

H₃⁺-synthesis on the surface of *d*-transition metals during the process of field desorption

AGNIESZKA TOMASZEWSKA, ZDZISŁAW M. STĘPIEN

Institute of Physics, Pedagogical University, al. Armii Krajowej 13/15, 42-200 Częstochowa, Poland.

A model of the formation process of a hydrogen molecule on the surface of metal in strong electric field is proposed based on the results of the experiment and quantum chemistry calculations. In the low-temperature process of field desorption from the surface of *d*-transition metals carried out in an atmosphere of hydrogen, the ions H₃⁺ of the hydrogen are recorded. The experimental work in which the ion energy distribution of hydrogen ions desorbed from a surface of Co has been recorded, reveals a strong dependence of the maximum yield of desorption ions on the electric field strength and the surface structure. In the case of Co and most other metals hydrogen molecules are formed on the terraces of low-index crystallographic planes. The total energy of the ionization potential of a molecule of three-fold symmetry has been calculated by employing a method of quantum chemistry.

1. Introduction

An atom of hydrogen has the simplest possible electronic structure among all the elements. It has only one valence electron and one orbital accessible to create a bond. In the ground state the electron may be described by using a wave function of 1s. This means that H atoms can join into pairs to form an H₂ molecule. As early as in 1912 Thompson, in the experimental way – by using mass spectrometry, recorded the mass 3 of hydrogen which was ascribed to an ion of H₃⁺. Molecules of H₃ are not stable as free particles in the space, which results both from theory and from experiment. An exception comes from Hersberg's observation [1], who recorded an optical spectrum of such particles in low temperature plasma. In that experiment, stable H₃⁺ ions recombined with free electrons into a neutral molecule of hydrogen. In the next years, a small amount of H₃⁺ ions was recorded by CLEMENTS and MÜLLER [2] who investigated a surface of tungsten in an atmosphere of hydrogen in the field ionization mass spectroscopy. The formation of hydrogen ions was ascribed to a field-promoted surface reaction. Although the reaction was investigated several times in the next years [3]–[13], its mechanism has not been sufficiently elucidated.

In the present paper H₃⁺ ion formation is discussed based on experimental results obtained by means of laser-light-stimulated field desorption of hydrogen from a surface of cobalt. The results are complemented with calculations by employing the techniques of quantum chemistry.

2. Experimental

The instrument used in this investigation was a high-resolution pulsed-laser time-of-flight atom-probe field (PLTFAP) ion microscope [14]. The ultra-high vacuum experimental conditions and the measurement procedure were the same as described in [15]. The field emitter tip was obtained from a cobalt wire of 99.99% purity by means of electropolishing. The specimen temperature was kept at 20 K in all the experiments and the operating pressure of hydrogen was 10^{-6} Pa. Before each experiment, the emitter surface was processed to an atomic end-form by low-temperature field evaporation in the presence of image gas.

The ion energy deficit was measured using a time-of-flight method as described by LIU *et al.* in [16] of Tsong's earlier studies. For this purpose, the ion energy deficits are calculated from the relation

$$\Delta E_c^n = ne \left(V_0 - \frac{M}{nC(t_0 - \delta)} \right) \quad (1)$$

where ne is the ion charge, V_0 – the tip potential, M – the ionic mass, C – the flight path constant, t_0 – the flight time and δ is the time delay constant.

Some quantum chemical calculations were done in order to explain the results obtained in the experiment. For numerical computations, the GAUSSIAN 98 program package [17] was employed. The *ab initio* method was used with the Hartree–Fock approximation. The total energy of the investigated species was calculated self-consistently (SCF method) using the molecular-orbital theory. The correlation energy within the Möller–Plesset perturbation theory of the second order was applied as a post-SCF method which enabled the correlation energy correction to be included.

3. Results and discussion

The field desorption experiment with the surface of cobalt yielded a spectrum of H^+ , H_2^+ and H_3^+ ions. Figure 1 shows the relative intensity of ionic desorption as a function of electric field strength at the emitter tip surface of cobalt. The H_3^+ ions in question were observed in the range 20–32 V/nm of electric field strength, with the largest amount of the desorption ions originated from edges of the (0001) plane of cobalt. Such amount of H_3^+ ionic desorption was observed also for Ir, Ni, W, Au, Fe, Re, Ta and Nb. Upon analyzing all the results it seems that the yield of H_3^+ ions in this process depends on both the surface structure and the type of atomic species that composes the surface. As to the structure, the most favorable atomic edges for the process seem to be edges of close packed crystallographic planes, which is particularly apparent in the experiments employing the pulsed-laser imaging atom-probe (PLIAP) techniques [7]. An interesting question arises if and where H_3 molecules appear on the surface of the emitter, as well as how the H_3^+ ions are formed in the desorption process. An answer to this question can be given in part by

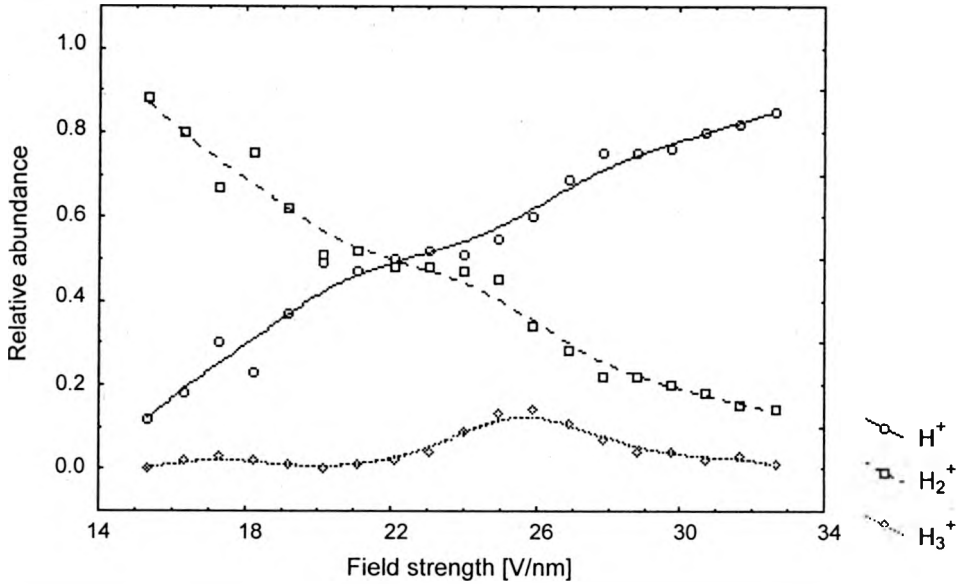


Fig. 1. Relative abundances of H^+ , H_2^+ and H_3^+ ions as a function of the applied field collected from the Co(0001) steps.

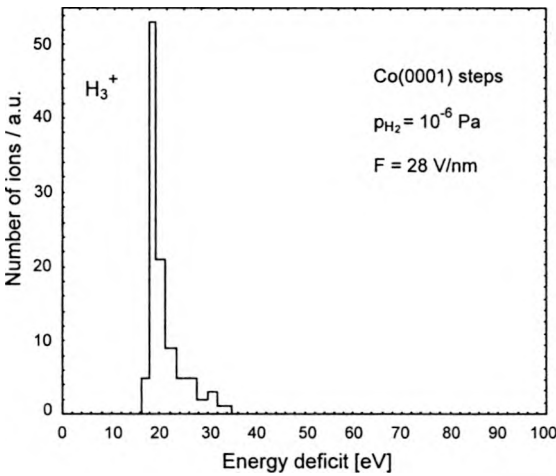


Fig. 2. Energy distribution of H_3^+ ions taken in 10^{-6} Pa H_2 and $F = 28$ V/nm.

performing the measurement of the energy distribution of desorption ions. A result for the edges of the Co(0001) plane is shown in Fig. 2.

As shown by FORBES [18], the field ion appearance energy (from an (hkl) plane) is related to the ion energy deficit by

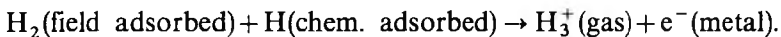
$$A_n^{hkl} = \Delta E_c^n + n\phi_{av} \tag{2}$$

where φ_{av} is the effective work function of the flight tube, assumed to be 4.5 eV. This parameter was derived, before each experiment, from the value of the appearance energy of He^+ , Ne^+ and Ar^+ , and was estimated in the same manner as in paper [16]. The appearance energy of n -fold charged field-desorbed ions can be expressed from a thermionic cycle by [18]

$$A_n^{hkl} = \sum_{i=1}^n I_i + A^{hkl}(F) - Q(F) \quad (3)$$

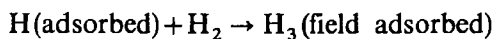
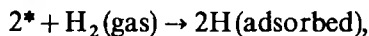
where I_i is the i -th ionization energy of an atom, A^{hk} is the binding energy of the atom (or the adsorption energy) in the high electric field at the (hkl) plane of the emitter and $Q(F)$ is the activation energy of field evaporation of the atom.

It results from our measurements that the appearance energy of an H_3^+ ion amounts to 13.1 ± 0.2 eV. This result is in good agreement with those obtained for the surfaces of other metals by TSONG and KINKUS [6], and ERNST [11]. Once the ionization potential of an H_3 molecule is known, one could estimate the binding energy of the molecule with the surface. A theoretical value of the ionization potential has been calculated for a molecule in the assumed form of an equilateral triangle (whose geometry has been optimized relative to the total energy minimum). Then, the H_3 ion is treated as an equilateral triangle as well, with a length of side equal 0.87 Å. The first ionization potential of such a molecule amounts to 9.03 eV. By neglecting temperature effects (in our case $T = 20$ K) and relatively low activation energy, the binding energy surface/molecule can be calculated from Eq. (3). In this case one obtains a value of 4.07 eV for the binding energy. In view of that the binding energy of hydrogen with the Co (0001), upon the adsorption process, amounts to about 2.6 eV [19]. The result obtained seems to be reasonable. Such a low value of the binding energy, when combined with the fact that the energy distribution of hydrogen ions does not exhibit a low-energy tail (or at most such one is exceptionally narrow), leads to the conclusion that the ions of interest originate in strictly defined conditions, just at the very surface of the emitter. During the course of the desorption induced by laser light pulses the heating rate of the surface is 200 K per ns. A desorption molecule excited in this way must be simultaneously ionized at the distance not exceeding 3 Å from the surface. ERNST and BLOCK [5], basing on their measurements of the field ionization of hydrogen at metallic surface, have proposed that hydrogen ions are formed owing to the reaction (H_3^+ ion is formed at the moment when a chemisorbed H atom combines with a field adsorbed H_2 molecule)

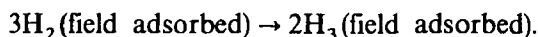
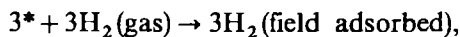


In view of that in our experiments the emitter temperature was 20 K, where hydrogen does not adsorb dissociatively, the above reaction path does not seem to be probable in the present case. Moreover, in the model mentioned above, the effect of both the substrate structure and the high electric field is not taken into account.

TSONG [20] has proposed two formation mechanisms for a hydrogen molecule on the surface of the emitter, a dissociative mechanism and an associative one:



or



An asterisk (*) here represents an adsorption site.

Basing on experimental results [6] Tsong suggests the associative mechanism to be more likely under the high field conditions.

From the energetic point of view a reaction is more probable to occur when the whole sum of its products is less than the energy of its substrates ($\Delta E = E_s - E_p$). The quantum chemistry techniques give a result of 2.6 eV and 4.37 eV for the former and the latter mechanism, respectively. Hence, the associative model appears to be energetically more favorable. On the other hand, a similar difference between the energies can be calculated in a direct way for an ion of hydrogen, which is shown in the Table.

Table. Changes of the investigated systems' total energy.

Type of reaction	$\Delta E = E_s - E_p$ [eV]
$H_2 + H^+ \rightarrow H_3^+$	1.81
$H_2^+ + H \rightarrow H_3^+$	6.18
$H + H + H^+ \rightarrow H_3^+$	6.08

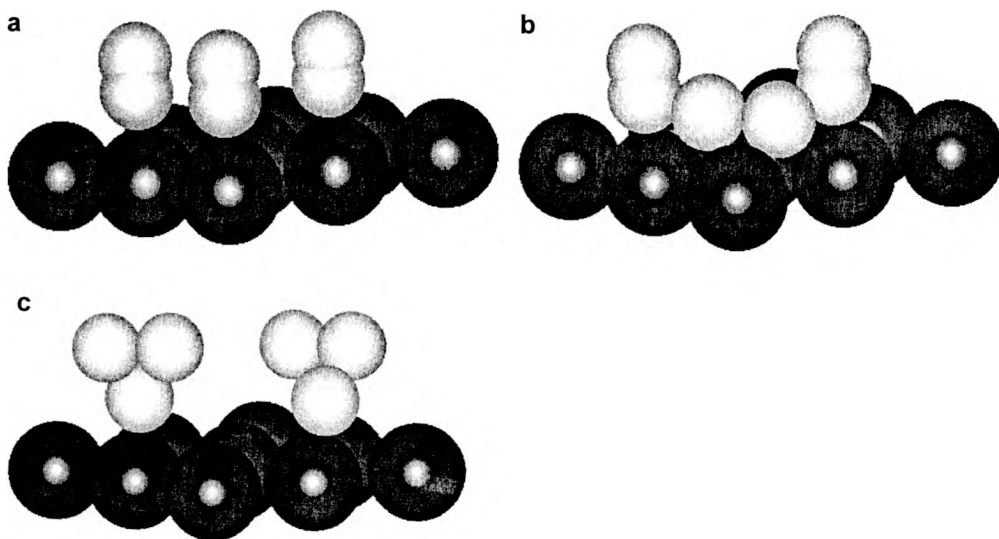


Fig. 3. Model of the synthesis reaction of H_3^+ (stages a, b, c) on the cobalt surface.

It results from the above argumentation that a hydrogen ion should be formed from an ionized H_2 molecule and an H atom. Another possibility should be excluded because of validity of the associative mechanism. Therefore, an H_3 molecule appears on the surface and only next produced is an H_3^+ ion.

Since most ions of hydrogen are recorded exactly on the edges of Co (0001) plane, in the following we will deal with namely this case. Figure 3a shows a situation in which three molecules of H_2 have been field adsorbed on the edge atoms. As the most protruding Co atom has the highest number of unsaturated bonds [21], the H_2 molecule gets a strong bonding with Co to produce cobalt hydride [22] (Fig. 3b). Owing to the fact that in the close proximity there are two field adsorbed molecules of H_2 , such a system would produce two molecules of H_3 . However, the bonding within this type of pseudo-molecule is realized in part by the atoms of substrate. Such a surface molecular species will be desorbed under the action of laser light pulses, and, still prior to its complete removal from the substrate, its field-desorbed fragment H_2 will get ionized (Fig. 3c).

In view of experimental and theoretical results such a model seems to be probable, however, other scenarios of the process are possible. A definite answer can be expected to appear from more precise calculations of the respective reaction stages, based on quantum chemistry.

Acknowledgments – The experimental part of this work was done in the laboratory of Professor Tien T. Tsong at the Institute of Physics, Academia Sinica, Taipei, Taiwan, ROC. Dr. Z. M. Stępień appreciates his hospitality and fruitful discussions during the visit to his laboratory.

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Received May 13, 2002