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Anomalous Near Infrared Emission Observed in High Energy Electron Excited Xe and Xe–Ar

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The near infrared emission spectra of Xe and Xe–Ar which were excited by the pulsed irradiation of electrons by using a 45 MeV linear accelerator were investigated. A new broad band, probably due to the transition between the upper molecular states, was observed at 1200 to 1400 nm. The effects of O_2 and SF_6 on this band were studied.

The emission spectra of excited rare gas atoms and excimers have been studied theoretically and experimentally in the vacuum ultraviolet region with respect to the development of bound-free lasers.[1–3] Recent studies are concentrated on the properties of the lowest excited states, 0_u^+ and 1_u, of the Xe excimer, which can be selectively excited by means of synchrotron radiation.[4–8] However, spectroscopic information on the upper molecular states has not been studied well because of the lack of experimental approaches. It is expected from theoretical estimations that the absorption of photons or emission related to the molecular transition should appear in the near infrared region.[9] Arai *et al.* have found the near infrared absorption bands which were assigned to the molecular transition from the first excimer states, ${}^{1,3}\Sigma_u^+$, for Ne to Xe, which were excited by electron beam pulses.[10] Distefano *et al.* observed the near infrared fluorescence due to the atomic transition from 6p to 6s configuration for vacuum ultraviolet irradiated Xe.[11]

We have investigated the near infrared emission spectra of Xe gas which had been excited by the pulsed irradiation of a high energy electron beam, and have found a new broad band; this is probably due to the transition of the upper to the lower molecular states where the excitation seems to be a nonionic process.

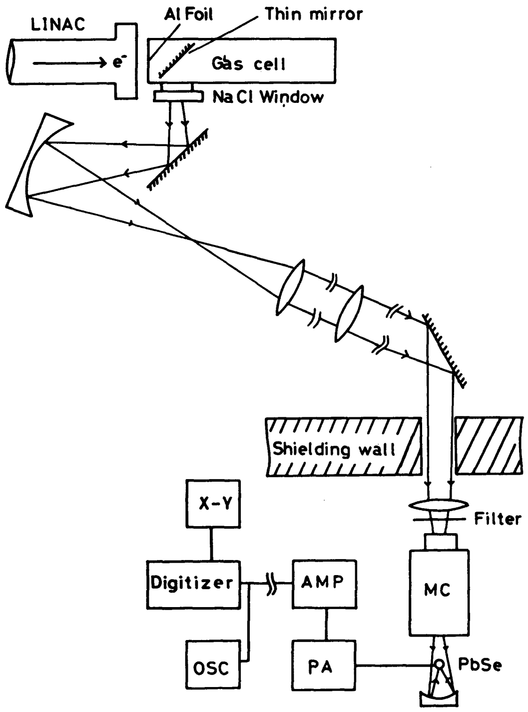

Fig. 1. Block diagram of experimental system.

Experimental

The electon beam pulses were generated by a 45 MeV linear accelerator installed at Hokkaido University. The duration of the pulses was 3 μs. The charge provided in one pulse was 5×10^{-6} C. The dose was estimated to be approximately 10 krad per pulse at 700 Torr (1 Torr = 133.32 Pa) of N_2O by means of its decomposition.[12]

A block diagram of the experimental system is shown in Fig. 1. A stainless steel cell of 60 mm in diam. by 350 mm long was used. The electron beam entered the cell at one end. The emissions from irradiated sample gases were reflected by a thin mirror which was fixed in the cell just behind the incident window at 45° to the electron beam axis, and directed to the NaCl window, which was attached at a right angle to the beam direction. Thus the emission from the samples was observed in the reverse direction to the electron beam so that interference by the intense Cerenko light in the Xe gas upon irradiation could be avoided in the infrared observation. The detection system for the emission consists of a Bausch and Lomb high-intensity grating monochromator and a PbSe detector (Hamamatsu TV, p 791) with a response time of 2.5 μs. The signals from the detector were amplified 10 fold by an ac amplifier (Keithlel 105) and were followed on a transient digitizer (Iwatsu DM901). All the data were recorded on an X-Y recorder. Typical signal traces are shown in the inserts in Fig. 2. Since the response time of the detector was much too long relative to the life time of this kind of emission, the spectra were obtained by plotting the peak intensity of the signal trace against the wavelength. The sensitivity of the detector is known to increase linearly from 1000 to 1600 nm but no correction for this was made. A filter for the cut-off at 650 nm was used to avoid the contribution of higher components.

Research grade Xe (99.995% pure from Nihon Sanso) and ultrahigh pure Ar (99.999% pure from Nihon Sanso) were used. The gases were introduced into the cell through a molecular sieve 5A trap. When necessary, a column of Ba getter at 190 °C was used before the trap to remove any O_2 contained as impurity.

Results

Emission Spectra in Xe. The emission spectrum in the irradiated Xe of 400 Torr is shown in Fig. 2(a). The well known emission lines due to the 6p-6s transitions were observed at 830, 890, and 990 nm, where each band is unresolved but consists of more than one line.

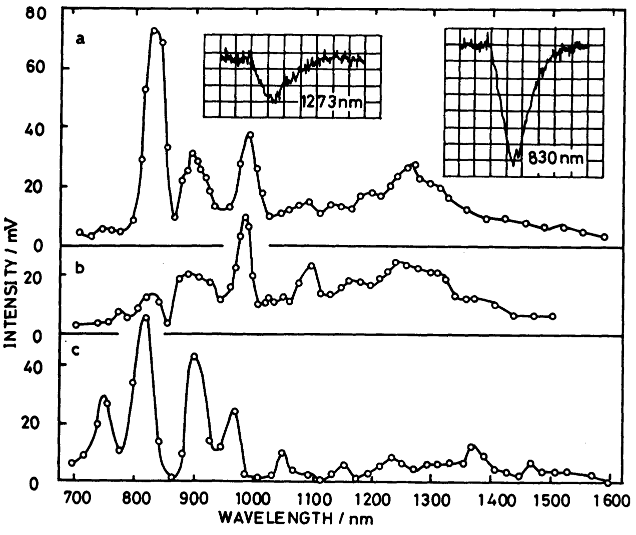

Fig. 2. Emission spectra of irradiated Xe, Xe–Ar and Ar. (a) 400 Torr Xe, inserts: 4 mV/div and 2.5 μs/div, (b) 400 Torr Ar+200 Torr Xe, (c) 500 Torr Ar.

In addition to these lines, a broad band was observed in the region of 1200 to 1400 nm with the maximum at 1270 nm; this has not been reported previously. Since this anomalous emission might originate from the window material having been excited by the Cerenkov light or the second continuum of Xe, the experiment was repeated with a quartz window instead of the NaCl window, and it was confirmed that the intensity of this emission band was not changed. Thus it was concluded that the origin of this band was the irradiated Xe gas.

Emission Spectrum in Xe–Ar. The mixtures of Ar and Xe at various compositions were irradiated. The total pressure of the mixtures was 600 Torr. Figure 2(b) shows the emission spectrum of the irradiated mixture of 200 Torr Xe and 400 Torr Ar. The atomic line at 830 nm, which was the most intense in pure Xe, disappeared, and the intense lines at 990 and 1080 nm were enhanced strongly as the Xe concentration decreased. The emission band similar to that obtained for pure Xe was also observed at around 1270 nm. Assuming that the ionization cross section of Xe is approximately twice that of Ar,[13] the absorption energy for this mixture was calculated to be approximately equal to that of 400 Torr Xe in Fig. 2(a). It is obvious from comparison between Fig. 2(a) and (b) that the equal intensity was obtained for the 1270 nm band under the equal absorption energy. Contrary to the intensity at 990 and 1080 nm lines, the intensity of this band decreased with the decrease of the Xe concentration.

In pure Ar this kind of broad band was not detected between 700 and 1600 nm, as shown in Fig. 2(c).

Effect of O_2. When the 0.01 Torr of O_2 was added to 430 Torr of Xe, the intensity of the broad band at 1270 nm decreased to one-half relative to that in pure Xe, whereas the intensity of the atomic lines was not influenced by the addition of such trace amounts of O_2. The 1270 nm band was quenched completely by 1 Torr of O_2.

Effect of SF_6. Figures 3 and 4 exhibit the effect of a trace amount of SF_6, which was added as a scanvenger of thermal electrons in Xe and in Xe–Ar respectively. In Xe, as shown in Fig. 3, the intensities of the three atomic lines decreased markedly on the addition of less than 0.05 Torr of SF_6, whereas the intensity of the 1270 nm band was unchanged except for a small increase at the same range of the concentration for which the significant decrease in the intensities of atomic lines occurred. The effect of SF_6 on the emission spectrum in Xe–Ar was essentially the same as in Xe. As shown in Fig. 4, the intensities of the two atomic lines at 990 and 1080 nm decreased to half on adding less than 0.1 Torr of SF_6, while the intensity of the 1270 nm band was almost unchanged except for the small decrease at less than 0.1 Torr of SF_6.

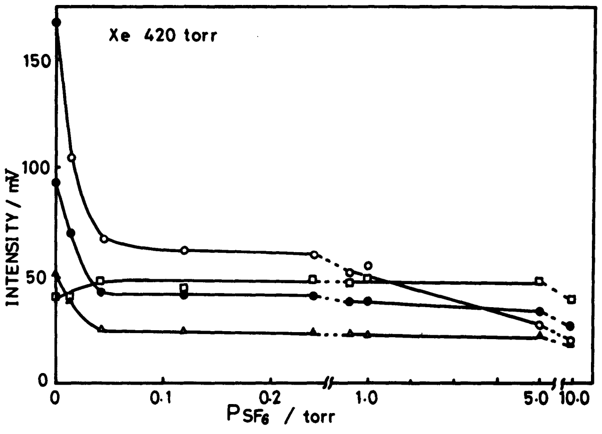

Fig. 3. Effect of SF_6 on the intensities of emission bands in Xe. ○: 830 nm. ●: 990 nm, △: 890 nm, □: 1270 nm.

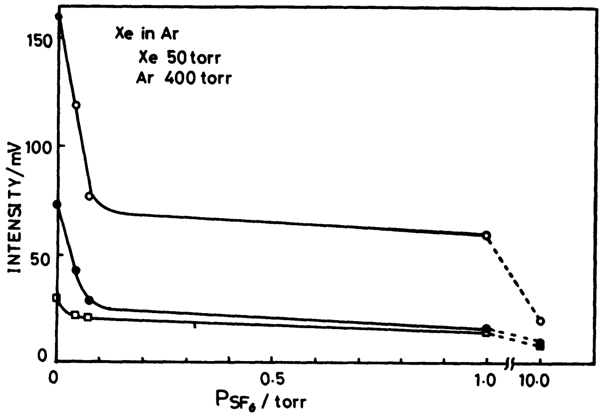

Fig. 4. Effect of SF_6 on the intensity of emission bands in Xe–Ar. ○: 990 nm, ●: 1080 nm, □: 1270 nm.

Discussion

A new emission band was observed at around 1270 nm in Xe gas on the bombardment of high energy electrons. Since O_2 is known to be the effective lasing component in the mixture with Xe, the possibility that this new emission band might be caused by contamination with air had to be considered. The result of the experiment on the addition of O_2 indicated that the origin of this emission band was not an impurity but the excited Xe itself. The large width of this band must be attributed to certain molecular transitions in excited Xe. The recent report by Keto *et al.* about the similar O_2 effect on the intensity of the second continuum in electron excited Ar[14] also supports the above assignment.

As shown in previous publications,[1-3] excited rare gas atoms are produced mainly from the dissociative recombination of Xe_2^+ with the secondary electron; they subsequently form the bound excimer, $^{1,3}\Sigma_u^+$, by three-body collision with atoms in the ground state. Accordingly, these excimer bands should be affected by the addition of SF_6. However, the result shown in Figs. 3 and 4 indicated that the 1270 nm band was not quenched by SF_6. This means that the precursor responsible for the 1270 nm band was not the excited atom. The excimer states observed in this experiment should thus be formed by some direct excitation not *via* the above mentioned ionic process. The small increase in the intensity at 1270 nm on the addition of SF_6 shown in Fig. 3 suggests that the small fraction of the excimer states observed here can be produced directly by the ion recombination of Xe_2^+ and SF_6^-. One of the possible paths of direct excitation under irradiation by high energy electrons is the excitation of the van der Waals (vdW) molecule, Xe_2, to vibrationally excited levels of the upper molecular states by inelastic collision with the secondary electrons, which have kinetic energy higher than thermal electrons. The emission band presented here might be attributed to the transition from the upper molecular states with the shallow minimums of the potential curves, which are located in the vicinity of the vdW distance. Since at least two shoulders were observed at both sides of the 1270 nm peak, several transitions could be associated. The radiative transitions from the 1_u of $7s[3/2]_1$ to the bound states of $6s'[1/2]_1$ or from the 0_u^+ of $6s'[1/2]_1$ to the bound states of $6s[3/2]_1$ were expected to give the emission band at 1200 to 1400 nm. According to Castex, the concentration of vdW bound and quasibound molecules is 0.6% at 760 Torr and at room temperature.[15] In the case of photon excitation, there has been some evidence for the excitation of vdW molecules to upper states both in absorption spectra[16] and in excitation spectra.[4,5,7,8,15,17,18] The vibrational progression was observed in the two-photon excitation spectra of high pressure Xe in the energy range of 6p and 5d configurations by Gornik *et al.*[18] They assigned the molecular bands to the transition from the bound vdW dimers. Recently work on this kind of excitation using monochromatic synchrotron radiation indicated that the red wing in the vicinity of $6s'[1/2]_1$ and $6s[3/2]_1$ excitation band,[4,5,7,8,17] was due to the transition of the vdW dimers to the vibrationally excited molecular states. Analogous with these results for photon excitation, then, the direct excitation of vdW molecules can occur in the high energy and high intensity electron excitation.

In the case of the Xe–Ar system, the disappearance of the emission line at 830 nm due to Xe $6p[1/2]_0$ and the enhancement of the 990 and 1080 nm lines due to Xe $6p[1/2]_1$, which were observed in Fig. 2(b), suggest that the dominant energy transfer occurs from the Ar excimer, $^{1,3}\Sigma_u^+$, to Xe atoms. However, concerning the 1270 nm band in Xe–Ar, the excitation process seems to be completely different, as indicated in Fig. 4, where similar mechanism to that considered in pure Xe can be applicable. The small decrease of the 1270 nm band shown in Fig. 4 can be interpreted to mean that in Xe–Ar the energy transfer from the Ar excimer to the vdW dimers of Xe occurs to a small extent.

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