Study of Photodissociation Dynamics Using Sub-Doppler Fluorescence Imaging Method: Photodissociation of ICN at 308 nm

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The sub-Doppler fluorescence imaging method has been developed to determine velocity distribution, angular distribution, and vector correlation of state-selected photofragments. Using this new method, photodissociation dynamics can be studied directly in the center-of-mass frame, even with an uncollimated molecular beam. We have performed the experiment of photodissociation of ICN at 308 nm to demonstrate that recoil velocities of photofragments can be obtained without collimating the parent beam. The forward- and backward-scattered CN($X\ ^2\Sigma^+$) photofragments are imaged simultaneously for the first time. The recoil velocities of the CN photofragments are measured and the bond dissociation energy D_0^0(I–CN) is determined to be 26960 ± 120 cm^{-1}, in agreement with the literature values reported recently.

1. INTRODUCTION

Recently, we have proposed and developed a "sub-Doppler fluorescence imaging method" (SFIM) to determine velocity distribution, angular distribution, and vector correlation of photofragments in the studies of photodissociation dynamics.[1] This method modifies the fluorescence imaging techniques which were first applied by Chen et al. to investigate photodissociation and reaction dynamics.[2-8] To obtain better velocity and angular resolutions using conventional fluorescence imaging techniques, the reaction zone has to be confined in a tiny volume, which can be achieved by crossing a well-collimated molecular beam with another well-collimated reagent beam or a focused laser beam. The drastic decrease in the number density of reaction products due to the expansion following the event of bimolecular collisions or photodissociation, unfortunately, has limited the number of fluorescence imaging experiments.[4-6] Nevertheless, it has been shown in our theoretical study of SFIM that three-dimensional (3D) dynamics of state-selected photofragments can be measured directly in the center-of-mass frame (CMF), even with an uncollimated molecular beam.[1] By doing such, the signal-to-noise ratio should be progressively improved because a larger number density of parent molecules can be retained. The relevant theories of SFIM have been derived using density matrix formalism. The feasibility of this new method has also been demonstrated by the experiment of laser ablation of B atoms at 248 nm.[1]

In this paper, we report the photodissociation experiment of cyanogen iodide (ICN) at 308 nm to demonstrate that recoil velocities of state-selected photofragments can be measured in an uncollimated molecular beam, as the original proposal claimed.[1] The forward- and backward-scattered CN photofragments are imaged simultaneously for the first time, from which the bond dissociation energy D_0^0(I–CN) is determined.

The rest of this paper is organized as follows. Section 2 gives an overview for the design of SFIM. Next, Section 3 describes the details of the ICN photodissociation experiment, and Section 4 presents and discusses the results. Finally, conclusions are addressed in Section 5.

2. OVERVIEW OF SFIM

Fig. 1a shows the experimental design of SFIM for the studies of photodissociation dynamics using a linearly polarized photodissociation laser. The time sequences for every experimental event are displayed in Fig. 1b. In general, the target molecular beam is expanded into the vacuum by a pulsed valve. A photodissociation laser crosses the molecular beam in the collisionless regions. Then a laser sheet, counter-propagating with the photodissociation laser, probes the photofragments distributed in the plane defined by the molec-

u lar and photodissociation la ser beams at a se lected de lay time with re spect to the on set of photodissociation. The bandwidth of the probe la ser should be much less than the Dopp ler widths of the photofragments for the pur pose of se lect ing certain ve loc i ties of photofragments along the prop a gat ing direc tion of the probe la ser. The in ter nal state dis tri bu tion of the photofragments is de ter mined by the probe la ser via a laser-induced flu o res cence (LIF) tech nique. A 2D im ag ing detec tor, e.g., an in ten si fied charge-coupled de vice (CCD) camera, is uti lized to reg is ter the spa tial po si tions of the photofragments by de tect ing the emit ted flu o res cence. The po lariza tion-states of the emit ted flu o res cence can be an a lyzed by mount ing a lin ear po lar izer in front of the CCD cam era.

As sume that the probe la ser prop a gates along the Y-direction and the CCD de tec tor is mounted in the X-direction (Fig. 2), then the di rect ex trac tion of 3D dis tri bu tion of the photofragments is accomplished by the following pro cedures. (1) The thin la ser sheet slices the YZ-plane of the expanded New ton sphere and se lects the photofragments with the ve loc ity com po nent $v_X = 0$ (Fig. 2a). (2) The sub-Doppler la ser fre quency se lects the photofragments with $v_Y = c(\nu - \nu_0)/\nu$ (Fig. 2b), where ν is the la ser fre quency, ν_0 is the Doppler-free mo lec u lar tran si tion fre quency, and c is the speed of light. (3) Finally, the dis tri bu tion of photofragments in the Z-dimension is de ter mined from flu o res cence im age us ing $v_Z = Z/t$ (Fig. 2c), where Z is the dis tance mea sured from the CM of photofragments, and t is the de lay time be tween the probe and photodissociation la sers with short pulse du ra tion (< 20 ns). Due to the Dopp ler ve loc ity se lec tion in the Y-direction, the par ent mo lec u lar beam need not be well collimated. For par al lel beams with mul ti ple photolysis cen ters, the im age of photofragments is like that de picted in Fig. 2c; for beams mov ing with a slight cur va ture, the im age is shown in Fig. 2d. It can be re al ized from Fig. 2c that the im age pat terns along the Z-dimension are the same for ev ery photolysis cen ter of dif fer ent ini tial Y-positions. There fore, the sig nals in the Y-dimension can be in te grated over to im prove the sig nal-to-noise ratio, and only the image profiles along the Z-dimension are nec es sary for de ter min ing the ve loc ity and an gu lar dis tri bu tion of photofragments.

Two schemes of SFIM have been pro posed.[1] De sign of Scheme I fixes the polarization vec tor ($\mathbf{E}_d$) of the photodissociation la ser at $\theta = 0°$ (Fig. 1) and scans the fre quency of the probe la ser. For each fre quency, i.e., for each se lected v_Y, the v_Z-com po nents of photofragments are de ter mined from the re corded im age. Af ter scan ning ν to cover the whole Dopp ler pro file of photofragments, ve loc ity and an gu lar distri bu tions of photofragments in a spe cific quan tum-state can

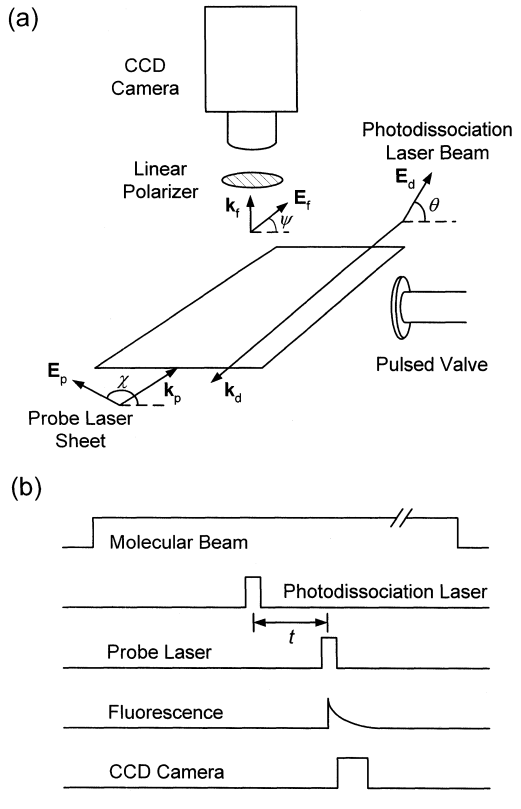

Fig. 1. (a) Schematic diagram of the experimental setup for the sub-Doppler flu o res cence im ag ing method. (b) The time se quences for ev ery exper i men tal event (not to scale).

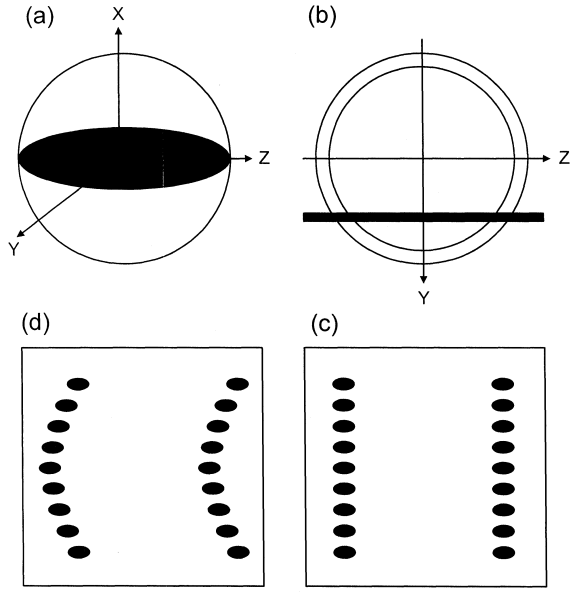

Fig. 2. Sche matic di a gram for di rect ex trac tion of the 3D dis tri bu tion of photofragments (see text).

be an a lyzed from $I_{exp}(v_X=0, v_Y, v_Z)$, where I_{exp} is the mea sured flu o res cence in ten sity as a func tion of ve loc i ties in the YZ-plane. On the other hand, Scheme II mea sures the flu o res-cence in ten sity $I_{exp}(v, \theta)$ as a func tion of ve loc ity and scat ter-ing an gle, i.e., the fre quency of the probe la ser is fixed at ν_0 to sin gle out the photofragments with $v_Y = 0$, and $\mathbf{E}_d$ is var ied (Fig. 1). At each se lected θ, the ve loc i ties along this scat ter-ing an gle are de ter mined from the im age. Scheme II is more versatile than Scheme I when using a linearly polarized photo dissociation la ser,[1] but Scheme I is more gen eral and can be ap plied for other ex per i ments of mo lec u lar dy nam ics. For ex am ple, Scheme I has been suc cess fully ap plied to study the la ser ab la tion mech a nisms of B at oms at 248 nm, which clearly dem on strates the fea si bil ity of SFIM.[1]

The rel e vant the o ries of SFIM have been de rived for Scheme I and Scheme II us ing den sity ma trix for mal ism by Chen and Chang[7] and Chang et al.,[1] re spec tively. For in-stance, the flu o res cence in ten sity for mula of Scheme II can be writ ten as[1]

$$I_{exp} = CP(v)P(\theta)I_p(J_1, J_2, J_3, v, \theta, \chi, \psi) \quad (1)$$

where C is a pro por tion con stant, $P(v)$ is the ve loc ity dis tri bu-tion func tion, $P(\theta)$ is the an gu lar dis tri bu tion func tion, and

$$I_p(J_1, J_2, J_3, v, \theta, \chi, \psi) = S_1 S_2 \sum_{kq} X_q^k(J_1, J_2, J_3, \chi, \psi)\rho_q^k(J_1, v, \theta) \quad (2)$$

where S_i is the tran si tion am pli tude, J_i is the ro ta tional quan-tum num ber, ρ_q^k is the state multipole of rank k with com po-nent q, and X_q^k is the cor re spond ing co ef fi cient of ρ_q^k.[1] The ef-fects of anisotropic dis tri bu tions of the photofragment ro ta-tional an gu lar momenta on the flu o res cence in ten si ties are em bed ded in I_p. Ex plicit forms of the above equa tions can be found in Refs. 1 and 7.

With out a pri ori knowl edge for the photodissociation sys tem of in ter est, the po lar iza tion ef fects of the photo frag-ment ro ta tional an gu lar momenta on the flu o res cence in ten si-ties should al ways be clar i fied be fore one can ex tract the ve-loc ity and an gu lar dis tri bu tions of photofragments from the LIF de tec tion scheme. That is, I_p in eq 2 ought to be de ter-mined prior to the mea sure ments of $P(v)$ and $P(\theta)$. In a 1+1 LIF de tec tion scheme, eight align ment pa ram e ters (i.e., ρ^2_{0-2} and ρ^4_{0-4}) can be uniquely de ter mined by vary ing the χ– and ψ–an gles through two types of tran si tions (e.g., P and Q or R and Q), for a min i mum num ber of 13 mea sure ments.[1] When the eight pa ram e ters are known for the photofragments with se lected v and θ, $P(\theta)$ can be de ter mined by vary ing θ, and $P(v)$ can be ob tained at the magic an gle (i.e., $\theta = 54.73°$) where $P(\theta)$ be comes a con stant for all v.[1]

3. EXPERIMENTAL SECTION

In or der to il lus trate that re coil ve loc i ties of photo-fragments can be ob tained with an uncollimated mo lec u lar beam, we have per formed a photodissociation ex per i ment of ICN at 308 nm. In the photodissociation of ICN at this wave-length, Fisher et al. mea sured the in ter nal en ergy dis tri bu-tions of the CN photofragments us ing LIF spec tros copy,[9] and Hall and co-workers stud ied vec tor cor re la tions of photo-fragments us ing high-resolution tran sient fre quency mod u-lated ab sorp tion spec tros copy.[10,11] The ex per i men tal setup for the photodissociation of ICN at 308 nm was sim i lar to that de picted in Fig. 1 ex cept that no po lar iza tion stud ies were made. The ex per i men tal pro ce dures have al ready been de-scribed in Sec. 2. Spe cifically, a neat beam of ICN (~110 Torr) was ex panded into vac uum (~10^{-6} Torr) by a pulsed valve (Gen eral Valve, Se ries 9) with an or i fice of 0.8 mm in di am e ter. The noz zle was kept at 100 °C dur ing the ex per i-ment. The pulse du ra tion of the par ent beam was ~800 μs, and the pres sure of the vac uum sys tem in creased to ~5×10^{-5} Torr when the pulsed valve was op er ated at 3 Hz.

The photodissociation la ser was the out put of a XeCl excimer la ser (Lambda Physik, Compex 200) and was aligned to cross the ICN beam ~12 mm down stream the noz zle. Note that when the photodissociation laser was positioned at shorter dis tances (< 6 mm) rel a tive to the noz zle, quite dif fer-ent im age pat terns were ob tained show ing that the CN photo-fragments col lided with the re main ing ICN mol e cules. The probe la ser was the out put of a dye la ser (Lambda Physik, LPD 3000) pumped by an other XeCl excimer la ser (Lambda Physik, LPX 200). The CN photofragments were de tected via LIF of the tran si tion CN($B\,^2\Sigma^+$, v = 0) ← CN($X\,^2\Sigma^+$, v = 0). The 2D im ag ing de tec tor was an ICCD (Prince ton In stru-ments, 576G/RB) with an elec tronic shut ter gated at a pulse of 100 ns. The time se quence for each in stru ment was con-trolled by a dig i tal pulse/de lay gen er a tor (Stan ford Re search, DG535).

4. RESULTS AND DISCUSSION

Fig. 3 de picts the ex ci ta tion spec trum of the na scent CN photofragments gen er ated from the photodissociation of ICN

at 308 nm in a flowing cell containing 15 mTorr ICN. The CN spectrum obtained in this work is consistent with that reported by Fisher et al.[9] While the P-branch peaks of the CN spectrum are clustered together for the B←X transitions, the R-branch peaks are well separated from each other (Fig. 3). A strong band-head is formed around 388.34 nm for the P-branch owing to $B' = 1.9701\ cm^{-1} > B'' = 1.8996\ cm^{-1}$.[12] The weak signals present in the vicinity of the $v'' = 0$ peaks are due to the CN($B\ ^2\Sigma^+$, $v' = 1$) ← CN($X\ ^2\Sigma^+$, $v'' = 1$) transitions. The images of the CN photofragments were taken at the resonance frequencies for the selected quantum-states.

Figs. 4a-4c show three images of CN probed at the delay times of 0.2, 1.1 and 2.1 μs, respectively, after the photodissociation of ICN at 308 nm. The images in Fig. 4a-4c were obtained by averaging 5, 600, and 1800 laser shots, respectively. The probe laser was tuned at the band-head of the P-branch (388.34 nm) to detect the CN($X\ ^2\Sigma^+$, $v'' = 0$, $N'' = 27$-30) photofragments.[12] Similar images with poorer signal-to-noise ratios (not shown) were also obtained for the CN fragments in a single ($v'' = 0$, N'') rovibrational state by the LIF of CN through the R-branch. As mentioned earlier in Sec. 2, the curvature in the vertical direction of Fig. 4 is due to uncollimated parent beams (cf. Fig. 2d), and only the image profile along horizontal direction is useful in the velocity determination. The image profiles of Figs. 4a and 4c are displayed in Figs. 5a and 5b, respectively. The following conclusions can be deduced directly from Figs. 4 and 5. (1) The forward- and backward-scattered photofragments are imaged simultaneously. Accordingly, the average recoil velocity of the CN photofragments can be determined to be 1800 ± 25 m/s, calculated directly from Fig. 5b where the distance between the forward and backward peaks is marked. Due to the conservation of (linear) momentum, the average recoil velocity of the counterpart I atomic photofragments is 369 ± 6 m/s. (2) The image profiles are symmetric and single-peaked in both the forward and backward directions (Fig. 5b) meaning that only one photodissociation channel is active, i.e., ICN + $h\nu$(308 nm) → I($^2P_{3/2}$) + CN($X\ ^2\Sigma^+$). The I*($^2P_{1/2}$) atoms were not produced in the photodissociation of ICN at 308 nm. The bond dissociation energy D_0^0(I–CN) can be calculated by

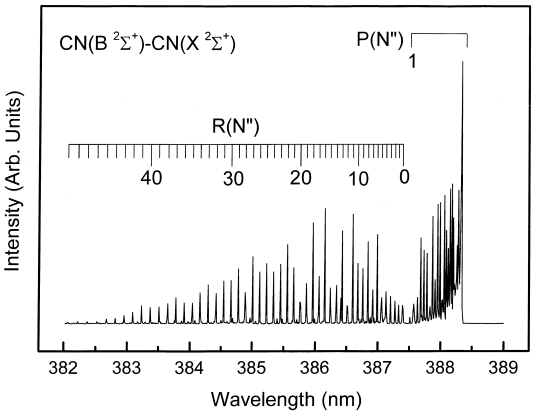

Fig. 3. Excitation spectrum of the CN($X\ ^2\Sigma^+$) photofragments generated from the photodissociation of ICN at 308 nm.

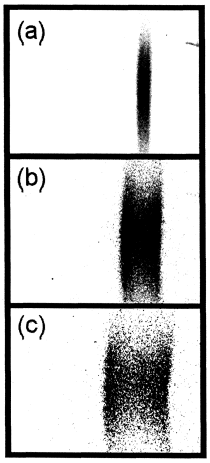

Fig. 4. Images of CN($X\ ^2\Sigma^+$) photofragments probed at 388.34 nm with a delay time of (a) 0.2, (b) 1.1, and (c) 2.1 μs after photodissociating ICN at 308 nm.

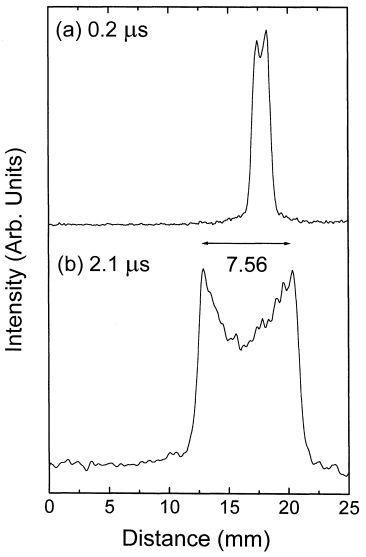

Fig. 5. Image profiles of CN taken from (a) Fig. 4a and (b) Fig. 4c. The arrows denote the distance between the forward and backward peaks.

$$D_0^0(\text{I-CN}) = h\nu + E_i(\text{ICN}) - E_i(\text{CN}) - \frac{1}{2}m_{\text{CN}}v_{\text{CN}}^2 - \frac{1}{2}m_{\text{I}}v_{\text{I.}}^2 \quad (3)$$

where $h\nu$ = 32647 cm^{-1} is the en ergy of a pho ton at 308 nm, E_i(ICN) = 340 cm^{-1} is the in ter nal en ergy of the par ent ICN mol e cules (see a later dis cus sion), E_i(CN) = 1600 cm^{-1} is the average internal (rotational) energy of the detected CN photo fragments (Fig. 4), and the last two terms are the ki netic en er gies of photofragments. By in sert ing all the above val ues into eq 3 and con sid er ing the un cer tainty in the mea sure ment of the CN ve loc i ties, one has D_0^0(I–CN) = 26960± 120 cm^{-1}. (3) Finally, the par ent ICN beams move at an av er age ve loc ity of 610 ±25 m/s in the lab o ra tory frame, de ter mined from the move ment of the CM of the CN photofragments (Figs. 4 & 5). This is due to the fact that the CM ve loc ity of photofragments is iden ti cal to that of the par ent mol e cules, since no ex ter nal forces are im posed on the photodissociation sys tem. Con se quently, once the im ages of photofragments are obtained, like those in Fig. 4, the anal y sis of photodissociation dy nam ics is quite sim ple and straight for ward.

In this work, the band width (~0.2 cm^{-1}) of the probe la ser was only slightly less than the width (~0.3 cm^{-1}) be tween the max i mum and min i mum Dopp ler shift of the CN photofragments. In ad di tion to the ef fects of re coil ve loc i ties, the im age pro files in Fig. 5 are there fore blurred by the photofragments scat tered at any an gle within the prob ing area of the la ser sheet, the ve loc ity spreads of the par ent beams, and the con tri bu tion from dif fer ent quan tum states. How ever, the im ages in Fig. 4 clearly dem on strate that the for ward- and back ward-scattered photofragments can be si mul ta neously de tected by the flu o res cence im ag ing tech niques. Hence, when the band width of the probe la ser is im proved to be sub-Doppler for a sin gle state of photofragments, the im age profiles will show two dis tinct and well-resolved peaks, which re sult from the re coil ve loc i ties of photofragments with minor con tri bu tions from ve loc ity spreads of the jet-cooled parent beams. Fol low ing the ex per i men tal pro ce dures pro posed by Chang et al.,[1] ve loc ity dis tri bu tion, an gu lar dis tri bu tion, and vec tor cor re la tion of state-selected photofragments can be de ter mined ac cord ingly.

Note that the in ter nal en ergy E_i(ICN) was not char ac terized in this work and was taken as 340 cm^{-1}, as sum ing that the CN photofragments are gen er ated pre dom i nately from ICN in its first vi bra tional state (bend, 304 cm^{-1})[13] with ro ta tional tem per a ture ~50 K, es ti mated from the mea sure ment of ro tational tem per a ture for NO_2 mo lec u lar beams. It is be lieved that vi bra tional hot bands play an im por tant role in the red wing of the ICN ab sorp tion spec tra in the Ã band con tin uum, such as at 308 nm.[9-11] We sup port this ar gu ment by the finding that the CN flu o res cence in ten si ties were re duced as the ICN mol e cules were seeded in 1 atm He serv ing as car rier gas. We there fore as sume that the vibrationally ex cited states are re spon si ble for the photodissociation of ICN at 308 nm. With out the as sump tion for the in ter nal en ergy of the ICN mol e cules, a lower bound for D_0^0(I–CN) = 26620 ± 120 cm^{-1} can be de ter mined by set ting E_i(ICN) = 0 in eq 3. The value of D_0^0(I–CN) = 26960 ± 120 cm^{-1} de ter mined in this work is in agree ment with the lit er a ture val ues re ported re cently, such as 26980 ± 100 cm^{-1} by Hall and co-workers[11] and 26500 ± 500 cm^{-1} by Wittig and co-workers.[14] In a pre lim i nary flu o res cence im ag ing ex per i ment of photodissociation of ICN at 248 nm,[4] however, the D_0^0(I–CN) was determined to be 28700 ± 100 cm^{-1}. This value was prob a bly over es ti mated because, in that work, only the for ward-scattered CN photofragments were de tected and the CM ve loc ity of the par ent beam was not mea sured. In con trast, si mul ta neous de tec tion of the for ward- and back ward-scattered photofragments (Fig. 4) al lows us to un am big u ously de ter mine the re coil ve loc i ties of photofragments di rectly in the CMF. As such, the CM ve loc ity of the par ent beam need not be mea sured, al beit it can be in ferred from the im ages of photofragments, as al ready shown above.

At this point, we shall com pare flu o res cence im ag ing with the well-developed ion im ag ing tech nique.[15,16] While flu o res cence im ag ing adopts LIF tech niques to probe re action prod ucts, ion im ag ing de tects prod ucts via res o nance-enhanced multiphoton ion iza tion (REMPI). It is gen er ally accepted that a REMPI tech nique is more sen si tive than LIF. In an ion im ag ing ex per i ment, how ever, only a very few ions can be gen er ated per la ser shot; oth er wise space charge effects can se ri ously de stroy the ve loc ity dis tri bu tion of the nascent prod ucts. To ob tain an ion im age with rea son able quality, the sig nals have to be av er aged for ~10^4 la ser shots. In sharp con trast, flu o res cence im ag ing de tects pho tons emitted from neu tral mol e cules; the num ber den sity of prod ucts can there fore be con trolled as high as pos si ble un der col li sion-free con di tions. It takes ~10^3 la ser shots to ac cu mu late a good flu o res cence im age (e.g., Fig. 4c). Be sides, both im ag ing tech niques are able to de ter mine not only ve loc ity and an gular dis tri bu tions, but also vec tor cor re la tions of state-resolved products. The usage of either technique will depend on wheth er the tar get mol e cules are suit able for the LIF or REMPI de tec tion schemes.

5. CONCLUSIONS

The new "sub-Doppler fluorescence imaging method" has been shown to be a useful tool in the studies of photodissociation dynamics. The photodissociation of ICN at 308 nm demonstrates that recoil velocities of state-selected photofragments can be measured with an uncollimated molecular beam. The forward- and backward-scattered CN($X\ ^2\Sigma^+$) photofragments are imaged simultaneously for the first time. The bond dissociation energy D_0^0(I-CN) is determined to be 26960 ± 120 cm^{-1}, in agreement with the literature values reported recently.

The preliminary results shown in this paper promise detailed investigations of photodissociation dynamics using this technique. It is most valuable if polarization experiments can be performed. By varying the vectors of the linearly polarized photolysis and probe lasers, anisotropy parameters and vector correlations can be measured for the state- and velocity-selected photofragments.[1] The experiment of ICN photodissociation including polarization studies is underway.

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Key Words

Sub-Doppler; Fluorescence imaging; Photodissociation; Cyanogen iodide.

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