



## Research paper

## The role of London dispersion interactions in strong and moderate intermolecular hydrogen bonds in the crystal and in the gas phase

Sergey A. Katsyuba<sup>a,\*</sup>, Mikhail V. Vener<sup>b</sup>, Elena E. Zvereva<sup>a,c</sup>, J. Gerit Brandenburg<sup>d,e,f</sup><sup>a</sup>A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, Arbuzov str. 8, 420088 Kazan, Russia<sup>b</sup>Department of Quantum Chemistry, Mendeleev University of Chemical Technology, Miusskaya Square 9, 125047 Moscow, Russia<sup>c</sup>Théorie-Modélisation-Simulation UMR CNRS UL 7565, Université de Lorraine, Boulevard des Aiguillettes 1, BP 70239 54506 Vandoeuvre-lès-Nancy, France<sup>d</sup>Department of Chemistry, University College London, 20 Gordon Street, WC1H 0AJ London, UK<sup>e</sup>London Centre for Nanotechnology, University College London, 17-19 Gordon Street, WC1H 0AJ London, UK<sup>f</sup>Thomas Young Centre, University College London, Gower Street, WC1E 6BT London, UK

## ARTICLE INFO

## Article history:

Received 9 January 2017

In final form 30 January 2017

Available online 1 February 2017

## ABSTRACT

Two variants of density functional theory computations have been applied to characterization of hydrogen bonds of the 1-(2-hydroxyethyl)-3-methylimidazolium acetate ([C<sub>2</sub>OHmim][OAc]), i.e. with and without inclusion of dispersion interactions. A comparison of the results demonstrates that London dispersion interactions have very little impact on the energetical, geometrical, infrared spectroscopic and electron density parameters of charge-assisted intermolecular hydrogen bonds functioning both in the crystal of the [C<sub>2</sub>OHmim][OAc] and in the isolated [C<sub>2</sub>OHmim]<sup>+</sup>[OAc]<sup>-</sup> ion pairs.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

The possible role of dispersion interactions and their contribution to noncovalently bound complexes [1–7], van-der-Waals crystals and molecular crystals with relatively weak hydrogen bonds (HBs) [8–11] has been widely discussed. In contrast, dispersion interactions in molecular crystals with strong and moderate intermolecular HBs have been considered in only a few cases [12–15]. Herein, the results of two variants of solid-state density functional theory (DFT) computations of the [C<sub>2</sub>OHmim][OAc] crystal (Fig. 1), i.e. with and without inclusion of dispersion interactions, were compared. Similar comparison was performed for DFT characterization of HBs in the isolated [C<sub>2</sub>OHmim][OAc] ion pairs (Fig. 2).

## 2. Methods used

## 2.1. Evaluation of the HB energies

According to our previous experience in studies of HBs formed by charged species [16,17], two different sets of the computed properties were used in the present study for evaluation of the HB energy/enthalpy: (i) the electron density features at the HB critical point [18,19] and (ii) the spectroscopic features of the stretch-

ing vibrations of XH group ( $\nu_{\text{XH}}$ ) involved into HB formation [20,21].

- (i) The energy of XH...A HB ( $E_{\text{HB}}$ ) can be estimated using the local electronic kinetic energy density,  $G_b$ , at the H...A bond critical point in electron density [19]:

$$E_{\text{HB}} [\text{kcal mol}^{-1}] = 269G_b [\text{atomic units}] \quad (1)$$

- (ii) Spectroscopic indicators of H-bond formation such as red shifts of  $\nu_{\text{XH}}$  vibrational frequencies and increases in infrared (IR) intensities [20,21] were used to evaluate the enthalpies ( $-\Delta H_{\text{HB}}$ ) of intermolecular HBs:

$$-\Delta H_{\text{HB}} [\text{kcal mol}^{-1}] = 0.29\Delta I^{1/2} [\text{kcal mol}^{-1}] \quad (2)$$

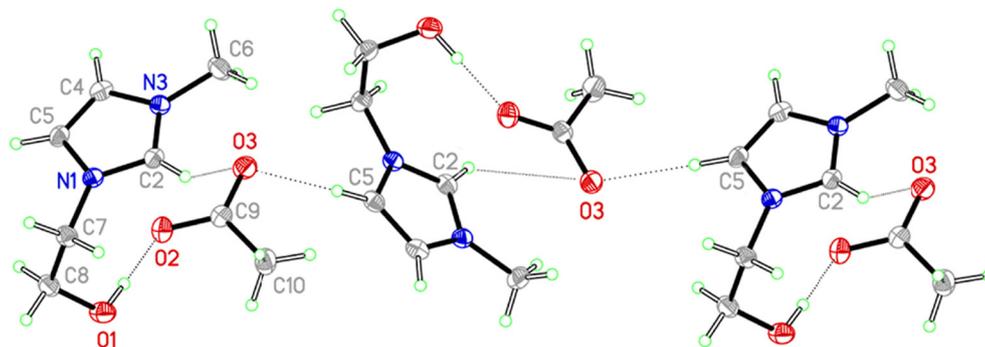
where  $\Delta I^{1/2} = I^{1/2} - I_0^{1/2}$ , and  $I$  is the IR intensity for the localized, uncoupled  $\nu_{\text{XH}}$  vibration of the X-H group participating in the H-bond compared to the non-interacting group ( $I_0$ ).

$$-\Delta H_{\text{HB}} [\text{kcal mol}^{-1}] = 0.33(\Delta\nu [\text{cm}^{-1}] - 40)^{1/2} \quad (3)$$

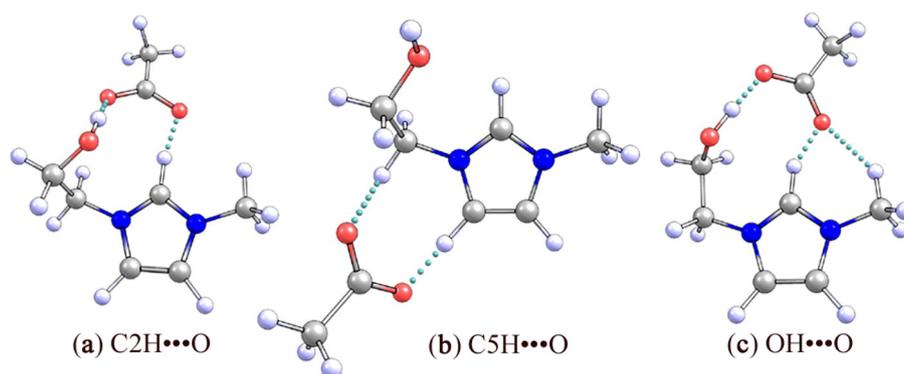
where  $\Delta\nu = \nu_{\text{XH}_{\text{free}}} - \nu_{\text{XH}_{\text{bonded}}}$  represents the red-shift value of the  $\nu_{\text{XH}}$  frequency caused by the formation of the HB with the XH group being the proton donor.

\* Corresponding author.

E-mail address: [skatsyuba@yahoo.com](mailto:skatsyuba@yahoo.com) (S.A. Katsyuba).



**Fig. 1.** ORTEP plot of the crystal structure of the 1-(2-hydroxyethyl)-3-methylimidazolium acetate ( $[\text{C}_2\text{OHmim}][\text{OAc}]$ ) showing the main interactions between adjacent molecules by dashed lines. Created on the basis of X-ray data [16].



**Fig. 2.** Examples of optimized structures of isolated ion pairs  $[\text{C}_2\text{OHmim}]^+ [\text{OAc}]^-$ . HBs are indicated with dashed lines.

## 2.2. London dispersion interactions

In non-covalently bound systems, the correct treatment of non-local London dispersion interactions is mandatory for accurate geometries and binding energies. These interactions are not included in any semi local density functional and require dispersion corrections, for reviews and overviews see Refs. [1,2,22–24]. We used the D3 London dispersion correction in the Becke-Johnson sampling scheme (indicated by “–D3” appended to the functional name) [3,4]. The accuracy of the scheme for noncovalently bound dimers, host-guest complexes, and van-der-Waals crystals is well documented [5–7]. DFT-D3 was recently benchmarked for interactions of various ions and found to provide results close to those of CCSD(T) benchmark quality [25].

## 2.3. DFT computations

The calculations of the isolated ion pairs were performed with the ORCA program of version 3.0 [26]. The equilibrium structures of the ion pairs were optimized with the B3LYP hybrid functional [27,28] and the standard 6-31G\*\* basis set. Obtained stationary points were characterized as minima by analysis of the Hessian matrices. The same combination of functional and basis set was employed for solid-state DFT computations conducted with the CRYSTAL suite of programs [29]. Further computational details can be found in Supplementary Material.

The following electron density features at the H...O intermolecular bond critical point were considered: (i) the values of the electron density  $\rho_b$ , (ii) its Laplacian  $\nabla^2\rho_b$ , and (iii) the kinetic energy density  $G_b$ . The  $G_b$  values computed from the theoretical periodic

electron density were used in the present study for evaluation of HB energy (Eq. (1)).

## 3. Results and discussion

HB-donor and HB-acceptor units in  $[\text{C}_2\text{OHmim}][\text{OAc}]$  are electrically charged, which results in strengthening of  $\text{XH}\cdots\text{A}$  intermolecular HBs. Owing to this phenomenon, called charge assistance [30–35] the energy of conventional  $\text{OH}\cdots[\text{OAc}]^-$  HBs and nonconventional  $\text{CH}\cdots[\text{OAc}]^-$  HBs in crystals of  $[\text{C}_2\text{OHmim}][\text{OAc}]$  amounts to ca. 10 and ca. 5 kcal mol<sup>−1</sup>, respectively [16]. In the gas phase the energy of the both types of charge-assisted HBs increases to ca. 11–13 kcal mol<sup>−1</sup> [16]. (For comparison: the energy of neutral nonconventional  $\text{CH}\cdots\text{O}$  HBs in the gas phase equals to ca. 2–4 kcal mol<sup>−1</sup> [36,37]). As indicated in the Introduction, little if anything is reported about the role of London dispersion forces in systems with HBs of similar strength. To quantify the contributions from dispersion interactions into the strength of the abovementioned charge-assisted HBs in the  $[\text{C}_2\text{OHmim}][\text{OAc}]$  crystal, we compared in Table 1 the geometrical, energetical, IR spectroscopic and electron density parameters of the strongest HBs computed with (B3LYP-D3/6-31G\*\*) and without inclusion of dispersion interactions (B3LYP/6-31G\*\*).

Data collected in Table 1 demonstrate that the introduction of London dispersive forces in the calculation leads to a moderate lengthening of the calculated C...O distances by ca. 0.01 Å and a concomitant almost negligible decrease of the electron density features at the HB critical point for the  $\text{CH}\cdots[\text{OAc}]^-$  HBs. Other computed structural, IR spectroscopic and electronic-topology characteristics of both conventional and nonconventional HBs do not significantly depend on the choice of the theoretical approxi-

**Table 1**  
The values of the X...O distances  $R(X...O)$  and angles  $\angle X-H...O$  of the X-H...O units, where X=O or C, in the  $[C_2OHmim][OAc]$  crystal from X-ray experiment and solid-state DFT computations (in parentheses). The electron density,  $\rho_b$ ; its Laplasian,  $\nabla^2\rho_b$ , the local electronic kinetic energy density,  $G_b$ , at the HB critical point; the HB energy,  $E_{HB}$ , and enthalpy,  $-\Delta H_{HB}$ ; frequencies,  $\nu$ , and intensities,  $I$ , of isotope-isolated XH stretching vibrations are given for each X-H...O unit.

	C2-H...O3 <sup>a</sup>	C5-H...O3 <sup>a</sup>	O1-H...O2 <sup>a</sup>
$R(X...O)$ , Å	3.245 (3.184, 3.194) <sup>b</sup>	3.104 (3.085, 3.096) <sup>b</sup>	2.651 (2.644, 2.641) <sup>b</sup>
$\angle X-H...O$ , deg	162 (164, 164) <sup>b</sup>	171 (172, 172) <sup>b</sup>	176 (174, 174) <sup>b</sup>
$\rho_b$ , a.u.	0.021, 0.020 <sup>b</sup>	0.026, 0.025 <sup>b</sup>	0.051, 0.052 <sup>b</sup>
$\nabla^2\rho_b$ , a.u.	0.051, 0.050 <sup>b</sup>	0.065, 0.063 <sup>b</sup>	0.140, 0.141 <sup>b</sup>
$G_b$ , a.u.	0.0150, 0.0135 <sup>b</sup>	0.0172, 0.0172 <sup>b</sup>	0.0379, 0.0375 <sup>b</sup>
$E_{HB}$ , kcal mol <sup>-1</sup>	4.0, 3.6 <sup>b</sup>	4.6, 4.6 <sup>b</sup>	10.2, 10.1 <sup>b</sup>
$\nu$ , cm <sup>-1</sup> ( $I$ , km mol <sup>-1</sup> ) for the crystal	3176 (544), 3166 (543) <sup>b</sup>	3183 (499), 3176 (498) <sup>b</sup>	3191 (1870), 3190 (1871) <sup>b</sup>
$\nu_0$ , cm <sup>-1</sup> ( $I_0$ , km mol <sup>-1</sup> ) for the isolated cation	3320 (47) 3321 (49) <sup>b</sup>	3303 (13), 3304 (13) <sup>b</sup>	3830 (74), 3833 (74) <sup>b</sup>
$-\Delta H_{HB}$ , kcal mol <sup>-1c</sup>	4.8, 4.7 <sup>b</sup>	5.4, 5.4 <sup>b</sup>	9.6, 9.6 <sup>b</sup>
$-\Delta H_{HB}$ , kcal mol <sup>-1d</sup>	3.4, 3.5 <sup>b</sup>	3.0, 3.1 <sup>b</sup>	8.1, 8.1 <sup>b</sup>

<sup>a</sup> The original numeration of atoms taken from Fig. 1.

<sup>b</sup> Values obtained with the use of B3LYP-D3/6-31G\*\* computations are given in *italics*.

<sup>c</sup> Evaluated using Eq. (2).

<sup>d</sup> Evaluated using Eq. (3).

**Table 2**  
The values of the X...O distances  $R(X...O)$  and angles  $\angle X-H...O$  of the X-H...O units, where X=O or C, in the  $[C_2OHmim][OAc]$  ion pairs (see Fig. 2). The electron density,  $\rho_b$ ; its Laplasian,  $\nabla^2\rho_b$ , the local electronic kinetic energy density,  $G_b$ , at the HB critical point; the HB energy,  $E_{HB}$ , and enthalpy,  $-\Delta H_{HB}$ ; frequencies,  $\nu$ , and intensities,  $I$ , of isotope-isolated XH stretching vibrations are given for each X-H...O unit.

	C2H...O(a) <sup>a</sup>	C5H...O(b) <sup>a</sup>	OH...O (c) <sup>a</sup>
$R(X...O)$ , Å	2.765, 2.756 <sup>b</sup>	2.803, 2.785 <sup>b</sup>	2.576, 2.570 <sup>b</sup>
$\angle X-H...O$ , deg	169.7, 169.6 <sup>b</sup>	176.4, 172.9 <sup>b</sup>	175.8, 175.1 <sup>b</sup>
$\rho_b$ , a.u.	0.057, 0.058 <sup>b</sup>	0.053, 0.055 <sup>b</sup>	0.065, 0.066 <sup>b</sup>
$\nabla^2\rho_b$ , a.u.	0.036, 0.037 <sup>b</sup>	0.034, 0.035 <sup>b</sup>	0.039, 0.037 <sup>b</sup>
$G_b$ , a.u.	0.040, 0.041 <sup>b</sup>	0.036, 0.038 <sup>b</sup>	0.047, 0.048 <sup>b</sup>
$E_{HB}$ , kcal mol <sup>-1</sup>	10.8, 11.0 <sup>b</sup>	9.8, 10.3 <sup>b</sup>	12.8, 13.0 <sup>b</sup>
$\nu$ , cm <sup>-1</sup> ( $I$ , km mol <sup>-1</sup> ) for the ion pair	2534 (1844) 2549 (1800) <sup>b</sup>	2527 (1863) 2508 (1662) <sup>b</sup>	2859 (1990) 2876 (1949) <sup>b</sup>
$\nu_0$ , cm <sup>-1</sup> ( $I_0$ , km mol <sup>-1</sup> ) for the isolated cation	3320 (47) 3321 (49) <sup>b</sup>	3303 (13) 3304 (13) <sup>b</sup>	3830 (74) 3833 (74) <sup>b</sup>
$-\Delta H_{HB}$ , kcal mol <sup>-1c</sup>	10.5 10.3 <sup>b</sup>	11.5 10.8 <sup>b</sup>	10.4 10.3 <sup>b</sup>
$-\Delta H_{HB}$ , kcal mol <sup>-1d</sup>	9.0 8.9 <sup>b</sup>	9.0 9.1 <sup>b</sup>	10.1 10.0 <sup>b</sup>

<sup>a</sup> The original numeration of atoms taken from the Fig. 1. Notation of ion pairs (in parentheses) corresponds to Fig. 2.

<sup>b</sup> Values obtained with the use of B3LYP-D3/6-31G\*\* computations are given in *italics*.

<sup>c</sup> Evaluated using Eq. (2).

<sup>d</sup> Evaluated using Eq. (3).

mation. Thus, the impact of dispersion forces on H-bonding in crystalline  $[C_2OHmim][OAc]$  is moderate.

The situation is similar for the gas phase ion pairs, see Table 2, where the introduction of London dispersive forces in the calculation leads to a moderate shortening of the C...O distances by ca. 0.01–0.02 Å for the CH...[OAc]<sup>-</sup> HBs and the O...O distances by ca. 0.01 Å for the OH...[OAc]<sup>-</sup> HBs. These changes result in a minor variation of electron density topological parameters,  $\rho_b$  and  $\nabla^2\rho_b$ , of the IR intensities of the  $\nu_{XH}$  bands and their vibrational frequencies. Consequently, estimates of the H-bonding strength, obtained with the use of the IR spectroscopic markers and Eqs. (2) and (3), as well as corresponding values obtained from Eq. (1), are close to each other and remain practically the same irrespective of the use of D3 correction or the neglect of dispersive forces in the computations.

Obtained results are in general agreement with the available literature data. The dispersion correction has a little influence on the atom–atom radial distribution functions and the infrared spectra of liquid water [38]. On the other hand, the dispersion interaction is

found to significantly affect some properties such as the density and the heat of vaporization [38]. According to [39], the dispersion-corrected DFT approach is needed for the accurate description of bulk water/ice equilibrium. We conclude that the applicability of the advanced computational methods with London dispersion corrections [40] for theoretical evaluation of the lattice energy of the two-component pharmaceutical crystals [41] and drug-receptor interactions [42] requires a special investigation.

It should be noted that computational predictions of IR vibrational intensities and frequencies are basis-set dependent, and B3LYP/6-31+G\* level of approximation is shown to offer excellent quantitative performance in the calculations of relative 'gas-phase' IR intensities for the bands of vibrations [43], while the use of smaller basis set may lead to unreliable intensity predictions. In order to check whether the results collected in Table 2 could be influenced by the choice of basis set, the computations of the IR intensities and frequencies have been repeated at the B3LYP-D3/6-31+G\* and B3LYP/6-31+G\* levels of approximation. A comparison of the latter two computations (supplementary material) demonstrates quite moderate influence of D3 correction on IR spectroscopic manifestations of H-bonding, similar to the case of use of 6-31G\*\* basis set (Table 2). Earlier we have shown that dispersion interaction has little influence on relative IR intensities computed with the hybrid DFT methods for the bands of vibrations with frequencies ( $\nu$ )  $\leq 2300$  cm<sup>-1</sup> [44]. Present results suggest that this conclusion can be extended to the case of  $\nu > 2300$  cm<sup>-1</sup>.

#### 4. Conclusions

In this letter we have shown that London dispersion interactions have little influence on the energetical, geometrical, IR spectroscopic and electron density parameters of medium to strong intermolecular HBs functioning both in the crystal of the 1-(2-hydroxyethyl)-3-methylimidazolium acetate ( $[C_2OHmim][OAc]$ ) and in the isolated  $[C_2OHmim]^+[OAc]^-$  ion pairs. In theoretical terms these results suggest that the role of dispersive forces in charge-assisted HB and in IR spectra formation is minor. In a more narrow and practical way the message is that simplified quantum chemical approaches unable to the correct treatment of nonlocal London dispersion interactions still can be applied to simulations of IR spectra. It should be noted though that the space groups and unit cell parameters of the  $[C_2OHmim][OAc]$  crystal were adopted in present solid-state DFT computations, and these constraints of crystal geometry might influence the results.

## Acknowledgements

M.V.V. and S.A.K. thank the Russian Foundation for Basic Research (Grants 14-03-01031 and 15-03-01058 A, respectively) for financial support of this study.

## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cplett.2017.01.070>.

## References

- [1] S. Grimme, Density functional theory with London dispersion corrections, *Wiley Interdisciplinary Rev.: Comput. Mol. Sci.* 1 (2) (2011) 211–228, <http://dx.doi.org/10.1002/wcms.30>.
- [2] J.G. Brandenburg, M. Hochheim, T. Bredow, S. Grimme, Low-cost quantum chemical methods for noncovalent interactions, *J. Phys. Chem. Lett.* 5 (24) (2014) 4275–4284, <http://dx.doi.org/10.1021/jz5021313>.
- [3] 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, *J. Chem. Phys.* 132 (15) (2010) 154104, <http://dx.doi.org/10.1063/1.3382344>.
- [4] S. Grimme, S. Ehrlich, L. Goerigk, Effect of the damping function in dispersion corrected density functional theory, *J. Comp. Chem.* 32 (7) (2011) 1456–1465, <http://dx.doi.org/10.1002/jcc.21759>.
- [5] L. Goerigk, S. Grimme, Efficient and accurate double-hybrid-meta-GGA density functionals—evaluation with the extended GMTKN30 database for general main group thermochemistry, kinetics, and noncovalent interactions, *J. Chem. Theory Comp.* 7 (2) (2011) 291–309, <http://dx.doi.org/10.1021/ct100466k>.
- [6] T. Risthaus, S. Grimme, Benchmarking of London dispersion-accounting density functional theory methods on very large molecular complexes, *J. Chem. Theory Comp.* 9 (3) (2013) 1580–1591, <http://dx.doi.org/10.1021/ct301081n>.
- [7] J.G. Brandenburg, S. Grimme, Dispersion corrected Hartree-Fock and density functional theory for organic crystal structure prediction, *Top. Curr. Chem.* 345 (2014) 1–23, [http://dx.doi.org/10.1007/128\\_2013\\_488](http://dx.doi.org/10.1007/128_2013_488).
- [8] A. Otero-de-la-Roza, E.R. Johnson, A benchmark for non-covalent interactions in solids, *J. Chem. Phys.* 137 (5) (2012) 054103, <http://dx.doi.org/10.1063/1.4738961>.
- [9] A.M. Reilly, A. Tkatchenko, Seamless and accurate modeling of organic molecular materials, *J. Phys. Chem. Lett.* 4 (6) (2013) 1028–1033, <http://dx.doi.org/10.1021/jz400226x>.
- [10] J.G. Brandenburg, M. Alessio, B. Civalleri, M.F. Peintinger, T. Bredow, S. Grimme, Geometrical correction for the inter- and intramolecular basis set superposition error in periodic density functional theory calculations, *J. Phys. Chem. A* 117 (38) (2013) 9282–9292, <http://dx.doi.org/10.1021/jp406658y>.
- [11] J.G. Brandenburg, T. Maas, S. Grimme, Benchmarking DFT and semiempirical methods on structures and lattice energies for ten ice polymorphs, *J. Chem. Phys.* 142 (12) (2015) 124104, <http://dx.doi.org/10.1063/1.4916070>.
- [12] R.L. Hayes, S.J. Paddison, M.E. Tuckerman, Proton transport in triflic acid hydrates studied via path integral Car–Parrinello molecular dynamics, *J. Phys. Chem. B* 113 (52) (2009) 16574–16589, <http://dx.doi.org/10.1021/jp907853p>.
- [13] A.A. Hoser, D.M. Kaminski, A. Matwijczuk, A. Niewiadomy, M. Gagos, K. Wozniak, On polymorphism of 2-(4-fluorophenylamino)-5-(2,4-dihydroxybenzeno)-1,3,4-thiadiazole (FABT) DMSO solvates, *CrystEngComm* 15 (10) (2013) 1978–1988, <http://dx.doi.org/10.1039/C3CE26778D>.
- [14] M.V. Vener, E.O. Levina, O.A. Koloskov, A.A. Rykounov, A.P. Voronin, V.G. Tsirelson, Evaluation of the lattice energy of the two-component molecular crystals using solid-state density functional theory, *Cryst. Growth Des.* 14 (10) (2014) 4997–5003, <http://dx.doi.org/10.1021/cg5005243>.
- [15] A.N. Manin, A.P. Voronin, A.V. Shishkina, M.V. Vener, A.V. Churakov, G.L. Perlovich, Influence of secondary interactions on the structure, sublimation thermodynamics, and solubility of salicylate:4-hydroxybenzamide cocrystals. Combined experimental and theoretical study, *J. Phys. Chem. B* 119 (33) (2015) 10466–10477, <http://dx.doi.org/10.1021/acs.jpcc.5b05082>.
- [16] S.A. Katsyuba, M.V. Vener, E.E. Zvereva, Z. Fei, R. Scopelliti, J.G. Brandenburg, S. Siankevich, P.J. Dyson, Quantification of conventional and nonconventional charge-assisted hydrogen bonds in the condensed and gas phases, *J. Phys. Chem. Lett.* 6 (21) (2015) 4431–4436, <http://dx.doi.org/10.1021/acs.jpclett.5b02175>.
- [17] S.A. Katsyuba, M.V. Vener, E.E. Zvereva, Z. Fei, R. Scopelliti, G. Laurency, N. Yan, E. Paunescu, P.J. Dyson, How strong is hydrogen bonding in ionic liquids? Combined X-ray crystallographic, infrared/Raman spectroscopic, and density functional theory study, *J. Phys. Chem. B* 117 (30) (2013) 9094–9105, <http://dx.doi.org/10.1021/jp405255v>.
- [18] R.W.F. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, New York, 1990.
- [19] I. Mata, I. Alkorta, E. Espinosa, E. Molins, Relationships between interaction energy, intermolecular distance and electron density properties in hydrogen bonded complexes under external electric fields, *Chem. Phys. Lett.* 507 (1–3) (2011) 185–189, <http://dx.doi.org/10.1016/j.cplett.2011.03.055>.
- [20] A.V. Iogansen, Direct proportionality of the hydrogen bonding energy and the intensification of the stretching  $\nu(\text{XH})$  vibration in infrared spectra, *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 55 (7–8) (1999) 1585–1612, [http://dx.doi.org/10.1016/S1386-1425\(98\)00348-5](http://dx.doi.org/10.1016/S1386-1425(98)00348-5).
- [21] K.F. Purcell, R.S. Drago, Theoretical aspects of the linear enthalpy wavenumber shift relation for hydrogen-bonded phenols, *J. Am. Chem. Soc.* 89 (12) (1967) 2874–2879, <http://dx.doi.org/10.1021/ja00988a013>.
- [22] L.A. Burns, Á.V.-. Mayagoitia, B.G. Sumpter, C.D. Sherrill, Density-functional approaches to noncovalent interactions: a comparison of dispersion corrections (DFT-D), exchange-hole dipole moment (XDM) theory, and specialized functionals, *J. Chem. Phys.* 134 (8) (2011) 084107, <http://dx.doi.org/10.1063/1.3545971>.
- [23] J. Klimeš, A. Michaelides, Perspective: advances and challenges in treating van der Waals dispersion forces in density functional theory, *J. Chem. Phys.* 137 (12) (2012) 120901, <http://dx.doi.org/10.1063/1.4754130>.
- [24] S. Grimme, A. Hansen, J.G. Brandenburg, C. Bannwarth, Dispersion-corrected mean-field electronic structure methods, *Chem. Rev.* 116 (9) (2016) 5105–5154, <http://dx.doi.org/10.1021/acs.chemrev.5b00533>.
- [25] S. Grimme, W. Hujo, B. Kirchner, Performance of dispersion-corrected density functional theory for the interactions in ionic liquids, *Phys. Chem. Chem. Phys.* 14 (14) (2012) 4875–4883, <http://dx.doi.org/10.1039/c2cp24096c>.
- [26] F. Neese, The ORCA program system, *Wiley Interdisciplinary Rev.: Comput. Mol. Sci.* 2 (1) (2012) 73–78, <http://dx.doi.org/10.1002/wcms.81>.
- [27] A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange, *J. Chem. Phys.* 98 (7) (1993) 5648–5652, <http://dx.doi.org/10.1063/1.464913>.
- [28] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B* 37 (2) (1988) 785–789, <http://dx.doi.org/10.1103/PhysRevB.37.785>.
- [29] R. Dovesi, V.R. Saunders, C. Roetti, R. Orlando, C.M. Zicovich-Wilson, F.C. Pascale, K. Doll, N.M. Harrison, I.J. Bush, P. D'Arco, M. Llunell, *Crystal06 User's Manual*, Università di Torino, Torino, 2006.
- [30] M. Meot-Ner, Update 1 of: strong ionic hydrogen bonds. *Chem. Rev.* 112(10) (2012), PR22-PR103, <http://dx.doi.org/10.1021/cr200430n>.
- [31] K.S. Kim, J.Y. Lee, S.J. Lee, T.-K. Ha, D.H. Kim, On binding forces between aromatic ring and quaternary ammonium compound, *J. Am. Chem. Soc.* 116 (16) (1994) 7399–7400, <http://dx.doi.org/10.1021/ja00095a050>.
- [32] F.M. Raymo, M.D. Bartberger, K.N. Houk, J.F. Stoddart, The magnitude of [C–H...O] hydrogen bonding in molecular and supramolecular assemblies, *J. Am. Chem. Soc.* 123 (38) (2001) 9264–9267, <http://dx.doi.org/10.1021/ja010443i>.
- [33] S. Scheiner, T. Kar, J. Pattanayak, Comparison of various types of hydrogen bonds involving aromatic amino acids, *J. Am. Chem. Soc.* 124 (44) (2002) 13257–13264, <http://dx.doi.org/10.1021/ja027200q>.
- [34] O.V. Shishkin, G.V. Palamarchuk, L. Gorb, J. Leszczynski, Opposite charges assisted extra strong C–H...O hydrogen bond in protonated 2'-deoxyadenosine monophosphate, *Chem. Phys. Lett.* 452 (1–3) (2008) 198–205, <http://dx.doi.org/10.1016/j.cplett.2007.12.052>.
- [35] B. Nepal, S. Scheiner, Anionic CH...X– hydrogen bonds: origin of their strength, geometry, and other properties, *Chem. Eur. J.* 21 (4) (2015) 1474–1481, <http://dx.doi.org/10.1002/chem.201404970>.
- [36] M.V. Vener, A.N. Egorova, D.P. Fomin, V.G. Tsirelson, *J. Phys. Org. Chem.* 22 (2009) 177–185, <http://dx.doi.org/10.1002/poc.1445>.
- [37] S. Scheiner, in: S. Scheiner (Ed.), *Noncovalent Forces*, Springer International Publishing, Cham, 2015, pp. 69–105.
- [38] A. Akin-Ojo, F. Wang, Effects of the dispersion interaction in liquid water, *Chem. Phys. Lett.* 513 (2011) 59–62, <http://dx.doi.org/10.1016/j.cplett.2011.07.064>.
- [39] J. Grdadolnik, F. Merzel, F. Avbelj, Origin of hydrophobicity and enhanced water hydrogen bond strength near purely hydrophobic solutes, *PNAS* 114 (2017) 322–327, <[www.pnas.org/cgi/doi/10.1073/pnas.1612480114](http://www.pnas.org/cgi/doi/10.1073/pnas.1612480114)>.
- [40] R. Sure, J.G. Brandenburg, S. Grimme, Small atomic orbital basis set first-principles quantum chemical methods for large molecular and periodic systems: a critical analysis of error sources, *ChemistryOpen* 5 (2) (2016) 94–109, <http://dx.doi.org/10.1002/open.201500192>.
- [41] A.P. Voronin, G.L. Perlovich, M.V. Vener, Effects of the crystal structure and thermodynamic stability on solubility of bioactive compounds: DFT study of isoniazid cocrystals, *Comput. Theor. Chem.* 1092 (2016) 1–11.
- [42] M. Kržan, R. Vianello, A. Maršavelski, M. Repič, M. Zakšek, K. Kotnik, E. Fijan, J. Mavri, The quantum nature of drug–receptor interactions: deuteration changes binding affinities for histamine receptor ligands, *PLOS ONE*, <http://dx.doi.org/10.1371/journal.pone.0154002>.
- [43] S.A. Katsyuba, E.E. Zvereva, T.I. Burganov, Is there a simple way to reliable simulations of infrared spectra of organic compounds?, *J. Phys. Chem. A* 117 (30) (2013) 6664–6670, <http://dx.doi.org/10.1021/jp404574m>.
- [44] E.E. Zvereva, A.R. Shagidullin, S.A. Katsyuba, Ab initio and DFT predictions of infrared intensities and Raman activities, *J. Phys. Chem. A* 115 (1) (2011) 63–69, <http://dx.doi.org/10.1021/jp108057p>.