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Kinetic Study of Excited Diatomic Molecules of Krypton and Xenon

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Excited diatomic molecules of krypton and xenon in $1^3\Sigma_u^+$ states, Kr_2^* and Xe_2^*, were produced by irradiating krypton and xenon in the presence of an excess of argon with short electron-beam pulses. The kinetic behaviors of Kr_2^* and Xe_2^* (monitored by near-IR absorption spectrophotometry) are explained quantitatively in terms of mechanisms involving three-body association and radiative decay. The rate constants were found to be $(6.5\pm0.8)\times10^{-33}\,cm^6\,s^{-1}$ for $Kr^*+Kr+Ar\rightarrow Kr_2^*+Ar$ and $(1.6\pm0.3)\times10^{-32}\,cm^6\,s^{-1}$ for $Xe^*+Xe+Ar\rightarrow Xe_2^*+Ar$. The rate constants for the quenching reactions of Kr_2^* were determined for Xe, H_2, O_2, N_2, CO, and NO.

The irradiation of rare gases with ionizing radiations results in the formation of excited atoms *via* direct excitation or ionization followed by charge neutralization. When pressures of rare gases are sufficiently high (10^2 Torr or higher), excited atoms are rapidly converted into excited diatomic molecules in a three-body association reaction involving one excited and two ground-state atoms.[1–3] Excited diatomic molecules of rare gases have broad and continuous vacuum UV emissions, which are attributed to the optical transitions between the bound excited and repulsive ground states.[4,5] Arai, Firestone, and their co-workers have demonstrated that rare gases irradiated with electron pulses exhibit two types of intense transient absorptions due to excited diatomic molecules in the near-IR region.[6–9] A comparison of the observed optical data with theoretical values leads to an assignment of the first absorption (at shorter wavelengths) and the second absorption (at longer wavelengths) to the transition $1^3\Sigma_u^+$ to $2^3\Pi_g$ and $1^3\Sigma_g^+$, respectively (potentical curves of diatomic molecules).[10] The two near-IR absorptions and the principal vacuum UV emission originate from a molecule in the same electronic state, *i.e.*, the lowest triplet state $1^3\Sigma_u^+$.

By observing the time dependence of the first absorption, several kinetic parameters have been determined for the excited diatomic molecules of rare gases in the $1^3\Sigma_u^+$ state.[7,9,11,12] The parameters are the rate constants of the formation and decay processes, together with quenching processes by many simple molecules. The absorption spectrophotometric method has also been applied to the kinetic study of helium molecules in the $1^3\Sigma_u^+$ state.[13]

The present paper reports on the kinetic parameters of the excited diatomic molecules of krypton and xenon. These parameters were determined by time-dependent observations of their first absorptions under various experimental conditions. The chemical reactions of excited atoms or excited diatomic molecules of rare gases should be studied more extensively, since information from such studies is important for constructing or testing theoretical models used in chemical kinetics.

Experimental

The experimental apparatus and procedures are essentially the same as those described in previous studies.[8,9,11–13] Therefore, only a few fundamental points will be briefly described.

All the samples were irradiated with 600-keV electron pulses generated from a Febetron 706. The profile had a pulse width of about 5 ns. The absorptions due to excited diatomic molecules of rare gases were measured spectrophotometrically as a function of time under various experimental conditions. The photomultiplier used was a Hamamatsu TV R316. The total rise time of the detection system was about 20 ns. Molecular absorptions were measured at a slit width of 0.30 mm, *i.e.*, a wavelength resolution of about 0.9 nm using a Narumi R23 monochromator. The widths of the 983-nm band due to an excited krypton molecule and the 1032-nm band due to an excited xenon molecule are much larger than the wavelength resolution.

Krypton and xenon purchased from Teikoku Sanso Co. and Takachiho Shoji Co., respectively, were of the highest grade and were used without further purification. The krypton used in the previous study contained xenon as an impurity. For the krypton used here, however, we could not detect any absorption due to an excited xenon atom, when 800 Torr (1 Torr=133.322 Pa) of krypton was irradiated with electron pulses. Since the energy transfer from excited krypton to xenon occurs very efficiently, the absence of excited xenon guarantees the high purity of krypton. Argon purchased from Nihon Sanso Co. did not show any sign of an impurity throughout all the observations. The other gases were obtained from Takachiho Shoji Co. and were used without further purification.

Results and Discussion

In this paper, the excited rare-gas atoms with an electronic configuration of $np^5(n+1)s^1$ are denoted by $X^*(^1P_1)$, $X^*(^3P_0)$, $X^*(^3P_1)$, and $X^*(^3P_2)$ in the L-S coupling notation, where X is a rare-gas atom and n is the principal quantum number of the outer shell of the ground state atom X. The excited diatomic molecules in the $1^3\Sigma_u^+$ state are denoted by X_2^*.

Formation of Excited Diatomic Molecules in Mixtures. The formation processes of Kr_2^* and Xe_2^* in the presence of excess argon were studied by measuring their near-IR absorptions as a function of time. Kr_2^* has its first absorption bands at 965.5, 974.3, 983.3, and 988.6 nm, and Xe_2^* has corresponding bands in the region of 1000—1120 nm.[6–9] The time dependencies of the absorptions were monitored at 983.3 nm for Kr_2^* and at 1032.0 nm for Xe_2^*. No change in shape was observed for the first absorption bands of Kr_2^* and Xe_2^* through their formation and decay processes in previous studies.[8,9]

Although the ionizing radiation interacts mainly with the excess argon at an initial stage, excitation energies are expected to be transferred rapidly to krypton and xenon in the mixtures examined here. For example, the energy-transfer rates from Ar*(^{3}P$_0$) and Ar*(^{3}P$_2$) to Kr(^{1}S$_0$) are estimated to be 1.5×10^6 and 3.7×10^6 s^{-1}, respectively, in a mixture of 930-Torr argon and 20-Torr krypton.[14] Our time-dependent absorption measurements for Ar*(3p^{5}4s^1) indicated a rapid disappearance (within 1 μs or so) after a pulse in the same mixture. Chang and Setser have measured two-body deactivation rate constants for Ar*(3p^{5}4p^1), which were produced by the laser-pulse excitation of Ar*(3p^{5}4s^1).[15] The constants range from 1×10^{-10} to 2×10^{-11} cm^3 s^{-1}. Therefore, the lifetimes of Ar*(3p^{5}4p^1) are estimated to be less than about 2 ns in 760-Torr argon at room temperature. We observed several visible and near-IR emission lines originating from Ar*(3p^{5}4p^1) and Kr*(4p^{5}5p^1) in irradiated argon-krypton mixtures. In all the mixtures examined, emissions terminated immediately after irradiation ceased. The excited argon and krypton atoms in higher states are, if produced, degraded almost instantaneously into those in the four lower states *via* radiative or collision processes. Although there are many visible and near-IR emission lines caused by excited rare-gas atoms at various high levels, such lines have not been observed in electron-irradiated rare gases at about 760 Torr except for those by X*(np^5(n+1)p^1).[6] The energy-transfer rate from Ar_2^* to Kr(^{1}S$_0$) is 6.4×10^7 s^{-1} in a mixture of 930-Torr argon and 20-Torr krypton.[11]

Charged species disappear very rapidly after irradiation ceases. Ion recombination coefficients for X_2^+ and e$^-$ have been summerized in the review by Bardsley and Biondi.[16] The coefficients are 7.5×10^{-7} cm^3 s^{-1} for Ar_2^+, 12×10^{-7} cm^3 s^{-1} for Kr_2^+, and 14×10^{-7} cm^3 s^{-1} fox Xe_2^+. Assuming that the electron pulse has an accelerating energy of 600 keV, a total output of 10 J, and a beam cross section of 2 cm^2, one can roughly estimate the initial ion concentration (n_0) from the energy loss of the incident electrons in 950-Torr argon.[17] The calculated initial lifetimes of X_2^+, *i.e.*, (recombination coefficient$\times n_0$)$^{-1}$ are less than 0.22 ns, indicating a rapid disappearance of charged species.

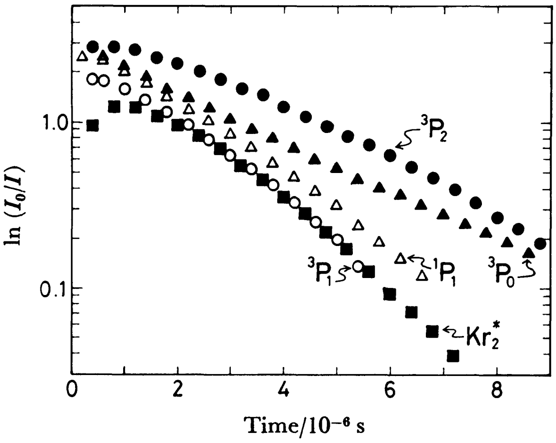

Fig. 1. Logarithmic plots of optical densities against time for Kr_2^* and Kr*(^{1}P$_1$, ^{3}P$_0$, ^{3}P$_1$, and ^{3}P$_2$) in the mixture of 60 Torr Kr and 890 Torr Ar. I_0, intensity of analyzing light transmitted in the absence of absorbing species; I, that in the presence of absorbing species. Absorption measurements, see text.

Figure 1 shows logarithmic plots of optical densities *vs.* time for Kr_2^*, Kr*(^{1}P$_1$), Kr*(^{3}P$_0$), Kr*(^{3}P$_1$), and Kr*(^{3}P$_2$) in the mixture of 890-Torr argon and 60-Torr krypton. Kr*(^{1}P$_1$), Kr*(^{3}P$_0$), Kr*(^{3}P$_1$), and Kr*(^{3}P$_2$) were monitored by observing absorption lines at 828.1, 785.4, 819.0, 892.9 nm, respectively (Fig. 1). The apparent lifetimes of these excited species range from 1.5 to 3 μs in the mixture. However, the Lambert-Beer law does not hold between optical density and concentration, because the bandpass of analyzing light used here (*i.e.*, about 0.35 nm) is larger than the widths of the atomic absorption lines. The net lifetimes should be shorter than the apparent ones by a factor between 1 and 2.[18]

The time dependence of the concentration of an excited diatomic molecule in a mixture can be explained by the following mechanism:

$$\mathrm{X}\ \text{in excess argon} \rightsquigarrow \mathrm{X}^*$$

$$\mathrm{X}^* \longrightarrow \mathrm{X}, \tag{1}$$

$$\mathrm{X}^* + \mathrm{X} + \mathrm{M} \longrightarrow \mathrm{X}_2^* + \mathrm{M}, \tag{2}$$

$$\mathrm{X}_2^* \longrightarrow 2\mathrm{X} + h\nu, \tag{3}$$

where M is a third body. The mechanism leads to the equation:

$$[\mathrm{X}_2^*] = \frac{k_2[\mathrm{X}][\mathrm{M}][\mathrm{X}^*]_0}{k_1+k_2[\mathrm{X}][\mathrm{M}]-k_3}\{\exp[-k_3t]-\exp[-(k_1+k_2[\mathrm{X}][\mathrm{M}])t]\}, \tag{4}$$

where k_n is the rate constant of the corresponding reaction and $[\mathrm{X}^*]_0$ is an initial concentration of X*. The absorption intensity *vs.* time curves observed for Kr_2^* and Xe_2^* exhibit an early growth and a subsequent slow decay after passing a maximum. The apparent decay and growth should correspond to the first and second exponential terms of Eq. 4, respectively, in the high-pressure region where $\{k_1+k_2[\mathrm{X}][\mathrm{M}]\}$ is larger than k_3. On the other hand, the relation is reversed in the low-pressure region where $\{k_1+k_2[\mathrm{X}][\mathrm{M}]\}$ is smaller than k_3, since the sign of Eq. 4 changes. As the result, the apparent first-order decay rate is equal to $\{k_1+k_2[\mathrm{X}][\mathrm{M}]\}$.

On the basis of Eq. 4, we have analyzed a series of absorption-intensity *vs.* time curves obtained with Kr_2^* and Xe_2^* in mixtures, where the total pressures were kept nearly constant and the partial pressures of krypton and xenon were varied over a wide range. In fact, the observed curves were found to approximately fit the difference of the two exponential terms, as shown in Fig. 2. Since the partial pressures of krypton and xenon are relatively low, the apparent first-order decay rates obtained here are expected to correspond to $\{k_1+k_2[\mathrm{X}][\mathrm{M}]\}$ in the second term. We determined the first-order decay rates from late portions of absorption-intensity *vs.* time curves, *i.e.*, portions later than 2 μs after pulses. Figures 3 and 4 present plots of $\{k_1+k_2[\mathrm{X}][\mathrm{M}]\}$ against [X] for krypton and xenon, respectively, where good linear relations are seen for both gases. The radiative decay rates, *i.e.*, k_3's of Kr_2^*

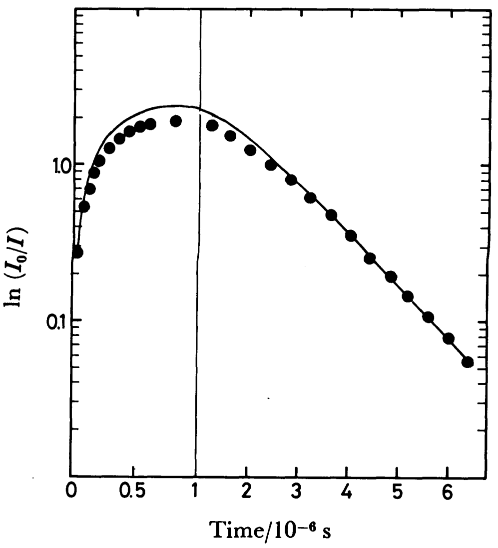

Fig. 2. Logarithmic plots of optical density at 983.3 nm against time for Kr_2^* in the mixture of 76 Torr Kr and 874 Torr Ar. Time scales are different between the regions before and after 1 μs. Solid curve was calculated from Eq. 4, where $k_3 = 1.8 \times 10^6$ s^{-1} and $k_1 + k_2[M][Kr] = 7.7 \times 10^5$ s^{-1}.

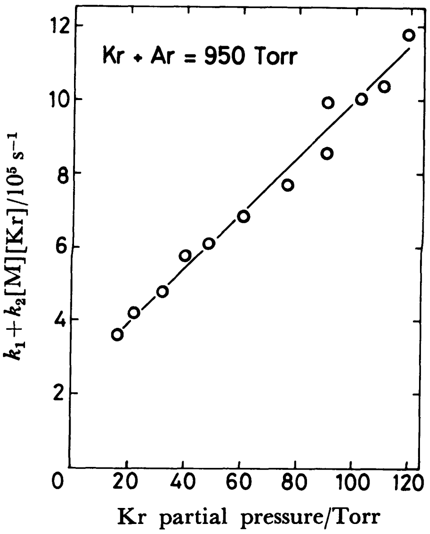

Fig. 3. Plot of $k_1 + k_2[M][Kr]$ against partial pressure of Kr.

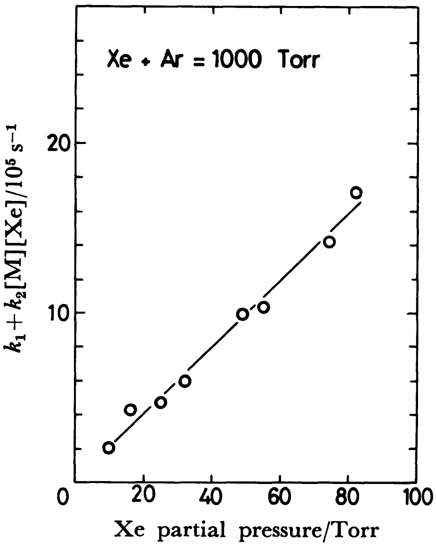

Fig. 4. Plot of $k_1 + k_2[M][Xe]$ against partial pressure of Xe.

and Xe_2^* have been reported to be 2.83×10^6 s^{-1} and 1.0×10^7 s^{-1}, respectively.[7,19] The decay rates are much larger than the apparent first-order decay rates shown in Figs. 3 and 4. The rate constants for the formation of Kr_2^* and Xe_2^* are tabulated in Table 1, together with those reported previously.[3,20,21] The rate constant determined here for Xe_2^* is a little smaller than that reported in the vacuum UV-emission study by Rice and Johnson.[20] However, it agrees with more recent determination by Gleason *et al.* within the error limits.[21]

It is generally accepted that the precursor responsible for the formation of X_2^* in the $1^3\Sigma_u^+$ state is one or more of the excited atoms $X^*(^1P_1)$, $X^*(^3P_0)$, $X^*(^3P_1)$, and $X^*(^3P_2)$. The observed results presented in Figs. 3 and 4 indicate that X_2^* is produced in a three-body reaction involving X, X*, and M, where the rate constant is given by the slope in each figure. If two or more precursors are involved in the formation of X_2^*, the corresponding three-body reactions should have almost the same rate constant among different precursors. There might be a possibility that some collisional processes induce the degradation of higher excited atoms, *i.e.*, $X^*(^1P_1)$, $X^*(^3P_0)$, and $X^*(^3P_1)$ into $X^*(^3P_2)$, and the resulting excited atom $X^*(^3P_2)$ acts as a precursor in the formation of X_2^*. However, it seems difficult to reconcile such a complicated mechanism with the simple relations presented in Figs. 3 and 4, except for the extreme case that collisional processes proceed much more rapidly than the three-body formation process of X_2^*. The results (Fig. 1) are inconsistent with the extreme case. The excited diatomic molecule in the $1^3\Sigma_u^+$ state is correlated to $X^*(^3P_2)$ and $X(^1S_0)$ at an infinite nuclear distance in theoretical studies.[10,22–27] The molecule in the $1^1\Sigma_u^+$ state is correlated to $X^*(^3P_1)$ and $X(^1S_0)$. Further, the combination of $X^*(^1P_1)$ and $X(^1S_0)$ leads to molecules in other states and that of $X^*(^3P_0)$ and $X(^1S_0)$ leads to repulsive potentials. These studies suggest that the most probable precursor is $X^*(^3P_2)$. The other excited atoms do not contribute appreciably to the formation of $X_2^*(1^3\Sigma_u^+)$, although they might produce $X_2^*(1^1\Sigma_u^+)$ in a similar three-body reaction.

Table 1. Rate constants of three-body association reactions

Reaction	Rate constant/cm^6 s^{-1}	
$Kr^* + Kr + Ar \rightarrow Kr_2^* + Ar$	$(6.5 \pm 0.8) \times 10^{-33}$	This work
$Xe^* + Xe + Ar \rightarrow Xe_2^* + Ar$	$(1.6 \pm 0.3) \times 10^{-32}$	This work
	$(2.15 \pm 0.25) \times 10^{-32}$	Ref. 21
	$(2.35 \pm 0.02) \times 10^{-32}$	Ref. 20

Quenching Reactions of Excited Krypton Molecule. Excited diatomic molecules of rare gases are very reactive with other molecules since they have large internal excitation energies. The energies are estimated to be 16.1 eV for Ne_2^*, 10.8 eV for Ar_2^*, 9.2 eV for Kr_2^*, and 7.7 eV for Xe_2^*. These values can be derived from the well depths of excited molecules in the $1^3\Sigma_u^+$ state and energy levels of excited atoms in $^3P_2$ states.[10,25,27,28] Rate constants of quenching reactions of He_2^*, Ne_2^*, and Ar_2^* by a number of simple gases were already determined using an absorption spectrophotometric technique.[11–13] However, those of Kr_2^* have been scarcely known in both absorption and emission studies.

The decay rate of Kr_2^* in pure krypton increases with increasing pressure of krypton (at low pressures). The apparent decay reflects the three-body association (similarly for the mixtures of argon and krypton). However, the decay becomes constant at pressures above 600 Torr. The radiative process now corresponds to the observed decay in the pressure region. This result is consistent with the previous one.[7] The rate was found to be $2.9\times10^6\ s^{-1}$. In 800-Torr krypton, Kr_2^* is produced much more rapidly as compared with the radiative decay process. The addition of a small amount of quenchers into 800-Torr krypton enhanced the decay rate of Kr_2^*. Plots of decay rates against partial pressures of quenchers gave straight lines for the quenchers examined here. Table 2 tabulates the rate constants and cross-sections obtained with Xe, H_2, O_2, N_2, CO, and NO. The reactivities of Kr_2^* toward these gases are more or less similar to those of Ar_2^*; the rate constants are relatively small for H_2 and N_2 in both Kr_2^* and Ar_2^*.[11]

TABLE 2. RATE CONSTANTS AND CROSS SECTIONS OF QUENCHING REACTIONS OF $Kr_2^*(1^3\Sigma_u^+)$

Quencher	Rate constant $10^{-11}\ cm^3\ s^{-1}$	Cross section $10^{-2}\ nm^2$
Xe	14±3	40±8
H_2	4.0±0.8	2.2±0.4
N_2	0.62±0.12	1.1±0.2
O_2	37±7	70±14
CO	12±2	21±4
NO	35±7	65±13

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