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INVESTIGATION OF THE LUMINESCENCE EMITTED BY PULSE-IRRADIATED D₂O ICE

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ABSTRACT- Purified D₂O ice was irradiated with pulses of 0.53 MeV electrons and the spectral distributions of the luminescence intensity and half-life were recorded between 200 and 800 nm. Emission peaks were observed at 390 and 540 nm and it was shown that none of these emissions was caused by luminescent impurities. The emission from D₂O ice was more intense than from H₂O ice at all wavelengths above 370 nm. The half-lives of the luminescence decay in D₂O ice varied from 170 ns at 390 nm to 60 ns at 540 nm and were longer than the corresponding values of ca. 140 ns and 25 ns for H₂O ice.

1. INTRODUCTION

Previous investigations by our research group have included studies of the luminescences emitted by H₂O ice excited by ultraviolet light [1] and by a 0.53 MeV pulsed electron beam [2,3,4]. The present investigation extends the latter studies to D₂O ice and also follows a recent study [5] of the luminescence emitted by electron pulse irradiated D₂O vapour.

Electron-irradiated H₂O ice emits luminescence extending from 280 nm to at least 600 nm and shows only one spectral peak [2,3]. This luminescence can be separated into three distinguishable bands possessing different decay kinetics [4] and different memory effects [3]. These three bands are comprised of [3,4] a weak emission around 280 nm, an intense band with a well developed peak around 385 nm and a broad, medium-intensity emission, extending from ca. 450 nm to 600 nm.

Published luminescence spectra of irradiated D₂O ice (Fig. 1) are surprisingly different from the above in that at least two spectral peaks have been reported. However, the number of peaks and their wavelengths and relative intensities vary from worker to worker. Thus

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the several publications referred to in Figure 1 variously report that the maximum of the second peak is at 534 nm [6], 490 nm [7] or ca. 530 nm [8]. Unfortunately, it is not always clear that the D2O samples used in such studies [6,8] have been freed from traces of organic impurities by appropriate oxidative purification regimes. It is therefore possible that the rather variable luminescence peak near 500 nm in D2O ice arises from the presence of trace(s) of light-emitting organic impurities.

![Fig. 1. Previously reported luminescence spectra of D2O ice at 77K showing the large variations between different studies. The intensities have been normalized to unit intensity at the highest peak in each case. These spectra are taken from references [6] (●●●), [7] (——) and [8] (▲▲▲).](image)

The present investigation thus uses samples of D2O which have been prepared by the same oxidative purification scheme which was used for the study [2,3,4] of H2O ice. These samples were irradiated with the same electron source used in that study in order to obtain a definitive comparison between the luminescence spectra of D2O and H2O ices, free from complications which luminescent impurities might introduce and free from any differences which might be caused by the use of exciting radiations of different energies or durations. A further aim of the present study was to obtain previously unavailable information about the half-lives of the various luminescences emitted by the D2O ice.

2. EXPERIMENTAL

2.1. Sample Purity

Although D2O samples can be obtained at relatively high levels of isotopic purity with respect to H2O and T2O, commercial suppliers give little information about the presence of organic contaminants. D2O was therefore purified in a four-stage still. Distillation from alkaline permanganate was followed by re-distillation, then distillation from acidified dichromate and a final re-distillation. High-purity oxygen, free from H2O [9], was bubbled through the still to provide an oxidizing atmosphere and to prevent 'bumping'. In some experiments, further oxidative purification was carried out by sealing 50 cm³ of the purified D2O in a 1000 cm³ round-bottom flask under an atmosphere of high purity oxygen and then subjecting it to 20 Mrad of 60Co γ-radiation. The D2O was then re-distilled into another flask after
degradation of any D$_2$O$_2$ using platinum-black catalyst on a platinum foil substrate. The isotopic purity of the D$_2$O was monitored using an infrared absorbance technique [10], and did not fall below 99.4% after distillation and transfer.

2.2. Preparation of D$_2$O Ice Samples

Liquid D$_2$O was first degassed by several freeze-thaw vacuum degassing cycles and was then slowly frozen under vacuum in the sample holder shown in Figure 2. When viewed under polarized light, these samples were seen to be composed of ca. 300 separately identifiable crystals per cm$^2$. Using H$_2$O, we have found that the extent of sample fragmentation does not affect the intensity or decay kinetics of the ice emissions. It was consequently not important that the present study was carried out on ice samples prepared in a sample holder (Figure 2) which produced more fragmentation of the ice than did the sample preparation technique used for the study [2-4] of H$_2$O ice.

![Fig. 2. Ice sample holder cross-sectional view](image)

a) liquid N$_2$ inlet/outlet, b) thermocouple, c) ice sample, d) copper block.

2.3. Pulse Radiolysis

Figure 3 contains a schematic diagram of the pulse radiolysis system. D$_2$O ice was excited by 0.53 MeV electrons from a Febetron 706 pulsed electron accelerator which produced approximately triangular pulses of about 3 ns duration [11]. The light detection system

![Fig. 3. A schematic diagram of the pulse radiolysis and light detection systems](image)
contained two lenses to focus luminescence from the D$_2$O ice sample on to the entrance slit of a Bausch and Lomb High Intensity Monochromator. The monochromated light was then passed to a Hamamatsu R928 photomultiplier tube with a fast response dynode chain. The photocurrent thus obtained was displayed as a function of time on a Tektronix 7834 storage oscilloscope. Permanent records of the photocurrent traces were made on 3000 ASA Polaroid film. Intensity measurements were made 20 ns after the commencement of the pulse to avoid any disturbances due to the effects of the strong Čerenkov and other early emissions on the photomultiplier tube. Appropriate neutral density filters were used to ensure the linearity of the photomultiplier response. The ice sample was maintained in a vacuum of less than 5 x 10$^{-5}$ Torr and was kept at a temperature of 77±1 K by circulating liquid nitrogen through the sample holder.

3. RESULTS AND DISCUSSION

3.1 Accumulation of the Emission Intensity

As in the case of H$_2$O ice [2,3], the intensity of the total emission from a previously-unirradiated D$_2$O sample increased to a plateau intensity with repeated irradiation. In the present case, this plateau was reached after some 35 to 40 irradiation pulses. This rise of intensity was attributed to the accumulation of a precursor species. The emission was divisible into two non-accumulating wavelength regions and one strongly accumulating region. These spectral subdivisions will be described more fully in a future publication. All subsequent measurements described in this paper were carried out on samples which had been brought to a plateau intensity by irradiating with more than 40 electron pulses.

3.2 Emission Spectrum

Figure 4 shows the emission spectra of D$_2$O ice and H$_2$O ice at 77±1 K. It can be seen that the emission from D$_2$O ice is more intense than that from H$_2$O in the 370-650 nm range. In order to check whether the oxidative purification regime used was sufficient to remove all luminescent organic impurities a D$_2$O sample was subjected to 20 Mrad of 60Co γ-radiation and a further distillation prior to freezing. Neither the luminescence spectrum nor the emission half lives were affected by this further purification. It is most unlikely that light emitting organic impurities would not be removed or at least reduced in concentration by such vigorous treatment.

The copper sample holder was cleaned by lightly abrading with 2400 grade emery paper in a calcium hexametaphosphate solution followed by frequently rinsing until the metal surface was bright. The surface was then rinsed thoroughly in triply distilled H$_2$O followed by quadruply distilled D$_2$O and then dried and stored under vacuum until used. The likelihood of Cu$^{2+}$ being the source of the emissions was discounted because samples containing up to 2.3x10$^{-4}$ mol l$^{-1}$ CuSO$_4$ showed the same emission spectrum as pure D$_2$O.

It is clear from the above experiments that the 540 nm peak from D$_2$O is not an artifact due to luminescent impurities in the ice. However, it is conceivable that contamination of D$_2$O ice samples by atmospheric H$_2$O could explain the variable 540 nm peak positions reported by previous workers [6,7,8], as the intensity in this region is known to be decreased [6] by the presence of relatively small
amounts of H\textsubscript{2}O in the D\textsubscript{2}O lattice. The time resolution with which the intensity measurements were made could also be a cause of the differences reported in the literature. The 390 nm peak decays over a much longer time period than the 540 nm peak, whence measurements of intensity at different times would show overlapping bands at different relative intensities.

3.3 Preliminary Investigation of the Luminescence Decay Kinetics

The work of Quickenden et al. [2,3,4] on the luminescence from electron-irradiated H\textsubscript{2}O ice suggests that the 450-650 nm emission therein arises from a process which is different from the one responsible for the main 385 nm emission band. Figure 5 shows the variation with wavelength of the first emission half-life of D\textsubscript{2}O ice (measured from 20 ns after the beginning of the excitation pulse), together with data for H\textsubscript{2}O ice from the work of Trotman et al. [4]. The 390 nm emission from D\textsubscript{2}O has a first half-life of ca. 170 ns and as the wavelength moves toward the 540 nm peak, the first half life decreases sharply to ca. 60 ns.

At most of the wavelengths shown in Figure 5, the differences between the D\textsubscript{2}O and H\textsubscript{2}O luminescence half-lives are larger than the error bars. Isotopic effects on the relative rates of quenching of excited OH by H\textsubscript{2}O and of OD by D\textsubscript{2}O can account [5] for only a ca. 4% change in half-life. These matters will be dealt with in a later, more detailed publication which will deal with the decay kinetics of the 540 nm emission and the identification of the emitting species and of the processes which lead to their formation.
Fig. 5. The first half-life of the luminescence decay, measured 20 ns after the commencement of the excitation pulse, for both D$_2$O ice (○) and H$_2$O ice (●) (H$_2$O data from reference 4).

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11. 'Febetron Operation Manual', Field Emission Corporation, McMinnville, Oregon, U.S.A.
Could you may be give at least a tentative assignment of the spectral data to actual species?

Answer:

The 390 nm peak has previously been assigned in H₂O (Trotman et al, J. Chem. Phys. 1986, in Press) to the A²⁺ X²⁻ transition of OH. Similarly, this emission in D₂O ice is assigned to OD A²⁺. The 540 nm emission shows different kinetic behaviour to the 390 nm emission. Preliminary investigations indicate that the species responsible are formed by geminate recombination in radiation spurs, probably an electron combining with D₃O⁺ or OD to give D₃O or OD⁻, which then undergoes a radiative transition. A full treatment of the kinetic behaviour and assignment of the emissions will be published in the near future.