

Automatic geometry optimization for molecules with *d*-orbitals

V.* EHT computational study of systems Pd and *n*H (*n* = 1—4)

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Received 22 February 1990

Dedicated to Professor L. Valko, DrSc., in honour of his 60th birthday

The possibilities of localization of the hydrogen atoms in Pd have been studied. The calculations were carried out by the EHT method with electrostatic correction. The unit cell of Pd was modelled by means of 14 Pd atoms. It has been shown that the occlusion of two H atoms is preferable from the energetic point of view while the occlusion of three or four H atoms is somewhat less favourable. Finally, the occlusion of one H atom is the least convenient. The optimum structural parameters of localization of the H atoms in the unit cell (keeping its geometry fixed at the observed one) have been found. The calculations predict the presence of H occluded in atomic form in Pd and suggest a possibility of a few different arrangements.

Изучены возможности размещения атомов водорода в Pd. Расчеты проводились по EHT методу с включением электростатической поправки. Элементарная ячейка Pd составлена с помощью 14-ти атомов Pd. Показано, что с энергетической точки зрения самой удобной является двухатомная окклюзия H, тогда как окклюзия состоящая из трех и четырех атомов, менее выгодна. Самой невыгодной является окклюзия одного атома H. Найдены оптимальные структурные параметры размещения H атомов в элементарной ячейке для ее геометрии фиксированной на наблюдаемых значениях. Расчеты предсказывают наличие H в Pd в атомарной форме, и показывают на возможности их нескольких различных расположений.

The first recent information [1, 2] about possible low-temperature nuclear fusion in Pd electrodes with occluded deuterium [3—11] stimulated the preceding study of this interesting system. Some aspects of this system were already earlier studied by using the tools of theoretical chemistry [12—19] but the methodical background did not allow to use the more advanced techniques of

* For Part IV see Ref. [35].

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automatic optimization of molecular geometry for this purpose then. A relatively considerable attention was also given to the problem of the temperature maximum of heat capacity of this system [20—24] as well as to interpretation of this problem on molecular level [25—30]. From the viewpoint of the cold fusion itself, the problem of possible muon catalysis [31, 32] may be theoretically the most interesting now. In whatever way the problem of the cold nuclear fusion may be solved, the molecular study of the hydrogen occluded in Pd represents a useful and interesting topic. This report contributes to understanding the problem, being based on automatic optimization [33—35] of molecular geometry by using the EHT method including the electrostatic correction.

Computational

The calculations were performed by using the EHT method [36], including electrostatic correction as proposed in papers [37, 38]. According to recommendation [38], the value of 2.25 was used for the constant in the Wolfsberg—Helmholtz approximation of nondiagonal elements H_{ij} . The atomic orbitals $5s$ and $4d$ with the ionization potentials suggested by *Vela* and *Gázquez* [39] as well as with the Slater exponents [40] were applied to description of the Pd atoms. The hydrogen $1s$ orbital was characterized by the parameters according to [38, 39]. The localization of stationary points on these hypersurfaces of potential energy was carried out by the automatic molecular-geometry optimization procedure applying an analytically constructed gradient of potential energy [33—35]. This procedure employs Cartesian coordinates of atomic nuclei and iteratively approximates the optimum geometry by using the variable metric method [41].

In this study the metallic palladium was modelled by the approach usual in cluster simulations of heterogeneous catalysis [42]. This metal exhibits a face-centred cubic lattice, the lattice constant of which reaches the value $a_0 = 4.020 \times 10^{-10}$ m provided the saturation with hydrogen is sufficient [24, 43]. A 14-atomic cluster corresponding to the unit f.c.c. cell of palladium was chosen for quantum-chemical simulation. Eight atoms of Pd were located in corners of the cube in the centre of which the origin of Cartesian coordinates was placed. The coordinates of these eight atoms were $(\pm a_0/2; \pm a_0/2; \pm a_0/2)$. The remaining six atoms of Pd were located in the centres of faces of this cube. The positions of all 14 atoms of palladium were fixed in the course of optimization so that only the hydrogen atoms located inside the model cluster were subjected to the optimization. On the whole, four different stoichiometries were taken into account, *i.e.* inclusion of one, two, three or four hydrogen atoms ($n = 1-4$). No conditions were imposed on the coordinates of hydrogen atoms so that the dimension of optimization process comprised three, six, nine or twelve Cartesian coordinates.

Results and discussion

Owing to dimension of the problem (especially for energy calculation) and to relatively slow convergence of geometrical optimization we had to do with a relatively extensive computational study. For accelerating the calculations, the starting structure was systematically changed, which also enhanced the possibility of finding another, alternative arrangements of hydrogen atoms leading to vanishing of the derivatives of energy with respect to hydrogen atoms coordinates. As the positions of all Pd atoms were fixed, the stationary points were not sought on the entire hypersurface of the dimension 3 ($14 + n$) but only within a certain partial hypersurface of the dimension reduced to the number of coordinates of the hydrogen atoms. In this reduced approach we cannot, however, use the standard treatment for characterization of the found stationary points, *i.e.* diagonalization of the matrix of the second derivatives constructed numerically in the space of Cartesian coordinates of all atoms of the system [44]. Nevertheless, we may follow numerical properties of the variable metric method [41] and reasonably well believe the obtained stationary points are really the local minima within the problem of the reduced dimension.

For characterizing the energetics of cluster systems, it is usual [35] to relate the found system energies to a certain unified reference state. In our case, it was the state where all hydrogen atoms under consideration were sufficiently far from the model cluster Pd₁₄ and from one another so that no significant interactions were present. Thus the changes in potential energy ΔE were obtained. The choice of reference state is a convention because other and different choices could also be possible. But the kind of reference state is not particularly important for our more or less qualitative purpose. However, for facilitating the direct comparison for different values of n , it is reasonable to use the relative energies referred to one hydrogen atom, *i.e.* the terms $\Delta E/n$.

The hydrogen atoms were not a priori considered to be present in the form of hydrogen molecule but in the form of dissociated particle. For characterizing the positions of these atoms, it is convenient to avoid any internal coordinates and to use Cartesian coordinates x_i , y_i , z_i of the hydrogen atoms in their equilibrium positions in the coordinate system which was already applied to description of the Pd₁₄ cluster. The energetic and structural data for the Pd₁₄ · n H complexes are given in Table 1.

In all the optimum arrangements found, the individual hydrogen atoms are so distant from one another that we cannot assume the presence of hydrogen molecule but more likely rather free hydrogen atoms. According to EHT calculations, the net charges on these atoms are slightly negative for all the optimum arrangements. The complex Pd₁₄ · 3H for which two alternative

Table 1

Energetics and structural parameters for optimized $\text{Pd}_{14} \cdot n\text{H}$ clusters ($n = 1-4$)

n	$\Delta E/n$	x_i	y_i	z_i
	eV			
1	-2.709	0.0	0.0	0.0
2	-4.124	1.057	1.057	1.057
		-1.057	-1.057	-1.057
3 ^a	-4.108	1.037	1.089	1.089
		-1.208	-1.031	-1.031
		1.217	-1.045	-1.045
3 ^a	-4.093	1.264	0.906	1.224
		-1.264	0.906	1.224
		0.0	-0.897	0.871
4	-4.083	1.190	1.054	1.054
		-1.190	1.054	1.054
		1.190	-1.054	-1.054
		-1.190	-1.054	-1.054

a) Two different arrangements of H atoms found.

arrangements of H atoms have been found is very interesting. As a matter of fact, it is a special case of cluster isomerism [44]. From the viewpoint of energy, both arrangements are close each other. We can expect that such alternative optimum arrangements should more frequently occur for higher numbers of hydrogen atoms. For obtaining an idea on the mobility of hydrogen atoms inside a cluster, it would be convenient to construct potential profiles around equilibrium positions along selected lines. For this purpose, the values of harmonic vibrational frequencies would be useful, but the vibrational analysis of cluster systems with partially fixed degrees of freedom has hitherto been only a seldom treated problem [45] (in contrast to usual molecular systems [44]).

The most interesting result presented in Table 1 is, however, a remarkable nearness of the terms $\Delta E/n$ for $n = 2-4$. Though the complex $\text{Pd}_{14} \cdot 2\text{H}$ appears to be the most stable according to this term, the stability of the complexes $\text{Pd}_{14} \cdot 3\text{H}$ and $\text{Pd}_{14} \cdot 4\text{H}$ is only slightly lower. If we neglect the entropic term, it indicates a comparable frequency of occurrence of these three complexes. If the number n continues to increase, it is, however, likely that the relationship between $\Delta E/n$ and n , exhibiting a minimum for $n = 2$ (Table 1) and a rather flat course in the interval $n = 2-4$, will show tendency to increase more appreciably.

All these findings represent a contribution to formation of the conception of nature of the hydrogen occluded in palladium. Further study continues in our

laboratory along these lines and includes the optimization for values beyond $n = 4$.

Finally, we must mention a great many more general methodical problems concerning this work though only a part of them has been adequately solved. That refers to such aspects as usability of semiempirical quantum-chemical methods for optimization of molecular structures, inclusion of relativistic effects (especially for heavy atoms), construction (including completion) of model cluster, *etc.* At present, these questions belong to crucial problems of theoretical chemistry in description of the interactions with solid phase and we may expect that the continuous progress along these lines will go on in oncoming years. These questions are accompanied by other key problems of semiempirical methods which involve the choice of the (in a certain sense) optimal set of parameters. In relation to the set of parameters chosen by us, the problem of its internal consistence should be mentioned. As far as possible, all parameters should correspond to the same reference electronic configuration which should resemble the conditions in the investigated compound. In the particular case of Pd atoms, the choice of the configuration $4d^9 5s^1 5p^0$, which is more adequate to cluster system (while for molecular complexes the configuration $4d^8 5s^2 5p^0$ would be more suited), comes into consideration besides the configuration $4d^{10} 5s^0 5p^0$ corresponding to the state of free atoms. The ionization energies can be obtained for different configurations of atoms from the Hartree—Fock or Dirac—Fock calculations. The sets of such parameters usable in relativistic methods are available in literature (*Pyykkö* and *Lohr* [46] and *Boča* [47—51]) and that is why the further research ought to be aimed to description of the investigated cluster system by using these more sophisticated approaches. However, the choice of the best combination of parameters and approximations for semiempirical methods is conditioned by the existence of a sufficient amount of reliable information characterizing the investigated particular system. From this point of view, we can state that the progress in our knowledge of the relations valid in the system containing hydrogen occluded in palladium is dependent on a further improvement in experimental characterization of this system.

Note added in proof

For a continuing survey of the literature on the presumed low-temperature nuclear fusion, see Ref. [52—55].

Acknowledgements. The author is indebted to Professor R. Boča for his valuable comments and information exchange on the subject. The study was finalized during a research stay at the Max-Planck-Institut für Chemie (Otto-Hahn-Institut) supported by the Alexander von Humboldt-Stiftung. The support is gratefully acknowledged.

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Translated by R. Domanský