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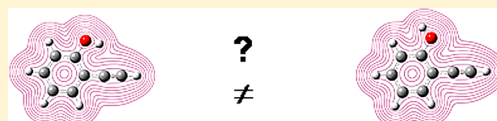
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# Characterization of Intramolecular Hydrogen Bonds by Atomic Charges and Charge Fluxes

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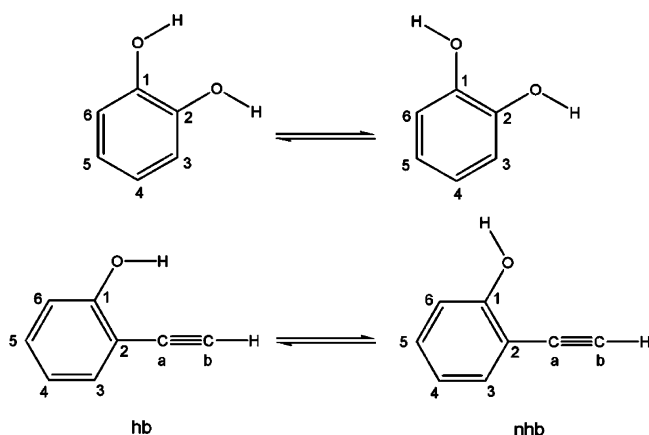
**ABSTRACT:** The electronic charge redistribution and the infrared intensities of the two types of intramolecular hydrogen bonds, O–H $\cdots$ O and O–H $\cdots\pi$ , of *o*-hydroxy- and *o*-ethynylphenol, respectively, together with a set of related intermolecular hydrogen bond complexes are described in terms of atomic charges and charge fluxes derived from atomic polar tensors calculated at the B3LYP/cc-pVTZ level of theory. The polarizable continuum model shows that both the atomic charges and charge fluxes are strongly dependent on solvent. It is shown that their values for the OH bond in an intramolecular hydrogen bond are not much different from those for the “free” OH bond, but the changes are toward the values found for an intermolecular hydrogen bond. The intermolecular hydrogen bond is characterized not only by the decreased atomic charge but also by the enlarged charge flux term of the same sign producing thus an enormous increase in IR intensity. The overall behavior of the charges and fluxes of the hydrogen atom in OH and  $\equiv$ CH bonds agree well with the observed spectroscopic characteristics of inter- and intramolecular hydrogen bonding. The main reason for the differences between the two types of the hydrogen bond lies in the molecular structure because favorable linear proton donor–acceptor arrangement is not possible to achieve within a small molecule. The calculated intensities (in vacuo and in polarizable continuum) are only in qualitative agreement with the measured data.



## 1. INTRODUCTION

Ortho-substituted phenols are very well-known as relatively simple systems occurring in two isomeric forms, one (*hb*) characterized by intramolecular hydrogen bond (H-bond) and the other (*nhb*) in which the hydroxyl group is described as free, i.e., positioned away from the substituent (Scheme 1).<sup>1</sup>

Scheme 1



Apart from the substituent effects, the solvent effects are unseparable part of the complete picture because the solvation and intramolecular H-bonding compete with each other. This has been demonstrated in numerous experimental studies. Nowadays each study of that type involves also use of the available theoretical models as well, especially so if a solvation model has been built in a standard program package for

electronic structure calculations. Such is the case, for example, with the polarizable continuum model (PCM)<sup>2</sup> as implemented in the Gaussian program suite.<sup>3</sup> The competition between solvation and intramolecular H bonding can thus be investigated by means of first-principle calculations. In this work we shall limit ourselves to the study of solvent effects on intramolecular H-bonds. Therefore, no explicit solvent molecules have to be introduced as is the case when intermolecular complexes are studied.

An intramolecular H-bond is different from an intermolecular one in the sense that no additional vibrational degrees of freedom occur in the system, and therefore, it is generally thermodynamically more stable. In other words, due to the smallness of the entropy term, the intramolecular H-bond although being generally weak is frequently observable even in polar solvents and at higher temperatures.<sup>4–6</sup> The corresponding frequency shifts and intensity changes are less dramatic, but still convincingly observable. Because a well-defined reference state is missing, the energy of the intramolecular H-bond is an ill-defined concept.<sup>7,8</sup> However, what can be experimentally more or less accurately measured is a free energy and/or enthalpy difference between the two isomers.<sup>9,10</sup> In performing such temperature studies by using IR spectroscopy, the *nhb* isomer is usually evidenced only by a weak band at the high frequency side of the strong band belonging to the *hb* isomer. Putting it differently, it is very difficult if not impossible to state quantitatively what are the intensity enhancements and bandwidth enlargements due to an intramolecular H-bond.

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The intramolecular H-bonds to be presently studied are those of an O—H group to another O—H group or to the  $\pi$ -system of a triple bond, with related intermolecular H-bonds of the type O—H $\cdots$ O,  $\equiv$ C—H $\cdots$ O, O—H $\cdots\pi$ , or  $\equiv$ C—H $\cdots\pi$ . In such a way *o*-ethynylphenol (EPOL) can be studied as an example of a relatively small molecule capable of acting simultaneously as both H-bond donor and acceptor. To reveal possible differences between the two types of intramolecular H bonds, the results for EPOL will be compared to those for catechol (*o*-hydroxyphenol, COL) in which another type of intramolecular H-bonding is realized (Scheme 1). In spite of the above-mentioned difficulties, we want to answer the following questions: (1) What is the strength of the intramolecular O—H $\cdots\pi$  bond in EPOL? Is it weaker than the intramolecular O—H $\cdots$ O bond in COL? (2) Are there any intensity changes due to changes of solvent? Are they predicted correctly by calculations? (3) Is there any difference in the charge distribution around the hydrogen atom participating in an intramolecular H-bond and the hydrogen atom of an intermolecular H-bond? (4) To what extent the distribution is changed in other parts of EPOL molecule, particularly at the ethynyl hydrogen; i.e., is the ability of EPOL to form an H-bonded intermolecular complex with a suitable acceptor affected by the presence of the intramolecular H-bond?

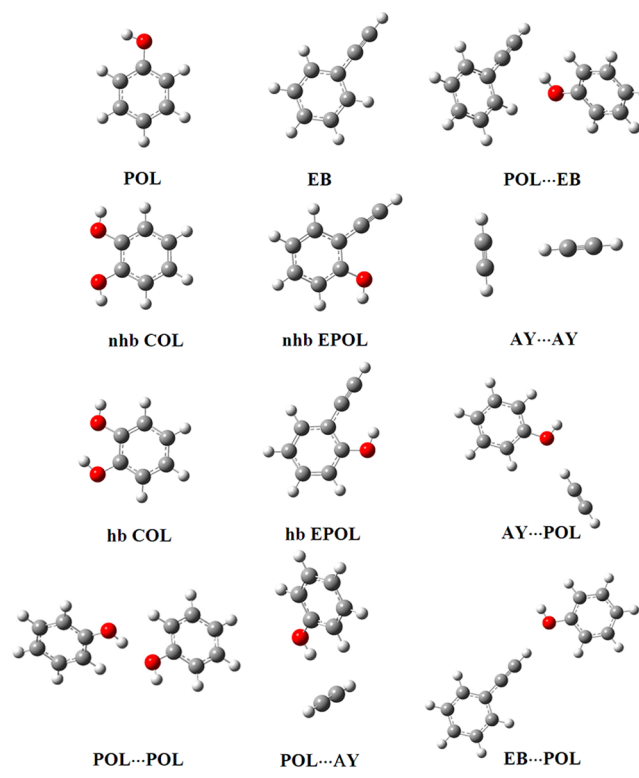
This actually brings us to the motivation for this study which is to attempt characterization of an intramolecular H-bond by means of the atomic charges and intramolecular charge fluxes<sup>11</sup> or, in other words, to decipher the changes of the electronic charge distribution due to formation of an intramolecular H-bond. The underlying assumption is that the corresponding changes can be followed through infrared intensity changes, i.e., the changes in atomic charges and charge fluxes. The latter are obviously worth discussion only if a comparison is made between the two conformers of the same molecule and/or within a group of carefully chosen molecules. With respect to EPOL, phenol (POL) and ethynylbenzene (EB) will be used as reference molecules. As mentioned above, COL is added to compare two types of intramolecular H-bonds, i.e., O—H $\cdots$ O and O—H $\cdots\pi$ . However, to discuss differences between inter- and intramolecular H-bonds, an introduction of six more intermolecular H-bonded dimers (proton donor monomer will always be written first), acetylene $\cdots$ acetylene (AY $\cdots$ AY) with a  $\equiv$ C—H $\cdots\pi$  bond, phenol $\cdots$ acetylene (POL $\cdots$ AY) and POL $\cdots$ EB with O—H $\cdots\pi$  bonds, AY $\cdots$ POL and EB $\cdots$ POL with  $\equiv$ C—H $\cdots$ O bonds, and finally the POL $\cdots$ POL dimer with an O—H $\cdots$ O bond, turned out to be very instructive (Scheme 2).

The theoretical predictions based on the density functional theory and the polarizable continuum model will be contrasted with experimental findings only for intramolecular H-bonding systems EPOL and COL, and for the reference molecules POL and EB in a series of solvents capable of forming only very weak, if any, H-bonds with the solutes [three nonpolar (petroleum ether, CCl<sub>4</sub>, and C<sub>2</sub>Cl<sub>4</sub>) and two polar, (CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub>)].

## 2. MATERIALS AND METHODS

**2.1. Experimental Section. Synthesis and Spectra Recording.** *o*-[(Trimethylsilyl)ethynyl]phenol was first synthesized starting from *o*-iodophenol and then EPOL according to Scheme 3. All other compounds and solvents (petroleum ether, CCl<sub>4</sub>, C<sub>2</sub>Cl<sub>4</sub>, CHCl<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub>) were obtained commercially and purified by standard methods. At least five low-

Scheme 2

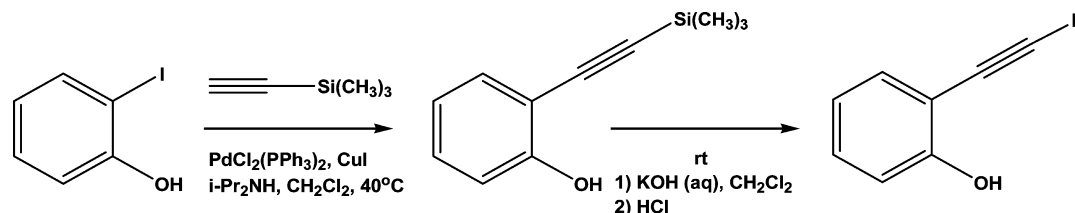


concentrated solutions (minimizing thus the probability of forming intermolecular complexes between solute molecules) of EB, EPOL, POL, and COL were prepared. The spectra were recorded with a Bomem MB102 spectrometer equipped with CsI optics and DTGS detector. The cell path lengths were determined interferometrically or by using secondary standards as described by Bertie et al.<sup>12</sup>

**Definitions of Terms and Analysis of Spectra.** By writing the Lambert–Beer law in the form  $\alpha = \epsilon \cdot C \cdot d$ , we define  $E \equiv \int \epsilon d\tilde{\nu} = 1/(C \cdot d) \int \alpha d\tilde{\nu} \equiv A/(C \cdot d) \equiv K/C$ . From the measured integrated absorbance values,  $A$  (cm<sup>-1</sup>), of a band, the integrated molar absorption coefficient  $E$  (mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-2</sup> = 10<sup>-2</sup> km mol<sup>-1</sup>) was determined by assuming that the integrated linear absorption coefficient  $K \equiv A/d$  (cm<sup>-2</sup>) depends linearly or quadratically on the analytical concentration  $C_0$  (mol dm<sup>-3</sup>). The analogous quantities measured at the band maximum are  $\alpha_m$ ,  $\epsilon_m$  (mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup> = 10<sup>-7</sup> km<sup>2</sup> mol<sup>-1</sup>) and  $\kappa_m \equiv \alpha_m/d$  (cm<sup>-1</sup>). To obtain them, the spectra have to be baseline corrected by drawing a tangent line to eliminate the contribution of neighboring (broad) bands. We have also used the apparent molar absorption coefficient  $\epsilon_{app} \equiv C/C_0 = (\kappa_m/C)_0$  where  $C_0$  is the initial (analytical) concentration. When  $C_0 \rightarrow 0$ ,  $\epsilon_{app}$  is expected to show linear behavior and the slope of  $\kappa_m$  at very low  $C_0$  should give  $\epsilon_m$ .

**Calculations.** All electronic structure calculations were performed by using the Gaussian suite of programs.<sup>3</sup> Molecular structures, vibrational frequencies, and IR intensities were determined at the B3LYP/cc-pVTZ and B3LYP/aug-cc-pVTZ levels of theory (three parameter exchange functional B3 of Becke<sup>13</sup> with the LYP correlation functional<sup>14</sup> and the correlation consistent basis sets of triple- $\zeta$  quality<sup>15</sup>). The use of the enlarged basis set aug-cc-pVTZ did not substantially improve the quality of the infrared intensity predictions; i.e., the results are more or less the same as for the cc-pVTZ basis set.

Scheme 3



What was different were the corrected charges and fluxes. For example, the corrected charge for the hydroxyl hydrogen in POL...AY dimer turned out to be negative and that, of course, should not be acceptable. This has to be traced back to the well-known fact that Mulliken charges do not converge to constant values by enlarging the basis set, particularly not by adding diffuse basis functions as has been attempted here. Although that was the only anomalous case for all the studied systems, it rendered the use of the augmented basis set in this study impractical.

The effects of solvent (only the dielectric constant value of  $\epsilon = 8.93$  corresponding to dichloromethane was considered) on the systems with intramolecular H-bond were studied within the polarizable continuum model (PCM)<sup>2</sup> with the same functional and the basis set. The Bondi atomic radii<sup>16</sup> (frequently used set of van der Waals radii) were used to build a cavity that contained the solute molecule. The cavity thus built follows closely the molecular shape and takes care about the hydrogen atoms what is obviously important when H bonding is studied.

**2.2. Partition of Atomic Polar Tensors.** Derivatives of a dipole moment over Cartesian atom coordinates for a molecule in the so-called standard orientation system (SOS) and infrared intensities are supplied by default as a part of frequency calculation.<sup>3</sup> An atomic polar tensor (APT) for a particular atom is formed by arranging the corresponding derivatives (all calculated at the equilibrium geometry) in a  $3 \times 3$  matrix:<sup>17,18</sup>

$$\mathbf{P}^\beta = \begin{pmatrix} \frac{\partial M_x}{\partial x_\beta} & \frac{\partial M_x}{\partial y_\beta} & \frac{\partial M_x}{\partial z_\beta} \\ \frac{\partial M_y}{\partial x_\beta} & \frac{\partial M_y}{\partial y_\beta} & \frac{\partial M_y}{\partial z_\beta} \\ \frac{\partial M_z}{\partial x_\beta} & \frac{\partial M_z}{\partial y_\beta} & \frac{\partial M_z}{\partial z_\beta} \end{pmatrix} \quad \text{or} \quad P_{ij}^\beta = \frac{\partial M_i}{\partial x_{\beta,j}}$$

$i, j = 1, 2, 3; \quad \beta = 1, \dots, N$

(We shall interchangeably use  $x_{\alpha,1}$  and  $x_{\alpha,2}$  and  $y_{\alpha}$   $x_{\alpha,3}$  and  $z_{\alpha}$ ).

An approach that has proved itself rather fruitful (this is the branching point for various approaches in interpretation of IR intensities) is to write the molecular dipole moment as a sum over atomic charges and positions,  $\mathbf{M} = \sum_{\alpha} q_{\alpha} \mathbf{r}_{\alpha}$  or  $\mathbf{M} = \sum_{\alpha} q_{\alpha} x_{\alpha,i}$  ( $i = 1-3$ ). Such a representation in which the charges are functions of atomic positions leads to the following partitioning of the APT:

$$\mathbf{P}^\beta = q_\beta^{(0)} \mathbf{I} + \sum_{\alpha} \mathbf{r}_{\alpha}^{(0)} (\nabla_{\beta} q_{\alpha})^{(0)} \quad \alpha, \beta = 1, \dots, N \quad (1)$$

(at the equilibrium positions, the superscript (0) will sometimes be omitted below). The charges and charge fluxes

occurring above are directly related to the experimentally derived charges and charge fluxes (ECCF).<sup>19</sup> However, the relation to the calculated charges and fluxes is not that straightforward. As shown by King and Mast,<sup>20</sup>

$$\mathbf{P}^\beta = \zeta_\beta \mathbf{I} + \sum_{\alpha} \mathbf{r}_{\alpha} \nabla_{\beta} \zeta_{\alpha} - \sum_{\alpha} \nabla_{\beta} \Phi_{\alpha\alpha} \quad (2)$$

where  $\zeta_\beta$  is Mulliken charge of atom  $\beta$  and the corresponding charge derivatives can be numerically calculated. The last term is known as the overlap tensor and as such has no classical counterpart. There are other ways to assign charges to atoms in a molecule, but only the Mulliken charges enable a satisfactory relationship to measured IR intensities to be made, as extensively discussed by Gussoni et al.<sup>11</sup> Let us write an APT as  $\mathbf{P}^\beta = \mathbf{P}^\beta(\text{C}) + \mathbf{P}^\beta(\text{CF}) + \mathbf{P}^\beta(\text{O})$ . The overlap term is not directly calculated but is obtained as the difference between  $\mathbf{P}^\beta$  and the sum of the two other terms. As stated by Choi and Kertesz, the charges  $q$  and  $\zeta$  are different and "there is no a priori reason that the Mulliken charge  $\zeta$  and [its] charge flux terms should be consistently similar to the classical concept of charge and charge flux irrespective of the basis set".<sup>21</sup>

To make the results of the above calculations directly comparable with the experimental results, the overlap term has to be somehow absorbed into the two first terms; i.e., to be compared with the experimental charges  $q_{\alpha}(0)$ , the corrected charges  $\sigma_\beta$  have to be defined such that  $\sum_{\alpha} \sigma_{\alpha} = 0$ ,  $\mathbf{M} = \sum_{\alpha} \sigma_{\alpha} \mathbf{r}_{\alpha}$  and therefore

$$\mathbf{P}^\beta = \sigma_\beta \mathbf{I} + \sum_{\alpha} \mathbf{r}_{\alpha} \nabla_{\beta} \sigma_{\alpha} \quad (3)$$

From eq 2 and 3 it is obtained

$$\sigma_\beta^{(0)} \delta_{ij} = \zeta_\beta^{(0)} \delta_{ij} - \sum_{\alpha} x_{\alpha,i}^{(0)} \left( \frac{\partial (\sigma_{\alpha} - \zeta_{\alpha})}{\partial x_{\beta,j}} \right)^{(0)} - \sum_{\alpha} \left( \frac{\partial \Phi_{\alpha\alpha,i}}{\partial x_{\beta,j}} \right)^{(0)} \quad (4)$$

The problem we want to solve is to find  $\sigma_\beta$  charges and their derivatives if  $\mathbf{P}^\beta$ ,  $\zeta_\beta$  and their derivatives have been calculated. That is generally not possible to do without additional assumptions. When a molecule possesses planar equilibrium configuration<sup>19,22</sup> and, therefore, for example,  $x_{\alpha,2}^{(0)} \equiv y_{\alpha}^{(0)} = 0$  for all  $\alpha$ , one obtains from eq 4 and for  $i = j = 2$

$$\sigma_\beta^{(0)} = \zeta_\beta^{(0)} - \sum_{\alpha} \left( \frac{\partial \Phi_{\alpha\alpha,2}}{\partial x_{\beta,2}} \right)^{(0)} = P_{22}^\beta \quad (5)$$

Also, from eq 4 and for  $j \neq i = 2$ , the overlap term turns out to be zero,  $\sum_{\alpha} (\partial \Phi_{\alpha\alpha,2} / \partial x_{\beta,i})^{(0)} = 0$ . However, by symmetry,  $(\partial \sigma_{\alpha} / \partial x_{\beta,2})^{(0)} \equiv (\partial \sigma_{\alpha} / \partial y_{\beta})^{(0)} = 0$ ,  $(\partial \zeta_{\alpha} / \partial y_{\beta})^{(0)} = 0$ , and  $\sigma_\beta^{(0)} \delta_{i,2} - \zeta_\beta^{(0)} \delta_{i,2} - \sum_{\alpha} (\partial \Phi_{\alpha\alpha,i} / \partial x_{\beta,2})^{(0)}$  or  $\sum_{\alpha} (\partial \Phi_{\alpha\alpha,i} / \partial x_{\beta,2})^{(0)} = 0$  for  $i \neq$

**Table 1. Bond Lengths (Å) and Angles of the Studied Systems at the B3LYP/cc-pVTZ Level of Theory Relevant to the H-Bond Formation**

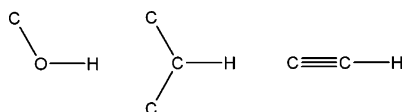
H-bond		$r(\text{O—H})$	$r(\equiv\text{C—H})$	$r(\text{C}\equiv\text{C})$	$r(\text{H}\cdots\text{O}/\text{C})$	$\angle(\text{O—H}\cdots\text{O}/\pi)$
O—H $\cdots$ O	POL	0.962				
	<i>nhb</i> COL	0.962				
	<i>hb</i> COL	0.961 <sup>a</sup>				
		0.965 <sup>b</sup>			2.146	113.6
O—H $\cdots$ O	POL $\cdots$ POL	0.962 <sup>a</sup>				
		0.969			1.925	171.6
O—H $\cdots\pi$	EB		1.061	1.202		
	<i>nhb</i> EPOL	0.963	1.061	1.202		
	<i>hb</i> EPOL	0.967	1.061	1.204	2.284 <sup>f</sup>	126.9 <sup>e</sup>
	POL $\cdots$ AY	0.966	1.063	1.197	2.464	177.1 <sup>e</sup>
O—H $\cdots\pi$	POL $\cdots$ EB	0.968	1.062	1.204	2.388 <sup>g</sup>	177.2 <sup>e</sup>
	AY		1.062	1.196		
$\equiv\text{C—H}\cdots\pi$	AY $\cdots$ AY		1.061 <sup>a,c</sup>			
			1.064 <sup>b,c</sup>	1.197	2.898	180.0 <sup>e</sup>
			1.062 <sup>a,d</sup>	1.196 <sup>d</sup>		
$\equiv\text{C—H}\cdots\text{O}$	AY $\cdots$ POL	0.962	1.066 <sup>b</sup>	1.197	2.289	175.7 <sup>h</sup>
$\equiv\text{C—H}\cdots\text{O}$	EB $\cdots$ POL	0.962	1.065	1.203	2.309	173.6 <sup>h</sup>

<sup>a</sup>Hydrogen atom not participating in the H-bond. <sup>b</sup>Hydrogen atom participating in the H-bond. <sup>c</sup>Monomer donor. <sup>d</sup>Monomer acceptor. <sup>e</sup>The angle O—H $\cdots$ center of the triple bond. <sup>f</sup>Shorter of the two H $\cdots$ C distances; the longer one is 2.737 Å. <sup>g</sup>Shorter of the two H $\cdots$ C distances; the longer one is 2.490 Å. <sup>h</sup>The angle  $\angle(\equiv\text{C—H}\cdots\text{O})$ .

2. Thus, for every atom of a planar molecule  $P_{1,2}^\beta = P_{2,1}^\beta = P_{2,3}^\beta = P_{3,2}^\beta = 0$ .

Because  $\mathbf{P}^\beta$  is a tensor, it is straightforward to evaluate it in any other Cartesian system. Of particular interest is a system defined by a specific bond that has the atom  $\beta$  at its end. For example, we will be interested in the following structural motifs of generally nonplanar molecules:

#### Scheme 4



Suppose that we are interested in an O—H bond Scheme 4. A bond attached system (BAS) is defined such that the O—H bond is along the Ox axis. The Oy axis is perpendicular to the plane defined by the bond and a third atom. The Ozx plane is thus a local symmetry plane and  $y_\alpha = 0$  for all  $\alpha \in \text{motif}$ . Again, the component  $P_{yy}^H$  is the static charge of the hydrogen atom, and the component  $P_{xx}^H$  describes how much the stretching of the X—H bond affects the total dipole moment. It is separated into two contributions, one from the motion of the hydrogen atomic charge  $P_{yy}^H$  and another from the charge flux, i.e., the change of that charge when it moves. For a planar molecule or for any planar part of a nonplanar molecule it is thus possible to rigorously redefine the Mulliken charge by adding one of the diagonal overlap terms, achieving thus unambiguous correspondence with the empirically determined charges and fluxes.<sup>23</sup> All the atomic charges to be discussed further on are the corrected Mulliken charges in the unit of elementary charge  $e$  that will be omitted.

The procedure that has been here applied to extract the dominant intensity terms was the following. Starting from the expression for the intensity of the  $p$ th fundamental transition:

$$A_p \propto \left| \frac{\partial \mathbf{M}}{\partial Q_p} \right|^2 = \sum_{i=1,2,3} \left( \frac{\partial M_i}{\partial Q_p} \right)^2 \quad (4)$$

the relationship that was further used was

$$\begin{aligned} \frac{\partial M_i}{\partial Q_p} &= \sum_{\beta,j} \frac{\partial M_i}{\partial x_{\beta,j}} \frac{\partial x_{\beta,j}}{\partial Q_p} \\ &\equiv \sum_{\beta,j} P_{ij}^\beta L_{(\beta,j)p}^X \\ &\equiv \sum_{\beta,j} (P_{ij}^\beta(\text{C}) + P_{ij}^\beta(\text{CF})) L_{(\beta,j)p}^X \\ &\equiv \sum_{\beta,j} \left( \sigma_\beta \delta_{ij} + \sum_\alpha x_{\alpha,i} \frac{\partial \sigma_\alpha}{\partial x_{\beta,j}} \right) L_{(\beta,j)p}^X \end{aligned}$$

where all the quantities are calculated at the equilibrium structure and in one and the same coordinate system. As already discussed, for planar molecules simplifications are possible. If  $x_{\alpha,2} \equiv y_\alpha = 0$  for all  $\alpha$ ,  $\partial M_2 / \partial Q_p \equiv \sum_{\beta,j} P_{2,j}^\beta L_{(\beta,j)p}^X = \sum_{\beta} \sigma_\beta L_{(\beta,2)p}^X$  and because  $L_{(\beta,2)p}^X = 0$  for in-plane (Ozx) modes, only for an out-of-plane mode can the intensity be proportional solely to the square of the atomic charge(s). For the normal modes that are dominantly X—H stretchings in their character, a few  $L^X$ -components will contribute multiplied by APT components that contain nonzero charge flux term:

$$\begin{aligned} \frac{\partial M_1}{\partial Q_p} &= \sum_{\beta,j} (P_{1,j}^\beta(\text{C}) + P_{1,j}^\beta(\text{CF})) L_{(\beta,j)p}^X \\ &= \sum_{\beta} (P_{1,1}^\beta(\text{C}) + P_{1,1}^\beta(\text{CF})) L_{(\beta,1)p}^X \\ &\quad + \sum_{\beta} P_{1,3}^\beta(\text{CF}) L_{(\beta,3)p}^X \end{aligned}$$

The APT element in the last term need not be zero for terminal hydrogen atoms, but the  $L^X$ -component is practically zero. This



**Table 2. Calculated Wavenumbers (cm<sup>-1</sup>), Integrated Absorption Coefficients (km mol<sup>-1</sup>), Dipole Moments (Debye) (B3LYP/cc-pVTZ), and Corrected Charges and Fluxes for the Hydroxyl Hydrogen in Vacuo for the  $\nu(\text{OH})$  Stretching Mode**

H-bond		$\nu(\text{O-H})$ ( $\Delta\nu$ ) <sup>a</sup>	$k^b$	$\sigma_{\text{H}}$	$\phi_{\text{H}}$	$E^c$	$M^d$
	POL	3817 (0)	8.153	0.315	-0.125	56	1.283
	<i>nbb</i> COL	3818 (-1) <sup>e</sup>	8.159	0.315	-0.121	51 <sup>f</sup>	1.049
	AY...POL	3816 (1)		0.309	-0.103	61	1.678
	EB...POL	3816 (1)		0.305	-0.102	59	1.220
	<i>nbb</i> EPOL	3814 (3)	8.142	0.315	-0.102	66	1.963
O-H...O	<i>hb</i> COL	3835 <sup>g</sup> (-18)	7.995	0.321	-0.100	74	2.367
		3780 <sup>h</sup> (37)	8.227	0.304	-0.039	92	
O-H...O	POL...POL	3819		0.331	-0.106	68	3.417
		3676		0.314	0.408	733	
O-H... $\pi$	POL...AY <sup>i</sup>	3734 (82)		0.275	0.272	394	1.936
O-H... $\pi$	POL...EB <sup>i</sup>	3706 (111)		0.288	0.244	452	2.053
O-H... $\pi$	<i>hb</i> EPOL	3724 (93)	7.761	0.282	-0.021	78	0.757

<sup>a</sup>Frequency shifts relative to POL. <sup>b</sup>OH stretching force constant, in 10<sup>2</sup> N m<sup>-1</sup>. <sup>c</sup>Integrated molar absorption coefficient, in mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-2</sup> = 10<sup>-2</sup> km mol<sup>-1</sup>. <sup>d</sup>Total dipole moment, in Debyes. <sup>e</sup>Antisymmetric OH stretching. <sup>f</sup>Half of the intensity of the antisymmetric O-H stretching mode. <sup>g</sup>Hydrogen atom not participating in the H-bond. <sup>h</sup>Hydrogen atom participating in the H-bond. <sup>i</sup>The O-H... $\pi$  bond with AY perpendicular to POL in POL...AY and with POL and EB planes only nearly perpendicular in POL...EB.

**Table 3. Calculated Wavenumbers (cm<sup>-1</sup>), Integrated Absorption Coefficients, Dipole Moments (B3LYP/cc-pVTZ), Corrected Mulliken Charges, and Charge Fluxes for Ethynyl Hydrogen ( $\nu(\equiv\text{CH})$  Stretching Mode)**

H-bond		$\nu(\equiv\text{C-H})$ ( $\Delta\nu$ ) <sup>a</sup>	$k^b$	$\sigma_{\text{H}}$	$\phi_{\text{H}}$	$E$	$M$
	AY	3415 (0) <sup>c</sup>	6.393	0.214	-0.008	89	0
	EB	3470 (0)	6.409	0.217	0.031	92	0.724
	<i>nbb</i> EPOL	3472 (-2)	6.416	0.218	0.027	90	1.963
O-H... $\pi$	POL...AY	3406 (9)	6.358	0.220	0.009	106	1.936
O-H... $\pi$	<i>hb</i> EPOL	3466 (4)	6.394	0.227	0.036	109	0.757
O-H... $\pi$	POL...EB	3461 (9)	6.376	0.228	0.035	111	2.053
$\equiv\text{C-H...}\pi$	AY...AY	3411 <sup>d</sup> (4)	6.378	0.211	0.004	96	0.328
		3396 <sup>e</sup> (19)	6.395	0.215	-0.011	170	
			6.300	0.186	0.170		
$\equiv\text{C-H...O}$	AY...POL	3381 <sup>f</sup> (34)	6.393	0.216	-0.010	274	1.678
			6.245	0.170	0.320		
$\equiv\text{C-H...O}$	EB...POL	3420 (50)	6.266	0.168	0.415	374	1.220

<sup>a</sup>In the first seven rows frequency shifts (in parentheses) are relative to the AY value. In the last five rows, relative to the EB value. <sup>b</sup>OH stretching force constant, in 10<sup>2</sup> N m<sup>-1</sup>; <sup>c</sup>Antisymmetric CH stretching of acetylene; <sup>d</sup>Antisymmetric CH stretching of the acceptor; <sup>e</sup>Hydrogen atom not participating in the H-bond; <sup>f</sup>Hydrogen atom participating in the H-bond; <sup>g</sup>Antisymmetric CH stretching of the donor.

simplification is preserved for all local systems attached to any of the bonds. The advantage of using local systems is in the possibility of directly comparing charges and charge fluxes of a particular bond to those of the others in the same or different molecules.

As a special case of the general one described above, for a two-atomic molecule X-H that either is free or is in an H-bonded complex the intensity of its stretching is given by  $A_{\text{str}} \propto |q_{\text{H}}^{(0)} + (\partial q_{\text{H}} / \partial r_{\text{XH}})^{(0)} r_{\text{XH}}^{(0)}|^2$ . The charge flux term is strongly affected by complexation and if both terms are of the same sign after complexation, the intensity increase takes place.<sup>24</sup> In polyatomic molecules such is the case of a terminal hydrogen atom and the corresponding stretching vibration and the intensity expression can be approximately reduced to this simple relationship. However, it will be later shown that not only the charge flux but also the charge itself is strongly affected by complexation.

### 3. RESULTS AND DISCUSSION

First we will discuss the results of calculations and then compare them with the experimental data. The perusal of Table 1 shows that the O-H bond length increases relative to that of

POL upon H-bond formation by only 0.005 Å. The slight lengthening of the  $\equiv\text{C-H}$  bond is found in AY...AY and EB...POL complexes, whereas the C $\equiv$ C bonds remain practically unaltered. Other geometry changes concern the valence angles  $\angle\text{C-C}\equiv\text{C}$  (180.0° in EB, 178.7° in *nbb* EPOL, 176.5° in *hb* EPOL) and  $\angle\text{C-C-O}$  (117.3° in *nbb* COL, 115.3° and 120.6° in *hb* COL). Thus, the calculated energy of the intramolecular H-bond in these systems identified as the free energy difference  $\Delta G = G_{\text{hb}} - G_{\text{nbb}}$  between the two conformers also contains the contributions due to the changed valence angles. These differences in vacuo are -4.178 and -3.311 kcal mol<sup>-1</sup> for COL and EPOL, respectively. The corresponding values in dichloromethane (with all non-electrostatic terms included) are -2.898 and -1.161 kcal mol<sup>-1</sup> for COL and EPOL, respectively. The EPOL value is small, suggesting an observable shift of the equilibrium *hb*  $\rightleftharpoons$  *nbb* to the right even around room temperature. Thus, these results indicate a stronger intramolecular H-bond in COL than in EPOL. We will see later that, when other indicators are taken into account, the answer to this question cannot be conclusive.

As detailed in the previous paragraph, when atomic charges and charge fluxes are discussed, it is important to specify the normal mode. Though only  $\sigma_{\text{H}}$  is enough to explain intensities

of an out-of-plane mode, both  $\sigma_H$  and  $\phi_H$  (charge flux) are needed to explain intensity enhancements of in-plane modes (Tables 2 and 3). In other words, for a planar molecule  $\phi_H = P_{2,2}^\beta(\text{CF}) = 0$ . However, for the intensity of the in-plane stretching  $\nu(\text{OH})$ ,  $P_{1,1}^\beta$  (and very often  $P_{1,3}^\beta$ ), with  $\phi_H = P_{1,1}^\beta(\text{CF}) \neq 0$  are responsible. In the case of nonplanar dimers (as are here considered POL...AY and POL...EB dimers), all the corrected charges and fluxes cannot be obtained by staying in only one, no matter how chosen, coordinate system. However, because all the atoms are locally in the planar surroundings, each APT can be calculated in the corresponding BAS, and the corrected charges and fluxes have physical meaning.

Accepting the (calculated) frequency downshift  $\Delta\nu$  (Tables 2 and 3) as a measure of the H-bond strength, it is observed that the frequency scale is generally consistent with the intensity scale. The exception is *hb* EPOL (Table 2) with its  $\Delta\nu$  comparable to those of intermolecular complexes, but with the predicted intensity 5–6 times weaker than in the H-bonded complexes. For the intensity increase in the complexes the corresponding charge flux term being positive and an order of magnitude greater in the absolute value can be taken as responsible. The reasons for such a behavior may be rationalized in terms of geometry differences. The distance from H to the center of the  $\text{C}\equiv\text{C}$  bond in *hb* EPOL is 2.448 Å with the concomitant deviation of the  $\angle\text{C}-\text{C}\equiv\text{C}$  angle from 180° by 3.5°. Thus, it can hardly be shorter without additional energetically very costly molecular deformations. The same distance in the intermolecular complex POL...EB (POL...AY) is 2.364 (2.391) Å, i.e., shorter by 0.084 (0.057) Å, a value that is reached without any significant intramolecular deformations of the monomers. For the angle  $\angle(\text{O}-\text{H}\cdots\text{C}\equiv\text{C} \text{ center})$  the same value of 177° is found for both complexes. At the same time, the angle between the normal of the  $\text{C}-\text{O}-\text{H}$  plane and the triple bond in the mentioned complex is 14° (0°), whereas in *hb* EPOL it is 90°; i.e., the H-bond is parallel to the molecular plane.

The increase of the O–H stretching intensity (Table 2) is not solely due to the charge-flux term. The charges  $\sigma_H$  of hydroxyl hydrogen atoms are always positive whereas the charge fluxes  $\phi_H$  are negative except in the intermolecular H-bonds. For example, for POL (no H-bond), *hb* EPOL (intramolecular H-bond) and POL...AY (intermolecular H-bond) they are –0.125, –0.021, and +0.273, respectively. The average values of atomic charges  $\sigma_H$  (Table 2) are  $0.29 \pm 0.02$  (*hb*) and  $0.32 \pm 0.02$  (*nbb*). Both values are in fair agreement with those obtained with a different functional and similar basis set (PBE1PBE/aug-cc-pVTZ<sup>25</sup>). The  $\sigma_H$  value for AY (0.214) in Table 3 is fairly close to the one obtained at the HF/6-31G(d, p) level.<sup>26</sup> To a limited extent, atomic charges can thus be considered as transferable between different molecules but not between a molecule and its H-bonded complex or between its *nbb* and *hb* isomers.

The ethynyl hydrogen atom has a positive  $\phi_H$  whenever it is H-bonded (Table 3). Because negative (positive) flux means covalent (ionic) bond,<sup>21</sup> the bond character changes only upon formation of inter- or intramolecular H-bond. A charge flux term is generally a weighted sum of charge derivatives and simple interpretation that the charge increases when  $\phi_H > 0$  is possible only in the simplest cases.

In the case of H-bonded complexes, the net charge transferred from the donor to the acceptor can be evaluated by calculating either of the sums  $\sum_{\beta \in \text{donor}} \sigma_\beta^{(0)}$  or  $\sum_{\beta \in \text{acceptor}} \sigma_\beta^{(0)}$ .

For the AY...AY ( $\equiv\text{C}-\text{H}\cdots\pi$ ), POL...AY ( $\text{O}-\text{H}\cdots\pi$ ), AY...POL ( $\equiv\text{C}-\text{H}\cdots\text{O}$ ), POL...EB ( $\text{O}-\text{H}\cdots\pi$ ), EB...POL ( $\equiv\text{C}-\text{H}\cdots\text{O}$ ), and POL...POL ( $\text{O}-\text{H}\cdots\text{O}$ ) complexes the values for the donors are –0.022, –0.083, –0.033, –0.012, –0.033, and –0.063, respectively; i.e., proton acceptors lose charge to donors. The value obtained for POL...AY is an order of magnitude greater than the one obtained within the natural-bond-orbital analysis at the B3LYP/6-311++G(d,p) level of theory.<sup>27</sup> However, they fairly well agree with the corresponding sums of Mulliken charges, particularly the value of –0.038 that has been calculated for the AY...AY dimer at the MP2/6-311++G(d,p) level.<sup>28</sup>

The changes in the electron charge distribution upon formation of an intra- or intramolecular H-bond is seen from the differences in atomic charges (Tables 4 and 5). As expected,

**Table 4. Changes of Corrected Atomic Charges Due to the Intramolecular H-Bond Formation in EPOL**

	<i>nbb</i> EPOL	<i>hb</i> EPOL	$\Delta(\text{nbb}-\text{hb})$
C 1 <sup>a</sup>	0.10	0.11	–0.01
O 1	–0.32	–0.31	–0.01
H 1	0.31	0.28	0.03
C 2	–0.01	–0.02	0.01
Ca	–0.03	–0.03	–0.00
Cb	–0.26	–0.27	0.01
Hb	0.22	0.23	–0.01
C 3	–0.09	–0.10	0.01
C 4	–0.15	–0.15	0.00
C 5	–0.11	–0.11	–0.00
C 6	–0.17	–0.16	–0.01
H 3	0.12	0.12	–0.00
H 4	0.14	0.14	0.00
H 5	0.13	0.13	0.01
H 6	0.14	0.14	–0.00

<sup>a</sup>Atom numeration as recommended by chemical nomenclature (substituent is at position 1, ortho is position 2, etc. (Scheme 1)).

significant changes are limited to the positions 1, whereas the other positions remain practically unaffected. They are several times smaller than the changes induced by solvation (Table 6 and 7). A molecule embedded in a dielectric has a dipole

**Table 5. Changes of Corrected Atomic Charges of POL Due to Formation of the Intermolecular O–H... $\pi$  Bond between POL and AY**

	POL	POL...AY	$\Delta$
C 1 <sup>a</sup>	0.09	0.12	–0.03
O 1	–0.35	–0.36	0.01
H 1	0.32	0.27	0.05
C 2	–0.17	–0.19	0.02
C 3	–0.12	–0.13	0.01
C 4	–0.16	–0.16	0.00
C 5	–0.12	–0.13	0.01
C 6	–0.16	–0.17	0.01
H 2	0.14	0.16	–0.02
H 3	0.12	0.13	–0.01
H 4	0.14	0.14	0.00
H 5	0.12	0.12	0.00
H 6	0.14	0.14	0.00

<sup>a</sup>See footnote to Table 4.

**Table 6. Changes of Atomic Charges of POL in Dichloromethane ( $\epsilon = 8.93$ ) Due to Solvent Polarization**

	POL	<i>s</i> POL	$\Delta(\text{vac-sol})$
C 1 <sup>a</sup>	0.09	0.13	−0.04
O 1	−0.35	−0.45	0.10
H 1	0.32	0.40	−0.08
C 2	−0.17	−0.22	0.05
C 3	−0.12	−0.16	0.04
C 4	−0.16	−0.20	0.04
C 5	−0.12	−0.16	0.04
C 6	−0.16	−0.21	0.05
H 2	0.14	0.19	−0.05
H 3	0.12	0.16	−0.04
H 4	0.14	0.18	−0.04
H 5	0.12	0.16	−0.04
H 6	0.14	0.18	−0.04

<sup>a</sup>See footnote to Table 4. H 1 is positioned away from C 2.**Table 7. Changes of Atomic Charges of *hb* EPOL in Dichloromethane ( $\epsilon = 8.93$ ) Due to Solvent Polarization**

	<i>hb</i> EPOL	<i>hbs</i> EPOL	$\Delta(\text{hb-hbs})$
C 1 <sup>a</sup>	0.11	0.16	−0.05
O 1	−0.31	−0.43	0.12
H 1	0.28	0.38	−0.10
C 2	−0.02	−0.02	0.00
Ca	−0.03	−0.04	0.01
Cb	−0.27	−0.33	0.06
Hb	0.23	0.27	−0.04
C 3	−0.10	−0.12	0.02
C 4	−0.15	−0.20	0.05
C 5	−0.11	−0.14	0.03
C 6	−0.16	−0.21	0.05
H 3	0.12	0.16	−0.04
H 4	0.14	0.17	−0.03
H 5	0.13	0.16	−0.03
H 6	0.14	0.18	−0.04

<sup>a</sup>See footnote to Table 4.

moment greater than in the gas phase (Table 2, 3, and 8), and because the geometry changes are generally minor, the increase is due to its polarizability. The corresponding changes of atomic charges describe this electronic charge redistribution very

convincingly (Table 6). The relationship between charge fluxes and  $\pi$ -electron mobility is not that obvious. Therefore, to discuss the effect of H-bond on the  $\pi$ -electron distribution, the latter should be first extracted from the calculated charge density matrix. The vibrational frequencies are uniformly downshifted by around 40  $\text{cm}^{-1}$ . The intensity enhancement in the polarizable continuum of 2–3 times is mainly due to the increase of atomic charges, not fluxes (Table 8).

Now, we turn to the experimentally determined characteristics of the intramolecular H-bonds. The *E* values for the OH stretchings (Table 9) and the  $\equiv\text{CH}$  stretchings (Table 10) were obtained in the limit of infinite dilution from the averaged *K*-spectra (recorded spectra were divided by path length) vs analytical concentration, as described in Experimental Section. The problems due to self-association or any other association taking place in solution were thus minimized, but apparently not fully eliminated in the case of COL.

In studying EPOL vibrational spectra, more precisely its OH and  $\equiv\text{CH}$  stretching bands, it is very instructive to compare them with those of POL, COL, and EB. Five H-bond nonaccepting solvents (petroleum ether,  $\text{CCl}_4$ ,  $\text{C}_2\text{Cl}_4$ ,  $\text{CHCl}_3$ , and  $\text{CH}_2\text{Cl}_2$ , the former three nonpolar and the latter two polar) have been chosen to measure the intensities of the OH and  $\equiv\text{CH}$  stretching bands of dissolved POL, COL, EPOL, and EB. Only the *hb* isomers were definitely observed, whereas the presence of the *nhb* isomers was only indicated by a very weak band at the high frequency side of the *hb* band in slightly polar solvents  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$ , or by its absence in nonpolar solvents (petroleum ether and  $\text{CCl}_4$ ).

The “free” OH oscillator of POL in  $\text{CCl}_4$  is found at 3611  $\text{cm}^{-1}$ , at 3609 in  $\text{C}_2\text{Cl}_4$ , and at 3598 and 3582  $\text{cm}^{-1}$  in  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$ , respectively. A weak band at around 3602  $\text{cm}^{-1}$  in  $\text{C}_2\text{Cl}_4$  and at 3585  $\text{cm}^{-1}$  in the last two solvents is present in EPOL spectra and is thus normally associated with “free” OH oscillators (Figure 1). The OH stretching of the H-bonded oscillator of EPOL,  $\nu(\text{OH})$ , is observed at 3533  $\text{cm}^{-1}$  in  $\text{CCl}_4$ , which is 78  $\text{cm}^{-1}$  lower. This shift is almost 2 times smaller than the shift of  $\Delta\tilde{\nu} = 127 \text{ cm}^{-1}$  due to the intermolecular hydrogen bond  $\text{OH}\cdots\text{OH}$  between POL molecules (3483  $\text{cm}^{-1}$ , also in  $\text{CCl}_4$ ).

An interesting case is that of COL. Two bands are observed in the vapor phase, at 3662 and 3604  $\text{cm}^{-1}$ , the latter being 2 times stronger. By calculations, four bands are predicted in vacuo, 3681 and 3629  $\text{cm}^{-1}$  for the *hb* isomer and 3666 and

**Table 8. Calculated Wavenumbers ( $\text{cm}^{-1}$ ), Integrated Absorption Coefficients ( $\text{km mol}^{-1}$ ), Dipole Moments (Debye) (B3LYP/cc-pVTZ), Corrected Mulliken Charges, and Charge Fluxes for the Hydroxyl and Ethynyl Hydrogen in Dichloromethane ( $\epsilon = 8.93$ )**

	$\nu(\text{O-H}) (\Delta\nu)^a$	$k^b$	$\sigma_{\text{H}}$	$\phi_{\text{H}}$	<i>E</i>	<i>M</i>
POL	3773 (0)	7.963	0.402	−0.093	130	1.771
<i>nhb</i> COL	3776 (−3)	7.977	0.425	−0.086	126 <sup>c</sup>	1.502
<i>nhb</i> EPOL	3767 (6)	7.941	0.404	−0.060	155	2.840
<i>hb</i> COL	3778 (−5)	7.984	0.413 <sup>d</sup>	−0.060	164	3.244
	3745 (28)	7.847	0.397 <sup>e</sup>	−0.010	190	
<i>hb</i> EPOL	3703 (70)	7.672	0.377	0.031	188	0.988
	$\nu(\equiv\text{C-H}) (\Delta\nu)$	$k^b$	$\sigma_{\text{H}}$	$\phi_{\text{H}}$	<i>E</i>	<i>M</i>
EB	3430 (0)	6.247	0.273	0.025	148	1.101
<i>nhb</i> EPOL	3433 (−3)	6.263	0.269	0.027	152	2.840
<i>hb</i> EPOL	3429 (1)	6.245	0.273	0.038	162	0.988

<sup>a</sup>Frequency shifts relative to POL or EB frequency. <sup>b</sup>OH stretching force constant, in  $10^2 \text{ N m}^{-1}$ . <sup>c</sup>Half of the intensity of the antisymmetric O—H stretching mode. <sup>d</sup>H atom not participating in the H-bond. <sup>e</sup>H atom participating in the H-bond.



**Table 9.** Measured Integrated Absorption Coefficients  $E$  ( $\text{km mol}^{-1}$ ), Peak Absorption Coefficients ( $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ), and Band Full Width at Half-Height (FWHH, in  $\text{cm}^{-1}$ ) of the  $\nu(\text{OH})$  Bands at Room Temperature in Different Solvents

solvent ( $\epsilon$ )	POL				<i>hb</i> COL				<i>hb</i> EPOL			
	$\nu(\text{O-H})(\Delta\nu)^a$	$\epsilon_{\text{max}}^b$	fwfh	$E^c$	$\nu(\text{O-H})^a$	$\epsilon_{\text{max}}^b$	fwfh	$E^c$	$\nu(\text{O-H})^a$	$\epsilon_{\text{max}}^b$	fwfh	$E^c$
petrol ether	3622 (−11)	238	12	45					3538 (73)	160	13	32
$\text{CCl}_4$ (2.228)	3611 (0)	231	16	45	3615	202	18	55				
					3569 <sup>d</sup> (42)	202	20	63	3533 (78)	137	22	42
$\text{C}_2\text{Cl}_4$ (2.3)	3609 (2)	233	15	52	3612	143	18	40				
					3568 <sup>d</sup> (43)	154	23	52	3532 (79)	140	20	43
$\text{CHCl}_3$ (4.806)	3598 (13)	158	30	58	3600	148	27	63				
					3557 <sup>d</sup> (54)	162	25	90	3526 (85)	50	36	26
$\text{CH}_2\text{Cl}_2$ (8.93)	3582 (29)	165	35	90	3581	146	34	77				
					3551 <sup>d</sup> (60)	181	39	116	3521 (90)	81	36	43
in vacuo	3817			56	3835			74				
					3780 <sup>d</sup>			92	3724			78
in dielectric (8.93)	3772			130	3778			164				
					3745 <sup>d</sup>			190	3703			188

<sup>a</sup>All  $\Delta\nu$  calculated relative to the POL value of  $3611 \text{ cm}^{-1}$ . <sup>b</sup>In  $\text{cm}^{-1} \text{mol}^{-1} \text{dm}^3$ . <sup>c</sup>In  $\text{km mol}^{-1}$ . <sup>d</sup>H atom participating in the H-bond.

**Table 10.** Measured Integrated Absorption Coefficients  $a$  of the  $\equiv\text{CH}$  Bands at Room Temperature in Different Solvents

solvent ( $\epsilon$ )	EB				<i>hb</i> EPOL			
	$\nu(\equiv\text{CH})(\Delta\nu)^a$	$\epsilon_{\text{max}}^b$	fwfh	$E^c$	$\nu(\equiv\text{CH})(\Delta\nu)^a$	$\epsilon_{\text{max}}^b$	fwfh	$E^c$
petrol ether	3324 (0)	121	10	18	3311 (0)	218	7	23
$\text{CCl}_4$ (2.228)	3314 <sup>d</sup> (10)	132	17	36	3307 (3)	207	10	33
$\text{C}_2\text{Cl}_4$ (2.3)	3312 (12)	118	17	34	3306 (5)	193	10	30
$\text{CHCl}_3$ (4.806)	3310 (14)	114	15	26	3303 (8)	64	19	16
$\text{CH}_2\text{Cl}_2$ (8.93)	3308 (16)	101	12	19	3297 (14)	130	19	36
in vacuo	3470			92	3466			109
in dielectric <sup>e</sup>	3430			148	3429			162

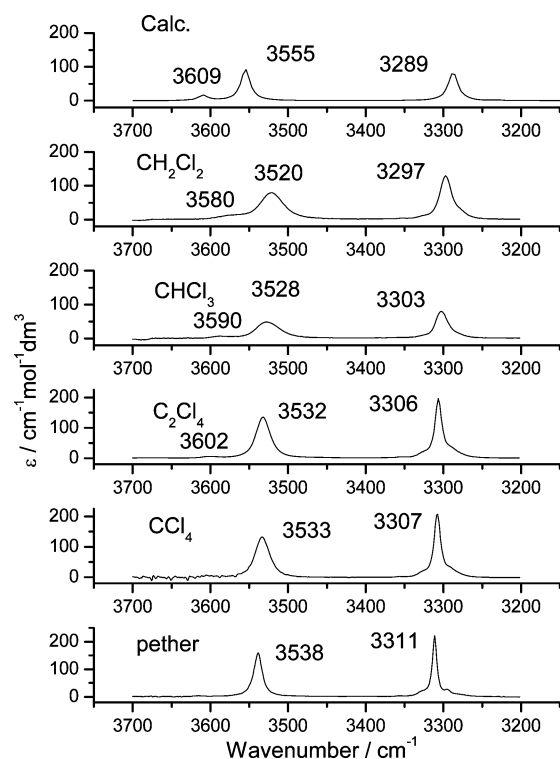
<sup>a</sup> $\Delta\nu = \nu(\equiv\text{CH}, \text{petrolether}) - \nu(\equiv\text{CH})$ . <sup>b</sup>In  $\text{cm}^{-1} \text{mol}^{-1} \text{dm}^3$ , from the baseline corrected averages of the  $K$ -spectra. <sup>c</sup>In  $\text{km mol}^{-1}$ . <sup>d</sup>The  $3314 \text{ cm}^{-1}$  band is the strongest; the other two are at  $3301$  and  $3286 \text{ cm}^{-1}$ , with relative peak absorbances 10:6:1, respectively. <sup>e</sup>B3LYP/cc-pVTZ, solvent as polarizable continuum with  $\epsilon = 8.93$  (dichloromethane).

$3665 \text{ cm}^{-1}$  for the *nhb* isomer (frequencies scaled by 0.96). The normal coordinate analysis in internal coordinates of *hb* and *nhb* COL shows complete absence of any vibrational dynamical couplings between the two OH stretching oscillators in the former isomer, whereas in the latter they participate equally in the two normal modes due to the symmetry reasons. In other words, the two OH stretching modes in *hb* COL are well localized. A closer look into the matrices of kinetic and potential energy reveals that the only coupling terms between any of the two OH stretchings and another internal oscillator are those with COH bending and CCO in-plane bending and not between them. Thus, two almost coinciding bands of the *nhb* isomer should be found between the two bands of the *hb* isomer. With negligible presence of the *nhb* isomer, the two bands of the *hb* isomer of comparable intensities, 10:12 (calculated) and 10:13 (average value, observed), should be the only OH stretching bands observed in the gas phase. This ratio increases with the solvent polarity from 1.1 to 1.5 (Figure 2). The free OH stretching in the *hb* COL appears slightly higher, around  $15 \text{ cm}^{-1}$  (calculated difference  $16 \text{ cm}^{-1}$ ), than in the gas-phase POL ( $3650 \text{ cm}^{-1}$ ).<sup>29</sup> In the  $\text{CCl}_4$  solution (Table 9), two strong bands at  $3615$  and  $3569 \text{ cm}^{-1}$  are assigned to the OH stretching vibrations. The shifts due to the intramolecular H-bond in COL are  $56 \text{ cm}^{-1}$  (gas phase<sup>29</sup>) and  $46 \text{ cm}^{-1}$  (solution), respectively. Thus, it seems that the intramolecular H-bond in COL is weaker than in EPOL.

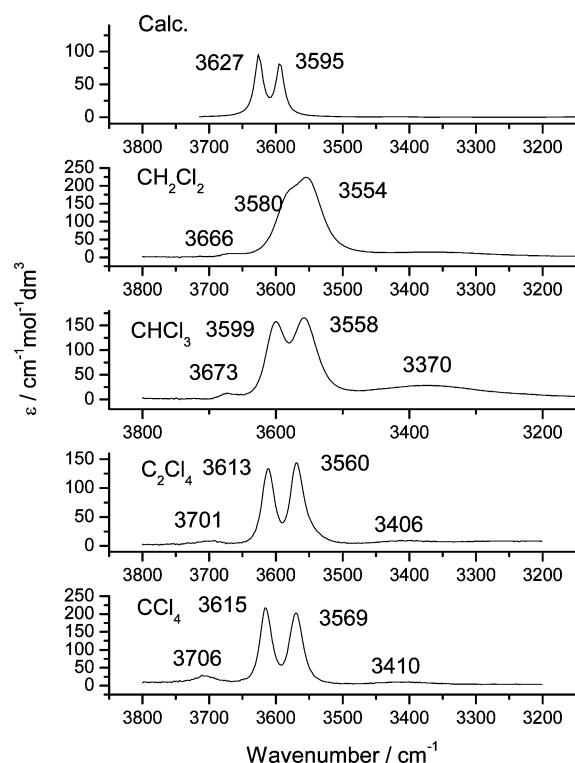
There is a problem with the  $\nu(\equiv\text{CH})$  band of EB (or EPOL) because it has a structure due to anharmonic couplings

(Fermi resonance). Therefore, the  $E$  values (Table 10) were determined by fitting of the baseline corrected spectra to three Lorentzians. In other words, it is not obvious that the integrated absorption coefficient of the strongest component band should be proportional to the solute concentration. In pure EB an IR band due to the acetylenic CH stretching,  $\nu(\equiv\text{CH})$  is a doublet with peaks at  $3309$  and  $3292 \text{ cm}^{-1}$  (fitted values for the spectrum recorded at  $95^\circ\text{C}$ ) and the ratio of the peak heights is 10:15. When EB is dissolved in  $\text{C}_2\text{Cl}_4$ , the band appears as a triplet. When again heated to  $95^\circ\text{C}$ , the peaks are found at  $3317$ ,  $3303$ , and  $3287 \text{ cm}^{-1}$  (fitted values) and the ratio of the peak heights 10:5:2 (the corresponding data at  $30^\circ\text{C}$  are  $3314$ ,  $3301$ , and  $3286 \text{ cm}^{-1}$  and 10:5:1). If the former two are taken to be the case of Fermi resonance (the sum of an overtone of the  $\equiv\text{CH}$  bending at  $1223 \text{ cm}^{-1}$  and the  $\text{C}\equiv\text{C}$  stretching fundamental at  $2113 \text{ cm}^{-1}$  is  $3336 \text{ cm}^{-1}$ , meaning that the anharmonic correction should be around  $30 \text{ cm}^{-1}$  to have the sum close to the  $\equiv\text{CH}$  stretching fundamental), the internally unperturbed acetylene CH oscillator in EB free of hydrogen bonding should be at  $3307 \text{ cm}^{-1}$ . When EPOL is dissolved in  $\text{CCl}_4$ , the triplet structure is still seen. However, the ratio of the peak heights at  $3328$ ,  $3307$ , and  $3289 \text{ cm}^{-1}$  is 9:207:20; i.e., the band at  $3307 \text{ cm}^{-1}$  is by far the strongest one. Thus, the  $\nu(\equiv\text{CH})$  vibration is observed at the same position as in EB.

The integrated absorption of the  $\nu(\text{OH})$  mode in POL is more sensitive to the solvent than in *hb* EPOL. This is not surprising because the OH group in *hb* EPOL is a part of the



**Figure 1.** Calculated (B3LYP/cc-pVTZ, PCM with  $\epsilon = 8.93$ , frequencies scaled by 0.96, *hb* EPOL + 0.20 *nhb* EPOL) and observed IR spectra of EPOL.



**Figure 2.** Calculated (B3LYP/cc-pVTZ, PCM with  $\epsilon = 8.93$ , frequencies scaled by 0.96, *hb* COL + 0.20 *nhb* COL) and observed IR spectra of COL.

intramolecular bond and therefore less exposed to the surrounding. The integrated absorption of the  $\nu(\equiv\text{CH})$  mode is about the same (around 33 km mol<sup>-1</sup>, Table 10),

but the peak heights and consequently the band widths are not. The solvent that does not fit into general pattern concerning absorption intensities is chloroform. Most probably this is due to its ability to form hydrogen bonds, although weak, not only with the oxygen lone pair but also with  $\pi$ -electron systems. The OH bands of intermolecular complexes are very broad and that is normally attributed to the contributions due to hot and combination transitions, i.e., anharmonic coupling with low-frequency deformation modes. From the observed full widths at half-heights (fwhh) (Table 9 and 10), this kind of coupling is evidently absent in the case of intramolecular H-bonds such as found in *hb* EPOL and *hb* COL.

The calculated integrated absorption coefficients are obviously highly overestimated. As expected, the calculated ratio  $E(\text{hb EPOL})/E(\text{POL})$  for the  $\nu(\text{OH})$  band is greater than 1 (1.4) (Table 2), whereas the ratios measured in a given solvent are all smaller than 1 (0.5–0.9) (Table 9). This discrepancy may qualitatively be accounted for by the ability of the OH groups of dissolved POL or COL to form H-bonds between themselves and/or weak H-bonds  $\text{O}-\text{H}\cdots\text{Cl}$  with the solvent molecules, resulting in a very weak and very broad band whereby the intensity of the nonbonded OH stretching is decreased on account of the H-bonded ones. The same ratio, either measured or calculated, for the  $\nu(\equiv\text{CH})$  band is around 1 (Table 3 and 10), pointing to the smaller acidity of the acetylene hydrogen.

#### 4. CONCLUSIONS

It is obviously justifiable to use the molecular charge distribution as determined from the calculated APTs only for the interpretation of gas-phase IR intensities. The  $\sigma_{\text{H}}$  and  $\phi_{\text{H}}$  values have been shown to be pertinent to the local molecular surrounding of a chemical bond; i.e., atomic charges and charge fluxes can actually be taken as good parameters in describing intramolecular charge redistribution from one molecule to another. All the studied systems have delocalized  $\pi$ -electrons, but nevertheless, the redistribution concerns mainly the atoms of the OH group.

The PC model predicts a uniform increase in intensities, but only due to the solvent polarization because other experimentally observable interactions are simply ignored and cannot be reproduced. However, from the PCM calculations it also follows that atomic charges are strongly dependent on the solvent and there are no such atomic charges that would be equally good for all types of molecular dynamics simulations.

As for the strength of the intramolecular  $\text{O}-\text{H}\cdots\pi$  bond in EPOL, it is weaker than the intramolecular  $\text{O}-\text{H}\cdots\text{O}$  bond in COL when the energy differences between *hb* and *nhb* isomers are compared. However, at the same time the observed frequency downshift in  $\text{CCl}_4$  and relative to POL is 78 cm<sup>-1</sup> for EPOL and only 42 cm<sup>-1</sup> for COL.

The well-known empirical characteristics of internal H-bonds (frequency downshifts only up to 100 cm<sup>-1</sup>, moderate increase in intensity and no enormous band broadening) have once again been experimentally documented in this paper. They are qualitatively well accounted for by the corrected Mulliken charges and charge fluxes. The trends in intramolecular effects are correctly predicted in the sense that the difference between the intra- and intermolecular H-bond can now be clearly stated in terms of electronic charge distribution. An intermolecular H-bond is characterized not only by enlarged charge flux term but also by decreased atomic charge. Both terms are positive and of comparable sizes and the net effect is enormous increase in

intensity. An intramolecular H-bond is characterized by values not much different from those of the “free” OH bond but changed in the direction of the intermolecular H-bond. The main reason for this is in the geometry differences between inter- and intramolecular H-bonds. In the latter case it is impossible to achieve favorable linear donor (D)–acceptor (A), D–H...A, geometry which is also known as directionality of H-bond. The origin of directionality in complexes is the polarization of the nonbonding orbital of A by the dipole moment of D–H group, resulting in deformation of the nonbonding orbital. However, in the case of intramolecular H-bond in small molecules this favorable arrangement is not possible due to the steric constraints imposed by the covalent bonds.

Finally, although the partition of an APT into two contributions, APT(C) + APT(CF), can be experimentally verified only for small molecules, it is generally useful as it clearly demonstrates that the equilibrium charge distortion with the motion of the hydrogen atom toward the electron donor system is significant only when the angle D–H...A is close to 180°. This is normally the case only for intermolecular H-bonds.

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### Notes

The authors declare no competing financial interest.

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