Sliced fluorescence imaging: a versatile method to study photo-induced dynamic processes
ABSTRACT

To reduce the image blurring which originates from contributions of a cylindrical array of photolysis events in a photo-induced experiment, a variant of fluorescence imaging techniques has been developed to study photodissociation dynamics and collisional relaxation processes in the bulk. The experimental arrangement utilizes sliced imaging techniques of photofragments by the laser-induced fluorescence detection scheme. An unconventional procedure is employed to guide the photolysis laser in the viewing direction of the imaging detector with a proper obstruction. The sliced image in the direction perpendicular to the photolysis laser is equivalent to a two-dimensional projection of the fluorescence image of photoproducts from a single photolysis center. Experimental images of state-selected CN photofragments from the ICN photodissociation are presented to illustrate the versatility of the present method.
中文摘要

為了降低在光誘發實驗中柱狀陣列光解中心所造成的影像模糊，建立一套新穎螢光成像實驗方法，研究流動環境中光解動態學及碰撞鬆弛過程。本實驗採用雷射誘發螢光偵測方法執行光解碎片的切片式成像技術。迥異於傳統步驟，光解雷射沿成像偵測器的觀測方向射入，並於偵測器前安置一塊擋板阻擋光解雷射。垂直於光解雷射方向的切片式影像，就等於來自於單一光解中心的光解產物螢光影像之二維投影。為闡明切片式螢光成像之廣泛適用性，本論文報導碘化氰光解產生之氰基光解碎片，具狀態選定螢光成像實驗結果。
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Chapter 1

Introduction

1.1 Background

With the advent of technological innovations in the past two decades, the study of gas phase dynamics has matured, and increasing amounts of detail have been revealed in both full (elastic, inelastic, and reactive) and half (photodissociative) collisions.\(^{1-18}\) Sixty years ago, flash photolysis was still at an early stage.\(^{19}\) Gas-phase dynamic studies of molecular photodissociation processes were not practical until Norrish and coworkers recorded the vibrational spectra of excited O\(_2\) molecules\(^{20}\) and Polanyi developed the infrared chemiluminescence method.\(^{21}\)

By the late 1970’s, with the introduction of tunable dye lasers, researchers in the field of reaction dynamics have developed many techniques to probe the population distributions of internal quantum states (rotational, vibrational, spin-orbit, etc.) in a wide range of products from both unimolecular (photodissociation) and bimolecular reactions. These techniques included laser induced fluorescence (LIF).\(^{22,23}\)
coherent anti-stokes Raman spectroscopy (CARS)\(^{(24)}\) and resonance enhanced multiphoton ionization (REMPI).\(^{(25)}\) Not all products can be detected using these techniques, either because they have no suitable optical transitions within the available laser tuning range, or because the allowed transitions lead to unresolved spectra. However, state-specific detection schemes are now common tools in the study of reaction dynamics.

The past few decades have witnessed the development of four major methods to measure flux-velocity contour maps of scattered products from photofragmentation processes, inelastic and reactive collisions. They are: time-of-flight mass spectrometry (TOF-MS),\(^{(26-30)}\) Doppler spectroscopy,\(^{(31-48)}\) ion imaging,\(^{(1-11,49-53)}\) and fluorescence imaging.\(^{(54-57)}\) These state-resolved methods adopt either laser-induced fluorescence (Doppler spectroscopy and fluorescence imaging) or REMPI (TOF-MS and ion imaging) spectroscopic techniques. None of them can be applied universally; each method has its advantages and limitations.

In this thesis, I will report the first experimental study on ICN photodissociation in the bulk by a variety of fluorescence imaging\(^{(54,55)}\) techniques, where image blurring can be reduced substantially. By
comparing this new technique with other methods, we can identify its advantages. Hence, in this chapter, we will give a brief account of existing methods and their limitations.

1.2 Time-of-flight mass spectrometry

TOF-MS was the first method\(^{(58,59)}\) developed to measure the velocity distribution of reaction products. It is widely applicable and allows sensitive measurements. On the other hand, this method lacks state specificity. TOF-MS provides information on the translational energy distributions of photofragments. In TOF-MS experiments, the molecule of interest is seeded in a molecular beam, photodissociated by pulsed laser, and then ionized by electron impact. The products are detected by a mass spectrometer which registers their arrival times. Usually, a quadrupole mass spectrometer is employed to determine their temporal distribution of mass-selected photofragments moving across a well-defined distance.

To measure the angular distribution of photofragments, TOS-MS
experiments have been modified to include the use of a polarized photolysis laser and/or rotating sources or detectors.\textsuperscript{(28)} These experimental methods have adopted similar techniques employed in crossed beams studies.\textsuperscript{(28)} These refinements can supply us with plenty of information about the dynamic information of reaction products.

Generally speaking, detection of neutral photofragments is achieved either by optical (spectroscopic) or nonoptical techniques. Nonoptical method which is usually adopted by the conventional TOF-MS experiments involved nonspecific ionization of neutral particles. It is commonly accomplished by electron impact, followed by mass selection and ion counting. Generality is one of its advantages, that is, all neutral molecules can be detected and branching ratios of different reaction channels are readily measurable. However, quantum state resolution is more difficult to achieve using this nonoptical detection method. On the contrary, the primary advantage of spectroscopic detection is the possibility of quantum state selectivity. In addition, spectroscopic probes can afford another unique opportunity to measure the alignment and orientation of product rotational motions.

To prepare the clearest route to product state selection, REMPI
techniques have been used to ionize the reaction products to replace the traditional electron impact method. This REMPI-TOF technique can also be applied to the study of photo-initiated bimolecular reactions. It has been extended into a number of techniques (core extraction techniques, position sensitive translational spectroscopy, Doppler-selected TOF technique and many other techniques) for measuring the state-to-state differential cross sections or 3D velocity distributions of reaction products. We note that Rydberg tagging techniques can offer higher TOF resolution, but its application is limited to the detection of H and O atomic products.

In 1999, TOF-MS was one of the most powerful methods for measuring the velocity and angular distribution of photofragments, especially after the apparatus design was improved by Y. T. Lee et al. The energy resolution of TOF-MS is usually limited to resolve vibrational state distributions. In some cases, such as Rydberg-TOF experiments, the resolution can be improved to resolve rotational states. Higher energy resolution is its major advantage. Nevertheless, TOF-MS methods have some drawbacks that are hard to overcome by the nature of its 1D detection feature.
Firstly, TOF-MS is not sensitive enough to correlate angular momentum with other vector properties. TOF-MS detection schemes are generally 1D, so angular distributions and \( \mathbf{k'} - \mathbf{J'} \) correlation of reaction products are often measured by rotating source modules or detectors, or by using polarized light for photolysis. To detect products with different recoil angles, the detector has to be rotatable in the experiment. Because of the physical restrictions of the experimental arrangement, some recoil fragments at certain angles may not be detected. Consequently, experimentalists should employ alternative methods to determine the vector correlations of reaction products.

Secondly, it is necessary for TOF-MS experiments to register counting rates at each angle for a long period of time, in order to improve the signal-to-noise ratio. The angular and speed distributions of photofragments can only be obtained simultaneously with a fixed experimental geometry by image techniques.
1.3 Doppler spectroscopy

In the previous section, the pros and cons of TOF-MS spectrometry have been analyzed, which can be combined with REMPI techniques for state-selected dynamic studies. However, there are many important transient species – OH, CN, HCO, etc. – which can be detected efficiently using LIF\(^{(22,23)}\) techniques. With high resolution Doppler spectroscopy, researchers have produced one-dimensionally projected profiles of Newton spheres of state-selected products.\(^{(31-36)}\) These techniques have found many applications in the study of photodissociation processes and photo-initiated chemical reactions, where LIF techniques are invariably employed. To be precise, both LIF and REMPI techniques can be used in Doppler spectroscopy to measure the velocity and angular distribution of photofragments. In addition, Doppler spectroscopy has two advantages, that is, a zero background and its simplicity. Doppler spectroscopy can be carried out either with a molecular beam or in a bulb. Nevertheless, this rather useful method also has its own limitations.

Firstly, to obtain the recoil speed of photofragments, researchers must tune the laser frequencies back and forth over a narrow range in
order to excite all the reaction products. If the laser bandwidth is not narrow enough, it is impossible to measure the Doppler shifts across the spectral linewidth. In fact, the bandwidth of the probe laser must be much narrower than the spectral width of a transition to obtain Doppler profile at its best resolution.

Secondly, the velocity \((v)\) of photofragments is estimated from the Doppler shift \((\nu_D)\) using the following equation:

\[
v_D = v_0 \left(1 - \frac{v_k}{c}\right) \text{, and } v_k = v \cdot \hat{k}_{\text{probe}}
\]  

(1.1)

where \(v_0\) is the absorption frequency of the system at rest, \(v_k\) is the projection of the velocity of photofragments onto the direction of the probe laser beam and \(c\) is the speed of light. Obviously, the Doppler shift is very small due to the fact that the frequency shift is \(v_k / c\), where the speed of light \(c\) is much larger than \(v_k\). As a result, Doppler spectroscopy is basically limited to probe fast moving products.

Thirdly, in Doppler spectroscopic LIF experiments, a photomultiplier tube (PMT) is generally used as the detector. Thus, the 1D projection of speed profiles is obtained from the full 3D velocity distribution by the Doppler spectroscopy in order to determine the original velocity distributions and angular momentum polarizations. On
the other hand, the 1D projection of a 3D distribution depends on the probe direction. A true 3D distribution can only be determined by exhausting all the possible Doppler experimental configurations. In other words, it is possible to have identical 1D projection from different 3D velocity distributions. Moreover, processes in which various channels lead to the same products at different velocities will induce complicated Doppler profiles, from which it is difficult to extract detailed information.

Because image techniques can provide us a 2D projection of velocities and \( \nu-J \) correlation information for a state-selected product in an image frame, it should be a powerful alternative method. It also enables detailed study of alignment and orientation of the products.

1.4 Ion imaging

In the past two decades, the superiority of ion imaging\(^{(1-3)}\) has been demonstrated extensively. Ion imaging is the state-of-the-art method in the experimental study of molecular photofragmentation processes,\(^{(4-6)}\) inelastic,\(^{(7,8)}\) and reactive scatterings.\(^{(9-11)}\)
The first ion imaging experiment, which combined REMPI techniques with a 2D detection scheme to study the photodissociation of methyl iodide, was pioneered by Chandler and Houston\(^1\) in 1987. These experiments involved pulsed laser photolysis of CH\(_3\)I molecules which were seeded in a molecular beam under the condition of a supersonic expansion. The photodissociated methyl radicals were ionized to CH\(_3^+\) by a 2+1 REMPI process. These state-selected methyl cations were accelerated by an electric field, and passed through a field-free drift tube onto a position-sensitive detector. It consisted of a microchannel plate (MCP) coupled to a fast phosphor screen. The images were registered by a CCD camera.

Grid electrodes were used in these conventional ion imaging experiments to extract and accelerate the ions toward the detector. One significant difficulty was encountered, that is, the detected species are all produced at different positions which cause image blurring and a reduction in energy resolution. To improve this drawback, velocity map imaging (VMI)\(^{(49,50)}\) and slice imaging (SI)\(^{(51-53)}\) techniques have been developed to reduce image blurring by orders of magnitude. With these refinements, all the required information about photofragments, including
kinetic energy and angular distributions, can be extracted from the high-resolution 2D projections or 3D sliced images. A profusion of research activities using VMI and SI have been undertaken\(^{(3,11)}\) and unprecedented levels of detail about the dynamics of chemically significant systems have been unveiled. On the other hand, there are still some limitations in ion imaging experiments.

Firstly, at least one complete set of ion imaging equipment has to be set up in a vast vacuum chamber, plus several sets of high vacuum pumps, MCP, CCD and so on. All of those equipments are very costly to set up and maintain. Secondly, ion imaging experiments involve many tricky techniques which require long experience to learn, such as the control of the electric field. Thirdly, ion imaging method employs the molecular beam environment and REMPI techniques. This means that fewer products can be detected than those experiments using a bulk condition and LIF techniques, due to the fact that the number density and transition probabilities are higher in the later case. To obtain an image, it is necessary to use \(10^4\) to \(10^5\) laser pulses. However, the longer the experimental time, the more uncertainties are involved. To sum up, ion imaging is a very powerful method. To accommodate the REMPI
detection scheme, it has to be executed in a beam environment. Furthermore, highly skillful procedures should be followed to obtain high quality ion images.

1.5 Fluorescence imaging

In 1994, Chen et al.\(^{54,55}\) proposed the first fluorescence imaging experiment. They used a molecular beam environment and combined laser sheet illumination and 2D imaging techniques to determine the 3D distribution of number density, angle and velocity of state-selected CN photofragments by slicing an expanding, spherical shell from the photodissociation center.

Similar to ion imaging experiments, fluorescence imaging techniques can be used for multiplex detection. In the fluorescence imaging experiment, the molecules of interest are seeded into a high vacuum chamber through a pulsed valve to form a molecular beam; these precursors are then photodissociated and recoiled on expanding Newton spheres by the pulsed photolysis laser. After a long time delay (usually in the microsecond range), the 3D Newton spheres are sliced by a laser
sheet. The laser sheet is positioned at a fixed distance relative to the molecular beam, and is in resonance with one of the allowed product transitions. The intensity patterns of species thus intercepted are recorded by an ICCD detector. It had been found that a horizontal laser sheet allows for better measurement of velocity distributions than a vertical one. On the other hand, angular distribution can be more easily measured using a vertical slice.

Fluorescence imaging is more sensitive than ion imaging and can be carried out in a bulk condition in the absence of space charge effects. However, only partial 2D projected images could be acquired in the previous experiments\(^{(55)}\) and the information of angular distribution was lost. Secondly, unlike ion imaging methods, the velocity and angular distribution cannot be obtained simultaneously in a single experimental configuration. Thirdly, it is impossible to reduce image blurring, which are caused by the contribution from a cylindrical array of photolysis events. As a result, there is an urgent need to develop a new detection scheme to solve the problems of the existing techniques.
Chapter 2
Photodissociation of ICN

For investigations of the photodissociation processes, triatomic molecules are a good experimental subject. The dynamics of the dissociation processes and the potential energy surfaces of triatomic molecules can be calculated and simulated theoretically. For large polyatomic systems, there are too many uncertain parameters to make the predictions of dynamic models reliable. By the same token, photodissociation of diatomics is too simple, because the photofragments lack vibrational and rotational degrees of freedom.\(^{(34,74-77)}\) From the experimental consideration, the precursor should be easily dissociated with available light sources and photolysis products should be easily probed using a variety of laser-based diagnostic techniques. As a result, cyanogen iodide (ICN) has long been a popular precursor for photodissociation experiments, and it serves as a prototypical case in the study of photodissociation processes for triatomic molecules. For this reason, ICN was chosen as the precursor in the present study. Much
details of ICN photodissociation have already been known, and previous results serve to confirm the feasibility and practicability of our novel technique.

Photolysis of ICN via its $\tilde{A}$ band continuum which extends from about 210 to 320 nm has been well studied. When the ICN molecules are photodissociated at the peak of the $\tilde{A}$ continuum (e.g., ~266 nm, 300 K), two spin-orbit states of the iodine atom are produced along with the ground electronic state CN ($X^2\Sigma^+$): (78,80,82)

$$\text{ICN} + h\nu \rightarrow \text{I} + \text{CN} (X^2\Sigma^+) \quad (a)$$

$$\quad \rightarrow \text{I}^* + \text{CN} (X^2\Sigma^+), \quad (b)$$

where I and I* refer to I ($^2P_{3/2}$) and I ($^2P_{1/2}$), respectively. These two electronically distinct pathways which originate from predominantly parallel transitions, (78) can describe the $\tilde{A}$ band photodissociation of ICN completely. Their photodissociation yields account for approximately 40% in the I channel and 60% in the I* channel. (78,82,89) The branching ratio of I/I* changes more with respect to the photolysis wavelength other than the temperature. (91,94) In the nascent CN ($X^2\Sigma^+$) fragments, little vibrational excitation (89-91) is found, but they display high rotational excitation and the distribution of rotational states is
For instance, when ICN molecules are photodissociated at 266 nm, the rotational distribution of CN fragments (see Fig. 1) extends from $N^* = 0$ to 60 and exhibits a bimodal distribution.\(^{(42,89,91,93,94)}\) From the results of Wittig et al.,\(^{(42,94)}\) co-fragments of low $N^*$ CN are $I^*$ atoms, while those of high $N^*$ CN are $I$ atoms.

Theoretically, at least three interacting potential energy surfaces contribute to the $\tilde{A}$ band absorption of ICN. Among them, the $\left| ^3 \Sigma_{0^+}, \Omega' = 0 \right\rangle \leftarrow \left| ^1 \Sigma_{0^+}, \Omega^* = 0 \right\rangle$ component exhibits the characteristics of a parallel-type transition. The other two components $\left| ^3 \Pi_1, \Omega' = \pm 1 \right\rangle \leftarrow \left| ^1 \Sigma_{0^+}, \Omega^* = 0 \right\rangle$ and $\left| ^1 \Pi_1, \Omega' = \pm 1 \right\rangle \leftarrow \left| ^1 \Sigma_{0^+}, \Omega^* = 0 \right\rangle$ are perpendicular transitions.\(^{(85,87,95-101)}\) The character of these transitions remains a disputed issue. Ling and Wilson\(^{(78)}\) claim that the products in both channels are primarily formed via parallel transitions. But Vigue et al. state that there is a small proportion of perpendicular transitions,\(^{(102)}\) implying that the transition has mixed characters. Morse et al. suggest that only parallel transitions contribute to the $I^*$ channel and that the $I$ channel arises from mixed transitions.\(^{(92)}\)

To sum up, there are experimental evidences which imply that the dominant initial transition is from the ICN ground electronic state to a
linear excited state. From the fact that I channel has a hotter CN rotational distribution than those of the I* channel, it suggests that the I* channel arises from an excited potential surface in a linear ICN configuration, while the I channel favors a bent geometry. In other words, it indicates that more than two excited states are involved in the process.\(^{(42,78,82,89,93)}\)
Chapter 3
Sliced fluorescence imaging experiments

3.1 Introduction

Before presenting this novel technique of sliced fluorescence imaging (SFI), it is necessary to distinguish the experimental conditions required for ion imaging and sliced fluorescence imaging. To avoid producing the repulsive force between ions due to Coulombic interactions (i.e. space charge effect), ion imaging experiments should utilize a molecular beam. On the contrary, neutral products are detected in a LIF scheme where the number densities of the excited state species have no limitation, provided that a collision-free condition is maintained. As a result, LIF experiments, including Doppler spectroscopy and sliced fluorescence imaging, can easily be carried out in a bulk condition.

Contrary to the beam environment, there are two most important characteristics to be considered for photodissociations in a bulb, namely, higher number densities and thermal energies of precursors. Thermal energies of precursors cause broadened image features. This issue will be
discussed in a later section. We shall focus on number density first.

In the present experiment which is executed in a flow cell at a partial pressure of 5 mTorr, the number density is estimated to be $1.63 \times 10^{20}$ molecules per liter. Under these conditions, the effective photolysis volume contains at least $10^7$ molecules which will be photodissociated. The photolysis volume from a single photolysis center is defined by a cube of 50 μm on each side (see later section). The parent molecules in the effective volume (see Fig. 2) with different spatial positions and different velocity vectors are dissociated. The resultant photofragments recoil on Newton spheres with their expansion rate determined by the energy conservation. They form a cylindrical array along the propagation direction of the photolysis laser (see Fig. 3a). This number density is about three orders of magnitude higher than those in molecular beam experiments. It implies that images with a better signal-to-noise ratio and a reasonable energy resolution are expected under the bulb environment.

Unless the photoproducts from a single photolysis center can be registered, the image will be blurred by the photolysis events along the intersection region between the photolysis laser and precursors, no matter which imaging technique is employed.
In ion imaging experiments, the cylindrical array of photolysis centers is created by the intersection of the photolysis laser with a molecular beam of finite width. When a REMPI detection scheme is employed, the resultant two-dimensionally (2D) projected image is blurred by the combination of ions from separate, spatially offset Newton spheres. To reduce the blurring, a new technique named velocity map imaging (VMI) was developed in 1999, and a dramatic improvement in image resolution was achieved. Employing electrostatic ion lenses (i.e., repeller plate, extractor and ground electrode), Eppink and Parker could refocus successfully all particles with the same initial velocity vector onto the same point of a 2D detector, irrespective of their birthplace in the ionization volume.

Obviously, this solution is not suitable for LIF techniques where the motion of photons cannot be altered by the electric field as in the case of ion imagings. It is therefore necessary to consider the key point of this issue: how can one avoid blurring of the image when an array of 3D Newton spheres is projected into a 2D image? Fig. 3b shows a recommended solution to this problem. Breaking a longstanding taboo, one should orient the detector directly in line with the photolysis laser.
This new detection scheme is an indispensable innovation in this technique (see later section).

Finally, we are confident that the obstruction which is utilized to protect the ICCD does not interfere with the image formation process seriously. As an example, a half-covered lens still can image a lighted candle faithfully, while the intensity of the registered pattern of the flame is reduced to half of those with an unblocked lens.

3.2 Design concept

The detail design concept which aims at the reduction of image blurring in a sliced fluorescence image experiment is quite straightforward and is illustrated in Fig. 4. A pulsed photolysis laser is deliberately guided to enter a flow cell along the viewing direction of an imaging detector. A suitable obstruction is employed to block the exiting laser beam without introducing any erroneous effects on image formation. Perpendicular to the photolysis laser, a probe laser sheet is employed to resonantly excite state-selected photofragments. Photofragments which
are in a specific product state with a recoil speed of $v_{\text{rec}}$ are distributed identically on an array of expanding Newton spheres with their photolysis centers along the path of the photolysis laser. If the delay time between the photolysis and probe lasers is $t$ and the origin is chosen to be their crossing point, the probe laser sheet can then only interact with photofragments on a limited number of Newton spheres, where their photolysis centers are within $\pm v_{\text{rec}} t$ with respect to the origin. Sliced crescents between various Newton spheres and the probe laser sheet inside the interaction region reside in different spatial locations, where they form a distribution characteristic of the excited state species (see Fig. 4). Most importantly, the resultant fluorescence image is equivalent to a 2D projection of the fluorescent Newton sphere from a single photolysis center at the origin. Thus, image blurring in the sliced fluorescence imaging experiment can be minimized by adopting this unconventional strategy.

Although we label this method “sliced” fluorescence imaging, it is important to distinguish between sliced ion imaging and sliced fluorescence imaging techniques. Sliced ion imaging registers only the central slice of the ion packet by a gated detector. On the other hand,
sliced fluorescence imaging intercepts cylindrical array of Newton spheres in the beam waist region of the photolysis laser, to obtain a 2D projected image of a single Newton sphere.

### 3.3 Apparatus setup and experimental procedures

A schematic diagram of the sliced fluorescence imaging experiment is depicted in Fig. 5. ICN photodissociation at 266 nm was executed in the bulk to demonstrate the simplicity of the present method. An ICN (ACROS, 98% purity) sample, which has been purified by vacuum sublimation, was introduced into a stainless steel flow cell (17 × 10 × 8 cm³) at a partial pressure of 5 mTorr. The fourth harmonic of a Nd: YAG laser (LOTIS TII, LS-2132 UTF) at 266 nm was guided into the flow cell to photodissociate ICN molecules. The linearly-polarized photolysis laser was loosely focused (beam waist at 50 μm) and delivered 8 ns pulses at 20 mJ per shot. The probe laser was a XeCl excimer pumped dye laser system (Lambda Physik, LPX 205i and LPD 3002E) and it delivered tunable laser pulses around 388 nm (3 mJ per pulse; BiBUQ dyes, LC
3860) with a bandwidth of about 0.2 cm\(^{-1}\) and a pulse duration of 15 ns. Before entering the reaction chamber, each laser beam passed through a polarizer and a waveplate in order to ensure complete linear polarization during experiment. A laser sheet (height of 3 cm and width of 150 μm) with an effective length of 10 cm was formed by passing the probe laser beam through a divergent and a cylindrical lens. The central region of the laser sheet which had a constant energy profile was crossed by the photolysis laser beam. With an appropriate delay between the photolysis and probe lasers, state-selected CN photofragments on an array of expanding Newton spheres can be probed by the LIF detection scheme. The net effect of spontaneous emissions from electronically excited species inside the interaction region was elucidated above. In essence, the sliced image in the direction perpendicular to the photolysis laser is equivalent to a 2D projection of the fluorescence image of photoproducts from a single photolysis center. Thus, the imaging detector has to be positioned along the propagation direction of the photolysis laser in order to register the fluorescence image on the excitation plane (see Fig. 4 and 5). The imaging detector in the present experiment was an intensified charge-coupled device (CCD) camera (Roper, PI-MAX, 512 RB) and was
protected against the photolysis laser by mounting an appropriate obstruction on the exit window of the 266 nm laser beam.

To trigger the photolysis and probe lasers, as well as the CCD detector properly, a delay generator (Stanford Research System, DG 535) was employed to provide the timing sequence. In order to avoid collisional relaxations of CN photofragments at high recoil speeds, the delay time between the photolysis and probe lasers was set at 800 ns. The relative pulse sequence is shown in Fig. 7. Concurrently, a reasonably good energy resolution of the resultant fluorescence images could be maintained at this delay time. These two consecutive laser pulses were monitored by a phototube (Hamamatsu, R1193U-02) and displayed on a digital oscilloscope (LeCroy, 9361). In addition, their shot-to-shot fluctuations of energies and pulse jitters could be watched closely. The imaging detector in a gated mode was triggered to register fluorescence images at a delay time of 25 ns after the probe laser pulse. Scattered photons from the photolysis and probe laser beams were rejected by properly gating the CCD camera. A 10 ns high voltage pulse, which activated the gain of the imaging detector, could guarantee that CN photofragments at a recoil speed of around $2000 \text{ms}^{-1}$ appear almost
stationary. Thus, the discord between collection efficiencies of fluorescent photons and image blurring induced by fast moving photofragments could be resolved.

3.4 Imaging processing and convolution fitting

A. Imaging processing

The raw image (see Fig. 8) from the experiment SFI was a 2D projection of the 3D distribution of CN photofragments. It was registered on the ICCD detector and transferred to a computer in the .spe format (this format can only be read by ICCD WinView32 software). To reconstruct the central slice of the 3D distribution of the fluorescent Newton sphere, inverse Abel transformation\(^{(104)}\) was executed. The Basex software package was employed to execute the inverse Abel transform. The input file of Basex must be either in ASCII-2 format (three columns: x, y and Intensity; columns x and y must be separated by a comma but there should be no comma between the y and Intensity columns), or a .dat file containing the matrix of intensities. Other software package
(OriginPro7.5) was utilized to convert these formats. There are two conditions that the images must meet before they can be input into the Basex software package:

(1) The image must be oriented such that the axis of cylindrical symmetry coincides with the vertical axis.

(2) The image must be centered exactly and must have an odd number of pixels in each dimension.

These limitations imply that a poorly centered image will cause reduction in resolution. This feature also can be used as an aid in centering the image. Actually, nine trial pixels around the chosen center were selected to find the best centered image.

As part of the image-centering process, the integral of pixel intensity along the $x$ and $y$ axes was displayed (see Fig. 9). This allows for an easier identification of the central pixel in the $512 \times 512$ matrix. It is necessary to reduce the dimensions of the matrix to an odd number (e.g. $401 \times 401$, see Fig. 10) such that a unique axis of cylindrical symmetry can be defined. Finally, the centered image can be filtered to subtract the background caused by dark currents. The digitized image in a matrix form is input into the Basex software (see Fig. 11) to generate a
reconstructed image (see Fig. 12).

By integrating the image intensity against radius (measured from the central pixel), we can determine the speed distribution of CN photofragments. A scale reference (see Fig. 13) is utilized to measure the physical distance between adjacent pixels such that the physical dimensions of the image can be determined exactly. The flight time of photofragments can be measured by a phototube and displayed on the oscilloscope. Velocity calibration is straightforward in SFI than those procedures employed in ion imaging experiments, where the magnification effect of ion images by the electrostatic field should be carefully determined. Because the speed distribution is observed in the laboratory frame, a convolution procedure is therefore necessary to obtain the photofragment velocity distribution in the center-of-mass frame.

**B. Convolution fitting**

Convolution is a mathematical operation on two functions \( f \) and \( g \), producing a third function that is typically viewed as a modified version
of one of the original functions. The observed laboratory-frame speed
distribution of the photofragments can be regarded as a convolution
between the distributions in the center-of-mass frame and the thermal
motions of precursors. Thus, we can obtain the recoil speed of
photofragments in the center-of-mass frame by a convolution fitting
process. The convoluted function has been derived by Cline et al.\textsuperscript{(105)} as
follows:

If we assume these parent molecules move in space randomly, they
should have an isotropic Maxwellian velocity distribution as follows:

\[ G(v) = \left( \frac{M}{2\pi kT} \right)^{\frac{3}{2}} \exp\left( -\frac{Mv^2}{2kT} \right), \]

where \( M \) is the mass of the parent molecule, \( k \) is the Boltzmann constant,
\( v \) is the speed of parent molecules and \( T \) is the equilibrium temperature.

The nascent laboratory-frame velocity distribution is given by

\[ F_{\text{c.m.}}(v, \theta) = \frac{f_{\text{c.m.}}(v)[1 + \beta_{\text{c.m.}} P_2(\cos \theta)]}{4\pi}. \]

The convolution integral can be written as follows:

\[ F([v], \theta) = \int d\nu' F_{\text{c.m.}}(v') G([v - v']). \]

Substituting Eq. (3.2) into Eq. (3.3), one obtains

\[ F(v, \theta) = \left[ \int_0^\infty \nu'^2 d\nu' \right] \sin \theta' d\theta' \left[ \int_0^{2\pi} \right. \left. d\phi' \right. \]

\[ \times f_{\text{c.m.}}(v') I(\nu') G([v - v']). \]
The various angles and vector are defined in Fig. 14 and $G(v)$ is defined in Eq. (3.1). By rotating the space-fixed coordinate system to one with the $z$ axis along $v$, one can have following equation in a new coordinate system.

$$F(v, \theta) = \int_{-\pi}^{\pi} \int_{0}^{\pi} \sin \theta'' d\theta'' \int_{0}^{2\pi} d\phi'' f_{\text{c.m.}}(v') \times \frac{1}{4\pi} [1 + \beta_{\text{c.m.}} P_2(\cos \theta')] G(\sqrt{v^2 + v'^2} - 2vv' \cos \theta'').$$  \hspace{1cm} (3.5)

Then spherical harmonic addition theorem is used to express $P_2(\cos \theta')$ in terms of the double-primed and unprimed angular coordinates, and the integrals over the angular coordinates are easily solved. Simplifying the remaining radial integrals over $v'$, one can obtain following equation:

$$F(v, \theta) = \frac{1}{4\pi} \left\{ h_0(v) + [h_0(v) + h_2(v)]\beta_{\text{c.m.}} P_2(\cos \theta') \right\},$$  \hspace{1cm} (3.6)

where

$$h_0(v) = \frac{\kappa}{\pi} \int_{0}^{\infty} \frac{v'}{v} f(v')(e^{-\kappa(v-v')^2} - e^{-\kappa(v+v')^2}) dv',$$  \hspace{1cm} (3.7)

$$h_2(v) = \frac{3}{2} \frac{\kappa}{\pi} \frac{1}{\kappa v^2} \int_{0}^{\infty} f(v') [e^{-\kappa(v-v')^2}] \left( \frac{1}{2\kappa v'} - 1 \right) \left( -e^{-\kappa(v+v')^2} \left( \frac{1}{2\kappa v'} + 1 \right) \right) dv'. \hspace{1cm} (3.8)$$
and \( \kappa = \frac{M}{2kT} \). If \( f_0'(v) = h_0(v) \) and \( f'_2(v) = h_0(v) + h_2(v) \), then \( F(v, \theta) \) can be written as
\[
F(v, \theta) = \frac{1}{4\pi} [f_0'(v) + f'_2(v) \beta_{\text{c.m.}} P_2(\cos \theta)]. \tag{3.9}
\]

If \( h_2(v) << h_0(v) \), then Eq. (3.9) can be written as
\[
F(v, \theta) \cong f_0'(v)[1 + \beta_{\text{c.m.}} P_2(\cos \theta)]. \tag{3.10}
\]

The velocity and angular distribution are almost separable and the function \( f_0'(v) \) is the isotropic speed distribution of the photofragments in the laboratory frame, broadened by the Maxwell speed distribution of the parent molecules. Taking it as a state function, one can simplify it as follows:
\[
f_0'(v) = \sigma \sqrt{\kappa} \frac{v'}{v} (e^{-\kappa(v-v')^2} - e^{-\kappa(v+v')^2}), \tag{3.11}
\]
where \( \sigma \) is a weighting factor, \( v \) is the speed of photofragments in the laboratory-fixed frame and \( v' \) is the speed of photofragments in the center-of-mass frame.

This function was employed as a best-fitting simulation in our data processing. The prerequisite to utilize this function is that the nascent photofragment speed is much larger than the thermal speed of the parent molecules. There are two fitting parameters \( (v' \text{ and } \kappa) \) in this equation. By fitting these two parameters, one can obtain the velocity of CN
fragments in the center-of-mass frame. By the way, the definition of $\kappa$ has been stated in Eq. (3.8), and the meaning of $\frac{1}{\sqrt{\kappa}}$ is the most probable thermal velocity of the parent molecules. It is consistent with the fact that the exponential terms in Eq. (3.11) are dimensionless. By fitting $\kappa$, it provides us the information of thermal temperature and thermal energy of parent molecules.

3.5 Results

The rotationally resolved fluorescence images of CN photofragments from ICN photodissociation at 266 nm were obtained by SFI experiments. The potential energy curves and the electronic transitions of CN radicals are shown in Fig. 15. Their excitation spectrum (see Fig. 16) has been calibrated against the high-resolution spectroscopic work by Miller and co-workers. The spin-rotation fine structure levels were not resolved under the present experimental conditions. Two representative raw fluorescence images of CN for $N = 3$ and 27 are shown in column (a) of Fig. 17 along with their physical dimensions and
polarization direction of the electric field of the photolysis laser. The polarization direction of probe laser is parallel to those of the photolysis laser in the present experiment. In particular, the coincidently-generated iodine co-fragments are exclusively in the excited $^2P_{1/2}$ state (I*) for CN in the $N = 3$ rotational state (see Fig. 17). For cases in which both the excited and ground state ($^2P_{3/2}$) iodine channels are open, a representative fluorescence image for CN in the $N = 27$ rotational state exhibits an expected double-ring feature.

From the scale reference, we estimate their diameters to be 3 mm and 5 mm for $N = 3$ and $N = 27$, respectively. These two images were the 2D projections of 3D Newton spheres of CN photofragments, which were detected after a flight time of 825 ns from the photolysis events. The raw data were obtained by averaging 18000 image frames, in which the experiment was controlled and processed by an appropriate software (Roper, Winview/32). To ensure that the angular distribution of photofragments was accurately registered, the frequency of the probe laser was scanned back and forth across the Doppler profile of a chosen transition. Before the inverse Abel transformation was executed, the raw data were centered and symmetrized according to image processing
procedures (section 2.4, part A).

The Abel transform of the original 2D projected images produces a central slice (see column (b) of Fig. 17) of the 3D Newton sphere, along with its velocity distribution. Beyond the branching ratio measurements, the anisotropy parameters, \( \beta \), for each ring in the fluorescence images can also be determined from the inversion process. The anisotropy parameters are \( \beta_{1s} = 1.9 \) \((N = 3)\), \( \beta_{1s} = 1.7 \) \((N = 27, \text{inner ring})\) and \( \beta_{1} = 1.3 \) \((N = 27, \text{outer ring})\).

To compensate for the contribution of the thermal velocity distribution and internal energies of ICN precursors to the observed speed of CN photofragments, the convoluted laboratory-frame velocity distribution function (see section B of chapter 2.4) is used to find the best fit for the experimental results (see column (c) of Fig. 17). The best-fit numerical values of the recoil speeds of CN in the center-of-mass frame are \( v_{\text{rec}} = 1695 \text{ m s}^{-1} \) \((N = 3)\), \( v_{\text{rec}} = 1367 \text{ m s}^{-1} \) \((N = 27, \text{inner ring})\) and \( v_{\text{rec}} = 2690 \text{ m s}^{-1} \) \((N = 27, \text{outer ring})\). The corresponding internal energies of ICN precursors are \( E_{\text{int}} \text{(ICN)} = 807 \text{ cm}^{-1} \) \((N = 3)\), \( E_{\text{int}} \text{(ICN)} = 922 \text{ cm}^{-1} \) \((N = 27, \text{inner ring})\) and \( E_{\text{int}} \text{(ICN)} = 421 \text{ cm}^{-1} \) \((N = 27, \text{outer ring})\). All the relevant results are summarized in Table 1.
These results were substituted into the following energy conservation equation to determine the bond dissociation energy \( D_0(\text{I–CN}) \):

\[
E(hv) + E_{\text{int}}(\text{ICN}) - D_0(\text{I–CN}) = E_T + E_{\text{so}} + E_{\text{int}}(\text{CN}) \tag{3.12}
\]

In the above equation, \( E(hv) \) is the photon energy (37594 cm\(^{-1}\) at 266 nm). \( E_T \) is the total kinetic energy of photofragments in the center-of-mass frame and \( E_T = \frac{m_{\text{CN}}(m_I + m_{\text{CN}})v_{\text{rec}}^2}{2m_I} \). \( E_{\text{so}} \) is the iodine spin-orbit energy (7603 cm\(^{-1}\) for \( \text{I}^* \), 0 cm\(^{-1}\) for I). \( E_{\text{int}}(\text{CN}) \) is the internal energy of CN fragments. When ICN is photodissociated at 266 nm, there is very limited CN vibrational excitation\(^{(81,90,94,95)}\) and no measurable \( \text{A}^2 \Pi \) excitation\(^{(81)}\), such that \( E_{\text{int}}(\text{CN}) \) is predominantly rotational excitations. Thus, \( E_{\text{int}}(\text{CN}) = B_0N(N+1) \), where the rotational constant \( B_0 \) is 1.973 cm\(^{-1}\).

The averaged bond dissociation energy \( D_0(\text{I–CN}) \) is calculated to be 26962 ± 105 cm\(^{-1}\), which is consistent with the previous result of 26980 ± 100 cm\(^{-1}\), obtained from high-resolution frequency modulated absorption spectroscopic measurements\(^{(48)}\). However, the internal energies of ICN for the \( \text{I}^* \) channel are consistently higher than those for the I channel by an amount of 400–500 cm\(^{-1}\).
3.6 Discussion

A. Comparison with previous works

A comparison between the results from SFI and other studies is presented. The $I^*/I$ branching ratios from SFI experiments are consistent with previous studies on ICN photodissociation at 266 nm$^{(42,48)}$ for quite a few selected rotational states of CN. Fig. 18 shows the results from sub-Doppler resolution (0.007 cm$^{-1}$) LIF experiments,$^{(42)}$ on the $I^*/I$ branching ratio and Doppler profile for rotational state $N = 30$. The spin-orbit splitting ($E_{so} = 7603$ cm$^{-1}$) of iodine atoms dictates the kinetic energies of $I^*$ channel to be much less than those of the $I$ channel. Thus, the recoil speeds of CN fragments in the $I$ channel are almost twice as fast as in the $I^*$ channel. From the SFI experiment, image feature which corresponds to the $I$ and $I^*$ channels can be discerned at a glance, in which the outer ($I$ channel) and inner ring ($I^*$ channel) of the fluorescence images in Fig. 17 (a) demonstrate the advantage of the present method.

However, in the sub-Doppler experimental results, the Doppler profile for the $I$ channel is just a shoulder (see Fig. 18) which is obscured by the contribution from the $I^*$ channel. It is due to the fact that the laser
bandwidth (0.007 cm\(^{-1}\)) is not narrow enough to resolve the Doppler profile definitely. To improve the resolution of Doppler spectra, Costen \textit{et al.} used high-resolution frequency modulated (diode laser bandwidth at 100 MHz) absorption spectroscopy to measure the Doppler profiles of nascent CN (\(X^2\Sigma^+\)) fragments from the \(\tilde{A}\) band photodissociation of room temperature ICN.\(^{48}\) The Doppler shoulders can be improved to Doppler wings (see Fig. 19), where the resolution has been much improved by this method. Unfortunately, the 7603 cm\(^{-1}\) difference in energy between the I and \(\tilde{I}\) channels is inconsistent with their experimental results.

In the SFI experiments, the spin–orbit splitting (\(E_{so} = 7603\) cm\(^{-1}\)) between I and \(\tilde{I}\) is in total conformity with the empirical measurements of speed distributions. The recoil speeds of CN fragments and the internal energies of ICN obtained from sliced fluorescence imaging techniques are more reliable than those from other experimental techniques.
B. Improvements of resolution

The energy resolution of the present method depends on the translational and internal motions of precursors, as well as the intensity profiles of the two crossed lasers and their delay times. For a loosely focused photolysis laser (266 nm) with a beam waist at 50 μm, its angular beam spread\(^{(108)}\) is 0.1°. For a finite viewing zone (±3 mm with respect to the origin) determined by camera lens, the contribution of laser beam divergence to the convoluted fluorescence image is negligible under the present experimental conditions.

The effective volume of photolysis events and the thickness of probe laser sheet could in theory affect the resolution of the images, but both effects are not significant in the present experimental conditions. In the absence of thermal energy contributions, the thickness of the expanded Newton-spherical shell is mainly determined by the beam waist of the photolysis laser and changes little over time. In other words, it can be assumed that the physical dimensions of Newton spheres will evolve with time, but the thickness of the shell remains the same. Therefore, the speed resolution could be estimated to be around 0.2 %, if the beam waist of the
photolysis laser is 50 μm and the diameter of Newton spheres expand to 5 mm. Consequently, the speed resolution could be improved by increasing the delay time between photolysis laser and probe laser. In the present experiment, the speed resolution is estimated to be 12 % which is far from the ideal case. We can clarify this issue by comparing molecular beam and bulb environments. In ion imaging experiments, the contributions of thermal energy are usually negligible. Because in a highly-collimated molecular beam, the precursor molecules have a narrow speed distribution and a low rotational temperature by the supersonic expansion and energy-transfer collisions. In contrast, the thermal energies of precursors in the bulk distribute to the energy balance in the photodissociation. This results in a broader speed distribution of CN fragments and widened crescents in the projected images. Therefore, the energy resolution of the present method could be much improved, provided that the translational and rotational temperatures of precursor molecules are lowered efficiently by the supersonic expansion technique.

Furthermore, the internal energies of ICN in the I* channel are consistently higher than those in the I channel by 400–500 cm⁻¹ in this work. This suggests that bending-mode excited ICN molecules (V_{ben}}
= 305 cm\(^{-1}\)) play an important role in the vertical transition which leads to the \(I^* + \text{CN}\) channel. This is due to the fact that the asymptote 
\[
\text{CN}(\Sigma^+, J'M'N', \frac{1}{2}) + \text{I}(^2\text{P}_{1/2})
\]
correlates to a bent repulsive state 
\[
^3\Pi_{0-}, \Omega' = 0
\]. In addition, the vertical transition favors the bending-mode excited ICN molecules from the Franck-Condon principle.
Chapter 4
Conclusions and prospective

A. Conclusions

We have demonstrated the simplicity of sliced fluorescence imaging in the study of a prototypical photodissociation system. Using this technique, image resolution has been significantly improved. A high quality image with medium speed resolution has been obtained in the experimental study of ICN photodissociation at 266 nm. The internal energies of ICN, recoil speeds of CN fragments and bond dissociation energy of I-CN have been accurately determined by this experimental technique.

In comparison with Doppler spectroscopy, the advantages of SFI are better energy resolutions, simpler data processing and more consistent results. SFI can be executed either in a bulb or in a molecular beam environment. In addition, the saturated absorption and space charge effects are absent in the probe laser sheet excitation scheme of the present method.
To improve the energy resolution of the present method, sliced fluorescence imaging experiments should be carried out in a beam environment, along with an elongated delay time between the pump and probe laser pulses.

**B. Prospective**

To acquire the central slice of three-dimensional product distributions, the SFI methods can be refined to a new experimental arrangement, namely, spatial-selected sliced fluorescence imaging. This novel approach involves three laser pulses to achieve the state-to-state detection scheme. A pulsed photolysis laser is guided to enter the reaction chamber along with the viewing direction of an imaging detector. Perpendicular to the photolysis laser, the first probe laser is employed to excite the photofragments to an excited state simultaneously. Both these two laser pulses are tightly focused for reducing the effective volume of a photolysis center. After a long time delay, these photoproducts are illuminated by the laser sheet of the second probe laser and the central
slice of fluorescent Newton sphere is registered by the ICCD detector. The main design concept is that a single photolysis center can be defined by crossing the photolysis laser with the first probe laser. As a result, the expanded Newton spheres sliced by the laser sheet come from photolysis centers inside a μm-sized spot.

The development of sliced fluorescence imaging techniques is cheerful and its advantages in the study of photo-initiated chemical reactions as well as collisional relaxations in a flow cell are highly expected. The collisional energy transfers including rotational (RET), vibrational (VET) and electronic energy transfer (EET) are ubiquitous and fundamental processes. For instance, they may increase or inhibit the reactivity of molecules. They can quench the radiative decay of molecular emissions and broaden spectral profiles of molecular absorption, such that a diagnostic probe on their environment can be established. They are the subject of very extensive experimental investigations, and still provide challenges to the highest levels of theory. To study more about collisional energy transfer from the measurement of vector properties (e.g., velocities and angular momenta), we will consider the inelastic energy transfer through RET, which may or may not be accompanied by
the others (VET and EET). This is because in the investigation of scalar properties, much of the detailed information is lost if the measurement of rotational quantum states before and after the collisions are not specified.

There are six distinctly different experimental approaches based on RET to investigate potential energy surfaces (PES). They are: velocity-map imaging, hexapole field selection, additional electrostatic field selection, Zeeman quantum beat spectroscopy, polarization spectroscopy and frequency-modulated spectroscopy. However, none of them is universally applicable. Now, sliced fluorescence imaging can offer another avenue to explore RET.

The results of a collisional relaxation study on nascent CN photoproducts are reproduced in Fig. 20. One can clearly see the decay in both velocity and anisotropy with increased pressures of the collider gas. Compared with conventional Doppler spectroscopic measurements, which are limited by their laser bandwidths, sliced fluorescence imaging techniques can be expected to provide insightful results in the study of collisional relaxation in a flow cell. In addition, sliced fluorescence imaging can be a versatile tool in the study of photo-induced dynamic processes.
References:


9. T. N. Kitsopoulos, M. A. Buntine, D. P. Baldwin, R. N. Zare and D. W.


Figure 1. Nascent CN rotational distribution. The first sharp peak is at low $N^\prime$ ($N^\prime=2$) and the second broad distribution peaks at high $N^\prime$ ($N^\prime=49$). The I$^*$ channel produces exclusively low $N^\prime$ with little population above $N^\prime=30$. The I channel is associated with a broad distribution at higher $N^\prime$. (From I. Nadler, D. Mahgerfeth, H. Reisler and C. Wittig, J. Chem. Phys., 1985, 82, 3885.)
Figure 2. Illustration of the effective photolysis volume (yellow area). Each circle represents a parent molecule whose velocity vector is shown as an arrow. The precursors with blue arrows will be excited, and those with red arrows will not. Those molecules which are not originally inside the photolysis volume still can be excited if they move into the volume during the duration of the laser pulse.
Figure 3. (a) Cylindrical array of Newton spheres. (b) Diagram on the relative orientation between the cylindrical array and the ICCD.
Figure 4. Illustration of the reduction of image blurring. The photolysis laser beam (purple) crosses the probe laser sheet (red) at the origin O. The combination of sliced crescents (blue) is equivalent to a 2D projection of the fluorescent Newton sphere from a single photolysis center at the origin.
Figure 5. Experimental apparatus. (a) Polarizer, (b) wave plate, (c) lens (15 cm focal length), (d) cylindrical lens, (e) lens (30 cm focal length), (f) divergent lens, (g) obstruction, (h) cutoff filter (> 370 nm), (i) bandpass filter (400 ± 50 nm), (j) phototube, (k) vacuum port and (l) sample port.
Figure 6. Photograph of the experimental apparatus.
Figure 7. Timing sequence for the sliced fluorescence imaging experiment.
Figure 8. Photofragment image for the CN (ν = 0, N = 27) products of ICN photodissociation at 266 nm. This raw image on a 512×512 pixel grid is off-centered and asymmetric due to the non-uniformity of the ICCD.
Figure 9. 1D projections of the raw image data (see Fig. 8) along the (a) X axis and (b) Y axis. The center of the image from these 1D projections can be found more easily.
Figure 10. A centered image. The center of the raw image (Fig. 8) is found to be $X=271$, $Y=262$, and the image size is reduced to $401 \times 401$ pixels. One can symmetrize the raw data using this centered image.
Figure 11. A Basex-adjusted image which has been centered and symmetrized. A central slice of the 3D distribution can be obtained by executing an inverse Abel transform on this raw image.
Figure 12. (a) A symmetrized raw image. It is the 2D projection of a 3D Newton sphere. (b) An inverse-Abel-transformed image. It is the central slice of a 3D Newton sphere.
Figure 13. A scale reference for the measurement of the image size. This scale reference is a squared grid paper in which the length of each grid is 1 mm.
Figure 14. Coordinate system for the convolution integral of Eq. (3.4).

(From J. I. Cline, C. A. Taatjes and S. R. Leone, J. Chem. Phys., 1990, 93, 6543.)
Figure 15. Potential energy curves for the CN $B^2\Sigma^+$, $A^2\Pi_i$, and $X^2\Sigma^+$ electronic states. In this work, the CN photofragments were detected by tuning the probe laser into the $R$-branch of the (0,0) band of the $B^2\Sigma^+ \leftarrow X^2\Sigma^+$ electronic transition. (From J. B. Halpern and Y. Huang, *Research in Chemical Kinetics, Volume 1*; ed. R. G. Compton and G. Hancock, Elsevier Science Publisher B. V., 1993, pp. 347-387)
Figure 16. Excitation spectrum of CN ($X^2\Sigma^+$) photofragments from ICN photodissociation at 266 nm. This spectrum is not corrected for probe laser power.
Figure 17. Fluorescence images of CN at $N = 3$ (upper panel) and $N = 27$ (lower panel). (a) Raw data. (b) Inverse-Abel-transformed images. (c) Speed distribution (dot: experimental result; solid line: simulation). The physical dimensions of images and polarization direction of the electric field of the photolysis laser are shown on the graph. The polarization direction of the probe laser is parallel to those of the photolysis laser in the present experiment. The anisotropy parameters, best-fitted recoil velocities and internal energies of ICN are listed in Table 1.
Figure 18. Illustration of Doppler shoulders. (From I. Nadler, D. Mahgerefteh, H. Reisler and C. Wittig, *J. Chem. Phys.*, 1985, 82, 3885.)
Figure 19. Experimental results on CN ($N=30$) from high-resolution transient FM spectroscopic experiment. In comparison with Doppler shoulders (see Fig. 18), signals between $I^*$ channel (inner peaks) and $I$ channel (outer peaks) can be better resolved into Doppler wings. Dashed line is the best fit with separately adjusted available energies for $I$ and $I^*$ channels. Solid line is the (poor) best fit obtainable without floating the $I^*$ channel available energy. (From M. L. Costen, S. W. North and G. E. Hall, *J. Chem. Phys.*, 1999, **111**, 6735.)
Figure 20. Fluorescence images of the collisional relaxation study. Two rotational states of CN ($B^2\Sigma^+$) were measured under various N$_2$ pressures. N$_2$ was employed as the quenching gas in these experiments.
Table 1: Experimental results on ICN photodissociation at 266 nm by the sliced fluorescence imaging technique

<table>
<thead>
<tr>
<th>Rotational states</th>
<th>Anisotropy parameters</th>
<th>Recoil velocities of CN</th>
<th>Internal energies of ICN</th>
</tr>
</thead>
<tbody>
<tr>
<td>of CN ($\chi^2\Sigma^+$, v = 0)</td>
<td>($\beta$)</td>
<td>(m s$^{-1}$)</td>
<td>(cm$^{-1}$)</td>
</tr>
<tr>
<td>N = 3</td>
<td>1.9</td>
<td>1695</td>
<td>807</td>
</tr>
<tr>
<td>N = 27, I$^*$ channel</td>
<td>1.7</td>
<td>1367</td>
<td>922</td>
</tr>
<tr>
<td>(inner ring)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N = 27, I channel</td>
<td>1.3</td>
<td>2690</td>
<td>421</td>
</tr>
<tr>
<td>(outer ring)</td>
<td></td>
<td></td>
<td></td>
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