Annual Progress Report on
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Vacuum Ultraviolet
Electronic Properties of Liquids

Linda R. Painter

Contract Period: Nov. 1, 1979 - Oct. 31, 1980

ORO-3861-32

THE UNIVERSITY OF TENNESSEE
Knoxville, Tennessee

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Electronic Properties of Liquids, 3#

Report No. ORO-3861-32

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Progress Report

I. Introduction

During the current contract period, starting November 1, 1979, the following activities were carried out.

Measurements on photoelectric emission from formamide were repeated in the 16 to 25 eV region. Yield curves, for the number of photoelectrons per incident photon and per absorbed photon, are similar over the energy range studied.

Photoionization measurements were made on the low vapor pressure organic solvent hexamethylphosphoric triamide (HMPT) in the 10 to 25 eV region. This data was combined with data derived in the 2-9 eV region using closed cell techniques. Optical functions and the energy loss function were determined from a Kramers-Kronig analysis of the reflectance data. Concomitant with photoionization studies on HMPT, electrons from the photon bombarded HMPT have been analyzed. Photoemission measurements on HMPT were determined in the 16.1 to 24.5 eV region. A model for photoemission has been proposed whereby the photon and photoelectron mean free paths in liquids can be determined from yield data. Several changes were made in the photoemission apparatus which adds credibility to the resulting photoemission data.

The optical properties of Kapton were obtained for wavelengths in the range 25,000 Å to 163 Å from reflectance measurements on Kapton films stretched over a sample holder. As a test of the data obtained, the measured k values of Kapton, which has a monomeric unit of

{$C_{22}H_{10}N_2O_5$} were combined with estimated values of k at shorter wavelengths to form a spectrum extending over the oscillator strength of the valence electrons. The "k-sum rule" was performed on these data and yields a total number of electrons consistent with the known number of valence electrons per monomeric unit.

Transmission measurements were made on four polycyclic aromatic hydrocarbons, benzene, toluene (methylbenzene), xylene (dimethylbenzene) and trimethylbenzene using the Cary-14 spectrophotometer in the 25,000 Å to 2500 Å. Reflectance measurements were made on these PAH's using the Seya monochromator. The data is to be refined with additional transmission measurements on the Seya.

Two papers were published since submission of the last progress report: "Optical Studies of Liquid Formamide in the Vacuum Ultraviolet," J. Chem. Phys. 71, 4641 (1979); and "Optical Properties of Polycrystalline Anthracene in the 3.2-9.3 eV Spectral Region," J. Appl. Phys. 51, 1747 (1980). One paper was accepted for publication during the current contract period: "Optical Properties of Polyethylene: Measurement and Applications," Radiation Research (proposed for publication in edition of July, 1980). Two papers were submitted for publication: "Photoemission from Liquid Formamide in the Vacuum Ultraviolet," Phys. Rev. [ORO-3861-33]; and "Optical and Dielectric Functions of Liquid Hexamethylphosphoric Triamide between 2 and 25 eV," J. Chem. Phys. [ORO-3861-34]. Two papers are currently in preparation: "Yield of Photoelectrons from Hexamethylphosphoric Triamide in the Vacuum Ultraviolet," J. Chem. Phys.; and "The Optical Properties of Kapton: Measurement and Applications," journal to be decided. Five papers were presented at meetings. Three papers were presented at the Southeastern Section, American Physical Society Meeting, Chattanooga, Tennessee, Nov. 8-10, 1979, "Photoemission from Liquid Formamide in the Vacuum Ultraviolet," Bull. Am. Phys. Soc. 25, No. 2, 130 (1979); "Optical Properties of Polycrystalline Anthracene in the 3.2 to 9.3 eV Spectral Region," Bull. Am. Phys. Soc. 25, No. 2, 130 (1979); "Optical Properties of Polyethylene: Measurement and Applications," Bull. Am. Phys. Soc. 25, No. 2, 130 (1979). One paper was presented at the Conference on Basic Optical Properties of Materials, Gaithersburg, Maryland, May 5-7, 1980, "The Optical Properties of Kapton: Measurement and Applications," NBS SP 574. One paper was presented at the VI International Conference on Vacuum Ultraviolet Radiation Physics, Charlottesville, Virginia, June 2-6, 1980, "Absolute Photoemission from Liquid Formamide in the Vacuum Ultraviolet," Proceedings of VI Int. Conf. on VUV Rad. Phys., Vol. 1, 88 (1980).

II. Optical and Dielectric Properties of Hexamethylphosphric Triamide

The reflectance of liquid hexamethylphosphoric triamide $[[(CH_3)_2N]_3PO]$ has been determined between 2 and 9 eV by the semicylinder method and between 10 and 25 eV by the double ionization chamber method. A Kramers-Kronig analysis of the data yielded the optical and dielectric functions and energy loss function. For the K-K analysis, the reflectance data were extrapolated to higher energies by a function $R = R_0(E_0/E)^{\beta}$ with $\beta = 4$. With this extrapolation over essentially the whole of the oscillator strength, calculation of the effective number of electrons participating in collective effects yields a total number of electrons consistent with the number of valence electrons per molecule of 68. A description of data for HMPT and interpretation of the results has been submitted for publication to J. Chem. Phys. [ORO-3861-34].

III. Photoemission from UV Irradiated Liquids

A. A major thrust of the current contract period has been a refinement of the techniques and theories concerning the photoemission effort. The first liquid for which photo-yield curves were determined was formamide [$HCONO_2$]. Questions relevant to credibility and interpretation of some of the initial photoemission measurements on this liquid prompted reinvestigation of the method.

The theory of operation of the double ionization chamber when used for photoemission measurements was given last year and has been incorporated in a paper submitted to The Physical Review [ORO-3861-33]. Briefly, the two ion currents to the incident beam ion chamber, I_0, and the reflected beam ion chamber, I (see Fig. 1), are measured as a function of pressure with a potential on the liquid sample cup of +2.5 volts to suppress photoemission. A plot of I/I_0 versus pressure extrapolates to P=0 to give the reflectance according to the formula

$$\frac{I}{I_0} = R \exp(-\alpha P x_3) \tag{1}$$

where α is the absorption coefficient due to ionization (the only attenuation mechanism when a rare gas is used in the chambers) and x_3 is the total optical path between the entrance to the I_0 chamber and the entrance to the I chamber. Determination of I and I_0 also enables a calculation of the absolute photon flux at the liquid surface I_s.

For photoemission measurements, the potential on the cup is changed to -1.5 volts in order to force electrons emitted from the liquid to leave it permanently. Thus the cup current I_c is given by:

$$I_c = YI_s + I_B + I_R$$

where Y is the electron yield per incident photon and I_B and I_R are currents of ions formed in the volume between the chambers and cup by the incident and reflected beams, respectively. These positive currents flowing to the cup increase the total current and must be evaluated before the time yield can be determined.

The solution to eq. 2 was given last year as

$$Y = \frac{I_c}{I_0} e^{\alpha P\delta} \left(e^{\alpha P x_1} - 1\right) - \left[\left(e^{\alpha P\delta} - 1\right) + R \left(1 - e^{-\alpha P\delta} \right)\right] \tag{3}$$

where x is the optical path in the I_c chamber, and x = x + 2 . Thus δ is the distance from either chamber to the cup. The equation may also be written in terms of the observables as

$$Y = \frac{I_c}{I_0} \left[1 - \frac{RI_0}{I}^{-\frac{x_2-\delta}{x_2+\delta}} \right] \left[\left(\frac{RI_0}{I} \right)^{\frac{x_2}{x_2+\delta}} \right]$$

$$- \left[\left(\frac{RI_0}{I}\right)^{\frac{\delta}{x_2+\delta}} - 1 \right] - R\left[1 - \left(\frac{RI_0}{I}\right)^{-\frac{\delta}{x_2+\delta}} \right] \tag{4}$$

$$Y \equiv \left(\frac{I_c}{I_0}\right) F_1\left(\frac{RI_0}{I}\right) - F_2\left(R, \frac{RI_0}{I}\right) \tag{5}$$

and the functions F_1 and F_2 have been programmed for the computer. The F_2 function is a correction for the ion drift mentioned above and can amount to a 50% correction.

One of the problems with these measurements has been the determination of the distances x_2 and δ. The former is the distance from the entrance to the I_0 chamber and the cup and is determined by the geometrical requirement that the photon beams after reflection must pass completely into the I chamber. <u>This geometrical condition is independent of voltages and pressures</u>, and we feel we know this distance to a high degree of accuracy from measurements of the system, i.e. $x_2 = 9.05$ mm.

The other dimension, δ, however is not so well known as it is the distance between some equipotential near the exit of the I_0 chamber, and the cup. We have estimated it as $\delta = 2.81$ mm. We accidently discovered a way to determine this distance in the following way this year. The exponentials in eq. 3 may be expanded in an approximation valid for low pressures. Using only the first two terms, we find:

$$Y = \left(\frac{I_c}{I_0}\right)\alpha P(x - \delta) - \alpha P\delta \qquad (6)$$

or solving for the observables

$$P\left(\frac{I_c}{I_0}\right) = \frac{Y}{\alpha(x_2-\delta)} + P\left(\frac{\delta}{x_2-\delta}\right) \qquad (7)$$

Clearly if we plot $P(I_c/I_0)$ versus pressure we should get a straight line with intercept $Y/[\alpha(x_2-\delta)]$ and slope $\delta/(x_2-\delta)$. From the latter we can get δ and then from the former, approximate the yield. This was done as shown in Fig. 2 and we find that $\delta = 2.84$ mm in good agreement with our previous estimate. For calculating Y however we continue to use the longer form, eq. 4, which is valid at all pressures.

B. Several changes were made in the photoemission apparatus which enhanced the reliability of the data.

1) A new sample cup was designed, constructed, and put in service. The previous model was built almost entirely of teflon (for its high resistance) with only the cup liner made of stainless steel. This had the disadvantage of poor structural rigidity so that the cup was not truly horizontal and allowed the liquid to leak out of the "low side." The other problem had to do with the cup resistance to ground whenever a liquid spill or boil-over would occur. The old design permitted the liquid to short the cup to ground thus changing the cup potential and adding error in the various measured currents. The new design has a stainless backing and support plate giving a good horizontal edge for the liquid containment. Also the ground support is hidden from exposure to spilled liquid so no short can occur. Further, the annular region around the cup contains a drain gutter to catch spilled liquid. Last the bottom of the cup was given a conical form which requires less liquid to fill the cup but, more importantly, seems to suppress surface waves on the liquid caused by apparatus vibrations. The angle of the cone was chosen to allow more effective "heaping" of the liquid above the cup edge thus allowing more time between cup refills. Surface tension forces are directed upward in the new design thus supporting the largest volume of liquid above the edge.

2) One of the problems we have experienced is the electrical and vacuum leakage of BNC electrical feedthroughs. The chamber is

occasionally filled with water vapor, and/or high vapor pressure impurities from the liquid sample, and these tend to collect on the feedthroughs, bypassing ion currents to ground. This year we redesigned the high voltage type of BNC feedthrough to give both lower vacuum and lower electrical leakage. This feedthrough apparently has a resistance well in excess of the 10^{16} ohms we need for our electrometers even in the presence of vapor in the system.

3) The potential on the cup has usually been of the order of the potential in the ion chambers. We discovered this year that reducing the cup potential from 6 volts to 2.5 volts gave somewhat smaller values of I/I_0 which were independent of further reductions in cup potential. Thus it was decided to operate with a cup voltage of 2.5 volts and a chamber voltage of 2.0 volts henceforth.

4) A new Bausch and Lomb grating was installed in the monochromator. The old grating had been used for about twelve years and was speckled with material evaporated from the light wource and liquid samples. The new grating produced a tripling of light source intensity in the region above 30 eV where it is badly needed.

5) The hood and vacuum pump exhaust system was installed. With eleven mechanical vacuum pumps in operation, the air was occasionally blue in the lab before the system was installed. Also we are now dealing with carcinogens, and the new hood and system will protect contract workers much better than before.

6) A heater was installed in the end plate where the electrometer feedthroughs emerge from the vacuum chamber to prevent sweating of the feedthroughs, and shorting of the electrometers.

C. Refined photoemission data was obtained for formamide. Photon fluxes were determined by filling the dual ion chambers with Ar and connecting an electrometer to the sample cup to measure electron currents leaving the cup. The number of photo-electrons per incident photon and per absorbed photon were obtained. The results of this work have been submitted to Phys. Rev. [ORO-3861-33]. The yield curves are similar over the 16-25 eV range of study, and show, per absorbed photon, a broad maximum reaching 13.5% at 18 eV and a minimum of 8.5% at 23 eV.

Concomitant with photoionization measurements on hexamethylphosphoric triamide, studies were also initiated on photoemission from this important liquid. As with our photoemission measurements on formamide, argon was used as a filling gas in order to determine the absolute photon flux in a manner reminiscent of the Sampson double ion chamber technique. Data were taken over the energy range from the argon ionization potential, 15.7 eV to 24.6 eV. This liquid proved much more difficult to use because of its high electrical conductivity, its lower surface tension and viscosity, and its carcinogenicity.

In general the data resembled the photoemission from formamide, with a broad maximum at the surface plasmon energy, a minimum near the volume plasmon energy, and a sharp rise at still higher energies. The absolute yield was somewhat lower than with formamide but the same structure appeared as shown in Fig. 3. The surface plasmon maximum is at about 8% for HMPT whereas it was about 12% for formamide. The minimum is at about 23 eV in both cases.

In formamide we attributed this minimum to a competition between plasmon creation and electron generation by the photoelectrons. If the former, then fewer secondaries would be available for escape--hence the minimum. A casual comparison with the absolute photoyield data of Sampson and Cairni[1] for aluminum showed that their data peaked at the plasmon energy (15 eV for Al).

We feel the matter becomes clarified when we correct the Al data to a per photon absorbed per unit optical attenuation length basis. That is, the electron yield per incident photon was divided by (1 - R), and then by $4\pi k/\lambda$, the reciprocal optical attenuation length. The HMPT curve still looks like Fig. 3 but the Al shown in Fig. 4 changes dramatically. For Al the emission starts at the surface plasmon energy (10 eV). It rises but starts to level off at the volume plasmon energy (15 eV). At higher energies it rises again presumably due to escape of photoelectrons after plasmon creation.

The new data in HMPT exhibits a similar behavior e.g. the rise due to surface plasmon creation and ecay, and a minimum due to volume plasmon creation and decay. These matters are under discussion at this time and it is hoped that the microdosimetry theorists at ORNL will be able to model this situation and confirm our explanation. It is interesting to speculate on the still higher energy data of Sampson and Cairni. This yield achieves a maximum

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[1] J.A.R. Sampson and R.B. Cairni, Rev. Sci. Instr. 36, 19 (1965).

at 19 eV and then declines possibly following decline in the plasmon excitation cross section. It starts up again at 25 eV where the photoelectron now has enough energy to excite both a surface and volume plasmon. The curve peaks at around 31 eV where the photoelectron has enough energy to excite two volume plasmons, and then declines as that excitation probably declines.

We will look for such features as our Monte Carlo modeling of radiation penetration develops during the next year.

IV. Photon and Photoelectron Mean Free Paths

One important application of photoemission measurements involves the calculation of photon and photoelectron mean free paths in liquids from photoyield data. The simplest model of photoemission proceeds as follows. A photon is normally incident on the surface and is exponentially attenuated, with a photon mean free path $\lambda_p = \left(\frac{4\pi k}{\lambda}\right)^{-1}$. In an element of depth dx it has a probability of producing a secondary electron dx/λ_p. This electron then has an exponential chance of returning to the surface and escaping with mean free path λ_e. Thus the differential probability for photoelectron production in dx and subsequent escape is:

$$dY(x) = e^{-x/\lambda_p} \cdot \frac{dx}{\lambda_p} \cdot e^{-x/\lambda_e} \qquad (1)$$

The total production and escape is then

$$Y = \int_0^\infty dY(x) = \frac{1}{\lambda_p}\int_0^\infty e^{-x\left(\frac{1}{\lambda_p} + \frac{1}{\lambda_e}\right)} dx \qquad (2)$$

$$Y = \left(\frac{1}{1 + \frac{\lambda p}{\lambda_e}}\right) \tag{3}$$

Now λ_p is typically of the order of hundreds of angstroms, whereas λ_e is usually thought of as being a few to a few tens of angstroms. Thus $\lambda_p/\lambda_e >> 1$ and eq. 3 becomes:

$$Y = \frac{\lambda_e}{\lambda_p}$$

Thus the quantity $Y\ \lambda_p = \lambda_e$ is the photoelectron mean free path. This quantity $Y\ \frac{\lambda}{4\pi k}$ has been reported for formamide where the electron mean free path is shown to be of the order of 10 angstroms. A convex characteristic in the vicinity of the surface plasmon frequency is due to photoelectron excitation of surface plasmons and is unrelated to the above model. The minimum in λ_e at the volume plasmon frequency is due to photoelectrons exciting plasmons and thus being less likely to reach the surface and escape.

Calculations of the mean free paths for photons and photoelectrons will be made for HMPT and for each liquid for which photoyield curves are determined. In addition, values of mean free paths in HMPT for electrons of energies from 10^2 - 10^4 eV will be calculated from the variation with photon wavelength of the energy loss function, Im $[-1/\varepsilon]$, obtained from optical parameters. The values determined for the liquid will be compared with those predicted by a recently proposed[2] simple expression for calculating electron mean free paths in

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[2] J.C. Ashley and M.W. Williams,"Electron Mean Free Paths in Solid Organic Insulators." Accepted for publication by <u>Radiation Research</u>.

solid organic insulators. The hiatus between mean free paths as determined from photoyield data (< 25 eV) and determined from optical data (> 100eV) can be reduced as photoemission data is extended to 50 eV using the newly proposed transmission monochromator.

V. Kapton

The study of Kapton, initiated during the last contract period, is a collaborative effort with E.T. Arakawa of ORNL. Kapton Type H polyimide film (manufactured by E.I. duPont de Nemours and Co.) has a monomeric unit of $\{C_{22}H_{10}N_2O_5\}$. The films are used extensively in situations demanding radiation resistance. The properties of Kapton are similar to those of Mylar polyester film (manufactured by E.I. duPont de Nemours and Co.), but Kapton is less affected by temperature changes and is ≈ 50 times more resistant to radiation damage.

The optical parameters were determined from a Kramers-Kronig analysis of measured reflectance values from 25,000 Å to 163 Å. These data were used to calculate the dielectric functions, energy loss function, and the effective number of electrons. In addition, the data was used to calculate values of the mean excitation energy of Kapton, electron mean free paths in Kapton and the stopping power of Kapton for electron.

A description of the Kapton data is included in the extended abstract from the Basic Optical Properties of Materials Conference appended to this report. Also appended are figures on Kapton which are to be included in a more comprehensive paper now in preparation.

VI. Polycyclic Organic Molecules

Transmission measurements have been made on the Cary 14 spectrometer on four polycyclic hydrocarbons, benzene, toluene (methylbenzene), xylene (dimethylbenzene), and trimethylbenzene in the 25,000 to 2400 Å region. In the UV, there is a shift in the onset of absorption to lower energy with increase in methyl groups. The onset for benzene is ∿ 4.49 eV, that for methylbenzene ∿ 4.44 eV, for dimethylbenzene ∿ 4.37 eV and trimethylbenzene is ∿ 4.30 eV.

Preliminary reflectance measurements have been made on these PAH's using the semicylinder technique in the 3 to 10 eV region. The data has been analyzed to yield the optical constants n and k. Structure near 6.5 eV in the absorption spectrum of liquid benzene is the strong allowed π excitation identified with the $^1A_{1g} \rightarrow {}^1E_{1u}$ transition in the vapor. There is a shift in the π-peak from 6.5 to 6.1 eV in going from benzene to trimethylbenzene (i.e. with the addition of methyl groups). This is consistent with the direction of shift observed in the onset of absorption observed in transmission data from Cary 14 studies. Structure above 8 eV, observed in the absorption spectrum of each of the liquids, is associated with $\sigma \rightarrow \sigma^*$ transition. The data must be refined before the magnitude and energy of this peak for each liquid can be specified with accuracy.

Transmission measurements using lithium fluoride plates encasing liquid films ∿ 500 Å will be made to investigate the weak vibrationally induced structure at 5 and 6 eV from symmetry forbidden $\pi \rightarrow \pi^*$ transitions.

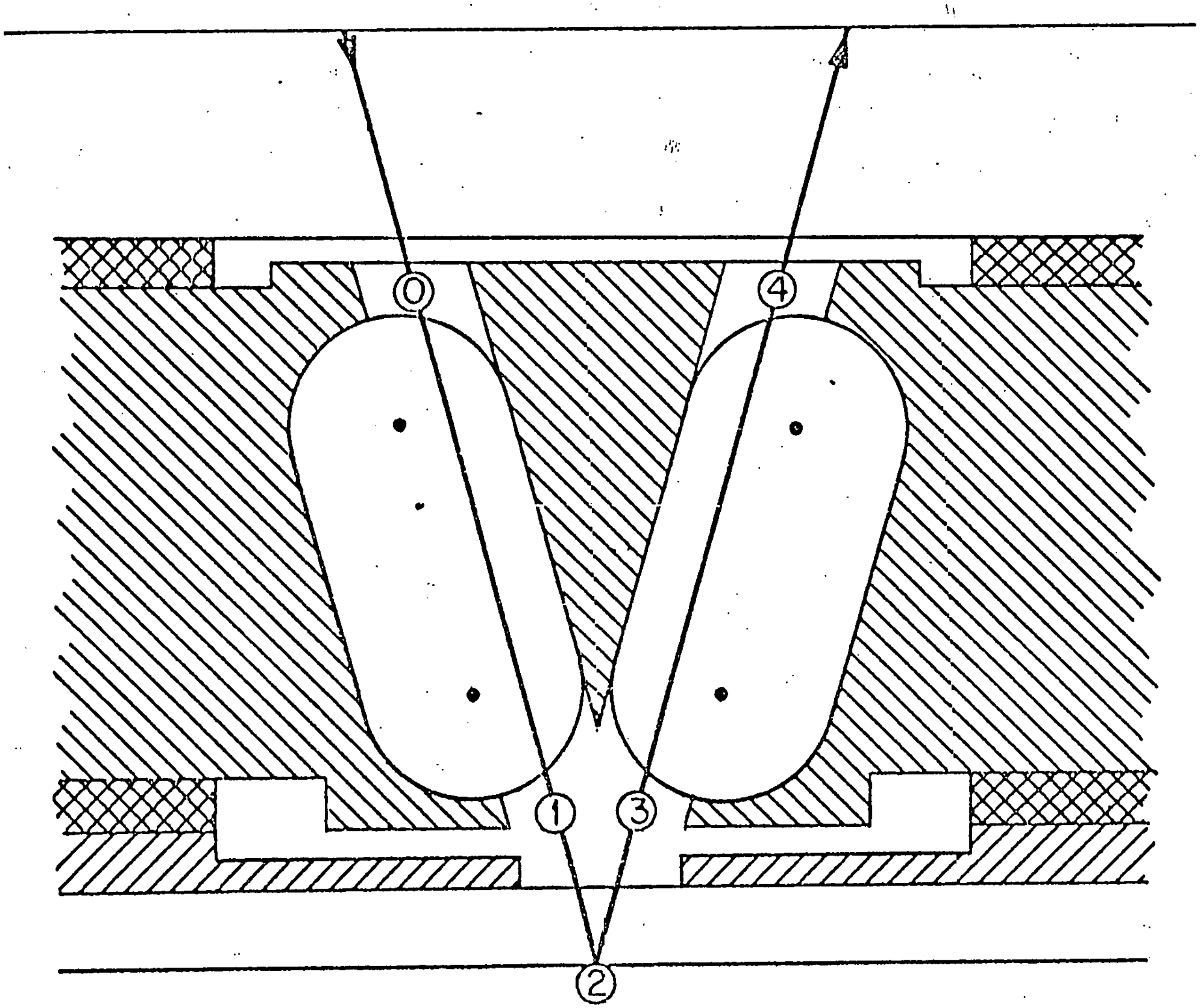

Figure 1

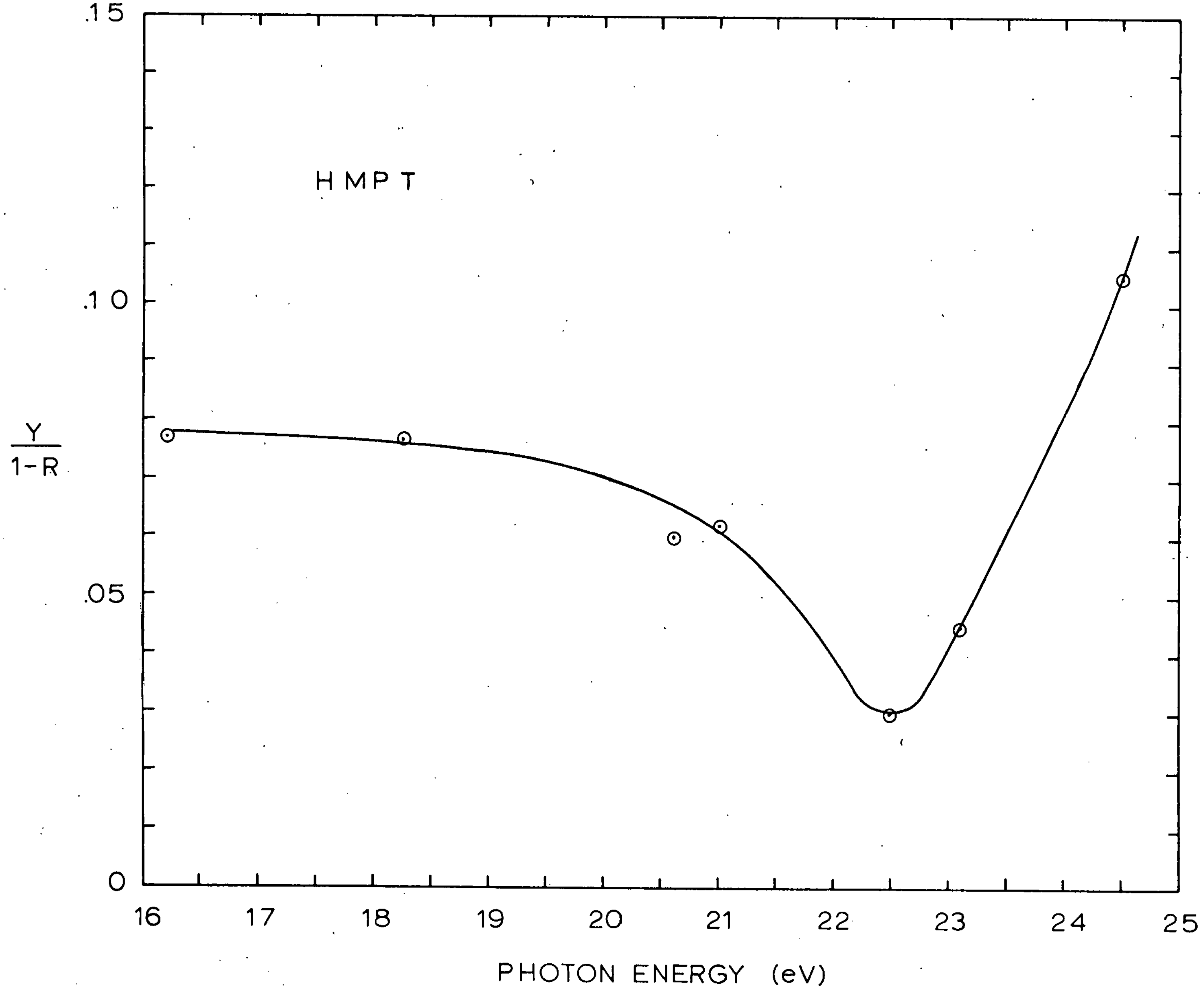

Figure 2

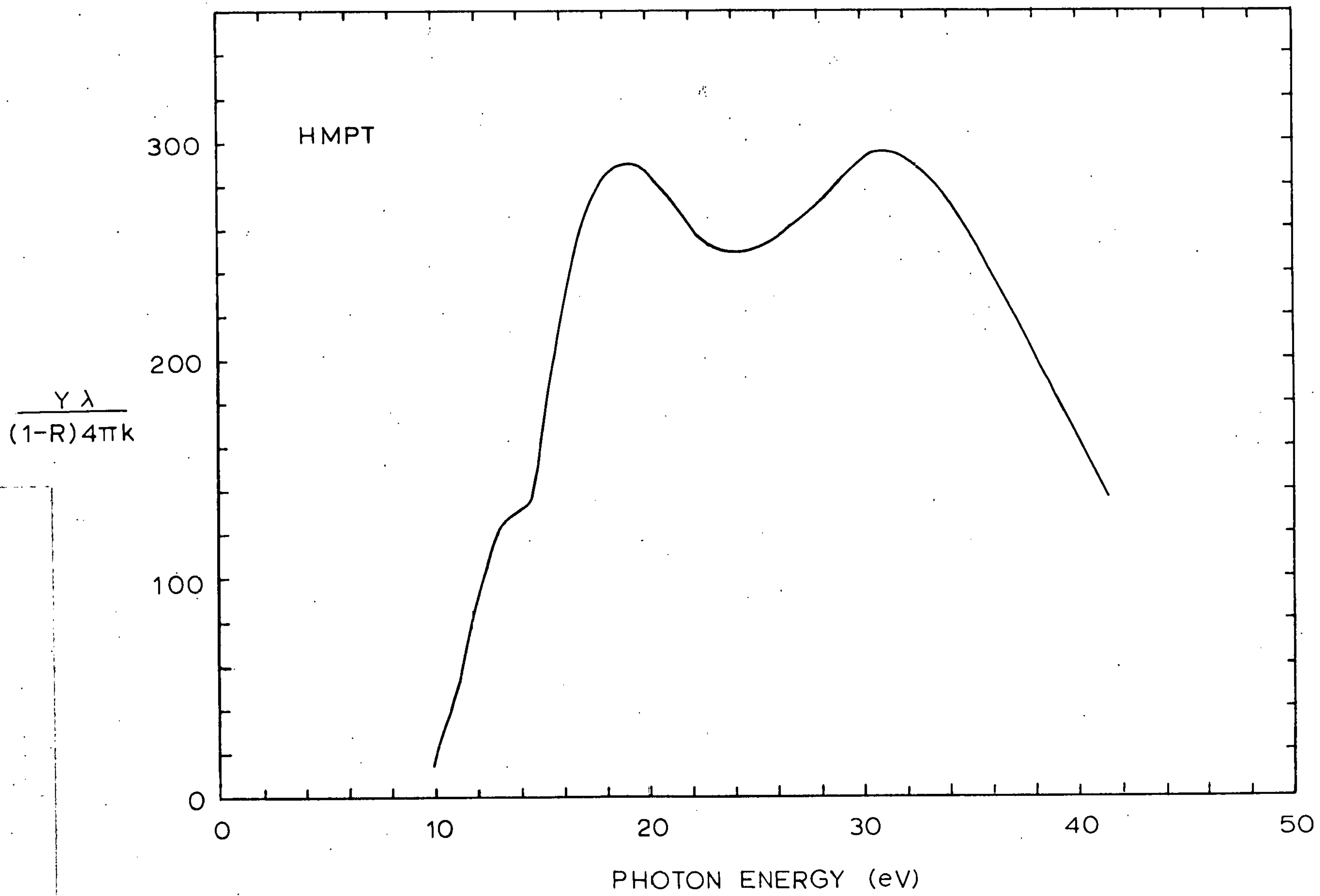
HMPT
300
200
100
0
$\frac{Y\lambda}{(1-R)4\pi k}$
0
10
20
30
40
50
PHOTON ENERGY (eV)

Figure 3

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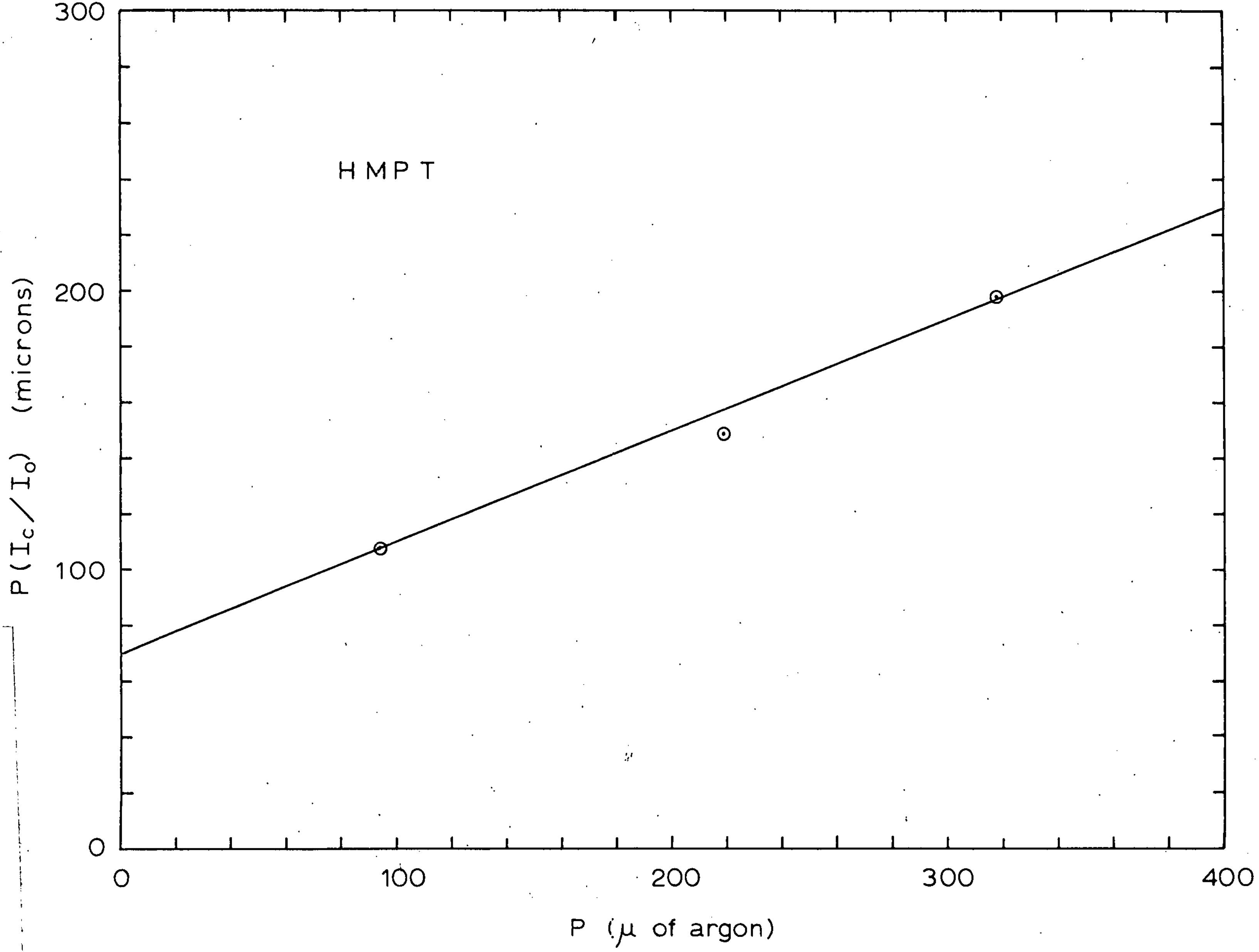

Figure 4