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Intermolecular Hydrogen Bond Energies in Crystals Evaluated Using Electron Density Properties: DFT Computations with Periodic Boundary Conditions

M. V. Vener,^{*,[a]} A. N. Egorova,^[a] A. V. Churakov,^[b] and V. G. Tsirelson^[a]

The hydrogen bond (H-bond) energies are evaluated for 18 molecular crystals with 28 moderate and strong O—H...O bonds using the approaches based on the electron density properties, which are derived from the B3LYP/6-311G** calculations with periodic boundary conditions. The approaches considered explore linear relationships between the local electronic kinetic G_b and potential V_b densities at the H...O bond critical point and the H-bond energy E_{HB} . Comparison of the computed E_{HB} values with the experimental data and enthalpies evaluated using the empirical correlation of spectral and thermodynamic parameters (logansen, *Spectrochim. Acta Part A* **1999**, *55*, 1585) enables to estimate the accuracy and applicability limits of the approaches used. The V_b — E_{HB} approach overestimates the energy of moderate H-bonds ($E_{HB} < 60$ kJ/mol) by ~20% and

gives unreliably high energies for crystals with strong H-bonds. On the other hand, the G_b — E_{HB} approach affords reliable results for the crystals under consideration. The linear relationship between G_b and E_{HB} is basis set superposition error (BSSE) free and allows to estimate the H-bond energy without computing it by means of the supramolecular approach. Therefore, for the evaluation of H-bond energies in molecular crystals, the G_b value can be recommended to be obtained from both density functional theory (DFT) computations with periodic boundary conditions and precise X-ray diffraction experiments. © 2012 Wiley Periodicals, Inc.

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Introduction

The enthalpy and energy of the hydrogen bond (H-bond) can be measured and computed with a high accuracy in the gas phase, for example, see Refs. [1–5]. logansen^[6] suggested an elegant approach to evaluate the enthalpies, ΔH , of intermolecular H-bonds in 1:1 acid-base complexes in liquid phases (solutions) by measuring the effect of H-bond on the infrared (IR) intensity of the OH stretching vibration (I) as compared to the noninteracting group (I_0):

$$-\Delta H = 12.2 \Delta I^{1/2}, \quad (1)$$

here, $\Delta I^{1/2} = I^{1/2} - I_0^{1/2}$; ΔH is in kJ/mol and the IR intensity is in 10^{-2} kM/mol. The upper limit of the H-bond enthalpies considered in Ref. [6] is ~60 kJ/mol. For systems with quasilinear O—H...O fragments (with angles O—H...O over 160°), the enthalpy $-\Delta H \sim 60$ kJ/mol corresponds to the O...O/H...O distances, $R(O\cdots O)/R(H\cdots O)$, equal to 2.60/1.60 Å.^[7–9] Applicability of the logansen approach to molecular complexes with strong H-bonds ($-\Delta H > 60$ kJ/mol) is problematic because I value is inversely proportional to the O...X distance ($X = O, N$) in these systems.^[10,11] The $-\Delta H$ value can also be evaluated from the frequency shift of the OH stretching vibrations, $\Delta\nu$, which occurs on formation of H-bonds. Accuracy of this empirical correlation appears below accuracy of the logansen approach.^[6] Applicability of the $\Delta\nu$ — ΔH approach to complexes with strong H-bonds is problematic because the OH stretching band becomes extremely broad in these systems and, in some cases; a continuous absorption appears in the IR spectrum.^[12,13]

In contrast to the gas and liquid phases, evaluation of the H-bond energy/enthalpy in molecular crystals is not straightforward^[14–18] and implies the extraction of the cohesive energy per a particular H-bond from the whole set of intermolecular interactions in a given crystal, for example, see Refs. [19–22]. To our best knowledge, this problem was completely solved only for urea, a benchmark molecular crystal with weak H-bonds ($-\Delta H < 25$ kJ/mol), for example, see Refs. [14,15]. Therefore, various approaches for estimation of the H-bond energy in crystalline compounds were suggested.

Rozenberg et al.^[23] established an empirical correlation between the H-bond enthalpy and the H...O distance ($R(H\cdots O)$, nm):

$$-\Delta H = 0.134 [R(H\cdots O)]^{-3.05} \quad (2)$$

The $R(H\cdots O)$ — ΔH approach gives reasonable $-\Delta H$ values for polycrystalline amino acids and peptides.^[24] The H...A distances in molecular crystals are often unknown accurately due to

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the weak scattering of the X-rays by the H atoms. This distance is usually extracted from the empirical correlation between $R(\text{H}\cdots\text{O})$ and $\Delta\nu$.^[23]

The H-bond energy, E_{HB} , in molecular crystals may be evaluated using the Lippincott and Schroeder model, for example, see Refs. [25,26]. It includes a large number of parameters which particular values are usually found from fitting the experimental data. In contrast to the isolated H-bonded species,^[27] computation of these parameters by the DFT methods with periodic boundary conditions is not straightforward in crystalline compounds.

Espinosa et al.^[28] suggested to estimate the H-bond energy, E_{HB} , in molecular crystals with $\text{A}\cdots\text{H}\cdots\text{O}$ H-bonds ($\text{A} = \text{O}, \text{N}, \text{C}$) using the local electronic potential energy density, V_{b} , at the $\text{H}\cdots\text{O}$ bond critical point in electron density^[29] (in atomic units):

$$E_{\text{HB}} = -0.5 V_{\text{b}} \quad (3a)$$

It was assumed in Ref. [28] that this equation is applicable to weak and moderate H-bonds ($R(\text{H}\cdots\text{O}) > 1.60 \text{ \AA}$ and $E_{\text{HB}} < 60 \text{ kJ/mol}$). Equation (3a) enables one to evaluate of the E_{HB} values in solid state using the experimental (X-ray diffraction) or theoretical potential densities.^[30–33] At the same time, the $V_{\text{b}}-E_{\text{HB}}$ approach was applied to crystals with strong H-bonds,^[34,35] where the $V_{\text{b}}-E_{\text{HB}}$ linearity is questionable, for example, see Refs. [36]. It was also used to estimate the energy of noncovalent interactions other than H-bond.^[37]

The expression which links the energy of H-bond and the local electronic kinetic energy density G_{b} , has been recently suggested^[38] (in atomic units):

$$E_{\text{HB}} = 0.429 G_{\text{b}}. \quad (3b)$$

It has been found that eq. (3b) gives the reasonable E_{HB} values in the range $3 < E_{\text{HB}} < 90 \text{ kJ/mol}$ in the gas-phase $\text{A}\cdots\text{FH}$ ($\text{A} = \text{H}, \text{Li}, \text{Al}, \text{Cl}, \text{CCH}$) complexes.^[38]

Accuracy of the E_{HB} values evaluated using eqs. (3a) and (3b) for crystals with moderate H-bonds is unknown. Applicability of these approaches for estimation of the E_{HB} values in crystalline compounds with strong H-bonds is uncertain. Meanwhile, the density functional theory (DFT) computations with periodic boundary conditions give us a unique possibility to calculate the geometrical, spectral, and electron density parameters of H-bonds in crystals and, therefore, to clarify the problems mentioned above. The aim of this article is to reveal the accuracy and applicability limits of the $V_{\text{b}}-E_{\text{HB}}$ and $G_{\text{b}}-E_{\text{HB}}$ approaches by comparison of the computed E_{HB} values with the literature data and the enthalpies evaluated using the logansen approach.

It should be noted that evaluation of the enthalpies/energies of the intramolecular H-bonds^[39] using the frequencies and IR intensities of the OH stretching vibration^[40,41] or electron density properties at the $\text{H}\cdots\text{O}$ bond critical point^[42] is out of the scope of this article.

Methodology

Quantum-chemical computations give the H-bond energy, E_{HB} . The experimental studies of H-bonded systems are usually performed at finite temperatures T and lead to the H-bond

enthalpy, ΔH . These quantities are connected with each other by the relation $\Delta H = -E_{\text{HB}} - 2RT$;^[43] thus, the absolute difference between ΔH and E_{HB} is $\sim 5 \text{ kJ/mol}$ at the room temperature.

Molecular crystals: the training set

In this study, 18 molecular crystals comprising 28 intermolecular $\text{O}\cdots\text{H}\cdots\text{O}$ bonds are considered (Supporting Information, Tables S1 and S2): 20 moderate H-bonds in potassium hydrogen carbonate (KHCO_3)^[44] formic acid,^[45] 1-hydroxycyclopropane-1-carboxylic acid ($\text{C}_4\text{H}_4\text{O}(\text{OH})_2$),^[46] monofluoroacetic acid (CFH_2COOH),^[47] ethane-1,2-diol ($\text{HO}(\text{CH}_2)_2\text{OH}$),^[48] methanol (CH_3OH),^[49] the proton-ordered forms of water ices,^[50–53] $\text{NaH}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$,^[54] and oxalic acid dihydrate ($(\text{COOH})_2\cdot 2\text{H}_2\text{O}$),^[55] 8 strong H-bonds in oxalic acid dihydrate, $\text{NaHC}_2\text{O}_4\cdot\text{H}_2\text{O}$, 1-hydroxyimidazole-3-oxide ($\text{H}_3\text{C}_3\text{N}_2\text{O}$),^[56] 2,3,5,6-pyrazinetetracarboxylic acid dihydrate ($\text{C}_8\text{H}_4\text{N}_2\text{O}_8\cdot 2\text{H}_2\text{O}$),^[16] potassium hydrogen oxydiacetate ($\text{KHO}(\text{CH}_2\text{COO})_2$),^[57] *N*-formylglycine,^[58] (5)-*N*-nitrosoazetidine-2-carboxylic acid ($\text{C}_4\text{H}_6\text{N}_2\text{O}_3$),^[59] and 3-deazauracil.^[60] These systems are taken by the following reasons: (i) the unit cell contains less than 70 atoms (mainly the first-row and hydrogen atoms); (ii) the $\text{H}\cdots\text{O}$ bond set fills evenly (i.e., without significant gaps) the range of $\text{O}\cdots\text{O}/\text{H}\cdots\text{O}$ distances from $\sim 2.45/1.40$ to $\sim 2.90/1.90 \text{ \AA}$ typical for strong and moderate H-bonds with $-\Delta H > 25 \text{ kJ/mol}$.^[9,61]

Different types of H-bonds exist in the aforementioned crystals, for example, the $\text{C}\cdots\text{H}\cdots\text{O}$ bond in formic acid,^[45] the $\text{N}\cdots\text{H}\cdots\text{O}$ bond in 3-deazauracil^[60] and so forth. We refer to only quasilinear $\text{O}\cdots\text{H}\cdots\text{O}$ bonds in this study.

Computational details

In the CRYSTAL06 calculations,^[62] the B3LYP/6-311G** level of approximation has been used. It produces the reasonable geometries, harmonic frequencies, and IR intensities of molecular crystals with moderate H-bonds.^[63–65] The default CRYSTAL06 computation options are used to achieve an appropriate level of accuracy in evaluating the Coulomb and Hartree–Fock exchange series and the XLGRID option is used in evaluating the DFT exchange–correlation contribution. Tolerance on energy controlling the self-consistent field convergence for geometry optimizations and frequencies computations is set to 1×10^{-8} and 1×10^{-9} hartree, respectively. The number of points in the numerical first derivative calculation of the analytic nuclear gradients is set equal to 2. The shrinking factor of the reciprocal space net was set to 3. Frequencies of normal modes are calculated within the harmonic approximation by numerical differentiation of the analytical gradient of the potential energy with respect to atomic position.^[66] The IR intensities for normal modes are calculated from the dipole moment derivatives determined using well-localized Wannier functions of the unit cell to calculate the Born charge tensors.^[66,67] It should be noted, that the frequency calculations have been performed for isotope-isolated samples of the corresponding crystal, for example, in the case of the water ices the partially deuterated water is surrounded by D_2O molecules.

The geometrical parameters obtained after the structure optimization have been used in the B3LYP/6-311G** computation of the periodical electronic wavefunctions by the CRYSTAL98 program.^[68] XLGRID option is used in evaluating the DFT exchange-correlation contribution. Tolerance on energy controlling the self-consistent field convergence for wavefunction computations is set to 1×10^{-8} hartree. The quantum-topological analysis of the periodical electron density is performed by the TOPOND computer program.^[69] Methodology is presented elsewhere.^[70,71] The following electron density features at the H...O intermolecular critical points are considered: (i) the values of the electron density, ρ_b , (ii) the Laplacian of the electron density, $\nabla^2\rho_b$, and (iii) the local electronic kinetic and potential energy densities, G_b and V_b .

The B3LYP functional is not able to account for van der Waals dispersion forces which contribute substantially the weak intermolecular interaction, for example, see Refs. [72–75]. However, in this study the molecular crystals with moderate or strong H-bonds^[9] are considered. H-bond energies in these crystals are larger ~ 25 kJ/mol and dispersion interactions are expected to play a minor role for the considered species. Also, it was recently shown that the dispersion correction has a little influence on the IR spectra.^[76]

Results

The space groups and unit cell parameters of the considered molecular crystals obtained in the neutron diffraction and single-crystal X-ray studies are adopted, and structural relaxations are limited to the positional parameters of atoms. This approximation yields a reasonable description of the harmonic frequencies and IR intensities in H-bonded crystals.^[77–81] The experimental values of the atomic positions are used as the starting point in the DFT computations with periodical boundary conditions. All the structures are found to correspond to the minimum point on the potential energy surface. The mean deviation of the computed values of the O...O distances from the experimental ones is less than 0.02 Å (Supporting Information, Tables S1 and S2). Moderate H-bonds in the considered crystals are characterized by $\nabla^2\rho_b > 0$ and $0.02 < \rho_b < 0.06$ a.u. (Supporting Information, Table S1) and, therefore, correspond to the case of the closed-shell atomic interactions.^[82–87] In accord with Refs. [7,9], the computed values of the frequency shift of the OH stretching vibrations, $\Delta\nu$, vary from 300 to 800 cm^{-1} . The calculated $\Delta\nu$ values in the proton-ordered ices agree nicely with the experimental data, see Tables 1 and 2 in Ref. [88]. Strong H-bonds in the considered crystals are characterized by $\nabla^2\rho_b > 0$ and $0.06 < \rho_b < 0.10$ a.u. (Supporting Information, Table S2) and correspond to an intermediate (transit) region separating the shared and closed-shell atomic interactions.^[82–84] In accord with Refs. [7,9], the computed $\Delta\nu$ values exceed 850 cm^{-1} . The calculated $\Delta\nu$ value in the 2,3,5,6-pyrazinetetracarboxylic acid dehydrate crystal, ~ 1500 cm^{-1} , agrees with the experimental shift of 1200–1400 cm^{-1} .^[16] We conclude that the level of approximation used in this study gives an adequate description of the geometrical,

Table 1. Computed values of the $R(\text{O}\cdots\text{O})$ and $R(\text{H}\cdots\text{O})$ distances, the enthalpy of H-bond, ΔH , and the H-bond energy E_{HB} , evaluated using Eqs. (1)–(3) for molecular crystals with moderate H-bonds.

Crystal ^[a]	$R(\text{O}\cdots\text{O})/R(\text{H}\cdots\text{O})$ Å	$-\Delta H$ (kJ/mol)		E_{HB} (kJ/mol)	
		(1)	(2)	(3a)	(3b)
KHCO ₃	2.593/1.593	54.4	36.3	80.4	55.4
Formic acid ^[b]	2.613/1.607	48.6	35.4	74.9	51.7
C ₄ H ₄ O(OH) ₂	2.632/1.630	53.1	33.9	68.6	48.6
CFH ₂ COOH	2.661/1.663	46.0	31.9	60.8	44.7
HO(CH ₂) ₂ OH	2.682/1.697	43.8	30.0	56.8	43.4
	2.698/1.725	38.9	28.5	50.6	40.2
CH ₃ OH	2.728/1.744	39.6	27.7	48.6	38.6
Ice IX	2.725/1.754	34.3	27.6	46.8	38.0
Ice XI	2.750/1.764	35.9	26.6	45.4	37.0
Ice II ^[c]	2.796/1.836	30.1	23.5	36.7	31.0
NaHC ₂ O ₄ ·H ₂ O	2.806/1.833	33.4	23.7	33.3	29.8
(COOH) ₂ ·2H ₂ O	2.855/1.899	33.0	21.3	26.7	24.5
Ice VIII	2.879/1.901	30.0	21.2	28.5	25.2

[a] see Table S1; in the case of proton-ordered ices only one H-bond is given. [b] The absolute value of H-bond energy available in the literature is 42–47.2 kJ/mol^[18]. [c] The absolute values of H-bond enthalpy available in the literature are 29.5^[17] and 28 kJ/mol.^[90]

spectral, and electron density parameters of the O—H...O fragment in the considered crystals.

The $-\Delta H/E_{\text{HB}}$ values depend linearly on the spectral and electron density parameters, see eqs. (1), (3a), and (3b). On the other hand, the H-bond energy increases monotonously with the H...O distance decrease in the H-bonded complexes.^[23,89] Studying the dependences of $\Delta I^{1/2}$, V_b , and G_b on $R(\text{H}\cdots\text{O})$ will give some hints on the applicability limits of the considered approaches for $-\Delta H/E_{\text{HB}}$ evaluation in molecular crystals.

Dependence of the computed $\Delta I^{1/2}$ values on $R(\text{H}\cdots\text{O})$ is given in Figure 1. For $R(\text{H}\cdots\text{O}) > 1.6$ Å, the $\Delta I^{1/2}$ value is inversely proportional to the H...O distance. Equation (1) fits a very few $-\Delta H/E_{\text{HB}}$ values available in the literature.^[17,18,90] According to Table 1, the accuracy of the logansen approach is ~ 2 kJ/mol. In strong H-bonded crystals ($R(\text{H}\cdots\text{O}) < 1.6$ Å), the $\Delta I^{1/2}$ versus $R(\text{H}\cdots\text{O})$ dependence becomes nonmonotonic. Similar results were obtained in Refs. [10,11] for the spectral properties of the strong H-bonded complexes in gas and liquid phases. It

Table 2. Computed values of the $R(\text{O}\cdots\text{O})$ and $R(\text{H}\cdots\text{O})$ distances, the enthalpy of H-bond, ΔH , and the H-bond energy E_{HB} , evaluated using Eqs. (2) and (3) for molecular crystals with strong H-bonds.

Crystal ^[a]	$R(\text{O}\cdots\text{O})/R(\text{H}\cdots\text{O})$ Å	$-\Delta H$ (kJ/mol) (2)	E_{HB} (kJ/mol)	
			(3a)	(3b)
H ₃ C ₃ N ₂ OH	2.467/1.404	53.4	154.5	83.9
C ₈ H ₄ N ₂ O ₈ ·2H ₂ O ^[b]	2.476/1.432	50.3	137.5	78.3
KHO(CH ₂ COO) ₂	2.483/1.423	51.3	141.3	78.4
(COOH) ₂ ·2H ₂ O	2.497/1.449	48.5	129.8	74.5
N-formylglycine	2.515/1.496	44.0	110.8	68.4
NaHC ₂ O ₄ ·H ₂ O	2.563/1.537	40.5	94.4	60.3
C ₄ H ₆ N ₂ O ₃	2.565/1.552	39.3	91.3	59.2
3-deazauracil	2.593/1.587	36.8	82.8	55.7

[a] see Supporting Information, Table S2. [b] The absolute value of H-bond energy available in the literature is 67 kJ/mol.^[16]

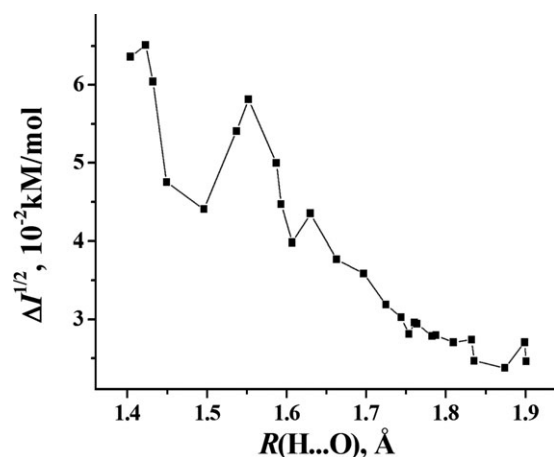


Figure 1. Dependence of $\Delta I^{1/2}$ on $R(\text{H}\cdots\text{O})$ in crystals with strong and moderate H-bonds. B3LYP/6-311G** computations with periodic boundary conditions.

implies that the logansen approach is not suitable for the estimation of $-\Delta H$ in the strong H-bonded complexes.

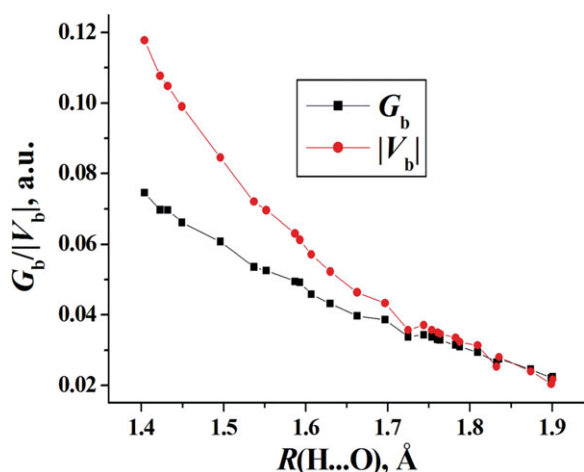


Figure 2. The local electronic kinetic G_b (black boxes) and potential V_b (red circles) densities at the $\text{H}\cdots\text{O}$ bond critical point versus the calculated $\text{H}\cdots\text{O}$ distances.

Dependences of the computed $|V_b|$ and G_b values on $R(\text{H}\cdots\text{O})$ are given in Figure 2. For $R(\text{H}\cdots\text{O}) > 1.7$ Å, the both electron density parameters are close to each other and are inversely proportional to the $\text{H}\cdots\text{O}$ distance. Indeed, eqs. (3a) and (3b) give similar E_{HB} values in molecular crystals with $R(\text{H}\cdots\text{O}) > 1.7$ Å which are close to the enthalpies evaluated using the logansen approach (Table 1). At $R(\text{H}\cdots\text{O}) < 1.7$ Å, the absolute values of V_b and G_b become essentially different (Tables 1 and 2). In strong H-bonded crystals, $|V_b|$ correlates with the inverse second power of the $\text{H}\cdots\text{O}$ distance (Fig. 2). The V_b-E_{HB} approach overestimates heavily the H-bond energy for $R(\text{H}\cdots\text{O}) < 1.7$ Å (see Tables 1, 2, and Fig. 3). Similar result was obtained for the gas-phase species with strong H-bonds in Ref. [36]. We conclude that eq. (3a) is appropriate for E_{HB} evaluation in molecular crystals with $R(\text{H}\cdots\text{O}) > 1.7$ Å. The

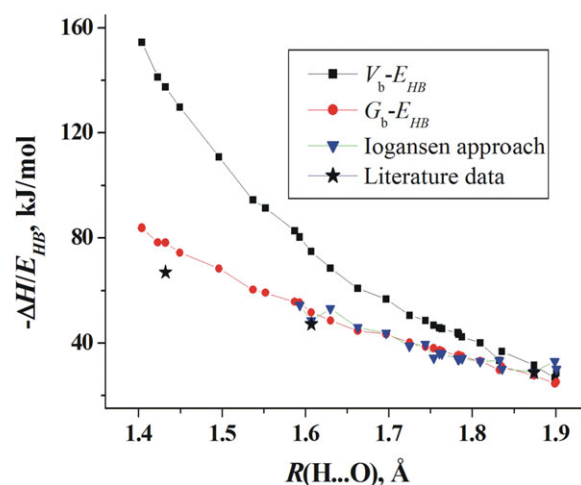


Figure 3. The H-bond enthalpies, $-\Delta H$ (eq. [1], blue triangles) and the energies, E_{HB} (eq. [3a], black boxes and eq. [3b], red circles) evaluated for the considered molecular crystals with the $\text{O}-\text{H}\cdots\text{O}$ fragment versus the calculated $\text{H}\cdots\text{O}$ distances. Black stars stand for the energy values available in the literature, see Tables 1 and 2.

G_b-E_{HB} approach, see eq. (3b), gives the E_{HB} values which agree with the available literature data and enthalpies evaluated using eq. (1), see Tables 1, 2, and Figure 3. Equation (3b) may be recommended for E_{HB} evaluation in molecular crystals with moderate and strong H-bonds. It is important that V_b and G_b values may be derived from the accurate X-ray diffraction data using the structural multipole model.^[91,92] Thus, eq. (3b) can be immediately applied to the experimental electron densities.^[28,87]

The $R(\text{H}\cdots\text{O})$ $-\Delta H$ approach, see eq. (2), gives the enthalpy values which are systematically lower those obtained by the logansen approach and eq. (3b) (Tables 1 and 2).

Applicability limits and accuracy of the considered approaches are summarized in Table 3. According to this Table 3 and Figure 3, only one approach, namely eq. (3b), affords reliable results for the $\text{H}\cdots\text{O}$ distance varying from ~ 1.40 to ~ 1.9 Å. This range corresponds to the $\text{O}\cdots\text{O}$ distances varying from ~ 2.45 to ~ 2.90 Å. The distance $R(\text{O}\cdots\text{O}) \sim 2.45$ Å may be considered as a border between the strong and very strong intermolecular $\text{O}-\text{H}\cdots\text{O}$ bonds. The inequality $R(\text{O}\cdots\text{O}) < 2.45$ Å is typical for the H_5O_2^+ ion in crystalline hydrates of different acids^[93] and aqueous acid solutions.^[94] This ion is characterized by $\nabla^2\rho_b < 0$ and $\rho_b \sim 0.15$ a.u. in crystals,^[84] it implies a partially covalent character of the very strong H-bond.^[95] The bridging proton is a subject to a large-amplitude motion in the H_5O_2^+ ion.^[77] It is difficult to determine the $\text{H}\cdots\text{O}$ distance precisely in this case.

Discussion

Different sets of the H-bonded systems described in the literature,^[4,5,9,96] it seems that the only intermolecular quasilinear $\text{O}-\text{H}\cdots\text{O}$ bonds fill eventually the range of the $\text{O}\cdots\text{O}/\text{H}\cdots\text{O}$ distances from $\sim 2.9/1.9$ to $\sim 2.4/1.2$ Å. This set exists in the gas^[5,97] and condensed phases.^[26,98] In the gas phase, the

Table 3. Applicability limits and accuracy of the empirical approaches used in the present study for evaluating the $-\Delta H/E_{\text{HB}}$ values in molecular crystals with moderate and strong H-bonds.

The approach ^[a]	Applicability limits (kJ/mol)	Accuracy of $-\Delta H/E_{\text{HB}}$
$-\Delta H = 12.2(I^{1/2} - I_0^{1/2})$	$R(\text{H}\cdots\text{O}) > 1.6 \text{ \AA}$, $-\Delta H < 60$	$\sim 2 \text{ kJ/mol}$
$-\Delta H = 0.134 [R(\text{H}\cdots\text{O})]^{-3.05}$	$R(\text{H}\cdots\text{O}) > 1.6 \text{ \AA}$, $-\Delta H < 60$	Underestimated $-\Delta H$ on $\sim 15\%$
$E_{\text{HB}} = -\text{const } 0.5 V_{\text{b}}$	$R(\text{H}\cdots\text{O}) > 1.7 \text{ \AA}$, $E_{\text{HB}} < 45$	Overestimated E_{HB} on $\sim 20\%$
$E_{\text{HB}} = \text{const } 0.429 G_{\text{b}}$	$R(\text{H}\cdots\text{O}) > 1.4 \text{ \AA}$, $E_{\text{HB}} < 85$	Overestimated E_{HB} on $\sim 10\%$

[a] I is in 10^{-2} kM/mol ; $R(\text{H}\cdots\text{O})$ is in nm; V_{b} и G_{b} are in a.u.; const = 2623 (kJ/mol)/a.u.

geometry and IR spectrum of the arbitrary H-bonded system may be computed at the high *ab initio* level. The O \cdots O distance and OH stretching frequency may be obtained experimentally for the molecular crystals. The theoretical/experimental data enables one to establish correlations between O \cdots O/H \cdots O distances and the frequencies of the OH stretching vibrations which are widely used for estimation of the geometrical parameters of H-bonded systems in liquid phase, for example, see Refs. [23,99]. To the experimental end, the O \cdots O distance is a tractable parameter, because it is obtained in the X-ray studies with high accuracy. It is not the universal one, because the shortest X \cdots A distance of the intermolecular H-bond, R_0 , is defined by the nature of the X and A atoms,^[4,84] for example, $R_0(\text{O}\cdots\text{O}) \sim 2.39 \text{ \AA}$,^[100–102] $R_0(\text{N}\cdots\text{O}) \sim 2.52 \text{ \AA}$,^[103] and $R_0(\text{F}\cdots\text{F}) \sim 2.23 \text{ \AA}$.^[104] This is why the $R(\text{X}\cdots\text{X})-R_0$ value was suggested to use in description of the static^[105] and dynamical^[106] properties of the H-bonded systems with the O—H \cdots O fragment in condensed phases. On the other hand, the H \cdots O distance is widely used in different structure/property correlations for H-bonds of different strength^[5,24,28,107,108] However, this parameter has a serious drawback caused by the usual lack of accuracy that X-ray structures have on the H atoms.

According to Table 2, the energy of strong O—H \cdots O bond in molecular crystals may reach $\sim 85 \text{ kJ/mol}$ ($\sim 20 \text{ kcal/mol}$). This value agrees with energies/enthalpies of strong H-bonds measured in the gas and liquid phases^[1,2,109] and estimated in molecular crystals.^[26] However, it appears to be much lower than the energies evaluated very recently for a set of strong H-bonded systems.^[110] To clarify this problem, the structure, harmonic frequencies, and electron density features of the bis(DL-Aspartic acid) oxalate crystal^[110] are computed at the B3LYP/6-31G** level. The calculated O \cdots O distance, 2.523 \AA , agrees nicely with the experimental value of 2.531 \AA . Computed value of the OH stretching vibration, $\sim 2560 \text{ cm}^{-1}$, implies that the intermolecular H-bond in this crystal is relatively strong, see Refs. [7,9] and Supporting Information, Table S2. The H-bond energy, evaluated using eq. (3b), appears to be 61.5 kJ/mol . This value is consistent with the energies, obtained for other strong H-bonded crystals, see Table 2. We can speculate that very large values of the H-bond energy, $\sim 580 \text{ kJ/mol}$, obtained in Ref. [110] for the considered system may be caused by deficiency in the geometry optimization.

Conclusions

Intermolecular H-bond enthalpies/energies in crystals are evaluated using various approaches based on the geometrical (the

H \cdots O distances), spectral (IR intensity of the OH stretching vibration), and quantum-topological electron density (the local electronic kinetic G_{b} and potential energy V_{b} densities at the H-bond critical point) properties. All these quantities are obtained from the B3LYP/6-311G** computations with periodic boundary conditions.

In the case of moderate H-bonds ($25 < -\Delta H < 60 \text{ kJ/mol}$; $1.60 < R(\text{H}\cdots\text{O}) < 1.90 \text{ \AA}$), the logansen approach gives the best results. It is inapplicable for strong H-bonds ($-\Delta H > 60 \text{ kJ/mol}$; $R(\text{H}\cdots\text{O}) < 1.6 \text{ \AA}$) because in this case the IR intensity of the OH stretching vibration does not increase monotonously with the H \cdots O distance decrease.

In the strong H-bonded crystals, the $V_{\text{b}}-E_{\text{HB}}$ approach overestimates heavily the H-bond energy, because $|V_{\text{b}}|$ correlates with the inverse second power of the H \cdots O distance at $R(\text{H}\cdots\text{O}) < 1.6 \text{ \AA}$. The $G_{\text{b}}-E_{\text{HB}}$ approach provides reliable estimates of the energies, because G_{b} is inversely proportional to the H \cdots O distance in the crystals considered.

The $G_{\text{b}}-E_{\text{HB}}$ approach can be recommended for evaluation of H-bond energies in molecular crystals, assuming that the local electronic kinetic energy density, G_{b} , at the H-bond critical point is obtained from DFT computations with periodic boundary conditions or extracted from precise X-ray diffraction experiments. The linear relationship between G_{b} and E_{HB} is basis set superposition error free and allows to estimate the H-bond energy (BSSE) without computing it by means of the supramolecular approach.

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Keywords: molecular crystals • H-bond enthalpies/energies • harmonic frequencies and IR intensities • electron-density analysis

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