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RECENT PROGRESS IN THE STUDY OF TRANSIENT SPECIES WITH VACUUM ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY

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ABSTRACT

Recent developments in the field of photoelectron spectroscopy (pes) of transient species are reviewed. An outline is given of the basic apparatus necessary for such studies and theoretical methods used to interpret the spectra are discussed. Examples are chosen of short-lived atoms and small molecules which have been studied by pes to illustrate the type of information to be obtained with this technique. Progress in studies of large molecules, van der Waals complexes, radicals adsorbed on surfaces and high temperature species, is also discussed. Suggestions are made regarding likely future developments in these areas.

INTRODUCTION

It is now some 20 years since the first vacuum ultraviolet photoelectron spectra of the rare gases were obtained (Turner *et al.*, 1969; Samson and Cairns, 1968). Since that time photoelectron spectroscopy (pes) has grown vigorously and found applications in many areas of physics and chemistry. Like all new branches of spectroscopy, it has carried with it the hopes of scientists from many disciplines and has exceeded its potential in some respects and disappointed in others. This review aims at reporting the progress in one such area—studies of the electronic structures of transient species and their positive ions, where in spite of somewhat faltering footsteps in the initial years, pes is now an established technique. The information which it provides is often complementary to that obtained by other methods and is of value to theoreticians, atmospheric chemists and spectroscopists from other disciplines, especially the optical and microwave areas. Although this review is not intended to be an exhaustive catalogue of examples, the studies chosen for discussion are taken from the literature up to September 1981. It sets out to give our purely personal views on the past and future significance of this field. Our bias towards small (i.e. few-atom) species will be evident. However, it is at this level that the most detailed theoretical treatments and spectral analyses can be made. Pes studies have been made on larger systems, but it is invariably the case that spectral interpretation is, by necessity, less detailed for these molecules and hence the information obtained is normally more qualitative in nature.

EXPERIMENTAL

The basic experimental concept involved in the study of transient species with pes has been given in a previous review (Dyke *et al.*, 1979a). Further details have also been given in other papers (Martensen, 1979; Frost *et al.*, 1977; Nagy-Felsobuki *et al.*, 1978).

Most pertinent perhaps to this present review is an assessment of the differences between the standard spectrometer and that used in studies of transients, and a discussion of the more important experimental developments that have been made since the earlier review (Dyke *et al.*, 1979a) was written. It is undoubtedly not by accident that nearly all pes studies have been carried out on custom built instruments. The standard commercial spectrometer is designed to satisfy the needs of the mass market and does not readily lend itself to the necessary adaptation required for transient studies. A spectrometer constructed on the building block principle, capable of being readily dismantled to facilitate cleaning and with large Helmholtz coils, instead of the more usual μ -metal shielding, will make for ease of access and is probably the best arrangement. A schematic diagram of such a spectrometer is shown in *Figure 1*. The main additional difference from conventional spectrometers apart from those already listed, is the incorporation of a fast pumping system onto the photoionization chamber. This secondary pumping arrangement is essential in order to minimize both the residence time in the chamber and the time between generation and observation.

Certain limitations of pes must be borne in mind when considering production of transient molecules. Firstly most spectrometers cannot operate at pressures much in excess of ~ 0.1 Torr. The spectral range for HeI (21.21 eV) radiation is typically about 10 eV (assuming a first ionization energy of say 11 eV), and also any one molecular species will occupy between 10 and 40% of the spectral region. Almost without exception the transient species signals are weak compared with those of precursors and/or stable products. Hence one has a tremendous 'overlapping band' problem unequalled in any other branch of spectroscopy. Coupled with this one has stability problems which inhibit spectrum accumulation over lengthy time periods. It is therefore not a simple matter to extract the required spectrum from the spectral bands normally observed.

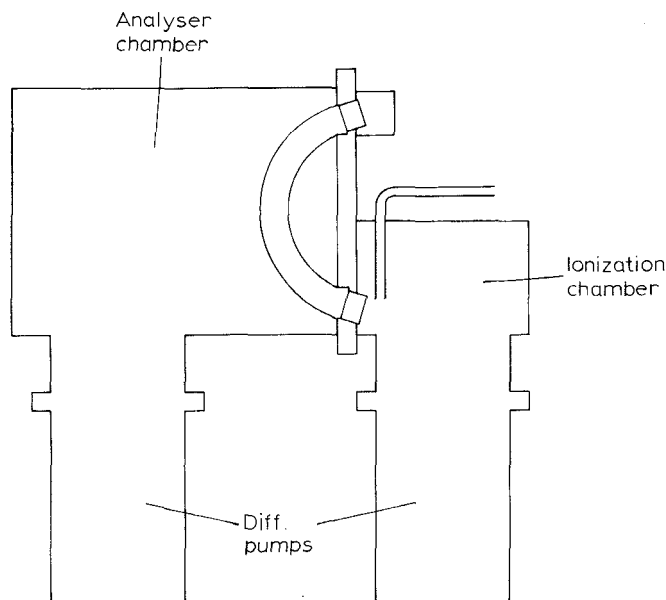


FIG. 1. Block diagram of a photoelectron spectrometer for the study of transient species.

The actual production of transient species relies heavily on standard gas kinetic techniques. Transients can sometimes be generated by microwave discharge dissociation of parent molecules; the microwave cavity being located sufficiently far from the ionization chamber so that the electrons and ions generated do not enter the photoionization zone. O_2 ($^1\Delta_g$), $SO(^3\Sigma^-)$, CS, CF_2 and halogen atoms are just some of the transients which have been generated in this way (Dyke *et al.*, 1979a). The chief drawback of this method is that the molecules of interest are produced at an appreciable distance (and hence time) before photoionization, and thus only relatively long-lived species have been studied in this way. Also, a microwave discharge is often an uncontrollable and indiscriminate way of producing short-lived species. A better way for studying shorter lived species involves gas-phase atom-molecule reactions. In this respect fluorine atom abstraction reactions have been especially useful. Many of these reactions have negligible activation energies and proceed at rates close to those corresponding to collision frequencies. Species such as FO, PH_2 , HO_2 and N_3 have been generated in this way from O_3 , PH_3 , H_2O_2 and HN_3 respectively.

So far there has only been one example of a short-lived species (atomic iodine) being generated by laser photolysis (Imre and Koenig, 1980). In theory, however, this method has great promise and its potential is yet to be fully realized.

High temperature pyrolysis can also be used to produce transient species for studies by pes. This has proved to be a particularly useful method of generating short-lived molecules in the gas-phase and studies at temperatures up to 2500 K have been made (Bulgin *et al.*, 1977; Dyke *et al.*, 1980g). The concept of being able to study molecules in isolation (i.e. free from intermolecular interactions) is particularly appealing if one is trying to unravel the more complex situation existing in the solid phase. Resistive heating is the most commonly used heating method. However, for pes studies this method seems to be limited to an upper working temperature of ≈ 1800 K, probably because the large currents required to achieve higher temperatures have associated fields which are difficult to eliminate in the photoionization region causing loss of count-rate and resolution. This problem can be avoided with radiofrequency induction heating. With this approach higher temperatures have been achieved whilst retaining reasonable instrumental sensitivity (Bulgin *et al.*, 1977; Dyke *et al.*, 1980g). Recently, radiative heating has been used to vaporize solid samples for photoelectron investigation (Berkowitz *et al.*, 1979). Although the advantages and disadvantages of this heating method have yet to be fully documented, this approach will obviously suffer from the same drawbacks as the heating method used to heat the radiator. Laser evaporation has also been used (Allen *et al.*, 1973; Streets and Berkowitz, 1976) but it seems that the strict long-term stability requirements imposed by pes do not favour this as a generally applicable method.

The highest temperatures so far reached in pes studies have been achieved using an rf inductively heated furnace. Rather than attempt elaborate screening methods in order to overcome the problem of interference from the operation of a high temperature furnace close to the photoelectron spectrometer, the rf heating supply was pulsed and the spectrometer detector gated accordingly (Bulgin *et al.*, 1977; Dyke *et al.*, 1980g). Graphite and tungsten furnaces have been successfully used and the main problems now being encountered in this work are not ones of temperature limitations or spectrometer sensitivity but are rather problems associated with furnace technology. At temperatures in excess of 2000 K, it is found that many compounds attack the furnace components and a great deal of effort is being spent in establishing the behaviour of high temperature materials e.g. in choosing ceramics, supports and furnaces which are unreactive towards each other and to the sample of interest at temperatures >2000 K. It may also be worth pointing out that although the basic technique is straightforward it

would be very difficult to apply to a spectrometer which was not constructed on the building block principle. There is a critical need for maximum space in the ionization chamber for easy access and for the ability to dismantle and reassemble apparatus quickly.

Whichever of the above methods is used to generate short-lived species, the problem of extracting the required spectrum from those of precursors and products remains. In theory, the use of a mass spectrometer with coincidence ion-electron counting would be the complete answer. In fact, such a method is impracticable because the weakness of the transient signal would require spectrum accumulation over prohibitively long time periods. This is not possible because changes in resolution and energy scale shifts, due to the gradual build-up of deposits in the photoionization chamber, nearly always occur. The first attempts to differentiate between transient and parent signals involved phase-sensitive detection and a pulsed microwave discharge technique (Morris, 1972). This worked reasonably well for oxygen discharges $\{O_2 \ ^3\Sigma_g^- \rightarrow O_2 \ ^1\Delta_g \text{ and } O(^3P)\}$ but attempts to extend the method to other species were less successful. Some improvement was achieved with a pulsed light source arrangement de Leeuw *et al.* (1976) while Peel and co-workers (Nagy-Felsobuki *et al.*, 1978; Livett *et al.*, 1978; Nagy-Felsobuki and Peel, 1980; Carnovale *et al.*, 1979 and 1980a,b) have used a spectrum-stripping technique, whereby the undischarged and discharged spectra are recorded separately and then subtracted by computer. A more refined version of this method has been developed by de Lange and co-workers (van Lonkhuyzen *et al.*, 1980) who have combined the use of a pulsed microwave discharge with computer accumulation. In this work high and low power discharge data are acquired simultaneously which circumvents some of the problems of the time-dependent quality of the spectra. It remains to be proven, however, as to whether the technique can be applied to atom-molecule reactions. In these cases the problems are much more severe because not only does one require to subtract the spectra due to the precursors but also those due to stable products. The latter will build up at different rates depending on the partial pressure of the transient. The transient may also be produced by secondary processes which are not necessarily in phase with the pulsed-atom supply. Hence, it seems unlikely that this will prove a generally applicable technique although it may prove useful in certain well chosen cases. Possibly the best method of obtaining improved transient spectra will involve the use of a multidetector (channel plate) spectrometer. Such an instrument has improved signal-to-noise characteristics of more than two orders of magnitude (Hicks *et al.*, 1980; Karlsson *et al.*, 1976) and hence stability problems can be minimized. A multidetector spectrometer has not yet been used for studies of transient species, but it seems highly promising, particularly for species generated at high temperatures where signal-to-noise problems are even more acute than those encountered in atom-molecule reaction studies.

THEORETICAL

The basic theoretical methods used in the interpretation of photoelectron spectra of transient species have been outlined in the earlier review (Dyke *et al.*, 1979a). However, over the last five years the use of semiempirical calculations has decreased markedly and an increased number of *ab initio* SCF calculations have been reported even in essentially experimental papers. Also, as noted earlier (Dyke *et al.*, 1979a), many short-lived molecules have open-shell electronic structures and Koopmans' theorem is not applicable in these cases. However, for these molecules vertical ionization potentials

can be estimated fairly readily by *ab initio* Δ SCF calculations. Koopmans' theorem also fails to give the correct ionic state ordering in a number of closed-shell molecules. A good example of this occurs in the calculation of ionization energies of transition metal complexes where relaxation energies are much larger for orbitals localized mainly on the metal atom than for ligand-based orbitals (Hillier *et al.*, 1974; Evans *et al.*, 1974; Hillier, 1979). *Ab initio* Δ SCF calculations again provide a more reliable estimate of the ordering of the low-lying ionic states in these molecules.

As well as the basic *ab initio* Δ SCF method, a number of other approaches have been used to predict vertical ionization energies and spectroscopic properties of molecular ions. Rather than attempt a full review of the subject, it is proposed to discuss three of the more important methods which are particularly appropriate for interpretation of photoelectron spectra of small transient molecules.

Ab initio SCF and MRD-CI calculations

The *ab initio* SCF multi-reference double-excitation (MRD-CI) method of Peyerimhoff, Buenker and co-workers has proved in recent years to be very useful in predicting ionization energies, spectroscopic constants and structural properties of small molecular ions (Bruna *et al.*, 1980a). The reliability of the vertical ionization potentials and spectroscopic constants predicted with this method for small diatomic and triatomic species often approaches the experimental uncertainty with which these quantities can be measured experimentally. For example, five ionization potentials have been observed for the SH radical with the HeI (21.22 eV) photon source (Dunlavey *et al.*, 1979a,b). The MRD-CI calculated vertical ionization potentials (Bruna *et al.*, 1980a) were all very close to the observed values except for the third vertical ionization potential corresponding to the process $\text{SH}^+(\text{}^1\Sigma^+) \leftarrow \text{SH}(\text{X}^2\Pi)$. This led to further experimental work which resulted in a reassignment of the third ionization process in agreement with the MRD-CI calculations. The MRD-CI predictions of vertical ionization potentials and spectroscopic constants for the low-lying states of PH (Bruna *et al.*, 1980a,b) are also proving extremely useful in analysing the ultraviolet photoelectron spectrum of PH. The observed first vertical ionization potential of PH is (10.19 ± 0.01) eV (Dyke *et al.*, unpublished) whereas the MRD-CI computed value is 10.05 eV (Bruna *et al.*, 1980a,b).

In a *pes* study of the NH_2 radical, the MRD-CI computed equilibrium geometries, potential curves and relative energies of the low-lying ionic states of NH_2^+ proved valuable in facilitating the assignment of the experimental spectrum. The separations of the adiabatic ionization energies to the ground (${}^3\text{B}_1$) and lowest excited (${}^1\text{A}_1$) ionic states has been measured as (0.99 ± 0.02) eV (Dyke *et al.*, 1980d) compared to the MRD-CI calculated value of 1.29 eV (Peyerimhoff and Buenker, 1979). A similar situation occurs for PH_2 . The HeI photoelectron spectrum of this radical shows that the ground state of the ion is the ${}^1\text{A}_1$ state and the ${}^3\text{B}_1$ state is the first excited state. This is confirmed by MRD-CI calculations and computed ionic potential curves obtained with this approach are proving useful in analysing the experimental photoelectron spectrum of PH_2 in more detail. The first vertical ionization potential of PH_2 has been measured as (9.83 ± 0.01) eV (Dyke *et al.*, unpublished) compared with the MRD-CI value of 9.57 eV (Bruna *et al.*, 1980a) for the $\text{PH}_2^+(\text{X}^1\text{A}_1) \leftarrow \text{PH}_2(\text{X}^2\text{B}_1)$ ionization.

At present, calculations of the MRD-CI type have been applied mainly to small diatomic and triatomic molecules and their low-lying ionic states. However, as the numerical accuracy of the MRD-CI method improves so it should be possible to make reliable predictions for larger molecules and their ions.

Use of Green's function methods

The most important contributions to the calculation of ionization energies by a many-body Green's function method have been made by Cederbaum and co-workers (1977). As with all *ab initio* calculations, large basis sets are often required to give reliable results. For example, for hydrogen sulphide a Green's function calculation of the ionization energies using a double-zeta basis gave poor agreement with experiment. However, extending the basis set by inclusion of polarization functions led to much better agreement (von Niessen *et al.*, 1977). Also, in small molecules the correction to ionization energies due to terms beyond third order in self-energy can be of major importance. For example, in the somewhat exceptional case of C_2N_2 the correct order of ionic levels is only obtained when the geometric approximation to the second- and third-order corrections is included (Cederbaum *et al.*, 1975). The Green's function method has, however, proved to be extremely useful in predicting ionization potentials and vibrational structure of transient species. For example, one of the first such species to be studied by pes was the CS molecule. In the HeI photoelectron spectrum of CS four relatively strong bands were observed (Jonathan *et al.*, 1972a,b,c; Frost *et al.*, 1972; McDowell, 1972; King *et al.*, 1972), whereas from a Hartree-Fock calculation only three ionization energies are predicted below 20 eV. Hence, one of the four observed bands must represent an unusually intense satellite band and because of this, the assignment of the CS spectrum was uncertain for several years after the original spectrum was recorded. This situation was resolved by a Green's function calculation (Domcke *et al.*, 1976) which showed that the first, second and fourth bands correspond essentially to one electron ionization of the outermost 7σ , 2π and 6σ levels. The third band, however, was assigned to a shake-up band corresponding essentially to ionization to the $^2\Sigma^+$ state formed by ionization of a 7σ electron and excitation of a 2π electron to an unoccupied 3π level. Related calculations have also been performed for PN and P_2 (Schirmer *et al.*, 1978). Three bands were observed in the HeI photoelectron spectra of both molecules (Bulgin *et al.*, 1976, 1977) and good agreement was obtained between the observed and predicted vertical ionization potentials in both cases. However, for CS, PN and P_2 weak bands were predicted in the ionization energy region 16.0–30.0 eV (Schirmer *et al.*, 1978). These bands have as yet not been observed and it would be of interest to investigate all three molecules with HeII radiation in order to test these predictions. Many-body Green's function calculations have also been performed on larger transient species. For example, in trans-diazene all calculated ionization potentials are within 0.3 eV of the measured values (von Niessen *et al.*, 1977b).

Results of many-body Green's function calculations show this method to be an extremely reliable one for predicting ionization energies of small molecules. For the same atomic orbital basis set, it gives results which are comparable to those obtained by the MRD-CI method. However, MRD-CI methods are more generally applicable than Green's function treatments. This arises because the Green's function method can only be used to predict ionization energies in cases where the equilibrium geometry of a molecule has previously been determined either experimentally or by another *ab initio* technique. Also, Green's function methods are incapable of making a direct prediction of an adiabatic ionization potential if there is a large equilibrium geometry change on ionization.

Molecular SCF Hartree-Fock-Slater calculations

As the area of pes applied to transient species has developed, the number of molecules composed of one or more heavy elements studied with this technique has increased. It is fairly clear, particularly with the continued development of high temperature pes, that

this trend will continue and as a result it is important that a theoretical method should be available for calculating reliable electronic wavefunctions for such systems. In practice, conventional *ab initio* calculations performed on molecules of this type require large amounts of computer time if the number of basis functions is large. This arises because in the *ab initio* method the number of two electron integrals to be evaluated varies approximately as the fourth power of the basis set size. Also, use of small basis sets in *ab initio* calculations on large systems casts considerable doubt on even the simplest calculated molecular properties. This problem can be alleviated by use of the so-called SCF-MSX α method (Johnson, 1966; Johnson and Smith, 1971, 1972; Slater and Johnson, 1972). This is based on the 'muffin-tin' approximation for the coulomb potentials and the Slater X α expression for the exchange terms in the Hartree-Fock-Slater (HFS) model Hamiltonian (Slater, 1951). However, the 'muffin-tin' approximation is most appropriate for large, nearly spherically symmetric systems and rather unreliable for systems with non-spherical charge distributions. An alternative approach has been devised for solving the HFS equations (Baerends *et al.*, 1973a,b; Baerends and Ros, 1973, 1978) which uses the Slater exchange approximation but has the advantage of not using a 'muffin-tin' approximation for potentials and densities. It involves expansion of the orbitals in terms of Slater functions together with a numerical scheme for the calculation of matrix elements of the Fock operator. Recently, a perturbation scheme has been developed which includes relativistic effects in the HFS method (Snijders and Baerends, 1978; Snijders *et al.*, 1979).

Hartree-Fock-Slater calculations both with and without relativistic corrections have been performed on a number of short-lived molecules, principally with the aim of interpreting their photoelectron spectra (de Leeuw *et al.*, 1978, 1979a,b,c; Baerends *et al.*, 1975; Baerends and Ros, 1973). For example, this method has been used in a recent study of TeCl₂ and TeBr₂ (Jonkers *et al.*, 1980) produced in the vapour phase by passing the corresponding molecular halogens over heated tellurium powder. Relativistic corrections to the ionization energies of TeBr₂ show that off-diagonal matrix-elements of the spin-orbit operator give rise to a splitting in the non-relativistically almost degenerate bromine 'lone-pair' orbitals, as observed experimentally. It has been found in general that HFS calculated ionization energies are of comparable quality or even slightly better than Δ SCF ionization energies obtained in the Hartree-Fock scheme when compared with experimental values. These calculations clearly demonstrate the HFS method to be an efficient computational scheme which can be applied to transition metal complexes or other molecules containing heavy elements in order to reliably interpret their photoelectron spectra and predict other molecular properties such as electronic excitation energies, and bond dissociation energies.

A review of transient species studied with vacuum ultraviolet photoelectron spectroscopy

Atoms

It was emphasized in the earlier review (Dyke *et al.*, 1979a) that the value of studying atomic species by pes lies not so much in determining ionization energies and relative energies of ionic states, as these have in most cases been determined more accurately by optical spectroscopy, but in determining relative intensities of both formally allowed and forbidden bands (Martin and Shirley, 1976; Manson, 1976). The relative intensity of these bands provides a useful way of investigating correlation and relativistic effects in atomic species and their ions (Süzer *et al.*, 1975; Hush and Süzer, 1977; Berkowitz *et*

al., 1974). Electron angular distribution measurements can also provide further information about the photoionization process (Manson, 1976, 1977).

The appearance of formally forbidden or shake-up bands involves a breakdown of the one-electron or single particle approximation. Four mechanisms have been identified by which these bands can gain intensity (Manson, 1976).

1. Initial state configuration interaction (ISCI).
2. Final state configuration interaction (FSCI) i.e. configuration interaction involving configurations of the ion.
3. Interchannel coupling. This is configuration interaction involving configurations derived from the ion plus the free electron.
4. Autoionization.

Good examples of initial state configuration interaction are provided by the Group IIA and IIB elements. The ground states of these elements are all 1S arising essentially from the ns^2 configuration. However, np^2 , nd^2 , nf^2 configurations can also mix into the ground state. This admixture causes ionic states arising from the nd^1 and nf^1 configurations to be observed as well as the 2S state arising from the ns^1 configuration. To date, ISCI has been reported in Zn (Hush and Süzer, 1977; Süzer *et al.*, 1976), Cd (Hush and Süzer, 1977; Süzer *et al.*, 1976; Süzer and Shirley, 1974) Hg (Berkowitz *et al.*, 1974; Süzer *et al.*, 1976; Süzer, 1980), Ca, Sr, Ba (Süzer *et al.*, 1976), Sm, Eu and Yb (Lee *et al.*, 1977). The HeI photoelectron spectra of Ba, Sm, and Yb also show strong effects arising from autoionization.

An example of FSCI occurs in the alkali atoms (Süzer *et al.*, 1980). The ground state of these atoms, 2S , can be considered to be mainly derived from the $np^6(n+1)s$ configuration. The higher nd levels are not populated and the $np^6nd^1\ ^2D$ state clearly will not interact with the 2S state. However, in the ion $^3P_{2,1,0}$ and 1P_1 states can be obtained from both the $np^5(n+1)s$ and np^5nd^1 configurations. Bands associated with ionization to the 3P and $^1P(np^5nd^1)$ ionic states will gain intensity by interaction with the corresponding states derived from the $np^5(n+1)s$ configuration and these have been observed experimentally in the photoelectron spectra.

Although examples can be chosen of ISCI, FSCI and autoionization, a complete separation of correlation effects in the initial and final (ion plus free electron) state is usually not possible. This is evident in the framework of configuration interaction because the description of configurations in terms of one-electron orbitals is somewhat arbitrary. As a result, it is extremely difficult to choose an example of interchannel coupling in the absence of either ISCI or FSCI. However, it is still valid to classify many cases as mainly ISCI or FSCI by analysis of the observed spectra and from the evidence of configuration interaction calculations.

Almost certainly more studies will be forthcoming in the above area. The availability of synchrotron radiation for variable wavelength and polarization studies has opened up many possibilities for providing more detailed investigations of angular distributions and photoionization cross-sections. These experiments would almost certainly be followed by the development of theoretical methods to aid in the understanding of these measurements.

One area where the use of synchrotron radiation would be particularly interesting would be in the measurement of the 4s and 3d photoionization cross-sections of the first row transition metals as a function of photon energy. Some measurements at the HeI (21.22 eV) wavelength suggest that the photoionization cross-section of the 3d shell is greater than that of the 4s shell and that this trend becomes more pronounced with decreasing atomic number (Dyke *et al.*, 1979b). However, laser photodetachment

measurements of some transition metal negative ions by Lineberger and co-workers (Corderman *et al.*, 1979; Engelking and Lineberger, 1979) using an argon ion laser (2.54 eV) show the 4s photoionization cross-section to be much greater than that of the 3d shell at this wavelength

The possible use of pes in kinetic studies of atom-molecule reactions anticipated earlier (Dyke *et al.*, 1979a) has yet to materialize. This is probably because of the overlapping band problem frequently encountered in pes and the relative insensitivity of the technique compared with other methods such as mass spectrometry and atomic resonance fluorescence. One exception to this has been the use of photoelectron spectroscopy to measure the concentration ratio of the $^2P_{1/2} : ^2P_{3/2}$ states of bromine atoms produced in the reaction of fluorine atoms with hydrogen bromide or deuterium bromide (Dyke *et al.*, unpublished) as (0.13 ± 0.04) . This value compared with values of (0.10 ± 0.04) and (0.07 ± 0.03) obtained by observing the $\text{Br}(^2P_{3/2}) \rightarrow \text{Br}(^2P_{1/2})$ emission (Sung and Setser, 1977; Brant *et al.*, 1979). The HeI photoelectron spectrum showing bands arising from electronically excited bromine atoms is shown in *Figure 2*.

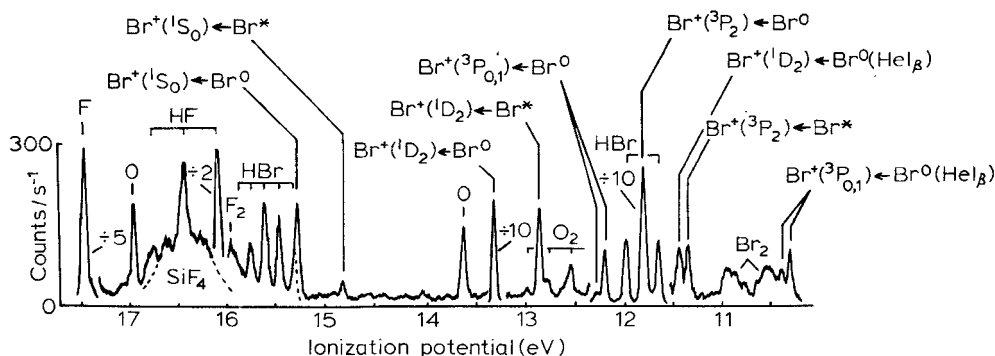


FIG. 2. The HeI photoelectron spectrum obtained from the reaction $\text{F} + \text{HBr}$ showing bands arising from ionization of the $\text{Br } ^2P_{3/2}$ state.

Five ionic states are formed from $\text{Br } ^2P_{1/2}$ or $^2P_{3/2}$ by removal of an electron from the outermost p orbital i.e. $^3P_{2,1,0}$, 1D_2 or 1S_0 . For ionization from $\text{Br } ^2P_{3/2}$ and $\text{Br } ^2P_{1/2}$ to the 3P_2 ionic state, the relative experimental band intensity ratio was measured as (0.013 ± 0.003) , whereas the corresponding values for the 1D_2 and 1S_0 states are (0.12 ± 0.03) and (0.11 ± 0.003) respectively. This ratio could not be measured for the 3P_1 and 3P_0 ionic states because of overlapping band problems.

In order to estimate the $\text{Br } ^2P_{1/2} : ^2P_{3/2}$ relative concentration from these intensity ratios, it is necessary to develop a simple model for the relative photoionization cross-sections of the ionizations involved. For the five ionic states, 3P_2 , 3P_1 , 3P_0 , 1D_2 and 1S_0 , the two $J=2$ and the two $J=0$ states will interact and an intermediate coupling scheme is necessary. This can be expressed equivalently in terms of an $L-S$ or $j-j$ basis for the lower $J=2$ and $J=0$ levels as:

$$\left. \begin{aligned} \psi_{(J=2)_{\text{lower}}} &= C_1 \left(\frac{3}{2}, \frac{3}{2} \right) + C_2 \left(\frac{3}{2}, \frac{1}{2} \right) \\ \psi_{(J=2)_{\text{lower}}} &= a_1 |^3P_2\rangle_{LS} + a_2 |^1D_2\rangle_{LS} \end{aligned} \right\} \quad (1)$$

and

$$\left. \begin{aligned} \psi_{(J=2)_{\text{lower}}} &= C_3 \left(\frac{3}{2}, \frac{3}{2} \right) + C_4 \left(\frac{1}{2}, \frac{1}{2} \right) \\ \psi_{(J=2)_{\text{lower}}} &= a_3 |^3P_0\rangle_{LS} + a_4 |^1S_0\rangle_{LS} \end{aligned} \right\} \quad (2)$$

The energies of the five ionic states arising from the s^2p^4 configuration can be written as (Ballard, 1978; Condon and Shortley, 1951),

$$\left. \begin{aligned} E(J=2) &= E_0 + 6F_0 - 2F_2 - \frac{\zeta}{4} \pm \sqrt{9F_2^2 - \frac{3F_2}{2}\zeta + \frac{9}{16}\zeta^2} \\ E(J=1) &= E_0 + 6F_0 - 5F_2 + \frac{\zeta}{2} \\ E(J=0) &= E_0 + 6F_0 + \frac{5}{2}F_2 + \frac{\zeta}{2} \pm \sqrt{\frac{225}{4}F_2^2 + \frac{15F_2}{2}\zeta + \frac{9}{4}\zeta^2} \end{aligned} \right\} \quad (3)$$

where ζ is the spin-orbit coupling parameter and F_0 and F_2 are electrostatic repulsion radial integrals.

The energy matrix coupling the $|^3P_2\rangle_{LS}$ and $|^1D_2\rangle_{LS}$ states (Condon and Shortley, 1951) is

$$\begin{array}{cc} & \begin{array}{c} |^3P_2\rangle_{LS} \\ |^1D_2\rangle_{LS} \end{array} \\ \begin{array}{c} |^3P_2\rangle_{LS} \\ |^1D_2\rangle_{LS} \end{array} & \begin{bmatrix} F_0 - 5F_2 - \frac{\zeta}{2} & -\frac{\sqrt{2}}{2}\zeta \\ -\frac{\sqrt{2}}{2}\zeta & [F_0 + F_2] \end{bmatrix} \end{array} \quad (4)$$

A similar matrix can also be written for the $|^1S_0\rangle_{LS}$ and $|^3P_0\rangle_{LS}$ states.

The three parameters F_0 , F_2 and ζ can readily be determined for the halogen ions by fitting the experimental term values (Huffman *et al.*, 1967, 1968; Moore, 1958) to the expression given in Eq. (3). In this fitting procedure, the sum of the positions of the two $J=2$ and two $J=0$ states has been used to eliminate the square root terms in Eq. (3).

Having determined F_0 , F_2 and ζ , these values can be substituted in Eq. (4) and the corresponding values of C as these are related to the α terms through the following (1)). A similar procedure can be followed to obtain the $J=0$ coefficients, α_3 and α_4 , in Eq. (2).

Once the α values are known, then it is straightforward to determine the corresponding values of C as these are related to the α terms through the following expressions which can be easily derived from a consideration of the limits of jj and LS coupling respectively.

$$\left. \begin{aligned} C_1 &= \sqrt{\frac{2}{3}}\alpha_1 + \sqrt{\frac{1}{3}}\alpha_2 \\ C_2 &= +\sqrt{\frac{1}{3}}\alpha_1 - \sqrt{\frac{2}{3}}\alpha_2 \\ C_3 &= \sqrt{\frac{1}{3}}\alpha_3 + \sqrt{\frac{2}{3}}\alpha_4 \\ C_4 &= \sqrt{\frac{2}{3}}\alpha_3 - \sqrt{\frac{1}{3}}\alpha_4 \end{aligned} \right\} \quad (5)$$

The values of C_1 , C_2 , C_3 and C_4 obtained in this way for Cl^+ , Br^+ , and I^+ from the optical data Huffman *et al.*, 1967, 1968) and Moore (1958) are shown in Table 1. It was not possible to derive the corresponding coefficients for F^+ because of uncertainties in the state positions (notably in obtaining a value for the relative position of the $F^+ ^1S_0$ state). Also, listed in this table are the coefficients obtained by Desclaux (1980) via a series of relativistic configuration interaction calculations. The α -coefficients derived by Berkowitz and Goodman (1979) from optical data can also be used to obtain values of C_1 , C_2 , C_3 and C_4 and these are also included in Table 1.

TABLE 1.

(a) Mixing coefficients for the halogen ions obtained from optical data*

	F ⁺	Cl ⁺	Br ⁺	I ⁺
C ₁	†	0.834 (0.834)	0.903 (0.902)	0.956 (0.954)
C ₂	—	0.552 (0.552)	0.431 (0.431)	0.293 (0.300)
C ₃	—	0.598 (0.598)	0.711 (0.710)	0.851 (0.851)
C ₄	—	0.801 (0.801)	0.704 (0.704)	0.525 (0.524)

(b) Mixing coefficients for the halogen ions obtained from relativistic configuration interaction calculations**

	F ⁺	Cl ⁺	Br ⁺	I ⁺
C ₁	0.824	0.837	0.890	0.941
C ₂	0.567	0.547	0.457	0.338
C ₃	0.582	0.599	0.684	0.813
C ₄	0.813	0.800	0.730	0.583

* Values in parentheses derived from α -coefficients of Berkowitz and Goodman, 1979; see text for details of method.† It was not possible to derive F⁺ values; see text.

** From Desclaux, 1980.

The agreement between the two sets of coefficients derived from optical data (*Table 1(a)*) is, as expected, very good, as also is the agreement with coefficients derived from relativistic calculations (*Table 1(b)*).

Using these coefficients (*Table 1(a)*), estimates can now be made of the relative intensity of observed photoelectron bands for ionization from a $J = \frac{1}{2}$ or $J = \frac{3}{2}$ initial state to a given ionic state. For example, writing the lower $J = 0$ state, as before as

$$\psi_{(J=0)_{\text{lower}}} = C_3 \left(\frac{3}{2}, \frac{3}{2} \right) - C_4 \left(\frac{1}{2}, \frac{1}{2} \right),$$

then the probability of reaching this ionic state will be proportional to C_3^2 from the $J = \frac{3}{2}$ neutral ground state and C_4^2 from the $J = \frac{1}{2}$ excited state.

This approach can be extended to the other ionic states involved in a straightforward way and the full results are listed in *Table 2*. It should be noted that allowance has also been made in this table for the degeneracy of the ionic states involved. Using the coefficients given in *Table 1(a)*, the relative band intensities for ionization from the ground $J = \frac{3}{2}$ and excited $J = \frac{1}{2}$ states of the halogens Cl, Br and I could then be calculated and the results are shown in *Tables 3* and *4*. For ionization from the $J = \frac{3}{2}$ state, *Table 3* shows that the agreement between the observed and predicted intensities is good for chlorine, bromine and iodine. Berkowitz and Goodman (1979) have also developed an intermediate coupling treatment which, although much more detailed than the simple model used here, also uses data derived from optical spectra to predict relative intensities for ionization from the ground $J = \frac{3}{2}$ state of the halogens. The results of these calculations are included in *Table 3*. Although Berkowitz and Goodman do not quote relative intensities for ionization from the $J = \frac{1}{2}$ state, their method can be readily extended to yield these values and these are included in *Table 4*. This table shows that, apart from the relative intensity measurements obtained for Br ($^2P_{1/2}$) (Dyke *et al.*, unpublished) (where the agreement between observed and predicted relative intensities is quite good) no measurements have yet been made for ionization from I $^2P_{1/2}$ or Cl $^2P_{1/2}$.

TABLE 2. Relative probabilities for the photoionization process $p^5 \rightarrow p^4 + e^-$

Ionic state	Wave function	Probability from the neutral atom state	
		$J = \frac{3}{2}$	$J = \frac{1}{2}$
$J = 0_{\text{upper}}$	$C_4 \left(\frac{3}{2}, \frac{3}{2}\right) + C_3 \left(\frac{1}{2}, \frac{1}{2}\right)$	C_4^2	C_3^2
$J = 2_{\text{upper}}$	$C_2 \left(\frac{3}{2}, \frac{3}{2}\right) - C_1 \left(\frac{1}{2}, \frac{1}{2}\right)$	$5 \left(C_2^2 + \frac{C_1^2}{2} \right)$	$5 \left(\frac{C_1^2}{2} \right)$
$J = 0_{\text{lower}}$ $J = 1$	$C_3 \left(\frac{3}{2}, \frac{3}{2}\right) - C_4 \left(\frac{1}{2}, \frac{1}{2}\right)$ $\left(\frac{3}{2}, \frac{1}{2}\right)$	C_3^2 $3 \cdot \frac{1}{2}$	C_4^2 $3 \cdot \frac{1}{2}$
$J = 2_{\text{lower}}$	$C_1 \left(\frac{3}{2}, \frac{3}{2}\right) + C_2 \left(\frac{1}{2}, \frac{1}{2}\right)$	$5 \left(C_1^2 + \frac{C_2^2}{2} \right)$	$5 \left(\frac{C_2^2}{2} \right)$

Attempts by Dyke *et al.* to observe excited halogen atoms produced by the reactions $F + HCl$ and $F + HI$ have proved unsuccessful although intense bands attributable to ionization of the ground state $^2P_{3/2}$ halogen atoms have been seen. However, it should be possible to observe ionization of Cl $^2P_{3/2}$ fairly easily by pes as at ~ 1200 K, the relative concentration ratio of the $J = \frac{1}{2}$ and $J = \frac{3}{2}$ states is ~ 0.17 . Hence, if, as seems likely, more pes measurements are made on the excited halogen atoms then *Tables 1 to 4* would prove very useful in analysing the experimental spectra. It should also be noted that no relative photoionization cross-section measurements have been made for ionization of atomic fluorine in the ground $J = \frac{3}{2}$ state. However, as the sensitivity of the pes technique improves it is anticipated that such measurements will be forthcoming and comparison can then be made with the predicted relative intensities given for F $^2P_{3/2}$ in *Table 3*.

TABLE 3. Comparison of experimental and predicted relative photoionization probabilities for the ground state halogen atoms $^2P_{3/2}$

Ionic state	Experimental		Predicted	
	Dyke <i>et al.</i>	Berkowitz and Goodman, 1979; Kimura <i>et al.</i> , 1978	This work	Berkowitz and Goodman, 1979
F^+ 3P_2	—	—	1.00*	—
3P_1	—	—	0.36	—
3P_0	—	—	0.08	—
1D_2	—	—	0.79	—
1S_0	—	—	0.16	—
Cl^+ 3P_2	1.00	1.00	1.00	1.00
3P_1	0.39 ± 0.03	0.44	0.35	0.35
3P_0	0.05 ± 0.01	0.06	0.08	0.09
1D_2	0.86 ± 0.05	0.81	0.77	0.77
1S_0	0.16 ± 0.03	0.16	0.15	0.15
Br^+ 3P_2	1.00	1.00	1.00	1.00
3P_1	0.40 ± 0.04	0.51	0.33	0.33
3P_0	0.12 ± 0.03	0.06	0.11	0.11
1D_2	0.70 ± 0.06	0.71	0.65	0.65
1S_0	0.07 ± 0.03	0.09	0.11	0.11
I^+ 3P_2	1.00	1.00	1.00	1.00
3P_1	0.39 ± 0.05	0.34	0.31	0.31
3P_0	0.18 ± 0.03	0.17	0.15	0.15
1D_2	0.80 ± 0.05	0.79	0.57	0.57
1S_0	0.04 ± 0.01	0.06	0.05	0.06

* For F^+ , the coefficients of Desclaux, 1980, *Table 1(b)* were used.

TABLE 4. Comparison of experimental and predicted relative photoionization probabilities for the excited state halogen atom ${}^2P_{1/2}$

Ionic state	Experimental	Predicted		
		This work	Berkowitz and Goodman, 1979*	
F ⁺	3P_2	—	1.00†	—
	3P_1	—	1.87	—
	3P_0	—	0.82	—
	1D_2	—	2.11	—
	1S_0	—	0.42	—
Cl ⁺	3P_2	—	1.00	1.00
	3P_1	—	1.97	1.98
	3P_0	—	0.84	0.85
	1D_2	—	2.29	2.30
	1S_0	—	0.47	0.48
Br ⁺	3P_2	1.00	1.00	1.00
	3P_1	—	3.23	3.23
	3P_0	—	1.07	1.07
	1D_2	3.94	4.40	4.37
	1S_0	1.14	1.09	1.08
I ⁺	3P_2	—	1.00	1.00
	3P_1	—	6.94	6.67
	3P_0	—	1.28	1.23
	1D_2	—	10.58	10.10
	1S_0	—	3.35	3.23

* These values were derived using the method and data quoted.

† For F⁺, the coefficients of Desclaux, 1980, Table 1(b) were used.

For bromine atoms produced in the $J = \frac{3}{2}$ and $J = \frac{1}{2}$ states by the F + HBr reaction, the relative band intensities for ionization from the two neutral atom states to a given ionic state can now be corrected to yield an estimate of the $J = \frac{1}{2} : J = \frac{3}{2}$ concentration ratio. For example, the experimental band intensity ratio for ionization to the 3P_2 ionic state, quoted earlier as (0.013 ± 0.003) , must be multiplied by a factor

$$\frac{2 \left(C_1^2 + \frac{C_2^2}{2} \right)}{C_2^2}$$

derived from Table 2. This yields an estimate of the concentration ratio as (0.13 ± 0.03) . A similar calculation for the 1D_2 and 1S_0 bands gives ratios of (0.16 ± 0.04) and (0.11 ± 0.03) respectively. The mean of these three values is (0.13 ± 0.04) . A similar study carried out on the analogous reaction with deuterium bromide showed that the fraction of excited bromine atoms formed was the same within the quoted uncertainty limits. Qualitative experiments also showed that the ${}^2P_{1/2}$ state of atomic bromine can be populated from the collision induced electronic-vibrational energy transfer reaction between the ground state atoms and vibrationally excited hydrogen fluoride. Unfortunately it has not yet proved possible to detect the vibrationally excited hydrogen fluoride directly. However, as apparatus sensitivity improves (by use, for example, of multichannel plate detectors) this situation should be rectified. At that time there may be some potential in the use of pes for determining initial vibrational energy distributions in simple atom-molecule reactions. Although there are obvious difficulties,

and there can be no hope of obtaining rotational distributions, the other methods such as infrared chemiluminescence and laser fluorescence also have severe limitations. Photoelectron spectroscopy may therefore prove to be a useful additional technique for such studies.

Similarly one can expect further developments in studies of atoms by pes particularly in view of the development of high temperature pes. Hence the study of thermally excited atomic states could become a rapidly developing and interesting area of research. Other examples where ionization of atomic excited states has been observed are in the photoelectron spectra of atomic germanium, tin and gallium (Dyke *et al.*, 1981d). In the case of germanium and tin, bands associated with ionization from the ground as well as the two lowest excited states have been seen. Intermediate coupling calculations (Dyke *et al.*, 1980d,f) have been used to calculate the experimental band intensities as a function of temperature and, from these calculations, the excitation temperature was estimated as (1600 ± 200) K for tin and (2000 ± 200) K for germanium. In the case of gallium, ionization of both the ground ($4s^24p^1$) $J = \frac{1}{2}$ and excited ($4s^24p^1$) $J = \frac{3}{2}$ state has been detected. Analysis of the observed photoelectron spectra yields an atomic excitation temperature of (1100 ± 150) K (Dyke *et al.*, 1981d).

These photoelectron studies highlight a problem which exists when ionization energies of atoms, generated in a high temperature source, are measured by electron impact mass spectrometry. In that method, population of low-lying excited states would lead to an erroneously low value for the first ionization potential. In practice, such mass spectrometric measurements may be the only source of ionization energies if no reliable optical measurements have been made, as is the case for example for a number of actinide and lanthanide elements. Although approximate corrections for this effect can be applied (Hildenbrand and Murad, 1974; Rauh and Ackermann, 1979), more precise values may be forthcoming with pes where in favourable cases excited state structure will be resolved.

Diatomic molecules

It is in the case of diatomic molecules that the most detailed information is obtained from pes studies. Usually for diatomic molecules composed of light atoms vibrational fine structure is well-resolved in the observed photoelectron bands. Analysis of the Franck–Condon envelopes allows ionic equilibrium bond lengths to be estimated to within ± 0.01 Å on the assumption that the electronic transition moment remains constant over the band. Also, if the dissociation energy of the neutral molecule is known from other studies, and the dissociation products of the molecule and ion can be determined, then the experimental adiabatic ionization energy can be used to estimate the dissociation energy of the ion. If a Morse potential is assumed for each electronic state of the molecule or ion, it is usually possible to construct potential energy diagrams for the molecule and the ionic states observed experimentally. Further details of this are given in the earlier review (Dyke *et al.*, 1979a). Such potential energy diagrams, although limited by the accuracy of the data provided by the pes method often provide information on ionic states which have not been observed by any other technique. These diagrams can also be used by optical spectroscopists to identify regions in which allowed transitions of molecular ions occur. In fact one can predict with some accuracy the region where the most intense vibronic transitions should be observed, thus solving not only a search problem but aiding in the spectroscopic analysis. Carrying out this procedure enables the spectroscopic constants derived by pes to be improved. Some studies of this type have already been made. For example, a comparison between the

experimental $S^2_2A^2\Pi_u - X^2\Pi_g$ emission spectrum and that derived from pes data shows the agreement between the observed vibrational band intensities and band positions and those derived from pes data to be very good (Dyke *et al.*, 1980h).

Another example occurs in the case of CS. This is one of the first transient species to be studied by pes. Ionization to the $CS^+X^2\Sigma^+$ and $B^2\Sigma^+$ states was observed in these experiments (Jonathan *et al.*, 1978a,b,c; Frost *et al.*, 1972). Using parameters derived from the experimental pe spectra, Franck-Condon factors have been computed for vibrational transitions between the lowest nine levels in both the upper and lower states. Also, the $CS^+B^2\Sigma^+ \rightarrow X^2\Sigma^+$ emission spectrum has recently been observed from Penning ionization of $CS(X^1\Sigma^+)$ (Tsuji *et al.*, 1980). Comparison of the relative intensities of vibrational components observed experimentally for the $B^2\Sigma^+ - X^2\Sigma^+$ transition with those computed from pes data (Figure 3) shows good agreement. For CS^+ , the spectroscopic parameters derived from optical data are, as expected, more precise than those obtained by pes e.g. for $CS^+(X^2\Sigma^+)$ $\bar{\omega}_e = (1384 \pm 40) \text{ cm}^{-1}$ from pes (Jonathan *et al.*, 1972a,b,c; Frost *et al.*, 1972) whereas the optical value is $(1376.6 \pm 0.5) \text{ cm}^{-1}$ (Tsuji *et al.*, 1980). Similarly the separation of the zeroth vibrational levels for the $CS^+B^2\Sigma^+ - X^2\Sigma^+$ transition was determined as $(36509 \pm 5) \text{ cm}^{-1}$ optically whereas

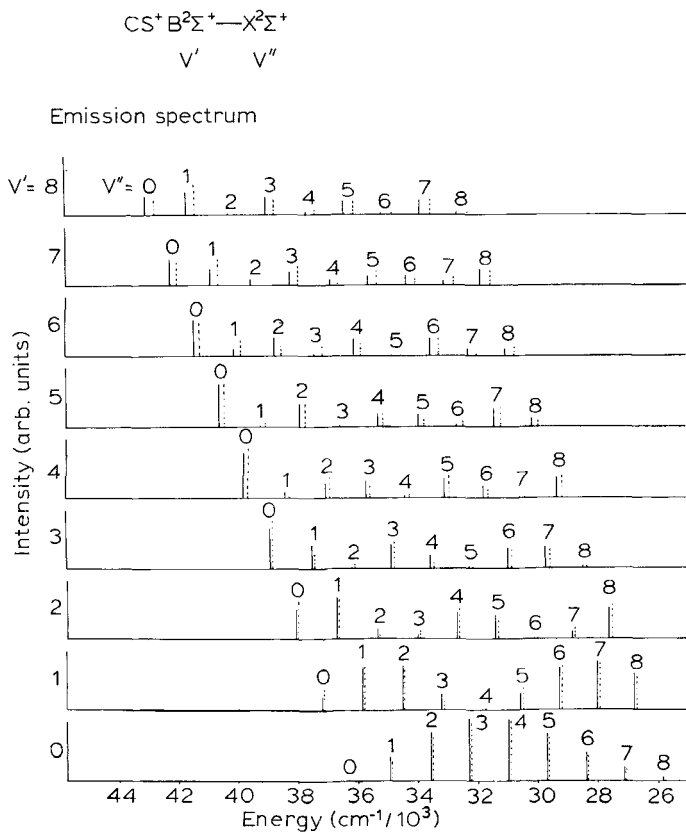


FIG. 3. Comparison between observed and predicted vibrational intensities for the $CS^+B^2\Sigma^+ - X^2\Sigma^+$ transition. --- from pes data, — from optical data. Pes data from Jonathan *et al.*, 1972a,b,c; Frost *et al.*, 1972; McDowell, 1972; King *et al.*, 1972. Optical data from Tsuji *et al.*, 1980.

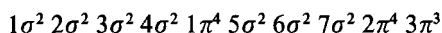
the earlier pes value is $(36297 \pm 200) \text{ cm}^{-1}$. It is expected that as more photoelectron spectra of diatomic molecules are recorded and analysed so it should be possible to make even greater use of the spectroscopic parameters obtained in order to assist in the analysis of molecular ion emission spectra.

A number of interesting short-lived diatomic molecules have been investigated by pes since the first review was written. It is clear, however, that the electronic structure of most of these molecules can be discussed by analogy with that of the diatomic molecules chosen in that review. For example, the photoelectron spectra of SnO and GeO can be interpreted by analogy with those of CO and SiO, and the photoelectron spectra of NF and PF can be interpreted from the known spectra of O₂ and SO. Attention can therefore be restricted to a limited number of examples.

The SH(X²Π) radical. This was produced in the gas phase by the reaction of fluorine atoms with hydrogen sulphide, and its HeI photoelectron spectrum has been recorded (Dunlavy *et al.*, 1979). The spectrum is complicated by bands associated with ionization of sulphur atoms, produced by the further reaction of fluorine atoms with SH. However, bands associated with SH(X²Π) and S(³P) could be identified by varying the mixing distance above the photon beam and the reactant concentrations. Five bands were observed attributable to SH and these have been assigned to ionization to the X³Σ⁻, ¹Δ, ¹Σ⁺, ³Π and ¹Π ionic states on the basis of the observed vibrational structure and from the results of *ab initio* ΔSCF calculations which include the effects of electron correlation. Similar calculations have also been performed for OH and, although only two bands have so far been observed in the photoelectron spectrum of this molecule, the positions of the higher ionic states have been reliably estimated. For SH⁺, predicted optical transition energies can be obtained from the observed spectra for the ³Π ↔ ³Σ⁻, ¹Π ↔ ¹Σ⁺ and ¹Π ↔ ¹Δ transitions. Of these, only the ³Π ↔ ³Σ⁻ transition has been observed previously and the separation of the zeroth vibrational levels determined optically of 3.71 eV compares well with a value of $(3.74 \pm 0.02) \text{ eV}$ obtained from the photoelectron spectrum.

The FO, ClO and BrO radicals. Pes studies of the ClO radical illustrated one of the major problems of investigating transient species by photoelectron spectroscopy, that of overlapping bands.

The ground state electronic configuration of ClO(X²Π) can be written as



and the 3π, 2π and 7σ levels should all be accessible via one-electron ionization with He(I) radiation (Bulgin *et al.*, 1979). As outlined previously (Dyke *et al.*, 1979a), three ionic states (³Σ⁻, ¹Δ, ¹Σ⁺) should arise from ionization from the 3π level, six ionic states (¹Σ⁻, ³Σ⁻, ³Δ, ³Σ⁺, ¹Δ, ¹Σ⁺) should be produced by ionization from the 2π level and two more ionic states (³Π and ¹Π) should result from ionization from the 7σ level. The experimental work (Bulgin *et al.*, 1979) showed that because of overlapping band problems, it was necessary to produce ClO by three different gas-phase reactions (Cl + O₃, Cl + ClO₂ and O + Cl₂O) in order to identify the bands associated with this radical. The three bands associated with the (3π)⁻¹ ionization and the two bands associated with the (7σ)⁻¹ ionization were clearly observed. However, the six bands associated with the (2π)⁻¹ ionization were not resolved and a long vibrational series extending over about 1 eV was observed which was assigned to all six bands. The most intense contributor to this latter band was the ³Δ state arising from the (2π)⁻¹ ionization. Although vibrational structure was observed in the bands associated with the ³Π and ¹Π states arising from the (7σ)⁻¹ ionization, the vibrational spacings in these bands could only be measured to

$\pm 100 \text{ cm}^{-1}$ as they were heavily overlapped by other features. Hence, because of this large error, potential curves could not be constructed for these states. In contrast, well-resolved vibrational structure was recorded for the three bands arising from the $(3\pi)^{-1}$ process and analysis of these bands allowed potential energy curves for the $X^3\Sigma^-$, $^1\Delta$ and $^1\Sigma^+$ states to be constructed (Bulgin *et al.*, 1979).

In the case of the FO radical, produced by the rapid reaction of atomic fluorine with ozone, only bands assigned to ionization to the lowest $^3\Sigma^-$, $^1\Delta$ and $^1\Sigma^+$ states were observed experimentally (Dyke *et al.*, 1980). However, the vibrational structure was well resolved in all three bands and, as a result, estimates could be made of the parameters $\bar{\omega}_e$, r_e and D_e in each ionic state and the corresponding potential energy curves could be constructed. The $X^3\Sigma^-$ and $^1\Delta$ states of SO and O_2 (which are isoelectronic with ClO^+ and FO^+) have been observed previously by laser photo-detachment of SO^- and O_2^- and the published spectra (Bennett, 1972; Lineberger, 1974; Celotta *et al.*, 1972) bear a marked similarity to the first two bands observed in the He(I) photoelectron spectra of ClO and FO.

The BrO radical was less well characterized by pes than FO or ClO. Only two vibrational components of the ionization $BrO^+(X^3\Sigma^-) \leftarrow BrO(X^2\Pi_{3/2})$ were observed experimentally. Nevertheless, from the separation of these vibrational components and their relative intensity, it was possible to estimate $\bar{\omega}_e = (830 \pm 30) \text{ cm}^{-1}$, $r_e = (1.66 \pm 0.01) \text{ \AA}$ and $D_e = (3.97 \pm 0.03) \text{ eV}$ for the $BrO^+(X^3\Sigma^-)$ state.

GeO and SnO. The photoelectron spectra of GeO and SnO have been recorded in order to characterize the ionic states observed and to correlate the observed spectra with those known for CO (Collin and Natalis, 1969; Gardner and Samson, 1973) and SiO (Colbourn *et al.*, 1978b). In these studies, GeO and SnO were both produced in the vapour phase by use of an inductively heated furnace (Bulgin *et al.*, 1977). GeO was obtained by heating an equimolar mixture of Ge and GeO_2 at $\sim 800 \text{ K}$ in a carbon furnace whereas SnO was produced by heating solid SnO_2 in an alumina-lined graphite furnace at $\sim 1300 \text{ K}$. For GeO, as in SiO and CO, three bands were observed corresponding to ionization to the $X^2\Sigma^+$, $A^2\Pi$ and $B^2\Sigma^+$ states (Colbourn *et al.*, 1978a). Vibrational structure was resolved in all three bands and analysis of this structure allowed potential energy curves for these states to be constructed. For SnO, only bands corresponding to ionization to the lowest lying $^2\Sigma^+$ and $^2\Pi$ states were clearly observed (Dyke *et al.*, unpublished) and these bands are shown in *Figure 4*. The sharp intense peak in this figure has a measured ionization energy of $(10.12 \pm 0.01) \text{ eV}$ whereas the underlying broad band has experimental vertical and adiabatic ionization potentials of $(9.98 \pm 0.01) \text{ eV}$ and $(9.60 \pm 0.02) \text{ eV}$ respectively. By analogy with the known photoelectron spectra of CO and SiO, the sharp band at 10.12 eV is assigned to ionization to the lowest lying $^2\Sigma^+$ ionic state whereas the broad band is assigned to ionization to the lowest-lying $^2\Pi$ state. Although no vibrational structure was observed for the band associated with the $SnO^+ ^2\Sigma^+$ state, a long vibrational series was clearly seen for the band associated with the $SnO^+ ^2\Pi$ state (*Figure 4*). Measurement of this structure gave a value of $\bar{\omega}_e = (700 \pm 40) \text{ cm}^{-1}$ in the $SnO^+(^2\Pi)$ state, which compares with $\bar{\omega}_e$ in $SnO(X^1\Sigma^+)$ of 822 cm^{-1} . The observed decrease in vibrational frequency on ionization is consistent with removal of an electron from the outermost π bonding orbital. No spin-orbit splitting was observed, although this is not unexpected as the electron removed is mainly localized on the oxygen atom.

This study shows that the ground state of SnO^+ is a $^2\Pi$ state. The correlation between the low-lying ionic states of CO, SiO, GeO and SnO is shown in *Figure 5* and calculations have been made (Dyke *et al.*, unpublished) using a number of theoretical methods to study the factors which control the ionic state ordering in these molecules.

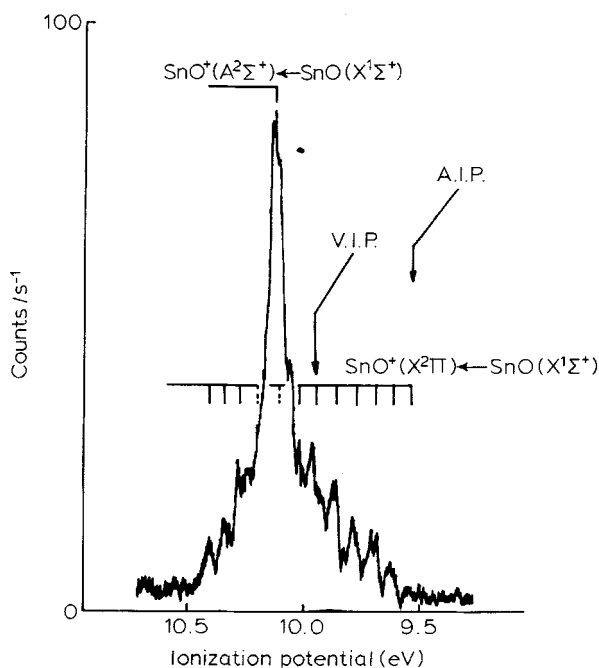


FIG. 4. Bands assigned to the first two ionization processes of the SnO molecule recorded with HeI radiation.

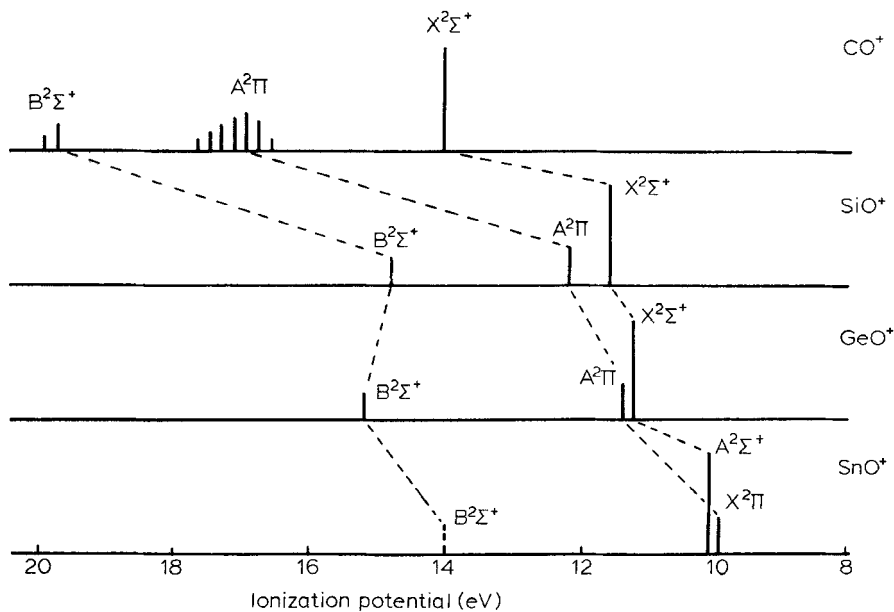
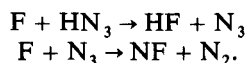


FIG. 5. Correlation of the low-lying ionic states of CO, SiO, GeO and SnO.

The NF and PF molecules. The NF molecule was produced in the gas phase for study by pes (Dyke *et al.*, unpublished) via the reactions



Both $\text{NF}(a^1\Delta)$ and $\text{NF}(X^3\Sigma^-)$ were found to be products of these reactions and the bands associated with ionization of these states to $\text{NF}^+(X^2\Pi)$ are shown in *Figure 6*. Calibration of these spectra led to $\bar{\omega}_e = (1520 \pm 40) \text{ cm}^{-1}$ for $\text{NF}^+(X^2\Pi)$ which is larger than the corresponding values in $\text{NF}(X^3\Sigma^-)$ and $\text{NF}(a^1\Delta)$ of 1141 cm^{-1} and 1184 cm^{-1} respectively. A similar increase in vibrational frequency occurs in the first band of oxygen, consistent with ionization of an electron from the outermost antibonding orbital. A Franck-Condon analysis of these bands using known spectroscopic constants for $\text{NF}(X^3\Sigma^-)$ and $\text{NF}(a^1\Delta)$ led to an estimate of $r_e = (1.183 \pm 0.01_e) \text{ \AA}$ for the $\text{NF}^+(X^2\Pi)$ state. Also, the separation of the $\text{NF } a^1\Delta$ and $X^3\Sigma^-$ states was measured from these spectra as $(1.45 \pm 0.02) \text{ eV}$ in good agreement with the optically determined value of 1.42 eV (Jones, 1967). As yet no higher bands attributable to NF have been observed, but, if they are observed, it is anticipated that the known photoelectron spectra of $\text{O}_2(X^3\Sigma_g^-)$ and $\text{O}_2(a^1\Delta_g)$ (Dyke *et al.*, 1979a) will be extremely useful in assisting the spectral analysis.

Preliminary spectra have also been recorded for the N_3 radical produced from the $\text{F} + \text{HN}_3$ reaction (Dyke *et al.*, unpublished). This molecule is similar to FO in that ionization of the outermost π^3 configuration will give rise to $X^3\Sigma^-$, $^1\Delta$ and $^1\Sigma^+$ states. Bands associated with ionization to these states from $\text{N}_3(X^2\Pi)$ have in fact been observed with an approximate intensity ratio of 3:2:1, as expected, and vertical ionization energies of 11.06, 12.19, and 12.87 eV respectively.

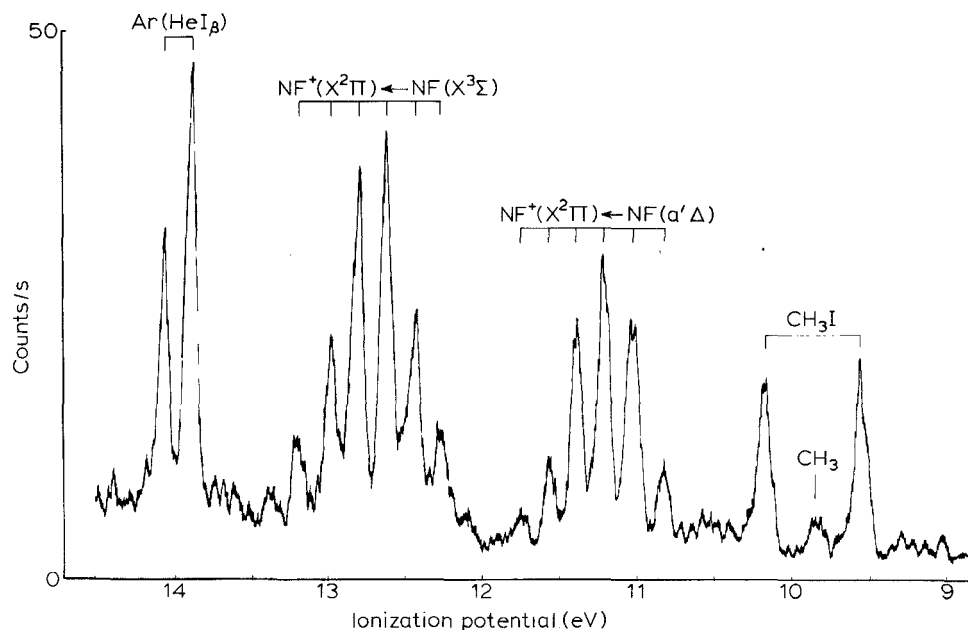


FIG. 6. Bands assigned to the ionizations $\text{NF}(X^3\Sigma^-) \rightarrow \text{NF}^+(X^2\Pi)$ and $\text{NF}(a^1\Delta) \rightarrow \text{NF}^+(X^2\Pi)$ recorded with HeI radiation. The NF radical was generated by the reaction of fluorine atoms with hydrazoic acid.

Photoelectron spectra recorded for the $F + PH_3$ reaction at three mixing distances above the photon beam are shown in Figure 7 (Dyke *et al.*, unpublished). At small mixing distances (Figure 7(a)) bands associated with ionization of PH_2 , PH , P and P_2 are observed and at large mixing distances (Figure 7(c)) bands associated with PF_2 , P_2 and P are observed. However, at an intermediate mixing distance (Figure 7(b)), a band is observed in the ionization energy region 9.5–10.0 eV which is assigned to the first band of PF . The vertical ionization potential of this band has been measured as (9.74 ± 0.01) eV and analysis of the vibrational structure gave $\bar{\omega}_e = (1030 \pm 30)$ cm^{-1} for the $PF^+(X^2\Pi)$ state. This value is in good agreement with the value of $\bar{\omega}_e = 1053$ cm^{-1} determined optically for $PF^+(X^2\Pi)$ and is, as expected, slightly higher than the corresponding value in $PF(X^3\Sigma^-)$ of $\bar{\omega}_e = 847$ cm^{-1} .

Some support for assigning this band to the PF molecule can be obtained by taking spectroscopic constants for $PF(X^3\Sigma^-)$ and $PF^+(X^2\Pi)$ determined optically and computing the Franck–Condon envelope of the first photoelectron band. Good

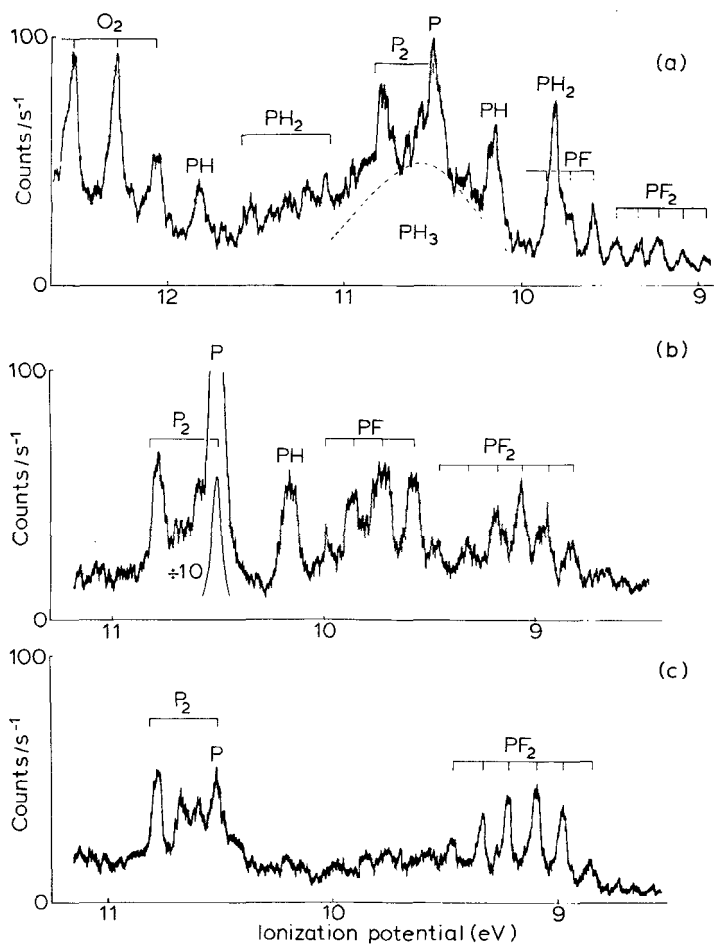


FIG. 7. Part of the HeI photoelectron spectrum obtained from $F + PH_3$ at mixing distances of (a) 0.7 cm, (b) 2.4 cm, and (c) 5.4 cm, above the photon beam.

agreement was obtained between the computed and observed vibrational intensities. As with NF, no higher bands associated with ionization of PF have, as yet, been observed.

Triatomic molecules

The HCO and FCO radicals. This is an interesting pair of molecules in that the positive ions are both expected to be linear and the neutral molecules are both known to be bent in their ground electronic states. Hence, on ionization a large equilibrium geometry change is expected and any observed vibrational fine structure should be characteristic of the deformation mode. Both molecules have been studied by pes (Dyke *et al.*, 1980c, 1981a) and were indeed found to exhibit a long series that could be attributed to the deformation mode in their first photoelectron bands. The band assigned to the first ionization process of DCO has also been observed and this shows the expected fractional reduction in frequency for the deformation mode on going from HCO^+ to DCO^+ .

For HCO, the upper state vibrational numbering in the first photoelectron band and hence the first adiabatic ionization potential were determined via a Franck–Condon calculation of the observed vibrational envelope. This was possible because the equilibrium geometries of both HCO and HCO^+ have been established from microwave spectroscopy (Woods *et al.*, 1975; Austin *et al.*, 1974; Bowater *et al.*, 1973; Boland *et al.*, 1978) and the vibrational frequency in the ion is known from analysis of the observed pe band. The validity of this procedure was confirmed by performing a parallel calculation on the vibrational envelope of $\text{A}^2\text{A}'' \leftarrow \text{X}^2\text{A}'\text{HCO}$ absorption process, where the vibrational numbering was well established from isotope shift measurements. The Franck–Condon calculations for the $\text{HCO}^+(\text{X}^1\text{A}') \leftarrow \text{HCO}(\text{X}^2\text{A}')$ process indicate that three vibrational components were too weak to be observed experimentally and allowance for these enabled the first adiabatic ionization potential of HCO to be determined as (8.27 ± 0.01) eV. Although the heat of formation of HCO^+ , $\Delta\text{H}_{\text{f}(298)}^\circ(\text{HCO}^+)$, is well established as (825.1 ± 4.2) kJ mol⁻¹, some uncertainty existed in the corresponding value of HCO. However, use of the above values gave a direct determination of the heat of formation of HCO, $\Delta\text{H}_{\text{f}(298)}^\circ(\text{HCO})$, as (28.0 ± 5.4) kJ mol⁻¹.

The first band in the photoelectron spectrum of FCO (Dyke *et al.*, 1981a) is very similar to that observed for HCO. However, unlike HCO the experimental equilibrium geometries of $\text{FCO}^+(\text{X}^1\text{A}')$ and $\text{FCO}(\text{X}^2\text{A}')$ have not been determined. Nevertheless, using minimum energy geometries for these states computed via *ab initio* molecular orbital calculations, the vibrational envelope of the first photoelectron band has been simulated using the method adopted previously. As before, these calculations lead to a determination of the vibrational numbering and first adiabatic ionization potential. However, because computed rather than experimental geometries have been used, the estimated experimental error in the adiabatic ionization potential is greater than in the HCO case.

The HO₂ radical. The $\text{HO}_2(\text{X}^2\text{A}'')$ radical has also been studied recently by photoelectron spectroscopy (Dyke *et al.*, 1981c). It was produced in the gas phase by the reaction of fluorine atoms with hydrogen peroxide. Only one band, corresponding to the ionization process $\text{HO}_2(\text{X}^2\text{A}'') + h\nu \rightarrow \text{HO}_2^+(\text{X}^3\text{A}'') + e^-$, was observed and this showed a regular vibrational series assigned to excitation of the O–O stretching mode in the $\text{HO}_2^+(\text{X}^3\text{A}'')$ state. The observed vibrational frequency of (1560 ± 50) cm⁻¹ compares with the corresponding value in $\text{HO}_2(\text{X}^2\text{A}'')$ of 1101 cm⁻¹ consistent with removal of an electron from an essentially anti-bonding molecular orbital between the

oxygen atoms. The first adiabatic ionization potential of HO_2 determined in this work, (11.35 ± 0.01) eV, allowed a considerably improved estimate of the heat of formation of HO_2^+ , $\Delta H_{f(298)}^\circ(\text{HO}_2^+)$, of (1104 ± 4) kJ mol⁻¹ to be made and this value in turn was used to calculate the bond dissociation energies in HO_2^+ , $\text{D}(\text{H}-\text{O}_2)^+$ and $\text{D}(\text{HO}-\text{O})^+$, as (278.0 ± 4.5) kJ mol⁻¹ and (438.2 ± 5.1) kJ mol⁻¹ respectively.

The $\text{NH}_2(\text{X}^2\text{B}_1)$ and $\text{PH}_2(\text{X}^2\text{B}_1)$ radicals. The study of the NH_2 radical by pes is of interest in that NH_2^+ is isoelectronic with CH_2 and the separation of the two lowest states of CH_2 has recently been a matter of some controversy. Recent laser photodetachment measurements on CH_2^- by Lineberger and co-workers places the separation of the two lowest states of CH_2 , the X^3B_1 and $^1\text{A}_1$ states, as (0.84 ± 0.03) eV (Zittel *et al.*, 1976; Engelking *et al.*, 1981), whereas indirect photochemical measurements and theoretical predictions favour a value of (0.35 ± 0.08) eV. It was hoped, therefore, that measurement of the corresponding $\text{X}^3\text{B}_1 - ^1\text{A}_1$ separation in NH_2^+ would provide some evidence for choosing between these alternatives.

The electronic ground state configuration of NH_2 is $1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^1$, where the $1b_1$ level consists essentially of the nitrogen $2p_\pi$ non-bonding orbital. The HeI photoelectron spectrum of NH_2 (Dyke *et al.*, 1980d), produced by the reaction $\text{F} + \text{NH}_3$, shows three bands attributable to NH_2 and these have been assigned on the basis of *ab initio* calculations to ionization to the $\text{NH}_2^+ ^3\text{B}_1$, $^1\text{A}_1$ and $^1\text{B}_1$ states produced via the $(3a_1)^{-1}$ and $(1b_1)^{-1}$ ionizations. Both the first and third bands, corresponding to ionization to the $^3\text{B}_1$ and $^1\text{B}_1$ ionic states, exhibit a long vibrational series attributed to excitation of the deformation mode in the ion. The observed vibrational frequency is (840 ± 50) cm⁻¹ in the $^3\text{B}_1$ state and (920 ± 150) cm⁻¹ in the $^1\text{B}_1$ state. Both of these are lower than the neutral molecule value of 1498 cm⁻¹, as expected for ionization from the $3a_1$ orbital which is bonding between the hydrogen atoms. In the second band, the adiabatic and vertical ionization potentials are, as expected, equal, although some weak structure was observed associated with excitation of ν_1 , the N-H symmetric stretch and ν_2 , the deformation mode, both close to the $\text{NH}_2\text{X}^2\text{B}_1$ values, consistent with ionization of a non-bonding orbital. The separation of the first two adiabatic ionization potentials measured in this work was (0.99 ± 0.02) eV. Also, minimum energy geometries of $\text{NH}_2^+ \text{X}^3\text{B}_1$ and $^1\text{A}_1$ were computed by *ab initio* configuration interaction calculations and the separation of the zeroth vibrational levels of these states has been obtained as 1.55 eV (Dyke *et al.*, 1980d). Similar calculations performed for CH_2 placed this separation as 0.88 eV. In view of the fact that the predicted $\text{NH}_2^+ ^3\text{B}_1 - ^1\text{A}_1$ separation is high, it was anticipated that the CH_2 computed separation will also be high. These results, therefore, favour the lower indirect photochemical value for the $\text{X}^3\text{B}_1 - ^1\text{A}_1$ separation in CH_2 .

The above investigations clearly indicate that the ground state of CH_2 and NH_2^+ is the lowest lying $^3\text{B}_1$ state in both cases. However, laser photodetachment experiments on SiH_2^- (Kasdan *et al.*, 1975) show that the ground state of SiH_2 is the lowest-lying $^1\text{A}_1$ state with the $^3\text{B}_1$ state being the first excited state. Preliminary investigations also confirm this is the case for PH_2^+ (Dyke *et al.*, unpublished). A preliminary uv photoelectron spectrum of PH_2 , obtained from the reaction $\text{F} + \text{PH}_3$ at small mixing distances above the photon beam (Figure 7(a)), shows a sharp band at (9.84 ± 0.01) eV, assigned to the ionization $\text{PH}_2^+(\text{X}^1\text{A}_1) \leftarrow \text{PH}_2(\text{X}^2\text{B}_1)$, and a broad band in the region 11.0–11.5 eV ionization energy assigned to the process $\text{PH}_2^+(\text{X}^3\text{B}_1) \leftarrow \text{PH}_2(\text{X}^2\text{B}_1)$. Further work is currently in progress to resolve the vibrational structure associated with this band (Dyke *et al.*, unpublished).

The PF_2 radical. The band assigned to the first ionization potential of the PF_2 radical has been observed from the $\text{F} + \text{PH}_3$ reaction at large mixing distances above the

photon beam (Figure 7(c)). As can be seen from this figure, a regular vibrational series was observed and this has been analysed to give $\bar{\omega}_e = (1000 \pm 30) \text{ cm}^{-1}$ for the vibration excited in the ion (Dyke *et al.*, unpublished). By analogy with the known NF_2 spectrum (Cornford *et al.*, 1971 and 1972), this band is assigned to ionization of the outermost, half-filled b_1 molecular orbital which is slightly anti-bonding in the P-F direction. Hence, the vibrational structure observed is assigned to excitation of the P-F symmetric stretching frequency in the ion increased from the corresponding value in $\text{PF}_2(\text{X}^2\text{B}_1)$ of 834 cm^{-1} (Burdett *et al.*, 1970).

FCP and CIBS. These molecules have been chosen together because they have both been studied by the joint use of photoelectron and microwave spectroscopy. Kroto and co-workers have applied this approach effectively to study a range of small short-lived molecules containing multiple bonds of the type C=S (Kroto *et al.*, 1974), C=Se (Hutchinson and Kroto, 1978), B=S (Kroto *et al.*, 1973), C=P (Hopkinson *et al.*, 1976a), and C \equiv P (Hopkinson *et al.*, 1976b). As the photoelectron technique detects all molecules produced in a reaction with a gas-phase lifetime greater than a certain value (typically $\sim 1 \text{ ms}$ (Dyke *et al.*, 1979a)), it can be used to optimize the conditions of production of a particular short-lived molecule. On the other hand, the microwave method is particularly sensitive to molecules which have a large dipole moment and hence once the conditions have been optimized by pes (e.g. for FCP or CIBS production) microwave measurements can be performed and rotational constants derived for the molecule under investigation.

The ground state of CIBS is a $^1\Sigma^+$ state arising from the electronic configuration

$$\dots (10\sigma)^2 (3\pi)^4 (11\sigma)^2 (4\pi)^4$$

Four bands were observed in the HeI photoelectron spectrum of this molecule (Kirby *et al.*, 1978), produced by passing S_2Cl_2 over heated boron, corresponding to the $(4\pi)^{-1}$, $(11\sigma)^{-1}$, $(3\pi)^{-1}$ and $(10\sigma)^{-1}$ ionizations.

The first band, corresponding to the $(4\pi)^{-1}$ ionization, shows the most structure with a vibrational splitting of $(1375 \pm 30) \text{ cm}^{-1}$, assigned to the B=S stretching mode, and a spin-orbit splitting of $(370 \pm 30) \text{ cm}^{-1}$. Microwave measurements have also been made for the two most abundant isotopic species $^{35}\text{Cl}^{11}\text{B}^{32}\text{S}$ and $^{37}\text{Cl}^{11}\text{B}^{32}\text{S}$ and these were analysed to yield the rotational constant for both isotopes. By assuming a reasonable geometry for CIBS with a B-Cl equilibrium bond length from F_2BCl and a B-S equilibrium bond length from HBS, a value for the rotational constant was derived for $^{35}\text{Cl}^{11}\text{B}^{32}\text{S}$ close to the observed value, consistent with the identity of the molecule involved as CIBS.

The study of F-C \equiv P by use of photoelectron and microwave spectroscopy is of interest in that it demonstrated that this molecule could be produced in the gas phase in a controlled way by eliminating two hydrogen fluoride units from CF_3PH_2 (Kroto *et al.*, 1978), by passing CF_3PH_2 over KOH at room temperature. This is a simple and efficient approach to be contrasted with high-temperature flow pyrolysis which has been found in other related cases to give lower yields and produce other reaction products. The observed microwave spectrum obtained from the $\text{CF}_3\text{PH}_2/\text{KOH}$ reaction can be attributed to a small linear molecule with an observed rotational constant close to that calculated from an estimated structure of F-C \equiv P. The photoelectron spectrum is also consistent with that expected for this molecule. Three bands were observed and these can be readily assigned by comparison with the known photoelectron spectra of H-C \equiv P and F-C \equiv N.

The SX₂ and SeX₂ molecules, where X=F, Cl and Br. These molecules have been studied in some detail by de Lange and co-workers (de Leeuw *et al.*, 1978, 1979b,c).

Correlations have been made between the observed photoelectron spectra and those obtained for other AB_2 molecules which are isoelectronic as far as their valence electrons are concerned. Also, the results of Hartree–Fock–Slater calculations have been used to interpret the observed spectra and, in general, the agreement between the observed and calculated vertical ionization potentials for these molecules is good.

Tetraatomic and polyatomic molecules

From an electronic structure point of view, the halogenated derivatives of the methyl radical would make an interesting series of molecules for study by pes. Unfortunately none of these has as yet been studied in detail. In fact the only possible observation has concerned the reported presence of Cl_3 in the spectrum of heated tetraiodomethane (Novak *et al.*, 1981). In this work tentative assignments were given for four electronic states of Cl_3^+ . However, one must view these assignments and even the identification of Cl_3 with extreme caution. The bands in question are extremely weak and have not been shown to arise from a short-lived molecule. Also, no bands corresponding to other pyrolysis products such as molecular or atomic iodine were observed. Further work is certainly needed before any conclusions can be drawn.

Some recent work on the chloramines NH_2Cl , $NHCl_2$, and NCl_3 and the methyl chloramines represents one of the most complete studies that have been made on unstable molecules by pes. These chloroamines were prepared either by direct gas phase reaction of ammonia and chlorine, or by the admixture of an aqueous solution of the appropriate amine with an aqueous solution of sodium hypochlorite. This latter method proved to be a very useful way of obtaining the pure chloroamines in the gas phase. In contrast, the spectra obtained from the gas-phase reaction of NH_3 and Cl_2 were contaminated either by residual NH_3 or Cl_2 . Peel and co-workers (Livett *et al.*, 1978) have recorded spectra from the reaction of ammonia with chlorine at various reactant gas partial pressures and have made use of spectrum-stripping to remove bands arising from NH_3 and Cl_2 . In this way, 'pure' spectra of NH_2Cl and $NHCl_2$ were obtained. These spectra are in good agreement with those reported by Frost *et al.* (Colbourne *et al.*, 1978a,b) who prepared the pure chloramines by the aqueous amine/hypochlorite route. Frost *et al.* have also used this preparative approach to study the photoelectron spectra of the methyl chloramines CH_3NHCl , CH_3NCl_2 and $(CH_3)_2NCl$ as well as NCl_3 . The spectra of $NHCl_2$ and NH_2Cl have been assigned with the aid of *ab initio* calculated eigenvalues, whereas the spectra of the methyl substituted chloramines have been assigned on the basis of observed substituent effects.

Of the substituted fluorides of ammonia, only the pes of HNF_2 and NF_3 have been recorded. NF_3 can hardly be classed as a transient molecule, and its photoelectron spectrum is well established (Bassett and Lloyd, 1972). For HNF_2 , evidence of seven ionization processes within the HeI region has been obtained (Colbourne *et al.*, 1980a). Extensive vibrational structure was observed in the first band of both HNF_2 and DNF_2 , and on the basis of this evidence and the results of *ab initio* molecular orbital calculations for the ground ionic state, it is concluded that the ion is planar in its ground state.

In the case of the bromamines, photoelectron spectra have been recorded for NH_2Br and $NHBr_2$ as well as the methylbromamines CH_3NHBr , CH_3NBr_2 and $(CH_3)_2NBr$ (Nagy-Felsobuki *et al.*, 1978; Nagy-Felsobuki and Peel, 1979; Carnovale *et al.*, 1978, 1979; Colbourne *et al.*, 1979). The spectra were found to correlate well with those of the corresponding chlorides.

The study by pes of polyatomic molecules which are short-lived in the gas-phase has developed rapidly in the last few years. Notable contributions have been made by the research groups of Frost (Colbourne *et al.*, 1978c, 1980b; Frost *et al.*, 1977a,b, 1978,

1980), Peel (Nagy-Felsobuki and Peel, 1980a,b), Kroto (Westwood *et al.*, 1979; Kirby and Kroto, 1978), de Lange (de Leeuw *et al.*, 1979; Jonkers *et al.*, 1981) and Bock (Block *et al.*, 1976; Solouki *et al.*, 1976; Bock *et al.*, 1977a,b). A detailed discussion of this work is not within the scope of this review as many of the experimental details or theoretical methods used are common to studies of smaller molecules which have been described in earlier sections. An exception to this is the work of Bock and co-workers who, as well as studying transient molecules in the gas-phase by pes as a method of investigating their electronic structure, have also used pes as a way of studying the course of chemical reactions (Bock *et al.*, 1978a,b). For example, the cyanation of benzene with a NCCN/HCN mixture has been studied as a function of temperature with pes (Bock *et al.*, 1978b). In the absence of a solid catalyst, the spectra show that cyanation starts at ≈ 1300 K to yield benzonitrile. However, on introducing a copper catalyst into the reaction vessel it was observed that there was a drop in the temperature at which cyanation occurred. Various catalysts were tested and the best result was obtained with a Cu/Al₂O₃ catalyst which gave a cyanation temperature of 700 K. It was also noted that on increasing the temperature above 700 K, the catalyst lost its activity only to become active again at 800 K. This was attributed to the temporary occupation of active sites by reaction products (Bock *et al.*, 1978b). One can readily believe that the progress of other heterogeneously catalysed reactions could be studied in this way, and possible industrial applications may be forthcoming.

Alkyl and aryl radicals

At the time of writing of the previous review, very little work had been carried out on alkyl radicals by pes and only the CH₃ molecule had been subjected to a detailed study (Dyke *et al.*, 1976). Since that time studies in this area have expanded considerably and partial pe spectra of some quite complex organic radicals have been obtained. It is unfortunate that the methods used for generation of these species have in general meant that overlapping band problems have restricted analysis to the band associated with the lowest ionization process. Nevertheless it is undoubtedly true to say that this first band contains the most important chemical information since it is used to obtain estimates of the heat of formation of the positive ion. In most cases the heat of formation of the parent radical is reasonably well established and only measurement of the first adiabatic ionization energy is required for ΔH_f° of the cation to be determined. Measurement of the adiabatic ionization potential may, however, be complicated if bands arising from ionization of the vibrationally excited neutral species are present—the so-called 'hot' bands. There is often a likelihood of these being present when radicals are generated by pyrolysis methods.

Some information on the structure of the radicals and ions has also been forthcoming from photoelectron studies. In this respect, it is worth mentioning the investigation of the *t*-butyl radical formed by pyrolysis of 2,2'-azoisobutane (Dyke *et al.*, 1977). The band associated with the lowest ionization potential showed resolvable fine structure. Even so the interpretation was not as straightforward as in the methyl radical case. In spite of this there was sufficient evidence for it to be concluded that the carbon skeleton is in fact non-planar and has C_{3v} symmetry. Also, the Franck-Condon envelope of the first band was used to estimate the out-of-plane distance of the central carbon atom from the other carbon atoms as (0.30 ± 0.05) Å. There has been considerable controversy regarding the symmetry of the *t*-butyl carbon skeleton, but it is interesting to note that a recent IR absorption study of this radical isolated in an argon matrix (Pacansky and Chang, 1981) is also consistent with a C_{3v} structure. Recently, the *t*-butyl photoelectron spectrum has been re-investigated by Houle and Beauchamp

(1979) as part of a comprehensive investigation of simple alkyl radicals. By using a low temperature method of production they were able to eliminate from the spectrum contributions arising from ionization of vibrationally excited molecules, and thus found a slightly higher value of 6.70 eV for the first adiabatic ionization energy compared with the previous value of 6.58 eV (Dyke *et al.*, 1977). This new value gave a heat of formation of the *t*-butyl cation in excellent agreement with a value determined from independent ion cyclotron resonance studies.

Two other features of interest arise from the work of Houle and Beauchamp (1979). Firstly, from accurate determinations of the first adiabatic ionization energies of the radicals CH_3 , C_2H_5 , CH_3CD_2 , CH_3CHCH_3 , and $\text{C}(\text{CH}_3)_3$, the heats of formation of the corresponding cations could be determined and the implications of these values to the gas-phase proton affinity scale were assessed. Secondly, some vibrational fine structure was observed in the first bands of these molecules and possible assignments were presented. The most interesting study in this respect was the work on the ethyl radical. A NeI spectrum of this radical, obtained by pyrolysis of the alkyl nitrite $\text{CH}_3\text{CH}_2\text{CH}_2\text{ONO}$, led to a redetermination of both the first adiabatic and vertical ionization energies as (8.39 ± 0.02) eV and (8.51 ± 0.02) eV respectively and showed that values obtained in an earlier study by the same authors (Houle and Beauchamp, 1977) were in error because of overlap with the first band of nitric oxide ionized by HeI_β radiation. The first band (Houle and Beauchamp, 1979) exhibited little vibrational structure except for the two peaks chosen as the adiabatic and vertical components. However, in contrast to this result, a recent study of the HeI photoelectron spectrum of the ethyl radical, obtained from the reaction of fluorine atoms with ethane, showed a first band which was more highly resolved and which exhibited extensive vibrational structure (Dyke *et al.*, unpublished). The adiabatic and vertical ionization energies were measured in this case as (8.32 ± 0.04) eV and (8.53 ± 0.02) eV respectively. Additionally the regular vibrational series showed an average peak separation of (370 ± 40) cm^{-1} . A similar spectrum has also been recorded by pyrolysis of azoethane (Dyke *et al.*, unpublished).

The interpretation of this structure is not straightforward. As Houle and Beauchamp (1979) indicated, two geometries are possible for the neutral molecule viz. an eclipsed and a staggered form, with the difference in energy between these structures being very small (≈ 0.01 – 0.04 eV). Two geometries are also possible for the positive ion, a classical and a hydrogen-bridged form. In this case, theoretical calculations indicate that the non-classical bridged form is the more stable by 0.13 to 0.30 eV.

On the basis of this evidence, Houle and Beauchamp put forward two possible assignment schemes. The first assumed that Franck–Condon transitions to the bridged ion are small and the band shape reflects the overlap of vibrational wavefunctions of the classical geometries. Thus vibrational structure would be expected in the (C–C) stretch (~ 800 cm^{-1}) and the CH_3 deformation mode (~ 1000 cm^{-1}) as well as the lower frequency torsion about the (C–C) bond. For this assignment to be correct one would expect a rather broad band with little or no resolvable fine structure. This would appear to be the case in Houle and Beauchamp's experimental spectrum and the one vibrational separation they resolved of 0.12 eV could be assigned to excitation of either a (C–C) stretching mode or a CH_3 deformation mode in the ion. However, this interpretation would seem inapplicable to *Figure 8* where the vibrational spacing is ~ 370 cm^{-1} .

The second interpretation, which is the one we favour, assumed that the bridged non-classical form of the ion is the more stable, in agreement with theoretical predictions. It also assumes that the adiabatic ionization process corresponds to formation of this bridged ion from the classical radical structure, whereas the vertical

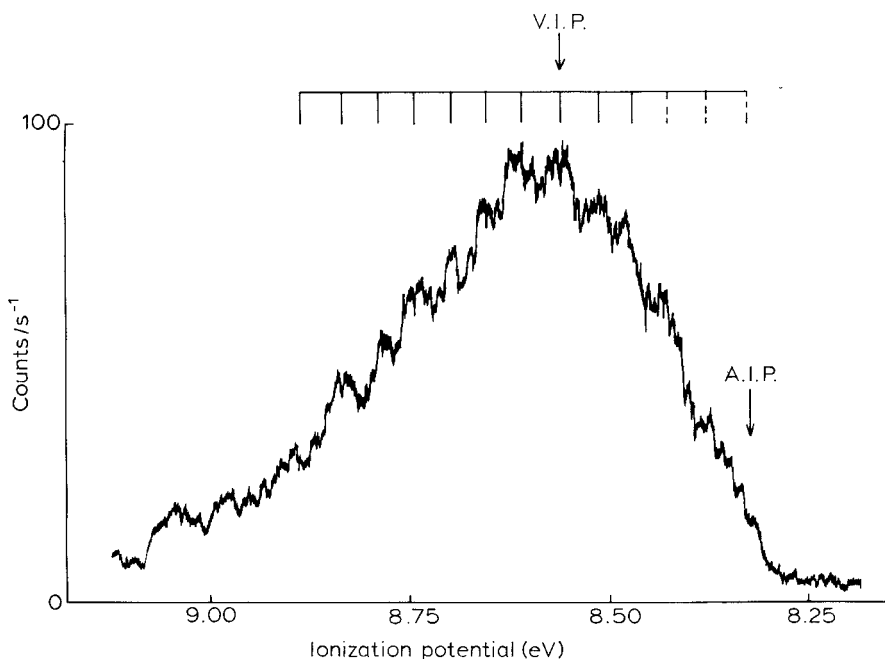


FIG. 8. The band assigned to the first ionization potential of the ethyl radical obtained from the reaction $F + C_2H_5$ recording with HeI radiation.

ionization energy would, on the Franck–Condon principle, be associated with formation of an ion with a structure closer to that of the neutral radical i.e. to a classical form. Support for this concept is given by the fact that the difference in vertical and adiabatic ionization energies is (0.21 ± 0.06) eV (measured from Figure 8) which is within the earlier mentioned range expected theoretically for the difference between the bridged and classical ions. The regular vibrational fine structure in Figure 8 should thus be associated with the equilibrium geometry change on ionization i.e. in this case, the vibration involving H-bridging to the radical centre. No estimate of such a vibrational frequency is available either experimentally or theoretically from either the ethyl radical or its ion. However, the out-of-plane bending vibration of the CH_2 group in the ethyl radical has been determined experimentally as 541 cm^{-1} (Pacansky *et al.*, 1977, and 1980; Pacansky and Dupuis, 1978) and it therefore seems reasonable that the H-bridging mode would be at a lower vibrational frequency. Thus, although this assignment is based on a number of assumptions and independent evidence as to the value of the bridging vibrational frequency would be invaluable, the non-classical structure for the equilibrium geometry of the ethyl cation seems the most likely on the basis of the available evidence.

Two other pieces of evidence need, however, to be considered. Firstly, the heats of formation of the radical and cation are well established as (117 ± 4) kJ mol^{-1} and (903 ± 2) kJ mol^{-1} respectively. These figures give the adiabatic ionization energy of the ethyl radical as (8.15 ± 0.06) eV which implies that the adiabatic i.p. has not been observed experimentally by pes. Secondly, the shape of the leading edge of the first photoelectron band of C_2H_5 observed via the reaction $F + C_2H_5$ is apparently different from that obtained by pyrolysis of the alkyl nitrite (Houle and Beauchamp, 1979). This

difference could conceivably be due to ionization of vibrationally excited radicals formed in the $F + C_2H_6$ case and further work on the ethyl radical is currently in progress to investigate this possibility.

The allyl and benzyl radicals have been the subject of similar studies (Houle and Beauchamp, 1978) and heats of formation for the two cations have been estimated from the measured adiabatic ionization energies. From the observed band envelopes and vibrational fine structure of the first photoelectron bands, it is concluded that the unpaired electron in the neutral molecule is essentially non-bonding and, as a result, virtually no change in geometry occurs between the cation and parent radical.

Larger radicals have also been studied. For example, Dewar and co-workers (Dewar and David, 1980) have obtained a partial photoelectron spectrum of the phenoxy molecule produced by thermal decomposition of allyl phenyl ether. A partial assignment was attempted on the basis of semiempirical (MNDO/HE) calculations and a value was also quoted for the heat of formation of the phenoxy cation derived from the first adiabatic ionization energy. However, in view of the fact that the first band assigned to ionization of the phenoxy radical was overlapped by other features arising from both the unpyrolysed parent molecule and the allyl radical, there must have been some difficulty in deriving a precise value for the adiabatic ionization energy. Also, no vibrational structure was resolved in any of the observed bands.

An even larger species which has been successfully studied by pes is the tropyli radical (Koenig and Chang, 1978). Clear vibrational structure was observed in the band associated with the first ionization process and a reliable value was thus obtained for the heat of formation of the cation. Evidence was presented to indicate a significant Jahn–Teller distortion of the parent radical away from a D_{7h} geometry, whereas the carbonium ion is almost certainly of this symmetry in its ground electronic state.

The degree of success achieved with even these large radicals indicates that this should be a fruitful research area in the immediate years ahead. One must, however, hope that rather cleaner methods of production are found than the presently used pyrolysis techniques. In this respect, fluorine atom abstraction (in the case of high symmetry molecules) or decomposition of metal alkyls might be profitable alternatives. One would probably not be restricted to analysis of the lowest ionization energy band if these methods were successful.

Molecular clusters and van der Waals molecules

Interest in spectroscopic studies of molecular dimers and higher molecular clusters has grown considerably in recent years. There are various possible experimental probes of molecular clusters of which pes is particularly attractive for a number of reasons. Firstly, the photoelectron spectrum yields directly the ionization energies of the cluster. Also, structural information can be obtained indirectly by relating the observed band shapes to computed Franck–Condon envelopes. Furthermore, a wealth of photoelectron spectra for free atoms and solids already exists and, as these are the two limits of decreasing and increasing cluster size, it should in principle be possible to observe the electronic structure changes in the condensation of free atoms or molecules to form solids. Overall the rate of progress in this area has been slow, largely because of experimental difficulties. Clusters are normally formed by adiabatic cooling in a high pressure supersonic expansion through a nozzle. However, the species of interest usually constitute <1% of the total gas pressure and under these conditions problems of overlapping bands from precursor species will be particularly severe in pes studies. Also, conventional pes studies of clusters is often impractical because a range of cluster sizes may be produced. This latter problem can be alleviated to some extent by varying

the supersonic nozzle diameter or nozzle stagnation pressure, so as to enhance the concentration of a particular cluster size. In this respect, photoionization mass spectrometry where identification of particle mass is straightforward, has a number of clear advantages as far as determination of the lowest ionization energy is concerned. However, this method also has some drawbacks and normally provides only a limited amount of information.

A good example of the complementary nature of pes and photoionization mass spectrometry is provided by some recent studies of the Xe_2 molecule. Although photoionization-mass spectrometric studies clearly identified the Xe_2 adiabatic ionization energy as (11.127 ± 0.010) eV (Ng *et al.*, 1976), the pes work (Dehmer and Dehmer, 1978a) showed no evidence of an increase in signal above the background in this region. The reason for this discrepancy is undoubtedly the very large change in equilibrium bond length (>1 Å) which occurs between the neutral and ionic ground states. Analysis of the spectrum was therefore not straightforward and there was also evidence that further complications existed because of the presence of heavier Xe clusters. However, detailed calculations, employing a Morse potential for the neutral molecule and a more realistic numerical potential to describe the ionic state, gave results which substantiated the arguments for a vertical ionization energy some 0.7 eV above the adiabatic value. Other features in the photoelectron spectrum were assigned to ionization to higher states of Xe_2^+ . Potential energy curves for all of the Xe_2^+ states dissociating to $\text{Xe}(^1\text{S}_0)$ and $\text{Xe}^+(^2\text{P}_{3/2}$ or $^2\text{P}_{1/2})$ were constructed primarily from the experimental results and compared with the results of theoretical calculations, thus providing new information on these weakly bound ionic dimers.

Pes (Dehmer and Dehmer, 1978b) and photoionization efficiency studies (Ng *et al.*, 1971a) have also been performed for Ar_2 and Kr_2 . These investigations are in many ways similar to those made on Xe_2 . In the pes study, dissociation energies were determined for the weakly bound $\text{B}^2\Pi_{3/2(\text{g})}$ and $\text{C}^2\Pi_{3/2(\text{u})}$ excited states of the dimer ions and these values were found to be approximately 30% greater than recent theoretical values. Also, optimum potentials were derived for both the Ar_2^+ and Kr_2^+ ground states by fitting calculated Franck–Condon envelopes to the observed photoelectron band shapes. As in the case of Xe_2 , for both Ar_2 and Kr_2 a large difference between the first adiabatic ionization energy determined from photoionization efficiency (PIE) curves and the first vertical ionization potential obtained from the pe spectra was observed because of a large equilibrium geometry change on ionization. Electron impact mass spectrometric experiments have also been performed on some mixed rare-gas dimers (Helm *et al.*, 1979, 1981) and the measured values of the first ionization potentials agree reasonably well with values determined from related photoionization studies (Ng *et al.*, 1977a,b). The molecular beam photoionization method has also been used to study the dimers of CO, N_2 and NO (Linn *et al.*, 1981). In this work, a quadrupole mass spectrometer was used to detect the dimer positive ions formed by photoionization using variable wavelength radiation. Photoionization efficiency curves were constructed for each dimer in the threshold region and hence ionization energies were accurately determined in each case. No comparable pes experiments have been performed and it seems likely that the low concentrations of the dimers would make such studies extremely difficult. This is unfortunate since, as shown in the xenon dimer case, the pes method should provide information on the ionic state potential surfaces. Also, the possibility of observing vibrational structure associated with the ionic states cannot be ruled out. Similar PIE studies have also been made on the clusters of O_2 and H_2 dimers (Anderson *et al.*, 1980). The photoionization thresholds for $(\text{O}_2)_n^+$, where $n = 1$ to 5, have been measured and the binding energy of $(\text{O}_2)_2^+$ was estimated as (0.26 ± 0.02) eV. However, it was found that binding energies for higher clusters $(\text{O}_2)_n^+$ for

removal of one O_2 molecule were much lower. These smaller values are roughly what is expected for a charge induced dipole interaction of $(O_2)_{n-1}^+$ with O_2 . In this work the photoionization spectra of $(H_2)_2$ to give $H_3^+ + H + e^-$ show that the mechanism of H_3^+ production involves competition between autoionization and vibrational predissociation of vibronically excited $(H_2)_2$. The PIE method has likewise been used to measure onset ionization energies for the species $(CS_2)_n$ where $n = 2$ to 5 (Ono *et al.*, 1980). From the measured ionization energy and the known dissociation energy for $(CS_2)_2$, the binding energy for the $CS_2^+ \cdot CS_2$ species was estimated. Similar work has since been carried out on the OCS dimer and trimer and on the OCS \cdot CS_2 mixed complex (Ono *et al.*, 1981). Since recent work in mass spectrometry of molecular clusters has shown that large cluster sizes can be readily prepared (e.g. $(CO_2)_n$ and $(H_2O)_n$ clusters up to $n = 100$ can be made (Stace, private communication)), there is little doubt that similar studies to those already mentioned will be performed on higher cluster sizes.

Some rather more strongly bound molecular complexes have been studied by Peel and co-workers (Carnovale *et al.*, 1979, 1980a,b) using pes. The basic technique is very similar to that used in the study of van der Waals complexes in that use is made of a high pressure nozzle inlet system as well as a 150° hemispherical electrostatic analyser. A typical example of this work has been the recent study of the formic acid dimer (Carnovale *et al.*, 1979). By varying the stagnation pressure above the nozzle, a spectrum containing contributions from only the monomer and dimer was recorded. By careful 'spectrum stripping' of the monomer components a complete HeI spectrum of $(HCOOH)_2$ was obtained. Fortunately, the geometry of $(HCOOH)_2$ has been determined by electron diffraction and was used in molecular orbital calculations from which the dimer spectrum was interpreted. It was found that the dimer shows considerable interaction of the monomer orbitals of σ -symmetry but little interaction of π -orbitals. Related studies have also been made on the monomers and dimers of acetic acid and trifluoroacetic acid and the dimethyl ether-hydrogen chloride complex (Carnovale *et al.*, 1980a,b respectively). However, in the $(CH_3)_2O \cdot HCl$ case some difficulty was experienced in interpreting the experimental spectrum because the geometry of this complex is not known. This could clearly be a major stumbling block in the pes study of such molecular complexes and again emphasizes the inter-dependent nature of different types of spectroscopic research. One would envisage that the pes technique alone may not be entirely satisfactory in that the size and relative number of the molecular clusters in the photoionization region is not known. Even when these problems are clarified monomer bands are usually the main contributors to an experimental spectrum and the possibility of errors in the 'spectrum stripping' procedure is apparent.

The study of transients on surfaces

Although the use of pes to detect species adsorbed on surfaces is not new, the subject is only recently showing signs of significant development. This has largely been because of lack of experimental resolution and other difficulties associated with relating photoelectron spectra of adsorbed species to those obtained for gas phase molecules. One of the most promising approaches for overcoming the latter problem has been to make comparisons between the spectra of the adsorbed species and gas-phase spectra of both the free ligand and appropriate metal complexes of the ligand. This approach has led to some success in, for example, understanding the pe spectra of carbon monoxide adsorbed on metal surfaces (Plummer *et al.*, 1968; Allyn *et al.*, 1977). It may, however, be difficult to obtain the gas-phase spectrum of the free ligand when this corresponds to a radical which is very short-lived in the gas phase. In addition,

open-shell effects will complicate the gas-phase radical spectra making comparison with those of the adsorbed species difficult. However, metal complexes containing radical groups are well known and a study of the spectra of these for comparison with the spectra of adsorbed species would be a logical development. Such a comparison may in any case be more valid than the direct use of the gas-phase radical spectrum because of possible charge transfer between the metal and the ligand in the metal complex and on a metal surface.

One recent study which illustrates the above approach has involved the assignment of the gas-phase HeI photoelectron spectra of the cluster complexes $\text{Co}_3(\text{CO})_9\text{CH}$ and $\text{Co}_3(\text{CO})_9\text{CCH}_3$ (Costa *et al.*, 1981). In this study, bands associated with ionizations from the C–H and CCH_3 groups in these molecules correlated well with bands assigned to ionization of the same species on metal surfaces. For the C–H group, all of the observations were consistent with the idea of the C–H axis being tilted away from the normal surface. For CCH_3 , although a reasonable correlation exists between spectra of the cluster complex and the adsorbed species on a metal surface, a firm distinction between adsorbed CCH_3 and CHCH_2 was not possible. In a related example (Demuth, 1980b), a particularly detailed study has been made of the reaction of acetylene with Ni(100) and Ni(110) surfaces using pes with HeI and HeII radiation as well as temperature programmed thermal desorption spectroscopy. Evidence was presented for the presence of C_2H , CH_2 and CH species on the surface studied, but the interpretation was by no means straightforward or definitive.

More than in most fields one has to correlate information from several experimental techniques. In this respect the results from LEED, thermal desorption, uv pes and especially high resolution electron energy loss spectroscopy (EELS), and more conventional vibrational spectroscopy are particularly important. For example, evidence has recently been presented for the existence of CH (Demuth, 1977, 1980b, Demuth and Ibach, 1978), CH_2 and C_2H_2 (Demuth, 1977) and C_2H_3 (Demuth, 1979 and 1980a, Fischer and Keleman, 1977; Kesmodel *et al.*, 1978) following dissociative adsorption of ethylene and acetylene on nickel, platinum and palladium surfaces, the data being provided by LEED, EELS, pes and thermal desorption. Also, recently EELS (Demuth and Ibach, 1979) and pes (Erskine and Bradshaw, 1980) have been used in studies of the methoxy species formed by decomposition of methanol on nickel(111) surfaces. The pes evidence is that the C–O–Ni bond is normal or near-normal to the metal surface, whereas the EELS data were interpreted in terms of a highly bent C–O–Ni bond. In this case, the arguments from pes seem to carry more weight. They were based mainly on the fact that some bands expected on the basis of a surface molecule with C_s symmetry were absent, whereas the observed bands could be accounted for if the adsorbed CH_3O group had C_{3v} symmetry. These findings are also consistent with photoelectron data obtained with linearly polarized synchrotron radiation.

In summary, it appears that the study of radical species on surfaces is a rapidly growing field of interest. It is clear that pes has a role to play along with a number of other techniques in elucidating the nature of chemisorbed species and possible surface reaction mechanisms.

High temperature photoelectron spectroscopy

High temperature pes has developed to such an extent over the past five years that it is probably now better classified as a research field in its own right rather than as a branch of the transient species area. The increase in activity in high temperature pes has arisen largely because vapour phase spectra can now be obtained from solids heated to

temperatures in excess of 2000 K (Bulgin *et al.*, 1977; Dyke *et al.*, 1980f; Colbourn *et al.*, 1978b) and hence the range of molecules accessible with this technique has been greatly expanded. Although examples of high temperature pes have been mentioned earlier in this review, there are a number of other recent investigations which further illustrate both the type of information that can be obtained and the recent developments in this area.

For example, Berkowitz *et al.* (1979) have recently described a high temperature photoelectron spectrometer which uses a radiatively heated double-oven assembly. This instrument has been used to study the gas-phase photoelectron spectra of the lithium halide monomers and dimers, an interesting series of molecules in that on heating any member of this group a mixture of the dimer and monomer is obtained in the vapour phase. Monomer to dimer ratios were varied by superheating part of the oven assembly. By studying spectra recorded under different conditions, pure monomer and dimer spectra were obtained for all the lithium halides. In a parallel study, Potts and Lee (1979) also studied the lithium halides (except the fluorides) with pes by making use of a resistively heated furnace. In this case, the monomer-to-dimer ratio was altered simply by varying the size of the furnace tubes used. Comparison of the spectra recorded by the two groups of investigators showed reasonably good agreement although some differences occurred in the lithium bromide dimer and lithium iodide monomer spectra. Nevertheless, these studies illustrate the value of superheating a high temperature vapour as this technique could be used to pyrolyze molecules produced by initial high temperature vaporization, or, as was done here, to reduce the concentration of polymeric species in the vapour phase above a heated solid. This superheating technique has also been used to distinguish between the HeI photoelectron spectra of the monomeric and trimeric forms of AgCl and AgBr in the vapour phase (Berkowitz *et al.*, 1980). The spectra attributed to the monomeric species were interpreted in terms of bands arising from ionization from the halide p orbitals and bands at higher ionization energy which arise essentially from the $\text{Ag}(4d)^{-1}$ ionization split by spin-orbit and ligand-field interactions. It was not possible to obtain a spectrum of pure monomeric AgI because of decomposition of the sample on heating. As well as this investigation, a number of other studies have been performed on the silver halide trimers in the vapour phase (Potts and Lee, 1979; Berkowitz *et al.*, 1980; Potts and Lyus, 1978; MacNaughton *et al.*, 1980; Vonbacho *et al.*, 1976). Comparison of the results of these experiments shows that spectra recorded in one of the earlier studies (Vonbacho *et al.*, 1976) are contaminated probably by iron halides arising from reaction of the silver halides with the stainless steel boat used to contain the samples. As indicated earlier, reaction of the oven material with the sample or with other furnace components can be a serious problem in high temperature pes. Consequently great care should be taken over choice of these materials when designing an oven assembly for vaporization of a particular solid sample.

Radiofrequency induction heating has also been used as a way of heating solid samples. In a recent study, it was used to vaporize the actinide tetrahalides UF_4 , ThF_4 , UCl_4 and ThCl_4 (Dyke *et al.*, 1980, 1981) from a carbon furnace and hence obtain their photoelectron spectra. HeI and HeII spectra were recorded for these molecules in the gas phase and $\text{AlK}\alpha$ X-ray photoelectron spectra have been recorded for solid samples. Comparison of the spectra of the uranium and thorium tetrahalides shows that their electronic structures are very similar both in the solid-state and in the gas-phase except for the presence of two non-bonding metal 5f electrons in the uranium compounds. Also, the experimental spectra are consistent with these molecules having an effective tetrahedral geometry in the gas phase. These conclusions are supported by the results of non-relativistic multiple-scattering SCF-X α calculations.

Over the last few years there has been considerable interest in the use of pes to study the first row transition metal dihalides. The main aim of these studies was to establish the role played by the metal 3d orbitals in such systems. Experimentally these compounds are relatively easy to study as they vaporize to give primarily the dihalide although in a few cases some decomposition takes place resulting in a mixture of the monohalide and dihalide. This occurs for example for CrF_2 and CuF_2 where some monofluoride is produced in the vapour phase. Also, for the iodides, bromides and chlorides intensity changes between HeI and HeII spectra can be used to distinguish between halogen np ionizations and metal 3d ionizations; the bands associated with the $(3d)^{-1}$ metal ionizations increasing in intensity in the HeII spectra relative to those associated with the ligand np ionizations. In the case of the fluorides, however, the metal 3d: fluorine 2p cross-section ratio remains approximately constant on going from the HeI to the HeII photon energy and hence no noticeable intensity changes are observed between these spectra. This arises because of the increase in the F 2p cross-section at the HeII wavelength compared with that of the heavier halogens. The interpretation of the experimental photoelectron spectra of the transition metal dihalides is complicated by a number of factors. Firstly, the equilibrium geometries of a number of transition metal dihalides are not known although, apart from the titanium dihalides which have a C_{2v} structure, it seems probable that they all have a linear geometry with both metal-halogen bonds equal (van Zee *et al.*, 1980). Also, the electronic ground states of many of the transition metal dihalides are not known. Furthermore, it has been found that for the metal dichlorides Δ SCF calculations are not sufficient for assignment of the observed experimental spectra and proper allowance for correlation energy correlations must be made to obtain reasonable agreement with experiment.

In view of the above difficulties, it is perhaps logical to consider the closed shell molecules ZnX_2 first and then the CuX_2 molecules which have a $^2\Sigma_g^+$ ground state. The experimental HeI photoelectron spectra of ZnCl_2 (Boggess *et al.*, 1973; Berkowitz, 1974; Cocksey *et al.*, 1973) and ZnF_2 (Lee *et al.*, 1980; Dyke *et al.*, 1980b) consisted of two distinct regions. The zinc dichloride spectra have been assigned on the basis of Green's function calculations (von Niessen and Cederbaum, 1981) and the ZnF_2 spectra were assigned using *ab initio* configuration interaction calculations (Lee *et al.*, 1980; Dyke *et al.*, 1980b). These assignments are essentially the same. The first group of bands is due to the outer valence orbitals which have mainly metal 4s and halogen np character whereas the second group of bands at higher ionization energy arise from orbitals which are essentially metal 3d in character. The observed HeI and HeII photoelectron spectra of CuF_2 consisted of nine bands in the ionization energy region 11–21 eV (Dyke *et al.*, 1980b). Configuration interaction calculations show that configurations derived from metal 3d and ligand 2p ionizations make significant contributions to the low-lying states of CuF_2^+ and the spectra can be assigned reasonably successfully on the basis of these calculations. No other copper dihalides have been studied with pes probably because they decompose readily to give the corresponding copper monohalide on heating.

For the NiX_2 molecules, HeI and HeII photoelectron spectra have been recorded for NiF_2 , NiCl_2 and NiBr_2 (Potts *et al.*, 1981; McNaughton *et al.*, 1981; Berkowitz *et al.*, 1979). These molecules have one electron less than the corresponding CuX_2 species and their ground state is thought to be the $^3\Pi_g$ state corresponding to the metal 3d orbital occupancy $\delta_g^4 \pi_g^3 \sigma_g^1$ (Lee *et al.*, 1980b; van Zee *et al.*, 1980). Detailed Green's function calculations have been performed for NiCl_2 in order to interpret its photoelectron spectrum (von Niessen and Cederbaum, 1981). These calculations assume, however, that NiCl_2 ground state is a closed-shell $^1\Sigma_g^+$ state corresponding to the metal 3d orbital configuration $\delta_g^4 \pi_g^4 \sigma_g^0$. Despite this assumption these calculations are of

interest in that they show that the nickel 3d electrons are valence in character and participate strongly in chemical bonding. They also show that correlation effects make strong contributions to the experimental spectrum with a number of weak low-lying satellite bands being predicted. An assignment has been presented (Potts *et al.*, 1981) for all the nickel dihalides using the more qualitative arguments of observed HeI/HeII intensity changes. This assignment placed all the bands arising from the nickel $(3d)^{-1}$ ionizations to lower ionization energy of the bands associated with the ligand $(np)^{-1}$ ionizations. Of the other transition metal dihalides HeI and HeII photoelectron spectra have been recorded for CoX_2 , FeX_2 , and MnX_2 (where $X = \text{F}, \text{Cl}$ and Br), CrCl_2 and MnI_2 (Potts *et al.*, 1981; Lee *et al.*, 1980a; McNaughton *et al.*, 1981; Berkowitz *et al.*, 1979). Although the analyses of these spectra is by no means clear-cut, Potts *et al.* (1981) have presented a reasonable assignment of the observed spectra based on HeI/HeII intensity changes and by comparing spectra within a series for a given transition metal with different halogen atoms and for a given halogen with different metal atoms. However, detailed calculations which include the effects of electron correlation are required to determine the electronic ground states of these systems and to predict the positions of ionic states accessible from the neutral ground state in order to assign accurately the experimental photoelectron spectra.

These studies of transition metal dihalides emphasize the dependence of high temperature pes on the results of theoretical calculations and other spectroscopic measurements. However, high temperature pes provides a unique way of probing the electronic structure of gaseous small molecules composed of heavy elements. Spectral features occur due to factors such as strong ionic bonding or relativistic effects which are rarely encountered in other branches of gas-phase pes. With the development of relativistic theories for calculating electronic properties of compounds containing heavy elements such experimental measurements will be extremely valuable in the future.

CONCLUSIONS

It is clear that the study of transient species by pes has developed rapidly since the first investigations were made. Some of the earliest molecules studied could hardly be classified as transient species in that they had relatively long gas-phase lifetimes e.g. CS, SO and $\text{O}_2(^1\Delta_g)$, whereas radicals with gas-phase lifetimes of the order of milliseconds can now be investigated. Undoubtedly, molecules with shorter lifetimes will be studied in the future but if major advances are to be made, improvement in the sensitivity of existing spectrometers by, for example, using a multidetector system will be essential. This would also allow improved spectra to be obtained for molecules for which weak spectra have already been recorded. For example, the band associated with the first ionization potential of NH has been observed at 13.49 ± 0.01 eV (Dyke *et al.*, 1980d) corresponding to the process $\text{NH}^+(\text{X}^2\Pi) \leftarrow \text{NH}(\text{X}^3\Sigma^-)$ but because only weak signals were detected it was not possible to identify any higher bands associated with the NH molecule. Such an improvement in sensitivity would also be extremely valuable in high temperature pes where weak signals of molecules produced by direct evaporation from a solid sample are the rule rather than the exception. Multichannel plate spectrometers also have the advantage of simultaneous recording of approximately 10% of the HeI spectral region. Not only does this lead to increased speed of recording of spectra, but also it eliminates spurious resolution or intensity changes over that energy range. Hence many of the difficulties presently inherent in spectrum subtraction techniques would be minimized. Perhaps most importantly the door may then be open for the use of pulsed methods for generation of transients e.g. flash photolysis or flash pyrolysis from solids.

It may also be possible to study short-lived species with other forms of electron spectroscopy. For example, synchrotron radiation with its variable wavelength and polarized nature is a particularly attractive photon source for such work. One use would be to make a very interesting study of the valence photoelectron spectra of the first row transition metals as a function of photon energy in order to establish the variation of 4s and 3d photoionization cross-sections as a function of photon energy. Investigations could then be extended to simple transition metal compounds. Also, spectroscopic studies of excited states of transient species could be made by techniques such as electron energy-loss spectroscopy and resonantly enhanced multiphoton ionization (Johnson, 1980). Both of these latter techniques offer the possibility of investigating one-photon forbidden excited states of molecules.

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