for glycine, with the previously discussed values for $\Delta H_f°(H^+)$ and $\Delta H_f°(\text{Gly})$ gives $\Delta H_f°(NH_2CH_2CO_2^-)(g) = -120.6$ kcal/mol. Results of similar calculations for the other amino acids used in this study are shown in Table I.

Conclusion

The gas-phase ion chemistry of low volatility molecules can be studied in pulsed ICR spectrometers by heating the analyzer system and adding the samples via a direct insertion probe. Only moderate heating is required since the ICR cell normally requires pressures in the range 10^{-7} to 10^{-5} torr.

In the gas phase glycine exists as a nonionic molecule in contrast with the zwitterionic structure which is dominant in the solid phase and in aqueous solution. This has been proven by examining methyl-substituent effects, and these effects in substituted glycines are typical of what has been found in previous studies for other classes of compounds.

The enthalpy of transfer of protonated glycine from gas phase to aqueous solution is −87.1 kcal/mol, and for $NH_2CH_2CO_2^-$ the solvation enthalpy is −90.7 kcal/mol. The enthalpies of formation for protonated and deprotonated glycine are found to be 58.4 and −120.6 kcal/mol, respectively.

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Registry No. Glycine, 56-40-6; alanine, 56-41-7; sarcosine, 107-97-1; glycine methyl ester, 616-34-2.

ENDOR Study of VO^{2+} Adsorbed on Y Zeolite

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Abstract: Over the past two decades electron paramagnetic resonance (EPR) has been used extensively in studies of the structure of transition metal ion exchanged zeolites. Use is made of the fact that data on *g* values and metal ion hyperfine splitting constants provide an insight into the structure of the cation binding site. In this contribution it will be shown that electron nuclear double resonance (ENDOR) makes it possible to measure the interactions between the unpaired electrons and nuclear spins in the vicinity of the paramagnetic cation. Generally, these interactions remain unresolved in the EPR spectra of these amorphous systems. The experimental results demonstrate that the ENDOR technique can be used to study cation solvation in the zeolite cavities and changes in cation environment induced by removal of solvent molecules or co-adsorbed molecules. It is shown that subtle structural changes that do not register in the EPR spectrum can have a profound effect on the ENDOR spectra. The results presented here suggest that ENDOR can be of great value in studies of transition metal ion adsorption on zeolites as well as other porous surfaces.

Zeolites are used as catalysts in a variety of chemical reactions. Their catalytic activity can be modified by cation exchange and changes in cation binding site. For this reason the study of the relation between structure and activity continues to be an important area of research. In cases where the exchanged cation is a transition metal ion, data on *g* values and metal ion hyperfine couplings derived from EPR spectra have proven to be a valuable source of structural information.[1-5] A more complete insight into the structure of these systems could be provided by measurement of hyperfine splitting constants of nuclear spins in the vicinity of the paramagnetic center.[6] Unfortunately, EPR measurements generally do not give access to this information. It will be shown that these interactions can be measured by using electron nuclear double resonance (ENDOR).

To explore the utility of ENDOR in this field of research the oxovanadium(IV) Y zeolite system was chosen for the following reasons. (1) Work performed in this laboratory has established that ENDOR spectra of vanadyl complexes in amorphous solids are obtained readily.[7-10] It has been demonstrated that the spectra give detailed information on hyperfine as well as quadrupole interaction components. (2) VO^{2+} adsorbed on Y zeolite has been the focus of an earlier EPR study by Martini and co-workers.[11] These workers proposed specific models for the various VO^{2+} complexes that could be generated. This offers the opportunity to investigate whether or not ENDOR can contribute new information that aids in the elucidation of the structure of the system.

Experimental Section

Linde Type NaY zeolite obtained from Alfa was used as received. Adsorption of VO^{2+} was achieved by stirring 5 g of zeolite with 100 mL of a 0.02-M solution of $VOSO_4{\cdot}5H_2O$ under an argon atmosphere for about 1 week. The exchanged zeolites were kept hydrated by storage in a water-vapor-saturated atmosphere. Evacuation (10^{-2} torr) at room temperature yielded the (partially) dehydrated samples used in this investigation.

EPR and ENDOR spectra were recorded with a Varian E9 X-band spectrometer with the home-built ENDOR accessory described before.[7,9] The optimum temperature for recording of the ENDOR spectra was found to be around 20 K. Other instrumental conditions were as follows: microwave power 5 mW, radio frequency power ~300 W, 10 kHz frequency modulation with a deviation of ±50 kHz.

Data and Discussion

The EPR spectrum of hydrated, VO^{2+}-exchanged Y zeolite recorded at 100 K is presented in Figure 1. The spectrum closely resembles that reported by Martini et al.[11] On the basis of the EPR parameters derived from the spectrum ($g_\parallel = 1.938$, $g_\perp = 1.986$, $A_\parallel = -0.0178$ cm^{-1}, $A_\perp = -0.0070$ cm^{-1}), these authors assigned the spectrum to the $VO(H_2O)_5^{2+}$ complex. The room-temperature spectrum of the hydrated system shows some line broadening and slight shifts of peak positions. This was attributed[11] to residual molecular motion of the complex. The penta-

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(1) Nicula, A.; Stamires, D.; Turkevich, J. *J Chem. Phys.* **1965**, *42*, 3684.

(2) Naccache, C.; Ben-Taarit, Y. *Chem. Phys. Lett.* **1971**, *11*, 11.

(3) Turkevich, J.; Ono, Y.; Soria, J. *J. Catal.* **1972**, *25*, 44.

(4) Peigneur, P.; Lunsford, J. H.; DeWilde, W.; Schoonheydt, R. A. *J. Phys. Chem.* **1977**, *81*, 1179.

(5) Kuznicki, S. M.; DeVries, K. L.; Eyring, E. M. *J. Phys. Chem.* **1980**, *84*, 535.

(6) Kevan, L. *J. Phys. Chem.* **1981**, *85*, 1628.

(7) van Willigen, H. *J. Magn. Reson.* **1980**, *39*, 37.

(8) Mulks, C. F.; van Willigen, H. *J. Phys. Chem.* **1981**, *85*, 1220.

(9) Kirste, B.; van Willigen, H. *J. Phys. Chem.* **1982**, *86*, 2743.

(10) Mulks, C. F.; Kirste, B.; van Willigen, H. *J. Am. Chem. Soc.* **1982**, *104*, 5906.

(11) Martini, G.; Ottaviani, M. F.; Seravalli, G. L. *J. Phys. Chem.* **1975**, *79*, 1716.

0002-7863/83/1505-4232$01.50/0

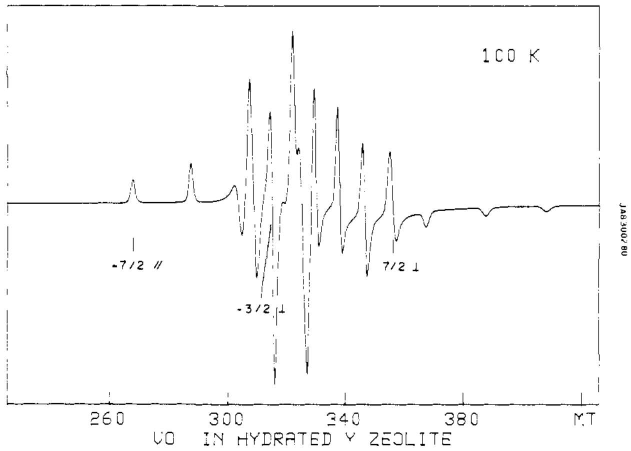

Figure 1. First derivative EPR spectrum of VO^{2+} adsorbed on Y zeolite (hydrated sample) recorded at 100 K.

Table I. Hyperfine Splittings (MHz)[a] of Axial Water Molecule Protons

system	field direction H ∥ V=O[b]	 H ⊥ V=O[c]
VO^{2+}/Y zeolite	6.49	3.03
VO^{2+}/0.1 N HCl	6.35	3.01
VO^{2+}/tutton salt	6.40	3.07

[a] Estimated uncertainty ±0.02 MHz. [b] Measured between low-frequency and high-frequency peak extremes (cf. Figure 2A). [c] Measured between zero crossings of low- and high-frequency peaks (cf. Figure 2D).

hydrate was presumed to be located in the zeolite supercavity.

Figure 2 shows the proton ENDOR spectra obtained with the magnetic field (H) set on the −7/2 parallel or −3/2 perpendicular peak in the EPR spectrum (field settings are marked in Figure 1). In ENDOR, NMR transitions induced by a strong radio frequency field are detected by their effect on the EPR signal amplitude at a chosen field value. By a suitable choice of field settings the range of molecular orientations contributing to the ENDOR signal can be controlled. With the −7/2 parallel field position a spectrum (Figure 2A) is obtained of those molecules that have the V=O axis parallel to H. This spectrum yields the proton hyperfine splittings along the V=O axis. The −3/2 perpendicular position generates a two-dimensional powder spectrum (Figure 2D) giving the hyperfine extremes in the plane perpendicular to the V=O axis.

The spectra make it possible to draw a number of conclusions regarding the structure of the system.

I. Except for the center region (close to the proton nuclear Zeeman frequency, ν_p), the spectra show a close resemblance to those obtained under identical conditions from $VO(H_2O)_5^{2+}$ in frozen aqueous solution (Figure 2, B and E) and in $Mg(NH_4)_2(SO_4)_2{\cdot}6H_2O$ powder (Figure 2, C and F). Therefore, the ENDOR data confirm the presence of the pentahydrate in hydrated Y zeolite.

II. Peaks due to protons of the axially coordinated H_2O[7,12] have been labeled H_{ax} in Figure 2. The hyperfine splittings for these protons are summarized in Table I. It has been shown[13] that the magnitudes of these splittings are proportional to r^{-3}, where r is the vanadium–proton distance. Evidently, the position of the axial water molecule is not affected significantly by interactions between the paramagnetic complex and the zeolite. The same applies for the equatorial water molecules. The isotropic splittings of protons of these molecules are sensitive to the location of the protons relative to the vanadyl cation.[13] Hence, the close correspondence of the three sets of ENDOR spectra shown in Figure 2 implies little variation in structure.

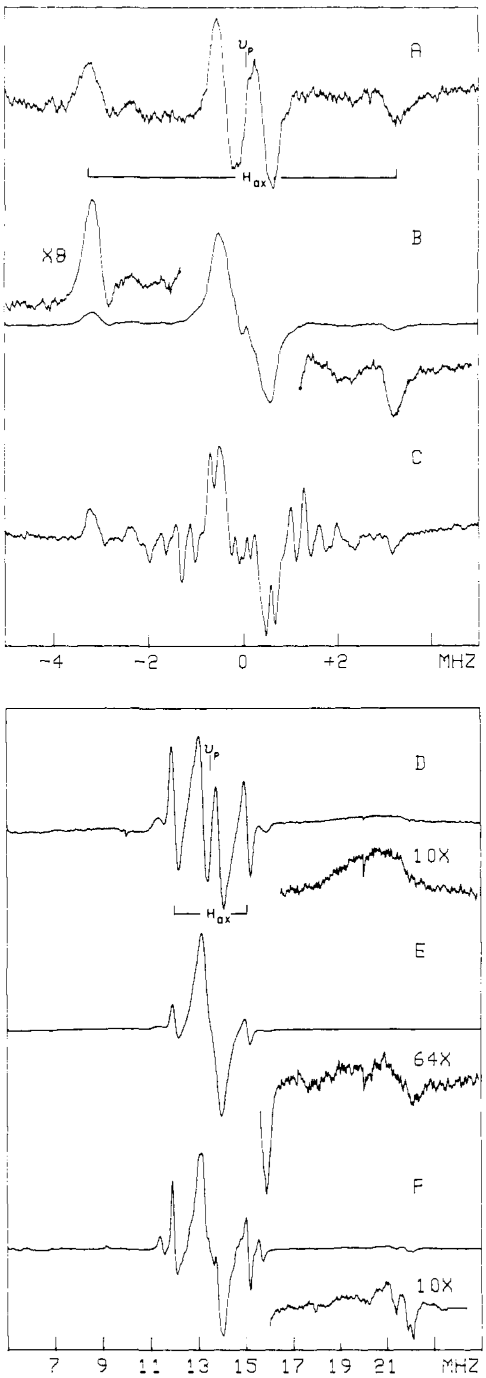

Figure 2. First derivative ENDOR spectra of VO^{2+} in (A, D) Y zeolite, (B, E) frozen aqueous solution (0.1 N HCl, glycerol added to ensure glass formation), and (C, F) $Mg(NH_4)_2(SO_4)_2{\cdot}6H_2O$ powder. Spectra A, B, and C obtained with the field set on the −7/2 parallel EPR line (cf. Figure 1). Frequencies relative to the proton Zeeman frequency (ν_p). Spectra D, E, and F obtained with the field set on the −3/2 perpendicular EPR line (cf. Figure 1). Spectra recorded at about 20 K.

III. Of interest is the absence of a matrix ENDOR peak (centered at ν_p) in the zeolite spectra (Figure 2, A and D). A matrix ENDOR peak, dominant in the frozen aqueous solution spectra (Figure 2, B and E), would be generated by (weakly coupled) protons outside the first coordination sphere of the cation. The distribution in position of these nuclei relative to the paramagnetic center is expected to give rise to a broad structureless absorption.[14] Its absence in the spectra from VO^{2+} in hydrated Y zeolite leads to the conclusion that the aquo complex is shielded

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(12) van Willigen, H.; Mulks, C. F.; Atherton, N. M. *Inorg. Chem.* **1982**, *21*, 1708.

(13) Atherton, N. M; Schackleton, J. F. *Mol. Phys.* **1980**, *39*, 1471.

(14) Kevan, L.; Kispert, L. D. In "Electron Spin Double Resonance Spectroscopy"; Wiley: New York, 1976; Chapter 4.

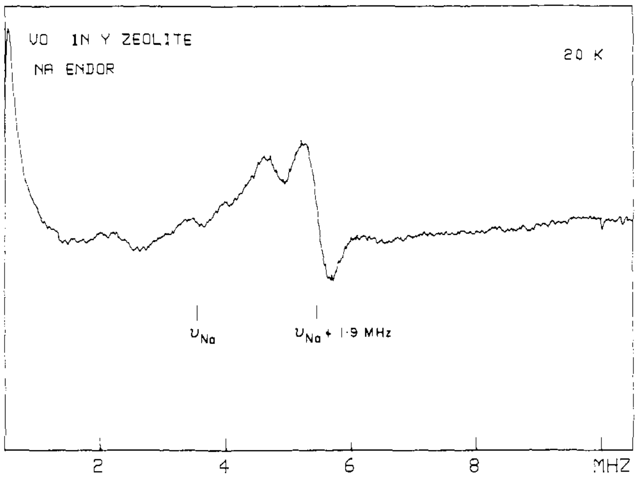

Figure 3. ^{23}Na ENDOR spectrum of VO^{2+} adsorbed on Y zeolite (partially dehydrated). Spectrum recorded with the field set on the −3/2 perpendicular EPR line (cf. Figure 1), temperature about 20 K.

from a close approach of bulk water molecules. Evidently, a model placing the aquo complex in the center of the supercage surrounded by one or more solvent molecule layers does not fit the ENDOR data. Such a structure also fails to account for the room-temperature EPR spectrum.[11] As noted earlier, this spectrum approaches the rigid matrix limit. The virtual absence of motion of the complex at room temperature implies that it is locked in place by interactions with the zeolite lattice. A structural model in which the complex is hydrogen bonded to the zeolite structure accounts satisfactorily for its shielding from solvent molecules.

Two more observations deserve mention. First, the low-frequency region (not shown) of the ENDOR spectrum reveals a weak resonance peak centered at the Zeeman frequency of Na (in the range of 3.5–4 MHz at the field settings employed). The presence of this peak shows that Na^+ ions must be in close proximity of VO^{2+}. No resonances due to Al have been detected; possibly quadrupole splittings render the peaks too weak to detect. Second, aging of the samples changes the spectra so that the center region more closely resembles that of the frozen solution spectra. *The EPR parameters do not reflect changes in structure due to this aging process.*

As reported by Martini et al.,[11] evacuation of the samples at room temperature does not cause a significant change in the low-temperature EPR spectrum. However, the room-temperature spectrum no longer shows the line broadening and peak shifts observed in the EPR spectrum of the hydrated samples. The absence of motional broadening has been attributed[11] to a complete localization of the vanadyl cation by bonding to four hydroxyl groups of the supercavity surface to form the $VO(OH)_4^{2-}\cdot H_2O$ structure. The EPR parameters suggest that the new paramagnetic species has retained a square-pyramidal configuration. For this reason it was postulated[11] that the cations bind to the square faces of the supercage surface (type III sites).[15]

It is found that VO^{2+}/Y zeolite systems that have been kept under vacuum overnight no longer show a proton ENDOR signal. On the other hand, a more complex Na ENDOR spectrum is generated by this procedure. It is noted that VO^{2+} in strongly basic solution, presumed to generate the $VO(OH)_3^-$ complex,[16] gives rise to strong proton ENDOR signals below 100 K.[17] Therefore, the ENDOR results argue against the formation of the $VO(OH)_4^{2-}\cdot H_2O$ complex. Rather, they suggest that dehydration at room temperature leads to binding of the cation to four oxygens of the zeolite structure and removal of the axial water molecule. Since exposure of the samples to water vapor restores the original ENDOR spectra, the structural integrity of the zeolite does not appear to be affected by the dehydration.

As Figure 3 shows, the spectrum obtained with the −3/2 perpendicular field setting reveals a fairly strong resonance in the low-frequency region. From the effect of changes in field setting (from −3/2 perpendicular to +7/2 perpendicular) on line positions, it can be deduced that this resonance is due to sodium atoms. The shoulders flanking the center peak represent quadrupole satellites.[18] The fact that the peaks have a "single-crystal-like" appearance, even though all molecular orientations with H perpendicular to V=O are probed, indicates that the hyperfine and quadrupole interactions must be fairly isotropic in this plane. From the peak positions it is derived that the hyperfine interaction A_{Na} equals 3.8 MHz. The quadrupole splitting (separation center line low-frequency satellite) is about 0.7 MHz. Spectrum simulations were performed on the assumption that the Na hyperfine interaction is isotropic and that the quadrupole interaction is virtually invariant in the plane perpendicular to the V=O bond. The calculations reveal that the low-frequency triplet of ENDOR lines (falling in the range from 1 to 3 MHz) has an intensity which is about 10% of the high-frequency peaks. This explains the absence of well-defined peaks in the low-frequency region. In view of the large number of variables involved, no attempt was made to search for a perfect match between calculated and experimental spectra. So far the −7/2 parallel field setting has failed to generate Na ENDOR signals.

The relatively large sodium hyperfine splitting measured shows that dehydration causes a decrease in distance between Na^+ and VO^{2+} ions. Furthermore, the relatively narrow ENDOR signal signifies a well-defined geometry. The observation that dehydration leads to the loss of proton ENDOR and appearance of Na hyperfine can be explained by assuming that the vanadyl ion moves along the fourfold axis toward the face of the sodalite cage. Binding of the VO^{2+} to this face could bring it in close proximity to sodium ions in the cage.[15]

Evidently, Al ENDOR could give more definitive information on cation position. Unfortunately, attempts to locate peaks that can be assigned definitely to Al have been unsuccessful so far. Work in progress focuses on resolving the problems associate with their measurement.

Conclusion

The results presented here show that ENDOR can be a valuable source of information in studies of transition metal ions bound to porous surfaces. While this investigation deals with a zeolite system, it is evident that the method should prove equally useful in studies of binding by silica, metal oxides, ion exchange resins, and clays. With the aid of this technique an insight can be obtained into the solvation structure of metal ions adsorbed on surfaces. Furthermore, measurements of hyperfine interactions of "ligand" nuclei can provide structural data on binding site location. The effect of co-adsorbed molecules on binding site location and cation solvation can be investigated as well. As is illustrated here, erroneous conclusions can be drawn if a structural model is based on EPR data alone. Complementary data provided by ENDOR make it possible to verify the validity of postulated models. Moreover, where spectra can be matched to those of model compounds of known structure, direct and detailed structural information is obtained. By comparison, EPR parameters are much less sensitive to changes in structure. Hence, a close match between two EPR spectra does not necessarily imply identical structures.

In a series of publications Kevan and co-workers[6,19–21] have shown that the electron spin echo (ESE) technique provides an alternative method for measuring small hyperfine interactions. Compared with ENDOR, this technique has the advantage of providing information on the number of nuclear spins responsible

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(15) Breck, D. W. In "Zeolite Molecular Sieves"; Wiley: New York, 1974; Chapter 2.

(16) Iannuzzi, M. M.; Rieger, P. H. *Inorg. Chem.* **1975**, *14*, 2895.

(17) Unpublished results from this laboratory.

(18) Cohen, M. H.; Reif, F. In "Solid State Physics"; Seitz, F., Turnbull, D., Eds.; Academic Press: New York, 1957; Vol. 5.

(19) Ichikawa, T.; Kevan, L. *J. Chem. Soc. Faraday Trans. 1* **1981**, *77*, 2567.

(20) Ichikawa, T.; Kevan, L. *J. Am. Chem. Soc.* **1981**, *103*, 5355.

(21) Suryanarayana, D.; Narayana, P. A.; Kevan, L. *J. Phys. Chem.* **1982**, *86*, 4579.

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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Registry No. VO^{2+}, 20644-97-7.

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

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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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[§] University of Wisconsin.

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

[⊥] Oak Ridge National Laboratory.

(1) D. Mehaffy, P. R. Keller, J. W. Taylor, T. A. Carlson, M. O. Krause, F. A. Grimm, and J. D. Allen, *J. Electron Spectrosc.*, **26**, 213 (1982).

(2) P. R. Keller, D. Mehaffy, J. W. Taylor, F. A. Grimm, and T. A. Carlson, *J. Electron Spectrosc.*, **27**, 223 (1982).

(3) P. R. Keller et al., unpublished results.

(4) D. Mehaffy, P. R. Keller, J. W. Taylor, T. A. Carlson, and F. A. Grimm, unpublished results.

(5) For a general overview on pyridine, see W. von Niessen, G. H. F. Diercksen, and L. S. Cederbaum, *Chem. Phys.*, **10**, 345 (1975), and references therein.

(6) For a general overview on azabenzenes, see W. von Niessen, W. P. Kraemer, and G. H. F. Diercksen, *Chem. Phys.*, **41**, 113 (1979), and references therein.

0002-7863/83/1505-4235$01.50/0