February, 1985] © *1985 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 58, 429—432 (1985)* 429

The Near Infrared Emission Band Observed in Electron Irradiated Xe and Xe in Other Rare Gases

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(Received August 6, 1984)

The near-infrared emission spectra were studied for xenon diluted with krypton, argon, and neon, respectively, in order to estimate the origin of an emission band at 1260 nm which was previously observed at several hundred Torr (1 Torr=133.2 Pa) of pure Xe irradiated with pulses of high-energy electrons. A continuous band around 1260 nm was observed only in Xe-Ar mixtures. This band appeared at Xe pressures above 20 Torr (diluted in 600 Torr of Ar) while it was detected above 190 Torr in pure Xe. In Xe-Ar mixtures, three emission lines due to Xe $5d(3/2)_1$were also observed at 1700, 2020, and 2650 nm. On the basis of the reported kinetic data for the reactions of rare gas mixtures, the present results led to the conclusion that the band at 1260 nm was due to emission from highly excited excimer states, of which the dissociation limits were higher Rydberg states above the energy level of the Xe_2^+ ion.

The spectroscopy and kinetics of rare gas excimers have been studied mainly in the VUV region. Here, the continuous emissions (due to transitions from the lowest bound states to the repulsive ground state) were observed. According to theoretical studies of the excited states of Xe by Mulliken,[1] the emission or absorption due to the transitions between the energy levels of excited diatomic molecules is expected to occur in the NIR region. In this regard, Arai and coworkers reported the presence of absorption bands in the NIR region and the reactivity of the excimer with a number of simple molecules.[2] On the other hand, the de-excitation processes of higher Rydberg states have not been well studied, especially at high pressures such as are used for excimer lasers. As previously reported, we have found a new continuous band in the emission spectra of Xe in the NIR region, which occurs upon the irradiation of Xe and Xe (diluted with Ar) with pulses of high-energy electron. This band seemed to be due to molecular transitions related to higher Rydberg states. However, an assignment has not yet been made.[3] In this paper the NIR emission spectra of Xe and Xe, which were diluted in other rare gases, were studied in order to estimate the excited states of Xe leading to the new band. The emission spectra were qualitatively interpreted on the basis of the recently reported kinetic models.

Experimental

The experimental apparatus has been previously described.[3] The source of the electron pulses was the 45 Mev linac at Hokkaido University and the duration of the pulses was 3 μs. The emissions from the sample gases were detected in the reverse direction to the electron beam so that interference due to intense Cerênkov light in the Xe gas (upon irradiation) could be avoided in the infrared observation. A Hamamatsu TV p791 PbSe detector with a time constant of 2.5 μs was used. The spectra were obtained by plotting the peak intensities of the time-resolved signals against wavelength. The spectra region examined was 800—1600 nm for Xe-Ne and Xe-Kr mixtures, and 800—3200 nm for pure Xe and Xe-Ar mixtures. The observed band width of the spectra was about 15 nm at 825 nm with the 1.5-mm slit used during most of the experiment. When using a narrower slit, the signal accumulation and averaging were performed by using a Sord M223 Mark III computer.

Research-grade Xe (99.995%), Ar (99.999%), and Kr (99.995%) supplied by Nippon Sanso, Ne (99.999%) by Takachiho Kagaku Kogyo were used.

Results and Discussion

Emission Spectra in Pure Xe. Th emission spectrum which was obtained upon the irradiation of 635 Torr of Xe is shown in Fig. 1. The spectrum is essentially the same as that reported peviously,[3] but the present one was measured with a better optical resolution. The emission lines observed at 830, 890—910, 990, and 1080 nm were due to known atomic transitions: 6p—6s and 6p′—6s′. The continuous band at around 1260 nm was first reported by the authors in a previous paper.[3] It starts at about 1100 nm and continues to 1350 nm. The insert in Fig. 1 shown this

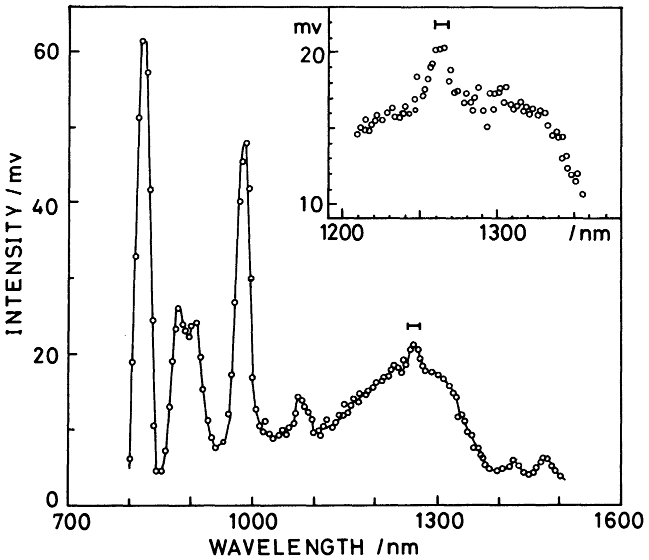

Fig. 1. The emission spectra of Xe in pure Xe at 630 Torr. The optical resolution is 20 nm. The spectrum in the insert was measured with 10 nm resolution.

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band measured at a resolution of less than 10 nm. A narrow peak, which had not been detected at lower resolution, appeared and was assigned to the emission due to one of the 7s—6p atomic transitions. The possibility that this band was due to a 7p—5d transition ($3p_{10}$—$3d_5$ in Paschen notation, 1259.4 nm) was excluded since it has been reported that the branching ratio to $3d_5$ is very low.[4] No vibrational structures were observed at a 10-nm resolution, as shown in the insert. The band began to appear clearly at pressures above 190 Torr, and the pressure dependence of the peak intensity at 1260 nm was quadratic, which indicates that the band was due to a molecular transition.

One of the most important results reported in the previous paper was that the intensity of the band at 1260 nm was not affected by adding a small amount of SF_6, while the intensities of atomic lines decreased significantly. It is known that ion recombination and collisional state mixing are effectively inhibited by a small amount of SF_6.[5–7] Therefore, the ionic processes such as dissociative recombination of Xe_2^+ were ruled out as being the entity responsible for the 1260 nm band. Instead, the contribution of the direct excitation by the interaction of high-energy electron was considered.

Emission Spectra of Xe in Ne. Figure 2 shows the emission spectra of Xe in Ne. When 50 Torr of Xe was added to 510 Torr of Ne, the emission due to Ne completely disappeared, and the emission lines of Xe, which are due to the transitions 6p—6s and 7s—6p, were observed. However, no continuum emission was observed at 1260 nm except for a sharp 7s—6p line. Among the 6p—6s emission lines, the intensities of the lines due to the transition from $6p(1/2)_1$ ($2p_{10}$ in Paschen notation) at 980 and 1080 nm were very intense when the Xe pressure was low. The intensities of all emission lines decreased in the same manner as the Xe pressure increased, which indicates that these emissions were produced by energy transfer from excited Ne, and that the collisional state mixing occurred efficiently. Since all of the excited states of the Ne atoms lie at levels higher than the level of Xe^+ (12.127 ev), the excited Ne atoms can induce Penning ionization of Xe atoms, which leads to the production of an excited Xe atoms as follows; $Ne^*+Xe \rightarrow Ne+Xe^++e^-$, $Xe^++Ne+Xe \rightarrow Xe_2^+ +Ne$, $Xe_2^++e^- \rightarrow Xe^*+Xe$. It was estimated that the resultant energy levels of Xe^* are the 6p states, if the electrons are thermalized and the dissociation energy of Xe_2^+ ion is about 1 ev.[6,8] Thus, it is considered that the 6p emissions which were observed in Fig. 2 were produced directly from the above-mentioned dissociative recombination. From the result that the 1260 nm band did not appear, it was concluded that the 6p states do not take part in the formation of the species responsible for the 1260 nm band.

Emission Spectra of Xe in Kr. The emission spectra in the irradiated Xe–Kr mixtures are shown in Fig. 3. Four emission lines due to 6p—6s transitions were observed at 830, 910, 980, and 1080 nm. The 7s—6p emission at 1260 nm, which was strong in the Xe–Ne mixtures, was very weak. The continuous band was not detected even at 100 Torr of Xe pressure.

It was considered that in this experiment the major part of the channel of energy transferred from the excited Kr to Xe was the excited Kr atoms in the 5s states. These were produced by deactivation in a cascade after the dissociative recombination of Kr_2^+. The role of the diatomic molecules, Kr_2^*, was less important, since the rate of the two-body collision of 5s Kr ($Kr^*+Xe \rightarrow Xe^*+Kr$) was much faster than that of the three-body collision ($Kr^*+2Kr \rightarrow Kr_2^*+Kr$) under the present experimental condition (P_{Xe}=higher than 5 Torr), where the former rate was 2.0×10^{-10} $cm^3 s^{-1}$[9] and the latter was 1.4×10^{-33} $cm^6 s^{-1}$.[9] An efficient dipole-dipole type energy transfer is possible between Kr $^3P_1$ and Xe $5d(7/2)_3$ and between Kr $^3P_2$ and Xe

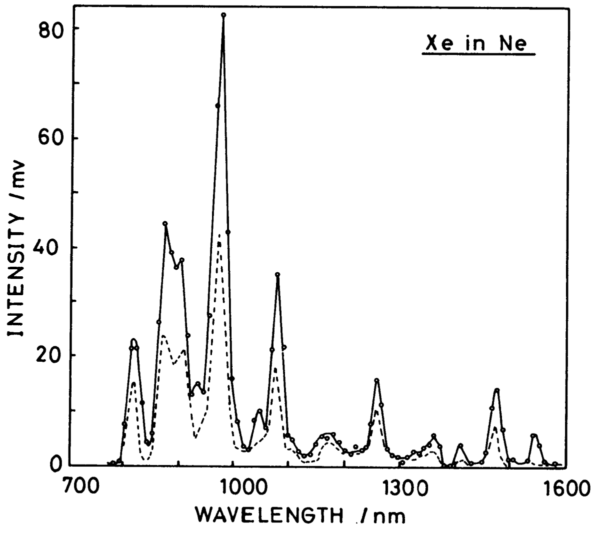

Fig. 2. The emission spectra of Xe in Xe–Ne mixtures at 50 Torr (——) and 80 Torr (----) of Xe in 510 Torr of Ne, respectively.

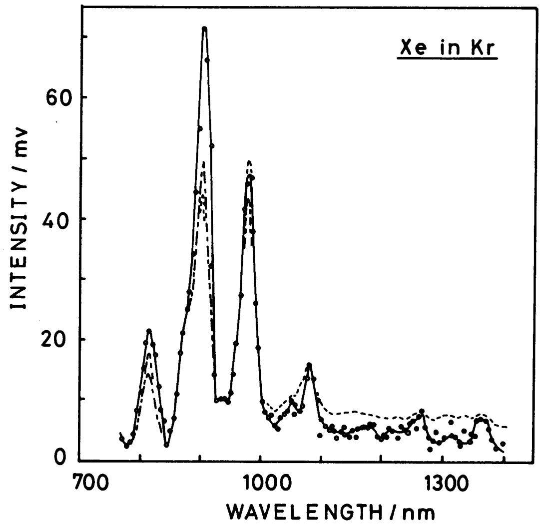

Fig. 3. The emission spectra of Xe in Xe–Kr mixtures at 20 Torr (——), 50 Torr (----), and 100 Torr (----) of Xe in 510 Torr of Kr, respectively.

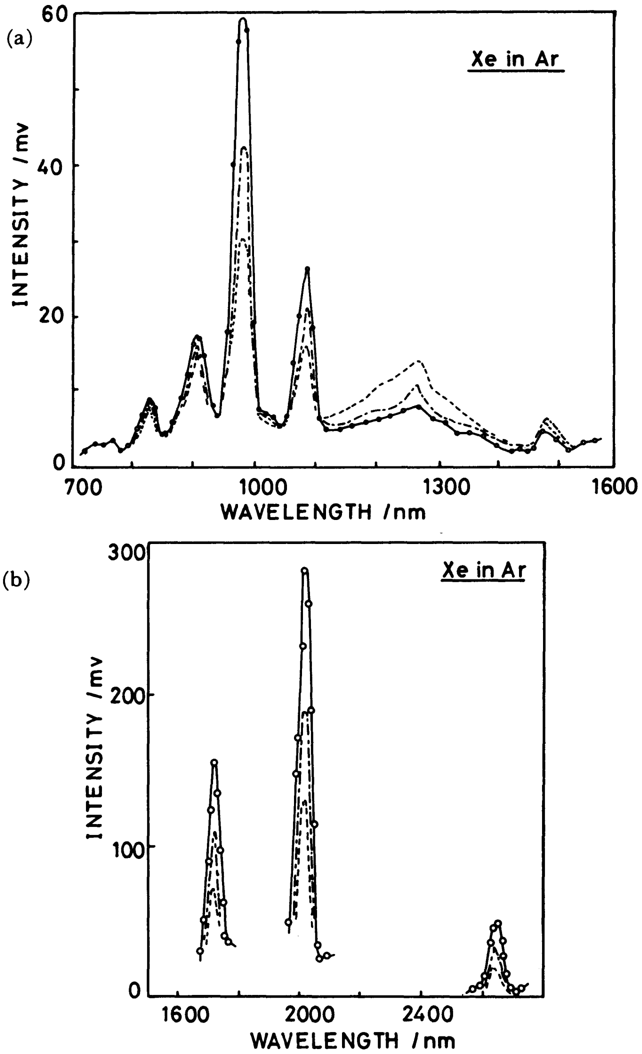

Fig. 4. (a) The emission spectra of Xe in Xe–Ar mixtures at 20 Torr (——), 50 Torr (---), and 80 Torr (----) of Xe in 640 Torr of total pressure, respectively.
(b) The emission bands of Xe $5d(3/2)_1$ in Xe–Ar mixtures at 5 Torr (——), 10 Torr (---), and 20 Torr (----) of Xe in 640 Torr of total pressure, respectively.

$5d(1/2)_1$. Similarly, the second resonant state of Kr, $^1P_1$, can correlate with Xe $7s(3/2)_1$. Accordingly, the observed emission lines due to 6p—6s transitions (Fig. 3) would be produced mainly by the de-excitation from lower 5d states and in a cascade from the 7s state. The absence of the continuous band at 1260 nm in the spectra implies that the lower 5d and 7s states of Xe are not involved in the formation of the species responsible for this band.

Emission Spectra in Xe–Ar Mixtures. In the Xe–Ar mixtures, the emissions due to the transition of 6p—6s of Xe and the 1260 nm band were observed, as shown in Fig. 4a. Figure 4b shows the emission lines due to Xe $5d(3/2)_1$ at the wavelength from 1600 to 2800 nm, where the lines at 1700, 2020, and 2650 nm were observed. The lower states of these emissions are $6p(5/2)_2$, $6p(3/2)_1$ and $6p(1/2)_0$ ($2p_9$, $2p_7$, and $2p_5$ in Paschen notation), respectively. The intensities of the emission due to $6p(1/2)_1$ (Paschen $2p_{10}$) at 980 and 1080 nm were the most intense and decreased as the Xe pressure increased, whereas the emission lines at 825 and 900 nm were weak and insensitive to the Xe pressure. The Xe pressure dependence of the 5d emission was very similar to the $2p_{10}$ emission. The band at 1260 nm began to appear at a Xe pressure greater than 20 Torr. The Xe pressure required to produce the appearance of this band was much lower in Ar compared with that observed in pure Xe, where the band began to appear above 190 Torr. Therefore, it is obvious that this band was induced by an energy transfer from Ar. The major part of the channel of the energy transfer from the excited Ar to Xe was considered to be the Ar atoms in 4s states rather than the lowest excimer state, Ar_2^*, as was considered for the reactions in Xe–Kr. Since all of the 4s states of Ar lie just below the ionization potential of Xe, the energy transfer from the excited Ar to Xe atoms will produce high Rydberg states in Xe. King, Piper and Setser studied the energy-transfer processes of metastable Ar atoms to Xe atoms and identified the emission lines extending from 7d to 10s[10] The production of similar highly excited states is possible in this type of experiment. In fact, the appearance of the emission due to Xe $5d(3/2)_1$, shown in Fig. 4b, indicates the production of excited Xe atoms at higher Rydberg states, because it is known that in Xe–Ar mixture, the excitation of Ar $^3P_1$, or the selective excitation of higher Rydberg states of Xe above Xe_2^+ state leads to the $5d(3/2)_1$ emission in VUV region.[11] The de-activation process of such higher Rydberg states has not been investigated except in studies of the collisional and radiative de-excitation of 7p states by Horiguchi and coworkers.[4] However, as the most probable reaction, the Hornbeck-Molner reaction, $Xe^* + Xe \rightarrow Xe_2^+ + e^-$, is known for the excited atoms above the energy state of Xe_2^+ ion (11.16 eV). According to the energetic model of the H–M reaction described by Hurst and Klots,[12] the formation of a highly excited diatomic molecule, Xe_2^{**}, would occur simultaneously with the H–M reaction, if the potential-energy curves for the collision of the highly excited atoms with a ground state atom are essentially parallel with those of the ion-atom system ($Xe^+ + Xe \rightarrow Xe_2^+$). Otherwise, the Xe_2^+ ions produced from the H–M reaction possibly undergo electron-ion recombination to form such highly excited excimers, as suggested by Mulliken[1] and Brodmann and coworkers.[13]

We attributed the band at 1260 nm to the emission from these highly excited excimer states. The Xe level closely resonant with Ar $^3P_1$ are the 9s states (11.58 eV). Then, if the potential minimum of the Xe_2^{**} formed from the 9s atom is as deep as that of the Xe_2^+ ion (0.97 eV), the lower state of this emission is estimated to be about 9.6 eV, which corresponds to the repulsive parts of the potential curves converging to the 6p levels. The band is so broad that it possibly involves several deactivation processes.

In pure Xe, such highly excited excimer states can be formed by the direct excitation of the ground-state atoms or the vertical excitation of van der Waals molecules. The occurrence of direct excitation is supported by the fact that the addition of a small amount of SF_6 did not affect the emission intensity of the continuous band. On the other hand, the small effect of the addition of SF_6 was observed for the emission of Xe in Ar, in which a small decrease in the emission intensity at 1260 nm was clearly seen. This small decrease is considered to indicate that the ionic processes, such as the dissociative recombination of Ar_2^+, were involved in the formation of Xe_2^{**} in the Xe–Ar mixtures. However, the effect of the SF_6 observed was too small to give a reasonable interpretation so far.

It is less likely that the present band is related to the NIR absorption bands which were observed by Arai and coworkers,[2] because the emission bands could be detected only in the pure Xe and in Xe–Ar mixtures. The species, Xe_2^{**}, in this experiment may have a larger internuclear distance than the $^3\Sigma_u^+$ type excimers.

In conclusion, the continuous band which was observed at 1260 nm in irradiated pure Xe and in the Xe in Ar can be attributed to a transition from molecular states which were related to high Rydberg states just below the ionization potential of Xe and were formed by the Hornbeck-Molnar reaction, followed by ion recombination, or were formed simultaneously with the H–M reaction.

The authors would like to thank Dr. Takeaki Enoto, and Messrs. Hiroaki Tanida and Koichi Sato for their help in the operation of the linac.

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