Temperature Dependence of the 7²P States Mixing and Quenching in Caesium-Deuterium Collisions *

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Temperature dependent mixing and effective quenching cross-sections for the 7²P doublet in caesium, induced in collisons 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 7²P 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 7²P 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 7²P doublet only is considered, excitation transfer to the 7²S, 5²P and 6²P states results in "total effective quenching" of the 7²P state. The steady-state solution of the kinetic equations for the 7²P and 6²S$_{1/2}$ 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.
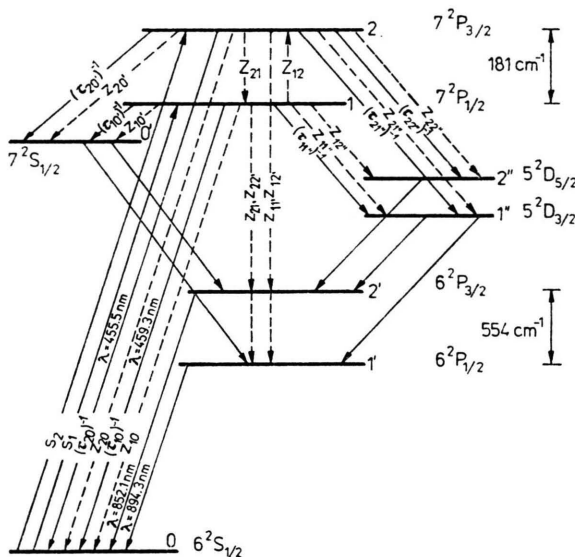

Fig. 1. Caesium energy diagram with transitions involved for the excited 7²P doublet.

The arrangement of the apparatus was a typical one for a sensitized fluorescence experiment. A Zeiss-Jena monochromator was used to separate the 7²P 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 · 10^5 cm/s. The fluorescence cell side arm was kept at 371 K, which correspondes to a caesium vapor pressure of 5 · 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 $136 \pm 4)$ 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 · 10^{-16} cm^2 for Q_{21}, and from 28.9 to 40.5 · 10^{-16} cm^2 for Q_{12}. They are about 1.5 times larger for deuterium then for
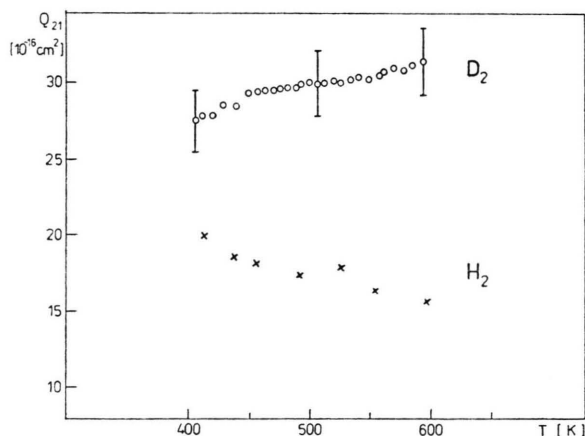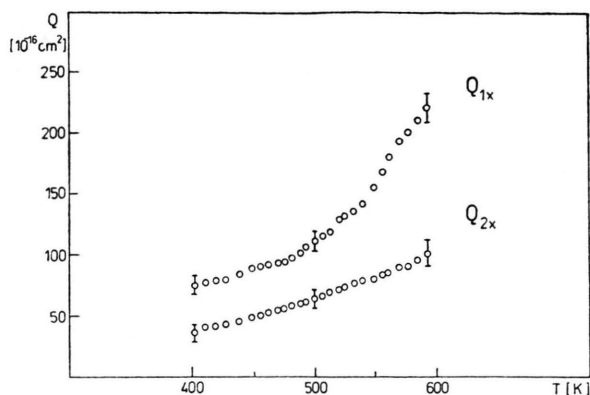

Fig. 3. Temperature dependence of the Q_{1x} and Q_{2x} cross-sections.

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 · 10^{-16} cm^2 for Q_{2x} and from 75.2 to 220.1 · 10^{-16} cm^2 for Q_{1x}. They also increase with temperature.

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

[1] E. Walentynowicz, R. A. Phaneuf, and L. Krause, Can. J. Phys. **52**, 589 (1974).
[2] I. N. Siara, H. S. Kwong, and L. Krause, Can. J. Phys. **52**, 945 (1974).
[3] I. N. Siara and L. Krause, Can. J. Phys. **51**, 257 (1973).
[4] L. Krause, I. N. Siara, and R. U. Dubois, IX ICPEAC, July 1975, Seattle, Wash. USA.

[5] R. A. Phaneuf and L. Krause, Can. J. Phys. **58**, 1047 (1980).
[6] M. Lukaszewicz, Bull. Acad. Pol. Sci. **23**, 501 (1975).
[7] P. W. Pace and I. B. Atkinson, Can. J. Phys. **53**, 937 (1975).