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Doppler-free multi-photon ionization: a proposal for enhancing ion images

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Abstract

We report on the use of Doppler-free 2 + 1 resonance enhanced multi-photon ionization (REMPI) to probe H atoms resulting from HBr photolysis at 243 nm. The Doppler-free technique allows almost all H atoms to be ionized at a single probe wavelength, regardless of their lab-frame velocities. This technique yields a significant enhancement in ionization efficiency of the product while leaving the background ionization essentially unaffected. We point out the utility of this technique for the ion imaging of reaction products.

1. Introduction

Ion imaging has proven to be a powerful means of investigating molecular reaction dynamics [1]. First used in 1987, ion imaging provides a measurement of the speed and spatial distributions of products of unimolecular or bimolecular reactions [2]. Imaging experiments became especially popular after the innovations of velocity mapping and event counting [3,4]. In ion imaging experiments, reaction products typically are ionized by the absorption of one or more photons from a UV laser. The ions are accelerated in a time-of-flight mass spectrometer and amplified by multichannel plates (MCP). The MCP signal is detected with a position sensitive detector, often a phosphor screen and CCD camera, which records the two-dimensional projection of the three-dimensional velocity distribution. The full velocity distribution is then reconstructed by applying an inverse Abel transform, a forward convolution, or a variety of newly developed methods [5–9].

The resolution of many imaging experiments is limited by the presence of space charge, which distorts the ion image. To achieve reasonable signal levels, researchers typically use laser powers that are high enough to create several hundred ions, but these ions interfere to some extent with each others' flight paths. Often, many of these ions are background ions, i.e., ionized species other than the prod- uct of interest. We present a method of Doppler-free multi-photon ionization that increases the efficiency of resonant ionization without increasing the laser power, thereby creating more signal ions without changing the amount of background ions. We suggest that Doppler-free multi-photon ionization can enhance ion imaging experiments.

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Doppler-free multi-photon ionization presents a means of ionizing all molecules whose natural transitions are in resonance with the laser field, regardless of the molecule's lab-frame velocity (Doppler shift). In essence, Doppler-free ionization results from the absorption of photons propagating in different directions with the geometry arranged such that the sum of the Doppler shifts of each absorbed photon vanishes. A molecule traveling in the lab frame with a velocity **v** in a laser field of frequency ω_{laser} and propagation direction **k** observes a frequency of

$$\omega = \omega_{\text{laser}} - \overline{k} \cdot \overline{v}. \tag{1}$$

If two photons are required for a resonant transition, the frequency necessary is

$$\omega_1 + \omega_2 = \omega_{1,\text{laser}} + \omega_{2,\text{laser}} - \left(\overline{k}_1 + \overline{k}_2\right) \cdot \overline{v}. \tag{2}$$

If two laser beams are used and the geometry is arranged such that $\mathbf{k}_1 + \mathbf{k}_2$ vanishes (the laser beams are counter-propagating), then all molecules, irrespective of their velocity **v**, absorb when $\omega_1 + \omega_2 = \omega_{1,\text{laser}} + \omega_{2,\text{laser}}$ (at the center of the Doppler lineshape). We note that this analysis ignores the relativistic quadratic Doppler effect; however, even for molecules moving at 20 km/s, the shift caused by this effect is several orders of magnitude smaller than the laser bandwidth in our experiment. Hence, we shall ignore the quadratic Doppler effect in what follows.

Doppler-free multi-photon spectroscopy was developed theoretically and experimentally in the 1970s and is still commonly used to measure high-resolution gas-phase spectra [10–13]. Those spectra typically involve measuring fluorescence from the two-photon absorption, and the elimination of the Doppler effect is used to achieve narrow lines. Because the excited molecule can ionize by absorbing additional, non-resonant photon(s), this technique can also be employed for resonance enhanced multi-photon ionization (REMPI) spectroscopy. In reaction dynamics, Vrakking et al. [14] have shown that Doppler-free REMPI can be a sensitive probe of quantum state distributions of reaction products. We propose the extension of this method to imaging experiments, in which the elimination of the Doppler effect will be advantageous because it allows the detection of all product velocities at a single laser wavelength. We present data showing that this technique can provide over two orders of magnitude in the ion signal for imaging.

2. Experimental

Fig. 1 presents a block diagram of the experimental setup. We use essentially the same experimental arrangement for this experiment as we have for our studies of the $H + D_2$ reaction [15]. A single laser pulse of 243 nm light photolyzes HBr and probes the H atom products through $2 + 1$ REMPI on the 1s–2s transition. The laser light is the doubled output of a dye laser (Lambda Physik LPD 3000) pumped by the third harmonic of a Nd:YAG laser; we typically need powers of only 100 μJ/pulse. A mixture of 10% HBr in He is introduced into a vacuum chamber through a pulsed nozzle with a backing pressure of 500 Torr. Ions

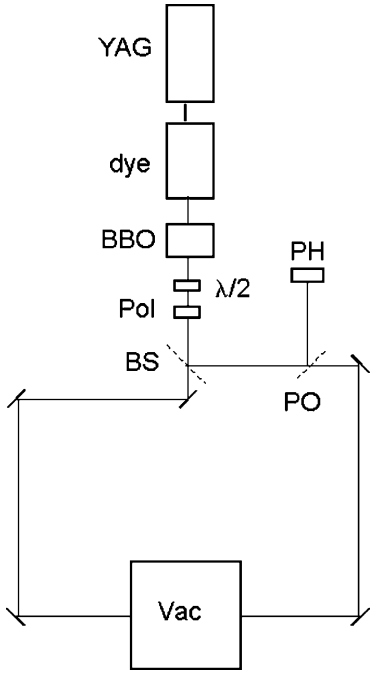

Fig. 1. Experimental block diagram. The waveplate ($\lambda/2$) and polarizer (Pol) are used to attenuate the power. The beam splitter (BS) divides the main beam into two almost equal halves. A pickoff (PO) and power head (PH) are used to measure the power in the half with slightly more power. Both halves have approximately the same path length to the vacuum chamber.

are accelerated in a Wiley–McLaren time-of-flight apparatus toward a MCP detector. An Einzel lens has been installed to facilitate collection of fast moving H atoms.

To achieve Doppler-free ionization, we separate the laser beam into two almost equally intense beams using a 1:1 beam splitter (CVI lasers Corp.). The beams are directed through separate delay lines to achieve temporal overlap, and they are focused into the center of the chamber with lenses of equal focal lengths. Beams are made to overlap by directing each one so it travels back through the other beam path, with a slight offset introduced to prevent feedback into the laser. As will be discussed, this slight offset does not impair the Doppler-free signal. Both lenses are held in XYZ translational stages to optimize spatial overlap. We note that Doppler-free REMPI could be achieved with a spherical mirror to reflect and refocus the beam, in place of the beam splitter, and advantages and disadvantages of this technique are discussed below.

Fig. 2 presents three spectra: the spectrum obtained with light propagating to the left only (L), the one obtained with light propagating to the right only (R), and the one obtained with both beams simultaneously overlapped (L&R). L and R are normal Doppler-broadened spectra. Each shape comes from the weighted sum of the two channels of HBr photolysis: H + Br (83%) with $\beta = -1$ and H + Br* (17%) with $\beta = -2$ [16]. Spectrum L&R contains two components. The first component results when the resonant transition arises from the absorption of two photons with the same propagation direction followed by (non-resonant) ionization from a photon going either direction; that component has the same shape as the normal Doppler profile (L or R). The second component is Doppler-free ionization. It results when the resonant transition arises from the absorption of one photon from each of the two propagation directions. In this case, the Doppler shifts cancel, so this component occurs almost exclusively only at the line center. Here, all H atoms are ionized regardless of their lab-frame velocity. Because the laser bandwidth is much smaller than the Doppler width, only a fraction of the H atoms are ionized at a single wavelength in the Doppler-broadened spectra. In contrast, for the Doppler-free case, all H atoms are ionized at the same wavelength, resulting in the strong peak at the line center.

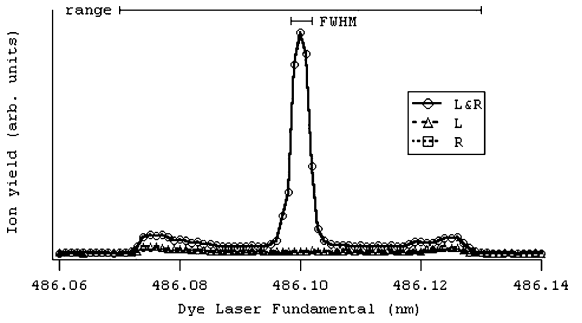

Fig. 2. Doppler profiles of H atoms from HBr photolysis. The spectra taken with the beam propagating to the left, L (dashed line) or right, R (dotted line) are almost identical and are barely seen on this scale. Spectrum L&R (solid line) shows an intense Doppler-free peak riding on a shallow Doppler-broadened pedestal. The amount of signal at the center of L&R is about 130 times larger than the average signal in spectrum L or spectrum R. That signal enhancement is the result of Doppler-free $2+1$ REMPI. The range and FWHM are defined in the text.

3. Theory

Several expressions for two-photon absorption have appeared in the literature [17–20]. Making the electric dipole approximation and neglecting relaxation and saturation of the resonant step, the probability for $2+1$ REMPI of a molecule with velocity $\overline{v}$ starting in a state $|i\rangle$, going through a virtual state $|n\rangle$ to a final state $|f\rangle$ and then to the ionization continuum is

$$\begin{aligned} P(\omega_1,\omega_2) = \Bigg[& \sigma_{11} I_1^2(\omega_1)\delta\{\omega_{fi} - 2(\omega_1 - \overline{k}_1\cdot\overline{v})\} \\ & + \sigma_{22} I_2^2(\omega_2)\delta\{\omega_{fi} - 2(\omega_2 - \overline{k}_2\cdot\overline{v})\} \\ & + \sigma_{12}\frac{\sqrt{2}}{\sqrt{\frac{\tau_1^2+\tau_2^2}{\tau_1\tau_2}}}\exp\left\{-\frac{(t_1-t_2)^2}{\tau_1^2+\tau_2^2}\right\} \\ & \times I_1(\omega_1)I_2(\omega_2)\delta\{\omega_{fi} - \omega_1 - \overline{k}_1\cdot\overline{v} - \omega_2 \\ & - \overline{k}_2\cdot\overline{v}\}\Bigg][I_1(\omega_1) + I_2(\omega_2)]^n, \end{aligned} \tag{3}$$

where the laser pulses are assumed to be temporally Gaussian with peak intensity I_i, temporal

center t_i, and width τ_i. The frequencies are defined as ω_i being the frequency of laser i and ω_{ij} being the frequency of the molecular transition between states $|i\rangle$ and $|j\rangle$. The resonant step is assumed unsaturated, and the ionization step has power law of n. The cross sections are sums over virtual states and are defined as

$$\begin{aligned}
\sigma_{11} &\equiv \left| \sum_n \frac{\langle f|\overline{\mu}\cdot\overline{E}_1|n\rangle\langle n|\overline{\mu}\cdot\overline{E}_1|i\rangle}{\omega_{ni}-\omega_1-\overline{k}_1\cdot\overline{v}} \right|^2, \\
\sigma_{22} &\equiv \left| \sum_n \frac{\langle f|\overline{\mu}\cdot\overline{E}_2|n\rangle\langle n|\overline{\mu}\cdot\overline{E}_2|i\rangle}{\omega_{ni}-\omega_2-\overline{k}_2\cdot\overline{v}} \right|^2, \\
\sigma_{12} &\equiv \left| \sum_n \frac{\langle f|\overline{\mu}\cdot\overline{E}_1|n\rangle\langle n|\overline{\mu}\cdot\overline{E}_2|i\rangle}{\omega_{ni}-\omega_2-\overline{k}_2\cdot\overline{v}} \right|^2 \\
&\quad + \left| \sum_n \frac{\langle f|\overline{\mu}\cdot\overline{E}_2|n\rangle\langle n|\overline{\mu}\cdot\overline{E}_1|i\rangle}{\omega_{ni}-\omega_1-\overline{k}_1\cdot\overline{v}} \right|^2 \\
&\quad + \left(\sum_n \frac{\langle f|\overline{\mu}\cdot\overline{E}_1|n\rangle\langle n|\overline{\mu}\cdot\overline{E}_2|i\rangle}{\omega_{ni}-\omega_2-\overline{k}_2\cdot\overline{v}} \right) \\
&\quad \times \left(\sum_n \frac{\langle f|\overline{\mu}\cdot\overline{E}_2|n\rangle\langle n|\overline{\mu}\cdot\overline{E}_1|i\rangle}{\omega_{ni}-\omega_1-\overline{k}_1\cdot\overline{v}} \right)^* \\
&\quad + \left(\sum_n \frac{\langle f|\overline{\mu}\cdot\overline{E}_1|n\rangle\langle n|\overline{\mu}\cdot\overline{E}_2|i\rangle}{\omega_{ni}-\omega_2-\overline{k}_2\cdot\overline{v}} \right)^* \\
&\quad \times \left(\sum_n \frac{\langle f|\overline{\mu}\cdot\overline{E}_2|n\rangle\langle n|\overline{\mu}\cdot\overline{E}_1|i\rangle}{\omega_{ni}-\omega_1-\overline{k}_1\cdot\overline{v}} \right).
\end{aligned} \tag{4}$$

Because the virtual states are not resonant with the laser light, the Doppler effect should have only a small effect on the cross sections. If both beams have the same frequency, temporal width, and polarization (as would result from using a beam splitter or a spherical mirror), the transition probability simplifies to

$$\begin{aligned}
P(\omega) = \sigma \Bigg[& I_1^2(\omega)\delta\{\omega_{fi} - 2(\omega - \overline{k}_1\cdot\overline{v})\} \\
& + I_2^2(\omega)\delta\{\omega_{fi} - 2(\omega - \overline{k}_2\cdot\overline{v})\} \\
& + 4\exp\left\{ -\frac{(t_1-t_2)^2}{\tau_1^2+\tau_2^2} \right\} I_1(\omega)I_2(\omega)\delta\{\omega_{fi} - 2\omega \\
& - (\overline{k}_1+\overline{k}_2)\cdot\overline{v}\} \Bigg] [I_1(\omega)+I_2(\omega)]^n.
\end{aligned} \tag{5}$$

The Doppler spectrum can be obtained by convoluting this probability by the distribution of molecular velocities. The first two terms are the absorption of two photons with the same propagation direction. If the beams are counter-propagating, then $\overline{k}_1 + \overline{k}_2 = 0$ and the final term contains no dependence on the molecular velocity; it represents Doppler-free ionization.

4. Application to ion imaging

The most popular means of analyzing imaging data require the detection of the entire product velocity distribution, but products typically move so quickly and laser bandwidths are usually so narrow that only a Doppler-selected subset of the products are ionized at a single wavelength. To overcome this problem, researchers typically scan the probe laser over the Doppler lineshape, attempting to produce a top-hat frequency profile [21]. The Doppler-free method, in which all molecules are ionized at a single laser wavelength, presents an alternative approach. This method has the advantage of obviating the need to scan the laser source over the line profile, which prevents having to correct for changes in detection efficiency during the course of an experiment. For example, any etaloning of laser power must be corrected for during a scan, but such a correction would be unnecessary in a Doppler-free setup.

The main advantage of the Doppler-free technique, however, is the large increase in ionization efficiency of the product of interest without a corresponding gain in background ionization. In our experiment, we measure the Doppler-free signal enhancement by comparing the yield of ionized H atoms obtained by allowing only one beam to enter the chamber to the yield obtained with both beams. With a single beam, the Doppler effect is significant, so the important quantity is the average signal obtained at each wavelength in the Doppler profile. With both beams, the Doppler effect is eliminated, so the important quantity is the signal obtained at the center of the line. We call these quantities important because they correspond to the amount of signal available in an imaging experiment. We assume here that the

power in each beam is equal, so there is twice as much power when both beams enter the chamber than when a single beam enters. The theoretical signal enhancement for two beams versus one beam is

$$4 \cdot 2^n \frac{\text{range}}{\text{FWHM}}. \quad (6)$$

The factor of 4 comes from the quantum mechanical interference between two indistinguishable paths for Doppler-free REMPI [22]. The factor of 2^n comes from the ionization of the excited molecule. We assume that non-resonant ionization takes place with a power law of n, so when the power is doubled the signal increases by 2^n. This term accounts for events like resonant absorption coming from two photons propagating to the left followed by ionization from the absorption of a photon propagating to the right. The biggest enhancement originates from the last term. The 'range' is the width of the Doppler-broadened spectrum and the 'FWHM' is the full-width at half maximum of the Doppler-free peak (see Fig. 2). This term represents the gain from ionizing all products at once versus ionizing only a Doppler-selected subset. We assume the resonant transition probability goes as the square of the intensity (unsaturated) and that all broadening factors are small compared to the laser bandwidth. In this case, the 'FWHM' is $\sqrt{2}$ times smaller than the laser bandwidth for a laser with a Gaussian frequency profile [23]. For our modest laser bandwidth of 0.38 cm^{-1}, the Doppler-free enhancement was a factor of 130. Some of this enhancement (about a factor of 7) arises simply from the doubling of the laser power, but the majority of the enhancement comes from the Doppler-free nature of the ionization process (about a factor of 20). Because the enhancement scales inversely with laser bandwidth, the use of a narrow bandwidth laser could further accentuate this effect.

The important point about this technique is that the efficiency of ionization occurs only for products that are resonantly ionized. Background molecules are typically ionized non-resonantly, so this technique would not cause such an increase in background ionization. If the laser beam is split, the total laser power is not increased and thus no increase in background ionization results; this case corresponds to a signal enhancement in our experiment of the factor of 20. If the laser were reflected with a spherical mirror, the laser power would increase by a factor of 2, so there would be some increase in background ionization; however, this case corresponds to a signal enhancement in our experiment of the factor of 130. The choice of whether to use a beam splitter or a spherical mirror would depend on the relative power laws for resonant versus non-resonant ionization. In either case, the signal-to-background ratio is greatly increased. In an imaging experiment, this benefit would allow the collection of a higher amount of signal without as much background ionization to cause space charge and therefore to lower the image's resolution. The amount of image degradation caused by background ionization varies with the experimental setup, so it is difficult to quantify the conversion of the signal-to-background ratio into a signal-to-noise ratio or image resolution.

This technique appears to be quite robust in its applications to imaging experiments. A potential problem could occur if the beams are not perfectly counter-propagating. In that case, the Doppler shifts do not exactly cancel, so slow moving molecules are ionized more efficiently than quickly moving ones. However, that effect will usually be quite small. If the beams are somewhat skewed, then $\overline{k}_1 + \overline{k}_2$ (the effective beam propagation direction) will be small in magnitude and will point almost perpendicular to the laser propagation directions. For our laser with 0.38 cm^{-1} bandwidth at 243 nm, if the laser beams are skewed by 1°, the theoretical efficiency of ionizing molecules traveling 20 km/s perpendicular to the laser propagation is still 98% of the efficiency of ionizing stationary molecules.

Detuning the laser from the center of the line could present another problem. Although detuning the laser would lower the ion yield, it would not introduce any bias toward slow or fast moving particles. Even if the beams are skewed as before, detuning the laser by 0.5 nm in the UV does not significantly increase the bias toward slow molecules.

In addition, imperfect temporal overlap does somewhat decrease the ionization efficiency.

However, for a beam of 4 ns FWHM, the theoretical ionization efficiency with delay lines mismatched by 10 cm is still 96% of the efficiency for perfectly overlapped beams. Fortunately, imperfect temporal overlap does not introduce any velocity bias.

A complication can occur in the analysis of imaging experiments for molecules moving perpendicular to the laser propagation direction. With the laser at the line center, those molecules can be ionized by both Doppler-free and Doppler-broadened methods. The Abel transform is most straightforwardly applied in the absence of the Doppler-broadened contributions, and there are several means to make this correction. The simplest method is to ignore that part of this ion image. This part is frequently along the symmetry axis of the image, which is often ignored anyway owing to the noise associated with the Abel transform. The second method is to subtract out the Doppler-broadened contribution. As can be seen in the ion yield expressions, Doppler-broadened ionization makes up one-third of the total signal for molecules traveling perpendicular to the propagation axis; thus, their contribution can be effectively removed. Finally, by changing the polarization of the laser beams, we could exploit the different selection rules for Doppler-free and Doppler-broadened ionization to suppress the Doppler-broadened background [13]. Similarly, we could use two lasers of different frequency such that the resonant transition cannot be achieved by either laser individually.

5. Conclusion

We have presented results on Doppler-free $2+1$ REMPI applied to the detection of H atom photofragments in the photolysis of HBr, and we have discussed the potential applications of this technique to ion imaging experiments. In the present experiment, two counter-propagating laser beams were employed to ionize the product of interest at one wavelength, regardless of the product's lab-frame velocity. If more photons are needed for the resonant transition, different geometries may be employed [13]. Ionizing all products simultaneously results in a large increase in the amount of signal, while keeping the laser power roughly constant prevents a large buildup in background ionization. For some imaging experiments in which only a subset of the products is ionized, this technique is not beneficial [24]. However, those methods often require an unacceptably high reduction in signal [25]. For imaging experiments in which the full three-dimensional velocity distribution of products is to be analyzed, this technique should be beneficial. Those experiments include ones in which either the distribution of the ion's arrival position or arrival time and position are measured (two- or three-dimensional detection). The utility of Doppler-free multi-photon ionization is especially apparent for quickly moving products or narrow-bandwidth lasers.

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