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A Far-IR Study of Irradiated Amorphous Ice: An Unreported Oscillation between Amorphous and Crystalline Phases

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Far-IR spectra have been recorded for amorphous H_2O ice irradiated at 13–125 K with 0.7-MeV protons. Little or no changes were seen in the spectra of ices irradiated above ~27 K. However, at lower temperatures, most prominently at 13 K, IR spectra showed that ice samples oscillated between a highly amorphous and a highly crystalline form with increasing radiation dose. A mechanism for the oscillation is proposed involving free radical storage.

Introduction

Amorphous water ice occupies an important position in the chemistry of comets, interstellar grains, and planetary satellites and rings.[1] In each of these objects, ice has been exposed to cosmic radiation, mostly in the form of high-energy protons.[2] Since the temperatures of comets, grains, and the planets from Saturn outward are nearly always below 100 K,[3] and often below 30 K, radiation chemical products, such as free radicals, are thought to be stored in the amorphous ice for long periods of time.

In contrast with the importance of irradiated amorphous ices in astronomical environments, very few laboratory radiation studies on amorphous H_2O ice have been reported. Excellent work has been done on ice mixtures, normally ices made by freezing solutions, often very acidic or alkaline ones, from the liquid state.[4] While these experiments have been invaluable for studies of ice structure and reaction mechanisms, the samples themselves were of little interest to astrochemists. Even in experiments where "neat" H_2O ice has been irradiated, it has nearly always been in the common hexagonal phase, I_h, irradiated at or above 77 K by radiation of low linear energy transfer (LET), such as electrons, X-rays, or ^{60}C γ-rays.[5] Our own literature search, summarized in the first five lines of Table I, uncovered but three spectroscopic[6] and two diffraction[7] studies of irradiated amorphous ice.

This paper presents our recent work on amorphous ice irradiated from 13 to 125 K with a 0.7-MeV H^+ beam. The experiments assess the stability of amorphous ice at low temperatures in a radiation environment. In addition, we describe an unusual radiation-induced oscillation between amorphous and crystalline phases of ice. A separate paper will explore the radiation chemistry of crystalline ice and its astrochemical implications.[8]

Experimental Section

A common method of forming amorphous H_2O ice is to slowly condense water vapor onto a surface cooled below 130 K, and preferably below 77 K.[9] Warming such an ice to 135–145 K causes crystallization to the cubic phase, and further warming produces the hexagonal phase above ~170 K.[10] Our experiments were done with these facts in mind.

TABLE I: Laboratory Studies of Irradiated Amorphous Ice

ref	T (K)	radiation used	method of study
6a	90	1.7-MeV e^-	mid-IR
6b	97	0.53-MeV e^-	UV–vis
6c	77	700-kV X-rays	ESR
7a	≥8	100-keV e^-	e^- diffraction
7b	≥25	80-, 100-keV e^-	e^- diffraction
this work	13–125	0.7-MeV p^+	far-IR

Figure 1 is a schematic representation of the experimental setup. Located perpendicular to the figure, and not shown, was a closed-cycle cryostat ($T_{\min} \approx 13$ K). Experiments began by cooling a polished, circular 5 cm^2 aluminum substrate to 13 K in the evacuated multisided sample chamber. Next, the source beam from a Mattson Polaris FTIR was reflected off the substrate, along the path shown in the figure, and then back to the spectrometer's detector. The resulting spectrum served as a background for spectral ratioing. Water vapor was then deposited slowly onto the cooled substrate under conditions chosen to assure that the solid formed was amorphous, as shown by its IR spectrum.[9–11] The ice thickness, based on the most recent optical constants,[12] was on the order of a few micrometers. IR spectra of the ice were recorded as 60-scan accumulations with 4-cm^{-1} resolution from 100 to 500 cm^{-1}

A heater and thermocouple adjacent to the ice (not shown in Figure 1) permitted irradiations and measurements at temperatures above 13 K. The heater also was used in forming crystalline ice by warming an amorphous sample from 13 to 155 K, holding at 155 K for 5 min, and then recooling to the temperature of interest. A dedicated quadrupole mass spectrometer (QMS), shown interfaced to the sample chamber in Figure 1, allowed the analysis of gas releases from the ices during either irradiation or warmings.

Irradiations were performed with 0.7-MeV protons (LET 430 MeV cm^{-1}, range 13 μm[13]) from a Van de Graaff accelerator at a current of 1×10^{-7} A. Since the range of the protons always was greater than the thickness of the sample, the protons passed through the ice and came to rest in the aluminum substrate where

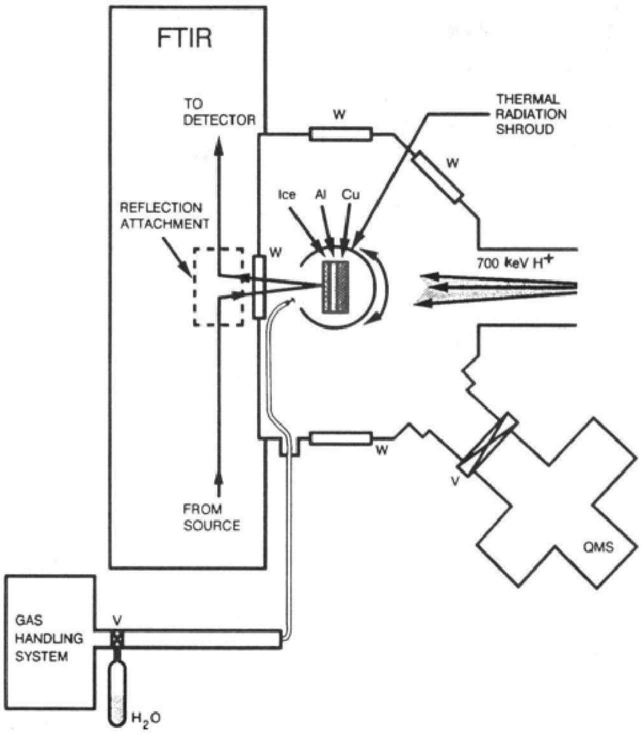

Figure 1. Schematic of experimental setup. The multiport sample chamber is vacuum-connected to the quadrupole mass spectrometer (QMS) and the Van de Graaff accelerator (W = window, V = valve).

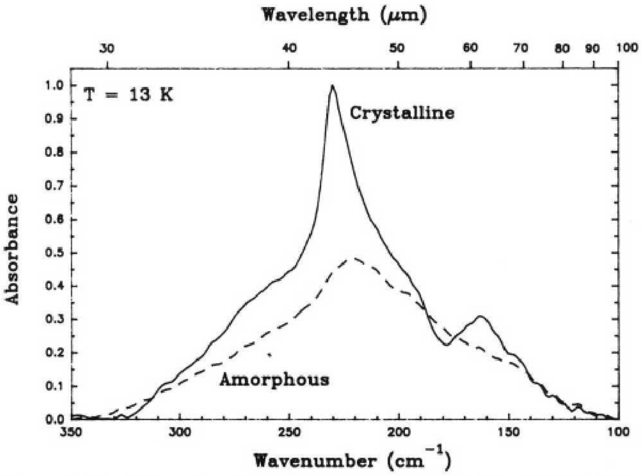

Figure 2. Far-IR spectra of amorphous and crystalline ice at 13 K. The ice thickness was 4.7 μm.

the resulting current was integrated. Current integration was possible only because the aluminum substrate was electrically, but not thermally, isolated from the cryostat. Other papers should be consulted for additional experimental details.[8,14]

Results

We were motivated to use the far-IR region in our work because of the rather dramatic difference in the spectra there of the amorphous and crystalline phases of H_2O ice, because of the scarcity of amorphous ice far-IR data, and because of our interest in astronomical observations in the far-IR region.[15] Figure 2 shows the far-IR bands of amorphous and crystalline ice at 13 K. When an amorphous ice was warmed, its spectrum became considerably and irreversibly sharper, with little change of position until the ice crystallized. Although the cubic and hexagonal forms of ice have virtually identical IR spectra,[11,16] our 5-min, 155 K annealing makes it likely that our crystalline samples were in the cubic phase.

Initial experiments were designed to search for changes in the far-IR spectrum of amorphous ice upon proton irradiation. Irradiations at temperatures from 125 to 46 K showed essentially no changes with doses as high as 39 eV molecule^{-1} (21000 Mrad = 210 MGy).[17] Irradiations from 46 to 27 K produced a decrease in the absorbance peak's position by 6–7 cm^{-1} and a slight shift of the baseline. These small changes are thought to have been caused by a buildup of radiation products in the ice. (It is not unusual for the IR bands of water to shift slightly when weakly or nonabsorbing "impurities" are added.[18]) This resistance to radiation-induced changes from 125 to 27 K was expected since crystalline ice was known to amorphize when exposed to 100-keV e^-,[7] 100-keV p^+,[19] or 3-keV He^+.[20]

We next irradiated amorphous ice at 13 K. To our surprise, once a dose of 1–2 eV molecule^{-1} was reached, the far-IR spectrum of the amorphous ice began to show dramatic and apparently erratic behavior, oscillating between the amorphous and crystalline band shapes during an irradiation. The oscillations continued until a dose of about 10 eV molecule^{-1} was reached, at which point the spectrum was that of amorphous ice but with the small changes in peak position and baseline mentioned in the previous paragraph. Only once, with a very large dose (>50 eV molecule^{-1}), were we able to reform crystalline ice from this heavily-irradiated amorphous form.

The amorphous–crystalline oscillations were put on a more predictive basis by using a mass spectrometer to monitor gas releases from the ice. During the initial dose of 1–2 eV molecule^{-1}, small sporadic bursts of H_2 and H_2O were observed but no oscillations were seen in the far-IR spectra. At doses of 2–10 eV molecule^{-1}, much larger and more regular bursts were detected. Above about 10 eV molecule,$^{-1}$ the bursts ceased.

Figure 3 follows three successive irradiations of a sample that had already received 4.8 eV molecule^{-1}. The breaks in the horizontal time scale between the first and second and the second and third parts of the figure were where the irradiation was halted for about 10 min to record IR spectra. Each of the three segments of Figure 3 consists of the mass spectral response for five different m/z values, corresponding to H_2^+, OH^+, H_2O^+, O_2^+, and $H_2O_2^+$, during an irradiation.

Figure 3 shows that, at roughly the same time, about 9 min after each irradiation was begun, a large burst of material was

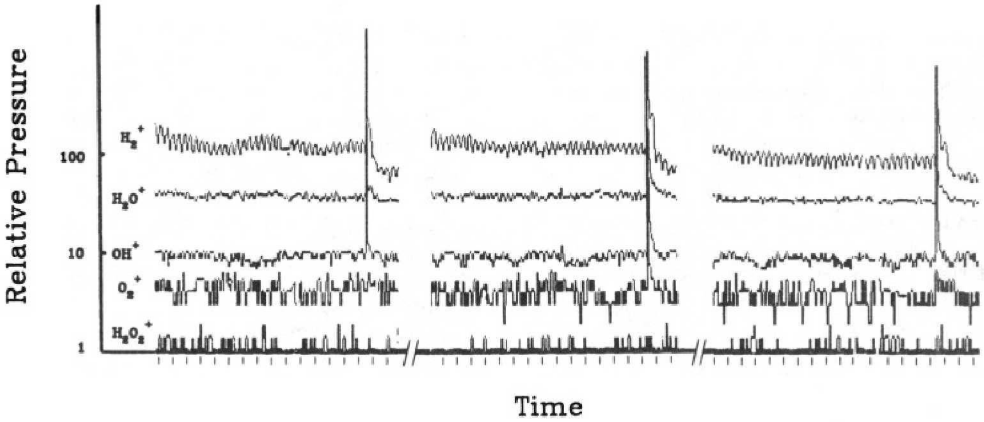

Figure 3. Mass-spectral intensities during 13 K irradiation of initially-amorphous ice (thickness 4.1 μm). The tick marks on the horizontal axis are 36 s apart. The two breaks in the horizontal scale are where the irradiation was halted for about 10 min to record IR spectra.

detected. The dose accumulated in each case was about 1.1 eV molecule^{-1} (≈590 Mrad = 5.9 MGy). In separate experiments at 13 K, the irradiation was continued without interruption during which time the bursts still appeared at a frequency of about 1.1 eV molecule^{-1}. Raising the irradiation temperature to 21 K reduced the number and intensity of the bursts, but not their frequency. No bursts were seen when the irradiation was done at 27 K. Thinner ices (~2 μm) showed about a 3-fold rise in the interval between bursts.

Raising the proton beam current (dose rate) reduced the time interval between bursts, and lowering the current delayed bursts. In another experiment, the sample was first irradiated until the bursts appeared regularly at about 9-min intervals, as in Figure 3. The irradiation was continued for 4.5 min past one burst, the irradiation stopped for 10 min, then resumed for 3.6 min, stopped again for 10 min, and then resumed. A burst appeared in about 1 min (total 9 min), showing that it was the total irradiation time and accumulated dose that brought about the bursts.

Of special interest is the physical state of the ice after various doses (along the horizontal axis of Figure 3). Although the unirradiated ice was amorphous, irradiated samples invariably gave the far-IR spectrum of *crystalline* ice when examined immediately after a pressure burst. As the irradiation was continued after a burst, IR spectra showed the ice was converted from a highly crystalline state back to the highly amorphous state with which the experiment began, until another burst was reached. With prolonged irradiation, radiolysis products appeared to build up enough to cause slight changes in position and baseline of the amorphous ice band, as described above. At this point, which was somewhat variable but above 10 eV molecule^{-1}, the bursts and phase oscillations ceased. Similar results were obtained at 13 K regardless of whether the original sample was freshly-deposited amorphous ice, amorphous ice that had been annealed at 60 K, or even 100% crystalline ice.

In other experiments the irradiated amorphous ice was warmed from 13 K, with the proton beam off, just before a burst was predicted to occur. The ice underwent at least partial crystallization at temperatures from 46 to 120 K, far below the usual transition temperature of 135–145 K.

On several occasions irradiated ices were viewed with the unaided eye but were always found to lack color. Exposure of irradiated ices to light from a 60-W tungsten lamp failed to change the observations of bursts and phase changes.

Irradiations of a blank aluminum substrate at 13 K failed to produce the bursts described above, failed to change the substrate's temperature, and failed to change its far-IR reflectance.

Discussion

The experiments above 27 K demonstrated the resistance of amorphous ice to radiation damage. No doubt water molecules were destroyed by the incident radiation, as described below, but a significant number were reformed by reactions in the solid phase. Therefore, we focus on the more novel findings, namely, the bursts and accompanying crystallizations seen at lower temperatures.

Our attempts to construct a reaction mechanism to explain the bursts begin with what we believe can be ruled out. We first exclude effects due to instrumental artifacts since blank experiments were negative. Beam charging of the ice can be ruled out since the protons passed through the sample to a metal substrate. Beam heating was not the source of the bursts since the IR spectrum of a thermally annealed amorphous ice was never observed, only the spectrum of an unannealed ice as deposited at 13 K. Large-scale recombinations of cations and trapped electrons are an unlikely reason for the bursts since the samples lacked the blue color usually associated with trapped electrons in ice,[21] and since the observations were unaffected by exposure of irradiated ices to bright visible light.[22] Finally, beam-induced crystallization, as seen in electron irradiations at 120 K and higher, can be excluded since the doses needed (>100 eV molecule^{-1} at 120 K) are beyond those available to us.[7]

A major difficulty in constructing a reaction mechanism is the lack of radiation chemical yields for ices. In most analyses reported for irradiated ices, the samples have been melted to determine product yields.[23] In such cases there is always an uncertainty as to whether the measured yield was formed during the low-temperature irradiation or during the subsequent warming. Nevertheless, despite uncertainties over yields, we believe it is possible to suggest a mechanism for our observations.

It is generally accepted that the initial event in the irradiation of ice is

$$H_2O \rightarrow H_2O^+ + e^- \qquad (1)$$

It is almost axiomatic in radiation chemistry that the yields of molecular and radical products depend on the incident radiation's LET.[24] For low LET radiations (e.g., X-rays, megaelectronvolt electrons, and ^{60}Co γ-rays), the ejected electron in (1) moves away from the H_2O^+ to create a track of events in regions referred to as spurs, blobs, and δ-rays. At the end of a track the electron will be trapped or will combine with a cation in a neutralization reaction. However, with higher LET radiation, such as our proton beam, events in the track are so close together that the track resembles a cylinder of events.[25] In such cases radical–radical combination is facilitated, raising molecular yields and dropping radical yields.

Unfortunately, although this LET effect explains the variation of e^-_{aq}, H, OH, H_2, and H_2O_2 yields in liquid water, its importance at 13 K is unknown. This makes it difficult to extrapolate from low-LET experiments on crystalline ice to our observations. The best that can be said is that our inability to see any color or bleaching effects attributable to trapped electrons suggests that dissociative combination probably follows (1):

$$H_2O^+ + e^- \rightarrow H_2O^* \rightarrow H + OH \qquad (2)$$

Alternatively, H atom transfer, or equivalently H^+ transfer, may occur after (1) so that the second and third steps will be

$$H_2O + H_2O^+ \rightarrow OH + H_3O^+ \qquad (2a)$$

$$H_3O^+ + e^- \rightarrow H_2O + H \qquad (2b)$$

Regardless of whether (2) or (2a) and (2b) occur, the free radicals that form are H and OH.

Some years ago Fontana observed light flashes and rapid, sharp drops in magnetic susceptibility when N atoms, formed by passing N_2 through a microwave discharge, were deposited at 4.2 K.[26] Each drop and flash corresponded to a loss of free radicals, as judged by the magnetic susceptibility measurements. Jackson interpreted the results in terms of the production and storage of free radicals followed by massive recombination and energy release.[27]

We interpret our observations similarly: production of free radicals, mainly H and OH, in the ice continues during the irradiation until some critical value is reached, after which explosive radical combination occurs. The radical–radical reactions raise the ice film's temperature very rapidly, causing release of products and ice crystallization. Schutte and Greenberg have invoked a similar argument in their studies of mixtures UV-photolyzed in the gas phase and then deposited at 10 K. Warming the mixtures produced explosions in the ice and an annealing comparable to that of heating the ice to 140 K.[28]

Tests of our interpretation are possible.

First, if radicals are being stored until large-scale recombination and energy release occurs, then it should be possible to trigger the crystallization by warming an irradiated ice just before a burst appears. Fluctuations in our proton beam current made timing of bursts difficult, but several warmings of irradiated amorphous ice were done. Crystallization was observed between 46 and 120 K in various irradiated ices, significantly below the usual transition temperature of 135–145 K.

A second test involved raising the irradiation temperature above 13 K to where the H atoms become mobile, about 20 K according to ESR experiments.[29] Our experiments at 21 K showed markedly reduced burst activity, and at 27 K the bursts were removed entirely, consistent with a *lack* of H atom storage.

A third test involved Jackson's derivation of an inverse relationship between ice thickness and the stable concentration of radicals in a sample.[27b] Although we performed only a few experiments along these lines, thinner ices did show a rise in the interval between bursts. It is significant that, in two recent papers on crystalline ice irradiated at 10 K, no mention was made of ice bursts or recrystallization.[20] Perhaps this is not surprising since the thickness of the ice samples (0.02 μm) was much less than our own (4–5 μm). Quantitative comparisons are difficult, but according to Jackson's model,[27b] reducing the ice thickness by 2 orders of magnitude can raise the radiation dose for bursts proportionally, to a value higher than available in most experiments.

Jackson's original treatment[27a] permits an estimate of the percent of free radicals accumulated in amorphous ice between bursts. Our Appendix gives the relevant equation and a reasonable choice of parameters for the calculation. The result is 0.6% for the percent of free radicals. This value can be compared with a rough estimate of the number of radicals contributing to each of the observed bursts. An amorphous ice initially at 13 K with 6.9×10^{19} H_2O molecules appears, after a burst, to have been warmed rapidly to ~155 K and recooled. Assuming an average heat capacity of 10 J K^{-1} mol^{-1} for the range 13–155 K,[30] the energy needed for the 142 K temperature rise would be 0.16 J or 1.0×10^{18} eV. Siegel and co-workers[31] have argued that the most likely reactions on warming irradiated ice from 4.2 K are

$$H + H \rightarrow H_2 \qquad (3)$$

$$H + OH \rightarrow H_2O \qquad (4)$$

Since each of these reactions releases about 4 eV, the number of reactions for 1.0×10^{18} eV is 2.5×10^{17} or 5.0×10^{17} radicals. This gives the percent of radicals as 0.7%, consistent with the value of 0.6% calculated above. The closeness is satisfying but probably shows only order-of-magnitude agreement.

An estimate also can be made for the radiation chemical yield of radicals, the G value, defined as the number of radicals produced per 100 eV of energy absorbed. For the production of 5.0×10^{17} radicals between bursts, corresponding to a dose of 1.1 eV molecule^{-1} given to 6.9×10^{19} water molecules, we calculate $G(\text{radicals}) = 100(5.0 \times 10^{17})/(1.1 \times 6.9 \times 10^{19}) = 0.7$. Siegel[31] measured $G(\text{radicals}) = G(\text{H}) + G(\text{OH}) = 0.9 + 0.8 = 1.7$ for γ irradiation of ice at 4.2 K, although the actual initial yield may be higher.[32] Our value of $G = 0.7$ does not appear unreasonable.

In light of our work on irradiated amorphous ice, it is appropriate to reconsider the earlier studies listed in Table I. The earlier spectroscopic experiments[6] were carried out at too high a temperature to see the effects reported here. The electron diffraction[7] experiments involved a low enough temperature, but the samples were much thinner than ours, down to a thousandth of our thicknesses, and so comparisons are difficult.

Additional experiments are needed to further quantify and test our proposed mechanism. We mention two of these involving techniques to which we do not have access. (1) ESR studies of ice irradiated below 77 K with intermediate- and high-LET radiation would be useful in establishing radical concentrations. (2) Our experimental arrangement does not permit luminescence measurements during irradiations. It would be helpful to search for and identify any such luminescence during bursts and sample crystallizations.

In summary, our experiments suggest that amorphous water ice in astronomical environments is resistant to radiation-induced changes between 27 and 125 K. Although water molecules will be destroyed by the radiation, as described above, reactions in the solid phase will regenerate H_2O. Below 27 K the situation is more complex. Although ionizing radiation will decompose the ice, the storage and eventual reaction of free radicals will crystallize the ice, even though the ice is being irradiated far below the usual temperature for crystallization. This is probably the case of most astrochemical interest since the doses needed for crystallization and bursts are only about 1 eV molecule^{-1}. By comparison, it has been estimated that during the lifetime of the solar system (4.6×10^9 years) cometary ice, thought to be amorphous, receives a radiation dose of tens of electronvolts per molecule at a depth of several meters below a comet's surface.[33] In a separate paper we intend to explore such astrochemical implications of our work as well as the temperature dependence of the spectra, the spectral band shapes, and the chemistry of irradiated crystalline ice.

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Appendix

The estimate of the percent of free radicals in irradiated amorphous ice between bursts is based on Jackson's original model, in particular his (9).[27a] Quantity α is $\langle C_{p,m} \rangle / R$ where we assume

$$\text{concn } (\%) = 76[\alpha k(T_f - T_i)/(\zeta W)]^{1/2}$$

an average molar heat capacity of 10 J K^{-1} mol^{-1} for the range 13–155 K.[30] Quantity ζ is 1 plus the number of nearest neighbors which we take as $1 + 4 = 5$.[9c] T_i is the irradiation temperature, 13 K, and T_f is the temperature where the radicals are mobile, which we take as 27 K. For W, the average energy release per radical–radical reaction, we use 4 eV, and for k, Boltzmann's constant, we have 8.6×10^{-5} eV K^{-1}. Combining these quantities according to the above equation gives a maximum stable radical concentration of 0.6%. Note that we have recalculated the numerical coefficient in Jackson's (9) to be "76" instead of the published value of "79".

Registry No. Ice, 7732-18-5.

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Red Emission in Chemically Produced Excited Oxygen Flow. 1. Attribution of the Emission Spectrum to $CuCl_2$

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Earlier observation of red chemiluminescence obtained by exposing heated copper to a chemically produced singlet oxygen flow was reproduced in a gas-phase reaction by mixing copper chloride vapor with singlet oxygen. This paper gives an identification of the emitter. The low-resolution spectrum of the red emission showed some progressions. They had a band spacing of 360 cm^{-1}, which was identical with that of the symmetric vibrational stretching of the ground electronic state of $CuCl_2$. The band intensity was calculated assuming that the emitter is $CuCl_2$ and at least a part of the observed spectrum is well explained. We thus attribute the red emission observed previously to the $^2\Pi_u \rightarrow {}^2\Pi_g$ transition in $CuCl_2$.

Introduction

Recently, Yoshida et al.[1] have observed a strong red chemiluminescence by exposing heated copper to a flow of excited oxygen produced via the chemical reaction

$$2NaOH + H_2O_2 + Cl_2 \rightarrow O_2(^1\Delta) + 2NaCl + 2H_2O \quad (1)$$

where unreacted chlorine and water vapor represent less than a few percent. Subsequently, some researchers observed the same emission using several metals.[2-4] The experimental results of those researchers are that the emission spectrum was identical with the metals used and also that chlorine greatly enhanced the red emission. Accordingly, it has been claimed that the heated metals played a catalytic role in producing the emitter. Huang et al.[2] have related the emission enhancement to refreshment of the catalyst by chlorine because of the volatility of copper chloride. Although a definite assignment could not be made from the spectra, Zhuang et al.[3] have discussed the possibility of the emitter being a compound of oxygen and chlorine, such as ClO, ClO_2, and Cl_2O_2, and give the ClCl–OO stretching mode of 359 cm^{-1} as most probable. Bacis et al.[4] reported nearly identical experimental results.

In our preliminary report,[5] we gave further reasons to suppose that $CuCl_2$ is responsible for the red emission. The proposal was deduced from the following experimental results: (1) Copper chloride deposition was observed on the reaction tube along the red emission tail when the heated metallic copper was placed in the chemically produced excited oxygen flow. (2) The emission intensities from copper were extremely strong relative to those from other metals. (3) The same emission due to copper chloride (produced by reaction of Cl_2 with copper compounds present as impurities in some metals) or due to copper chloride contaminating the thermocouple, the heater, etc. was observed even when no copper compound was present in the flow. (4) The previous experiment in which the red emission was obtained by mixing copper chloride vapor with the excited oxygen flow suggests that the chemiluminescence reaction is not catalytic. We also reported that the red emission was always accompanied by a strong near-infrared emission and concluded that the emitter may be $CuCl_2$ from the infrared spectrum analysis.[6]

Although spectroscopic studies for CuCl have been widely performed and the emission understood in detail, the spectroscopic data for $CuCl_2$ are poor. Emission data for $CuCl_2$ are absent, except for the far-infrared region.[7] Absorption results show that $CuCl_2$ has peaks at 19 000 and at 9000 cm^{-1}.[8-11] Accordingly, we consider it important to clarify spectroscopically the identity of the present emitter. In the present study, we analyze the visible emission spectrum and simulate the distribution of the band intensity of the emission spectrum due to excited $CuCl_2$.

Experimental Section

The excited oxygen flow system was analogous to that used for a chemical oxygen–iodine laser.[12] It was constructed of a singlet oxygen generator, a water vapor trap, a reaction tube including a copper chloride vapor injector, and a high pumping speed vacuum system. The apparatus is made of poly(vinyl chloride) except for the vapor trap tube and the reaction tube. The pressure was measured with an MKS Baratron capacitance manometer

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