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**Electronic Structure  
and Magnetism of  
Inorganic Compounds  
VOLUME 6**

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Magnetism of Inorganic  
Compounds**

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**Volume 6**



A Specialist Periodical Report

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# Electronic Structure and Magnetism of Inorganic Compounds

Volume 6

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A Review of the Recent Literature

Senior Reporter

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# *Preface*

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This is the sixth in the series of Specialist Periodical Reports dealing with electronically excited states and the magnetic properties of inorganic compounds. Several reviewers of recent volumes commented on the disappearance of photoelectron spectroscopy from the list of techniques covered, and therefore I am pleased to say that this field, which has been of great significance for the development of theories about electronic structure of inorganic molecules and solids, is included once again. With a backlog of several years' references to catch up on, Drs. Egdell and Potts have been obliged to be more selective in their coverage, but we hope to include this topic regularly from now on. Also this year, for the first time since the inception of the series, I have not been responsible for the chapter on electronic spectroscopy, a task which has now been taken up by Dr. Flint. At the same time the opportunity has been taken to amalgamate coverage of absorption and emission spectra into a single chapter, since both are complementary ways of looking at electronically excited states. In all other respects the principles and extent of our coverage remain unchanged. A final point of concern to the editors, contributors, publishers and, it seems, reviewers of Specialist Periodical Reports is the length of time between the publication of a significant paper and its evaluation in one of our chapters. Unfortunately there is no simple answer to this problem. Writing long comprehensive reviews is a time-consuming business and reviewers are busy people with other calls on their time. Consequently some chapters may deal with papers which are 3—4 years old by the time the review appears. Of course, everyone would like to see reviews as up to date as possible. Nevertheless a comprehensive assessment of a field remains valid even after a year or two has elapsed, and passing time may even serve to bring events into a better perspective. As always, comments on these or any other questions about our Reports are welcome: we want to be as useful to the inorganic chemistry community as we can.

P. DAY  
August 1979





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# Gas-phase Photoelectron Spectroscopy

BY R. G. EGDELL AND A. W. POTTS

## 1 Introduction

Previous articles<sup>1,2</sup> in the Specialist Periodical Reports series dealing with photoelectron spectroscopy (p.e.s.) have adopted a broad approach reviewing all aspects of the technique. To keep this contribution for the extended period 1973—1977 within manageable bounds we have restricted our attention to gas-phase p.e.s. While our canvas is clearly defined for ultraviolet p.e.s. there is less distinction between gas- and solid-phase X-ray work; core levels are of a largely atomic nature irrespective of the phase under investigation. This article aims to provide comprehensive coverage of the literature up to the end of 1976 and a more selective discussion of papers published in 1977.

During the period covered by this Report the field has continued to expand and the production of p.e. spectra is now a largely routine procedure in many laboratories. Review articles proliferate and may usefully be divided into three categories. First and least numerous are those that provide a thorough coverage of the literature of a given period. Within this group the u.v.-p.e.s. field from 1973 to 1975 has been covered by Baker *et al.*<sup>3</sup> and the earlier period from 1971 to 1973 by Betteridge and Williams.<sup>4</sup> The X-p.e.s. work published between 1972 and 1975 has been dealt with by Hercules.<sup>5,6</sup> The second type of review still has a broad scope but adopts a rather more selective and sometimes personalized approach. Such reviews have been given by Price,<sup>7,8</sup> DeKock and Lloyd,<sup>9</sup> Jonathan,<sup>10</sup> Carlson,<sup>11</sup> Schweitzer,<sup>12</sup> Bahr,<sup>13</sup> and Siegbahn.<sup>14</sup> In this section we must

<sup>1</sup> S. Evans and A. F. Orchard, in 'Electronic Structure and Magnetism of Inorganic Compounds', ed. P. Day (Specialist Periodical Reports), The Chemical Society, London, 1973, Vol. 2.

<sup>2</sup> A. Hamnett and A. F. Orchard, in 'Electronic Structure and Magnetism of Inorganic Compounds', ed. P. Day (Specialist Periodical Reports), The Chemical Society, London, 1974, Vol. 3.

<sup>3</sup> A. D. Baker, M. A. Brisk, and D. C. Liotta, *Analyt. Chem.*, 1976, **48**, 281R.

<sup>4</sup> D. Betteridge and M. A. Williams, *Analyt. Chem.*, 1974, **46**, 125R.

<sup>5</sup> D. M. Hercules and J. C. Carver, *Analyt. Chem.*, 1974, **46**, 133R.

<sup>6</sup> D. M. Hercules, *Analyt. Chem.*, 1976, **48**, 294R.

<sup>7</sup> W. C. Price, *Adv. Atom. and Mol. Phys.*, 1974, **10**, 131.

<sup>8</sup> W. C. Price, in 'Wave Mechanics—the First Fifty Years', ed. W. C. Price, S. S. Chissick, and T. Ravensdale, Butterworths, London, 1973, p. 315.

<sup>9</sup> R. L. DeKock and D. R. Lloyd, *Adv. Inorg. Chem. Radiochem.*, 1974, **16**, 66.

<sup>10</sup> N. Jonathan, in 'Essays in Chemistry', ed. J. N. Bradley, R. D. Gillard, and R. F. Hudson, 1973, 5, 1.

<sup>11</sup> T. A. Carlson, *Ann. Rev. Phys. Chem.*, 1975, **26**, 211.

<sup>12</sup> G. K. Schweitzer, *Appl. Spectroscopy Rev.*, 1975, **10**, 257.

<sup>13</sup> J. L. Bahr, *Contemp. Phys.*, 1973, **14**, 329.

<sup>14</sup> K. Siegbahn, *Endeavour*, 1973, **32**, 51.

mention the detailed and regular reviews produced by Siegbahn.<sup>15-17</sup> While dealing with the general field of p.e.s. these lean heavily upon the substantial contributions made by the Uppsala laboratory.

Finally and forming by far the largest part of this section are the reviews or articles addressing themselves to a specific aspect of p.e.s. Thus the field of high-temperature inorganic studies is admirably covered by Berkowitz<sup>18,19</sup> while articles by Heilbronner<sup>20,21</sup> and Maier<sup>22</sup> deal with organic u.v.-p.e.s. A useful review of instruments commonly used in p.e.s. with particular emphasis on their performance is given by Wannberg *et al.*<sup>23</sup> while Krause<sup>24</sup> deals with the experimental principles of electron spectroscopy. The close affinities between u.v.-p.e. and Rydberg absorption spectra observed in the vacuum u.v. have been stressed by Sandorfy.<sup>25</sup> A review of gas phase X-p.e.s. carried out at Uppsala has been given by Gelius.<sup>26</sup> This deals with the fine high-resolution work carried out with monochromatic X-rays by the Swedish group. A general article on photoemission from atoms and small molecules has been given by Samson.<sup>27</sup> This dwells particularly on accurate intensity measurements in u.v.-p.e.s. and on the measurement of asymmetry parameters.

Although many of the articles mentioned so far include consideration of photoionization theory and the calculation of binding energies, there are now a number of articles dealing specifically with these topics. These tend to deal either with the process of photoionization (Cooper<sup>28</sup> and Marr<sup>29</sup>) and the associated theory of shake-up and shake-off (Fadley<sup>30</sup>) or with the various approximations used in the calculation of binding energies. For X-p.e.s. this includes the calculation of chemical shifts as covered by Basch,<sup>31</sup> Shirley,<sup>32</sup> Schwartz,<sup>33</sup> and Gelius.<sup>34</sup> As regards valence ionization energies, although there have been significant developments in theoretical techniques (see Section 4) no general review on this topic came to our attention. At an elementary level molecular

<sup>15</sup> K. Siegbahn, *J. Electron Spectroscopy*, 1974, **5**, 3.

<sup>16</sup> K. Siegbahn, U.U.I.P. 909: A survey presented at the XVIIIth Colloquium Spectroscopium Internationale, Grenoble, France, Sept. 1975.

<sup>17</sup> K. Siegbahn, ref. 50, p. 227.

<sup>18</sup> J. Berkowitz, in 'Vacuum Ultraviolet Radiation Physics', Pergamon/Vieweg, Braunschweig, 1974, p. 107.

<sup>19</sup> J. Berkowitz, ref. 41, p. 355.

<sup>20</sup> E. Heilbronner, J. P. Maier, and E. Haselbach, in 'Physical Methods in Heterocyclic Chemistry', ed. A. Katritzky, Academic Press, New York, 1974, p. 1.

<sup>21</sup> E. Heilbronner, ref. 50, p. 422.

<sup>22</sup> J. P. Maier, *Ann. Reports (B)*, 1974, **71**, 75.

<sup>23</sup> B. Wannberg, U. Gelius, and K. Siegbahn, *J. Phys. (E)*, 1974, **7**, 149.

<sup>24</sup> M. O. Krause, in 'Atomic Inner Shell Processes', Vol. II, ed. B. Crasemann, Academic Press, 1975, p. 34.

<sup>25</sup> C. Sandorfy, *J. Mol. Structure*, 1973, **19**, 183.

<sup>26</sup> U. Gelius, *J. Electron Spectroscopy*, 1974, **5**, 985.

<sup>27</sup> J. A. R. Samson, *Phys. Reports*, 1976, **28**, 303.

<sup>28</sup> J. W. Cooper, ref. 24, Vol. I, p. 160.

<sup>29</sup> G. V. Marr, 'An Introduction to the Theory of Photoelectron Spectroscopy for Experimentalists', Science Research Council, Daresbury Laboratory, DL/SRF/R4.

<sup>30</sup> C. S. Fadley, ref. 49, p. 895.

<sup>31</sup> H. Basch, *J. Electron Spectroscopy*, 1974, **5**, 463.

<sup>32</sup> D. A. Shirley, *Adv. Chem. Phys.*, 1973, **23**, 85.

<sup>33</sup> M. E. Schwartz, in 'Theoretical Chemistry', ed. C. A. Coulson, MTP International Review of Science, Physical Chemistry Series Two, Vol. 1, Butterworths, London, 1976, p. 189.

<sup>34</sup> U. Gelius, *Phys. Scripta*, 1974, **9**, 133.

orbital theory is discussed in relationship to u.v.-p.e. by Bock and Mollère<sup>35</sup> while a more thorough treatment with discussion of various semi-empirical MO models is given by Bock *et al.*<sup>36,37</sup>

In addition to the articles so far discussed a number of books devoted to p.e.s. have been published. A text by Carlson<sup>38</sup> deals with Auger spectroscopy as well as X-p.e.s. and u.v.-p.e.s. and a recent volume by Rabalais<sup>39</sup> devoted to u.v.-p.e.s. places particular emphasis on the theoretical aspects of the subject. A most useful general book on gas-phase u.v.-p.e.s. written by Eland<sup>40</sup> deals with the elementary theory and practice of the technique in a very readable manner. Two recent volumes bringing together important articles on a wide range of photoelectron topics are those edited by Baker and Brundle<sup>41</sup> and by Briggs.<sup>42</sup> The former work is Part I of a projected three-volume series.

We should also mention the published proceedings of the series of NATO advanced study institutes which have dealt with various aspects of p.e.s., in particular in relation to other techniques used to study the electronic structure of molecules and solids.<sup>43-45</sup> In a similar vein p.e.s. has been set against other forms of electron spectroscopy including Auger and energy-loss spectroscopy by Brion<sup>46</sup> and in relation to u.v. absorption measurements in a two-volume work by Robin.<sup>47</sup>

Finally there have of course been several conferences in the period covered by this Report either devoted to or touching on p.e.s. The first of these, held at Namure in 1974, was biased towards X-ray work although it did include a useful review by Frost of developments in u.v.-p.e. at that time.<sup>48</sup> The proceedings of the conference were published as Volume 5 of the *Journal of Electron Spectroscopy and Related Phenomena* and also in a volume edited by Caudano and Verbist.<sup>49</sup> Photoelectron work also occupied a considerable portion of the proceedings of the Sixth Conference on Molecular Spectroscopy held at Durham, England in 1976.<sup>50</sup> The most recent conference dedicated to p.e.s. was held at Uppsala in 1977 and the proceedings are published in *Physica Scripta*.<sup>51</sup>

<sup>35</sup> H. Bock and P. Mollère, *J. Chem. Educ.*, 1974, **51**, 506.

<sup>36</sup> H. Bock, *Angew. Chem. Internat. Edn.*, 1977, **16**, 613.

<sup>37</sup> H. Bock and B. G. Ramsey, *Angew. Chem. Internat. Edn.*, 1973, **12**, 734.

<sup>38</sup> T. A. Carlson, 'Photoelectron and Auger Spectroscopy', Plenum Press, New York, 1975.

<sup>39</sup> J. W. Rabalais, 'Principles of Ultraviolet Photoelectron Spectroscopy', Wiley, New York, 1977.

<sup>40</sup> J. H. D. Eland, 'Photoelectron Spectroscopy', Butterworths, London, 1974.

<sup>41</sup> 'Electron Spectroscopy, Theory, Techniques and Applications', Vol. 1, ed. C. R. Brundle and A. D. Baker, Academic Press, London, 1977.

<sup>42</sup> 'Handbook of X-ray and Ultraviolet Photoelectron Spectroscopy', ed. D. Briggs, Heyden, London, 1977.

<sup>43</sup> 'Electron Emission Spectroscopy', ed. W. Dekeyser, L. Fiermans, C. Vander Kelen, and J. Vennick, Reidel, Dordrecht, 1973.

<sup>44</sup> 'Chemical Spectroscopy and Photoemission in the Vacuum U.V.', ed. C. Sandorfy, P. J. Ausloos, and M. B. Robin, Reidel, Dordrecht, 1974.

<sup>45</sup> 'Electronic States of Inorganic Compounds, New Experimental Techniques', ed. P. Day, Reidel, Dordrecht, 1975.

<sup>46</sup> C. E. Brion, in 'Mass Spectrometry', ed. A. Maccoll, MTP International Review of Science, Physical Chemistry Series One, Vol. 5, Butterworths, London, 1972, p. 550.

<sup>47</sup> M. B. Robin, 'Higher Excited States of Polyatomic Molecules', Academic Press, London, Vol. I, 1974; Vol. II, 1975.

<sup>48</sup> D. C. Frost, *J. Electron Spectroscopy*, 1974, **5**, 99.

<sup>49</sup> 'Electron Spectroscopy, Progress in Research and Applications', ed. R. Caudano and J. Verbist, Elsevier, Amsterdam, 1974.

<sup>50</sup> 'Molecular Spectroscopy', ed. A. R. West, Heyden, London, 1977.

<sup>51</sup> *Phys. Scripta*, London, 1977, Vol. 16.

In this introduction we have attempted to mention and in some cases comment on the review material currently available in the p.e. field. It should be noted however that refs. 41–45 contain many excellent articles both of a general and of a specialized nature by established authors. They are, however, too many in number to list here and the reader is advised to consult the original collections of articles for further details.

## 2 Advances in Experimental Techniques

Since the scope of this Report is essentially limited to gas-phase p.e.s. only developments directly relevant to this aspect of the technique will be discussed. In general one of the three basic electrostatic deflection analysers, *i.e.* the 127° cylindrical, the cylindrical mirror, or the spherical sector, forms the basis of most spectrometers. A few novel arrangements have been described during the period of this Report, most notably the threshold photoelectron or photoionization resonance spectrometer in its various forms.<sup>52</sup>

As might have been expected the principal growth area for p.e.s. in its simple form (*i.e.* the energy analysis of photoelectrons) has been in techniques associated with the ionization chamber and sample handling. This is exemplified by the recent work of Bulgin *et al.*<sup>53</sup> who describe a spectrometer incorporating a molecular beam unit which may be operated at temperatures up to 2500 K. Also, in the context of 'unstable' target species, there has been impressive use of laser p.e.s. to study negative ions. This work has been largely associated with the University of Colorado.<sup>54,55</sup> The p.e. spectrum of a negative ion is obtained using the argon ion laser line at 2.34 eV as photon source and yields highly accurate values for the electron affinity of the neutral species.

The field of e,2e coincidence spectroscopy has also been a growth area and it is now possible to obtain much of the information available from p.e.s. by coincidence work, albeit at a considerable sacrifice in resolution<sup>56</sup> (FWHM  $\approx$  1.5 eV).

**Electron Energy Analysers.**—During the period of this Report a number of treatments comparing analyser performance and giving analyser theory have appeared. A particularly thorough study was made by Wannberg *et al.*<sup>23</sup> who compared a variety of analysers commonly used in p.e.s. Amongst other things they discuss the use of preretardation coupled with fixed-energy analysis and hence fixed-energy resolution as a means of improving the signal (luminosity). This theory also indicates how energy resolution may be profitably increased without sacrifice of signal by using low fixed pass energies in analysers with preretardation facilities.<sup>57,58</sup> Read *et al.*<sup>59</sup> and Baker *et al.*<sup>60</sup> have also considered

<sup>52</sup> R. Frey, B. Gotchev, W. B. Peatman, H. Pollak and E. W. Schlag, *Internat. J. Mass Spectrometry Ion Phys.* 1978, **26**, 137.

<sup>53</sup> D. Bulgin, J. Dyke, F. Goodfellow, N. Jonathan, E. Lee, and A. Morris, *J. Electron Spectroscopy*, 1977, **12**, 67.

<sup>54</sup> M. W. Siegel, R. J. Celotta, J. L. Hall, J. Levine, and R. A. Bennett, *Phys. Rev. (A)* 1972, **6**, 607.

<sup>55</sup> R. J. Celotta, R. A. Bennett, and J. L. Hall, *J. Chem. Phys.*, 1974, **60**, 1740.

<sup>56</sup> A. Hamnett, W. Stoll, G. Branton, C. E. Brion, and M. J. Van der Wiel, *J. Phys. (B)*, 1976, **9**, 945.

<sup>57</sup> O. Edqvist, E. Lindholm, L. E. Selin, and L. Asbrink, *Phys. Scripta*, 1970, **1**, 25.

<sup>58</sup> A. W. Potts, A. Gabriel, T. A. Williams, and W. C. Price, in 'X-ray Photoelectron Spectroscopy', Academy of Sciences of the Ukrainian S.S.R., Kiev Naukova Dumka, 1977.

<sup>59</sup> F. H. Read, J. Comer, R. E. Imhof, J. N. Brunt, and E. Horting *J. Electron Spectroscopy*, 1974, **4**, 293.

<sup>60</sup> M. E. Gellender and A. D. Baker, *J. Electron Spectroscopy*, 1974, **4**, 249.



design requirements for electron energy analysers. The latter authors derive general expressions for transmission in terms of source and analyser dimensions. Arnow<sup>61</sup> has given a general theoretical treatment for the cylindrical electrostatic focusing field while Wannberg *et al.*<sup>62</sup> considered the focusing properties of a toroidal electrostatic field. They concluded that in certain situations where a large sector angle is not inconvenient a toroidal spectrometer will have a superior transmission to an equivalent hemispherical analyser.

A number of accounts of more or less standard analysers have appeared in the literature. Dromey and Peel<sup>63</sup> describe a computer-controlled 127° cylindrical analyser for u.v.-p.e. work with the facility for on-line deconvolution of spectra. Neddermeyer<sup>64</sup> *et al.* have described a spherical sector analyser with a mean radius of 109.56 mm capable of use in the study of gases or solids, *i.e.* with a base pressure of 10 nPa. This system is also computer controlled. Several analysers specifically designed to investigate angular dependence of photoemission in the u.v. have also been described. Leng and Nyberg<sup>65</sup> describe a computer-controlled retarding potential device while Mason *et al.*<sup>66</sup> have given details of a system based on a computer-controlled 180° hemispherical deflection analyser with a mean radius of 38 mm and an acceptance angle of 4.2°. Dehmer *et al.*<sup>67</sup> have also given an account of a spherical sector analyser with a 22.5 mm mean radius designed for measurement of the asymmetry parameter  $\beta$  in u.v.-p.s. In all of these cases the value of  $\beta$  is derived assuming that the light source is unpolarized by measuring the electron emission at two<sup>68</sup> or more angles with respect to the direction of the photon beam. The relationship between electron flux and angle is that given previously.<sup>2</sup> Where the photon beam is completely or partially polarized, as is the case when synchrotron radiation is used to excite the spectra,  $\beta$  may be deduced simply by measuring the variation in electron emission in a plane at right angles to the photon beam. The analyser for these measurements may be simply a retarding grid device<sup>69</sup> or for more accurate work a deflection analyser as described by Houlgate *et al.*<sup>70</sup> (Figure 1). Measurements of the p.e. signal as the analyser is rotated about the photon beam then define  $\beta$  for the particular photoionization process. The relationship between intensity and angle for partially polarized light is also given in the previous Report.<sup>2</sup> To establish  $\beta$ ,  $g$ , the degree of polarization, must be known. This is normally accomplished by making asymmetry measurements for He 1s<sup>-1</sup> ionization for which it is assumed that  $\beta = 2$  as expected theoretically for a pure s-orbital.

In connection with asymmetry measurements two polarizers designed for use with He-I 58.4 nm radiation have been described. Both are based on multiple reflection from plane gold surfaces. In the case of the design given by Karlsson *et*

<sup>61</sup> M. Arnow, *J. Phys. (E)*, 1976, **9**, 372.

<sup>62</sup> B. Wannberg, G. Engdahl, and A. Sköllermo, *J. Electron Spectroscopy*, 1976, **9**, 111.

<sup>63</sup> R. G. Dromey and J. B. Peel, *Austral. J. Chem.*, 1975, **28**, 2353.

<sup>64</sup> H. Neddermeyer, D. Heimann, and H. F. Roloff, *J. Phys. (E)*, 1976, **9**, 756.

<sup>65</sup> F. J. Leng and C. L. Nyberg, *J. Phys. (E)*, 1977, **10**, 686.

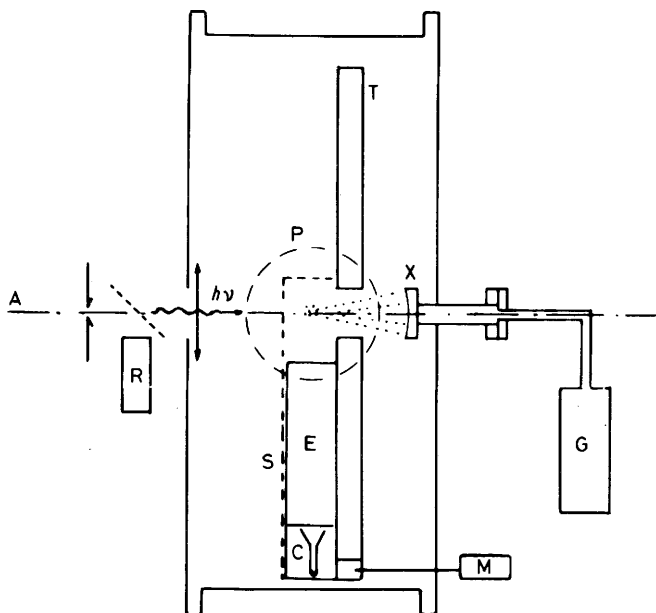
<sup>66</sup> D. C. Mason, D. M. Mintz, and A. Kuppermann, *Rev. Sci. Instr.*, 1977, **48**, 926.

<sup>67</sup> J. L. Dehmer, W. A. Chupka, J. Berkowitz, and W. T. Jivery, *Phys. Rev. (A)*, 1975, **12**, 1966.

<sup>68</sup> J. J. Huang, J. W. Rabalais, and F. O. Ellison, *J. Electron Spectroscopy*, 1975, **6**, 85.

<sup>69</sup> W. S. Watson and D. T. Stewart, *J. Phys. (B)*, 1974, **7**, L466.

<sup>70</sup> R. G. Houlgate, J. B. West, K. Codling, and G. V. Marr, *J. Phys. (B)*, 1974, **7**, L470.



**Figure 1** 127° cylindrical analyser designed to measure  $\beta$  as a function of wavelength using synchrotron radiation; E, analyser; C, gas supply; R, reference photomultiplier; T, rotating table; X, focusing capillary array (for gas)  
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*al.*<sup>71</sup> (Figure 2) four reflections result in a polarization of 97% or greater but a reduction in the photon intensity by approximately two orders of magnitude. The second polarizer designed by Hancock and Samson<sup>72</sup> involves three reflections and produces a polarization of only 84%. The arrangement however has a transmission of 10%. To make use of the polarizers the degree of polarization  $g$  must be known. Since He  $1s^{-1}$  ionization is obviously outside the He-I 58.4 nm range the Ar  $3p^{-1}$  ionization was used, a value for  $\beta$  of  $0.95 \pm 0.02$  being assumed. In Samson's work,  $g$  was initially measured using an optical method and this measurement was used to give the value of  $\beta$  for argon as a secondary standard. The particular beauty of the technique is that simple rotation of the polarizer gives all the information necessary for the determination of  $\beta$  while the electron analyser can remain fixed throughout the measurements.

While measurement of asymmetry in the photoemission process is clearly important it is also desirable to be able to measure the relative populations of different ionized states produced at a particular photon energy. These so-called branching ratios are given by the relative intensities of photoelectron bands either corrected for asymmetry or recorded at the 'magic angle' of  $54^\circ 44'$ . While spectrometers designed to measure  $\beta$  can therefore be used to give corrected branching ratios, detection at the 'magic angle' can result in a higher electron flux

<sup>71</sup> L. Karlsson, L. Mattson, R. Jadrny, K. Siegbahn, and K. Thimm, *Phys. Letters (A)*, 1976, 58, 381.

<sup>72</sup> W. H. Hancock and J. A. R. Samson, *J. Electron Spectroscopy*, 1976, 9, 211.