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TRANSFER CALIBRATION OF THE TRANSMISSION OF ELECTRON-ENERGY SPECTROMETERS

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ABSTRACT

Relative intensities of strong peaks in the HeI photoelectron spectra of N_2, CO, CO_2, and O_2 are tabulated. These data have been measured with an electron energy analyzer whose relative transmission has been calibrated to an accuracy of ±5%. The tables thus will be useful for calibrating the transmission of other analyzers for electron energies below 9 eV. Correction for angular distribution effects is discussed.

Introduction

Quantitative photoelectron spectroscopy requires that the transmission of the energy analyzer be known as a function of the electron energy. Comparatively few attempts have been made to measure the transmission of photoelectron energy analyzers.[1-4] For deflection analyzers that do not include a retarding lens, the transmission has been assumed to be determined purely by the geometry and thus independent of the electron energy, except in the low energy region where contact potentials and magnetic fields have their strongest effect. For analyzers incorporating a lens, the transmission has been calculated on the basis of the energy-brightness law of the retarding optics;[5-8] however, these calculations assume source geometry, such as a point source, which may not be true in a practical analyzer, and predict infinite transmission for zero energy electrons if aperture limitations are not included.

We have previously reported[4] the calibration of the transmission of a cylindrical mirror energy analyzer with a retarding lens, using two independent methods. The first involved measuring the number of photoelectrons detected from a known number formed; this method requires the use of a monochromator and light source producing a number of lines in the vacuum ultraviolet, and also requires that a calibrated photodetector be used to measure the intensity of the radiation. The second method involved a measurement of the energy-brightness relationship of the retarding lens. Good agreement was found between the two sets of results over most of the range covered (0 to 27 eV), such that the relative transmission of our analyzer is known to within estimated limits of ±5%. It follows that any other analyzer may have its relative transmission calibrated to an accuracy approaching these limits by comparing the relative intensities of peaks appearing in photoelectron spectra with data obtained from our analyzer, provided systematic errors generated by differing angular distributions or differential scattering are accounted for.

Experimental

The cylindrical mirror energy analyzer used in this study has been described in detail elsewhere.[2] The photon beam enters on axis and electrons ejected within a narrow cone of angles about $54^{\circ}44'$ to the axis pass through a pair of retarding slits normal to the electron beam into the deflecting region. Slit to slit focusing on the inner cylinder is employed. The electrons are detected with a channel electron multiplier placed on axis. The energy is swept by scanning the potential difference across the retarding slits with a potentiometer driven by a stepping motor, which is driven synchronously with the advance of a multichannel store.

Multiple passes through the spectrum were added to average the effect of slow variations in the target gas pressure and the intensity of the source. The HeI radiation was produced in a DC glow discharge and dispersed by a 1/2 m Seya Namioka monochromator set to pass the dominant 584 Å line.

Spectra were recorded with a pass energy of 3 eV, corresponding to a constant resolution of 45 meV across the spectrum, for which the transmission was known most accurately. Some data for oxygen were recorded with 30 meV resolution to better delineate the background between the peaks. Peak areas were taken as a measure of the peak intensity, after the spectra had been corrected point by point for the known transmission. For the data presented here, statistical errors in the peak areas were generally less than 1% and results from several spectra were averaged to obtain the final data.

Systematic Errors in the Transfer Calibration

Systematic errors in the transfer calibration arise mainly from energy dependent scattering, causing pressure dependent intensities, and from varying electron angular distributions.

Pressure dependent effects are minimised in energy analyzers where the electrons traverse a small path with different energies and are then retarded or accelerated to enter a deflection region at a fixed energy,[2] as in the present analyzer. The data presented here were obtained with pressures of the order of 10^{-4} Torr in the deflection region; varying the pressure small amounts had negligible effect on the relative intensities, although a large variation was found in the absolute intensities.

If the peaks in a photoelectron spectrum have different angular distributions, the relative intensities observed can vary widely with different analyzer geometries and with the polarization of the incident radiation.[9,10] The general dependence of photoelectron intensities on angular distributions and degree of polarization of the radiation is presented elsewhere.[11,12] The data presented here were obtained with "magic-angle" geometry and are inherently free of such effects.

Most photoelectron energy analyzers sample a cone of angles at right angles to the photon beam. In that case, the observed intensity I_{obs}

for a given peak is related to the true intensity I_{true} (that is, a fixed fraction of the total number of electrons ejected into a solid angle of 4π steradians) by [11]

$$I_{obs} = I_{true} \{1 - \cos\gamma + \frac{1}{4}\beta \frac{g-2}{g+1} (\cos^3\gamma - \cos\gamma)\} , \qquad (1)$$

where γ is the half angle of the cone of acceptance, β is the angular distribution asymmetry parameter for the peak, and g is the degree of polarization of the radiation (defined as the ratio of intensities of the polarization components in the X and Z directions, respectively, where the photon beam is incident along the Y axis and the analyzer samples along the Z axis). If the cone half angle is small, the expression (1) reduces, after dropping a constant factor γ because we are interested only in relative peak intensities, to

$$I_{obs} = I_{true} \{1 - \frac{1}{2}\beta (g-2)/(g+1)\} . \qquad (2)$$

Must HeI photoelectron spectra are recorded with undispersed light for which the radiation is unpolarized (g=1), provided no asymmetric metal collimators are used to define the light path. Thus in the most usual case,

$$I_{obs} = I_{true} \{1 + \beta/4\} . \qquad (3)$$

In the tables that follow measured angular distribution parameters are given with the peak intensities, so that the data may be corrected for different analyzer geometries or polarization, using whichever of equations (1), (2), or (3) are applicable.

Results

Tables 1 through 4 list peak intensities measured in the 584 Å HeI photoelectron spectra of N_2 CO, CO_2, and O_2 respectively, after correction for the analyzer transmission. The kinetic energies of the electrons are listed, together with the angular distribution parameters determined by others.[13-17] The intensities represent peak areas, not peak heights, so that the rotational band shapes and unresolved or partially resolved doublets are accounted for. Several spectra were recorded for each gas, with the peak areas determined to better than 1% (except in the case of O_2, noted below). For each gas, the intensities of the peaks shown in the tables were normalized to the same sum and averaged to give the distributions shown. The intensities shown are renormalized to 100 at the strongest peak, and the errors quoted represent one standard deviation obtained from the averaging procedure.

In the case of oxygen, a smaller number of channels was available between the peaks, giving rise to larger errors. For O_2 data were recorded at both 45 and 30 meV resolution; the transmission for the latter case was not as accurately known as for the former.

All of the intensities shown are subject to a further ±5% error, representing the uncertainty in the transmission calibration.

Conclusion

The data presented in tables 1 through 4 will enable the transmission of an energy analyzer to be calibrated in the range 0 to 9 eV, without recourse to a calibrated source of dispersed radiation at a number of wavelengths. The energy vs. brightness method[4] is applicable to analyzers with retarding lens for energies of a few eV and higher. Similarly, deflection type analyzers without lens may be assumed to have constant transmission for electrons above a few eV in energy (provided focusing effects at the detector are not energy dependent). Thus, the data presented here is sufficient to determine the relative transmission of an energy analyzer over the energy range covered in vacuum ultraviolet photoelectron spectroscopy.

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TABLE 1

Relative Intensities in the HeI Photoelectron Spectrum of N_2

N_2^+				Angular Distribution Parameter β		
Level		Energy (eV)	Intensity	a	b	c
X $^2\Sigma_g^+$	v=0	5.64	100.0±0.3	+0.5±0.1	+0.69±0.03	+0.65±0.05
A $^2\Pi_u$	v=0	4.51	39.9±0.2	+0.3±0.1	+0.43±0.04	+0.33±0.05
	1	4.28	48.4±0.2			
	2	4.05	34.5±0.2			
	3	3.83	21.5±0.2			
	4	3.61	8.0±0.1			
B $^2\Sigma_u^+$	v=0	2.47	25.8±0.3	+1.25±0.1	+1.25±0.04	+1.38±0.05

a. Carlson and Jonas (ref. 13)

b. Morgenstern, Niehaus, and Ruf (ref. 14)

c. Samson and Hancock (ref. 15)

TABLE 2

Relative Intensities in the HeI Photoelectron Spectrum of CO

CO^+ Level		Energy (eV)	Intensity	Angular Distribution Parameter	
				a	b
X $^2\Sigma^+$	v=0	7.20	100.0±0.6	+0.8±0.1	+0.72±0.05
A $^2\Pi$	v=0	4.67	14.3±0.1	+0.3±0.1	+0.31±0.05
	1	4.48	30.4±0.1		
	2	4.30	37.0±0.2		
	3	4.11	32.3±0.2		
	4	3.93	25.3±0.2		
	5	3.76	19.3±0.2		
	6	3.58	9.5±0.2		
B $^2\Sigma^+$	v=0	1.54	24.8±0.1	+1.0±0.2	+0.24±0.05
	1	1.34	9.2±0.1		

a. Carlson and Jonas (ref. 13)

b. Samson and Hancock (ref. 15)

TABLE 3

Relative Intensities in the HeI Photoelectron Spectrum of CO_2

CO_2^+ Level	Energy (eV)		Intensity	Angular Distribution Parameter β	
				a	b
$\tilde{X}\ ^2\Pi_g$	(0,0,0)	7.44	72.8±0.4	-0.1±0.1	-0.2±0.05
	(1,0,0)	7.28	13.1±0.2		
$\tilde{A}\ ^2\Pi_u$	(0,0,0)	3.90	5.9±0.1	+0.8±0.1	+0.64±0.05
	(1,0,0)	3.76	14.4±0.2		
	(2,0,0)	3.62	17.6±0.2		
	(3,0,0)	3.49	14.8±0.1		
	(4,0,0)	3.35	10.6±0.3		
$\tilde{B}\ ^2\Sigma_g^+$	(0,0,0)[c]	3.17	100.0±0.8	-0.4±0.1	-0.59±0.05
	(1,0,0)	3.01	14.7±0.2		
$C\ ^2\Sigma_g^+$	(0,0,0)	1.86	12.6±0.1	+1.3±0.2	+1.15±0.05

a. Carlson and McGuire (ref. 16)

b. Samson and Hancock (ref. 15)

c. Includes A $^2\Pi_u$ (5,0,0) and (6,0,0)

TABLE 4

Relative Intensities in the HeI Photoelectron Spectrum of O_2

O_2^+ Level	Energy (eV)	Intensities	Angular Distribution Parameter β a	b	c
$X\ ^2\Pi_g$ v=0	9.14	46.7±1.8	-0.3±0.1	+0.04±0.05	-0.32±0.05
1	8.90	100.0±5.0			
2	8.67	91.6±3.2			
3	8.45	46.1±2.1			
4	8.23	15.4±0.3			
$b\ ^4\Sigma_g^-$ v=0	3.05	79.3±4.4	+0.7±0.1	+0.73±0.05	+0.57±0.05
1	2.90	68.5±1.3			
2	2.76	44.6±1.2			
3	2.63	27.3±0.5			
4	2.50	15.2±0.2			
$B\ ^2\Sigma_g^-$ v=0	0.92	32.1±1.8	----	+1.35±0.07	+1.04±0.05
1	0.78	38.3±2.[illegible]			
2	0.65	31.9±2.9			
3	0.53	21.4±1.9			
4	0.40	12.5±0.5			

a. Carlson _et al_., (ref. 17)

b. Morgenstern, Niehaus, and Ruf (ref. 14)

c. Samson and Hancock (ref. 15)

References

1. B. P. Pullen, T. A. Carlson, W. E. Moddeman, G. K. Schweitzer, W. E. Bull, and F. A. Grimm, J. Chem. Phys., 53 (1970) 763.
2. J. L. Gardner and J. A. R. Samson, J. Electron Spectrosc., 2 (1973) 267.
3. R. T. Poole, R. C. G. Leckey, J. Liesegang, and J. G. Jenkin, J. Phys. E., Sci. Instr., 6 (1973) 226.
4. J. L. Gardner and J. A. R. Samson, J. Electron Spectrosc., 6 (1975) 53.
5. J. C. Helmer, Amer. J. Phys. 34 (1966) 222.
6. J. C. Helmer and N. H. Weichert, Appl. Phys. Lett., 13 (1968) 266.
7. P. C. Kemeny , A. D. McLachlan, F. L. Battye, R. T. Poole, R. C. G. Leckey, J. Liesegang and J. G. Jenkin, Rev. Sci. Inst., 44 (1973) 1197.
8. H. G. Noller, H. D. Polaschegg, and H. Schillalies, J. Electron Spectrosc., 5 (1974) 705.
9. T. A. Carlson, Chem. Phys. Letts., 9 (1971) 23.
10. J. A. Kinsinger and J. W. Taylor, Int. J. Mass Spectrom. Ion Phys., 10 (1972/73) 445.
11. J. A. R. Samson and J. L. Gardner, J. Opt. Soc. Am., 62 (1972) 856.
12. J. A. R. Samson and A. F. Starace, J. Phys. B8 (1975) 1806. ?
13. T. A. Carlson and A. E. Jonas, J. Chem. Phys., 55 (1971) 4913.
14. R. Morgenstern, A. Niehaus and M. W. Ruf, Proc. Intern. Conf. Phys. Electron At. Collisions 7th, Amsterdam, (1971).
15. J. A. R. Samson and W. H. Hancock, unpublished data.
16. T. A. Carlson and G. E. McGuire, J. Electron Spectrosc., 1 (1972/73) 209.
17. T. A. Carlson, G. E. McGuire, A. E. Jonas, K. L. Cheng, C. P. Anderson, C. C. Lu, and B. P. Pullen, Electron Spectroscopy, ed D. A. Shirley, North Holland, Amsterdam (1972), p. 207.