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Intramolecular resonance-assisted hydrogen bonds: A theoretical description by means of atomic charges and charge fluxes

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HIGHLIGHTS

- Quadratic correlation charge fluxes ϕ_H vs. molecular IR absorption coefficients E is shown.
- The transition "free" → intramolecular → intermolecular H-bond is gradual.
- The hydrogen charge flux provides a quantitative and simple parameterization of H-bond strength.

GRAPHICAL ABSTRACT
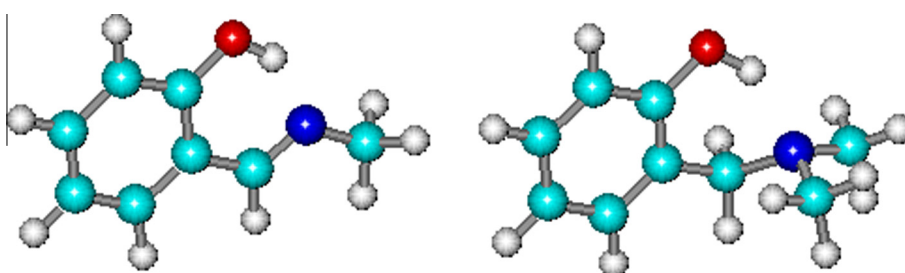
ABSTRACT

The characterization of intramolecular H-bonds in terms of atomic charges and charge fluxes (at the B3LYP/cc-pVTZ level of theory) has been extended to the case of the so called resonance-assisted (RA) H-bonds. A quadratic correlation between the charge fluxes ϕ_H and the molecular IR absorption coefficients E that includes the entire family of the studied systems (31 of them) containing both intra- and intermolecular hydrogen bonds (O–H···O/N) confirmed the critical importance of the charge fluxes on the IR intensity enhancements. Since they reflect changing of the atomic charge distribution during the normal modes of vibrations, the dynamic nature of hydrogen bonding properties has been re-emphasized. The changes of the charge flux of the hydroxyl hydrogen in an RA intramolecular H-bond are between those for "free" OH bonds and the values calculated for intermolecular H-bonds. The transition "free" → intramolecular → intermolecular is gradual and therefore the hydrogen charge flux can be considered as practically sufficient to give quantitative measure to the intuitively obvious statement that "intramolecular H-bonding is somehow in between no H-bonding situation and intermolecular H-bonding" and thus provide a quantitative and yet simple parameterization of H-bond strength. In strictly planar molecules, the difference of the sums of charges of atoms participating in the 6-membered H-bond ring $\Delta\Sigma$ can serve as a measure of the charge delocalization after the H-bond is formed. The electronic charge is withdrawn from the group of six atoms when the H-bond is formed in nitrophenol ($\Delta\Sigma = -0.07$), while the opposite is true ($\Delta\Sigma = +0.03$) for 2-hydroxy benzylidene amine. The corresponding values of the geometrical resonance parameter Δ are 0.39 and 0.37, respectively, similar to those found for 2-hydroxy acetophenone and 2-hydroxy benzaldehyde. The extent of the π-electron delocalization as measured by the resonance parameter Δ does not follow the strength of H-bond as measured by the charge flux ϕ_H.

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Introduction

Strong *intra*molecular hydrogen (H) bonds (as a part of six-membered *intra*molecular rings), also known as resonance assisted (RA) H-bonds [1] will be studied here. The observed characteristics of the H-bonds in enol forms of β-diketones [2] were supposed to occur due to the charge redistribution resulting in resonance stabilization. In addition, it is generally considered acceptable to relate the properties of RA H-bonds with π-electron delocalization although only in a qualitative way and indirectly [2,3] (the π-electron charge density is not calculated). Thus, one of the main

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characteristics of RA H-bonds is the existence of conjugated single and double bonds [1,2]. However, in a number of recent studies it has been shown [4,5] that the RA H-bond effect is not the primary reason behind the strength of the corresponding intramolecular H-bonds, rather it is simply a consequence of the structure of the σ skeleton of the system that puts constraints on the intramolecular ring containing the H-bond. As systems within which RA H-bond O—H···N″ exists, a Schiff base 2-hydroxy-benzylidene methyl amine (**sbm**) [6], has been chosen and contrasted with a Mannich base 2-hydroxy-dimethyl benzyl amine (**mbm**) having O–H···N′ H-bond [7] (single primed and double primed atom symbols refer to the nitrogen hybridization state). The integrated intensities of the OH bands in Mannich and Schiff bases are generally lower than in the related intermolecular H-bonded complexes because the intramolecular bonds are all bent. In Mannich bases, the tendency of the OH-group to align itself tetrahedrally with respect to the other three bonds of nitrogen atom means actually that the six-membered ring cannot be planar (the angle ∠(C1,C6,C,N) (Scheme 1) in **mbm** is 44°). In Schiff bases the same angle is 0°, i.e. the six-membered ring is strictly planar. In order to make more useful comparisons and put more weight on the possible conclusions concerning the properties of RA H-bonds in **sbm** and **mbm**, some other similar molecules having intramolecular O—H···O″ or O-H···O′ H-bonds and their isomers without H-bonds (**n** is appended to the abbreviated name of a molecule) and the corresponding intermolecular H-bonded complexes too have been added (Fig. 1, for more detailed description see below).

Although the strength of *intra*molecular H-bond is an ill-defined concept due to lack of a suitable reference system [8–10], it is nevertheless extensively used, most often for qualitative purposes. It is generally possible to describe a particular intramolecular H-bond XH···Y as stronger then the other one by using suitable quantity such as the XY distance or the electron density at the critical point from X to Y [4,5]. In this work, the strength of an H-bond will be discussed in terms of calculated, but *measurable* spectroscopic quantities, the frequency shift of the OH stretching vibrations, $\Delta \tilde{\nu}(OH)$, the enhancement of its absorption coefficient, ΔE and the H-bond enthalpy or free energy difference between the two conformers. The latter quantity can be considered as the most suitable one for the characterization of the H-bond strength.

Recently a characterization of intra- and intermolecular H-bonds in terms of atomic charges and charge fluxes [11] has been proposed [12]. Based on the spectroscopic criteria, the intramolecular H-bonds studied in that work (O–H···O and O–H···π as
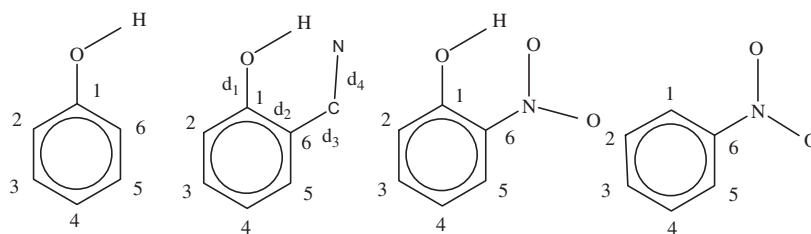
Scheme 1. Atom numbering.
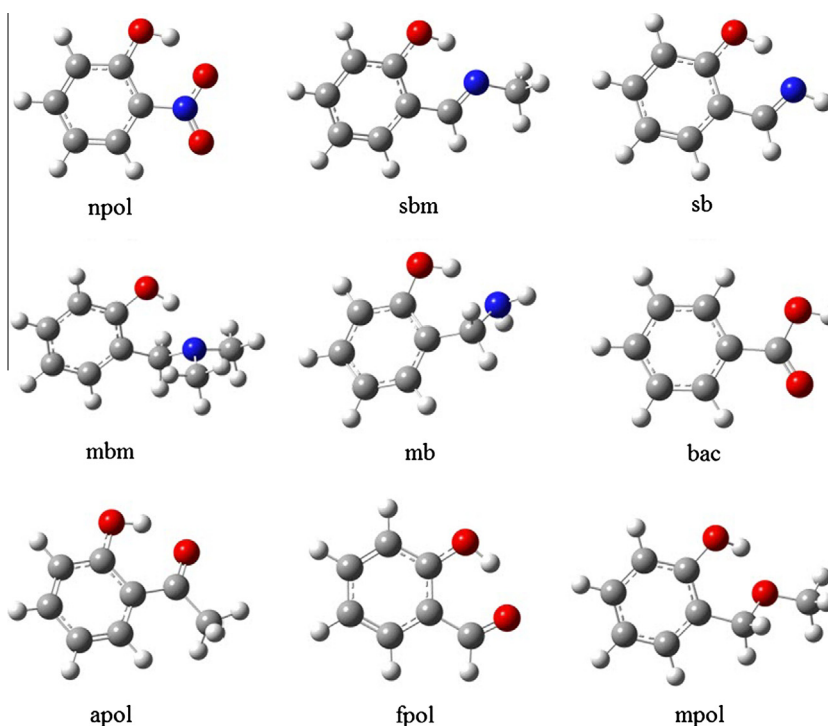
Fig. 1. Molecules with intramolecular H-bonds (except **bac**): group **A** – nitrophenol (**npol**); group **B** – 2-hydroxy benzylidene methylamine (Schiff base, **sbm**) and 2-hydroxy benzylidene amine (**sb**); group **C** – 2-hydroxy dimethyl benzylamine (Mannich base, **mbm**) and 2-hydroxy benzylamine (**mb**); group **D** – benzoic acid (**bac**); group **E** – 2-hydroxy acetphenone (**apol**), 2-hydroxy benzaldehyde (**fpol**); group **F** – 2-methoxy methyl phenol (**mpol**).

a part of five-membered rings) are weak with respect to those in **mbm** and **sbm**. The OH bond in a weak intramolecular H-bond is not much different from the "free", non-hydrogen bonded, OH bond, but the changes of the hydrogen atomic charge and charge flux are toward the values calculated for intermolecular H-bonds. The intermolecular H-bond is characterized not only by the somewhat decreased atomic charge but also by the enlarged charge flux term of the same sign producing thus an enormous increase in IR intensity. Having in mind their spectroscopic characteristics, strong intramolecular H-bonds as found in **mbm** and **sbm**, are expected to show little differences in terms of atomic charges and charge fluxes when compared to the corresponding intermolecular H-bonds. If the strength of an H-bond is measured by the spectroscopic quantities, the frequency shift of the OH stretching vibrations, $\Delta\tilde{v}(OH)$, and the enhancement of its absorption coefficient, ΔE, it is quite normal to expect their strong correlation to the structural parameters of the σ-skeleton, like, for example, the distance $r(H \cdots O/N)$, the angle $\angle(OH \cdots O/N)$ and the dihedral angle $\angle(C–O \cdots O–N)$ or $\angle(C–O \cdots N–C)$ or $\angle(C–O \cdots O–C)$ (the latter angle being chosen to characterize the non-planarity of the intramolecular ring to which the H-bond belongs). Thus, the structure of the σ-skeleton of the system plays a decisive role in the dynamics of the intramolecular ring containing the H-bond [12]. The same conclusion, though in somewhat different context, has been reached recently [5].

In this work an attempt will also be made to quantitatively estimate the π-electron delocalization by comparing atomic charges and atomic fluxes of, for example, **mbm** and **sbm** benzene rings with the unperturbed values of benzene itself. An additional way to do it is by comparing the force constants of the relevant stretching vibrations because longer bond means smaller stretching force constant. Unlike other approaches concentrating on the static picture of the electronic charge distribution [3], a dynamical aspect of the H-bond characteristics is being re-introduced here through charge fluxes because they are dependent on the vibrational movements of atoms. It is our expectation that the charge and the charge flux of hydrogen atom in an OH bond will be smoothly changing as it goes from non-H-bonded to *intra*molecularly (five- to six-ring) H-bonded and then to *inter*molecularly H-bonding situation thus providing a quantitative and yet simple parameterization of H-bond strength.

Computational details

All calculations have been performed by using Gaussian03 suite of programs for electronic structure calculations [13]. The hybrid functional B3LYP (three parameter exchange functional B3 of Becke [14] with the LYP correlation functional [15]) was employed with the correlation consistent basis set of triple-zeta quality cc-pVTZ [16,17]. All the fully optimized geometries are true minima on the potential energy surfaces (no imaginary frequency obtained). Different geometries for H-bonded dimers were reached by choosing different initial configurations. With regard to the aims of this work, it was not necessary to search for the lowest-energy monomer or dimer configurations. For example, the initial configuration of an **mbm** conformer without the intramolecular H-bond was generated by 180° rotation of the OH group around the CO bond. The optimized structure was not further examined against internal rotations around other single bonds. In case of dimers, the energy of an optimized structure was not further calculated as a function of the ring-ring dihedral angle, i.e. of the rotation around the O-H···O/N bond. Due to the smallness of the rotational barriers hindering the transitions between the conformers, it was considered fully acceptable to assume that the H-bond characteristics will not critically depend on these angular variables. Derivatives of Mulliken charges were calculated numerically with a step of 0.01 Å. All the atomic charges and charge fluxes are expressed in units of electron charge e without stating that explicitly.

The model of the IR intensity parameterization that is going to be presently applied has been developed long ago and is certainly well established [11]. Only for the purpose of avoiding misunderstandings the basic relationships will be now summarized. The dominant intensity terms were extracted starting from the expression for the integrated absorption coefficient of the p-th fundamental transition:

$$E_p \propto \left|\frac{\partial \boldsymbol{M}}{\partial Q_p}\right|^2 = \sum_{i=1,2,3}\left(\frac{\partial M_i}{\partial Q_p}\right)^2, \tag{1}$$

($p = 1,2,\ldots,3N$) the relationship that was further used was

$$\frac{\partial M_i}{\partial Q_p} = \sum_{\beta,j}\frac{\partial M_i}{\partial x_{\beta,j}}\frac{\partial x_{\beta,j}}{\partial Q_p} \equiv \sum_{\beta j}\boldsymbol{P}_{ij}^\beta(\boldsymbol{L}_p^X)_{\beta,j}, \tag{2}$$

($\beta = 1,2,\ldots,N$) where $\boldsymbol{P}^\beta$ is the atomic polar tensor (APT) of atom β [18] and $\boldsymbol{L}^X$ is the transformation from normal to Cartesian coordinates and all the quantities are evaluated at the equilibrium structure and in one and the same coordinate system. The coordinate system can always be chosen such that for an XH stretching mode only two terms of the $\boldsymbol{L}^X$ matrix significantly contribute [19] (the so called bond attached system, see below). The problem arises when one whishes to split P_{ij}^β into two contributions, atomic charge and charge flux, each having an appealing chemical interpretation and heuristic value, but not directly measurable.

It is assumed that a molecular dipole moment has the form $\boldsymbol{M} = \sum_\alpha \sigma_\alpha \boldsymbol{r}_\alpha \equiv \sum_{\alpha=1}^N \sigma_\alpha(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N)\boldsymbol{r}_\alpha$, i.e. the atom α at $\boldsymbol{r}_\alpha$ bears a point charge σ_α that is a function of the relative positions of all atoms in the molecule. The charges σ_α at the equilibrium have the property that $\boldsymbol{M}^{(0)} = \sum_\alpha \sigma_\alpha^{(0)}\boldsymbol{r}_\alpha^{(0)}$ and $\sum_\beta \sigma_\beta^{(0)} = 0$ for a neutral molecule. The atomic polar tensor (APT) of atom β is $\boldsymbol{P}^\beta = \sigma_\beta \boldsymbol{I} + \sum_\alpha \boldsymbol{r}_\alpha \nabla_\beta \sigma_\alpha$. Here, the second term is called charge flux because it takes into account the atomic charge dependence on vibrational motion of all atoms in the molecule. By introducing charge fluxes the atomic charges become the characteristic of the molecule as a whole, i.e. the additivity of atomic charges expressed as $\boldsymbol{M} = \sum_\alpha \sigma_\alpha^{(0)}\boldsymbol{r}_\alpha$ has been given up [20]. The charges $\sigma_\beta^{(0)}$ are known as effective charges and this model is known as the effective charges and charge fluxes (ECCF) model [11,21] (for more details see Supplemental Information where also the so-called corrected charges and charge fluxes [22] are explained).

Going now back to Eq. (2), and when $x_{\alpha,2} \equiv y_\alpha = 0$ for all α, i.e. for a planar molecule,

$$\frac{\partial M_2}{\partial Q_P} \equiv \sum_{\beta,j}\boldsymbol{P}_{2j}^\beta(\boldsymbol{L}_p^X)_{\beta,j} = \sum_{beta}\sigma_\beta(\boldsymbol{L}_p^X)_{\beta,2} \tag{3}$$

In a coordinate system attached to, say, an OH bond which is a part of the moiety C–O–H, the Ox axis is along the OH bond, the Oz axis is in the plane C–O–H and the Oy axis is perpendicular to that plane. If an OH stretching is the p-th normal mode, only $(L_p^X)_{O,1}$ and $(L_p^X)_{H,1}$ are different from zero. In other words, $\frac{\partial M_i}{\partial Q_p} \approx P_{i,1}^O(L_p^X)_{O,1} + P_{i,1}^H(L_p^X)_{H,1}$. In this particular case, only the $P_{1,1}$ term is significant and therefore its partition into two contributions, atomic charge and charge flux, enables the type of discussion here performed.

Since $(L_p^X)_{\beta,2} = 0$ for in-plane (Ozx) modes, only for an out-of-plane mode the intensity can be proportional solely to the square of the atomic charge(s). For the normal modes that are dominantly, for example, O-H stretchings in their character, a few $\boldsymbol{L}^X$-components multiplied by the APT components that contain non-zero charge flux term will contribute:

$$\frac{\partial M_1}{\partial Q_p} = \sum_{\beta} (P_{1,1}^{\beta}(C) + P_{1,1}^{\beta}(CF))(L_p^X)_{\beta,1} + \sum_{\beta} P_{1,3}^{\beta}(CF)(L_p^X)_{\beta,3}, \qquad (4)$$

where β = O and H (all the quantities in Eqs. (3) and (4) are evaluated for the equilibrium structure). The APT element in the last term need not be zero for terminal hydrogen atoms, but the L^X-component is practically zero. This simplification is preserved for all the local systems attached to any of the terminal bonds. The advantage of using local systems is in the possibility to directly compare charges and charge fluxes of a particular bond to those of the others in the same or different molecules. How good is the interpretation in terms of effective atomic charges and charge fluxes for a non-planar molecule will be estimated by putting in correlation these parameters with observable quantities.

Thus, there is no problem in calculating corrected charges for any molecule. However, only for planar molecules the ECCF model parameters can be experimentally determined and safely used in discussing the charge redistribution when an H-bond is formed [23,24]. This limits any possible conclusion on the electronic charge redistribution within a molecule only to planar molecules. For all other molecules, atomic charges and charge fluxes have usefulness only when comparing the properties of, for example, O–H bond in different molecules. More fundamental is, however, the problem of non-additivity [20] upon which every attempt to ascribe a well defined property to a structural subunit is deemed to failure.

There are 31 of molecular systems treated in this work (monomers and dimers) that are grouped into 6 groups with phenol (**pol**), as a reference, standing aside (Table 1). The total number is that large because two conformers, one with an H-bond and the other without it, and the corresponding H-bonded complex had to be considered. In group **A** (O–H···O, 5 members), nitrobenzene (**nb**), **pol**···**nb** (**a**) and nitrophenol (**npol**) are planar. **npol** without H-bond (**npoln**) is not planar because the two lone pairs of the

oxygen atoms come too close (∠(C, C, N, O) = 28°). In group **B** (O–H···N″, 8 members), only 2-hydoxy-benzylidene amine (**sb**), **sbn** and benzylidene amine (**bda**) are strictly planar, while **sbm**, and benzylidene methylamine (**bdma**), posses a plane of symmetry. It is interesting that the optimized planar dimer **pol**···**bda** is not stable (one imaginary frequency). The angle between the two ring planes in the stable **pol**···**bda** dimer is 64°. In group **C** (O–H···N′, 8 members) 2-hydroxy-benzyl dimethylamine (**mbm**), 2-hydroxy-benzyl amine (**mb**), phenol···dimethyl benzyl amine (**pol**···**dmba**), phenol···benzyl amine (**pol**···**ba**)), there is no planar molecule. Benzyl amine (**ba**) and **mb** are not planar, but have C$_s$ symmetry. In group **D** (O–H···O″, 3 members), benzoic acid monomer (**bac**) and dimer **bac**···**bac** (**a**) are planar. In another dimer, **bac**···**bac** (**b**), that is not planar, there is no carboxylic ring. In group **E** (O–H···O″, 4 members), 2-hydroxy benzaldehyde (**fpol**) is planar and 2-hydroxy acetophenone (**apol**) has C$_s$ symmetry. In group **F** (O–H···O′, 2 members), 2-methoxy methyl phenol (**mpol**) has C$_s$ symmetry.

Molecular (non)planarity had to be pointed out in the preceding paragraph because, as has already been mentioned, effective atomic charges can be rigorously defined only for planar molecules [23,24]. However, the restriction of the model to only planar molecules need not be a drawback of the present approach as long as we are interested, first, in the relation between the H-bond strength and π-electron delocalization because the latter is also rigorously defined only for planar systems. Second, it will be obvious from the results below that there exists the transferability of atomic charges and charge fluxes of a chosen atomic group between different molecules irrespective of their (non)planarity.

Results and discussion

The geometrical aspects of the H-bond formation in the chosen systems will be considered first. When there is no H-bond, the OH

Table 1
Bond lengths (Å), angles $\theta = \angle(\text{O–H}\cdots\text{O/N})$ and $\varphi = \angle(\text{C–O}\cdots\text{O–N})$ or $\angle(\text{C–O}\cdots\text{N–C})$ or $\angle(\text{C–O}\cdots\text{O–C})$ (°) and the resonance parameter Δ (see text) of the studied systems at the B3LYP/cc-pVTZ level of theory relevant to the H-bond formation.

H-bond		$r(\text{O–H})$	$r(\text{H}\cdots\text{O/N})$	θ	φ	Δ
	pol	0.962				
O–H···O	**pol**···**nb(a)**[b]	0.968	2.936	160.2		
Group **A**	**pol**···**nb(b)**	0.967	2.908	163.7	55.5	
	npol	0.984	2.560	144.5		0.395
	npoln	0.963				
O–H···N″[a]	**pol**···**bdma**	0.985	2.828	171.7	76.0	
Group **B**	**pol**···**bda**	0.984	1.853	172.7	57.0	
	sb	0.993	1.726	147.2		
	sbn	0.963				0.367
	sbm	0.994	2.631	147.9		
	sbmn	0.963				0.332
O–H···N′[a]	**pol**···**dmba**	0.988	2.821	163.9	59.4	
Group **C**	**pol**···**ba**	0.988	1.851	172.9	90.4	
	mb	0.983	1.850	146.8	35.9	
	mbn	0.962				−0.056
	mbm	0.986	2.737	148.5	33.6	
	mbmn	0.962				−0.084
O–H···O″	**bac**	0.968				
Group **D**	**bac**···**bac(a)**[b]	1.003	1.637	178.6		
	bac···**bac(b)**	0.975	1.997	151.7		
		0.986	1.842	144.8		
O–H···O″	**apol**	0.989	1.667	147.9	0.0	0.334
Group **E**	**apoln**	0.963			0.0	
	fpol	0.985	1.743	147.0	0.0	0.358
	fpoln	0.963			0.0	
O–H···O′	**mpol**	0.971	1.761	146.1	30.0	−0.126
Group **F**	**mpoln**	0.962				

[a] Single primed and double primed atom symbols refer to the atom hybridization state;
[b] Planar dimers.

bond length is 0.963 Å, with an exception of **bac** where it is 0.968 Å. The OH bonds in **pol**···**nb** dimers are 0.968 Å long, while in **mpol** and **bac**···**bac(b)** are somewhat longer, 0.971 Å and 0.975 Å, respectively. Then, there is a gap of 0.010 Å to the next nearest of the molecules containing H-bond. The second interval is from 0.984 to 1.003 Å (Table 1, Fig. 2). The non-planar benzoic acid dimer **bac**···**bac(b)** is thus an interesting case with two types of intermolecular H-bonds simultaneously present, O′–H′···O′ (0.975 Å) and O′–H′···O″ (0.986 Å). According to the wavenumber downshift the former is weaker, while their absorptions are equal (Table 2). The longest OH bond is found in the planar **bac**···**bac(a)** dimer and it will be no surprise to learn later that its other characteristics are also extreme.

The bond lengths d_1, d_2, d_3 and d_4 (Scheme 1) can be used to define a resonance parameter $\Delta = 1/2[(\Delta d^o_{3,2} - \Delta d^c_{3,2})/\Delta d^o_{3,2} + (\Delta d^o_{4,1} - \Delta d^c_{4,1})/\Delta d^o_{4,1}]$, where $\Delta d_{ij} = d_i - d_j$ and o and c stand for open and close conformer, respectively [3]. Δ is zero for no bond length differences between the two conformers, and 1 for all four bonds becoming equally long. The values obtained are 0.395 (group **A**), 0.367 and 0.332 (group **B**), −0.056 and −0.084 (group **C**), 0.334 and 0.358 (group **E**), −0.126 (group **F**), what expectedly confirms the greater extent of the π-electron delocalization in the systems with unsaturated substituents.

Instead of discussing the OH bond lengths, the force constant of the OH stretching vibration can equally serve the purpose. Two straight lines can be visualized when the stretching force constant f_{OH} is plotted against the bond length $r(OH)$, one for the molecules with intramolecular H-bond and the other for the H-bonded complexes. At the same time, since it does not depend solely on the force constant f_{OH}, the relationship between the wavenumber $\tilde{v}(OH)$ and the bond length $r(OH)$ is described by a single straight line. In solving normal coordinate problem for a pair of isomers, with and without intramolecular H-bond, in order to ensure valid comparisons between them, the stretching H···O/N has not been used. However, for intermolecular H-bonded complexes, it is practically unavoidable one and the coupling constants $g_{OH,H···O/N}$ and $f_{OH,H···O/N}$, belonging to the **G**- and **F**-matrix, respectively, are non-negligible. This can be also formulated as the question of the strength of coupling between the OH bond stretching and any other internal coordinate. As is well known, within harmonic approximation, this type of coupling is generally weak.

Among the most dramatic manifestations of the H-bond formation are the intensity and frequency changes of the OH stretching band in infrared. It is empirically very well known that the $v(OH)$ band intensity of intramolecular H-bonds is lower when compared with the intermolecular H-bonded dimers. This is nicely reproduced in the present calculations (Table 2). In full agreement with experiment, the $\Delta v(OH)$ in **npol** is 409 cm^{-1}, i.e. four times larger than in the planar **pol**···**nb(a)** dimer. The integrated absorption coefficient in **npol** is two to three times smaller than in the dimer, while greater by the same amount than in **npoln**. In particular, the intensities in **mbm** and **sbm** (E = 712 and 390 km mol^{-1}, respectively) are substantially lower than in the corresponding intermolecular complexes, **pol**···**dmba** and **pol**···**bdma** (1537 and 1578 km mol^{-1}, respectively). The frequency downshifts for **mbm** and **sbm** are 481 and 637 cm^{-1}, respectively, and 539 and 480 cm^{-1} for **pol**···**dmba** and **pol**···**bdma**, respectively. Obviously, if the H-bond strength is measured by ΔE a different order is obtained than if $\Delta v(OH)$ are used. The observation that the intensities in Schiff bases are decreased relative to those in Mannich bases, while the opposite is observed for the H-bonded complexes [6,7] can be attributed to the unfavorable geometries of the σ-skeleton in the former.

One more spectroscopic observable relevant to the present considerations is worth of discussing. Experimentally more complex, although very appealing, is the characterization of the H-bond strength by the frequency of the torsional vibrations $\tau(CO)$ [28]. In the absence of H-bond it is in the interval 410–340 cm^{-1} (356 cm^{-1} in **pol**, 384 cm^{-1} in **npoln**, 399 cm^{-1} in **sbmn**, 409 cm^{-1} in **sbn**, 343 cm^{-1} in **mbmn**, 342 cm^{-1} in **mbn**). When there is an intramolecular H-bond it is found between 870 and 820 cm^{-1} (810 and 792 cm^{-1} in **npol**, 863 cm^{-1} in **sbm**, 863 cm^{-1} in **sb**, 846 and 843 cm^{-1} in **mbm**, 825 cm^{-1} in **mb**), i.e. it is around two times higher. Estimating from the frequency differences (417 cm^{-1} in **npol**, 464 cm^{-1} in **sbm**, 454 cm^{-1} in **sb**, 502 cm^{-1} in **mbm**, 483 cm^{-1} in **mb**), the strongest intramolecular H-bond would be that in **mbm**. The normal modes here assigned to the torsional vibration $\tau(CO)$ are in most cases pure (for example, in **pol** and **sbmn**). This means that sum in Eq. (3) can be reduced to one term only ($(L^X_p)_{\beta,2}$ is around 0.9 for β = H, and for other atoms zero or an order of magnitude smaller).

Concerning the electronic charge redistribution associated with the H-bond formation some interesting aspects emerge from the present analysis. It is important to keep in mind that all the charges and charge fluxes (Tables 3 and 4, S3–S8, Supplemental information) are calculated in local, bond-attached coordinate systems and therefore the obtained values reflect the local environment of an atom what make the comparison of different molecules fully justified. The charges and charge fluxes of other, non-terminal atoms cannot be so directly related to IR band intensities. However, they are related to their positions within the molecular structure.
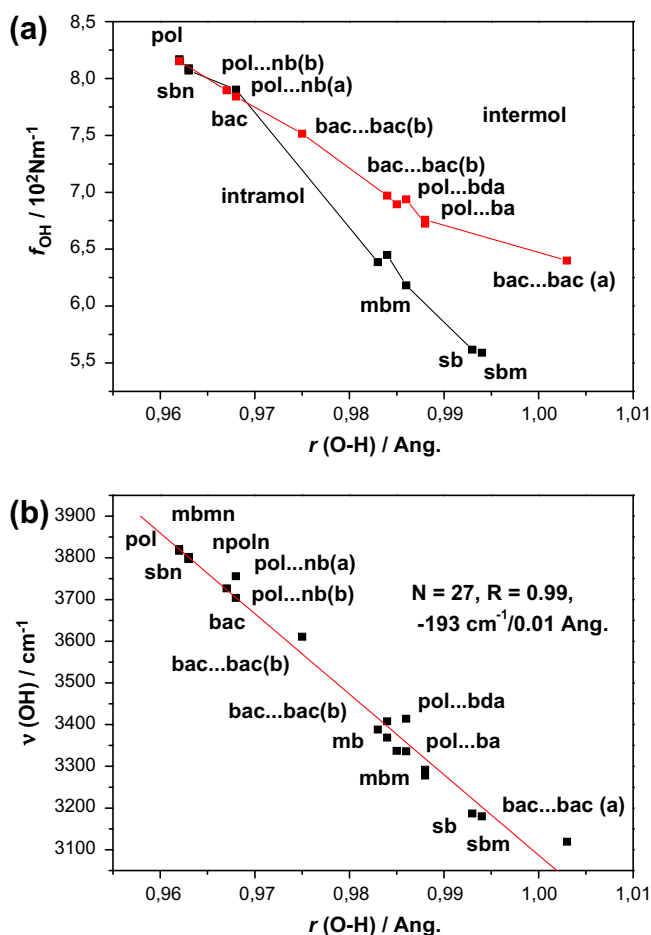

Fig. 2. (a) Longer bond means smaller stretching force constant, but the slope depends on the H-bonding circumstances (force constants were evaluated by solving the normal coordinate problem also in the redundancy-free set of internal coordinates); (b) $\bar{v}(OH)$ decreases linearly (-193 cm^{-1}/0.01 Å, $N = 27$, $R = 0.99$) with $r(OH)$ irrespective of the H-bonding situation.

Table 2
Calculated (B3LYP/cc-pVTZ) and observed wavenumbers (cm^{-1}), stretching force constant k (10^2 N m^{-1}), corrected charges and fluxes for the hydroxyl hydrogen *in vacuo*, integrated absorption coefficients E (km mol^{-1}) for the ν(OH) stretching mode and dipole moments M (debye).

H-bond		ν(OH)$_{calc}$ (Δν)	ν(OH)$_{exp}$ (Δν)	k	σ_H	ϕ_H	E	M
	pol	3817 (0)	3611	8.153	0.315	0.125	56	1.283
O–H···O	**pol···nb(a)**	3704 (113)		7.842	0.267	0.545	779	7.537
Group **A**	**pol···nb(b)**	3727 (90)		7.896	0.290	0.280	540	4.764
	npol	3408 (409)	3252[a] (359)	6.449	0.279	0.206	255	3.571
	npoln	3802 (15)		8.089	0.317	0.096	73	5.635
O–H···N″	**pol···bdma**	3337 (480)		6.895	0.312	0.800	1578	4.025
Group **B**	**pol···bda**	3369 (448)		6.971	0.292	0.754	1634	4.665
	sb	3187 (630)		5.617	0.248	0.344	331	2.551
	sbn	3798 (19)		8.072	0.310	0.124	52	1.963
	sbm	3180 (637)	2764[b] (847)	5.589	0.248	0.422	390	2.382
	sbmn	3797 (20)		8.071	0.309	0.127	50	1.468
O–H···N′	**pol···dmba**	3278 (539)		6.725	0.318	0.788	1537	3.040
Group **C**	**pol···ba**	3292 (525)		6.759	0.257	0.797	1524	3.646
	mb	3388 (429)		6.387	0.270	0.452	531	3.232
	mbn	3821 (−4)		8.169	0.311	−0.119	56	0.418
	mbm	3336 (481)	2970[b] (641) 3020[c]	6.181	0.243	0.617	712	2.812
	mbmn	3819 (−2)		8.161	0.311	−0.117	56	0.969
O–H···O″	**bac**	3756 (61)		7.902	0.321	0.061	90	2.036
Group **D**	**bac···bac(a)**	3119 (698)		6.399	0.259	1.513	6330	0
	bac···bac(b)	3611 (206)[d]		7.514	0.290	0.538	966	3.570
		3414 (403)[e]		6.938	0.251	0.650	966	
O–H···O″	**apol**	3282 (535)		5.959	0.269	0.294	343	3.166
Group **E**	**apoln**	3795 (22)		8.062	0.310	−0.124	53	3.578
	fpol	3367 (450)	3120–3190[f]	6.294	0.275	0.201	249	3.013
	fpoln	3798 (19)		8.075	0.313	−0.108	62	4.195
O–H···O″	**mpol**	3618 (201)	3409[f]	7.311	0.287	0.312	374	2.761
Group **F**	**mpoln**	3821 (−4)	3614[f]	8.168	0.308	−0.110	58	1.283

[a] Gas phase [25].
[b] In CCl$_4^9$.
[c] Gas phase [26].
[d] O–H···O′ H-bond.
[e] O–H···O″ H-bond.
[f] Solution [27].

The charges of carbon atoms C2, C3, C4 and C5 (Scheme 1) deviate, of course, from the benzene carbon values (for benzene (unperturbed aromatic ring) σ_C = 0.13, ϕ_C = 0.11, σ_H = + 0.13, ϕ_H = 0.24), expressing the changes brought by the substituent. The electronic charge distribution around these atoms is thus hardly affected by the formation of an H-bond ring.

In Tables 3 and 4, the atoms H′–O′–C1–C6–C–N′/N″ form a 6-membered ring. In Table S5 (Supplemental information), the ring is made of atoms H′–O′–C1–C6–N–O″ (primed and double primed atom symbols describe the hybridization type). The sum of their charges for the two pairs of neutral planar molecules, **npol** and **npoln** (Table S5, Supplemental information), **sb** and **sbn** (Table 3), indicate that for the former pair, the electronic charge is withdrawn from the group of six atoms when the H-bond is formed ($\Delta\Sigma$ = −0.07), while for the latter pair, the opposite is true ($\Delta\Sigma$ = +0.03). The $\Delta\Sigma$ values can thus serve as a measure of the charge delocalization when the H-bond is formed. For the non-planar systems, **sbm** and **sbmn** (Table S3, Supplemental information), **mb** and **mbn** (Table 4), **mbm** and **mbmn** (Table S4, Supplemental information), $\Delta\Sigma$ = +0.03, −0.01 and −0.15, respectively, but the interpretation in the aforementioned sense is not possible. Similarly, only in the case of planar dimers, the net charge transferred from acceptor to donor is $\sigma(A \rightarrow D) = \sum_{i \in A}\sigma_1 = -\sum_{i \in D}\sigma_i$. Thus, for the planar **pol···nb** dimer, $\sigma(A \rightarrow D)$ = 0.08 (Table S5, Supplemental information). When the two monomers are symmetry related as in the benzoic acid dimer **bac···bac (a)**, they both remain neutral. Although no charge transfer takes place, strong H-bond is formed. The sum of atomic charges of the carboxylic group atoms

in **bac** is −0.08 and in a monomer of **bac···bac** (**a**) −0.06 (Table S8, Supplemental information). The monomer dipole moments are 2.04 D and 1.61 D, respectively.

One of the important and attractive characteristics of the ECCF model is the role played by the charge fluxes. That actually has been demonstrated for *inter*molecular H bonded complexes in a series of papers by Ramos et al. [29,30] and also for *intra*molecular H-bonds within five-membered rings [12]. The main result of the present paper is that such an exceptional role the charge flux has also for the RA *intra*molecular H-bonds. In Tables 3 and 4 and S3–S8 (Supplemental information) the atomic charges, σ, and charge fluxes, ϕ, are arranged so as to enable useful comparisons within a group of similar molecules and also between the groups. When comparing, for example, **sb** and **sbn** (Table 3) or **mb** and **mbn** (Table 4), it is seen that the charge fluxes are, as expected, more sensitive to the H-bond formation than the atomic charges. This remains true also for all other pairs of molecules, **npol** and **npoln**, **sbm** and **sbmn**, **mbm** and **mbmn** (Tables S3–S5, Supplemental information). The hydroxyl group is everywhere present and the corresponding atomic charges, σ_o = −0.32 ± 0.02 and σ_H = +0.28 ± 0.02 (averaged over all the systems) can be considered practically constant. This is very useful property of the model because it emphasizes the role of charge fluxes in generating IR intensities. Since the charge fluxes are directly connected with the vibrational movements of atoms, the fundamental relation, $E_p \propto \left(\frac{\partial M_i}{\partial Q_p}\right)^2$, is here re-stated in a way that enables an intuitive understanding of IR intensity changes upon formation of all types of H-bond including the RA *intra*molecular H-bonds. By comparing,

Table 3
Changes of corrected atomic charges and charge fluxes due to formation of the inter- and intramolecular OH···N″ bond between **pol** and **bda**, and in **sbn** (group **B**).

	pol		pol in pol···bda		bda in pol···bda		bda		sb		sbn	
	σ	φ	σ	φ	σ	φ	σ	φ	σ	φ	σ	φ
H	0.32	−0.12	0.29	0.75					0.25	0.34	0.31	−0.12
O	−0.35	−1.18	−0.35	−1.68					−0.31	−1.03	−0.31	−1.03
C1[a]	0.09	0.35	0.12	0.54	−0.10	0.17	−0.08	0.05	0.14	0.31	0.12	0.39
C6	−0.17	0.00	−0.18	−0.02	−0.04	−0.15	−0.04	−0.08	−0.07	−0.39	−0.05	−0.29
C					0.08	1.27	0.04	1.08	0.06	1.32	0.04	1.12
N″[b]					−0.41	−1.05	−0.41	−0.55	−0.40	−0.69	−0.41	−0.55
H(C)					0.24	−0.18	0.13	−0.34	0.12	−0.30	0.12	−0.34
H(N″)					0.12	−0.31	0.22	−0.23	0.23	−0.19	0.22	−0.25
C2[c]	−0.16	−0.01	−0.17	−0.07	−0.13	0.02	−0.13	0.03	−0.17	−0.17	−0.17	−0.14
C3	−0.12	0.28	−0.13	0.31	−0.10	0.16	−0.12	0.14	−0.10	0.46	−0.11	0.38
C4	−0.16	−0.04	−0.17	−0.04	−0.12	−0.08	−0.14	0.06	−0.17	−0.28	−0.16	−0.16
C5	−0.12	0.30	−0.14	0.34	−0.09	0.08	−0.11	0.13	−0.11	0.40	−0.11	0.32
$\sum$[d]									−0.33		−0.30	

[a] In all the cases presented here, hydroxyl group is bonded to C1 and nitro group bonded to C6. Thus, C1 in **pol** and C6 in **nb** are to be compared, but C1 in **pol** and C1 in **pol···nb**, **npol**, **npoln** and C6 in **nb** and C6 in **pol···nb**, **npol** or **npoln** (Scheme 1).

[b] Nitrogen atom participating in the H-bond.

[c] ∠(C2,C1,O,H) = 180°, ∠(C6,C1,O,H) = 0°, i.e. hydroxyl hydrogen and C2 are at opposite sides of the C1–O bond.

[d] The sum of σs for the first six atoms comprising the H-bond ring.

Table 4
Changes of corrected atomic charges and charge fluxes due to formation of the inter- and intramolecular OH···N′ bond between **pol** and **ba**, and in **mbn** (group **C**).

	pol		pol in pol···ba		ba in pol···ba		ba		mb		mbn	
	σ	φ	σ	φ	σ	φ	σ	φ	σ	φ	σ	φ
H	0.32	−0.12	0.26	0.80					0.27	0.45	0.31	−0.12
O	−0.35	−1.18	−0.33	−1.07					−0.28	−1.19	−0.34	−1.09
C1	0.09	0.35	0.12	0.52	−0.12	0.08	−0.14	0.08	0.11	0.21	0.11	0.30
C6	−0.17	0.00	−0.19	−0.01	−0.08	0.10	−0.02	−0.09	−0.11	−0.18	−0.04	−0.18
C					−0.26	0.67	−0.35	0.80	−0.19	0.63	−0.30	0.77
N′					−0.37	−0.34	−0.08	−0.60	−0.30	−0.32	−0.39	−0.28
H(C)					0.09[a]	−0.25[a]	0.12	−0.25	0.08	−0.27	0.08[a]	−0.26[a]
H(N′)					0.28[a]	−0.26[a]	0.33	−0.33	0.27	−0.27	0.29[a]	−0.30[a]
C2	−0.16	−0.01	−0.17	−0.08	−0.14	0.11	−0.14	0.15	−0.18	−0.06	−0.18	−0.06
C3	−0.12	0.28	−0.13	0.31	−0.13	0.11	−0.14	0.08	−0.13	0.32	−0.13	0.30
C4	−0.16	−0.04	−0.17	−0.04	−0.13	0.09	−0.13	0.17	−0.17	−0.08	−0.17	−0.05
C5	−0.12	0.30	−0.14	0.34	−0.10	0.04	−0.14	0.05	−0.14	0.30	−0.12	0.26
ΔΣ									−0.50		−0.65	

[a] H(C) and H(N′) refer to methylene and amine hydrogen atoms, respectively and the arithmetic mean values are given.

for example, **pol** with **pol** in **pol···nb** and **nb** with **nb** in the same dimer, the changes caused by formation of intermolecular H-bond are coming forth. For example, on going from **pol** to **pol···nb** and from **pol** to **npol**, the atomic charges in the OH bond change, $\Delta\Sigma_O$ = + 0.02 and +0.05, $\Delta\Sigma_H$ = −0.05 and −0.04, respectively. Similar values are found for other cases too. The hydrogen atom becomes less positive when participating in H-bonding.

If only the isomers without internal H-bond are considered, the averaged values for the atomic charge and charge flux are σ_H = 0.312 ± 0.004 and ϕ_H = −0.111 ± 0.020 with E = 61 ± 12 km mol^{-1}. When the atomic charge σ_H is added to the list containing both intra- and intermolecular H-bonds, an overall averaged value σ_H = 0.28 ± 0.02 is obtained. A correlation has been found between the integrated molar absorption coefficient E of the OH stretching vibration and the charge flux ϕ_H (Table 2 and Fig. 3). It is a quadratic growth curve given by $E = (1660 \pm 91) \times (0.28 + \phi_H)^2$ with N = 18 and R^2 = 0.92. Since all the charges and charge fluxes have been calculated in the corresponding local coordinate systems, even the non-planar systems fit in. Having in mind that even eight different H-bond types have been included (intra- and intermolecular O–H···Y, Y = O′, O″, N′ or N″), the correlation nicely demonstrates that the charge flux is the main reason for the increase of the integrated IR intensity upon formation of H-bond. However, this is very simplified picture because the v(OH) band is not only downshifted and intensified, but also very much
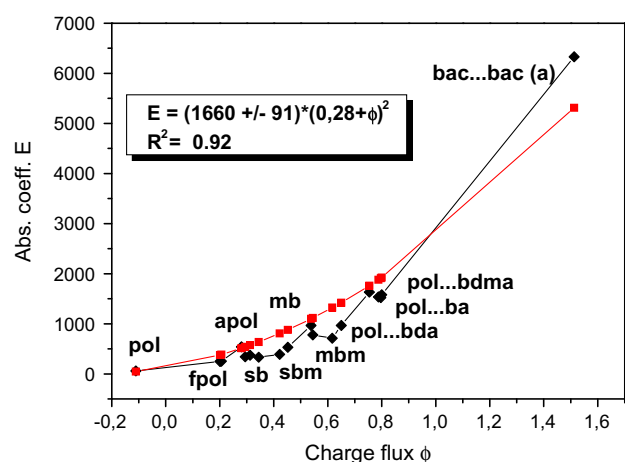
Fig. 3. Charge flux ϕ contributes essentially to the IR intensity changes of the v(OH) vibration.

broader and often accompanied with complicated substructure due to the anharmonic couplings between the high-frequency OH stretching and low-lying COH bending and CO torsion vibrations and a bath of surrounding solvent oscillators. The solvent effects include the changed values of atomic charges and charge fluxes

[12] and most often formation of intermolecular complexes without breaking the intramolecular H-bond [26]. Therefore, the comparison with experimental results is not that straightforward and had to be kept only at qualitative level.

The strength of an H-bond can thus be quantitatively measured by its position on the correlation curve. For five molecules possessing intramolecular H-bond, **mbm** and **mb** with saturated substituents, **npol**, **sbm** and **sb** with unsaturated substituents, the charge flux ϕ_H is 0.617, 0.452, 0.206, 0.422 and 0.344, respectively. Thus, the intramolecular H-bond in **mbm** would be the strongest, in agreement with the scale based on the wavenumber of the torsional vibration $\tau(CO)$. In the same order of molecules, the frequency shifts $\Delta\nu(OH)$ are 481, 429, 409 (350–370 cm^{-1} measured [25]), 637 and 630 cm^{-1} and the H-bonds in **sbm** would be stronger than H-bonds in **mbm**. Of course, and that is a part of the excitement in studying H-bonding, this need not be in agreement with the scale obtained by using, for example, the relative free energies or enthalpies of the two isomers, with and without the internal H-bond. If one is interested in explaining experimental data, the difference has to be taken between the H-bonded and the lowest-energy non-H-bonded conformer because that is quantity measured in spectroscopic experiment [31]. In this work the OH bond was simply pointed away from the acceptor site and the geometry optimization performed. The major conformational change for **mbm** and **mb**, other than in the angle $\angle$(C6,C1,O,H) is the change of the angle $\angle$(C1,C6,C,N) from 45° to 78° in **mbmn** and **mbn**. Similarly, $\angle$(C6,C1,N,O) changes from 0° in **npol** to 28° in **npoln**. The (calculated) free energy differences for **mbm**, **mb**, **npol**, **sbm** and **sb** are 6.2, 6.4, 9.9 (6.2 kcal mol^{-1} measured [21]), 12.2 and 12.6 kcal mol^{-1}, respectively. They refer to the thermodynamical stability of the isomers with H-bonds and can be taken as the measure of the H-bond strength. It is the H-bond that gives the stability to the closed forms like, for example, **mbm** and **sbm**. It is of secondary importance that the energy differences contain not only the H-bond term, but other contributions as well.

Conclusions

The characterization of intramolecular H-bonds in terms of atomic charges and charge fluxes (at the B3LYP/cc-pVTZ level of theory) has been extended to the case of the so called resonance-assisted H-bonds. That strong intermolecular H-bonds are formed only for linear arrangement of XH⋯Y is known as directionality of the H-bond. The angle $\angle$(O–H⋯O/N) in the studied systems has the values 120° and 150° in 5- and 6-membered intramolecular H-bonding rings, respectively. In intermolecular complexes it is most often greater than 170°. The geometrical constraints are relaxed in 6-membered rings relative to 5-memberd rings and the corresponding H-bonds are therefore stronger.

Only in strictly planar molecules, the difference of the sums of the atomic charges of the 6-membered H-bond rings $\Delta\Sigma = \Sigma^{open} - \Sigma^{closed}$ can serve as a measure of the charge delocalization after the H-bond is formed. The electronic charge is withdrawn from the group of six atoms when the H-bond is formed in **npoln** ($\Delta\Sigma = -0.07$), while the opposite is true ($\Delta\Sigma = +0.03$) for **sbn**. The corresponding values of the resonance parameter Δ are 0.39 and 0.37, similar to those found for **apol** and **fpol**. The extent of the π-electron delocalization as measured by the resonance parameter Δ does not follow the strength of H-bond as measured by the charge flux ϕ_H.

As regard to the wavenumber downshifts of the intramolecular H-bonds, they can be larger than in the corresponding intermolecular complexes, while, at the same time, the opposite is true for the intensity enhancements. Quite expectedly, quadratic correlation between the charge fluxes ϕ_H and the molecular IR absorption

coefficients E that includes the entire family of the studied systems containing both intra- and intermolecular hydrogen bonds confirmed the critical importance of the charge fluxes on the IR intensity enhancements. Since they reflect the dependence of the atomic charges on the atomic vibrations, the dynamic nature of hydrogen bonding properties has again been emphasized. The changes of the charge flux of the hydroxyl hydrogen in an RA intramolecular H-bond are between those for "free" OH bonds and the values calculated for intermolecular H-bonds. The transition "free" → intramolecular → intermolecular is gradual and therefore the hydrogen charge flux can be considered as practically sufficient to give quantitative measure to the intuitively obvious statement that "intramolecular H-bonding is somehow in between no H-bonding situation and intermolecular H-bonding" and thus provide a quantitative and yet simple parameterization of H-bond strength.

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.saa.2013.08.024.

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