for a particular interaction. Furthermore, isotropic and dipolar contributions to the hyperfine tensors can be distinguished. On the other hand, the difficulties associated with the analysis of the time-domain data are avoided by using ENDOR. Also the range of hyperfine and quadrupole interactions that can be measured with ENDOR is much broader than that currently accessible to the ESE technique.

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Angular Distribution Parameter as a Function of Photon Energy for Some Mono- and Diazabenzenes and Its Use for Orbital Assignment[†]

M. N. Piancastelli,[‡,§] P. R. Keller,[§] J. W. Taylor,*[§] F. A. Grimm,[∥] and T. A. Carlson[⊥]

Contribution from the Departments of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, and the University of Tennessee, Knoxville, Tennessee 37916, and Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830. *Received September 7, 1982*

Abstract: Angle-resolved photoelectron spectra were obtained on a series of nitrogen-containing aromatic systems using synchrotron radiation as the ionizing source. The angular distribution parameter, β, was measured in the photon energy range 12–27 eV for the first three orbitals of 2-fluoropyridine, pentafluoropyridine, and pyridine, and for the first four orbitals of pyrimidine and pyrazine. The angular distribution parameter as a function of photon energy is shown to be of value in the assignment of bands in photoelectron spectra and has been applied to the photoelectron spectra of pyridine. The fluoro-substituted pyridines provided information on the trend of the β values for nonbonding orbitals with predominant nitrogen lone-pair character. The diazines demonstrated that β values as a function of photon energy could be used for orbital assignments even in the case of partial band overlap. For pyridine the overlap of the first two ionic levels, consisting of a π and a nonbonding orbital, is so severe that unambiguous assignment has been difficult but is now possible. Experimental evidence is presented for the sequence of these levels to be the nonbonding (n) orbital at lower ionization energy followed by the π orbital. The relevance of systematic investigations of the angle-resolved photoelectron spectroscopy of a homologous series of molecules as a function of photon energy is discussed.

Introduction

A systematic study of the angle-resolved photoelectron spectra of molecules as a function of photon energy offers the opportunity to characterize the behavior of molecular orbitals. As yet, there are only a few studies reported in the literature that make use of synchrotron radiation to study comprehensively the partial cross section and angular distribution parameter, β, for large polyatomic molecules. In the case of 100% polarized light and randomly oriented molecules, the angular distribution parameter, β, can be defined in the following equation for the differential cross section, $d\sigma/d\Omega$

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{\text{total}}}{4\pi}\left[1 + \frac{\beta}{2}(3\cos^2\theta - 1)\right]$$

where θ is the angle between the polarization vector and the direction of the ejected photoelectron. This relationship is developed further in previous references to β values as a function of photon energy for the unsaturated hydrocarbons[1–4] and the chloromethanes.[3] This, however, is the first systematic study of β as a function of photon energy to be reported for heterocyclic compounds.

In particular, it was decided to characterize the behavior of the π and nonbonding, n, orbitals of a series of azabenzenes. The relative ordering of π and nonbonding ionic states in the whole class of azabenzenes has been the object of several studies[5,6] both experimentally and theoretically. The many-body calculations of von Niessen et al.[5,6] indicate that a characteristic of this series of molecules is the presence of nonuniform many-body effects which strongly shift the ionization energies of nonbonding, n, electrons to lower values with respect to those of π electrons. Therefore, Koopmans' approximation is inadequate to reproduce the relative ordering and spacings of ionic states in the azabenzenes. Assignments in the azabenzenes have not always been straightforward, since the simplest and most readily available calculations based on Koopmans' theorem cannot be used for reliable assignments.

In particular, there was disagreement in the relative ordering of the first two ionic states in pyridine.[5,6] In this molecule, the

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[‡] Permanent address: Istituto di Chimica Generale, Università di Roma, I00185 Roma, Italy, CNR sponsored Fellow, 1982.

[§] University of Wisconsin.

[∥] Theoretician in Residence, Synchrotron Radiation Center; Stoughton, WI, 1982.

[⊥] Oak Ridge National Laboratory.

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nitrogen nonbonding n orbital ($7a_1$) and the highest π orbital ($1a_2$) are expected to be ionized at approximately the same energy. The two theoretical methods, which have been the most reliable in providing assignments in these systems,[5-8] give two different orderings for the first two orbitals in pyridine. These two methods are the many-body Green's function calculations of von Niessen et al.[5,6] and the empirical HAM/3 method of Åsbrink et al.[7] Both these methods consider many-body effects and are not limited to Koopmans' theorem, with von Niessen et al. concluding the ordering for pyridine to be 9.45 eV ($1a_2$) and 9.64 eV ($7a_1$) (the authors do not consider the calculated values to be of sufficient accuracy unambiguously to assign the order of ionizations), whereas the HAM/3 calculations give 9.68 eV ($7a_1$) and 10.03 eV ($1a_2$).

In the experimental photoelectron spectrum, these orbitals give rise to only one broad band around 9.7 eV, so there is almost complete overlap of the two expected bands. Two experimental techniques have been applied to the problem of the orbital assignment in pyridine. Berg et al.[9] used multiphoton spectroscopy to demonstrate that ionization of the n-electron occurs at the lowest energy in pyrazine in accord with the conclusions based on PES data by Fridh et al.[10] and Gleiter et al.[11] that in all azabenzenes a nonbonding electron is removed first. Berg et al. also investigated pyridine and concluded that the ordering of the orbitals is (1) n, (2) π, the same as in pyrazine. Their conclusions for pyridine, however, depended upon a questionable but likely assignment of the Rydberg state. Thus, the assignment of Berg et al. has not been completely accepted in the literature. Utsunomiya et al.[12] used the angular distribution parameter measurements provided by a HeI lamp to give evidence that the first two levels in pyridine were (1) n and (2) π on the grounds of the trend of β values plotted against ionization energy over the whole first band.

However, it is important to observe the nature of β as a function of photon energy and not just at one wavelength. In addition, the use of the angular distribution parameter for orbital assignments can be challenged when only one-photon energy is used because of the difficulties which arise from the possible presence of autoionization resonances and/or shape resonances. These resonances can have a major effect on the value of β such that it is conceivable that the β values at a given photon energy could be reversed and show a higher value for σ orbitals than for a π orbitals.[13-17]

In this paper we report data on the photon energy dependence of β values in the range 12–27 eV for the first three ionic levels in pyridine, 2-fluoropyridine, and pentafluoropyridine, and for the first four ionic levels in pyrimidine and pyrazine. The general aim was to develop a method of determining the ordering of orbitals in molecules by using the characteristics of the dependence of the angular distribution parameter, β, on photon energy. Studying molecules in which the orbital assignments of bands are known permits determination of molecular orbital ordering in analogous molecules for which the assignment is uncertain. There is a large set of data available on β distributions for π orbitals[1-4] that shows that β for a π orbital is characterized as starting from a low value near the ionization threshold and rapidly increasing as the kinetic energy of the ejected electrons increases. It will be shown in this paper that the nitrogen nonbonding n orbitals have a behavior with regard to β that is in contrast to the π orbital. Fluorosubstituted pyridines were studied to utilize the fact that upon fluorosubstitution for hydrogen, σ orbitals are shifted toward higher ionization energies more than π orbitals. This provided a way to obtain information on the behavior of the nitrogen n orbitals without the complication of overlap with a π orbital. The diazines were studied to explore the effect on β where there was partial overlapping of bands corresponding to nonbonding and π levels. For pyridine, the aim was to obtain experimental evidence using information on the behavior of β to determine the sequence of the two first ionic states in the overlapping PES band.

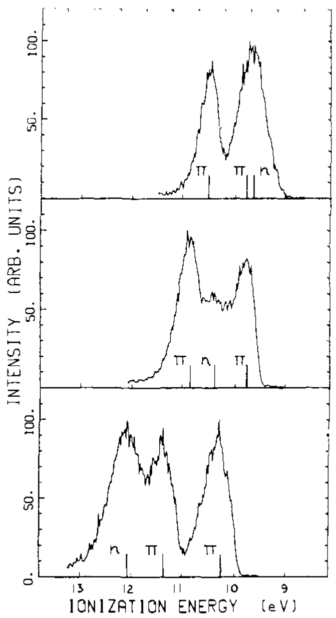

Figure 1. Photoelectron spectra at photon energy of 21.22 eV and 0° angle for (top to bottom) pyridine, 2-fluoropyridine, and pentafluoropyridine.

Experimental Section

The 240-MeV Tantalus I electron storage ring at the Wisconsin Synchrotron Radiation Center (SRC) was used as a continuum source of eliptically polarized light for this investigation. The synchrotron radiation was passed through a 1-m Seya-Namioka monochromator equipped with a 1440 lines/mm osmium coated grating in order to obtain monochromatic photons in the 10 to 30 eV range. The bandpass of the monochromator was held constant at 2 Å. A spherical sector electron spectrometer having a radius of 3.6 cm was utilized. A detailed description of the general instrumental characteristics is presented elsewhere.[18]

In order to determined the angular distribution parameter for a given orbital, spectra were obtained at two angles, in the plane and perpendicular to the plane of polarization, for each photon energy. The experimental value of the angular distribution parameter, β, is obtained from the expression

$$\beta = \frac{4(R-1)}{3P(R+1)-(R-1)}$$

where $R = I(0°)/I(90°)$ and $I(0°)$ and $I(90°)$ are the intensities of the photoelectron peaks measured parallel and perpendicular, respectively, to the polarization vector. P is the degree of polarization of the photon beam. The derivation has been given previously.[1] Using a polarization analyzer modeled after one described by Samson,[19] we found the polarization of the photon beam under our experimental conditions to be between 0.90 and 0.95. A value of 0.925 was used at all wavelengths.

The angular distributions of Ar and Kr were measured as a check on calibration.[20] A correction of the ratio R by a constant factor was found

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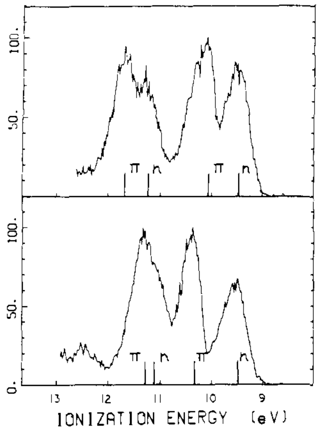

Figure 2. Photoelectron spectra at photon energy of 21.22 eV and 0° angle for (top to bottom) pyrazine and pyrimidine.

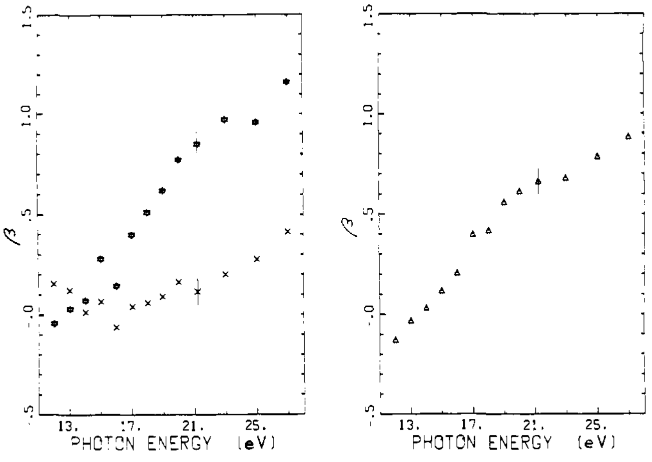

Figure 3. Left: plots of β values as a function of photon energy for the first (☆) and the second (×) ionic level in 2-fluoropyridine. Right: plot of β values as a function of photon energy for the third (△) ionic level in 2-fluoropyridine.

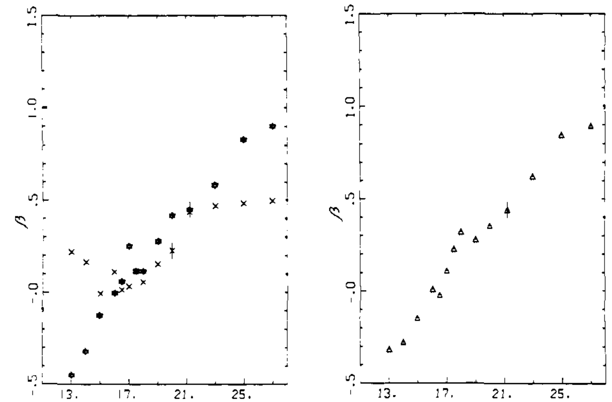

Figure 4. Left: plots of β values as a function of photon energy for the first (☆) and the third (×) ionic level in pentafluoropyridine. Right: plot of β values as a function of photon energy for the second (△) ionic level in pentafluoropyridine.

to be necessary in order to obtain the correct β values for the calibrant gases. The correction was attributed to sampling volume differences at the two angles. It was also found that the sampling volume, and thus the correction factor, was dependent upon the alignment of the instrument with respect to the photon beam. The error bars given in the figures were determined primarily by consideration of the agreement between replicate runs although consideration was also given to the counting statistics.

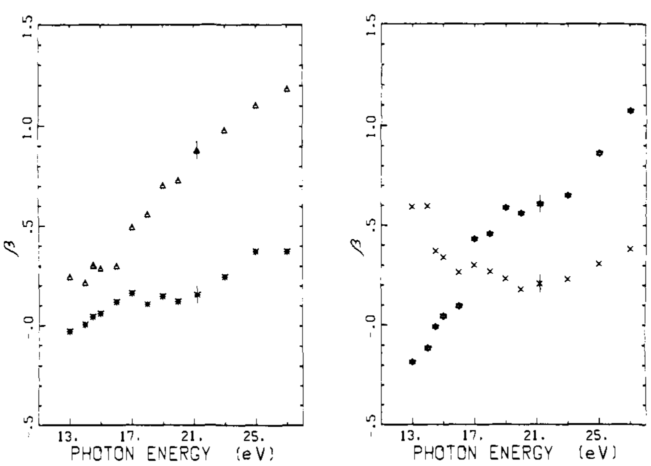

Figure 5. Left: plots of β values as a function of photon energy for the first (*) and the second (△) ionic level in pyrazine. Right: plots of β values as a function of photon energy for the third (×) and the fourth (☆) ionic level in pyrazine.

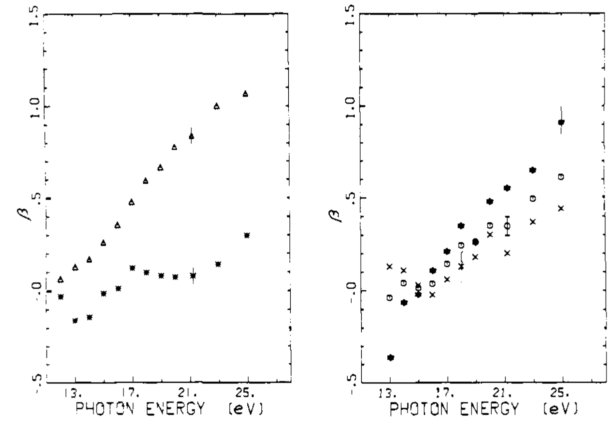

Figure 6. Left: plots of β values as a function of photon energy for the first (*) and the second (△) ionic level in pyrimidine. Right: plots of β values as a function of photon energy for the whole third band (○), for the high-energy side (☆) and for the low-energy side (×) in pyrimidine.

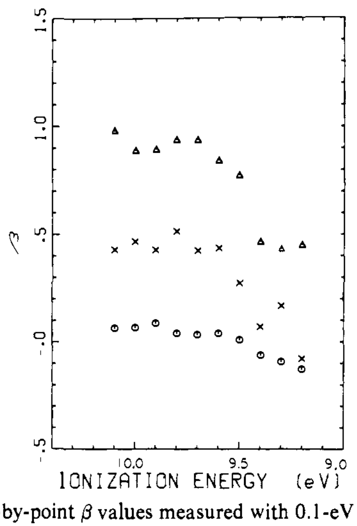

Figure 7. Point-by-point β values measured with 0.1-eV spacing for the first band of pyridine plotted as a function of ionization energy for three different photon energy values and, namely, (○) 13 eV, (×) 21.22 eV, (△) 27 eV.

The pyridine was purchased from Fisher Scientific Co. The 2-fluoropyridine, pentafluoropyridine, pyrazine, and pyrimidine were purchased from Aldrich Chemical Co. All chemicals were used as received and were 99% purity of greater.

Results and Discussion

Typical photoelectron spectra for all molecules measured with synchrotron radiation at 21.22 eV and at 0° angle are shown in

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Figures 1 and 2. Plots of β values for various bands and molecules as a function of photon energy (E_p) are shown in Figures 3–7. The spectrum of 2-fluoropyridine (Figure 1) shows three bands at 9.9, 10.5, and 10.8 eV. In accordance with the literature assignment,[21] the first band corresponds to the ionization of the first π orbital, the second band to the nonbonding orbital, and the third band to the second π orbital. In Figure 3, β values are plotted as a function of photon energy (E_p) for the first ionic level (☆), for the second ionic level (×), and for the third ionic level (△). The (☆) and the (△) curves are very similar in shape and exhibit the expected trend for a π orbital of an unsaturated hydrocarbon[1-4] (low values near threshold and much higher β values at 10–15 eV above threshold). The (×) curve is very different from the other two and does not show a rapid increase in β values as the photon energy increases. Therefore, this provides evidence that the β (E_p) trend of a nonbonding orbital is clearly different from that of a π orbital in the fluorosubstituted pyridines. This difference in the shapes of the β cures can be used to differentiate n orbitals from π orbitals.

The spectrum of pentafluoropyridine shows three bands at 10.27, 11.37, and 12.08 eV. On the basis of consideration of band shape and on the different fluoro-induced shifts for the π and σ orbitals, the assigned sequence is π–π–n.[21,22] In Figure 4 plots of β vs. photon energy for the first (☆), second (△), and third (×) ionic level of pentafluoropyridine are reported. The first (☆) and the second (△) β (E_p) curves clearly show an energy dependence expected for π orbitals, while the third one (×) is similar to the (×) curve in 2-fluoropyridine (Figure 3). Therefore, this confirms the trend for the n orbitals in contrast to π orbitals.

The spectrum of pyrazine (Figure 2) shows four bands at 9.63, 10.18, 11.35, and 11.77 eV. The sequence that has been proposed is n–π–n–π.[6,11] In Figure 5 the plots of β vs. photon energy for the first (*), the second (△), the third (×) and the fourth (☆) ionic level are reported. The (△) and the (☆) curves are typical for π orbitals, while the (*) and the (×) curves are rather flat and can be considered typical for n orbitals.

The spectrum of pyrimidine (Figure 2) exhibits, in the low energy region, four bands at 9.73, 10.41, 11.23, and 11.39 eV, and the literature sequence for these four ionic states is n–π–n–π.[6,11] In Figure 6, plots of β vs. photon energy for the first band (*) and for the second band (△) are displayed. Because of the partial overlap of the third and the fourth band, β values for the two corresponding orbitals cannot be directly obtained from the peak maximum. Therefore, β values were obtained on a point-by-point basis over the entire overlapping bands with 0.1 eV spacing. Separately plotted in Figure 6 are the β values obtained from (1) the total area of both overlapping bands, (2) the β values averaged over the region of ionization energy from 11.5 to 11.9 eV (high-energy side), and (3) the β values averaged over the region of ionization energy from 10.9 to 11.2 eV (low-energy side). The β values for the high-energy side of the overlapping bands of pyrimidine are given in curve (☆) of Figure 6. This curve shows the trend expected for a π orbital. The β values for low energy side are given in curve (×). This latter curve does not rapidly increase and is similar to the β curves reported in all the other cases for n orbitals.

The photoelectron plots of β (E_p) derived from the first and second ionization band (Figure 6) show that the first orbital (curve *) has a much flatter dependence of β on energy than the second orbital (curve △). This behavior is consistent with our generalization for n and π orbitals of azabenzenes. Therefore, the β distributions are shown to be usuable even in the case of naturally overlapping bands.

From our studies a generalization can be attempted for the different behavior of π and n orbitals in azabenzenes. For each molecule the shape of a plot of β values vs. photon energy for π orbitals looks distinctly different from β (E_p) plots for n orbitals. Plots of π orbitals always show a slope higher than that for nonbonding orbitals, rising to a value of about 1 at the end of the measurement at 27 eV. Then, the two types of orbitals can be easily distintinguished. Furthermore, β plots for π orbitals in this series of molecules have similar characteristics to all other π orbitals studied so far in unsaturated organic molecules.[1-4]

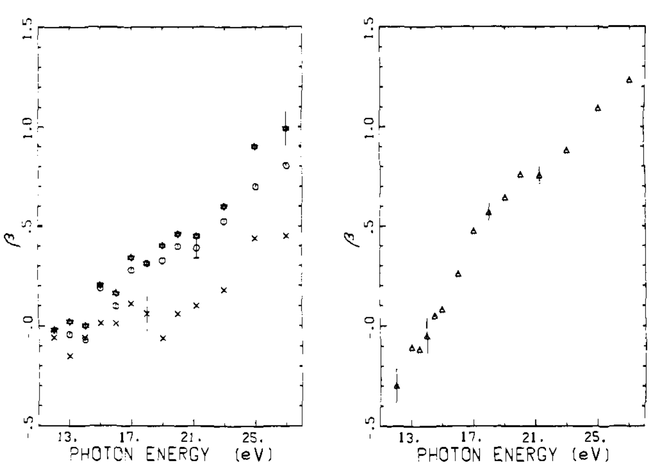

Figure 8. Left: plots of β values as a function of photon energy for the whole first band (○), for the high-energy side (☆) and for the low-energy side (×) in pyridine. Right: plot of β values as a function of photon energy for the third (△) ionic level in pyridine.

In contrast to the β (E_p) curves for the olefins, the lone pair n orbitals have a much flatter dependence, and the β values do not rise above 0.5 unit. Nonbonding orbitals do not exhibit universal behavior as π orbitals do. For example, the lone pair orbitals of halogen compounds rise rapidly above threshold.[3] Our generalizations on nonbonding n orbitals are meant to pertain only to the azabenzenes until further data become available. The different behavior of n and π orbitals for the azabenzenes is consistent with the β values measured with a line source at photon energy of 21.22 eV.[12,23] In almost all cases, the values measured for π orbitals are higher than β values for n orbitals.

The generalizations on β (E_p) established empirically for n and π orbitals of azabenzenes do not as yet have a theoretical basis. However, calculations based on multiple scattering theory have been done on the β values for the π orbitals of ethylene, acetylene, and benzene. Good agreement is obtained between theory and experiment. It is hoped that further analysis of these theoretical calculations will eventually allow a better basis to rationalize the experimental trends. With the generalizations derived from our study of the n and π orbitals of azabenzenes, we shall next attack the analysis of pyridine.

The photoelectron spectrum of pyridine (Figure 1) shows two bands in the energy region between 9 and 11 eV, the first band receiving contributions from two orbitals. The broad band at 9.7 eV arises from the ionization of the $7a_1$ (nonbonding) orbital and of the $1a_2$ (π) orbital. The single band at 10.5 eV corresponds to the ionization of the $2b_1$ (π) orbital.[5,10,11] Because the first two levels are accidentally degenerate, β values for the whole band and point-by-point β values over all the band were obtained. This is shown in Figure 7, where β values measured all over the band with 0.1 eV spacing are plotted as a function of ionization energy for three different photon energy values. The corresponding plots for the β values obtained for the total area of the two overlapping bands (○), the β values averaged over the region of ionization energy from 9.2 to 9.4 eV (low energy side) (×), and the β values averaged over the region of ionization energy from 9.8 to 10.1 eV (high energy side) (☆) are reported in Figure 8. The β (E_p) curve for the third and (△) is also reported in Figure 8.

The β (E_p) curve for the third ionic level (△) shows the energy dependence expected for a π orbital. For the first two levels, if the π level were the upper one, a plot of β derived from the low energy side of the ionization band would have the higher slope.

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The opposite would be expected for a reversed ordering of these levels. What is actually seen (Figure 8) is that at higher photon energy the high- and the low-energy sides of the band give distinctively different β values, the ones for the low-energy side being systematically lower. In this analysis, the implicit assumption is that the β over a vibrational envelope is fairly constant. When there is extensive overlap in the photoelectron spectrum between two bands, however, vibronic interaction might occur.[4] In addition, a skewing of the broad distribution of the band shape may give rise to a spectrum that is not free from contribution of both orbitals. Nevertheless, it is believed that at these extreme ends one or the other orbital is dominant so that at least the qualitative behavior of β (E_p) can be plotted. The low-energy side β (E_p) curve (×) (Figure 8) does not show a rapid increase in β values as the photon energy increases. The behavior of the low-energy side (×) curve is also similar to the β curves reported for nonbonding orbitals in the other azabenzenes and it appears to be consistent with an assignment to a nonbonding orbital.

The high-energy side β (E_p) curve (☆) (Figure 8) does rise with photon energy reflective of a contribution from the π orbital which was lacking for the low-energy side. Therefore, the relative ordering for the first two ionic levels in pyridine is confirmed to be n at lower ionization energy followed by π. A subtle difference in the β values as a function of photon energy is shown by the data for pyridine and fluorosubstituted pyridines. There is a shift to lower β values for π orbitals due to the presence of fluorine. For the second π orbital the maximum β values in pyridine at electron kinetic energy of 16.5 eV is 1.233; in 2-fluoropyridine at an electron kinetic energy of 16.3 eV the β value is 0.884; and in pentafluoropyridine at electron kinetic energy of 15.6 eV the β value is 0.895. This effect was previously seen for benzene and hexafluorobenzene[3,4] and appears so far to be a general effect on β.

When the β values reported here are compared to the 21.22-eV He I values[12] for pyridine and pentafluoropyridine, it is seen that the He I data are systematically higher by approximately 0.2 β unit. It is also obvious from the shape of the β curve with photon energy that orbitals which are measured with line sources at 21.22 eV must yield electron kinetic energies sufficiently high to circumvent the threshold effects. If this is not the situation, the β values for n and π orbitals appear to be identical. For example, for pentafluoropyridine the 21.22-eV line source gives identical β values of 0.6 for the first and third bands identified as π and n, respectively. The data presented here at 21.22 eV show identical β values of 0.45, but at a photon energy of 27 eV, the β values are 0.9 and 0.5, respectively. Clearly, the ability to produce electrons of different kinetic energies provides another dimension in distinguishing the orbital producing the photoelectron.

Conclusion

A systematic study of the angular distribution parameter, β, has been determined for a series of azabenzenes over the photon energy range from 12 to 27 eV. From these results generalizations can be made regarding the relative behavior of β for the π and n orbitals. The value of β for the π orbitals rises more rapidly with photon energy than the n orbitals to a value close to or greater than 1.0 for energies approximately 15 eV above the ionization threshold. In contrast, the value of β for the nonbonding n orbitals is fairly constant as a function of photoelectron energy and remains relatively low (below a value of 0.5 unit of β). Using these generalizations, it has been possible to assign the order of binding energy levels in pyridine. Generalization on the behavior of β as a function of orbital types must be approached with great caution. They should be made preferably for a limited series of homologous compounds. Nevertheless, as in the present case of the azabenzenes such generalizations do seen appropriate. In evaluating the systematic behavior of β as a function of photon energy for various molecular orbitals, it may be desirable to extend the energy range. It is hoped that theoretical calculations on the angular distribution parameters will lead to a better understanding of the observed behavior of β for different molecular orbital types. Besides offering a means of fingerprinting an orbital, and thus helping the assignment of the ionization levels in a molecule, a systematic study of the energy dependence curves of β gives an opportunity to characterize the nature of molecular orbitals and the dynamics of the photoionization process in molecules.

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Registry No. Pyridine, 110-86-1; 2-fluoropyridine, 372-48-5; pentafluoropyridine, 700-16-3; pyrazine, 290-37-9; pyrimidine, 289-95-2.

Chemical Properties of the Gas-Phase Benzvalene Radical Cation

D. L. Miller and M. L. Gross*

Contribution from the Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588. *Received November 15, 1982*

Abstract: The nature of the gas-phase benzvalene radical cation has been explored by means of comparative ion–molecule reactions studied by Fourier transform mass spectrometry and by comparative collision-induced dissociation spectra obtained by mass spectrometry/mass spectrometry. It is found that this C_6H_6 radical cation has a unique structure different from previously studied C_6H_6 radical cations, including ionized benzene. We conclude that the structure is similar to that of its neutral precursor. The rate constant of the reaction with neutral butadiene has also been measured and compared with the rate constant of the reaction of ionized fulvene and butadiene.

Perhaps one of the most studied systems in gas-phase ion chemistry is that of the C_6H_6 radical cation,[1-28] in particular that of ionized benzene. This is due in large part to questions concerning the nature of the gas-phase ion structure. Benzene requires

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