

ROTATIONAL ENERGY DISTRIBUTION OF THE CsH FORMED IN
THE REACTION BETWEEN Cs($7P_{1/2}$) AND H₂.

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The nascent rotational distribution of the CsH molecules formed by the reaction between a cesium atom in the $7P_{1/2}$ state and a hydrogen molecule has been measured in a cell. A thermal distribution at the temperature of the cell is reported.

1. INTRODUCTION

For a few years now, the formation of CsH by the reaction between an excited cesium atom in the $7P$ state and a hydrogen molecule has motivated several studies /1-6/. A particular interest has been directed towards understanding the mechanism responsible for the formation of CsH. In a cell experiment, it was shown that a direct and an indirect reaction, which, in this last case, may involve a vibrationally excited H₂ molecule, contribute to CsH formation /4/. More recently, in a beam experiment, evidence was obtained of the direct process, with the observation that the cesium in the $7P_{1/2}$ sublevel reacts more efficiently than that in the $7P_{3/2}$ /6/. Two mechanisms were proposed for the alkali-hydride formation : Crepin et al /6/ suggested a harpooning

process in the colinear geometry for CsH formation and Sevin and Chaquin /7/ considering $\text{Na}(4P \text{ or } 5P) + \text{H}_2$ proposed a mechanism involving a rearrangement of the NaH_2 complex passing from a triangular to a colinear geometry. As shown by Hijazi and Polanyi /8/, the kinematics of the collision in an exchange reaction plays a role in the energy distribution of the products. Information about this mechanism can be obtained through the measurement of the rotational energy distribution of the CsH molecules produced in the reaction between a $\text{Cs}(7P_{1/2})$ and a H_2 molecule.

2. EXPERIMENTAL METHOD AND SET UP

The principle of the experiment is to excite the cesium to the $7P_{1/2}$ level with a pulsed laser, and to detect the rotational states of the CsH. This molecule is formed in its ground electronic and vibrational level (the formation of vibrationally excited CsH being endoergic by more than 900 cm^{-1} is less probable). The CsH detection is performed by laser induced fluorescence. The photoexciting laser pulse is divided in two parts: one part is sent a short time after the cesium excitation to detect the nascent CsH, and the other is delayed so that a large number of collisions will have thermalized the rotational distribution, but not so late for the CsH to have diffused out of the observation region /4/. Consequently the ratio of the two fluorescence intensities gives the ratio between the nascent and the thermal populations without necessitating knowledge of the relative transition probabilities, photoexcitation

efficiencies, reactant densities etc...

The mixture of cesium and hydrogen is contained in a heated glass cell ($T=650\text{K}$). The densities are maintained at moderate values (about 10^{15} and $7.10^{15} \text{ cm}^{-3}$ for Cs and H_2 , respectively).

A N_2 laser pumps two dye lasers. Laser 1 photoexcites the cesium to the $7P_{1/2}$ state and laser 2 is used to detect the CsH. The CsH which is formed in the $X^1 \Sigma^+ v''=0, J''$ state is excited to the $A^1 \Sigma^+ v'=10, J''^{\pm} 1$ state and the fluorescence toward another ro-vibrational state of the $X^1 \Sigma^+$ level is measured. The tuning of the laser 2 wavelength is performed by sending the beam through a discharge cell containing $\text{Cs}+\text{H}_2$ /9/.

Optical fibers are used to guide and to delay the various laser pulses. The laser 2 beam is divided in two parts (2' and 2'') which are focused on the entrances of two fibers, a short (6m) and a longer (200 m) one to create delays of 30 and 1000 ns, respectively. These time delays will be justified later on. The divergent beams emerging from these fibers are reoriented parallel to the axis of propagation and combined with laser 1 beam so that the three pulses (1, 2' and 2'') propagate along the same fiber to the cell before being focused inside.

The fluorescence is observed at a right angle to the laser beam through a monochromator followed by a photomultiplier and a system which counts the photons over a large number of laser pulses. A microprocessor is used to monitor the experiment. In order to subtract the background signal, laser 2 is periodically tuned out of resonance with a piezoelectric ceramic acting on the end

mirror of the Littman cavity. Another photomultiplier controls the relative power of the pulses 2' and 2'' to correct for any evolution in the transmission of the optical system.

Further the power of laser 1 must be maintained low enough to avoid various non-linear effects leading to the creation of large densities of excited Cs atoms in other states than the 7P which can also react with $H_2/4/$.

3. RESULTS

The ratio between the nascent and the thermal distributions at the temperature of the cell is presented in figure 1. From these results we deduce a rotational temperature ($610 \pm 70K$) close to that of the cell (650K) in an energy range of about 2kT ($J''=1$ to 17).

Such a result indicates a thermal distribution of the nascent CsH. However, other explanations might be a complete thermalisation in less than 30 ns or no thermalisation at all after 1 μ s. The cross sections of rotational transfer of $CsH(X^1 \Sigma^+)$ by collision with H_2 are not known, but are most probably of the same order as those measured for the $LiH(X^1 \Sigma^+) / He / 10 /$ or $CsH(A^1 \Sigma^+) / H_2 / 11 /$ systems : a few tens of \AA^2 . Considering the densities in the cell, the cross sections needed to have a complete thermalisation after 30 ns or no thermalisation after 1 μ s would be $\gg 3000 \text{\AA}^2$ or $\ll 0.5 \text{\AA}^2$, respectively. These possibilities seem unrealistic. Consequently we have good reason to believe that the measured distribution is really the nascent CsH distribution.

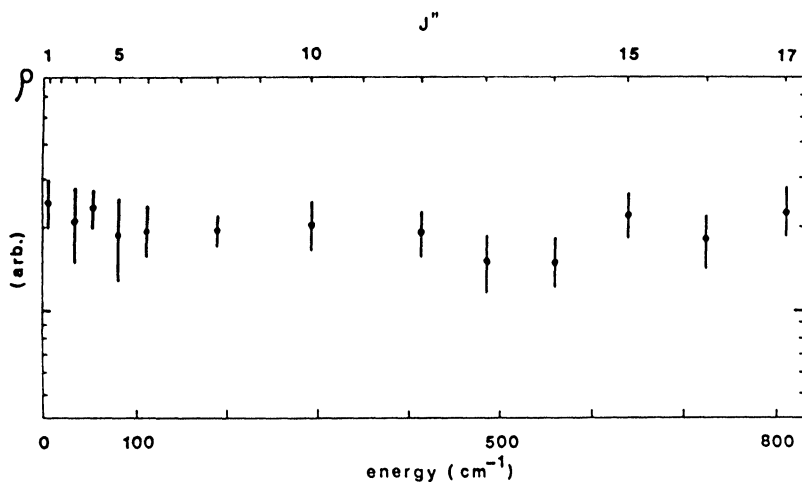


FIGURE 1 Ratio of the fluorescence intensities of CsH lines excited by laser 2' (nascent) and 2'' (thermal). The upper horizontal scale gives the rotational number of the photoexcited CsH state and the lower the corresponding rotational energy.

4. DISCUSSION

For some widely exoergic reactions like $\text{Mg}(3P_1) + \text{H}_2$ / 12 / or $\text{O}(^1D_2) + \text{H}_2$ /13/ a rather large rotational energy in the product was interpreted as the energy release from a bent triangular configuration /8/. In the case of $\text{H} + \text{D}_2$ the reaction is energetically balanced, but a large relative velocity is needed to overcome the energy barrier and a large rotational energy is measured in the product /14, 15/. The reaction that we have investigated is also balanced /16, 17/, but there is apparently no barrier /5, 18/, and no results for such a reaction are

available. The results concerning the rotational distribution seem compatible with either a colinear approach of the reactants or with the dissociation of a long living CsH_2 complex, if such a complex does exist.

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