The Cd*$_2$ excimer: Fluorescence band shape and decay rates

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Recent interest in HgCd as an excimer laser molecule[1] has created a need for better knowledge of the Cd$_2$ excimer. In this Note we report the visible fluorescence spectra and discuss its temperature and pressure dependence as well as some preliminary measurements of the decay rate for this fluorescence.

Figure 1 shows the fluorescence band from the low-est radiating excimer state (i.e., a state originating from the 5 $^3P_1$ atomic asymptote), while Figure 2 shows the observed decay times for the fluorescence following pulsed excitation. Following the procedure used in previous work on mercury,[2] the Cd was carefully prepared in quartz cells and excited by optical radiation in the wings of the atomic intercombination line at 326 nm. The steady state spectra were produced using cw exci-
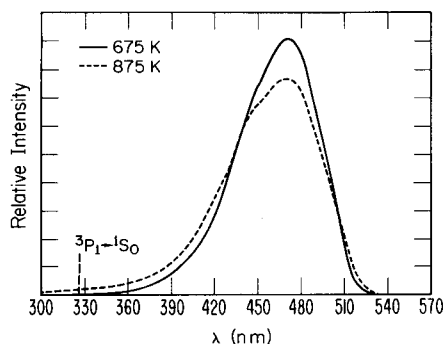
FIG. 1. The Cd_2^* fluorescence band shape; normalized to unit area and calibrated in relative units of quanta per unit wave length per unit time.

FIG. 2. The observed decay times for the Cd_2^* fluorescence following pulsed excitation.

tation from a He–Cd laser operating at 325 nm. Note that this excitation lies some 100 cm^{-1} to the *blue* of the resonance line but its effectiveness as a pump shows that it lies within the pressure broadened wing of the line. A search of Ref. 3 has revealed a total lack of detailed, quantitative information about the self broadening of this Cd 326 nm line. The decay data were produced by using the 10 ns pulse from a nitrogen laser at 337.1 nm for excitation and observing the total fluorescence through a wide band filter (470±20 nm).

The Cd_2^* (excimer) fluorescence band shape showed no pressure dependence at the densities we observed ($N \geq 10^{18}$/cc) but did show the broadening and shifting with temperature one would expect from a thermalized excimer population (see Ref. 2). Figure 1 shows the spectra at two different temperatures, normalized to unit area to show the broadening and calibrated in relative units of quanta per unit wavelength per unit time. The band is typified by the marked shoulder at about 450 nm, mild undulations between 390–420 nm (not visible on the scale of Fig. 1) and a precipitous decrease on the red side. The only sign of the trimer band analogous to the mercury visible band, was a low flat emission observed at lowest temperatures and highest pressures to extend to the red beyond 650 nm. The intensity at this radiation relative to the dimer band did scale linearly with pressure as it should for a trimer in equilibrium with its dimer parents. The trimer may have been observed in matrix isolation[4] with a band centered at 645 nm.

The decay data of Fig. 2 show a strong dependence on both temperature and pressure. Following the pulsed excitation, the fluorescence intensity shows a fast "spike," then a slower rise to the main fluorescence and finally an exponential decay. The decay from 0.1–5τ (decay period) is a simple exponential within the accuracy of our data ($< 1\%$ deviation). These decay times, when plotted on a $-\ln\tau$ vs $1/kT$ plot again in analogy to the mercury work,[5] gave slopes of approximately 1 eV, the meaning of which is not understood at this time. The intensity "spike" and subsequent rise of the fluorescence band intensity observed at early time (0–0.1τ) may be indicative of rapid dissociation of the
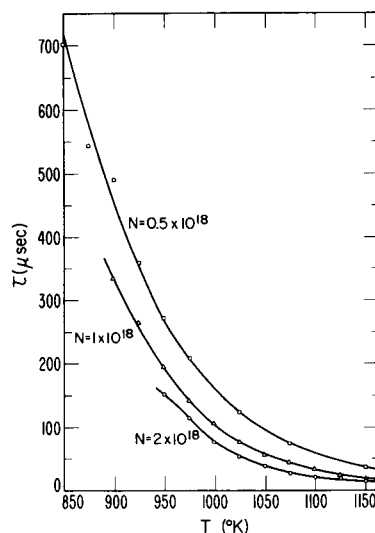
initially formed vibrationally hot excimers and subsequent reformation by three body recombination. This process has been observed in the case of Hg_2^* formed in a similar way.[5-7] However, time resolved spectra of the Cd_2^* band show the radiation at very early times (during the "spike") is dominated by atomic line emissions produced by a small amount of multiphoton excitation during the laser pulse. Therefore, the rapid dissociation and subsequent recombination before thermalization and emission is not conclusively demonstrated in this case. And before one attempts to use this early time behavior for the analysis of recombination and vibrational relaxation rates, proof of the mechanism would have to be obtained, for example, by observing the atomic $5\,^3P_1$ or $5\,^3P_0$ populations.

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[1] G. R. Fournier and M. W. McGeoch, Optics Commun. **18**, 121 (1976); also M. W. McGeoch and G. R. Fournier, J. Appl. Phys. (to be published).

[2] R. E. Drullinger, M. M. Hessel, and E. W. Smith, J. Chem. Phys. **66**, 5656 (1977) and Earl W. Smith, R. E. Drullinger, M. M. Hessel, and J. Cooper, *ibid.* **66**, 5667 (1977).

[3] J. R. Fuhr, W. L. Wiese, and L. J. Roszman, Natl. Bur. Stand. (U.S.) Spec. Pub. 366, Suppl. 1 and 2.

[4] H. J. Vreede, R. F. C. Claridge, and L. F. Phillips, Chem. Phys. Lett. **27**, 1 (1974).

[5] M. Stock, E. W. Smith, R. E. Drullinger, M. M. Hessel, and J. Pourcin, "Analysis of the Decay of Molecular Fluorescence in Optically Excited Mercury Vapor," J. Chem. Phys. **68**, 1785 (1978).

[6] M. Stock, E. W. Smith, R. E. Drullinger, and M. M. Hessel, "Relaxation of the Mercury $6\,^3P_0$ and $6\,^3P_1$ States", J. Chem. Phys. **67**, 2463 (1977).

[7] M. Stock, E. W. Smith, R. E. Drullinger, and M. M. Hessel, "Relaxation of the First Excited 1_u State of Hg_2," J. Chem. Phys. (accepted).