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Comment on “Assessment of new DFT methods for predicting vibrational spectra and structure of cisplatin: Which density functional should we choose for studying platinum(II) complexes?” [Spectrochim. Acta A125 (2014) 431–439]



As researchers in the field of Pt(II) and Pd(II) compounds as potential anticancer agents, we were surprised by the recent paper by Malik and Michalska (hereafter MM) on the application of DFT methods to cisplatin <http://dx.doi.org/10.1016/j.saa.2014.01.107>. All of the work described in MM is based on the isolated molecule approximation, *i.e.* cisplatin is treated as a gas phase molecule. There is an immediate contradiction here, in that all of the experimental data used (including that generated by MM) refers to the solid state. In fact, isolated molecule calculations should not be expected to accurately represent systems where there are significant intermolecular interactions present, as in cisplatin where the N–H...Cl hydrogen bonding is responsible for the ordering along the *c*-axis and within the *ab* plane [1]. Further, isolated molecule calculations do not allow for the possibility of polymorphism and we note that cisplatin exists as two polymorphs, α and β . Polymorphism is of vital concern to the pharmaceutical industry and to ignore its existence is a disservice to the field.

In contrast, density functional theory with periodic boundary conditions (periodic-DFT) treats the entire unit cell, thus it explicitly includes the intermolecular interactions. This is shown by the excellent agreement between the observed and calculated geometries we obtain [2,3]. Moreover, although it may be true that periodic-DFT methods are not straightforwardly applied to very large systems, they can already handle up to a few hundred atoms already (*e.g.* the low temperature phase of C₆₀ that contains 240 atoms in the primitive cell [2]), so this is a limitation that will continue to recede as computing power increases.

Studies by simultaneous Raman and inelastic neutron scattering (INS) techniques allow the observation of all the low energy

vibrational modes of these complexes, including the ones of most interest, those involving the metal centre [3]. INS has a further advantage in that it is straightforward to generate a calculated spectrum from only the vibrational transition energies and the atomic displacements, the more complicated (and less reliable) calculation of infrared and Raman intensities is avoided. Thus the combination of INS spectroscopy with periodic-DFT calculations provides a much more stringent test of a calculation than consideration of transition energies alone. It should be highlighted that these type of experiments have been performed and published for cisplatin [3], as well as periodic-DFT calculations for solid cisplatin, transplatin and carboplatin [4].

In conclusion, the peer-revision essential to all submitted manuscripts should be an accurate and thorough process.

References

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