Kinetics and Mechanism of the CS$_2^{(3A_2)}$ Decay.

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Summary. — From the rate constants for the CS$_2^{(3A_2)}$ decay obtained by laser-induced fluorescence and using a vibrational cascade model we have calculated the average value of the vibrational quantum transferred on each deactivating collision, as well as the second-order rate constants for vibrational and electronic quenching.

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1. – Introduction.

Fluorescence studies of CS$_2$ vapour have been carried out in the past using a typical fluorescence technique (1), electrical discharge (2) or shock-heated CS$_2$-Ar mixtures (3). Brus (4) measured the laser-excited fluorescence of CS$_2$ vapour, detecting a double exponential decay. This suggested that two emitting states exist. One of the lifetimes was in good agreement with the one observed by Douglas (5). The same observations have been achieved by resolving the fluorescence by interference filters (6).

All the previous work ascertained that the long-lived state is the $^3A_2$-state, observed in absorption by Kleman (7).

A recent study (s) shows that vibrational relaxation occurs in the excited triplet state. This is inferred from the similarities in the quenching rate constants of CS$_2$ by CO$_2$ for the two long-lived states observed (s).

Lambert and Kimbell (9) had to invoke a vibrational cascade model in order to account for their observations on the CS$_2$ fluorescence. The same mechanism was proposed (10,11) to explain the decay of NO$_2$, a molecule that, as is well known, behaves like CS$_2$.

In this work, we use a vibrational cascade model to explain the CS$_2(^3A_2)$ decay from laser-excited-fluorescence data (s,8), obtaining the values for the average number of the vibrational quantum transferred on each collision as well as the rate constants for the vibrational and electronic quenching. This vibrational relaxation in the $^3A_2$-state could be a possible explanation for the «continuum» observed in the emission spectrum of CS$_2$.

2. Theory.

The results presented in a previous work (s) suggest that a simple Stern-Volmer mechanism with only one excited level is not good enough to explain how the quenching rate constant for the $^3A_2$-state varies with the emission wave-length. Therefore, we need to assume a vibrational cascade model for the $^3A_2$-state of CS$_2$. Hence, we can write the following equations:

$$\frac{d[CS_2(1)]}{dt} = (K_{11} + K_{a1}[CS_2] + K_{v1}[CS_4])[CS_2(1)] - K_4I_x[CS_2],$$

$$\frac{d[CS_2(2)]}{dt} = (K_{12} + K_{a2}[CS_2] + K_{v2}[CS_4])[CS_2(2)] - K_v[CS_2][CS_2(1)],$$

$$\frac{d[CS_2(i)]}{dt} = (K_{ii} + K_{ai}[CS_2] + K_{vi}[CS_4])[CS_2(i)] - K_{v(i-1)}[CS_2][CS_2(i-1)],$$

where $[CS_2]$ is the concentration of CS$_2$ in the ground state, $[CS_2(i)]$ are the concentrations of CS$_2$ in the vibrational levels of the $^3A_2$-state; $K_1$ is the radiative rate constant; $K_a$ and $K_v$ are the rate constant for electronic and vibrational quenching, respectively; $K_a$ is the absorption coefficient and $I_x$ is the intensity of the exciting radiation.