Pt-M

$Pt_2H$

1990

**3 Д50. Поверхности потенциальной энергии для взаимодействий $Pt_2+H_2$ и Pt+H.** Potential-energy surfaces for $Pt_2$+H and Pt+H interactions / Balasubramanian K., Feng P. Y. // J. Chem. Phys.— 1990.— 92, № 1.— С. 541—550.— Англ.

Методом МК ССП в варианте полного пространства активных орбиталей и многоссылочным методом КВ, учитывающим вклады конфигураций, одно- и двукратно возбужденных по отношению к исходным, выполнены расчеты поверхностей потенц. энергии большого числа низколежащих электронных состояний систем $Pt_2$—H и Pt—H. Учет спин-орбитального взаимодействия в системах проводился с использованием релятив. метода КВ. Найдено, что основным состоянием системы Pt H является состояние $2\Delta_{5/2}$, а системы $Pt_2H$ — состояние *E* группы $C_{2v}^2$, соответствующее равновесной мостиковой структуре. Для рассмотренных электронных состояний найдены зависимости дипольного момента от межъядерного расстояния и основные спектроскопич. постоянные.

А. Н. К.

М.Л.

Ⓗ ☒

ф.1991, № 3

PtH

$Pt_2H$

$PtH$

1990

**112: 165437s Potential-energy surfaces for diatomic platinum + atomic hydrogen and atomic platinum + atomic hydrogen interactions.** Balasubramanian, K.; Feng, P. Y. (Dep. Chem., Arizona State Univ., Tempe, AZ 85287-1604 USA). *J. Chem. Phys.* 1990, 92(1), 541-50 (Eng). Potential-energy surfaces for ten electronic states of $Pt_2H$ as a function of $Pt_2$–H distance are constructed using the complete active space multiconfiguration SCF followed by multireference singles plus doubles configuration interactions which included up to 407,000 configurations. In addn., the spin-orbit effects were included through the relativistic CI method. The potential-energy curves of low-lying electronic states of PtH and spectroscopic consts. of 11 states of PtH are also computed using the same method. The exptl. $A'-X_2$ spectroscopic bands of PtH are reassigned to the $^2\Sigma^+$ (II)–1/2(I) transition. A tentative reassignment of the obsd. $B'-X_1$ system is also suggested. The ground state of $Pt_2H$ is found to be of E(I) symmetry when spin-orbit effects are incorporated with a bridged structure [$R_e$(Pt–Pt) = 2.46 Å, $R_e$(Pt–H) = 1.68 Å]. A very low-lying excited state E(II)

расчет
электрон.
состоян.,
м.п., $D_0$

C.A. 1990, 112, N18

($T_e$ = 0.14 eV) was found for $Pt_2H$. The $D_e(Pt_2H)$ = 59 kcal/mol compared to the $D_e(PtH)$ = 72 kcal/mol, indicating lower stability of the $Pt_2H$ bridge compared to PtH diat. Some of the low-lying electronic states of PtH, esp. 3/2 states, exhibit avoided crossings.

$Pt_3H$ 1992

низколежащие электрон- состояния

116: 181577a **Potential energy surfaces for platinum ($Pt_3$) + hydrogen atom and palladium ($Pd_3$) + hydrogen atom interactions.** Dai, Dingguo; Balasubramanian, K. (Dep. Chem., Arizona State Univ., Tempe, AZ 85287-1604 USA). *J. Phys. Chem.* 1992, 96(8), 3279-82 (Eng). The CAS MC-SCF MR-CI calcns. were carried out which included up to 3.1 million configurations on $Pt_3$ + H and $Pd_3$ + H systems. Three low-lying electronic states were identified for $Pd_3$ + H while for $Pt_3$ + H four electronic states were found. Both $Pd_3H$ and $Pt_3H$ were found to form triangular-pyramid structures in which the H atom is at the apex. The $^2A_2$ electronic state ($C_{3v}$) was found to be the lowest for both $Pd_3H$ and $Pt_3H$. Spin-orbit effects were found to be significant for $Pt_3H$. The energy to sep. the H atom from the trimers was found to be comparable to the corresponding energy for the dimers. $Pd_3H$ was found to be fluxional in its ground state while in contrast $Pt_3H$ is rigid.

(+) $Pd_3H$

C. A. 1992, 116, N18

$PtH_2$

1993

**119: 80731c Relativistic effects on the bonding and properties of the hydrides of platinum.** Dyall, Kenneth G. (Eloret Inst., Palo Alto, CA 94303 USA). *J. Chem. Phys.* 1993, 98(12), 9678-86 (Eng). The ground state of $PtH_2$ and several low-lying states of $PtH^+$ and PtH has been studied at the all-electron SCF level of theory to examine the importance of relativistic effects. The results of calcns. based on Dirac-Hartree-Fock theory, nonrelativistic theory, and the spin-free no-pair relativistic approxn. of Hess are compared to sep. the effects of the spin-free terms and the spin-orbit terms of the Hamiltonian on the relativistic corrections to the mol. properties. Comparison is also made between first-order perturbation theory including the one-electron spin-free terms and the method of Hess to det. the size of effects beyond first order. The spin-orbit interaction significantly affects the properties and energetics of these mols. because of the participation of the Pt 5d orbitals in the bonding; effects beyond first order in perturbation theory are large. Any treatment of Pt compds. will have to include both the spin-free and spin-orbit interactions for an accurate description.

теор. расчет
стабильн. и
структуры

⑪ ☒ ● PtH, $PtH^+$

C.A. 1993, 119, N8

Pt-H

1994

**121: 187672c Bimetallic Thermochemistry: Perturbations in M-H and M-C Bonds Due to the Presence of M'.** Reynolds, G. Gregg; Carter, Emily A. (Department of Chemistry and Biochemistry, Los Angeles, CA 90024-1569 USA). *J. Phys. Chem.* **1994,** 98(33), 8144-53 (Eng). The effect of perturbing the environment of a transition metal-ligand (M-L) complex by the addn. of another metal atom, M', was investigated by ab initio generalized valence bond/correlation-consistent CI methods. The authors have examd. the properties of low-lying states of Pt-X, Zr-X, and (PtZr)-X, where X = {H, CH$_3$}. The bonding trends of the transition metal diat.-ligand complexes have been compared to their monometallic analogs. The authors find that Zr acts as an electron donor in all the diat. complexes and that in these complexes the hydride-diat. bond strengths are increased much more on av. than the methyl-diat. bonds relative to the monometallic complexes. For example, the PtZr-H bond strength is increased by over 14 kcal/mol relative to Zr-H, while the Zr-CH$_3$ bond strength increases only by 4 kcal/mol in the bimetallic complex. The Pt-ligand bond strengths also both increase upon "alloying" the transition metal, but the magnitude of the changes are more similar-8 kcal/mol for the hydride vs. 6 kcal/mol in the Me complex. The authors comment on the implications of these results for the potential use of PtZr alloys as dehydrogenation catalysts.

стабильность,
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сост., теор-
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☒ (44)

C.A. 1994, 121, N16

$Pt_3 + H_2$

1995

**123: 93897u Potential energy surfaces for $Pt_3 + H_2$ and $Pd_3 + H_2$ systems.** Dai, Dingguo; Liao, D. W.; Balasubramanian, K. (Dep. Chem. Biochem., Arizona State Univ., Tempe, AZ 85287-1604 USA). *J. Chem. Phys.* 1995, 102(19), 7530-9 (Eng). Potential energy surfaces of $Pt_3 + H_2$ and $Pd_3 + H_2$ systems are computed for different modes of approach using the complete active space multiconfiguration SCF theory (CAS-MC-SCF). The equil. geometries and the dissocn. limits were computed using multireference singles + doubles configuration (MRSD-CI) method which included up to 1.54 million configurations. For both in-plane and out-of-plane approaches barriers arise from the crossings of the $Pt_3 + H + H$ (or $Pd_3 + H + H$) surface and the $Pt_3 + H_2$ (or $Pd_3 + H_2$) surface. Three potential min. were found in the in-plane potential energy surface in the post-barrier region. One of these min. exhibited two Pt-H-Pt (or Pd-H-Pd) bridge bonds. For $Pd_3H_2$ this structure was found to be stable, while for $Pt_3H_2$ two nearly degenerate structures were found as candidates for the ground state. The barrier for $H_2$ dissocn. in the out-of-plane approach was found to be larger and the out-of-plane

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C. A. 1995, 123, N8

$Pd_3 + H_2$

min. was higher in energy compared to the in-plane min. for both $Pt_3H_2$ and $Pd_3H_2$. The barrier for $H_2$ dissocn. was found to be considerably smaller for $Pt_3$ compared to $Pd_3$ and thus $Pt_3$ is more reactive towards $H_2$ compared to $Pd_3$, a finding consistent with expt. The dissocn. energy of $Pd_3H_2$ was found to be larger than $Pt_3H_2$. These trends, the nature of bonding, Mulliken populations, and avoided crossings in the potential energy surfaces are discussed.

$Pt_2-H_2$

1995

**122: 248798t Theoretical studies of the $Pt_2$–$H_2$ interaction.** Poulain, E.; Castillo, S.; Cruz, A.; Bertin, V. (Division de Posgrado y Estudios Superiores, ITTLA, Tlalnepantla de Baz, Mex. 54070). *Rev. Mex. Fis.* **1995,** 41(1), 50–61 (Span). The capture and activation of mol. hydrogen by the platinum dimer has been studied by perturbative and variational MRCI calcns., using relativistic pseudopotentials. Both singlet and triplet $A_1$ states are found to be efficients in the activation of the H–H bond. The results are compared with those previously obtained for the Pt monomer, for which only the singlet states are active. A Pt/H = 1/1 relationship is obtained, in agreement with the exptl. chemisorption results of $H_2$ in Pt catalysts. Also it is found that the reaction channel for the H–Pt dissocn. is closed since the systems present large energies barriers. At the min. the hydrogen mol. is dissocd. and forms a weak Pt–H bond.

синглетн-
и триплетн-
состояние,
теор. расч

C. A. 1995, 122, N 20

1996

F: Pt2H
P: 3

16Б126. Неэмпирическая электронная структура PtH{+}, PtH, Pt[2] и Pt[2]H на основе расчета с использованием одноэлектронного псевдопотенциала [для атома Pt в основном состоянии]. Ab initio electronic structure of PtH{+}, PtH, Pt[2], and Pt[2]H from a one-electron pseudopotential approach / Zurita Silvia, Rubio Jaime, Illas Francesc, Barthelat Jean Claude [Journal of Chemical Physics] // J. Chem. Phys. - 1996. - 104, N 21. - С. 8500-8506. - Англ.

РЖХ 1997

F: Pt-H2

P: 3

18Б135. Расчет с помощью релятивистского эффективного остовного потенциала реакций H[2] с Pt, Os, Re. Систематическое сопоставление. RECP calculations for reactions of H[2] with Pt, Os, Ir, and Re-A systematic comparison / Gropen O., Sjovoll M., Stromsnes H., Karlsen E., Swang O., Faegri K. // Theor. chim. acta. - 87, 4-5. - С. 373-385. - Англ.