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# Spatial discrimination of Rydberg tagged molecular photofragments in an inhomogeneous electric field

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A new approach to detecting the spatial and energetic distribution of photodissociation products is demonstrated, in which an inhomogeneous electric field is used for spatially selective field ionization of Rydberg molecules. State-selected NO fragments from NO<sub>2</sub> photodissociation in a supersonic beam are excited to high-*n* Rydberg states and allowed to expand through the inhomogeneous field provided by an octopole. The field in the octopole results in the field ionization of those fragments that have moved to large radial distances (~5 mm) from the beam axis, and therefore this device transmits only those Rydberg molecules with a low velocity component in the direction perpendicular to the beam. A detailed characterization of the properties of this "steradiancy analyzer" is carried out and factors limiting the energy resolution (currently approximately 100 cm<sup>-1</sup> at an excess energy of 250 cm<sup>-1</sup>), along with possible improvements, are discussed in detail. © 2001 American Institute of Physics. [DOI: 10.1063/1.1408286]

### I. INTRODUCTION

### A. Spatially selective field ionization

The application of ion-imaging techniques to measure the spatial anisotropy and the energy distribution of product molecules from simple gas-phase chemical processes has been a rapidly developing field in recent years.<sup>1,2</sup> The measurements provide fundamental tests of the quality of ab initio potential energy surfaces and of the dynamics on those surfaces. In our own laboratory we have developed an interest in the near-threshold dynamics,<sup>3</sup> as these may be sensitive to more subtle features of the potential energy surface and a wider range of nuclear configurations. In this paper a new approach for obtaining spatial and energetic information is described, which is potentially of value in these nearthreshold studies and in a wider sphere. Product molecules from a photodissociation event are excited into high-n Rydberg states, and are then subjected to a pulsed inhomogeneous electric field. The probability of field ionization depends on the spatial position of the fragments at the time the field is applied. Thus by detecting either the Rydberg-tagged molecules surviving the applied pulsed field, as in the present experiments, or by detecting the ions produced by field ionization in the inhomogeneous field, spatial discrimination is achievable. Furthermore, it should be possible to establish a complete picture of the spatial distribution by varying the field magnitude and its time of application. In this paper we discuss how the field configuration and other

experimental parameters might be optimized so as to obtain the best spatial resolution in such an experiment.

The first system investigated and reported here uses an electrostatic octopole, comprising eight cylindrical electrodes of alternating polarity equally spaced around a circle, to provide the inhomogeneous field. The photodissociation of  $NO_2$  in a supersonic beam is the simple reaction under study. The experimental apparatus is illustrated schematically in Fig. 1. After photodissociation of NO<sub>2</sub> in Region I, the NO photofragments are excited to high-n Rydberg states (n  $\sim$ 120) by the probe lasers and the fragment cloud is allowed to expand as the beam passes centrally through the octopole in Region II. A pulsed voltage is applied to the octopole when the fragment cloud is well inside this device and the resulting field rises sharply with radial distance from the beam axis. Fragments produced at energies very close to a dissociation threshold have essentially zero kinetic energy in the center-of-mass frame and remain in the molecular beam. Fragments produced at energies significantly above the relevant dissociation threshold may have high velocities perpendicular to the molecular beam axis. These fragments travel to a region where the field strength is large when the pulsed voltage is applied, and are field ionized. The ions produced in the octopole are discarded, while the Rydberg states that survive the octopolar field are transmitted into Region III, where they are ionized and accelerated onto a detector.

The octopole provides a mechanism for discriminating against fragments produced with nonzero kinetic energies, thus representing a first step in the direction of a *tunable* kinetic energy aperture. The effective size of the aperture is changed by varying either the principal quantum number of Rydberg states excited (i.e., the excitation wavelength) or the

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FIG. 1. Schematic of the experimental setup.

applied octopole voltage. The device has been fully characterized and its behavior is analyzed in detail using a combination of ion imaging and Mass Analyzed Threshold Ionization (MATI) spectroscopy. The octopole constitutes an example of a more general class of experiments employing inhomogeneous electric fields and Rydberg excitation to manipulate<sup>4,5</sup> or analyze spatial distributions of neutral atoms or molecules.

#### B. NO<sub>2</sub> photodissociation

The dissociation process under study may be written as

$$NO_2 + h\nu \rightarrow NO(\upsilon'', J'') + O({}^3P_J).$$
(1)

The photodissociation channels are defined by the possible vibration-rotation states of the NO fragments (v'',J'') and the three possible spin-orbit states (J) of the oxygen atom  ${}^{3}P_{2}$ ,  ${}^{3}P_{1}$ , and  ${}^{3}P_{0}$ . Energy conservation requires that

$$h\nu = D_0 + E(v'', J'') + E(J) + KE,$$
(2)

neglecting the initial energy of the parent NO<sub>2</sub> molecule, where *KE* is the total kinetic energy of both products, and  $D_0$  is the dissociation energy. The NO fragments are detected state-selectively in the present experiments, fixing E(v'', J''), and thus the quantity  $E_{avl}$  is defined here as the available excess energy for distribution among the kinetic energy of the products and the spin–orbit energy of the O atom,

$$E_{\rm avl} = KE + E(J) = h\nu - D_0 - E(v'', J'').$$
(3)

For any detected quantum state (v'', J'') of NO the total kinetic energy of the products, *KE*, will be equal to  $E_{avl}$ ,  $E_{avl}-158 \text{ cm}^{-1}$  and  $E_{avl}-226 \text{ cm}^{-1}$  for the NO  $(v'', J'') + O({}^{3}P_{J})$ , J = 2,1,0 channels, respectively.

 $NO_2$  photodissociation was chosen as the system to test the octopolar device, building on the previous measurements of angular distributions for near-threshold photodissociation of this molecule in our laboratory. The state-selected Rydberg tagging of NO was demonstrated in previous experiments,<sup>3</sup> guaranteeing the long lifetimes necessary for a successful application of the octopole. Furthermore the photodissociation anisotropy parameters, of importance in the present work, were investigated in detail in Ref. 3 for the channels studied here.



FIG. 2. MATI probing scheme for NO photofragments (v''=0, J''=17/2) as used in the PHOMPFI (photofragment multiphoton pulsed-field ionization) and imaging experiments (see Sec. III).

#### **II. EXPERIMENT**

### A. Excitation and detection

The experimental set-up, illustrated in Fig. 1, is a modification of the apparatus described in Ref. 3. The pulsed supersonic beam of NO<sub>2</sub>, seeded in He at 0.5% molar fraction, is introduced into the experimental chamber (maintained at less than  $10^{-7}$  mbar) via a 0.5 mm diameter skimmer. The molecular beam is intersected at right angles by the photolysis laser beam and by two additional laser beams required to excite the NO fragments to the high-n Rydberg states. The probing scheme is illustrated in Fig. 2. The nascent NO fragment molecules in the  $v''_{NO} = 0$ ,  $J''_{NO} = 17/2$  state are probed in a (1+1') mass analyzed threshold ionization (MATI) scheme via the  $Q_{11}/P_{21}(17/2)$  transitions in the  $\tilde{A} \leftarrow \tilde{X}(0,0)$ band of NO. The detection of the J'' = 17/2 channels for the NO product was chosen because the population of this level in the background NO impurities contributed negligibly to the NO<sup>+</sup> ion yield at the rotational temperature of 5-8 K in the supersonic expansion. Also, the chosen rotational transition from J'' = 17/2 corresponds to an isolated line in the (1+1') REMPI (resonance-enhanced multiphoton ionization) spectrum via the  $\tilde{A}$  state and, as shown below, the broad MATI peaks converging to the various accessible ionic thresholds of NO are widely separated. Therefore, high-n Rydberg states with a single core angular momentum and narrow range of n could be tagged when probing the fragments.

The linearly polarized output of a frequency-doubled, Nd:YAG-pumped optical parametric oscillator (Quanta Ray GCR 190/MOPO 730, 10 Hz, 8 ns pulse, ~2 mJ per pulse), acts as the tunable photolysis source in the near-threshold region at  $\lambda \sim 390$  nm. The photolysis laser is weakly focused and has a linewidth  $\Gamma_{\text{phot}} \approx 0.3 \text{ cm}^{-1}$ . The frequency-tripled output of a Nd:YAG-pumped dye laser (Spectron 4000G/ SL800, Pyridine-1/DCM dye mixture, ~226 nm, 300  $\mu$ J per pulse) is used to excite the desired NO fragment mol-

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ecules to the *A* state. A second, frequency-doubled Nd:YAGpumped dye laser (Spectron 4000G/SL800, DCM dye, ~326 nm, 4 mJ per pulse), is used to excite from the *A* state to the high-*n* Rydberg states. The probing laser beams are introduced coaxially and are perpendicular to both the molecular beam axis and the photolysis laser beam. They are gently focused by a cylindrical fused-silica lens (f=15 cm). The laser providing excitation to the high-*n* Rydberg states is constantly monitored by a pulsed wavemeter (Burleigh WA 4500) so as to correct for any wavelength drifts in the course of the experiments. This ensures that, throughout the data acquisition, only states within the selected range of principal quantum number *n* are excited.

The photodissociation and fragment excitation take place in Region I between the skimmer plate and a fine-mesh electrode, both kept at ground potential. The fragment cloud travels into Region II at the beam velocity, where it passes centrally through the octopole. A positive voltage pulse,  $+U_{8n}$ , of 4  $\mu$ s duration and 50 ns rise time is applied to every second octopole rod, while a carefully matched negative voltage pulse,  $-U_{8p}$ , is applied simultaneously to the remaining rods. A small constant repelling field is applied across Region II to suppress any signal due to prompt ions or NO Rydberg states field ionized in the octopole. The fragments that are not ionized by the discrimination or octopole fields in Region II, enter Region III, where a 200 V/cm electric field pulse is applied. The Rydberg-tagged NO molecules are field-ionized by the pulse and this field serves also to accelerate the fragment cloud towards the detector. The electric field pulse is carefully timed so as to ionize the whole fragment sphere.

The ionized fragment cloud is accelerated further by a stack of dynodes and crushed onto a microchannel plate detector (Gallileo, 40 mm diameter) coupled to a phosphor screen. The total ion signal can be detected by a photomultiplier tube, amplified, averaged over typically ten shots in a boxcar integrator, and fed via an analog-digital converter to a computer. In the imaging mode, the phosphor screen output is recorded by a fiber-optically coupled CCD camera (Proxitronic HR0, 768×576 pixels). The captured frames are sent to a frame grabber (Coreco Ultra II) and the acquisition is controlled from a PC. Images are averaged over 20 shots using standard image acquisition and analysis software (Visilog 5, Noesis S.A.) and accumulated over typically 300 cycles. Fewer than 100 ions are obtained per laser shot. Owing to the low kinetic energy of the fragments, the probing lasers do not need scanning over the Doppler profile during image acquisition. The acquired images are centered, symmetrized and filtered prior to Abel inversion,<sup>6</sup> which generates the original three-dimensional fragment distribution.

### B. MATI spectrum of NO

Figure 3 shows an overview of the (1+1') MATI spectrum of NO produced by photolysis of NO<sub>2</sub> just a few cm<sup>-1</sup> above the dissociation threshold for the channel detected. The NO (J''=17/2) fragments are excited via the  $A(v'_{NO}=0, N'_{NO}=8)$  intermediate with the J'=17/2 and 15/2 levels unresolved (see Fig. 2). A discrimination field of 1.8



FIG. 3. Overview MATI spectrum of nascent NO  $(J_{NO}'^{2}=17/2)$  produced by near-threshold photodissociation of NO<sub>2</sub> (excitation via N'=8 as shown in Fig. 2).

V/cm is employed to reject prompt ions and no voltage is applied to the octopole. The spectrum shows a group of broad features associated with the field ionization of high-n Rydberg series converging to the various ionic thresholds,  $N^+=5$  to 10, accessible from  $N'=8.^{3,7}$  The Rydberg series converging to the  $N^+ = 10$  threshold corresponds to the highest series accessible with significant oscillator strength. The sharp peaks within the  $N^+ = 5$  to 9 broad features, for example, the peak at 74710  $\text{cm}^{-1}$  or the series in the range  $74730-74760 \text{ cm}^{-1}$ , are due to channel interactions between the Rydberg states converging on a higher threshold (higher  $N^+$ , lower n) and the detected high-n pseudo-continuum.<sup>8</sup> The intensity associated with the  $N^+=9$  threshold is derived almost entirely from such interactions. The  $N^+ = 10$  feature is the only one not to show obvious perturbations due to these channel interactions, and it is therefore ideally suited for characterizing the octopole. However, in some of the experiments shown below it was necessary to use the  $N^+ = 8$ MATI peak in order to gain sufficient transition intensity. The substructure in the main  $N^+ = 8$  feature reveals strong final-state interactions with the series converging to the  $N^+$ = 9 and  $N^+$  = 10 thresholds. The Rydberg series, simulated with an average quantum defect of  $\overline{\delta}_p = 0.7$ , are indicated in Fig. 4.

#### C. Potential and field of an octopole

An ideal multipole with 2n poles at potential  $\Phi_0$ , is defined as one for which the electric potential  $\Phi(r,\varphi)$  and field magnitude *F* are given in a plane perpendicular to the axis by<sup>9</sup>

$$\Phi(r,\varphi) = \Phi_0 \hat{r}^n \cos n\varphi, \tag{4}$$

$$F = \left| -\vec{\nabla} \Phi(r, \varphi) \right| = \frac{\Phi_0}{r_0} n \hat{r}^{n-1},$$
(5)

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FIG. 4. MATI spectrum via N' = 8 in the vicinity of the  $N^+ = 8$  threshold. The Rydberg series converging to the  $N^+ = 8$ , 9 and 10 thresholds are simulated with an average *p*-quantum defect of  $\overline{\delta}_p = 0.7$  and are displayed to a maximum of n = 100. The dashed-line box indicates the region where the mixed diabatic/adiabatic field-ionization efficiency due to the repelling field ( $F_{\text{rep}} = 1.8$  V/cm) drops from one (at the high-energy edge, IP- $3.1\sqrt{F_{\text{rep}}}$ ) to zero (at IP- $6.1\sqrt{F_{\text{rep}}}$ ). The arrow marks the energy at which the probe lasers were fixed when recording images and PHOMPFI spectra.

where *r* and  $\varphi$  are two-dimensional polar coordinates in a coordinate system with its origin at the center of the device,  $r_0$  is the characteristic dimension of the multipole, and  $\hat{r} = r/r_0$ . The electric field magnitude varies only with the radial distance from the center, and as *n* increases the electric field strength rises more steeply as a function of radial distance. It is thus possible to have a region of negligible electric field magnitude in the center and considerable field strength at small distances from the center.

A good approximation to the ideal multipole can be obtained using 2n cylindrical rods equally spaced on an inscribed circle of radius  $r_0$  with the diameter of the rods dchosen to fulfill

$$r_0 = \frac{(n-1)d}{2}.$$
 (6)

The octopole in our experimental setup consisted of eight polished stainless steel rods of diameter 6.66 mm and length 10 mm arranged on a circle with  $r_0 = 10$  mm internal radius. Figures 5(a) and 5(b) show SIMION<sup>TM</sup> simulations of the electric potential and the electric field magnitude in the plane bisecting the octopole. Note that the electric field magnitude around the eightfold axis of the octopole is indeed approximately cylindrically symmetric. The radial variation of the field is also shown in Fig. 5(c) for a range of applied voltages and for the chosen experimental geometry. When voltages of more than  $\pm 100$  V are applied, the field strength is already 0.4 V/cm at a position within 1 mm from the center. Although this field will only ionize Rydberg states with n $\geq$  200, it is sufficient to cause full *l* mixing for states with  $n \ge 100$  and may affect the lifetimes of these states (see below).



FIG. 5. SIMION<sup>TM</sup> simulations of (a) the electric potential and (b) lines of constant electric field strength inside an infinitely long octopole. (c) Simulated electric field strengths as a function of the radial distance from the central axis of the octopole, for the experimental geometry employed, with various potentials applied to the octopole.

### III. RESULTS: CHARACTERIZATION OF THE OCTOPOLE PERFORMANCE

### A. Fragment yield as a function of available excess energy $(E_{avl})$

By fixing the probe lasers to a given position in the MATI spectrum ( $N^+ = 8$ ,  $n \sim 125$  in this case), and scanning the photodissociation laser, the total fragment yield for the selected rotational state of NO can be recorded as a function of available excess energy  $(E_{avl})$ . The Photofragment Multiphoton Pulsed-Field Ionization (PHOMPFI) spectrum thus obtained for J'' = 17/2 is shown in Fig. 6(a). This spectrum is analogous to the photofragment multiphoton ionization (PHOMPI) spectra reported in Ref. 3 (with any differences due to the parent molecular beam temperature), and is proportional to the partial photodissociation cross section into the NO(J''=17/2) + O $({}^{3}P_{J})$  channels, convoluted with the detection efficiency function. The spectrum shows the characteristic broad overlapping resonances associated with the excited potential energy surface of the NO<sub>2</sub> parent molecule. These "Ericson fluctuations" are observed near threshold in the partial photodissociation cross-sections for all channels.<sup>10</sup> Figure 6(b) shows the effect on the PHOMPFI spectrum of applying a  $\pm 60$  V pulsed voltage to the octopole. The de-



FIG. 6. PHOMPFI spectra with (a) 0 V and (b)  $\pm 60$  V applied to the octopole, pulse duration 4  $\mu$ s. Both spectra are recorded by scanning the photodissociation wavelength and detecting NO in the state  $X^2 \Pi_{1/2}, v_{NO}^{"} = 0$ ,  $J_{NO}^{"} = 17/2$ , by excitation to the  $N^+ = 8$ ,  $n \sim 125$  Rydberg states, followed by field ionization after transmission through the octopole. (c) The effective transmission function obtained by dividing the signal shown in (b) by that in (a). The available excess energy  $E_{avl}$  is defined in Eq. (3).

tected fragment flux in the PHOMPFI spectrum starts to decrease with respect to the spectrum at 0 V at an available excess energy of greater than  $120 \text{ cm}^{-1}$ , due to discrimination against the more energetic fragments by field ionization in the octopole. The discrimination is demonstrated more clearly in Fig. 6(c), which shows the ratio of the spectra in (a) and (b), effectively the transmission function for the octopole.

This effect can be investigated in a different manner by recording the remnant pulsed-field ionization (PFI) signal intensity at various excess energies,  $E_{\rm avl}$ , as a function of the voltage applied to the octopole, as shown in Fig. 7. For near-zero excess energy, the Rydberg-tagged photofragments survive even when moderately large voltages are applied to the octopole rods, while at higher excess energies the signal due



FIG. 7. The relative transmission efficiency (MATI signal normalized to 1 at  $U_{8p}=0$ ) for Rydberg states passing through the octopole as a function of the applied voltage. The octopole voltage tuning curves are shown for three different available energies  $E_{avl}$  [defined in Eq. (3)] with excitation to Rydberg states near  $N^+=8$ , n=125.



FIG. 8. Abel-inverted images with  $E_{\rm avl}$ =325 cm<sup>-1</sup>, and voltages applied to the octopole (a) 0 V, (b) ±30 V, (c) ±40 V, and (d) ±60 V. The signal amplification is steadily increased from (a) to (d) such that the intensity in (d) is effectively magnified by a factor of ~100 compared to (a).

to more energetic fragments decreases rapidly with applied octopole voltage. It is interesting to observe that if the octopole voltage is increased beyond approximately  $\pm 40$  V the PFI signal decreases markedly even for a negligible fragment kinetic energy. At the highest voltages investigated ( $\sim 100$ V), any kinetic energy discrimination is impossible, since neither fast nor slow fragments survive the inhomogeneous electric field region. As discussed in Sec. II C, when a large voltage pulse is applied to the octopole, an electric field sufficient to induce rapid *l*-mixing in the high-*n* Rydberg states is expected, even at very short radial distances. In NO this has been shown to lead to enhanced predissociation of the Rydberg-tagged fragments.<sup>11,12</sup> Therefore it is probable that field-induced predissociation plays a role in the loss of signal at higher voltages even for low energy fragments. It is thus clear that there exists an optimal voltage range to achieve discrimination between low and high energy fragments in this device, the magnitude of which depends on the photofragment excess energy range to be investigated.

### B. Images of the transmitted photofragment signal

A more visual demonstration of the effect of the octopole in discriminating against fast photofragments is seen in the images, recorded at a single photolysis wavelength, illustrated in Fig. 8. Four images of NO fragments are shown at  $E_{\text{avl}} = 325 \text{ cm}^{-1}$  and  $n \approx 125$ ,  $N^+ = 8$ , using different voltages  $(0-\pm 60 \text{ V})$  applied to the octopole. The data shown are the inverse Abel transforms of the original ion images, the transform being carried out after filtering and renormalization. The direction of the photolysis laser polarization is indicated at the bottom of image (a). At  $E_{avl}=325 \text{ cm}^{-1}$ , three channels are accessible, associated with  ${}^{3}P_{2}$ ,  ${}^{3}P_{1}$ , and  ${}^{3}P_{0}$ O-atom states, with total kinetic energies of 325, 167, and 99  $cm^{-1}$ , respectively. The rings in the images of Fig. 8 signify the predicted positions of the fragment shells corresponding to the three accessible channels. The positions of the outer two rings are coincident with the main features in (a), and the inner ring is coincident with the main feature in (d). The



FIG. 9. The radial intensity of the backprojected images as in Fig. 8, integrated over polar angle  $\theta \in [3^{\circ},90^{\circ}]$  plotted as a function of the total fragment kinetic energy. The asterisk indicates a feature arising from an artifact in the center of the image.

relative intensities of the rings with no applied voltage on the octopole are consistent with spin-orbit ratios measured close to threshold<sup>13,14</sup> that are of the order  $1:10^{-1}:10^{-2}$  for J = 2:1:0. A number of small artifacts, due primarily to center-line noise, are visible in images (c) and (d) inside the innermost circle. Note that the total intensities of the four images shown are not on the same scale: the gain has been increased by almost two orders of magnitude in (d) to show the remnant structure more clearly, i.e., the images are only a guide to the *relative* intensities of the transmitted signal in the three channels at a given voltage.

With increasing voltage on the octopole rods, the outermost, initially dominant ring becomes progressively weaker and the inner shells gain in relative intensity. Figure 9 shows this effect more clearly in a radial intensity plot, integrated in the polar angle  $\theta$  over the range of  $\theta \in [3^\circ, 90^\circ]$ . The inner two shells, corresponding to NO( $v_{NO}^{"}=0$ ,  $J_{NO}^{"}=17/2$ )+O ( ${}^{3}P_{0,1}$ ), are barely visible at 0 V, but become dominant at the higher voltages used at this excess energy. The reduction in fragment flux observed in the PHOMPFI spectrum of Fig. 6(b) is thus demonstrated to result from the selective discrimination against fast fragments in the octopole.

## C. Effect of the octopole on the observed MATI spectrum

One key measurement in the characterization of the octopole is the effect of the octopole on the MATI spectrum, as illustrated in Fig. 10. The spectra, showing just the  $N^+ = 10$ threshold, are recorded for a range of pulsed voltages (0– ±80 V) applied to the octopole rods and at a fixed photolysis energy giving  $E_{avl}=516 \text{ cm}^{-1}$ . The high-energy edge of the main feature changes significantly as the pulsed voltage applied to the octopole is increased, as discussed in detail in Sec. IV A. Simulations based on a diabatic field ionization model (see below) are also shown and agree very well with the threshold behavior in the experimental data sets. The position of the  $N^+ = 10$  threshold shown in Fig. 10, 74806.7



FIG. 10. A series of MATI spectra in the region of the  $N^+ = 10$  threshold [IP  $(N^+=10)$ ] with a voltage pulse applied to the octopole of  $0,\pm 30,\pm 45$ ,  $\pm 60,\pm 80$  V and a duration of 4  $\mu$ s. The total available excess energy is  $E_{\rm avl} = 516 \text{ cm}^{-1}$  and the discrimination field is 2.1 V/cm. The bold lines correspond to simulations based on a diabatic field ionization model (see the text).

cm<sup>-1</sup> relative to the J'' = 17/2 ground state level, is determined from the ionization energy in Ref. 15, the ground state rotational energy tabulated in Ref. 16 and the ionic rotational constants given in Ref. 17. The well-resolved *np* Rydberg series appearing at the low-energy side of the figure converge to a limit within 0.5 cm<sup>-1</sup> of the calculated threshold.

### **IV. DISCUSSION**

## A. Field ionization processes in an octopole: analysis of the MATI spectra

Our analysis focuses initially on the MATI spectra reported in Sec. IIIC and shown in Fig. 10 as this analysis provides the key to understanding the performance of the octopole. The low-energy region (red edge) of the MATI profile at a given threshold is determined in part by the fieldionization pulse in Region III and also by the decay behavior of the lower-*n* Rydberg states (n < 100). The red edge is not affected by the field due to the octopole and therefore we concentrate our analysis on the high-energy (blue) edge of the  $N^+ = 10$  MATI feature. The slope of the blue edge becomes smaller as the voltage applied to the octopole is increased, and the peak of the rise of this edge (i.e., where the flat top of the peak begins in the simulations) is shifted to lower energy. This point falls almost into the region where individual Rydberg states are resolved for the highest voltage applied ( $\pm 80$  V).

The high-energy edge of the MATI signal is simulated using a hydrogenic diabatic field ionization model,<sup>18,19</sup> combined with a spatial distribution of Rydberg-tagged fragments determined by the fragment kinetic energy and the angular anisotropy in the photodissociation. The fragments experience a range of fields when the voltage is applied to the octopole owing to their distribution of radial positions at that time, derived from the distribution of kinetic energies and angles of fragment ejection. They will therefore have a



FIG. 11. Hydrogenic field ionization probability vs the Rydberg electron energy  $E_{\text{Ryd}} = E_{\text{probe}} - \text{IP}$ , with a comparison of the analytical approximation, Eq. (7), and the diabatic field ionization model based on Ref. 18 for a pulsed electric field of 5 V/cm.

range of field ionization probabilities. Thus the overall field ionization probability in the octopole  $P_{oct}$ , for a given Rydberg excitation energy and given photofragment kinetic energy/angular distribution, is given by the weighted average of the field ionization probabilities for the spatial probability distribution of the fragments. The observed signal is proportional to the fraction of the Rydberg states surviving the pulsed octopole field (i.e., proportional to  $1 - P_{oct}$ ).

In the regime of high principal quantum number (n > 100) employed in the present investigations, and given the relatively fast rise-time of the octopole voltage pulse, *diabatic* field ionization is expected to be the dominant ionization process. In that case the field ionization probability decreases from one to zero over the range  $IP - 3.1\sqrt{F}$  to  $IP - 4.6\sqrt{F}$  where IP is the ionization threshold as is shown in Fig. 11.<sup>19</sup> To obtain this plot we used Eq. (40) of Ref. 18 to calculate the hydrogenic Stark energies in the field and Eq. (72) of the same reference to calculate the ionization rate. Rydberg states with a calculated ionization rate of less than  $10^9 \text{ s}^{-1}$  are assumed to survive. Although only m=0 states are included in the calculation, the overall field ionization profile changes very little if all *m*-states are included. Figure 11 also shows an analytical approximation of the form

$$\Phi^{\text{diab}}(E_{\text{probe}};F) = \sqrt{\frac{2}{3\sqrt{F}}(E_{\text{probe}} - (IP - 4.6\sqrt{F}))}, \quad (7)$$

where  $\Phi^{\text{diab}}(E_{\text{probe}};F)$  is the field ionization efficiency for a given field magnitude F (in V/cm) at excitation energy  $E_{\text{probe}}$  (in cm<sup>-1</sup>). The agreement between the two curves is satisfactory for the present purposes, and Eq. (7) was used in the simulations.

When modeling the spatial distribution of the Rydberg tagged fragments at the point of application of the inhomogeneous field, the angular distribution of photofragment velocity vectors has an important effect. Depending on the anisotropy parameter,  $\beta$ , a varying fraction of all photo fragments will be ejected along the molecular beam



FIG. 12. A schematic of the fragment cloud (dashed line) and the electric field strength in the octopole. Concentric circles (bold lines) in the xz-plane are lines of constant electric field magnitude.

axis where they experience only a negligible electric field. These fragments will contribute to the remaining signal intensity in the high-n region of the MATI spectrum even if they have substantial kinetic energy. The angular distribution is assumed to have the normalized form

$$I(\theta) = \frac{\sigma}{4\pi} (1 + \beta P_2(\cos\theta)), \tag{8}$$

where  $\theta$  is the angle between the fragment velocity vector and the laser polarization vector. Figure 12 gives a schematic representation of the geometry and the variables involved. Note that the photolysis laser polarization is horizontal (the *z* direction in the figure) and thus perpendicular to the principal symmetry axis of the octopole (the *y* direction); with this definition, the experienced field strength changes with  $\varphi$  the azimuthal angle, even though the angular probability distribution does not.

In order to calculate the MATI spectrum for a given  $E_{avl}$ and octopole voltage, it is assumed that the fragment cloud is subjected to the inhomogeneous electric field due to the octopole when the center-of-mass is found half-way into the device, i.e., after approximately 12  $\mu$ s. A given spin-orbit state of the oxygen atom is assumed (i.e., the calculation is performed separately for each channel) and then the spatial distribution can be calculated using the appropriate kinetic energy and anisotropy parameter for that channel. The field ionization probability, weighted by the spatial probability distribution, is numerically integrated over all angles and radial positions to obtain  $P_{oct}$ .

The overall field ionization probability due to the octopole must be multiplied by the probability of ionization by the discrimination field  $F_{rep}$ . We assume that this field is approximately homogeneous and acts between the octopole and the grid dividing Regions II and III. For simplicity, the mixed diabatic/adiabatic field ionization process due to this constant repelling field is modeled in analogy to Eq. (7) as

$$\Phi^{\text{adiab}}(E_{\text{probe}};F_{\text{rep}}) = \sqrt{\frac{1}{3\sqrt{F_{\text{rep}}}}} (E_{\text{probe}} - (IP - 6.1\sqrt{F_{\text{rep}}})),$$
(9)

### with $F_{\rm rep}$ in V/cm and $E_{\rm probe}$ in cm<sup>-1</sup> as before.

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Any Rydberg states at an energy higher than  $E = IP - 3.1\sqrt{F_{\text{rep}}}$  are assumed to decay with 100% probability in the presence of the repelling field, while Rydberg states at an energy lower than  $E = IP - 6.1\sqrt{F_{\text{rep}}}$  are assumed to survive the repelling field. Finally, all the MATI profiles corresponding to each spin-orbit channel are added together in the appropriate ratio to yield a normalized MATI spectrum.

Figure 10 shows the excellent agreement between the experimental spectra and the simulations. The simulations do not include the effects of nonzero translational temperature in the parent beam or the finite interaction width of the laser beams, which will lead to a finite width of the fragment shells at a given excess energy. In reality, fragments ejected into the same solid angle and with the same excess energy, but from different starting positions, may experience a range of electric field strengths. Not included either is the spread of excess energies due to the rotational distribution of NO<sub>2</sub>. All these effects are expected to have only a minor influence on the appearance of the MATI spectra, since the electric field strength does not vary drastically on the scale associated with the resulting spread of the spatial distribution. A spin-orbit branching ratio of  $p(O^3P_2):p(O^3P_1):p(O^3P_0)$ = 1:0.20:0.044 for the *f*-component of the NO  $\Lambda$ -doublet is the only state-resolved reported value for the channel series with  $J''_{NO} = 17/2$ , determined at an energy of  $E_{avl}$ =256 cm<sup>-1</sup>.<sup>13</sup> This spin-orbit branching ratio was used in the calculations. In the energy range of interest, this distribution has been shown to be strongly nonstatistical and to fluctuate when averaged over all accessible rotational and electronic NO states.<sup>13,14</sup> However, the simulated MATI spectra are in fact very insensitive to the exact population of the different fine structure states of the oxygen atom, as it is the outer shell that dominates. For example, a simulated spectrum with  $p(O^3P_2):p(O^3P_1):p(O^3P_0) = 1:0.16:0.07$ does not differ visibly from one using  $p(O^3P_2)$ :  $p(O^{3}P_{1}):p(O^{3}P_{0})=1:0.20:0.04.$ 

### B. Influence of the anisotropy parameter on the MATI spectra

As might be expected from the spin-orbit branching ratio, it is primarily the value of the anisotropy parameter  $\beta$  for the dominant outer shell which has a significant effect on the simulated MATI spectrum. It would be expected that as  $\beta$ approaches the limiting value of 2.0, the cut off between the *n* values surviving and the *n* values ionized by the octopole field should become sharper, since the proportion of fragments moving in the direction of the rods and thus into the high-field region is larger (given the specific direction of the photodissociating laser polarization  $\vec{E}_{diss}$ ). The angular anisotropy of the photofragment distribution for the outermost and dominant ring can be determined from the ion image with the octopole turned off. A value of  $\beta = 1.6 \pm 0.1$  is obtained at  $E_{avl} = 516 \text{ cm}^{-1}$ , as expected from Ref. 3 where a high-energy limiting value for NO<sub>2</sub> of  $\beta_{\text{lim}} = 1.54$  was calculated. The inner rings are however significantly weaker and the angular anisotropy parameter for the two higher-energy channels cannot be easily determined from these images. Values of  $\beta = 1.3$  and 1.0 have been assumed for the shells



FIG. 13. A simulation of MATI spectra (bold line,  $U_{8p}=0$ ; dotted/dashed lines,  $U_{8p}=\pm 60$  V) in the vicinity of the  $N^+=10$  threshold using a variety of different anisotropy parameters ( $\beta$ ) for the outermost fragment shell with  $E_{avl}=516 \text{ cm}^{-1}$ .

corresponding to NO produced in conjunction with the O  $({}^{3}P_{1})$  and O $({}^{3}P_{0})$  states respectively, but the simulations are insensitive to the anisotropy of the inner shells at this excess energy. Even with a value of  $\beta = 0.1$  for the shell corresponding to the formation of O $({}^{3}P_{1})$ , the difference in the simulated spectrum is marginal. The small effect of the inner shells is due to both the relatively low percentage of these excited fine structure states and the slowly rising field strength as a function of the radial distance in the octopole. The major action of the octopole field is on the outermost ring, while the inner rings are much less affected for the voltages investigated in this series of spectra.

Figure 13 shows four simulated MATI spectra ( $E_{avl}$ =516 cm<sup>-1</sup>,  $U_{8p} = \pm 60$  V) with values of  $\beta$  for the outer shell ranging from -1 to 2 ( $\beta$  for the inner shells held constant) together with the simulated MATI spectrum without the octopole. At n = 112, discrimination ratios (the ratio of field-ionized fragments to surviving fragments at the given excess energy and applied field) vary from 5:1 to 10:1, respectively. Even with a maximum anisotropy parameter of  $\beta = 2$  there is still a significant fraction of fragments flying on trajectories in such a way that they experience relatively low electric fields only. As a result, these fragments escape from the octopole region unaffected. Conversely, even for a fully isotropic angular photofragment distribution ( $\beta = 0$ ) the probability of fragments entering a high-field region remains high, leading to field ionization of a significant proportion by the octopole field.

### C. Modeling the effect of the octopole on the PHOMPFI spectrum

Using the same model as outlined in Sec. IV A, the relative transmission probability of the fragments through the octopole can be calculated as a function of  $E_{avl}$  for fixed Rydberg state energy and octopole voltage. For simplicity, the anisotropy parameter  $\beta$  is assumed to be independent of  $E_{avl}$ . As shown in Fig. 14, excellent agreement is obtained between this calculated function and the experimentally ob-



FIG. 14. The simulated transmission probability (bold line) as a function of excess energy in the octopole, assuming a population of n=126 and with anisotropy parameters  $\beta = 1.60$ , 1.3, and 1.0 for the O(<sup>3</sup>P) J=2,1,0 channels, respectively. The experimental ratio of the MATI intensities with the octopole on and off is shown by the diamonds [from Fig. 6(c)]. The contributions to the simulations from the three different channels are shown separately.

served ratio of the PHOMPFI signals with the octopole on and off [from Fig. 6(c)]. Small deviations between experiment and simulation could be in part due to the variation of  $\beta$  with  $E_{avl}$ .<sup>3</sup> The simulated data shown for the separate channels indicate that the fragments of lower kinetic energy associated with  ${}^{3}P_{1}$  and  ${}^{3}P_{0}$  channels make a significant contribution to the transmitted signal at higher  $E_{avl}$ . The level of agreement demonstrates that our model encapsulates the major factors controlling the effect of the octopole on the MATI and PHOMPFI spectra.

## D. Factors affecting the discrimination of the kinetic energy aperture

The experimental results and their agreement with simulations show clearly that the pulsed-field octopole acts effectively as a discriminator against high kinetic energy fragments, and that its behavior is well understood. As can be determined from Fig. 14, the kinetic energy resolution is  $\sim 100 \text{ cm}^{-1}$  (defined as the energy range over which the transmission function falls to from 1.0 to 0.5) at an excess energy of 200 cm<sup>-1</sup> (the midpoint of the transmission function decay curve). The major factor contributing to the resolution is the range of angles over which the photofragments are ejected, i.e., fragments of the same kinetic energy are not all experiencing the same field. Improved discrimination in favor of low kinetic energy fragments could be achieved by fast gating of only those fragments arriving at the same time as the parent molecular beam center-of-mass, with the more energetic fragments arriving earlier or later. Given the current experimental set-up using a slow phosphor screen (P20) and a slow amplifier, such discrimination in time-of-flight is not possible, but improvements in this direction are underway.

Another factor contributing to the photofragment kinetic energy resolution is the diabatic field ionization mechanism. The ionization efficiency in the diabatic model does not rise as a step function of the field for a given *n* (energy  $E_n$ ) but increases from 0 to 1 over a range of fields given by  $\sqrt{F}$  $=E_n/4.6$  to  $E_n/3.1$ . The underlying physical reason for this is that the blue-shifted Stark states are field ionized at higher fields than the red-shifted Stark states, and a mixed population of such states are excited by the probe lasers. If a mechanism for selective population of the red-shifted states could be devised, then this field-ionization profile could be sharpened. It would also be sharpened by Rydberg tagging at higher n values, but this would require a lower discrimination field (see below). It should be noted that a range of nvalues is typically populated in the present experiments because of the finite laser bandwidth, and this contributes to the spread in the field-ionization behavior. These factors would not be limiting if the field gradients in the octopole were infinitely steep. The use of higher-order multipoles with steeper field gradients is discussed below.

A further factor that needs to be considered in optimizing the resolution is the finite duration of the voltage pulse applied to the rods. In order to obtain a well-defined voltage pulse, where ringing and similar distortions are kept at a minimum, a duration of 4  $\mu$ s was chosen for the present experiments. However, in the duration of this pulse, the center-of-mass of the molecular beam travels approximately 6 mm, a good fraction of the length of the octopole. The tagged fragments will experience a change of electric field strength due to the expansion of the fragment sphere during the voltage pulse. The contribution to the energy resolution  $\Delta E_{\rm avl}$  can be calculated to be

$$\Delta E_{\rm avl} = E_{\rm avl}^{\rm lim} \left( 1 - \frac{t_{\rm on} + t_{\rm off}}{2t_{\rm off}} \right), \tag{10}$$

where  $E_{\text{avl}}^{\text{lim}}$  is the limiting value of the available kinetic energy beyond which all fragments are field-ionized (assuming ejection perpendicular to the molecular beam direction), and  $t_{\text{on}}$  and  $t_{\text{off}}$  are the times at which switching occurs. For the experimental values  $t_{\text{on}} = 10 \ \mu\text{s}$  and  $t_{\text{off}} = 14 \ \mu\text{s}$  and an estimated  $E_{\text{avl}}^{\text{lim}} = 400 \ \text{cm}^{-1}$ , based on Fig. 6, we obtain a contribution to the limiting resolution of

$$\Delta E_{\rm avl} = 57 \ \rm cm^{-1}. \tag{11}$$

When using a fairly long voltage pulse it is also necessary to consider the variation of the octopole-generated field with axial distance along the octopole. The field strength simulations presented earlier are based on an infinitely long device and do not take into account the presence of further electrodes on either end (in the present set-up a grid is mounted at each end perpendicular to the beam axis). The field is least perturbed in the middle of the octopole, but its magnitude at given radius varies with distance along the axis creating a funnel-shaped field region instead of the ideal cylinder shape. In fact this effect tends to compensate the previous factor [given by Eq. (10)] as the field becomes smaller for a given radial distance when the fragment cloud moves towards the exit of the octopole.

The employed repelling field also affects the performance of the kinetic energy aperture as it limits how high the detected n values can be. This field is present to suppress the signal due to any prompt ions and ions formed by field ion-

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FIG. 15. Simulation of MATI spectra,  $U_{8p} = 0$  V (solid line) and  $U_{8p} = \pm 45$  V (dotted line), in the vicinity of the  $N^+ = 10$  threshold and for repelling fields of 0.5 and 2.1 V/cm, with  $E_{avl} = 516$  cm<sup>-1</sup>.

ization of the high-n Rydberg states in the octopole. The higher this electric field, the fewer the number of Rydberg states with very high n that can survive; yet these are precisely the states which would give the best kinetic energy discrimination, because they are most susceptible to the octopole field. In principle the spatial separation between ions formed in Region II, and those produced in Region III, could be achieved by applying a lower discrimination field over a longer flight distance. However, this might reduce the signal owing to the finite lifetime of the Rydberg states.

Figure 15 compares the simulated MATI spectrum (with 0 and  $\pm 45$  V on the octopole,  $E_{avl} = 516 \text{ cm}^{-1}$ ) for a repelling field of 2.1 V/cm (as used in the present experiments) with that for a field of 0.5 V/cm. With the higher repelling field, reasonable signal levels are obtained at n=112 ( $E_{probe}=74795.6 \text{ cm}^{-1}$ ), where the discrimination ratio (field-ionized versus surviving) is 6:1. Meanwhile, for the lower repelling field a discrimination ratio of 35:1 is obtained at n=157 ( $E_{probe}=74800.2 \text{ cm}^{-1}$ ) for a similar signal level. This difference is further accentuated at higher operating voltages of the octopole.

One last point addresses the decay mechanism of the high-*n* Rydberg states. Predissociation is the most likely major decay channel for the Rydberg-tagged fragments. Additionally, as discussed above and exemplified in Fig. 7, electric-field induced predissociation becomes dominant in the higher range of applied voltages. It leads to a general decay of high-*n* Rydberg states, independent of their associated kinetic energy. To some extent the detection of NO is not ideal in this type of experiment because predissociation of the optically accessed Rydberg states is known to be fast. Interestingly, however, both the excellent agreement between simulated and experimental MATI spectra in Fig. 10 and evidence obtained from ion images suggests that the multipole operates largely by field-induced ionization of the tagged fragments.

#### E. Imaging the effect of the kinetic energy aperture

Ion imaging provides an excellent way of obtaining direct spatial information on the results of the discrimination process. Figures 8 and 9 show very clearly how the intensity of the fragment shell corresponding to the lowest  $O({}^{3}P_{2})$ dissociation channel decreases rapidly as a function of applied voltage, such that the highest energy channel  $O({}^{3}P_{0})$ provides the dominant feature in image (d). Figure 9 also reveals how the center of the outermost ring gradually moves inwards as the voltage increases; this ring in image (d) constitutes the tail of the blurred shell for the lowest dissociation channel. Similar effects are seen in images obtained at other excess energies, although the discrimination against the outer ring becomes less as the maximum excess energy decreases. Note that the additional shoulder in the 60 V profile at a fragment kinetic energy of 40  $\text{cm}^{-1}$  is caused by an artifact in the center of the image.

It is interesting to consider whether the Abel transform, used to obtain Fig. 8, is actually valid in the experiments presented in this paper. The transform requires cylindrical symmetry around an axis in the plane of the image. In principle, this is provided by the linearly polarized electric field vector of the photolysis source. The octopole itself possesses also approximate cylindrical symmetry; the symmetry axis is, however, *perpendicular* to the imaging plane. Fragments ejected at the same polar angle  $\theta$  but different azimuthal angle  $\varphi$  (refer to Fig. 12 for a definition of these angles) experience different electric field strengths and are thus not affected in the same way by the device. The required axial symmetry breaks down, so that the Abel transform is not strictly valid, and the reconstructed images presented above must be interpreted with caution. Some of the artifacts may potentially be attributed to the break-down of this symmetry. For this reason it is not generally possible to extract anisotropy parameters from the images when the octopole voltage is nonzero. Nevertheless the ion images consolidate the characterization of the octopole and the features revealed agree well with the expected spin-orbit distributions and the expected positions of the various fragment shells. The octopole acts as an approximately cylindrically symmetric steradiancy analyzer.

### F. Conclusion: The road towards a zero kinetic energy photodissociation spectrometer

In the previous section, factors contributing to the kinetic energy resolution of the present device were discussed. These include the inherent angular distribution of the photofragments, the intrinsic diabatic field ionization mechanism, the voltage pulse duration of 4  $\mu$ s, the speed of the detection system, the field gradients in an octopole, and some minor effects due to finite interaction volume, the range of principal quantum number *n*, and the rotational temperature of the parent.

It is interesting to compare the present experimental results with work performed in the group of Houston.<sup>20</sup> In their experiment, the *atomic* oxygen fragments from NO<sub>2</sub> photodissociation are excited to high-*n* Rydberg states and left to drift in a long time-of-flight tube for  $360 \,\mu$ s. The detection



FIG. 16. (a) The electric field strength as a function of the radial distance in a dodecapole. (b) Simulated MATI spectra in the vicinity of the threshold for  $N^+$  = 10 after transmission through a dodecapole at an excess energy of 516 cm<sup>-1</sup>.

assembly consisted of an ion detection set-up with a mask of fixed size in front of the PMT and in the center of the phosphor screen. This allowed them to detect fragments arriving within a small solid angle centered on the molecular beam, i.e., predominantly low kinetic energy fragments. The spectra, termed zero kinetic energy photofragment spectra (ZKE), were recorded in the range of  $D_0$  to  $D_0 + 150$  cm<sup>-1</sup>. They show the sequential opening of the channels corresponding to the various rotational states of NO, in accordance with OTS-PST (orbiting transition-state phase-space theory). From these spectra it was possible to deduce a maximum allowed orbital angular momentum of  $l_{\text{max}} = 5\hbar$ , owing to the estimated experimental resolution of 0.5 cm<sup>-1</sup>. The instrumental resolution reported by Houston and co-workers is currently superior to that provided by the octopole. It is however not tunable, except by replacing the aperture with a different size. The detection of the O atom fragment rather than NO allowed them to benefit from a much longer Rydberg state lifetime, and hence flight time.

In addition to optimizing the factors discussed in Sec. IV D, such as the use of a faster gating and detection system, it is desirable to consider whether there is a better electrode configuration that would improve on the present device. A promising example, using a dodecapole (a 12-rod multipole), is illustrated in Fig. 16. The radial variation of the electric field strength is shown for a dodecapole with rods of radius 2 mm arranged on a circle of radius 12 mm, demonstrating the steeper field gradients than in Fig. 5. A set of simulated MATI spectra are also shown for a dissociation event at  $E_{avl}=516 \text{ cm}^{-1}$  and a repelling field of 2.1 V/cm. Moderate voltage pulses in the range of several hundred to a thousand volts produce a relatively steeply rising electric field that has

nevertheless negligible strength in the center of the device. The simulated MATI spectra show that a strong bias against the faster fragments can be achieved at this excess energy. The discrimination ratio is better than the octopole example in Fig. 13, as measured at the top of the rise in the blue edge.

The present experiments clearly demonstrate the principle of using field-ionization of high-n Rydberg states in inhomogeneous electric fields to obtain information about the spatial/energetic distribution of photofragments. Given the potential for substantial improvements, we are confident that multipole devices of the kind presented here will provide a valuable tool in photodissociation or reaction dynamics studies. The testing of a variety of different field configurations should be carried out, and the possibility of detecting selectively the ions produced by the inhomogeneous field, rather than rejecting them, should be explored, especially in alternative field configurations. We believe that such investigations will lead to a novel means for providing detailed three-dimensional pictures of the trajectories of reaction products, and hence details of the potential energy surfaces for the reaction.

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