Structure of Xe 6*s* Rydberg States in Supercritical Ar

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Previous photoabsorption studies [1-4] of the energy and intensity of the Xe 6*s* Rydberg transition in supercritical argon presented the energy shift and lineshape changes induced by the perturber number density. The appearance of two blue satellite bands was explained as arising from the formation of stable ground state XeAr dimers and XeAr excimers. However, these former studies did not explore the temperature dependence of the Xe 6*s* transition near the critical density and temperature of the perturber. Moreover, the asymmetric experimental lineshape was inaccurately modeled by assuming a symmetric Gaussian lineshape [3-4]. Recently, Egorov, *et al*. [5] have presented a new approach to modeling the 6*s* Rydberg state of CH_3I in argon. Here, the absorption lineshape of a Rydberg transition is given by

$$I(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\; e^{-i\,\omega\,t}\left\langle e^{i\,\omega(R)\,t}\right\rangle \quad = \quad \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\; e^{-i\,\omega\,t}\left(e^{A_1(t)+A_2(t)+\cdots}\right) \quad ,$$

where $A_1(t)$ and $A_2(t)$ are dependent on (i) the density of the perturber, (ii) the distribution of the perturber around the dopant, and (iii) the ground and excited state dopant/perturber intermolecular potentials. In the present paper, we present lineshape simulations for the Xe 6s Rydberg state doped into argon that include the primary Xe 6*s* transition and the two satellite bands using the Egorov model with appropriate ground and excited state potentials. These simulated lineshapes are compared to photoabsorption spectra obtained by us from low argon number density to the density of triple point liquid, at both noncritical temperatures and near (+0.5°C) the critical temperature of argon. The term energy for the Xe 6*s* Rydberg state doped into supercritical argon is analyzed as a function of argon number density for noncritical temperatures and on an isotherm near the critical temperature to show the striking perturber critical point effect on low-*n* dopant electronic transitions.

References

1. M. C. Castex, J. Chem. Phys. **66**, 3854 (1977).
2. D. E. Freeman, K. Yoshino, and Y. Tanaka, J. Chem. Phys. **67**, 3462 (1977)
3. I. Messing, B. Raz, J. Jornter, J. Chem. Phys. **66**, 2239 (1977).
4. I. Messing, B, Raz, J. Jortner, J. Chem. Phys. **66**, 4577 (1977).
5. S. A. Egorov, M. D. Stephens, J. L. Skinner, J. Chem. Phys. **107**, 10485 (1997).

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