LIQUID AND SOLID ORGANIC PHOTOCATHODES

V. Peskov^{1,2)}, G. Charpak¹⁾, P. Miné^{1*)}, F. Sauli¹⁾, D. Scigocki¹⁾,
J. Séguinot³⁾, W.F. Schmidt^{1,4)} and T. Ypsilantis³⁾

ABSTRACT

We have investigated the possibility of creating photocathodes for gaseous detectors with a high sensitivity in the photon spectral region between 105 and 300 nm. Metal cathodes covered with liquid or solid organic layers, such as tetrakis(dimethylamine)ethylene (TMAE) and tetramethyl-p-phenylenediamine (TMPD) and solutions of these substances, were studied using two different experimental set-ups: a proportional wire chamber and a single-wire counter. Three effects were observed. First, a thin film of adsorbed vapours led to the efficiency of the metallic cathode being increased by more than one order of magnitude at photon wavelengths up to $\lambda \approx 400$ nm. Secondly, a thick layer of liquid strongly increased the cathode efficiency Q for radiations of $\lambda < 270$ nm: e.g. with TMAE we obtained a yield of about 0.5%, for $\lambda = 235$ nm. Thirdly, we found that some solid layers, such as neopentane + TMAE, give a maximum efficiency $Q \approx 3\%$ at $\lambda = 235$ nm. The quantum yields of liquid and solid photocathodes increase with increasing applied electric field. Some applications of the liquid and solid photocathodes are discussed.

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- 1) CERN, Geneva, Switzerland.
 - 2) Institute for Physical Problems, Moscow, USSR.
 - 3) Collège de France, Paris, France.
 - 4) Hahn-Meitner Institute, Berlin, Fed. Rep. Germany.
 - *) Now at the Ecole polytechnique, Palaiseau, France.

1. INTRODUCTION

The photoionization process in a gas is of intrinsic interest in understanding the propagation of electron avalanches in an electric field around a wire, i.e. the gain mechanism in proportional and Geiger counters. Practically, this process served as the basis for the development of gas-phase single UV photon detectors for Cherenkov ring-imaging [1, 2] and for plasma diagnostics [3]. Data made available in a recent review [4] give relative quantum efficiencies versus photon wavelength for noble, simple organic and simple inorganic gases. Absolute quantum efficiencies are now measured for some complex organic molecules [tetrakis(dimethylamine)ethylene (TMAE), tetramethyl bi-imidazolidine (TMBI), triethylamine (TEA)] which have the lowest ionization thresholds and high efficiencies [5–8].

The photoionization process is also observed in liquids (both neat and doped), and a recent review giving relative quantum efficiencies is available [9]. In liquids, as compared with gases, there are several new related factors which tend to reduce the quantum yield: e.g. geminate recombination (due to the short electron thermalization length r_0 in liquids) and low electron mobility μ . If, in addition, transfer of the photoelectrons from the liquid to the gas phase is required (where amplification is possible), then additional loss of efficiency may occur [10]. The threshold energy for photoionization in liquids is, however, generally lower than in gases owing to the polarization energy P_+ of the positive ion and to the lowering of the electron conduction band V_0 . The relation between the gas-phase ionization energy threshold E_{gas} and the liquid threshold E_{liq} is

$$E_{\text{liq}} = E_{\text{gas}} + P_+ + V_0. \quad (1)$$

The polarization energy is always negative, whereas V_0 may be of either sign. Relation (1) will, for example, allow some photosensitivity in liquid TMAE ($V_0 = -0.26$) up to 330 nm [11], whereas for TMAE gas, the sensitivity ends at 230 nm.

A characteristic of these liquids when they are specially purified is that the electron lifetime τ is long (many microseconds); so if the electron mobility is high ($\mu > 10 \text{ cm}^2/\text{V}\cdot\text{s}$), the electron mean free path $\ell_e = \mu E \tau$ will be long. As an example: for $\mu = 10 \text{ cm}^2/\text{V}\cdot\text{s}$, $\tau = 10 \mu\text{s}$, and an electric field $E = 10 \text{ kV/cm}$, the electron mean free path is $\ell_e = 1 \text{ cm}$. Such a long mean free path would allow all photoelectrons that escape geminate recombination to drift and be collected at the liquid surface, since the liquid (or solid) photocathode is only microns (10^{-4} cm) thick. Its thickness is determined by the photon absorption length $\ell_{\text{ph}} = 1/n\sigma$, which is about $0.1 \mu\text{m}$ (n is the number of molecules per cubic centimetre of liquid $\approx 3 \times 10^{21}/\text{cm}^3$ and σ is the molecular absorption cross-section $\approx 40 \text{ Mb}$). A $1 \mu\text{m}$ thick cathode therefore absorbs 99.995% of the incident photons. In this simple model the final quantum efficiency is determined by geminate recombination and the extraction probability of the electrons at the liquid–gas interface. An electric field that is large enough for efficient extraction will also reduce the geminate recombination. The condition that $\ell_e \gg \ell_{\text{ph}}$ is completely satisfied for high-mobility liquids is the primary reason for their high quantum efficiency.

Anderson [12, 13] proposed to use a liquid-TMAE layer as the photocathode in a wire chamber. With liquid photocathodes, one can expect to build UV detectors with good sensitivity in the wavelength range up to 300 nm, which opens up new prospects for applications in high-energy physics and in other areas of science. Subsequent investigations, however, have shown conflicting indications. The existence of liquid-TMAE photosensitivity was also demonstrated by Schotanus et al. [14] using spectral measurements. Other investigators [15, 16] have failed to confirm Anderson's results, although Holroyd [8] observed an effect in TEA which could be explained as a manifestation of a liquid photocathode.

The aim of this work is to investigate liquid-TMAE photocathodes as well as other organic liquid and solid photocathodes, and to understand the conflicting results previously indicated. We

have repeated the conditions of Anderson [13] based on the detection of UV scintillation light emitted from BaF₂, and have extended this work with a photocathode coupled to a monochromatic light source of variable wavelength and with a counter capable of efficiently detecting single photoelectrons.

2. EXPERIMENT WITH BaF₂ SCINTILLATOR AND A LOW-PRESSURE MWPC

2.1 Experimental set-up

This experiment, which followed closely the set-up of Anderson [12, 13] in observing a liquid-photocathode effect, was performed with the assembly shown schematically in Fig. 1. This consisted of: a low-pressure (≤ 30 mbar) multiwire proportional chamber (MWPC) assembled inside a thermostatic box; a gas-flow system; a liquid-cathode receptacle; a pump; and detection electronics. A BaF₂ crystal was coupled to the MWPC as previously described [17] and as shown in Fig. 1. The aluminium cathode had a groove ('cathode bath') which held the liquid on the cathode. It was filled either by vapour condensation as the chamber was cooled, or from a liquid reservoir. An overflow bottle coupled to the grooved channel prevented accidental spillage of the liquid across the rim of the cathode bath. If there was a need to fill the chambers with vapour alone, special valves were used to open the vessels containing the appropriate liquids. The cathode bath [(e) of Fig. 1] was earthed ($V_c = 0$), whereas the BaF₂ plane (a), the MWPC cathodes (b, d), and the MWPC anode (c) potentials could be varied independently. Depending on the voltages chosen, it was possible to work with or without gas amplification in spaces A and C (Fig. 1). In this way, by adjusting polarity and voltages, the signals from volumes A, B, and C could be measured separately. Signals from the anode wires (c) were amplified and sent in parallel to a pulse analyser and to an oscilloscope. The thermostatic box (and the gas and liquid fill lines) could be operated between -20 °C and $+70$ °C.

2.2 Results with BaF₂ scintillator and low-pressure MWPCs

For these measurements the UV scintillation light from the BaF₂ crystal was excited with γ -rays from ⁶⁰Co (1.17 and 1.33 MeV) or by X-rays from ²⁴¹Am (59 keV). The number of UV photons is estimated, from the measurements of Laval et al. [18] and of Schotanus et al. [14], to be 2000/MeV of energy lost in the crystal in the wavelength interval 180 to 230 nm. As a result of the overlapping of this radiation spectrum with the TMAE-vapour quantum efficiency, the number of photoelectrons created inside a wire chamber at room temperature (~ 20 °C) was less than one per millimetre gas gap. For this reason, when the signal from the MWPC region A or C of Fig. 1 was recorded on the pulse analyser, the shape of the spectrum displayed a low pulse-height noise peak and an exponential single-electron distribution. The electronics noise peak was eliminated by a discriminator so as not to overload the analyser.

When the chamber was filled with purified TMAE vapour, with 30 mbar CH₄, the count rate from region B (Fig. 1) was slightly higher than the rates from regions A or C. Injection of purified TMAE liquid into the cathode bath did not substantially change the count rate from region C, indicating that the gas-phase photoionization was dominant. Therefore, in order to obtain clearer observations of the liquid-cathode effect, we usually proceeded by cooling the chamber. When TMAE was cooled from 20 °C to 4 °C, the saturated vapour pressure fell from 0.46 to 0.13 mbar [13, 19].

After filling the chamber with saturated TMAE vapour at 4 °C, methane was added up to a pressure of 30 mbar. The working voltage of the chamber was determined mainly by the methane pressure. At 4 °C, however, we were unable to obtain a gas amplification large enough to record all pulses reliably in the wire chamber (region B), but it was possible to obtain preamplification in the drift space and to record signals from regions A and C [see Fig. 2 (solid lines)]. A comparison with

room temperature indicated that the count rates from regions A and C fell by a factor of approximately 5, which shows fairly good agreement with the expectation from the reduction of the gas-phase TMAE pressure.

When liquid TMAE at 4 °C was injected into the cathode bath the gas conditions in the chamber did not change, because the chamber was again filled with the saturated pressure of TMAE at 4 °C plus 30 mbar CH₄. So the working voltages, the gas amplifications, and the pulse-height spectrum were exactly the same as before injection. This allowed us to make an accurate comparison of the count rates from regions A and C. The results of the measurements are presented in Fig. 2 (dashed line). As can be seen, when liquid TMAE (4 °C) was injected into the cathode bath, the count rate from region C rose by a factor of 7 to 10 and that from region A by a factor of 3 (because of the low condensation). This demonstrated the liquid-TMAE photocathode effect, with transfer of electrons from the liquid phase to the gas phase. It also showed that a liquid-cathode effect occurred at the BaF₂ surface. In all cases when there were vapours inside the chamber, a thin photosensitive liquid layer was formed on all the chamber surfaces, including that of the BaF₂ crystal. This can open up a range of applications for photocathodes created directly on the entrance windows of gas detectors.

In another experiment we tried to obtain a liquid photocathode by means of stronger condensation. To do this, the chamber was filled with TMAE vapour at a temperature of 20 °C and then cooled down to 0 °C. Here the highest count rate was from region A, indicating that photoelectron emission from the thick TMAE layer condensed on the BaF₂ crystal is dominant. The performance of the chamber at -12 °C, which is below the freezing point of TMAE, was also tested. In this case, the count rate from region A changed only very slightly, whereas from region C it actually decreased (see dash-dotted line in Fig. 2). This shows that emission takes place mainly from TMAE in its solid state formed on the window, and that as a result of the absorption and scattering of the radiation in this layer, the signal from region C decreases.

Similar experiments were performed with purified liquid tetramethyl pentane (TMP) in which 3% TMAE was dissolved; TMP was chosen because of its low vapour pressure (≈ 6 mbar at 0 °C) and its long thermalization length r_0 (≈ 10 nm) and electron mobility μ (≈ 30 cm²/V·s). All these factors decrease the recombination rate of TMAE ions and therefore increase the quantum yield.

The experimental procedures were the same: first we introduced TMP + TMAE vapour into the chamber, added CH₄ to a pressure of 30 mbar, and carried out the measurements; then we filled the cathode bath with the liquid and compared the results. The high-voltage gas amplification and pulse-height spectrum remained unchanged. The experiments were carried out at room temperature and at 0 °C. At room temperature a small ($\sim 20\%$) increase in the count rate was noticeable when the bath was filled with liquid. To make the effect stand out more clearly, we cooled the chamber down to 0 °C. When the liquid was placed in the cathode bath, the following changes were observed, which were not seen when the detector was filled with vapour alone: the count rate from region B remained almost the same, but the rates from regions A and C increased by a factor of 2 to 3 (see Fig. 3).

A large number of other control experiments were carried out. For example, the detector was filled with a vapour mixture of TMAE and TMP and heated to about 38 °C (the gas amplification was kept constant by voltage adjustment). In this case, because of the rise in vapour pressure, the signal from region B increased, but the signals from regions A and C decreased owing to the evaporation of the thin, liquid, surface film and a consequent loss of sensitivity in these parts of the chamber.

All the experiments described were stable and easily reproduced.

2.3 Discussion and interpretation

The measurements given in the preceding subsection show conclusively the existence of a liquid-TMAE photocathode effect.

Two sources could give rise to the increased sensitivity of the chamber: the formation of a thin adsorbed film, and the extraction of photoelectrons from the liquid (thick condensed layer and cathode bath). Since the introduction of liquid into the cathode bath between 0 °C and 4 °C increased the quantum efficiency for both TMAE and TMP + TMAE by a factor of more than 3, it could be expected that the liquid would provide a contribution that is at least three times larger than that of the adsorbed film. At room temperature, the difference between the adsorbed film and the liquid is lower. This is due to the fact that with a greater partial vapour pressure, the adsorbed film [8] is thicker, thus reducing the difference between the film and the liquid itself.

If we ignore the effect of the adsorbed film at low TMAE vapour pressure, the fact that the sensitivity increases as the cathode is filled with liquid leads us to conclude that for temperatures between 0 °C and 4 °C the emission of electrons from the liquid is at least three times higher than that from the ionization of the gas. Therefore at room temperature, when the TMAE vapour pressure rises by a factor of 4 to 5, the contribution to the full current by the charges that are extracted from the liquid will be at least 60% for a gap thickness of 2 mm. For a 1 cm thickness the contribution from the liquid will amount to about 15%, whilst that coming from the surface films will be lower than 15%, which is too small from the practical point of view.

In the case of TMP + TMAE, cooling to 0 °C caused the counting rate to drop by less than a factor of 4, indicating the existence of a surface effect. In addition, even at room temperature the difference between the liquid and the adsorbed layer could be seen. In qualitative terms this means that a greater sensitivity was obtained with a TMP + TMAE liquid cathode than with TMAE alone.

Thus the idea of Anderson was confirmed. There clearly exists a photoelectric enhancement effect due to the condensation of photoionizable vapours in wire chambers used for detecting the UV component of BaF₂. But the absolute quantum yield of a liquid photocathode could not be estimated from this experiment, so measurements with monochromatic light and a single-wire counter were then performed.

3. EXPERIMENTS WITH A UV MONOCHROMATOR AND A SINGLE-WIRE COUNTER

3.1 Experimental set-up

The apparatus shown in Fig. 4 was built for the precision measurement of the quantum yield from different photocathodes. It consists of a D₂-filled UV arc lamp with a MgF₂ window (Hamamatsu L879-01), a UV photon monochromator (Jobin-Yvon H20 UVL) with 2 nm resolution at 150 nm, and a single-wire counter which operates in such a way that single electrons can be detected with near 100% efficiency. The photon beam from the monochromator was split into a reflected beam (intensity I_R) and a transmitted beam (intensity I_T) by means of a 4 mm thick CaF₂ crystal [(3) in Fig. 4] placed at 45° to the beam direction. The reflected beam was monitored by an RCA8850 phototube (14) whose glass window was coated, in vacuum, with a 1000 nm thick film of p-terphenyl wavelength shifter [(13) in the figure]. The transmitted beam I_T was parallel-focused by a CaF₂ lens of 100 mm focal length and 25 mm diameter. The 3 mm diameter beam entered the single-wire gas counter (6) after traversing a neutral density filter station (4) which could reduce I_T by calibrated amounts, a CaF₂ exit window (15), and two parallel, 81% optically transparent meshes (5) which were biased to trap photoelectrons produced by possible TMAE deposits on the CaF₂ window (15).

Figure 4 shows the design of the single-wire counter. It consists of a 40 mm diameter stainless-steel cylinder with two transverse flanges placed along an axis in the middle of the cylinder.

The counter was linked to the monochromator by one of the flanges. Cathodes of differing design, manufactured from various materials, could be fixed on the other flange. This figure shows the most frequently used design, which permits the copper cathode to be cooled or heated. The vapour can be condensed by cooling, and a liquid or solid photocathode obtained; by heating, it can be evaporated. A 0.2 mm diameter wire was used as an anode.

The gas supply (12) passed through a flowmeter (11) and could be bypassed through liquid TMAE (10). A supply of liquid TMP, tetramethyl silane (TMS), or neopentane (NP) was available (9) in the circuit. All these liquids and the TMAE were specially purified.

Different mixtures of gases could be flushed through the counter: methane, argon, and isobutane with (or without) TMAE, TMP, TMS, NP, or diethyl ferrocene vapours at total pressures from 0.03 to 1.6 bar.

3.2 Calibration

The system was calibrated before starting measurements with the single-wire counter. Calibration of I_T relative to I_R was achieved by replacing the single-wire counter [(6) of Fig. 4] with a second photomultiplier, which was also covered with a 1000 nm thick vacuum-deposited film of p-terphenyl [identical to (13) and (14) of Fig. 4]. The wavelength shifter efficiency has been measured to be constant ($\pm 10\%$) over the range 100 to 300 nm [20], relative to sodium salicylate which itself is constant over this interval [21]. Measurement of the photomultiplier current ratio $R = I_T/I_R$ serves to calibrate the transmitted flux: in terms of the reflected flux, $I_T = RI_R$ for any wavelength. The count rate C of the single-wire counter is proportional to I_T and to the quantum efficiency Q (for 100% single-electron counting efficiency); thus

$$C = kI_TQ = kI_RRQ, \quad (2)$$

where the second equality expresses the count rate in terms of the monitored flux $I_R(\lambda)$ and the calibration ratio $R(\lambda)$. The proportionality constant k is evaluated by measuring, at wavelength λ_0 , a count rate C_0 and reflected flux I_{R_0} when the single-wire counter is filled with TMAE vapour with known quantum efficiency Q_0 . Thus $k = C_0/I_{R_0}R_0Q_0$, where $R_0 = R(\lambda_0)$ is from the calibration. The TMAE-vapour relative quantum efficiency versus wavelength has been measured by Ekelin and Fransson; their results were published a few years ago [6, 7]. Normalization of this curve to a maximum quantum efficiency $Q_{\max} = 0.67$ at $\lambda = 145$ nm leads to agreement with the Cherenkov ring-imaging data [7] which gave the Cherenkov quality factor [1] $N_0 = 95 \text{ cm}^{-1}$ for an argon-gas Cherenkov radiator and a TMAE-vapour-filled, single-photon detector with quartz windows. With this normalization the quantum efficiency at $\lambda_0 = 200$ nm is $Q_0 = 0.21$. The more recent absolute measurement of Q for TMAE vapour by Holroyd et al. [8], gives a value $Q_0 = 0.23$. We adopt a value $Q_0 = 0.22$ at $\lambda_0 = 200$ nm for full photon absorption.

Special care was taken to suppress short wavelength light coming from second-order diffraction and the tail of the zeroth-order (undispersed) beam. For example, when taking measurements at $\lambda = 250$ nm, light of $\lambda = 125$ nm may be present from second-order diffraction. Even though the zeroth and second orders have only $\sim 1\%$ of the intensity of the first order, the counter was much more sensitive to this shorter wavelength light; a signal from this parasitic light was approximately one order of magnitude larger than the useful signal. A filter system [(4) of Fig. 4] was therefore always used to suppress this component, and the level of this light as well as of the tails of the zeroth order was regularly checked.

It should be noted that when the counter was flushed with Ar and isobutane or with isobutane alone, it was possible to achieve the Geiger regime. In this case the amplitudes of all pulses were approximately equal. This makes it possible to reach almost 100% probability in photoelectron

recording, which is of extreme importance for precision measurements of the photocathode efficiency. When the counter was filled with methane, only a restricted proportional regime was possible, with a counting plateau at about 200 to 300 V. To estimate the efficiency of this counter, a calibration procedure was then carried out. We measured the count rate from a Geiger counter filled with isobutane + TMAE vapour, at $\lambda = 200$ nm. Then the same measurements were repeated with the counter filled with methane + TMAE vapour. In the region of the counting plateau, the two rates agreed, showing that efficient single-electron counting in methane is possible, as previously shown by Ekelöf et al. [22].

3.3 Liquid and solid photocathodes containing TMAE

3.3.1 TMAE photocathodes

The quantum efficiency Q of an uncoated copper cathode at room temperature (20 °C) was measured at atmospheric pressure in argon + 10% methane versus wavelength λ , as shown in Fig. 5. The admittance of an extremely low partial pressure of TMAE ($p < 0.1$ mbar) over a period of 20 hours was sufficient to form a photosensitive layer with the quantum yield increasing by more than a factor of 10, even up to $\lambda = 380$ nm. This test was repeated with an initially clean aluminium cathode (see Fig. 5). During the first 10 to 12 hours, the results obtained with the aluminium cathode were similar to those with the copper cathode, but after 20 hours the sensitivity at $\lambda = 380$ nm dropped. The quantum yield of this type of photosensitive layer did not depend on the counter pressure or on the type of gas filling (see Fig. 6). The photosensitive layer is extremely tenacious, as is shown in Fig. 7a. The whole single-wire counter system had to be heated to about 60 °C for two days and gas-flushed (argon + 50% methane) for nine days in order to recover the initial low quantum efficiency of the copper cathode. The formation time of the TMAE cathode at 20 °C is shown in Fig. 7b. The previous TMAE thin-film cathode was replaced at time zero with a clean copper cathode, and then flushed with gas (without TMAE). The TMAE film cathode was formed by TMAE trapped in the gas system, and reached its previous value in about 20 hours.

When the external part of the copper cathode is cooled to $t_{\text{cath}} = 0$ °C, intensive TMAE condensation begins, because the gas input is at room temperature and TMAE gas is cryopumped onto the copper cathode. The quantum efficiency grows by factors of between 10 and 1000 at $\lambda < 250$ nm. A new, steeper dependence of Q on λ appears in the region of the increased quantum efficiency. At the same time, because of absorption in a comparatively thick liquid layer, the sensitivity to radiation between 290 and 400 nm is reduced by two orders of magnitude.

The same results were obtained at a TMAE pressure of $p > 0.1$ mbar. Typical data are shown in Fig. 8a (curve 2). In this experiment, the gas mixture flowing in the counter contains TMAE vapour at 0.45 mbar, which is almost its room-temperature equilibrium vapour pressure. At this partial pressure the photon absorption mean free path is about 20 mm at $\lambda = 200$ nm [19], hence 86% of these photons are absorbed in the counter gas path (36 mm) before reaching the cathode. Since the TMAE vapour is ionized by radiation from $\lambda < 230$ nm downwards, the observed quantum yield in this region is due to ionization of the vapour. There is good agreement between the present measured shape of $Q(\lambda)$ and the measurements of Holroyd et al. [8] and Arnold et al. [19]. This demonstrates the reliability of our calibration system.

At $\lambda > 230$ nm the gas-phase quantum efficiency is negligible and the full signal is due to the liquid cathode. When the TMAE cathode was heated to $t_{\text{cath}} = 40$ to 50 °C for several minutes, the sensitivity for $\lambda > 230$ nm decreased significantly (compare curves 3 and 2 of Fig. 8a), showing that the cathode effect is due to condensation. All these results are easily reproducible, although they depend very much on the deposited cathode material. Corrections are necessary to account for absorption of photons in the counter gas before they reach the cathode. This correction was measured experimentally and, depending on temperature and wavelength, amounted to a factor of

about 5 to 7, which is in agreement with the absorptance measurements of Holroyd [8] and Arnold et al. [19]. The results, corrected for absorption, are presented in Fig. 8b (curve 2). The corrected quantum efficiency for TMAE is 0.4% at $\lambda = 235$ nm, to be compared with Holroyd's value of 0.56% [11] as measured in a liquid ionization chamber where the photoelectrons are not extracted into the gas phase.

Several control experiments have verified that the $\lambda > 230$ nm signal originates at the cathode. They include: i) changing the bias on the entrance meshes so as to allow photoelectrons produced at the entrance CaF_2 window to be collected (no effect was observed); ii) cooling the counting gas to 0 °C, which caused the signal to increase, as expected, owing to less photon absorption in the counter gas; iii) moving the copper cathode closer to the entrance window (and wire), which increased the signal, also as expected, owing to a reduced absorption path length; and iv) using a copper cathode with a hole, $\varnothing$ 7 mm, in the centre, which caused an almost complete loss of signal. These independent measurements with a single-wire counter showed also that the sensitivity of the cathode to UV light is increased by the TMAE film. With the cathode at room temperature we observed effects that are intermediate between those of the thin and thick layers.

At $t_{\text{cath}} < -5$ °C the TMAE layer becomes solid. The quantum efficiency of this layer was approximately equal to the sensitivity of the liquid layer.

3.3.2 Photocathodes with TMAE in solution

We also tested liquid photocathodes obtained from TMS + TMAE, TMP + TMAE, and NP + TMAE condensation. The electrons in these liquids have the highest drift mobility and the longest thermalization lengths r_0 of any known organic compound [9, 23]; hence the maximum quantum yield can be expected from them. Before the measurements, however, it was not evident which of the three liquids was the best, since one has maximum μ , the second has maximum r_0 , and the third has maximum V_0 (see Table 1).

Attempts were made to form photocathodes from these mixtures when the copper cathode was at room temperature. Liquid condensation did not occur, but a thin adsorbed film was formed which had some photosensitivity; however, the liquid cathode was three times better.

In our experiments we obtained a mixture of liquids by cooling the cathode down to $t_{\text{cath}} < 0$ °C when vapours of TMAE (with TMS, or TMP, or NP) were flushed through the counter. It is difficult to calculate the TMAE concentration accurately in this kind of liquid photocathode, but we consider it to be at least equal to the ratio of partial vapour pressures. The TMAE concentration could be slightly altered by changing the velocities at which a gas was flushed through the system. The maximum efficiencies attained are given in Figs. 8a and 8b. Curves 5 and 6 of Fig. 8b show the best liquid-cathode efficiencies obtained. As can be seen, the sensitivity of TMAE in NP and of TMAE in TMS gave $\sim 2\%$ at $\lambda = 235$ nm. The TMAE + TMP cathode was always a factor of 1.5 to 2 times less efficient than the TMAE + TMS cathode.

The best result is, however, given by a solid photocathode formed at $t_{\text{cath}} = < -20$ °C. Curve 7 in Fig. 8b shows the results for a solid mixture of TMAE + NP. The efficiency achieved in this case is $\sim 3\%$ at $\lambda = 235$ nm.

The quantum yield of the liquid or solid photocathodes increased with increasing electric field at the cathode surface, as shown in Fig. 9. A large variation of the field strength at the cathode surface was not possible because of a concomitant increase of the electric field at the wire, causing breakdown or instability. Even though the surface electric field increased from 1.08 to only 1.10 kV/cm, the count rate doubled, showing a very strong field dependence at $\lambda = 240$ nm. No electric-field effect is seen at $\lambda = 200$ nm, because the signal is due to gas photoionization. A striking confirmation of this dependence was provided by replacing the solid copper cathode by a cathode of parallel 100 μm wires with 1 mm spacing. At the wire surface the electric field is calculated to be a

factor of 5 higher than for a corresponding uniform cathode. The measured quantum efficiency at $\lambda = 235$ nm for a TMAE + TMS cathode was $(6 \pm 1)\%$ at room temperature, which should be compared with 1% for the flat cathode also at room temperature. This indicates that it is possible to have high-efficiency cathodes at room temperature, given a large extraction field.

In all the measurements of Figs. 8a and 8b methane was always flushed through TMAE and the other liquids (TMS or TMP or NP), and it was the main constituent of the counting gas in the single-wire counter. If, however, isobutane was used for the same purpose, the quantum yields from the liquid cathode were reduced by a factor of 2 to 3 as has been previously noted [24]. This is due to little-known effects at the cathode surface.

The stability of the liquid and solid photocathode mixtures was tested as follows. After forming the mixed cathodes as previously described, pure methane was flushed through the single-wire counter by bypassing the TMAE and TMS (or TMP) reservoirs (see Fig. 4), and by increasing the flow velocity, by a factor of about 40, to several litres per minute. The results are shown in Fig. 10. At $\lambda = 200$ nm the signal fell quickly because it was predominantly due to the gas-phase photoionization of TMAE, whereas at $\lambda = 245$ nm the signal initially increased in both the TMS and TMP cathodes because of increased gas transparency. The intensity of the pulses from the solid-TMP cathode continued to increase, and stabilized after 20 minutes to a value about five times the initial value (this is the correction for photon absorption), whereas the TMS cathode reached a peak after 10 minutes and then decreased to a negligible value after 25 minutes. This shows that the liquid cathode (TMS + TMAE) evaporated, whilst the solid cathode (TMP + TMAE) remained stable for many hours.

3.4 Other photocathodes

Since solid (or liquid) photocathodes at atmospheric pressure could have many important practical applications (see Section 4), we tested other substances in addition to TMAE, such as tetramethyl-p-phenylenediamine (TMPD), caesium iodide (CsI), anthracene ($C_{14}H_{10}$), diazobicyclo-octane (DABCO), and diethyl ferrocene ($C_5H_4-C_2H_5)_2Fe$, which have a low ionization potential. The best results were obtained with a TMPD cathode. The molecular structure of TMPD is related to that of TMAE, but it is solid even at room temperature and is not reactive with the oxygen in air (for short exposures). A TMPD cathode of about $1\ \mu m$ thickness was obtained by vacuum evaporation on the standard copper cathode. A second TMPD cathode was fabricated by rapid evaporation of a solution of TMPD in ethyl alcohol (100%) on a warm copper-cathode substrate. Typical results are shown in Fig. 11. The curves labelled 1, 2, and 3 are liquid ionization chamber measurements [25, 26] of TMPD in TMS, TMP, and NP, respectively (without electron extraction into the gas). The points on the figure show our measurements of quantum efficiency versus wavelength, with electron extraction: (Δ) for solid TMPD; ($\times$) for TMPD in TMP; ($\bullet$) for TMPD in TMS; and ($\square$) for TMPD in NP. We note that the solid-TMPD result is lower than that of liquid TMAE by a factor of more than 5 at $\lambda = 235$ nm. The mixed cathodes were made by flushing the cooled copper cathode covered by TMPD (from $t_{cath} - 5^\circ C$ to $-40^\circ C$) with methane plus the vapours of TMS (or TMP or NP): a solution was probably formed by the absorption of these vapours in the TMPD. The measured points are, as before, somewhat lower than the liquid ionization measurements. However, some of the difference could be recuperated by increasing the electric field. The measurements of TMPD in NP were not very reproducible, because the NP has such a high vapour pressure that it tends to evaporate quickly. The cathode, however, could not be cooled too much (for better stability) because neopentane solidifies at $-20^\circ C$. The data ($\square$) shown in Fig. 11 are those considered to be the most reliable for a solution of TMPD in NP. The solid TMPD + NP cathode (at $t_{cath} < -20^\circ C$) shows an efficiency of about 4% for $\lambda = 235$ nm, but this cathode has a spontaneous emission of about 10 to 30 photoelectrons per second.

Another solid cathode was tested: diethyl ferrocene, whose gas-phase photoionization threshold is $\lambda = 184$ nm. The result, given as curve 8 in Fig. 8a, showed lower efficiency than with the TMAE liquid, but still with a factor of 80 increase over the bare copper cathode up to $\lambda = 260$ nm.

3.5 Discussion

Measurements with a single-wire counter confirm and extend, in a totally independent way, the qualitative results obtained from a wire chamber. Three effects which increase the sensitivity to photons were observed; these were due to a thin adsorbed film; ii) real liquid condensation; iii) the formation of a solid layer. Let us discuss these three effects separately.

3.5.1 Thin adsorbed film

Generally speaking, the effect of a thin molecular film on the efficiency of the cathode may have a simple explanation: in order to escape from the surface of the metal, the electron must overcome a barrier defined by the work function ϕ . When there is contact between a metallic surface and a liquid film possessing a conduction band energy V_0 , the work function of the metal decreases if $V_0 < 0$. In this way, electrons find it easier to overcome the metal-liquid barrier than the metal-gas barrier. However, to escape from the liquid film, the electrons must overcome the conduction band energy. Depending on the relationship of these two factors, the liquid film can either increase or reduce the quantum efficiency of the cathode. In the particular case of thin TMAE and TMPD films, the metal work-function is evidently lowered—owing to the predominant orientation of the adsorbed molecules—in such a way that the π -electrons enter the metal and form an electric dipole layer (for details see, for example, Refs. [27] and [28]). This explains why, in the case of a copper or an aluminium cathode, we observed an increase in sensitivity, of one order of magnitude, up to 400 nm. This also explains why it is so difficult to remove the TMAE layer from a metallic surface: it is only by heating for a period of a few days that the surface can be completely cleansed.

3.5.2 Liquid layer

If there is real liquid condensation, the sensitivity to short wavelength radiation ($\lambda < 270$ nm) rises sharply. In this case the radiation does not reach the metal because of absorption in liquid, and electrons are produced mainly through photoionization of the liquid molecule. In this way, the metallic cathode itself plays no direct part in the generation of photoelectrons^{*)}. The following mechanism seems plausible. It was found that for liquid cathodes with $V_0 \approx -0.2$ eV, a quantum yield Q is close to the value obtained with liquid ionization chambers. For example, the authors of Refs. [11] and [25] have measured, in a liquid ionization chamber, a quantum efficiency Q_{liq} of 0.56% at $\lambda = 235$ nm in pure TMAE, of 4.6% for 1% TMAE in 2,2',4-trimethyl pentane (closely related to TMP = 2,2',4,4'-tetramethyl pentane), and of 0.2% for TMPD in trimethyl pentane. Our measurements give 0.4% for pure TMAE, 2% for TMAE in TMS, and 0.1% for TMPD in TMP. For liquids with $V_0 \approx -0.5$ eV, $Q = (0.2 \text{ to } 0.3) Q_{\text{liq}}$. Indeed, at $\lambda = 235$ nm, Q_{liq} is 16% for 1% TMAE in TMS, $\sim 3\%$ for TMPD in TMS, and 0.15% for TMPD in NP [11, 25, 26]. Our measurements, with electron extraction, give 2% for TMAE in TMS, 0.3% for TMPD in TMS, and 0.05% for TMD in NP at the same λ . This may be explained in the following way. In experiments with a liquid ionization chamber the true quantum yield of the liquids was measured. However, in the case of the liquid photocathode, the electrons have to be extracted from the liquid to the gaseous

*) This fact may explain results obtained with an Al cathode (see subsection 3.3 and Fig. 5) if one supposes that the attachment of Al to TMAE is stronger than that of Cu, and therefore that a thicker layer of TMAE can be formed after 20 hours.

phase. To do so, the kinetic energy of their random motion (not of the drift motion, which is smaller) has to be higher than $-V_0$; in other words the electric field at the cathode must be greater than a given value E_{crit} . For example, for liquid Ar, $V_0 \approx -0.2$ eV and $E_{\text{crit}} \approx 5$ kV/cm [29]. In a recent work of Anderson et al. [30] the full extraction of electrons from liquid TMP to the gas phase has been observed with $E \approx 30$ kV/cm. In our case, however, the electric field at the cathode was $E \approx 1$ kV/cm, which is not great enough for efficient extraction. This explains why, in the case of $V_0 < -0.2$ eV, $Q < Q_{\text{liq}}$.

One way of increasing the quantum yield is therefore to apply the maximum possible electric field at the cathode. This will increase the probability of the electrons overcoming the potential barrier and reduce the likelihood of geminate recombination and trapping by impurities. In fact, in the experiments with the multiwire cathode plane with $E \approx 5$ kV/cm, we were able to obtain $Q \approx 5$ to 7% for $\lambda = 235$ nm (TMAE + TMS at 20 °C).

If an electron is born inside the liquid, it has the kinetic energy $K = h\nu - E_{\text{liq}}$, where E_{liq} is the ionization threshold of the liquid [see Eq. (1)]. If the electron is close to the surface, and if $K > -V_0$, it will have a high probability of escaping from the liquid, even in a relatively weak electric field. The thermalization length $r_0 \approx 10$ nm in TMS and NP is 5 to 10 times less than the photon absorption length in solutions with TMAE, so that only a small fraction of the photoelectrons can be extracted in this way.

The results obtained make it possible to link up all the disparate findings of earlier published literature which were mentioned in the Introduction. This literature may be arbitrarily divided into research of two kinds: i) measurements without spectral resolution, and ii) measurements with spectral resolution. In the experiments without spectral resolution, efforts were made to observe the part played by a thin adsorbed TMAE film in wire chambers; this was seen from the time structure of the sequences of pulses coming from the different electrodes and the different gas gaps [15, 16]. Based on our measurements with a single-wire counter, the proportion of the signal due to surface photoeffect can be estimated. To do this, it is enough to calculate the convolution of the spectrum of the BaF₂ emission [31] in the 180 to 300 nm range with the quantum efficiency of TMAE vapour and of the surface photoeffect. Our calculations show that for a wire chamber with a 1 cm gap and with methane flushing, the surface contribution would be 6% for TMAE and 12% for TMS + TMAE. This is in good agreement with our measurements mentioned in subsection 2.3. For isobutane the effect would be half as much, i.e. it would correspond to 3% and 6%. For gaps of > 1 cm the contribution would be correspondingly lower. Such a small contribution from the surface relative to the gas can only be observed under conditions of very good statistics, which was not the case in most attempts referred to above.

Let us now turn to experiments carried out with spectral resolution. In our Introduction we pointed out that in Ref. [14]—where, as in our own case, a monochromator was used—the photoeffect from TMAE condensed on the surface was clearly observed. In Ref. [8] the surface photoeffect was investigated on a dielectric window, so that to compare these results with our own would be incorrect. In Ref. [15] the spectral measurements were carried out by means of filters, and the authors obtained the following estimates: $\text{signal}_{230\text{ nm}} \text{ to } \text{signal}_{210\text{ nm}} = 7 \times 10^{-2}$ and $\text{signal}_{250\text{ nm}} \text{ to } \text{signal}_{210\text{ nm}} = 3 \times 10^{-3}$, which coincide closely with our own measurements (see Fig. 8a).

As can be seen from this cursory analysis, the results of our experiments do not conflict with any work known to us.

3.5.3 Solid photocathode

In this work we have discovered that some solid photocathodes have a sensitivity that is equal to or even better than that of the corresponding liquids. This fact has a natural explanation because, in

the solid state, V_0 as well as μ is usually higher than in liquids [23]. These two factors contribute to achieving higher sensitivity for VUV. In the special case of neopentane, V_0 becomes positive in the solid phase [23, 32]. This explains why, in the case of solid NP, we observe the highest efficiency: about 3% at $\lambda = 235$ nm.

4. APPLICATIONS

Liquid and solid organic photocathodes can find a wide range of applications in diversified fields. The main interest of such photocathodes lies in the fact that large surfaces, in the square metre range, are relatively easy to produce without having to go to the high vacuum technique. Also, they are compatible with most of the gases used in wire chambers or in other gaseous amplifying structures. This permits position accuracies in the millimetre range coupled to time resolutions of better than a nanosecond, since the absence of parallax in the film absorbing the UV photons suppresses a major cause of position and time jitter. It is foreseen to use such cathodes to read out scintillation light from liquid argon or xenon. This would probably improve the energy resolution of liquid Ar or Xe chambers [33]. On the other hand, a solid photocathode in contact with liquid Ar would allow us to build fast calorimeters [34]. The present efficiency reached in our work, i.e. 3% at 235 nm, is far from being the maximum achievable with this method. In high-energy physics, one often encounters situations where the number of photons is large enough to make this efficiency attractive.

These cathodes can be used in plasma diagnostics, astrophysics, X-ray spectroscopy, and medical imaging.

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Table 1
 Electron mobilities and band energies at 295 K
 and thermalization lengths at $h\nu - E_{\text{liq}} \geq 1$ eV [9, 22]

	μ (cm ² /V·s)	V_0 (eV)	r_0 (nm)
TMS	100	−0.55	~ 10
NP	70	−0.43	~ 20
TMP	24	−0.33	~ 10

Figure captions

- Fig. 1 Schematic drawing of the apparatus used to observe the liquid-cathode effect. It includes: a BaF₂ crystal; a wire plane (a) touching the crystal; wire planes (b, d), which are cathodes; wire plane (c), which is the anode of a MWPC; and finally a liquid-cathode receptacle (e). The voltages V_a , V_b , V_c , and V_d could be independently varied, whilst $V_e = 0$, so as to provide signals from region A, B, or C.
- Fig. 2 Observed pulse amplitudes from regions A and C of fig. 1 when working with a cooled low-pressure wire chamber:
- 1) In this experiment the chamber was cooled to 4 °C and filled with TMAE vapour at 4 °C and 30 mbar CH₄.
 - 2) The cathode bath was then filled with liquid TMAE at 4 °C: $p_{CH_4} = 30$ mbar. The working voltage on the chamber was kept at the same value as for the first experiment.
 - 3) Signals from the BaF₂ detector cooled to -12 °C: $p_{CH_4} = 30$ mbar.
- Fig. 3 Observed pulse amplitudes from regions A, B, and C of fig. 1 when
- 1) the MWPC was filled with TMP + TMAE vapour + 30 mbar CH₄ at 0 °C; 2) the same gas filling was used, but with the bath (e) containing liquid.
- Fig. 4 Apparatus for cathode quantum efficiency measurements. The components are as follows:
- 1) D₂ arc lamp; 2) UV monochromator; 3) CaF₂ beam splitter; 4) filter station; 5) transparent meshes; 6) single-wire counter; 7) copper cathode; 8) cryogenic bath; 9) TMS, TMP, or neopentane liquid container; 10) TMAE liquid container; 11) gas flowmeter; 12) gas bottle supply; 13) p-terphenyl wavelength shifter deposit on (14) the photomultiplier; 15) CaF₂ exit window.
- Fig. 5 The quantum efficiency Q of a copper and an aluminium cathode without and with exposure to TMAE vapour ($p < 0.1$ mbar) for a period of 20 hours versus wavelength. The single-wire counter gas was argon + 10% methane at a pressure of 1 bar. The cathode was at room temperature (20 °C).
- Fig. 6 The relative quantum efficiency at $\lambda = 380$ nm (unless otherwise noted) of the copper cathode (20 °C) as a function of the single-wire counter gas pressure for the following gas fillings: (*) argon + 50% methane; (□) methane; (×) argon + 50% methane, $\lambda = 240$ nm; (Δ) isobutane; (▽) methane + TMAE.
- Fig. 7 a) Measurements illustrating the destruction of a thin TMAE layer on the upper cathode as a function of time. After formation of the TMAE layer at time zero, for the whole nine days of measurements, argon + 50% methane (no TMAE) was flushed through the system at the rate of 3 l/h (counter volume = 0.25 l). For the first three days, the entire single-wire counter system was heated to 50 to 70 °C. Measurements were at $\lambda = 380$ nm.
- b) Formation of a photosensitive layer on a copper cathode (20 °C) versus time. The deposit is due to TMAE impurities in the gas system. After heating the entire system for 10 h, a new, clean cathode was installed at time zero. The gas flow was 3 l/h of argon + 10% methane (without TMAE). The TMAE deposit resulted from TMAE impurities in the system. Measurements were at $\lambda = 380$ nm.

- Fig. 8 a) Experimental results of quantum efficiency Q versus photon wavelength λ for various liquid and solid cathodes deposited on a copper cathode at a pressure of 1 bar unless otherwise noted: 1) and 1') are the full curves of Fig. 5; 2) methane + TMAE, $t_{\text{cath}} = 0\text{ }^{\circ}\text{C}$; 3) the same as 2, but with the cathode heated for several minutes to 40 to 50 $^{\circ}\text{C}$; 4) methane + TMP + TMAE, $t_{\text{cath}} = -15\text{ }^{\circ}\text{C}$; 5) methane + TMS + TMAE, 1.5 bar, $t_{\text{cath}} = -5\text{ }^{\circ}\text{C}$; 6) methane + NP + TMAE, $t_{\text{cath}} = 0\text{ }^{\circ}\text{C}$; 7) methane + NP + TMAE, $t_{\text{cath}} < -20\text{ }^{\circ}\text{C}$; 8) methane + diethyl ferrocene, $t_{\text{cath}} = -40\text{ }^{\circ}\text{C}$.
b) Experimental results presented in Fig. 8a, but corrected for light absorption in the counter gas.
- Fig. 9 Count rate versus cathode voltage (or cathode electric field) for two different photon wavelengths, $\lambda = 200\text{ nm}$ and 240 nm . The gas flow was methane + TMS + TMAE at $20\text{ }^{\circ}\text{C}$ and 1 bar, with the copper cathode at $t_{\text{cath}} = 0\text{ }^{\circ}\text{C}$. At $\lambda = 200\text{ nm}$ the count rate is mostly due to gas-phase photoionization of TMAE, but at $\lambda = 240\text{ nm}$ the signal is mainly due to a liquid photocathode.
- Fig. 10 Count rate versus time when TMAE is bypassed and pure methane is flushed through the single-wire counter at an accelerated rate of 2 l/min. The curve labelled (Δ) is for $\lambda = 200\text{ nm}$ and an initial TMS (or TMP) + TMAE photocathode; ($\bullet$) for $\lambda = 245\text{ nm}$ and for an initial liquid TMS + TMAE photocathode; (+) for $\lambda = 245\text{ nm}$ and an initial solid TMP + TMAE photocathode.
- Fig. 11. Quantum efficiency of TMPD cathodes versus photon wavelength λ : (Δ) is for solid TMPD; ($\times$) for TMPD in TMP; ($\bullet$) for TMPD in TMS; ($\square$) for TMPD in NP. The curves labelled (1), (2), and (3) are liquid ionization chamber measurements [24, 25] of TMPD in TMS, TMP, and NP, respectively.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11