

Unusual Bonding in Platinum Carbido Clusters

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Supporting Information

Basin Hopping Algorithm

Recent developments in computing power and the efficiency of electronic structure codes have lead a number of groups to develop global optimization methods which directly explore the energy landscape described by electronic structure methods¹⁻⁴ rather than using a prescreening with an empirical potential. We will not try to provide a comprehensive review of these developments here, but give some details of the choices we made in extending basin hopping (BH) to use DFT calculations for the local optimization and energy evaluation at each Monte Carlo step. Our basin hopping program is written in Fortran 90 and interfaces to TURBOMOLE using the TMOLE

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script, versions are also available which work with TURBOMOLE's DEFINE program or with Gaussian, and extension to other electronic structure codes should be reasonably straight forward. Code can be obtained from DJH (email: daniel.harding@mpibpc.mpg.de).

The greatest difference between BH with a model potential and DFT-BH is the computational cost of the local optimization. A second, related, factor is the sensitivity of the electronic wavefunction self consistent field (SCF) convergence to the cluster geometry. This typically manifests itself in problems with the first step of the geometry optimization if any of the atoms are too close together. The solution to both of these problems is to check that the interatomic distances in the new candidate structure are reasonable, neither too close nor too far, which we also use to prevent the cluster from fragmenting.

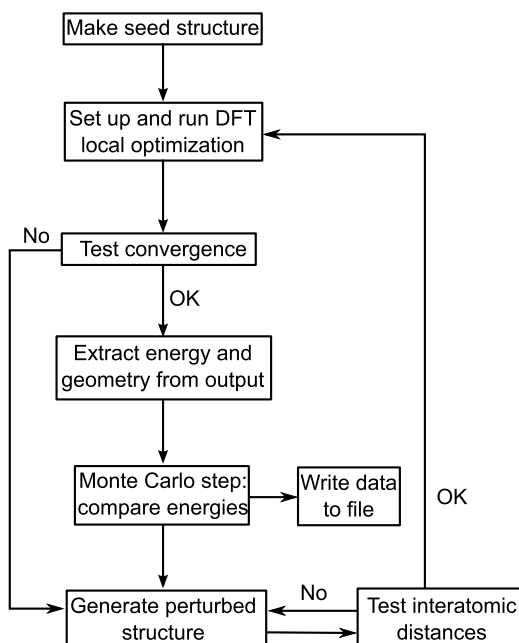


Figure 1: Flow chart showing the most important steps in the DFT-BH routine.

Figure 1 shows a flow chart of the most important part of the DFT-BH routine. We start a BH run with a seed geometry rather than a completely random structure, the geometry is then written to an input file for TURBOMOLE, where the functional, basis set and convergence criteria are specified. All of the options available in TURBOMOLE can, in principle, be used, allowing mixed clusters or ions to be investigated. In order to increase the number of MC steps we typically use

relatively small basis sets with effective core potentials and reduce the SCF convergence criteria to 10^{-4} compared to the default 10^{-6} . We found it less fruitful to lower the convergence threshold for the geometry optimization and typically use the default settings.

Following the DFT calculation the optimized coordinates and energy are extracted from the output files of the electronic structure program, and a test is also made to ensure that the calculation has converged. If the calculation has not converged, either during an SCF step or the geometry optimization, a new input geometry is generated and the optimization restarted. The energy of the new, converged structure is compared to that of the current reference structure using the standard Metropolis criteria.⁵ Given the relatively high cost of the DFT calculations and our interest in exploring the full range of low energy isomers we save all of the converged structures to allow an off line analysis.

A new candidate structure is then generated, using either a single atom move, where one atom is moved around the cluster, or a 'jiggle', where all of the atoms in the cluster are moved. We use the significant structures variant of BH, where the current reference structure is perturbed to generate the new candidate structure. The interatomic distances of the candidate are then checked and, if they fall within the preset criteria, the structure is used to start a new DFT optimization, otherwise another candidate is generated. It is sometimes necessary to go around this loop a relatively large number of times, but the computational cost is insignificant compared to the time savings made by the increased success of the DFT optimizations.

The number of MC steps used varies depending on the system, for the small Pt_nC^+ clusters only a few hundred steps were used, but for larger systems thousands of steps are possible at reasonable computational cost.

Pt_2C^+

Figure 2 shows the experimental and calculated spectra of Pt_2C^+ . We were only able to measure a high quality spectrum in a limited, low frequency, range. We clearly observed a strong band at 276 cm^{-1} and possibly a weak band at 1110 cm^{-1} . The primary cause of the low signal-to-

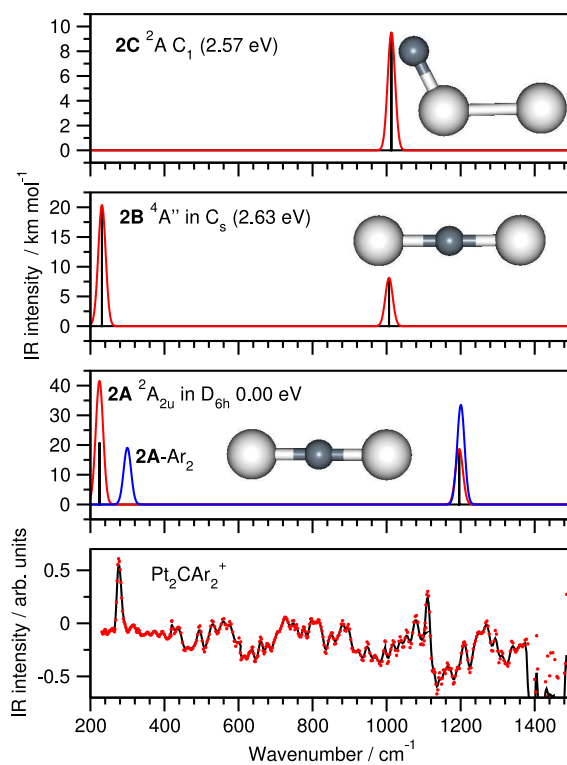


Figure 2: Experimental spectrum of argon tagged Pt_2C^+ and calculated spectra of low-energy isomers. The blue line shows the spectrum of isomer **2A** with two argon atoms included explicitly in the calculation.

noise ratio appears to be the low intensity of this species in the cluster distribution, which was optimized for the larger sizes. A second potential complication may be a low density of vibrational states at higher energy in this small cluster, leading to relatively slow intramolecular vibrational redistribution (IVR) following IR excitation of the high frequency mode around 1100-1200 cm^{-1} . Slow IVR may make it more difficult for the cluster to absorb the multiple photons necessary to drive dissociation, in turn leading to a smaller apparent cross section. The calculated spectrum of the linear isomer **2A** is a reasonable match to the band position in the experimental spectrum and if the argon atoms are included explicitly the position of the low frequency band is matched very well. The other isomers do not match the experiment so well, suggesting the linear structure is present in the experiment.

Cartesian coordinates

The Cartesian coordinates of the structures discussed in the article are available in a plain text file PtCarbides.xyz.

References

- (1) Yoo, S.; Zhao, J.; Wang, J.; Zeng, X. C. *J. Am. Chem. Soc.* **2004**, *126*, 13845.
- (2) Goedecker, S.; Hellmann, W.; Lenosky, T. *Phys. Rev. Lett.* **2005**, *95*, 055501.
- (3) Gehrke, R.; Gruene, P.; Fielicke, A.; Meijer, G.; Reuter, K. *J. Chem. Phys.* **2009**, *130*, 034306.
- (4) Drebov, N.; Oger, E.; Rapps, T.; Kelting, R.; Schoos, D.; Weis, P.; Kappes, M. M.; Ahlrichs, R. *J. Chem. Phys.* **2010**, *133*, 224302.
- (5) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. *J. Chem. Phys.* **1953**, *21*, 1087.

4				Pt	1.8065988	0.0002533	0.0000000
3A	Energy = -395.8389680936			Pt	-1.8066020	0.0002533	0.0000000
Pt	0.0000000	0.0000000	2.0730384	C	0.0000513	-0.0082269	0.0000000
Pt	-1.2972727	0.0000000	-1.0449103	3			
Pt	1.2972727	0.0000000	-1.0449103	2C	Energy = -276.3638495908		
C	0.0000000	0.0000000	0.272568	Pt	1.3243400	-0.6015995	1.1811428
4				C	-2.1604197	-0.5620866	0.5684195
3B	Energy = -395.8379863883			Pt	-0.6803383	-0.5214634	-0.2504771
Pt	1.7933737	0.0000110	-0.6800214	5			
Pt	-1.7933737	0.0000110	-0.6800214	2a-Ar2	Energy = -1331.593224710		
Pt	0.0000000	0.0000023	1.3900547	Pt	-1.7491548	0.0000000	0.0000000
C	-0.0000000	-0.0003941	-0.4874398	Pt	1.7491712	0.0000000	-0.0000000
4				C	0.0000149	-0.0000000	0.0000000
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Pt	0.0019418	1.4092290	0.0000069	PtC+	doublet Energy = -156.9390086443		
C	0.0043606	3.0783574	-0.0000642	Pt	-0.1012879	0.0000000	0.0000000
5				C	1.6450745	0.0000000	0.0000000
4A	Energy = -515.2185847258						
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Pt	1.6141266	0.7817250	-0.1532202				
Pt	-0.5452560	2.0177770	0.2370600				
C	0.5057586	-0.6760060	-0.1303519				
5							
4B	Energy = -515.2158134890						
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Pt	-0.5164093	1.6951142	1.0174199				
Pt	0.8658784	1.0135710	-1.0286744				
Pt	0.5169978	-1.6982141	1.0139045				
C	0.0030557	-0.0002496	0.4290294				
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4C	Energy = -515.2125605238						
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Pt	-1.2031933	1.3041303	-0.3925567				
C	0.1456413	-0.0437598	-0.5079686				
6							
5A	Energy = -634.5990477496						
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Pt	-0.5417503	-1.1911622	0.0473782				
Pt	0.3569045	1.6909336	0.0347072				
Pt	-2.9016293	0.0798178	0.0024449				
Pt	1.5141928	-0.2955859	-1.2982264				
C	-1.1629473	0.5946693	0.0522985				
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Pt	-0.2231987	0.5029804	-1.4998436				
Pt	-0.2363175	-1.4413782	0.6559629				
Pt	0.9737174	1.2623617	1.1252514				
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Pt	0.2790146	1.3249573	-1.7374520				
Pt	-1.5140982	-0.3041391	-0.0170862				
C	-0.3473699	1.2158683	-0.0143163				
3							
2A	Energy = -276.4584721518						
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Pt	0.0000000	0.0000000	1.7385707				
C	0.0000000	0.0000000	0.0000000				
3							
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