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First principles predictions of van der Waals bonded inorganic crystal structures: Test case, $HgCl_2$

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Abstract

We study the crystals structure and stability of four possible polymorphs of $HgCl_2$ using first principles density functional theory. Mercury (II) halides are a unique class of materials which, depending on the halide species, form in a wide range of crystal structures, ranging from densely packed solids to layered materials and molecular solids. Predicting the groundstate structure of any member of this group from first principles, therefore, requires a general purpose functional that treats van der Waals bonding and covalent/ionic bonding adequately. Here, we demonstrate that the non-local van der Waals density functional paired with the C09 exchange functional meets this bar for $HgCl_2$. In particular, this functional is able to predict the correct groundstate among the structures tested as well as having extremely good agreement with the experimentally known crystal structure. These results highlight the maturity of this functional and open the door to using this method for truly first principles crystal structure predictions.

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Keywords: vdW-DF; crystal structure prediction; van der Waals; London dispersion; density functional theory

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1. Introduction

The need for low cost, efficient, robust, and in some cases lightweight, materials for modern devices, such as photovoltaics (PVs), sensors, batteries and solid state lighting has driven the research into molecular crystals (MCs). These materials have a wide range of physical, chemical and electrical properties, such as being electrically

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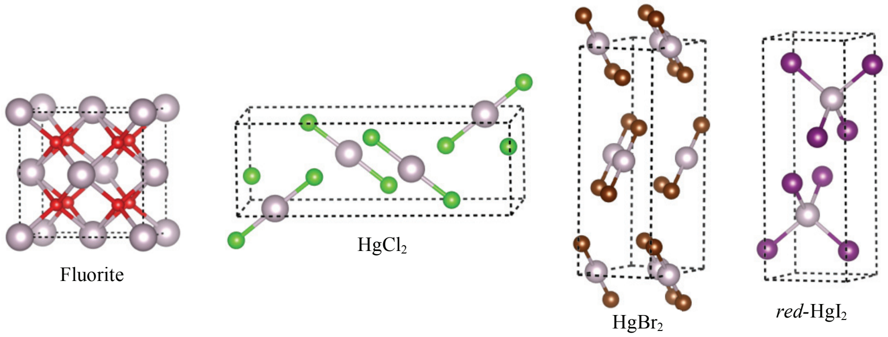
conducting, semiconducting, insulating, ferroelectric, magnetic and optically active, which are strongly linked to their crystal structures [1-5]. In addition, organic MCs have building blocks, comprised mainly of elements such as C, N, O and H, which make them suitable for lightweight applications. Furthermore, the solution based, low temperature and reproducible synthesis of MCs make them ideal candidates for fulfilling many of the demands of our energy needs. In a nutshell, MCs are highly tunable, cheap, easily processed, flexible and light. However, real world applications still call for materials with significant improvements in efficiency and thermal stability.


Fluorite

$HgCl_2$

$HgBr_2$

red-HgI_2

Figure 1 Crystal structure types studied for the $HgCl_2$ periodic solid. The Hg atom is in grey in each case.

Given the enormous variability in possible crystal polymorphs and the small differences of their corresponding cohesive energies to the groundstate structure, the computational discovery of molecular crystals is a daunting but vital task. A striking example of the effect of polymorphism can be found in the antiretroviral drug, Ritonavir. Shortly after it was introduced to market, it had to be recalled due to the unfortunate precipitation of a competing, insoluble, polymorph; which rendered the drug ineffective [6]. Such dramatic changes demonstrate the need to understand not only the properties of the crystal form that one intends to use, but to know how environmental conditions such as temperature, pressure and even synthesis conditions can affect the structure and what consequences this may have on function. From an energy relevant standpoint, the challenge is to understand the complex relationships between molecular identity, structure and electronic properties.

Central to this challenge is the reality that our grasp of the London dispersion interactions, or van der Waals (vdW) forces, that control intermolecular π-π stacking interactions, is still quite rudimentary. In particular, the computational demands of highly, accurate quantum chemical (QC) calculations and the poor description of dispersion interactions within standard density functional theory (DFT) have severely limited our use of theory/computation in addressing this issue. Motivated by this deficiency, the past decade has seen enormous progress in the way vdW interactions are treated within DFT. New techniques run the gamut from post-processing, empirical corrections to the development of new, self-consistent, correlation functionals; with varying computational demands, accuracies and transferability [7-20]. Irrespective of the method, however, it is clear that the inclusion of vdW interactions is paramount to our ability to properly simulate the structure of MCs and hence they are fundamental to predicting the function of these materials [11, 21-24]. These breakthroughs are now mature enough that it is possible to use theory to explore crystal packing and stacking interactions within MCs thereby moving us into a new era of computational materials research.

Here, we employed a state-of-the-art vdW-DF (DFT) method [7, 25] to explore the crystal structure energy landscape of a test case: $HgCl_2$. Mercury dihalides are known to crystalize in a variety of structures [26, 27] (see Figure 1): which span the group of densely packed solids (i.e. the fluorite structure of HgF_2) to layered materials (*red*-HgI_2) and molecular crystals ($HgCl_2$ and $HgBr_2$). The preference for one structure over another is a result of a subtle balance between ionic bonding (giving rise to strong internal permanent dipoles) and dispersion interactions (particularly for the larger halide species). The $HgCl_2$ molecular crystal structure is particularly interesting as it lies along the boundary in the mercury dihalide series between the ionic fluoride case and the cases where significant dispersion interactions engender sparsely packed molecular crystal structures. As such, this system poses a challenge not only for dispersion bound complexes, but for densely packed solids and thus provides a unique testing ground for any general purpose functional for materials modeling.

Using the vdW-DF non-local correlation functional paired with the C09x exchange functional [14], we demonstrate that this method is indeed capable of modeling the subtle differences between the aforementioned crystal structures. In particular, we find that traditional methods that do not include dispersion interactions find the incorrect crystal structure, and that dispersion interactions are necessary for predicting the correct groundstate as well as for more accurate predictions of lattice parameters; both defining features that determine many crystal structure electronic properties.

Ultimately, these results demonstrate the importance of accurately modeling dispersion interactions in order to understand the correlations between differing crystal packing, which may include in other cases π-π stacking and hydrogen bonding interactions and electronic structure. They provide a stepping-stone to developing a theoretical understanding of the principles through which the macroscopic phenomena related to the generation of excitons and polarons, electronic transport and charge carrier separation can be tuned in molecular crystals for use in opto-electronic and ferroelectric applications. Simultaneously, these results illustrate that the vdW-DF framework is indeed a streamlined and accurate approach for examining the physical properties of molecular crystals, polymers and perhaps weakly bound biologically relevant complexes in a manner now more fully developed for traditional inorganic materials.

Methods

All DFT calculations were performed using the van der Waals density non-local correlation functional with the C09 exchange functional (vdW-DF-C09) and ultrasoft pseudopotentials as implemented in the Quantum Espresso simulation package [28]. All calculations employed a 140 Ry planewave cutoff and 1×1×1 and 8×8×8 k-point meshes for the isolated $HgCl_2$ molecule/dimer and the periodic solids, respectively. We explored four crystal structure types: fluorite, $HgCl_2$, $HgBr_2$ and *red*-HgI_2. The forces on the atoms were relaxed until they were less than 5 meV/Å and all lattice constants were optimized. The effects of dispersion interactions were analyzed through comparisons with the generalized gradient approximation of Perdew-Burke-Erzenhoff (GGA-PBE) exchange-correlation functional, which does not account for dispersion interactions. It should be noted, that although the vdW-DF class of functionals were designed to treat dispersion interactions within DFT, recent studies of condensed matter systems (e.g. $PbTiO_3$) indicate that the functional is indeed a general purpose functional [20]; capable of modeling systems with ionic/covalent bonds and non-bonding interactions on the same footing. Condensation energies $E_{condens.}$ were computed relative to the isolated monomer structure as follows:

$$E_{condens.} = E_{mol} - \frac{1}{n} E_{solid} \; [1]$$

where E_{mol} and E_{solid} are the total energies of the isolated $HgCl_2$ molecule and solid, respectively. n is the number of $HgCl_2$ formula units in the solid.

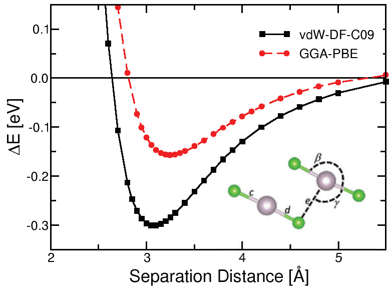


Figure 2 (Color online) Interaction energy as a function of Hg-Hg separation distance for the $HgCl_2$ dimer as computed with GGA-PBE (red circles, dashed line) and vdW-DF (black squares, solid line). Inset: Structural parameters for dimer geometry.

Results and Discussion

To calibrate our first principles calculations we first compare the geometry and interaction energies with highly accurate QC calculations. Table 1 lists the structural parameters and dimer interaction energies for the $HgCl_2$ dimer as determined using second-order Möller Plesset theory (MP2) [29, 30] and from DFT using both vdW-DF-C09 and GGA-PBE. Here, we see that both exchange-correlation functionals do an excellent job in reproducing the MP2 geometries. This is largely because the dimer configurations are strongly defined by the interactions of the internal permanent dipoles which result in a shifted parallel configuration (see inset of Figure 2). Figure 2 shows the $(HgCl_2)_2$ interaction energy as a function of separation distance *e* obtained using GGA-PBE and vdW-DF-C09. Interestingly, we find that the GGA-PBE dimer interaction energy is half of the vdW-DF-C09 calculations. MP2 simulations give a value of -0.24 eV at the optimized separation, suggesting that the vdW-DF-C09 results may be more in line with the true value. The large underestimation of the GGA-PBE calculations is once again indicative of the poor description of dispersion interactions inherent in these semi-local exchange-correlation functionals. Nevertheless, these results signal that vdW-DF-C09 may indeed be a suitable starting point for exploring the relative stability and structure of bulk $HgCl_2$.

Table 1 Geometrical parameters *c*, *d*, *e*, *β* and *γ* (defined in inset of Figure 2) and dimer interaction energies ΔE for the $HgCl_2$ dimer obtained with MP2 [29, 30], vdW-DF-C09 and PBE.

Method	***c* [Å]**	***d* [Å]**	***e* [Å]**	***β* [°]**	***γ* [°]**	**Δ*E* [eV]**
MP2	2.229	2.251	3.166	176.9	96.9	-0.24
vdW-DF-C09	2.256	2.285	3.074	175.3	98.1	-0.30
GGA- PBE	2.270	2.295	3.242	175.8	98.9	-0.15

Table 2 lists optimized structural parameters for the 4 different crystal structure types studied for the $HgCl_2$ solid obtained using vdW-DF-C09 and GGA-PBE. First, we see that for the experimentally determined $HgCl_2$ groundstate structure [27, 31], vdW-DF-C09 gives lattice parameters that are in excellent agreement with experiment (<2.6%). GGA-PBE, however, consistently overestimates the lattice parameter; by almost 10% along the *b*-axis direction. A comparison of the lattice parameters of other crystal structure types again shows that GGA-PBE results predict lattice parameters that can be as much as 16% and 50% larger than the vdW-DF-C09 predictions for $HgBr_2$ and HgI_2, respectively. For HgF_2, however, we find that the GGA-PBE and vdW-DF-C09 calculations give lattice parameters that are in reasonable agreement of each other (~2%). Once more, this is indicative of the excellent behaviour of both functionals in predicting the properties of densely packed solids. Nevertheless, the severe overestimation of lattice constants is typical of GGA-PBE for describing dispersion bound complexes, such as layered graphite, and is often accompanied by significant underbinding [32].

Table 2 Lattice parameters (*a*, *b* and *c*) and space group symmetries for the crystal structure types studied for the $HgCl_2$ solid. Experimental lattice parameters for the *Pnma* phase were taken from [31].

Crystal Structure	**Space Group**	**Method**	***a* [Å]**	***b* [Å]**	***c* [Å]**
Fluorite	$Fm\bar{3}m$	GGA-PBE	6.679		
		vdW-DF-C09	6.534		
$HgCl_2$	*Pnma*	GGA-PBE	13.373	6.578	4.514
		vdW-DF-C09	12.458	5.873	4.220
		Expt.	12.776(4)	5.986(3)	4.333(2)
$HgBr_2$	$Cmc2_1$	GGA-PBE	5.029	6.735	12.723
		vdW-DF-C09	4.320	6.527	11.337
red-HgI_2	$P4_2/nmc$	GGA-PBE	4.134		11.965
		vdW-DF-C09	4.392		7.925

Figure 3 depicts the condensation energies for the four crystal structure types. Similar, to the dimer, we note a large difference in condensation energies between the GGA-PBE and vdW-DF-C09 calculations. As expected, the inclusion of dispersion interactions significantly enhances the condensation energies for the sparsely packed structures. Surprisingly, we also find that dispersion interactions stabilize the densely packed fluorite structure. Furthermore, we find that GGA-PBE calculations incorrectly predict the $HgBr_2$ $Cmc2_1$ structure to be the groundstate by 29 meV/formula unit (f.u.) over the $HgCl_2$ *Pnma* structure. This is corrected with vdW-DF-C09,

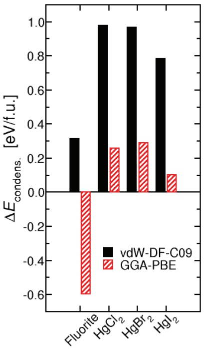


Figure 3 Condensation energies for the 4 crystal structure types studied. Black solid and red hashed bars are for vdW-DF-C09 and GGA-PBE calculations, respectively.

which predicts the $HgCl_2$ *Pnma* structure to be the most stable structure (by 12 meV/f.u. over the $HgBr_2$ structure). The failure of GGA-PBE to predict the correct groundstate can be understood on the basis of the differences between the two crystal structures and the inadequate treatment of dispersion interactions at the GGA-PBE level. In the $HgBr_2$ structure type, unlike the $HgCl_2$ form, the molecular units are aligned such that the Hg-Cl bonds are parallel and shifted to ensure that opposing dipoles interact with each other. Thus, in the absence of dispersion interactions one might expect that this structure would be favoured over one in which the molecules are arranged perpendicularly to each other, as in $HgCl_2$. The closeness in energy of the $HgBr_2$ $Cmc2_1$ and $HgCl_2$ *Pnma* crystal types suggests that one should expect to find the $HgBr_2$ structure in the phase diagram of $HgCl_2$. However, although $HgBr_2$ $Cmc2_1$ has not been observed mercury dichloride, it resembles other polymorphs that are known to exist at moderate pressures; i.e. the $P2_1/m$ (Phase IV) and $R\overline{3}$m (Phase II) phases [27].

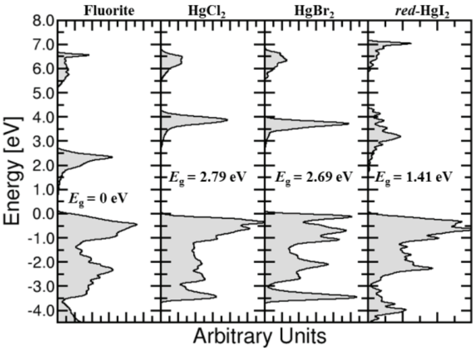


Figure 4 Density of states for the 4 crystal structure types studied for the $HgCl_2$ system. Electronic band gaps E_g are denoted in the plots.

Finally we examine the electronic structure of these materials. Figure 4 shows the density of states (DOS) for the four crystal structures obtained using the vdW-DF-C09 functional. Here, we observe significant differences in the electronic band gaps E_g of the four different crystal structure types. Most notably, the densely packed fluorite structure has a negligible band gap while the layered structure (*red*-HgI_2) is semi-conducting with a band gap of 1.41 eV, and finally the molecular crystals ($HgCl_2$ and $HgBr_2$) have very similar (<2.5 eV) band gaps. These results further highlight the importance of correct crystal structure predictions as it is clear that in this case, stabilization of any of the covalently bonded solids could signify a dramatic reduction in the predicted band gap.

Conclusions

In summary, we have employed the vdW-DF non-local correlation functional with the C09 exchange functional, to explore the structure and stability of possible polymorphs of the $HgCl_2$ crystal. Our results demonstrate that the inclusion of dispersion interactions is not only necessary in order to use density functional theory to predict the correct groundstate structure of sparsely packed materials, but that they have significant effects on predicted condensation energies. These affect both whether a crystal would form and at what temperatures it would vaporize/melt. Furthermore, we show that the traditional GGA-PBE functional fails to predict the correct groundstate and, for van der Waals bonded axes, it overestimates lattice parameters. Of equal importance is the link between crystal structure and electronic structure. Here, we observe a range of band gaps (from metallic to 2.79 eV) that arise in the four different crystal structures studied. Naturally, here the correct prediction of crystal structure would have dramatic consequences when attempting to predict functionality of these materials. In essence, these results highlight the need for a method that can accurately predict crystal structure and stability (even in sparsely packed solids) and demonstrate that vdW-DF-C09 is a general purpose method. As such, this work provides a necessary benchmark for true crystal structure predictions in a wide range of materials.

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References

[1] F. Garnier, A. Yassar, R. Hajlaoui, G. Horowitz, F. Deloffre, B. Servet, S. Ries, P. Alnot, Molecular engineering of organic semiconductors: design of self-assembly properties in conjugated thiophene oligomers, J. am. Chem. Soc., 115 (1993) 8716-8721.
[2] B. Servet, G. Horowitz, S. Ries, O. Lagorsse, P. Alnot, A. Yassar, F. Deloffre, P. Srivastava, R. Hajlaoui, Polymorphism and Charge Transport in Vacuum-Evaporated Sexithiophene Films, Chem. Mater., 6 (1994) 1809-1815.
[3] D.J. Gundlach, Y.Y. Lin, T.N. Jackson, S.F. Nelson, D.G. Schlom, Pentacene organic thin-film transistors-molecular ordering and mobility, IEEE Electron Device Lett., 18 (1997) 87.
[4] R. Hajlaoui, D. Fichou, G. Horowitz, B. Nessakh, M. Constant, F. Garnier, Organic transistors using α-octithiophene and α, ω-dihexyl-α-octithiophene: Influence of oligomer length versus molecular ordering on mobility, Adv. Mater., 9 (1997) 557.
[5] H. Sirringhaus, P.J. Brown, R.H. Friend, M.M. Nielsen, K. Bechgaard, B.M.W. Langeveld-Voss, A.J.H. Spiering, R.A.J. Janssen, E.W. Meijer, P. Herwig, D.M. de Leeuw, Two-dimensional charge transport in self-organized, high-mobility conjugated polymers, Nature, 401 (1999) 685.
[6] J. Bauer, S. Spanton, R. Henry, J. Quick, W. Dziki, W. Porter, J. Morris, Ritonavir: An Extraordinary Example of Conformational Polymorphism, Pharm. Res., 18 (2001) 859.
[7] M. Dion, H. Rydberg, E. Schröder, D.C. Langreth, B.I. Lundqvist, van der Waals Density Functional for General Geometries, Phys. Rev. Lett., 92 (2004) 246401.
[8] S. Grimme, Accurate description of van der Waals complexes by density functional theory including empirical corrections, J. Comput. Chem., 25 (2004) 1463.
[9] S. Grimme, J. Antony, T. Schwabe, C. Muck-Lichtenfeld, Density functional theory with dispersion corrections for supramolecular structures, aggregates, and complexes of (bio)organic molecules, Org. Biomol. Chem., 5 (2007) 741.
[10] O.A. Vydrov, Q. Wu, T. Van Voorhis, Self-consistent implementation of a nonlocal van der Waals density functional with a Gaussian basis set, J. Chem. Phys., 129 (2008) 8.
[11] E.R. Johnson, I.D. Mackie, G.A. DiLabio, Dispersion interactions in density-functional theory, Journal of Physical Organic Chemistry, 22 (2009) 1127-1135.
[12] A. Tkatchenko, M. Scheffler, Accurate Molecular Van Der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data, Phys. Rev. Lett., 102 (2009) 073005.
[13] O.A. Vydrov, T. Van Voorhis, Nonlocal van der Waals Density Functional Made Simple, Phys. Rev. Lett., 103 (2009) 063004.
[14] V.R. Cooper, Van der Waals density functional: An appropriate exchange functional, Phys. Rev. B., 81 (2010) 161104(R).
[15] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, Journal of Chemical Physics, 132 (2010).
[16] J. Klimeš, D.R. Bowler, A. Michaelides, Chemical accuracy for the van der Waals density functional, J. Phys.: Condens. Matter, 22 (2010) 022201.
[17] O.A. Vydrov, T. Van Voorhis, Implementation and assessment of a simple nonlocal van der Waals density functional, J. Chem. Phys., 132 (2010) 164113.
[18] A. Tkatchenko, D. Alfe, K.S. Kim, First-Principles Modeling of Non-Covalent Interactions in Supramolecular Systems: The Role of Many-Body Effects, Journal of Chemical Theory and Computation, 8 (2012) 4317-4322.
[19] K. Berland, P. Hyldgaard, Exchange functional that tests the robustness of the plasmon description of the van der Waals density functional, Phys. Rev. B, 89 (2014) 035412.
[20] K. Berland, C.A. Arter, V.R. Cooper, K. Lee, B.I. Lundqvist, E. Schroder, T. Thonhauser, P. Hyldgaard, van der Waals density functionals built upon the electron-gas tradition: Facing the challenge of competing interactions, J. Chem. Phys., 140 (2014) 18A539.
[21] D.C. Langreth, B.I. Lundqvist, S.D. Chakarova-Kack, V.R. Cooper, M. Dion, P. Hyldgaard, A. Kelkkanen, J. Kleis, L.Z. Kong, S. Li, P.G. Moses, E. Murray, A. Puzder, H. Rydberg, E. Schroder, T. Thonhauser, A density functional for sparse matter, J. Phys.: Condens. Matter, 21 (2009) 15.
[22] V.R. Cooper, L. Kong, D.C. Langreth, Computing dispersion interactions in density functional theory, Phys. Proc., 3 (2010) 1417-1417.
[23] J. Klimes, A. Michaelides, Perspective: Advances and challenges in treating van der Waals dispersion forces in density functional theory, The Journal of Chemical Physics, 137 (2012) 120901-120912.
[24] K. Berland, V.R. Cooper, K. Lee, E. Schröder, T. Thonhauser, P. Hyldgaard, B.I. Lundqvist, van der Waals forces in density functional theory: a review of the vdW-DF method, Rep. Prog. Phys., (in press) (2015).
[25] T. Thonhauser, V.R. Cooper, S. Li, A. Puzder, P. Hyldgaard, D.C. Langreth, Van der Waals density functional: Self-consistent potential and the nature of the van der Waals bond, Phys. Rev. B, 76 (2007) 125112-125112.
[26] M. Hargittai, Molecular structure of metal halides, Chem. Rev., 100 (2000) 2233.
[27] M. Hostettler, D. Schwarzenbach, Phase diagrams and structures of HgX_2 (X = I, Br, Cl, F), C. R. Chimie, 8 (2005) 147.
[28] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G.L. Chiarotti, M. Cococcioni, I. Dabo, A.D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C.S. andSandro Scandolo, G. Sclauzero, A.P. Seitsonen, A. Smogunov, P. Umari, R.M. Wentzcovitch, QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials, J. Phys.: Condens. Matter, 21 (2009) 395502.
[29] M. Kaupp, H.G. von Schnering, Dominance of linear 2-coordination in mercury chemistry: Quasirelativistic and nonrelativistic *ab Initio* pseudopotential study of $(HgX_2)_2$ (X = F, Cl, Br, I, H), Inorg. Chem., 33 (1994) 2555.
[30] K.J. Donald, M. Hargittai, R. Hoffmann, Group 12 dihalides: Structural predilections from gases to solids, Chem.-Eur. J., 15 (2009) 158.
[31] V. Subramanian, K. Seff, Mercuric chloride, a redetermination, Acta Crystallogr. B, 36 (1980) 2132.
[32] H. Rydberg, M. Dion, N. Jacobson, E. Schroder, P. Hyldgaard, S.I. Simak, D.C. Langreth, B.I. Lundqvist, Van der Waals density functional for layered structures, Phys. Rev. Lett., 91 (2003) 126402-126402.
[33] B.J. Aylett, in: J.C. Bailar, A.F. Trotman-Dickenson (Eds.) Comprehensive Inorganic Chemistry, Pergamon Press: Oxford, England, 1973.

[34] R.E. Taylor, S. Bai, C. Dybowski, A solid-state 199Hg NMR study of mercury halides, J. Mol. Struct., 987 (2011) 193.