

PCCP

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

On the Nature of Hydrogen Bonds to Platinum(II) – Which Interaction can Predict their Strength?

Cite this: DOI: 10.1039/x0xx00000x

Rocío Sánchez-de-Armas^a and Mårten S.G. Ahlquist^a

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

The interaction between hydrogen bond donors and platinum has been analysed. Our results point to an interaction that can be entirely predicted from the dz^2 orbital energy of the platinum centre indicating strong charge transfer, with significant dispersion contribution to the bonding, very different from classical hydrogen bonds.

Platinum is one of the most commonly used metals for catalysis, due to its combination of high stability against oxidation and high catalytic activity. There are many applications where the interaction of platinum with the solvent is highly important such as in fuel cell electrode dissolution.^{1,2,3,4,5} To fully understand these processes the interaction with water and other hydrogen bond donors is crucial. Computational chemistry can provide insight into these types of interactions complementing the information obtained by experimental techniques, and this knowledge will make predictions of the structure and reactivity of platinum easier.

Hydrogen bonds are unusually strong intermolecular interactions which have intrigued chemists since their discovery.⁶ This interaction plays a key role in many chemical and biological systems and it has classically been described as the interaction between a H atom bound to an electronegative residue (X-H) and a region with high electron density (a lone pair of electrons, a π molecular orbital or a σ -bonding pair) (Figure 1). However, it has been observed that transition metals can also participate in hydrogen bonds, despite the electropositive nature of these elements.^{7,8} In 2011 an IUPAC Task Group recommended a modern evidence-based definition of hydrogen bonding.⁹ It is described as an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X-H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation. This short definition is followed by a list of criteria, which can be used as evidence for the presence of the hydrogen bond, being the first one related to the forces involved in the formation of the hydrogen bond. These forces include those of an electrostatic origin, those arising from charge transfer between the

donor and acceptor leading to partial covalent bond formation between H and Y, and those originating from dispersion.



Figure 1. Hydrogen bond (left) and non-classical hydrogen bond, where a metal acts as hydrogen bond acceptor (right).

In the last few years a few papers have appeared reporting that platinum(II) complexes bind to water molecules via the hydrogen, with platinum acting as a hydrogen bond acceptor.¹⁰ Also on Pt(111) surface, H₂O has been found to bind to Pt both through H and O atoms.¹¹ In ab initio molecular dynamics simulations by Lledós et al. the radial distribution functions showed an unusually short Pt-H average distance.¹² Neutron diffraction studies of the platinum complex *trans*-[PtCl₂(NH₃)(N-glycine)]·H₂O, showed that a water molecule points its hydrogen towards the axial position of the platinum center.¹³ The authors performed calculation at the HF and MP2 level and they only found a bonding interaction when MP2 was used. It was concluded that the interaction was driven by London dispersion, since Hartree-Fock cannot describe electron correlation and dispersion is a medium to long range interaction originating from the correlated motion of electrons. This explanation is problematic for several reasons. Firstly, if dispersion is driving the interaction why would water not point the oxygen towards the platinum centre? This would result in similar strength of the dispersion interaction while the electrostatic interaction should be greatly favoured. Now the positive positive Coulomb interaction would be replaced by a positive negative one. Secondly, the interpretation that dispersion comes last is based on the way the methods are created. One could, at least in principle, imagine a method where orbital overlap was not included but dispersion was, and upon inclusion of orbital overlap the interaction changed from

non-bonding to bonding. This would not mean that dispersion was less important for the bonding compared to orbital overlap. Finally, the difference between MP2 and Hartree-Fock does not necessarily need to stem from London dispersion but could be due to charge transfer correlation. In fact, more recently it has been suggested that the O-H...Pt interactions in both *trans*-[PtCl₂(NH₃)(N-glycine)]·H₂O and [NBu₄][Pt(C₆F₅)₃(8-hydroxyquinoline)] complexes are mainly closed-shell in nature with significant charge transfer based on B3LYP/6-311++G** calculations together with the atoms in molecules (AIM) theory and the NBO method.¹⁴ In a very recent paper the water-to-Pt(II) interaction has been analysed for several neutral platinum complexes with various polar ligands in their *cis* and *trans* configurations at MP2 level, using the AIM theory and the topological analysis of the electron localization function (ELF) to characterize the interaction.¹⁵ It was concluded that the stabilization energy is dominated by a dispersive component for all the complexes. However, the charge transfer from the complex to the water molecule and the Laplacian of the density at the bond critical point between water and Pt are identified as interesting AIM descriptors of this H-bond. There are several more recent theoretical works on this topic,^{16,17} but it is clear that the nature of this non-conventional H-bond remains controversial.

In this report we use three different strategies to analyse the nature of the non-classical hydrogen bonds to platinum: (1) In silico chemical modification to see bonding/property relationships, (2) analysis of the wavefunction using NBO and ALMO-EDA to decompose the interactions and (3) vibrational frequency analysis of different hydrogen bond donors and comparison with typical hydrogen bonds.

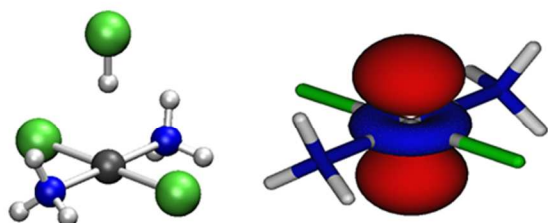


Figure 2. Non-classical hydrogen bond between Cl-H and *trans*-bisammine-dichlorido platinum(II) (left) and complex dz₂ orbital (right).

As a model to simplify our analysis we chose HCl as the initial hydrogen bond donor. Its linear geometry makes it easier to decompose the different interactions compared to a non-linear molecule such as water. When we calculate the potential energy of interaction between HCl and *trans*-bisammine-dichlorido platinum(II) (Figure 2) using B3LYP we find a significant negative interaction energy. B3LYP is known for being incapable of describing purely dispersive interactions and we find this as a first indication that the interaction is not solely driven by dispersion. We modified the ligands on the platinum complex as it is described in Figure 3 and Table 1 and, using the M06 functional, which has been found to be capable of describing midrange dispersion, we found strong correlation ($r^2 = 0.94$) between the interaction energy between the fragments and the energy of the dz² orbital of the platinum fragment (Figure 4 top). This correlation indicates that charge transfer from this orbital is important for the binding energy. Interestingly, we found no correlation between the partial charge and the energy of interaction. One extreme is the complex *trans*-bisammine-difluoro platinum(II) (Entry 11 in Table 1), which has a

high partial charge on the platinum due to the strongly electronegative fluorido ligands, but where the dz² energy is high due to d_π-p_π-repulsion. This complex was found to have among the strongest interaction with HCl, despite the large positive charge on platinum.

Reasoning that the total dispersion interaction in the series of complexes is close to the D3 dispersion correction for B3LYP by Grimme, we plotted this D3 interaction energy against the total bond energy (Figure 4 bottom). The correlation is very poor with an r^2 value of 0.38. One could see a tendency that the more strongly interacting complexes also have stronger dispersion interaction; however, some complexes with almost identical interaction energy have very different dispersion interactions. We see this as an indication that dispersion might not be the main driving force of the interaction, although it is always present and a substantial contribution to all complexes.

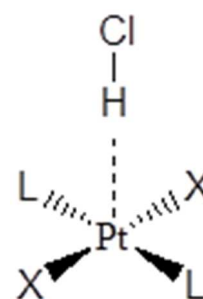


Figure 3. Model employed to study the interaction with HCl.

Table 1. Partial charge on Pt (a.u.), energy of the dz² orbital (a.u.), D3 dispersion correction for B3LYP interaction energies (kcal mol⁻¹) and M06 energy of the interaction of for the different Pt complex with HCl (kcal mol⁻¹)

Label	X	L	NPA	Ed _{z²}	D3	E _{int}
1	CH ₃	NH ₃	0.522	-0.211	-4.26	-9.61
2	CN	CO	0.392	-0.364	-3.00	0.88
3	CN	NH ₃	0.539	-0.287	-3.66	-3.13
4	CN	PH ₃	0.189	-0.305	-4.03	-2.91
5	OH	NH ₃	0.745	-0.233	-3.62	-6.11
6	Br	NH ₃	0.419	-0.266	-4.01	-5.11
7	Br	PH ₃	0.050	-0.283	-4.50	-4.66
8	Cl	CO	0.381	-0.339	-3.16	-0.84
9	Cl	NH ₃	0.536	-0.262	-3.84	-5.19
10	Cl	PH ₃	0.171	-0.281	-4.29	-4.61
11	F	NH ₃	0.875	-0.248	-3.27	-5.33

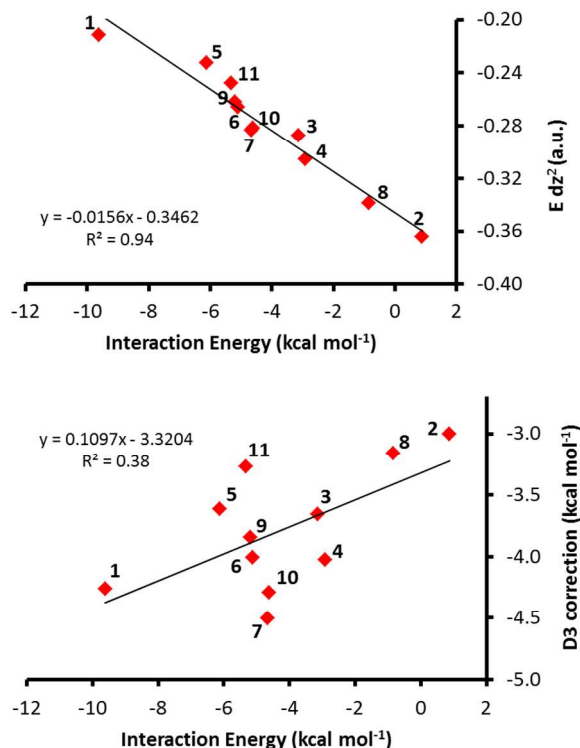


Figure 4. Plots of dz^2 orbital energy (top) and D3 dispersion correction to B3LYP interaction energies (bottom) versus the energy of interaction for the different platinum complexes described in Table 1 and HCl.

Next we look at the interaction of *trans*-bisammine-dichlorido platinum(II) complex with different hydrogen bond donors (Figure 5). We used the series HF, HCl, HBr, and HI. For classical hydrogen bonds with acceptors such as water the bond energy decreases over the series HF>HCl>HBr>HI. For hydrogen bonding to platinum a clear trend is not seen. The interaction is calculated to be around 5 kcal mol⁻¹ for all hydrogen halides. This difference in the interaction compared to regular hydrogen bonds we believe is an indication that the interaction with metals has a different composition.

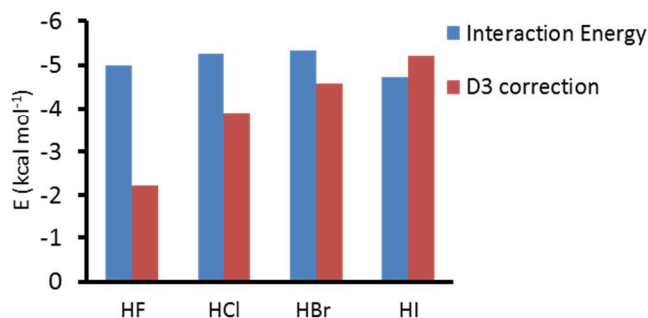


Figure 5. Energy of the interaction of *trans*-bisammine-dichlorido platinum(II) complex with different hydrogen bond donors at M06 level (blue) and D3 correction to B3LYP interaction energy (red).

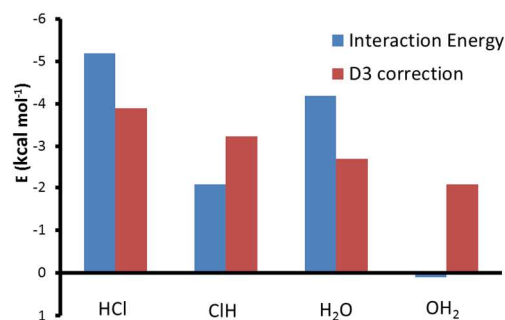


Figure 6. Energy of the interaction of *trans*-bisammine-dichlorido platinum(II) complex with HCl (H atom pointing Pt), ClH (Cl atom pointing Pt) and H₂O (H atom pointing Pt) at M06 level (blue). D3 correction to B3LYP interaction energy (red).

The energy of the interaction between HCl and *trans*-bisammine-dichlorido platinum(II) has been calculated to be -5.2 kcal mol⁻¹. This interaction is more than 3 kcal mol⁻¹ more favorable than the interaction of the complex with the same molecule when Cl is pointing to platinum (Figure 6). Nevertheless, the dispersion correction has been found to be very similar for both interactions. The hydrogen bonded water complex was found to have a similar interaction energy and distribution between total binding and dispersion correction to that of HCl, however, slightly lower for both components. We have also optimized a water complex with the oxygen pointing to the metal centre, which had to be enforced by locking the Pt-O-H angles to 109°. As for the HCl complex the hydrogen bonded complex the bond energy is lower, however for water the interaction vanishes (+0.1 kcal/mol). However, again the dispersion interaction is close to that of the hydrogen bonded complex. Results from an Absolutely Localized Molecular Orbital Energy Decomposition Analysis (ALMO-EDA) are shown in figures 7 and 8. For the interaction of *trans*-bisammine-dichlorido platinum(II) complex with different hydrogen bond donors we find that despite the total interaction energy being close to identical for all donors, the components of the interactions are different (Figure 7). In the HF complex the charge transfer term is -4.66 kcal mol⁻¹, which changes to -7.66 and -9.14 kcal mol⁻¹ in the HCl and HBr complexes, respectively. Simultaneously the frozen density interaction, the interaction between the two fragments before polarization and charge transfer, increases in the series HF<HCl<HBr, leading to a very similar total interaction. When we compare the components with those of normal hydrogen bonds, where the acceptor is water, the picture is very different (Figure 8). The interaction energy decreases in the series HF>HCl>HBr, while the charge transfer component in the ALMO-EDA is close to constant. The main difference is instead in the frozen density interaction and the polarization interaction, both favoring the H₂O-HF complex.

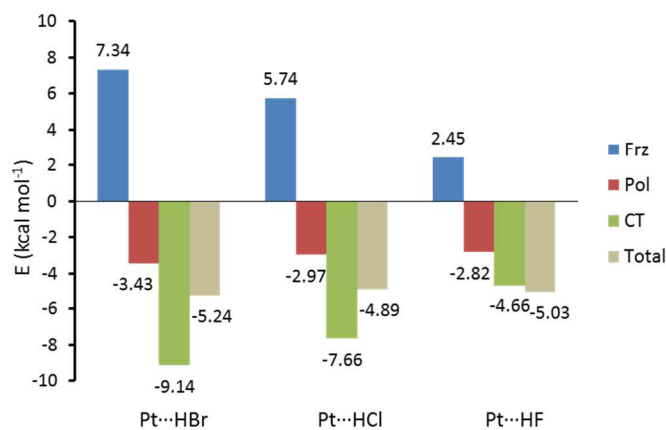


Figure 7. ALMO-EDA results for the interaction of *trans*-bisammine-dichlorido platinum(II) complex with different hydrogen bond donors: frozen density interaction (Frz, blue), polarization interaction (Pol, red), Charge transfer term (CT, green) and total interaction energy (Total, brown).

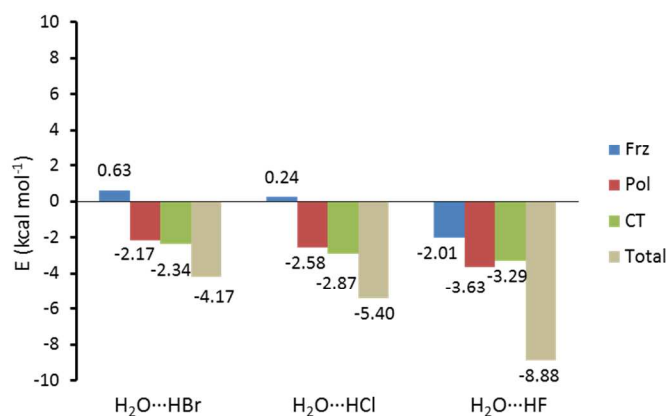


Figure 8. ALMO-EDA results for the interaction of water with different hydrogen bond donors: frozen density interaction (Frz, blue), polarization interaction (Pol, red), Charge transfer term (CT, green) and total interaction energy (Total, brown).

Finally we compared the shift of the H-X stretching frequency for HF, HCl and HBr after interacting with *trans*-bisammine-dichlorido platinum(II) and with water. An interaction with significant charge transfer should give a large red shift due to weakening of the σ -bond from donation of electrons into the σ^* -orbital. Electric fields are also known to give significant shifts,¹⁸ while dispersion interactions only have minor impact on the vibrational frequency.¹⁹ We calculated the shifts of the H-X vibrational frequencies and found these to be quite substantial and larger for complexes with higher charge transfer contributions. Again the trend differs substantially from the water H-X complexes.

Table 2. H-X stretching frequency for different hydrogen bond donors taking part in a non-classical H-bond with *trans*-bisammine-dichlorido platinum(II) complex as H-bond acceptor (second column) or in a normal H-bond with water as H-bond acceptor (third column).

HX	H-X vibrational	H-X vibrational
----	-----------------	-----------------

	frequency shift (cm ⁻¹) Pt-HX	frequency shift (cm ⁻¹) H ₂ O-HX
HF	-253 (-6.1%)	-281 (-6.7%)
HCl	-370 (-12.5%)	-226 (-7.6%)
HBr	-332 (-12.7%)	-140 (-5.4%)

Conclusions

We have presented a series of analyses of hydrogen bonds to platinum(II) centres. They all point towards charge transfer being the driver for the interaction.

1. Strong correlation between the dz^2 orbital and the total interaction energy indicates that charge transfer from this orbital to the anti-bonding orbital of the hydrogen bond donor is important. The extent of the interaction can hence be predicted from the energy of the dz^2 orbital.

2. The directionality of the interaction of the Pt-HCl bond is quite strong. If only dispersion was responsible for the favourable interaction one would expect the opposite directionality, Pt-ClH, since this would have a favourable electrostatic interaction.

3. Poor correlation between the D3 dispersion correction and the interaction energy indicates that dispersion is a consequence of the close contact, however, not the driving force. The interaction energy of an unknown complex cannot be predicted from the extent of the dispersion interaction.

4. ALMO-EDA analysis shows that charge transfer is a major interaction between metals and hydrogen bond donors. As expected for an interaction dominated by charge transfer the total interaction does not decrease when changing the hydrogen bond donor from the polar HF to HCl and HBr. For typical hydrogen bonds between hydrogen halides and water the interaction energy decreases significantly in as the polarity of the HX molecule decreases, likely due to the large electrostatic component of the interactions.

5. The vibrational energy shifts of the H-X fragments indicate large charge transfer. The water-HX interactions also show significant shift, however, this is likely to be largely due to the electric field of water. If dispersion was the only favorable interaction one would not expect the large shift as observed here.

All these point show that the interaction between platinum(II) and hydrogen bond donors is driven by charge transfer, and that the extent of the interaction can be predicted from the amount of charge transfer. Dispersion is important but it is merely a consequence of the close contact, which is crucial for understanding of how to manipulate these interactions. Prior theoretical studies on *trans*-[PtCl₂(NH₃)(N-glycine)]•H₂O indicated that charge transfer was important in the hydrogen bonding.^{14,15} However, while electronic density decomposition schemes can give insight in different interactions they do not necessarily help with the understanding of which of the interactions that can be manipulated in order to change the interaction.

Notes and references

^a Division of Theoretical Chemistry & Biology School of Biotechnology, Royal Institute of Technology, S-10691, Stockholm (Sweden)

† DFT calculations were carried out with Jaguar 7.6 program package,²⁰ using B3LYP²¹ and M06²² exchange-correlation functionals and LACV3P**++ basis set.²³ All the geometries were optimized at the level of theory for which the interaction is reported. To avoid mixing with other intermolecular interactions the geometries were optimized in Cs symmetry with the X-Pt-H and the Pt-H-Y angles fixed at 90 and 180 degrees, respectively (X anionic ligand on platinum, Y halogen on hydrogen bond donor). D3 dispersion corrections for B3LYP were calculated using the DFT-D3 software.²⁴ NBO analysis has been

performed in order to analyze partial charges.²⁵ All the reported values are corrected for basis set superposition error.²⁶ A modified version of Q-Chem 3.1 were used for the ALMO-EDA²⁷ calculations with the M06 functional and the Stuttgart-Bonn pseudopotential and basis set augmented with two f-functions on Pt, and the 6-311++G(3df,2pd) on all main group atoms.

Electronic Supplementary Information (ESI) available: [geometries of all the platinum complexes]. See DOI: 10.1039/c000000x/

- 1 A. Kloke, F. von Stetten, R. Zengerle and S. Kerzenmacher, *Adv. Mater.*, 2011, **23**, 4976.
- 2 R. R. Adzic, J. Zhang, K. Sasaki, M. B. Vukmirovic, M. Shao, J. X. Wang, A. U. Nilekar, M. Mavrikakis, J. A. Valerio and F. Uribe, *Top Catal*, 2007, **46**, 249.
- 3 Y. Shao-Horn, W. C. Sheng, S. Chen, P. J. Ferreira, E. F. Holby and D. Morgan, *Top Catal*, 2007, **46**, 285.
- 4 K. Yasuda, A. Taniguchi, T. Akita, T. Ioroi, and Z. Siroma, *Phys. Chem. Chem. Phys.*, 2006, **8**, 746.
- 5 E. Antolini, *J Solid State Electrochem*, 2011, **15**, 455.
- 6 T. Steiner, *Angew. Chem. Int. Ed.*, 2002, **41**, 48.
- 7 L. Brammer, *Dalton Trans.*, 2003, 3145.
- 8 L. R. Falvello, *Angew. Chem. Int. Ed*, 2010, **49**, 10045.
- 9 E. Arunan, G. R. Desiraju, R. G. Klein, J. Sadlej, S. Scheiner, I. Alkorta, D. C. Clary, R. H. Crabtree, J. J. Dannenberg, P. Hobza, H. G. Kjaergaard, A. C. Legon, B. Mennucci and D. J. Nesbitt, *Pure Appl. Chem.*, 2011, **83**, 1619.
- 10 L. Brammer, J. M. Charnock, P. L. Goggin, R. J. Goodfellow, A. G. Orpen and T. F. J. Koetzle, *Chem. Soc. Dalton Trans.*, 1991, 1789.
- 11 H. Ogasawara, B. Brena, D. Nordlund, M. Nyberg, A. Palmenschikov, L. G. M. Pettersson, and A. Nilsson, *Phys. Rev. Lett.*, 2002, **89**, 276102.
- 12 P. Vidossich, M. A. Ortuño, G. Ujaque, and A. Lledós, *ChemPhysChem*, 2011, **12**, 1666.
- 13 S. Rizzato, J. Bergès, S. A. Mason, A. Albinati, and J. Kozelka, *Angew. Chem. Int. Ed.*, 2010, **49**, 7440.
- 14 G. Zhang, X. Li, Y. Li and D. Chen, *Mol. Phys.*, 2013, **111**, 3276.
- 15 J. Berges, I. Fourné, J. Pilme and J. Kozelka, *Inorg. Chem.*, 2013, **52**, 1217.
- 16 M. Baya, U. Belío and A. Martin, *Inorg. Chem.*, 2014, **53**, 189.
- 17 O. A. Filiopov, N. V. Belkova, L. M. Epstein, A. Lledós and E. S. Shubina, *ChemPhysChem*, 2012, **13**, 2677.
- 18 K. Hermansson, *J. Chem. Phys.*, 1993, **99**, 861.
- 19 D. T. Anderson, S. Davies and D. J. Nesbitt, *J. Chem. Phys.*, 1997, **107**, 1115.
- 20 Jaguar, version 7.6, Schrödinger, LLC, New York, NY, 2009; www.schrodinger.com.
- 21 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098; J. P. Perdew, Eds: P. Ziesche, H. Eschrig, Akademie Verlag: Berlin, 1991, 11-20; J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B*, 1992, **46**, 6671.
- 22 Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.* 2008, **120**, 215.
- 23 The LACV3P basis set is a triple-zeta contraction of the LACVP basis set developed and tested at Schrödinger, Inc.
- 24 S. Grimme, S. Ehrlich and L. J. Goerigk, *Comput. Chem.*, 2011, **32**, 1456.
- 25 E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales and F. Weinhold, NBO 5.0; Theoretical Chemistry Institute: University of Wisconsin, Madison, WI, 2001.
- 26 S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553.
- 27 R. Z. Khaliullin, E. A. Cobar, R. C. Lochan, A. T. Bell and M. Head-Gordon, *J. Phys. Chem. A*, 2007, **111**, 8753.