

Temperature Dependence of the 7^2P States Mixing and Quenching in Caesium-Deuterium Collisions*

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Temperature dependent mixing and effective quenching cross-sections for the 7^2P doublet in caesium, induced in collisions with molecular deuterium, were determined experimentally using the sensitized fluorescence method. The character of the temperature dependence exhibits an isotope effect compared to the data for caesium-hydrogen collisions obtained earlier.

Investigations of the energy transfer between $2P$ levels in alkali atom-molecule collisions show that the measured cross-sections exhibit an isotope effect involving the mass of the colliding molecule [1–5]. This had led us to the conclusion that the excitation transfer proceeds by a mechanism which involves electronic-to-rotational energy transfer.

In this note we report on the temperature dependence of the 7^2P mixing and the “effective” quenching cross-section of caesium in collisions with deuterium molecules. The results are compared with data for caesium-hydrogen collisions obtained earlier [6]. The values of the cross-sections were determined using the sensitized fluorescence method.

A caesium atom, excited to the 7^2P state, can either decay radiatively or, due to inelastic collisions, be transferred to other states as shown in Figure 1. The latter processes manifests themselves in sensitized fluorescence. When the fluorescence from the 7^2P doublet only is considered, excitation transfer to the 7^2S , 5^2P and 6^2P states results in “total effective quenching” of the 7^2P state. The steady-state solution of the kinetic equations for the 7^2P and $6^2S_{1/2}$ state populations gives us relationships for the mixing and the total effective quenching collision number Z , which can be obtained from the 455.5 nm and 459.3 nm component intensity [6]. The total collision cross-section Q was determined from the slope of the $Z = f(p)$ plot (p = gas pressure), which should be linear.

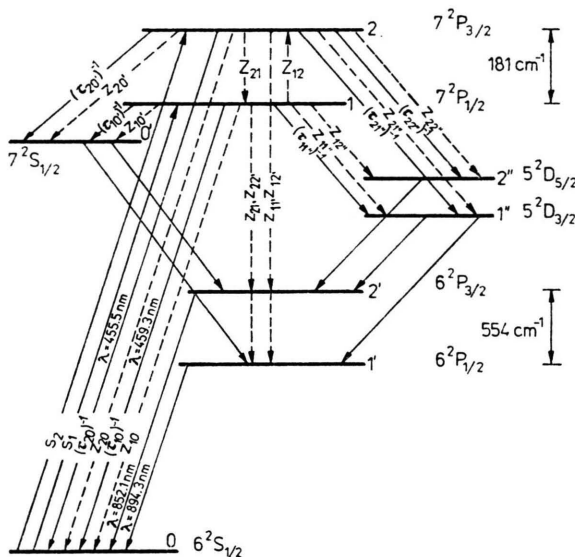


Fig. 1. Caesium energy diagram with transitions involved for the excited 7^2P doublet.

The arrangement of the apparatus was a typical one for a sensitized fluorescence experiment. A Zeiss-Jena monochromator was used to separate the 7^2P doublet components emitted by a caesium-xenon discharge powered by 100 W r.f. generator. The light was focused in to a pyrex fluorescence cell mounted in the oven and containing caesium vapor and a molecular gas. The fluorescence observed perpendicularly was resolved into its two components by a second Zeiss monochromator and monitored by an EMI 6256 S P.M. tube. A lock in technique was employed to measure the intensity of the light signals.

The mixing cross-sections Q_{12} and Q_{21} as well as the effective quenching cross-sections Q_{1x} and Q_{2x}

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have been determined over the temperature range 403–593 K corresponding to a relative velocity of the Cs and deuterium partners in the range 1.48 – $1.81 \cdot 10^5$ cm/s. The fluorescence cell side arm was kept at 371 K, which corresponds to a caesium vapor pressure of $5 \cdot 10^{-4}$ Torr. The molecular deuterium pressure was varied in the range 0.1 to 1 Torr. The effective lifetimes used in the calculations were taken to be (158 ± 5) ns and (136 ± 4) ns for the $7^2P_{1/2}$ and $7^2P_{3/2}$ states, respectively [7].

The temperature dependence of the mixing and effective quenching cross-sections for caesium-deuterium collisions is presented in Figs. 2 and 3. The experimental values for the mixing cross-sections vary from 27.5 to $31.4 \cdot 10^{-16}$ cm 2 for Q_{21} , and from 28.9 to $40.5 \cdot 10^{-16}$ cm 2 for Q_{12} . They are about 1.5 times larger for deuterium than for

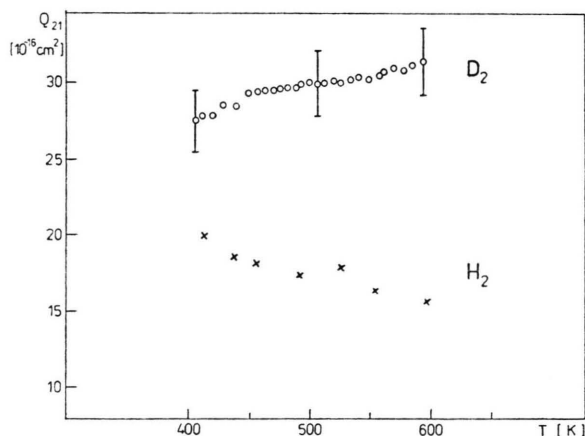


Fig. 2. Temperature dependence of the Q_{21} cross-section. x: data for Cs- H_2 collisions [6].

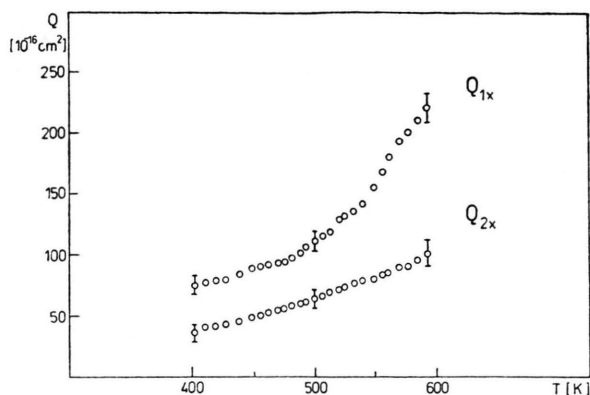


Fig. 3. Temperature dependence of the Q_{1x} and Q_{2x} cross-sections.

hydrogen and are in good agreement with the detailed balance principle. As is seen in Fig. 2, the variation of the Q_{21} cross-section with temperature differs from the Cs- H_2 data indicated in the graph.

The theory, which has satisfactorily explained the temperature dependence for Cs- H_2 collisions [6], fails in this case. Our calculations suggest a change in the $7^2\pi$ term splitting for the CsD_2 molecule, assumed to be 181 cm $^{-1}$. The effective quenching cross-sections for the Cs- D_2 collisions are of the same order as for hydrogen and lie in the range from 35.4 to $101.3 \cdot 10^{-16}$ cm 2 for Q_{2x} and from 75.2 to $220.1 \cdot 10^{-16}$ cm 2 for Q_{1x} . They also increase with temperature.

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