Photoelectron Spectrum of Potassium Hexacyanoferrate(II) measured by a Millikan Condenser Method

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Summary A new method of measurement of photoelectron spectra is described with potassium hexacyanoferrate as an example.

HAVING previously determined[1] by a Millikan condenser method the photoionization threshold energy and the photoelectric emission spectrum of potassium hexacyanoferrate(II) we now report the measurement of its photoelectron spectrum.

The method of measurement consists in the suspension against gravity of a droplet of solution by means of an electric field, D, between the plates of a condenser so that at balance,

$$Dq = mg \tag{1}$$

where q is the electric charge on the droplet, m is the mass and g is the gravitational force constant. The volume within the condenser is maintained at atmospheric pressure with an inert gas such as nitrogen and the droplet is irradiated with monochromatic light of frequency, ν^j, so that photoelectrons of energy, ϵ_i^j, are released from the i'th electronic level of photoionization energy, I_i. Einstein's equation gives,

$$\epsilon_i^j = h\nu^j - I_i \tag{2}$$

Photoelectrons of maximum kinetic energy, $\epsilon^j_{\max}$, originate from the level of threshold ionization energy, I_t. Confining discussion to positively charged droplets there will be a minimum energy, E, of escape from the droplet given by,

$$E = -eq/R \tag{3}$$

From equation (1)

$$E = -emg/RD \tag{4}$$

R being the radius of the droplet.

The continuous irradiation of the droplet increases the charge and hence the escape energy until $E = \epsilon^j_{\max}$ when,

$$h\nu^j - I_t = -emg/RD^j \tag{5}$$

When equation (5) is satisfied photoionization ceases and the droplet is in equilibrium with light of energy $h\nu^j$. By increasing the light energy it is possible to obtain further equilibria and a plot of light energy against $1/D^j$ gives I_t as intercept[2] and the constant, $-emg/R$ as slope.

The desired photoelectron spectrum is some function, $f(\epsilon^j)$, plotted against ϵ^j with the property that,

$$\int_E^{\epsilon^j_{\max}} f(\epsilon^j)d\epsilon^j = i(E) \tag{6}$$

where i is the photoelectron current emitted by the drop, measurable as the rate of increase of $1/D$.

Because i is zero when $E = \epsilon^j_{\max}$,

$$\frac{di}{dE} = -\left\{f(\epsilon j)\right\}_{\epsilon^j = E} \tag{7}$$

$f(\epsilon^j)$ cannot be negative hence,

$$di/dE \leqslant 0 \tag{8}$$

The slope on the left of equation (7) is measurable and thus the photoelectron spectrum can be found.

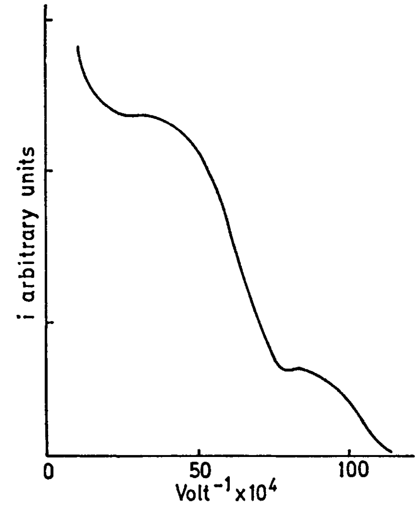

FIGURE 1. *Photoelectron current,* i, *against the reciprocal of the balancing voltage, V, across the condenser plates for a droplet of potassium hexacyanoferrate*(II) *in glycerol solution,* −7 °C, *light wavelength* 200 nm (6·2 eV).

Figure 1 shows a plot of i against $1/D$ for a glycerol solution of potassium hexacyanoferrate(II) in nitrogen under irradiation with light of wavelength 200 nm (6·2 eV) isolated by a double monochromator from a deuterium arc. The derived photoelectron spectrum is given in Figure 2 together with that of solid potassium hexacyanoferrate(II) obtained by the same method, using a volatile solvent *viz.* water.

The $1/D$ volt^{-1} of plot 1 were converted to E cm^{-1} of plot 2 by determining the constant factor, $-emg/R$, of equation

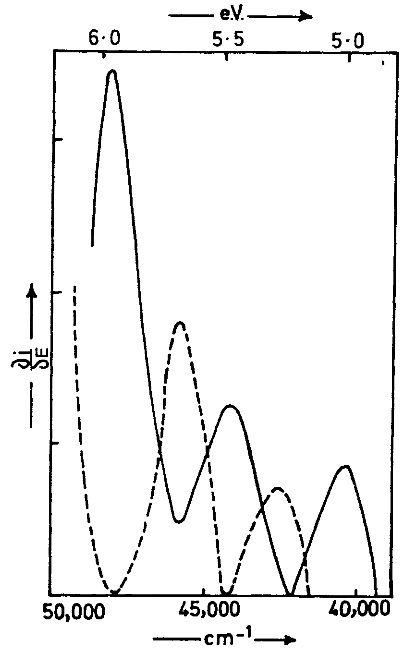

Figure 2. *The photoelectron spectrum of potassium hexacyanoferrate*(ii) *solid* (*full line*) *and glycerol solution* (*dashed line*) at 25° *and* −7 °C *respectively. The energy scale is chosen so that ionization potentials can be read off in* eV *or* cm^{-1}.

(4) by bringing the drop to equilibrium with light of known energy; threshold energies, I_t, previously found[1] were also used for this purpose. Near equilibrium *i* approaches zero asymptotically causing difficulties in measurement and uncertainty in the photoelectron spectrum near threshold; equilibrium balancing fields, D^j, were obtained therefore in conditions of higher light intensity than required for the photoelectron spectra.

We shall discuss the spectra of Figure 2 elsewhere. The similarity of the solid and the solution results, apart from the threshold displacement of 2,300 cm^{-1} (0·29 eV), indicates that the spectra obtained are those of potassium hexacyanoferrate(ii). Thus the Millikan method described is applicable to liquids, solids and solutions—and possibly to the measurement of photoelectron spectra of biochemicals *in vivo* in algae, *etc.*

Since atmospheric or higher pressures are used liquid solutions can be studied. A limitation on the energy of the radiation is imposed by either the absorption limit of the gas or the ionization threshold of the solvent; the solvent used here, glycerol, gave zero ionisation current when no potassium hexacyanoferrate(ii) was present.

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