

**Enhancement of the Photomultiplier Detection
of Cherenkov Light from Water using a Fluorescent Dye
in the Sudbury Neutrino Observatory (SNO) Detector**

M.E. Moorhead, E. Bonvin, N.W. Tanner and D.L. Wark

Abstract

The spectrum of Cherenkov light from fast electrons in (heavy) water varies as $\frac{1}{\lambda^2}$ down to the water cut-off at $\lambda = 195$ nm (Fig. 2). However only 40% of the light reaches the photomultipliers in the case of the SNO detector (Fig. 1) because of the cut-off at $\lambda = 310$ nm imposed by the acrylic container for the heavy water. The question is whether a fluorescent dye (sometimes referred to as a wavelength shifter) exists, or could be made, which in water would absorb light in the range 195 to 310 nm and re-emit within, say, ± 50 nm of 400 nm (the optimum wavelength for the photomultipliers) with an efficiency approaching 100%? There are a number of constraints discussed below including (a) absorption length (e^{-1} attenuation) of ≤ 10 cm for a few ppm of dye, (b) short fluorescence lifetime $\tau_F \leq 3$ ns, (c) minimal attenuation (absorption or scattering) of the Cherenkov light in the range 310 to 550 nm, (d) no appreciable deposition of the dye on the surface of the acrylic vessel and in particular no risk of chemical reaction with the acrylic which might impair the mechanical strength of the acrylic over ten years, and (e) no interference with the extraction of trace quantities of Radium and Thorium via absorbers (MnO_2 and $HTiO$) from the heavy water at a purification rate of 1000 tons per week.

1. Introduction

The SNO detector, which is currently under construction, will observe solar neutrino interactions in heavy water by collecting the Cherenkov radiation produced by relativistic electrons. Each electron produces an instantaneous burst (< 0.2 ns spread) of Cherenkov photons along its 5 cm track. These Cherenkov photons travel out of the heavy water through the acrylic containment vessel and through ~ 2.5 m of H_2O shielding until they reach the spherical array of 10,000 photomultipliers where they are detected, see Fig. 1. The number of detected photons determines the energy of the electron, and the relative time and location of the photomultiplier hits are used to reconstruct the location and initial direction of the electron track in the detector.

Cherenkov photons are produced with a $\frac{1}{\lambda^2}$ spectrum, see Fig. 2 where the efficiency of detecting these photons as a function of wavelength is also shown. This efficiency is the product of the transmission coefficients of D_2O , acrylic, H_2O and glass and the quantum efficiency of the photocathode. It has a relatively sharp cut-off at about 310 nm which is caused by absorption in

the acrylic vessel. The purpose of using a fluorescent dye (sometimes called wavelength shifter) in SNO is to shift the photons from below 310 nm (which would otherwise be absorbed in the acrylic vessel) to above 310 nm so that they can pass through the acrylic vessel and can be detected by the photomultipliers. The aim is to **maximize** the number of detected photons. Ideally, all the Cherenkov photons between 195 nm and 310 nm (and none of the photons above 310 nm) would be shifted with 100% quantum efficiency to exactly 400 nm. In this case the total number of detected photons would be increased by a factor of 2.5 with respect to the case without dye, i.e. the number of wavelength shifted photons detected would be 1.5 times the number of Cherenkov photons detected directly without the dye. For our purposes, the minimum acceptable gain in the total number of detected photons is a factor of 2 increase with respect to the case without dye, i.e. the number of wavelength shifted photons detected would be equal to the number of directly detected Cherenkov photons. This corresponds to a minimum overall dye efficiency of 67%, as calculated by comparing with the ideal case described above. This overall dye efficiency includes dye quantum efficiency, loss due to self-absorption and loss due to not shifting to exactly 400 nm.

2. Solubility in water

We would expect to use a dye at a concentration level of $\lesssim 10$ ppm, i.e. $\lesssim 10$ Kg in 1,000 tons. As the D_2O will be continuously purified (with the dye in solution) it would be preferable to use a dye which is more soluble than the operating concentration by a factor of up to 100 so that there is no danger of precipitation during the numerous processing stages (Ultra-filtration, ion exchange, and possibly U.V. sterilization and reverse osmosis). The temperature of the water will be $10^\circ C$.

3. Absorption Spectrum

The most important feature is that the dye should absorb efficiently in the wavelength range 195–310 nm. Below 195 nm the D_2O will itself be strongly absorbing [1], see Fig. 3.

In order to preserve the small volume of the origin of light in the detector, it is desirable to have an attenuation length for the dye in water of $\Lambda \leq 10$ cm over most of the range 195–310 nm, (e.g. an extinction coefficient of 10^4 mol liter $^{-1}$ cm $^{-1}$, a molecular weight of 230 and a concentration of 1 ppm correspond to an attenuation length of 10 cm).

Ideally, the condition $\Lambda \leq 10$ cm would occur throughout the range 195–310 nm and then the absorption would cut-off sharply so that $\Lambda \sim 10$ m at 310 nm (this corresponds to an extinction coefficient of 10^2 mol liter $^{-1}$ cm $^{-1}$ in the example of the paragraph above). This sharp cut-off is desired in order to absorb or scatter as few as possible of the Cherenkov photons

which (without a dye) would pass through the acrylic vessel and would be detected directly, see Fig. 4. These direct Cherenkov photons are required to reconstruct the direction of the relativistic electron from the Cherenkov cone. It is not absolutely necessary that the cut-off in absorption should occur at 310 nm. It could be at a slightly longer wavelength (up to 350 nm) as we might be able tolerate absorbing or scattering up to 20% of the direct Cherenkov photons (as calculated by assuming a 6 m path length). Nevertheless, we would like to minimize the absorption or scattering of direct Cherenkov photons. As an approximate guideline, the percentage of the total number of direct Cherenkov photons which are below a given wavelength cut-off are respectively 1.5%, 4.5%, 9%, 14%, and 20% for infinitely sharp cut-offs at 310, 320, 330, 340 and 350 nm.

4. Emission Spectrum

From the detection efficiency as a function of wavelength shown in Fig. 2 it is clear that the ideal emission spectrum would be centered on 400 nm. This might correspond to an impossibly large Stokes shift, so that it may be necessary to accept an emission spectrum at slightly lower wavelengths. This will obviously reduce our efficiency for detecting the wavelength shifted photons with respect to the ideal case. As an approximate guideline, we estimate that this reduction in efficiency is respectively 10%, 20% and 30% for emission spectra centered on 370, 355 and 340 nm.

Self absorption is another reason for preferring large Stokes shifts. It is highly desirable to limit this effect to $\leq 10\%$ absorption or scattering of the dye emission spectrum (for a 6 m path length).

5. Quantum Efficiency

The dye quantum efficiency (Q.E.) should really be as high as possible so that the overall dye efficiency defined in the introduction (which includes dye quantum efficiency, loss due to self-absorption and loss due to not shifting to exactly 400 nm) is at least 67%. This will probably mean a Q.E. of $> 90\%$, but it could possibly be lower if all the other requirements of the dye are met. It should also be noted that the Q.E. of interest is not the Q.E. as measured by exciting the dye at the peak of its absorption spectrum, but instead the average Q.E. when the dye is excited by a $\frac{1}{\lambda^2}$ Cherenkov spectrum between 195 and 310 nm.

6. Fluorescence lifetime

A short fluorescence lifetime (τ_F) for emission is necessary so that the shifted photons can be used in the reconstruction of the location of the neutrino event from the relative timing

of the photomultiplier signals. Ideally τ_F should be less than about 1.5 ns but anything with τ_F up to 3 ns is worth considering, particularly if the overall dye efficiency is very high ($> 90\%$). Again, the relevant τ_F is the average τ_F measured by exciting the dye with a $\frac{1}{\lambda^2}$ Cherenkov spectrum between 195 and 310 nm.

7. Chemical Compatibility

Our main concern here is that the dye could attack the acrylic vessel over the lifetime of the detector (~ 10 years). Any crazing of the acrylic vessel could be fatal to the experiment. The acrylic vessel is both optically and mechanically an extremely sensitive part of the experiment.

The D_2O will be operated in three different phases: 1) pure D_2O , 2) D_2O with 2.5 tons of NaCl or $MgCl_2$, making a 0.25% salt solution and 3) D_2O with 1,000 nickel tubes of length 1 m and diameter 5 cm suspended from the acrylic vessel. We require the dye to operate in all three of these environments, without reacting chemically with any of the above components, or the polypropylene plumbing or polysulphone filters.

It is also very important that the dye does not form complexes with the trace quantities of Radium or Thorium that will be present in the water (as for example EDTA would do). The contamination level of these ions ($\simeq 10^{-15}$ g/g) will be continuously monitored by performing extractions onto MnO_2 and $HTiO$ absorbers at a purification rate of 1000 tons per week. A dye which complexed Thorium or Radium into a non-absorbable form or was itself absorbed would not be very useful.

8. Stability

It is essential that the dye should be both optically and chemically stable for periods of order months or better years. In this context it should be noted that the D_2O will be degassed (Oxygen should be removed) and contained in an almost totally dark environment, but that it might be U.V. sterilized in the D_2O continuous purification plant at a turnover rate of about once every couple of weeks (the decision on U.V. sterilization has not yet been taken).

[1] T.I. Quickenden and J.A. Irvin, J. Chem. Phys., 1980, 72(8), 4416.

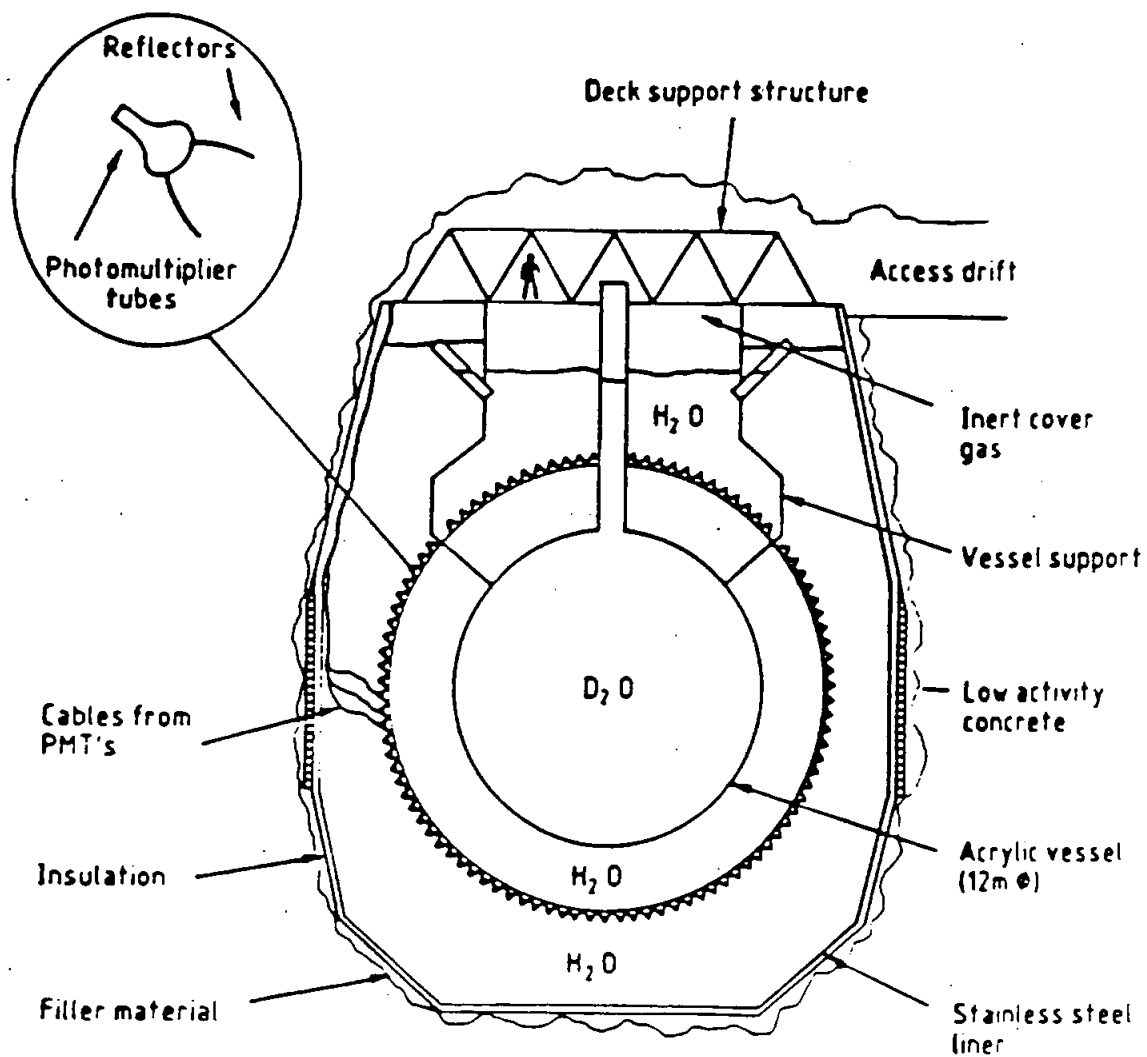


Figure 1: Schematic representation of the SNO detector.

Fig.2 :

Cerenkov spectrum and Detection efficiency

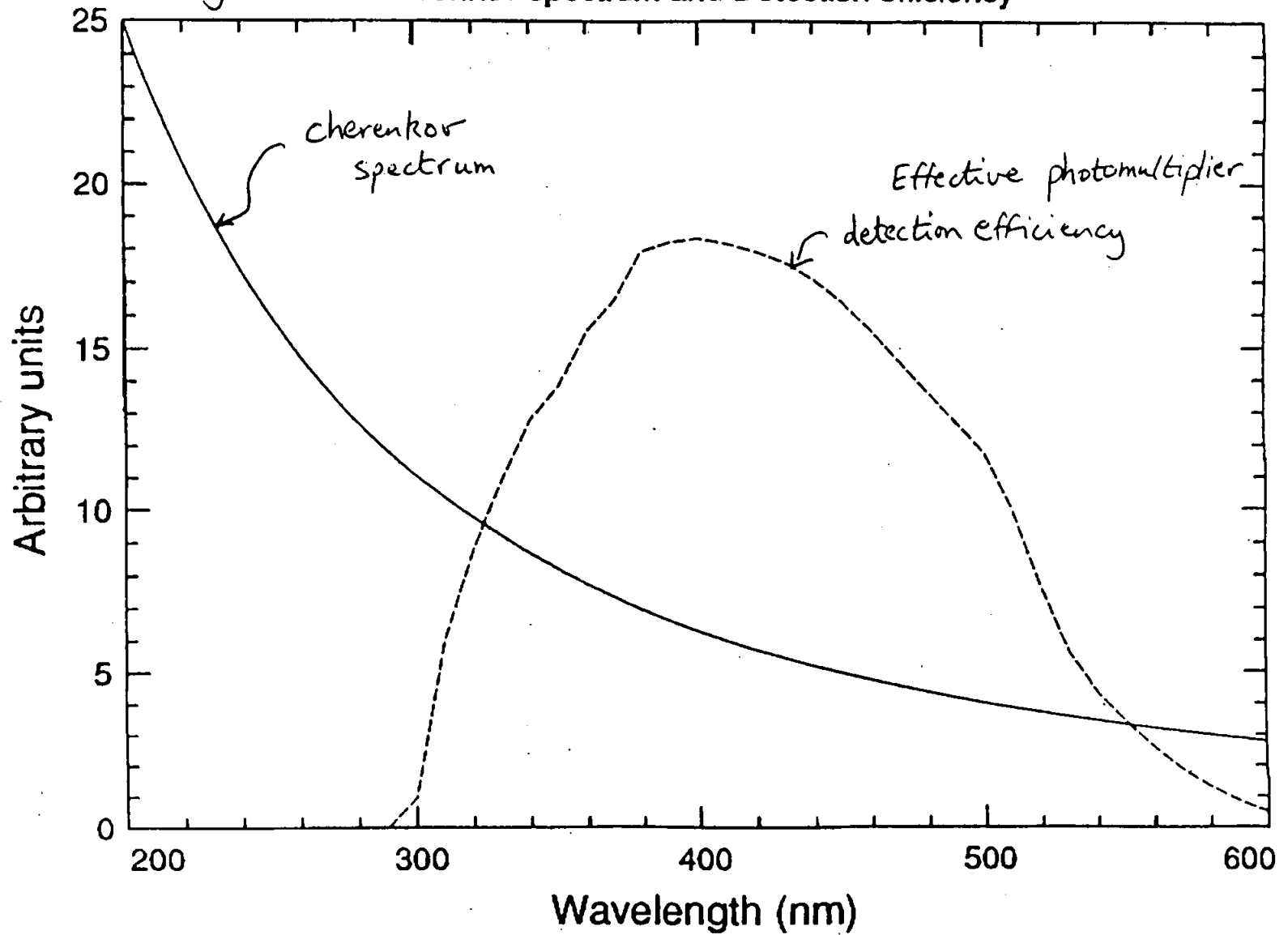


Fig. 3:

Absorption coefficients in water

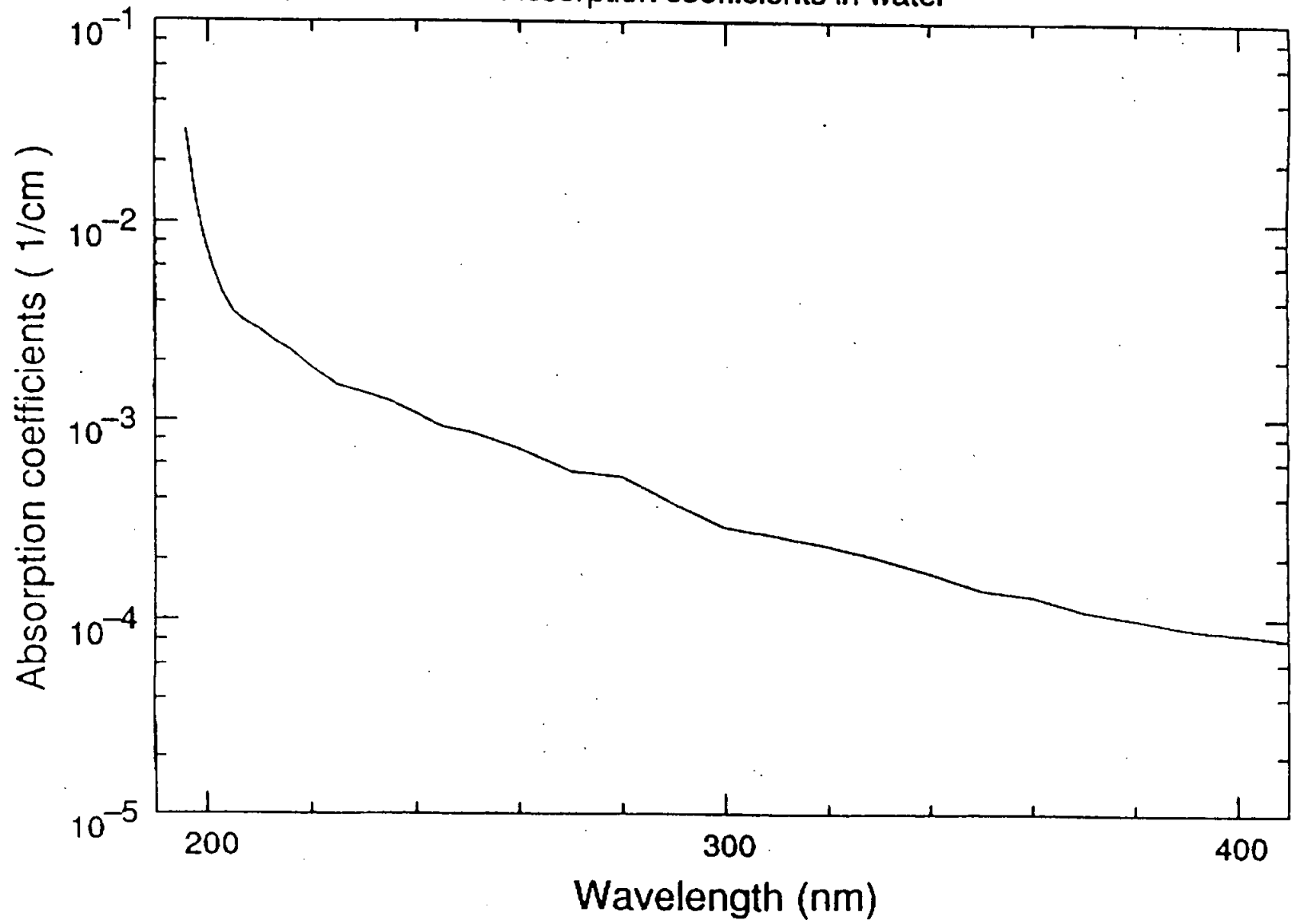
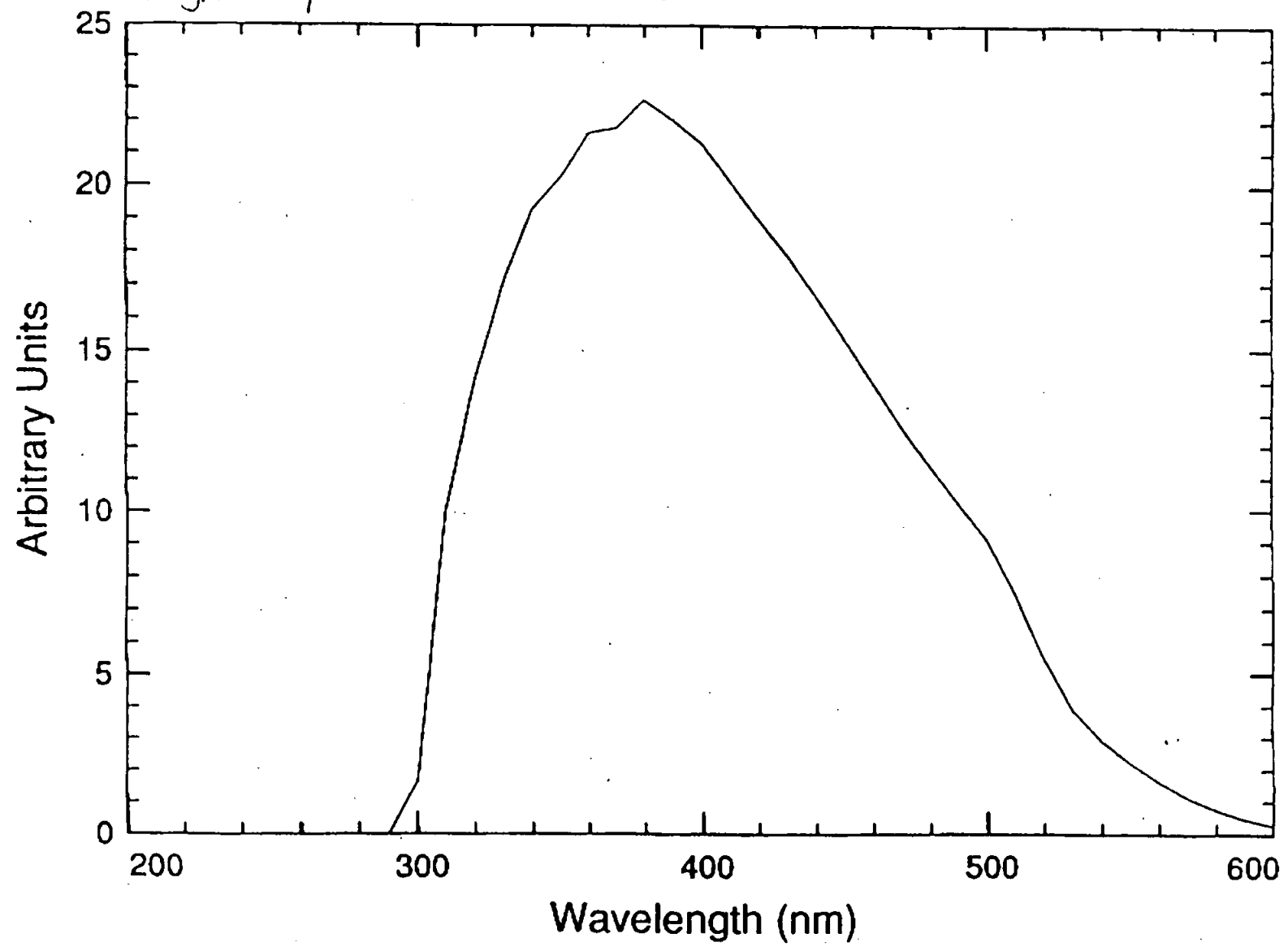


Fig.4: Spectrum of Directly Detected Cherenkov Photons.



PHYSICAL CHEMISTRY LABORATORY
OXFORD UNIVERSITY

From: K.A. McLauchlan F.R.S.

Tel: 0865-275424

Fax: 0865-275410

E-Mail: KAMCL@UK.AC.OX.Physchem



SOUTH PARKS ROAD
OXFORD
OX1 3QZ

24 March 1993

Dr. N.W. Tanner,
Hertford College

Dear Neil,

I have taken a look at your paper. It is admirably clear, and completely sensible, in defining what you would like, but I doubt that there is anyone who can answer your questions.

There are two major problems. Firstly, because of the media in which solution physicists and physical chemists work, there are very few who have performed experiments at short wavelengths, and I doubt that anyone has done much work on wavelength up-conversion from around 195nm. Laser dyes do exist which are pumped at 248nm, and emit at higher wavelengths, and some people are working on frequency quadrupled infra-red and visible lasers at lower frequencies than the KrF 248nm laser, but it is a very specialised field with maybe less than 5 working in it world-wide. The best person, who uses these techniques to contact is an Englishman working in the Dept. of Chemistry in the University of Chicago, Prof. Graham Fleming. He is a nice man who is very much one of the leaders of the field. I know him reasonably well and you could mention that I have suggested he may be able to help you, if you write to him. Most of the standard wavelength shifters I have heard about work by converting near U.V. radiation into the visible. This implies that even if someone can suggest a water-soluble molecule that would do the job, it is extremely unlikely that he could give the chemical guarantees you need - the knowledge simply does not exist.

My other worry is on the radiative lifetime, associated with high quantum efficiency. You are looking for quite a sizeable wavelength shift, and this implies that following the initial absorption of Cherenkov light the system must cross from its initial electronic state to another. With the size of shift required, I would be thinking in terms of inter-system crossing to a triplet state, which could well be fast enough in itself, but this would be followed by slow, spin-forbidden, phosphorescence (by definition) to the ground state. Phosphorescence lifetimes are usually of the order of a tenth of a microsecond or so in solution. Also the molecule persists so long in this state that it is often the source of photochemistry, lowering the emissive quantum yield, and possibly causing you chemical difficulties, eg. with your acrylic. In particular, free radicals are usually produced, and these would almost certainly attack it, especially at the interface. All this implies that the system you need is one involving "internal conversion" in which the initial excited singlet state undergoes a very rapid radiationless transition to a lower excited singlet state (the excess energy being dumped into the lattice) from which it then fluoresces. Such systems are known, but whether in the frequency range you need I do

not know.

Altogether, I think that the problem you have posed is a major research programme in its own right, with a real possibility that it would not be solved within several years. A good organic chemist can tailor molecules to adjust their absorption, emission, lifetime and solubility characteristics, but it is all pretty empirical and your only real hope is to discover someone who has been doing this sort of thing as a hobby for years. I honestly do not know who this might be (certainly no-one in Oxford), and my initial reaction would be to write to all the manufacturers of laser dyes just in case they have molecules which would be suitable and which they might not yet be marketing. The quantities you would require would certainly be enough for them not to ignore your letter!

I am sorry to be unable to offer any further advice.

Yours,

A handwritten signature in cursive script, appearing to read "J. K. Stille".

UNIVERSITY OF OXFORD

Department of Physics

Telephone: Switchboard (0865) 273333
Direct Line (0865) 273319
Telex: 83295 NUCLOX G
Fax: (0865) 273418
Email: TANNER@UK.AC.OX.PH

PARTICLE & NUCLEAR PHYSICS
Nuclear Physics Laboratory
Keble Road
Oxford OX1 3RH

NWT/BAR

17th March 1993

Drs. K.A. McLauchlan & C. Schofield
Hertford College
Oxford

Dear Keith and Chris

I am enclosing a paper, written to the best of our ability in chemists' language, which specifies the problem which we are trying to solve. We are aware that there may be no solution to the problem, or more exactly no solution unless we relax some of the constraints, in particular the possible requirement that the dye should survive U.V. sterilization and reverse osmosis.

We have been sufficiently encouraged by your previous comments that we feel that it may be worth circulating (fully corrected to chemists' jargon) to possible sources of a suitable dye. Could you have a look at the paper and advise us whether it is worth pursuing, and if so in what direction? The only names I have at the moment are Gus Hancock and xxx at Lake Constance.

Yours



N.W. Tanner

Enc.

I have not passed this to Chris since the information you require
is more in my brief-park than his

K



DIPARTIMENTO DI CHIMICA
 LABORATORIO DI CHIMICA FISICA
 UNIVERSITÀ DI PERUGIA
 Via Elce di Sotto, 8 - 06100 PERUGIA
 Tel. (075) 5855570 - 5855571 - Fax 5855599

2 pages

Dr. Martin Moorhead
 Oxford Physics
 Oxford OX1 3RH

Perugia, March 18, 1993

fax: 0044-0865-273418

Dear Martin,

I read with interest your report and have now a better view of your requirements. In the meantime, Fausto Masetti has measured for you two of the several parameters needed:

- 1) solubility of PPO in water: 1.5 ppm (± 0.1) at ca. 18°C;
- 2) absorption spectrum of PPO in water at short λ (see attached sheet). We could not evaluate the self-quenching from the measured emission and absorption spectra since we cannot make reliable measurements of extinction coefficients above 340 nm with our cells (max. 10 cm) in such dilute solutions.

Other comments:

Absorption properties: the scintillators and/or dyes for lasers commercially available seem to be not suitable to your requirements: usually they have the required band around 280-300 nm with a satisfactory cut-off at 310-340 but they absorb very little (window) around 250 nm. The 1,2-diphenyl-indole would be interesting but it is not available in our catalogues. The use of two solutes with compensating absorption spectra could be a solution but they certainly would complicate the transfer and lengthen the lifetime.

Solubility: This is a big problem for all candidates. PPO seems to be the best candidate from this point of view. It is widely used and this could be a reason of confidence; however, we found that it is not much stable to the light. Anyway, even with PPO, one cannot go over $\sim 7 \times 10^{-6}$ mole liter⁻¹ (1.5 ppm) at room temperature (even less at 10°C).

A long-term project should plan the chemical synthesis of compounds bearing polar groups in order to improve the solubility in water.

Possibly, people more expert than us in the field of scintillators in water will be more helpful.

I hope to meet you soon. Best regards and wishes

Ugo
 Ugo Mazzucato