channels differs only slightly, so for most observed speeds the signal will be a weighted sum of each channel's contribution. As Fernández-Alonso et al. [20] have discussed in detail, the slow channel is expected to make a small contribution under the present experimental conditions; the fraction of slow H atoms is 18%, but the effective contribution to the DCS also depends on the state-specific total reaction cross section, the collision rate, and the angular distribution. Knowing the full 3D velocity distribution, it is possible in principle to separate the contributions of the two reaction channels by their different spatial anisotropies. The speed-dependent anisotropy of the reaction products can be written as [19]

$$I(|v_i|, \gamma) \propto 1 + \beta_{obs}(|v_i|)P_2(\cos \gamma), \qquad (1)$$

where γ is the angle of recoil with respect to the laser polarization, P_2 is the second Legendre polynomial, and $\beta_{obs}(|v_i|)$ is an anisotropy parameter that can be obtained by fitting the image and ranges from −1 to 2. If the image contains contributions from two photolysis channels with known anisotropies β_{phot} and β'_{phot}, then

$$\beta_{obs}(|v_i|) = c_i\beta_{phot}P_2(\cos \alpha_i) + c'_i\beta'_{phot}P_2(\cos \alpha'_i), \qquad (2)$$

where α_i and α'_i are uniquely determined for each photolysis channel and laboratory speed as shown in Fig. 2, and the coefficients c_i and c'_i can be readily obtained by requiring the solution to be normalized. In practice, we have enough signal to determine $\beta_{obs}(|v|)$ reliably only near a peak in the speed distribution. Fig. 4 compares the effective speed-dependent anisotropy for $HD(v' = 1, j' = 8)$ products arising from the fast or slow channel alone with that of the measured image. For bins with too few events, the fitting procedure fails; for bins in the speed distribution that contain more than ~300 events $\beta_{obs}(|v|)$ is in good agreement with the curve for the fast channel alone. Also,
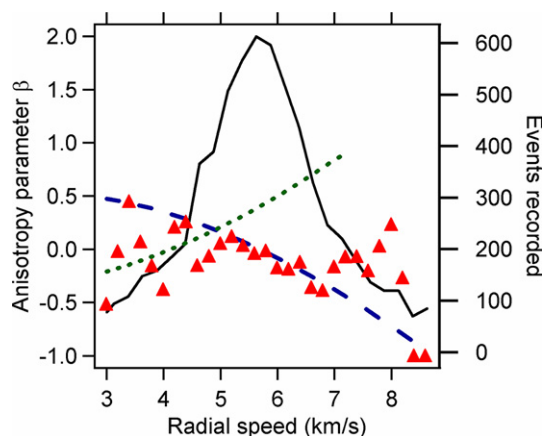

Fig. 4. The 3D image of $HD(v' = 1, j' = 8)$ is fit for the speed-dependent anisotropy parameter $\beta(|v|)$ (filled triangles) and compared with $\beta_{eff}(|v|)$ for the reaction with only fast-channel (dashed line) or slow-channel (dotted line) H atoms. The speed distribution (solid line) is shown for comparison.

after background subtraction, the radial speed distribution (Fig. 1) has essentially no signal outside the allowed speed range for reaction with fast H atoms. We observe similar behavior for $HD(v' = 1, j' = 1, 5)$ and conclude that the slow channel should not appreciably change the shape of the DCSs under the present experimental conditions, thus confirming the arguments of Fernández-Alonso et al. [20]. Averaging more scans together should in principle allow us to separate the contributions of the fast and slow channels better, except at speeds where both channels have the same effective anisotropy. This approach would be especially useful for reactions that use HI as the photolytic precursor because the fraction of slow H atoms can be as high as 40%.

Residual discrepancies between experiment and theory may arise from not comparing exactly the same quantities, such as slight differences in collision energy between the experiment and the calculations (Table 1) as well as rotational excitation of the D_2 reagent. We also cannot rule out convergence errors in the calculations, small errors in the BKMP2 surface, or experimental errors whose origins are presently unknown to us.

3.2. Two-color Doppler-free detection

Qualitatively we find that the two-color signal is of the same order of magnitude as the one-color Doppler-free signal measured when both lasers are tuned to the center of the line. For this proof-of-principle experiment we used two lasers with different bandwidths and modes, so we cannot comment quantitatively on the detection efficiency. While the sensitivity is already adequate for the difficult task of measuring DCSs of bimolecular reactions, we anticipate that the detection efficiency might be improved by several methods. One simple modification would be to improve the spatial overlap by using two identical dye lasers pumped by the same Nd:YAG laser and to narrow the two laser linewidths, for example, by use of etalons.

If only one dye laser is available, this technique could also be implemented by using a Raman cell and sending the Stokes-shifted light and the fundamental into the chamber in a counterpropagating geometry.

Reduced-Doppler ion imaging of D atoms using one dye laser and broadband 266 nm light from the 4th harmonic of a Nd:YAG laser has recently been demonstrated [17], but Doppler-free signal enhancement is greatest when the two lasers are of similar frequency and have a narrow line-width, so we expect that our technique would allow for lower laser power and thus be more appropriate for experiments that are extremely sensitive to space charge such as bimolecular reactions with small cross sections. Because we use two dye lasers, we also have the flexibility to detune each laser from the line center by an arbitrary amount in the event of nearby accidental resonances that would otherwise contribute unwanted background ions. In addition, we may easily block one of the lasers and scan over the Doppler profile with the other laser to obtain relative state distributions without modifying the imaging setup.

One characteristic of Doppler-free techniques is that the signal enhancement is greatest for fast-moving products. We expect that the technique we describe here will be most useful for forward- or side-scattered products that move quickly in the laboratory frame, and for reactions at high collision energies where more energy is available for product translation.

4. Conclusions

We have demonstrated the first use of Doppler-free ionization for 3D imaging of bimolecular reaction products. The combination of event-counting detection with Doppler-free ionization appears well suited to the difficult task of imaging reaction products with small state-specific cross sections that are especially susceptible to blurring from space charge. This method was applied to the reaction H $+ D_2 \rightarrow D + HD(v' = 1, j' = 1, 5, 8)$ and we observed previously unresolved features in the differential cross sections at 1.7 eV collision energy. The two-color Doppler-free technique can be used for both 2D and 3D imaging; it should be applicable to a wide range of reaction systems, and offers potential advantages over other ionization methods in detection efficiency, background suppression, and flexibility. The most useful application of the technique should be for reactions at high collision energies and for

scattering distributions that are side-to-forward scattered. The outlook is thus most promising for the study of non-adiabatic effects at high collision energies as well as for detecting forward-scattered resonance signatures.

Acknowledgments

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