PHOTOELECTRON SPECTROSCOPY IN CHEMISTRY

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Contents

I. Introduction

Early in the past decade, two research groups[1-5] independently discovered a new spectroscopy based on measurement of energies of photoelectrons emitted from molecules in the presence of monochromatic uv radiation. This new spectroscopic method, which was appropriately named photoelectron spectroscopy by Al-Joboury and Turner,[2] has been investigated extensively in recent years and is potentially of as great value to the chemist as are the well-established nmr, ir, and mass spectrometry techniques.

Photoelectron spectroscopy (PS) provides not only adiabatic and vertical ionization potentials[6] of molecules but also uv spectra of the ions. As an ionization potential measurement technique, PS has two attributes that are not generally possessed by other well-established methods such as electron impact, photoionization, and uv spectroscopy. First, whereas the older conventional methods usually provide only first ionization potentials (I_1), which correspond to ionization of the highest occupied energy level of the molecule, PS is capable of yielding all those molecular ionization potentials (I_n, $n = 1, 2, \ldots$) corresponding to removal of single electrons from molecular orbitals which are more energetic than $-h\nu$, the excitation energy. Thus, PS is a valuable tool with which the quantum chemist can test molecular energy level calculations. Second, because PS is not a threshold technique, it is not generally complicated by autoionization processes (ionization from a bound excited molecular state) as are the three threshold methods mentioned above. In high-resolution PS, vibrational structure in the ionization bands can often be resolved; the same structure would be observed in direct uv spectra of the various ions. This structure provides the physical chemist with Franck–Condon factors (related to ionization probability) and information about the geometries of the ions and about the bonding characters of the orbitals from which the electrons are removed. Possibly of greatest general interest is the potential of the method as an analytical tool for gases. A parallel technique, electron spectroscopy for chemical analysis (ESCA),[7,8] in which the energies of K-shell electrons ejected in the presence of X-rays are measured, is currently being used effectively by chemists as a complement to mass spectrometry and nmr for liquid and solid samples.

The basic principles of PS, the instrumentation, and data reduction and interpretation procedures have been discussed in several classic papers[2,3,9-11] and have been reviewed

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(3) M. I. Al-Joboury and D. W. Turner, *ibid.*, 4434 (1964).

(4) F. I. Vilesov, B. L. Kurbatov, and A. N. Terenin, *Dokl. Akad. Nauk SSSR*, 138, 1329 (1961); *Sov. Phys. Dokl.*, 6, 490 (1961).

(5) B. L. Kurbatov, F. I. Vilesov, and A. N. Terenin, *Dokl. Akad. Nauk SSSR*, 140, 797 (1961); *Sov. Phys. Dokl.*, 6, 883 (1962).

(6) An adiabatic ionization potential is the difference in energy between the ground vibrational levels of the molecule and the resulting ion, while a vertical ionization potential is the difference in energy between the ground vibrational level of the molecule and some vibrational level of the ion, the nature of which is dictated by the Franck–Condon principle.

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thoroughly.[12-20] Thus, in this review, these concepts will be mentioned only briefly to orient those readers who are not familiar with PS. The main goal of this review is rather to outline the experimental work done in the field through early 1970 on polyatomic molecules, with emphasis on the interpretation of the photoelectron spectra using quantum molecular orbital (MO) procedures. The high-resolution spectra of diatomic, triatomic, and small polyatomic molecules have been discussed extensively in the previous review articles[12-20] and thus will not be treated in this review. A partial description of the theoretical procedures currently being used by the photoelectron spectroscopist and a section on the current areas of research in PS and possible future applications will also be included. Extensive tabulation of data will be avoided because complete tables of ionization potentials derived from photoelectron spectra will soon be available.[21]

II. Principles of Photoelectron Spectroscopy

The photoelectron spectrometer is an inherently simple device consisting of two basic components: a vacuum uv excitation source and an electron-energy analyzer. The excitation source is commonly one or more of the intense resonance lines produced by a dc or a microwave discharge through one of the rare gases. Radiation from the excitation source is normally passed through two aligned sections of narrow-bore capillary into an ionization chamber that is directly linked to some type of electron-energy analyzer. A chamber separating the two sections of capillary is evacuated to minimize mixing of the inert gas from the lamp and the sample gas from the ionization chamber. Alternatively, a continuous excitation source can be used in conjunction with a vacuum monochromator to produce a monochromatic beam of photons. In the presence of the high-energy photons ($h\nu$) collimated into the ionization chamber, electrons are removed from all molecular orbitals of the sample molecules that have appreciable ionization cross sections and that are more energetic than $-h\nu$. These electrons possess kinetic energies T_n^- (n referring to the MO; $n = 1$ designating the highest occupied MO, $n = 2$ the first inner orbital, etc.) given by the Einstein relation

$$T_n^- = h\nu - (I_n + T_n^+ + E_{vib}^+ + E_{rot}^+) \quad (1)$$

In eq 1, I_n is the adiabatic ionization potential for MO n, T_n^+ is the translational energy imparted to the ion, and E_{vib}^+ and E_{rot}^+ are the vibrational and rotational energies of the ion. The T_n^+ term is negligible because, upon ionization, conservation of momentum requires that the translational energy be almost entirely imparted to the electron. The E_{rot}^+ term also may be neglected, because it is also quite small, being at most a few thousandths of an electron volt. Rotational fine

structure has not been observed in a PS ionization band, although rotational broadening is observed in the vibrational structure of very highly resolved bands for some small molecules. High-resolution PS readily resolves vibrational structure in the ionization bands for diatomic molecules and many small polyatomic molecules; i.e., the E_{vib}^+ term can be appreciable (on the order of 0.05–0.5 eV). For high-resolution PS, eq 1 then becomes

$$T_n^- = h\nu - I_n - E_{vib}^+ \quad (2)$$

In low-resolution PS, vibrational structure is usually not resolved, such that only the adiabatic ionization potentials can be measured (from the onset of the bands). Thus the measurement of the various T_n^- for a molecule provides the I_n for the various molecular orbitals and, for high-resolution, the vibrational spacing within the various ionization bands as well.

Figure 1 shows a hypothetical photoelectron spectrum in which vibrational structure is resolved. The first band (I_1) contains several peaks corresponding to transitions from the molecule in its ground vibrational state to the ion in the various vibrational levels of its electronic state. The first peak represents the $0 \leftarrow 0$ transition, or the adiabatic I_n, while the most intense peak relates to the Franck–Condon transition, or the vertical I_n. The integrated area of each peak is related to the probability of producing the ion in each vibrational state (Franck–Condon factor). The width of the band is an indication of the geometry reorganization upon passing from the molecule to the ion; the hypothetical I_1 band represents a considerable alteration of geometry. The vibrational frequency ν_{ion} excited upon ionization can be measured from the peak spacing and is an indication of the bonding character of the MO from which the electron was removed. If a bonding electron is removed, ν_{ion} should be less than the corresponding vibrational frequency for the molecule (ν_{mol}); removal of an antibonding electron should give $\nu_{ion} > \nu_{mol}$. The second band (I_2) in Figure 1 consists of only one vibrational peak. This implies that there is little geometric reorganization upon ionization, such that the adiabatic transition is the Franck–Condon one. Such a band would be expected for removal of a nonbonding ("lone-pair") electron. Figure 2 shows a hypothetical low-resolution photoelectron spectrum from which only the peak onset can be accurately measured. For this type of spectrum, I_1 is a true adiabatic ionization potential, but higher I_n, corresponding to removal of inner electrons, may be somewhat larger than the adiabatic values due to the overlapping nature of the bands. Nevertheless, higher I_n values obtained under low resolution are quite useful in testing quantum MO calculations and as a guide for future high-resolution studies. In any case, for large polyatomic molecules (e.g., n-hexane), many of the bands resemble those in Figure 2 even under the highest resolution because there are many closely spaced molecular energy levels and symmetry is low.

The most common excitation source in PS used to date is the 584-Å (21.22 eV) resonance line of helium;[2,10] this copious source is capable of inducing ionization of at least one energy level in all molecules except helium and neon, and many I_n values are obtained for polyatomic molecules such as benzene. The other inert gases have also been used recently,[22] but the doublet nature of the exciting lines and their low energies (e.g., 16.65, 16.83 eV for Ne) render them less useful than the

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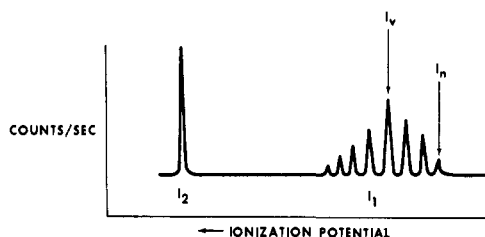(22) See, *e.g.*, J. E. Collin and P. Natalis, *Int. J. Mass Spectrom. Ion Phys.*, 2, 231 (1969).

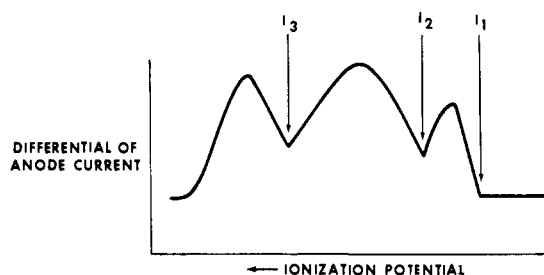**Figure 1.** Hypothetical high-resolution photoelectron spectrum.
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Figure 2. Hypothetical low-resolution photoelectron spectrum.

He I line. Very recently, the 537-Å (23.09 eV) line of helium generated in a microwave discharge in 2% of the intensity of the 584-Å line was successfully used to obtain the PS of neon.[23] Also, the He II line at 304 Å (40.82 eV) is currently being employed to study molecular orbitals lying below −21.22 eV, which are not accessible to the He I line.[24,25] The fabrication[26] and purification[27] of the various excitation lamps have been discussed recently. The spectra discussed in this review should be assumed to have been excited by the 21.22-eV line of helium, unless stated otherwise.

Many types of electron-energy analyzers have been described, including several variations of the retarding potential analyzer,[2,4,10,24,28−33] the magnetic deflection analyzer,[9] the parallel-plate analyzer,[34] the 127° cylindrical electrostatic-field analyzer,[11] the 180° spherical electrostatic analyzer,[23,35] and the steradiancy analyzer.[36] Retarding potential analyzers generally provide low-resolution spectra resembling the hypothetical spectrum in Figure 2; the other analyzers mentioned above provide high-resolution spectra which are ideally represented in Figure 1. The "resolving power" commonly claimed for high-resolution analyzers ranges between 0.01 and 0.05 eV; low-resolution analyzers, at worst, are capable of distinguishing between two ionization processes separated in

energy by 0.5 eV. The general resolving power criterion in PS is the width at half-maximum of the rare gas $^2P_{3/2}$ and $^2P_{1/2}$ peaks. Of the high-resolution analyzers, the one designed by Turner[11] has received the widest acclaim, and a similar instrument is being marketed by Perkin-Elmer. For complete details about the various analyzers, the reader is referred to the original papers; one of the review articles[13] is also especially helpful.

III. Theoretical Methods

Photoelectron spectroscopists have employed several types of MO calculations in correlating their measured ionization potentials with theoretical predictions, both as an aid to making spectroscopic assignments and as a test of the theoretical procedures. This section will deal with the important differences between the various methods and their relative merits for the photoelectron spectroscopist, i.e., their accuracy in predicting ionization energies. The mathematical formulation of the methods and the general principles of MO theory will not be discussed; for additional information the reader is referred to the original papers and two excellent reference books.[37,38]

A. MO METHODS FOR π SYSTEMS

The historical Hückel (HMO) method[39] has been used for predicting π-orbital energies for a limited number of conjugated hydrocarbons.[40−42] In this method, the Hückel parameters α_x and β_{xy} must be evaluated empirically for each type of atom x in the π system. Since these parameters vary markedly as new atoms are introduced, the method is of limited use. The perturbational MO method (PMO)[37] has also been employed recently in interpreting photoelectron spectra of π systems.[43,44] This method is quite successful in comparing closely related molecules. When used in conjunction with π HMO theory, the PMO method involves parameterizing small changes in α_x or β_{xy}.

A major shortcoming of the HMO method is its failure to take into account electronic interaction. Several variations of the semiempirical Π SCF (self-consistent field) method based on the original work of Pople[45] have been used with great success in predicting π-orbital energies[46−54] for conjugated mole-

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cules. In the Π SCF–MO method, the σ electrons of the molecule are treated as localized, but the π electrons are allowed to interact.

All of the MO methods mentioned thus far depend on Koopmans' theorem[55] for predicting ionization potentials. Under this widely employed approximation, the molecular ionization potentials are equated to the negatives of the MO energies. Inherent in the use of this approximation are the assumptions that, upon ionization, there is no change in molecular geometry and the wave functions describing the remaining electrons are not altered. These assumptions could not be made for "exact" calculations. However, the current theoretical procedures for large molecules are of necessity more or less semiempirical in nature. Thus, through proper choice of a minimum number of parameters, decent agreement of orbital energies and ionization potentials can be obtained, as will be shown in this review. Since Koopmans' approximation does not allow for geometrical reorganization upon ionization, orbital energies should better be correlated to vertical ionization potentials than to adiabatic ones. Vertical I_n's are commonly 0 to 0.3 eV larger than the corresponding adiabatic I_n's, which is within the error limits of any current theoretical method; therefore, orbital energies can often be usefully correlated with adiabatic ionization potentials as well. Richards has pointed out some of the pitfalls of indiscriminate use of Koopmans' approximation.[56]

Because of the limitations of Koopmans' theorem, direct SCF calculations on the molecule and the ion are preferable, the ionization potential being the difference in total energy between the molecule and ion. Such calculations normally require an "open-shell" SCF–MO treatment[57] for the ion radical; open-shell iterative calculations often diverge, or converge very slowly;[58] thus they have not received wide attention. Dewar, Hashmall, and Venier[59] have developed an extension of the Π SCF–MO method ("half-electron method") in which ion radicals can be treated with the usual closed-shell procedure. By varying the geometries of both molecule and ion to achieve an energy minimum, adiabatic ionization potentials can be calculated directly by this method.[59] Alternatively, the geometry of the ion can be set equal to that corresponding to the energy minimum of the molecule, in which case the calculated ionization potential is vertical. Unfortunately, this new method often fails for I_n ($n > 1$) because of convergence problems, but it always works well for the first ionization potential.

B. MO METHODS FOR ALL VALENCE ELECTRONS

The problem with all of the methods discussed in the previous section is that only π ionization potentials can be obtained. One of the most interesting aspects of photoelectron spectroscopy is the correlation of the experimental I_n values with theoretically predicted molecular energy levels. To do this properly, one must use a theoretical approach which treats all of the valence electrons as being delocalized, i.e., a method which predicts both π and σ MO energies or ionization poten-

tials. In any case, the large majority of molecules do not contain conjugated π systems, such that the Π SCF–MO methods have very limited application. Three general types of MO calculations which consider both π and σ electrons are currently being used by photoelectron spectroscopists. These are the "extended Hückel" method, semiempirical SCF–MO methods, and ab initio approaches.

1. Extended Hückel Method

The extended Hückel method of Hoffmann[60] is based on the HMO method, but overlap is included; i.e., $S_{ij} \neq \delta_{ij}$. The diagonal matrix elements H_{ii} are set equal to valence-state ionization potentials, and the off-diagonal elements H_{ij} are estimated by the Mulliken approximation

$$H_{ij} = 0.5K(H_{ii} + H_{jj})S_{ij} \qquad (3)$$

where K is an empirical constant. Hydrogen 1s and carbon 2s,-2p Slater orbitals are employed, the carbon 1s electrons being treated as part of the core, and the $4n + m$ Hückel secular determinant (for a molecule C_nH_m) is solved in the usual manner. Ionization potentials for hydrocarbons obtained by this method and Koopmans' theorem are commonly 2 eV too large.

2. Semiempirical SCF–MO Methods

Several semiempirical SCF–MO methods have been used to estimate orbital energies and ionization potentials for a wide variety of molecules. Thus far, the most widely employed of these has been the CNDO (complete neglect of differential overlap) SCF–MO method of Pople, Santry, and Segal.[61–64] This method is an extension of the original Pople method[45] to include all of the valence electrons; as in the extended Hückel method, the carbon 1s electrons are included in the carbon core. The original CNDO treatment is analogous to the Pople Π SCF–MO method in that all integrals involving differential overlap are neglected; however, the electron–electron repulsion integrals in CNDO are evaluated theoretically rather than parametrically, as in the Π method. An improved version of CNDO (CNDO/2) employs empirical atomic matrix elements and neglects certain penetration terms,[63] but the two-center electron repulsion integrals (ii,jj) are still evaluated theoretically. Ionization potentials estimated by CNDO/2 and Koopmans' theorem are usually 4 eV too high.[65,66] In part, this is a result of the failure of all SCF–MO methods based on Koopmans' theorem to account for the reorganization in geometry that occurs upon ionization and the difference in correlation energy between the molecule and the ion. Sichel and Whitehead have shown that CNDO/2 in conjunction with Koopmans' theorem gives ionization potentials in better agreement with experiment than does the extended Hückel method if the electron repulsion integrals and the bonding parameters are evaluated empirically.[67] The CNDO/2 method has been extended[63] to open-shell systems, such as ion radicals.

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A refinement of the CNDO method is the INDO (intermediate neglect of differential overlap) SCF–MO method developed by Pople, Beveridge, and Dobosh.[68] The primary difference between INDO and CNDO is that all one-center exchange integrals (ij,ij) are retained in INDO. The retention of the one-center exchange integrals allows distinction of multiplet states. A major limitation of the CNDO method is its failure to predict the energy differences between states arising from the same configuration; viz., the splitting of the $^1\Delta_g$ and $^3\Sigma_g^-$ states arising from the $(\sigma_g)^2 (\sigma_u)^2 (\pi_u)^2$ configuration of linear methylene.[68] Ionization potentials predicted by INDO and Koopmans' theorem are slightly lower than those predicted by CNDO/2, but are still 4 eV too large.[69,70] The CNDO/2 and INDO techniques have been shown to be at variance with each other in predicting the energy ordering of two of the inner orbitals of methyl cyanide,[71] although this does not appear to be the general case for the few molecules[69–71] treated by both methods. The INDO method can be extended to open-shell systems;[68] indeed, this was the primary reason for its development.

Dewar, Baird, and Sustmann[72,73] have developed a semiempirical SCF–MO approach similar to the INDO method,[68] but which gives a better account of ground-state molecular properties. This modified INDO method (MINDO) differs from the INDO method of Pople, Beveridge, and Dobosh[68] in three important aspects.[72] First, the Slater–Condon parameters used to describe the one-center electron-interaction integrals are all evaluated empirically from atomic spectral data. Second, the two-center integrals are treated empirically rather than by direct quadrature as in INDO. A third difference between the two methods involves the empirical evaluation of the two-center resonance integral (H_{ij}^{core}). In the INDO method, these integrals are empirically evaluated to reproduce results obtained by ab initio methods, whereas in MINDO they are chosen to give correct ground-state energies for a small number of reference molecules. In the original version of MINDO (henceforth MINDO/1),[72,73] the core–core repulsion and the electron–electron repulsion for pairs of neutral atoms are set equal at all distances. This leads to bond lengths that are too short. Consequently, standard bond lengths and angles[72,73] must be used, and the SCF energy minimum does not correspond to the experimental molecular geometry. A more recent version of MINDO (MINDO/2)[74,75] employs a more realistic nuclear repulsion term.[76] MINDO/2 also differs slightly from MINDO/1 in the parameterization of the resonance integrals, but, in all other aspects, the two versions are the same. Unlike MINDO/1, experimental geometries can be used in MINDO/2, because the SCF energy minimum does correspond to the experimental molecular geometry. Both versions of MINDO predict orbital energies

with high accuracy (usually within a few tenths of an electron volt), which is an unexpected windfall since the methods are parameterized to predict total molecular energies (heats of formation), not orbital energies. Both variations of MINDO can be used for open-shell systems[72,74] when the "half-electron" approach[59] is employed.

3. Ab Initio Methods

Ab initio SCF–MO methods[77–82] have been used recently with fair success[25,83–85] in predicting orbital energies and ionization potentials of small polyatomic molecules. These methods have been described in two recent review articles.[86,87] Ab initio calculations for polyatomic molecules involve all of the electrons and normally employ contracted Gaussian basis sets which are treated in the SCF formalism. Approximations such as the neglect of differential overlap are not invoked; all integrals are evaluated theoretically. Thus, of the methods mentioned in this review, these computations are the most closely related to so-called "exact" calculations. However, because the basis sets must be contracted for molecules of appreciable size (due to the extensive nature of the calculations for complete basis sets), the computations only approximate true Hartree–Fock calculations. It should be noted that configuration interaction is commonly employed in conjunction with ab initio approaches in predicting electronic transition energies.[77,78,87] Clementi has studied[79–81] several polyatomic molecules as large as pyridine with an ab initio approach, but accurate calculations for larger molecules of chemical interest (e.g., anthracene) are not feasible at this time.

The ionization potentials obtained from orbital energies predicted by ab initio methods for the few molecules studied thus far[83–85] are too large by 8% (ca. 1.5 eV); the inadequacies of Koopmans' theorem are usually blamed for this discrepancy. Ionization potentials obtained from separate SCF treatments of molecules and ions are too small because of correlation-energy differences in the two states. An average of the ionization potentials obtained from the two approaches often agrees well with experimental results.[83]

Newton, Boer, and Lipscomb[88,89] have developed a "nonempirical" SCF–MO approach that represents a compromise between ab initio and the usual semiempirical procedures in that the parameters are not chosen empirically. All electrons, including carbon 1s, are treated, and the zero differential overlap approximation is not invoked. The ionization potentials[89] predicted by this method are often too low; the error increases with molecular complexity.

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4. General

Of the theoretical methods discussed in section B, the semi-empirical MINDO SCF–MO method[72–75] has been employed in predicting ionization potentials for the largest number and variety of molecules. In general, it is also the most accurate method, at least in terms of providing absolute values that agree with experiment. MINDO requires much less computation time than do the *ab initio* methods; with a large computer (*e.g.*, CDC6600), polyatomic molecules such as fluoranthene can be treated in less than 1 min. Such molecules cannot be handled by *ab initio* methods at the present time. This is not to say that *ab initio* methods and other semiempirical methods (*e.g.*, CNDO/2 and INDO) should not be used by photoelectron spectroscopists in correlating their data. Indeed, these other approaches often correctly order molecular energy levels and even occasionally predict correct relative magnitudes of ionization potentials within groups of molecules. However, in general, MINDO seems to do as well as the other methods in these respects, and, since it also gives good absolute values for a wide variety of organic molecules, it appears to be the best current theoretical approach available to chemists initiating research in photoelectron spectroscopy.

IV. Photoelectron Spectra of Polyatomic Molecules

In this section, the photoelectron spectra of polyatomic molecules reported through spring 1970 will be reviewed. Theoretical calculations used in the interpretation of the spectra will also be discussed. Because of the vast number of theoretical papers on ionization potentials that have appeared, this review will be confined mainly to those calculations reported in the experimental works.

A. ALKANES, SUBSTITUTED ALKANES, AND RELATED COMPOUNDS

The photoelectron spectra of the open-chain unsubstituted alkanes are characterized by broad, diffuse bands from which little information, other than a few of the I_n values, can be obtained. Watanabe, Nakayama, and Mottl[90] have encountered similar difficulties with the paraffins in their photoionization threshold experiments, yields near the low-frequency threshold being very low and the yield curves not showing marked breaks. The I_n's from the low-resolution photoelectron spectra (LRPS) of 11 alkanes have been reported,[3,91–93] but little high-resolution work (HRPS) has been done, probably because the diffuse bands for higher members of the alkane series contain little resolved vibrational structure.

Of the alkanes, only methane and ethane have been investigated at high resolution.[94] The "adiabatic" first ionization potential of methane, corresponding to loss of an electron from the triply degenerate $1t_2$ MO, has been measured from the LRPS[91–93] to be 12.98–12.99 eV in agreement with data obtained from other methods (*e.g.*, ref 90). However, the HRPS[94]

and recent high-resolution photoionization work[95,96] suggest that the adiabatic I_1 should be closer to 12.70 eV. The MINDO/1 calculations of Dewar and Worley[93] predict an I_1 of 12.98 eV; since MINDO/1 generally predicts ionization potentials to be a few tenths of an electron volt too large, it is suspected that the LRPS value is too high. A possible explanation for the apparent discrepancy is that the adiabatic transition is of very low probability because of extensive geometrical reorganization upon ionization, such that it is not distinguished in the LRPS. The HRPS[94] of CH_4 and CD_4 both exhibit a double maximum in the I_1 band with a splitting of *ca.* 0.7 eV. This is probably indicative of Jahn–Teller distortion of the triply degenerate ion; *i.e.*, transitions occur from the ground state of the molecule (T_d symmetry) to two different ionic states of lower symmetry (C_{3v} and C_{2v}).[94] It should be pointed out that methane is one of few molecules for which the first ionization potentials obtained from LRPS and HRPS are not in close agreement. One might anticipate other such discrepancies when geometry reorganization is very large.

The second ionization potential of methane, corresponding to ionization from the $2a_1$ orbital, has been of recent interest.[24,97,98] Molecular orbital calculations[93,99,100] predict that the $2a_1$ orbital will lie below −25 eV and hence will not be accessible to PS when the 21.22-eV resonance line of helium is the excitation source. This indeed appears to be the case, for no evidence of a second ionization band has been found using He I excitation.[91–94] Moreover, Price and Wilkinson[24] have used 40.82-eV excitation (He II) to observe a second ionization band that occurs between 22 and 24 eV at about one-third the intensity of the first band. This second band almost certainly corresponds to the $2a_1$ orbital, which would be expected to contain one-third the electron population of the $1t_2$ level. This second band has also been observed at 23.1 eV in LRPS excited by X-rays;[97,98] however, the intensity ratio of the two bands corresponding to $1t_2$ and $2a_1$ was inverted. Apparently, the cross section for ionization induced by X-rays of 2s electrons is much larger than that for 2p electrons.[98] For He II uv radiation, the intensity seems to be governed more by the degeneracy of the orbital undergoing ionization.

The adiabatic first ionization potential of ethane obtained from the HRPS[94] is 11.56 eV, while LRPS values[3,93] of 11.49 and 11.51 eV have been measured. Thus, even within a closely related series of molecules, the LRPS does not necessarily give ionization potentials higher than those derived from HRPS (*cf.* methane). Vibrational structure was resolved in the first and fourth bands of the HRPS. The spacing between the vibrational peaks in the I_1 band, which corresponds to ionization of the doubly degenerate $1e_g$ orbital, was 0.145 eV or 1170 cm⁻¹, which was assigned to the symmetric C–H deformation. The spacing in the I_4 band at 20.13 eV was 0.144 eV or 1160 cm⁻¹; this was assigned to the C–C stretch on grounds that the similar vibration in the molecule occurs at lower frequency and that deuteration (to C_2D_6) shifts the frequency to 1070 cm⁻¹. Both of these observations would be expected for ioniza-

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tion of the $2a_{2u}$ orbital which is C–C antibonding.[94] As for methane, a double maximum was observed in the I_1 band. This double maximum was again attributed to Jahn–Teller distortion of the ion. The second and third ionization bands at 13.4 and 14.7 eV were assigned to $3a_{1g}$ and $1e_u$ ionization, respectively.

Ethane has also been studied at high resolution in conjunction with methylsilane and disilane.[24] The adiabatic I_1 obtained for ethane was 11.65 eV, which differs considerably from that measured in the other HRPS investigation. This indicates that high-resolution studies are not necessarily better than low-resolution ones from the standpoint of accuracy and reproducibility of adiabatic first ionization potentials; the superiority of high-resolution analyzers exists mainly in their ability to resolve vibrational structure and inner ionization potentials. Replacement of carbon atoms in ethane by silicon atoms to form methylsilane and disilane would be expected to lower the ionization potential of the $3a_{1g}$ orbital by more than the $1e_g$ or $1e_u$ orbital, because the $3a_{1g}$ orbital has greater contribution from the carbon atoms (relative to hydrogen) than do the $1e_g$ and $1e_u$ orbitals.[24] While the ionization potentials corresponding to the $1e_g$ and $3a_{1g}$ orbitals are not clearly separated in the spectrum of ethane,[24,94] they are in disilane.[24] Thus, a comparison of the HRPS of ethane and disilane indicates an energy-level ordering of $1e_g > 3a_{1g} > 1e_u > 2a_{2u}$ in agreement with the other high-resolution study.[94] This is also the ordering predicted by *ab initio* calculations,[101] although the theoretical I_1 is too high by 1.5 eV. The semiempirical MINDO/1 method predicts 11.38 eV ($3a_{1g}$), 11.92 eV ($1e_g$), 14.15 eV ($1e_u$), and 20.96 eV ($2a_{2u}$), thus reversing the ordering of the two closely spaced highest occupied orbitals.[93]

Both of the LRPS studies[8,93] of straight-chain and branched alkanes have shown that branching does not necessarily cause a decrease in I_1; *i.e.*, the old classical argument tht branching stabilizes the ion and hence leads to a lower I_1 is now in doubt. However, it is possible that the cross section for the adiabatic transition for the branched alkanes is sufficiently low to have escaped detection, such that the observed values of I_1 for these compounds were too high. The MINDO/1 method[93] supports the PS results in this respect, but overestimates the magnitudes of the changes.

Dewar, Shanshal, and Worley[102] have employed LRPS in conjunction with the MINDO/1 SCF–MO method to study a series of nitroalkanes, alkyl nitrites, and methyl nitrate. The breaks in the LRPS (especially those for I_1) of these compounds were markedly more pronounced than were those for the unsubstituted alkanes.[103] Also, the first ionization potentials for all these molecules are considerably lower than are those for the corresponding alkanes; *e.g.*, $I_1(CH_4) = 12.98$ eV, $I_1(CH_3NO_2) = 11.23$ eV, and $I_1(CH_3NO_3) = 11.53$ eV. These two observations suggest that the highest occupied orbital for each of these molecules containing N and O is largely confined to the heteroatoms. The MINDO/1 method indeed predicts this to be the case and correctly predicts the ordering and, in some cases, the relative magnitudes of the I_1 values for this series of compounds.

The halomethanes have been investigated recently by several research groups.[36,69,93,104–106] Two studies of carbon tetrafluoride[69,104] at "intermediate" resolution have revealed three structureless bands between 15.9 and 21.22 eV. These bands were assigned to orbitals in the sequence $3t_2$ (C–F bonding) > $1t_1$ (nonbonding) > $1e$ (nonbonding), based on CNDO/2 and INDO SCF–MO calculations.[65,69] The calculated orbital energies, especially those predicted by INDO, were in good agreement with the observed ionization potentials after a 4-eV correction to all the orbital energies was made. For SiF$_4$ and GeF$_4$, four bands were observed[104] below 21.22 eV and were assigned in the order $4t_2 > 1t_1 > 1e > 3t_2$. The $3t_2$ orbital was placed above $2a_1$ on grounds that the spectra of the analogous chlorides contained a fifth band at higher ionization potential which was one-third the intensity of the fourth band. Evidence of d-orbital participation in SiF$_4$ and GeF$_4$ based on the $1t_1$–$1e$ separation was also presented.[104] A high-resolution study of CF$_4$ and SiF$_4$ has also been made.[106] Based on *ab initio* calculations for CF$_4$ and the "center of energy" of the $1t_1$–$1e$ splitting, the authors suggested the revised assignment $1t_1 > 3t_2 > 1e$. The highest ionization band for CF$_4$ ($1e$) and SiF$_4$ (?) contained resolved vibrational structure; the similarity of the structure for the two compounds prompted the assignment $1t_1 > 4t_2 > 3t_2 > 1e$ for SiF$_4$, in disagreement with the previous study.[104] No spin–orbit splitting or Jahn–Teller splitting of the type[94] reported for CH$_4$ was observed in the HRPS[106] of CF$_4$ or SiF$_4$.

The HRPS[105] of CH$_3$I, CH$_3$Br, and CH$_3$Cl show clearly vibrational and spin–orbit fine structure in the first ionization band. This first band (I_1) corresponds to removal of a halogen lone-pair electron to produce a $\ldots 2e^3$ configuration (^2E ionic state). The I_1 band of CH$_3$I contains two strong peaks of equal intensity corresponding to the transitions $^2E_{3/2}$ ($v = 0$) $\leftarrow$ $^1A_1$ ($v = 0$) and $^2E_{1/2}$ ($v = 0$) $\leftarrow$ $^1A_1$ ($v = 0$) with the $^2E_{3/2}$ state at lowest energy; small vibrational peaks corresponding to $^2E_{3/2}$ ($v = 1$) $\leftarrow$ $^1A_1$ ($v = 0$) and $^2E_{1/2}$ ($v = 1$) $\leftarrow$ $^1A_1$ ($v = 0$) in ν_1 of the ion and the analogous $\Delta v = 1$ transitions in ν_2 of the ion (very weak) were also observed. For CH$_3$Br, the magnitude of spin–orbit splitting is decreased, and the $^2E_{3/2}$ and $^2E_{1/2}$ states begin to overlap, causing an extensive redistribution of intensity in the fine structure. Transitions to the $^2E_{3/2}$ ($v = 1$) state of the ion borrow intensity from that to the $^2E_{1/2}$ ($v = 0$) state; in this manner new vibration peaks corresponding to $\Delta v = 1$ transitions in ν_4, ν_5, and ν_6 of the $^2E_{3/2}$ ion appear with a reduction in intensity of the $^2E_{1/2}$ ($v = 0$) $\leftarrow$ $^1A_1$ ($v = 0$) peak. For CH$_3$Cl, the spin–orbit splitting is decreased more, and resolution becomes poor, such that assignments are difficult. Higher ionization potentials are also reported for the three methyl halides, but vibrational structure was not resolved in any of the bands. A study[36] of the zero kinetic energy electrons of CH$_3$I also has revealed the $^2E_{3/2}$–$^2E_{1/2}$ splitting. The magnitude of the splitting in the latter study[36] (0.617 ± 0.010 eV) is in excellent agreement with that[105] (0.626 eV) in the former.

The LRPS of the four chloromethanes[93] indicate that the highest occupied MO for each molecule is almost entirely confined to the heteroatom(s) and that inductive effects are small; *i.e.*, there is only an increase of 0.21 eV in I_1 upon passing from CH$_3$Cl (11.26 eV) to CCl$_4$ (11.47 eV). The LRPS value[93] of I_1

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for perfluoropropane (13.38 eV) is more than 2 eV higher than that[93] of its hydrocarbon analog, propane (11.06 eV). The lone-pair ionization potential of fluorobenzene has been reported[107] to be 14.1 eV. Thus, the highest occupied orbital of perfluoropropane is either mainly confined to fluorine (lone-pair orbital) or is delocalized extensively throughout the molecule. If the latter is true, the fluorines must introduce a large perturbation to the highest σ MO that is confined essentially to the carbon skeleton of propane (MINDO/1 prediction[108]). In this respect, an investigation of the photoelectron spectra for a series of fluoroalkanes having varying numbers of fluorine substituents should prove illuminating.

B. ALKENES, DIENES, AND RELATED COMPOUNDS

The photoelectron spectra for molecules containing π electrons are generally better resolved than are those for molecules containing only σ electrons. Deciding which bands in the spectra correspond to the two types of electrons is one of the more interesting and difficult problems in photoelectron spectroscopy.

Of the alkenes, only ethylene[23,41,85,94] and several haloethylenes[108] have been studied extensively at high resolution. The results obtained and the conclusions drawn in the four independent investigations of ethylene are basically the same. One of the studies[23] employed C_2D_6 spectra and another[85] He II spectra and diborane results in making assignments and analyzing vibrational structure. The general consensus seems to be that the orbital ordering is b_{3u} (π) > b_{3g} > a_g > b_{2u} > b_{1u} > a_k, in agreement with semiempirical SCF-MO calculations,[67] although one of the works[94] does suggest that the above ordering of b_{3g} and a_g should be reversed. The ionization potentials measured by the four groups are in reasonable agreement, particularly I_1, which corresponds to ionization of the π MO. The I_1 reported in all of the studies was 10.51 eV, in accord with results of two low-resolution studies[8,93] (10.48 and 10.50 eV, respectively). In fact, the higher I_n's measured from the LRPS[93] are within the range of values obtained by the several HRPS studies, demonstrating once again that LRPS give accurate values of adiabatic ionization potentials when the bands are well defined. A recent X-ray determination[98] indicates that the lowest a_g orbital should lie at -24.5 ± 1 eV.

Lake and Thompson[108] have measured the HRPS of several haloethylenes. Twelve molecules of the form CWX=CYZ, where W, X, Y, and Z are H, Cl, or F, are discussed in terms of vibrational structure, assignment of the various I_n values to the π and nonbonding (nb) orbitals, and the relative importance of inductive and mesomeric effects on the I_n values.

The LRPS of several higher members of the alkene series have been described.[93] While the highest occupied MO in ethylene is completely π in nature, the MINDO/1 SCF method predicts that the corresponding orbitals in propene, 1-butene, etc., contain some σ contribution, the amount of σ increasing with molecular size. Thus it is risky tacitly to attribute I_1 for all such molecules to ionization of the "double bond." However, it is of interest that the I_1 values for the cis and trans isomers of 2-butene are exactly the same[93] (9.12 eV), but that the corresponding higher I_n's for the two compounds

differ by several tenths of an electron volt; similar observations have been reported for cis- and trans-dichloroethylene[108] and the two isomers of 1,3-dichloropropene.[18] These results imply that the highest occupied MO for each of these molecules is largely confined to the double bond. On the other hand, the high I_1 of perfluoro-2-butene[93] (11.25 eV) would seem to indicate that the π MO is not at all "pure" (see below for effect of fluorine substitution on π orbitals of butadiene).

trans-2-Butene (1) has also been studied in connection with the related compounds trans-N-ethylidenemethylamine (2) and trans-azomethane (3).[109] Vertical ionization potentials of
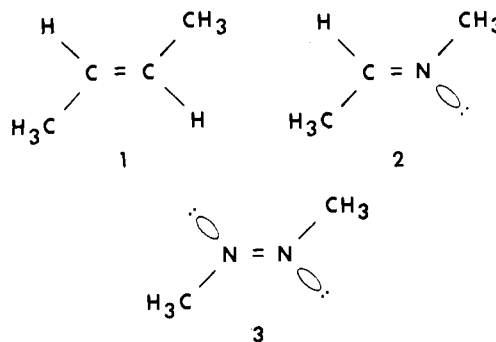
9.11 eV for 1, 10.66 eV for 2, and 11.84 eV for 3 were assigned to the orbitals that are mainly π; vibrational fine structure, which is characteristic of the C=C and N=N, was resolved in the π bands of 1 and 3, respectively. The first ionization potential (9.49 eV) of 2 and values of 8.98 and 12.3 eV for 3 were assigned to nb orbitals. The interaction between the two nb orbitals of azomethane is thus quite large (3.3 eV). Semiempirical MINDO/1 calculations agreed qualitatively with the experimental results. The calculated lone-pair splitting was 2.2 eV, in reasonable accord with experiment, and was insensitive to changes of the C—N=N angle in the range 110–130°.

Of the dienes, trans-1,3-butadiene has received the widest attention.[3,41,93,110] It is generally accepted that I_1 for butadiene (9.07 eV) must correspond to π ionization $(1b_g)$; however, there is some question about the MO assignment of the second ionization band in the photoelectron spectrum. The MINDO/1 SCF-MO method[93] predicts there to be two σ energy levels above the lowest π level $(1a_u)$, the second σ at only 0.1 eV above the π. On the other hand, ab initio calculations predict that both of the π levels lie above the highest occupied σ orbital.[78] Introduction of fluorine atoms into an unsaturated molecule causes a shift of the σ ionization potentials to higher energy (by ca. 3 eV) due to the inductive destabilization of the ions, while the π ionization potentials are almost unchanged.[20,110] Comparison of the HRPS of trans-1,3-butadiene with those of 1,1,4,4-tetrafluorobutadiene and hexafluorobutadiene indicates that the second band in the spectrum of butadiene should be assigned to σ ionization[110] in agreement with the semiempirical calculation.[93] This conclusion was based on the large shift observed for I_2 and a very small one for I_3 upon fluorine substitution. One of the two σ ionizations predicted by MINDO/1 to lie between the two π bands evidently is not resolved; it could correspond to a weak band that lies beneath the tail of the I_1 band, or both σ ionizations could comprise the I_2 band. (Vibrational structure was not resolved in this

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band.) Thus, whereas the *ab initio* orbital ordering seems to be more accurate than MINDO for ethane, the reverse is clearly true for butadiene. The vibrational structure resolved in the I_1 bands of butadiene[41,110] and 1,1,4,4-tetrafluorobutadiene[110] mainly corresponds to the C=C stretching mode.

The *ab initio* and semiempirical calculations are again at odds for *cis*-1,3-butadiene. Buenker and Whitten[78] predict 9.63 and 9.78 eV for the *ab initio* first ionization potentials of the cis and trans isomers of butadiene. Dewar and Worley[111] have performed calculations with three different semiempirical SCF–MO methods (MINDO/1, II (Koopmans' theorem), and II half-electron method), all of which predict I_1(cis) > I_1-(trans). The latter workers also studied the LRPS of *trans*-1,3-butadiene at temperatures up to 150° and saw absolutely no evidence of ionization below 9.07 eV, the established I_1 for the trans isomer. Since the amount of cis isomer should increase at higher temperatures, the only tenable conclusion is that I_1(cis) ≥ I_1(trans), in accord with the semiempirical predictions.

The LRPS of the cis and trans isomers of 1,3-pentadiene and of the three stable isomers of 2,4-hexadiene have also been investigated.[93,103] In contrast to the I_1 values of the isomers of 2-butene, those of the diene isomers differ appreciably: *i.e.*, *cis,cis*-2,4-hexadiene (8.28 eV); *cis,trans*- (8.23 eV); and *trans,-trans*- (8.19 eV). The corresponding higher I_n values for these molecules differed considerably. Resolution was best for the cis isomer of 1,3-pentadiene and the cis,cis isomer of 2,4-hexadiene.

The HRPS of allene and ketene reveal well-resolved vibrational structure in most of the bands.[112] The first band in the spectrum of ketene corresponds to ionization of an orbital mainly confined to oxygen but partly delocalized over the C=C region, while I_1 for allene involves the loss of a C=C π electron. A double maximum was observed in the first band of the allene spectrum; this was attributed to Jahn–Teller distortion in the ion. It is interesting that the I_1 of allene (9.83 eV) measured from the LRPS[93] is 0.14 eV higher than that (9.69 eV) measured from the HRPS;[112] a similar situation exists for I_1 of methane, for which Jahn–Teller distortion has also been observed (section A).

C. ALKYNES, SUBSTITUTED ALKYNES, AND RELATED COMPOUNDS

The LRPS[3,113] of acetylene contained three bands which were assigned to ionization of orbitals in the sequence $1\pi_u > 3\sigma_g > 2\sigma_g$. Baker and Turner[114,115] have also studied the molecule at high resolution. Vibrational structure was resolved in all three bands, that in the I_1 band, which corresponds to the $1\pi_u$ orbital, being characteristic of the ν_2 stretching mode of the ion. The sets of ionization potentials reported in the four investigations[3,113–115] vary somewhat, but, in this case, the low-resolution values are smaller than the corresponding high-resolution ones.

In addition to acetylene, Baker and Turner[115] have investigated the HRPS of several polyacetylenes ($R(C≡C)_nR'$,

where R and R′ = H or CH_3) and of related aza compounds (*e.g.*, N≡C—C≡N). This is an especially useful paper for consultation for those beginning photoelectron spectroscopists who are interested in vibrational structure assignments. Conjugative and inductive effects for the series of compounds are discussed; greater inductive changes appear to occur for the σ energy levels than for the π levels.

The HRPS of methyl cyanide and methylacetylene have been studied in conjunction with semiempirical CNDO/2 and INDO calculations.[71] The predicted ordering of the highest two orbitals of methyl cyanide was reversed for the two theoretical procedures. The authors concluded that, in this case, the predicted ordering (e > a_1 > a_1 > e) of CNDO/2 was correct; as usual for these two methods, a 4-eV correction to the orbital energies was necessary. The HRPS of the two compounds showed no evidence of Jahn–Teller splitting.

The HRPS of several dihaloacetylenes (XC≡CY; X and Y = Cl, Br, or I)[116] and cyanogen halides (XC≡N; X = Cl, Br, or I)[117] have been reported recently. Spin–orbit splitting was observed in those bands corresponding to ²Π ionic states. The π energy levels for the dihaloacetylenes lie above those corresponding to axially symmetric lone-pair ionization.[116]

D. CYCLIC HYDROCARBONS AND DERIVATIVES

1. Benzene

Benzene has been the subject of more PS investigations than any other single molecule.[3,5,42,91,93,107,118–124] There are several reasons for the current interest in the photoelectron spectrum of this compound. The LRPS of benzene is characterized by sharp band onsets, enabling the determination of very accurate adiabatic I_n values. The HRPS possesses appreciable vibrational structure, which is not usually the case for a polyatomic molecule of the complexity of benzene. The most intriguing problem related to benzene is the assignment of the various I_n values to π or σ ionization.

Photoelectron spectroscopists and theoreticians agree that the doubly degenerate π orbital is the highest occupied MO (corresponding to I_1). However, the majority of experimentalists disagree with the theoreticians as to the assignment of the next few I_n values. Quantum MO calculations of all types that treat all valence electrons (semiempirical, *ab initio*, and extended Hückel) predict that one or more σ energy levels lie above the lowest occupied π level.[60,76,77,89,93,125–127] The HRPS excited by 21.22-eV radiation[118,120] seems to indicate that no direct ionization processes occur between I_1 (9.25 eV) and I_2 (11.50 eV); both of these potentials are commonly assigned to

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π ionization. But not all photoelectron spectroscopists concur with this point of view, and the question has developed into a lively controversy.

Using a vacuum monochromator to provide a 10- to 11-eV excitation source, Kurbatov, Vilesov, and Terenin[5] first observed structure in the LRPS of benzene between the 9.25- and 11.50-eV breaks (at ca. 10.75 eV). The extra break was attributed to a preionization process. The high-resolution photoionization threshold curve[128] reveals two breaks at 10.35 and 10.85 eV in addition to the ones at 9.24 and 11.50 eV. Natalis, Collin, and Momigny[119] have observed structure in the 10- to 11-eV region of the LRPS when neon (16.65 to 16.83 eV) and argon (11.61 to 11.82 eV) were used in the excitation lamp, but none when helium (21.22 eV) radiation was employed. The conclusion drawn from each of the latter two studies[119,128] was that the cross sections for σ ionization increase as the excitation energy decreases such that the breaks in the 10- to 11-eV region should be assigned to direct σ ionization in agreement with the theoretical studies. This conclusion has been vigorously attacked by Baker, Brundle, and Turner,[120] who have studied the HRPS excited by radiation from discharges through helium, a helium and argon mixture, and hydrogen; no evidence of additional structure that could be attributed to σ ionization was observed with the low-energy excitation sources. These workers[120] suggest that the structure observed by Natalis, Collin, and Momigny[119] was caused by impurity lines in their light source and that the apparent discrepancies between PS and theoretical calculations can be attributed in this case to the failure of Koopmans' theorem. Presumably, the two extra breaks in the high-resolution photoionization curve[128] would then have to be assigned to some type of indirect ionization process (viz., autoionization). The London group[120] suggests that the use of He I (21.22 eV) radiation as the excitation source aids in interpretation of spectra in that such indirect processes are not usually present, at least not in the low I_n region of the spectra. Momigny and Lorquet[121] have recently replied to the criticisms raised by Baker, Brundle, and Turner. They[121] analyzed the light emitted by their argon lamp with a monochromator; no Lyman α impurity was observed. Also, they report that Comes,[129] in a high-resolution study, has observed I_n at 9.24, 10.3, 10.8, and 11.48 eV, the bands being completely resolved and especially easy to detect at photon energies between 14.3 and 16 eV. Above 16 eV, the bands mix to form a broad band starting at 9.24 eV and going up to 11.48 eV.[129] Using the photoionization resonance technique, Peatman, Borne, and Schlag[122] have also observed two processes in the vicinity of 10.4 eV. However, Samson[123] investigated the spectrum of benzene at moderate resolution using excitation at many wavelengths between 1253 and 584 Å (filtered by a monochromator) and found no evidence of additional ionization processes between 9.25 and 11.50 eV. Furthermore, he suggests that the apparent structure observed in the photoionization resonance experiment[122] is due to autoionization and shows that the extra bands observed in the LRPS excited by argon and neon[119] can be explained by impurities in the light source, as suggested earlier.[120] It should be pointed out that two closely spaced ionization potentials at 11.5 and 11.7 eV have been measured from the HRPS;[120] the vibrational analysis for the 11.5-eV band indicated that it

might be due to σ ionization, but, based on a comparison with the spectrum of C_6D_6, the authors favor a π assignment. A very recent study,[124] in which the HRPS of benzene was excited by He II (304 Å) radiation, places the highest σ level at -11.5 eV but the lowest π at ca. -12 eV. Eland has suggested that 11.5 eV is a limiting value for the first σ ionization potential for aromatic systems.[41]

In the opinion of the author, the work of Samson[123] is the most convincing yet reported; i.e., true σ ionization has not been observed between 9.25 and 11.50 eV. However, it is still quite possible that one or more σ orbitals have a very low cross section for ionization, such that they have not been resolved in the spectra. The adiabatic first σ ionization potentials of cyclohexane,[98] cyclohexene,[8] and 1,4-cyclohexadiene[130] are, respectively, 9.81, 10.29, and ca. 10.6 eV; as the amount of unsaturation (and s character) in the cyclic C_6 systems increases, the σ ionization potential also increases. The geometries of these three molecules are significantly different from that of benzene, so a prediction of I_1 (σ) for the planar aromatic molecule from the data for this series of compounds is clearly tenuous. However, it is tempting to suggest that it will be greater than that for cyclohexadiene by at least 0.3 eV. Whether it is actually greater by more than 0.9 eV (I_2 of benzene is 11.5 eV) is open to question. In any case, there is no reason to assume that Koopmans' theorem is a worse approximation for σ ionizations than for π ones, especially for the lower I_n values. Dewar and Worley[93] have shown that the MINDO/1 method predicts the σ-orbital energies quite accurately for a large number of saturated cyclic hydrocarbons of widely varying geometry. Moreover, MINDO/1 predicts these σ ionization potentials to be too high by several tenths of an electron volt. Why should the semiempirical SCF method suddenly predict values of the I_n (σ) to be too low for benzene?

2. Substituted Benzenes

Baker, May, and Turner[107] have reported the vertical ionization potentials of benzene and 44 of its monosubstituted and 1,4-disubstituted derivatives. This paper should be of considerable interest to all organic chemists, because the data have been interpreted in terms of the inductive and mesomeric effects of the substituents. Introduction of a substituent removes the degeneracy of the highest occupied π MO of benzene in a manner such that two bands should result in the photoelectron spectrum, one being almost unchanged in energy from the I_1 (π) band for benzene. An electron-releasing substituent should stabilize the ion and thus cause a shift of I_1 to lower energy; on the other hand, an electron-withdrawing substituent should destabilize the ion, causing a higher I_1. The splittings of the two π bands induced by 20 different substituents are reported in the above work.[107] For most of the 23 1,4-disubstituted benzenes studied, the splitting was roughly the sum of the separations observed for the corresponding monosubstituted compounds.

A few additional studies of substituted benzenes have been reported, including amines,[4] methyl derivatives,[5] styrene,[12,98] chlorobenzene,[131] several fluorobenzenes,[42,118,119] and others.[12] Bloor and Breen[66] have shown that the CNDO/2 SCF-MO method gives poor results for substituted benzenes.

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3. Polycyclic Aromatic and Related Compounds

The work on this series of compounds has been essentially confined to that of two research groups, mainly because of the low volatility of the compounds. Eland and Danby[40] have studied the HRPS of indene, naphthalene, azulene, and biphenyl; Eland[41] has also reported the HRPS of biphenylene. Of course, "high resolution" here refers to the nature of the analyzer used, not the appearance of the spectra, because very little vibrational structure was resolved. The first several peaks in the spectra tended to be sharper than those beginning at ca. 11 eV. This might indicate that the first bands correspond to π ionization with σ ionization commencing around 11 eV. The ionization potentials were correlated with orbital energies predicted by HMO theory. The intensity of the second ionization band for biphenyl was about twice that of the first, in accordance with the twofold degeneracy of the second π orbital, as predicted by HMO.

The LRPS of those molecules mentioned above (except biphenylene) and of phenanthrene, fluoranthene, acenaphthylene, acenaphthene, and fluorene have been measured recently.[132] For the less volatile compounds, it was necessary to heat the ionization chamber and sample inlet system. The agreement between the independent measurements[40,132] is excellent for the first ionization potentials and, in general, quite good for the higher I_n. The I_1's in the latter study[132] were correlated with orbital energies predicted by the Π SCF–MO method, MINDO/1, and MINDO/2 and with adiabatic ionization potentials predicted by the Π half-electron method. The latter Π method and the MINDO/2 SCF–MO method predicted the better absolute values (in accord with experiment), but MINDO/1 seems to estimate higher I_n values with greater accuracy (see below).
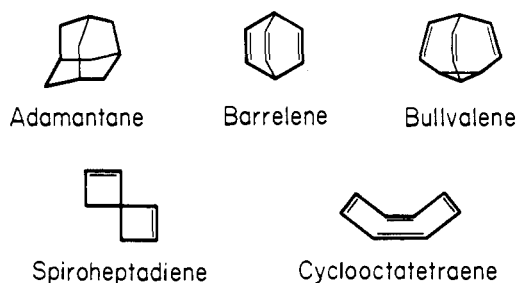
The first ionization potentials for this series of compounds tend to decrease as the number of π electrons increases, notable exceptions being biphenyl, acenaphthene, and azulene. Since biphenyl is not planar, complete overlap of the 12 p_z atomic orbitals to form "pure" π molecular orbitals is impossible. Thus the I_1 of biphenyl (8.23 eV) should be expected to be greater than those of acenaphthylene (8.02 eV) and fluorene (7.93 eV), both of which have planar π systems. Acenaphthene and azulene have only 10 p_z orbitals contributing to the π molecular orbitals but have the lowest values of I_1 found for this series (7.73 and 7.43 eV, respectively), whereas naphthalene has a higher I_1 of 8.11 eV. The low value for acenaphthene probably can be attributed to ring strain. The highest occupied MO of a molecule that possesses considerable ring strain should be of higher energy than that of a similar nonstrained molecule, and it is possible that the strain energy of the ion relative to that of the molecule is reduced. Both of these factors should lead to a lower first ionization potential. Azulene has a much lower I_1 than the isomeric naphthalene because it is in effect a monocyclic aromatic hydrocarbon, being best regarded as a slightly perturbed version of [10]annulene;[87] i.e., azulene is less stable than naphthalene and hence has a lower ionization potential. The various semiempirical SCF approaches mentioned above reproduce these trends nicely.

Dewar and Worley[93] have also pointed out that the first few bands in the LRPS of aromatic hydrocarbons appear to correspond to π ionization. The MINDO/1 method, which estimates both σ and π orbital energies, was used to predict the ionization potentials below 21.22 eV for naphthalene and azulene. The first five breaks in the LRPS of naphthalene (8.11, 8.79, 9.96, 10.90, and 12.26 eV) correlate best with the five π orbital energies predicted by MINDO/1, although seven σ orbitals are also predicted to lie in this region. The same result was found for azulene; however, in this case, several σ orbital energies were also close, but no nearer, to the experimental I_n. An ab initio calculation on nahpthalene predicts the four highest occupied orbitals to be π, but then three σ levels higher than the lowest π level.[133] Brundle and Robin[20] have studied the HRPS of naphthalene and octafluoronaphthalene, concluding that at least the first four bands in the spectra can be assigned to π ionization. So the question again arises. What has happened to the σ ionization processes in the spectra or why has the semiempirical method failed for unsaturated systems?

4. Other Cyclic Hydrocarbons and Derivatives

The LRPS and MINDO SCF–MO calculations for 35 cyclic and polycyclic hydrocarbons and their derivatives, including such exotic molecules as adamantane, cubane, nortrycyclene, bullvalene, and spiroheptadiene, have been reported;[93,134] some of these molecules to be discussed are shown below.

Adamantane   Barrelene   Bullvalene

Spiroheptadiene   Cyclooctatetraene

One of the most surprising discoveries for this series was that substitution in the 1 and in the 2 positions of adamantane (I_1 = 9.25 eV) caused almost no change in the first ionization potential, but alteration of the connectivity of the carbon skeleton or its geometry caused large shifts; i.e., I_1(1,3,5,7-tetramethyladamantane) = 9.23 eV, while I_1(congressane) = 8.93 eV and I_1(adamantanone) = 8.76 eV. Evidence of interaction between the π electrons in the isolated double bonds of norbornadiene (bicyclo[2.2.1]heptadiene) and barrelene (bicyclo[2.2.2]octatriene) was observed. The splitting of π bands ($I_2 - I_1$) for norbornadiene was 0.8 eV, in good agreemtnt with values of 0.83 and 0.85 eV obtained in independent[20,130] high-resolution studies. The first few I_n values of barrelene are[134] 8.24, 9.22, 9.63, 11.11, and 11.49 eV. In the original paper,[134] the 9.22- and 11.49-eV potentials were attributed to a possible benzene impurity, for I_1 and I_2 of benzene are 9.24 and 11.50 eV, respectively.[93] However, an HRPS study[130] of bicyclo-[2.2.2]octadiene has revealed a π-band splitting of 0.58 eV. The lowest occupied π MO in barrelene is doubly degenerate and should be split from the highest π level by approximately three-halves the amount for the two π levels of bicyclo[2.2.2]-

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octadiene, or 0.87 eV. Thus the 9.22-eV break in the LRPS of barrelene is probably genuine. Strong interaction was also observed in the LRPS of bullvalene. For this interesting molecule, the interaction occurs between the degenerate pair of cyclopropane-type orbitals and the degenerate pair of olefinic-type ones. Photoelectron spectroscopy has also been used to predict splittings of 1.0 and 0.6 eV, respectively, for the interaction of the isolated π electrons in 1,4-cyclohexadiene[130] and hexamethyl(Dewar benzene);[20] 1,4,5,8-tetrahydronaphthalene[185] gave the same interaction parameters as those for 1,4-cyclohexadiene. No evidence of spiroconjugative interaction between the double bonds in the dicyclobutene isomer of spiroheptadiene was observed.[134] The HRPS of nine compounds in this series, three of which have been mentioned above, have also been measured.[130] An independent LRPS study[3] also treats several cyclic compounds.

Cyclooctatetraene has been the subject of several PS investigations[3,41,134] and of a very thorough theoretical study.[136] The experimental values of I_1 are 8.04 (adiabatic),[3] 8.5 (vertical),[41] and 8.21 eV (adiabatic).[134] In the theoretical study,[136] the MINDO/2 SCF–MO method was applied to molecular cyclooctatetraene and to the ground ionic state. Four different geometries were used in the calculations; these were planar and nonplanar (tub) with equal bond lengths and with alternating bond lengths. In each case, the bond lengths were chosen to minimize the energy of the molecule or ion. The calculations predicted the stable geometry of the molecule to be the "tub" with alternating bond lengths; the same was true for the ion, except that the departure from planarity and equal bond lengths was less. An adiabatic I_1 of 8.17 eV was calculated from the difference in energy between molecule and ion in their equilibrium states. A vertical I_1 of 8.81 eV was estimated from the difference in energy between the molecule and ion, both having the equilibrium geometry of the molecule. The adiabatic I_1 is in excellent agreement with experiment;[3,134] the vertical I_1 appears to be 0.3 eV too high.

An extensive HRPS study of cyclopropane, including correlations with ab initio calculations, has been reported.[83] The first band, corresponding to a vertical I_1 of 10.53 eV and containing resolved vibrational structure, could be assigned to ionization of the 3e' orbital, but the second band at a vertical potential of 11.3 eV did not correlate with the second highest orbital (1e''). Rather, the 1e'' orbital correlated best with the third band in the spectrum. The workers suggested that Jahn–Teller distortion in the doubly degenerate lowest ionic state could be a possible explanation for the second band, as is apparently the case for the double maxima observed in the spectra of methane and allene. The adiabatic I_1 derived from the HRPS is less than 10 eV (see spectrum in ref 83), while that measured from the LRPS[93] is 10.06 eV. Thus, in analogy to methane and allene, the adiabatic I_1 for cyclopropane is quite a bit lower for the HRPS. This analogy lends support to the Jahn–Teller argument. However, an I_2 of 11.07 eV is clearly resolved in the LRPS, but the double maxima caused by Jahn–Teller distortion of the ions in methane and allene were not resolved at all in the LRPS.[93] Therefore, it is not clear whether the second band is part of a double maxima or the true second ionization potential. If the latter is the case, the ab initio calcu-

lations for this molecule are not reliable. The semiempirical MINDO/1 method predicts the 3e' and 1e'' orbital energies to be −10.14 and −11.95 eV, respectively, but only one orbital is predicted to lie between −15 and −17 eV;[93] the HRPS clearly contains two bands in this region (at 15.7 and 16.5 eV).

The HRPS of bromocyclopropane[20] contains a sharp peak at 10.6 eV, which may be assigned to the bromine lone-pair ionization.

E. AZABENZENES AND AZANAPHTHALENES

1. Azabenzenes

A point of controversy in photoelectron spectroscopy has been which of the first few ionization potentials of the azabenzenes and the azanaphthalenes correspond to removal of electrons from π molecular orbitals and which should be assigned to nonbonding (nb) ionization. Although theoretical calculations of all types (ab initio,[80,81] MINDO,[44] and extended Hückel[137]) predict that the lone-pair electrons on N in the azines are partially delocalized throughout the molecular framework, the nb orbitals are largely confined to N, such that the lone-pair concept is useful in interpreting spectra. Early studies[3,91] of pyridine LRPS excited by 584-Å radiation revealed the first few adiabatic I_n values to be 9.28, 10.54, and 12.22 eV. The appearance of the bands in the spectra and a comparison with the LRPS of benzene indicated that the first three I_n values might be assigned to orbitals in the order $\pi_3 > $ nb $> \pi_1$, the π_2 band not being resolved. A later HRPS study[118] by the same group supported the assignment of the 12.2-eV band to π_1 ionization, but the π_3, π_2, and nb ionizations were not discussed. Six ionization potentials at 9.17, 9.50, 10.45, 10.80, 11.37, and 12.16 eV have been derived from the pyridine LRPS excited by 736-Å radiation and from a high-resolution photoionization threshold curve.[138] The six ionizations, of which I_2 and I_4 are uncertain, were assigned to energy levels $\pi_3 > \pi_2 > $ nb $> \sigma > \pi_1 > \sigma$, based on the ordering predicted by ab initio calculations.[80] Pyrazine has also been studied recently at high resolution.[41] The extensive nature of the vibrational structure resolved in the I_1 band suggests strongly that I_1 for pyrazine can be assigned to π_3 ionization.[41] It should be pointed out that none of the studies mentioned above proved conclusively that I_1 for pyridine corresponds to π_3 ionization, although this might reasonably be inferred by analogy from the high-resolution pyrazine work.[41]

Not only the photoelectron spectroscopists but also the theoreticians disagree about the ordering of the energy levels in the azines. The ionization energies and assignments predicted by seven theoretical studies are listed in Table I; the first few ionization potentials derived from the LRPS[44] are also included for comparison. Table I shows that the ab initio orbital orderings for pyridine[80] and pyrazine[81] are quite different. The ordering of nb $> \pi_3$, i.e., $I(\mathrm{nb}) < I(\pi_3)$, for pyrazine[81] is not in accord with the HRPS experiment.[41] The semiempirical MINDO/1 SCF–MO method[44] predicts the highest occupied π and nb orbitals to have almost the same energy for pyridine and for pyrazine, the π_3 level being the highest; however, the ordering is reversed for pyrimidine, the nb level being 0.4 eV higher than π_3. The MINDO/1 calculations for pyridazine failed to converge. The "nonempirical" calculations[89] also

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(136) M. J. S. Dewar, A. Harget, and E. Haselbach, *J. Amer. Chem. Soc.*, 91, 7521 (1969).

(137) R. Hoffmann, *J. Chem. Phys.*, 40, 2745 (1964).
(138) J. Momigny, C. Goffart, and P. Natalis, *Bull. Soc. Chim. Belg.*, 77, 533 (1968); *Int. J. Mass. Spectrom. Ion Phys.*, 3, 371 (1969).

Table I

Ionization Potentials and Orbital Assignments for the Azabenzenes[a]

Method	Ref[b]	Pyridine	Pyrazine	Pyrimidine	Pyridazine
Ab initio	80, 81	12.17 (π_3), 12.48 (π_2), 12.66 (nb), 15.77 (σ), 16.93 (π_1)	12.01 (nb), 12.56 (π_3), 13.43 (π_2), 14.50 (nb), 16.62 (σ), 17.67 (π_1)		
MINDO/1	44	9.65 (π_3), 9.66 (nb), 10.37 (σ), 10.39 (π_2), 12–12.5 (4σ), 12.97 (π_1)	9.61 (π_3), 9.70 (nb), 10.72 (nb), 11.14 (π_2), 12–12.6 (3σ), 13.38 (π_1)	9.70 (nb), 10.12 (π_3), 10.40 (nb), 11.00 (π_2), 12.12 (σ), 12.19 (σ), 13.31 (π_1)	
Nonempirical	89	8.10 (nb), 8.11 (π_3), 9.07 (π_2), 12.2–16.2 (5σ), 16.21 (π_1)			
CNDO/2	139c	13.02 (σ)	12.50 (σ)	12.82 (σ)	12.71 (σ)
CNDO/2	140c	10.75 (π_3)	10.71 (π_3)	11.05 (π_3)	10.99 (π_3)
Π	52	9.27 (π_3), 9.72 (π_2), 10.5 (nb), 12.78 (π_1)	9.32 (π_3)c	9.50 (π_3)c	
PMO	44	9.24 (π_3),d 9.42 (nb),e 10.04 (π_2)	9.24 (π_3),d 9.42 (nb),e 10.84 (π_2)	9.42 (nb),e 9.64 (π_3), 10.44 (π_2)	8.91 (nb), 9.64 (π_3), 9.93 (nb), 10.44 (π_2)
Observed	44	9.31, (9.51),f 10.45, 12.30, (13.83)	9.36, (9.51), 10.15, 11.14, 11.73, 13.13	9.42, (9.64), 10.39, 11.06, 13.62	8.90, (9.22), 10.53, 11.16, 13.63

a All values are in electron volts. b See references in main text. c Only I_1 was reported. d The observed I_1 for benzene.93 e The observed I_1 for pyrimidine.44 f The breaks defining the I_n in parentheses were less marked than the others, but reproducible (see ref 44).

predict the π_3 and nb orbitals of pyridine to have nearly the same energy. Both of these methods[44,89] place several σ orbitals above π_1 (as for benzene). The two sets of CNDO/2 calculations differ only in parameterization. The first set,[139] which employed the original CNDO/2 parameters, predicts that the first ionization potential for each of the four compounds should correspond to ionization of a σ orbital that is largely delocalized throughout the molecule. The second set,[140] using revised parameters, indicates that I_1 for each molecule should correspond to π ionization. The modified Π SCF calculations[52] for pyridine agree with assignments suggested in the early PS studies.

Two recent independent PS investigations have clearly shown that the π_3 and nb orbitals of pyridine have almost the same energy as predicted by the MINDO/1 method[44] and the nonempirical calculations.[89] In the first, Heilbronner, Hornung, Bock, and Alt[141] compared the spectra of 2-methyl-pyridine and 2-trimethylsilylpyridine. The spectrum of 2-methylpyridine is quite similar to that of pyridine, except that the bands appear at slightly lower ionization energy. Upon replacement of the methyl substituent by trimethylsilyl, the first band split into two components. One component remained at approximately the same energy as the π_3 band in 2-methylpyridine; the other appeared at more than 0.2 eV lower ionization energy. Since the ionization potential of Si-(CH₃)₄ is significantly higher than that corresponding to either of the components, the first band in 2-methylpyridine (and presumably pyridine) must actually correspond to two ionization processes; *i.e.*, either π_3 and nb or π_3 and π_2. The electronic spectra ($\pi^* \leftarrow$ n) and reduction half-wave potentials established that the nb orbital of trimethylsilylpyridine is 0.2 eV higher in energy than that of 2-methylpyridine. Thus the two processes composing the first band in the photoelectron spec-

trum of 2-methylpyridine and of pyridine must be ionization of the π_3 and nb orbitals.

The other definitive study has been made by Dewar and Worley,[44] who used simple first-order perturbation theory in their interpretation of the LRPS of the azabenzenes. In the perturbational MO method (PMO),[37] the difference in energy ($\delta\epsilon_\mu$) of a given π MO (μ) between an aromatic hydrocarbon and an isoconjugate heteroaromatic molecule is given by

$$\delta\epsilon_\mu = \sum_i q_{\mu i}\delta W_i \qquad (4)$$

where $q_{\mu i}$ is the orbital charge density at atom i, and δW_i is the difference in valence-state ionization potential between the heteroatom in position i and carbon. Using real forms for the two highest occupied π orbitals in benzene (eq 5 and 6), which are of course degenerate, Dewar and Worley[44] determined

$$\psi(E_{1a}) = 12^{-1/2}(2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6) \qquad (5)$$

$$\psi(E_{1b}) = 0.5 (\phi_2 + \phi_3 - \phi_5 - \phi_6) \qquad (6)$$

values of $q_{\mu i}$ for each of the azabenzenes. An analogous treatment was used for the lowest unoccupied π^* orbitals. Experimental $\pi^* \leftarrow$ n transition energies for these molecules[142] were employed in estimating a value of -2.4 eV for δW_N (see original paper[44] for complete details). To a first approximation, the nb orbitals of pyridine, pyrazine, and pyrimidine should have the same energy, while the nb levels of pyridazine, in which the two nitrogens are adjacent, should be split due to lone-pair interaction. Thus, comparison of the $\pi^* \leftarrow$ n transition energies for pyrimidine and pyridazine, which have the same π^* energy, gives a splitting (2ϵ) of 1.02 eV. Table I shows the ionization potentials estimated by the PMO method using the empirical values of δW_N and ϵ. The first ionization potentials of pyridine and pyrazine should equal that of benzene to a first-order approximation. The observed differences (*ca.* 0.1 eV) among the three compounds can be attributed to second-order effects. The predicted π_3 ionization energies of

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(141) E. Heilbronner, V. Hornung, H. Bock, and H. Alt, *Angew. Chem.*, **81**, 537 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 524 (1969).

(142) S. F. Mason, *J. Chem. Soc.*, 493 (1962).

pyrimidine and pyridazine are 0.4 eV greater than that for benzene, pyridine, and pyrazine; therefore, I_1 for pyridazine must correspond to ionization of the highest nb orbital. The observed "break" at an I_1 of 9.22 eV in the LRPS of pyridazine was very weak and probably corresponds to ionization of an impurity. However, the second break in each of the other spectra was more pronounced and may reasonably be assigned to nb ionization for pyridine and pyrazine. Since the I_2 for pyrimidine (9.64 eV) is in exact agreement with the estimated π_3 potential, the I_1 for this compound can be assigned also to nb ionization in accord with the MINDO/1 prediction. The difference in I_1 values between pyrimidine and pyridazine is 0.52 eV, almost exactly the 0.51 eV predicted by the PMO method for the spacing between the first nb levels for the two compounds. It should be pointed out that the *ab initio* and MINDO/1 methods predict there to be significant interaction between the lone-pair orbitals in pyrazine and pyrimidine, such that the nb levels are split nonsymmetrically. This splitting is assumed to be negligible in the first-order approximation discussed above; however, MINDO/1 predicts that the highest occupied nb orbitals lie at essentially the same energy for pyridine, pyrazine, and pyrimidine, so the arguments based on $\pi^* \leftarrow$ n transition energy data should not be affected. Thus the LRPS and PMO theory indicate that I_1 for pyridine should be assigned to π_3 ionization and that the nb ionization potential should be only a few tenths of an electron volt above I_1.

A very recent HRPS study of the pairs of compounds furan–isoxazole and pyrrole–pyrazole has revealed that an appreciable increase (more than 1 eV) in the π ionization potentials occurs upon introduction of N into a region of high π electron density on the furan and pyrrole rings.[143] The implication of this experiment is that, upon N introduction to form pyridine, the π_2 ionization potential of benzene (9.3 eV) should be shifted above 10 eV. A vertical ionization potential for pyridine of 9.8 eV was then reported[143] for the nb ionization in satisfactory agreement with the adiabatic value (*ca.* 9.5 eV) measured earlier by Dewar and Worley.[44]

The HRPS of perfluoropyridine[20] is another good illustration of fluorine substitution causing a greater shift in σ-type orbitals than π, for the ordering is now apparently $\pi_3 > \pi_2 >$ nb.
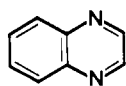
2. Azanaphthalenes

Dewar and Worley[44] have also reported the LRPS of quinoline, isoquinoline, quinoxaline, quinazoline, cinnoline, and phthalazine. It was necessary to heat the ionization chamber to 70° in order to obtain a sample pressure of 25 μ for phthalazine. Because of the low volatility of cinnoline and phthalazine, first ionization potentials measured earlier from the
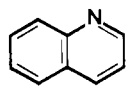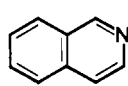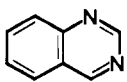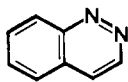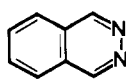

| Quinoline | Isoquinoline | Quinoxaline |
| Quinazoline | Cinnoline | Phthalazine |

(143) A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Chem. Commun.*, 286 (1970).

photoionization threshold curves[144] (obtained at only 10% absorption) were too high, corresponding to I_2 in the photoelectron spectra. The two methods were in excellent agreement for I_1 of quinoline, isoquinoline, and quinoxaline. As for the azabenzenes, the LRPS of this series were interpreted[44] with the aid of first-order perturbation theory. However, in this case, the $q_{\mu i}\delta W_i$'s were evaluated empirically from the PS data for quinoline and isoquinoline, because $\pi^* \leftarrow$ n data were incomplete and because, unlike benzene, the coefficients of the π orbitals of naphthalene are not determined by symmetry. In this manner, the first two ionization potentials for the azanaphthalenes were assigned to π or nb orbitals. For cinnoline and phthalazine, I_1 definitely corresponds to nb ionization, while, for quinoline and isoquinoline, the highest occupied MO is π. The π and nb orbitals of quinoxaline and quinazoline are very close in energy, such that only one break was resolved at low ionization energy, and a definite assignment cannot be made. The HRPS of quinoline and isoquinoline has also been measured;[40] most of the I_n's reported in the independent studies[40,44] are in good agreement.

F. METAL CARBONYL COMPOUNDS

1. Organometallic Carbonyl Complexes

Cyclobutadiene (CB) and trimethylenemethane (TMM) are molecules that have long been of considerable interest to quantum organic chemists. These compounds are not stable at room temperature, and there has been no attempt to study them directly by photoelectron spectroscopy. However, Dewar and Worley have obtained estimates of the two π ionization potentials for both molecules[93,145] by employing appropriate theoretical computations and comparing the LRPS of the iron tricarbonyl complexes of CB, TMM, and *cis*-1,3-butadieneiron tricarbonyl (A) with that of *trans*-1,3-butadiene. In brief, the first two measured I_n's for *trans*-1,3-butadiene[93] were used in conjunction with the Π SCF–MO method and the half-electron method[59] to estimate the two π ionization energies of *cis*-1,3-butadiene. Comparison of the I_2 and I_4 measured from the LRPS of the iron carbonyl complex of *cis*-butadiene (A) with the I_1 and I_2 of free *cis*-butadiene then gave estimates of the perturbing influence of $Fe(CO)_3$ on the two π orbitals of the ligand. The observed I_2 and I_4 for the complex were assigned to π ionization because they were quite different from the corresponding values measured from the LRPS of cyclobutadieneiron tricarbonyl (B); the I_1 and the I_3 values for the two complexes (A and B) were almost exactly the same, indicating ionization of orbitals essentially confined to the $Fe(CO)_3$ moiety. The first ionization potential for B was in fact exactly equal to that (8.04 eV) for A, while the corresponding value varied over several tenths of an electron volt for four monosubstituted derivatives of A and B. This result implies that the perturbing influence of $Fe(CO)_3$ in A and B is the same. Based on this assumption, values of 8.50 and 11.66 eV were estimated from the spectrum of B for the two π ionization potentials of CB.[93] The I_1 obtained in this manner is in excellent agreement with the 8.51 eV adiabatic value for CB predicted by a direct SCF computation. It also supports a recent electron-impact study of CB (generated by flash vacuum pyrolysis of photo-α-pyrone),[146] in which the I_1

(144) A. J. Yencha and M. A. El-Sayed, *J. Chem. Phys.*, 48, 3469 (1968).
(145) M. J. S. Dewar and S. D. Worley, *ibid.*, 51, 1672 (1969).
(146) E. Hedaya, R. D. Miller, D. W. McNeil, P. F. D'Angelo, and P. Schissel, *J. Amer. Chem. Soc.*, 91, 1875 (1969).

was reported to be between 8.2 and 8.6 eV. The predicted second π ionization energy of CB also agrees with the II SCF–MO calculations, but, in view of the findings of Brundle and Robin[110] on the origin of I_2 for trans-1,3-butadiene (section B), the I_2 estimated for CB is questionable. However, the first σ ionization potential of trans-butadiene is apparently only a few tenths of an electron volt lower than the second π ionization potential, so 11.66 eV is probably close to the true value. Employing similar arguments and the LRPS of trimethylenemethaneiron tricarbonyl, Dewar and Worley[145] have estimated the two π ionization potentials of TMM to be 8.63 and 11.07 eV.

2. Metal Carbonyls and Complexes

The HRPS of manganese pentacarbonyl and seven complexes, $Mn(CO)_5X$, where $X = H$, Cl, Br, I, CH_3, CF_3, or $COCF_3$,[147a] and those of vanadium hexacarbonyl and chromium hexacarbonyl[147b] have been studied. The low ionization potential region of the spectra for most of these compounds is thought to relate to ionization of molecular orbitals largely composed of the metal 3d atomic orbitals; for $Mn(CO)_5X$, these ionization bands depend markedly on the nature of the substituent X. However, when $X = $ Cl, Br, or I, the first ionization potential relates instead to an MO that is largely of halogen character. This was ascertained from a 0.3-eV spin–orbit splitting in the first band of $Mn(CO)_5I$. The ionization potentials above ca. 12 eV can be assigned to ionization of orbitals that are largely carbonyl; these I_n's are relatively insensitive to X. The low I_1 for each of the manganese carbonyl halides (8.3–8.8 eV), relative to that found for each corresponding methyl halide (9.5–11.3 eV), strongly suggests that metal–halogen d_π–p_π bonding exists in the former.
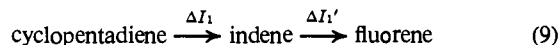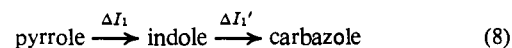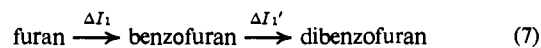
The photoelectron spectra of iron pentacarbonyl and nickel tetracarbonyl have also been measured.[148] The I_1 value (8.00 eV) for $Fe(CO)_5$, which again may be assigned to ionization of an MO which is essentially metal 3d, is very close to the 8.04-eV value reported[93] for the two iron carbonyl complexes mentioned previously.

G. FURANS, PYRROLES, AND THIOPHENES

The HRPS of furan, benzofuran, dibenzofuran, pyrrole, indole, thiophene, and benzothiazole have been measured by Eland.[41] Several bands in the spectrum of furan contained well-resolved vibrational structure, but only the first band for pyrrole and thiophene was structured. The HMO method was used in making assignments (π or σ) for most of these molecules, exceptions being thiophene and benzothiazole, for which suitable parameters for sulfur could not be found. Turner has also reported the HRPS of furan and α-chlorofuran.[15]

The LRPS of the furans and pyrroles mentioned above have also been measured.[149] While the band structure of the first ionization band for furan[15,41] is indicative of π ionization, there is some question about the energy of the lone-pair orbital on oxygen. That I_1 for the furans corresponds to π ionization is clearly demonstrated from comparison of the

first ionization potentials of the analogous hydrocarbons and pyrroles; i.e.

$$\text{furan} \xrightarrow{\Delta I_1} \text{benzofuran} \xrightarrow{\Delta I_1'} \text{dibenzofuran} \qquad (7)$$

$$\text{pyrrole} \xrightarrow{\Delta I_1} \text{indole} \xrightarrow{\Delta I_1'} \text{carbazole} \qquad (8)$$

$$\text{cyclopentadiene} \xrightarrow{\Delta I_1} \text{indene} \xrightarrow{\Delta I_1'} \text{fluorene} \qquad (9)$$

The value of ΔI_1 for all three cases[93,132,149] is -0.44 eV, and $\Delta I_1'$ is -0.21 for eq 7 and 9. Since the addition of an aromatic ring to furan should affect the π orbitals more than the nb one, and since the highest occupied MO's of pyrrole and cyclopentadiene are clearly π, the I_1 for furan must correspond to π ionization. The MINDO/1 method correctly predicts this result; it also predicts the second highest MO to be π, in accord with the HRPS finding.[41] Furthermore, MINDO/1 estimates the density on the hetero groups to be very small in the highest occupied MO of benzofuran, indole, and indene, so it is not surprising that $\Delta I_1'$ for eq 7 and 9 is the same. The density is zero, of course, in the highest π orbital of the symmetrical molecules. Thus the nb orbital in furan apparently lies below the two highest π orbitals. Carbazole was not sufficiently volatile for measurement, even at 150°, but the analogies in eq 7 and 9 strongly imply that $\Delta I_1'$ should be -0.21 eV in eq 8, leading to an estimated I_1 of 7.87 eV for this compound.

There have been several II SCF studies for this series of compounds.[49,51,53,54,149] An ab initio study of pyrrole has also been reported.[79]

H. AMINES AND HYDRAZINES

Al-Joboury and Turner have measured the low-resolution spectra of 15 saturated and unsaturated amines[3,12] and hydrazine.[14] The LRPS of hydrazine was very similar in appearance to that of ammonia, except that the two bands for NH_3 were broadened to the point at which a split into a pair of bands for N_2H_4 was barely evident. The LRPS of aziridine, 2,2-dimethylaziridine, three benzylamines, and eight derivatives of hydrazine (ABN–NCD, where A, B, C, and D $= $ H, CH_3, C_6H_5, or $C_6H_5CH_2$) have also been reported.[150] The I_1 bands in many of the spectra were quite diffuse. The MINDO/2 method predicts the lone-pair electrons in all of these molecules to be moderately delocalized. The diffuse nature of the I_1 band onsets confirms this prediction, for ionization of localized lone-pair electrons would lead to little or no change in geometry, and the breaks in the LRPS would then be very sharp. Vertical first ionization potentials computed by MINDO/2, employing both Koopmans' theorem and the half-electron approximation,[59] have also been reported.[150] In general, the I_1 values obtained from the latter version of MINDO/2 were in better agreement with experiment than were those estimated by Koopmans' theorem.

Of the amines, the simplest member of the series, ammonia, has naturally received the most attention.[3,24,70,151] The first band in the HRPS[70] of both NH_3 and ND_3, which corresponds to the $3a_1$ nb orbital, contains well-resolved vibrational structure that may be assigned to the totally symmetric out-of-plane bending mode. The second ionization band of NH_3,

(147) (a) S. Evans, J. C. Green, M. L. H. Green, A. F. Orchard, and D. W. Turner, Discuss. Faraday Soc., 47, 112 (1969); (b) S. Evans, J. C. Green, A. F. Orchard, T. Saito, and D. W. Turner, Chem. Phys. Lett., 4, 361 (1969).

(148) D. R. Lloyd and E. W. Schlag, Inorg. Chem., 8, 2544 (1969).

(149) M. J. S. Dewar, A. J. Harget, N. Trinajstic, and S. D. Worley, Tetrahedron, 26, 4505 (1970).

(150) N. Bodor, M. J. S. Dewar, W. B. Jennings, and S. D. Worley, ibid., 26, 4109 (1970).

(151) D. C. Frost, C. A. McDowell, and D. A. Vroom, Can. J. Chem., 45, 1343 (1967).

which may be assigned to the degenerate 1e MO, does not exhibit well-resolved structure;[70] however, a small Jahn–Teller splitting has been observed in this band.[24] The INDO and CNDO SCF methods predict the correct ordering of the $3a_1$ and 1e orbitals, but the calculated ionization potentials are 4 to 6 eV too large.[70]

The HRPS of bicyclo[2.2.2]octane (1), quinuclidine (2), and 1,4-diazabicyclo[2.2.2]octane (DABCO) (3) have been studied
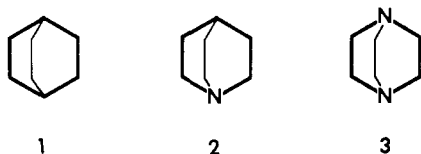
recently.[152] Extended Hückel calculations[153] predict that the highest two occupied orbitals of DABCO should be nb (a_1'-$(n_+) = -11.85$ eV; $a_2''(n_-) = -13.42$ eV), with a 1.57-eV splitting between the two levels. The first two vertical ionization potentials of DABCO are 7.52 and 9.65 eV; therefore, the experimental splitting is 2.13 eV, in satisfactory accord with the theoretical estimation. The mean of these two I_n values is 8.59 eV, which is higher than I_1 for quinuclidine (8.02 eV); i.e., the splitting is not symmetrical. This result is also predicted correctly by the extended Hückel method.[153] Furthermore, an analysis of the vibrational patterns in the first two bands of the HRPS of DABCO has confirmed that the $a_1'(n_+)$ level is the higher of the two nb levels (corresponding to I_1).[154] Thus DABCO is an example of a molecule that can be treated successfully by the extended Hückel method. The MINDO/2 SCF method makes the same qualitative predictions for DABCO, and, although it estimates the splitting to be slightly lower (1.36 eV), it gives much better absolute values of the orbital energies (-8.46 and -9.82 eV).[155] The MINDO/2 method also predicts that the splitting is due almost entirely to indirect interaction via the $p\sigma$ components of the C–C bonds rather than a direct interaction across space. In view of this finding, it is difficult to reconcile the reported zero experimental HRPS splitting[152] for piperazine. However, it should be pointed out that the LRPS[103] of piperazine ($I_1 = 8.21$ eV, $I_2 = 8.53$ eV) and piperidine ($I_1 = 8.30$ eV) also indicate that the splitting for piperazine should be quite small (ca. 0.32 eV). Possibly, for piperazine, the orientations of the atomic orbitals containing the two lone pairs are unfavorable for interaction through the C–C bonds, as in DABCO.

The I_1 of hexamethylenetetramine has been measured from the LRPS[93] to be 8.26 eV, while that for its hydrocarbon analog, adamantane, is 9.25 eV. This suggests that the highest occupied MO in the amine must be largely confined to nitrogen. The I_2 measured for the former compound was 11.80 eV, but it is certain that several ionization bands between 8.26 and 11.80 eV were not resolved, so no estimate of lone-pair interaction could be made in this case.

An extensive high-resolution study of aziridine (ethylenimine), in conjunction with several other saturated three-membered ring compounds, has been reported.[83] The spectra

were correlated with orbital energies estimated by *ab initio* Gaussian-type orbital calculations.

I. ALCOHOLS, ALDEHYDES, KETONES, ACIDS, AMIDES, ETHERS, AND OXIDES

For the carbonyl compounds, it is often difficult to distinguish which bands in the photoelectron spectra should be assigned to the nb and carbonyl orbitals. The MINDO/1 SCF method predicts that the highest occupied MO of alcohols, ethers, and carbonyl compounds should be largely, but by no means entirely, composed of oxygen atomic orbitals.[93] The extent of delocalization of the lone-pair electrons increases as the size of the alkyl group increases. Experimental work on this series of molecules has been relatively sparse.

Al-Joboury and Turner[92] have examined the LRPS of methanol and concluded that I_1 should be assigned to a weakly bonding orbital, i.e., the nb one mainly localized on oxygen. They have also assigned the other I_n for methanol to various molecular energy levels, which differ somewhat in ordering from that suggested in two theoretical studies. Recently, the photoelectron spectrum of chemisorbed methanol has been measured.[156] The first band (I_1) was broadened, but not shifted, upon passing from the vapor to the chemisorbed state, indicating that the methanol molecule continues to exist on the surface. The second band, corresponding to a π-type orbital of the CH_3 group, was displaced by ca. 1 eV; this observation suggests that the hydrogen atoms are affected by bonding to the surface. The definitive nature of this work has been questioned on grounds that the surface was not prepared under ultrahigh vacuum.[20,156] The I_n's derived from the LRPS of several other alkyl alcohols have been tabulated.[3,12,93]

Of the compounds included in this series, the aldehydes have been the most widely investigated by PS. The HRPS of formaldehyde and of D_2CO each contain four bands with well-resolved vibrational structure.[94,157] The I_1 band structure for each (at ca. 10.9 eV) shows that all three totally symmetric modes are weakly excited, the frequencies for the ion being fairly close (within 200 cm^{-1}) to the corresponding ones for the molecule. Thus, the highest occupied MO clearly is of nb character. The I_2 band (14.1 eV) contains the C=O stretching frequency as the main series; therefore, I_2 can be assigned to the carbonyl π MO. These two assignments are also predicted by the CNDO/2 SCF method.[65] A study of the HRPS of acrolein and several of its derivatives[15,16] has shown that the first ionization potential for this unsaturated aldehyde corresponds to the oxygen lone pair and that bands can also be distinguished for the C=C and C=O π ionizations. Acetaldehyde,[12,93] propionaldehyde,[93] and furfural[93] have been studied at low resolution.

The I_1 of hexafluoroacetone (11.68 eV) is 2 eV greater than that (9.68 eV) of acetone.[93] It has been shown that the "inductive effect" plays a very minor role in influencing the I_1 values of the chloromethanes,[93] which correspond to lone-pair ionization; therefore, it seems unlikely that the large 2-eV increase upon passing from acetone to its hexafluoro derivative can be attributed to a long-range inductive effect on a localized lone pair. It is more reasonable to attribute the increase to extensive delocalization of the nb orbital, as predicted by

(152) P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Tetrahedron Lett.*, 4025 (1969).
(153) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, 90, 1499 (1968).
(154) E. Heilbronner and K. A. Muszkat, *ibid.*, 92, 3818 (1970).
(155) M. J. S. Dewar and J. S. Wasson, *ibid.*, 92, 3506 (1970).

(156) W. T. Bordass and J. W. Linnett, *Nature*, 222, 660 (1969).
(157) C. R. Brundle and D. W. Turner, *Chem. Commun.*, 314 (1967).

the MINDO calculations. However, the first ionization potential of p-benzoquinone (9.95 eV) is larger than that for acetone or 2-butanone (9.51 eV). A similar observation has been noted for I_1 of acrolein (10.10 eV) and propionaldehyde (9.94 eV) and attributed to the electron-withdrawing inductive effect of the vinyl group predominating over direct conjugation with the ionic center.[12]

The HRPS of formic acid, formamide, N-methylformamide, and N,N-dimethylformamide have been measured.[84] Based on *ab initio* Gaussian-type orbital calculations on the molecules and ions, the first ionization potentials of formic acid and formamide were assigned to oxygen nb ionization (n_0), while I_2 for the two compounds corresponded to ionization of the antisymmetric π_2 orbital. Similar calculations on the molecular states only (Koopmans' theorem) reversed the ordering for formamide, but the authors considered the former calculations to be more accurate. Similar *ab initio* calculations could not be performed for the two N-methylamides, presumably because of the prohibitive size of these compounds. However, analogies observed between the vibrational structure of the first two bands for the N-methylformamides and the first two bands of formamide indicated that methyl substitution caused a reversal in ordering, such that now I_1 should be assigned to π_2 and I_2 to n_0.

The first ionization potential for aliphatic ethers basically corresponds to oxygen nb ionization, but MINDO/1 predicts the nb orbital to be very extensively delocalized in these molecules. Consequently, the breaks in the LRPS of these compounds tend to be diffuse except for the smaller members of the series. The I_n's for dimethyl ether,[93] diethyl ether,[3,93] and diphenyl ether[41] have been reported. The first few bands in the spectrum of the latter compound correspond to π ionization from the aromatic rings.[41]

The HRPS of ethylene oxide has been correlated with *ab initio* calculations; again the highest occupied MO is predicted to be largely confined to oxygen.[83] The I_1 band for this oxide is well resolved, and the Franck-Condon envelope is narrow (only three vibrational peaks are evident, the adiabatic one being the most intense), supporting the *ab initio* prediction.

## J. COMPOUNDS CONTAINING BORON

1. Diborane and Boron Halides

Diborane has been the subject of several types of theoretical computations[67,85,99,101,158,159] and two PS investigations.[85,160] The various theoretical methods predict different ordering of the energy levels; the experimental I_n assignments were based on *ab initio* calculations. An HRPS study[85] compared the spectra and MO calculations with those for the isoelectronic hydrocarbon, ethylene. In contrast to ethylene, the π-type MO in diborane is shifted below the first three σ orbitals. A small amount of HCl as an impurity in the diborane sample led to an incorrect assignment of the I_2 band in the LRPS[160] of B_2H_6.

Boyd and Frost[161] first studied the photoelectron spectra of BF_3, BCl_3, and BBr_3; the semiempirical theoretical method of

Sichel and Whitehead[67] was employed in making band assignments. This method[67] placed the three highest occupied orbitals in the order $e'(\sigma) > a_2'(\sigma) > e''(\pi)$, while the semiempirical CNDO/2 method[65] predicts $e' > e'' > a_2'$, and an *ab initio* calculation[162] gives $a_2' > e'' > e'$. A recent high-resolution study[163] of BF_3 by Bassett and Lloyd has shown that all of the theoretical interpretations are questionable. The vibrational structure in the I_3 band is indicative of B-F bonding, and the I_1 band is twice as intense as the I_2 one, leading to an experimental ordering[163] of $e'' > a_2' > e'$. The I_3 band appears to be *twice* as intense as the I_1 band, which at first seems peculiar since the assigned levels have the same degeneracy. Of course, there is no reason why π- and σ-type ionization processes should have the same cross section, so the assignment is tenable from this standpoint. However, the I_5 band was assigned[163] to a σ-bonding e' orbital. It is of similar intensity to the I_1 band, which is also peculiar, given that I_1 was thought to correspond to a π-type ionization. Thus, from the relative band intensities, the ordering $e' > a_2' > e''$ suggested in the earlier PS study[161] would seem more logical. Evidence of Jahn-Teller distortion was observed in the I_5 band, supporting the e' assignment.[163]

2. 10,9-Borazaronaphthalene

The compound 10,9-borazaronaphthalene (1) is of considerable chemical and theoretical interest because it is aromatic and isoelectronic with naphthalene (2). The MINDO/1 CF


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      +
     1             2             3
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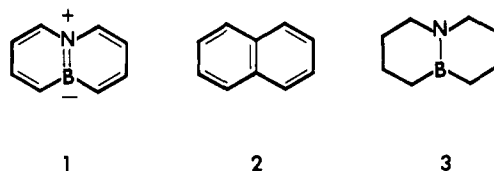
method predicts that the first five bands in the LRPS of **2** correspond to ionization of the five occupied π molecular orbitals.[93] Although no SCF calculations on **1** are available, the arguments to follow suggest strongly that the first five I_n's of **1** may also be assigned to π ionization.

The π orbitals of **2** are either symmetric or antisymmetric to reflection in the plane passing through the 9,10 carbon atoms and normal to the molecular plane. The two antisymmetric π orbitals have a node passing through the 9,10 centers; consequently, replacement of the 9,10 carbons by N and B to form **1** should affect these orbitals little. The MINDO/1 method predicts that I_1 and I_4 for **2** should correspond to ionization of the two antisymmetric orbitals. On the other hand, the symmetric π orbitals of **2**, corresponding to I_2, I_3, and I_5, should be perturbed markedly by N and B. The sign of the perturbation can be derived from first-order perturbation theory; *i.e.*, the change in orbital energy $\delta\epsilon_\mu$ upon forming **1** from **2** is (see eq 4 in section E for definition of terms)

$$\delta\epsilon_\mu = q_{\mu 9}\delta W_N + q_{\mu 10}\delta W_B \qquad (10)$$

Since for **2** $q_{\mu 9} = q_{\mu 10}$, and since δW_N is negative with $|\delta W_N| > |\delta W_B|$,[164] $\delta\epsilon_\mu$ must be negative, which means that the symmetric π orbitals in **1** should have lower energies (higher ionization potentials) than those in **2**. Table II shows the first five

(158) F. P. Boer, M. D. Newton, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **88**, 2361 (1966).
(159) L. Burnelle and J. J. Kaufman, *J. Chem. Phys.*, **43**, 3540 (1965).
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Table II

Ionization Potentials of Naphthalene and
10,9-Borazaronaphthalene (eV)

	I_1	I_2	I_3	I_4	I_5
Naphthalene (2)	8.11	8.79	9.96	10.90	12.26
10,9-Borazaronaphthalene (1)	8.24	10.07	10.95	12.23	13.07

I_n values for **1** and **2** measured from the LRPS.[43] Based on the foregoing arguments, it seems clear that the I_n values at 10.07, 12.23, and 13.07 eV for **1** should correlate with the I_n's at 8.79, 9.96, and 12.26 eV, respectively, for **2**. The values of 8.24 and 10.95 eV for **1** must correlate with those of 8.11 and 10.90 eV for **2**.

The LRPS of 9-aza-10-boradecaline (**3**) has also been studied.[43] The I_1 for **3** is 8.47 eV, while that for its hydrocarbon analog, *trans*-decalin,[93] is 9.35 eV. This result implies that the highest occupied MO of **3** is largely confined to nitrogen. However, I_1 for **3** is significantly higher than those of typical tertiary amines ((CH$_3$)$_3$N, 8.12 eV; (C$_2$H$_5$)$_3$N, 7.84 eV).[3] Since the B–N σ bond is more polar in the sense B$^+$–N$^-$ than is a C–N σ bond, the negative charge on nitrogen should reduce its lone-pair ionization potential, not raise it; therefore, the high I_1 of **3** must indicate relatively strong π bonding. Thus, whereas I_1 for **1** corresponds to ionization of an antisymmetric π MO confined entirely to carbon, the first ionization potential of **3** seems to correspond to ionization of a two-center π MO largely concentrated on nitrogen.

3. Borazines

The ordering of the I_1 values measured from the LRPS[103] of *B*-trimethylborazine (9.50 eV), *N*-trimethylborazine (8.97 eV), and hexamethylborazine (8.47 eV) is the same as that predicted by semiempirical SCF–MO calculations.[165] It is noteworthy that N substitution causes a much larger decrease in I_1 of borazine than does B substitution. The HRPS of the parent borazine[166] has been reported recently, the adiabatic I_1 being 10.01 eV. The CNDO and INDO methods predict that the highest occupied MO of this molecule should be e'(σ).[166]

K. COMPOUNDS CONTAINING PHOSPHORUS, ARSENIC, AND SULFUR

The HRPS of the phosphonitrilic fluorides (NPF$_2$)$_n$, where $n = 3$ to 8, show that the I_1 values alternate in magnitude as the size of the ring increases; *i.e.*, vertical I_1's of 11.4, 10.7, 11.4, 10.9, 11.3, and 10.9 eV were measured for $n = 3, 4, \ldots, 8$, respectively.[167] The first few I_n values for these compounds probably correspond to π ionization.[167] The nature of the d orbitals on phosphorus that contribute to the π systems is of interest. The (NPF$_2$)$_{3,4}$ rings are planar, and those for (NPF$_2$)$_{5,6}$ approach planarity, so the simple HMO method might provide useful information about the d-orbital participation in these compounds. The above work included such HMO calculations, in which two models were used. In one (homomorphic π system), the 3d$_{z^2-y^2}$ orbital, which is symmetric with respect to σ_v, is the participant; in the other (hetero-

morphic π system), the participant is the 3d$_{zz}$ orbital, which is antisymmetric with respect to σ_v. The HMO calculations based on the former model predict the I_1 values to alternate in the same manner as the observed trend, while the latter model incorrectly predicts all of the I_1 to be equal (11.4 eV). Thus, the highest occupied MO for these compounds is π with the 3d$_{z^2-y^2}$ orbital on phosphorus apparently being the major d contributor. For the odd-membered rings, the π orbitals containing 3d$_{z^2-y^2}$ and 3d$_{zz}$ are apparently in near coincidence.

The HRPS of phosphine[168] and arsine[168] are quite similar to that of ammonia.[70] The first ionization potential for all three compounds relates to loss of an nb electron (a$_1$), the I_2 values corresponding to ionization of the e orbital; structure corresponding to the totally symmetric out-of-plane bending mode was observed in the first band of each. The adiabatic I_1 and I_2 for the three compounds are NH$_3$ (10.15, 14.92 eV), PH$_3$ (10.13, 12.5 eV), and AsH$_3$ (10.06, 11.9 eV).

The LRPS values of several sulfur compounds of the type CA$_3$S$_n$CB$_3$, where A and B = CH$_3$ or CF$_3$ and $n = 1$ to 4, have been measured.[169] The first ionization potentials for these compounds decrease as n increases and seem to be converging to the I_1 of S$_8$. An HRPS study[170] of sulfur hexafluoride has revealed a very high I_1 of 15.30 eV and four higher I_n values below 21.22 eV.

L. OTHER COMPOUNDS

Phenyltrimethylsilane and *p*-fluorophenyltrimethylsilane have been studied at high resolution.[171] The Si(CH$_3$)$_3$ substituent was found to cause a reduction in I_1 of benzene by 0.4 eV, but a splitting of the π_3, π_2 levels of less than 0.2 eV (not resolved). The lower I_1 for the silane relative to that for benzene indicates that the electron-releasing effect of the three methyl groups overrides any negative mesomeric effect associated with the empty silicon d orbitals.[171] For the disubstituted benzene, a π_3, π_2 splitting of 0.45 eV was measured; this is what would be predicted from the additivity rule for para-disubstituted benzenes,[107] since the corresponding splitting is 0.3 eV for fluorobenzene and less than 0.2 eV for phenyltrimethylsilane. The HRPS of ferrocene[13,14] and carbon suboxide[172] have also been reported, and the ionization potentials of the chlorine 3p electrons of 25 chloro-substituted compounds have been tabulated.[15,16]

Very recently, methane, silane, germane, and the fluoromethanes have been studied at high resolution.[173] Jahn–Teller splitting was observed in the first band (corresponding to ionization of the t$_2$ orbital) for CH$_4$ (0.7 eV), SiH$_4$ (0.5 eV), and GeH$_4$ (0.5 eV). The HRPS of series of mercury(II) compounds,[174] dichloroethylenes,[175] and alkyl bromides[176] have also been reported in the past several months. For some of the mercury compounds, it was necessary to heat the inlet system of the spectrometer to temperatures as high as 140°.[174]

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V. Current and Future Research

Current research in photoelectron spectroscopy can be classified into six broad areas. The one which has received the widest attention in the early going is the analyses of HRPS of diatomic and small polyatomic molecules. Most of the work in this area has dealt with the assignment of the ionization bands to the various molecular energy levels based on measured vibrational frequencies. The extent of the Franck–Condon envelope has been employed often also in determining the nature of the orbitals (bonding, antibonding, or nonbonding). Although ionization cross sections are related to the integrated peak areas, little work toward measuring these important parameters has been done. Recently, the emphasis of the high-resolution work has shifted to larger polyatomic molecules, many of which have been discussed in this review. Clearly, the future of HRPS lies in the study of the larger compounds, because virtually all of the diatomic, triatomic, and even tetratomic molecules have been thoroughly investigated. Of course, there is always the hope that, eventually, rotational fine structure for small molecules will be resolved, but, at present, this seems out of reach for existing electron-energy analyzers. Although many bands in the HRPS of large molecules do not possess resolved vibrational structure, the inner adiabatic I_n's measured by high-resolution analyzers are usually more accurate than those determined by low-resolution ones.

A research area that is becoming quite popular is the measurement of angular distributions of the photoelectrons removed from the various molecular energy levels.[31,177-183] Thus far, only the rare gases, cadmium and zinc atoms, and a few diatomic molecules have been studied in this respect. These angular-distribution investigations should be extended to larger molecules. It is quite possible that the cross sections for ionization of the various orbitals of a molecule may vary appreciably with the angle of ejection of the photoelectrons (measured relative to the electric vector of the exciting photon). If this is shown to be the case, the spherical-grid analyzer[10,28] should prove to be the most useful from the standpoint of observing all the ionization processes.

While most photoelectron spectra have been excited by the 21.22-eV resonance line of helium, other spectral lines are currently being tested (section II). Since ionization cross sections depend somewhat on the energy of the excitation source, it is conceivable that some direct ionization processes may be overlooked when only one exciting energy (e.g., 21.22 eV) is used. However, photoelectron spectroscopists should be aware that indirect ionization processes (autoionization) may be excited in the spectra when a bound molecular state lies at exactly the energy of the excitation source. Also, hydrogen and nitrogen impurity lines are difficult to remove from rare-gas lamps.

An area of PS that definitely has merit is its use as an analytical tool; preliminary work[18] in this area has been reported. Clearly, X-ray electron spectroscopy (ESCA) is better than

photoelectron spectroscopy for qualitative and quantitative analyses of large molecules. However, PS should be useful in these respects for studying small molecules present in the upper atmosphere; such work is now being planned at the NASA Manned Spacecraft Center. The method also could prove to be useful in studying various pollutants in the atmosphere.

In addition to its usefulness as an analytical tool, PS can be used to solve a variety of chemical problems. Several examples of this have been discussed in this review, e.g., measurement of lone-pair interaction energies and measurement of perturbation energies. The ionization potentials derived from the photoelectron spectra of large aromatic compounds should be useful in interpreting the properties of π-molecular complexes. To study such compounds, the ionization chambers and sample-inlet systems of the spectrometers must be heated, and, since the photoionization cross sections of these molecules appear to be quite small,[132] grid-type spectrometers will probably be required to collect a sufficient photoelectron output. Already, a spectrometer has been developed that operates at temperatures as high as 250°; preliminary results for anthracene, pyrene, perylene, and many other large aromatics have been obtained with this apparatus.[184] Also, photoelectron spectroscopy, in conjunction with uv spectroscopy, has been used to predict a ground-state molecular geometry.[110] Chemists certainly will uncover other clever applications of PS to the field.

Possibly the most important area of PS is its use in testing quantum MO procedures. In the opinion of the author, the most perplexing problem that today jointly confronts photoelectron spectroscopists and quantum chemists is the assignment of the first several I_n for conjugated molecules to π or σ ionization (section IV.D). To date, the most successful experimental effort in this respect has been the low-resolution study of benzene at a variety of exciting energies.[123] This early work[123] should be extended to other aromatic compounds. A higher resolution study would also be desirable, for the published LR spectra of benzene[123] do not clearly demonstrate a *complete* lack of structure between the adiabatic I_1 and I_2 breaks; i.e., it is not obvious that a weak band could not lie under the I_1 band. But, in any case, an analyzer capable of collecting electrons at all ejection angles (spherical analyzer), or one that can be mechanically moved to the various angles, should be employed to ensure observation of all the ionization processes. The most likely approach to resolving the present controversy between the experimentalist and the theoretician would seem to be the development of more sophisticated theoretical procedures. Since it has been suggested that the current controversy stems from the use of Koopmans' theorem in estimating the I_n values from the calculated orbital energies,[120] the validity of Koopmans' approximation for aromatic molecules should be tested. The first few π and σ ionization potentials for these complex molecules could be predicted from the SCF energy differences between the ground molecular state and the various ionic states. The calculations on the ionic states present a difficult problem because the ionic geometries are not known. Many trial geometries (theoretically an infinite number) will have to be employed in computing the approximate minimum energy for each ionic state. The immense nature of a complete treatment of the first few ionic

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states of an aromatic molecule, even benzene, renders current *ab initio* SCF methods quite useless; from a computational-time standpoint, the semiempirical SCF methods (*e.g.*, MINDO) seem to provide the most hope for a resolution of the π,σ controversy in the near future. A second possible theoretical approach to the problem is the calculation of the cross sections for ionization of the various occupied molecular orbitals. Such calculations could indicate that one or more of the first σ ionizations have low probability for 21.22-eV excitation; on the other hand, the calculations may confirm the consensus of photoelectron spectroscopists, *i.e.*, that the first σ ionization potential of benzene is greater than or equal to 11.5 eV. It should be pointed out that a very recent benzene study at extremely high resolution has suggested strongly that the I_2 band should be assigned to ionization of a σ orbital.[185] Cross-section computations for both π and σ levels of aromatic molecules present a formidable theoretical problem that probably will not be solved soon; however, a recent theoretical study of the photoionization cross sections of the π levels of benzene and several other π systems has been performed.[186] It should be noted that a technique for the construction of electronic continuum wave functions for large molecules has been described.[187] Whether the photoelectron spectroscopists or the quantum chemists are correct in the current π,σ controversy is of secondary importance. The important issue is the reason why certain ionization processes are not detected in the spectra or why Koopmans' theorem fails for σ orbitals in conjugated systems. This question will be resolved only if research in both areas is continued.

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