AB INITIO COMPUTATIONS FOR H_3^+ ION ON THE SURFACE OF COBALT IN A HIGH ELECTRIC FIELD

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ABSTRACT

Interaction between hydrogen and a surface of cobalt in the presence of electric field of the strength of a few volts per nanometer leads to the formation of the H_3^+ ion which has been studied both experimentally (by using pulsed- laser time- of- flight atom- probe field ion microscope) and theoretically (quantum chemical calculations).

The binding characteristics of triangular H_3^+ , calculated by ab initio method with a wide variety of approximations have been compared. On the basis of the results of computations the pathway of synthesis of H_3^+ has been proposed.

The total energy potential surface scan for $Co - H_3^+$ system in the presence of external electric field has been done. The binding energy of H_3^+ ion has been also determined.

It has been proved that the ion of H_3^+ is formed right on the surface in a saddle point in a parallel position to the edge of the plane.

INTRODUCTION

The ion of H_3^+ is known to exist since its first observation by Thompson in 1912 [1]. The results of this experiment suggest that H_3^+ is formed as a product of ionization of H_3 .Then this ion was observed by Clement and

Mũller in 1962 [2]. This experiment seems to indicate that the H_3^+ ion as a product of a·field induced surface chemical reaction. Since these dates similar observations have been repeated many times while examining the surface of d-transition metals carried out in the atmosphere of hydrogen in the presence of an electric field of the order of a few V/nm [3- 8]. Apart from experimental works many theoretical studies have appeared [9- 14]. Although the existence of H_3^+ in the field desorption process is common known the mechanism of synthesis pathway is systematically studied.

In present paper we are interested in how the formation of considered ions is related to the substrate structure, and the applied external electric field strength . An attempt of explaining the reaction mechanism leading to the formation of H_3^+ has been undertaken. All the quantitative date presented here come from laser- light- stimulated field desorption experiment of hydrogen from a surface of cobalt, complemented with the quantum chemical computations.

EXPERIMENT AND COMPUTATIONS

The experiment was performed by using high- resolution pulsed- laser time-of-flight atom- probe field ion microscope.The details of construction have been described in Ref. [5]. Field ion images were observed with neon as the image gas. The experiment was carried out the atmosphere of hydrogen at a pressure of 10^{-6} Pa. The field emitter tip was obtained from a cobalt wire of 99.99% purity by means of electropolishing. During all measurements the temperature of the field ion emitter was 20 K in order to assure field adsorption of hydrogen on the surface of emitter tip.

Some quantum chemical calculations have been performed in order to explain the results obtained in the experiment. For this purpose Gaussian 98 program package [15] has been employed. It has been used ab initio method with the Hartree- Fock, the Local (LSDA)and Non- Local Spin Density Approximations (NLSDA).

The LSDA and NLSDA were used earlier for investigations field effects of the adsorption characteristics of hydrogen on rhodium cluster [12] and studies field dissociation mechanism of H_3^+ [13]. The basis set established in computation has been 6-31 G(d), which gives the best accuracy in the all electron calculations for cobalt.

RESULTS AND DISCUSSION

During the process of a field desorption of hydrogen from a surface of cobalt the ions of H^+, H_2^+ and H_3^+ were recorded.

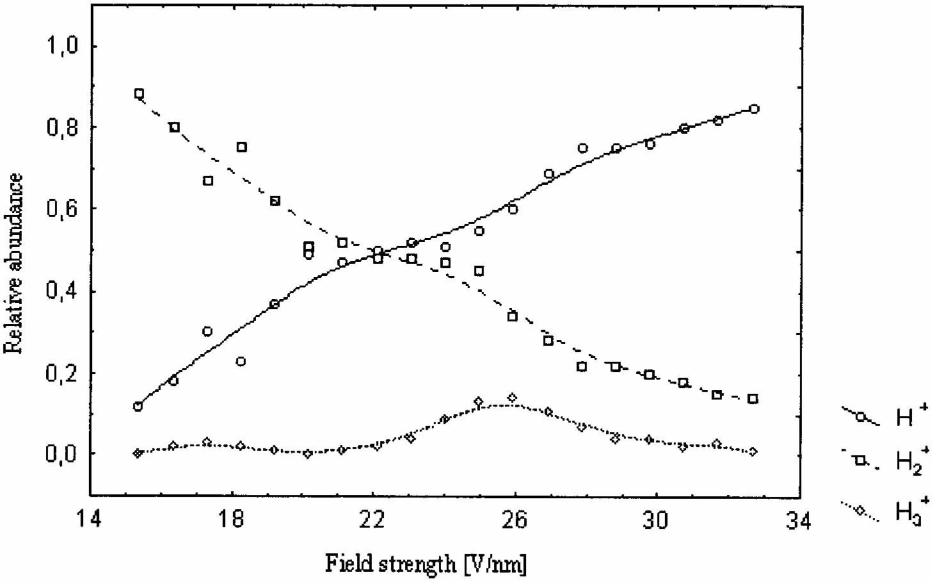

Figure 1. The relative abundances of H^+, H_2^+ and H_3^+ ions as a function of the applied field collected from the Co(0001) steps

Figure 1 shows the relative abundance of ionic desorption as a function of electric field strength at the emitter tip of cobalt. The H_3^+ ions in question were observed in the range 20- 30 V/nm [16]. The largest amount of ionic desorption were observed being desorped from the edges of (0001) plane of cobalt.

It results from another experiments that the amount of H_3^+ in a field desorption process depends on the material. The most favorable atomic edges for the process seem to be edges of close packed crystallographic planes. The binding characteristics of H_3^+ have been established for an ion of H_3^+ in the assumed form of an equilateral triangle which geometry has been optimized relative to the total energy minimum. It has been made an attempt of optimization of geometry of H_3 molecule which has resulted in a failure. It results from the fact that H_3 molecule does not exist free in space. It has been reported by Reckzügel [14] that linear H_3 can be stable only on the surface.

Table 1. Binding characteristics of triangular H_3^+

	Hartree- Fock approximation	LSDA	NLSDA
Bond length (Å)	0.84	0.88	0.89
Total energy (hartree)	-1.27	-1.32	-1.22
Dipole moment (debye unit)	0.0002	0.0002	0.0002

The characteristics for H_3^+ performed in Table 1 are in good agreement with those obtained by Ye at al [12] . The LSDA gives the lowest energy level comparing with other applied approximations, which means that this approximation gives the best accuracy of reading for H_3^+. It has been also studied the energy level- structures of H_3^+ and the results are presented in Table 2. It results from presented dates that the energies of the occupied states have the same values.

Table 2. Energy level- structure of H_3^+ (hartree unit)

	Hartree- Fock approximation	LSDA	NLSDA
occupied	-1.02 -1.02	- 0.99 - 0.99	- 0.95 - 0.95
virtual	- 0.37 - 0.37 0.09 0.45 0.45	- 0.38 - 0.38 0.12 0.48 0.48	-0.35 -0.35 0.15 0.51 0.51

Ernst at al [9] based on their measurements of the energy distributions and appearance energy of H_3^+ have proposed that an H_3^+ ion is formed at the instant a diffusion chemisorbed H atom jumps to interact with an apex site field adsorbed H_2 molecule, or

$$H_2(field-adsorbed)+H(adsorbed)\rightarrow H_3^+ + e^-(metal).$$

The above reaction pathway involves molecular and atomic hydrogen being adsorbed in a permanently applied electric field. In view of that in our experiment the temperature of emitter tip was 20 K, where hydrogen does not adsorbed dissociatively, the above mechanism does not seem to be probable.

A more direct way of finding out the most probable mechanism of synthesis of H_3^+ relays on calculations of the total energy of substrates and products for several probable types of reaction. From the energetic point of view reaction is more likely to occur when the total energy of its substrates is more than the total energy of its products. In the Table 3, the differences between the total energy of substrates and products are performed.

Table 3. The model of the reaction pathway of H_3^+ synthesis on the surface

Type of reaction	ΔE= $E_s - E_p$ (hartree)		
	Hartree- Fock approximation	LSDA	NLSDA
$H_2 + H^+ \rightarrow H_3^+$	0.10	0.12	0.11
$H_2^+ + H \rightarrow H_3^+$	0.23	0.30	0.28
$H + H + H^+ \rightarrow H_3^+$	0.22	0.29	0.27

Although these values may not be very accurate, they give some information of favorable mechanism of reaction taking place.

H_3^+ ion is formed from an ionized H_2 molecule and a hydrogen atom.

A qualitative understanding of described process can be achieved by examining the occupied orbital levels of H_2^+, H and H_3^+.

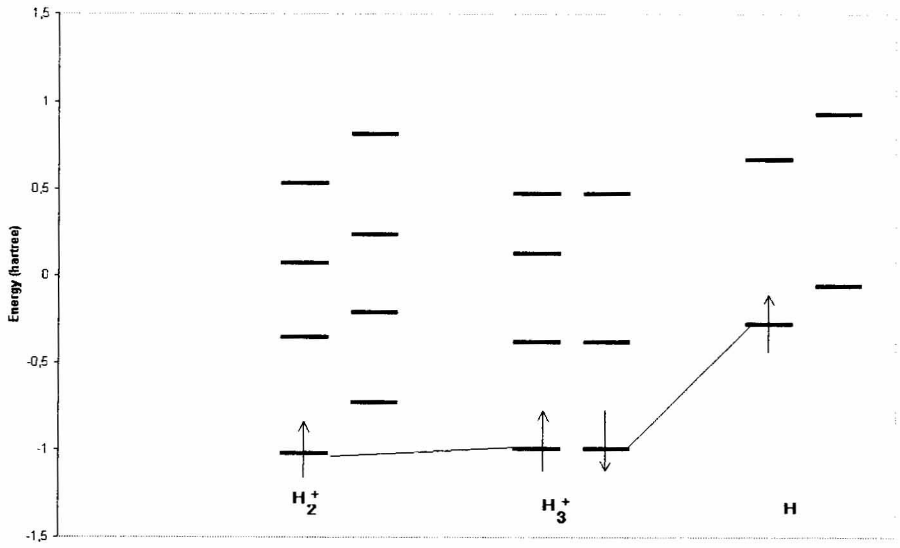

Figure 2. Model of electronic structure of H , H_2^+ , H_3^+

In Fig. 2 compared energy levels of substrates and a product of favorable mechanism are shown. In the light of presented diagram the proposed model of formation of H_3^+ seems to be credible.

An interesting question to be addressed in this paper is whether H_3^+ ions are formed right on the surface of emitter tip or in the ionization zone as a product of ionization of H_3 .

In view of that H_3 molecule does not exist free in space the process of formation of H_3^+ ions is not the case of ionization of H_3 . The formation of H_3^+ is predicted to occur right on the surface.

It is known that the local electric field is enhanced around a single metal atom on the top of closely packed crystallographic planes. It has been assumed that the process of adsorption of H_3^+ must take place only on the protruding surface atom.

To confirm the correctness of above assumption the calculations of the total energy scan for $Co - H_3^+$ system have been performed (Fig. 3).

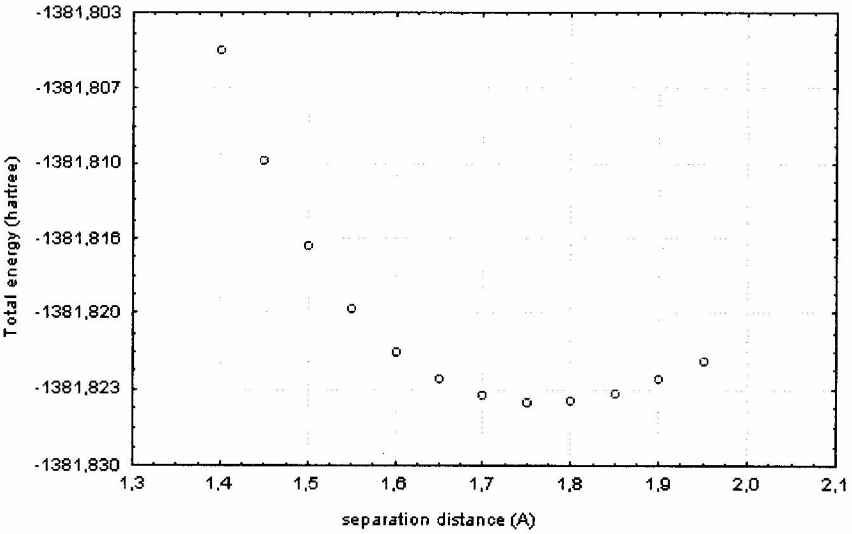

Figure 3. Calculated total energy changes in dependence on the distance between and a single cobalt atom in the absence of electric field

A minimum of the total energy is seen for the separation distance equal to 1.7 Å. The binding energy has been determined to be 2.66 eV. Then the cluster consisting of a single metal atom and the adsorbing H_3^+ ion has been put into constant external fields of the strength of 10, 15 and 20 V/nm. An electric field has been taken into account by introducing an electric dipole field in the direction corresponding to the symmetry axis of the ion.

The function curves (Fig. 4) of the total energy do not reveal any minimum. That surprising result has proved that H_3^+ are not formed on the top of the atom in the presence of electric field.

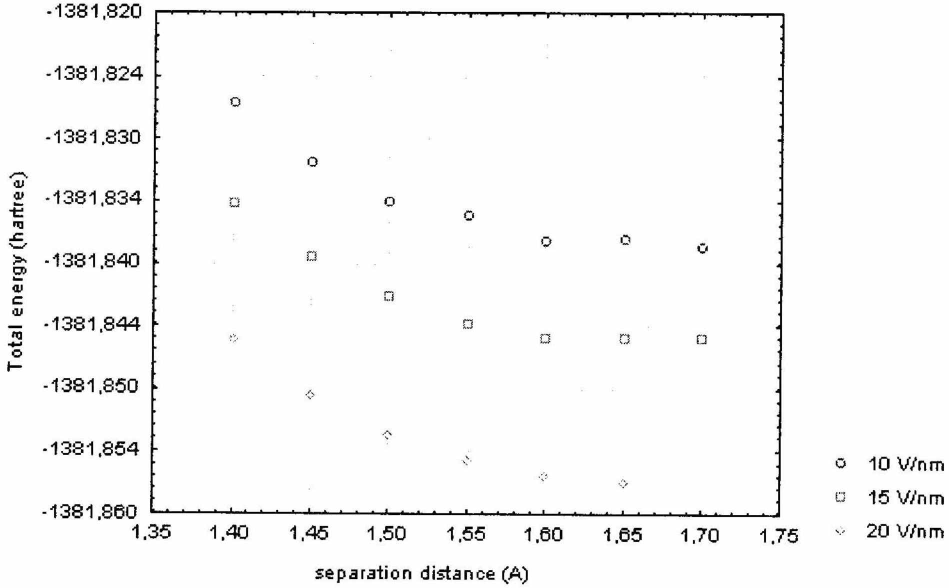

Figure 4. Calculated total energy changes in dependence on the distance between H_3^+ and a single cobalt atom in the presence of electric field

It has been considered another solution to a problem of the formation of H_3^+ on the surface- adsorption of this ion in a saddle point. It has been examined two cases- adsorption of the ion in a saddle point in a direction parallel and perpendicular to the edge of the plane. In both cases the total energy scans in dependence on the distance between H_3^+ and a saddle point. The results are presented in Fig.5 and Fig.6.

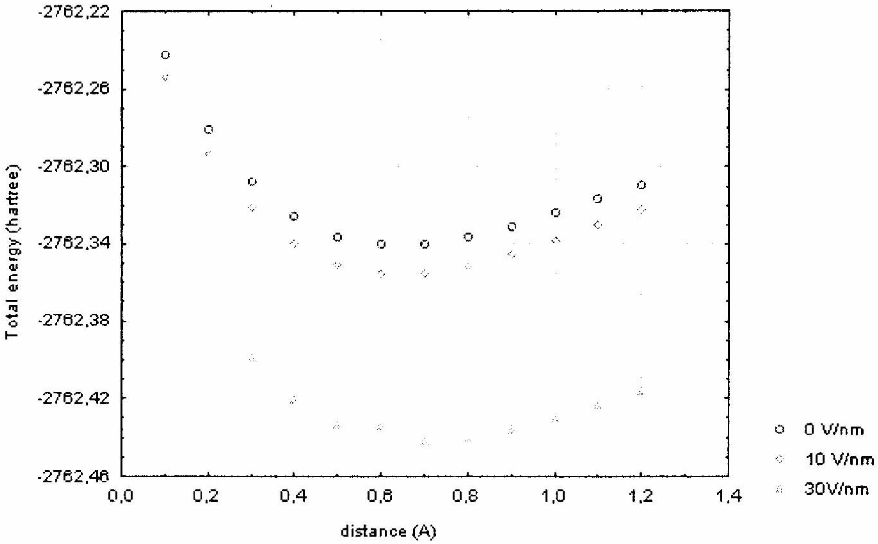

Figure 5. Calculated total energy changes in dependence on the distance between H_3^+ and two- atom cobalt cluster in the case of a parallel approach position of the ion to the saddle point

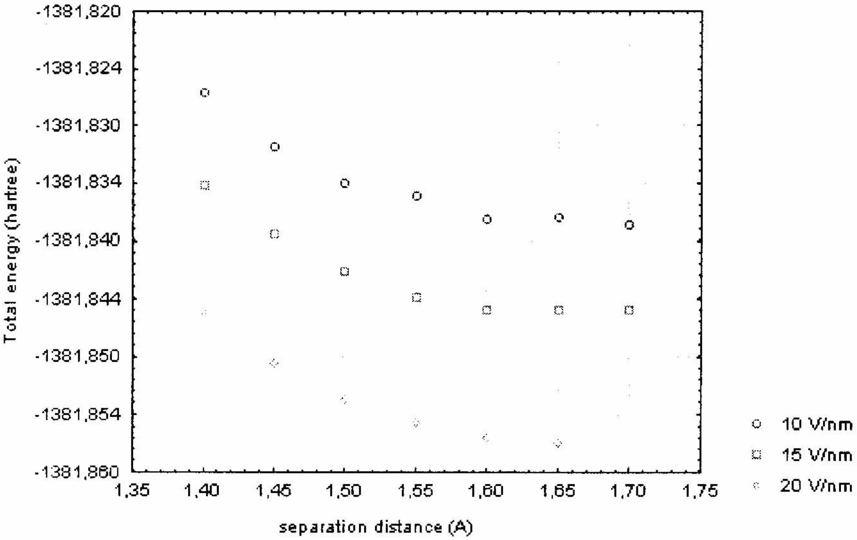

Figure 6. Calculated total energy changes in dependence on the distance between H_3^+ and two- atom cobalt cluster in the case of a perpendicular approach position of the ion to the saddle point

In the case of a parallel approach position of H_3^+ to the saddle point decreasing of the total energy minimum according to the increasing of electric field strengths has been observed.

In the second case the results could not prove any such regularity due to insufficient number of atoms in a cluster.

We hope that in our future quantum chemical calculations carried on a bigger cluster we will be able to show more credible results.

CONCLUSIONS

From presented studies the following conclusions can be drawn.

H_3^+ ions are formed in the low temperature field desorption process of hydrogen from a surface of cobalt;

The ions were observed in the range of 20- 30 V/nm;

The ions are expected to be formed in the process:

$$H_2^+ + H \rightarrow H_3^+;$$

They are created in a saddle point in the case of an parallel approach position to the edge.

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