Collision Induced Decay in Rare Gases: The $\text{Kr } 5s'[1/2]_1(^1P_1)$ Decay in Dense Ar

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The decay of the krypton $5s'[1/2]_1(^1P_1)$ state in argon has been investigated for several argon densities from the gas to the liquid and for krypton concentrations in the ppm range. The experimental results demonstrate that no quenching of the 1P_1 state occurs due to argon interactions even at liquid argon densities. This result is discussed on the basis of the possible quenching mechanisms and the recently calculated Kr^*Ar molecular potentials.

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The spectroscopy and excited state dynamics of rare gases have attracted considerable attention in the past. The interest is partly related to their closed-shell electronic structure which motivated their characterization as prototypes in atoms, molecules, ions, liquids, solids, and, more recently, clusters of different sizes. Additional motivation for these studies is the importance of the excited state dynamics in the understand, and the improvement, of gas lasers emitting from the vacuum ultraviolet to the infrared region. As is well known, most of these lasing systems involve rare gases in their operation.

Selective excitation has proven to be a valuable tool in the interpretation of excited state dynamics in pure and mixed rare gases [1,2]. Its combination with time resolved techniques significantly enhances the experimental capabilities in excited state dynamics studies [1,3–5]. These techniques and the availability of theoretical molecular potentials are a prerequisite for the correct interpretation of the role of collisions on the decay from excited states.

The purpose of this Letter is to present experimental results demonstrating that collisions *per se* (i.e., without change in transition moment with internuclear distance, appropriate molecular potential crossings, or collisional mixing) are not sufficient to quench an excited state. This requires a system which fulfills at least the condition of well separated molecular potentials between the excited state and lower lying molecular levels. The molecular potentials of the system chosen for this study, KrAr , were recently calculated by Spiegelmann, Gadea, and Castex [6] and are reproduced in Fig. 1. As seen in the figure, the crossings between the molecular potentials related to the $\text{Kr}^*\text{Ar}(^1P_1)$ and lower lying molecular levels occur at much higher energies than the kinetic energies involved in room temperature collisions. This fact makes this system

a potential candidate for demonstrating the inefficiency of collisional quenching.

The experimental method has been described elsewhere [7]. Briefly, the measurements were performed using monochromatized synchrotron radiation at the HIGITI system at HASYLAB, DESY. The radiation (<0.2 mm diameter) enters a cell through a LiF window and the emitted light is monitored through a MgF_2 window perpendicular to the entrance window. The cell can withstand high pressure and is connected to a cryostat. An exit LiF window allows us to record the transmitted light.

FIG. 1. Lower lying excited states of Kr^*Ar according to Ref. [6].

The excitation volume serves as an entrance slit for the secondary monochromator. Most emission spectra were obtained using two independent time windows that record the emission emitted in the time intervals 1–8 and 35–210 ns, hereafter referred to as the fast and slow windows, respectively. The spectra recorded in the liquid and at supercritical densities were obtained with a single time window, 1–482 ns [8].

Since our intent was to focus specifically on the Kr-Ar interactions and avoid the efficient Kr-Kr interactions [9,10], it was crucial to perform the measurements using concentrations in the ppm range as in our previous work on rare gas mixtures [5,11,12].

The luminescence associated with Kr $5s'[1/2]_1(^1P_1)$ excitation in Ar actually confirms the extremely inefficient excitation transfer to the lower levels of krypton, $5s'[1/2]_0(^3P_0)$, $5s[3/2]_1(^3P_1)$, and $5s[3/2]_2(^3P_2)$, and to the Kr*Ar exciplexes related to the 3P_1 and 3P_2 krypton levels [12]. This is illustrated in Fig. 2 which displays the luminescence spectra recorded with the fast [Fig. 2(a)] and slow [Fig. 2(b)] time windows after 1P_1 excitation takes place in a room temperature sample at 73 bars. The Kr concentration in the sample is 1 ppm. As seen in Fig. 2(a), only the emission from the 1P_1 to the 1S_0 ground state is detected during the fast time window. The weak emission spectrum recorded with the slow time window has a peak corresponding to the $^1P_1 \rightarrow ^1S_0$ transition and two additional small contributions. The one around 10.0 eV corresponds to the $^3P_1 \rightarrow ^1S_0$ transition. The broad emission centered at 9.3 eV is due to the decay of the Kr*Ar $\Omega = 1(^3P_2)$ exciplex [12]. The 1P_1 emission appearing in Fig. 2(b) is actually the tail of the fast component at times included in the slow window. This is demonstrated in Fig. 3(a) which exhibits the decay curve associated with the 1P_1 emission. As evident from the figure, almost all the decay occurs according to a quasisingle exponential law with a decay time of $\tau \approx 4$ ns. This time is slightly longer than the Kr 1P_1 atomic radiative lifetime

FIG. 2. Emission spectrum recorded after excitation at 10.63 eV (1P_1). (a) Fast component; (b) slow component. The sample density and temperature are $1.8 \times 10^{21} \text{ cm}^{-3}$ and 305 K, respectively. The Kr concentration is 1 ppm.

FIG. 3. Time resolved emission of (a) Kr (1P_1); and (b) Xe (1P_1) in argon. The sample densities and concentrations are (a) $1.7 \times 10^{21} \text{ cm}^{-3}$ and 1 ppm; (b) $1.8 \times 10^{21} \text{ cm}^{-3}$ and 0.3 ppm.

(3.18 ns [13]). The reason for the longer measured lifetime and the deviation from a pure exponential decay is a residual radiation trapping effect as discussed in Ref. [5] for the Xe*Ar case.

It is illustrative to compare the decay of the Xe $6s'[1/2]_1(^1P_1)$ level to that of the Kr $5s'[1/2]_1(^1P_1)$ level in dense argon gas since the radiative lifetimes in the isolated atom are only slightly different [13]. Figure 3(b) displays the decay curve associated with the Xe 1P_1 emission in an argon sample at very similar thermodynamical conditions to those of Fig. 3(a). As opposed to the results presented in Fig. 3(a), two decay times are observed in Fig. 3(b). The faster time contains the quenching from the 1P_1 level to the 3P_0 level. The long decay time is due to the decay of the 3P_0 by means of two parallel channels; endothermal collisions to 1P_1 and emission from this level, and quenching to lower levels as detailed in Ref. [5].

Additional measurements performed under similar thermodynamical conditions and using higher Kr concentrations allowed us to conclude that the $^3P_1 \rightarrow ^1S_0$ emission and the exciplex emission observed in Fig. 2(b) are due to the quenching of the 1P_1 by Kr and not by Ar. Actually, the quenching processes at such high pressures are dominated by three body collisions. From the spectra and from the decay curves we obtain $3.5 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$ for the quenching rate of the 1P_1 due to Kr-Kr-Ar interactions.

An additional and complementary demonstration that the quenching of the 1P_1 is not due to pure interactions with Ar can be obtained from measurements performed at very high argon densities doped, again, with a minimal amount of Kr. Such a sample minimizes the probability of having a Kr atom in the first shell surrounding the excited Kr, or a Kr atom approaching the excited one during its lifetime. Figure 4 shows the luminescence spectrum obtained after exciting into the Kr (1P_1) level in a sample at supercritical density containing only 1 ppm Kr. We note that in this spectrum the time window is set to record

FIG. 4. Emission spectrum recorded after excitation at 10.64 eV (1P_1). The sample density and temperature are $1.2 \times 10^{22} \text{ cm}^{-3}$ and 154 K, respectively. The Kr concentration is 1 ppm.

all emissions occurring between 1 and 482 ns. As shown in the figure only one emission, that from the Kr^*Ar (1P_1) to the ground state, is observed.

The specific behavior reported above, i.e., the absence of quenching of the $\text{Kr } ^1P_1$ by argon, combined with some recent experimental and theoretical results, provides the opportunity to discuss the question of collision induced decay through radiative or nonradiative processes.

Several processes that can explain the quenching of the lower lying atomic levels and their related molecular states have been identified in rare gases:

(i) Changes in transition moment with internuclear separation. These changes have been theoretically predicted [14,15] and experimentally observed in the decay from highly excited vibrational levels of the $1u(^3P_2)$ state to the ground state [16]. In the case of the relaxed excimers, the change results in radiative lifetimes to the ground state of 100, 265, and 3150 ns for Xe, Kr [7], and Ar [17], respectively. An example of a large transition moment change between Kr excited molecular states, $0_g^+(^1P_1)$ and $1_u(^3P_2)$ has been recently proposed on the basis of experimental data [10] and unpublished theoretical results [18].

(ii) Quenching mechanisms that occur at crossings of molecular potentials even when they are not of the same symmetry. This is the reason for the efficient energy transfer from the 3P_1 to the 3P_2 as established in the case of pure rare gases [9,10,19,20]. This is, most probably, also the reason for the efficient $\Omega = 0^-, 1(^3P_2)$ exciplex formation in rare gas mixtures [12,21]. The more familiar case of quenching at avoided crossings between molecular potentials is well known [2].

(iii) Collisional mixing. This process has been invoked in experiments performed at low density and room temperature by several authors [22,23] in connection with the relaxed $^3\Sigma_u^+$ and $^1\Sigma_u^+$ Xe excimer states which are not so far in energy. The process is reversible in nature, and

its temperature dependence is given by an $\exp[-(\Delta/kT)]$ law, where Δ is the energy separation and k is the Boltzmann constant. We point out that the change in the refractive index as a function of the density, and not collisional mixing, explained the change in the Ar and Kr excimer lifetimes from the gas to the solid [7]. The same was found for the Xe excimer lifetime in cold liquid Xe [7]. These results have been recently extended to the Kr^*Ar exciplex [12] showing, again, a purely refractive index dependence versus density of the $1(^3P_2)$ relaxed molecular state lifetime.

To our best knowledge, the transition moments related to the molecular states correlated to the Kr^*Ar (1P_1) have not yet been calculated. Our experimental results demonstrate no significant transition moment increase in the relevant internuclear distances between molecular states correlated to the Kr^*Ar (1P_1) and lower lying excited molecular states in contrast to that discussed in pure krypton [10].

The calculations performed by Spiegelmann, Gadea, and Castex [6] and illustrated in Fig. 1 show that the crossings between the molecular potentials related to the Kr^*Ar (1P_1) and lower lying molecular levels occur at kinetic energies inaccessible in the present experiments. This discards a quenching process as the one discussed in (ii). On the other hand, recent calculations by Hickman, Huestis, and Saxon [24] indicate a short distance energy crossing between the $\text{Xe}^*\text{Ar } \Omega = 1(^1P_1)$ and $\Omega = 0^-(^3P_0)$ levels. This explains the significant differences between the two systems as illustrated in the decay curves displayed in Figs. 3(a) and 3(b).

From the published Kr^*Ar molecular curves [6] one realizes that the only possibility for collisional mixing could be between the 1P_1 and 3P_0 related molecular states along their molecular curves 0^+ and 0^- . Our results indicate that this process is negligible for the energy separations calculated in Ref. [6].

In summary, we have shown experimentally that collisions *per se* cannot quench an excited state. Although this has been demonstrated in a specially selected system, Kr^*Ar , our results show the close connection between collisional quenching efficiency and excited molecular potentials. Furthermore, the present results indicate that theoretical molecular potential curves are a prerequisite in the interpretation of excited state kinetics.

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