

LASERS AND REACTIVE COLLISIONS: THE Cs\* - H<sub>2</sub> REACTION

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The detailed study of the collision between two reacting molecules is the necessary step for the understanding of elementary processes of reaction. Modification, breaking and creation of chemical bonds are determined by a number of parameters, internal energy, kinetic energy, relative orientation of reagents ..., whose control is essential before, during and after the collision. This is the aim of state-to-state chemistry to follow as closely as possible the evolution of these parameters and to evaluate the individual cross-sections.

During the last two decades, the search for an "ideal" experiment where the whole set of parameters could be determined has made considerable progress with the advent of new sophisticated techniques. Among them, the technique of supersonic molecular beams offers unique possibilities, in particular with the good definition of internal and external energies of reagents which can be achieved. Use of two crossed beams of fixed geometry leads to product analysis after a unique collision has taken place, i.e., the analysis is free of complications due to successive encounters; variation of the kinetic energy allows for the determination of activation barriers; angular analysis of the product distribution yields information about the geometry of the reactive collision.

Although extremely powerful, this technique is generally

restricted to atoms and molecules in their ground state. Furthermore, chemical systems of interest for a useful comparison between theory and experiment are still relative to simple ones: this is due to the fact that the methods of Quantum Chemistry are able to provide accurate potential energy surfaces for systems implying a small number of atoms only, typically up to three or four. Moreover, the dynamics of collision of these surfaces is still in its infancy since, even for simple systems, one is able to evaluate state-to-state cross-sections for a limited number of circumstances only, a collinear approach of non-rotating reagents for example.

In this context, use of tunable lasers is obviously of great interest for state-to-state chemistry. To schematize, state-selective excitation of reagents (electronic, vibrational, rotational) is easily accomplished and the subsequent effect on reactivity can be observed; second, large amounts of energy can be deposited into the system, hence the possible study of endoergic reactions; third, polarization of laser beams allows for the study of the orientation dependence of the cross-section; fourth, photodissociation products and unstable species (radicals) can be obtained in the zone of collisions by use of intense (pulsed) laser beams. Finally, the technique of laser-induced fluorescence offers two advantages in the detection of nascent products: a quasi-infinite energy resolution and a high sensitivity.

It comes therefore that the combined use of molecular beams and laser beams approaches the conditions required for an "ideal" state-to-state experiment, can multiply the number of experimental situations of interest and lead to the observation of new features. Up to now, there exists only a few experiments of this kind, but numerous data have been gained already by use of less versatile and less sophisticated experiments. Let us mention briefly several results of major importance (a non-exhaustive list!) <sup>1-7</sup>.

The Vibrational Enhancement

Perhaps the most striking effect was observed in the lightly endo-ergic reaction:  $\text{HCl} + \text{Br} \rightarrow \text{HBr} + \text{Cl}$ , where the vibrational excita-tion of HCl molecules with a pulsed HCl laser beam in the infrared yields an increase of the reaction rate by a factor  $10^{11}$  from  $\text{HCl}(v=0)$  to  $\text{HCl}(v=2)^8$ . It can be explained simply by considering that the vibrational excitation is used to overcome the activation barrier of the reaction. This experiment was conducted in "bulk" phase but was extended later on to other species in beam + gas ar-rangements; study of the reactions:  $\text{HCl} + \text{K}$ ,  $\text{HF} + \text{Ca}$ ,  $\text{Sr}$ ,  $\text{Ba}$  led to some generalization of the efficiency of vibrational/translational excitation of reagents<sup>9-13</sup>. For instance, theory confirmed by ex-periment predicts that for an exoergic reaction, vibrational ener-gy is most effective at promoting reaction when the potential en-ergy surface shows a late barrier (mostly an attractive surface) whereas translational energy is most effective in the case of an early barrier. In many cases, the vibrational distribution of prod-ucts is out of equilibrium.

Similar experiments were performed with a rotational excita-tion of reagents, but with less spectacular effects. It was shown for example that for endoergic reactions of the type:  $\text{HX} + \text{Na} \longrightarrow \text{NaX} + \text{H}$  ( $\text{X} = \text{F}, \text{Cl}$ ) the rate constant shows a minimum for interme-diate values of the rotational quantum number<sup>14</sup>.

Electronic Excitation of Reagents

Electronic excitation by tunable lasers (pulsed or C.W.) is widely used in bulk experiments for a number of simple or heavy molecules<sup>4</sup>; it is not the case in beam arrangements although, compared to others (electronic bombardment, photodissociation), this technique offers the advantage of selectivity and simplicity. Let us mention the following cases:  $\text{I}_2^* + \text{F}_2^{15}$ ;  $\text{Mg}^* + \text{H}_2$ ,  $\text{D}_2^{16,17}$ ;  $\text{Ca}^* + \text{HCl}$ ,  $\text{Cl}_2$ ,

$\text{CCl}_4^{18-20}$  and more recently  $\text{Cs}^* + \text{H}_2^{21}$ .

Perhaps the most appealing example is the one of  $\text{Ca}^* + \text{HCl} \rightarrow \text{CaCl} + \text{H}$ , for which laser excitation of Ca atoms in a beam + gas arrangement directly demonstrates the influence of reagent's orientation. During the reaction,  $\text{CaCl}$  molecules form preferentially in ( $\text{A}^2\Pi$ ) or ( $\text{B}^2\Sigma^+$ ) states, depending on the approach direction of Ca p orbitals which is determined by the laser beam polarization: a parallel approach with respect to HCl favors the formation of  $\text{CaCl}$  in the B state. Other effects are observed with  $\text{Cl}_2$ . Interpretation suggests that in an electron-jump model, the symmetry of reagents must be conserved.

$\text{Cs}^* + \text{H}_2 \rightarrow \text{CsH} + \text{H}$  is a case where laser excitation of one species is used to compensate the large endoergicity of the reaction; first observed in a bulk experiment<sup>22</sup>, the reaction is now studied in a crossed-beam arrangement, with laser excitation of Cs atoms and laser detection of CsH products. Study of this reaction is the main subject of this Lecture.

#### The $\text{Cs}^* - \text{H}_2$ Reaction

The reaction of Cs atoms with molecular hydrogen in their ground state is known to be highly endoergic:  $\Delta H = 2.7$  eV, the difference between the energy of dissociation of  $\text{H}_2$  and that of  $\text{CsH}$ . The spectrum of  $\text{CsH}$  could be studied years ago, production of  $\text{CsH}$  molecules being ensured by heating Cs and  $\text{H}_2$  in high-pressure cells<sup>23,24</sup>. In 1975, however, W. Happer and coll. discovered that by sending an  $\text{Ar}^+$  laser beam at  $\lambda = 4579 \text{ \AA}$  or  $\lambda = 4545 \text{ \AA}$  in such cell, quantities of particulates formed in the region of the beam ("laser snow"<sup>22</sup>). This phenomenon was interpreted by initial laser-induced formation of  $\text{CsH}$  molecules since, Cs atoms being excited to one of the two levels  $7P_{1/2,3/2}$ , the endoergicity of the reaction is just compensated (Figure 1); crystallisation of  $\text{CsH}$  molecules can occur further on. Other experiments conducted in gas cells with tunable

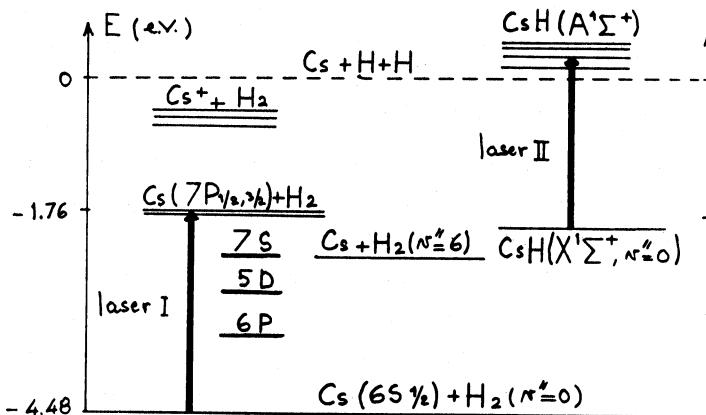
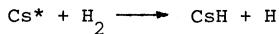


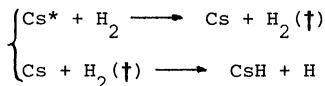
FIGURE 1 Potential energy diagram of the system

lasers confirmed this interpretation<sup>25-27</sup>.

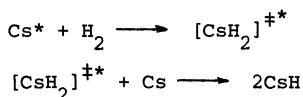
These experiments and energy considerations also put into evidence one other aspect of the problem. When Cs atoms are excited to the 7p state, the amount of energy which is available above threshold is drastically small: 0.0016 eV and 0.024 eV for  $7P_{1/2}$  and  $7P_{3/2}$  respectively. Furthermore, the initial system ( $\text{Cs}^* + \text{H}_2$ ) is at least on the 11th potential energy surface from the ground state, implying that many surface crossings must necessarily occur during the reaction. Under these conditions, is a unique collision able to promote the direct reaction:



with simultaneously electronic deexcitation and bond breaking, or is it necessary to invoke more complicated processes whose energetics is more favorable? For instance, one could think to the following two-collision processes<sup>28</sup>:



and



the first one with transfer of electronic excitation in Cs to vibrational energy of  $\text{H}_2$ , the second with formation of an intermediate excited complex.

The experiments mentioned previously are not able to yield definite answers to this problem since, in gas cells, multiple encounters can occur between atoms and molecules; furthermore the relative kinetic energy is not perfectly determined for each collision. One could attribute the formation of CsH observed in 30's, to multiple collisions between particles of high energy which exist in the tail of the velocity distribution.

Quantum Chemistry on the other hand yields interesting preliminary predictions in the case of  $(\text{Cs} + \text{H}_2)^{28}$ . Calculations performed with ab initio methods including relativistic pseudo-potentials, large basis sets, accurate configuration interaction show that the adiabatic ground state potential surface does not present any saddle-point between the entrance valley and the exit plateau, in the case of a collinear approach of the reagents. Therefore  $\text{Cs}^*$  and  $\text{H}_2$  could in principle react during the course of a unique collision, but with a small cross-section.

A positive (or negative) answer can come from a crossed-beam experiment: in this case, one is able to observe the effect of a unique collision of well-defined geometry and energy. The facile interfacing with laser beams allows for Cs excitation and CsH detection by use of the technique of laser-induced fluorescence.

#### Experimental

Figure 2 shows schematically the experiment which has been realized at Laboratoire Aimé Cotton, Orsay. A supersonic beam of molecu-

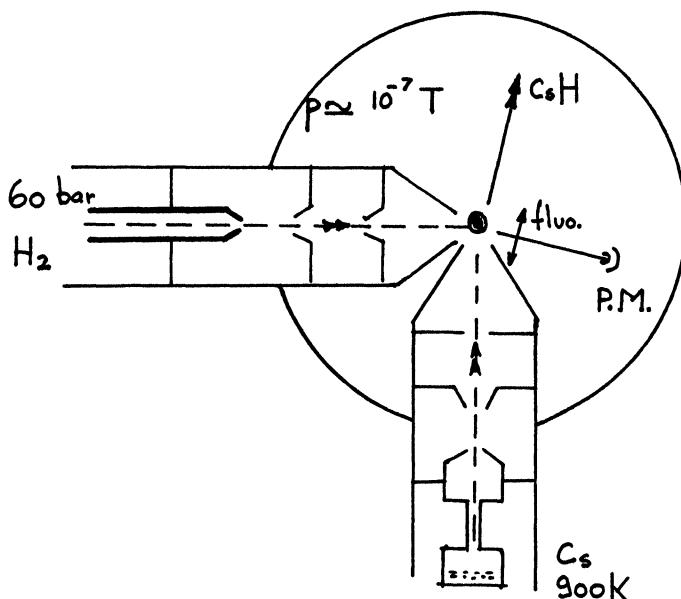


FIGURE 2

lar hydrogen and a supersonic beam of atomic cesium enter a collision chamber and cross at right angle. Perpendicularly to the plane of collision, a first laser beam excites Cs atoms at the crossing and a second laser beam excites CsH molecules to the ( $A^1\Sigma^+$ ) state from which they fluoresce. The fluorescence light is collected and sent to a photomultiplier through a series of filters; the P.M. signal is analyzed and stored.

The supersonic beam of hydrogen has been built according to technique developed by R. Campargue<sup>29,30</sup>. A high pressure of H<sub>2</sub> (60 bars typically) is established in a first chamber separated from a second one by a nozzle through which the molecule expand. In the second chamber, which is maintained at low pressure by high-velocity pumping, a region of hydrodynamical regime is created, separated from the molecular regime by a shock wave; in the hydrodynamical region, molecules propagating on the axis suffer many

collisions and acquire large velocities to the expense of rotational and vibrational energies. A skimmer allows for these molecules to enter a third high-vacuum chamber without perturbation; then they enter the collision chamber through a collimator. This beam offers interesting characteristics since molecules are rotationally and vibrationally cooled (typically up to 1 K and 10 K respectively) and their velocity distribution is narrowed (typically  $\Delta V/V \sim 0.1$ ). Furthermore high densities of particles are obtained (typically  $10^{13}$  molecules/cm<sup>3</sup> at the crossing point).

The beam of cesium is obtained by evaporation of the metal held in an alkali-resistant oven heated at 900 K; Cs atoms effuse through a nozzle maintained at 1000 K and two successive diaphragms which define the geometry of the beam. These diaphragms are cooled at 300 K to avoid secondary emission. Migration of liquid metal and trapping of atoms not directly used in the beam permit the use of moderate quantities of cesium. Typical densities of  $10^9$  atoms/cm<sup>3</sup> at the crossing point are obtained. By heating more the oven and the nozzle, one should obtain a supersonic regime with the subsequent reduction of the velocity distribution and a larger density of particles.

The two laser beams are provided by C.W. tunable dye lasers; they are mixed on a beam-splitter and they enter the collision chamber through a Brewster-angle window. Light baffles reduce the stray light inside the collision chamber. The two beams are concentrated at the crossing point so that their waist is adapted to the dimensions of the particle beams, 2 mm - diameter typically. The first beam is frequency-locked on the most intense hyperfine component of one resonance line of Cs, at  $\lambda = 4555 \text{ \AA}$  or  $\lambda = 4593 \text{ \AA}$ , by means of a servo-controlled system which uses the blue fluorescence signal due to Cs atoms excited at the crossing point. The second beam is frequency-locked on the center of a Doppler-broad-

ened line of CsH molecules produced in a sealed-off cell outside the collision chamber, by means of the fluorescence signal at this wavelength. By changing CsH transitions in the ( $A\ ^1\Sigma^+$  -  $A\ ^1\Sigma^+$ ) system, it is possible to monitor the population distribution of products on each rovibrational level of the X state.

A small fraction (~4%) of the total fluorescence due to CsH molecules produced at the crossing point is collected by an optical system and detected by a low-noise photomultiplier through a series of filters which eliminate stray light and fluorescence light due to excited Cs atoms. Under these conditions the level of the background is typically of 3 photons/second; as one expects very weak signals photon-counting techniques and data storage must be used.

#### First Results

In search of a signal due to CsH molecules, it has been necessary first to determine accurately the frequency of the relevant (A - X) transitions of the molecule. This has been performed by use of laser-induced fluorescence techniques, by recording simultaneously the spectrum of CsH provided by the sealed-off cell and the spectrum of an I<sub>2</sub> cell<sup>31</sup>. In this manner, 40 lines have been identified, involving the v"=0 and v"=1 levels of the X  $\ ^1\Sigma^+$  state<sup>32</sup>; according to energy considerations, the CsH molecules created in the crossed-beam experiment must involve these two levels only (see Figure 1 and Figure 3).

A weak signal has been detected for several values of the rotational quantum number ( $1 \leq J'' \leq 13$ ) in the v"=0 level<sup>21</sup>. This signal is characteristic of CsH molecules produced at the crossing point of the collision chamber since it vanishes:

- i) in the absence of hydrogen;
- ii) without excitation of Cs atoms;
- iii) by slightly detuning the second laser from line center;

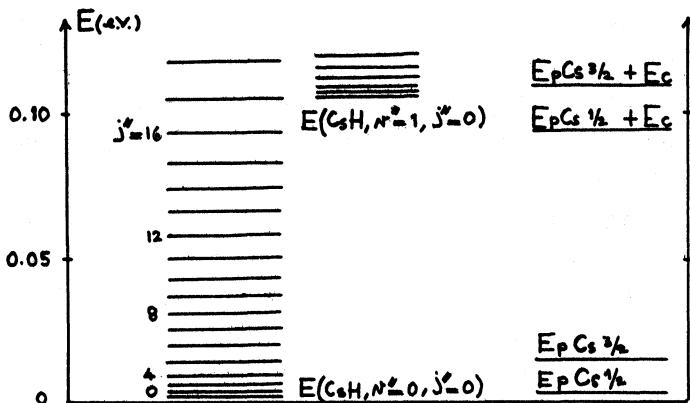


FIGURE 3 Energy diagram of the system. Left: rotational levels of  $\text{CsH}$  ( $X^1\Sigma^+$ ,  $v''=0$ ). Center: rotational levels of  $\text{CsH}$  ( $X^1\Sigma^+$ ,  $v''=1$ ). Bottom right: potential energy of  $\text{Cs}(7P_{1/2}, 3/2) + \text{H}_2$ ). Top right: potential energy + kinetic energy.

for instance, no signal could be detected for detunings as small as  $2 \cdot 10^{-3} \text{ cm}^{-1}$ . This indicates that the spectral width of the signal is of the same order, or less, in accordance with the residual Doppler width which is expected in these beam experiments. This test is probably the most sensitive one.

No signal could be detected for transitions involving the  $v''=1$  levels. The surprising result of these measurements however, is in the fact that for a  $7P_{1/2}$  excitation of Cs atoms, the signal is larger than for a  $7P_{3/2}$  one. Figure 4 shows an example of the data which has been obtained on the ( $v'=5, J'=7 \leftarrow v''=0, J''=6$ ) transition. The signal is multiplied by a factor 6 by simply changing the wavelength of the first laser from  $\lambda = 4555 \text{ \AA}$  to  $\lambda = 4593 \text{ \AA}$ . According to the ratio of excited populations of cesium ( $n 7P_{3/2}/n 7P_{1/2} \sim 1.7$ ) which can be deduced from the measurement of atomic fluorescence, this means that the reactive cross-section is roughly 10 times larger for a  $7P_{1/2}$  excitation of Cs atoms.

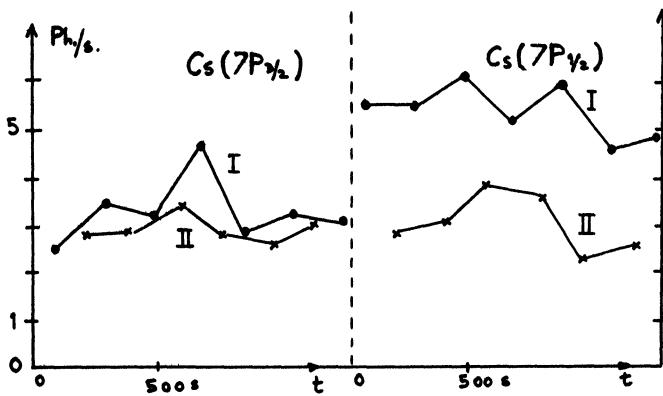


FIGURE 4 Histogram of the signal recorded on the transition  $A(v'=5, J'=7) \leftarrow X(v''=0, J''=6)$  in a series of trials performed under same experimental conditions except Cs excitation. Left: Cs(7P<sub>3/2</sub>) excitation: curve I with H<sub>2</sub>, curve II without H<sub>2</sub>. Integration time: 100 s. Second laser output power: 170 mW.

A theoretical interpretation of this result has been suggested by J. P. Malrieu by consideration of the relevant potential energy surfaces of the system<sup>21</sup>. Calculations show that a crossing exists at low energy between the  $(\text{Cs}(7P) + \text{H}_2)$  neutral surface and the  $(\text{Cs}^+ + \text{H}_2^-)$  ionic one, and that the ground state of CsH is strongly polar, i.e.,  $(\text{Cs}^+ + \text{H}^-)$ . Therefore, one can imagine that the system enters the  $(\text{Cs}(7P) + \text{H}_2^-)$  valley, jumps on the  $(\text{Cs}^+ + \text{H}_2^-)$  surface and remains diabatically on the  $(\text{Cs}^+ + \text{H}^- + \text{H})$  ionic one when the distance between H atoms increases, despite avoided crossings with the lower neutral surfaces related to Cs(7s), (5d), (6p), and (6s). In this manner, the suggested mechanism of reaction should be a type of harpooning leading to a molecular "zwitterion" and one atom. The interesting feature is that  $\text{Cs}(7P_{1/2})$  with  $\text{H}_2$  generates  ${}^2\Sigma^+$  states which have the same symmetry as that of the ionic states, whereas  $\text{Cs}(7P_{3/2})$  generates  ${}^2\Pi$  states which are not relevant for the jump onto the ionic surface, in a collinear

approach of the reagents. Similar considerations were already suggested to explain this "fine structure" effect<sup>33,34</sup>.

Other data can be extracted from these measurements. First, observation of a signal for  $J''$  values up to 13 in the  $v''=0$  level (see Figure 3) indicates that the relative kinetic energy is necessarily transformed into rotational energy during the course of the collision since the only potential energy is not sufficient. For a system at threshold like this one, it is mostly interesting to determine the rotational distribution of products, as can be done by laser-induced fluorescence techniques. Second, by evaluating the density of excited Cs atoms, the efficiency of collection of fluorescence of CsH molecules and their probability of excitation , it is possible to get the value of the reactive cross-section, here  $10^{16} \text{ cm}^2$  for a  $7P_{1/2}$  excitation of Cs atoms. Due to present experimental uncertainties, this value must be considered as an order of magnitude only, but the same experimental data indicate that a two-collision process would require cross-sections of the order of  $10^{-13} \text{ cm}^2$  for each collision to lead to the same signal. Consequently a two-collision process is rather unlikely to occur in this experiment.

#### Possible Developments

As explained above, determination of the rotational distribution of products is of major importance in such system at threshold. However, there are other aspects of the laser excitation of Cs atoms which could be interesting; for instance, excitation to Rydberg levels should lead to different values of the reactive cross-section and to different rotational and vibrational distributions of products. In this case , the optical electron of the atom is less and less bound to the nucleus and the harpooning mechanism which is suggested to occur in the reaction, should become more and more

efficient. Up to now, there is no systematic result concerning this question, for endoergic and for exoergic reactions.

Second, comparison between the efficiency of photon excitation versus kinetic energy is made possible by use of the technique of "seeded" beams; addition of a light carrier gas in the beam of cesium should allow, at least partially, for compensation of the endoergicity of reaction. Also, vibrational excitation of hydrogen could be possible by electronic bombardment; unfortunately, this technique is not yet selective in energy.

Third, the technique of Doppler tuning developed for atom-atom scattering could yield the angular distribution of products. In this technique, the laser beam which induces the fluorescence of CsH molecules is sent into the collision chamber, in the direction of relative velocities at the center of mass of the system. Then, there is a unique relation between the angle of deflection of CsH molecules and the detuning of the laser with respect to line-center: only respond those molecules whose velocity projection on the laser beam obeys the Doppler relation. However, this technique suffers from an important loss in sensitivity due to the angular resolution it-self.

To conclude, the crossed-beam experiment with laser excitation of reagents and laser detection of products which has been described here, appears to have versatile applications in many aspects of reactive collisions. It should be emphasized once more that the necessary need for interpretation implies Quantum Chemistry calculations which are still limited to simple situations. The author is pleased to acknowledge with thanks his colleagues of Laboratoire Aimé Cotton, Orsay, and Laboratoire de Physique Quantique, Toulouse, for participation to the experiment and interpretation of the data.

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