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The Hydrogen Bond - Practice and QTAIM Theory.

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Abstract.

The direct proportionality between the energy (enthalpy) of the hydrogen bond and the intensification of the infrared stretching mode of the AH group on formation of the H-complex A-H···B [Iogansen, A.V., *Spectrochim. Acta*, 1999, **A55,** 1585] is compared empirically with the linear correlation of stabilization energies, in the range of 1-70kJ.mol^{-1},with the electron density of the H-bond critical point, which follows from the published computational results of the quantum theory of atoms in molecules (QTAIM). Very close similarity is seen between the increase in IR intensity on H-bond formation as $\Delta A^{1/2} \equiv A_H^{1/2} - A_0^{1/2}$ (subscripts H and 0 relate to bound and free AH groups, respectively) and the electron density, ρ, in their relevance to the energy. Despite the fact that both parameters, ρ and $\Delta A^{1/2}$, are defined by the same wave functions of the electronic and vibrational states of a system, the direct interrelation between two parameters of different dimensionalities is not obvious. The suggestion is made that IR intensities in the spectra of H-complexes, in addition to the results of diffraction methods, can be a source of electron-density data as $\rho(r_c)$ (e.a^{-3}) = $10^{-2}(\Delta A^{1/2})$ (cm.mmol^{-1})

IR intensities in the spectra of H-complexes as a source of electron-density data
$\rho(r_c)(e.a^{-3})=10^{-2}(\Delta A^{1/2})(cm.mmol^{-1/2})$

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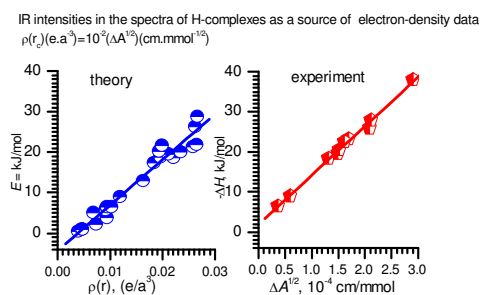
Key words: H-bonding energy, IR spectra, intensity, proton stretching vibration, electron density, QTAIM .

The quantum theory of atoms in molecules (QTAIM) is now accepted as a powerful instrument in studies of intermolecular interactions including those involved in hydrogen bonding.[1] The topological properties of electron density at the critical point of the H-bond have been used to obtain information on the nature of this interaction. Electron density ($\rho(r_c)$) and the Laplacian of the electron density ($\nabla^2\rho(r_c)$) at the critical point of a hydrogen bond have been used as the criteria for quantifying the H-bonding interaction. It was found that both topological parameters are linearly related to the stabilization energy of the H-bond, i.e with H-bond strength.[1] It is remarkable that the energy of interaction is governed by only one parameter - $\rho(r_c)$ - over the whole range of interaction energies, from the very weak (van der Waals) level up to that of strong hydrogen bonds. This approach is the opposite of the usual description of hydrogen bonds as a sum of different components – electrostatic, polarization, delocalization, charge-transfer - whose contribution varies as the energy of interaction and the whole range of H-bonding cannot, obviously, depend on one parameter.

Besides the theoretical approach of QTAIM, quite a long time ago the experimental direct proportionality was suggested, which also described the whole range of H-bond energies with only one parameter – the intensification of the IR stretching mode ν_s of the acidic group AH on H-complex formation.[2] Taking into account that both - theoretical and experimental - approaches are formally very similar, the comparison of the two is attempted here on the basis of published in literature data. The rationale for a such comparison is justified because the electron density $\rho(r_c)$ and IR intensity $A_i \infty (\partial\mu/\partial Q_i)^2$ (or the square root of the intensity of a fundamental IR band ($A_i^{1/2}$)), which in the harmonic approximation, correspond to the derivative of the dipole moment μ with respect to the normal coordinate Q_i of the particular (nondegenerate) vibration, are defined by the same wave functions of electronic and vibrational states of a system.

There are many studies of H-bond complexes of separate systems with the QTAIM theory (see f.e.[1]). Here, several reports were chosen, in which a large number of the model intermolecular binary complexes was systematically studied [3-21, 23-28] - from the weak van der Waals to the typical H-bonds - with the H-bond strength from almost zero to approximately 70kJ.mol^{-1}. The results of the chosen studies, which include a comprehensive number of systems, are presented in the Table.

The most recent data on more complex H-bonded cyclic molecules are added to those found in.[15] All these studies, which were mainly calculated on the MP/2 level of the theory with some variations, result in the linear relations $E = a + b\rho(r_c)$ between the calculated

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stabilization energy E and the critical-point electron density $\rho(r_c)$ with a correlation coefficient R very close to unity. The results obtained by different authors are close (the slopes differ by not more than 30%). The deviations resulted possibly because of differences in the computational techniques and complexity of computed systems. The small intercepts (as compared to the whole energy range) which are about $\pm 6 kJ.mol^{-1}$, make these relationships closely related to the straight proportionalities. Being summarized these separate results can be expressed as a general relationship (with standard deviations shown in parentheses)

$$E(kJ.mol^{-1}) = -6.6(8.0) + 1215(440) \, \rho \,(e.a^{-3}) \qquad (1)$$

From the data presented in the Table, it follows that the QTAIM theoretical approach indeed predicts the existence of linear correlation, close to proportionality, between the energy of hydrogen bonding (the energy of stabilization) and its topological property - the electron density $\rho(r_c)$.

The proportionality of the increase in intensity of the ν_s stretching mode of the acidic AH group on H-bond formation[2], which is compared with the theoretical approach above, was initiated by the well known experimental fact: "….the integrated absorption coefficient of the fundamental ν_s increases many-fold when a H-bond is formed…".[29] It was later confirmed experimentally and published in a final form as the direct proportionality of the intensification, $\Delta A^{1/2}$, of the ν_1 band and hydrogen-bond enthalpy, ΔH. The parameter $\Delta A^{1/2} \equiv A_H^{1/2} - A_0^{1/2}$ (subscripts H and 0 refer to a bound and free AH group, respectively) is based on the suggested simple additive model $(\partial\mu/\partial r) = (\partial\mu_0/\partial r_0) + (\partial\mu_H/\partial r_H)$ of the effective charges of the A−H and H···B bonds of a binary hydrogen-bonded complex.[30,31] An essential feature of the model is that the A−H bond retains, in the hydrogen bond, the magnitude $(\partial\mu_0/\partial r_0)$ of a free A−H bond and the intensification of the ν_s-band as a whole derives from $(\partial\mu_H/\partial r_H)$. This is the direct additive "intrinsic" contribution of the H···B hydrogen bond to the total moment of the ν_s-vibration and its effective charge $(\partial\mu/\partial r)$. The direct proportionality

$$-\Delta H \,(kJ.mol^{-1}) = 12.2\Delta A^{1/2} \qquad (2)$$

(A in $cm.mmol^{-1}$) holds with a correlation coefficient r=0.999 for over a 200-fold range of energy $(0.3 - 60kJ.mol^{-1})$ for a large number of different A−H···B hydrogen bonds. These range from the great diversity of dimers to the continuous three-dimensional network of liquid water and ice with a standard deviation of $0.4kJ.mol^{-1}$.[31] Infrared intensities have been discussed in the framework of QTAIM [32,33] but not in connection with the spectral properties of hydrogen bonding. Very recently the infrared intensity enhancements observed in the water and hydrogen fluoride dimers and in $HF:H_2O$ heterodimer were investigated using

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QTAIM/Charge-Charge Flux-Dipole Flux model but without correlation with H-bond energy.[34]

The parallelism of the two correlations (1) and (2) is striking and shows the direct connection of the effective charge $A^{1/2} \propto (\partial\mu/\partial r)$ with the electron density $\rho(r_c)$ in the H-bond. The mean value of the computed proportionality coefficient **b** in relation (1) (taking into account the constant factor (10^2) in the abscissa) agrees well – within 1% - with the experimental value of relation (2).The comparison of both relations is shown in the Figure.

The illustrative example of the similarity of the theoretical (from[3]) with experimental correlations (from Table 1 in[31]) is shown in the Figure inset. The data for very weak binary complexes with Xe are practically in the origin of the Graph on the Figure.[35]

Thus it can be concluded that the mutual interconnection between both theoretical $\rho(r_c)$ and experimental $\Delta A^{1/2}$ parameters does exist. It is also clear from the Figure that the two bold lines – solid and dashed - are very close. It should be pointed out that experimental correlation pertains to the association *enthalpies* (-ΔH), whereas theoretical calculation yields bond *energy* values. If it is taken into account that the difference between the two entities may be estimated not to exceed $RT \approx 2.5 kJ.mol^{-1}$, then at room temperature and for freely translating molecules, the two correlations are practically coincident.

In conclusion, it can be stated that the empirical comparison reveals the correlation of the QTAIM electron-density parameter $\rho(r_c)$ with the experimentally measurable spectral parameter $\Delta A^{1/2}$ as

$$\rho(r_c) \ (e.a^{-3}) = 10^{-2}(\Delta A^{1/2}) \ (cm.mmol^{-1}) \qquad (3)$$

and the relationship (3) can be a new source of information about $\rho(r_c)$, which is usually obtained from diffraction experiments.

The empirical correlation -ΔH =12.2 $\Delta A^{1/2}$ may possibly receive solid theoretical grounds for the first time and can serve as proof of the theory. From the practical point of view, the experiment, which is applicable to many different acid-base H-complexes in condensed phases (in diluted solutions and pure solvents), that cannot be computed because of their complexity, can be used as an instrument for a probe of the theory.

The possibility of measurement of electron density with equation (3) can be important for theoretical and practical construction of the of H-bond acidity and basicity scales.

It is of note, that practically in all the literature devoted to the theory of the H-bond, the red shift of the ν_s band is indicated as one of the crucial characteristics of H-bond formation, (see f.e[21, 22]), despite the fact that its relative change from the free state does not exceed 30% for

strong H-bonds, which are those usually discussed. However, the integral intensity changes by a factor of a hundred and is obviously the most impressive and fundamental characteristic of the H-bond. Up to now, the work of Iogansen[31] and those which were done before it, remain unique in the field of hydrogen bonding. Furthermore, these IR-intensity studies, which cover a very large body of H-bond complexes, were possibly the first experimental evidence for the covalency of the hydrogen bond. These, study of together with other experimental results, such as an NMR spin–spin coupling[36] and X-ray scattering[37], which relate to discrete systems, showed the inconsistency of the classical picture of H-bond interaction, as a sum of different components – electrostatic, polarization, delocalization, charge-transfer - and were not compatible with the "partial or non-covalent" nature of the H-bond.[38]

From very general point of view the H-bond can always be considered a covalent chemical bond – it is directional, short-range and, in general, saturated. The correlation between the energy of the H-bond and its force constant, which was found to be the same as those for the first-row hydrides[39], also supported this conclusion.

The only property, for which the H-bond differs from the usual chemical bond with energy of $400kJ.mol^{-1}$, is its weakness – the limits of energy, $1-60kJ.mol^{-1}$, with the strongest not exceeding $150kJ.mol^{-1}$. As a result, it follows that the low-frequency intermolecular deformational modes are excited at room temperature and this affects the width of the infrared bands of the proton modes, at least in condensed phase. If other causes of broadening, such as intermolecular vibrational interaction or crystal disorder, are removed, the bands become at low temperature narrow as usual in molecular spectra[40].

References.

1.   R. Parthasarathi, V. Subramanian, V. in *Hydrogen Bonding-New Insight,* Grabowski,S.J., Ed.; 2006, Springer,1-50.

2   A.V. Iogansen, *Dokl.Akad.Nauk SSSR,* 1965**, 164,** 610

3   R. Parthasarathi, V. Subramanian, N. Sathyamurthy N, *J. Phys. Chem*, 2006**, 110***,* 3349-3351.

4   R.J Boyd, S.C. Choi, *Chem.Phys.Lett*., 1985, **120(1),** 80-85.

5   R.J Boyd, S.C. Choi, *Chem.Phys.Lett.,*1986, **129(1),** 62-65.

6   R.D. Parra, X.C. Zeng, *J. Chem. Phys.,* 1999, **110(13)** 6329-6338.

7   M.T. Carroll, R.F.W. Bader, *Molecular Physics*,1988, **65(3),** 695-722.

8   S.J. Grabowski, *J Phys. Chem, A*, 2001**, 105**, 10739-10746

9   S.J. Grabowski, *Chem. Phys. Lett.,* 2001, **338,** 361-366.

10   S.J. Grabowski, *J. Mol.Struct.* 2002, **615***,* 239-245.

11   J. Poater, X. Fradera,, M. Sola, M. Duran, S. Simon, *Chem.Phys.Lett.,* 2003, **369,** 248-255.

12   P. Kolandaivel, V. Nirmala, *J. Mol. Struct.,* 2004, **694**, 33-38.

13   F.-Q, Shi, J.-Y, An, J.-Y. Yu, , *Chinese J.Chem.* 2005, **23**, 400-403.

14.   B.G. Oliveira, F.S. Pereira, R.C.M.U. de Araujo, M.N. Ramos, *Chem.Phys.Lett.,* 2006, **427,** 181-184.

15   B.G. Oliveira, R.C.M.U. Araujo, A.B. Carvalho, M.N. Ramos, *J.Mol.Model.* 2009**, 15***,* 123-131.

16   M. Ziolkowski, S.J. Grabowski,J. Leszczynski, *J. Phys. Chem.A*, 2006**, 110**, 6514-6521.

17   D. Hugas, S. Simon, M. Duran, *J Phys. Chem, A*, 2007, **111,** 4506-4512.

18   A.M. Navarrete-Lopez, J.Garza, R.Vargas, *J.Phys.Chem.,A*, 2007, **111**, 11147-11152.

19   A. Zabardasti, S. Amani, M. Solimannejad, M. Salehnassaj, *Struct. Chem.*, 2009, **20,** 1087-1092.

20   S.J. Grabowski, P. Lipkowski, *J Phys. Chem, A*, 2011**, 115**, 4765-4773.

21   F. Weinhold, R.A. Klein, *Molec.Phys*. 2012, **110(9-10),** 565-579.

22   B.G. de Oliveira, *Phys,Chem.Chem.Phys*.,2013, **15,** 37-79.

23   D. Hugas, L. Guillumes, M. Duran, S. Simon, *Comp.Theor. Chem*., 2012, **998**, 113-119.

24   H. Raissi, M.Yoosefian, F. Mollania, *Int.Journ.Quant.Chem.,* 2012,**112**,2782-2786.

25   S.J. Grabowski, *Phys.Chem. Chem. Phys*., 2013, **15**, 7249-7259.

26   S.J. Grabowski, *J. Mol. Model.* 2013, **19,** 4713-4721.

27   P. Durlak, K.Mierzwicki, Z.Latajka,, *J Phys. Chem, B,* 2013**, 117**, 5430-544023.

28   X. Zhang, X. Li, Y. Zeng ,L. Meng, S. Zheng, *Int. J.Quant. Chem.*, 2014, **114**, 400-408.

29   G.C. Pimentel, A.L. McClellan, *The Hydrogen Bond,* 1960, W. H. Freeman and Co.; San Francisco and London, p.70.

30   A.V. Iogansen, in: N.D. Sokolov (Ed), *Vodorodnaya Svyaz (The Hydrogen Bond),* Izd. Nauka, Moscow, 1981, 112-155, Russian.

31   A.V. Iogansen, , *Spectrochim. Acta,* 1999**, 55A**, 1585-1612.

32   R.F.W. Bader, A. Larouche, C. Gatti, M.T. Carrol, P.J. MacDougall, K., *Chem. Phys.* 1987**, 87(2),** 1142-1152.

33   T.A. Keith, in *The Quantum Theory of Atoms in Molecules,* ed. C.F. Matta and   R.J. Boyd, 2007,Wiley-VCH, pp.61-94.

34   A.F. Silva, W.E. Richter, L.A.Terrabuio, R.L.A. Haiduke, R.E. Bruns, *J. Chem.Phys*.,2014, **140**, 084306.

35   D. Gaszowski, M. Ilczyzyn, *Int. J. Quant. Chem*., 2014, **114**, 473-480

36   N.S. Golubev, Shenderovich, S.N. Smirnov, G.S. Denisov, H-H. Limbach, *Chem.Eur.J.* 1999, **5(2),** 492-497.

37   E.D. Isaacs, A. Shukla, P.M. Platzman, D.R. Hamann, B. Barbiellini, C.A. Tulk, *Phys.Rev. Lett.,* 1999**, 82(3),** 600-603.

38   S.J. Grabowski, *Chem. Rev.* 2011, **111,** 2597-2625.

39   A.V. Iogansen, M.S. Rozenberg, *Doklady Akademii Nauk SSSR* , 1971, **197(1***,)* 117,

40   A.V. Iogansen, *Izvestia Akademii Nauk SSSR Ser.Fiz.,* 1989 , **53 (9),** 1741-1745; Engl.

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Table. Calculated linear correlations $E=a+b\rho$ of the energy E (kJ.mol^{-1}) and the electron density, ρ, (e.a^{-3}) of the H-bond critical point; n- number of complexes

| №	a	b	n	references
1	-6.5	**1671**	34	4, 5, 6
2	-6.5	**1222**	4	7
3	0.78	**986**	14	8
4	-2.9	**967**	7	9
5	-10.7	**1416**	19	10
6	-2.8	**1002**	20	11
7	-6.65	**1515**	15	12
8	-16.2	**2152**	14	13
9	0.5	**690**	8	14
10	-1.1	**878**	28	3, 15
11	-14.3	**1791**	9	16
12	-5.4	**996**	24	17
13	4.4	**820**	11	18
14	1.8	**786**	11	
15	-27.8	**1781**	4	19
16	1.9	**703**	22	20
17	6.6	**1151**	15	21
18	-0.09	**850**	23	23
19	-10.6	**732**	30	24
20	-16.4	**991**	30	
21	-10.0	**1629**	6	25
22	-22.3	**2112**	6	26
23	-2.11	**1107**	11	27
24	-7.6	**1220**	14	28
mean values				
	-6.6 (s=8.0)	**1215** (s =440)	377	

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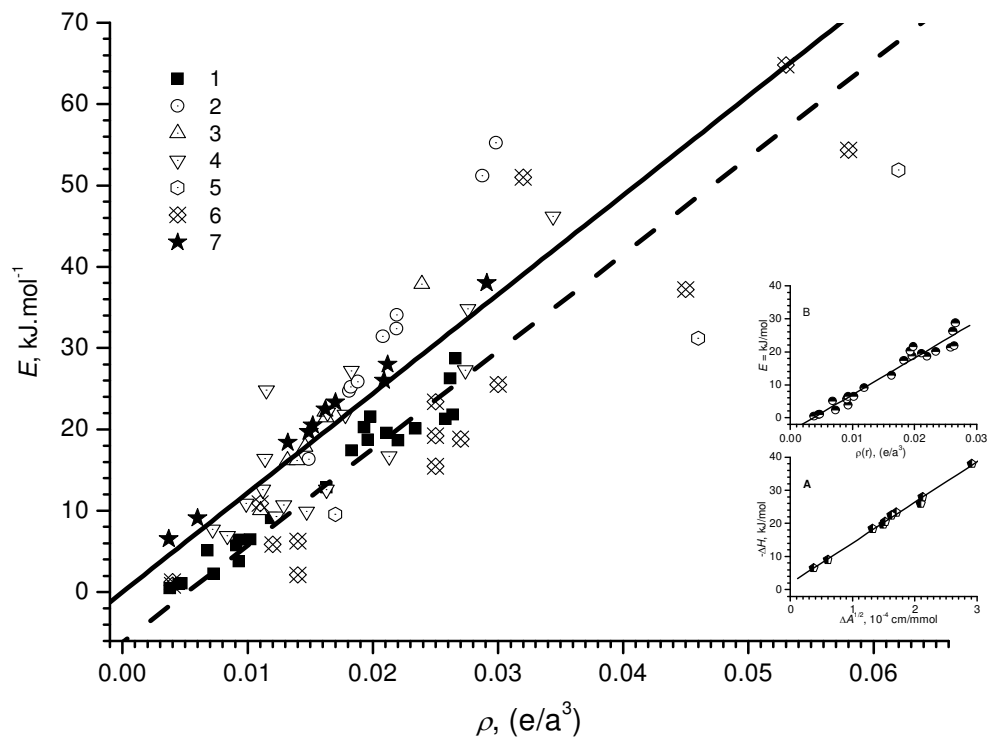
Figure. The comparison of H-bond energy correlations with electron density at the critical point and increasing of intensity of ν_s mode of the AH group. Data 1-[3], 2-[9], 3-[9], 4-[11], 5-[13], 6-[4], 7-[31], Solid line – correlation from [31], bold dashed line –mean theoretical result; inset – A-data-[31], B-data [3].