VACUUM ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY OF INORGANIC MOLECULES

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I. Introduction

The study of the photoelectric effect, and particularly of the energies of photoelectrons, contributed considerably to the establishment of the quantum theory at the beginning of this century, but from then until about 1960 there was only occasional interest in the topic on the part of a few physicists. During the last decade the detailed examination of the energy spectra of electrons photoejected from both solids and gases has shown that a great deal of information of interest to chemists, and others, can be obtained from such spectra, and in consequence the field is rapidly expanding. Partly because of practical problems in obtaining the necessary monochromatic photons, work has been largely restricted either to the soft X-ray region, with wavelengths ~1 nm, or to the vacuum ultraviolet region, with wavelengths in the region from 30–100 nm. The techniques used and the information obtained in these two spectral regions are rather different, so that different names have been applied. Work with X-rays is often called ESCA [electron spectroscopy for chemical analysis (*158*)] or XPS (X-ray photoelectron spectroscopy), while the UV work of most interest to chemists has been entirely on molecules and has been called molecular photoelectron spectroscopy by Turner (*180*). The rather unfortunate convention has grown up that the term photoelectron spectroscopy (PES) used without qualification usually refers to ultraviolet work, and we use it in this way here. The term UPS has been proposed, to distinguish from XPS, but has not yet found wide acceptance in the literature.

The X-ray work is most readily carried out on solids, and most of the published spectra are of atomic core levels, though gas phase work, and valence level studies, are possible (*175*). This has been extensively reviewed, and the earlier reviews are referenced by Nordling (*158*) so we do not consider it further here. In almost all PES studies carried out so far the molecules have been examined as vapors, and since the photon energies are insufficient to ionize core electrons, except in unusual cases (*63*, *91*), the technique is restricted to the valence levels. Since the valence levels, in principle, can be delocalized over the entire molecule, interpretation of the spectra can be quite difficult, and this, with the restriction to volatile species, means that the technique is unlikely to become a routine tool for the chemist. However, in small molecules where complete assignments are possible very detailed information on the bonding can be extracted, and in larger molecules partial analyses of the spectra can be very useful. In this chapter we attempt to provide a concise account of the necessary background to an understanding of the method and to illustrate with a few examples the type of information which has been obtained, giving particular attention to those aspects we think are of most interest to inorganic chemists.

Many other aspects of PES have been reviewed elsewhere, and we refer only to the more recent ones (*6a, 17, 34, 112, 178, 179, 187*). The Specialist Periodical Reports of the Chemical Society (*112*) will provide a continuing series of comprehensive reports. Perusal of the published proceedings of three international conferences (*79a, 160, 174a*) will give some indication of the wide range of interest in both PES and ESCA. Considerable experimental detail is given in the earlier reviews, so in this chapter we have included only those points which we think are essential to a critical reading of the literature. However, we have given considerable emphasis to the question of assignment of spectra, since there are disputed assignments for several molecules in published papers. Although we have not attempted a comprehensive discussion of the literature, we have included a tabulation of references to indicate the range of molecules to which the technique has been applied. The examples we have chosen for discussion inevitably reflect a personal bias, and in some of these examples we have attempted to relate PES data to information available from other techniques.

II. Theory

When a photon of energy $h\nu$ ionizes an electron from an isolated atom, the kinetic energy E of the emitted electron is given by

$$E = h\nu - I \tag{1}$$

where I is the ionization potential, i.p. (strictly, ionization energy), of the atom. Conservation of momentum between ion and electron leads to a very slight correction to this which is less than the experimental accuracy of measurement of E and will be ignored subsequently. So long as the photons are monochromatic and ν is known, measurement of E leads directly to I. This has assumed that there is only one possible energy state of the ion; when we extend this to molecules, it is likely that there will be several molecular ionic states which can be produced by ionizing the electrons in different molecular orbitals. This is illustrated schematically in Fig. 1. Ionization of a tightly bound electron gives electrons of low E; ionization from higher-lying orbitals gives electrons of higher E. It is necessary to distinguish these different ionizations, and by convention the energies required for the three ionizations shown in Fig. 1, I_1, I_2, and I_3, each of which produces a *singly charged ion*, with different excitation energies, are referred to as first, second, and third i.p.

This is, of course, different from the usage for atoms where the second i.p. refers to the minimum energy required to remove a second electron from a singly charged ion.

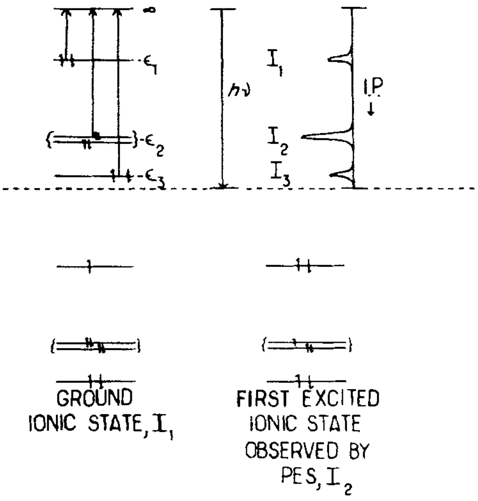

FIG. 1. Energy levels and ionization potentials. [Adapted from Brundle (*34*) and Turner (*178a*)].

A. IONIC STATES

Figure 1 does not represent a real spectrum since it does not take account of possible vibrational or rotational energy of the ion or molecule. Vibrational excitation of the molecule is usually ignored,* so we have for each of the ionic states

$$E_n = h\nu - (I_n + E_{\text{vib}} + \Delta E_{\text{rot}})$$

where I_n refers to the *n*th i.p. in the absence of vibrational and rotational excitation (other than zero-point), called the *adiabatic* i.p., and E_{vib} refers to vibrational excitation of the ion. Except in H_2 (*3*), the changes in rotational quanta ΔE_{rot} have not been resolved, although the expected rotational shading has been observed in H_2O (*4*), and effects due to grouping of rotational levels have been observed in H_2S (*82*).

Some of the vibrational levels can often be resolved, particularly for small molecules, and provide a great deal of information both as to the

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* In a few cases weak features due to vibrationally excited molecules, so-called hot bands, have been detected; see Section VI, A.

nature of the ionic state and indirectly to the nature of the orbital from which the electron was ejected. This is illustrated schematically in Fig. 2 for a diatomic molecule AB. If the electron is ejected from a nonbonding orbital, the resulting photoelectron band will be sharp with little or no vibrational fine structure. On the other hand, ejection from a bonding (or antibonding) orbital will lead to vibrational fine structure, the relative intensities of the components being controlled by the usual Franck–Condon factors, exactly as in a transition between two molecular states

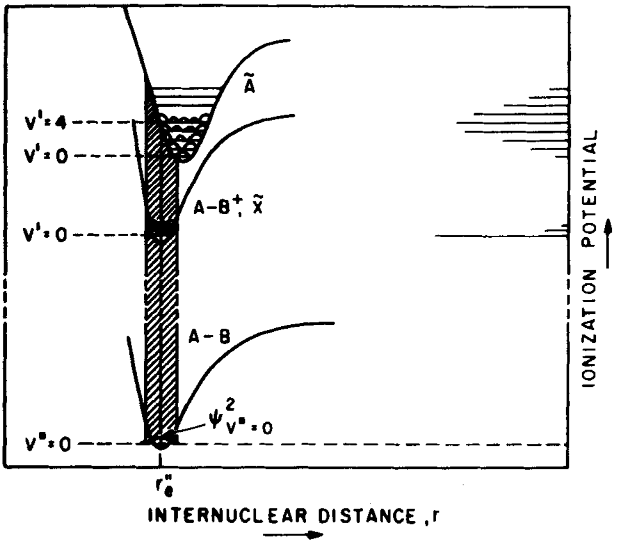

FIG. 2. Formation of ionic states and illustration of the Franck–Condon effect. [Reproduced from Brundle (*34*) with permission.]

(*117*). Comparison of the vibrational interval with the corresponding one for the molecule can provide information on the bonding character of the corresponding molecular orbital. In many cases no structure is observed but only a broad band; this may be due to a variety of reasons, including insufficient instrumental resolution, and ion decomposition, but even so the breadth of the band gives an indication of bonding character (but see comments in Sections IV, D and VI, C). The *vertical* i.p., which corresponds to ionization from the undisturbed molecular configuration and, hence, is the quantity related to molecular orbital energies, is taken as the most probable ionization transition (to $v' = 4$ for Ã in Fig. 2) or as the maximum of an unresolved band.

B. SELECTION RULES

As in electronic spectroscopy the probability of a particular ionization transition is given by the transition moment between the lower (molecule) and upper (ion) states. In the electronic spectra of symmetric molecules the symmetry leads to zero values of the electronic transition moment, i.e., to forbidden transitions, if the group theoretical species of the product of ground and excited state does not include the species of the dipole operator (*58*). However, in ionization, the "excited state" to be considered is the product of the ionic state and the ejected electron. Since the species of the ejected electron wave can be any of the representations of the molecular point group,* all transitions to ionic states produced by removal of a single electron are possible, so there are no orbitals whose ionizations are symmetry forbidden.

In electronic spectroscopy two-electron transitions are rare, and when observed are very weak. Double ionization is not possible energetically using the usual He(I) source (Section III, A), but may be possible with the He(II) source; it has been observed at higher photon energies (*42*). A very large number of ionic states can be derived by removal of one electron and excitation of another, but examples of PE processes leading to these are rare. Weak features in some PE spectra which are unaccounted for on the basis of single electron transitions have been assigned to such ionization + excitation transitions; their occurrence with measurable intensity has been ascribed to "intensity borrowing" through configuration interaction with single electron transitions leading to ionic states of the same symmetry (*81*, *136*, *148*, *166a*). All these instances were observed using the He(II) source (30.4 nm), but there is one He(I) spectrum, that of CS, in which a band of intensity comparable to that of a single electron ionization has been assigned to such a configuration interaction state (*129a*).

For a nondegenerate electronic state, the vibrational progressions (Fig. 2) observed in ionic states correspond to the completely symmetric modes. This is a direct result of the selection rule derived in electronic spectroscopy (*117*), which states that for an electronically allowed transition, no intensity will be achieved unless the vibrations in the excited state are completely symmetric.

The Jahn–Teller effect allows nonsymmetric vibrations for degenerate electronic states (*117*) and observations of such modes can be useful in making assignments (*11*, *132a*, *166b*). In many small symmetric molecules

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* In a molecule with a center of symmetry, the Laporte rule applies, i.e., if the molecular ground state is totally symmetric, then ionization of a *gerade* orbital requires an *ungerade* wave, and vice versa.

a splitting of photoelectron bands from degenerate orbitals is observed; this is also ascribed to the operation of the Jahn–Teller effect (see Section IV, C).

C. DISSOCIATION OF MOLECULAR IONS; TIME SCALES

If the vibrational energy levels in the $\tilde{A}$ state (Fig. 2) were observed up to the dissociation limit, there would be a dramatic break in the vibrational fine structure. This effect has been seen in several cases including HCN (*180*) and HF (*16, 29*). For a diatomic molecule the dissociation must occur along the only vibrational coordinate available. However, in the case of polyatomic molecules it quite often happens that dissociation to the observed photoionization fragments cannot occur along the particular vibrational mode which is being excited. In these cases, there must be curve crossing by other states leading to the correct products. This effect has been discussed at length for N_2O (*28, 180*) and mentioned in the case of XeF_4 (*35*) and NO_2 (*30*).

The PES time scale must be at least as fast as that for ultraviolet spectroscopy, 10^{-15} sec (*152*). This is much shorter than the time required for a molecular vibration or for molecular dissociation, so that spectra can be observed as broad bands even if the ionic state is a repulsive one with no potential minimum. It has been suggested that in cases, such as CCl_4, where no parent ion is observed in the mass spectrum, the PE spectrum is that of the fragment ion (*131*) rather than the molecule, but since ion transit times in a mass spectrometer are at least 10^{-7} sec, this is clearly false.

D. AUTOIONIZATION

In addition to the occupied orbitals of a molecule, there are a very large number of unoccupied, virtual orbitals. The energy required for an allowed transition from the highest occupied level to the lowest virtual orbital is usually approximately three-quarters of the first i.p., and between this and the first i.p., even for such a simple molecule as H_2, there is a vast complex of accessible states, shown by the emission and absorption spectra below the first i.p. For a photon energy slightly above the first i.p. it is quite probable that, in addition to the direct photoionization process of Fig. 1, there will be a transition at this energy to a state of the *molecule*, produced by exciting one of the electrons from the second highest occupied level, or a lower one, to one of the virtual orbitals. Even if such a transition has only a small oscillator strength it will still be much more probable than direct ionization since the oscillator strength for ionization is spread throughout the continuum, whereas the molecular excitation is relatively sharp. Such a state of the molecule is unstable with respect to ionization, but may exist at least for molecular rotation times [$\sim 10^{-10}$ sec (*43a*)] before falling to the ionic ground state and emitting an electron. This process of excitation followed by spontaneous ionization is known as autoionization, and is one of the major reasons why threshold techniques for ionization potential measurement, varying photon or electron energy in a mass spectrometer, are usually unsuccessful in detecting ionization onsets other than the first one. Photoelectron spectroscopy may also be affected by this if there is an orbital whose i.p. is greater than the photon energy but from which a transition to one of the virtual orbitals is possible at exactly the photon energy. In such a case, in addition to the true photoelectron spectrum, there will also be a spectrum due to the autoionizing electrons. Several cases of this are known when relatively low energy photons are used (e.g., *48*, *49*, *49a*, *49b*, *155*, *157*). The classic case is that of O_2. The sharpness of the "resonance" process has been elegantly demonstrated by Price who has shown that the effect, manifested as an abnormal intensity distribution in the vibrational progression on the first band, is present for photons of wavelength 73.6 nm but not for those of wavelength 74.4 nm (*167a*). For the usual He(I) 58.4 nm radiation the effect is much less common, probably because there are fewer possible occupied levels which can be excited, but in some fluorides, particularly SF_6, autoionization is probably responsible for some abnormally intense bands. Use of the even more energetic He(II) radiation at 30.4 nm "overshoots" the occupied valence levels and removes the abnormal intensity (*163*).

E. OPEN SHELLS

When a molecule with only one electron in an orbital or group of orbitals ("shell") is ionized, ionization of this unpaired electron gives only one ionic state, a singlet. However, ionization from any of the other orbitals gives both singlet and triplet states from the coupling, *via* exchange interaction, of the outer unpaired electron with the electron "hole" left by the ionized electron. The energy splitting of these spin states may be quite high; for NO all the expected spin states are observed (*167*, *180*) and the splittings are about 1–2 eV. In other cases little or no splitting is observed (Section VI, E). If both the outer electron and the hole have orbital angular momentum, as in ionization from the π_u orbital of NO, then coupling of these angular momenta causes further splitting (*180*). Finally, if the open shell contains more than two electrons, then coupling of the angular momenta within the open shell can give splittings into different states, so that, for example, the *d* electrons of $V(CO)_6$ (*94*) and $Cr(C_5H_5)_2$ (*62*) have several ionization bands in the PE spectra. The expected intensities of the bands in such cases have been discussed (*60*, *62*).

III. Some Experimental Points

In principle, the equipment required is quite simple, consisting of a light source, an ionization region, an electron energy analyzer, and an electron multiplier detector with appropriate recording system. Because of the lack of window materials at wavelengths below 100 nm, the various sections of the apparatus are separated by differential pumping.

A. PHOTON SOURCES

The most generally useful and convenient source is a d.c. (or microwave) discharge in helium. Other than the visible emission, which is incapable of causing ionization, the major photon emission is at 58.4 nm with a photon energy of 21.22 eV*

$$^1S(1s^2) \leftarrow {}^1P(1s2p)$$

this is usually referred to as He(I) radiation following the spectroscopic convention that radiation from an unionized atom is designated I, that from 1+ ions II, etc. The notation He(I)α is sometimes used to distinguish the main emission from the small amounts (1–3%) of He(I)β radiation

$$^1S(1s^2) \leftarrow {}^1P(1s3p)$$

The presence of small numbers of electrons ionized by He(I)β (23.09 eV) in He(I)α spectra has led to at least one mistaken assignment in the literature (*96a*).

The helium discharge often emits small amounts of photons from N or H impurity and these can give rise to weak features at the high i.p. end of a PE spectrum which have sometimes been assigned as part of the He-induced spectrum (*28*, *139*, *180*).

By careful design of the discharge tube, working with high voltages and low helium pressures, the discharge can be made to emit a substantial fraction of radiation from helium ions, principally the He(II)α line at

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* The electron volt (eV), despite disapproval by the S.I. Committee, is universally used in PES. It is directly related to the voltage calibration of most instruments and is of a convenient magnitude, where the corresponding S.I. units are much too large or inconveniently small (1 eV per molecule $\equiv 1.6021 \times 10^{-19}$ J per molecule or 96.49 kJ per mole).

30.4 nm, 40.8 eV. Only a few laboratories have been successful so far in work with this source, but it can be very useful even when there is a large amount of He(I) radiation as well. Recent work with filters to remove the He(I) radiation allows the study of *all* valence levels, except those derived from 2*s* of F (*166a*). Lower energy photons, particularly those from discharges in neon, argon, and hydrogen, are used occasionally for study of autoionization, or to increase resolution as indicated in Section III, C below.

B. SAMPLE INTRODUCTION

In most instruments constructed so far, particularly the commercial ones, the sample pressures required in the ionization region to obtain sufficient signal strength are from 0.1–10 Nm^{-2}, so that at present the technique is less sensitive than mass spectrometry. The use of electron analyzers with wider acceptance angles can give a great increase in sensitivity, and one such instrument has been operated with a molecular beam source (*14*). Instruments are now being manufactured in which less volatile samples can be heated to over 300°C in the ionization region and this should extend the range of compounds which can be studied. A further new development is the study of transient species produced by thermal or discharge methods immediately before or in the ionization region (*128*, *129a*, *132*).

The question of decomposition of the sample in the ionization region by the photon beam has arisen on occasion, but since the output from the lamp is about 10^{10}–10^{11} photons sec^{-1} (*15*) and the flow of molecules through the ionization region is at least 10^6 times greater than this, the probability of observation of spectra from photochemically produced impurities is very low. However, *thermal* decomposition of relatively unstable or reactive species may occur in the inlet system, and this may be responsible for the only case so far in which different laboratories have reported qualitatively different spectra for the same compound, $Pt(PF_3)_4$ (*108*, *119*). Reaction of hydrolytically unstable compounds with adsorbed water in the instrument is common, but the spectra of the most likely volatile products are well known and easily recognized.

C. ELECTRON ANALYZERS AND THE PRESENTATION OF SPECTRA

Early instruments performed the electron energy analysis by retardation between grids (*180*), but almost all instruments now in use employ electrostatic deflection analyzers, most commonly the 127° cylindrical sector illustrated in Fig. 3, but other designs have been used

(*14, 22, 90, 180*). As the voltage between the cylindrical plates is varied, electrons of different energy are focused on to the exit slits; those which emerge are detected by the multiplier, and normally the rate of arrival of electron pulses is registered on the vertical axis of a recorder, although multichannel analyzers can be used, as in Mössbauer spectroscopy. Since the electron count rate is low, often below 100 sec^{-1}, the noise level of a spectrometer using a ratemeter and recorder is determined almost exclusively by $N^{1/2}$, where N is the product of the count rate and the ratemeter integration time constant. In consequence, PE spectra which are accurately reproduced often have a much higher noise level on them than spectra from other instruments familiar to chemists, and this noise is highest at the top of peaks.

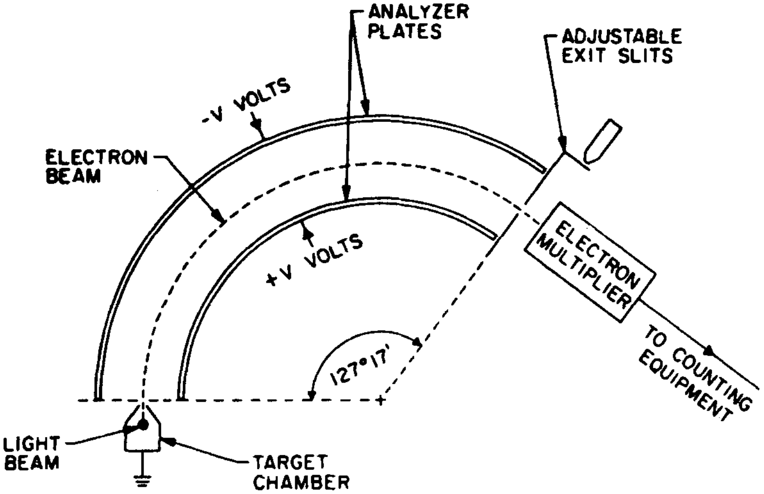

FIG. 3. 127° electrostatic electron energy analyzer. [Reproduced from Brundle (*34*) with permission.]

There are several other points concerned with the presentation of spectra. Some workers plot spectra with i.p. increasing from left to right, others in the reverse direction, and though in most work nowadays the ordinate is labeled in units of i.p., in some early work units of electron kinetic energy were used. For an electrostatic analyzer with fixed slit widths, the theoretical energy resolution ΔE increases linearly with E, i.e., $E/\Delta E$ is constant; for most modern instruments this quantity may be as high as 400. The variation of ΔE means that the electron transmission also increases linearly with E. In consequence, spectra obtained from instruments where the analyzer voltages are varied all show an apparent decrease in intensity to high i.p. (low E). For example, a band at i.p. 17.2 eV which appears to have only half the intensity as one at i.p. 13.2 eV is really of the same intensity, if 21.2 eV photons were used. Since this effect is dependent only on the electron energy within the analyzer, it may be partially overcome by accelerating the electrons by a few volts before they enter the analyzer (*166a, 168*). An alternative which has been used is to keep the analyzer voltages fixed and to accelerate or retard the electrons into the analyzer. If the instrument geometry is appropriate this method can produce spectra with a true intensity presentation (*97*), but this is not true of all such instruments with the voltage scan before the analyzer (*88a*).

It is thus possible to compare band intensities in published spectra, but, in order to do so, a knowledge of the method of scan is necessary; at present (1972) all commercial instruments operate with the voltage scan applied to the analyzer.

According to the discussion above, it is possible to improve resolution ΔE by reducing E, and some work has been carried out using lower energy photons, which reduces E and hence ΔE (*165, 166b*). Electron retardation before the analyzer has also been used for this purpose (*23, 88a, 97*), but in either case it is difficult to obtain a routine practical resolution of much better than 20 meV because of contamination of the slit surfaces by the compounds being studied; most of the spectra discussed here were obtained with resolution between 25 and 75 meV for He(I) ionization of argon, i.e., for electrons of 5 eV kinetic energy.

D. CALIBRATION ACCURACY

Measurements of electron energy are always carried out by comparison with substances of accurately known i.p., since absolute kinetic energy measurements are liable to gross errors from stray fields, especially electrostatic fields in the ionization region from deposition (often reversible) on the slit surfaces. Some of the spectra illustrated here have been obtained with xenon present for this calibration. In principle, with a resolution of 20 meV an accuracy of at least 10 meV would be expected, and the reproducibility of individual measurements on sharp bands is frequently better than this. However, measurements from different laboratories do not always agree at this level of precision, although agreement to 50 meV is usually attained. The important sources of error are analyzer nonlinearities, and the fact that some instruments show a strong dependence of electron energy on the pressure in the ionization region. This latter may be due to space charge effects from the cloud of positive ions around the photon beam (*67a*). Disagreements of up to

100 meV sometimes occur for broad unresolved bands; some of this may be merely subjective error in assessing the top of a peak, but the actual position of the band maximum may depend on the instrument resolution (*180*).

IV. Assignment of Bands

In NMR spectroscopy, for example, signals specific to types of atoms can be obtained, but each orbital in an asymmetric molecule can be delocalized and, in consequence, each band in the PE spectrum is a function of the entire molecule. The problem of assignment is thus similar to that in IR spectroscopy, where, in principle, coupling of all the molecular deformations may take place. The delocalization may be symmetry-restricted, and certain orbitals such as halogen "lone pairs" or transition metal *d* orbitals may be recognizable because of their small delocalization, analogous to the "group frequencies" in IR spectra. Other criteria which may be used to help in assignment include an examination of the fine structure, width, and relative intensities of the bands. Information obtained from this spectral data may be compared with the expected ionic states obtained from molecular orbital calculations or simple symmetry considerations. A comparison of related molecules combined with chemical intuition can also be extremely useful and especially with larger molecules this is often the most effective approach.

A. KOOPMANS' THEOREM

The idea, implicit in the discussion of Fig. 1, that an i.p. is the negative of the corresponding orbital energy, is known as Koopmans' theorem. The theorem is only valid for closed-shell molecules, and several approximations are involved; the general usefulness of the theorem is probably due to the cancellation of opposing terms which are ignored in the approximations (*172*). The vertical i.p. is used since this maximum ionization probability corresponds to the most probable ground state arrangement of nuclei. On this basis it is usual to suppose that the i.p. can be compared directly with calculated orbital energies and that discrepancies are due to inaccuracies in calculation. However, there is definitely one example, the N_2 molecule, where this is not so. The calculations available for N_2 are of a very high quality, the orbital energy sequence is $\ldots \sigma_u \sigma_g \pi_u$, but the first band in the PE spectrum is due to ionization from the σ_g orbital, i.e., there is an inversion of the two highest lying orbitals (*172*).

B. SYMMETRY CONSIDERATIONS

With the application of group theoretical principles (*58*) one can readily derive the number and degeneracy of the occupied molecular orbitals. Consideration of the averaged valence state ionization energies (*8*) or i.p. data for atoms obtained directly from optical spectra (*151*) allows estimation of the number of orbitals expected in a given energy region, e.g., 0–20 or 0–40 eV. This approach is especially useful for molecules containing a threefold or higher axis of symmetry, since the resultant degeneracies simplify the spectrum considerably.

As an example we consider the 0–30 eV range for BF_3. We need only count the fluorine $2p$ electrons* and the three valence electrons on boron, for a total of eighteen valence electrons. Simple group theory tells us that these eighteen electrons must reside in the orbitals: $a_2' + 2e' + e'' + a_2'' + a_1'$. In fact, six PE bands are observed between 16 and 22 eV (*163*). The actual ordering of these orbitals must then be decided on the basis of the spectral features (e.g., relative intensity, fine structure), nodal arguments, intuition, and/or molecular orbital calculations.

In many cases fewer bands are observed than are predicted by symmetry. For XeF_6 a total of eight valence molecular orbitals are predicted ($2a + e + 5t$), whereas only three or four bands are observed in the PE spectrum (*35*). We can only conclude that several bands are overlapping. Such band overlapping is a major limitation in extension of PES to the study of large molecules, and in this respect the technique resembles visible–UV spectroscopy.

C. FINE STRUCTURE

The "one band per orbital" concept of Fig. 1 can become complicated by vibrational fine structure as shown in Fig. 2. In this case, the second band consists of several sharp peaks due to vibrations in the ion.

Extra structure can also result from spin-orbit coupling for orbitally degenerate electronic states. This becomes more important for heavier atoms, and is clearly shown (*166*, *180*) for the rare gas atoms, where ionization of the valence p electrons results in two states $^2P_{3/2}$ and $^2P_{1/2}$, split by 0.11 (Ne), 0.18 (Ar), 0.67 (Kr), and 1.31 eV (Xe). A similar effect is observed for the halogen acids which are isoelectronic with the corresponding rare gases. Here the observed splitting (*166*, *180*), is 0.03, 0.08, 0.33, and 0.66 eV for the ground state ions of HF, HCl, HBr, and HI, respectively. These states arise from halogen p electron ionization and are designated $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$.

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* The fluorine $2s$ electrons are expected to ionize at much higher energy (*151*).

A particularly striking example which illustrates a combination of spin-orbit and vibrational fine structure is provided by the cyanogen halides (*122*). Figure 4 illustrates the $\tilde{X}\ ^2\Pi$ bands for ClCN, BrCN, and ICN. The observed spin-orbit splitting is 0.028, 0.184, and 0.546 eV for the ground state ions of ClCN, BrCN, and ICN, respectively. This allows us to conclude that these bands can be assigned to ionization from the halogen p_π orbitals by virtue of the observed spin-orbit splitting, but that since the values are somewhat smaller than in the halogen acids the electrons are spending less time in the neighborhood of the heavy nucleus, i.e., there is some delocalization to the CN group.

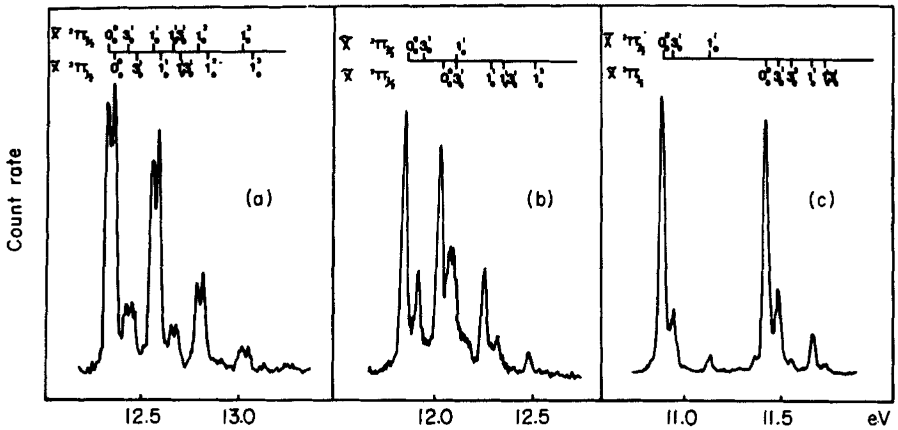


FIG. 4. Photoelectron spectras howing the first two band systems associated with the ionization producing the X $^2\Pi_{3/2}$ and X $^2\Pi_{1/2}$ components of the ground states of (a) ClCN$^+$, (b) BrCN$^+$, and (c) ICN$^+$. The notation $n^\alpha{}_\beta$ refers to the nth vibrational mode arising in the β electronic state with α vibrational quanta. [Reproduced from Hollas and Sutherley (*122*) with permission.]

The vibrational fine structure illustrated in Fig. 4 also provides an example of the vibrational selection rule discussed in Section II, B. Vibrations corresponding to $\nu_1[\nu(\text{C–N})]$ and $\nu_3[\nu(\text{X–C})]$ are both observed; however, the antisymmetric ν_2 bending mode is not detected. The vibrational fine structure was used to calculate bond lengths in the ion (*122*). These authors emphasize that precautions should be observed when making deductions from intensity patterns in Franck–Condon envelopes about the bond lengths in the ion and about the bonding in the molecules.

A further mechanism for splitting of orbitally degenerate states in nonlinear molecules is provided by the Jahn–Teller effect. This is expected under some circumstances to give vibrational progressions with more than one intensity maximum, and although this has not been observed, a number of asymmetrically broadened or split bands have been observed, particularly with hydrides, e.g., NH_3 and CH_4 (Section VI, C), compounds containing $-BH_3$ and $-CH_3$ (Table I), but also in P_4 (*96b*). Recognition of such band shapes in related series of molecules can be a useful aid in assignment.

D. Band Width

Sharp bands with a short Franck–Condon envelope such as those illustrated in Fig. 4 are often indicative of ionization from nonbonding electrons. However, this criterion appears to be valid only for molecules which are of predominantly covalent character. Berkowitz (*15*) has shown that for the thallium halides (TlX) where the bonding is probably largely ionic, removal of a halogen p_π "lone pair" electron results in a broad band in the photoelectron spectrum (Fig. 5). By analogy with BF and on the basis of extended Hückel calculations and relative intensities the first (sharp) band is assigned to the thallium $6s^2$ "lone pair" and the second (broad) band to the halogen "lone pair."

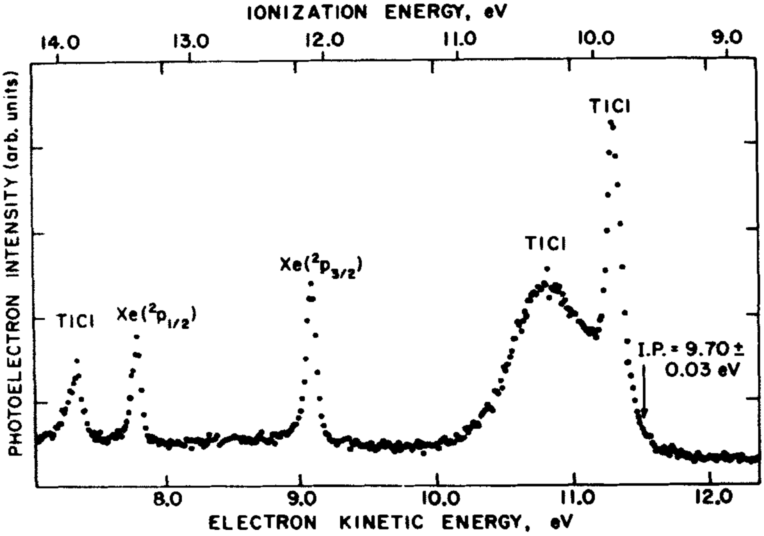


FIG. 5. Photoelectron spectrum of thallium chloride, TlCl. [Reproduced from Berkowitz (*15*) with permission of the American Institute of Physics.]

E. RELATIVE INTENSITY

The relative intensity of bands in PES is also useful in assigning bands. In Fig. 1, we have implied that the intensity of a band is directly related to its orbital degeneracy. This is true only for closed-shell molecules (*62*) and for orbitals which have similar localization properties. This latter criterion is satisfied best by the *d* electrons in the transition metal organometallic and carbonyl compounds. The first two bands in ferrocene occur at 7.2 and 6.8 eV in an intensity ratio 1:2 and can therefore be assigned to the $(a_{1g})^2$ and $(e_{2g})^4$ orbitals (*180*) derived from the iron 3*d* orbitals. Likewise, the first two bands of iron pentacarbonyl and nickel tetracarbonyl exhibit relative intensities of 1:1 and 2:3; on this basis they can be assigned to the orbital sequence ... $(e')^4(e'')^4$ and ... $(e)^4(t_2)^6$, respectively (*138*).

Aside from these restricted cases, the use of relative intensity as an assignment criterion is unwise without supporting data. The PE spectrum of BF_3 (*11*, *163*) shows that the first band is more intense than the second. Yet on the basis of SCF calculations (*2*, *182*) and comparison with the isoelectronic species NO_3 and CO_3^- (*112*), it is probable that the first band belongs to a singly degenerate state and the second to a doubly degenerate state (*11*, *132a*).

F. PHOTOIONIZATION CROSS SECTION

The photoionization cross section of any orbital is known to change with the excess photon energy. Since all orbitals will not change in the same manner, it often happens that a He(I) spectrum will exhibit different relative intensities from a He(II) spectrum. Robin and coworkers have shown this effect to be particularly striking in the case of molecular orbitals predominantly derived from Cl 3*p* and P 3*p* orbitals (*173*). The photoionization cross section decreases dramatically on changing from the He(I) to He(II) photon source. This has allowed an assignment of the Cl 3*p* orbitals in C_2Cl_4 and Cl_3CCN. Relative intensities dependent on the photon source have also been observed for other compounds (*32*, *35*, *37*, *73*, *150*, *163*, *167a*). Some of these effects are due to autoionization as discussed in Section II, D.

It has been generally assumed that the photoionization cross section of a particular orbital will increase with atomic number (*70*, *167*). Recent semiempirical calculations on HF and HCl provide support for this idea (*176*). The absolute cross section of the fluorine 2*p* electrons was calculated to be 0.48×10^{-19} cm^2 compared to 8.03×10^{-19} cm^2 for the chlorine 3*p* electrons. Progress is being made in the theory of photoionization cross sections (*40*, *147*, *174*).

G. Chemical Intuition

The advantage of comparing i.p. in related molecules is obvious and one illustration has been given by Brundle *et al.* (*38*, *39*). These workers have noticed the *perfluoro* effect in which "... the substitution of fluorine for hydrogen in a planar molecule has a much larger stabilizing effect on the σ MO's than on the π MO's." This effect has proven useful in assigning i.p. of several organic substances. Among the inorganic species studied are H_2O–F_2O, and $B_3N_3H_6$–$B_3N_3H_3F_3$. The results for F_2O and H_2O are shown in Fig. 6 and illustrate the very small shift in the oxygen electrons

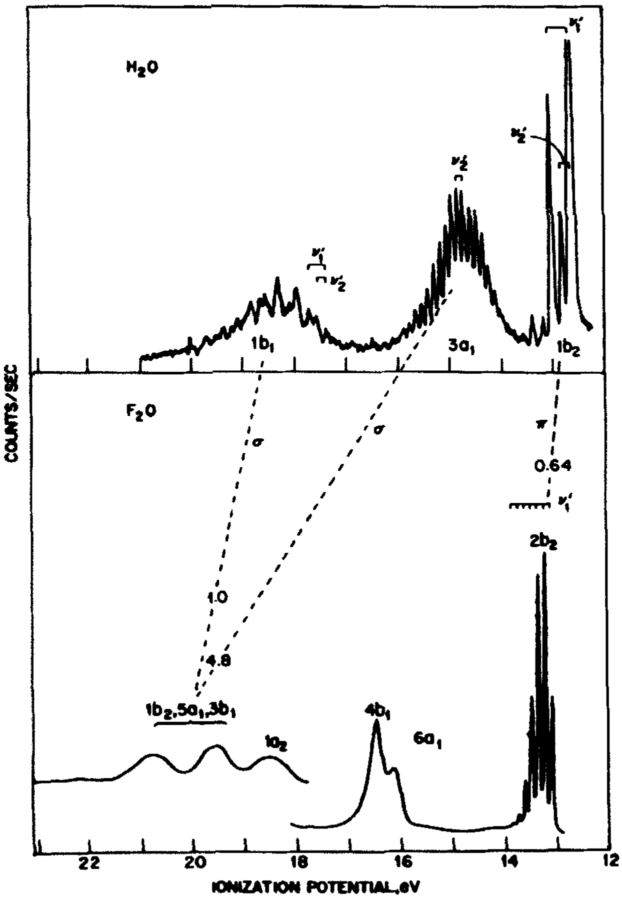


FIG. 6. Photoelectron spectra of H_2O and F_2O. [Reproduced from Brundle *et al. J. Amer. Chem. Soc.* **94**, 1451. Copyright 1972 by the American Chemical Society. Reprinted with permission of the copyright owner.]

perpendicular to the plane of the molecule (b_2). The "extra" orbitals $1b_2$, $1a_2$, $4b_1$, and $6a_1$ are due to the four additional fluorine lone pairs (see below).

Another useful illustration of comparing related molecules is provided by the hydrogen halides. Plots of i.p. for both the π and σ electrons versus the Pauling electronegativity results in a linear correlation (*6b*). The same group has shown by comparison of a large number of complex organic molecules containing halogen, S, N, and O atoms, that characteristic i.p. regions exist for the "lone-pair" electrons on such atoms (*6c*). Such an approach can be very useful with organic compounds with a reasonably constant charge distribution, but in inorganic molecules with varying charge separations it needs to be used with great caution. For instance, the PE spectrum of $Mn(CO)_5I$ exhibits a first i.p. of 8.35 eV (*95*), much closer to that of Mn (7.43 eV) than I (10.4 eV) (*151*). Yet both the observed spin-orbit splitting (*95*) and molecular orbital calculations (*100*) indicate that the topmost orbital in $Mn(CO)_5I$ is iodine "lone pair." This ordering can then be rationalized in terms of the charge separation $Mn^{\delta+}$ $I^{\delta-}$ and d_π–p_π backbonding with the carbonyl ligands, both effects tending to stabilize the metal *d* orbitals. Although Cl, Br, and I "lone-pair" orbital ionizations are usually fairly sharp, this is not true for F; the only sharp band attributable to F "lone-pair" electrons is the first band in the HF spectrum (Section VI, C).

H. ANGULAR DISTRIBUTION OF PHOTOELECTRONS

In general, the distribution of photoelectrons varies with the azimuthal angle to the photon beam, and is characterized by an asymmetry parameter β which can be measured by measuring spectra at different angles to the beam ($\beta = 0$ corresponds to isotropic distribution). The value of β varies between ionization bands in a way which is not yet understood, but this variation means that if a band is a composite of different ionizations, it may be possible to detect this by angular dependence studies. So far this has been demonstrated only for benzene (*43b*), CH_2F_2, and CF_4 (*43c*), but it is probable that angular distribution studies will become more common in the future, and may well be of use for assignment purposes. Values of β have been determined for several molecules (*43b, 43c, 43d, 150a*).

V. Compilation of Photoelectron Spectra

As indicated in the introduction we make no claim that this list is comprehensive. However, we have included examples of all the different types of molecules which have been studied. If a molecule was studied by both retarding grid and electrostatic deflection analyzers, normally only the most recent and best resolved spectrum is referenced. This will allow the reader to trace the earlier references if necessary. The compilation covers spectra published up to May 1972 and is given in Table I.

TABLE I

COMPILATION OF REFERENCES TO INORGANIC COMPOUNDS STUDIED BY PHOTOELECTRON SPECTROSCOPY

Compound	Ref.	Compound	Ref.
	Diatomics		
H_2	*3, 51, 180*	HX	*16, 29* (F), *184* (Cl); *137* (F, Cl, Br, I); *180* (Cl, Br, I)
N_2	*48, 85, 139, 166a, 174, 180*		
$O_2(^3\Sigma_g^-)$	*23, 48, 85, 86, 155, 167, 180*	SO	*128*
$O_2(^1\Delta_g)$	*126, 127*	CS	*129, 129a, 132*
X_2	*52, 164* (F_2, Cl_2, Br_2, I_2); *98* (Cl_2, Br_2, I_2)	ClF	*1, 70*
		BrF	*70*
CO	*48, 85, 180*	IX	*98, 164* (Cl, Br)
NO	*49, 87, 88b, 180*	TlX	*15* (Cl, Br, I)
	Triatomics		
H_2O	*4, 38, 166, 166a, 180*	NSF	*59, 71, 83*
H_2S	*74, 75, 82, 84, 103, 166*	NF_2	*53*
H_2Se	*74, 166*	ClO_2	*54*
H_2Te	*166*	X_2O	*38* (F), *55* (F, Cl)
CO_2	*28, 180*	HCN	*180*
CS_2	*28, 49b, 180*	XCN	*114, 122, 134*
COS	*28, 49b, 180*	KrF_2	*36*
N_2O	*28, 49b, 180*	XeF_2	*32, 26*
NO_2	*30, 88a, 156*	HgX_2	*91* (Cl, Br, I)
SO_2	*90, 180*	PbX_2	*14* (Cl, Br, I)
O_3	*180*		
	Tetraatomics		
H_2CO	*180*	BX_3	*11, 163* (F, Cl, Br, I); *135* (F)
X_2CO	*38* (F), *177* (F, Cl, Br); *47* (Cl)		
		NX_3	*12* (F), *163* (F, Cl)
Cl_2CS	*47*	PX_3	*12, 119, 150, 153* (F); *163* (F, Cl, Br)
HN_3	*65, 92*		
HNCO	*65, 92*	AsX_3	*163* (F, Cl)
HNCS	*65, 92*	*trans*-N_2F_2	*38*
NH_3	*23, 166, 180, 185*; *113* (assign. disc.)	P_4	*37, 96b*
		XF_3	*70* (Br, Cl)
PH_3	*24, 150, 166*	$(CN)_2$	*180*
AsH_3	*24, 166*	SOX_2	*47a*
SbH_3	*166*		

TABLE I—*continued*

Compound	Ref.	Compound	Ref.
Pentaatomics			
CH_4	*33, 165, 168, 180*	$HSiCl_3$	*104*
SiH_4	*165, 168*	CX_4	*163, 180* (F, Cl, Br); *10, 43c* (F, Cl); *33, 41* (F); *107* (Cl, Br)
GeH_4	*63, 165, 168*		
SnH_4	*168*		
CH_3X	*43c, 163, 180* (F, Cl, Br, I); *170* (Cl, Br, I); *33, 168* (F)	SiX_4	*10* (F, Cl), *41* (F), *107* (Cl, Br)
		GeX_4	*10* (F, Cl), *168* (Cl, Br), *63* (F)
SiH_3X	*64* (F, Cl, Br, I), *104* (F, Cl)		
		SnX_4	*10* (F, Cl), *107* (Cl, Br)
GeH_3X	*64* (F, Cl, Br, I)	TiX_4	*107* (Cl, Br), *61* (Cl)
CH_2X_2	*163, 180* (F, Cl, Br, I); *43c* (F, Cl); *33, 168* (F)	VCl_4	*61*
		SO_2X_2	*72* (F), *47a* (F, Cl)
SiH_2X_2	*64* (F, Cl, Br, I), *104* (F, Cl)	ClO_3F	*72*
		ONF_3	*12, 105*
GeH_2X_2	*64* (F, Cl, Br, I)	$OPCl_3$	*12*
HCX_3	*180* (F, Cl, Br, I); *163* (F, Cl, Br); *43c* (F, Cl)	C_3O_2	*180, 169a*
		XeF_4	*35*
CF_3X	*33, 168* (F); *162a* (Br, I)		
Hexaatomics			
CH_3HgX	*91* (Cl, Br, I)	BH_3CO	*141*
N_2H_4	*21, 166a*	CH_3SH	*66, 106*
BrF_5	*73*	SiH_3SH	*66*
IF_5	*73*	GeH_3SH	*66*
Heptaatomics			
SF_6	*73, 163, 180*	SF_5Cl	*73*
SeF_6	*163*	CH_3X	*92* (NCO, NCS), *65* (NCO, NCS, N_3)
TeF_6	*163*		
UF_6	*163*	SiH_3X	*65* (NCO, NCS, N_3)
XeF_6	*35*	GeH_3X	*65* (NCO, NCS, N_3)
Boron Compounds			
BX_3	*11, 132a, 163* (F, Cl, Br, I), *135* (F)	$(BXNY)_3$	*18* (X/Y: H/H, H/CH_3, CH_3/H, Cl/H, CH_3/CH_3, Cl/CH_3, F/CH_3), *142* (X/Y: H/H, F/H), *102* (X/Y: H/H), *144* (X/Y: CH_3/H, H/CH_3)
B_2H_6	*31, 142*		
BH_3CO	*141*		
BH_3NH_3	*141*		
BH_3PF_3	*118*		
B_4Cl_4	*145*		
B_2X_4	*149* (F, Cl)		
$(R_nNH_{3-n})BH_3$	*141* ($n = 0$–3)		

continued

TABLE I—*continued*

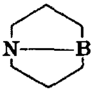
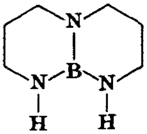
Compound	Ref.	Compound	Ref.
Boron Compounds—continued			
$(CH_3)_2NBX_2$	*19*, *132a* (H, CH_3, F, Cl, Br)	$(CH_2{=}CH)_3B$	*123*
		$(CH_2CH_3)_3B$	*123*
$[(CH_3)_2N]_2BX$	*19*, *132a* (H, CH_3, F, Cl, Br)	$(CH_3)_3NBF_3$	*135*
		$(CH_3)_2NHBF_3$	*135*
$[(CH_3)_2N]_3B$	*19*	$B_2[N(CH_3)_2]_4$	*46*, *132a*
	19		19
Silicon Compounds			
SiH_4	*165*, *168*	SiH_3SH	*66*
SiH_3X	*64* (F, Cl, Br, I), *104* (F, Cl)	$(CH_3)_nSi(CH{=}CH_2)_{4-n}$	*183* ($n = 0, 2, 3$)
		$(CH_3)_nSiCl_{4-n}$	*109* ($n = 0$–4), *20* ($n = 4$)
SiH_2X_2	*64* (F, Cl, Br, I), *104* (F, Cl)	$[(CH_3)_2N]_nSiCl_{4-n}$	*109* ($n = 0, 1, 2, 4$)
$HSiCl_3$	*104*	$[(C_2H_5)O]_nSiCl_{4-n}$	*109* ($n = 0$–4)
SiX_4	*10* (F, Cl), *41* (F), 107 (Cl, Br)	$R(SiR_2)_nR$	*20* ($n = 1$–4)
		$(SiR_2)_n$	*20* ($n = 5, 6$)
		$(MH_3)_2Y$	*66* (M = C, Si, Ge; Y = O, S, Se, Te)
SiH_3X	*65* (NCO, NCS, N_3)		
$Si(CH_3)_3X$	*65* (NCO, NCS, N_3)		
Nitrogen and Phosphorus Compounds			
$(NPF_2)_n$	*25* ($n = 3$–8)	$(CH_3)_nNH_{3-n}$	*56*, *166a* ($n = 1$–3), *135* ($n = 2, 3$)
Sulfur Compounds			
SO	*128*	CH_3SH	*66*, *106*
CS	*129*, *129a*, *132*	SiH_3SH	*66*
H_2S	*74*, *75*, *82*, *84*, *103*, *166*	GeH_3SH	*66*
CS_2	*28*, *49b*, *180*	SF_6	*73*, *163*, *180*
COS	*28*, *49b*, *180*	SF_5Cl	*73*
SO_2	*90*, *180*	$(CH_3)_2S_x$	*106* ($x = 1$), *67* ($x = 1$–3)
NSF	*59*, *71*, *83*	$(CF_3)_2S_x$	*67* ($x = 1$–4)
SO_2X_2	*72* (F), *47a* (F, Cl)	C_6H_5SH	*106*
$(MH_3)_2Y$	*66* (M = C, Si, Ge; Y = O, S, Se, Te)	$C_6H_5CH_2SH$	*106*

TABLE I—*continued*

Compound	Ref.	Compound	Ref.
	Transition Metal Compounds		
TiX_4	*107* (Cl, Br), *61* (Cl)	$RFe(CO)_3$	*76*, *186* (R = dienes and substituted dienes); *77* [$R = C(CH_2)_3$]
VCl_4	*61*	$(\pi\text{-}C_5H_5)_2M$	*180* (Mg, Fe, Cr, Co, Ni), *178* (Fe), *62* (Cr)
$Ni(CO)_4$	*108*, *138*	$(\pi\text{-}C_5H_4CH_3)_2Cr$	*62*
$Fe(CO)_5$	*138*	$(\pi\text{-}C_6H_6)_2Cr$	*99*
$Cr(CO)_6$	*180*	$(\pi\text{-}C_6H_5CH_3)_2Cr$	*99*
$Mo(CO)_6$	*180*	$(\pi\text{-}C_6H_6)(\pi\text{-}C_5H_5)Mn$	*99*
$W(CO)_6$	*180*	$(\pi\text{-}C_6H_6)(\pi\text{-}C_5H_5)Cr$	*99*
$V(CO)_6$	*94*	$(C_3H_5)_2M$	*146* (Ni, Pd)
$M(PF_3)_4$	*108*, *119* (Ni, Pt)		
$M(hfa)_3$[a]	*96a*, *140* (Fe), *140* (Fe, Cr, Co, Al), *143* (Co), *99a* (Sc, Ti, V, Cr, Mn, Fe, Co, Ga)		
$Mn(CO)_5Y$	*95* [Y = H, Cl, Br, I, CH_3, CF_3, $COCF_3$, $Mn(CO)_5$]		
	Zinc and Mercury Compounds		
$(CH_3)_2Zn$	*91*	HgX_2	*91* (Cl, Br, I)
R_2Hg	*91* ($R = CH_3, C_2H_5$)	CH_3HgX	*91* (Cl, Br, I)

[a] hfa = enolate anion of hexafluoroacetylacetone.

VI. Discussion of Selected Results

A. THE HALOGENS

The photoelectron spectra of the diatomic halogens (X_2) have been reported by three groups (*52*, *98*, *164*). The spectra are presented in Fig. 7 and illustrate several features of interest. First, three band systems are observed for each molecule: ${}^2\Pi_g$, ${}^2\Pi_u$, and ${}^2\Sigma_g{}^+$.* The order and number of bands is exactly that predicted from simple molecular orbital theory for a homonuclear diatomic (*57*), involving a relatively small amount of *s–p* mixing. Second, both the ${}^2\Pi_g$ and ${}^2\Pi_u$ bands are split by spin-orbit interaction, increasing with atomic number. As the molecular weight

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* The ${}^2\Sigma_g{}^+$ state of $F_2{}^+$ has not been definitely observed, but may be at about 21 eV (*52*, *164*).

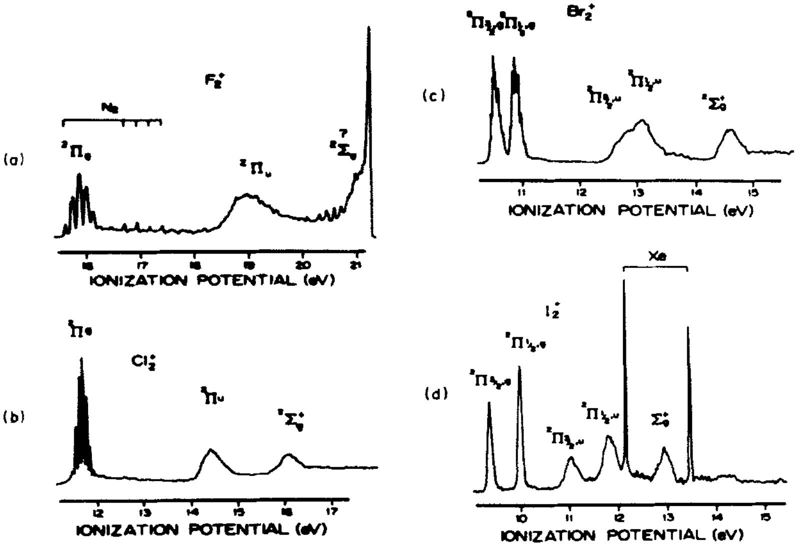

FIG. 7. The photoelectron spectra of the halogens. [Reproduced from Cornford *et al.* (*52*) with permission of the American Institute of Physics.]

increases, the stretching frequency decreases. This factor combined with the opposite sequence for spin-orbit interaction results in $\zeta < \omega_e'$ for F_2^+, $\zeta = \omega_e'$ for Cl_2^+, and $\zeta > \omega_e'$ for Br_2^+ and I_2^+ as shown in Fig. 8 for the X $^2\Pi_g$ states.

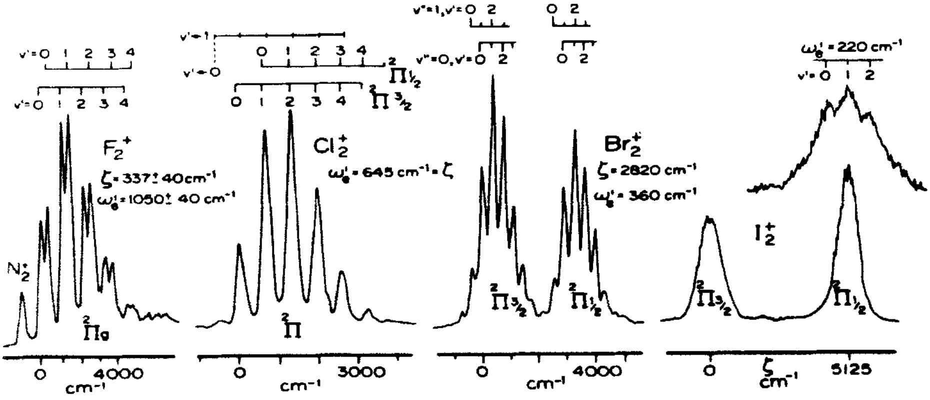

FIG. 8. Spin-orbit splittings and vibrational levels in the ground states of the halogen molecule ions. [Reproduced from Cornford *et al.* (*52*) with permission of the American Institute of Physics.]

Table II illustrates a comparison of bond lengths and vibrational frequencies for the molecular ground state and the lowest ionic state of each molecule. The bond length shortening and the increase in vibrational stretching frequency for each of the molecules indicate that the X $^2\Pi_g$ state of the ion has a stronger bond than the molecular ground state. This result is exactly that predicted on the basis of molecular orbital theory which indicates that the uppermost occupied orbital is π antibonding. The antibonding character is greatest for F_2, and this is probably at least partly responsible for the low dissociation energy of F_2 (Section VI, D).

TABLE II

PHOTOELECTRON AND SPECTROSCOPIC DATA FOR THE HALOGEN X $^1\Sigma_g^+$ AND X $^2\Pi_g$ STATES[a]

Halogen	r_e(Å) X_2	r_e(Å) X_2^+	ω_e(cm^{-1}) X_2	ω_e(cm^{-1}) X_2^+
F_2:F_2^+	1.435	1.326	892.1	1054.5
Cl_2:Cl_2^+	1.988	1.892	564.9	645.6
Br_2:Br_2^+	2.283	~2.2	323.2	360 ± 40
I_2:I_2^+	2.666	—	214.6	~220

[a] After Cornford *et al.* (*52*).

Most of the data given in Table II was obtained from optical spectroscopy, which is of inherently higher resolution than that obtainable from photoelectron spectroscopy. Approximate values of the bond lengths in the X $^2\Pi_g$ states can also be estimated from the Franck–Condon envelopes and in all cases the results are consistent with those obtained from optical spectroscopy (*52, 164*).

Reference to Fig. 7 illustrates that in each case the $^2\Pi_u$ band is broader than the corresponding $^2\Pi_g$ band. This is a good indication that the $^2\Pi_u$ states result from electron ejection out of strongly bonding orbitals. In fact, simple molecular orbital theory predicts the π_u orbital to be strongly bonding. The only vibrational progression observed in a $^2\Pi_u$ state was by Potts and Price (*164*) for Cl_2^+. Their value of 323 ± 20 cm^{-1} corresponds to a decrease from the molecular value of 564.9 cm^{-1} (Table II), indicative of the strong bonding character for this orbital.

Two other features are of general interest in Fig. 8. First is the presumed equal value (645 cm^{-1}) of the spin-orbit splitting and vibrational spacing for the $^2\Pi_g$ state of Cl_2^+. This is supported nicely by the PE spectra of HCl (*137*), CH_3Cl (*170*), and ClF (*70*), where the observed spin-orbit splitting is 645, 630, and 630 cm^{-1}, respectively. Because this spin-orbit splitting is predominantly due to the chlorine atom, it is expected to be nearly identical in all cases. Second, the presence of "hot" bands ($\nu'' = 1$, i.e., vibrationally excited molecules) is clearly observed on the low energy side of the spectra for both Cl_2 and Br_2 (Fig. 8). Hot bands can normally be assigned as such simply on the basis of the general shape of the Franck–Condon envelope, but experimental proof would be provided only by variation of the sample temperature, and no such temperature-dependent studies have yet been made. Failure to assign hot bands properly can result in incorrect assignments of the adiabatic i.p. and the vibrational progressions (*59*, *83*).

Fortunately, the assignment for the halogens is on a firmer foundation than for most molecules because optical spectra have been observed for the two lowest ionic states of both F_2^+ and Cl_2^+, and these show that both states in these species are of $^2\Pi$ character (*161*, *124*). The calculated molecular orbital sequence is not as straightforward as the intuitive ordering mentioned above: $\pi_g > \pi_u > \sigma_g$. Even the most sophisticated *ab initio* calculations (*133*, *181*) have produced the sequence $\pi_g > \sigma_g > \pi_u$. However, the most recent calculations on F_2^+ (*7*) seem to agree that the two lowest ionic states are $^2\Pi_g$ and $^2\Pi_u$. This simple example illustrates that calculations should not always be taken at face value in making assignments. This caution holds especially for semiempirical types of calculations. Comparison of the diatomic interhalogen spectra with those of the halogens is straightforward (*70*, *98*, *164*).

With very small molecules, particularly diatomics and triatomics, there is often information available from high-resolution visible and UV spectra which can be used to confirm PE assignments. Conversely PE data can be used to help the assignment of such high-resolution UV–visible gas phase spectra, e.g., H_2S (*82*). Recently there has been considerable interest in the dihalogen cations as isolable chemical species, and PE data for Br_2 have been used to assign the (low-resolution) solution spectrum of Br_2^+ in the visible region and to confirm the Raman spectrum assignment (*89*).

B. N_2, CO, AND CS AND THEIR BONDING CAPABILITIES TOWARD METAL COMPLEXES

An elementary molecular orbital approach to the bonding in N_2 suggests the electron arrangement, ignoring core levels, of $(\sigma_g 2s)^2$ $(\sigma_u 2s)^2 (\sigma_g 2p)^2 (\pi_u 2p)^4$ with a triple bond from cancellation of the bonding and antibonding characters of $\sigma_g 2s$ and $\sigma_u 2s$. However, it is widely appreciated that this simple picture has to be modified by the introduction of s–p mixing leading to a stabilization of $\sigma_g 2s(1\sigma_g)$ and $\sigma_u 2s(1\sigma_u)$

and a destabilization of $\sigma_g 2p$ ($2\sigma_g$) (*57*). The PE spectrum shows that, in fact, $1\sigma_u$ and $2\sigma_g$, rather than being antibonding and bonding, respectively, are almost nonbonding with very little vibrational excitation in the corresponding bands (*180*), while ionization of $1\pi_u$ gives a long vibrational progression with a smaller interval than in the molecule (Table III), as expected for a strongly bonding orbital. The great stabilization of $1\sigma_g$ and the presence of configuration interaction states (Section III, B) in this region have made detection of this orbital difficult in photoelectron spectra, but it has recently been observed at about 36.5 eV (*162b*, *166a*) confirming the earlier observations by ESCA (*175*).

TABLE III

PHOTOELECTRON AND SPECTROSCOPIC DATA FOR N_2, CO, AND CS[a]

Molecule	Electronic state	Vertical i.p./eV	Vibrational frequency[b] (cm^{-1})
N_2	X $^1\Sigma_g^+$	—	2331
N_2^+	X $^2\Sigma_g^+(2\sigma_g)^1$	15.60	2175
N_2^+	A $^2\Pi_u(1\pi_u)^3$	16.98	1850
N_2^+	B $^2\Sigma_u(1\sigma_u)^1$	18.78	2373
CO	X $^1\Sigma^+$	—	2143
CO^+	X $^2\Sigma^+(3\sigma)^1$	14.01	2184
CO^+	A $^2\Pi(1\pi)^3$	16.91	1535
CO^+	B $^2\Sigma^+(2\sigma)^1$	19.72	1678
CS	X $^1\Sigma^+$	—	1272
CS^+	X $^2\Sigma^+(3\sigma)^1$	11.33	1330
CS^+	A $^2\Pi(1\pi)^3$	12.9_5	980
CS^+	B $^2\Sigma^+(2\sigma)^1$	16.0_6	840

[a] Data from Refs. *116*, *129*, *129a*, and *180*.

[b] Table 3.2 of Ref. *180* contains an error in that they have not employed $\nu = \omega_e - 2\omega_e x_e$ for the molecular frequencies.

In comparing CO with N_2, the effect of the difference in atomic orbital energies is that 3σ, corresponding to $2\sigma_g$ of N_2, becomes largely localized as a carbon lone pair, with a correspondingly lower i.p. than in N_2, but still with very little vibrational excitation. The 1π orbital is very similar in ionization behavior to that in N_2, but 2σ is more stable than $1\sigma_u$ of N_2, because of its mainly O character, and it has acquired some bonding character as shown by the reduction in vibrational frequency (Table III). 1σ has been observed at about 37 eV by both PES (*162b*) and ESCA (*175*). CS has only recently been observed as a semitransient species produced in discharges (*129*, *129a*, *132*); in addition to ionizations from one-electron transitions there is an intense configuration interaction band (Section III, B). The lower electronegativity of S means that all i.p. are less than the corresponding ones in CO, and this is particularly true of the S-localized 1π and 2σ; 2σ has considerably more bonding character than in CO as indicated by a long vibrational progression on the third PE band and by the frequency reduction (Table III).

The bonding of these species to metals is often discussed in terms of donation to metal from the ligand and π "back donation" from the metal. If the basic assumption is made that electron donation is equivalent to partial ionization, then the behavior of the ligand on ionization may give information pertinent to a discussion of the bonding to metal atoms. Similarly, the effect on the ligand of π back donation may be related to the effect of exciting an electron to the π^* orbital (*159*).

Examination of the first i.p. shows that CS is expected to be the best donor since its i.p. is lowest (11.33 eV). This allows a larger interaction of the lone pair on CS with empty metal orbitals. Furthermore, σ donation is expected to lead to a CS stretching frequency *increase* since ν(CS) is 1330 cm^{-1} in the $\tilde{X}\ {}^2\Sigma^+$ state (*129a*) compared to 1272 cm^{-1} in the molecular ground state (Table III). Although the π orbital of CS occurs at the low i.p. of 13 eV, its interaction with the metal is expected to be less important since it is more localized on the sulfur atom (*171*).

Comparing CO and N_2 we see that CO is expected to be a better σ donor since its first i.p. occurs at 14.01 versus 15.60 eV for N_2. This energetic factor will be further enhanced by the fact that the lone pair on CO is fairly localized on the carbon atom, whereas in N_2 the σ_g orbital must be equally distributed over both nitrogen atoms by symmetry. The associated stretching frequencies in the $\tilde{X}\ {}^2\Sigma^+$ states show that σ donation will result in a stretching frequency *decrease* in N_2 and an *increase* in CO. This fact alone could account for the observation that the CO stretching frequency in $NiCl_2CO$ and CO adsorbed on ZnO occurs at a *higher* frequency than in free CO (*27*, *69*). Likewise, the large ν(NN) decrease observed (*101*) in transition metal dinitrogenyl complexes can be compared to the large drop in ν(NN) in going from free N_2 to $\tilde{X}\ {}^2\Sigma_g{}^+$ of $N_2{}^+$.

An indication of any modifications to this discussion of σ effects by π back donation may be obtained from the spectroscopic data for the lowest molecular singlet states in which an electron is excited from the highest occupied σ level to the lowest unoccupied π level, although several states should be considered (*154*). In this lowest ${}^1\Pi$ state the vibration frequencies are reduced for all three molecules, compared to the ground state, and the percentage reductions are 29 (N_2), 31 (CO), and 17 (CS) (*116*). Thus, any back donation will have least effect in CS, so it is not surprising that CS complexes have a higher vibration frequency than the free molecule. [It has been suggested that, in fact, CS is a better π acceptor than CO (*171*).]

The effects of π back donation in N_2 may well be similar to those in CO; certainly the observed larger frequency shifts for N_2 complexes compared to CO complexes can be rationalized entirely in terms of σ effects.

C. A COMPARISON OF THE ISOELECTRONIC SERIES Ne–HF–H_2O–NH_3–CH_4

Theoretical correlation of orbitals based on the "united atom" approach has been employed for many years; the photoelectron spectra of the species listed above are shown in Fig. 9 and they provide a very interesting correlation from an experimental point of view (*166*).

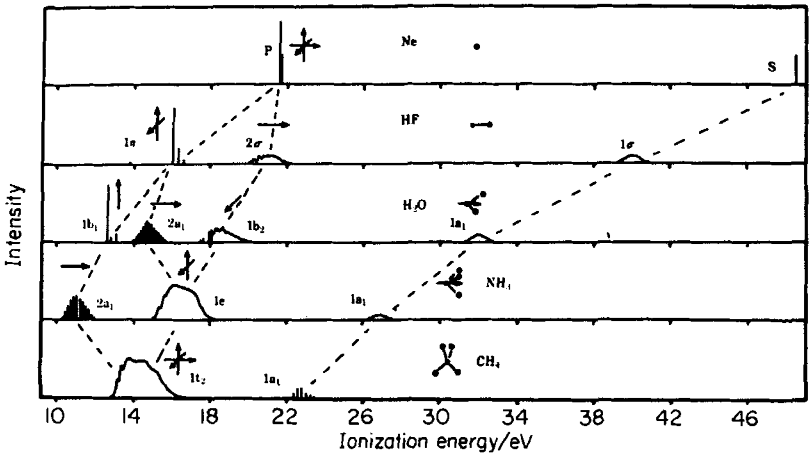

FIG. 9. Diagrammatic photoelectron spectra of hydrides "formed" by proton withdrawal from neon. [Reproduced from Potts and Price (*166*) with permission of the Royal Society.]

As the central atom nuclear charge decreases the 2*s* orbital of neon is seen to decrease continuously in i.p. to the $1a_1$ orbital of CH_4. The orbitals derived from the *p* electrons suffer a less drastic change in energy owing to their larger participation in bonding and shielding from the nucleus by the *s* electrons. The $2p^5$ shell of Ne^+ is split into two components ($^2P_{3/2}$, $^2P_{1/2}$) by virtue of spin-orbit interaction. The corresponding spin-orbit splitting in HF (0.03 eV) is too small to be shown in Fig. 9. No spin-orbit splitting is possible in the first bands of H_2O and NH_3 since these orbitals are nondegenerate, and although spin-orbit interaction is possible in the $1t_2$ band of methane, it is expected to be very small and will be masked by the complex vibrational progression (*166*) and Jahn–Teller effects.

The vibrational structure in $2a_1$ bands of H_2O and NH_3 correspond to the HOH bending and NH_3 "umbrella" modes, respectively. This is expected by virtue of the symmetry of the orbitals which is depicted by the arrows in Fig. 9. The production of a broad band is here related to the "bonding character" of the orbital in that the electron removed contributes to the bond *angles* but not greatly to the bond *distances.* Generally, the observation of a broad unresolved band indicates that the molecular geometry changes upon ionization, but only when vibrations can be resolved and assigned is it possible to decide whether bond distortions or angle deformations are involved. The particular examples here are clearly related to the current ideas of determination of molecular geometry by lone pairs. However, it should be pointed out that the electron pairs of the Gillespie–Nyholm theory correspond to localized orbitals which are obtained from linear combinations of the delocalized molecular orbital "observed" in PES. Discussion of the $2a_1$ orbital of NH_3, for instance, as a "lone pair" implicitly assumes that the three localized bond pairs are made up from $1e$ and $1a_1$ and that the localized lone pair is almost identical with $2a_1$, with little mixing in of the other orbitals. The observations on Lewis acid–base systems reported in Section VI, G seem to indicate that at least in some systems it is reasonable to discuss the lone-pair orbital independently of the other orbitals.

D. EXPERIMENTAL AND THEORETICAL POTENTIAL ENERGY CURVES FOR THE $^2\Sigma^+$ STATE OF HF^+, AND THE BOND DISSOCIATION ENERGY OF F_2

The photoelectron spectrum of HF provides an ideal example of the high precision data obtainable from careful work. In a pair of papers which appeared back-to-back in *Chemical Physics Letters*, Julienne, Krauss, and Wahl (*130*) compare their Hartree–Fock calculations to the PE spectrum of Berkowitz (*16*). A fuller exposition of some of the background to the following discussion is provided in the paper of Berkowitz *et al.* on the photoionization of HF and F_2 (*13*).

A point of particular interest is the HF dissociation energy $D_0°$ (HF), which can be directly related to $D_0°$ (F_2):

$$D_0^\circ\,(F_2) = 2D_0^\circ\,(HF) + 2\Delta H_f^\circ\,(HF) - D_0^\circ\,(H_2)$$

The previously accepted value for D_0° (F_2) of 1.59 eV was apparently called into question by photoionization mass spectroscopic measurements on F_2, HF, and ClF, all of which indicated a value of 1.34 eV (*78*, *79*). This work has been criticized, and new measurements on F_2 and HF indicate a value of 1.59 eV again (*13*). A final decision can be made with the aid of the photoelectron study and the calculations.

Removal of an electron from the F $2p_\pi$ orbital of HF produces the ground state of HF^+, $\tilde{X}\ ^2\Pi$, with the very small amount of vibrational excitation seen in Fig. 9, so the dissociation limit of HF^+ is inaccessible through this photoelectron process. However, the dissociation limit of the $^2\Sigma^+$ state produced by removal of an electron from the H–F bonding orbital gives the same products, $H^+ + F\ (^2P)$: the only difference is that $^2\Sigma^+$ correlates with $F(^2P_{1/2})$, and $\tilde{X}\ ^2\Pi$ with $F(^2P_{3/2})$. From the value of 1.34 eV for $D_0^\circ(F_2)$ a value for $D_0^\circ(HF)$ can be calculated and, hence, from the i.p. of H and the spin-orbit splitting in F, a dissociation limit for HF^+ ($^2\Sigma^+$) of 19.37 eV is predicted. The critical point in this discussion is that the photoelectron spectrum of HF shows vibrational states *above* this limit, the last at 19.505 eV. Although there is a small potential energy barrier to dissociation in $^2\Sigma^+$, the agreement of the calculations and the PE spectrum is such that this barrier height is very probably about 70 meV, whereas, the limit of 19.37 eV would require a barrier much greater than 130 meV. Thus, the value of 1.34 eV for the dissociation of F_2 is unacceptable.

The above discussion has focused on only part of the data obtained in the HF study. Altogether, Berkowitz (*16*) obtained values for ω_e, $\omega_e x_e$, D_e, and r_e for both $\tilde{X}\ ^2\Pi$ and $^2\Sigma^+$ states of HF^+ and an estimate for the $^2\Pi_{1/2}$–$^2\Pi_{3/2}$ spin-orbit splitting.

E. TRANSITION METAL COMPOUNDS

A glance at Table I will show that the majority of transition metal compounds studied are either organometallic or carbonyl compounds. These are almost the only compounds which have sufficient vapor pressure to be studied at ambient temperature or slightly above. In this section we pick out some features of general interest, and then discuss a few systems in more detail.

A comparison of the PE spectra of $TiCl_4$ and VCl_4 shows one extra weak band at low i.p. in the latter which is assigned to the single 3*d* electron. The rest of the VCl_4 spectrum also shows some band splittings which are probably due to spin coupling with this single electron (*61*). A detailed analysis of the spectra of first-row transition metal tris complexes with hexafluoroacetylacetone (hfaH) shows that as the atomic number of the metal increases there is a rapid increase in i.p. of the *d* electrons, so that with the later ones the ionization is in the same region as the first ligand ionization (*99a*). In contrast to VCl_4 (*61*) and $V(CO)_6$ (*94*), no spin splitting of the ligand ionizations is observed in these complexes. A similar increase in metal 3*d* orbital i.p. with increase in atomic number has been noted in the closed shell metal carbonyls (*138*), but there is no such simple variation in metal bis-π-cyclopentadienyl compounds (*99a*). Few studies of vertical comparisons within a group of the Periodic Table have yet been reported, but the spectra of $Ni(PF_3)_4$ and $Pt(PF_3)_4$ and of $Ni(C_3H_5)_2$ and $Pd(C_3H_5)_2$ have been interpreted as showing a greater splitting of the *d*-type orbitals in the compounds of the heavier metals (*119*, *146*).

In metal carbonyls the ligand i.p. begins at about 13 eV, appreciably less than that of free CO, 14.01 eV. This trend is not reproduced by calculations (*44*, *45*, *121*) and it has been proposed that there is a greater electron rearrangement on ionization in complexed CO than in free CO, i.e., that Koopmans' theorem cannot be applied here (*121*). A comparison of $Ni(PF_3)_4$ with $Ni(CO)_4$ suggests that PF_3 is a better π acceptor than CO (*108*).

Evans, Green, and Jackson (*99*) have published an interesting article on the PE spectra of $(\pi\text{-}C_6H_6)_2Cr$, $(\pi\text{-}C_6H_5CH_3)_2Cr$, $(\pi\text{-}C_6H_6)(\pi\text{-}C_5H_5)Mn$, and $(\pi\text{-}C_6H_6)(\pi\text{-}C_5H_6)Cr$. Each of these molecules has the formal d^6 configuration except the last which is d^5. Hence, the first three have the same metal configuration as ferrocene. In all cases the low i.p. bands are assigned to the "metallic" *d* electrons. In contrast to ferrocene though, the closed shell molecules exhibit an intensity ratio in the low energy i.p. of 1 : 2 (increasing i.p.) compared to the opposite sequence for ferrocene. It is concluded that the *d* orbital sequence is ... $(a_{1g})^2\,(e_{2g})^4$ in ferrocene, but ... $(e_{2g})^4\,(a_{1g})^2$ in the bis-π-arene compounds. This switch over in energy can be rationalized in terms of the valence state i.p. of the metals. The a_{1g} orbital follows the same trend as the valence state i.p. since it is relatively nonbonding, as indicated by the sharp PE band. However, the e_{2g} orbitals show less shift with metal atom because this orbital contains more ligand character. The bonding character of the e_{2g} orbital is exhibited by its greater width (*99*).

In these arene compounds the "metallic" i.p. occurs at about 6 eV, whereas the ligand i.p. does not begin until nearly 9 eV. Evans *et al.* (*99*) have pointed out the remarkable similarity between the ligand portion of the PE spectrum for the bis-π-arene complexes and free benzene itself. The reviewers note that this resemblance is much more marked than in the CO, $Cr(CO)_6$ spectra and may be due to less ligand–ligand interaction in the bis-π-arene complexes. The alternative explanation, of weaker metal–ligand interaction, is not borne out by the strength of the metal–ligand bond, the low i.p. of the bis-π-arene compounds or the substantial split of the "metal" e_{2g}, a_{1g} orbitals (up to 1 eV).

As the last part of this discussion on transition metal compounds, we turn our attention to the $Mn(CO)_5X$ compounds studied by Evans *et al.* (*95*). We have already indicated in Section IV, G how the first i.p. in the case of the halides was interpreted as electron ejection from a mainly halogen orbital. This is in direct contrast to the above discussion on VCl_4, metal carbonyls, $M(\pi\text{-}C_5H_5)_2$, and $M(\pi\text{-}C_6H_6)_2$ in which the first i.p. was assigned to the metal *d* electrons.

The rest of the ionization bands before 12 eV were assigned to the metal *d* electrons, the configuration d^6 being split into $b_2{}^2 + e^4$ components by the C_{4v} symmetry. This leaves no ionization assigned to the a_1 Mn–(X*np*) bonding orbital; it has been assumed that the ionization due to this orbital lies underneath the broad region of ionization from the CO ligands (*95*). In the case of X = Cl, this means a splitting between the Cl p_π and Cl p_σ (bonding to Mn) of nearly 5 eV. Calculations (*100*) on $Mn(CO)_5Cl$ had predicted the p_σ–p_π splitting to be only about 2 eV, placing the i.p. of the M–Cl bond in the same region as the metal 3*d* electrons. While the earlier interpretation (*100*) tended toward a fault in the calculations, the reviewers feel that sufficient data exist now to support a p_σ–p_π splitting of only 2 eV.

The chlorine p_σ–p_π energy difference can be obtained from the published spectra of several compounds where the assignments are more certain. The following rough values are obtained* in decreasing order: ClF (5.5 eV), HCl (3.8 eV), TlCl (3.5 eV), CH_3Cl (3.1 eV), SiH_3Cl (1.8 eV), SF_5Cl (2 eV), and ICl (1.5 eV). Hence, we see that the chlorine p_σ–p_π splitting depends drastically on the attached group and may be less than 2.0 eV in some cases. We would not expect the chlorine p_σ–p_π energy difference to be greater in $Mn(CO)_5Cl$ than in SF_5Cl, so it is probable that the Mn–X bonding orbital ionization is in the metal *d* ionization region.

Recently spectra of $Mn(CO)_5CH_3$ and $Mn(CO)_5CF_3$, obtained by the same group but with better definition than in Ref. 95 have been presented, together with some calculations, and on the basis of these calculations it is proposed that the Mn–C σ-bonding orbital ionization also lies in the region of the metal "*d*" ionizations (*111*). An argument similar to that used for the Cl p_σ–p_π splitting may also be applied to the CH_3 group, since the *e* and higher-lying a_1 orbitals of CH_3 correspond approximately to p_π and p_σ of Cl. Values of the separation $\Delta(a_1 - e)$ for CH_3 in various compounds are CH_3–F (4.0 eV), CH_3–H (0 eV), CH_3–Cl (−1.0 eV), CH_3–Br (−1.6 eV), CH_3–I (−2.3 eV), and CH_3–$Mn(CO)_5$ (−3.5 eV) if the

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* From the papers referred to in Table I.

reassignment (*111*) is accepted. The inversion of a_1 and e for CH_3 as the substituent changes is due to the fact that the e orbital has a large H atom component and so is less sensitive to the substituent. The above sequence follows the substituent i.p. order quite well, but the earlier assignment would probably give a zero or positive value, so again it seems probable that the Mn–ligand bonding orbital is in the *d* ionization region. Since the CF_3 C–F bonding orbital ionization energies have not been identified, we use the F lone-pair e orbitals to compare with the C–Mn bond orbital. Using the new assignment for $CF_3Mn(CO)_5$, values for the difference $\Delta(a_1 - e)$ are CF_3–H (−1.4 eV), CF_3–Br (−2.2 eV), CF_3–I (−2.8 eV), and CF_3–$Mn(CO)_5$ (−5.3 eV), which again is an intuitively reasonable sequence. It seems probable that in all the compounds containing $Mn(CO)_5$ the bonding orbital to the substituent has a similar i.p. to the metal *d* electrons. The importance of this conclusion is that the earlier work suggested that the methyl group was a strong π acceptor; this new assignment (*111*) removes any need to postulate π-acceptor properties for CH_3.

F. EVIDENCE FOR OUTER *d* ORBITAL INVOLVEMENT

One of the aspects of chemical bonding which inorganic chemists find interesting is the possible involvement of outer *d* orbitals in compounds containing Si, Ge, P, S, Cl, Kr, and Xe or any other element with empty low-lying *d* orbitals. Unfortunately, outer *d* orbital involvement in the occupied molecular orbitals is not a direct physical observable and can only be inferred by making certain logical deductions.

The above discussions on energy level trends in molecules were inferences on the basis of Koopmans' theorem, so in making deductions about *d* orbital involvement we must keep in mind that we are one more step removed from the primary i.p. data. As with the conclusions drawn from other physical methods, a controversy concerning the importance of *d* orbitals has developed. In this short review we only attempt to indicate the range of the discussion, but for details of the arguments the original papers must be consulted.

In a series of three papers (*64–66*) Cradock and co-workers have examined a total of forty-six compounds, mainly involving the CH_3, SiH_3, and GeH_3 groups. By examining i.p. trends of electrons belonging predominantly to the attached group they conclude that outer *d* orbital involvement is important for silyl- and germyl-containing compounds. On the basis of calculations Hillier and co-workers (*110*, *120*) believe that *d* orbital involvement at the sulfur atom aids in the assignment of the PE spectrum of SO_2. However, employing a slightly larger *s*, *p* basis set, the assignment of the NSF spectrum has been achieved without involving *d* orbitals (*71*).

Possible *d* orbital involvement does not appear to be critical for the interpretation of PE spectra of ClF (*70*), ClF_3 (*70*), ClO_2 (*54*), Cl_2O (*55*), KrF_2 (*36*), XeF_2 (*32*), XeF_4 (*35*), XeF_6 (*35*), $(CH_3)_nSiCl_{4-n}$ ($n = 0$–4) (*109*), P_4 (*37*), and several sulfur-containing organic compounds (*106*). However, interpretations invoking *d* orbitals have been employed for vinyl-silicon compounds (*183*), $(NPF_2)_n$ ($n = 3$–8) (*25*), PF_3 (*12*, *150*), PF_3O (*12*, *105*), PF_3BH_3 (*118*), SiF_4 (*10*, *41*), and SF_6 (*73*). As can be seen, no clear trend is emerging and the argument may be developing into one of semantics. It has been suggested that a large enough *s*,*p* basis set (*36*, *70*, *71*) can obviate the need for invoking *d* orbitals. All the published calculations on SF_6 indicate the uppermost occupied orbital to be e_g if S 3*d* orbitals are not included. The PE spectrum can only be rationalized if the first i.p. is assigned to a t_{1g} orbital (*73*), a result which is readily obtained in the calculations when S 3*d* orbitals are included.

Two research groups (*64*, *104*) have examined the halosilanes and both

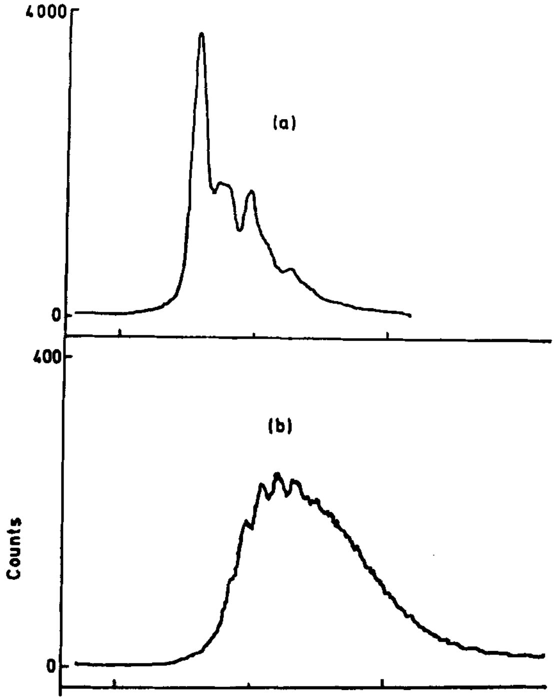

FIG. 10. The first band in the photoelectron spectrum of CH_3Cl (a) and SiH_3Cl (b). [Reproduced from *J. Chem. Soc.*, *D*, 57 (1971) with permission.]

conclude, but for different reasons, that by comparison with the analogous carbon compounds, *d* orbital involvement is evident. The spectra of CH_3Cl and SiH_3Cl (Fig. 10) illustrate some of the pertinent data. Cradock and Whiteford (*64*) conclude that *d* orbital involvement is the most likely explanation to rationalize the shift to higher i.p. of the first band (halogen lone pair). This shift is exactly the opposite of that predicted on electronegativity considerations. Also the first band is broader in the SiH_3Cl spectrum than in CH_3Cl indicating more bonding character in the orbital. In contrast, Frost *et al.* consider that these effects could be due to the antibonding interaction of the occupied Cl p_π and SiH_3 *e* orbitals, and present calculations which support this (*104*). However, by studying the complete series SiH_nCl_{4-n} they show that the effects of mixing the halogen orbitals with other orbitals may be allowed for, and that when allowance is made there is still a stabilization of the halogen i.p. relative to those in the corresponding carbon compounds. This is most reasonably interpreted as due to Si 3*d* orbital involvement, but, of course, the same effects are produced by participation of Si 4*s*, Si 4*p*, etc.

G. LONE-PAIR INTERACTIONS IN LEWIS ACID–BASE ADDUCTS

The transition metal compounds $Cr(CO)_6$, $Ni(CO)_4$, and $Ni(PF_3)_4$ can be considered in the Lewis acid–base sense, but these have already been discussed in Section VI, E. We now discuss the more conventional adducts such as PF_3BH_3, BH_3CO, ONF_3, OPF_3, R_3NBF_3, and R_3NBH_3.

Although much can be learned by an examination of trends in all the energy levels, we concentrate our attention here on the change in energy of the donor lone pair upon complexation. As expected, the donor lone pair is stabilized and the amount of stabilization is ONF_3 (3.15 eV), OPF_3 (3.38 eV), NH_3BH_3 (3.07 eV), $(CH_3)_2NH\text{–}BF_3$ (3.23 eV), $(CH_3)_3N\text{–}BF_3$ (3.74 eV), PF_3BH_3 (0.3 eV), and BH_3CO (0.1 eV) (Table I). In each case the stabilization amounts to 3–4 eV except for PF_3BH_3 and BH_3CO, where it is much smaller. This effect has been ascribed to back donation from the BH_3 *e* orbital into empty low-lying π orbitals on the donor ligand (*118, 141*). However, at least for BH_3CO, the effect may also be due to breakdown of Koopmans' theorem (*141*) in the same way as has been suggested for $Cr(CO)_6$ (Section VI, E).

VII. Conclusion

It is clear that the technique of PES is becoming of greater interest to inorganic chemists, and we hope in this chapter to have given some of the reasons for this interest; a great deal of information concerning the details of bonding in individual molecules can be obtained. It is not immediately obvious, however, that these details are directly related to more conventional chemical observations, and until much more work has been carried out it will be difficult to provide a detached assessment of the general utility of the technique. The technique itself, is, of course, developing rapidly, and future developments may add greatly to its usefulness. Two obvious advances in this direction are the extension to higher temperatures, particularly with molecular beam studies, and the development of new photon sources with slightly higher energy. An extremely important prospect is the possibility of vacuum UV studies of solids, and studies on this are proceeding in several laboratories, usually with the He(II) source. Such studies may also aid in bringing together the interests of workers in PES and ESCA.

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