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An Isotope Effect on $6^2P_{1/2} - 6^2P_{3/2}$ Mixing in Cesium,
Induced in Collisions with CH_4 and CD_4

by

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An Isotope Effect on $6^2P_{1/2} - 6^2P_{3/2}$ Mixing in Cesium,
Induced in Collisions with CH_4 and CD_4 ¹

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ABSTRACT

$6^2P_{1/2} - 6^2P_{3/2}$ excitation transfer in cesium, induced in collisions with CH_4 and CD_4 molecules, has been studied in relation to the temperature of the vapor-gas mixtures. The variation with temperature of the cross section ratio $Q(CH_4)/Q(CD_4)$ is ascribed to an isotope effect which is interpreted on the basis of the theory of absolute reaction rates.

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The results of a recent investigation of sensitized fluorescence in cesium, in mixtures with N_2 , H_2 , HD and D_2 , suggested that the atomic $6^2P_{1/2} \leftrightarrow 6^2P_{3/2}$ transitions induced in collisions with these molecules might proceed according to a mechanism different from that governing the same process induced in collisions with noble gas atoms (McGillis and Krause 1968). In order to explore this question further, a series of precise determinations of the $6^2P_{1/2} - 6^2P_{3/2}$ mixing cross sections was carried out over a range of temperatures, with CH_4 and CD_4 molecules used as collision partners.

The apparatus and experimental method have been described elsewhere, as has the derivation of the necessary formulae connecting the sought cross sections with the experimental observations (McGillis and Krause 1968). The cesium-methane mixtures were irradiated continuously with a single component of the cesium resonance doublet and the relative intensities of both the components present in the fluorescence monitored at right angles to the direction of irradiation, were determined over a range of gas pressures, using a refrigerated photomultiplier followed by an electrometer-amplifier. This procedure, which was carried out with both CH_4 and CD_4 , at four different temperatures ranging from $300^\circ K$ to $450^\circ K$, yielded the appropriate mixing cross sections for each gas and at each temperature. The gases* were gettered with hot Cs vapor for several days before use, and their pressures were measured with a trapped McLeod gauge. Molecular transpiration in the capillary (2 mm bore) connecting the fluorescence cell to the vacuum and gas-filling system, was reduced

* Research grade CH_4 of 99.99% purity, supplied by the Matheson Company, and 99% isotopic CD_4 , supplied by Merck, Sharp and Dohme, were used.

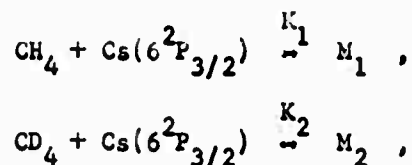
to a minimum by working at pressures in the range 0.2 - 0.8 Torr. Small optical depths were maintained by keeping the cesium vapor pressure at about 10^{-6} Torr and by restricting the light paths in the vapor to about one millimeter. The fluorescent intensity ratios of the cesium resonance lines were obtained reproducibly with both increasing and decreasing gas pressures and temperatures. The influence of quenching collisions on the measured mixing cross sections was established by plotting the reciprocal of the mixing cross section against CH_4 or CD_4 pressure. The slope of such a plot is proportional to the quenching cross section and its intercept gives the mixing cross section separated from the quenching effects. Such analyses of the experimental results led to an upper limit of 2 \AA^2 on the quenching cross sections for both CH_4 and CD_4 , and showed unequivocally that changes in quenching efficiency with temperature had no significant influence on the mixing cross sections.

3. 1.

Figure 1 shows the variation of the experimentally determined mixing cross sections, $Q_{12}({}^2P_{1/2} \rightarrow {}^2P_{3/2})$ and $Q_{21}({}^2P_{1/2} - {}^2P_{3/2})$, with the temperature of the vapor-gas mixtures. In all cases the ratios Q_{12}/Q_{21} are in exact agreement with the values predicted by the principle of detailed balancing. It may be seen that, for both upward and downward transitions, the ratio $Q(\text{CH}_4)/Q(\text{CD}_4)$ decreases with temperature. Such an effect is not expected on the basis of the gas-kinetic collision theory, unless one were to assume a different velocity dependence of the partial cross sections $\sigma(v)$ for CH_4 and CD_4 , which is not likely as the Cs - CH_4 and Cs - CD_4 interaction forces ought to be identical. Even though the experimental temperature range and the observed effects are small, the trend is considered to be real and beyond the limits of experimental error.

The large magnitudes of the mixing cross sections which range from 19 to 25 Å², arise presumably because the atomic excitation energy is transferred from excited cesium atoms to internal molecular degrees of freedom rather than to the kinetic energy continuum. If this transfer of energy were of a 'resonant' character, then even a slight shift in the thermal populations of the molecular vibrational and rotational states, caused by an increase in temperature, would be reflected in a temperature dependence of the mixing cross sections. This is unlikely in the case of CH₄ and CD₄ molecules whose vibrational states have frequencies of at least 1000 cm⁻¹ and whose rotational states are too closely spaced to envisage a particular resonance with the ²P_{1/2} → ²P_{3/2} transition in cesium which corresponds to an energy transfer of 554 cm⁻¹.

It is possible, on the other hand, that the excitation transfer takes place by a mechanism which involves the formation of a relatively long-lived transition state complex of definite configuration. Such a mechanism has been accepted for some time as being instrumental in the quenching of alkali resonance radiation by molecules which, in colliding with the excited atoms, cause the radiationless decay of the ²P states (see, for instance, Laidler 1942, Mori 1962, Nikitin 1965). Let us consider the transition state equilibria:



where M₁ and M₂ are the appropriate transition state complexes, and K₁ and K₂ are the activation equilibrium constants which are proportional to the

rate constants k_1 and k_2 for the corresponding mixing processes involving CH_4 and CD_4 , respectively. It follows from transition state theory that the ratio k_1/k_2 is proportional to the factor $\exp \left\{ (hc/2kT)[\nu(\text{CH}_4) - \nu(\text{CD}_4)] \right\}$, where ν is the stretching frequency of the C-H or C-D bond involved in the energy transfer (Melander 1960). Since for all the corresponding modes, $\nu(\text{CH}_4) > \nu(\text{CD}_4)$, this factor should decrease with temperature, as should the ratio k_1/k_2 and, consequently, $Q(\text{CH}_4)/Q(\text{CD}_4)$.

The above argument provides a qualitative explanation for the observed effect which should be investigated further with other isotopic molecules and over a wider temperature range.

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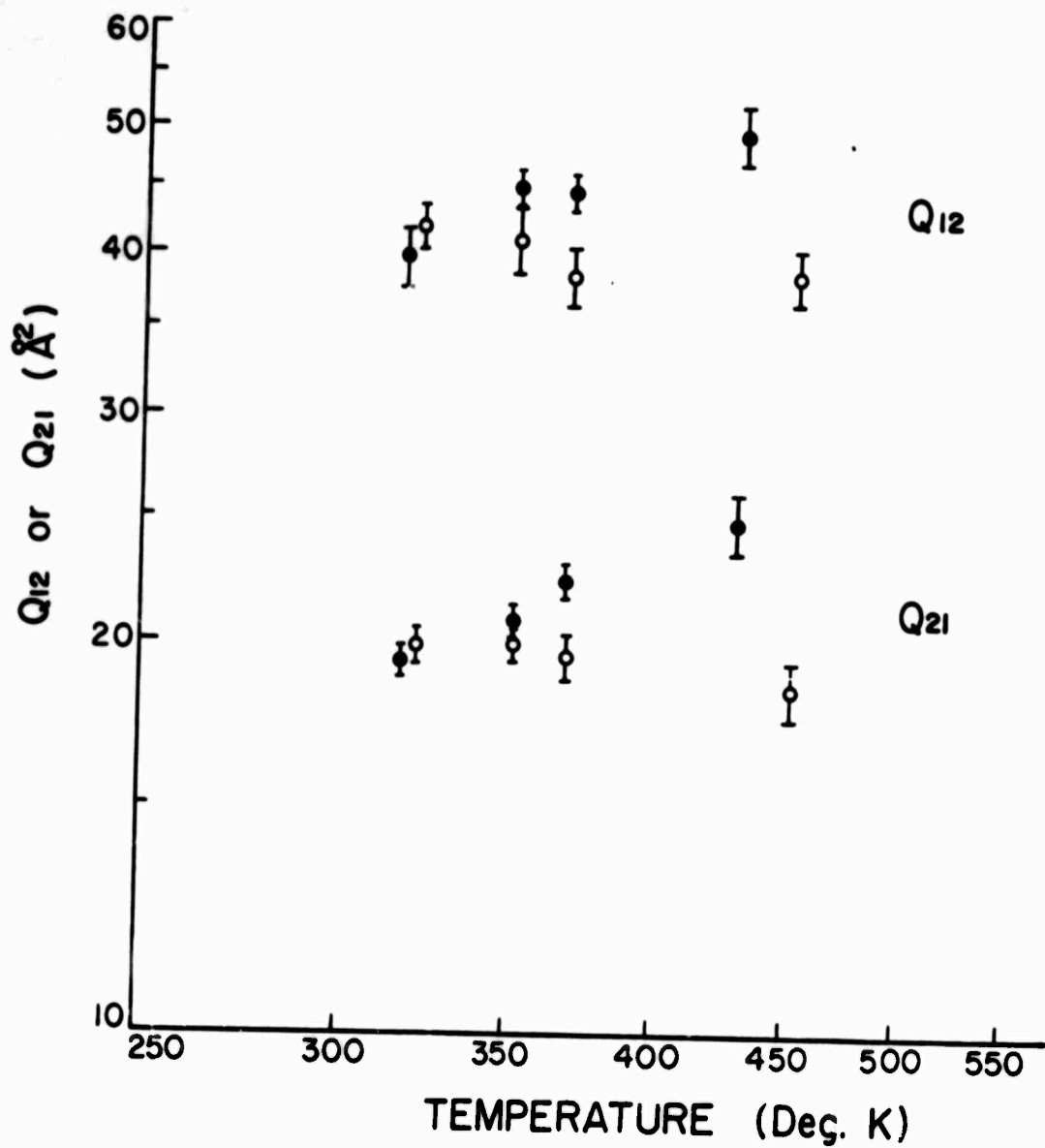
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FIGURE CAPTIONS

Fig. 1. The variation of ${}^2P_{1/2} - {}^2P_{3/2}$ mixing cross sections with temperature. o, Cs - CH₄; •, Cs - CD₄. The measured values Q_{12} were divided by the Boltzmann factor $\exp(-\Delta E/kT)$ before plotting. The error bars were obtained from the statistical scatter in the measurements and represent 95% confidence limits.



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Fig. 1

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The $C.P.(1/2) = (1/PK) \text{ result}$			