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Collisional and radiative excitation transfers in Kr-Xe mixtures: Emissions from the Xe($^3P_1$) resonant level and the Xe first continuum region

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Time-dependent and time-independent measurements of emissions from Xe in Kr-Xe mixtures are reported. Kr host gas pressure was varied from 100 to 900 Torr, and Xe impurities were varied from 1% to 10% of total Kr pressure. This work has shown that the Xe($^3P_1$) resonant state is depopulated by collisions with both Xe and Kr ground-state atoms. In particular, a two-body quenching rate of $10^4P_{\mathrm{Xe}}+2100P_{\mathrm{Kr}}$ is reported. This two-body rate is assigned to represent a collisional transition to the Xe($^3P_2$) metastable state. A three-body rate of $97P_{\mathrm{Xe}}P_{\mathrm{Kr}}+7P_{\mathrm{Kr}}{}^2$ was also found. The rate $7P_{\mathrm{Kr}}^2$ is assigned to represent the formation of (KrXe)* molecules, while the rate $97P_{\mathrm{Xe}}P_{\mathrm{Kr}}$ represents either formation of $\mathrm{Xe}_2^*(\mathrm{O}_u{}^+)$ or (XeKr)*. Time-dependent measurements made in the Xe first continuum region at about 1500 Å indicate that these emissions follow the Xe($^3P_1$) state.

INTRODUCTION

This Brief Report continues the presentation of the results that we have obtained from a vacuum-ultraviolet (vuv) study of Kr-Xe binary gas mixtures.[1] We have previously discussed the quenching of Kr excited states by Xe impurities. In the present work, we discuss results obtained from vuv emissions associated with atomic and molecular Xe states.

Reference 1 gives a thorough discussion of our data analysis and our measured two- and three-body collisional deexcitation rates for Kr. We have used data analysis techniques in work that has allowed us to obtain results that are compared to other time-dependent measurements obtained in pure Kr. A similar approach is taken in the analysis of emissions from Xe so that results that can be compared to pure Xe are obtained.

This study should help provide information about the energy-transfer mechanisms in the Kr-Xe system. This is important because knowledge of pathways that populate and depopulate the lower-lying states of Xe could lead to greater efficiency in excimer laser design. When the costs of Kr and Xe are compared, it becomes clear that high-pressure Kr-Xe systems can provide an attractive alternative to pure Xe in populating metastable states that ultimately energize excimer lasers such as Xe-Cl$_2$.

EXPERIMENTAL METHOD

The experimental equipment and techniques used in this experiment are described in Ref. 1. Briefly, we have used electron-beam excitation and time-of-flight techniques to make time-dependent measurements for observed vuv Xe spectral lines in Kr-Xe mixtures. These measurements have been made over a wide range of Kr host gas pressures and Xe impurity concentrations.

EXPERIMENTAL RESULTS

Typical time-independent spectra of vuv emissions from Xe in Kr-Xe mixtures were shown in Ref. 1. This discussion makes use of those spectra. Of particular interest in this paper is the Xe($^3P_1$) to Xe($^2S_0$) transition at about 1470 Å and the associated molecular continuum that immediately follows it (1470–1530 Å). We report time-dependent measurements on both of these emissions.

Figure 1 shows a typical time-resolved spectrum made at 1470 Å. The time evolution of the Xe($^3P_1$) emissions shows a rapid increase in intensity at early times followed by an exponential decay. The solid curve is a least-squares fit to the data. The curve is of the form

$$I(t)=A_1e^{-k_0t}+A_2e^{-k_1t} . \tag{1}$$

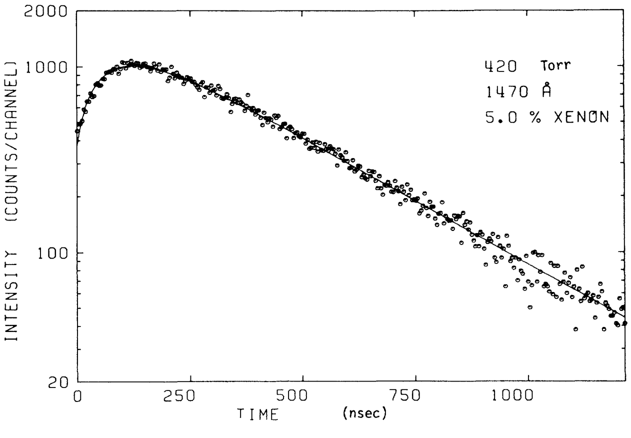

FIG. 1. Typical decay curve of the Xe($^3P_1$) emissions in Kr-Xe mixtures. Krypton partial pressure is 400 Torr and Xe partial pressure is 20 Torr.

In this equation, $I(t)$ represents the emission intensity at time t, A_1 and A_2 represent initial amplitudes at $t=0$, and k_0, k_1 are the decay constants of interest and, in general, are pressure dependent. The first term represents an initial buildup; the second term represents a fast decay component.

The time-dependent measurements of the initial buildup were inconclusive due to the small number of data points and the complexity of the transfer mechanisms between Kr and Xe. Therefore, we do not report on this component at this time. Briefly, we note that there are at least four mechanisms that could be represented in the initial buildup, as discussed in Refs. 1–8.

Figure 2 illustrates the decay constant associated with the fast-decay component obtained in Eq. (1) as a function of Kr and Xe pressure. The Xe concentrations are shown as a percentage of Xe impurity. To obtain Xe partial pressure the relationship

$$P_{\mathrm{Xe}}=f(\%)P_{\mathrm{Kr}}/100 \qquad (2)$$

is used. Here P_{Xe} represents Xe partial pressure, P_{Kr} is the Kr host gas pressure, and $f(\%)$ is the fractional Xe percent displayed in Fig. 2.

Least-squares fitting the data displayed in Fig. 2 yields the pressure-dependent decay rate as a function of Xe and Kr partial pressures. The total pressure-dependent decay rate is written (all decay rates are in units of $\sec^{-1}$)

$$k_1(1470)=\beta_0(1470)+10^4P_{\mathrm{Xe}}+2100P_{\mathrm{Kr}} +(97P_{\mathrm{Xe}}+7P_{\mathrm{Kr}})P_{\mathrm{Kr}}\ . \qquad (3)$$

The solid lines displayed in Fig. 2 represent this fit. The constant term $B_0(1470)$ represents resonance trapping[9] and is not numerically important in this work.

The quenching rates of the Xe($^3P_1$) resonant state by Kr ground-state atoms presented here have not been found in the literature; therefore, no direct comparisons can be made. The two-body rate 10 $^4P_{\mathrm{Xe}}$ can be compared to the work of Leichner *et al.*,[10] who have reported a rate of about $9150P_{\mathrm{Xe}}$, in good agreement with our measured rate. No three-body rate in Xe was found in our study because of the low Xe total pressures used.

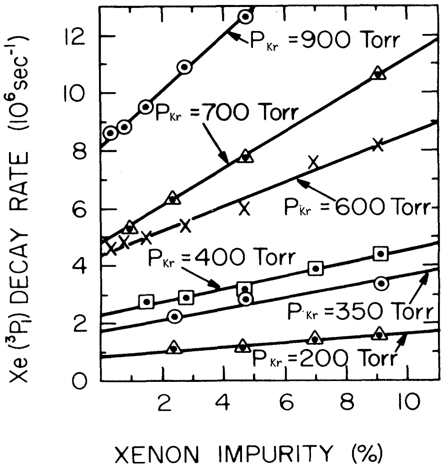

FIG. 2. Xe($^3P_1$) decay rate in Kr-Xe mixtures as a function of Xe impurity and Kr pressures ranging from 200 to 900 Torr. Xe impurity is plotted as a percentage of Kr partial pressure.

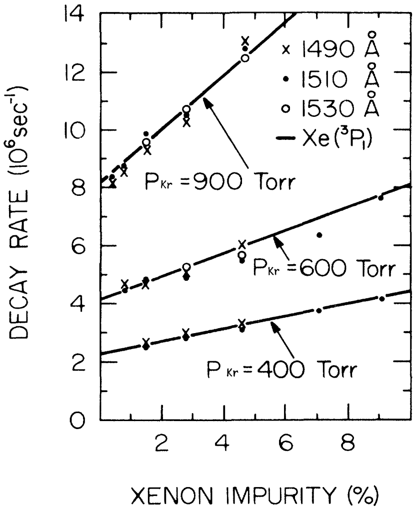

FIG. 3. Decay rates of the 1500-Å emissions in Kr-Xe mixtures. Xe impurity is plotted as a percentage of Kr partial pressure. The solid line represents the decay of the Xe($^3P_1$) emissions as obtained from least-squares fitting the data in Fig. 2.

Figure 3 shows time-dependent measurements made at various points in the molecular continuum that follows the resonant line at 1470 Å. The solid line is the fit obtained for the Xe($^3P_1$) transition. Within experimental error (10%) these emissions exhibit the same pressure dependence as the fast decay component of the Xe($^3P_1$) resonant state.

KINETIC ANALYSIS

Before analyzing the results presented in this study of Kr-Xe mixtures, it is useful to first review a previous study of pure Xe conducted by the current authors,[10] where we showed that the X3($^3P_1$) resonant state is depopulated at the rate

$$K_1(1470)=\beta_0(1470)+9150P_{\mathrm{Xe}}+46P_{\mathrm{Xe}}^2\ . \qquad (4)$$

It is generally known that the two lowest-lying states of Xe, the Xe($^3P_1$) resonant state and the Xe($^3P_2$) metastable state, are energetically isolated from other excited states of Xe. At room temperature the Xe($^3P_2$) lies about 3 kT lower in energy than the Xe($^3P_1$) resonant state. The pressure-dependent decay of Xe($^3P_1$) atoms in pure Xe displayed in Eq. (4) is then explained by three mechanisms and illustrated in Fig. 4. The constant term represents the escape of resonant radiation from cell, while $9150P_{\mathrm{Xe}}$ is the rate at which the Xe($^3P_1$) population is converted to Xe($^3P_2$) atoms in two-body collisions with Xe($^1S_0$) ground-state atoms. The three-body rate $46P_{\mathrm{Xe}}^2$ is commonly assigned to the formation of Xe_2^* (0_u^+) molecules, which radiate immediately on the long-

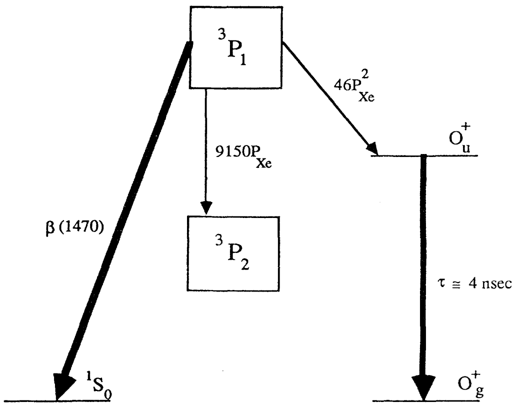

FIG. 4. Decay scheme of Xe($^3P_1$) in pure Xe as proposed by Leichner *et al.* (Ref. 10). The thick lines represent radiative transitions.

wavelength side of the 1470-Å resonant line. This is considered well established and is supported by time-dependent measurements made in the Xe_2^* first continuum and the theoretical work of Mulliken,[11] which links the Xe($^3P_1$) to excited $O_u{}^+$ molecular levels. The understanding of the model shown in Fig. 4 and the isolation of the two lowest-lying states of Xe are very useful in analyzing the decay of the Xe($^3P_1$) in Kr-Xe mixtures shown in Eq. (3).

The linear relationships presented in Figs. 2 and 3 indicate that the decay of the Xe($^3P_1$) resonant state in Kr-Xe mixtures can also be explained in terms of the escape of resonant radiation and two- and three-body collisions with Kr and e ground-state atoms. Figure 5 shows our model for the decay of the Xe($^3P_1$) resonant state in Kr-Xe mixtures. From this figure it is seen that two-body collisional deexcitation indicates energy transfers to the Xe($^3P_2$) metastable state, while the three-body rates would be responsible for the molecular continuum shown in Ref. 1.

In the case of the two-body terms ($10\,000P_{Xe}$ $+2100P_{Kr}$), the only possible atomic receptor state is the Xe($^3P_2$) metastable state. No other atomic state in either Kr or Xe is energetically close enough to be considered a candidate to interact with the Xe($^3P_1$) resonant state.

The three-body terms ($7P_{Kr}^2+97P_{Kr}P_{Xe}$) represent heteronuclear three-body collisions between Xe($^3P_1$) atoms and combinations of Kr($^1S_0$) and Xe($^1S_0$) atoms. These terms cannot represent the formation of Kr molecular levels because of energy limitations and radiative lifetime considerations associated with the long-lived krypton state, $Kr_2^*(^3\sum_u^+)$. This lowest Kr molecular energy state radiates with maximum intensity at about 1425 Å and the intensity falls off rapidly on the longer-wavelength side, which indicates that this state cannot energetically be formed from the Xe($^3P_1$) resonant state. The decay through the Kr molecular state channel would also be rate limited by the Kr_2^* radiative lifetime (about 250–300 μsec).[12] This is not observed in the molecular continuum following the 1470-Å line.

The time-dependent results shown in Fig. 3 indicate the molecular states formed from the Xe($^3P_1$) resonant state radiate in the molecular continuum immediately following the resonant line. In our proposed scheme, the two molecular states [$O_u{}^+$ and/or (KrXe)*] are depopulated as rapidly as they are formed and follow the pressure dependence of their atomic precursor. Time-independent spectra presented in Ref. 10 also support our assignment because the intense molecular continuum shown in Ref. 1 is not present in low-pressure Xe.

The time-independent results presented by Gedanken *et al.*[3] and Salamero *et al.*,[2] indicate that no other emissions have been found in either the vuv or visible region that can be linked to the Xe($^3P_1$) resonant state.

Finally, we note the time-dependent measurements made by Salamero *et al.*[2] at about 1700 Å in the Xe_2^* second-continuum region. They have found that the time-dependence of emissions in that continuum consists of three separate decay components. These are an initial buildup, a fast-decay component, and a slow-decay component. In their work, they have attempted to find the pressure-dependent decay of the Xe($^3P_1$) resonant state in Kr-Xe mixtures by associating the slow-decay component of the time-dependent decay of emissions in that region to the Xe($^3P_1$) state. They propose that this slow-decay component represents emissions from collisionally relaxed $^1\sum_u^+$ and $^3\sum_u^+$ molecular states that follow their atomic precursor; in this case, the Xe($^3P_1$) resonant state. They have reported a three-body decay rate of about $(40+100P_{Xe})P_{Kr}$ for the rate we show in Eq. (3), which is about half of what we observe. While not a direct measurement, their work provides an order-of-magnitude comparison with our results.

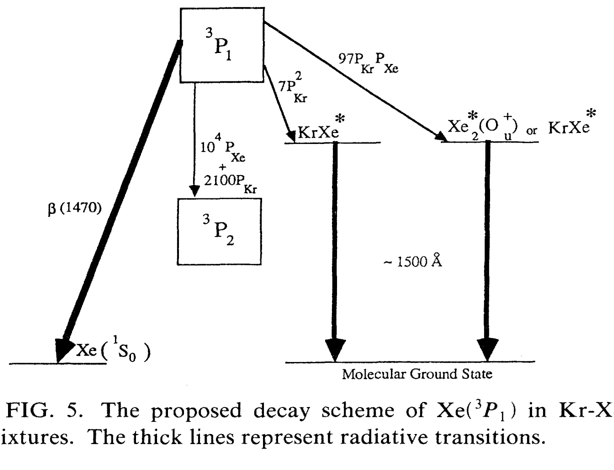

FIG. 5. The proposed decay scheme of Xe($^3P_1$) in Kr-Xe mixtures. The thick lines represent radiative transitions.

SUMMARY AND CONCLUSION

We have made time-dependent measurements on the Xe($^3P_1$) resonant state and the molecular continuum immediately following the resonant state. For the first time, direct measurements on a resonant state have been reported that give the production rate of (KrXe)* heteronuclear molecules which are formed at the rate of $7P_{\mathrm{Kr}}^2$ sec^{-1}. Time-independent spectra and time-dependent measurements in the Xe first continuum region indicate that these heteronuclear molecules radiate in the Xe first continuum. We have also found that Xe($^3P_1$) atoms are collisionally deexcited to the Xe($^3P_2$) metastable state by Kr ground-state atoms at the rate of $2100P_{\mathrm{Kr}}$.

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