Photodetachment of Electrons from Anions of High Symmetry. Electron Photodetachment Spectra of the Cyclooctatetraenyl and Perinaphthenyl Anions

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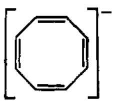
Abstract: The reported experimental photodetachment cross sections for the cyclooctatetraenyl radical anion **1** and the perinaphthenyl anion **2** provide the first examples of detachment from molecular orbitals of very high angular momentum, and theoretical aspects of the electron photodetachment of highly symmetric molecules are discussed. Partially orthogonalized plane wave (POPW) theory is used to estimate the vertical electron detachment energy of cyclooctatetraenyl anion at about 1 eV and the adiabatic electron affinity of the perinaphthenyl radical at 1.07 ± 0.1 eV. Resonances in the photodetachment cross section at 330 nm for **1** and at 420 and 530 nm for **2** are assigned to autodetaching π to π^* excited states of the respective anions.

Introduction

In 1948 Wigner developed a theory[1] which predicts generalized cross section shapes at threshold. For photodetachment processes of anions

$$A^- + h\nu \rightarrow e^- + A$$

the Wigner theory predicts the cross section near threshold to depend only on the angular momentum of the final state. We have extended the Wigner theory to molecules and shown how to determine the energy dependence of the cross section given the shape of the orbital from which detachment occurs.[2] Since this treatment should hold only at the onset, we have also developed a simple one-electron treatment (POPW theory)[2,3] to calculate the photodetachment probability. The intrinsic dependence of these theories on symmetry suggests that an investigation of highly symmetric molecules would be valuable. In this paper we present the experimental photodetachment cross sections for the cyclooctatetraenyl radical anion **1** and for the perinaphthenyl anion **2**. These anions provide the first examples for which the theory predicts the lowest allowed outgoing waves to be d and f waves, respectively. The observations agree with theory but the expected shallowness of the cross section curves for these processes precludes us from following them all the way to onset experimentally. Thus we use the theory to estimate the electron affinity of cyclooctatetraene and of the perinaphthenyl radical. Finally we discuss the resonances which are present in the higher energy part of the cross section curves.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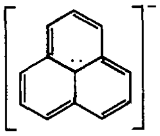
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Experimental Section

Perinaphthene was obtained by reduction of commercially available perinaphthenone (Aldrich).[4] It was chromatographed under nitrogen on a silica gel column with pentane as the solvent. Cyclooctatetraene (Baker) was used as received. Both anions, **1** and **2**, were generated and trapped (typical trapping times about 0.5 s) in a modified Varian V5900 ion cyclotron resonance spectrometer.[5] Cyclooctatetraene forms its parent negative anion **1** by electron capture at 2 eV (electron energy minus trapping). Typical pressures were around 5×10^{-6} Torr. The perinaphthenyl anion was formed via proton abstraction by F^- (obtained by dissociative electron capture from NF_3 at 1.35 eV). The total pressure was about 10^{-6} Torr, about 10% of which was NF_3.

The light sources for the photodetachment experiments were a 1000-W Xe arc lamp and a 1000-W Hg-Xe arc lamp used with a grating monochromator.[6] A grating blazed at 300 nm and the Hg-Xe arc lamp were used to obtain data below 400 nm. All other data were collected using the Xe lamp and a grating blazed at 600 nm. The resolution of the data for **1** was 14.1 nm (fwhm) below 400 nm and 39.6 nm above 400 nm. For **2** the data have a resolution (fwhm) of 23.8 nm below 600 nm and 39.6 nm above 600 nm. The collection and analysis of the data have been previously described.[5]

The solution spectrum of the lithium salt of perinaphthene was recorded on a Cary 17 spectrometer. A sample of perinaphthene was dissolved in absolute ether, and the solution was degassed and covered with argon. After addition of butyllithium, the orange solution was transferred to a sealed 1-mm optical cell filled with argon.

Results

The photodetachment cross section spectra obtained for **1** and **2** are given in Figures 1 and 2, respectively. The signal decrease never exceeded 10% of the total signal for **1**, and for **2** the maximum percentage signal decrease was 27%. The signal decrease for **1** was about 0.5% at 1020 nm, for **2** about 0.8% at 930 nm. These low values correspond approximately to the detectability limit of the apparatus.

Above threshold a resonance peak at ~330 nm is observed for **1**. The cross section for **2** exhibits a peak at about 420 nm with a shoulder around 530 nm.

The absorption spectrum of the lithium salt of perinaphthene in ether is shown in Figure 3.

Discussion

For noninteracting product particles the cross section σ near threshold is predicted[1] to depend on the energy ΔE above threshold as

$$\sigma \propto (\Delta E)^{l^* + 1/2} \tag{1}$$

where l^* is the lowest angular momentum of the product state for which the cross section does not vanish by symmetry. Thus the higher the lowest angular momentum of the continuum state, the more slowly the cross section will increase above threshold.

In order for a dipole transition to be allowed, the direct product of the irreducible representation of the initial state, one of the Cartesian axes, and the final state must contain the totally symmetric representation of the respective group. If we represent the (final) continuum state as a plane wave and expand it in terms of s, p, d, and f waves, etc., we can find the lowest allowed continuum state for any anion from the symmetry of the highest occupied orbital (initial state). For example, the lowest allowed continuum state from an s atomic orbital would be a p wave, since the s orbital is totally symmetric and each p wave transforms like one of the axes. Thus

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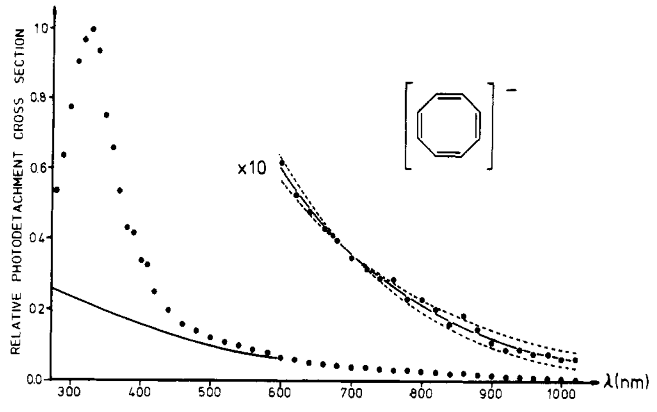

Figure 1. Relative experimental (●) and theoretical (——) photodetachment cross sections for the cyclooctatetraenyl anion **1** plotted as a function of incident photon wavelength. The solid curve extrapolates to the threshold 0.83 eV; the dashed lines correspond to thresholds ±0.1 eV from this value.

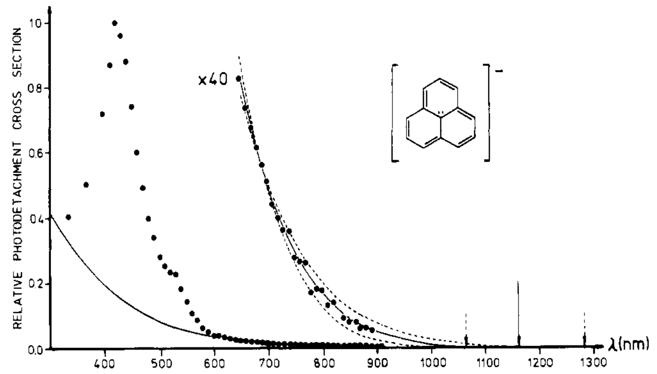

Figure 2. Relative experimental (●) and theoretical (——) photodetachment cross sections for the perinaphthenyl anion **2** as a function of incident photon wavelength. The large arrow points to the threshold at 1.07 eV. Dashed lines and arrows indicate the theoretical curves with thresholds offset by ±0.1 eV from the best fit.

the product of the three factors is totally symmetric. Similarly a p orbital gives rise to an s wave, and a d orbital gives rise to a p wave. These considerations can be extended to molecules by using group theory to assign an effective angular momentum to the molecular orbital of the outermost electron. For illustration, consider the model arrangement of p orbitals given in Figure 4 which could represent molecular orbitals. The orbitals in arrangement II transform like a d function, those in arrangement III like an f function, and those in arrangement IV like a g function. Now the lowest outgoing wave allowed from these arrangements are $l^* = 1$, $l^* = 2$, and $l^* = 3$, and we predict energy dependences of $\Delta E^{3/2}$, $\Delta E^{5/2}$, and $\Delta E^{7/2}$ for the arrangements II, III, and IV, respectively.

Since this argument should hold only at the onset, it is of interest to see how the more complete POPW theory[2] deviates from the threshold behavior higher above the onset. We have calculated[7] photodetachment probabilities, σ, for these model arrangements and plotted them in Figure 4. As we have previously shown,[2] our POPW calculation gives the correct limiting slope at threshold, since the plane-wave calculation can be expanded in the power series:

$$\sigma = \alpha_1 \Delta E^{l^*+1/2} + \alpha_2 \Delta E^{l^*+3/2} + \alpha_3 \Delta E^{l^*+5/2} + \ldots \quad (2)$$

where the α_i's are nonzero coefficients and at threshold only the first term is important. At higher excess energies ΔE, the subsequent terms also become important, causing the overall function no longer to be purely a simple power law. This can be seen by inspecting the slope[8] of a plot of log σ vs. log ΔE.

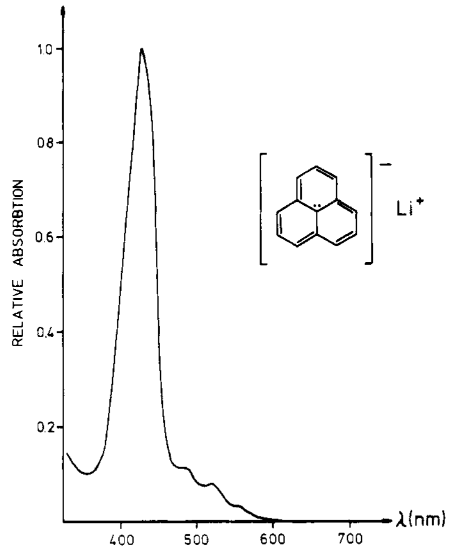

Figure 3. Absorption spectrum of the lithium salt of perinaphthene in ether obtained by reaction with butyllithium.

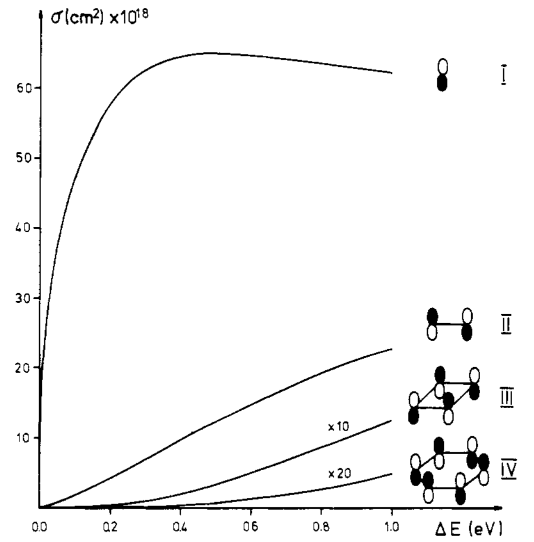

Figure 4. Calculated model cross section curves for different symmetries.

Slopes for our model cases are listed in Table I. Even a few millielectron volts above threshold the slope deviates in a negative direction from the threshold value. However, even within 0.5 eV above threshold the maximum deviation is only about 0.5, and thus it is possible to use experimental slopes near threshold as a guide to symmetry if the location of the threshold is known. The limiting law argument can also be useful in predicting the position of an unknown threshold, but this should be done with caution since for large extrapolations the deviation of the POPW curve from the threshold law becomes substantial. Since the threshold power law curve is more shallow within ~1 eV of threshold, onsets estimated will be at lower energies than those obtained using POPW theory for extrapolation.

Now we turn to real examples. The applicability of the Wigner approach to *atomic* photodetachment as in arrangement I has been discussed previously.[9] Examples of molecular anions whose highest occupied molecular orbitals (HOMOs) correspond to arrangement II include O_2^- and the allyl anion.[3,10] These, along with the cyclopentadienyl anion,[11] which should also give rise to a p wave, agree well with the calculated model.[2] Representative molecular anions whose

Table I. Instantaneous Slope[a] $n = (\partial \log \sigma)/(\partial \log \Delta E)$ Calculated for the Arrangements of Figure 4 as a Function of the Excess Energy, ΔE, above Threshold

arrangement	symmetry of initial state	symmetry of final state	excess energy ΔE, eV 0	0.05	0.25	0.50	0.75	1.00	1.50	2.00
I	p	s	0.50	0.43	0.18	−0.01	−0.06	−0.03	0.08	0.08
II	d	p	1.50	1.44	1.23	1.03	0.89	0.80	0.67	0.55
III	f	d	2.50	2.45	2.27	2.08	1.93	1.81	1.62	1.45
IV	g	f	3.50	3.46	3.29	3.11	2.95	2.81	2.59	2.39

[a] See ref 8.

HOMOs correspond to arrangements III and IV are the cyclooctatetraenyl radical anion **1** and the perinaphthenyl anion **2**, respectively. The solid lines in Figures 1 and 2 are from the POPW calculations. Since the HOMOs for these anions are determined by symmetry, no additional theoretical uncertainty arises from the choise of the method used for evaluating the orbital coefficients. The basis functions are those chosen previously.[2]

Because of the extreme shallowness of the cross section curves of the photodetachment process for **1** and **2**, it is not possible experimentally to obtain data close to threshold. Thus in order to estimate the actual onsets we must rely on our extrapolation procedure. The discussion above suggests the use of POPW curves. For the fitting procedure a normalization factor and a relative shift on the energy scale between the calculated[12] and the experimental data have been varied to minimize the squares of the deviations of the experimental from the calculated points. At first this procedure was checked with the previously published photodetachment probability curve for cyclopentadiene.[11] The extrapolated threshold, including data from 380 to 660 nm or from 380 to 520 nm, agrees well with the previously determined threshold within the experimental error (±0.03 eV). This gives us some confidence in applying the procedure to **1** and **2**. The fitted curves are those indicated in Figures 1 and 2. For **1** data ranging from 600 to 1020 nm and for **2** data ranging from 650 to 900 nm were included in the fitting procedure. At shorter wavelengths the shape of the curves is governed not only by the direct photodetachment process but also by autodetachment from an excited state of the anion (see below). At longer wavelengths the experimental data are indistinguishable from noise. The fitted curves shown as solid lines in Figures 1 and 2 extrapolate to 0.83 and 1.07 eV for the cyclooctatetraenyl radical anion and the perinaphthenyl anion, respectively. The dashed lines show the fits corresponding to thresholds at ±0.1 eV, where only the normalization factor was optimized. They are obviously a significantly worse fit to the experimental data.

The extrapolated values can be affected by Franck-Condon problems. If a significant geometry change occurs between the ground states of the ion and neutral, the transition intensity originates from several vibronic transitions, each of which gives rise to a new onset. The radical anion **1** is essentially planar[13] while the neutral cyclooctatetraene is tub shaped.[14] Therefore we expect large Franck-Condon factors for transitions other than the 0-0 transition. Moreover, the radical anion will exhibit a Jahn-Teller distortion.[15] Although this perturbation will affect a shallow curve less than a steep one, the problem of 0-0 identification is still difficult. In order to analyze this problem, we convoluted the POPW curve calculated for **1** with a peaked Franck-Condon envelope (0-0, 0-1, 0-2, 0-3, 0-4; 0.05, 0.24, 0.42, 0.24, 0.05) and the resulting curve was treated as if it were experimental data. The result suggested that the extrapolated threshold lies between the 0-0 transition and the most intense vibronic transition, being close to the latter. Thus our "experimental" value, 0.83 eV, is probably closer to the vertical electron detachment energy than to the adiabatic one. Under these circumstances it is not possible to assign a rational error limit, but we would judge the vertical detachment energy to be at least this large, and in the neighborhood of 1 eV. The vertical detachment energy should be the sum of the adiabatic electron affinity plus the strain energy for the planar neutral. The strain energy has been estimated at 0.6 eV as an upper limit[16] which would imply an adiabatic EA of ≥0.2 eV. The only reported[17] adiabatic EA is 0.577 ± 0.043 eV. A theoretical prediction[18] of EA = 0.87 eV for planar COT is in good agreement with our result.

It is generally believed that there is a low-lying triplet state of cyclooctatetraene (COT). Since production of this state is allowed via photodetachment and since the Franck-Condon factors are likely to be at least as good as those for singlet COT, one might hope to observe a change in the cross section when this state becomes accessible, thereby determining its energy. Unfortunately, the same consequence of high angular momentum which makes the initial threshold to the singlet rise so slowly also applies to the onset of transitions to the triplet state. Thus, this threshold would also rise initially with a slope of $(\Delta E)^{5/2}$, and it would be very difficult to observe, assuming that the cross section for detachment to the singlet state is already substantial at that point. The problem is compounded by the resonances associated with the optical transitions below 500 nm (see below) which make changes in the direct photodetachment cross section hard to observe in this region.

In the case of the perinaphthenyl anion **2** both the anion and the neutral radical possess a common, rather rigid skeleton, and the geometry of the anion is predicted not to change much on electron detachment.[19] The value of 1.07 ± 0.1 eV can therefore be directly taken as an estimate of the adiabatic electron affinity of the perinaphthenyl radical. No other experiments determining the electron affinity of the radical have been published to our knowledge.

Resonances

Resonances in photodetachment cross sections have been suggested previously[20] to correspond to autodetaching electronic excited states of the anion. The absorption spectrum of **1** in liquid ammonia[13d] and frozen glasses[13i,21] exhibits peaks near 325 and 395 nm. Calculated transitions,[22] albeit in poor numerical agreement with the experiment, assign both of the two peaks to $E_{2u} \rightarrow E_{1g}$ (D_{8h}) transitions. The peak in our data at 330 nm can be tentatively attributed to the same transition as the 325-nm solution peak. While no transition corresponding to the weaker and sharper solution peak at 395 nm is resolved in the photodetachment cross section, the overall appearance of the photodetachment resonance suggests that it may be an envelope which includes both transitions. It is not certain whether the detail at about 400 nm is an actual peak or merely noise.

The broad peak on the blue side of Figure 2 of the perinaphthenyl anion at 420 nm (fwhm = 100 nm) compares very well with the solution absorption spectrum of Figure 3 which has an intense peak near 430 nm (fwhm = 50 nm). Furthermore, a shoulder appears in the photodetachment cross section at about 530 nm corresponding to a series of weak peaks in the solution spectrum. Taking into account that the resolution of the photodetachment spectrum is lower than that of the solution experiment, and that the photodetachment spectrum reflects both direct photodetachment into the continuum and indirect loss of an electron via the excited state, the agreement is excellent and suggests strongly that indeed $\pi \rightarrow \pi^*$ transitions cause the enhanced photodetachment probability in this region. The strong and the weak peaks are also in agreement with a PPP calculation[23] which predicts a degenerate intense $A_1'' \rightarrow E''$ transition well removed from the higher energy transitions and a forbidden $A_1'' \rightarrow A_2''$ transition about 100 nm to the red of the first one (D_{3h}).

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Stereospecificity in Reactions of Activated η^3-Allyl Complexes of Molybdenum

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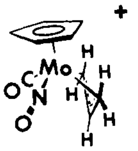
Abstract: Nucleophilic attacks on endo and exo η^3-allyl complexes, such as $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(1,3\text{-dimethylallyl})^+$ cation, are stereospecific. The structures of the olefinic derivatives formed by the addition of the nucleophile are consistent with nucleophilic attack trans to NO in the endo isomer and cis to NO in the exo isomer. The relative configuration of the newly formed chiral center implies that the attack occurs on the face of the allyl opposite to the metal and not directly at the metal center. The crystal structure determinations of two neutral olefin derivatives, $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(\eta^2\text{-}C_8H_{14}O)$ and $(\eta^5\text{-}C_5H_5)Mo(CO)(NO)(\eta^2\text{-}C_9H_{16}O)$, formed by addition of the enamine of isobutyraldehyde are reported. The olefinic bond tends to be aligned parallel to the molybdenum-carbonyl vector rather than parallel to the $\eta^5\text{-}C_5H_5$ plane. This orientational preference, which can readily be rationalized by back-bonding arguments, appears to have a profound effect on the selectivity of the reactions.

Introduction

Complexation of organic molecules to transition metal atoms leads to systematic variations in their reactivity and this forms the basis for an emerging branch of organic synthesis.[1] Nucleophilic addition to unsaturated ligands is of intense interest.[2] Recently we reported the preparation and rearrangement pathway of cationic $\eta^5\text{-}C_5H_5Mo(CO)(NO)$ (1).[3] These



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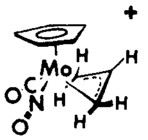

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