EXPLORATORY

On chemisorption-type sticking of H onto graphitic/graphenic surfaces

- Report -

ISMO (Orsay) – LPIIM (Marseille) – LCAR (Toulouse)

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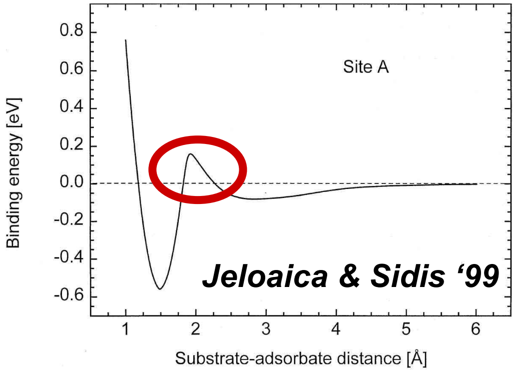
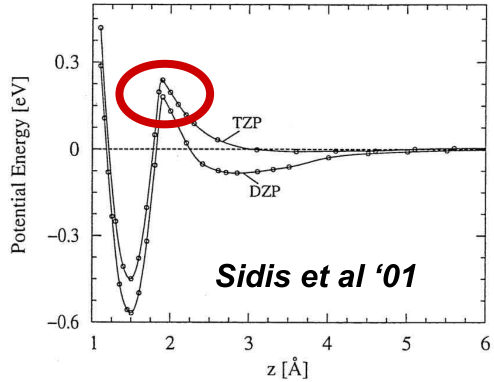
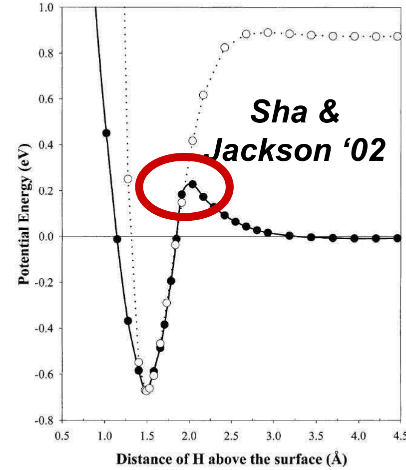
V. Sidis
D. Teillet-Billy
N. Rougeau
F. Aguillon

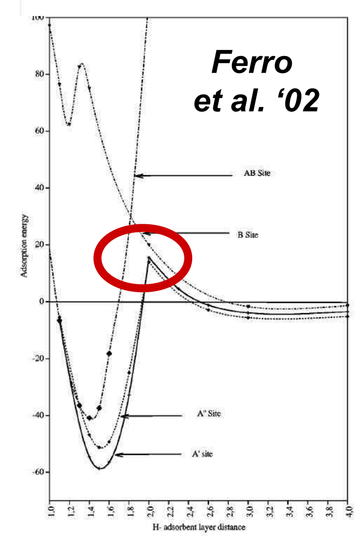
S. Morisset
A. Allouche
Y. Ferro

B. Lepetit
D. Lemoine

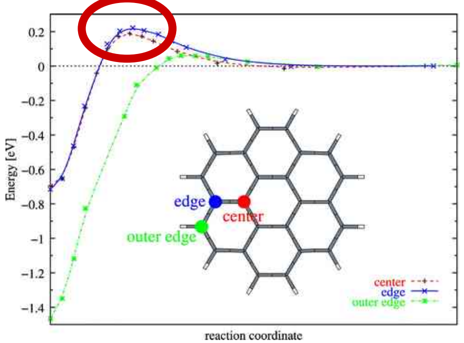








Rauls & Horneckaer '08



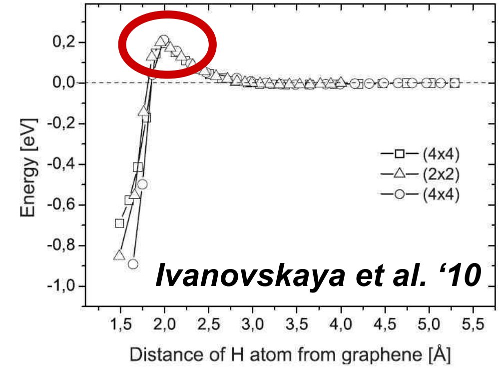
H adsorption on a graphenic surface

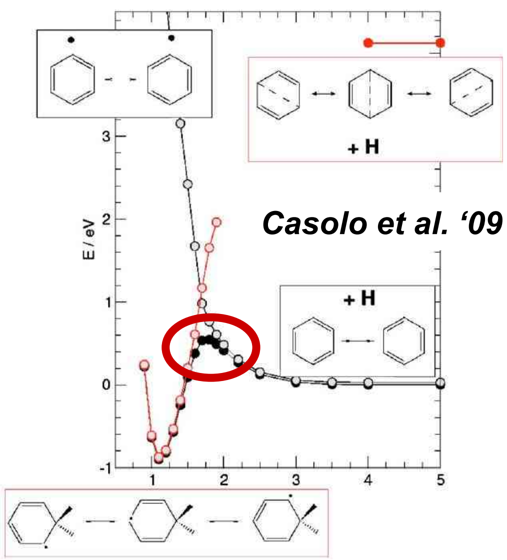
Experiments: Hot H atom source 1600 K – 2000 K

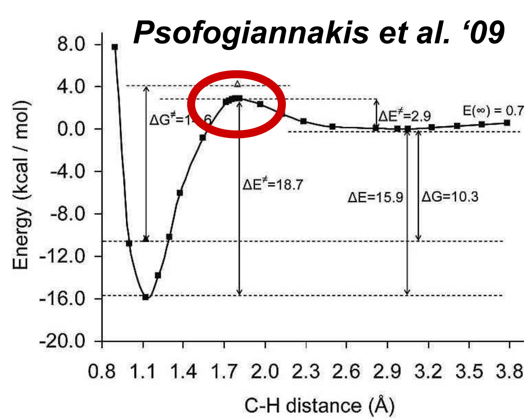
Zecho et al. JCP 2002, CPL 2002

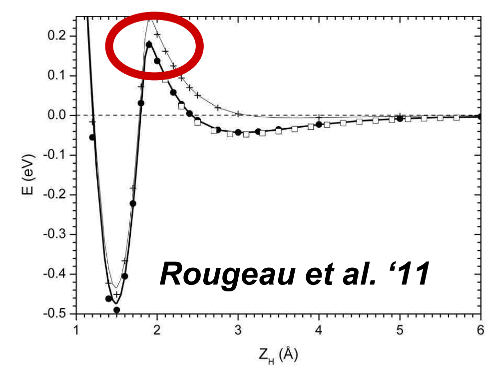
Horneckaer et al. PRL 2006

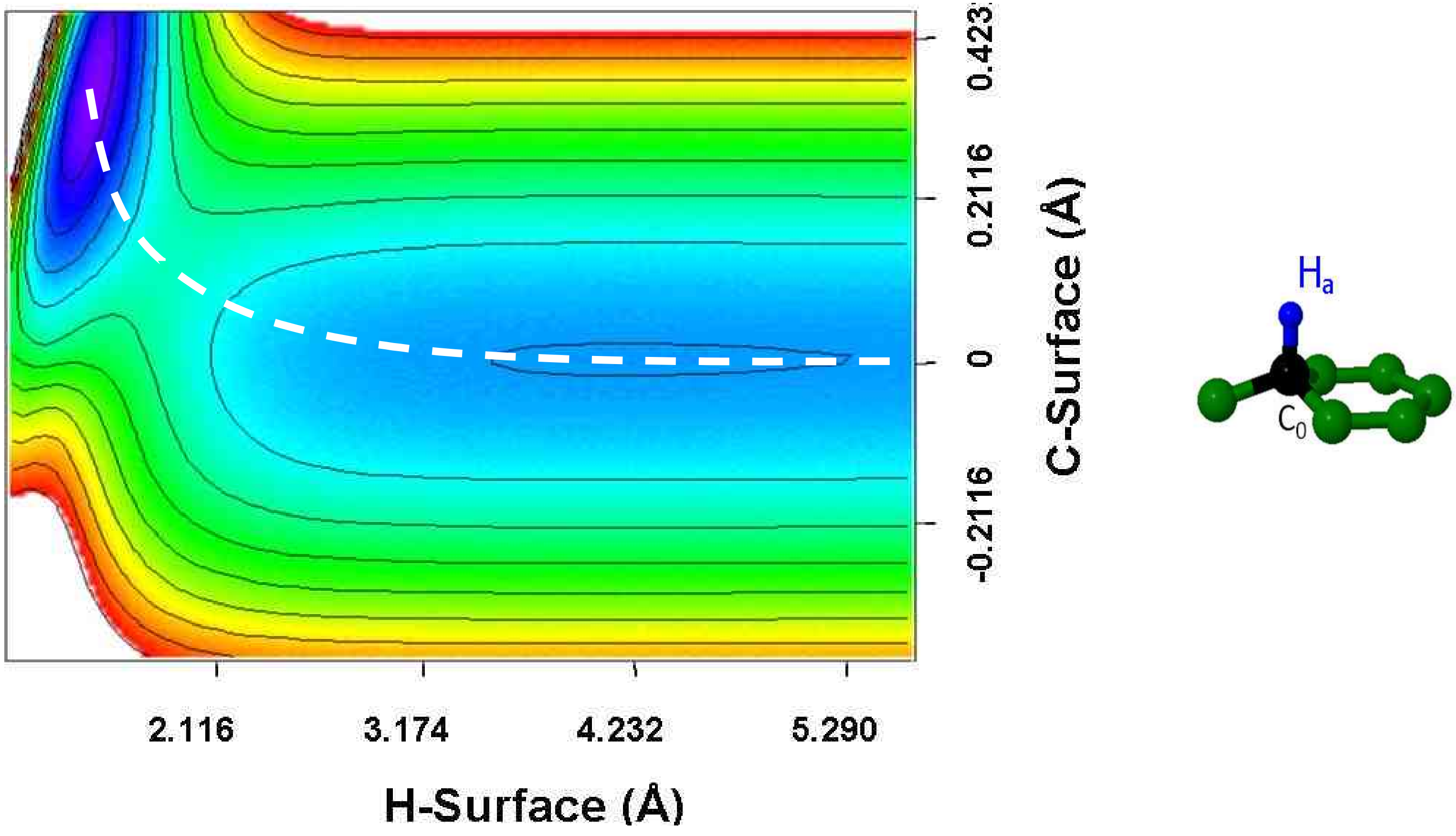
Aréou et al. JCP 2011











0.423
0.2116
0
-0.2116
C-Surface (Å)
2.116
3.174
4.232
5.290
H-Surface (Å)
H_a
C_0

B. Jackson H trapping and sticking on graphite
S. Morisset Sticking of an H atom on a graphite surface

Réunion Plénière du GDR ARCHES 2009
http://www.u-cergy.fr/GDR-ARCHES/

B. Lepetit Physisorption of hydrogen on graphene

Réunion Plénière du GDR ARCHES 2011

Physisorption

Medina and Jackson JCP 2008
Quantum : Colinear w/o corrugation
small displacements of the surface atoms

Lepetit et al. JCP 2011
Quantum : Colinear with corrugation
small displacements of the surface atoms

Chemisorption

Sha, Jackson, Lemoine & Lepetit JCP 2005
Quantum : Colinear 2D (z_H, z_C) + Q

Kerwin & Jackson JPC B 2006
Classical vs Quantum : Colinear 2D (z_H, z_C) + Q
Classical 3D (z_H, z_C, ρ) + Q

Morisset & Allouche JCP 2008
Quantum coupled 1D wp's : Colinear (z_H, 671 phonons modes)
small displacements of the surface atoms wrt mep

Kerwin & Jackson JCP 2008
Classical : Classical 3D – coupled to Aixawa force field

Bachellerie et al PCCP 2009
Adaptation of the Brenner model : H + H-graphene
Eley Rideal recombinative abstraction

Morisset et al. JCP 2010
Mixed quantum classical 1D wp : Colinear (z_H, phonons classical)
small displacements of the surface atoms wrt mep

$$H = T + H_b + V$$

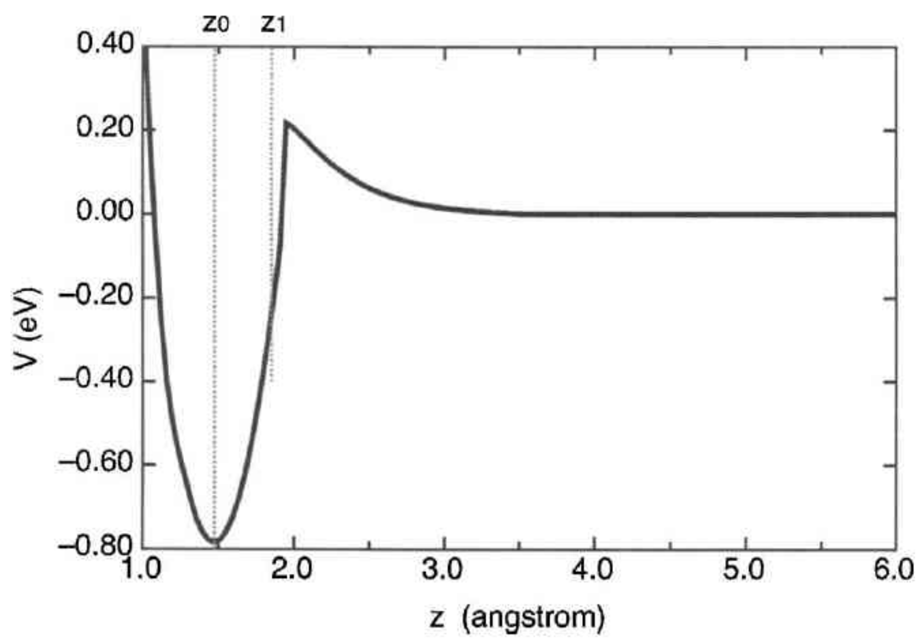
$$H_b = \sum_{\mathbf{q}=1}^{N} \sum_{j=1}^{M} \hbar\omega_{\mathbf{q}}\left(a^{+}_{\mathbf{q}j} a_{\mathbf{q}j} + \tfrac{1}{2}\right)$$

$$V(z,\{u_i\}) = V_0(z,\{u_i^{\text{rel}}(z)\}) + \sum_{i=1}^{N_{\text{at}}} \left.\frac{\partial V(z,\{u_i\})}{\partial u_i}\right|_{u_i=u_i^{\text{rel}}} \times(\mathbf{u}_i - \mathbf{u}_i^{\text{rel}}(z)) + \cdots ,$$

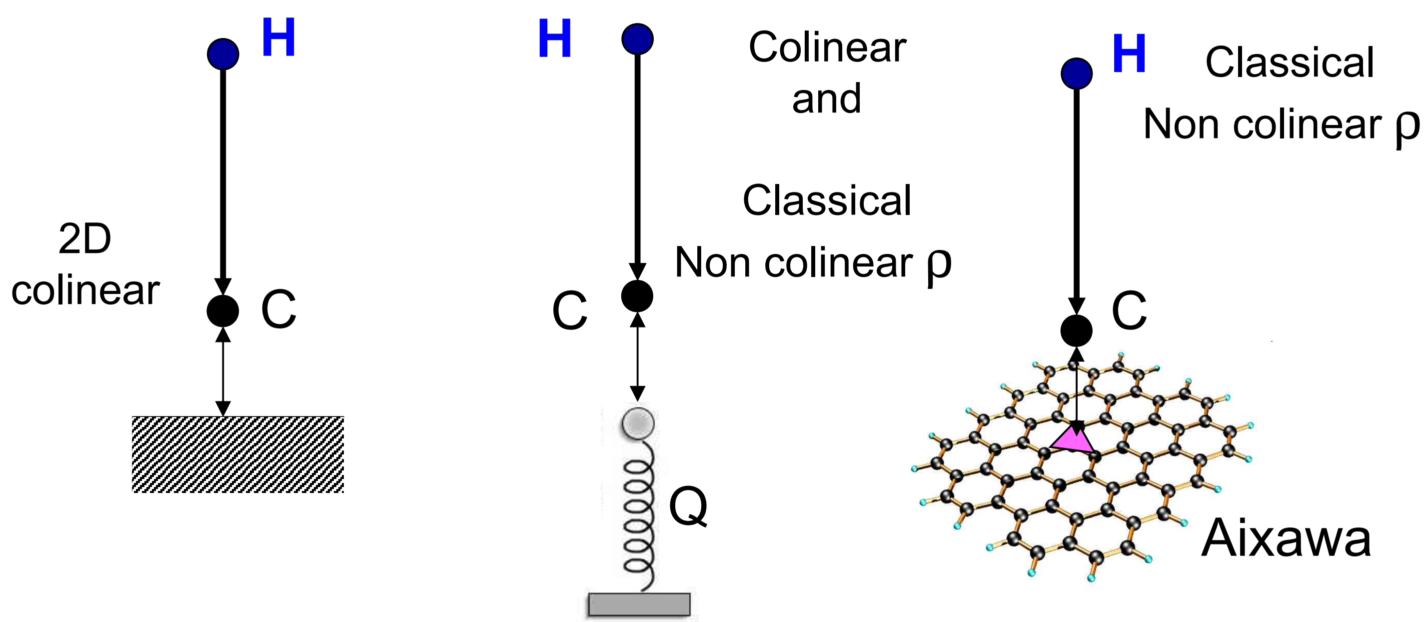
$$V_{\text{mb}} = \sum_{i=1}^{N_{\text{at}}} \left.\frac{\partial V(z_0,\{u_i\})}{\partial u_i}\right|_{u_i=u_i^{\text{rel}}} (\mathbf{u}_i - \mathbf{u}_i^{\text{rel}})$$

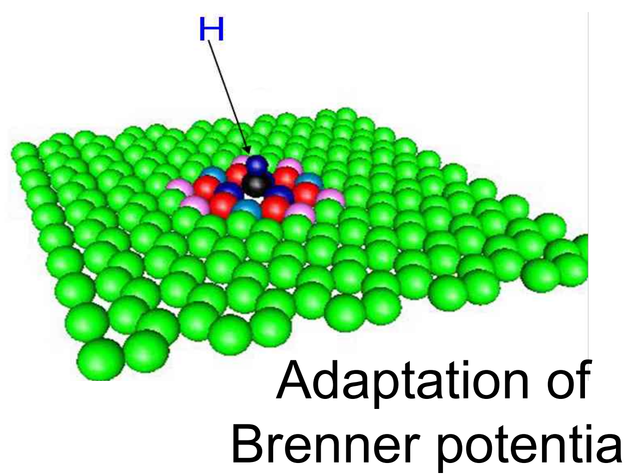
J. Chem. Phys. **129**, 024509 (2008)

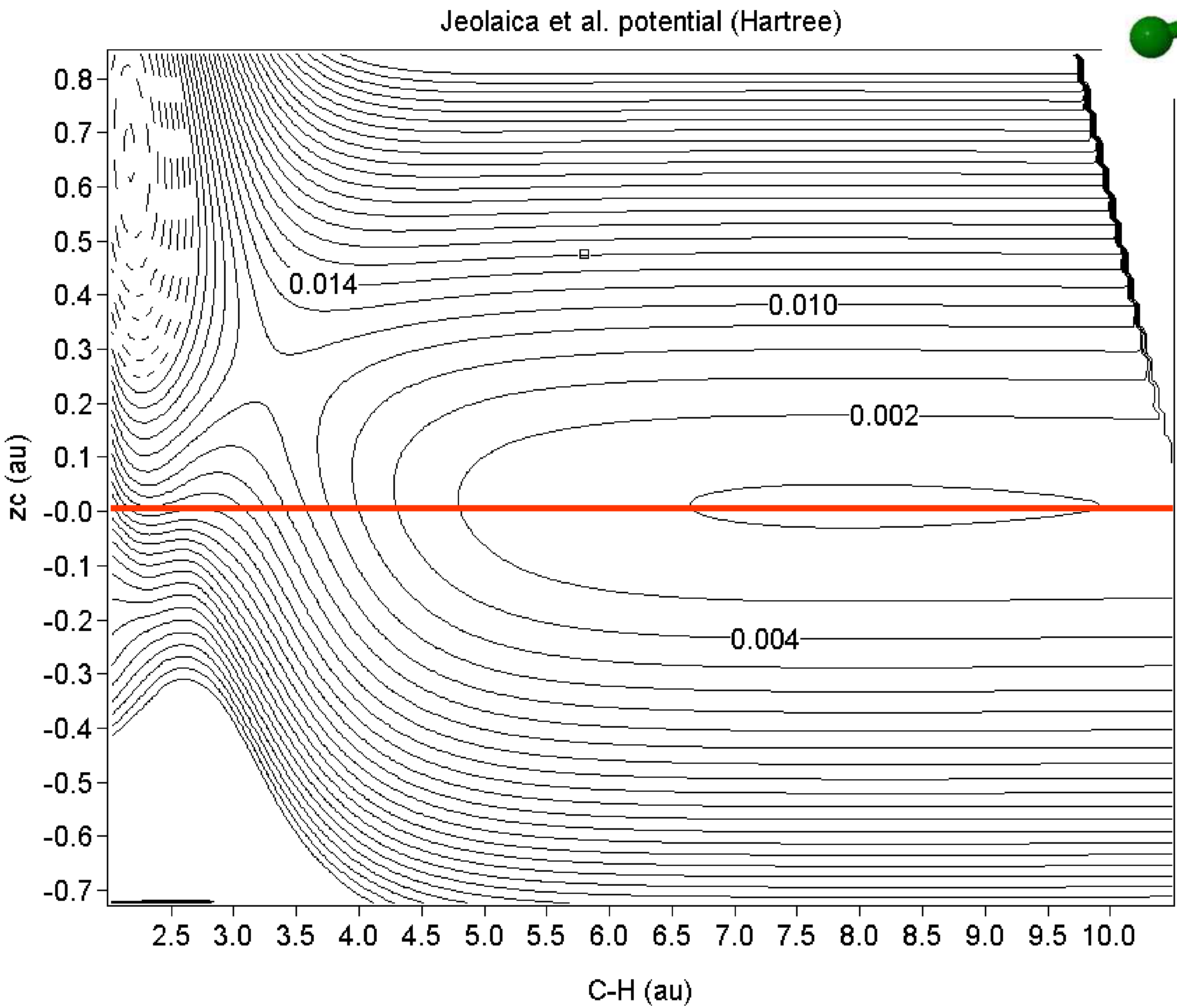
$$H_b = \sum_{i=1}^{N} \sum_{j=1}^{M} \frac{1}{2}\omega_{ij}(q_{ij}^2 + p_{ij}^2)$$



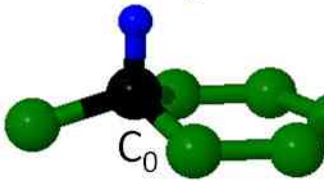
$V(z_H, z_C)$ $\quad$ $V(z_H\text{-}Q, z_C\text{-}Q)$ $\quad$ $V(z_H\text{-}Q, z_C\text{-}Q) + V_{Aix}(z_C,\{z_{other}\})$





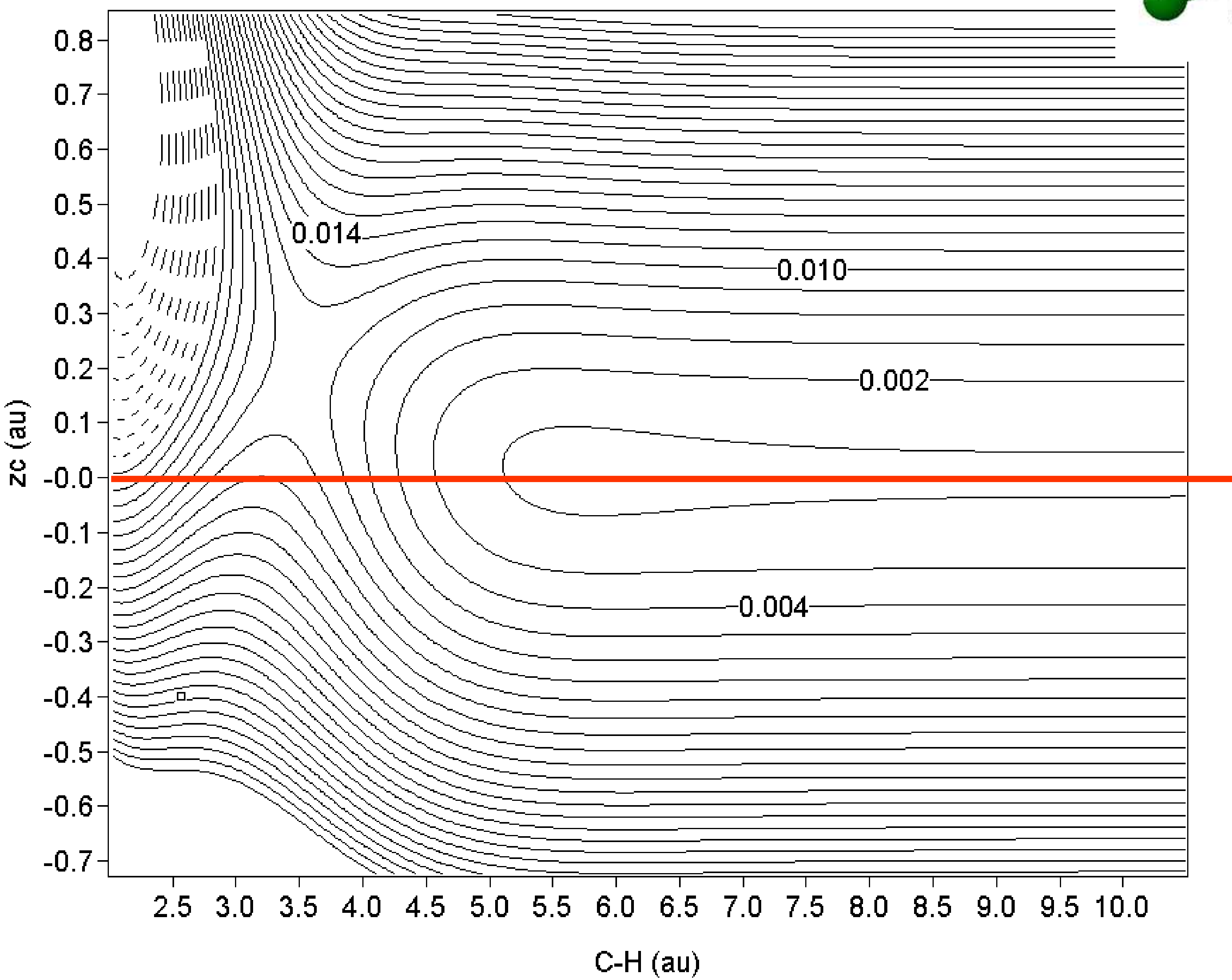


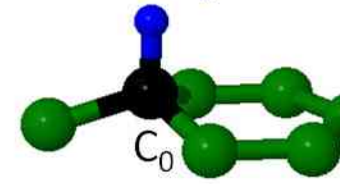
Jeolaica et al. potential (Hartree)
0.014
0.010
0.002
0.004
zc (au)
C-H (au)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
-0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0



C_0

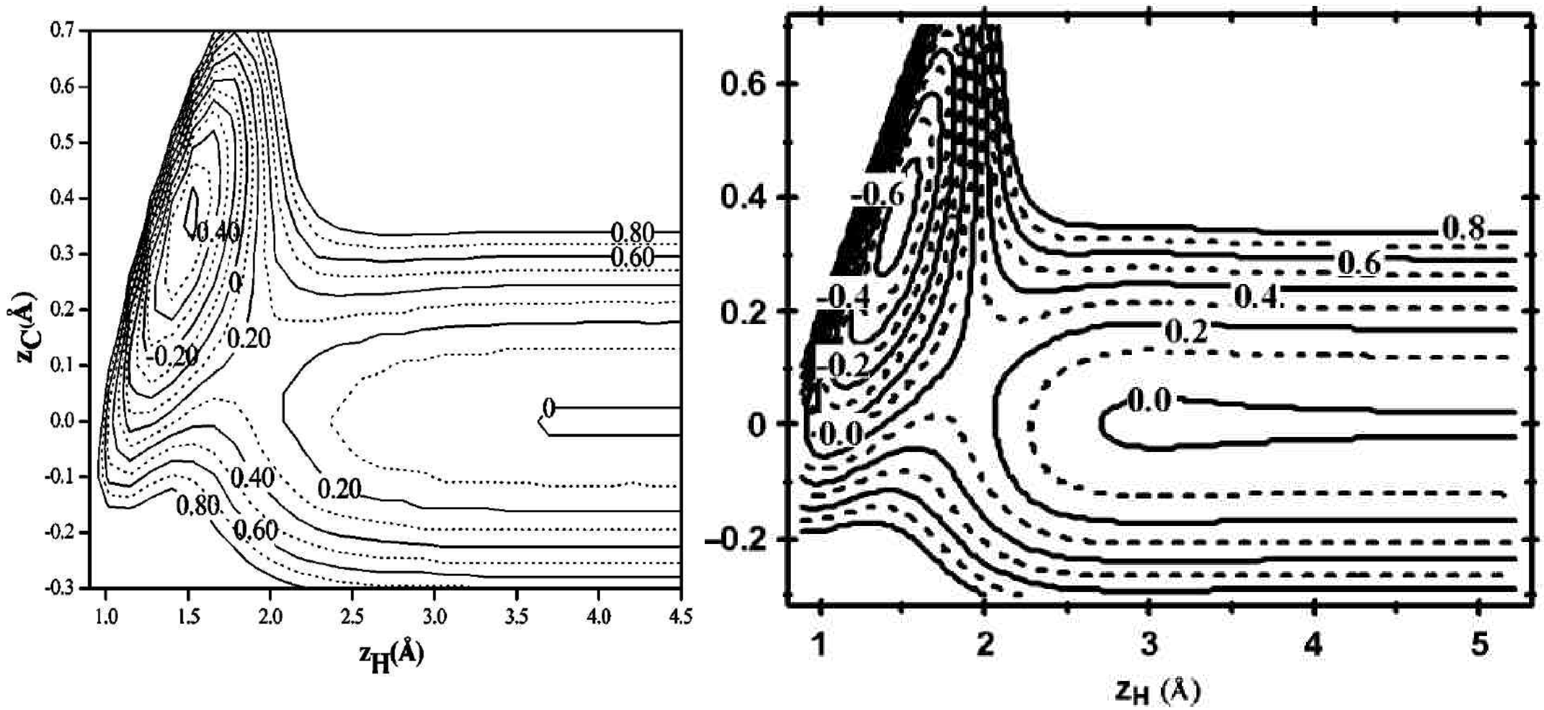
Jackson et al. potential (Hartree)





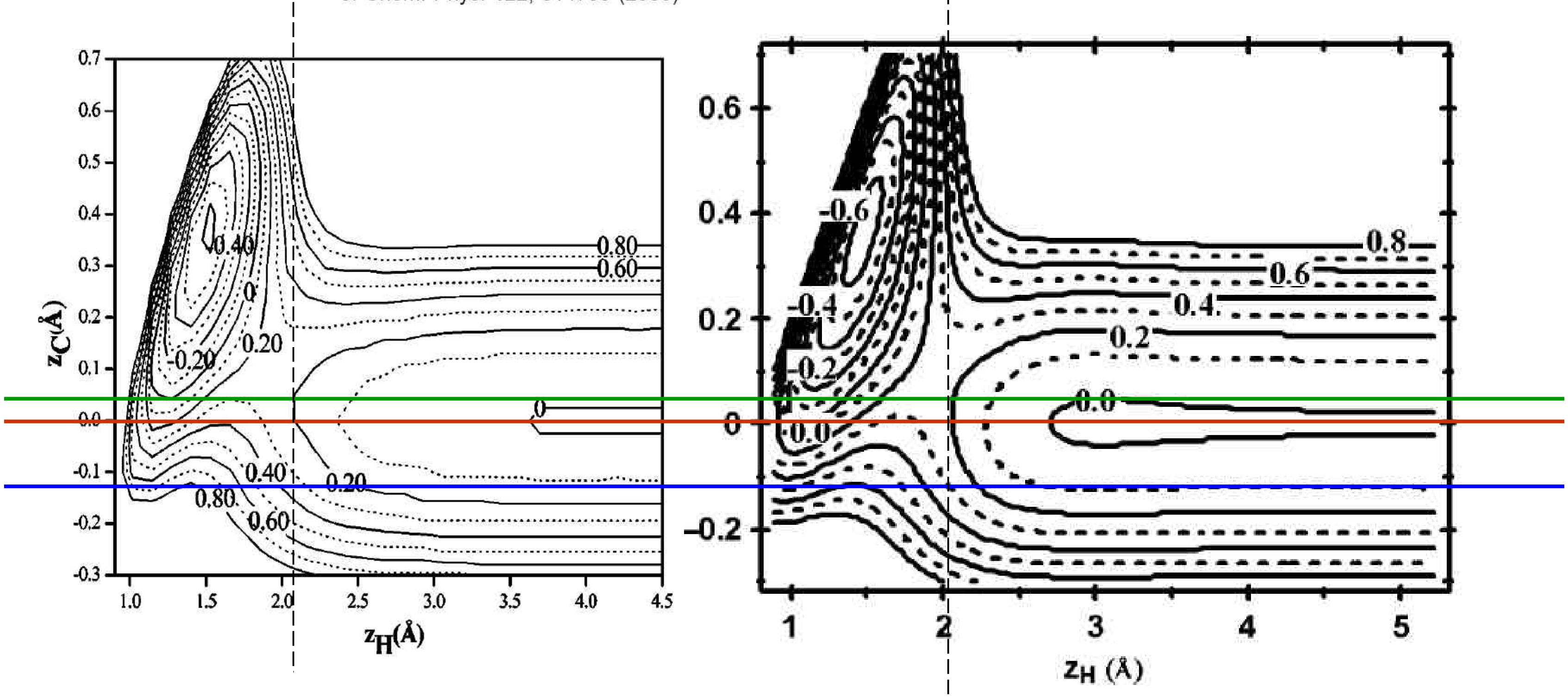
J. Phys. Chem. B, Vol. 110, No. 38, 2006

J. Chem. Phys. **122**, 014709 (2005)

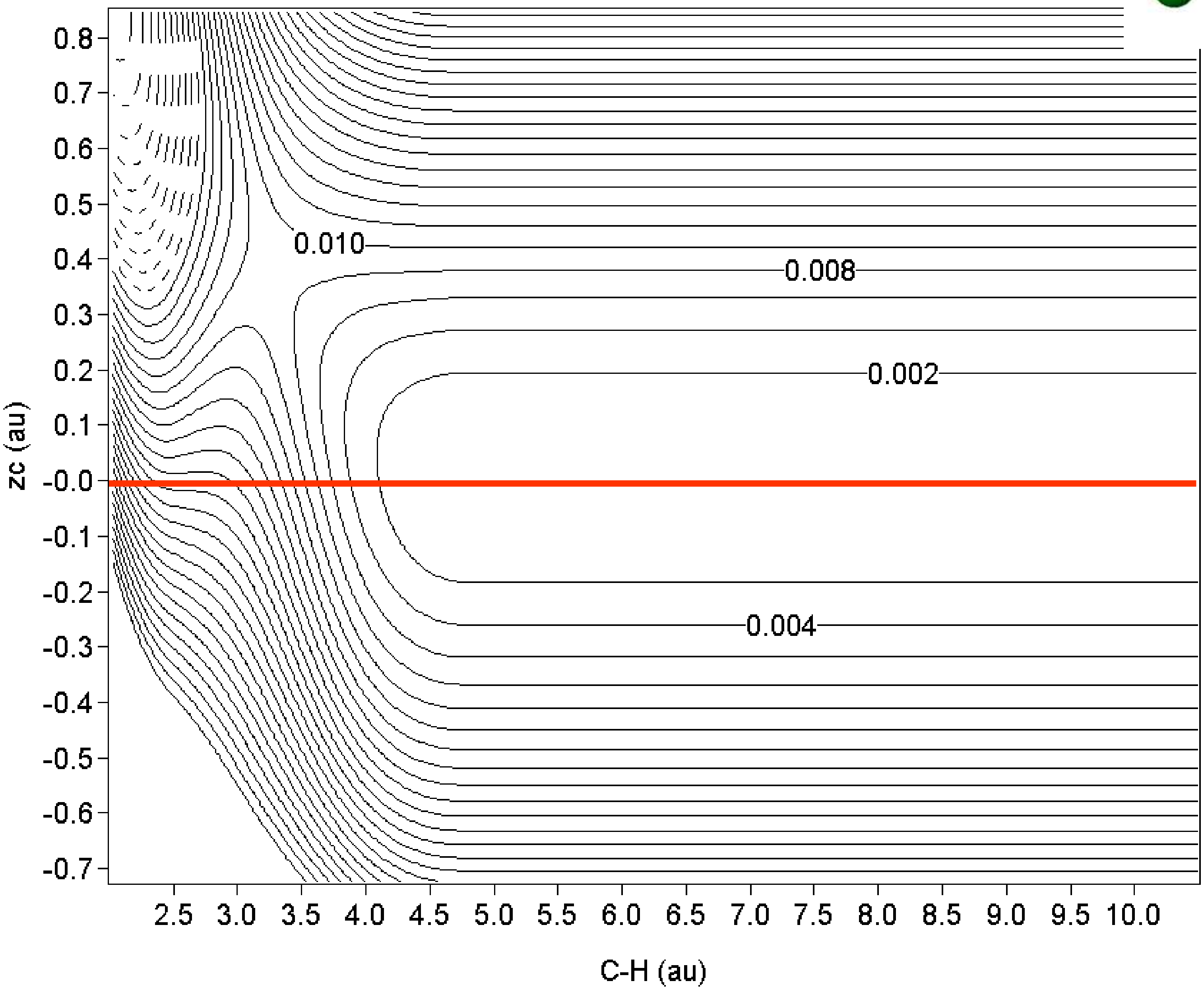


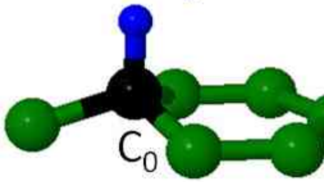
J. Phys. Chem. B, Vol. 110, No. 38, 2006

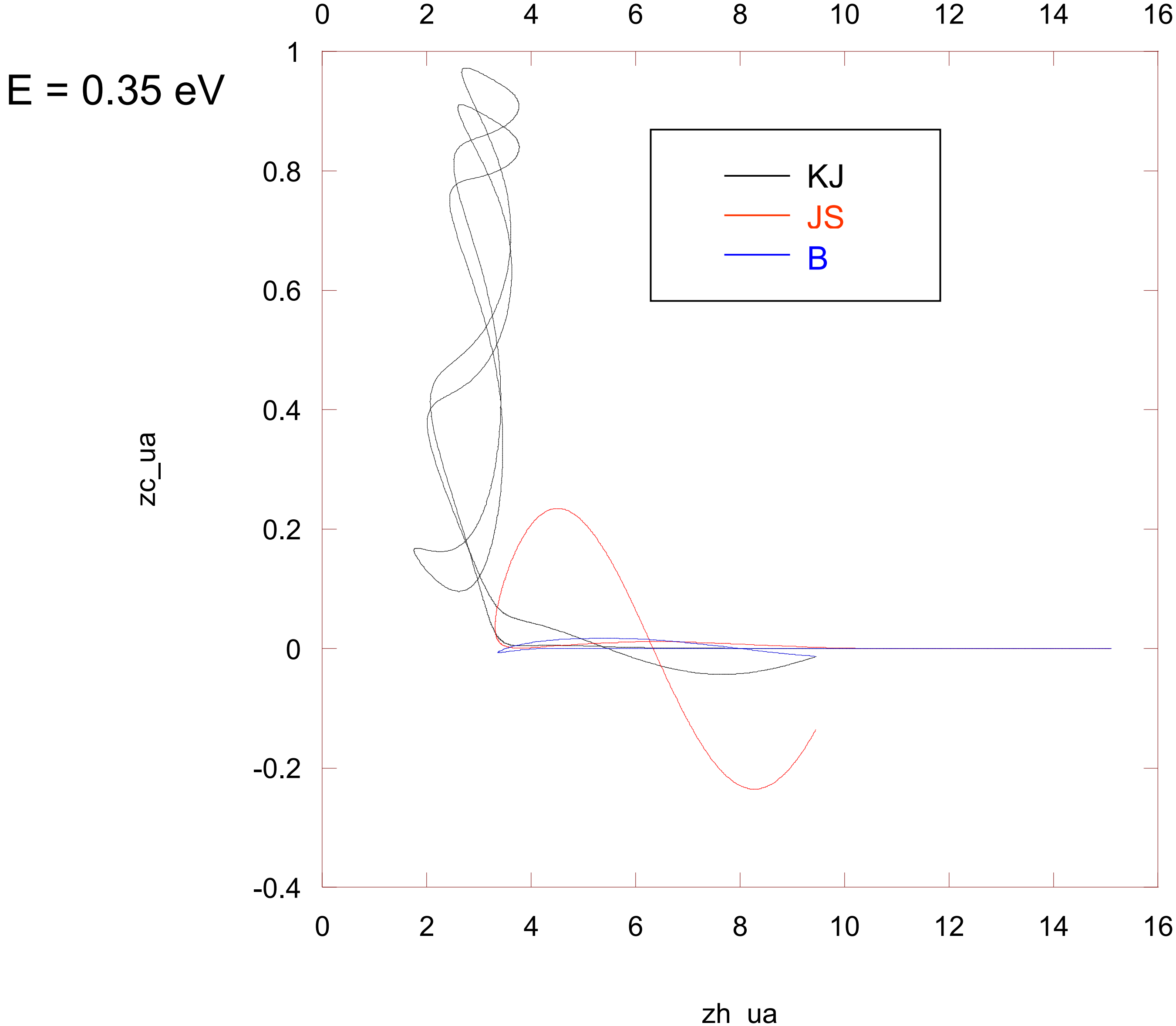
J. Chem. Phys. **122**, 014709 (2005)

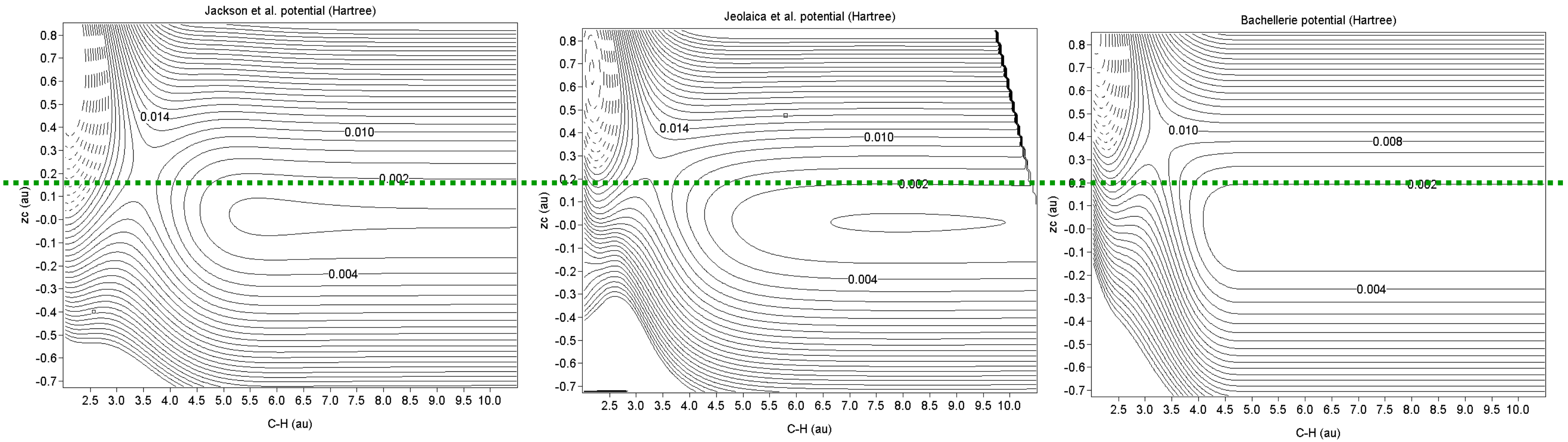


Bachellerie potential (Hartree)



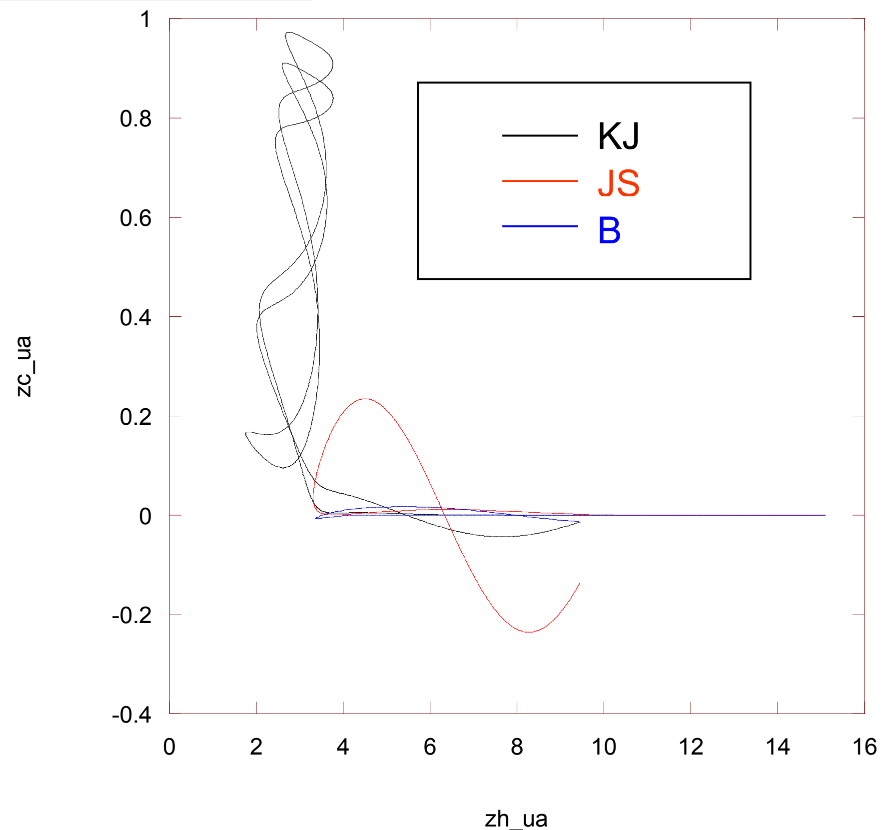



E = 0.35 eV
KJ
JS
B
zc_ua
zh_ua
0
2
4
6
8
10
12
14
16
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4



Jackson et al. potential (Hartree)
Jeolaica et al. potential (Hartree)
Bachellerie potential (Hartree)
zc (au)
C-H (au)
0.014
0.010
0.008
0.002
0.004

E = 0.35 eV



KJ
JS
B
zc_ua
zh_ua

X section T=10 K E = 0.3 eV	0. Å^2	K &J (T=0.):	0.25 Å^2
X section T=10 K E = 0.5 eV	0.76 Å^2	K &J (T=0.) :	1.5 Å^2
X section T=150 K E = 0.3 eV	0.06 Å^2	K &J :	0.4 Å^2
X section T=150 K E = 0.5 eV	0.68 Å^2	K &J :	1.3 Å^2

K & J J. Chem. Phys. **128**, 084702 (2008)

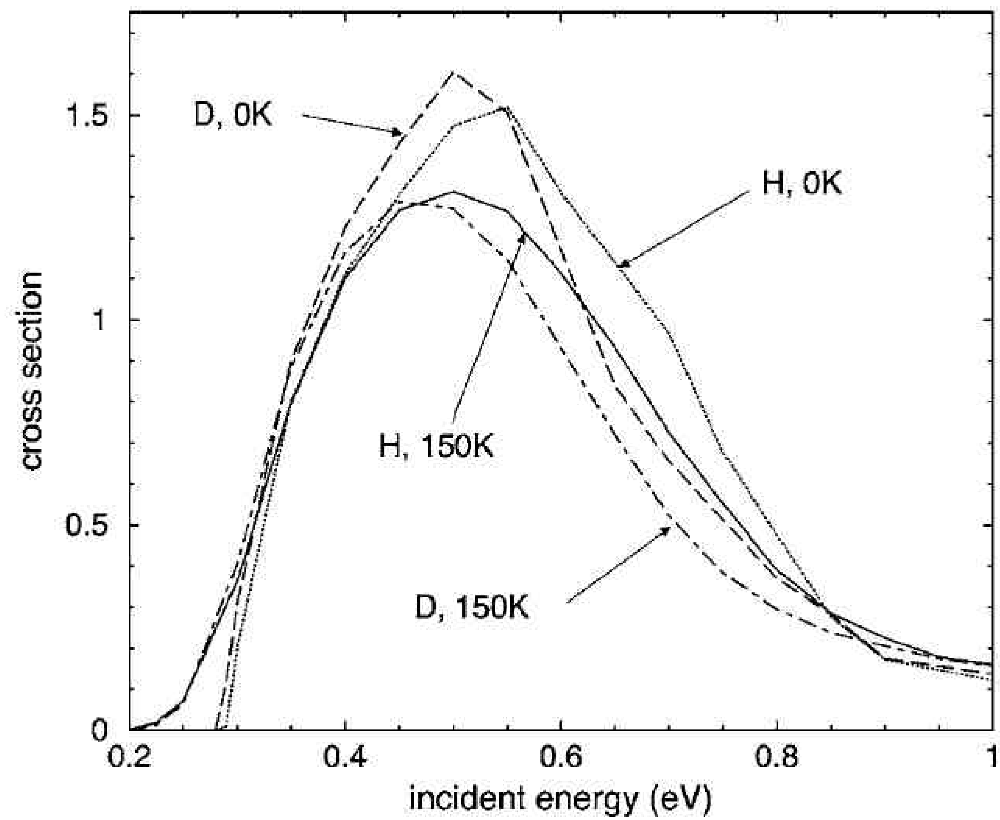
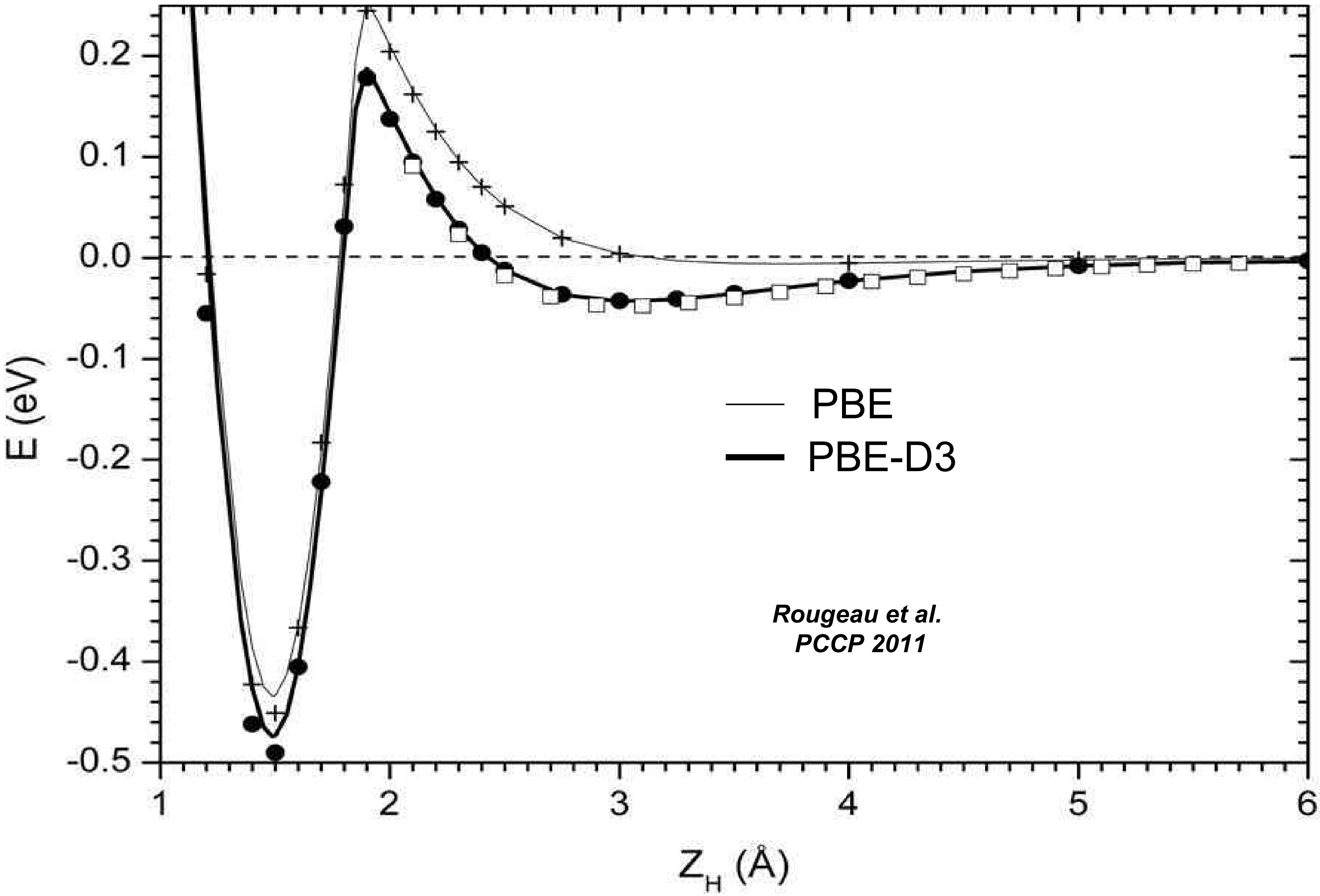
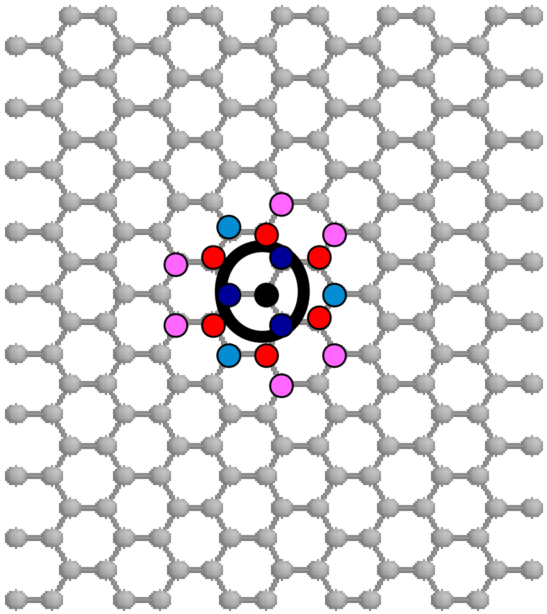


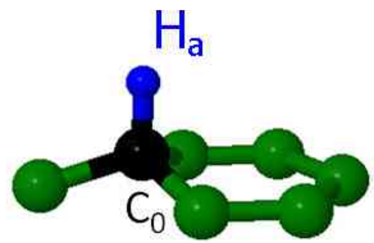
FIG. 4. The trapping cross section (in Å^2) as a function of the incident energy, for H or D normally incident on a 0 or 150 K graphite surface, as labeled. The results for H correspond to 0.3 ps and the results for D to 0.34 ps.



0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
E (eV)
1
2
3
4
5
6
Z_H (Å)
PBE
PBE-D3
Rougeau et al.
PCCP 2011

Graphenic surface





« ***puckering*** »
Tetrahedrization
$sp_2 \rightarrow sp_3$

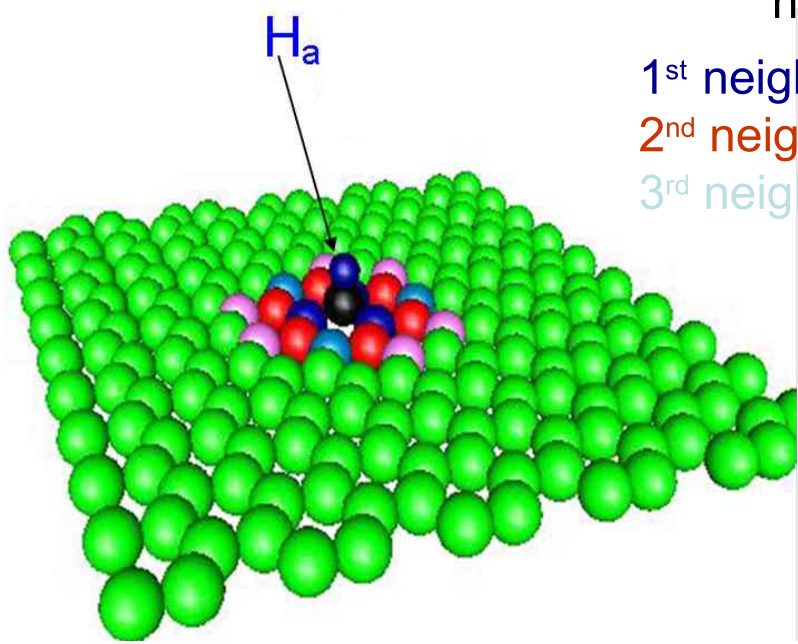
« ***extended puckering*** »

hillock

1^{st} neighbors : 0.21 Å

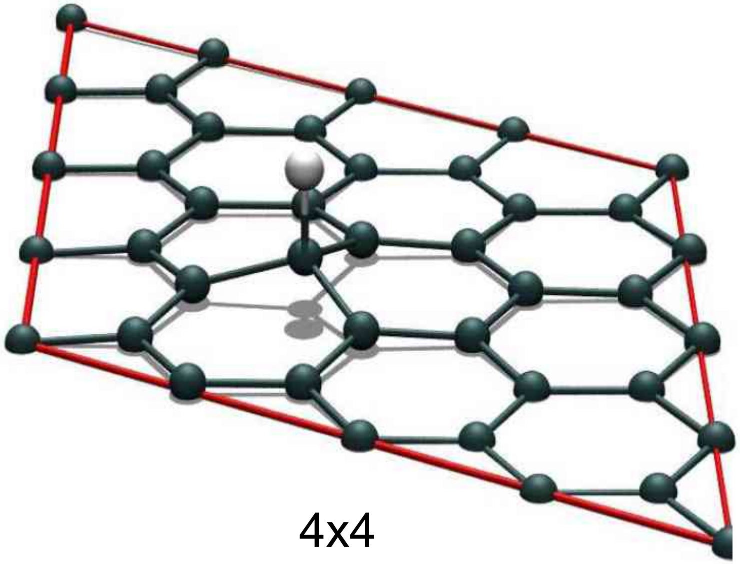
2^{nd} neighbors : 0.04 Å

3^{rd} neighbors : 0.005 Å



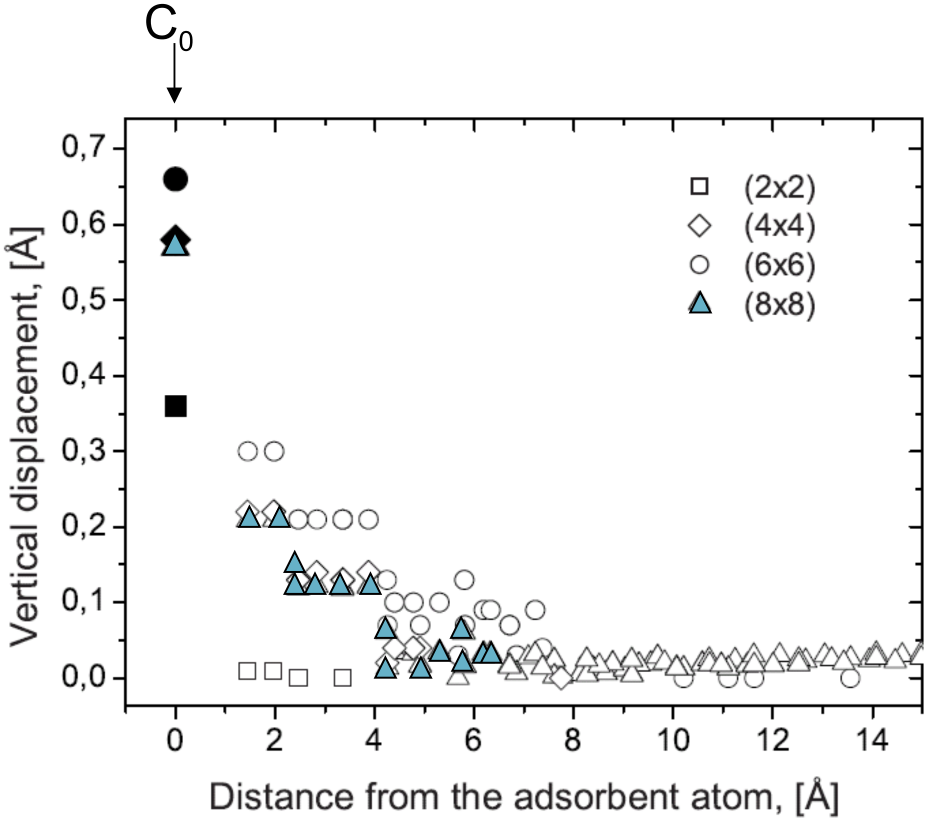
Bachellerie et al. PCCP 2009
(adaptation of Brenner potential force field)

Ferro et al. PRB 2008
DFT



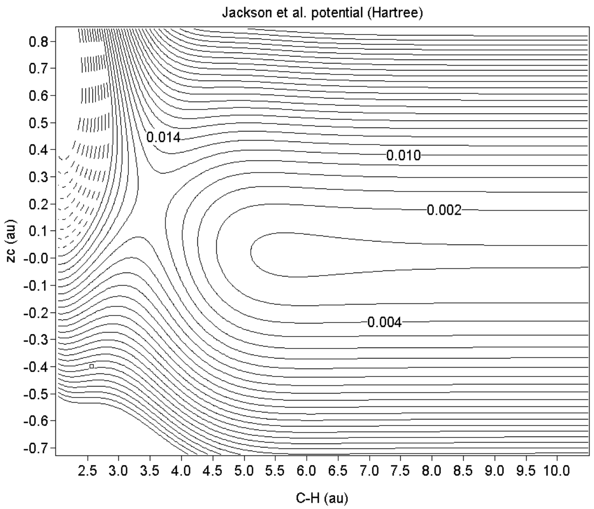
4x4

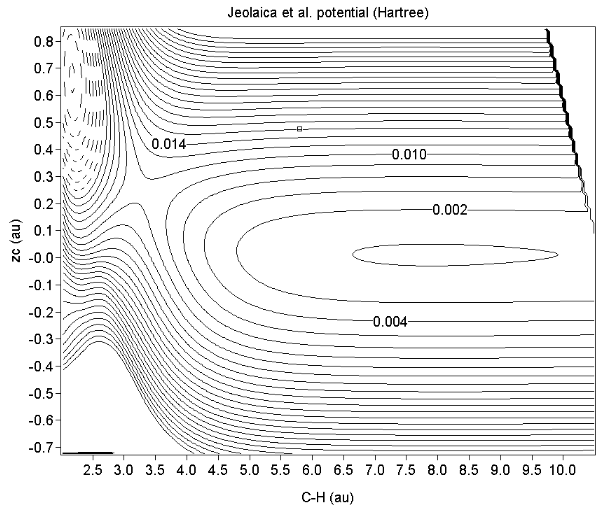
Periodic calculations
DFT-GGA (PBE)
AIMPRO
Gaussian orbital basis



Sticking

Ivanovskaya et al. EPJB (2010)


Jackson et al. potential (Hartree)
0.014
0.010
0.002
0.004
zc (au)
C-H (au)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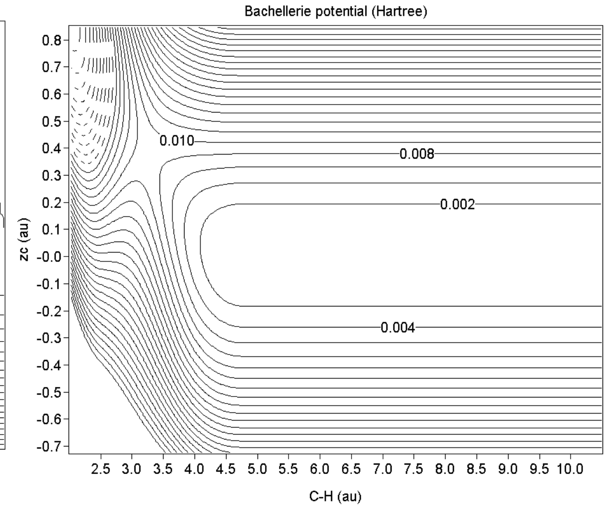
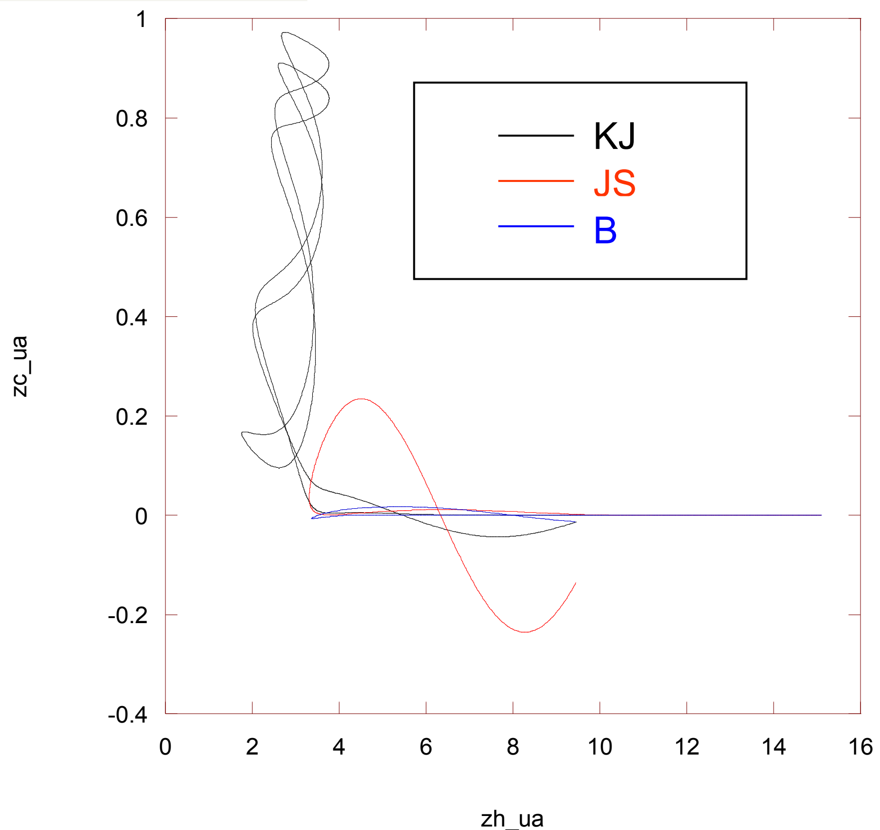
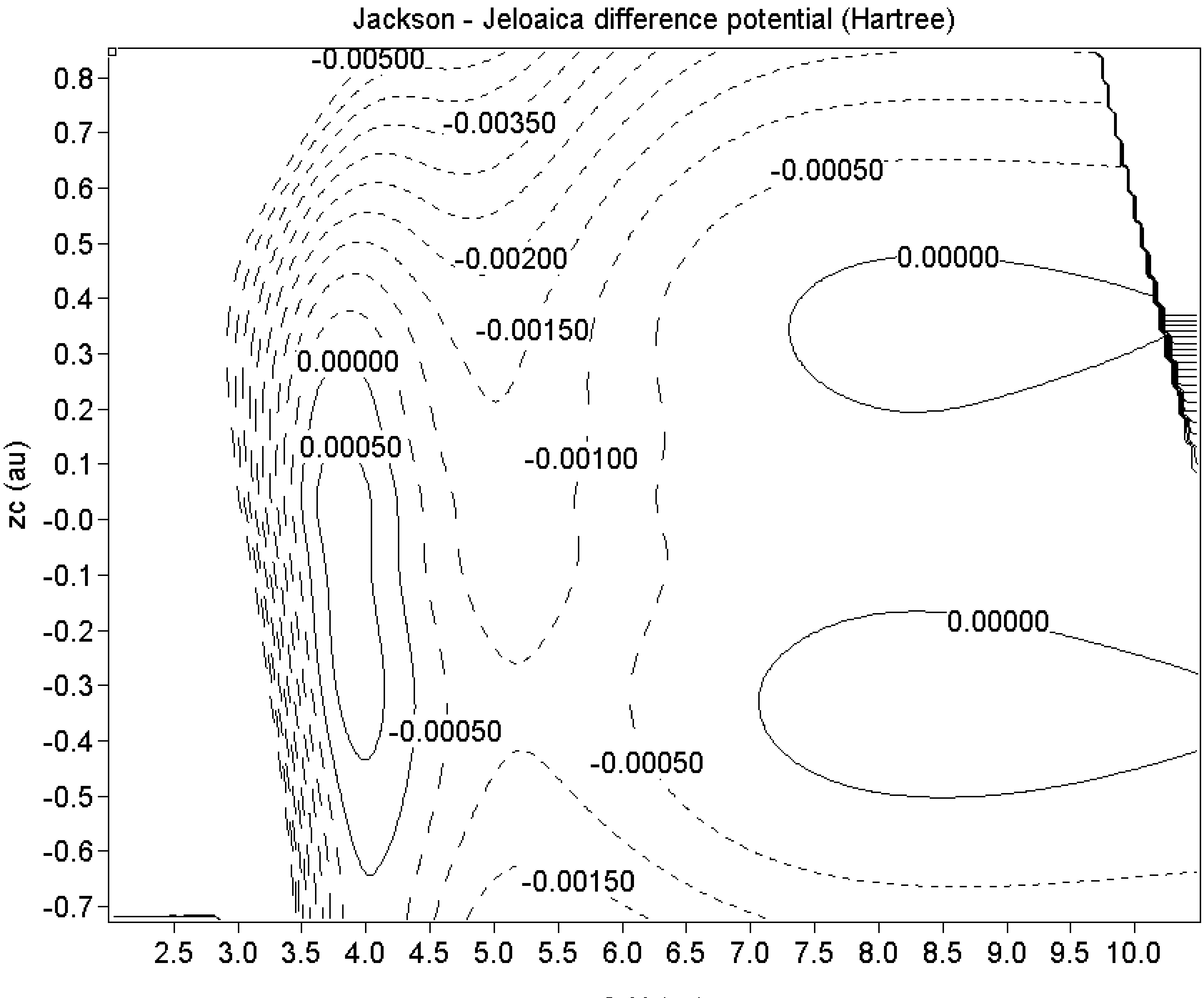
0.010
0.002
0.004
zc (au)
C-H (au)

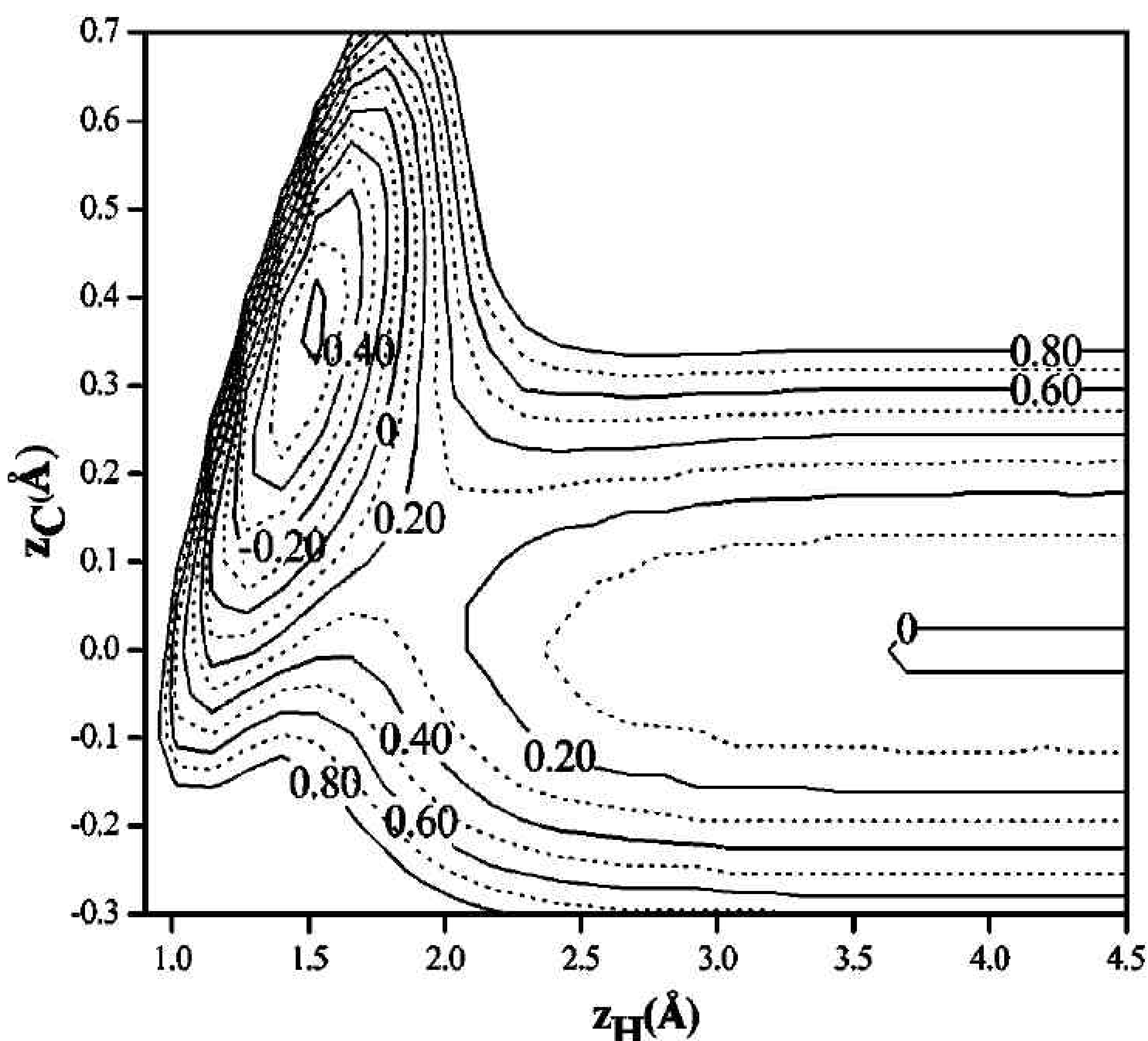

Bachellerie potential (Hartree)
0.010
0.008
0.002
0.004
zc (au)
C-H (au)

E = 0.35 eV


KJ
JS
B
zc_ua
zh_ua



Jackson - Jeloaica difference potential (Hartree)
-0.00500
-0.00350
-0.00050
-0.00200
0.00000
-0.00150
0.00000
0.00050
-0.00100
0.00000
-0.00050
-0.00050
-0.00150
zc (au)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
-0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0


0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
z_C(Å)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
z_H(Å)
-0.40
0
-0.20
0.20
0.80
0.60
0
0.40
0.20
0.80
0.60

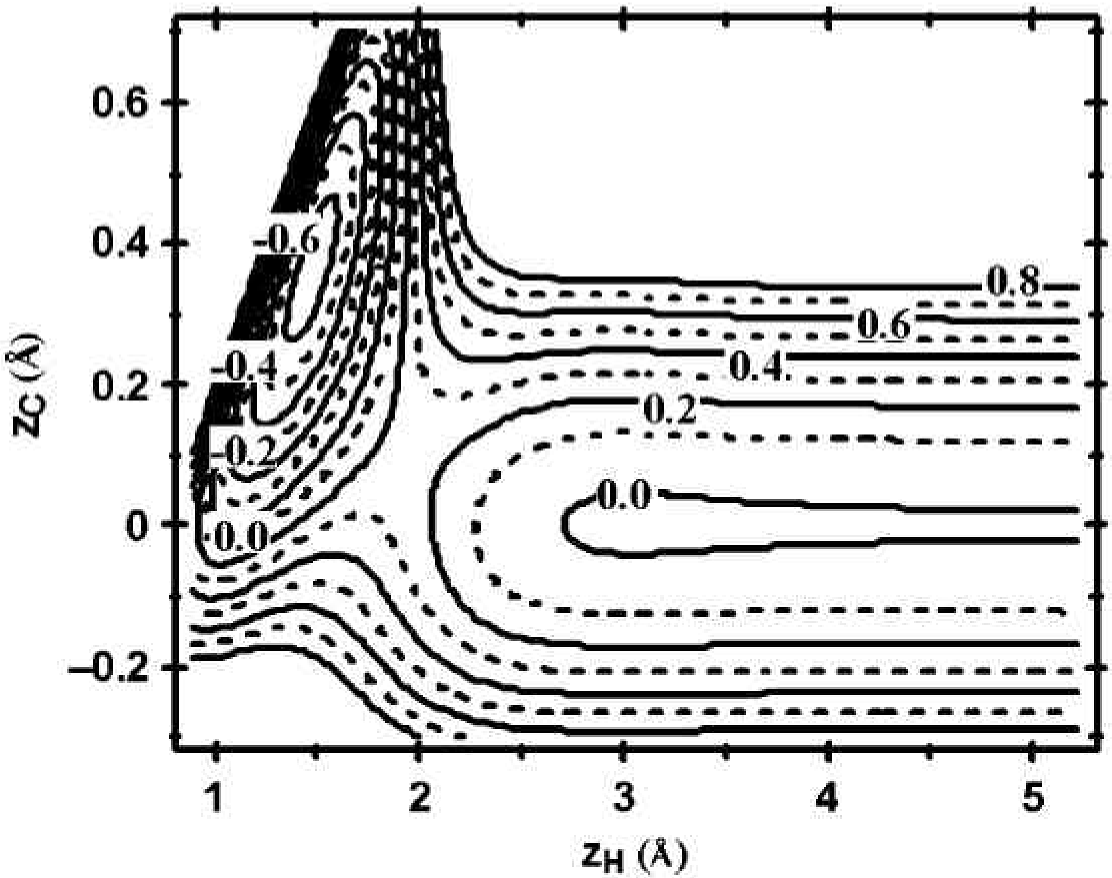
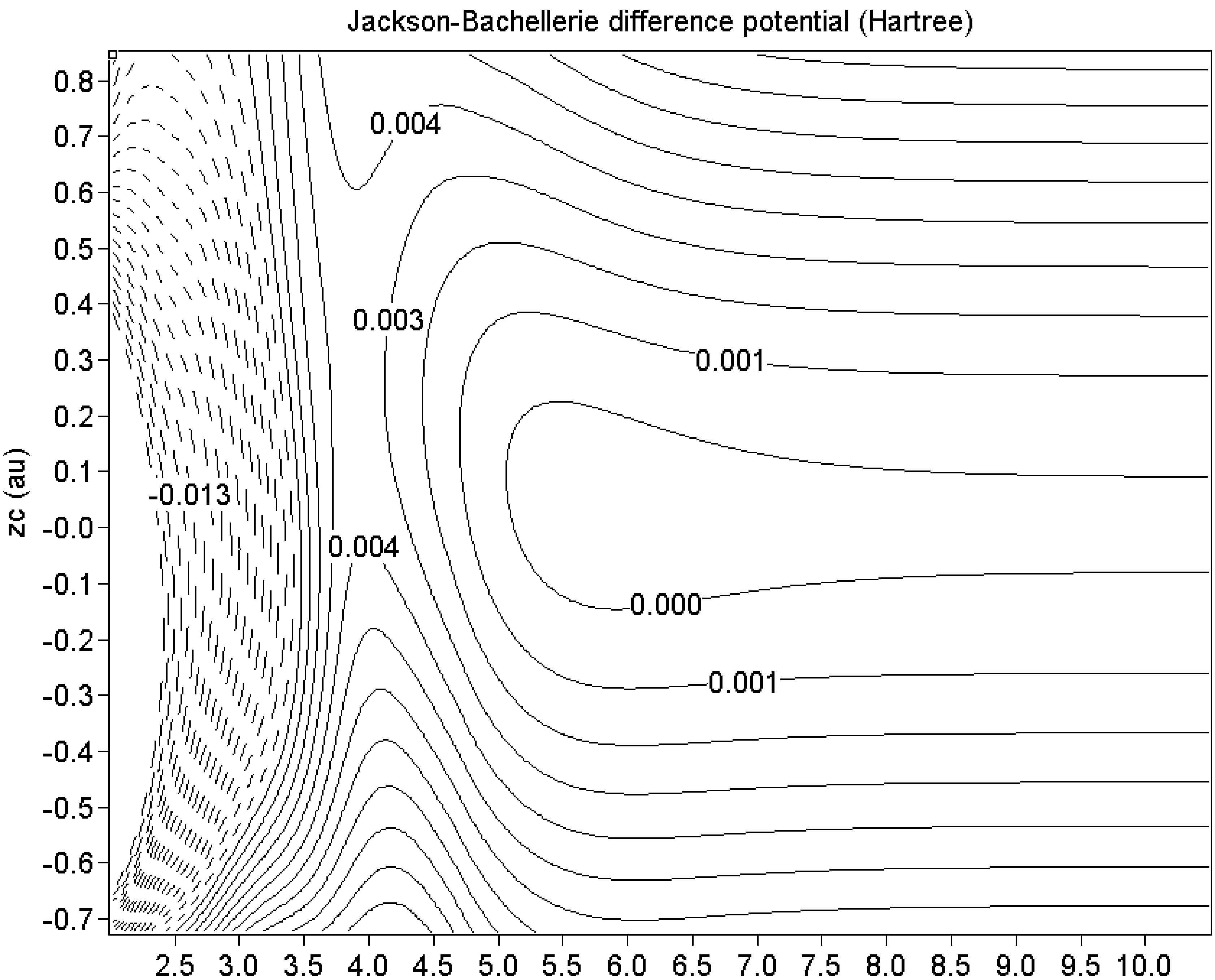


Figure 1. Potential energy contours for the collinear configuration, as a function of z_H, the distance of the H atom above the surface plane, and z_C, the height of the carbon above the surface. The contour spacing is 0.1 eV, and the contour labels are in eV.



Jackson-Bachellerie difference potential (Hartree)
zc (au)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
-0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
0.004
0.003
0.001
-0.013
0.004
0.000
0.001