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On the excitation of the krypton 123.6 nm emission by metastable argon atoms

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In studies of chemiluminescent excitations, or of excitations produced in energy-transfer reactions, it is generally desirable to determine absolute excitation rate coefficients for the reaction under study. In general, the easiest method for doing this is to compare intensities of emissions from the reaction under study with those produced from a standard reaction, the excitation rate coefficient of which is already known. In chemiluminescence studies, the role of the standard reaction has been filled admirably by the O/NO continuum emission, the intensity and spectral distribution of which has been shown to depend only upon the concentrations of O and NO, but not upon pressure in the range of 0.1–12 torr.^{1–3} In the case of energy transfer reactions involving metastable argon atoms, the $\text{Ar}^* + \text{Kr}$ reaction has been shown to serve as a useful standard reaction, both in the visible-infrared and in the vacuum ultraviolet.^{4–6} In the near infrared, it was shown that the emission intensities of the lines of krypton which were excited by metastable argon did show a slight dependence on neutral argon pressure even at pressures as low as 1 torr.⁵ However, this pressure dependence has been characterized so that corrections may be made. It turns out that in the vacuum ultraviolet, the intensity of emission of the 123.6 nm transition does not show a significant pressure dependence in the range of 0.5–8 torr. We wish to show why this is so. In addition, we wish to correct several errors which appeared in the detailed discussion by Gundel *et al.*⁶ on the excitation of the 123.6 nm transition of krypton by metastable argon atoms.

Two excited states of krypton, $5p\left[\frac{3}{2}\right]_{2,1}$, are the primary products from the interaction of Kr with $\text{Ar}(^3P_2)$.⁵ Col-

lisional cascade from these two states populates the $5p\left[\frac{3}{2}\right]_{3,2}$ levels. Figure 1 shows the energies of these

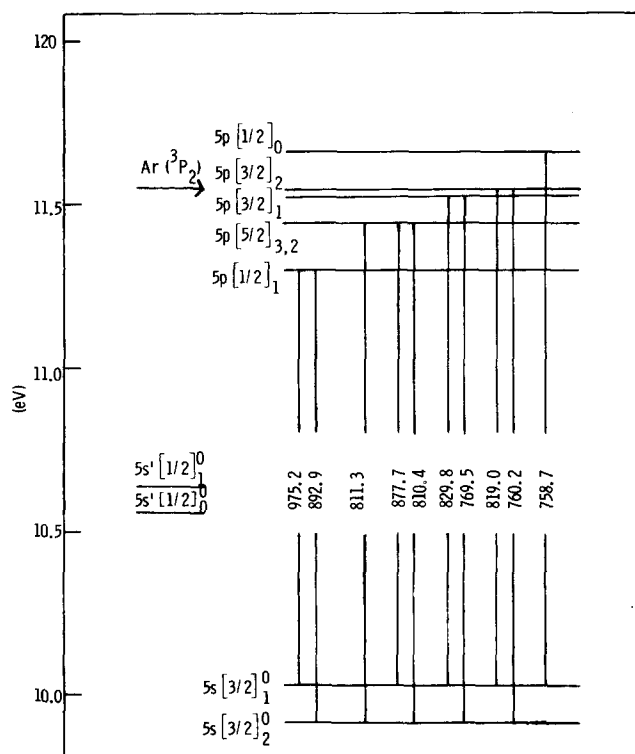


FIG. 1. Energies of the Kr $5p$ and $5s$ and $\text{Ar}(^3P_2)$ levels and the wavelengths, in nm, of radiative transitions coupling the $5p$ to the $5s$ levels. Radiative transitions from $5p$ to $5s'$ levels are unimportant and have been ignored.

states and the wavelengths of emissions from them. Three of these levels are radiatively connected to the $5s[3/2]_1$ level of krypton (which radiates to the ground state at 123.6 nm), so we must consider the pressure dependence of the relative populations of these levels in order to see how the emission intensity from the $5s[3/2]_1$ level may be affected by pressure:

$$\frac{I_{123.6}}{I_{\text{total}}} = F_{5p[3/2]_2} \frac{I_{5p[3/2]_2}}{I_{\text{total}}} + F_{5p[3/2]_1} \frac{I_{5p[3/2]_1}}{I_{\text{total}}} + F_{5p[5/2]_2} \frac{I_{5p[5/2]_2}}{I_{\text{total}}} \quad (1)$$

where the I 's represent the total emission intensities from the subscripted Kr levels and the F 's are the fraction of the radiative cascade from a given level which populates the Kr $5s[3/2]_1$ state. Kinetic expressions for the intensity ratios on the right hand side of Eq. (1) as a function of bulk argon pressure have been given previously.⁵

Murphey's calculations⁷ have shown that the contribution to the total radiative rate from the $5p$ levels to the $5s'$ levels of krypton is less than one half per cent. Thus, in order to establish the fraction of emission from a given $5p$ level which radiates to the $5s[3/2]_1$ level, only the ratio of two emission line intensities is required. In our earlier work,⁵ we measured the ratio of 760.2 to 819.0 and 769.5 to 829.8 nm lines to be 3.26 ± 0.15 and 0.158 ± 0.012 , respectively. Thus the fraction of emission from the $5p[3/2]_2$ and $5p[3/2]_1$ levels of krypton which populate the $5s[3/2]_1$ level is 0.235 and 0.864, respectively. These numbers had been quoted erroneously as 0.30 and 0.82.⁶ Murphey's calculations⁸ give 0.245 and 0.849. We were unable to measure the branching ratio for the 877.7 to 810.4 nm lines which connect the $5p[5/2]_2$ level of krypton to the $5s[3/2]_{2,1}$ states. Murphey's calculations indicate that the fraction of emission from the $5p[5/2]_2$ level to the $5s[3/2]_1$ level is 0.649. Any uncertain-

ties in this value are not particularly important since this level contributes less than 3% to the total radiative cascade from the $5p$ levels at pressures below 8 torr.

Using the branching ratios given above and the kinetic expressions from previous results,⁵ we may calculate the fraction of total krypton excitation which radiatively cascades to the $5s[3/2]_1$ level, hence the fraction of total krypton excitation which is observed as emission at 123.6 nm in the vacuum ultra violet. Figure 2 shows a plot of Eq. (1) versus pressure. Also shown in Fig. 2 are the experimental data from the previous study⁵ for the sum of the intensities of all lines connecting the $5p$ and the $5s[3/2]_1$ levels divided by the total observed $5p$ emission intensity as a function of pressure. The cascade ratio is seen to have only a weak pressure dependence. If the experimental data shown in Fig. 1 are averaged, we obtain an average cascade fraction of 0.306 ± 0.006 . This average cascade fraction is of course more convenient to use computationally than the cascade fraction calculated from the kinetic fit and deviates from the fit by less than 1.5% over the pressure range 0.5–9 torr. The cascade ratio quoted by Gundel *et al.*⁶ was 0.36, 18% higher than the present average value. Their quoted ratio was apparently a typographical error as the data in their paper was analyzed using a ratio of 0.30.⁸

Two competing processes occur in the collisional cascade within the $5p$ levels of krypton which effectively cancel each other and thereby maintain the constant ratio of $5s[3/2]_1$ excitation to total excitation as a function of pressure. On the one hand, collisional cascade tends to increase the population of the $5p[3/2]_1$ level relative to the total excited-state population, and this effect favors increased radiative cascade to the $5s[3/2]_1$ level. Balancing this out is the collisional cascade populating the $5p[5/2]_3$ level which does not radiate to the $5s[3/2]_1$ level at all.

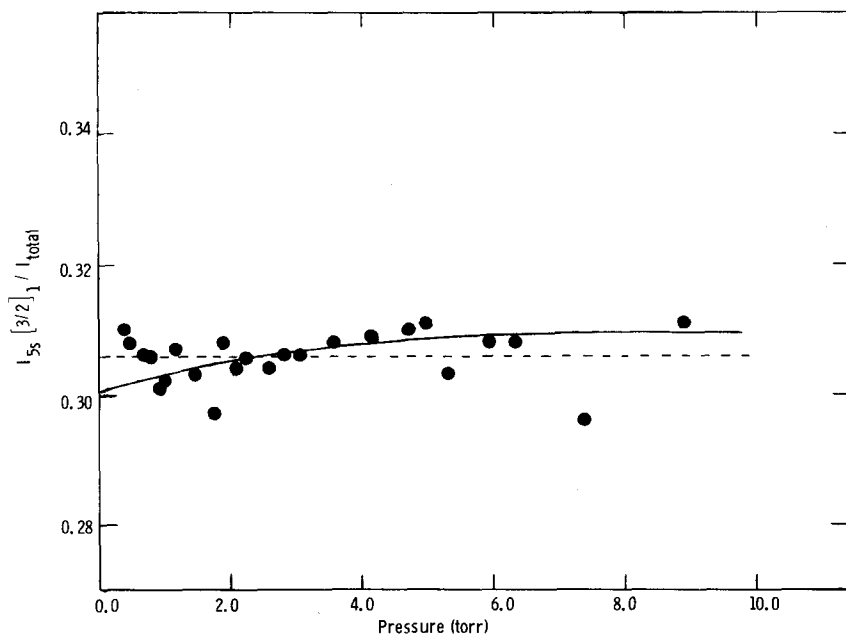


FIG. 2. The fraction of the total excitation of Kr by Ar^* (3P_2) which populates, via radiative cascade, the Kr $5s[3/2]_1$ level as a function of pressure. The solid line is the pressure dependence calculated from Eq. (1) using the kinetic parameters from Ref. 5. The dashed line indicates the arithmetic mean of the data points, 0.306 ± 0.006 .

Note added in proof: Clyne and Nip, *J. Chem. Soc. Faraday II* **73**, 161 (1977), have reported rate coefficients for excitation of atomic Cl from $\text{Ar}^*(^3P_2) + \text{Cl}_2$ and Cl. Their values are based upon the incorrect Kr^3P_1 excitation rate constant given by Gundel *et al.*⁶ and are therefore 18% too large.

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¹⁴N quadrupole resonance of *p*-azoxyanisole and related compounds

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Blinc and co-workers have recently reported the ¹⁴N nuclear quadrupole resonance (NQR) spectra of a few substances that exhibit a nematic liquid crystalline phase.¹ The purpose of the present contribution is to present evidence favoring an alternative assignment of the spectra. We have also recalculated the angles subtended by the principal axes of the ¹⁴N field gradient tensors and the axis of molecular rotation in the nematic phase of *p*-azoxyanisole (PAA).

The ¹⁴N NQR frequencies for several compounds of relevance are presented in Table I. These data were obtained in our laboratory on samples at 77 K, using the double resonance level-crossing technique.²⁻⁷ The spectrum obtained by us for PAA is the same as that reported in Ref. 1. However, we differ in the assignments of the observed resonances.

In assigning the PAA transitions, Blinc and co-workers did not recognize that the N-oxide nitrogen possesses a low field gradient. The NQR parameters for the pyridine-N-oxide and γ -picoline-N-oxide nitrogen atoms (Table I) are dramatically different from those for the free bases. In azoxybenzene all the transitions can be assigned unambiguously to two nitrogen atoms with substantially different field gradient parameters. A similar assignment accounts perfectly for all the observed signals of PAA. Furthermore, this assignment is in accord with the crystallographic work on PAA, which shows the presence of only one type of site in the unit cell.⁸ The assignment in Ref. 1 for diheptiloxazoxybenzene (HOAB) should also be reinterpreted along the same lines.

Using the new values of e^2Qq/h and η for the chemical-

ly distinct nitrogen atoms of PAA it is of interest to interpret the nematic phase quadrupole splittings observed by Cabane and Clark.⁹ It is not clear which quadrupole splitting in the nematic phase corresponds to which nitrogen. Equation (1) expresses the relationship between V_{mm} , the component of efg along the axis of molecular rotation in the nematic phase, to V_{zz} , the largest component of efg in the principal axis system centered at nitrogen in the molecular frame

$$V_{mm} = V_{zz} \left\{ \frac{3}{2} \cos^2 \theta - \frac{1}{2} + \frac{1}{2} \eta \sin^2 \theta \cos 2\phi \right\}. \quad (1)$$

The θ and ϕ in Eq. (1) are defined so that $(\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$ are the direction cosines of the molecular rotation axis (shown in Fig. 1) with respect to the molecular efg principal axes, X , Y , and Z , respectively. There are two unknowns, θ and ϕ , to be determined; one of these must be estimated.

The microwave data indicate that in pyridine¹⁰ and pyridazine,¹¹ the principal Y axis lies perpendicular to the molecular plane and the principal Z axis lies along

TABLE I. ¹⁴N NQR transitions at 77 K. (All frequencies in kHz.)

Compound	ν_+	ν_-	ν_0	$\frac{e^2Qq}{h}$	η
4-Methylpyridine-N-oxide ^a	1171	931	240	1401	0.343
Pyridine-N-oxide ^b	1110	730	380	1227	0.619
Azoxybenzene	3842	2803	1039	4430	0.469
	963	724	239	1125	0.425
<i>p</i> -Azoxyanisole	3836	2816	1020	4435	0.460
	951	877	...	1219	0.121

^aThese results are a correction to those reported in Ref. 2.

^bY. N. Hsieh (unpublished observations).