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LETTERS

Ice Triboluminescence

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Bursts of triboluminescence (200 count s^{-1} over ca. 1 s) were observed when 5 mL blocks of purified H_2O ice (Ih) at temperatures just below 0 °C were dropped into liquid nitrogen while viewed by a photon counter. The triboluminescence was neither quenched nor enhanced by oxygen. The spectrum contained a broad emission between 200 and 350 nm and another emission between 450 and 500 nm. We calculate that a photon counter in a space probe viewing the shadowed icy surface of an outer solar system body might be able to map mechanical stresses in the ice surface by measuring this triboluminescence.

1. Introduction

Triboluminescence (mechanically excited luminescence) was first reported in 1605 by Francis Bacon[1] who observed light when sugar was scraped. Sugar is probably the most frequently investigated triboluminescent substance. Figure 1A presents the measurements by Zink,[2] which show fine structure in the sugar emission spectrum. The peak positions agree well[2] with the $^3\Pi_u \rightarrow {}^3\Pi_g$ emission series[3] of excited molecular nitrogen.

Harvey[4] in his major review of luminescences reported prior to 1900 suggests that the first mention of ice triboluminescence was made by Wässtrom[5] in 1798 while the first report recorded by Hobbs[6] is a very brief mention by Precht[7] in 1902. Hobbs[6] has speculated that some of the light emission seen at night in the polar regions of the earth might possibly be due to ice triboluminescence. In 1940, Wick[8] also made a very brief reference to triboluminescence from ice, which was crushed with a mortar and pestle. Although no indications of absolute intensity or spectral distribution were presented, it was noted that prior irradiation of the ice with light from an electric spark increased the triboluminescence intensity somewhat.

Following the above qualitative reports, there have been no subsequent accounts of ice triboluminescence in the scientific literature. Unfortunately, such visual observation of extremely weak luminescence by the dark-adapted eye are notoriously unreliable and prone to subjective effects. Furthermore, the above early reports give no detail about the purity of the ice. Unpurified water will often contain organic contaminants, many of which may have stable excited states and may thus be excited during mechanical stress. Previous publications[9,10] from this laboratory have emphasized the importance of water purity in studies of the luminescences emitted by optically excited and electron-excited ice.

The aim of the present paper was to determine whether H_2O ice does emit triboluminescence when subjected to a temperature shock and, if it does, to spectrally resolve any such emission.

2. Experimental Section

The present study used blocks of H_2O ice made from highly purified water.[11] The ice blocks were frozen at a temperature of ca. 263 K and were thus in the stable Ih form[6] of ice. The ice blocks were dropped into liquid nitrogen while being viewed

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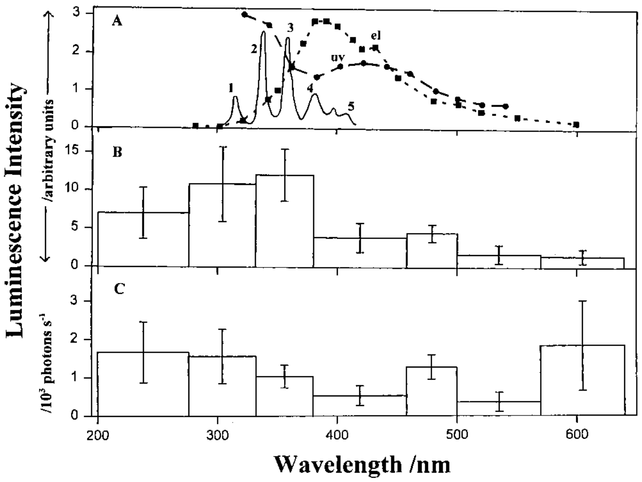

Figure 1. Triboluminescence spectra of sugar and ice. Spectrum A shows the triboluminescence of sugar measured by Zink[2] (solid line). The numbers 1−5 show the different vibrational transitions for the $^3\Pi_u \rightarrow {}^3\Pi_g$ series of transitions of molecular nitrogen. These were assigned by Zink[2] from Herzberg[4] as follows: peak 1, 316 nm, $\Delta v = 1$; 2, 337 nm, $\Delta v = 0$; 3, 358 nm, $\Delta v = -1$; 4, 380 nm, $\Delta v = -2$; 5, 406 nm, $\Delta v = -3$. The short-dashed line is the luminescence spectrum of electron excited ice from ref 11, and the long-dashed line is the UV excited ice luminescence spectrum from ref 14. Spectrum B is the uncorrected spectrum of the triboluminescence of ice. The intensity at each wavelength range is the mean of 48 replicate measurements, each on a new ice sample, and the error bars are 95% confidence intervals in these means. Spectrum C is the triboluminescence spectrum of ice corrected for filter transmission and spectral variations in the quantum efficiency of the photomultiplier tube.

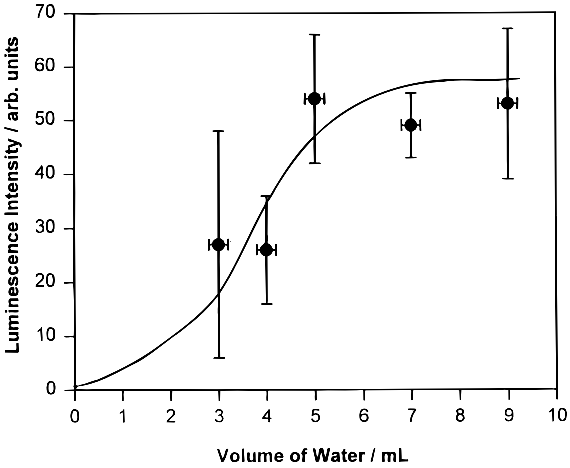

Figure 2. Variation of triboluminescence intensity when blocks of ice of varying size are dropped into liquid nitrogen. Each point is the mean of five replicate measurements on different ice samples. The vertical error bars are 95% confidence intervals in these means.

by a sensitive photon counter equipped with an EMI 9813 QAM photomultiplier tube. The transient (ca. 1 s) increase in count rate was of the order of 200 counts per 5 mL of ice block and corresponded to ca. 600 photons of 200−650 nm light reaching the photomultiplier tube cathode. The effect of ice block volume on light intensity is shown in Figure 2, which indicates that the luminescence intensity plateaus at ice volumes of around ca. 5 mL. The error bars (95% confidence intervals) are large, partly because the total photon count from each block is small and possibly also because the amount of light is affected somewhat by the way in which the ice block is orientated and moves about in the highly agitated liquid nitrogen.

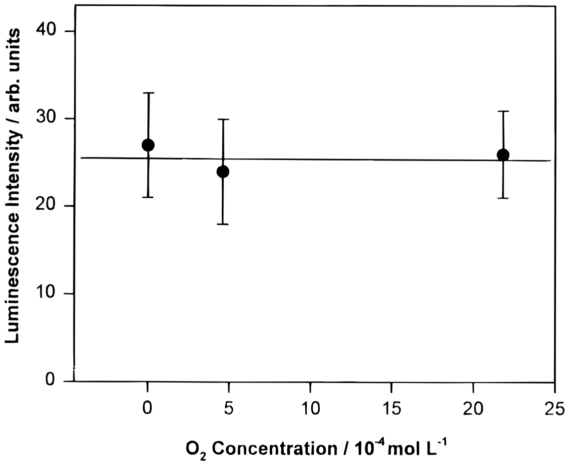

Figure 3. Effect of dissolved oxygen on the triboluminescence intensity of ice. Each point is the mean of 24 replicates, and the error bars are 95% confidence intervals in these means. The oxygen concentrations were measured values[19,20] for liquid water at 0 °C.

Because of the low intensity and short duration of each burst of luminescence from an ice block, it was quite tedious to obtain a spectrum at even low resolution. However, Figure 1B,C shows that a broad band-pass spectrum can be obtained but that it is necessary to carry out many (in this case 48) replicate ice block measurements at each wavelength interval. Furthermore, there was not sufficient light to use a conventional monochromator, and so a filter wheel containing a series of broad band-pass optical filters was used for monochromation purposes. The detailed spectral responses of the filters used have been described in a previous publication.[12]

3. Results and Discussion

A brief investigation of the effect of oxygen on the luminescence indicated that dissolving nitrogen or oxygen in the water used to make the ice caused (Figure 3) negligible increase or decrease in the triboluminescence intensity. It was also found that the addition of liquid oxygen to the liquid nitrogen had no substantial effect on the triboluminescence. These observations are important for two reasons. First, they indicate that the triboluminescence does not arise from the excitation of singlet oxygen or its dimers, which are known to produce red chemiluminescence in some systems.[13] Second, these observations indicate that oxygen does not quench the triboluminescence significantly.

The spectra obtained from averaging 48 replicate measurements of the 1 s transient for each wavelength interval are shown in Figure 1B,C. Figure 1C has been corrected for the spectral characteristics of both the photomultiplier tube and filters.

The corrected and uncorrected spectra have the same general features except that the poor sensitivity of the photomultiplier tube around 600 nm appears to enhance the 600 nm band. In summary, the corrected spectrum suggests that there is some emission at each wavelength in the 200−650 nm range but that the main emissions lie between 200 and 350 nm and between 450 and 500 nm.

In view of the extensive presence of liquid nitrogen in the present experiments, it is tempting to attribute at least some of the emission wavelengths to the $^3\Pi_u \rightarrow {}^3\Pi_g$ series of molecular nitrogen, which seems[2] to be responsible for the triboluminescence of sugar as seen in Figure 1A. The nitrogen lines could account for one portion (the ca. 300−400 nm region) of our spectrum but would fail to account for the broad emission regions around 250 and 475 nm.

Alternative assignment of the triboluminescence can be attempted by considering the spectra (Figure 1A) of UV-excited ice (long-dash line) and electron-excited ice (short-dash line). The UV-excited emissions in the region below 380 nm have been previously assigned[9] to the Herzberg I $A^3\Sigma^+{}_u \rightarrow X^3\Sigma^-{}_g$ system or the Herzberg III $C^3\Delta_u \rightarrow X^3\Sigma^-{}_g$ system of excited O_2 formed photolytically in the ice lattice. The UV-excited emissions above 380 nm have been assigned[14,15] to the spin-forbidden $^4\Sigma^- \rightarrow X^2\Pi$ transition of OH.

The electron-excited emissions[10] from ice have been assigned[16] to the excimer $C^1B_1 \rightarrow A^1B_1$ transition between upper states of the water molecule. Unfortunately, the spectrum of the electron-excited emissions in Figure 1A has fallen to negligible intensity at 320 nm and below, whereas the ice triboluminescence spectrum contains a significant portion of its emission below 320 nm. However, the Herzberg (<380 nm) region of the UV-excited emissions in Figure 1C shows reasonable agreement with a portion of the triboluminescence spectrum, except in the short wavelength (<300 nm) region where no data for UV-excited emission are available. However, the absence of UV-excited spectral data below 300 nm does not necessarily mean the absence of UV-emitting states below 300 nm. The 300 nm limit to the UV-excited spectrum merely results from the impracticality of measuring fluorescences close to the exciting wavelength[17] of 260 nm.

4. An Astrophysical Application

It is possible that ice triboluminescence produced by mechanical stresses in the icy surfaces of outer solar system bodies[18] might be detectable by a space probe when the body's surface is shadowed from the sun. The following calculation suggests that this may be a reasonable expectation.

We will assume that the present measurement of ca. 600 photons s^{-1} cm^{-2} of ice surface is typical of ice triboluminescence in general and that the outer solar system body has a radius of 200 km and that the space probe is 20 km above the body's surface. If the probe's detector area is 0.1 m^2 and if the detector views all the ice-covered surface of the body, a simple geometric integration suggests that the photon rate at the detector would be of the order of 8×10^7 photons s^{-1}.

To identify regions of particular mechanical stress, it will be assumed that instead of viewing the whole surface, one selects telescopically ca. 1/10000 of the outer solar system body's surface area. The measured photon arrival at the detector would then be expected to ca. 8×10^3 photons s^{-1}, which should be well within the detection capabilities of a modern photon counter. This estimate bears some similarity to that previously calculated[18] for potentially detectable plasma-excited luminescence from shadowed, icy outer solar system bodies.

5. Conclusions

From the above considerations, at least the short wavelength portions of the triboluminescence spectrum might tentatively be attributed to the Herzberg transitions of O_2 formed from H_2O fragments during mechanical disruption of the ice lattice. An alternative assignment might be to the excited states of N_2, which are also observed in the spectrum of sugar triboluminescence.[2] More definite assignments would only become possible when higher resolution spectra are obtained.

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References and Notes

(1) Bacon, F. *Of the Advancement of Learning*; 1605, as cited in ref 4.

(2) Zink, J. I. *Acc. Chem. Res.* **1978**, *11*, 289.

(3) Herzberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand: New York, 1950.

(4) Harvey, E. N. *A History of Luminescence*; American Philosophical Society: Philadelphia, PA, 1957.

(5) Wässtrom, O. *Crell's Chem. Ann.* **1799**, 392, as cited in ref 4.

(6) Hobbs P. V. *Ice Physics*; Clarendon Press: Oxford, 1974.

(7) Precht, T. *Phys. Z.* **1902**, *3*, 457.

(8) Wick, F. G. *J. Opt. Soc. Am.* **1940**, *30*, 302.

(9) Matich, A. J.; Bakker, M. G.; Lennon, D.; Quickenden, T. I.; Freeman, C. G. *J. Phys. Chem.* **1993**, *97*, 10539.

(10) Quickenden, T. I.; Trotman, S. M.; Sangster, D. F. *J. Chem. Phys.* **1982**, *77*, 3790.

(11) Quickenden, T. I.; Irvin, J. A. *J. Chem. Phys.* **1980**, *72*, 4416.

(12) Tilbury, R. N. Ph.D. Thesis, University of Western Australia, 1987.

(13) Quickenden, T. I.; Litjens, R. A. J.; Bakker, M. G.; Trotman, S. M.; Sangster, D. F. *Radiat. Res.* **1988**, *115*, 403.

(14) Quickenden, T. I.; Green, T. A.; Lennon, D. *J. Phys. Chem.* **1996**, *100*, 16801.

(15) Quickenden, T. I.; Hanlon, A. R.; Freeman, C. G. *J. Phys. Chem.* **1997**, *101*, 4511.

(16) Vernon, C. F.; Matich, A. J.; Quickenden, T. I.; Sangster, D. F. *J. Phys. Chem.* **1991**, *95*, 7313.

(17) Quickenden, T. I.; Litjens, R. A. J.; Freeman, C. G.; Trotman, S. M. *Chem. Phys. Lett.* **1985**, *114*, 164.

(18) Johnson, R. E.; Quickenden, T. I. *J. Geophys. Res.* **1997**, *102*, 10985.

(19) Washburn, E. W., Ed.; *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, 1st ed.; National Research Council: New York, 1928; Vol. 3.

(20) Lide, D. R., Ed.; *CRC Handbook of Chemistry and Physics*, 73rd ed.; CRC Press: Boca Raton, FL, 1992−1993.