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Ultraviolet Photoelectron Studies of Unstable Molecules with Relevance to Synthesis, Quantum Chemistry, and Spectroscopy

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1 Introduction

Ultraviolet photoelectron spectroscopy (UPS), since its inception in the early sixties, has demonstrated fully its utility for the determination of the electronic structures of a wide range of stable molecules, both organic and inorganic.[1–3] Detailed analysis of photoelectron spectra can provide information on bonding, and in combination with semi-empirical and *ab initio* quantum mechanical methods can substantiate the molecular orbital picture of molecules.

In its maturity, the method has developed into a technique *par excellence* for following the course of a variety of chemical reactions, especially those designed (often with ingenuity) for the generation of transient/unstable molecules. These species produced by, for example, pyrolysis, discharge, atom–molecule, molecule–molecule, and molecule–solid reactions are often new, and frequently chemically interesting. Such studies can provide the impetus for investigating new synthetic procedures, new classes of compounds, can provide a rich testing ground for the whole gamut of quantum mechanical methods, and can lead to other, higher resolution, spectroscopic studies. This central role of photoelectron spectroscopy can be illustrated as in Figure 1, and it is the happy synergism of these methods that will be discussed in this review.

The range of transient/unstable molecules can extend from very short lifetime (10^{-6}—10^{-3} s) radicals, *e.g.* CH_3,[4] HCO,[5] through to semistable molecules with lifetimes of minutes in the gas phase at low pressure, *e.g.* FCP,[6] Cl_2CCO.[7] This suggests that such photoelectron studies can be divided broadly into two camps, A and B, shown in Table 1. These two areas are by no means distinct; much

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[1] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, 'Molecular Photoelectron Spectroscopy', Wiley-Interscience, London, 1970.

[2] K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, and S. Iwata, 'Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules', Halsted Press, New York, 1981.

[3] R. L. DeKock and D. R. Lloyd, 'Advances in Inorganic Chemistry and Radiochemistry', Academic Press, 1974.

[4] J. M. Dyke, N. Jonathan, E. P. F. Lee, and A. Morris, *J. Chem. Soc., Faraday Trans. 2*, 1976, **72**, 1385.

[5] J. M. Dyke, N. Jonathan, A. Morris, and M. J. Winter, *Mol. Phys.*, 1980, **39**, 629.

[6] H. W. Kroto, J. F. Nixon, N. P. C. Simmons, and N. P. C. Westwood, *J. Am. Chem. Soc.*, 1978, **100**, 446.

[7] D. Colbourne, D. C. Frost, C. A. McDowell, and N. P. C. Westwood, *J. Chem. Soc., Chem. Commun.*, 1980, 250.

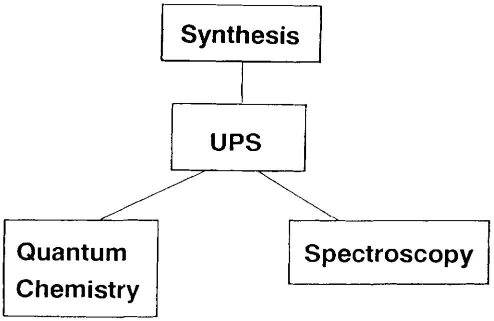

Figure 1 *The symbiosis between ultraviolet photoelectron spectroscopy, synthesis, spectroscopy, and quantum chemistry*

Table 1 *Ultraviolet photoelectron studies of transient molecules*

Type A:

Small molecules and radicals
2—5 atoms
Short lifetime (10^{-6}—10^{-1} s)
High resolution (150—200 cm^{-1} !)
Spectroscopically and theoretically interesting
Detailed investigation of ground and excited ionic states

Type B:

Larger molecules and radicals
4—12 atoms
Lifetime (s to min)
Medium resolution (200—400 cm^{-1})
Synthetically and chemically interesting
Investigation of chemical and physical properties

overlap can, and does occur. However, the focus of this work will be on species that come into category B, since most previous attention has centred around those belonging (primarily) in A.[8,9]* Of particular interest will be the interplay of synthesis, UPS, quantum chemistry, and spectroscopy, with the goal of demonstrating how a specific technique like photoelectron spectroscopy can provide information to a variety of chemists. These four principal themes will be followed by some unifying case studies.

2 Synthesis of Unstable Molecules

A. General Principles.—Synthesis in the context described above refers to the generation, detection, and characterization of small molecules sufficiently long-

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[8] J. M. Dyke, N. Jonathan, and A. Morris, in 'Electron Spectroscopy: Theory, Technique, and Applications', Vol. 3, ed. C. R. Brundle and A. D. Baker, Academic Press, London, 1979.

[9] J. M. Dyke, N. Jonathan, and A. Morris, *Int. Rev. Phys. Chem.*, 1982, 2, 3.

* Many of the smaller species mentioned *en passant* in this review have been covered in some depth in references 8 and 9, to which the reader will be directed for the appropriate citations.

lived at low pressure to undergo minimal decomposition. The emphasis is on furnishing organic and inorganic species in *high yield* with a view to further spectroscopic investigation, and use as reactive intermediates in a true synthetic sense. The accent is not on the isolation, establishment of a crystal structure, melting point, and full characterization, *etc.* associated with professionals in the synthetic field.

UPS lends itself to such an *in situ* or 'on-line' approach, and can provide the impetus for further genuinely synthetic work, or spectroscopic and quantum mechanical investigations. A classic example of this approach driving synthesis would be the unstable $2p_\pi—3p_\pi$ $>C=P<$ and $-C\equiv P$ species, *e.g.* $H_2C=PH$,[10] $FC\equiv P$,[6] $CH_3C\equiv P$,[11] produced in sufficient yield by on-line methods that the essential features can be modified in the preparative laboratory, leading to the formation of a variety of transition metal complexes,[12,13]

Although the emphasis in UPS is often on the molecular properties of the species, it should not be forgotten that *in situ* synthesis can demonstrate that a species can be made; that it has a definite lifetime, and that the opportunity exists to work further with it. In general, the molecules are small, easily recognizable, spectroscopically interesting, and are tractable by reasonable quality quantum mechanical (QM) calculations for many of their electronic and structural properties. The species of interest often turn out to be the unstable analogues of larger, but similar, compounds that are stabilized by bulky groups (Table 2).

In many cases even the completely unsubstituted species cannot be detected by UPS, and yet partially substituted species can; $H_2Si=SiH_2$ is unknown by spectroscopy, but can be stabilized by bulky groups, *e.g.* mesityl.[34] Similarly, CH_3SCN is known (it can be bought) and yet HSCN is unknown. Of course, it is precisely in this netherworld that quantum chemistry can play a role, both of the preceding examples having been subjected to a wide variety of theoretical methods.[35,36]

B. Techniques.—Having indicated the range of lifetimes and properties of interest, and having given the mandate that the molecules should be synthetically interesting, one is limited to attempting to generate them at low pressure in a flow system, since many such species are often thermodynamically and/or kinetically unstable. These requirements therefore determine the techniques used to probe them, and it is here that UPS makes a real contribution. Other related

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[10] M. J. Hopkinson, H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *J. Chem. Soc., Chem. Commun.*, 1976, 513.

[11] N. P. C. Westwood, H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, *J. Chem. Soc., Dalton Trans.*, 1979, 1405.

[12] H. W. Kroto, *Chem. Soc. Rev.*, 1982, **11**, 435.

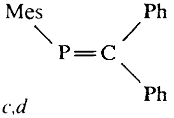
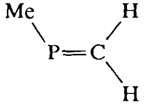
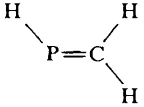
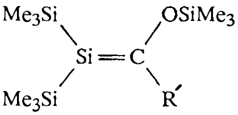
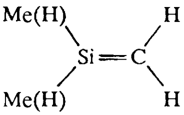
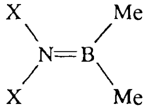
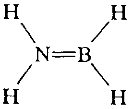
[13] J. C. T. R. Burckett-St. Laurent, P. B. Hitchcock, M. A. King, H. W. Kroto, M. F. Meidine, S. I. Klein, S. I. Al-Resayes, R. J. Suffolk, and J. F. Nixon, *Phosphorus Sulfur*, 1983, **18**, 259.

[34] R. West, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1201.

[35] G. Olbrich, *Chem. Phys. Lett.*, 1986, **130**, 115.

[36] V. Barone, P. Cristinziano, F. Lelj, and N. Russo, *J. Mol. Struct., Theochem.*, 1982, **86**, 239.

Table 2 *Some molecules that have been stabilized by bulky ligands, and spectroscopic and theoretical studies of their unstable analogues*

Stable[a] Molecules	*Unstable Analogues*	*Spectroscopic Studies*	*QM[b] Calculations*
 *c,d*		UPS[e]	*g,h*
		MW[f]	
RN=NR	HN=NH	UPS,[i] IR[j]	See *i,k*
 *l*		UPS[m,n,o] IR[p]	*q,r,s*
 *t*		UPS[u] MW[v] IR[w]	See *u*

[a] Mes = mesityl (2,4,6-trimethylphenyl); R = alkyl; R′ = 1-adamantyl, X = halogen. [b] Only representative recent studies are given. [c] Ref. 14; [d] Ref. 15; [e] Ref. 16. [f] Ref. 10; [g] Ref. 17. [h] Ref. 18. [i] Ref. 19. [j] Ref. 20. [k] Ref. 21. [l] Ref. 22. [m] Ref. 23. [n] Ref. 24. [o] Ref. 25. [p] Ref. 26. [q] Ref. 27. [r] Ref. 28. [s] Ref. 29. [t] Ref. 30. [u] Ref. 31. [v] Ref. 32. [w] Ref. 33.

[14] R. Appel, F. Knoll, and I. Ruppert, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 731.
[15] C. N. Smit and F. Bickelhaupt, *Organometallics*, 1987, **6**, 1156.
[16] H. Bock and M. Bankmann, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 265.
[17] W. W. Schoeller and E. Niecke, *J. Chem. Soc., Chem. Commun.*, 1982, 569.
[18] L. L. Lohr, H. B. Schlegel, and K. Morokuma, *J. Phys. Chem.*, 1984, **88**, 1981.
[19] D. C. Frost, S. T. Lee, C. A. McDowell, and N. P. C. Westwood, *J. Chem. Phys.*, 1976, **64**, 4719.
[20] K.-E. J. Hallin, J. W. C. Johns, and A. Trombetti, *Can. J. Phys.*, 1981, **59**, 663.
[21] H. J. Aa. Jensen, P. Jørgensen, and T. Helgaker, *J. Am. Chem. Soc.*, 1987, **109**, 2895.
[22] A. G. Brook, S. C. Nyburg, F. Abdesaken, B. Gutekunst, G. Gutekunst, R. K. Kallury, Y. C. Poon, Y.-M. Chang, and W. Wong-Ng, *J. Am. Chem. Soc.*, 1982, **104**, 5667.
[23] T. Koenig and W. McKenna, *J. Am. Chem. Soc.*, 1981, **103**, 1212.
[24] P. Rosmus, H. Bock, B. Solouki, G. Maier, and G. Mihm, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 598.
[25] J. M. Dyke, G. D. Josland, R. A. Lewis, and A. Morris, *J. Phys. Chem.*, 1982, **86**, 2913.
[26] G. Raabe, H. Vančik, R. West, and J. Michl, *J. Am. Chem. Soc.*, 1986, **108**, 671.
[27] R. Ahlrichs and R. Heinzmann, *J. Am. Chem. Soc.*, 1977, **99**, 7452.
[28] M. W. Schmidt, M. S. Gordon, and M. Dupuis, *J. Am. Chem. Soc.*, 1985, **107**, 2585.
[29] P. v. R. Schleyer and D. Kost, *J. Am. Chem. Soc.*, 1988, **110**, 2105.
[30] H. Steinberg and R. J. Brotherton, 'Organoboron Chemistry', Vol. 2, Wiley, New York, 1966.

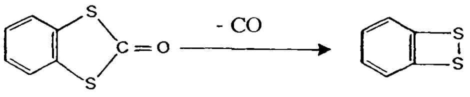
techniques could include microwave spectroscopy, Fourier transform infrared (FTIR), and various laser techniques. However, it should be remembered that in order to follow the on-line chemistry, a method is required that does not focus in on very fine spectroscopic details, *e.g.* fractions of a wavenumber (diode laser spectroscopy), or perhaps miss some product due to selection rules, *e.g.* lack of a dipole moment (microwave spectroscopy). Rather, one requires a technique that follows the complete reaction, monitors all products, gives an estimate of relative amounts, and is reasonably fast with good sensitivity. UPS comes close to this, since the experimental configuration permits the reaction products to be generated directly into the spectrometer. Certainly there is a sacrifice in resolution, and indeed some sensitivity, and often there are overlapping bands, since many ionization events occur in a relatively small (*ca.* 10 eV) range. This is more than offset, however, by the gain in flexibility, and the ability to see all species in real time.

Experiments generally divide between those demonstrating that a transient is formed—with often only the first ionization potential observed, the rest of the spectrum obscured by precursors, other unstable molecules, or final products—and those leading to a high yield of product. Our approach is essentially the latter, thereby permitting further spectroscopic characterization.

C. Generation of Small Unstable Molecules for Detection by UPS.—(i) *Controlled thermolysis* of a pure precursor with the intention of *selectively* eliminating a thermodynamically good leaving group is a favoured method. Tidy examples involving HX,[37,38] N_2,[39] CO,[40] or H_2[31] elimination include the formation of substituted ketenes (equation 1), or the aminoborane molecule (equation 4).

$$XH_2CCOCl \xrightarrow{-HCl} XHC{=}C{=}O \qquad (1)$$

$$\text{Azides} \xrightarrow{-N_2} \text{Imines} \qquad (2)$$



(3)

$$H_3NBH_3 \xrightarrow{-H_2} H_2NBH_2 \qquad (4)$$

In all of the above cases the yield of product is virtually 100%. Such thermolyses, judiciously chosen, often have the intention of producing multiply

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[31] N. P. C. Westwood and N. H. Werstiuk, *J. Am. Chem. Soc.*, 1986, **108**, 891.

[32] M. Sugie, H. Takeo, and C. Matsumura, *J. Mol. Spectrosc.*, 1987, **123**, 286.

[33] M. C. L. Gerry, W. Lewis-Bevan, A. J. Merer, and N. P. C. Westwood, *J. Mol. Spectrosc.*, 1985, **110**, 153.

[37] D. Colbourne and N. P. C. Westwood, *J. Chem. Soc., Perkin Trans. 2*, 1985, 2049.

[38] H. Bock, T. Hirabayashi, and S. Mohmand, *Chem. Ber.*, 1981, **114**, 2595.

[39] H. Bock and R. Dammel, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 504.

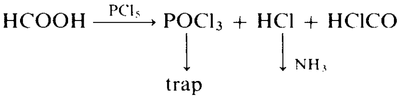
[40] M. Breitenstein, R. Schulz, and A. Schweig, *J. Org. Chem.*, 1982, **47**, 1979.

bonded molecules, a rapidly developing area of research. It should, however, be stated that in many instances the desired yields are not so high. For exceedingly transient species (category A, Table 1), or incomplete thermolysis, yields can be low, *e.g.* pyrolysis of nitrites with elimination of NO leads to the formation of alkyl radicals with observation of only weak first ionization potentials. Nonetheless, thermochemical and structural information on carbonium ions can be extracted.[41]

(ii) *Gas–solid* reactions at, or close to, *ambient* temperatures, in which control is exerted over flow rates, and the solid packing, are reasonably successful. Illustrative examples would include dehydrochlorination using $KOBu^t$ (equation 5),[42] the formation of halogen azides, isocyanates,[43] or thiocyanates[44] by means of a halogen/solid salt reaction (equation 6), or the formation of formyl chloride by on-line chlorination of formic acid with PCl_5 (equation 7).[45]

$$CH_3NHCl \xrightarrow{KOBu^t} H_2C{=}NH \tag{5}$$

$$X_2 \xrightarrow[\substack{AgNCO\\AgNCS}]{NaN_3} \begin{matrix} XN_3 \\ XNCO \\ XSCN \end{matrix} \tag{6}$$



$$\begin{tikzcd}[column sep=small] HCOOH \arrow[r, "PCl_5"] & POCl_3 \arrow[d] & + & HCl \arrow[d, "NH_3"] & + & HClCO \\ & \text{trap} & & & & \end{tikzcd} \tag{7}$$

The latter example illustrates how the side-products of the reaction can be removed *en route* into the spectrometer, an expedient often used to enhance the yield.

(iii) *Gas–solid* reactions at *elevated* temperatures, again with control over the conditions, can also lead to high yields of products as shown in equations 8—10, for the formation of HBX_2,[46,47] X_2CCO,[7,37] and SiF_2,[48,49] respectively.

$$BX_3 \xrightarrow[150\,°C]{NaBH_4} HBX_2 \tag{8}$$

$$X_3CCOCl \xrightarrow[300\,°C]{Zn} X_2C{=}C{=}O \tag{9}$$

$$SiF_4 \xrightarrow[1000\,°C]{Si} SiF_2 \tag{10}$$

[41] J. C. Schulz, F. A. Houle, and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1984, **106**, 3917.
[42] H. Bock and R. Dammel, *Chem. Ber.*, 1987, **120**, 1961.
[43] D. C. Frost, C. B. MacDonald, C. A. McDowell, and N. P. C. Westwood, *Chem. Phys.*, 1980, **47**, 111.
[44] D. C. Frost, C. B. MacDonald, C. A. McDowell, and N. P. C. Westwood, *J. Am. Chem. Soc.*, 1981, **103**, 4423.
[45] D. C. Frost, C. A. McDowell, and N. P. C. Westwood, *Chem. Phys. Lett.*, 1977, **51**, 607.
[46] D. C. Frost, C. Kirby, C. A. McDowell, and N. P. C. Westwood, *J. Am. Chem. Soc.*, 1981, **103**, 4428.
[47] D. P. Chong, C. Kirby, W. M. Lau, T. Minato, and N. P. C. Westwood, *Chem. Phys.*, 1981, **59**, 75.
[48] N. P. C. Westwood, *Chem. Phys. Lett.*, 1974, **25**, 558.
[49] T. P. Fehlner and D. W. Turner, *Inorg. Chem.*, 1974, **13**, 754.

(iv) *Molecule–molecule* reactions, invariably in the gas phase under conditions where collision-controlled reactions can occur, can lead, *e.g.*, to the formation of unstable halogeno-amines[50–52] (equation 11), and halogen thiocyanates[44,53] (equation 12).

$$RNH_2 + X_2 \longrightarrow RNHX \text{ and/or } RNX_2 \qquad (11)$$

$$(SCN)_2 + X_2 \longrightarrow XSCN \qquad (12)$$

(v) *Decomposition* of higher *n*-mers, *e.g.* dimers or trimers, to give a transient monomer can often result in a very high yield of product. One of the first species to be investigated by this route was the NF_2 radical[54] produced from the dimer. Other studies include the formation of substituted imines,[55] and thiocarbonyls.[12] Equation 13 shows the formation of heterocyclic SN radicals sampled from the vapour over the corresponding radical dimers.[56] *

$R = CF_3,Cl,Ph,NMe_2$ (13)

The UPS of such a radical species with $R = NMe_2$[57] (Figure 2) shows the low lying SOMO expected for ionization from the $^2A_2$ radical. The strong/weak bands with an approximate 3:1 intensity between 8 and 9 eV correspond to the $^3B_2$ and $^1B_2$ excited states of the cation separated by 2 K; higher ionization potentials (IP) relate to ring and ligand orbitals.

(vi) *Efficient* in situ *atom–molecule* reactions, frequently with no activation energy, can lead to the detection of very short-lived species, since the mixing zone (often movable) can be placed very close to the ionization point, *e.g.* $O(^3P)$ atoms can be reacted with Br_2, leading to the detection of $Br(^2P)$ atoms,[58] and the $OBr(^2\Pi)$ radical.[59] More recently, elegant experiments have been performed by Dyke *et al.* using ^2P F-atoms (generated in a microwave discharge) to produce small transient species, particularly di-, tri-, and tetra-atomics.[8,9]

[50] D. Colbourne, D. C. Frost, C. A. McDowell, and N. P. C. Westwood, *Can. J. Chem.*, 1979, **57**, 1279.

[51] M. K. Livett, E. Nagy-Felsobuki, J. B. Peel, and G. D. Willett, *Inorg. Chem.*, 1978, **17**, 1608.

[52] F. Carnovale, T.-H. Gan, and J. B. Peel, *Aust. J. Chem.*, 1979, **32**, 719.

[53] G. Jonkers, O. Grabandt, R. Mooyman, and C. A. de Lange, *J. Electron Spectrosc. Rel. Phenom.*, 1982, **26**, 147.

[54] A. B. Cornford, D. C. Frost, F. G. Herring, and C. A. McDowell, *J. Chem. Phys.*, 1971, **54**, 1872.

[55] D. C. Frost, C. B. MacDonald, C. A. McDowell, and N. P. C. Westwood, *J. Electron Spectrosc. Rel. Phenom.*, 1978, **14**, 379.

[56] R. T. Boeré, R. T. Oakley, R. W. Reed, and N. P. C. Westwood, *J. Am. Chem. Soc.*, 1989, **111**, 1180.

[57] A. W. Cordes, J. D. Goddard, R. T. Oakley, and N. P. C. Westwood, *J. Am. Chem. Soc.*, 1989, **111**, 6147.

[58] D. C. Frost, S. T. Lee, C. A. McDowell, and N. P. C. Westwood, *J. Electron Spectrosc. Rel. Phenom.*, 1977, **12**, 95.

[59] S. J. Dunlavey, J. M. Dyke, and A. Morris, *Chem. Phys. Lett.*, 1978, **53**, 382.

* The dimer structure, as shown, is cofacial, although structures with rings rotated with respect to each other are also known (ref. 57).

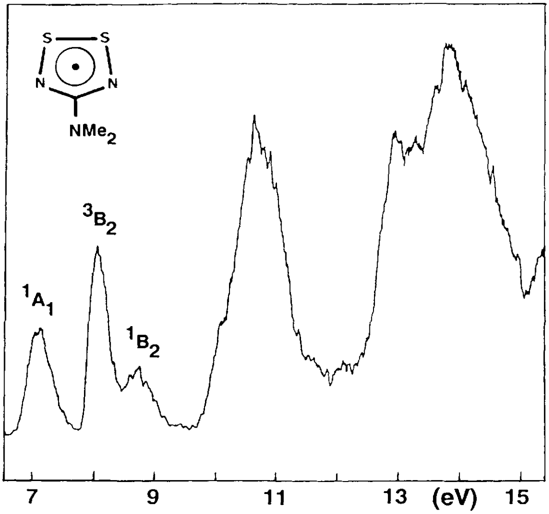


Figure 2 *The* HeI *photoelectron spectrum of the* 4-*dimethylamino*-1,2,3,5-*dithiadiazolyl radical obtained from the radical dimer, showing the relative energies of the ground and first excited* (*triplet and singlet*) *state cations*

$$F^{\cdot} + N_3 \longrightarrow NF + N_2 \qquad (14)$$

Equation 14 illustrates the formation of NF, isoelectronic with O_2, which is produced in ground ($X^3\Sigma$) and excited ($a^1\Delta$) states, both of which can be detected. Often the methods are based on previously known kinetic data, although in principle the UPS technique could provide a method for following the kinetics of such processes. As a synthetic route however, this approach is lacking.

(vii) *Discharge techniques*, especially of the microwave type at 2.45 GHz, are not particularly controllable, but can, with care, be used to produce high yields of specific species. Some of the early papers in the field used this method to produce *e.g.* $O_2(^1\Delta_g)$, $SO(^3\Sigma^-)$, $CS(^1\Sigma^+)$, and CF_2 (references 8 and 9). The last three species were obtained in reasonably high yield. Larger molecules can be obtained, *e.g.* HN=NH[19] and H_2C=NH,[58] from hydrazine and methylamine precursors, respectively, but for success, the discharge cavity has to be detuned to the point of instability. Alternative methods for these species turn out to be superior.[19,42]

(viii) *Thermal decomposition* of solids also appears to be an uncontrollable method of generating unstable compounds, *e.g.* the exothermic decomposition of AgNCO at 150 °C must be rated as particularly arbitrary, and yet UPS spectra of essentially pure NCNCO have been recorded from this reaction.[60] Other

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[60] D. C. Frost, H. W. Kroto, C. A. McDowell, and N. P. C. Westwood, *J. Electron Spectrosc. Rel. Phenom.*, 1977, **11**, 147.

examples of this type include the formation of PN,[8] S_3N_3[61] (equation 15), and $S_2(^3\Sigma_g^-)$[8] (equation 16).

$$(SN)_x \xrightarrow[120\,^\circ C]{\Delta} S_3N_3 \tag{15}$$

$$HgS \xrightarrow[400\,^\circ C]{\Delta} S_2 \tag{16}$$

(ix) *Thermal vaporization* of solids has been used for involatile compounds up to, say, 1 000 K. This method is often employed for investigation of alkali metal halides, compounds of Groups IIb, IIIa, IVa, and Va, and a variety of other species including transition metals halides. Some of these results have been summarized previously.[9,62]

(x) *Very high temperature methods* for the gas phase generation of refractory materials, *e.g.* transition metals, metal oxides, *etc.*, have been developed. This is a very specialized area, admirably investigated by Dyke, Morris, *et al.*[63] using radiofrequency induction heating with sufficient power to permit the attainment of temperatures in excess of 2 100 K with the appropriate susceptors. These techniques can be thought of as the spectroscopic analogues of metal vapour synthesis, although the measurement techniques require skilful experimentation. In addition to the experimental challenge, the species themselves, typically with $Z > 21$ pose a real test for quantum mechanical methods since relativistic effects are often involved.

(xi) *Isentropic expansions* using molecular or pseudo-molecular beams to form atomic or molecular clusters, or generate discrete gas phase adducts also merit attention. Often both dimers and higher *n*-mers are formed under a given set of experimental conditions, such that spectra of discrete dimers or trimers have to be obtained by spectral subtraction procedures. Many examples involving the use of UPS and photoionization mass spectrometry have been covered previously[9] for both strongly bound molecular complexes, *e.g.* acid dimers, $(CH_3)_2OHCl$, and weakly bound van der Waals molecules such as Xe_2, Ar_2, and Kr_2. More recently, Kimura,[64] Peel,[65] and co-workers have been active in these areas.

D. Synopsis.—From the synthetic chemist's point of view the first five methods are the most appropriate for general synthetic adaption. It should be pointed out that there are essentially no UPS groups engaged in collecting or trapping the species that are generated. In most cases, irrespective of the method, the photoelectron spectroscopist invariably pumps the products away, and makes no

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[61] W. M. Lau, N. P. C. Westwood, and M. H. Palmer, *J. Am. Chem. Soc.*, 1986, **108**, 3229.

[62] R. G. Edgell, in 'Electronic Structures and Magnetism of Inorganic Compounds,' A Specialist Periodical Report, ed. P. Day, The Royal Society of Chemistry, London, 1982, Vol. 7, p. 1.

[63] A. Morris, J. M. Dyke, G. D. Josland, M. P. Hastings, and P. D. Francis, *High Temp. Sci.*, 1986, **22**, 95.

[64] S. Tomoda and K. Kimura, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1768.

[65] F. Carnovale, J. B. Peel, and R. G. Rothwell, *J. Chem. Phys.*, 1988, **88**, 642.

use of them for further reaction. Given the time and energy that goes into some of the work it would seem that here is a promising area for further investigation. Some of the semistable products have lifetimes that would permit co-condensation reactions with subsequent work-up.

3 Ultraviolet Photoelectron Spectroscopy

The technique, which became available in the early-sixties has been well documented in the literature,[1–3,66–68] and it is not necessary to go into all the details except to mention those features that make the method so appealing for study of transients. UPS involves the ejection of electrons from molecules by ultraviolet radiation, and the subsequent kinetic energy (KE) analysis of these ejected electrons. This provides a measure of the binding energies of electrons in molecules, which for the valence region (unlike the complementary XPS technique which uses *X*-rays to probe core levels[66,69]), gives a handle on those energy levels intimately involved in bonding. The relationship between the available energies is given by the Einstein photoelectric equation.

$$\mathrm{KE} = h\nu - \mathrm{IP} \tag{17}$$

With a fixed energy light source (HeI, 58.4 nm, 21.22 eV), and analysis of the electron KEs, the technique, to a first approximation, maps out the orbital energies of a molecule. This provides a means of investigating the electronic structures of molecules, the primary value of the method. It should be noted that since the technique involves transitions between ground state molecules and the various states of the cation, UPS is one of the few techniques to provide information on excited ionic states. Indeed, since the PE spectrum corresponds to the ultraviolet spectrum of the cation, this relationship can often provide mutually useful information.[70]

An approximation that is often invoked to explain the orbital relationship is Koopmans' theorem (KT),[71] a disarmingly simple statement that expresses the experimental IP as equal to the negative of the orbital energy. This relationship, as discussed later, neglects electron correlation and orbital relaxation (or reorganization). In addition, the assumption is made that relativistic effects are the same in the molecule and the ion. This can be reasonably ignored in molecules containing first and/or second row atoms, although explicit inclusion, *e.g.* in $\mathrm{CI_4}$[72] or $\mathrm{HgI_2}$,[73] is

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[66] T. A. Carlson, 'Photoelectron and Auger Spectroscopy', Plenum, New York, 1975.

[67] J. W. Rabalais, 'Principles of Ultraviolet Photoelectron Spectroscopy', Wiley, New York, 1977.

[68] J. H. D. Eland, 'Photoelectron Spectroscopy', Butterworths, London, 1984.

[69] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johanssan, T. Bergmark, S.-E. Karlsson, I. Lindgren, and B. Lindberg, *Nova Acta Regiae Soc. Sci. Ups., Ser. IV*, 1967, 20.

[70] F. G. Herring and R. A. N. McLean, *Inorg. Chem.*, 1972, **11**, 1667.

[71] T. Koopmans, *Physica*, 1934, **1**, 104.

[72] G. Jonkers, C. A. de Lange, and J. G. Snijders, *Chem. Phys.*, 1982, **69**, 109.

[73] E. J. Baerends, J. G. Snijders, C. A. de Lange, and G. Jonkers, in 'Local Density Approximations in Quantum Chemistry and Solid State Physics', ed. J. P. Dahl and J. Avery, Plenum, 1984.

required in order to obtain full agreement between calculated and experimental IPs.

A feature which becomes apparent upon detailed study is the accessibility of excited vibrational states of the cation. Such information carried away by the ejected electron manifests itself as vibrational structure on photoelectron bands. Consideration of the Franck–Condon principle of verticality enables one to ascertain, in theory, the type of orbital from which the electron was ejected. This may be used for identification, and is therefore of value in the investigation of previously unknown species. Of course, molecules have multi-dimensional surfaces and it is only with small molecules, or unique types of ionization *e.g.* localization within a particular functional group, that this structure is resolvable. This is a particularly good *raison d'etre* for looking at small molecules, with a limited number of degrees of freedom.

Cross-section studies with different energy light sources can also provide a guide to orbital assignments. Additional features also observed include rotational structure; this is only found in specific cases, and under very high resolution (30—60 cm^{-1}), *e.g.* H_2 or HF/DF.[67] Details derived from the lifting of orbital degeneracies can also be investigated; these include Jahn–Teller distortions in degenerate states, and Renner–Teller distortions in linear molecules.[68] Spin–orbit effects, which essentially compete with Jahn–Teller distortion to lift degeneracies, are also observed; both are evident in the series of methyl halides, CH_3X, $X =$ Cl, Br, and I.[74] The identification of these effects can provide evidence for the generation of high symmetry molecules. It should also be mentioned that since the ejected electron carries away any value of angular momentum it requires to satisfy the conservation rules, all one electron processes are allowed, unlike other techniques that often have restrictive selection rules. Hence UPS monitors all species. This also implies that a study of the angular distributions of the outgoing electrons can give additional information, which it does; it is, however, rarely performed in the investigation of transients. The minimalist nature of the selection rules is the feature of UPS that makes it so powerful as an on-line technique. It is however, as practitioners in the field admit, one of the lowest resolution forms of spectroscopy around (short of *X*-ray methods); typical resolution ranges from 15—40 meV (120—320 cm^{-1}). For those groups engaged in the study of transient/unstable molecules, it is also one of the dirtiest forms of spectroscopy, and often the resolution limitations are set by perturbations of the electrostatic potentials used to analyse the ejected electrons. In high resolution work further limitations are provided by the light source line width, Doppler motion of the target molecules, and by stray magnetic fields. For transient work these are rarely of concern due to contamination of the electron optics. Despite these limitations, a rather good way to investigate unstable molecules is to tee up the preparative method(s) using UPS, and then move to higher resolution spectroscopy for detailed molecular parameters.

A block diagram of a typical photoelectron spectrometer for the study of

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[74] J. L. Ragle, I. A. Stenhouse, D. C. Frost, and C. A. McDowell, *J. Chem. Phys.*, 1970, **53**, 178.

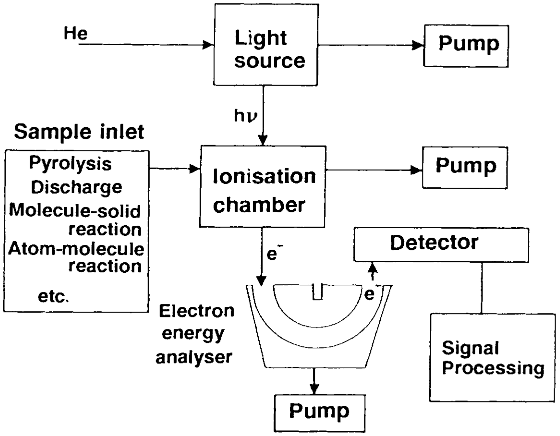

Figure 3 *Block diagram of an ultraviolet photoelectron spectrometer designed for the study of transient species. The key features include a versatile inlet system, and a separately pumped ionization chamber*

unstable molecules is shown in Figure 3. It is generally the case that instruments for this purpose are custom built, to incorporate enhanced pumping capabilities, versatile inlet systems, modular construction, and resistance to contamination.[8,9,58,75–80] Most home-built instruments feature such facilities, and in addition, may include some enhancement features built into the driving software. These can be designed to enhance the signal due to the transient, *e.g.* by using phase-sensitive detection techniques,[8,76] or, once spectra have been collected, by invoking some kind of spectrum stripping routine to obtain a spectrum of the 'pure' transient.[65,76] Of course, a preferred approach is to improve the chemistry of the process to enhance the yield. It is also true that careful and judicious use of commercial instruments, sometimes with minor modifications, can provide worthwhile results,[12,81–85] especially for semistable species.

UPS is thus a superb technique for following gas phase reactions; one sees all the products and the conditions of the experiment can then be optimized in real time to enhance the yield of desired species. Overlap of photoelectron bands in

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[75] G. Jonkers, C. A. de Lange, and J. G. Snijders, *Chem. Phys.*, 1980, **50**, 11.

[76] O. Grabandt, H. G. Muller, and C. A. de Lange, *Computer Enhanced Spectroscopy*, 1984, **2**, 33.

[77] F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.*, 1978, **100**, 3290.

[78] E. Nagy-Felsobuki, J. B. Peel, and G. D. Willett, *J. Electron Spectrosc. Rel. Phenom.*, 1978, **13**, 17.

[79] Y. Achiba, K. Nomoto, and K. Kimura, *J. Phys. Chem.*, 1982, **86**, 681.

[80] M. J. S. Dewar and T.-P. Tien, *J. Chem. Soc., Chem. Commun.*, 1985, 1243.

[81] T. Koenig, R. Wielesek, W. Snell, and T. Balle, *J. Am. Chem. Soc.*, 1975, **97**, 3225.

[82] D. M. de Leeuw, R. Mooyman, and C. A. de Lange, *Chem. Phys. Lett.*, 1978, **54**, 231.

[83] H. Bock and B. Solouki, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 427.

[84] J. Kreile, N. Munzel, A. Schweig, and H. Specht, *Chem. Phys. Lett.*, 1986, **124**, 140.

[85] C. Lafon, D. Gonbeau, G. Pfister-Guillouzo, M. C. Lasne, J. L. Ripoll, and J. M. Denis, *Nouv. J. Chim.*, 1986, **10**, 69.

those cases where yields are low can be a problem. However, the major concern is often one of identification; how does one establish the carrier of a new spectrum, or how can the components of a mixture be deciphered? There is no one answer to this; one must rely on chemical intuition, alternative routes, comparison with similar molecules, independent evidence, QM calculations (see below), and detailed spectroscopic information if resolved bands are obtained. To this end a valuable aid is to monitor the concomittant ion, either by time-of-flight, or by using a quadrupole mass analyser operating in the electron impact or photoionization mode.[61,86,87] For transient work this is not done in coincidence, although such photoelectron–photoion coincidence techniques have been used to investigate state-selected ions.[68,88]

A recent development for electron spectroscopy in general, but also applicable to the study of transients,[89] is the replacement of a single channel detector by a position-sensitive device, thereby permitting the simultaneous aquisition of a complete portion of the spectrum. Providing that contamination of the microchannel plates is minimized, this adaption permits an improvement in the data rate of up to 75, which is significant for the study of weak bands, and more importantly, reduces the inevitable energy drift associated with time-dependent contamination of the electron optics.

4 Quantum Chemistry

A. Calculation of IPs and Orbital Assignments.—The molecular orbital energies can, in principle, be obtained from QM calculations. Since the Schrödinger equation cannot be solved explicitly for a multi-electron system, all computational methods have to rely on some approximations. Despite these inadequacies the range of methods for calculating orbital energies is vast, ranging from simple Hückel calculations, to extensive and expensive *ab initio* methods which can include some form of post-SCF treatment. Some of these and their applicabilities to the topic at hand will be touched on here.

From the photoelectron spectroscopist's point of view the simplest approach is to perform a single calculation on the ground state molecule, and make the assumption that KT holds. Although electron correlation, reorganization, and relativistic effects are neglected, the first two almost cancelling, and the latter of no significance for light elements, this method turns out to be reasonably viable only in those cases where the cationic states are well separated. There are, of course, some notable exceptions, since the assumption is made that reorganization and correlation are the same from state to state, which they are not. Thus even 'good' calculations get the state ordering wrong in N_2 and F_2, and indeed, when the density of states increases, the method becomes unreliable; one is simply assuming that what is good for the molecule is also good for the cation, which is

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[86] D. C. Frost, W. M. Lau, C. A. McDowell, and N. P. C. Westwood, *J. Phys. Chem.*, 1982, **86**, 3577.

[87] M. H. Palmer, W. M. Lau, and N. P. C. Westwood, *Z. Naturforsch., Teil A*, 1982, **37**, 1061.

[88] J. Dannacher, *Org. Mass. Spectrom.*, 1984, **19**, 253.

[89] A. Morris, N. Jonathan, J. M. Dyke, P. D. Francis, N. Keddar, and J. D. Mills, *Rev. Sci. Inst.*, 1984, **55**, 172.

obviously unrealistic. In addition, KT holds only for closed shell molecules; when radicals involving open shells are considered, the eigenvalues have no physical meaning, and since unpaired outer shell electrons can couple with the electrons remaining after inner shell ionization, a multiplicity of states can arise (*e.g.* Figure 2), and the simple view of one orbital—one band does not hold.

Molecular orbital calculations take many forms; a requirement is to solve the Hartree–Fock (HF) self-consistent field (SCF) equations using Roothaan's method,[90] which employs a linear combination of basis functions. With basis functions, $\varphi_1, \varphi_2, \ldots \varphi_N$, an individual molecular orbital ψ_i is,

$$\psi_i = \sum_{\mu=1}^{N} c_{\mu i}\varphi_\mu \tag{18}$$

In the *ab initio* approach, after choosing a basis set of atomic orbitals, all of the integrals in the Roothaan equations are evaluated with no further approximations, the unknown expansion coefficients, $c_{\mu i}$, being obtained by the variational method. Details of the principles can be found elsewhere.[91] The basis functions can be atomic orbitals of the constituent atoms (hence LCAO), but are more commonly Slater-type orbitals (STOs), or Gaussian-type functions. The choice of basis set is crucial if one wishes to obtain results close to the HF limit. In the most widely used set of *ab initio* molecular orbital programs (Gaussian 86 and its predecessors),[91] Gaussian-type functions are employed since evaluation of the integrals in STOs is difficult. Thus, STOs can be replaced by linear combinations of Gaussian functions; *e.g.* three Gaussians are sufficient to mimic an STO, and thus provide a minimal basis set, STO-3G. More Gaussians could be used, *e.g.* STO-6G, 6-13G* *etc.*, the latter providing the flexibility of a split-valence basis set, and the inclusion of higher angular quantum numbers (*d* functions) which can be added to each heavy atom to incur some measure of polarization. Additional refinements would be expected to lead to results close to the HF limit, and it is generally true that most small transients can be treated to a fairly high level of theory. Experience gained with 'exact' HF calculations, indicates that calculated orbital energies will be too high due to the dominance of the reorganization energy, and so the approximation (equation 19),

$$I_{\text{vert}} = -0.92\varepsilon_i \tag{19}$$

is often used in *ab initio* calculations to correct the calculated Koopmans' IPs.[92]

The number of two-electron integrals goes approximately as the fourth power of the number of atomic orbitals, and so the logistics of evaluating all of the time consuming integrals in *ab initio* methods is reduced in the semi-empirical methods. Depending on the method employed, some are not calculated precisely,

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[90] C. C. J. Roothaan, *Rev. Mod. Phys.*, 1951, **23**, 69.

[91] W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, '*Ab initio* Molecular Orbital Theory', Wiley, New York, 1986.

[92] C. R. Brundle, M. B. Robin, H. Basch, M. Pinsky, and A. Bond, *J. Am. Chem. Soc.*, 1970, **92**, 3863.

others are obtained from experimental data, and still others are obtained from parametric functions mimicking the integrals. Indeed, some are even completely neglected. These may sound like severe limitations, but carefully crafted semi-empirical methods can provide a very cost-effective approach to the calculation of many molecular parameters. For some of the larger molecules investigated by UPS, semi-empirical methods are the only feasible approach. At the outset, most methods consider only valence electrons, with the inner electrons as a fixed potential. Then can follow a variety of ways in which the atomic orbitals can overlap. Hence, *e.g.*, CNDO, Complete Neglect of Differential Overlap;[93] INDO, Intermediate NDO;[94] NDDO, Neglect of Diatomic Differential Overlap,[93] although there are others. Perhaps the most commonly encountered, which have undergone a process of refinement over many years, are those emanating from the Dewar group, *viz.* MINDO/3,[95] (modified INDO); MNDO,[96]culminating in AM1.[97] These procedures have a demonstrated performance for evaluating many one-electron parameters, including orbital energies, and many a medium-sized unstable molecule has been investigated by such procedures.

One other semi-empirical method that has met with some success for the calculation of IPs is the HAM/3 method, initially based on intuitive arguments,[98] but now shown to be an example of density functional theory.[99] It is parametrized with the IPs of some 80 molecules, and involves a half-electron method for calculating IPs. Although limited in its present form to first row elements excluding Li, Be, and B, it provides a rapid and reasonably reliable means of calculating IPs.[100,101]

Whether or not the results of semi-empirical methods mean anything is another matter; as has been charmingly shown,[102] a comparison of observed and calculated IPs can achieve a perfectly satisfactory correlation even when numbers are generated in a random fashion and ordered!! The motto is therefore, *caveat emptor*, with other procedures necessary to confirm the proposed assignments.

An illustration of some of the procedures discussed above, and some of the refinements to be covered below, and the validity, or otherwise, of KT is demonstrated by comparing the photoelectron spectrum of the explosive NHF_2[103] molecule (obtained carefully, by hydrolysis of 1,1-difluorourea), with a variety of calculations (Figure 4). Cpu times on an Amdahl V6 computer are shown, illustrating both the qualitative (ordering), and quantitative (accuracy) performance.

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[93] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys. Suppl.*, 1965, **43**, 5129.

[94] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 1967, **47**, 2026.

[95] R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, 1975, **97**, 1285, 1294, 1302, 1307.

[96] M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899, 4907.

[97] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.

[98] L. Åsbrink, C. Fridh, and E. Lindholm, *Chem. Phys. Lett.*, 1977, **52**, 63, 69, 72.

[99] E. Lindholm and L. Åsbrink, 'Molecular Orbitals and Their Energies, Studied by the Semiempirical HAM Method', Lecture Notes in Chemistry, Springer-Verlag, Berlin, 1985, p. 38.

[100] D. P. Chong, *Theor. Chim. Acta*, 1979, **51**, 55.

[101] D. C. Frost, W. M. Lau, C. A. McDowell, and N. P. C. Westwood, *J. Mol. Struct. Theochem.*, 1982, **90**, 283.

[102] E. Heilbronner and A. Schmelzer, *Nouv. J. Chim.*, 1980, **4**, 23.

[103] D. Colbourne, D. C. Frost, C. A. McDowell, and N. P. C. Westwood, *Chem. Phys. Lett.*, 1980, **72**, 247.

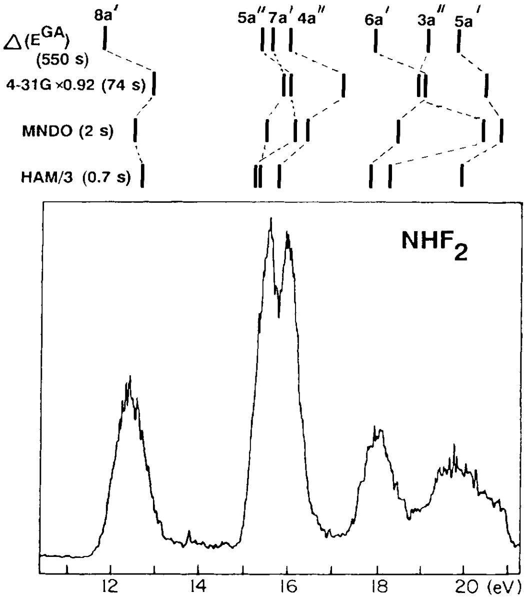

Figure 4 *The* HeI *photoelectron spectrum of* NHF_2 *illustrating the performance and cpu times (in seconds) for semi-empirical and* ab initio *calculations on* NHF_2 *at the microwave geometry. These include those involving perturbation corrections to Koopmans' theorem to third order with a geometric approximation,* $\Delta(E^{GA})$. *All calculations were performed on an Amdahl V6 computer*

B. ΔSCF Calculations.—Given what was said earlier about the approximations inherent in the use of KT, the best approaches are obtained by doing separate calculations, to as high a level as possible, for the molecule and all the states of the ion at the same geometry as the molecule, and subtracting the total energies. This ΔSCF approach accounts for the reorganization energy, but since correlation still exists, albeit smaller in the cation, the calculated IPs will be too small. In addition, from the variational principle, access to the lowest state only of each particular symmetry is permitted. Also, since separate calculations are required, this can be very time consuming even for small transients. There is still no guarantee of correct ordering since reorganization and correlation is different from state to state.

C. The Correlation Problem.—The HF method is a single configuration approach based on a single determinant wavefunction. The next step would be to include a correction for electron correlation, and there are several techniques for doing this post-SCF step. One approach is to regard long-range correlation as a perturbation to be added on to the HF problem. This method, involving many-body perturbation theory initiated by Møller and Plesset,[104] is adopted in the later versions of the Gaussian series of programs.[91] Corrections to KT have also been

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[104] G. Møller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618.

performed with ordinary third order Rayleigh–Schrödinger perturbation theory (RSPT) carried up to third order in the energy of the parent and the cation, and then estimating the vertical IP from a geometric approximation[105] (see Figure 4). This method is capable of giving vertical IPs of valence molecular orbitals with an average error of *ca.* 0.5 eV for a double zeta basis set.[105,106]

Although a single configuration comprises most of the ground electronic state, it is obviously far better to mix in other configurations, especially those that can contribute to the final wavefunction. This can lead to a massive computational problem involving hundreds of thousands of configurations, and so some method of selection is required. The CI methods are often described by acronyms, *e.g.* the PNO (pseudo-natural orbital) and CEPA (coupled electron pair) approximations of Meyer;[107,108] MRD-CI (multi-reference double-excitation configuration interaction) method of Buenker and Peyerimhoff.[109] Perhaps the most successful technique has been that of Cederbaum and co-workers,[110] involving the use of Green's functions. This method, which follows a good quality *ab initio* SCF calculation, involves many-body corrections to KT. The real value of this approach, apart from the very accurate values obtained for IPs using the outer valence Green's function (OVGF),[111] is shown in the use of the extended two-particle-hole Tamm–Dancoff approximation (2ph-TDA) where inner valence effects can be calculated.[112] These involve the observation of weak bands in UPS, attributable to a final-state correlation effect, and evidenced by a redistribution of intensity from the inner-valence orbital. This breakdown of the molecular orbital picture is becoming increasingly evident in UPS, as illustrated in Figure 5 which shows the photoelectron spectrum of the semistable molecule S_2N_2,[113] with weak satellite structure beginning as low as 13 eV.[114]

Other methods that have also proven useful include the X_α method based on density functional theory, and equations of motion methods. The former has demonstrated its strength in those cases where heavy elements are involved, including transition metal compounds, and where *ab initio* methods involving all electrons are infeasible. An extension of this approach, the SCF Hartree–Fock–Slater (HFS) method developed by Baerends *et al.*,[115] has been used extensively for the calculation of IPs of small heavy transients with, and without, the inclusion of relativistic effects.[72,73] The increase in computational power over

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[105] D. P. Chong, F. G. Herring, and D. McWilliams, *J. Chem. Phys.*, 1974, **61**, 78, 958, 3567.

[106] D. C. Frost, C. Kirby, W. M. Lau, C. A. McDowell, and N. P. C. Westwood, *J. Mol. Struct.*, 1983, **100**, 87.

[107] W. Meyer, *J. Chem. Phys.*, 1976, **64**, 2901.

[108] W. Meyer, *J. Chem. Phys.*, 1973, **58**, 1017.

[109] P. J. Bruna, G. Hirsch, R. J. Buenker, and S. D. Peyerimhoff, Proceedings of a NATO Advanced Study Institute, Kos, Greece, 1980; Plenum, New York, 1983.

[110] L. S. Cederbaum and W. Domcke, *Adv. Chem. Phys.*, 1977, **36**, 205.

[111] W. von Niessen, G. H. F. Diercksen, and L. S. Cederbaum, *J. Chem. Phys.*, 1977, **67**, 4124.

[112] L. S. Cederbaum, W. Domcke, J. Schirmer, and W. von Niessen, *Adv. Chem. Phys.*, 1986, **65**, 115.

[113] D. C. Frost, M. R. LeGeyt, N. L. Paddock, and N. P. C. Westwood, *J. Chem. Soc., Chem. Commun.*, 1977, 217.

[114] W. von Niessen and G. H. F. Diercksen, *J. Electron Spectrosc. Rel. Phenom.*, 1980, **20**, 95. W. von Niessen, J. Schirmer, and L. S. Cederbaum, *J. Chem. Soc., Faraday Trans. 2*, 1986, **82**, 1489.

[115] E. J. Baerends and P. Ros, *Int. J. Quantum Chem.*, 1978, **512**, 169.

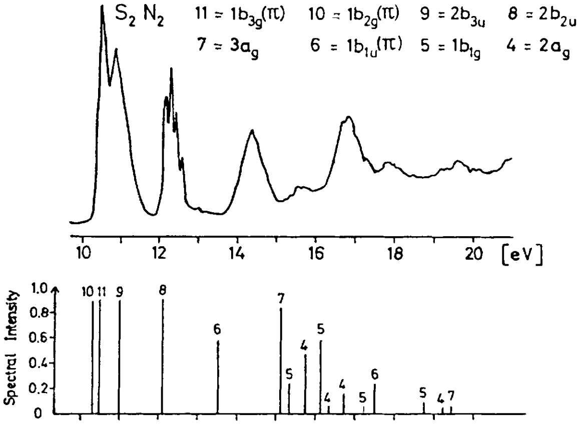

Figure 5 *The photoelectron spectrum of* S_2N_2 *compared to many-body calculations for the IPs and satellite structure in the outer valence region; Green's function results from the largest basis set, and 2ph-TDA results from an intermediate basis set*
(Reproduced by permission from *J. Electron Spectrosc. Rel. Phenom.*, 1980, **20**, 95)

recent years has also meant that direct CI methods have become more feasible.[116] The end result of the surge in computational power brought about by supercomputers has meant that calculations have become larger and more elaborate, and have moved to higher levels of accuracy.

D. Calculation of Structures and Stabilities for Unknown Molecules.—Of perhaps more interest to the synthetic chemist is the ability to explore now the structures and stabilities of hitherto unknown molecules at a consistent level of theory, with larger basis sets, and possibly with the inclusion of correlation. Part of this has been helped by the substantial advances in geometry optimization techniques; analytical gradient methods are capable of accurately locating points on the potential surface corresponding to equilibrium structures and transition states.[117] Hence it is feasible to determine if a proposed synthetic target has a minimum on the potential surface. From a spectroscopist's point of view it is important to have some structural information to hand before attempting some assignments. Given that most high resolution spectroscopy is performed on small molecules, it is here that calculations can be of real benefit. It is often the case that quantum chemistry can drive the synthetic chemist and spectroscopist (not just of the photoelectron variety) to search for new molecules, or other isomeric forms of a base formula.

Figure 6 demonstrates the utility of a computational method (MNDO) for the energies of eight possible isomers of a reasonable sized molecule with a base formula C_3H_4O.[118] Acrolein is predicted to be the thermodynamically most

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[116] V. R. Saunders and J. H. van Lenthe, *Mol. Phys.*, 1983, **48**, 923.
[117] H. F. Schaeffer and Y. Yamaguchi, *J. Mol. Struct., Theochem.*, 1986, **135**, 369.
[118] H. Bock, R. Dammel, and B. Roth, in 'Inorganic Rings and Clusters', ed. A. H. Cowley, *ACS Symp. Ser. No. 232*, American Chemical Society, Washington, 1983.

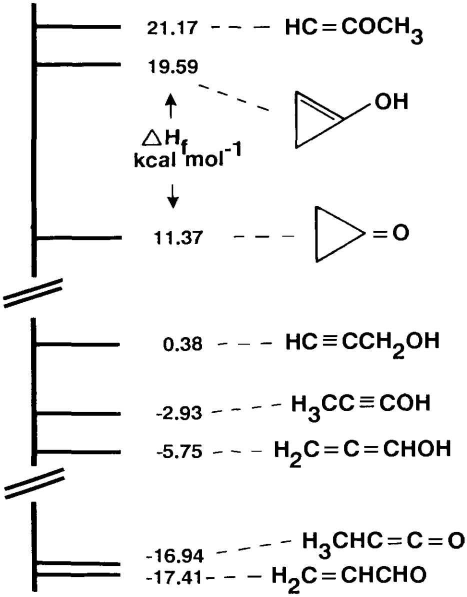

Figure 6 *MNDO calculations for the energetics of eight* C_3H_4O *isomers; heats of formation in* kJ mol^{-1}. (*Adapted from ref.* 118)

stable, although some of the others have been observed by a variety of techniques. Of course, nothing is indicated of the kinetic stability of these species. Only acrolein[1] and methylketene[119] have been seen by UPS.

5 Spectroscopy

Since the UPS method is a low pressure technique, the symbiosis between spectroscopic methods is restricted to those procedures that can be adapted from photoelectron experiments, or *vice versa*; immediate examples are microwave spectroscopy, FTIR, diode laser spectroscopy, and other varieties of laser spectroscopy. The essential difference between these and UPS is the much higher resolution, from which more fundamental information may be obtained.

A. Microwave Spectroscopy.—This involves the investigation of transitions between quantized rotational energy levels in a molecule.[120] It is high resolution and very specific, transitions being measured to 1 part in 10^6, although it is not, in general, used as an analytical technique because of the need for specialist equipment. It does, however, provide unambiguous identification of molecules,

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[119] D. P. Chong, N. P. C. Westwood, and S. R. Langhoff, *J. Phys. Chem.*, 184, **88**, 1479.

[120] W. W. Gordy and R. L. Cook, 'Microwave Molecular Spectra', Interscience, New York, 1970.

and by analysis of the energy levels, their splittings or Stark shifts, can give precise gas phase structures, molecular dipole and quadrupole moments, and information on rotational isomers including energy differences. Since molecules must have no centre of inversion in order to be observed, this immediately excludes, *e.g.*, homonuclear diatomics such as H_2, N_2 or X_2, which are often some of the very species observed in elimination reactions, *e.g.* equations 2 and 4. Nonetheless, the method is good for low concentrations of molecules with reasonable dipole moments.

Molecules can be classified as either linear, spherical rotors, symmetric rotors, and asymmetric rotors, and there are well known equations relating to the frequency of a transition for these situations, although there are no closed solutions for asymmetric rotors. Although the analysis of microwave spectra is not trivial, there are certain standard procedures, and, as pointed out,[12] there are often distinct patterns that emerge from the apparent jumble of lines, and these help to identify the class and nature of the molecule; especially important when the species is unknown.

An example of this is provided by the microwave spectrum of BrNCO, a molecule that had previously been observed by UPS, and for which the generation procedure had been refined.[43] Figure 7 shows clumps of *a*-type *R* branch transitions spaced at intervals of approximately 4 200 MHz which enable one to obtain preliminary *B* and *C* rotational constants. Of course, there are some details in here, including the presence of two isotopes, ^{79}Br and ^{81}Br, and quadrupole splittings which turn out to be perturbed for some transitions, thereby permitting the accurate determination of *A* and χ_{ab} from a global fit to the spectroscopic constants.[121]

The use of microwave spectroscopy for following the formation of transients is becoming more common, although one limitation of conventional Stark modulated microwave spectroscopy is the need to fill a metal waveguide, often one or two metres long, with a continual supply of the transient. There are therefore limitations on the lifetime. More recently free-space cells have been used for very short-lived molecules.[122]

B. FTIR.—Weak absorption in the infrared (IR) region has been assisted by the use of interferometric methods, and the development of long pathlength cells for weakly absorbing, or low pressure species.[123] All the advantages of IR including species identification, and observation of all products (except those without electric dipole allowed transitions) are retained, together with high sensitivity. High resolution studies (to 0.003 cm^{-1}, essentially Doppler limited in the mid-IR) can provide spectroscopic and structural information for small molecules. Consider the HBF_2 molecule, generated pure by equation 8 for UPS studies, and

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[121] H. M. Jemson, W. Lewis-Bevan, N. P. C. Westwood, and M. C. L. Gerry, *J. Mol. Spectrosc.*, 1986, **118**, 481.

[122] E. Hirota, *J. Phys. Chem.*, 1983, **87**, 3375.

[123] P. R. Griffiths and J. A. de Haseth, 'Fourier Transform Infrared Spectrometry', Wiley-Interscience, New York, 1986.

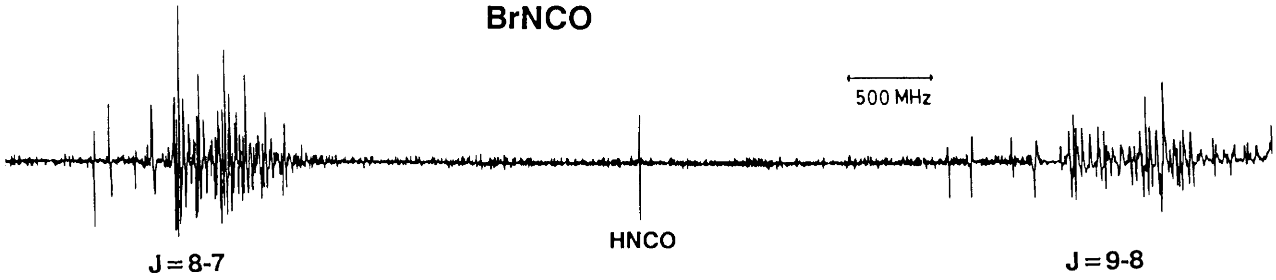

Figure 7 *Broadband scan of the microwave spectrum of* BrNCO *from* 32.7—38.6 GHz, *showing the distinct* a-*type* R *branch transitions* (*separated by* ~B + C)
(Reproduced by permission from *J. Mol. Spectrosc.*, 1986, **118**, 481)

investigated by RSPT for assignment of the IPs.[47] High resolution FTIR of the 2^1_0 and 4^1_0 bands[124,125] (see Figure 8 for the latter) necessitated good ground-state parameters, which were established by concomitant microwave studies.[126]

D. Laser Spectroscopy.—A variety of laser driven methods including diode laser spectroscopy, laser induced fluorescence, laser magnetic resonance, photoacoustic spectroscopy. multiphoton ionization, and some double resonance techniques have been used for the investigation of fundamental short-lived molecules and ions.[127,128] Although these methods provide superb sensitivity and resolution, they are not the method of choice for the on-line approach advocated here since they are too specific, and require specialist equipment. Nevertheless, as spectroscopic methods, they are state-of-the-art, and many of the molecules described herein are amenable to such studies. Multiphoton ionization using pulsed visible lasers coupled with KE analysis of ejected electrons is demonstrating potential for the study of excited states,[129] and considerable work in this area is to be anticipated.

6 Some Case Studies

The following brief survey of some of the more interesting molecular species from our laboratory is not intended to be all encompassing; by necessity it covers some aspects of the UPS of transients that can best illustrate the technique and its virtues. In most cases the molecules are small, they have been generated in high yield, and they are spectroscopically and theoretically interesting. Some examples of such molecules, *e.g.* XBS and RCP have already been covered in the review by Kroto,[12] with the phosphaethynes, as mentioned, having spawned new synthetic endeavours.

A. 'Linear' Triatomic Groupings with Off-axis Substituents.—Molecules of the type, XNCO, XOCN, XN_3, XSCN, XNCS (X = halogen or CN) are of considerable interest for a variety of reasons. They represent molecules, which, in the cyanate and thiocyanate cases, can be bound to the substituent X through N or the Group 6 element, O or S.[130]

viz. –N=C=O or –O–C≡N
–N=C=S or –S–C≡N

A priori it is not clear which isomer is likely to be the more stable although, as mentioned earlier, the parent HNCO and HNCS molecules are known, whereas

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[124] M. C. L. Gerry, W. Lewis-Bevan, D. J. MacLennan, A. J. Merer, and N. P. C. Westwood, *J. Mol. Spectrosc.*, 1986, **116**, 143.

[125] M. C. L. Gerry, H. M. Jemson, W. Lewis-Bevan, D. J. MacLennan, and N. P. C. Westwood, *J. Mol. Spectrosc.*, 1987, **122**, 135.

[126] N. P. C. Westwood, W. Lewis-Bevan, and M. C. L. Gerry, *J. Mol. Spectrosc.*, 1984, **106**, 227.

[127] *Faraday Discuss. Chem. Soc.*, No. 71, 1981.

[128] E. Hirota, 'High-Resolution Spectroscopy of Transient Molecules', Springer Series in Chemical Physics, Vol. 40, Springer, Berlin, 1985.

[129] K. Kimura, *Int. Rev. Phys. Chem.*, 1987, **6**, 195.

[130] S. Patai, 'The Chemistry of Cyanates and Their Thio Derivatives', Wiley, New York, 1977.

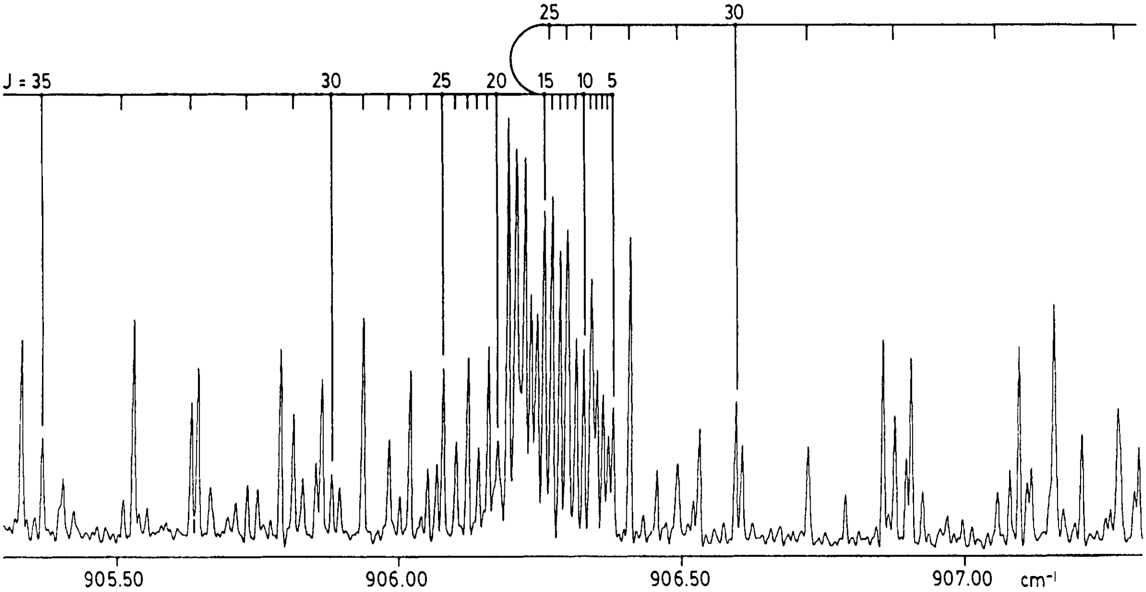

Figure 8 *The* $^{P}Q_5$ *branch of the* 4_0^1 *band of gaseous* $H^{11}BF_2$ *from* 905.3 *to* 907.3 cm^{-1}. *The* J *assignments are indicated, and intensity alternations arising from the two equivalent* F *atoms are evident*
(Reproduced by permission from *J. Mol. Spectrosc.*, 1986, **116**, 143)

the HOCN and HSCN molecules are not. Substitution by a halogen, or CN group, modifies the properties such that of the eight species below,

Isocyanates	*Cyanates*	*Isothiocyanates*	*Thiocyanates*
XNCO	XOCN	XNCS	XSCN
NCNCO	NCOCN	NCNCS	NCSCN

only NCSCN may be regarded as stable, and XNCS and the two substituted ethers have not been observed. The isocyanates and the thiocyanate species can be generated as unstable intermediates in high yield for UPS observation[43,44,131] according to equation 6, which has parallels to previously known solution chemistry. They can be reasonably easily handled in the gas phase, such that IR spectra of these species can be obtained.[132] In contrast, NCNCS is obtained by *in situ* thermal isomerization of NCSCN.[133] The halogeno- and cyano-azides, are explosive, and the generation procedures reflect the avoidance of liquid or solid phases.[43] FN_3 has been recently obtained from HN_3 and F_2, and the microwave and UPS spectra recorded.[134]

Synthetically, these molecules can act as precursors to a wide range of organic compounds,[130] *e.g.* thiocyanates or cyanates, as can the archetypal pseudohalogen $(SCN)_2$ which was known and used as a solution intermediate in addition and substitution reaction well before it was generated for the first time in the gas phase for UPS observation (equation 20).[135]

$$X_2 + 2AgSCN \longrightarrow (SCN)_2 + 2AgX \tag{20}$$

Either Cl_2 or Br_2 will yield the desired product, although care must be taken to avoid excess halogen (equation 12). A disulphide structure was proposed, based on the UPS spectrum, and CNDO/2 and minimal basis set *ab initio* calculations. This structure has, to date, not yet been confirmed by microwave spectroscopy.

Structurally, the known azide and isocyanate molecules all possess a close-to-linear triatomic grouping with an off-axis substituent;[136] the magnitude of the angle depends on the triatomic grouping, *e.g.* ~108—120° for azides, compared to wider angles, 120—140° for various substituted isocyanates. The UPS results[43] for these molecules reflect the size of the off-axis angle through a splitting of the π orbitals. Calculated orbital energies over a range of angles (Walsh-type diagram), even with a minimal (STO-3G) basis set, can be used to predict a bond angle in these molecules, by matching the theoretical π splittings to the experimental spectra. This is illustrated in Figure 9 for ClNCO.

Although UPS can, from the form of the spectrum,[44] predict for example, that

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[131] H. Leung, R. J. Suffolk, and J. D. Watts, *Chem. Phys.*, 1986, **109**, 289.

[132] T. C. Devore, *J. Mol. Struct.*, 1987, **162**, 287.

[133] M. A. King and H. W. Kroto, *J. Am. Chem. Soc.*, 1984, **106**, 7347.

[134] P. Rademacher, A. J. Bittner, G. Schatte, and H. Willner, *Chem. Ber.*, 1988, **121**, 555.

[135] D. C. Frost, C. Kirby, W. M. Lau, C. B. MacDonald, C. A. McDowell, and N. P. C. Westwood, *Chem. Phys. Lett.*, 1980, **69**, 1.

[136] C. Glidewell, *Inorg. Chim. Acta*, 1974, **11**, 257.

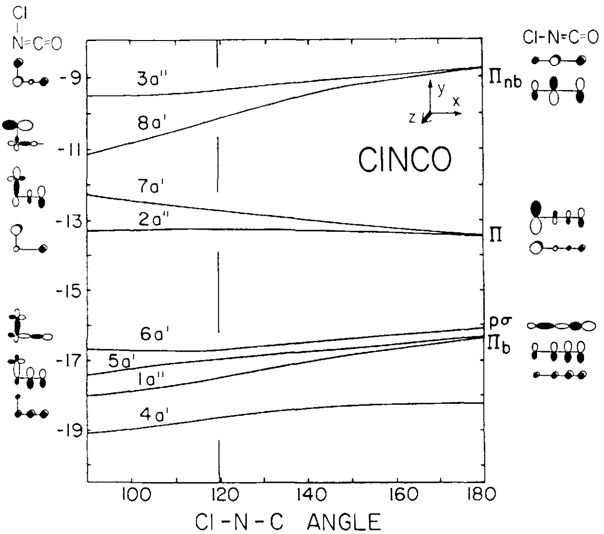

Figure 9 *Calculated Walsh type diagram (STO-3G basis set) for the valence orbitals of ClNCO: the UPS (ref. 43) closely matches the calculated π-splittings at the experimental angle,* 119.4° *(vertical line)*
(Reproduced by permission from *Chem. Phys.*, 1980, **47**, 111)

ClSCN is not ClNCS, and give an estimate of the bond angle (*ca.* 100°), it cannot provide information on the non-linearity of the triatomic grouping, a subtle effect that is a feature of many pseudo-halide structures.[136] This can only be established by high resolution microwave studies of several isotopic species.[137] As it turns out, high level *ab initio* calculations can also demonstrate this *trans*-bent structural feature, in addition to confirming that the thiocyanate forms are more stable than the isothoocyanate species.[131] The only halogeno- or pseudo-halogeno-isothiocyanate to be studied, NCNCS, shows quasilinear behaviour.[138]

B. Multiply Bonded Compounds of Boron.—Boron with its vacant p_π orbital is well known to form adducts involving σ donation from Lewis bases. These species can, with care, be induced to eliminate H_2 (equation 4) or HX to form, in high yield, species of the type H_2NBX_2 with a nominal double bond, isoelectronic with the corresponding ethylenes. These B-substituted aminoboranes admirably satisfy the requirements for spectroscopic and theoretical interest; they are small, amenable to high level calculations, and the double bond character can be tuned by changing the substituent, X. Although microwave spectra were obtained previously for the parent H_2NBH_2 molecule,[32] thereby establishing the planarity, and the short BN bond length (r = 139.1 pm), the preparative method (discharge/thermolysis of B_2H_6 and NH_3) was poor. A simplification, involving careful

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[137] E. J. Richards, R. W. Davies, and M. C. L. Gerry, *J. Chem. Soc., Chem. Commun.*, 1980, 915.
[138] M. A. King, H. W. Kroto, and B. M. Landsberg, *J. Mol. Spectrosc.*, 1985, **113**, 1.

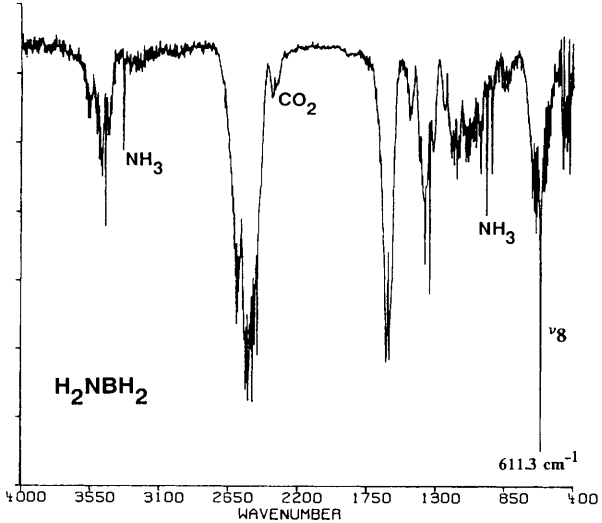

Figure 10 *The IR spectrum of* H_2NBH_2 *from* 4 000 *to* 400 cm^{-1} *obtained from the* 85° C *thermolysis of* H_3NBH_3. *Note the new C-type band at* 611.3 cm^{-1} *assigned to* ν_8 (*compare ref.* 33). *The IR active* ν_{12} *band is still unidentified*

thermolysis of the H_3NBH_3 adduct (equation 4), gives a high yield of H_2NBH_2 as shown by the gas phase IR spectrum (Figure 10). This spectrum shows a new *C*-type band at 611.3 cm^{-1}, attributable to ν_8 which was not seen in the earlier work.[33]

Having established the conditions for generating the molecule, the UPS spectrum[31] provides information on the electronic structure, and *ab initio* calculations support the assignment of the PE spectrum, and provide information on the charge distributions in this molecule, and the B-halogeno-derivatives.[139] Interestingly, the calculations show that the H_2NBH_2 cation is twisted by 90° in the ground state, with a 1,2-shifted distonic form, $H_3\overset{+}{N}\overset{\bullet}{B}H$ more stable on the global surface at the MP3/6-31G* level.[140]

The monoaminoboranes, once generated, can be reacted with excess NH_3 to form bis(aminoboranes) which show some essential differences to the monoaminoboranes, including a weakening of the individual BN bonds, and a destabilization of the HOMO since it is now an antibonding a_2 combination.[141] Figure 11 shows the MNDO calculated orbital energies for a series of bis(amino)boranes.

The observed first IPs for the H, F, and Cl molecules at 8.6, 8.9, and 8.8 eV, respectively, track the calculated first IPs, and indicate the virtual independence from ligand substitution. It remains to be seen whether the tris(aminoborane) $(H_2N)_3B$, can be generated; it has been claimed to have been synthesized in amounts up to 60 kg![142]

[139] C. A. Kingsmill, N. H. Werstiuk, and N. P. C. Westwood, *J. Am. Chem. Soc.*, 1987, **109**, 2870.
[140] N. P. C. Westwood, *J. Mol. Struct.*, 1988, **173**, 227.
[141] C. A. Kingsmill and N. P. C. Westwood, to be published.
[142] Cetesel S. a. r. l., Ital. Pat., 508 919, 1955; *Chem. Abstr.* 1958, **52**, 4996h.

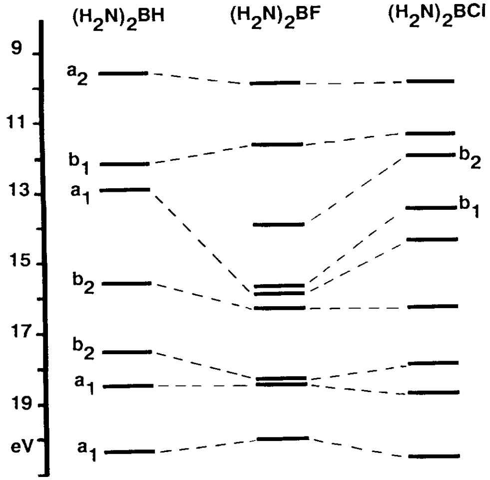

Figure 11 *Calculated (MNDO) orbital energies in* eV *for the bisaminoboranes*, $XB(NH_2)_2$, (X = H, F, *and* Cl), *indicating the relative insensitivity of the HOMO to ligand substitution*

C. Sulphur–Nitrogen Ring Molecules.—The work involved in this area is truly representive of collaborative efforts in spectroscopy, synthesis, and quantum chemistry. SN molecules have a fascinating and wide chemistry,[143] and because of their abundance of π electrons provide rich UPS data. The fundamental molecule NS has been generated through thermolysis, and the first IP has been observed.[144] The subsequent oligomers, S_2N_2,[113,145] S_3N_3,[61] and S_4N_4,[144] have been studied by UPS, although S_2N_2 (see Figure 5) is unstable, S_3N_3 is a transient radical, and S_4N_4 is only marginally volatile and somewhat explosive. The relationship between these species may be summarized as in Figure 12.

The S_4N_4 molecule is the precursor to almost all SN molecules, and the S_2N_2 molecule is the precursor to the $(SN)_x$ polymer, which can itself be vaporized to yield, depending on the conditions, S_4N_4, S_2N_2, and S_3N_3. Interestingly the latter two species can, upon condensation, reform the polymer; these processes can be followed using UPS.[61] In addition, the electronic structures of the dimer,[146] trimer,[61] and tetramer[147] have been investigated by *ab initio*/CI methods to a high level. The same is also true for the related S_4N_2 molecule where the UPS can be assigned on the basis of *ab initio*/CI calculations.[87] To illustrate the quality of the methods the calculated structure of S_4N_2[148] is compared (Figure 13) with that obtained from *X*-ray diffraction,[149] and shows remarkable agreement.

[143] R. T. Oakley, *Prog. Inorg. Chem.*, 1988, **36**, 299.

[144] J. M. Dyke, A. Morris, and I. R. Trickle, *J. Chem. Soc., Faraday Trans. 2*, 1976, **73**, 147.

[145] R. H. Findlay, M. H. Palmer, A. J. Downs, R. G. Egdell, and R. Evans, *Inorg. Chem.*, 1980, **19**, 1307.

[146] M. H. Palmer, *Z. Naturforsch., Teil A*, 1984, **39**, 102.

[147] M. H. Palmer, *Z. Naturforsch., Teil A*, 1983, **38**, 378.

[148] M. H. Palmer, J. R. Wheeler, R. H. Findlay, N. P. C. Westwood, and W. M. Lau, *J. Mol. Struct., Theochem.*, 1981, **86**, 193.

[149] T. Chivers, P. W. Codding, and R. T. Oakley, *J. Chem. Soc., Chem. Commun.*, 1981, 584.

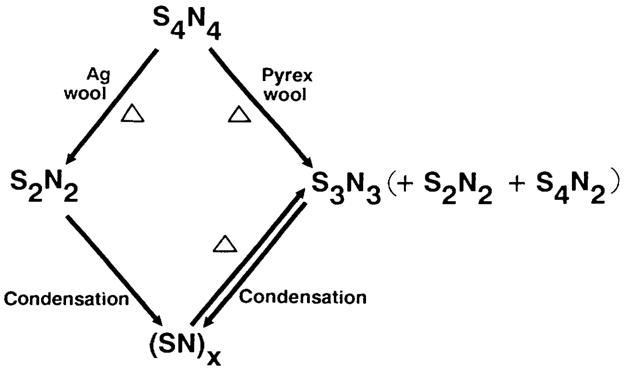

Figure 12 *Interconversions between simple binary* S–N *molecules. Note that the* S_3N_3 *radical is the major product from the thermolysis of* $(SN)_x$ *and (in part) from* S_4N_4

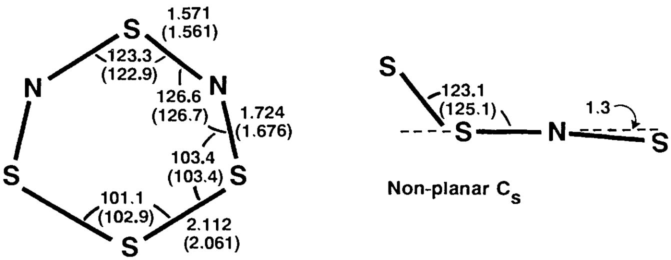

Figure 13 *Comparison of the* S_4N_2 *X-ray structure (parentheses, ref.* 149) *with that obtained from a big basis set* ab initio *calculation (ref.* 148). *Angles in degrees, and bond lengths in Ångstrom*

More recently, several SN heterocyclic rings have been investigated by UPS and QM methods, including 1,2,3,5-dithiadiazolyl radicals of the type illustrated in Figure 2 (equation 13), and 1,2,4,6-thiatriazinyl radicals obtained by on-line reduction of the corresponding *S*-chloro molecules,[56,57]

D. Substituted Ketenes.—The >C=C=O moiety also has a rich chemistry, since ketenes may be used in cycloaddition reactions in solution.[150] Substituted derivatives XHC=C=O and X_2C=C=O, with X = halogen, methyl, or phenyl are unstable species, although Ph_2C=C=O, with some additional stability conferred by the phenyl groups, can be isolated with care. The theoretical interest arises from investigation of the electronic structures, the geometric structures, and photodissociation routes to substituted carbenes. Spectroscopically these molecules provide fertile ground, although the unstable derivatives have not been as extensively investigated as the parent H_2C=C=O molecule.

The general strategy used for generating these species in high yield involves

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[150] S. Patai, 'The Chemistry of Ketenes, Allenes and Related Compounds', Wiley, New York, 1974.

either thermal dehydrohalogenation (equation 1), or metal dehalogenation using Zn (equation 9). The distinctive UPS can be used to monitor the reactions, and analysis of the resulting spectra provides information on the electronic structures, including perturbations of the C=C=O-based π orbitals,[37] and conformational information in the case of phenyl substitution.[151] Although MNDO methods can provide a reasonable assessment of the orbital ordering, *ab initio* methods with RSPT corrections to KT[119,152] provide unequivocal confirmation.

Structurally, these molecules present no surprises, the microwave spectra of monochloro- and monobromo-ketene indicating planar structures with a linear C=C=O grouping.[153] The details of the spectroscopy are interesting, however, with substantial perturbations being observed in the quadrupole structure; analysis of the quadrupole data required a least-squares fit to the exact quadrupole Hamiltonian for χ_{aa}, $(\chi_{bb} - \chi_{cc})$, *and* χ_{ab}. From Stark measurements on the monochloro-species the dipole moment was ascertained to bisect the ClCC angle, a pertinent observation since in the dichloro-substituted species, a close to zero dipole moment was estimated.[154]

There is a paucity of data on fluoro-substituted ketenes, although the monofluoro-species was recently observed by microwave spectroscopy.[155] The difluoro-species has been the subject of a reasonable quality *ab initio* calculation[156] with the conclusion that it is thermodynamically unstable with respect to singlet CF_2 and CO. As mentioned above, the ability of theoretical methods to predict stabilities will assume an increasing role, and even now is of considerable utility in providing, to a high level, the energetics and structures of those hitherto unknown species that are so synthetically and spectroscopically interesting.

Acknowledgements. It is a pleasure to acknowledge the many people who have contributed to some of the work mentioned herein, and whose names appear repeatedly throughout the references. NPCW thanks the Natural Sciences and Engineering Research Council of Canada for grants in support of this work.

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[152] S. R. Langhoff and D. P. Chong, *Chem. Phys. Lett.*, 1983, **100**, 259.

[153] M. C. L. Gerry, W. Lewis-Bevan, and N. P. C. Westwood, *J. Chem. Phys.*, 1983, **79**, 4655, and unpublished work.

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[155] R. D. Brown, P. D. Godfrey, and B. Kleibömer, *Chem. Phys.*, 1986, **105**, 301.

[156] E. H. N. Rice, Ph.D. Thesis, Monash University, Australia, 1985.