PHASE-SHIFT STUDY OF THE QUENCHING AND TRAPPING OF Cd 228.8 nm RESONANCE RADIATION

PETER D. MORTEN, COLIN G. FREEMAN, RODNEY F. C. CLARIDGE and
LEON F. PHILLIPS

Chemistry Department, University of Canterbury, Christchurch (New Zealand)

(Received June 3, 1974)

Summary

Cadmium vapour at ~ 560 K has been irradiated with 228.8 nm radiation from a microwave discharge lamp modulated at 30 kHz. The phase angle of 228.8 nm fluorescence, relative to a fixed reference signal, has been measured as a function of the partial pressure of quenching gas. Rate constants k_Q for the quenching of Cd (5^1P_1) have been calculated from:

$$T_0/T = 1 + k_Q N_Q T_0$$

where T is the trapping time for resonance radiation in the presence of N_Q molecules of quencher per cm^3, and T_0 is the trapping time in absence of quencher. Trapping times were determined from the phase shift between the exciting light and the fluorescence; the phase angle corresponding to zero phase shift was obtained by an extrapolation procedure. Values for k_Q are given for Q = He, Ar, H_2, N_2, NH_3, N_2O, CO_2, CO, propene and n-butane. The values range from 5.2×10^{-12} to 1.5×10^{-9} cm^3 molecule^{-1} s^{-1}; T_0 was typically 1.4 μs.

Introduction

The possibility of using phase-shift measurements to estimate radiation trapping times and quenching rates in systems of large optical depth was previously investigated by computer simulation [1]. We now report a practical application of the results of that study. For fluorescence excited by a modulated source of radiation, the phase delay, δ, between the fundamental components of the exciting radiation and the fluorescence defines a trapping time, T, such that:

$$\tan \delta = 2\pi f T \qquad (1)$$

where f is the modulation frequency. T_0, the trapping time calculated from the phase-shift measured in the absence of a quencher, is not the same as the trapping times which are characteristic of either the quenching of steady-state

fluorescence or the decay of fluorescence when excitation ceases. If the concentration of quencher is not too large the trapping time T derived from phase-shift measurements in the presence of quencher obeys a Stern–Volmer equation of the form:

$$T_0/T = 1 + k_Q N_Q T_0 \qquad (2)$$

where k_Q is the rate constant for quenching by a species whose concentration is N_Q molecules cm^{-3}. In the present experiments the observed phase-shifts were sufficiently large that T_0 could be determined with reasonable precision directly from the phase-shift data. This is in contrast to a previous study of quenching and trapping of Lyman α-radiation [2], where T_0 was obtained by extrapolation on the basis of the assumption that the trapping time governing the intensity of steady-state fluorescence was equal to T_0.

Several studies have been reported of the quenching of resonance radiation from $Cd(^3P_1)$ at 326.1 nm [3 - 5] but, apart from a few preliminary measurements [4, 6], there appear to be no data for the quenching of resonance radiation from $Cd(^1P_1)$ at 228.8 nm.

Experimental

The experimental system was similar to that described previously [7, 8]. The main differences from the system described in ref. [8] were that the filter between the lamp and reaction cell was removed and that the configuration of the cell was rotated through 90 ° so that the exciting radiation entered the fluorescence cell along a line perpendicular to the entrance slit of the McPherson Model 218 monochromator. This was necessary in order to minimize errors arising from variation of phase angle with distance from the point of entry of the exciting beam [1]. Observations were made with a slit width of 0.8 mm, the fluorescence being viewed through a collimating system of aperture ~ 1 °. The viewing region of the cell was approximately 1.5 cm from the window through which the exciting radiation entered. The experimental procedure consisted simply of measuring the phase angle at a point of quadrature of the modulated 228.8 nm fluorescence signal, relative to the internal reference signal of the lock-in amplifier, over a range of pressures of the quenching gas. All experiments were carried out with a modulation frequency of 30 kHz. The pressure of Cd remained constant at 9×10^{-3} Torr (saturated vapour pressure at 255 °C) during the experiment. Quenchers used were research grade materials, or were purified as previously described [7].

Results

Representative curves showing the variation with pressure of the observed phase angle Φ (relative to the internal reference signal of the lock-in amplifier) are shown in Fig. 1. At infinite pressure of quencher the phase
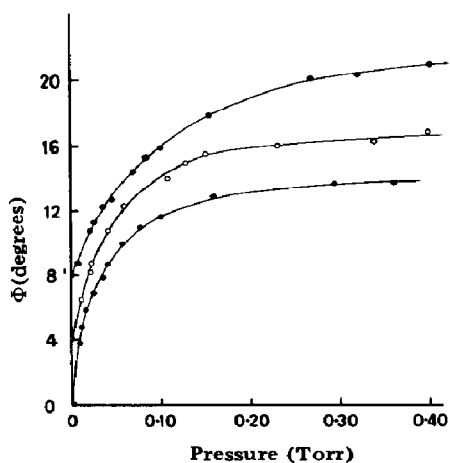
Fig. 1. Variation of observed phase angle, Φ, with quencher gas pressure (modulation frequency 30 kHz). Φ_0 has arbitrarily been set at values shown below. From top to bottom curves are for: N_2 (Φ_0 = 8.0°, δ_0 = 16.6 ± 0.2°); N_2O(Φ_0 = 4.0°, δ_0 = 14.7 ± 0.2°); n-butane (Φ_0 = 0°, δ_0 = 15.0 ± 0.2 °).
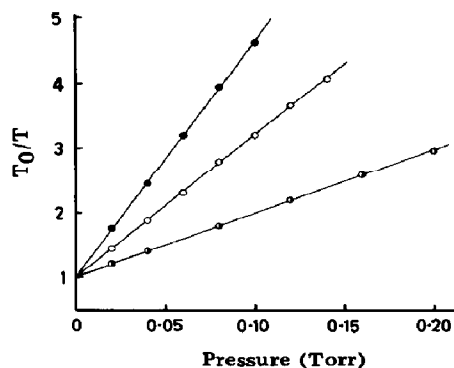
Fig. 2. Stern—Volmer plot of T_0/T against quencher gas pressure for data shown in Fig. 1. ●, n-butane; ○, N_2O; ◑, N_2. (Points are read from smooth curves of Fig. 1.)

delay due to quenching and trapping must become zero, while at zero pressure of quencher the phase delay will be due solely to the trapping time T_0. Thus δ_0 must be given by the difference in observed phase angles at the two extremes, *i.e.*

$$\delta_0 = \Phi_\infty - \Phi_0 \tag{3}$$

At intermediate pressures the phase delay due to trapping and quenching is given by:

$$\delta = \Phi_\infty - \Phi \tag{4}$$

Hence

$$T_0 = \frac{\tan(\Phi_\infty - \Phi_0)}{2\pi f} \tag{5}$$

and

$$\frac{\tan(\Phi_\infty - \Phi_0)}{\tan(\Phi_\infty - \Phi)} = \frac{T_0}{T} = 1 + k_Q N_Q T_0 \tag{6}$$

Of the quantities which are required for the evaluation of T_0 and k_Q, Φ_0 and Φ are readily available. However, as the pressure of quencher is increased to a large value the intensity of fluorescence decreases sharply, which prevents Φ_∞ from being determined directly. Φ_∞ was found by an iterative procedure in which the first estimate of Φ_∞ was based upon the high pressure limit of the observed curve of Φ against quencher pressure. Thereafter Φ_∞ was adjusted to obtain optimum linearity of a plot of T_0/T *vs.* the pressure of quencher

TABLE 1

Results for quenching and trapping of Cd 228.8 nm resonance radiation

Quencher	$T_0/\mu s$	k_Q/cm^3 molecule^{-1} s^{-1}	$\sigma_Q \times 10^{16}/cm^2$	Temperature/K
He	0.98	5.2×10^{-12}	0.30	563
Ar	1.19	7.0×10^{-12}	1.10	561
H_2	1.69	2.6×10^{-10}	10.7	558
N_2	1.58	3.6×10^{-10}	50	557
NH_3	1.60	5.2×10^{-10}	58	557
N_2O	1.39	9.1×10^{-10}	149	556
CO_2	1.33	9.2×10^{-10}	150	567
CO	1.33	1.01×10^{-9}	138	568
propene	1.42	1.46×10^{-9}	234	562
n-butane	1.42	1.49×10^{-9}	267	568

(eqn. 6) at low pressures. In this way Φ_∞ could be estimated to within 0.2 ° (*i.e.* a variation of more than 0.2 ° in the value of Φ_∞ in either direction caused a perceptible curvature in the plot of T_0/T *vs.* N_Q). The uncertainty in Φ_∞ resulting from this procedure, together with scatter in values of Φ, leads to a total uncertainty in δ_0 of ± 0.5 °. This in turn leads to an estimated uncertainty of ±4% in values of T_0, and an uncertainty of ±10% in the final values of k_Q. Figure 2 shows a test of eqn. (6) for some representative quenchers. Table 1 lists the results obtained for the 10 different quenching gases used. In addition, measurements were made with O_2 as quencher but are not listed because of their lack of reproducibility. These results indicated that k_Q for O_2 is certainly greater than that for n-butane (1.5×10^{-9}) and this is therefore considered a lower limit for O_2. Quenching cross-sections, σ_Q were calculated from:

$$\sigma_Q = k_Q (\pi\mu/8RT)^{1/2} \tag{7}$$

where the symbols have their usual meaning.

In addition to the experiments with 228.8 nm radiation, some measurements were made for quenching by NH_3 of $Cd(^3P_1)$ at 326.1 nm, in order to compare results obtained by the present technique with those of other workers. Values of quenching cross-sections for $Cd(^3P_1)$ with NH_3 are shown in Table 2, and it can be seen that the various results agree within the combined experimental uncertainties. The trapping time, T_0, measured for 326.1 nm radiation was 2.5 μs which is identical with the lifetime of $Cd(^3P_1)$ [9].

Furthermore, the value of k_Q measured for $Cd(^1P_1)$ with H_2 (2.6×10^{-10} cm^3 molecule^{-1} s^{-1}) is in good agreement with the figure of $\sim 3.5 \times 10^{-10}$ estimated by Breckenridge and Callear [6].

With the exception of H_2, the values of k_Q listed in Table 1 generally reflect the size of the quenching molecule. For the larger molecules k_Q values are greater than the collision numbers (by up to an order of magnitude in the case of propene and n-butane). It is apparent that in these cases there must be

TABLE 2

Quenching cross-sections for ammonia with Cd 326.1 nm radiation

Study	$\sigma_{NH_3} \times 10^{16}/cm^2$
This work	0.049
Lipson and Mitchell [3]	0.041
Steacie and LeRoy [4]	0.052

appreciable attractive forces acting between $Cd(^1P_1)$ and the quenching molecule during the quenching process. Variations in the values of T_0 outside the range of the uncertainty quoted above are due to differences in the distance between the point of entry of exciting radiation and the viewing region between different experiments. The values of T_0 observed in the present system lie between 500 and 800 times the natural lifetime of $Cd(^1P_1)$ $(2 \times 10^{-9}$ s) [9], i.e. the experiments were indeed carried out under conditions of large optical depth. Some preliminary quenching results were obtained with a system in which the exciting light entered the cell along a line parallel to the entrance slit of the monochromator, the length of the incident beam viewed by the monochromator being about 1 cm. These results would be expected to err on the large side because or the effect of variation of trapping time with distance from the point of entry of the exciting light [1]. In fact the difference amounted to approximately a factor of 3 in k_Q. Because of the very narrow angle of acceptance of the present optical system we consider that this effect causes a negligible error in the results of Table 1.

Acknowledgements

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