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

E.D. POLIAKOFF ‡, S.H. SOUTHWORTH, D.A. SHIRLEY
Materials and Molecular Research Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, California 94720, USA

and

K.H. JACKSON and R.N. ZARE
Department of Chemistry, Stanford University, Stanford, California 94305, USA

Received 9 May 1979; in final form 4 June 1979

Linearly polarized synchrotron radiation (1100–1700 Å) is used to photodissociate ICN, and emission from the CN ($B\,^2\Sigma^+$) fragment is analyzed for its degree of polarization, which is found to vary between 0 and 8%. This measurement establishes the direction of the absorption transition dipole moment in the molecular frame.

1. 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_{fl}, 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 (see for example ref. [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, $\boldsymbol{\mu}_{abs}$ and $\boldsymbol{\mu}_{fl}$. Specifically, the fluorescence polarization is given by

$$P = (3\langle\cos^2\gamma\rangle - 1)/(\langle\cos^2\gamma\rangle + 3)\,, \qquad (1)$$

where γ represents the angle between $\boldsymbol{\mu}_{abs}$ and $\boldsymbol{\mu}_{fl}$ 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.

‡ Present address: Argonne National Laboratory, Argonne, Illinois 60439, USA.

2. 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 Å $\leqslant \lambda \leqslant$ 3000 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 ns and repetition period of 780 ns. 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, collisional 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., no. 3850 BBC) was placed in front of the polarization analyzer (Melles Griot sheet polarizer, no. 03FPG003) and phototube (RCA 8850) to reject all radiation except CN(B → X) fluorescence. The interference filter (200 Å fwhm) has its peak transmission at 3850 Å to transmit principally the $\Delta v = 0$ sequence [10]. Low fluorescence intensity necessitated the use of a large band-pass (8.7 Å 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 mTorr, 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.

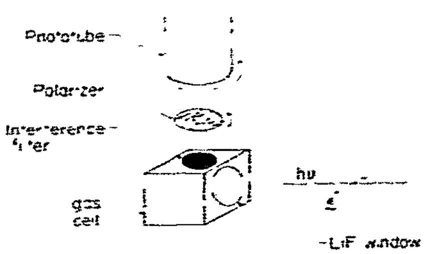

Fig. 1. Schematic diagram of the experimental setup.

3. Results and discussion

The data analysis revealed no effects of pressure on the polarization; only the 50 mTorr 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 $t_1 = 6$ ns and $t_2 = 50$ ns (see fig. 2). It was found that other choices for t_1 and t_2 yielded the same value for the fluorescence polarization,

$$P \equiv (I_\parallel - I_\perp)/(I_\parallel + I_\perp), \quad (2)$$

but with poorer signal to noise ratios. We chose t_1 to be 6 ns rather than 0 ns to exclude Rayleigh-scattered stray light. The observed time-independent behavior suggests that collisional depolarization (alignment destruction) does not occur to an appreciable extent during the short lifetime of the CN $B\,^2\Sigma^+$ state [11]. The 50 mTorr results are shown graphically in fig. 3. Corrections resulting from our finite acceptance angle (θ = 11° half-angle) were found to be insignificant [12] ($\leqslant 1\%$) 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, population of the first three members of the lowest-lying Rydberg series (λ_{ex} = 1698 Å, 1331 Å, 1247 Å) all led to vanishing values of the degree of polarization in the diatomic fragment fluorescence. Second, there is a strong variation in P in the neighbor-

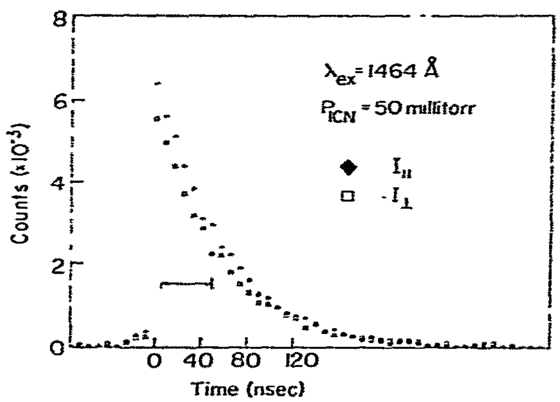

Fig. 2. Fluorescence decay curves of the polarized emission (background subtracted). The horizontal bar indicates the time period in which data were analyzed (see text).

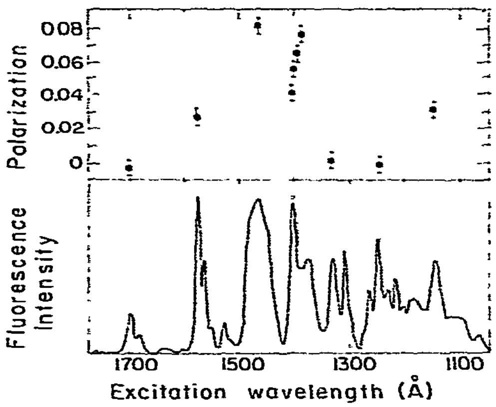

Fig. 3. Degree of polarization and fluorescent intensity of the CN fragment as a function of excitation wavelength. The latter is not corrected for the variation of synchrotron flux with wavelength.

hood of 1400 Å as the excitation wavelength is scanned over a peak. Finally, we note that the observed polarizations were all positive. Our results imply [2] that the transition dipole moment, μ_{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.

Acknowledgement

We wish to thank Michael G. White, Richard A. Rosenberg, and Javed Husain for many helpful discussions and experimental assistance. This work was performed at the Stanford Synchrotron Radiation Laboratory which is supported by NSF Grant No. DMR 73-07692 A02, in cooperation with the Stanford Linear Accelerator Center. The work was supported in part by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract No. W-7405-Eng-48 and by the National Science Foundation under NSF Grant No. PHY 77-02252. K.H.J. thanks the National Fellowship Fund for support.

References

[1] R.J. van Brunt and R.N. Zare, J. Chem. Phys. 48 (1968) 4304.

[2] G.A. Chamberlain and J.P. Simons, J. Chem. Soc. Faraday Trans. II 71 (1975) 2043;
M.T. Macpherson, Ph.D. thesis, Birmingham (1978);
M.T. Macpherson, J.P. Simons and R.N. Zare, Mol. Phys., submitted for publication.

[3] J.H. Ling and K.R. Wilson, J. Chem. Phys. 65 (1976) 881;
M. Kawasaki, S.J. Lee and R. Bersohn, J. Chem. Phys. 63 (1975) 809.

[4] J. Solomon, J. Chem. Phys. 47 (1967) 889.

[5] M. McClintock, W. Demtröder and R.N. Zare, J. Chem. Phys. 51 (1969) 5509.

[6] M.N.R. Ashfold and J.P. Simons, J. Chem. Soc. Faraday Trans. II 73 (1977) 858.

[7] A.P. Baronavski and J.R. McDonald, Chem. Phys. Letters 45 (1977) 172.

[8] M.D. Morse, K.F. Freed and Y.B. Band, Chem. Phys. Letters 44 (1976) 125.

[9] E. Matthias, R.A. Rosenberg, E.D. Poliakoff, M.G. White, S.-T. Lee and D.A. Shirley, Chem. Phys. Letters 52 (1977) 239.

[10] R.J. Spindler, J. Quant. Spectry. Radiative Transfer 5 (1965) 165.

[11] W.M. Jackson and J.L. Faris, J. Chem. Phys. 56 (1972) 95;
C.K. Luk and R. Bersohn, J. Chem. Phys. 58 (1973) 2153.

[12] P.E. Zinsli, J. Phys. E 11 (1978) 17.