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6 Photoelectron Emission from Cyclooctatetraene Dianion Solution.

10 Iwao Watanabe and James Proscia

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The quantum yield for photoelectron emission into the gas phase by dipotassium cyclooctatetraene dianion in solution (0.1 to 0.4 M) in tetrahydrofuran was measured at 1.5°C as a function of photon energy from 3.5 to 6.7 eV. The resulting quantum yield spectrum consists of a broad band at 5.4 eV which coincides with a peak in the absorption spectrum. The threshold for photoionization in solution is approximately 3.7 eV. It is concluded that photoionization occurs predominantly via

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autoionization of an excited bound state into the continuum of a transition at lower photon energies.

Photoelectron Emission from Cyclooctatetraene Dianion Solution

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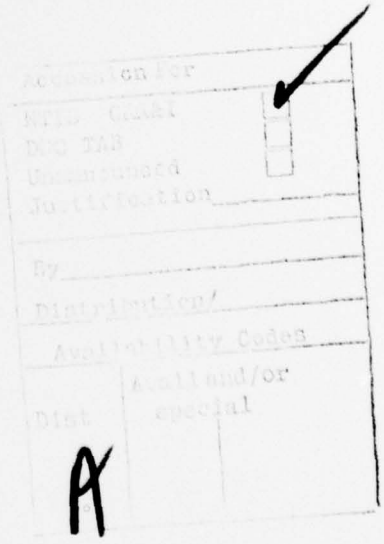
Abstract of Communication to the Editor

The quantum yield for photoelectron emission into the gas phase by dipotassium cyclooctatetraene dianion in solution (0.1 to 0.4 M) in tetrahydrofuran was measured at 1.5°C as a function of photon energy from 3.5 to 6.7 eV. The resulting quantum yield spectrum consists of a broad band at 5.4 eV which coincides with a peak in the absorption spectrum. The threshold for photoionization in solution is approximately 3.7 eV. It is concluded that photoionization occurs predominantly via autoionization of an excited bound state into the continuum of a transition at lower photon energies.



Photoelectron Emission from Cyclooctatetraene Dianion Solution

Sir:

We propose to show that the study of photoelectron emission by organic anions in solution by means of methods developed in this laboratory[1] provides a simple way of ascertaining the photoionization mechanism. The quantum yield spectrum[2] of cyclooctatetraene (COT) dianion is determined in this work, and it is shown that this dianion photoionizes predominantly via autoionization of an excited bound state. This dianion was selected because it is of interest in theoretical chemistry and its photoionization had been studied previously[3] in a 2-methyltetrahydrofuran glass at 77K.

Solutions of dipotassium COT dianion in tetrahydrofuran (THF) were prepared according to Ref. 4. A film of the solution was formed on a rotating glass disk (2 mm thick, 5 cm diameter) in a vertical position in a vessel containing the sample at 1.5°C. This film was irradiated (GCA/McPherson monochromator model 235, xenon lamp) through a sapphire window covered with a gold mesh serving as an electron collector electrode. The rotating disk assembly was evacuated to reduce the pressure to that of THF vapor. The quantum yield spectrum was independent of the voltage applied between the liquid film and the collector electrode (2 mm gap) in the 20- to 200-volt range.[5] The photon flux was monitored with a photomultiplier tube with salicylate converter. Signals were stored in and processed by a PDP 11/34 (Digital Equipment Corp.) minicomputer. Details on instrumentation are available.[6]

The quantum yield spectrum (Figure 1) for photoelectron emission by the COT anion in solution into the gas phase (THF vapor) consists of a broad band with a maximum at 5.4 eV. This spectrum was independent of

concentration of COT dianion in the 0.1 to 0.4 M range that was investigated. The photon energy at the maximum of the quantum yield spectrum very nearly coincides with a peak (5.25 eV, log ε_{max} = 2.87) in the absorption spectrum.[7] This coincidence is indicative of photoionization of COT dianion via autoionization of an excited bound state into the continuum of a transition at lower photon energies.[1] Autoionization thus provides a more efficient channel than direct bound-continuum transition.

The foregoing interpretation supports the conclusion of Dvorak and Michl[3] that COT dianion photoionizes via autoionization in 2-methyltetrahydrofuran glass at 77K. The photoionization threshold of 3.7 eV reported by these authors is approximately the same as in this work (insert of Figure 1). The threshold photon energy is an operational datum in the photoionization of solutions which depends on instrument sensitivity, and no accurate value therefore can be reported. It should be emphasized that the onset of photoionization was inferred in Ref. 3 from the rapid decrease of fluorescence at ca. 3.7 eV whereas the present approach provides direct proof of photoionization.

Systematic application of this approach to a variety of organic anions will be pursued in this laboratory.

Acknowledgment. This work was supported by the Office of Naval Research and the National Science Foundation. The authors are indebted to Professor P. Delahay for his support and for discussions.

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(8) On leave from Department of Chemistry, Faculty of Sciences, Osaka University, Toyonaka, Osaka, Japan.

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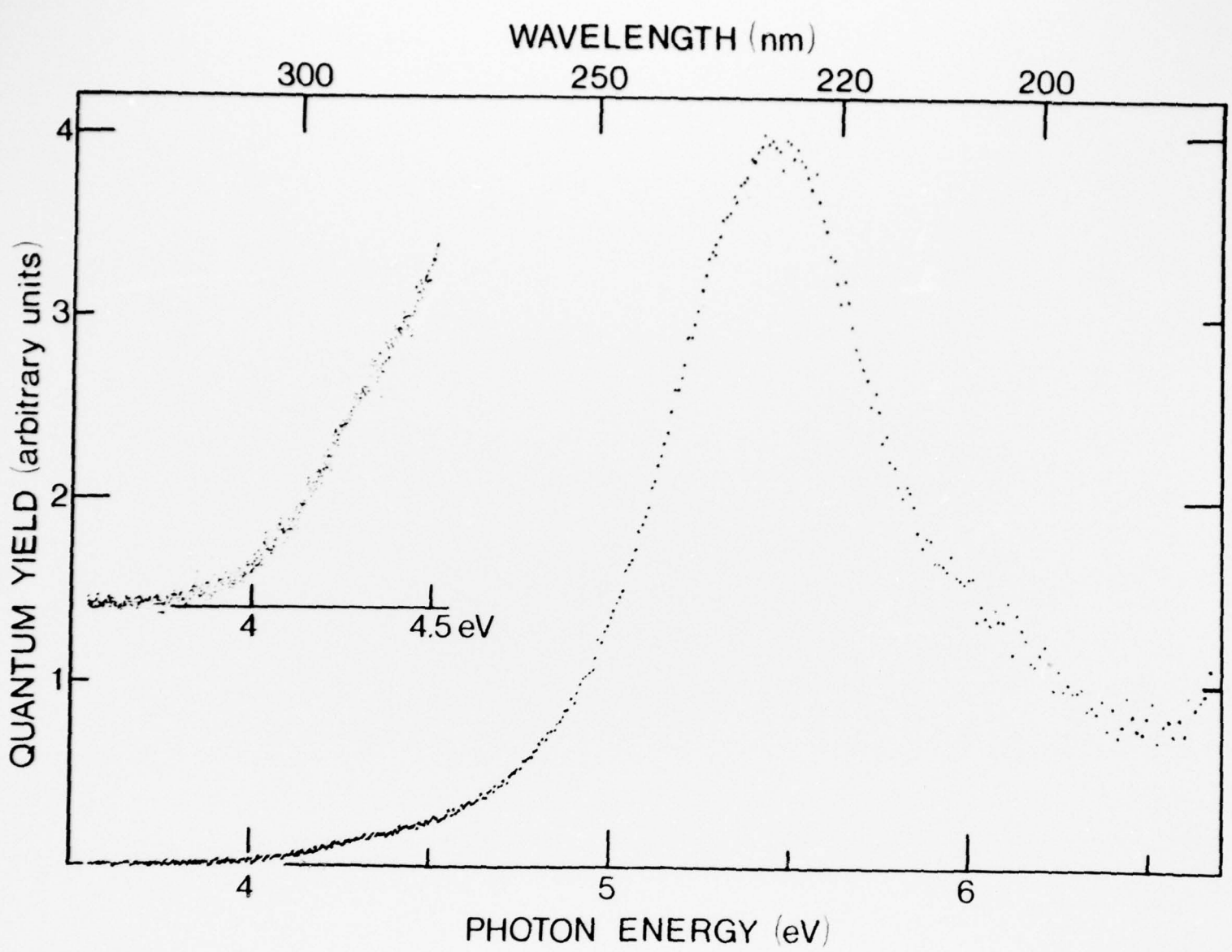
Caption to Figure

Figure 1. Quantum yield versus photon energy for photoelectron emission by 0.36 M cyclooctatetraene dianion in tetrahydrofuran at 1.5°C. Threshold region in insert. Photoelectron emission currents did not exceed 5 picoamp.


WAVELENGTH (nm)
300
250
220
200
QUANTUM YIELD (arbitrary units)
4
3
2
1
4
4.5 eV
4
5
6
PHOTON ENERGY (eV)

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