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Visible excimer bands of the K–noble-gas and Na–noble-gas molecules: Comparison of experiment with theory

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The visible emission bands from K(5S)Xe, K(5S)Kr, Na(4S)Xe, and Na(4S)Kr excimers have been observed experimentally, the potassium excimers being produced by a violet Kr^+ laser excitation and the sodium excimers by a discharge. These observed profiles are compared with calculated profiles based on Gallagher's quasistatic theory and Pascale's molecular potentials and oscillator strengths. Qualitative conclusions are drawn concerning the shapes and depths of the molecular-potential curves and the accuracies of the computed oscillator strengths. The theoretical emission profile is approximated by an analytical form, and the emission linewidth is predicted to vary as $T^{1/2}$, where T is the absolute temperature. This is verified experimentally for KXe in a limited temperature range.

I. INTRODUCTION

Emission bands from the lower excimer states of alkali-metal–noble-gas molecules (correlated with the lowest excited P alkali-metal atom and unexcited noble-gas atom) have been studied extensively by Gallagher and co-workers[1,2] in the past several years. Recently, emission bands from higher excimer states (correlated with the lowest excited S alkali-metal atom and unexcited noble-gas atom) were observed,[3] and several further investigations of these higher excimer bands have followed. These investigations include emission spectroscopy with selective laser excitation[4-10] or with discharge excitation,[10-12] and absorption spectroscopy.[13,14] However, a quantitative understanding of the line shapes of these higher excimer bands was lacking, although a local part of the CsXe absorption band near the Cs ($5D \leftarrow 6S$) forbidden atomic doublet has been calculated[15] and compared to experimental observation[14] with some success. Recently, Pascale[16] calculated the oscillator strengths of the higher excimer bands correlated with forbidden alkali S-S or S-D transitions, and he reported oscillator strengths as large as 10^{-1} at certain interatomic separations. Using the calculated oscillator strengths[16] and molecular potential curves,[17] Sayer *et al.*[18] have recently calculated some of the higher excimer bands in alkali-metal–noble-gas molecules, and they have made comparisons of the calculated bands with available experimental data. For the case of K–noble-gas and Na–noble-gas bands, only a very rough comparison was made, because the published experimental data[10] were not detailed enough. In this paper, we present some clearer emission profiles in these systems, and we present more detailed comparisons with theoretical profiles. Such comparisons provide a critical test of the calculated molecular potential curves[17] and oscillator strengths,[16] and we shall draw some qualitative conclusions about these calculated parameters.

II. EXPERIMENT AND ANALYSIS

The emission profile of the KG (G being a noble-gas atom) green band near 5200 Å owing to the K(5S)$G \rightarrow$ K(4S)G molecular transition has been reported previously.[10] This green band was excited by the 4579-Å Ar^+ laser line, and the emission profile[10] was somewhat distorted by strong alkali-metal dimer emission bands and by atomic emission lines. We find that a much stronger emission profile of the KG green band can be obtained by exciting with the 4067-Å Kr^+ laser line, which populates the K(5P) excited state through absorption in the noble-gas-induced red wing of the 4045 and 4047-Å resonance doublet. The K(5P) state can undergo either a radiative decay or an excitation-transfer collision and produce the K(5S) excited atom or K(5S)G excited molecules. A strong K(5S)$G \rightarrow$ K(4S)G green band is then produced. The emission spectrum in the visible for the case of KXe, excited by the violet multiline output of a Kr^+ laser (4067 Å at about 140 mW; 4131 Å at about 240 mW and 4154 Å at less than 20 mW) is shown in Fig. 1 for a Xe density of 2.4 amagats (1 amagat $= 2.69 \times 10^{19}$ cm^{-3}) and cell temperature of 253 °C. We note that the entire visible spectrum is dominated by the single green band peaked near 5215 Å.

The origin of the KG green band, as discussed previously,[10] can be understood by examining the molecular potential curves calculated by Pascale and Vandeplanque,[17] and the relevant KXe curves are shown in Fig. 2. Rapid collisions in our high-density systems favor population of the K(5S)Xe

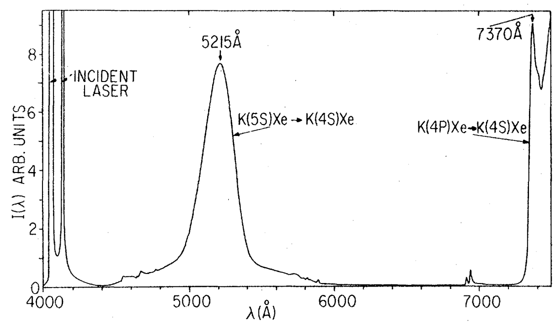

FIG. 1. Visible emission spectrum from a KXe cell (Xe density is 2.4 amagats; cell temperature is 253 °C) excited by the violet Kr^+ laser lines at 4067 Å (140 mW) and 4131 Å (240 mW).

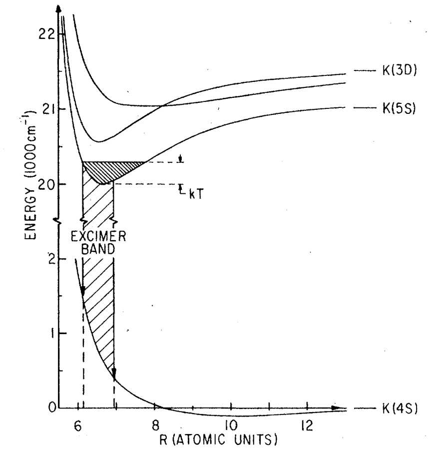

FIG. 2. Relevant theoretical molecular potential curves (from Ref. 17) showing the origin of the green excimer band in KXe. The Boltzmann population of the K(5S)Xe potential well within a depth of $kT \sim 350$ cm^{-1} is indicated. The limits of R for approximately half intensities of the green band are also shown. For larger R, emission intensity rapidly decreases because of vanishing oscillator strength; and for smaller R, emission intensity also rapidly decreases because of vanishing Boltzmann population in the K(5S)Xe state.

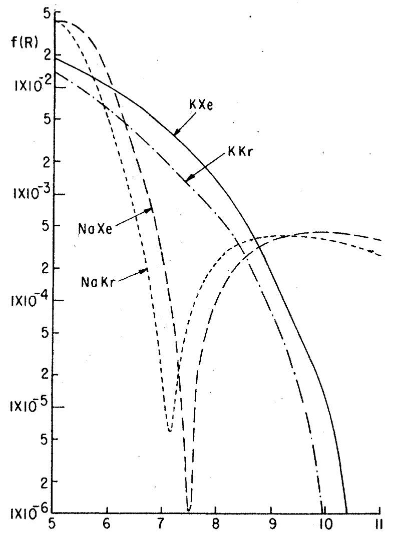

FIG. 3. Theoretical oscillator strength $f(R)$ calculated by Pascale (Ref. 16) for the K(5S)G → K(4S)G and for the Na(4S)G → Na(3S)G transitions.

potential curve near the bottom of the well, and this population can radiate either to the K(4P)Xe states (radiation bands in the ir) or to the K(4S)Xe dissociative ground state (green excimer band). While the K(5S)Xe → K(4S)Xe transition is highly forbidden for large interatomic separation R, it is strongly allowed near the bottom of the potential well. [A very similar emission band is the Xe-induced green band in oxygen, O(^1S)Xe → O(^1D)Xe, which has received much attention because it is a proven[19] lasing transition.] The relevant calculated oscillator strengths[16] f are shown in Fig. 3. For KG, we see that f decreases rapidly with increasing R, and at $R > 10$ a.u., f becomes $<1\%$ of the oscillator strength at the bottom of the potential well (at $R \approx 6$ a.u.). Hence the excimer band we observed [K(5S)G → K(4S)G for the case of potassium] is bound on the red side (small R) by the Boltzmann factor in the upper-state population, and on the blue side (large R) by vanishing f.

The emission intensity $I(\nu)$ at frequency ν owing to the K(5S)G → K(4S)G molecular transition can be calculated by the quasistatic theory of Gallagher and co-workers,[1,2] as done by Sayer *et al.*[18]:

$$I(\nu)\,d\nu = a\,N_u N_g\,\nu^3 f(R)\,R^2\,dR \times \exp\{[V^*(\infty) - V^*(R)]/kT\}, \tag{1}$$

where a is a constant, N_u and N_g are the K(5S) and Xe atomic densities, respectively, and $V^*(R)$ is the K(5S)G potential energy at separation R. The calculated green bands for KXe and KKr are found to be rather similar in shape to the observed green band, except for two points: (a) the calculated band peak is on the blue side of the observed peak: the discrepancy is about 55 Å for KXe and about 60 Å for KKr; since the calculated ground-state potential curve [K(4S)G] is believed to be fairly accurate,[2] this indicates that the theoretical K(5S)G potential well is not deep enough, and it should be deeper by about 200 cm^{-1} for KXe and by about 230 cm^{-1} for KKr to bring the predicted peak position into agreement with experiment; (b) the predicted linewidths (315 Å for both KXe and KKr) are noticeably broader than the observed line-widths (260 Å for

KXe and 240 Å for KKr); this may indicate that the calculated upper-state potential well is too broad. The comparison is shown in Fig. 4, where the theoretical emission profiles have been red-shifted by 200 cm^{-1} for KXe and by 230 cm^{-1} for KKr to facilitate comparison with experimental profiles. Despite the difference in widths, the theoretical calculations do predict a rather structureless band with a slight asymmetry (falling off faster on the red side) in agreement with experimental observations.

Further understanding of this type of excimer emission band can be gained in a less accurate but more analytical approach by expanding Eq. (1) near the equilibrium separation R_0, where the upper-state potential V^* is a minimum. Let us approximate $V^*(R)$ near R_0 by a parabola (simple harmonic oscillator):

$$V^*(R) = -D + \tfrac{1}{2}K(R-R_0)^2 + V^*(\infty)\,, \tag{2}$$

where D is the dissociation energy measured from the bottom of the potential well and K is the "spring constant" of the harmonic oscillator. Now, the first-order expansion of the emitted frequency ν is

$$\nu(R) = \nu_0 + (R-R_0)\frac{d\nu}{dR}\,, \tag{3}$$

where $\nu_0 = \nu(R_0)$. Substituting (3) into (2), we get

$$V^*(R) = -D + \tfrac{1}{2}K(\nu-\nu_0)^2\left(\frac{d\nu}{dR}\right)^{-2} + V^*(\infty)\,. \tag{4}$$

Substituting (4) into (1) and using first-order expansion for $\nu^3 f R^2 (d\nu/dR)^{-1}$, we have

$$\begin{aligned} I(\nu) &\approx \text{const} \times \left\{1 + (R-R_0)\frac{d}{dR}\ln\left[\nu^3 f R^2\left(\frac{d\nu}{dR}\right)^{-1}\right]\right\} \exp\left[-\tfrac{1}{2}K(\nu-\nu_0)^2\left(\frac{d\nu}{dR}\right)^{-2}\Big/kT\right] \\ &\approx \text{const} \times \exp\left[\frac{(\nu-\nu_0)}{d\nu/dR}\frac{d}{dR}\ln\left(\frac{\nu^3 f R^2}{d\nu/dR}\right) - \tfrac{1}{2}K(\nu-\nu_0)^2\left(\frac{d\nu}{dR}\right)^{-2}\Big/kT\right] \\ &= \text{const} \times \exp\frac{-(\nu-\nu_0-\delta\nu_0)^2}{2kT(d\nu/dR)^2/K}\,, \end{aligned} \tag{5}$$

where the line shift is

$$\delta\nu_0 = \frac{kT}{K}\frac{d\nu}{dR}\frac{d}{dR}\ln\frac{\nu^3 f R^2}{d\nu/dR}\,. \tag{6}$$

Using the following values for the parameters in Eq. (6) (based on Pascale's potential curves[17]): $K \approx 10\,000\ \mathrm{cm}^{-1}/\text{Å}^2$, $d\nu/dR \approx 1500\ \mathrm{cm}^{-1}/\text{Å}$, $d(\ln f)/dR \approx -2\ \text{Å}^{-1}$, and neglecting $d\ln[\nu^3 R^2/(d\nu/dR)]/dR$, we estimate that $\delta\nu_0 \approx -0.1T\ \mathrm{cm}^{-1}$ for KXe, where T is the temperature in °K. This is not large in the range of temperatures we have studied (about 150–250 °C) and it has not been unambiguously observed. The full width at half maximum w of the emission profile, according to (5), is

$$w = 1.7\left(\frac{2kT}{K}\right)^{1/2}\frac{d\nu}{dR}\,. \tag{7}$$

Again, using $K \approx 10\,000\ \mathrm{cm}^{-1}/\text{Å}^2$ and $d\nu/dR \approx 1500\ \mathrm{cm}^{-1}/\text{Å}$, we estimate that $w \approx 600\ \mathrm{cm}^{-1}$ at 250 °C for KXe. This can be compared with an experimental full width at half maximum for KXe of 960 cm^{-1}. Furthermore, Eq. (7) predicts that w should increase as $T^{1/2}$; this is found experimentally to be approximately the case. For example, the measured full widths of the green band of KXe at 2.4 amagats Xe for various cell temperatures are listed in Table I, and $w/T^{1/2}$ is observed to be constant to within our experimental error for the

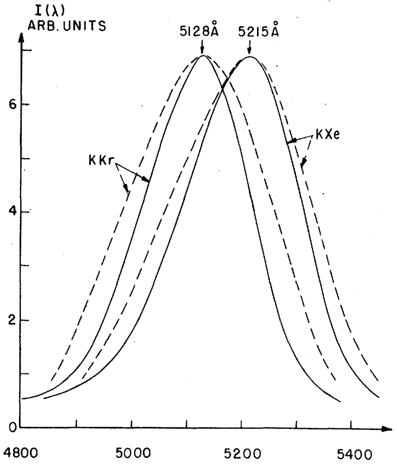

FIG. 4. Full lines indicate experimental emission profile from the $K(5S)G \rightarrow K(4S)G$ transition due to violet Kr^+ laser excitation: for KXe, the Xe density is 2.4 amagats and cell temperature is 253 °C; for KKr, the Kr density is 5.1 amagats and the cell temperature is 250 °C. Peak positions of the observed bands are given. Note that the forbidden atomic $K(5S) \rightarrow K(4S)$ transition is at 4754 Å. The dashed lines represent calculated profiles according to Eq. (1): for KXe, the calculated profile has been red-shifted by 200 cm^{-1}; and for KKr, the calculated profile has been red-shifted by 230 cm^{-1}.

TABLE I. Variation of the experimental linewidth w (full width at half maximum) of the green KXe excimer band with cell temperature. Xe density is 2.4 amagats.

w (Å)	235	246	252	259
Temperature (°C)	148	185	216	253
$T^{1/2}$ ($K^{1/2}$)	20.5	21.4	22.1	22.9
$w/T^{1/2}$ (Å/$K^{1/2}$)	11.45	11.5	11.4	11.3

temperature range of 148–253 °C. Thus we conclude that the analytical emission profile given by Eq. (5) is a rough but useful form for understanding the shape of the visible excimer bands in KG or NaG molecular systems.

We have also calculated the emission profile according to Eq. (1) for the blue excimer bands of NaG owing to the Na(4S)G → Na(3S)G molecular transitions. These bands have been observed in Na–noble-gas discharges as reported previously,[10] and presumably these blue bands will be much stronger if the Na–noble-gas system can be excited with a laser line of wavelength near the second resonance doublet at 3302 and 3303 Å (similar to the laser excitation of KG discussed above). Such a laser line not being available to us yet, we use the previously reported profile[10] for comparison with theory. One problem with the calculation of the NaG blue band is that Pascale's theoretical oscillator strength[16] of NaG (see Fig. 3) undergoes a strong minimum at $R \approx 7.5$ a.u. and it varies by more than three orders of magnitude within 0.5 Å. This strong variation is definitely unusual, and one might expect the variation of the oscillator strength of NaG to resemble that of KG. Hence, in Eq. (1), we have calculated $I(\nu)$ with two sets of oscillator strengths, one being the calculated NaG, and the other being the calculated KG oscillator strengths. The resultant spectrum $I(\nu)$ is found to resemble the observed spectrum only for the latter case (e.g., for NaXe the observed emission band linewidth is 230 Å, while the theoretical linewidth is 160 Å in the former case and 235 Å in the latter case). Hence we conclude that the NaG oscillator strengths may be similar to the calculated KG oscillator strengths given in Fig. 3. The comparison of the calculated blue emission bands of NaG, using either the calculated NaG oscillator strengths or the calculated KG oscillator strengths, with the observed blue NaG emission bands is shown in Fig. 5, where the calculated profiles have been red-shifted by amounts indicated in the figure caption. The calculated profiles using the gently varying KG oscillator strengths agree very well with the observed profiles, but not those calculated using the abruptly varying NaG oscillator strengths.

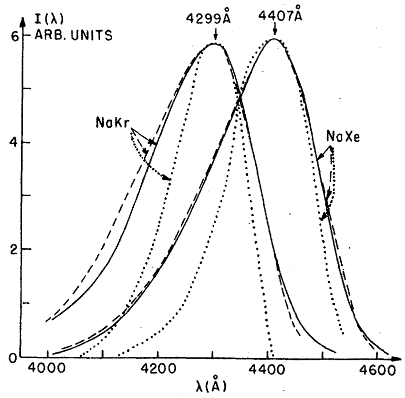

FIG. 5. Solid lines are experimental profiles from the Na(4S)G → Na(3S)G transition due to discharge excitation, reported previously (Ref. 10): for NaXe, the Xe density is 0.58 amagats and for NaKr, the Kr density is 0.86 amagats. Cell temperature is ≈ 150 °C. The forbidden atomic Na(4S) → Na(3S) transition is at 3884 Å. The dashed lines are calculated profiles (red-shifted by 735 cm^{-1} for NaXe and by 445 cm^{-1} for NaKr), using Pascale's calculated KG oscillator strengths. The dotted lines are calculated profiles (red-shifted by 470 cm^{-1} for NaXe and by 200 cm^{-1} for NaKr), using Pascale's calculated NaG oscillator strengths.

We note that the theoretical Na(4S)G potential well[17] is much narrower than the K(5S)G potential well [e.g., the half width of the Na(4S)Xe well is 3.4 a.u., while that of the K(5S)Xe is 5.0 a.u.], and this may explain why the predicted profiles are too broad for the KG cases but not for the NaG cases.

III. CONCLUSION AND DISCUSSION

The visible excimer band in an alkali-metal–noble-gas system correlated with the lowest forbidden S-S atomic transition is very strong compared to the other excimer bands (except those bands[1,2] in or near the ir correlated with the lowest P-S resonance doublet); this visible excimer band frequently dominates the entire visible spectrum for selective laser excitation in the case of Xe (Ref. 3, and present work for KXe), and it is also a very prominent feature for other noble gases or for other experimental configurations (e.g., discharges[10–12] or absorption measurements[13,14]). In this paper, we have attempted to make a semiquantitative comparison of the calculated profiles of such visible excimer bands with experimental observations for the cases of KG and NaG. We have calculated the visible excimer emission bands due to the K(5S)G → K(4S)G and Na(4S)G → Na(3S)G molecular transitions, using Gallagher's quasistatic theory and Pascale's potentials and oscillator strengths. In all cases studied, the upper-state potential well is found to be too shallow, and they should be deeper by about 200, 230, 735, and 445 cm^{-1} for the K(5S)Xe, K(5S)Kr, Na(4S)Xe, and Na(4S)Kr molecular excited states, respectively, in order to produce the observed peak positions of the emission profiles. A similar conclusion was drawn by Sayer *et al.*[18] The predicted linewidth is too broad by about 25% for the green KG excimer bands; this may be owing to the calculated K(5S)G potential curves being too broad. The calculated Na(4S)G emission linewidths are in excellent agreement with the observed blue band linewidths if the oscillator strengths in the NaG system are taken to be the calculated oscillator strengths[16] in the KG system.

The case of Na(4S)Xe is probably the most interesting, because the strong binding in the upper state (estimated as 1900 cm^{-1} at the equilibrium separation R_0) and the strong repulsion of the lower state (1150 cm^{-1} at R_0) and the large value for the oscillator strength (~10^{-2}) at R_0 greatly favor the Na(4S)Xe → Na(3S)Xe transition for possible excimer laser applications similar to the O(^1S)Xe → O(^1D)Xe case.[19]

By approximating the theoretical emission profile in an analytical form, we have predicted that the visible excimer band linewidth w should increase with temperature roughly as $T^{1/2}$. This prediction is borne out in our experimental observations for KXe in a limited temperature range. A line shift δV_0 proportional to T is also predicted but not clearly observed.

We have been concerned only with the main emission band in the KG or NaG system, at $R \sim 6$ a.u. A much weaker satellite band has been predicted[18] very near the forbidden atomic S-S transition, owing to the upper and lower adiabatic potential curves being parallel at $R \sim 11$ a.u. Perhaps one of the small peaks near 4700 Å in Fig. 1 is actually this predicted weak satellite band.

In the present investigation, we have studied only relatively low noble-gas densities, where mainly binary molecules are important. We found that at high Xe densities (e.g., 10 amagats) and low cell temperatures ($\lesssim 150$ °C), polyatomic exciplex molecules K(5S)Xe$_n$ (with n being 2, 3, or 4 mainly) become very important radiating species in the KXe system excited by the 4067-Å Kr$^+$ laser line. Such exciplex radiation occurs in the spectral region of 5400–6400 Å, and the study of these exciplexes shall be reported elsewhere.

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