**Solid and vapour phase UV photocathodes
for gaseous detectors**

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To be published in
Nuclear Instruments and Methods in Physics Research A

X-LPNHE 95-12

SW 9551

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Abstract

We measured the relative quantum efficiency of four organic materials: tetrathiafulvalene and bis(cyclopentadienyl)magnesium in the solid phase and t-butylferrocene and n-butylferrocene in the vapour phase. The measurements were performed in the wavelength range of 150-220 nm. We also present a new quantum efficiency measurement of ethylferrocene. The three ferrocene derivatives exhibit relatively high quantum efficiency.

1 Introduction

Large area photosensitive gaseous wire chambers can provide a cheap and unique solution for fast and high accuracy localisation of UV photons emitted by Cherenkov radiation or by scintillators. As a photocathode, in the vapour phase, TMAE (tetraakis[dimethylamine]ethylene) is used in a large number of experiments operating in high energy physics, astrophysics, and nuclear medical imaging [1, 2]. In the solid phase, cesium iodide is the most popular candidate envisaged in future RICH devices [3, 4]. The vapour phase photocathode presents several advantages: the light absorption length can be controlled by the gas flow and the temperature, the photosensitive material is constantly renewed and thus does not suffer from aging. On the other hand the use of a solid photocathode is favourable for fast timing and parallax-free imaging, as all photoelectrons are emitted from a well defined surface. Devices based on this principle do not require complex temperature regulation of the gas system of the detectors.

An important drawback of the photocathode is its reactivity to oxygen and to other materials. TMAE is difficult to handle from this point of view, and a great deal of effort has been devoted in recent years to search for compounds which exhibit a comparable quantum efficiency (QE) and are easier to handle[5]. CsI has received a lot of attention because it can be handled for a reasonable time in air[6]. The QE of CsI is however lower than that of TMAE by more than a factor 2 for wavelengths higher than 190 nm[7].

In this article we will present for the first time a measurement of the QE of four organic materials, known for their low ionization potential : TTF(tetrathiafulvalene) [8],

bis(cyclopentadienyl) magnesium ($C_5H_5)_2Mg$, t-butylferrocene ($(CH_3)_3CC_5H_4Fe(C_5H_5)$) and n-butylferrocene ($C_4H_9C_5H_4Fe(C_5H_5)$). The last three belong to a family of metallocenes to which the attention was drawn by Anderson [9]. We also present a new measurement of the QE for ethylferrocene $C_2H_5C_5H_4FeC_5H_5$.

Several authors [10, 7, 11] reported that the standards used for light flux calibration, for absolute QE measurements may be unreliable. We have been confronted with this problem following a recalibration of our reference photomultipliers (Hamamatsu R1460) [7]. As a consequence of this recalibration the absolute value of TMAE QE as measured by us is a factor of 2 larger than the widely accepted value of Holroyd et al.[12]. The problems encountered in absolute determination of QE will be presented in a separate communication[13]. We express therefore our present results in a relative form by comparing them to the results obtained from the measurements on TMAE and CsI. To avoid any problem of calibration when comparing solids and vapours in this study, the results of the compounds in the solid and vapour phase are compared to those of CsI and TMAE respectively.

2 Bis(cyclopentadienyl)Magnesium, TTF

Since both these compounds are in powder form, (STREM Chem. Inc. and Aldrich-Chimie-SARL, respectively), the samples were prepared by vacuum deposition of a thin layer on a copper disk. The samples were stored under argon atmosphere. A small exposure to air, of about 5 min, was necessary during the transport to the measuring apparatus.

For the first compound, Bis(cyclopentadienyl)magnesium, a sample with a 500nm thickness was measured both in vacuum and in methane. In both cases no measurable signal was detected.

The second compound, tetrathiafulvalene (TTF), was measured only in vacuum. Two samples of different thickness, 300nm and 500nm, were studied. No influence of thickness was observed. The results, relative to the QE of CsI obtained from these measurements

are shown in figure 1. The detected signal was weak in both cases, resulting in a low QE throughout the whole spectral range.

3 Ferrocenes

As was mentioned earlier, three sets of measurements were performed with Ferrocene compounds. Two of these materials, namely the ethylferrocene and the t-butylferrocene are air-stable liquids, while the third one, n-butylferrocene, is not. All three compounds were purchased from STREM Chem. Inc. The procedures of measuring the QE of these liquids is described in detail in [14]. In addition, different gas flow and temperature schemes were used to ensure that there were no systematic errors during the measurements.

Figure 2 shows the results obtained for ethylferrocene vapour normalised to TMAE measurements. In addition the curve that corresponds to an indirect measurement performed by Charpak et al.[15] is shown in dashed line. For comparison purposes it is normalised to TMAE QE as measured by Holroyd et al. [12]. The two other curves correspond to two different gas flow. Both measurements were performed at 20°C. A measurement performed on a sample from a different source [16] exhibited no significant difference in the QE.

The QE measured, in both cases, gave similar results within the experimental errors. The QE reaches at best 30% of that of TMAE. A third measurement at 30°C, not shown here, gave also a similar result. Comparing our data with the one reported in [15], we notice a strong disagreement in the region around 180-190 nm. Our results do not peak, while the latter show a clear increase of the QE. Except from the fact that the curve shown in [15] is based on an indirect measurement of the QE, it should be noted that the measurements was done at 70°C.

Similar measurements were done with the t-butylferrocene (TBF) sample, shown in figure 3. The measured QE is lower than that of EF. The distribution is rather flat, reaching about 15% of the value of TMAE at 150nm followed by a decrease, with a cutoff around 200nm. Again here, the two curves stand for the different gas flow. These

measurements were performed at 30°C.

Finally figure 4 shows the results obtained for the n-butylferrocene (NBF) compound. The results obtained at two different flows are markedly different. Different results occurred either when changing the flow of gas or when changing the orientation of the detector from vertical to horizontal position. A possible explanation could be related to the fact that this liquid has a much more viscous form than the previous ones. Taking into account that with our current setup, it is not possible to raise the temperature of the bubbler to more than 40°C, the uniformity of the gas mixture during the period of the measurement might not be very stable. This could introduce a non controllable variation of the NBF vapour pressure. We therefore cannot precisely conclude on the QE of NBF. From the two plots of Fig.4 one could estimate that the QE lies within 10% and 20% of the TMAE value, up to 180nm, falling monotonically towards a cutoff around 200nm.

4 Conclusions

Several photosensitive compounds were measured by us in previous works: decamethylferrocene, tris(cyclopentadienyl)cerium [17], 1,1'-dimethylferrocene, bis(cyclopentadienyl)ruthenium and amorphous silicon with different doping levels [18].

Including in our survey the present data of TTF, ethylferrocene, bis(cyclopentadienyl)magnesium, n-butylferrocene and t-butylferrocene, we can draw the following conclusion concerning the QE. Only the derivatives of ferrocenes exhibit potentially useful QE values. Similar organometallic compounds, containing different metallic elements, (cerium, ruthenium, magnesium) have much lower QE than those containing iron. Decamethylferrocene has some unique characteristics: it is solid, its QE is non negligible at 220 nm and it is not air-sensitive. The three liquids, ethylferrocene, n-butylferrocene and t-butylferrocene have a QE in the range 10% to 30% of the TMAE QE between 150 and 190 nm. At larger wavelengths their QE drops abruptly. They could be used in some cases as alternatives to TMAE.

5 Acknowledgements

We would like to thank A.Breskin and R.Chechik of the Weizmann Institute of Science, Rehovot, Israel for constant support and fruitful discussions.

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Figure captions

1. The Quantum efficiency of tetrathiafulvalene (TTF) relative to CsI.
2. The Quantum efficiency of ethylferrocene (EF) gas photocathode relative to TMAE. The dashed curve is from [15]. Measurements were made at two different flows of methane at 1 atm.
3. The Quantum efficiency of t-butylferrocene (TBF) relative to TMAE for two different flows of methane at 1 atm.
4. The Quantum efficiency of n-butylferrocene (NBF) relative to TMAE for two different flows of methane at 1 atm.

Figure 1.

Figure 2.

Figure 3.

Figure 4.