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Strong New Emission Bands in Alkali-Noble-Gas Systems*

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Strong new visible emission bands are observed when mixtures of Cs of Rb with noble gases are excited with blue lines of an argon-ion laser. The bands in Cs are believed to be due to transitions between $7s\sigma$ bound excited states and dissociating $6s\sigma$ ground states of alkali-noble-gas molecules, and they may have potential for excimer laser systems.

The emission and absorption spectra of alkali-noble-gas systems have been the subject of detailed investigation over a period of many years. Therefore, we were very surprised recently to discover that when we illuminated Cs vapor in a few atmospheres of Xe with any one of several blue lines from an argon-ion laser we observed a striking yellow fluorescence which has apparently never before been observed. We at first mistook this to be resonance fluorescence from a sodium impurity. A check with a grating monochromator, however, revealed that a large fraction of the emission from the vapor in the entire spectral region from the violet to the near infrared (9000 \AA), which includes the first two resonance doublets, was concentrated in a single band about 50 \AA wide, peaked at 5723 \AA , which did not correspond to any known feature of the Cs-Xe spectrum. Similar bands were observed at slightly different wavelengths with other noble gases. These bands are not present in the emission from pure Cs vapor with similar excitation and no corresponding feature has been observed in optical-absorption studies of similar Cs-noble-gas mixtures.¹ The existence and surprising intensity of the emission bands we observe may have significance for laser applications,² and a detailed analysis of their structure should provide extensive information about molecular potential curves and transition moments of previously unknown bound excited states.

Typical emission spectra, recorded with a

scanning monochromator with a resolution of 1 \AA and an extended S-20 photomultiplier tube, are shown in Fig. 1. To obtain these spectra, cells of alkali-resistant glass (Corning 1720) were

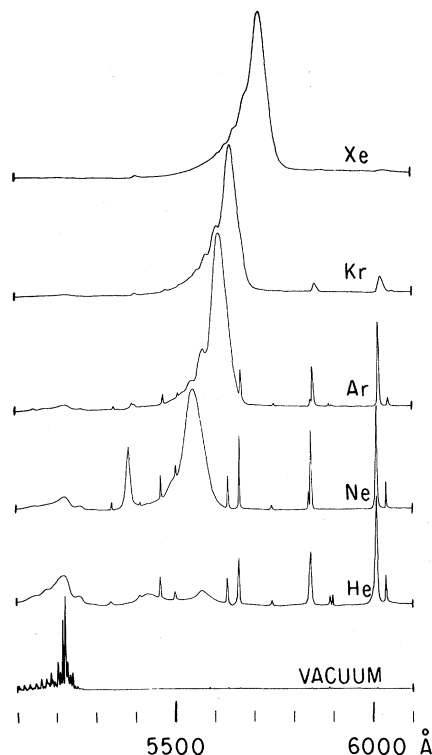


FIG. 1. Yellow emission bands of cesium in noble gases.

baked at 500°C under a vacuum of 10^{-6} Torr, then filled with cesium and a noble gas. The cells were then placed in an oven and illuminated with an argon-ion laser. For all the data shown in Fig. 1 the excitation was by the 4579-Å Ar^+ line with an intensity of 220 mW focused into a beam diameter of approximately 0.005 cm. The noble-gas pressure was approximately 3 atm at room temperature and the cell temperature was 310°C.

Molecular Cs_2 bands^{1,3} are visible in Fig. 1 near 5200 Å and a number of atomic-cesium lines are also visible, as reported by McClintock and Balling.⁴ The dominant features of the spectrum for the heavier noble gases, however, are the yellow emission bands, whose peak wavelengths shift systematically toward the red for the heavier noble gases. The peaks occur at approximately 5548, 5616, 5648, and 5723 Å in Ne, Ar, Kr, and Xe, respectively. In Ne an additional prominent narrow peak occurs at 5383 Å, and less prominent but noticeable peaks also occur around 5400 Å for Ar, Kr, and Xe. Helium is clearly different from the other noble gases; the two weak bands at approximately 5425 and 5570 Å are apparently due to Cs_2 dimers, since they can also be observed when no noble gas is present. Dimer emission bands in cells with noble gas can also be distinguished from the yellow bands of interest since, in contrast to the yellow bands, the dimer bands vanish very rapidly at lower cell temperatures or when the vapor is superheated. In addition, the shape of the dimer bands is strongly dependent on the wavelength of the exciting light, while the shape of the yellow emission bands is independent of this wavelength.

The relative intensities of the emission bands shown in Fig. 1 were 1, 3, 11, and 88 for Ne, Ar, Kr, and Xe, respectively. A part of this striking increase in intensity for the heavier noble gases is the result of the variation in the amount of 4579-Å laser light absorbed, which was 12%, 17%, 30%, and 70% for Ne through Xe, respectively. The path length in the vapor was 2.1 cm. The yellow bands were excited most strongly by the 4579-Å line, but substantial excitation could also be produced by other laser lines. Strong nonthermal self-defocusing of the laser beam was observed for some lines. The resonance fluorescence at 4555, 4593, 8520, and 8943 Å was strongly self-absorbed. The band intensity was approximately proportional to the intensity of the laser light in the limit of low laser intensity. This implies that the bands do not in-

volve multiphoton or stepwise excitation by the laser. The band intensity also increased at least linearly with increasing noble-gas pressure.

The yellow band occurs just to the red side of the forbidden $7s$ - $6s$ cesium atomic transition. We believe that the band arises from a transition between a bound $7s\sigma$ Cs-noble-gas excited molecular state and a dissociative $6s\sigma$ ground state. The general properties of such bound-free transitions are well known.⁵ There seems to be no spectroscopic datum on the $7s\sigma$ potential and the only theoretical potential of which we are aware was recently calculated by Pascale and Vandepanque.⁶ We have reproduced several of their potentials in Fig. 2. It is reasonable to associate the strong yellow bands with radiative transitions occurring at small internuclear separations R where the transition moment for the $7s\sigma$ - $6s\sigma$ transition is large, while the weak peaks around 5400 Å are associated with large R where the transition moment is more nearly zero. The structures in the blue wings of the bands for the heavier gases (Fig. 1) could be due to the vibrational states of the bound excited $7s\sigma$ state. The absence of noticeable emission bands for helium is consistent with a repulsive molecular potential curve for the $7s\sigma$ state of CsHe . However, the fairly well developed band for neon may indicate that the $7s\sigma$ potential of CsNe is attractive, rather than repulsive as indicated by theory.⁶

We were also able to observe broad, weak

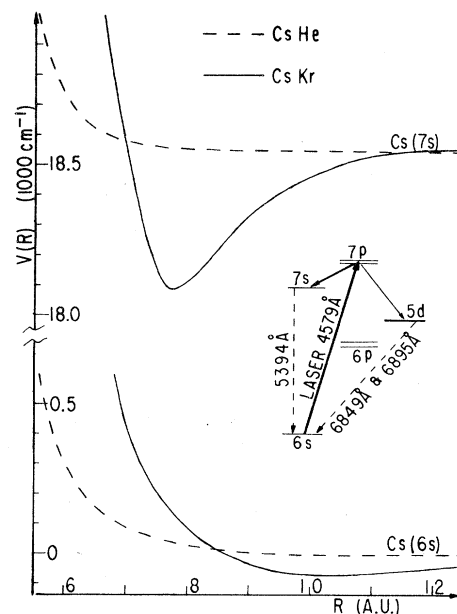


FIG. 2. Typical molecular-potential curves, from Ref. 6.

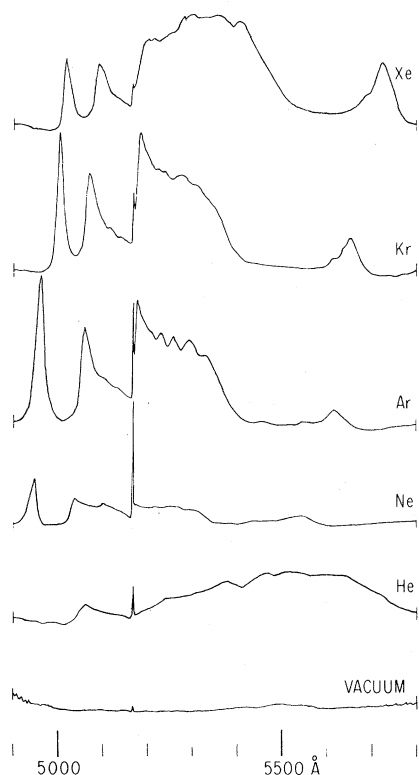


FIG. 3. Green emission bands of rubidium in noble gases.

emission bands extending for several hundred angstroms on either side of the forbidden $5d-6s$ transitions, which were visible as sharp lines at 6849 and 6895 Å. These bands were much less striking than the yellow bands of Fig. 1 and they were partially obscured by Cs_2 emission bands and by atomic Cs lines.

We have made similar studies of Rb. Green emission bands were observed near the 4966-Å $6s-5s$ and 5165-Å $4d-5s$ forbidden transitions and typical data obtained with 4579-Å excitation at about 350°C are shown in Fig. 3. The noble-gas pressure was approximately 3 atm. The green bands of Rb are considerably more complicated than the yellow bands of Cs. This is qualitatively what one would expect since the $6s$ and $4d$ states of Rb are nearly degenerate, and pronounced avoided crossings can be expected to occur in the molecular potential curves.⁶ The narrow 5165-Å forbidden $4d-6s$ atomic transition is visible in all of the data of Fig. 3. The yellow Cs bands can also be seen in Fig. 3, even though the Cs contamination of our Rb sample was only 80 ppm.

Absorption spectra with features very similar to our emission spectra of Fig. 3 were obtained

by Besombes, Granier, and Granier.⁷ They associated the absorption bands solely with the forbidden $5d-5s$ transition, ignoring any possible $6s-5s$ contribution. Our data for Cs (Fig. 1) strongly suggest that emission bands associated with $s-s$ transitions in the alkali atoms can be more intense than those associated with $d-s$ transitions, which have heretofore received exclusive attention.⁸

It is natural to expect that similar bands exist for K, Na, and Li. We may also assume that the bands are accompanied by strong emission bands in the infrared due to transitions between molecular terms associated with the lowest excited s and p atomic states. Since some of these bands will involve transitions between discrete molecular states, an analysis of the vibrational structure should yield very precise information about some of the same molecular-potential curves studied by Hedges, Drummond, and Gallagher⁹ as well as unique information about the still unmeasured potential curves for the $7s\sigma$ state of Cs-noble-gas pairs.

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