

Quenching Cross-sections of Excited Sodium Atoms

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THE rates of the processes by which atoms and molecules in excited electronic states lose their excitation energy are of considerable interest in photochemical reactions and in other systems in which excited species play a part. These rates are one of the main factors which determine the steady-state concentration of the excited species, and hence the rate of photochemical reactions. A knowledge of them also enables the rate of the excitation process to be calculated from measurements of the steady-state concentration of the excited species.

The simplest case to consider is that of atoms in the first excited state which can lose their excitation energy only by radiative transitions or by quenching collisions with other atoms or molecules. The quenching of sodium atoms by some molecular gases in the $3p,^2P$ state has been studied previously, notably by Norrish and Smith¹ but the method used is susceptible to errors due to self-absorption, compound formation of sodium with the quenching gases and pressure broadening effects. A method which can be used for many elements and is free from these sources of error has been developed and used to obtain quenching cross-sections for sodium. Some of the cross-sections obtained refer to gases that have not been studied previously and values for those gases that have been studied previously differ significantly from the earlier determinations.

The method is an extension of the experiment of Boers *et al.*² The fluorescent emission of a modulated beam of resonance radiation is measured for groups of flames which are isothermal but differ widely in composition. From the variation

of the intensity of fluorescence with flame composition the contribution of each bulk species in the flame to the quenching rate can be deduced. The amount of radiation absorbed, ΔP , from the primary beam is measured for each flame, as well as the total fluorescence, and the total quenching rate is deduced from the difference between the two measurements. There are three principal advantages of this method. Firstly, as ΔP is measured for each flame, errors due to line-broadening effects are eliminated. Secondly, as the optical density of sodium in the flame can be varied isothermally, it is possible to investigate, and correct for, the self-absorption of the fluorescence. Thirdly, compound formation is of no consequence since the ΔP measurements refer to the actual concentration of sodium atoms in each flame.

The fluorescence of sodium has been studied in hydrogen-oxygen flames diluted with the gases helium, argon, nitrogen, and carbon monoxide at temperatures of 1400, 1600, and 1800° K. This has yielded the following values (in Å²) for the quenching cross-sections, defined as the square of the distance between the centres of the colliding species, σ^2 :

$$\begin{aligned}\sigma_{\text{H}_2}^2 &= 2.87 \pm 0.1; \sigma_{\text{N}_2}^2 = 6.95 \pm 0.15; \\ \sigma_{\text{H}_2\text{O}}^2 &= 0.5 \pm 0.3; \sigma_{\text{CO}}^2 = 11.9 \pm 0.4; \\ \sigma_{\text{CO}_2}^2 &= 17.0 \pm 0.4; \sigma_{\text{O}_2}^2 = 12.3 \pm 0.5; \\ \sigma_{\text{He}}^2 &< 0.1; \sigma_{\text{Ar}}^2 < 0.1.\end{aligned}$$

No temperature-dependence was observed for any of these cross-sections. The measurements for oxygen were made at 1800° K only.

For the atomic species the cross-sections are very small, as would be expected, and only an upper limit for these values could be found. The most interesting result is the new result for the cross-section for quenching by water. It is very strong evidence that quenching occurs not by a resonance with the internal energy-levels of the quenching molecules but by incipient compound formation as in the case for nitrogen and hydrogen.^{3,4} The cross-sections found for hydrogen, nitrogen, and carbon monoxide are about half as large as those determined by earlier resonance

radiation quenching experiments.¹ Estimates of the amount of self-absorption show that this difference is at least partly due to a neglect of this factor in the earlier work. In the case of hydrogen it is likely that compound formation with sodium occurs at the lower temperatures used in this earlier work and that failure to allow for this made the apparent cross-section too large.

Further details of these measurements will be published in due course, as well as the results for other atoms.

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¹ R. G. W. Norrish and W. MacF. Smith, *Proc. Roy. Soc.*, 1940, *A*, **176**, 295.

² A. L. Boers, C. T. J. Alkemade, and J. A. Smit, *Physica*, 1956, **22**, 358.

³ Y. Mori, *Bull. Chem. Soc. Japan*, 1962, **25**, 1584.

⁴ K. J. Laidler, *J. Chem. Phys.*, 1942, **10**, 34.