Preliminary Investigations About the $\text{Cs}^* + \text{H}_2$ Collision

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The possible photoreactions leading to the formation of “laser snow” in cell experiment by laser irradiation of Cesium atoms to the ($7p$) level will be analyzed through crossed beam experiment. A single collision process would be excluded if an activation barrier was present in the inverse ground state reaction $\text{CsH} + \text{H} \rightarrow \text{Cs} + \text{H}_2$; accurate *ab initio* calculations exclude the existence of such a barrier. The ionic state $\text{Cs}^+ + \text{H}_2^-$ is suggested to make possible the electronic into vibrational energy transfer in the perpendicular collision.

1. INTRODUCTION

The formation of laser snow in cell experiments^{1–3} from the excitation of the Cs atom to the $7p\ ^2P_{1/2}$ level may be interpreted in several ways:

(1) the first possibility would involve a single collisional process insuring both the bond breaking and the electronic deexcitation

(2) one may also suppose that a first collision insures the deexcitation of the Cs atom and the conversion of the electronic energy of the Cs atom into vibrational energy of the H_2 molecule while a *second* collision of the vibrationally excited H_2 molecule with a ground state

Cs atom (the same or another) would lead to the photoproducts

(3) an intermediate excited complex might be formed from the first collision between Cs^* and H_2

while a second collision with a second (ground state) Cs atom would lead to the formation of two CsH molecules.

Among these three mechanisms, the first one should be easily studied from beam experiments, which are less suited for the second and third (two collisional) processes. However the rate dependence of the CsH formation in the $[\text{Cs}(6s)]$ concentration, demonstrated in cell experiments¹ supports these two-collision processes.

The following discussion is devoted to a preliminary study of the possibility of these various mechanisms.

The main energetic characteristics of the problem are summarized in Figure 1. It should be noticed that some uncertainty remains about the position of the final state $\text{CsH}(v=0) + \text{H}$ since the well depth D_e of CsH, which was estimated to be about $17\,200 \pm 500 \text{ cm}^{-1}$ by Tam and Happer,⁴ is now estimated to be about $14\,805 \pm 30 \text{ cm}^{-1}$ by S. C. Yang,⁵ in better agreement with other spectroscopic measurements,⁶⁻⁸ beam scattering experiments⁹ and theoretical calculations.¹⁰⁻¹² Using this last value for D_e , the excess energy for the first two mechanisms

$$\{E[\text{Cs}(7p)] + E[\text{H}_2(v=0)]\} - \{E[\text{CsH}(v=0)] + E(\text{H})\}$$

falls down to 0.05 eV; such a small value makes rather unlikely the single collisional process (1) or lets little hope for the second mechanism itself (2).

If it occurred through a single collision, the reaction might be viewed as a strongly perturbed analog of the basic reaction

which received the most careful theoretical efforts, since the Cs atom only brings its single valence electron in the chemical process.

FIGURE 1 Basic energetic features for various processes leading to CsH . (A) concerns process (1) and (2) while (B) concerns process (3).

However the ground state chemical reaction is terribly endoenergetic

and the reaction starts from the eleventh surface of the (CsH_2) complex. For an arbitrary geometry (C_{2v} symmetry) $\text{Cs}(6s)$ generates one surface $^2A'$ (and so does $\text{Cs}(7s)$), $\text{Cs}(6p)$ generates two surfaces $^2A'$ and one $^2A''$, while $\text{Cs}(5d)$ generates three surfaces $^2A'$ and two surfaces $^2A''$. If the reaction starts from the lowest $^2A'$ surface dissociating into $\text{Cs}(7p)$, this surface is the 8th one of its symmetry; if the reaction starts from an A'' surface, three A'' surfaces lie below it.

The paradox of this reaction, in either schemes (1) or (2), is that one should fall down from the eleventh surface to the ground state one without losing more than 0.05 eV!

2. FIRST PROBLEM

Where may the deexcitation occur, and how?

The deexcitation process is impossible in the $\text{CsH} + \text{H}$ region since all the excited surfaces are much too high. It can therefore only occur

in the Cs + H₂ region, and the mechanism is easily understood from an analogy with the electronic-into-vibrational energy transfer in the collision

which has been well studied both experimentally¹³⁻¹⁵ and theoretically.¹⁶⁻¹⁸ Translating the interpretation to our problem one may draw a qualitative picture of the potential curves for a perpendicular collision (Figure 2); the 2B_2 curves originated from Cs(*p*) states are attractive and cross the (Cs(6*s*) + H₂) 2A_1 ground state potential curve which is rapidly repulsive, due to the exclusion of the Cs(6*s*) and H₂ σ_g^2 electronic distributions of the same symmetry. The stabilization of the 2B_2 state is due to:

- (1) The lack of such a repulsion;

FIGURE 2 The lowest 2A_1 (full lines) and 2B_2 (dotted lines) potential curves for a perpendicular collision ($r_{\text{HH}} = 0.7 \text{ \AA}$). Energies and distances are in a.u. (non-empirical results).

(2) the possible charge transfer delocalization from the H₂σ_g to the empty Cs(6s) orbital;

(3) an inverse delocalization of the 7p electron in the σ_u^{*} orbital of H₂.

as expressed through the schematic steric and energetic diagrams.

The ²B₂ state coming from Cs(6p) crosses the repulsive wall of the ²A₁ ground state at short distances according to Figures 2 and 3.

The physical origin of the energy conversion is easy to understand since the stabilization factors of the ²B₂ excited state (σ_g → 6s and 6p → σ_u^{*} charge transfer) both weaken and lengthen the H···H bond. The qualitative shapes of the ²B₂ and ²A₁ potential surfaces $E(r_{\text{Cs} \cdots \text{H}}, r_{\text{H} \cdots \text{H}})$ for θ = 90° are given in Figure 3 where the ²B₂ surface appears as a closed valley going down to a lake while the ground state valley goes up rapidly. The surface change occurs for elongated HH distances and the H₂ molecule is vibrationally excited when the system enters the ground state surface.

However these comments are essentially valid for the Cs(6s) + H₂/Cs(6p) + H₂ intersection, and one should analyze:

(1) Whether the deexcitation occurs through this state and how the system may go from the Cs(7p) + H₂ surface(s) to the Cs(6p) + H₂ surface.

(2) Whether a more direct process cannot occur.

FIGURE 3 Schematic view of the 2A_1 ground state potential surface (full lines) with the 2B_2 ($\text{Cs}(6p) + \text{H}_2$) surface (dotted lines). The thick line represents the intersection.

The $[\text{Cs}^+\text{H}_2^-]^2B_2$ configuration plays an important role in the stabilization of the 2B_2 surfaces, and takes a large component in the short distance $\text{Cs}(6p) + \text{H}_2$ 2B_2 minimum. This configuration might cross the $\text{Cs}(7p) + \text{H}_2$, 2B_2 surface through an avoided crossing at large $\text{Cs} \cdots \text{H}_2$ distances and might allow to reach the lowest 2B_2 surface through a cascade of avoided and non avoided crossings (such a cascade is exemplified on the CsH problem, cf. Jeung *et al.*, 1983.¹²)

An other possibility might be that the system after entering the Cs(7p) + H₂ surface passes into the Cs⁺ + H₂⁻ system at a large Cs...H₂ distance for a short H₂ interatomic distance, while the Cs⁺ + H₂⁻ surface crosses the ground Cs(6s) + H₂ surface for large HH distances.

3. SECOND PROBLEM

Activation energy of the Cs + H₂ → CsH + H ground state reaction

Assuming that the excitation energy has been fully converted into H₂ vibrational energy, the main question concerns the ground state surface characteristics: if the reverse reaction CsH + H → Cs + H₂ presents an activation energy larger than the excess energy (i.e., 0.05 eV), the reaction will be impossible (except for a weak tunnelling effect). The order of magnitude of this activation energy is the preliminary quantity to be calculated before studying the whole surface.

From electronic evidences (and the experience on the H₂D problem) the saddle point for the ground state reaction must be searched in the colinear collision Cs - H_A - H_B.

Precise calculations have been performed (cf. Appendix) which lead to the picture of the ground state surface as the perpendicular crossing of two valleys; the Cs + H₂ valley goes up slowly when $r(\text{Cs} + \text{H}_A)$ diminishes, without any significant lengthening of the H_AH_B bond. When $r(\text{CsH}_A)$ reaches the molecular bond, a high valley leading to CsH + H region opens in the left side wall of the Cs + H₂ valley, slowly going up to the CsH + H limit *without any saddle point*.

The potential surface shape is very unusual for two reasons:

- (1) The turn occurs for a very compact geometry where both CsH and HH bond lengths take their diatomic values (while in most cases the XY and Y₂ distances are both increased in the corner of the XYZ collision minimum energy path);
- (2) There is not any barrier along the process.

The later conclusion makes possible the reaction

but it shows that the CsH molecules should disappear as soon as they meet an H atom. One may imagine that a recombination has no

opportunity to occur in beam experiments but for cell experiments, one must invoke a stabilizing process; the dimerization energy of $(\text{CsH})_2$

is under study.

4. DISCUSSION

The first (single collision) process is not demonstrated to be impossible. It suffers from a contradiction since the energy transfer seems to be more efficient for perpendicular collision while the ground state reaction prefers the colinear collision. An answer would require calculations for $\theta \neq 90^\circ$ and 0° , since the surface hopping may occur for avoided crossings and the barrier on the ground state surface may remain low enough for $\theta \neq 0$.

FIGURE 4 The ground state $^2\Sigma^+$ potential surface for the colinear collision. The valence energies are (a) $= -1.31$ a.u., (b) $= -1.30$ a.u., etc. . . . The distances are in a.u. (non-empirical results).

One may also imagine some coupling with the rotation of the H_2 system along the reaction.

From a theoretical point of view, the rejection of the single collision mechanism requires both estimations of the whole surfaces and dynamic calculations. But the answer certainly came from the beam experiment described hereafter.

5. EXPERIMENTAL TECHNIQUE

The crossed-beam experiment that has been built to determine the mechanism at the origin of CsH formation is now ready to run. It consists mainly in a supersonic molecular beam of hydrogen which crosses perpendicularly a supersonic beam of cesium atoms in a collision chamber (cf. Figure 5). A first laser beam (laser 1) provided by a single mode c.w. laser tuned to one of the second resonance lines

FIGURE 5 Schematic description of the crossed beam experiment apparatus.

of Cs ($\lambda = 459.3$ nm or 455.5 nm) excites the atoms to the $7P_{1/2}$ or $7P_{3/2}$ levels. It is sent into the collision chamber, at the crossing point of the two beams, perpendicularly to the plane of collisions. A second laser beam (laser 2) provided by a single mode ring laser is sent colinearly to the first one; it is tuned to an absorption line of the CsH molecule ($X^1\Sigma^+ - A^1\Sigma^+$). The fluorescence light of the $A^1\Sigma^+$ rovibrational levels is then collected from the collision volume and sent to a photomultiplier.

The advantages of such a technique are well-known. Supersonic beams provide large densities of molecules or atoms (in our case, 10^{13} mole/cm³ in the collision volume for the H₂ beam, typically); the vibrational and rotational temperatures of the molecules are lowered in the nozzle expansion, providing reactants in well-defined energy states (internal and external). The use of crossed beams and lasers thus leads to "ideal" conditions for observing the effect of a unique collision of well-defined energy and geometry.

In a first step, we intend to determine whether the CsH formation proceeds via a single-collision process or a two-collision one. The geometry of the set-up could be managed if it appeared that a second collision is necessary to produce the reaction. The detailed analysis of the distribution of rovibrational states of the products is the necessary second step of development giving rise to information on the state-to-state mechanism of formation. Other experiments are prospected.

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Appendix

QUANTUM CHEMICAL CALCULATIONS, METHODOLOGY AND RESULTS

The Cs atom is considered as bringing one valence electron only. The core is first treated through a relativistic pseudopotential extracted from Pauli type calculations on the atom in Cs(6s), (6p) and (5d) configurations. This pseudopotential incorporates the spatial and energetic effects of the mass-velocity correction on the valence levels.

The core polarizability being important in such heavy atom, the core-polarization and core-valence correlation effects have been included through an original method¹⁹⁻²⁰ which goes through the calculation of the electric field created by the valence distribution and outer nuclei on the Cs atom and the fluctuation of this field. This method avoids the artefacts of the r^{-4} operators proposed by Bottcher *et al.*²¹ Bardsley *et al.*²² for the same purposes.

The basis set involves 4s, 4p, 2d atomic orbitals for Cs, 3s, 2p for each H atom.

The precision of the method may be estimated from the calculated characteristics of CsH reported in Table I.

The ground state potential surface reported in Figure 4 for the colinear collision has been calculated from a multiconfigurational zeroth-order wave-function including 198 determinants built from properly orthogonalized atomic orbitals. The resulting zeroth order wave-function was perturbed to the second order by all other valence determinants and by the core-valence excited determinants.

TABLE I
CsH electronic states $X\ ^1\Sigma^+$ and $A\ ^1\Sigma^+$; calculated and experimental characteristics

		Theory	Experiment
$X\ ^1\Sigma^+$	D_e	1.80 eV	1.836 ^a eV (2.13 ^b eV)
	r_e	2.36 Å	2.49 Å
	ω_e	871 cm ⁻¹	891 cm ⁻¹
$A\ ^1\Sigma^+$	D_e	1.07 eV	1.08 eV
	r_e	4.28 Å	3.96 Å
	ω_e	196 cm ⁻¹	165.7 cm ⁻¹

^a Ref. 5.

^b Ref. 4.

As a preliminary report about the perpendicular collision, the potential curves for $r_{\text{HH}} = 0.7\ \text{\AA}$ are given in Figure 2. The crossing between the ground 2A_1 and lowest 2B_2 excited states appears very well. At short Cs—H₂ distances the 2B_2 state is strongly ionic Cs⁺...H₂⁻, with a strong mixing with Cs($5d_{xy}$) + H₂. Numerous avoided crossings appear in this figure. The details of the potential surfaces for the perpendicular collision and their interpretation will be given later on.