Inorg. Chem. **1999,** *38,* 4023−4027

Reevaluation of the Gas-Phase Valence Photoelectron Spectra of Octaethylporphyrin and Tetraphenylporphyrin

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Received March 10, 1999

Gas-phase valence photoelectron spectra are reported for 2,3,7,8,12,13,17,18-octaethylporphyrin ($OEPH_2$) and 5,10,15,20-tetraphenylporphyrin ($TPPH_2$). Comparison of spectra collected with He I and He II sources gives an empirical assignment of the relative order of the low-energy ^2A_u and $^2B_{1u}$ ion states in the gas phase. For $OEPH_2$, the first ionization at 6.24 eV is assigned to the ^2A_u ion state, with the $^2B_{1u}$ ionization located 0.25 eV to higher energy. The photoelectron spectrum reported here is quite different from the previously reported spectrum of $OEPH_2$. The first ionization of $TPPH_2$ is assigned to the $^2B_{1u}$ ion state, with the ^2A_u ionization 0.27 eV to higher energy. The reversal of the ordering of the first two ionizations of $OEPH_2$ and $TPPH_2$ is due to the different site of the substituents and the different nodal properties of the porphyrin orbitals.

Introduction

Porphyrins have been studied extensively due to their importance in biology[1] and usefulness in other catalytic systems.[2] Much attention has been given to electronic structure calculations on porphyrins[3−14] and metalloporphyrins,[15−17] with particular attention in recent years given to understanding the effect of substituents on the electron distributions and energies[18−23] and subsequent changes in reactivity.[21,24] Computational results are often compared to spectroscopic results, such as absorption and photoelectron spectra. Specifically, the quality of a computational method for describing a system is often judged by the method's ability to calculate accurate ionization energies,[12] because an ionization energy is one of the most basic physical properties that can be measured for a molecule. Analysis of computational results for porphyrins has been hindered by a lack of photoelectron spectroscopic data for comparison. To this time there are only a few reports of the gas-phase photoelectron spectroscopy of porphyrins.[25−28] Some comparison has been made between calculations and solid-state XPS results,[7,18,21] but these are somewhat hindered by problems associated with intermolecular interactions in the solid phase and are not as useful for understanding reactivity as are the valence ionizations that are much more closely related to thermodynamic cycles[29] and the orbitals associated with the reactivity of molecules. Gas-phase measurements are particularly important for comparison to computational results because other spectroscopic methods are often affected by solution or other intermolecular interactions.

We have recently begun further investigation of the gas-phase valence photoelectron spectra of substituted porphyrins and metalloporphyrins. As part of our initial studies we remeasured the PES of 2,3,7,8,12,13,17,18-octaethylporphyrin (referred to as $OEPH_2$ from this point), which has previously been reported[27] and often referred to by computational chemists for matching substituent effects.[18−20,22,23] Our results do not agree with this previously reported spectrum. Here, we report He I PES and accurate ionization energies for $OEPH_2$. We also report a new He I spectrum of 5,10,15,20-tetraphenylporphyrin ($TPPH_2$), for

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10.1021/ic990279o CCC: $18.00

which we measure ionization energies in good agreement with the previous literature spectrum,[26] although the actual spectrum was not shown, so complete comparison is difficult. In addition to He I spectra we also report He II spectra for each of these porphyrins. Our primary goal is to assign and accurately measure the relative energies of the first two vertical ionization energies of each compound. These two ionizations correspond to π orbitals of the porphyrin ring that are each influenced differently by substituents (vide infra) and are the values most often reported from calculations.

Experimental Section

Sample Preparation. Two different samples of $OEPH_2$ were used, and both gave the same spectrum. One sample of $OEPH_2$ was prepared in 1970 by published procedures[30] and purified by column chromatography, and another was purchased from Aldrich and used without any further purification. The sample of $TPPH_2$ was prepared and purified by published methods.[31]

Photoelectron Spectroscopy. Photoelectron spectra were recorded using an instrument that features a 36-cm hemispherical analyzer (McPherson), which has been described in more detail previously.[32] The ionization energy scale was calibrated using the $^2E_{1/2}$ ionization of methyl iodide (9.538 eV), with the argon $^2P_{3/2}$ ionization (15.759 eV) used as an internal energy scale lock during data collection. During data collection the instrument resolution, measured using the full width at half-maximum of the argon $^2P_{3/2}$ ionization, was 0.020−0.030 eV. All data are intensity corrected with an experimentally determined instrument analyzer sensitivity function that assumes a linear dependence of analyzer transmission (intensity) to the kinetic energy of the electrons within the energy range of these experiments.

The spectra collected with a He Iα ($1s^2 \leftarrow 1s2p$, 21.218 eV) source were corrected for the He Iβ line ($1s^2 \leftarrow 1s3p$, 23.085 eV, and 3% of the intensity of the He Iα line), and the He IIα ($1s \leftarrow 2p$, 40.814 eV) spectra were corrected for the He IIβ line ($1s \leftarrow 3p$, 48.372 eV, and 12% the intensity of the He IIα line). These corrections are necessary because discharge sources are not monochromatic.[33]

Samples sublimed cleanly with no detectable evidence of decomposition products in the gas phase or as a solid residue. The sublimation temperatures (in °C, at 10^{-4} Torr) were as follows: $OEPH_2$, 260−315; $TPPH_2$, 280−320 (monitored using a "K" type thermocouple passed through a vacuum feedthrough and attached directly to the ionization cell). A stainless steel sample cell that had been used previously to collect gas-phase PES of compounds with sublimation temperatures of up to 400 °C was used to accommodate the high temperatures.[34] The spectrum of each compound was measured several times on different days with no discernible difference between the spectra, and the spectra did not vary as the temperature was raised through the sublimation range.

Data Analysis. In the data figures, the vertical length of each data mark represents the experimental variance of that point.[35] The valence ionization bands are represented analytically with the best fit of asymmetric Gaussian peaks.[35] The bands are defined with the position, amplitude, half-width for the high binding energy side of the peak, and half-width for the low binding energy side of the peak. The peak positions and half-widths are reproducible to about ±0.02 eV (≈3σ level). For each compound, the He I spectrum was fit first, where the number of peaks used in the fit was based on the features of the band profile and the number necessary for a statistically good fit. The He I fit was then used to fit the He II spectra, with the peak positions and half-widths fixed to those of the He I fit and the peak amplitudes allowed to vary to account for the changes in photoionization cross section as the source energy is varied (vide infra).

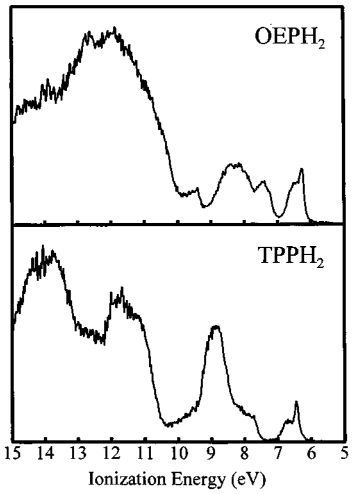

Figure 1. Valence photoelectron spectra of octaethylporphyrin ($OEPH_2$) and tetraphenylporphyrin ($TPPH_2$).

Table 1. Analytical Representation of PES Data

	ionization band		half-width (eV)		rel area			
compd	label	energy (eV)	high	low	He I	He II	He II/ He I	assignment
$OEPH_2$	1′	6.17	0.16	0.16	1.00	1.00	1.00	^2A_u
	1	6.24	0.18	0.15				
	2	6.49	0.38	0.31	1.61	2.15	1.34	$^2B_{1u}$
	3	7.35	0.95	0.34	2.98	3.02	1.01	
	4	7.89	0.69	0.24	1.18	1.62	1.37	
	5	8.20	0.71	0.42	2.32	2.73	1.18	
	6	8.58	0.56	0.47	1.77	1.98	1.12	
	7	9.40	0.59	0.25	0.79	1.23	0.56	
$TPPH_2$	1′	6.26	0.16	0.15	0.69	0.96	1.39	$^2B_{1u}$
	1	6.43	0.16	0.15				
	2	6.70	0.42	0.36	1.00	1.00	1.00	^2A_u

Confidence limits for the relative integrated peak areas are about 5%, with the primary source of uncertainty being the determination of the baseline, which is caused by electron scattering and is taken to be linear over the small energy range of these spectra. The total area under a series of overlapping peaks is known with the same confidence, but the individual peak areas are more uncertain. The fitting procedures used are described in more detail elsewhere.[35]

Results

The gas-phase valence photoelectron spectra of $OEPH_2$ and $TPPH_2$ from 5 to 15 eV ionization energy are shown in Figure 1. The ionizations located above about 10 eV for each compound arise from removal of electrons from orbitals primarily associated with σ bonds and the most stable π bonds. The rather intense ionization at about 9 eV in the spectrum of $TPPH_2$ is due to the π orbitals of the phenyl substituents that derive from the e_{1u} orbital of benzene. Close-up spectra of the regions of interest for each compound will be described in the following sections. Data from the fits used to model these close-up spectra analytically are listed in Table 1.

$OEPH_2$. The He I and He II close-up spectra of $OEPH_2$ from 6 to 10 eV are shown in Figure 2. The first set of ionizations, located between 6 and 7 eV, has two distinct features labeled 1 and 2 in Figure 2 with vertical ionization energies of 6.24 and 6.47 eV. A small shoulder is also visible on the low binding energy side of the band. This shoulder is likely due to a partially resolved hot band, and it requires an additional Gaussian that is labeled 1′ and is 0.07 eV (~600 cm^{-1}) lower in energy than

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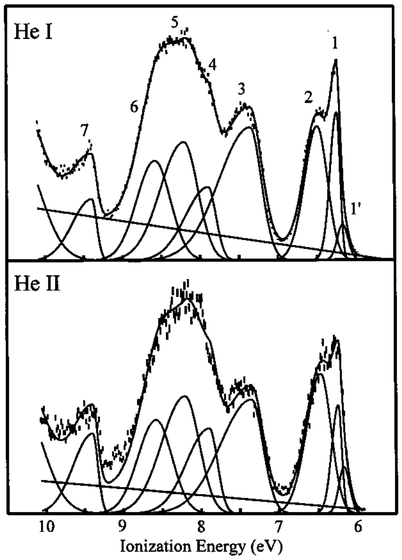
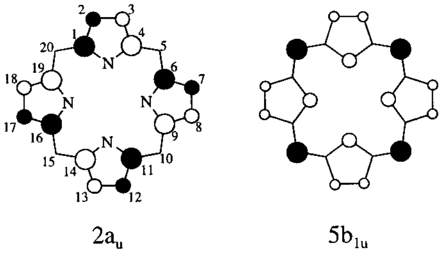


Figure 2. He I and He II close-up spectra of $OEPH_2$.



$2a_u$ $5b_{1u}$

Figure 3. Representations of the general nodal characteristics of the $2a_u$ and $5b_{1u}$ orbitals (D_{2h} symmetry) of a porphyrin.

1, to best describe the overall shape of the band. The intensity of the hot band relative to the first ionization is difficult to determine confidently because it is not completely resolved, but at this temperature and vibrational spacing the hot band would be about one-fourth the intensity of the first ionization. Bands 1 and 2 represent two different ion states because their intensity ratio changes between He I and He II excitation (vide infra). It is difficult to unambiguously assign any of the ionizations above 7 eV, but the positions and relative intensities of the Gaussians used to represent the ionization bands from 7 to 10 eV are listed in Table 1 for comparison.

According to Gouterman's four-orbital model,[36] it is expected that two porphyrin π orbitals with labels a_u and b_{1u} in D_{2h} symmetry (a_{1u} and a_{2u}, respectively, in D_{4h} symmetry) and general nodal properties as shown in Figure 3 should be separated from all of the other filled orbitals and close to each other in energy. For comparison, the photoelectron spectrum of unsubstituted porphine has an ionization band at 6.9 eV[28] and does not show two clear vertical ionizations as this spectrum of $OEPH_2$ does. For unsubstituted porphine, the ^2A_u and $^2B_{1u}$ ionizations are very close in energy, as expected, and appear under one ionization band. Addition of eight ethyl substituents in the 2, 3, 7, 8, 12, 13, 17, and 18 positions will split the near degenerate ^2A_u and $^2B_{1u}$ ionizations further apart. While alkyl substituents are overall electron donating, the primary electron perturbation of an alkyl group in place of a hydrogen in an unsaturated organic compound is a hyperconjugative π interaction rather than a σ inductive one.[37] The amount of interaction and destabilization of the porphyrin π orbitals with the ethyl substituents will be dependent on the π overlap with the π symmetry combination of the σ bonds within the substituents. As the representations in Figure 3 show, the a_u orbital has more electron density at the substituted sites than the b_{1u} orbital does, and the a_u orbital will therefore be destabilized more than the b_{1u} orbital, causing the energy splitting between the ^2A_u and $^2B_{1u}$ ionizations seen in the photoelectron spectrum. The total destabilization of the ^2A_u ionization of $OEPH_2$ from its position in unsubstituted porphine is ~0.7 eV. For comparison, the first ionization of benzene is destabilized 0.42 eV by a single methyl substitution to form toluene. The ~0.7 eV destabilization with two alkyls per pyrrole ring of $OEPH_2$ is consistent with the expected shift.[38] The assignment of the first two ionizations is then that ionization 1 represents the ^2A_u state, while ionization 2 represents the $^2B_{1u}$ state.

The He II spectrum gives additional support for the particular assignment of the relative ordering of the ^2A_u and $^2B_{1u}$ ion states of $OEPH_2$. After corrections for instrument resolution and sensitivity, and for other excitation lines in the sources, photoelectron spectra obtained with different ionization sources differ only in the relative intensities of the ionization bands. This behavior is primarily due to the different inherent photoionization cross sections of atomic orbitals, which vary as the incident photon energy changes. From theoretical estimates,[39] the photoionization cross section of N 2p orbitals increases by about 25% as compared to C 2p orbitals when comparing spectra from He II and He I sources. Assuming that atomic orbital cross sections are additive in molecular orbitals (the Gelius model[40]), comparison of the He I and He II spectra of a molecule can therefore give an indication of the relative amount of atomic character in orbitals from which ionizations arise. The a_u orbital is composed of only C 2p character, while the b_{1u} orbital has appreciable character from N 2p orbitals. It would therefore be expected for a porphyrin that the $^2B_{1u}$ ionization would increase in relative intensity in the He II spectrum as compared to the ^2A_u ionization.

The He I and He II spectra of simpler aromatic organic compounds that contain nitrogen and have well-separated π orbital based ionizations for which the assignment is well understood can be used to verify the general theoretical prediction of the cross-section behavior of N and C 2p orbitals. For example, the first ionization in the photoelectron spectrum of pyrrole[41] corresponds to removal of an electron from the π-based a_2 orbital, which similar to the a_u orbital of a porphyrin is composed of only C 2p character. The second ionization of pyrrole corresponds to removal of an electron from the π orbital of b_1 symmetry, which contains a mixture of C 2p and N 2p character similar to the b_{1u} orbital of porphyrin. Comparison of the He I and He II spectra of pyrrole indicates that the $^2B_1$ ionization increases in area by 25% as compared to the $^2A_2$ ionization. Another simple molecule that can be used as an example is aniline, for which the $^2B_1$ π-based ionization (a mix of C 2p and N 2p character) is seen to increase in area by 44% in the He II spectrum as compared to the $^2A_2$ π-based ionization (only C 2p character). For $OEPH_2$, band 2 increases in area by 34% compared to band 1 when the He II spectrum is compared

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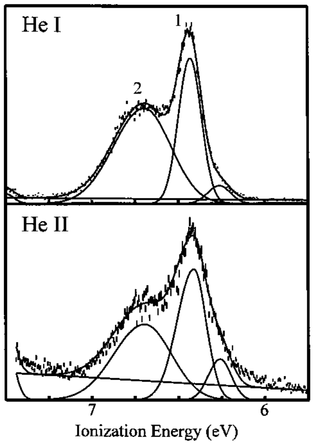

Figure 4. He I and He II close-up spectra of $TPPH_2$.

to the He I spectrum. This behavior agrees with the assignment of the first ionization of $OEPH_2$ at 6.24 eV to the ^2A_u ion state and the second ionization at 6.49 eV to the $^2B_{1u}$ ion state.

$TPPH_2$. Due to the presence of the ionization from the phenyl π orbitals that obscures the rest of the spectra of $TPPH_2$ from about 8 to 10 eV, close-up spectra were only collected of the first band, which is expected to contain the ^2A_u and $^2B_{1u}$ ion states. The He I and He II close-up spectra of this region are shown in Figure 4. There is a small feature on the low ionization energy side of the band that necessitates the use of the third Gaussian in the fit to fully describe the contour of the band. This third Gaussian is 0.17 eV ($\sim$1400 cm^{-1}) lower in energy than the first vertical ionization labeled 1 in Figure 4 and, as in $OEPH_2$, is likely due to hot band structure.

The substituents in $TPPH_2$ will affect the relative energies of the $2a_u$ and $5b_{1u}$ orbitals differently than the substituents in $OEPH_2$. In $TPPH_2$, the four electron-donating phenyl substituents are in the 5, 10, 15, and 20 positions. The $2a_u$ orbital has nodes passing through these positions, while the $5b_{1u}$ orbital has significant electron density at these positions and will be destabilized relative to the $2a_u$ orbital. It would then be expected that for $TPPH_2$ band 1 will be the $^2B_{1u}$ ionization with band 2 the ^2A_u ionization, the opposite ordering observed for $OEPH_2$. Comparison of the He I and He II spectra of $TPPH_2$ shows that band 2 decreases in relative intensity to band 1 in the He II spectrum, which is also in agreement with the assignment for $TPPH_2$ that the $^2B_{1u}$ ion state is the first ionization, with a vertical ionization energy of 6.43 eV, and the ^2A_u ion state is the second ionization with a vertical ionization energy of 6.70 eV. For both $OEPH_2$ and $TPPH_2$ the ionization that orbitally interacts with the substituents on the porphyrin ring and is destabilized to become the first ionization is also the ionization with the more narrow vibrational manifold, indicating a smaller change in bonding with ionization.

Comparison to Previous Studies

A comparison of the ionization energies of the ^2A_u and $^2B_{1u}$ ion states of $OEPH_2$ and $TPPH_2$ to those from previously reported spectra is shown in Table 2. The photoelectron spectra that we have collected for $OEPH_2$ are quite different from the He I spectrum previously reported.[27] Our first vertical ionization energy of 6.24 eV compares to a previously reported first vertical ionization energy of 6.39 eV. The relative spacing of the ionizations is very different. We find a 0.25 eV difference between the first and second ionizations, while the previously reported difference between the first and second ionizations was 0.44 eV. The relative intensity of the first two ionizations also differs greatly between the two spectra of $OEPH_2$, and the ionization bands at higher ionization energy are also quite different. The spectrum of $OEPH_2$ previously reported[27] much more closely resembles the spectra also reported at that time for metallooctaethylporphyrins than it does our spectrum of $OEPH_2$. The validity of the spectra of $OEPH_2$ reported here is supported by the facts that these spectra were collected over several different days and using samples from two different sources, with no differences observed in any of the data collected.

Table 2. Comparison to Previous Studies

compd	ionization energy (eV) ^2A_u	ionization energy (eV) $^2B_{1u}$	ref
$OEPH_2$	6.24	6.49	this work
	6.39	6.83	27
$TPPH_2$	6.70	6.43	this work
	6.72	6.39	26
	6.55		25

Our spectrum of $OEPH_2$ is much more what would be expected on the basis of the spectra of porphine and other octaalkylporphyrins reported in 1980.[28] The general shape of our spectrum of $OEPH_2$ is similar to that of porphine, although the ionization energies of $OEPH_2$ have all been destabilized 0.3 to 1.0 eV from their position in the spectrum of unsubstituted porphine and the first ionization band of $OEPH_2$ is broader than that of porphine (vide supra). Our spectra of $OEPH_2$ are strikingly similar to the spectra of etioporphyrin-I, -II, and -III.[28] The first ionization energy of each of the etioporphyrins is 6.3 eV, in excellent agreement with our first ionization energy of 6.24 eV for $OEPH_2$ as would be expected for such similar compounds. The spectra of etioporphyrins also have energy separations between the first and second ionizations similar to our spectrum of $OEPH_2$. The previous report of the He I spectrum of $TPPH_2$ also briefly mentions a preliminary spectrum of $OEPH_2$ with ionization energies of 6.25, 6.53, and 7.46 eV,[26] in reasonable agreement with our results.

The quality of the previously reported spectrum of $OEPH_2$ also makes the spectra of the metallooctaethylporphyrins reported in this same paper questionable. Accurate measurement of the spectra of each complex is important to ensure that comparisons and trends are being measured precisely. We have collected preliminary data of (octaethylporphyrin)Zn(II) for comparison to the previously reported spectra and find, for example, a first ionization energy of 6.18 eV as compared to a reported ionization energy of 6.29 eV.[27,42]

Our He I spectrum of $TPPH_2$ is in good agreement with the previously reported spectrum.[26] The first two ionization energies in both spectra are within or close to experimental error, and both are also in decent agreement with the one ionization energy reported for a low-resolution spectrum.[25] From the previous study[26] using only a He I photon source a definitive assignment of the lowest ionization energy was not possible, but our comparison of He I and He II spectra indicates a $^2B_{1u}$ ground excited-state-cation for $TPPH_2$ in the gas phase.

These gas-phase relative ionization energies of the ^2A_u and $^2B_{1u}$ states are also in good agreement with results obtained for one-electron oxidation of $OEPH_2$ and $TPPH_2$ and their respective Zn(II) and Mg(II) complexes in various solvents. On the basis of the EPR spectra of the π cation radicals, the $[OEPH_2]^+$ radical was shown to have the unpaired electron in the a_u orbital (a_{1u}

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orbital for the D_{4h} metal complexes),[43−46] while the EPR spectra of $[TPPH_2]^+$ and other meso-substituted porphyrins are consistent with the unpaired electron being in the b_{1u} orbital (a_{2u} for the D_{4h} metal complexes).[43,47,48]

Conclusions

To summarize, we report gas-phase photoelectron spectra of $OEPH_2$ and $TPPH_2$ that give accurate ionization energies for the ^2A_u and $^2B_{1u}$ ion states. For $OEPH_2$, the first ionization is assigned to the ^2A_u ion state, while for $TPPH_2$, the first ionization is assigned to the $^2B_{1u}$ ion state. These results indicate the strong influence that substituents can have upon the electronic structure of porphyrins and show that variable photon energy photoelectron spectroscopy is useful for assigning the photoelectron spectra of porphyrins without reliance on calculations. This is an especially valuable finding considering that different computational methods give different relative ordering of the orbitals and ionization energies of substituted porphyrins.[23] Hopefully the results we present here will serve to clarify the current literature regarding the PES and electronic structure of porphyrins. Further study of the valence gas-phase photoelectron spectra and electronic structure of other substituted porphyrins and metalloporphyrins is currently underway in our laboratory.

Acknowledgment. D.L.L. acknowledges support by the U.S. Department of Energy (Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, DE-FG03-95ER14574), the National Science Foundation (Grant No. CHE9618900), and the Materials Characterization Program, Department of Chemistry, The University of Arizona. F.A.W. acknowledges support by the National Institutes of Health (Grant No. DK31038).

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