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Chemiluminescence in molecular beams: Statistical partitioning of electronic energy in the $\text{Cl} + \text{K}_2$ reaction

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The chemiluminescent reactions of alkali metals with halogens have recently been studied under the single collision conditions provided by crossed molecular beams^{1,2} as well as in the multiple collision environments of "beam + gas" experiments³ and diffusion flames.⁴ Emission is observed from a wide range of excited alkali atom states produced by the very exothermic reaction of halogen atoms and diatomic alkali molecules, $\text{X} + \text{A}_2 \rightarrow \text{AX} + \text{A}^*$. In the crossed beam experiments,² the intensity distribution of this emission indicated a statistical partitioning of electronic energy among the excited A^* . An approximate phase space theory⁵ was found to give good agreement with the data, although the comparison was handicapped by low spectral resolution. According to the theory, the cross section for producing an excited A^* state is proportional to the electronic degeneracy of that state and to the square of the available energy, the initial collision energy plus the reaction exoergicity for that state. Here we report a crossed-beam study of the chemiluminescent $\text{Cl} + \text{K}_2$ reaction with improved resolution. The results again are consistent with the phase space theory and, interestingly, show distinct differences from the flame spectra.

The experimental procedure and apparatus were essentially the same as described previously,² except for the radiation detector. An optical train mounted directly above the reaction zone led to a $\frac{1}{2}$ -m grating monochromator (Jarrell-Ash 82-000, dispersion 16 Å/mm, ruled 1180 lines/mm, blazed at 3000 Å in first order) and a S-20 photomultiplier (EMI 9558 QB, refrigerated at 240° K). Slit widths were typically 0.3 mm with an effective resolution of ~10 Å, about the same as that in the flame study.⁴

Since the relative spectral response of the detection system is subject to inaccuracy over broad wavelength regions, we confined attention to intensity comparisons for transitions of similar energy. Several correspond-

ing pairs of lines were examined for the two series $(m-2)^2D \rightarrow n^2P$ and $m^2S \rightarrow n^2P$, for which the upper states occur at nearly the same energy. For example, Fig. 1 shows the $5^2D \rightarrow 4^2P$ and $7^2S \rightarrow 4^2P$ transitions, each with $J = 1/2, 3/2$ spin-orbit splitting. The phase space theory predicts an intensity ratio of 2:1 for the spin-orbit components ($3/2:1/2$) and a ratio of 1.7 for the pair of transitions ($D \rightarrow P: S \rightarrow P$), including contributions from cascading.⁵ We find a 2:1 ratio for the spin-orbit components of both transitions, and a ratio of 1.9 for the pair of transitions. The intensity ratios were determined by planimeter integration of line areas and include a small correction (~5%) for the spectral response of the photomultiplier.² For the same lines in

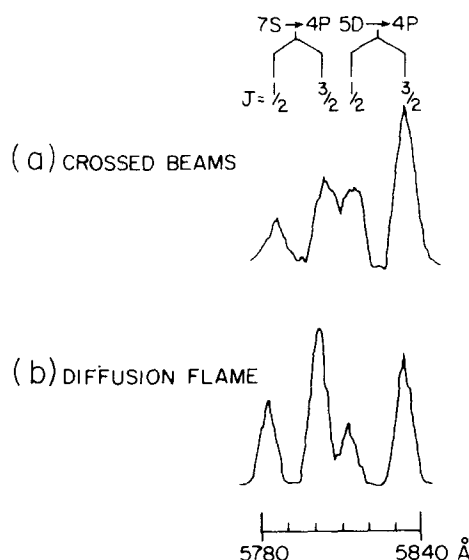


FIG. 1. Comparison of emission lines from excited 7^2S and 5^2D states of potassium atoms formed (a) in reaction of $\text{Cl} + \text{K}_2$ in our crossed-beam experiment and (b) in Ham's Cl_2 , K diffusion flame study (Ref. 4).

the flame spectra,⁴ intensity ratios were determined in the same way. A 2:1 ratio was again found for the spin-orbit components whereas 0.7 was obtained for the pair of transitions.

Table I gives corresponding results for three other pairs of transitions. For these transitions some of the lines were not fully resolved and when deriving the pair intensity ratios we assumed a 2:1 ratio of spin-orbit components, as observed for all the resolved lines. Results from the phase space theory are given for several collision energies; in the beam experiment $E \approx 5.7$ kcal/mole. The line intensities were calculated from

$$I_{i \rightarrow j} = N_i A_{i \rightarrow j} = \left[\left(\sigma_i + \sum_h N_h A_{h \rightarrow i} \right) / \sum_l A_{l \rightarrow i} \right] A_{i \rightarrow j}, \quad (1)$$

where N_i is the steady-state population of the upper state, σ_i the phase space cross section for its formation, and $A_{i \rightarrow j}$ the transition probability.⁶ The sum \sum_h accounts for cascading from higher levels, and \sum_l for cascading to lower levels. The predicted intensity ratios show a strong energy dependence for the $(m, n) = 9, 4$ transitions, for which the upper states lie near the maximum energy available.² This introduces uncertainty in the comparison with experiment, since the available energy depends on the difference in K_2 and KCl bond strengths, which is only known within about ± 3 kcal/mole. Accordingly, the initial vibration-rotation energy of the alkali dimer was neglected; it is only ~ 0.6 kcal/mole because the internal temperature of the supersonic beam is low.⁷ The predicted line intensities are also subject to errors in the radiative transition probabilities,⁶ some of which are only known within $\pm 50\%$, although this uncertainty tends to cancel out in the intensity ratios.⁸ Although these uncertainties prevent a strong test, the phase space theory appears consistent with our data.

Comparisons with intensity ratios from the flame spectra are included in Table I. These ratios are also roughly consistent with the phase space theory, although distinctly different from the beam results. At the pressures used in the flame experiments (~ 10 Torr), the time interval between collisions is comparable to the radiative lifetimes. Collisional quenching hence competes with the emission and in particular the cascading contributions are likely to be attenuated. Ratios (marked with an asterisk) calculated from Eq. (1) omitting the \sum_h and \sum_l terms indeed prove to be closer to the flame results. The flame spectra might involve some self-absorption as well as contributions from reactions other than $Cl + K_2$. In any case, since the phase space calculations indicate that the minor differences in reactant energy are not significant, the appreciable differ-

TABLE I. Intensity ratios, $R_{mn} = [(m-2)^2 D \rightarrow n^2 P] / [m^2 S \rightarrow n^2 P]$.

(m, n) :	(6, 4)	(7, 4)	(8, 4)	(9, 4)
Beam ^a	< 0.059	1.9	~ 10	> 10
Flame ^b	...	0.7	2.3	2.5
Phase Space ^c				
$E = 4.6$	0.0470	1.78	4.89	∞
$E = 5.0$	0.0465	1.75	4.64	10.6
$E = 5.7$	0.0461	1.70	4.40	7.13
$E = 5.7^*$	0.0194	0.476	1.37	2.21
Thermal	0.0463	1.73	4.50	8.17
Thermal*	0.0193	0.479	1.37	2.54

^aThis work.

^bDerived from Fig. 2 of Ref. 4.

^cCalculated from theory of Ref. 5 for various collision energies E (kcal/mole), with the dimer molecules in ground vibrational and rotational states. For the "thermal" case, the collision energy was taken as $E = 3.2$ and the vibrational energy as 2.1 kcal/mole, corresponding to most probable values for conditions of Ref. 4. The asterisks indicate results obtained when the cascading contributions to the steady-state level populations are omitted.

ences between the flame results and our beam data may be attributed to multiple vs single collision conditions.

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