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POLARIZED FLUORESCENCE FROM PHOTODISSOCIATION FRAGMENTS: A STUDY OF ICN PHOTOLYSIS USING SYNCHROTRON RADIATION

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ABSTRACT: The photolysis of ICN in the wavelength range between 1100Å and 1700Å has been studied using linearly polarized synchrotron radiation as an excitation source. CN fragments were formed in the $B^2\Sigma^+$ state and the polarization of the fluorescence ($B \rightarrow X$) of these fragments was analyzed. The fluorescence polarization, $P_{f\ell}$, varied between 0 and 8%. This measurement establishes the direction of the absorption transition dipole moment in the molecular frame.

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I. INTRODUCTION

Polarized fluorescence has been observed in the CN(B → X) transition following VUV photolysis of cyanogen iodide (ICN). Highly polarized radiation ($P_{ex} > 95\%$) from the Stanford Synchrotron Radiation Laboratory (SSRL) was used as an excitation source, and the fluorescence polarization, $P_{f\ell}$, varied between -0.002 ± 0.01 and $+0.08 \pm 0.01$, depending on excitation wavelength. It appears that fluorescence polarization is a sensitive probe of photodissociation mechanisms, and the correlation between excitation and fluorescence polarization will elucidate the dynamics of simple photodissociative systems.

The basis of these experiments has been discussed by Van Brunt and Zare [1] and by Simons and coworkers [2]. The experiment generates some of the same information obtainable from photofragment spectroscopy [3] or photolysis mapping [4]; i.e., the symmetry of the excited dissociative state and the time scale of the dissociation can be determined. Analysis of the fluorescence polarization is straightforward, assuming classical Hertzian dipole oscillators for the excitation and fluorescence transition dipoles, $\underset{\sim}{\mu}_{abs}$ and $\underset{\sim}{\mu}_{f\ell}$. Specifically, the fluorescence polarization is given by

$$P = \frac{3\langle \cos^2\gamma \rangle - 1}{\langle \cos^2\gamma \rangle + 3} \qquad (1)$$

where γ represents the angle between $\underset{\sim}{\mu}_{abs}$ and $\underset{\sim}{\mu}_{f\ell}$ and $\langle\ \rangle$ denotes an ensemble average. There are, however, differences

in the kinds of information gained from photofragment spectroscopy and polarization experiments when the photodissociation leads to excited diatomic fragments. In contrast to photofragment spectroscopy, measurement of the fluorescence polarization yields information regarding the orientation of the diatomic rotational angular momentum [5] (the M_J value, in a quantum-mechanical sense). Perhaps some of the puzzling questions regarding the high rotational excitation of molecular photolysis products [6,7], as well as the possible explanations of this rotational excitation [8], can be addressed with simple polarization studies.

II. EXPERIMENTAL

The characteristics of synchrotron radiation make it ideally suited as an excitation source for such experiments. The work reported here was performed at the 8° branch line of SSRL. Photons with $350\text{Å} \leqslant \lambda \leqslant 3000\text{Å}$ are transmitted with an incident polarization $\geqslant 0.95$ at all wavelengths. This photon wavelength range is capable of producing excited fragments from a large number of systems via photodissociation or photoionization. In addition, the radiation at SSRL is pulsed with a duration of 0.4 nsec and repetition period of 780 nsec. Because of these excellent timing parameters, polarized fluorescence was measured as a function of time following the pulse, i.e., decay curves were generated [9] for both the parallel and perpendicular fluorescence components. Thus,

collisonal and time-dependent depolarization could be investigated.

The experimental apparatus was similar to that of Ref. 9. The traditional right-angle geometry was employed for excitation/observation (see Fig. 1). An interference filter (Microcoatings, Inc., #3850 BBC) was placed in front of the polarization analyzer (Melles Griot sheet polarizer, #03FPG003) and phototube (RCA #8850) to reject all radiation except $CN(B \rightarrow X)$ fluorescence. The interference filter (200Å FWHM) has its peak transmission at 3850Å to transmit principally the $\Delta v = 0$ sequence [10]. Low fluorescence intensity necessitated the use of a large band-pass (8.7Å FWHM) on the monochromator used to select the excitation wavelength. Extensive checks were made for spurious polarization signals. In particular, the stray light level was found to be negligible.

Data were collected at ICN pressures from 10 to 100 millitorr, measured using a capacitance manometer (MKS 315 BHS-10) and held constant by a servo-driven leak valve to pressure deviations of 0.5% or less.

III. RESULTS AND DISCUSSION

The data analysis revealed no effects of pressure on the polarization; only the 50 millitorr results are presented here. The data were analyzed by subtracting the dark count background from both the parallel and perpendicular decay curves, then summing counts between t_1 = 6 nsec and t_2 = 50 nsec (see Fig. 2). It was found that other choices for t_1

and t_2 yielded the same value for the fluorescence polarization,

$$P \equiv (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp}) \qquad (2)$$

but with poorer signal to noise ratios. We chose t_1 to be 6 nsec rather than 0 nsec to exclude Rayleigh-scattered stray light. The observed time-independent behavior suggests that the collisional quenching cross-section is so large [11] that the collisional depolarization (alignment destruction) is not competitive. The 50 millitorr results are shown graphically in Fig. 3. Corrections resulting from our finite acceptance angle (Θ = 11° half-angle) were found to be insignificant [12] ($\leq$1%) in comparison to the variations in reproducibility of the results, which are given as error bars in Fig. 3.

Several interesting trends can be noted in the results. First, the degree of vibrational excitation of the parent ICN, which subsequently predissociates, appears to have a profound effect on the degree of polarization observed in the neighborhood of 1400Å. Second, populating the first three members of the lowest-lying Rydberg series (λ_{ex} = 1698Å, 1331Å, 1247Å) all led to vanishing values of polarization in the diatomic fragment fluorescence. Finally, we note that the observed polarizations were all positive. Our results imply [2] that the transition dipole moment, $\underset{\sim}{\mu}_{abs}$, lies in the triatomic plane or along the triatomic axis if the equilibrium geometry of the ICN dissociative state is bent or linear, respectively. A more detailed analysis is under study.

IV. ACKNOWLEDGEMENTS

We wish to thank Michael G. White, Richard A. Rosenberg, and Javed Husain for many helpful discussions and experimental assistance.

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FIGURE CAPTIONS

Figure 1. Schematic diagram of the experimental setup.

Figure 2. Fluorescence decay curves of the polarized emission (background subtracted). The horizontal bar indicates the time period in which data were analyzed (see text).

Figure 3. Degree of polarization and fluorescent intensity of the CN fragment as a function of excitation wavelength.

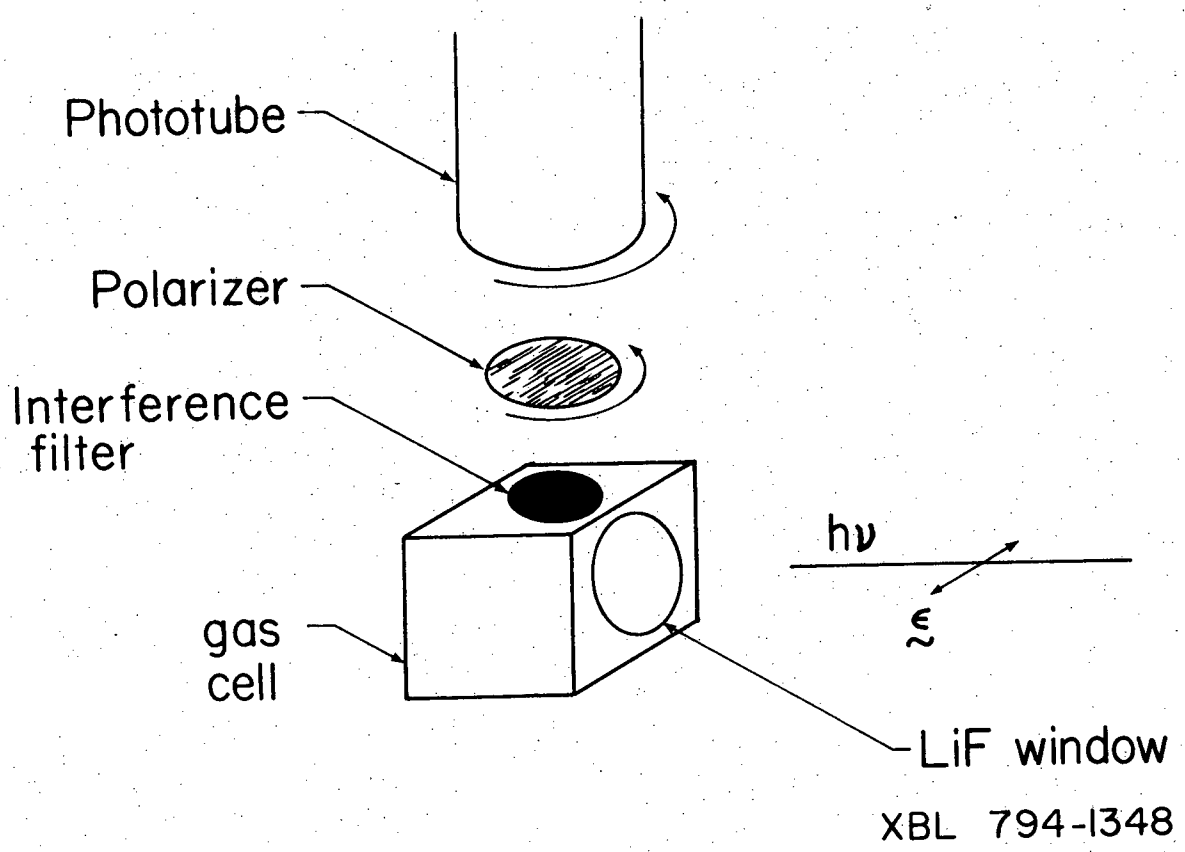
Phototube
Polarizer
Interference filter
gas cell
hν
ε
LiF window
XBL 794-1348

Figure 1

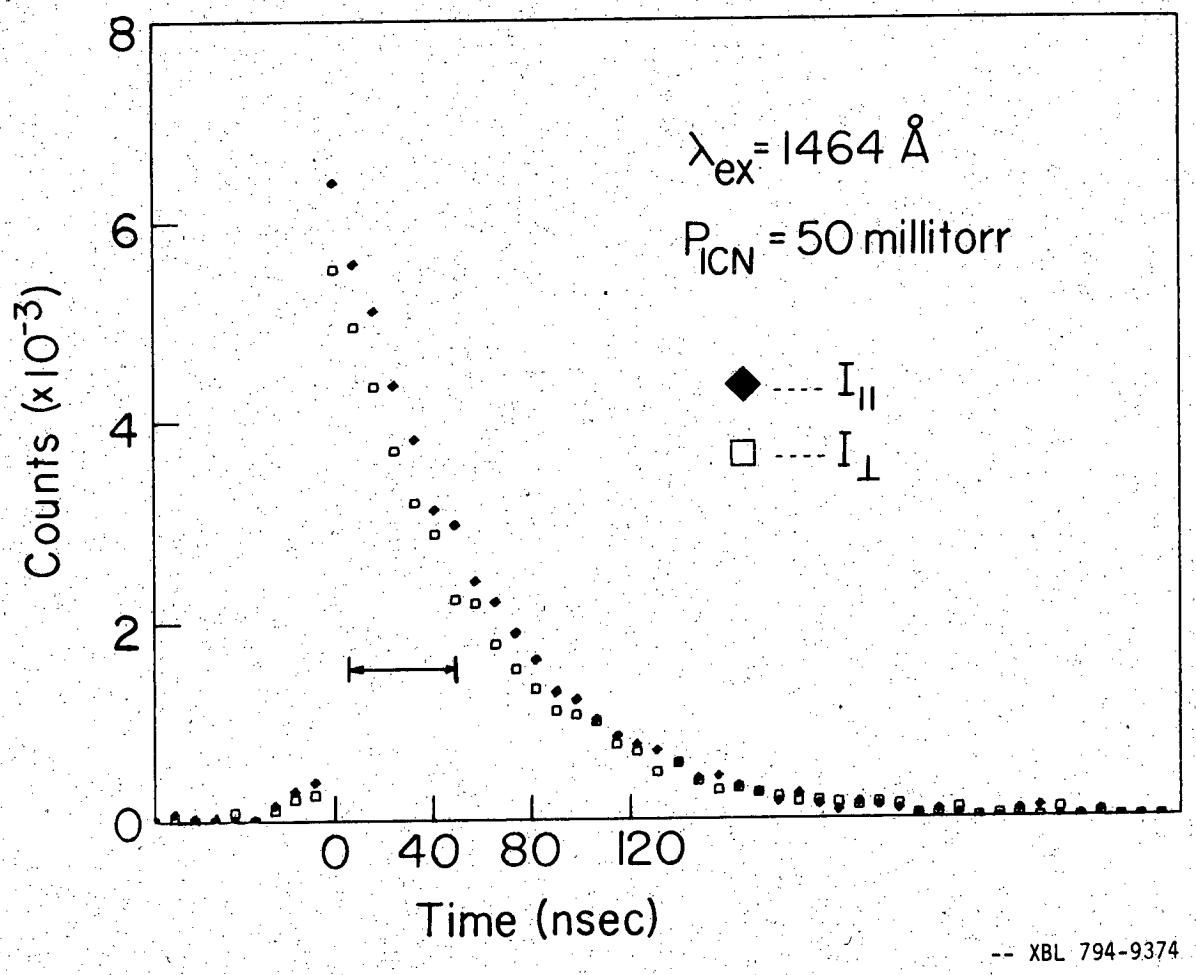
8
6
4
2
0
Counts (x10^{-3})
λ_{ex}= 1464 Å
P_{ICN} = 50 millitorr
$I_{||}$
$I_{\perp}$
0
40
80
120
Time (nsec)
-- XBL 794-9374

Figure 2

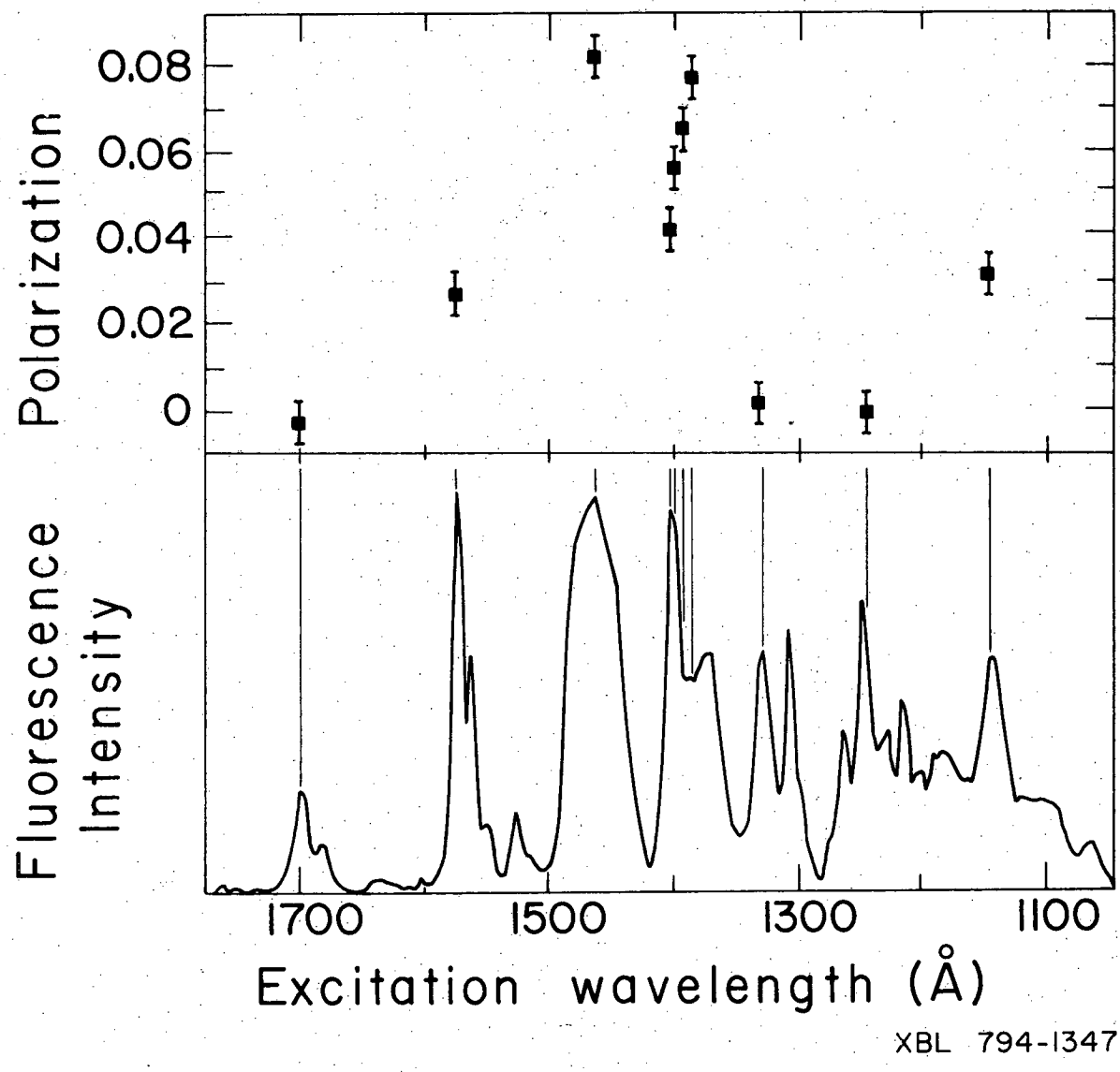
0.08
0.06
0.04
0.02
0
Polarization
Fluorescence
Intensity
1700
1500
1300
1100
Excitation wavelength (Å)
XBL 794-1347

Figure 3

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