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Photodissociation Spectroscopy of Alkane Radical Cations

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Abstract: Photodissociation spectra are reported for gas-phase radical cations of straight-chain and cyclic alkanes C_5 to C_8 (along with *n*-butane). Large photodissociation cross sections, in the neighborhood of 10^{-17} cm^2, are observed for these ions. The spectrum of cyclopentane ion suggests ring opening to give a pentene ion structure, but the other cycloalkane ions appear to retain a saturated hydrocarbon structure. The *n*-alkane ion spectra are compared with photoelectron spectra of the neutrals and do not correspond very closely. Calculations of the predicted optical spectra of the ions are made by using a conformationally averaged MINDO/3 approach with the inclusion of transition moment weighting, and the correspondence of theory and experiment is encouraging. The long-wavelength portions of the spectra of hexane and octane ions are unexpectedly weak, and some influence by threshold truncation effects is suggested.

Introduction

It was first reported in 1976[1] that the gas-phase radical cations of saturated hydrocarbons have strong optical absorptions in the visible region of the spectrum. The strongly colored nature of the alkane radical ions is in striking (through not unpredictable) contrast to the neutral alkanes, and study of the optical spectroscopy of these ions using photodissociation spectroscopic techniques has continued.[2,3] We report here a set of photodissociation spectra for the series of linear and cyclic alkanes from C_5 to C_8 (as well as *n*-butane) and give more quantitative theoretical attention to the features of these spectra than has been reported previously.

Experimental Section

The photodissociation spectra were collected by two variations of the ion cyclotron resonance (ICR) photodissociation technique. Some spectra were obtained by the steady-state method described previously.[4,5] Ions are continuously formed by electron impact until the ion population reaches a steady-state level. Photodissociation is monitored by measuring the decrease in the steady-state level upon irradiation. The steady-state method was found to be extremely difficult for alkane ions because the parent ions are highly reactive. Many of the primary ionization fragments, photofragments, and ion-molecule reaction products are much less reactive than the parent radical

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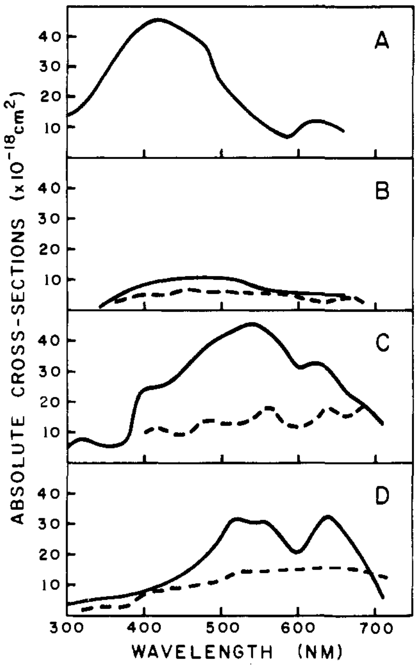

Figure 1. Photodissociation spectra for straight chain alkane cations. [A] Pentane; [B] *n*-hexane (—); cyclohexane (- - -); [C] *n*-heptane (—); cyclohexane (- - -); [D] *n*-octane (—); cyclooctane (- - -).

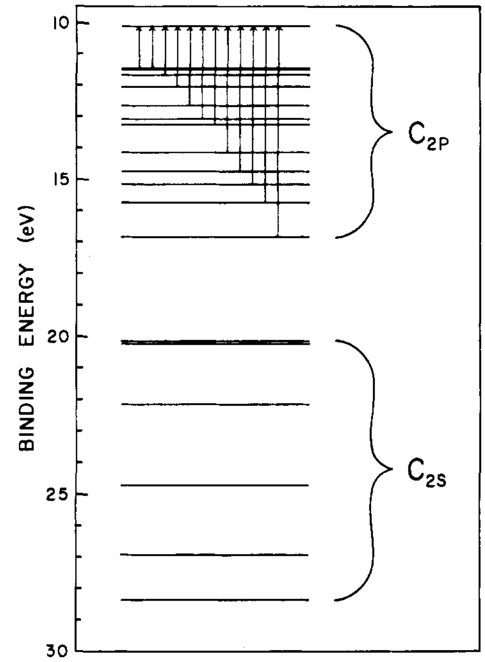

Figure 2. Ab initio analysis (minimal basis set, STO-3G) of the molecular orbitals of *n*-hexane.[1] The arrows show possible electronic transition responsible for the optical spectrum of the radical cation.

ion, and it was found difficult to maintain sufficient concentration of the latter under steady-state conditions.

Many of the spectra were taken by using the pulsed mode of operation described previously.[6,7] The problem of parent ion reactivity is greatly reduced in this method because there is less time for reactions to occur and for nonreactive species to build up. In this method ions are formed by a 50-ms pulse of electrons, trapped, and irradiated with light for a period of time of typically 2 s, observed by the pulsed ICR electronics, and then ejected from the ICR cell. Photodissociation was measured, in this case, by integrating the ion signal with a boxcar integrator, measuring the decrease in signal when the ICR cell was irradiated. The ions were irradiated by light from a 2.5-kW mercury-xenon arc lamp with wavelengths in the UV region selected by a Schoeffel GM-250 monochromator with a band width of 14 nm. The visible region was examined by using interference filters with a band width and a spacing of 20 nm. An Eppley thermopile was used to obtain the relative fluxes of the monochromator and filters. The absolute cross sections were determined by comparing the photodissociation rates with the toluene $C_7H_8^+$ cation, whose cross section at 400 nm is a convenient standard.[8]

The data acquisition in the later part of this study was achieved by interfacing the boxcar integrator to a microprocessor and a PDP 11/45 computer. The integrated signal is first converted to a digital form by an analogue-to-digital converter, then stored in a 12K memory bank of a 6800 based microprocessor. After the data are accumulated in the microprocessor, they are transferred to the PDP 11/45 computer, where the actual photodissociation cross sections are computed.

Results and Discussion

Figure 1 shows the photodissociation spectra for straight chain and cyclic alkane cations C_5–C_8. The spectra are given with absolute photodissociation cross sections, determined by comparing relative cross sections at 4000 Å with the toluene cation standard, which has an absolute cross section[8] of 5.2×10^{-18} cm^2. Absolute cross sections determined by this method have usually been considered reliable within a factor of two.

The photodissociation spectrum of methane has been previously reported[9] showing a maximum around 340 nm with very little dissociation in the visible region.

Butane was examined and has a dissociation maximum in the area of 340–360 nm with a tail extending slightly past 400 nm. The absolute cross sections in the visible region are estimated to be less than 1×10^{-18} cm^2.

As generalizations, one may note that the photodissociation cross sections are large and (remembering that photodissociation cross sections give a lower limit to the optical absorption intensities) indicate peak molar absorptivities for these ions of the order of 10^4 or larger. With increasing length of the carbon chain, there is a trend toward longer wavelengths in the photodissociation peak, and also a general broadening of the photodissociation feature.

***n*-Alkanes.** The strong optical absorptions of the *n*-alkane radical cations, extending across the visible wavelength region for ions larger than butane, are readily understood in molecular orbital terms. Extending down from the highest occupied molecular orbital (HOMO) is a rather closely packed set of valence molecular orbitals (MO's), clearly displayed in the photoelectron (PES) spectra of the neutral alkanes.[10,11] In the radical cations, the HOMO is half-filled, and it is optical transitions carrying electrons from the filled MO's into the hole in the HOMO which give the cluster of strong optical absorptions whose sum leads to the observed photodissociation spectrum. In Figure 2 orbitals and transitions giving the optical spectrum are illustrated for a typical ion, the hexane ion.[11] In the following, a more quantitative picture of the distribution of the MO's and of the optical transitions among them is sought. In particular, we would like to account for the position of the broad photodissociation maxima for the various ions, for the line shapes, and for the systematic shift to longer wavelength of the spectral maxima as the chain is lengthened.

Serious theoretical treatments of the molecular orbitals of straight chain alkanes began with the equivalent orbital (EO) treatment of Lennard-Jones and Hall.[12] With the impetus given by photoelectron spectroscopic results,[10,11] theoretical work has continued, and a recent comparison of photoelectron spectra and ab initio calculations[11] suggest that the essential features of the problem are adequately described by current theory. There is good separation between the C_{2P} region, extending over roughly 10–17 eV binding energy, and the C_{2S} region over 20–30 eV. The PES spectra of the C_{2S} region are more tractable than the poorly resolved spectra of the C_{2P} region and have accordingly received more attention, but it is the

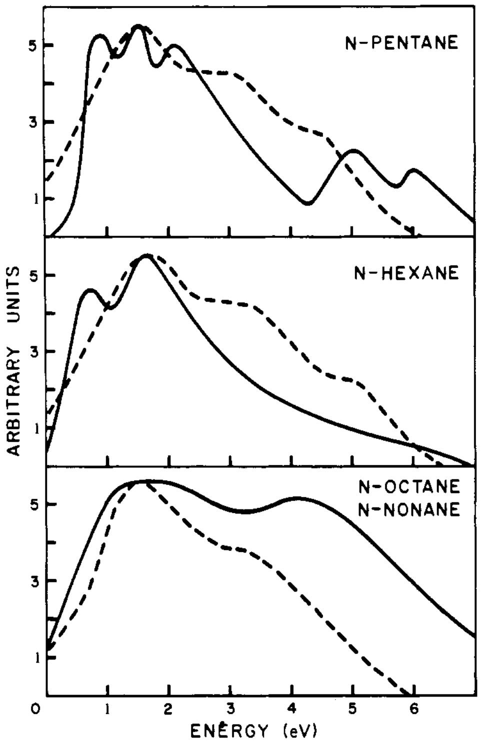

Figure 3. Comparison of photoelectron spectra[10,11] (—) with calculated density of states (- - -) for *n*-alkanes: pentane, hexane, and octane (nonane).

C_{2p} orbitals which are relevant to the interpretation of the photodissociation spectra, and we will give them some consideration here.

An aspect of alkane MO's which has not received much emphasis is the dependence of the orbitals on the geometrical conformation of the molecule: most calculations have looked only at a single conformation, which, as our own calculations described below have suggested, does not give an adequate picture of the MO's of the flexible molecules. In order to explore this feature, and to obtain some calculated spectra for comparison with the photodissociation results, we have chosen to use the relatively rapid MINDO/3 program to construct MO's for a representative range of stable geometrical conformations of the neutrals. In the results discussed below, eight conformations of each molecule were used, chosen to cover what seemed to represent a good selection of the stable (noneclipsed, nonoverlapping) conformations available to the chain. The conformations were equally weighted and were combined to give a rough density-of-states profile of the C_{2p} region. This density-of-states curve should be directly comparable with the photoelectron spectrum.

Density-of-states curves were calculated for pentane, hexane, and octane and are shown in Figure 3. These should be directly comparable to the PES spectra of the neutrals, which are displayed on the same figure. (Since for comparison with the photodissociation results, it is the energy above the HOMO which is of interest, the energy scales have been shifted to put the HOMO at zero energy, and to put the onset of the PES spectrum at zero. In the absence of a PES spectrum of octane, the spectrum of nonane has been displayed, assuming that for alkanes this large there will be little difference.) The PES spectra are seen to differ in detail from the calculation (indeed the PES spectra from different laboratories differ substantially), but the position of the maxima is in satisfactory agreement, and it seems that the conformationally averaged MINDO/3 approach does generate a generally satisfactory density of valence orbitals in the C_{2p} region.

The optical spectrum of the radical ion also reflects the density-of-states profile of the C_{2p} region, but it weights each state according to the transition probability for optical excitation to the corresponding hole state from the radical-ion ground state (see ref 13 for details of transition moment calculations). Plotting the resulting transition probabilities as a function of energy (for the same set of eight geometrical conformations) gives a spectrum which should be directly comparable to the optical spectrum of the radical cation. In comparing such a spectrum with the photodissociation spectrum, it must be remembered, as always, that the photodissociation spectrum is not necessarily the same as the optical spectrum, but is only a lower limit to the optical absorption spectrum. For the purpose of comparison of theory and experiment, each of the orbitals given by theory has been artificially broadened by an arbitrary Gaussian line function with $\sigma = 0.5$ eV, and the resulting broadened lines summed, in order to smooth the theoretical curves to be comparable with the poorly resolved, bandlike experimental spectra.

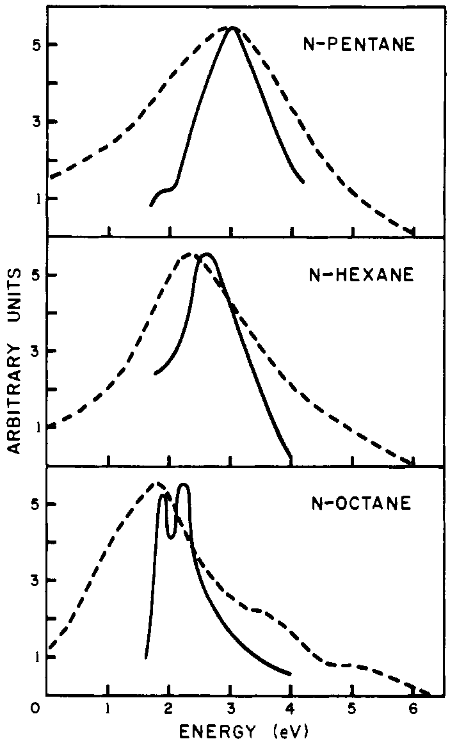

Figure 4. Photodissociation spectra (—) and weighted density-of-states (- - -) for *n*-alkanes: pentane, hexane, and octane.

In Figure 4 are shown the similar MINDO/3 results with the inclusion of transition-moment weighting. These curves should be directly comparable with cation optical spectra, and thus perhaps with the photodissociation spectra, which are also shown in the figure. It may be noted first that the inclusion of transition-moment weighting gives substantial changes from the unweighted density-of-states curve: for pentane the maximum shifts by 1.5 eV and the curve shape is wholly different; for hexane the maximum shifts by 0.6 eV with considerable narrowing of the curve; while for octane the shift is small (0.2 eV) but the shape is substantially altered.

In comparing these curves with the photodissociation spectra, the possible effects of threshold truncation should be borne in mind: little photodissociation is expected at photon energies below that necessary for the easiest rapid bond cleavage, so that truncation of the photodissociation spectrum at some wavelength in the red or near IR is expected. Unfortunately, ambiguities of product structure and uncertainties in the thermochemical data make it impossible to give reliable thresholds for these ions, particularly for the channel involving loss of H. It appears, however, that the threshold for loss of

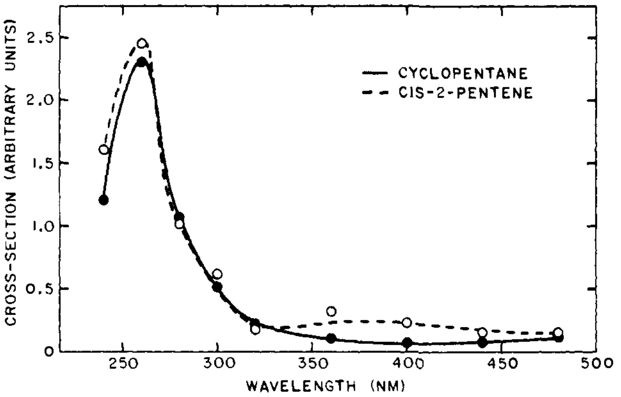

Figure 5. Cyclopentane (—) and *cis*-2-pentene photodissociation spectra. The photodissociation cross-section scales, while not absolute, are similar for the two curves.

$CH_3\cdot$ in heptane and octane ions lies in the red part of the visible spectrum,[14] and it can be suspected that truncation or distortions of the photodissociation spectra of the larger alkane ions due to proximity to threshold might be important at red wavelengths.

It is seen that the theoretical curve gives a very good fit to the pentane photodissociation spectrum and a reasonable approximation to the hexane spectrum; the fit is less good for octane, which, however, might be partly accounted for by threshold truncation of the photodissociation spectrum. The theoretical curves account for the shift to longer wavelength as the alkane chain is lengthened; they also agree with the observation that there is much less photodissociation at short wavelengths than a prediction from PES spectra would lead one to expect. We may conclude that the conformationally averaged MINDO/3 calculations are a useful approximation, and that the inclusion of transition-moment weighting is essential in calculating the optical (or photodissociation) spectra. The long-wavelength portions of the calculated curves are not all in good agreement with experiment: it would be of interest to compare optical absorption spectra with the photodissociation spectra to assess the effect of proximity to the thermochemical threshold on the latter.

Cycloalkanes. The ions formed from cyclopentane have a photodissociation spectrum which is entirely uncharacteristic of alkane ions, but, as the comparison with the spectrum of *cis*-2-pentene ions in Figure 5 illustrates, is characteristic of alkene radical ions. It is clear that the cyclopentane ring opens up upon ionization to give a pentene ion.[15] The spectra of the large cycloalkane ions, by contrast, are characteristic of alkane structures. The cycloalkanes have very low photodissociation thresholds (extending well into the IR): it is seen that the cycloalkane spectra generally extend further to the red than the corresponding *n*-alkanes, which strengthens the suspicion that the *n*-alkane spectra are distorted in the long-wavelength region as the thermochemical threshold is approached. The observation that the cyclopentane ring opens, while the larger ones do not, corroborates the similar conclusion of Borchers et al.,[16] from collisional activation and field ionization kinetic results.

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