

Intramolecular hydrogen bond: Can it be part of the basis set of valence internal coordinates in normal mode analysis?

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Abstract. It has been shown earlier¹ that the relaxed force constants (RFCs) could be used as a measure of bond strength only when the bonds form a part of the complete valence internal coordinates (VIC) basis. However, if the bond is not a part of the complete VIC basis, its RFC is not necessarily a measure of bond strength. Sometimes, it is possible to have a complete VIC basis that does not contain the intramolecular hydrogen bond (IMHB) as part of the basis. This means the RFC of IMHB is not necessarily a measure of bond strength. However, we know that IMHB is a weak bond and hence its RFC has to be a measure of bond strength. We resolve this problem of IMHB not being part of the complete basis by postulating ‘equivalent’ basis sets where IMHB is part of the basis at least in one of the equivalent sets of VIC. As long as a given IMHB appears in one of the equivalent complete VIC basis sets, its RFC could be used as a measure of bond strength parameter.

Keywords. Hydrogen bond; intramolecular; relaxed force constant; normal mode analysis; bond strength parameter.

1. Introduction

The advantages of the compliance constants (the inverse of the force constant matrix elements) over the regular force constants were addressed by several authors.^{1–6} The relaxed force constant (RFC), reciprocal of the diagonal compliance matrix element, which was first introduced by Jones,⁷ was realized as a “more chemically meaningful bond strength parameter than the regular (force) constant.”⁸ Grunenberg explicitly showed this for covalent bonds in a series of papers and also extended the idea from covalent to noncovalent interactions like hydrogen bonding.⁵ However, it was pointed out that the RFCs of several nonbonded pairs have similar values as bonded pairs in several molecules.^{9,10} Hence, to use the RFCs as a measure of bond strength parameter we have to separate the bonded atom pairs from the nonbonded ones. The RFCs are the measure of bond strength for the bonded atom pairs alone and not necessarily for nonbonded atom pairs.¹

In a recent paper,¹ we showed that if we use the valence internal coordinates (VIC) as the basis, the bonded pairs appear as stretching coordinates in VIC.

In the case of dimers, there should be connecting bonds between monomers, which could be identified as bonded pairs in the dimer. The idea could be extended to larger clusters. Thus, the intermolecular hydrogen bonds will be part of the basis in VIC.¹ The intramolecular hydrogen bonds need not be a member in the complete basis set of VIC defined in the standard normal mode analysis. Here we address this problem by defining ‘equivalent’ VIC basis sets by choosing intramolecular H-bonds (IMHBs) as part of at least one basis. Since the complete basis sets are equivalent, the RFCs of bonds in all equivalent basis sets could be used as bond strength parameters.

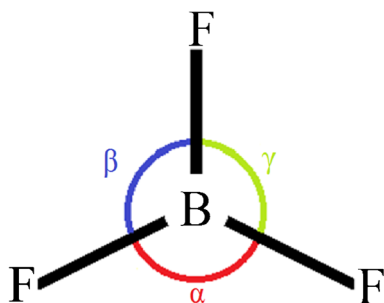
2. Methodology

A polyatomic molecule having N atoms has $3N-6/3N-5$ vibrational degrees of freedom, depending on whether it is nonlinear or linear. As a result, we have to choose $3N-6/3N-5$ suitable coordinates to address the vibrational problem. However, in most cases, the numbers of VIC are more than the number of vibrational degrees of freedom. As a result, we have to make the basis set linearly independent by making suitable linear combinations of VIC. We defined a complete basis set as

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the minimum number of required VIC to describe the normal modes as completely as possible.¹ Since the normal modes depend on the symmetry of the molecule, this definition automatically includes all the VICs required to maintain the symmetry of a molecule. For example, in BF₃, although three angles are linearly dependent, we need all of them to retain the D_{3h} symmetry in the complete basis set.

If we draw the normal mode pictures obtained from the mass-weighted cartesian force constants, the stretching frequency modes clearly indicate all the covalent bonds.¹ The covalent bonds represent regions of electron density in between the bonded atoms, and the electron density is invariant. As a result, all the covalent bonds should be part of all the equivalent complete sets. Whenever redundancies are involved, usually in angles and torsions, there is no unique way to choose the angles and/or torsions as members of the

**Set 1**¹²

$$S_1 = \frac{1}{\sqrt{6}} (2\alpha - \beta - \gamma);$$

$$S_2 = \frac{1}{\sqrt{2}} (\beta - \gamma)$$

Set 2¹³

$$S_2 = \frac{1}{\sqrt{2}} (\beta + \gamma);$$

$$S_2 = \frac{1}{\sqrt{2}} (\beta - \gamma)$$

Set 3¹⁴

$$S_1 = \alpha;$$

$$S_2 = \frac{1}{\sqrt{2}} (\beta - \gamma) \quad (\text{normalized})$$

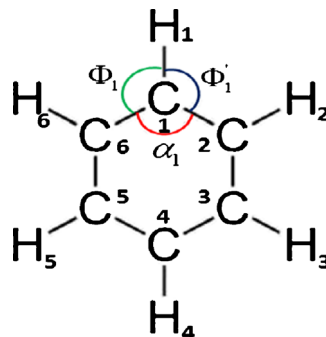
Set 4¹⁵

$$S_1 = \alpha;$$

$$S_2 = \frac{1}{2} (\beta - \gamma) \quad (\text{unnormalized})$$

VIC basis. For example, the three angles in BF₃ are handled in different ways in the literature, as shown in figure 1.¹¹⁻¹⁵ Similarly, the 18 angles in benzene are handled in different ways in the literature, as shown in figure 2.¹⁶⁻¹⁸

In all the coordinate systems shown in figures 1 or 2, the different sets produce *the same set of normal modes* of BF₃ or benzene. Hence, they are *equivalent sets*. The equivalent basis sets are the sets of complete VICs giving the same set of normal modes for a given molecule.

**Set 1**¹⁶

C-H rocking: $\beta_1, \beta_2, \beta_3, \beta_4, \beta_5, \beta_6$

$$\text{where } \beta_i = \frac{1}{2} (\Phi_i - \Phi_i') \text{ unnormalized};$$

or,

$$\beta_i = \frac{1}{\sqrt{2}} (\Phi_i - \Phi_i') \text{ normalized}^{17}.$$

In-plane deformation of ring, B_(1u):

$$q_{19} = \frac{1}{\sqrt{6}} (\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6)$$

In-plane deformation of ring, E_(2g):

$$q_{20a} = \frac{1}{\sqrt{12}} (2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6)$$

In-plane deformation of ring, E_(2g):

$$q_{20b} = \frac{1}{2} (\alpha_2 - \alpha_3 + \alpha_5 - \alpha_6)$$

Set 2¹⁸

CCC bend

$$R_{13} = \frac{1}{\sqrt{6}} (2\alpha_1 - \Phi_1 - \Phi_1'); R_{19} = \frac{1}{\sqrt{2}} (\Phi_1 - \Phi_1')$$

$$R_{14} = \frac{1}{\sqrt{6}} (2\alpha_2 - \Phi_2 - \Phi_2'); R_{20} = \frac{1}{\sqrt{2}} (\Phi_2 - \Phi_2')$$

$$\dots\dots\dots$$

$$R_{18} = \frac{1}{\sqrt{6}} (2\alpha_6 - \Phi_6 - \Phi_6'); R_{24} = \frac{1}{\sqrt{2}} (\Phi_6 - \Phi_6')$$

Figure 1. Equivalent sets representing the 3 angles in BF₃.

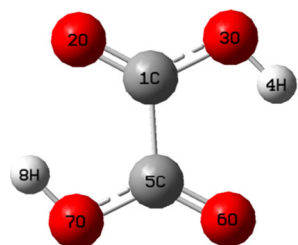
Figure 2. Equivalent sets representing the 18 angles around the carbon atoms in C₆H₆.

In the present work, equivalent VICs are defined for oxalic acid, 1,4-butanediol, and 1,2-ethanediol, where the IMHB is part of one of the equivalent basis sets. The RFCs and the normal modes are computed for each molecule using the equivalent VIC. The calculated normal modes show that the different VIC basis sets are indeed equivalent and the RFCs give the strength of IMHB in each system. For electronic structure calculations, Gaussian 09¹⁹ was used and the RFCs were calculated using a locally developed computer

program based on UMAT.²⁰ All the optimized geometries of conformers are verified for the minima in potential energy surface by doing frequency calculations.

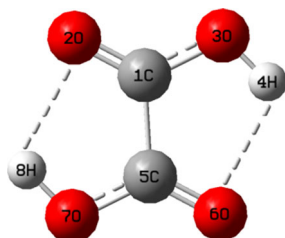
3. Results and Discussion

The main idea here is that the IMHB can be chosen as part of the VIC in at least one of the equivalent basis



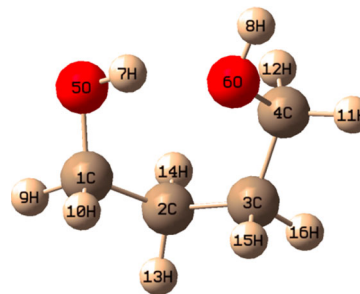
Bonds: 7 (covalent bonds indicates by the connecting lines)	Local* 7
Angles: 8 (2 \angle COH, 3 angles around each C \times 2)	6
Out of plane: 2 (2 $>$ C=O)	2
Torsions: 3 (τ C-C, 2 τ C-O)	3

Figure 3. VIC of Oxalic Acid without H-bonds. (*Local coordinates are 3N-6 linear combinations of VIC obtained as non-zero eigen vectors of suitable internal G-matrix⁶).



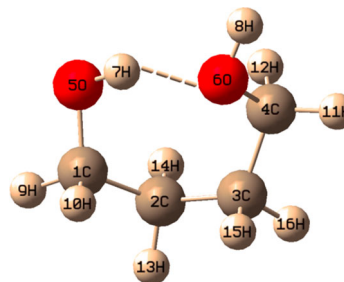
Bonds: 9 (covalent bond:7, H bonds: 2)	Local* 9
Angles: 10 (each ring has 5 internal angles \times 2)	4
Out of plane: 0	0
Torsions: 12 (each ring has 5 torsion \times 2 + 2 connecting the rings)	5

Figure 4. VIC Oxalic Acid with H-bonds. (*Local coordinates are 3N-6 linear combinations of VIC obtained as non-zero eigen vectors of suitable internal G-matrix⁶).



Bonds: 15 (all covalent bonds connected as lines)	Local* 15
Angles: 26 (2 \angle COH + 6 angles around each C \times 4)	22
Torsions: 5 (3 τ CC + 2 τ CO)	5

Figure 5. VIC of 1,4-Butanediol without H-bond. (*Local coordinates are 3N-6 linear combinations of VIC obtained as non-zero eigen vectors of suitable internal G-matrix⁶).



Bonds: 16 (covalent bonds: 15 + 1H bond)	Local* 16
Angles: 24 (6 angles around each C \times 4)	20
Angles: 5+Torsions : 4 [2 \angle COH+ \angle OHO(576)+ \angle HOC(764) + \angle HOH(768)+ τ C-O(15)+ τ O-H(57) + τ O \cdots H(76)+ τ C-O(64)]	6

Figure 6. VIC of 1,4-Butanediol with H-bond. (*Local coordinates are 3N-6 linear combinations of VIC obtained as non-zero eigen vectors of suitable internal G-matrix⁶).

sets. As a result, the IMHB also can be included as a bonded pair in the VIC. The IMHB structure usually contains a ring as compared to the structure without the IMHB. Since the standard selection of VIC for a ring and an open chain compound is well documented in the literature,²¹ the complete VIC that describes the normal modes as completely as possible can easily be selected. In the present work, we have two equivalent basis sets for each molecule: one corresponding to the ring structure and the other corresponding to the open chain structure. We used two molecules, one planar (oxalic acid) and the other nonplanar (1,4-butanediol), as examples for this procedure. The two equivalent VIC are defined in figures 3 and 4 for oxalic acid and figures 5 and 6 for 1,4-butanediol, respectively. Using

these VICs, we formed suitable $3N-6$ linear combinations as local coordinates. These local coordinates are obtained as non-zero eigenvectors of a suitable internal G-matrix.⁶ The local coordinates thus formed are converted into symmetric coordinates and the normal mode analysis is done in symmetric coordinates to get the normal mode frequencies corresponding to different irreducible representations. All the normal mode frequencies and their corresponding eigenvectors matched for the equivalent basis sets. These results clearly show that the two basis sets for each of the molecule are really equivalent. The required results are given in the supplementary material (tables S1–S4). All the *covalent bonds* should be part of all of the equivalent basis sets for a given molecule.

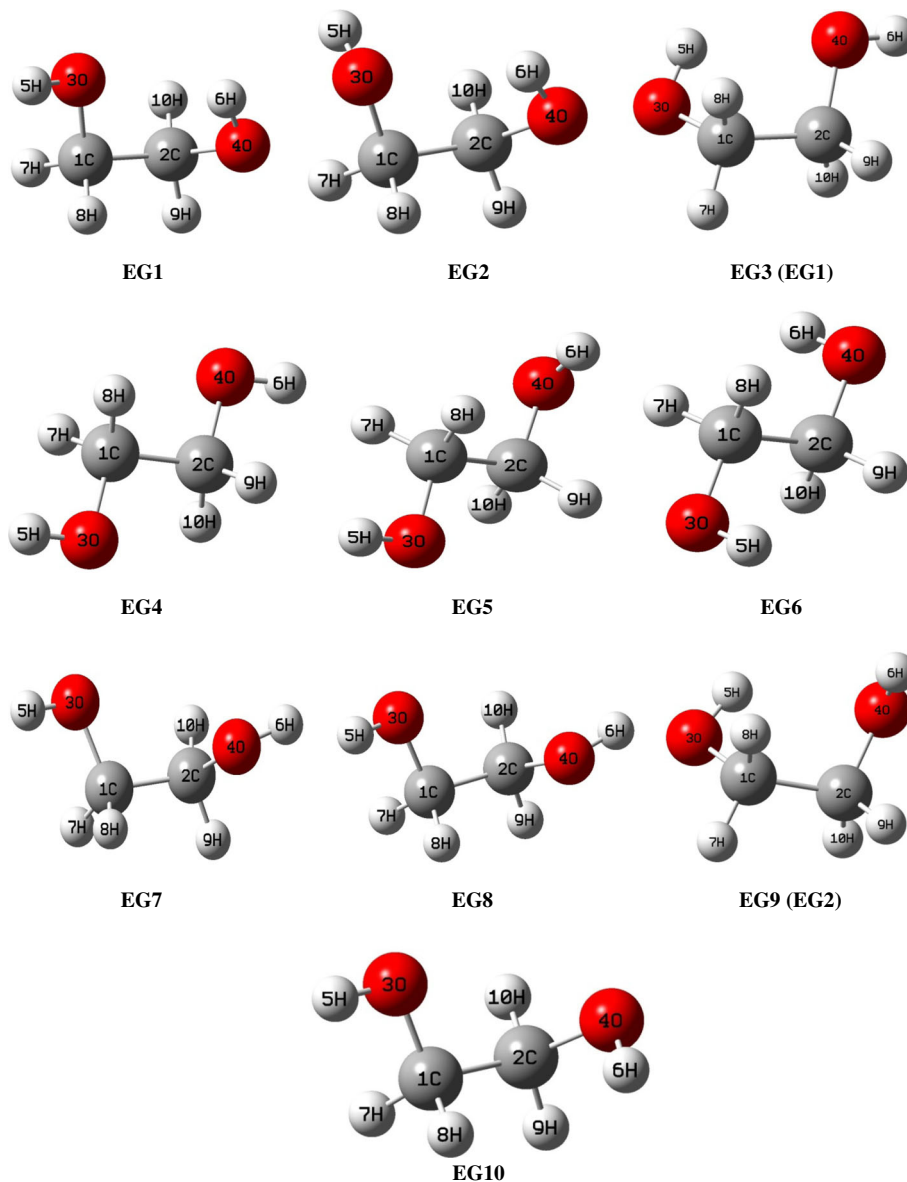


Figure 7. Optimized 1,2-ethanediol conformers at the MP2/cc-pvtz level.

RFC values of IMHB were computed for oxalic acid and 1,4-butanediol using MP2/aug-cc-pvtz and the values are 0.21 mdyn/Å and 0.23 mdyn/Å, respectively. The IMHB bond distances are 2.096 Å and 1.834 Å, respectively, at this level of theory. The $\angle\text{CO}\dots\text{H}$ and $\angle\text{OH}\dots\text{O}$ are 81° , 118° in oxalic acid and 103° , 156° in 1,4-butanediol, respectively. When the angles are close to 180° , usually the strongest bonds are formed. So the geometry explains that the IMHB of oxalic acid is weaker than that of 1,4-butanediol.

3.1 Hydrogen bonding in 1,2-ethanediol

Hydrogen bonding in 1,2-ethanediol received considerable attention in the literature.^{22–26} The full conformational space when scanned gave ten locally stable

conformers: three hydrogen bonded and seven non-hydrogen bonded.^{22–24} The energy differences between these conformers are not very large. Overall, the results of different workers are consistent although the relative stability of different conformers is dependent on the method and basis sets used in the calculations as expected. We extended the calculations to higher basis sets MP2/cc-pvtz and MP2/aug-cc-pvtz. The results are shown in figures 7 and 8 and tables 1 and 2. Our results are in agreement with the earlier results. The RFCs of the hydrogen bonded conformers are 0.09, 0.09, 0.09 mdyn/Å (MP2/cc-pvtz) and 0.08, 0.08, 0.01 mdyn/Å (MP2/aug-cc-pvtz), respectively. The low values of RFCs of the IMHB imply that the IMHB is extremely weak to be of any significance in 1,2-ethanediol in agreement with the previous reports.

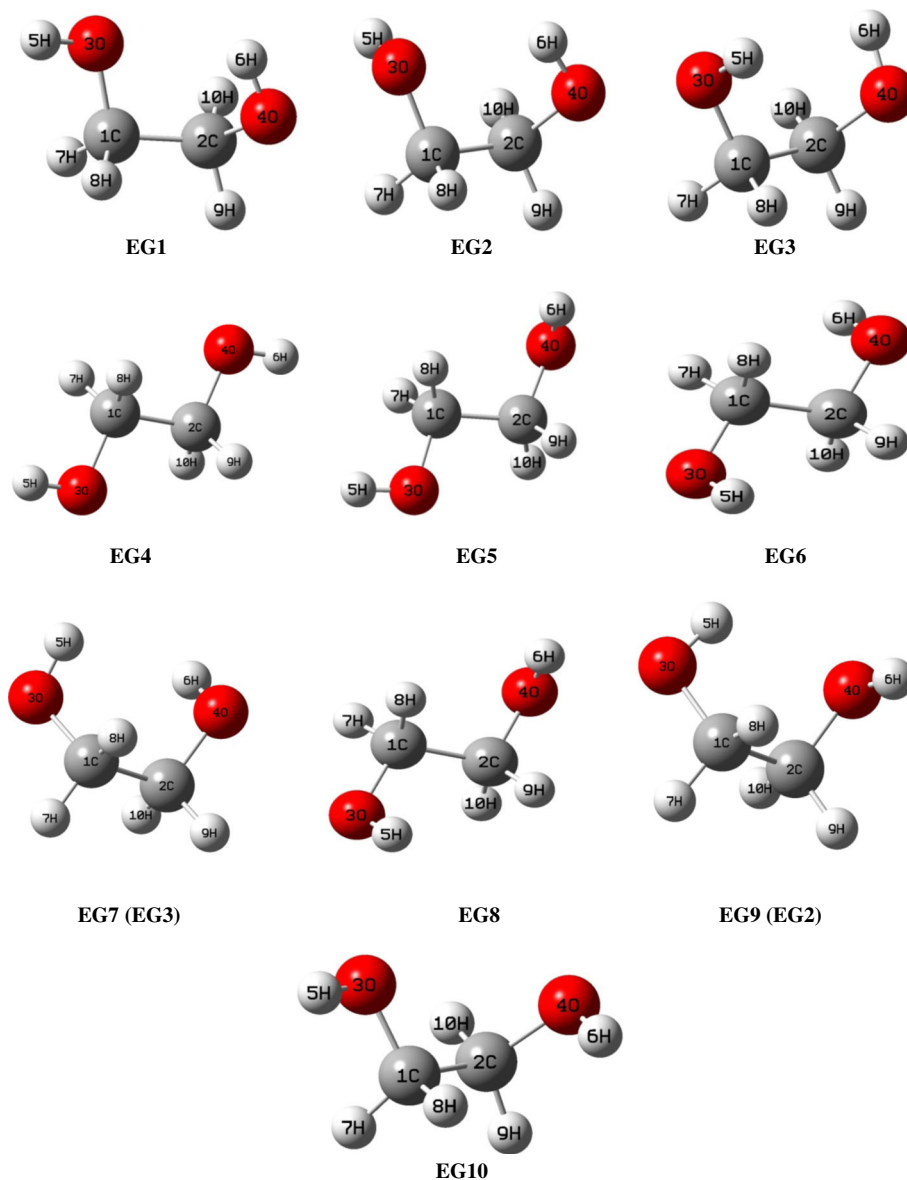


Figure 8. Optimized 1,2-ethanediol at the MP2/aug-cc-pvtz level.

Table 1. Geometric parameters and relative energies of 1,2-ethanediol (MP2/cc-pvtz).

Bonds**	EG1	EG2	EG3*	EG4	EG5	EG6	EG7	EG8	EG9*	EG10
1 1 2	1.502	1.506	1.502	1.503	1.508	1.512	1.498	1.512	1.506	1.503
2 1 3	1.423	1.423	1.411	1.417	1.415	1.415	1.415	1.414	1.410	1.412
3 2 4	1.411	1.410	1.422	1.417	1.415	1.415	1.415	1.414	1.423	1.412
4 3 5	0.958	0.960	0.962	0.958	0.958	0.959	0.958	0.960	0.963	0.959
5 4 6	0.962	0.963	0.958	0.958	0.959	0.959	0.958	0.960	0.960	0.960
6 1 7	1.089	1.089	1.084	1.088	1.088	1.086	1.090	1.083	1.085	1.091
7 1 8	1.088	1.084	1.090	1.088	1.091	1.088	1.088	1.092	1.093	1.093
8 2 10	1.090	1.093	1.088	1.088	1.083	1.088	1.088	1.083	1.084	1.084
9 2 9	1.084	1.085	1.089	1.088	1.088	1.086	1.090	1.092	1.089	1.091
Angles**										
1 3 1 2	105.8	110.3	111.0	106.8	106.9	111.9	108.3	111.9	110.8	108.6
2 4 2 1	111.0	110.8	105.8	106.8	111.6	111.9	108.3	111.9	110.3	113.7
3 5 3 1	108.5	107.6	105.1	107.9	108.2	107.6	108.1	107.8	105.2	108.0
4 6 4 2	105.1	105.2	108.5	107.9	107.7	107.6	108.1	107.8	107.6	107.6
5 7 1 2	110.1	110.9	109.9	108.9	108.8	109.5	108.7	109.1	110.2	108.2
6 8 1 2	109.2	109.5	108.9	108.9	109.2	109.3	108.3	109.7	109.3	109.1
7 10 2 1	108.9	109.3	109.2	108.9	109.2	109.3	108.3	109.1	109.5	108.8
8 9 2 1	109.9	110.2	110.1	108.9	109.3	109.5	108.7	109.7	110.9	108.4
Dihedral Angles**										
1 3 1 2 4	60.7	56.3	60.5	180.0	179.1	180.0	73.3	176.2	56.3	64.3
2 5 3 1 2	-166.7	72.9	-49.5	-180.0	-175.8	69.2	-166.6	64.7	-42.4	-179.1
3 6 4 2 1	-49.7	-42.4	-167.3	180.0	70.4	-69.2	-166.6	64.7	72.7	56.1
4 7 1 2 4	-178.9	-179.4	179.0	59.0	57.8	62.8	-165.8	58.4	175.2	-174.3
5 8 1 2 4	-58.8	-59.4	-62.3	-59.0	-60.1	-55.0	-47.9	-59.4	-66.4	-57.3
6 10 2 1 3	-62.2	-66.5	-59.0	59.0	61.6	55.0	-47.9	58.4	-59.4	-53.5
7 9 2 1 3	179.2	175.1	-179.0	-59.0	-56.2	-62.8	-165.8	-59.4	-179.4	-170.9
Relative energies**										
HF	0.00	2.87	0.00	6.37	7.85	8.64	11.53	9.92	2.87	13.62
MP2	0.00	1.61	0.00	11.98	12.53	12.40	14.58	13.27	1.61	6.15
Conformers										
EG1										
EG2 (EG9)										
EG3 (EG1)										
RFC Values for (O- - -H)										
EG1	0.09									
EG2 (EG9)	0.09									
EG3 (EG1)	0.09									

* After optimization EG3 goes to EG1 and EG9 goes to EG2 conformer.

** Bond lengths in Angstrom(Å), bond angles and dihedral angles in Degree(°), relative energies in kJ/mole and RFC values in mdyn/Å.

Table 2. Geometric parameters and relative energies of 1,2-ethanediol (MP2/aug-cc-pvtz).

Bonds**	EG1	EG2	EG3	EG4	EG5	EG6	EG7*	EG8	EG9*	EG10
1 1 2	1.502	1.505	1.506	1.503	1.508	1.512	1.506	1.512	1.505	1.503
2 1 3	1.425	1.425	1.421	1.420	1.419	1.418	1.421	1.417	1.412	1.416
3 2 4	1.414	1.412	1.421	1.420	1.418	1.418	1.421	1.417	1.425	1.415
4 3 5	0.959	0.961	0.960	0.959	0.959	0.960	0.960	0.960	0.964	0.960
5 4 6	0.963	0.964	0.960	0.959	0.960	0.960	0.960	0.960	0.961	0.960
6 1 7	1.091	1.091	1.088	1.090	1.090	1.088	1.088	1.085	1.087	1.093
7 1 8	1.090	1.086	1.090	1.090	1.093	1.090	1.090	1.093	1.095	1.094
8 2 10	1.092	1.095	1.090	1.090	1.085	1.090	1.090	1.085	1.086	1.086
9 2 9	1.086	1.087	1.088	1.090	1.090	1.088	1.088	1.093	1.091	1.093

Table 2. (Continued)

Bonds**	EG1	EG2	EG3	EG4	EG5	EG6	EG7*	EG8	EG9*	EG10
Angles**										
1 3 1 2	106.2	110.6	111.3	106.6	106.9	111.7	111.3	111.8	111.1	108.7
2 4 2 1	111.3	111.1	111.3	106.6	111.3	111.7	111.3	111.8	110.6	113.8
3 5 3 1	108.9	108.1	107.2	108.4	108.6	108.2	107.2	108.3	106.0	108.6
4 6 4 2	105.9	106.0	107.2	108.4	108.2	108.2	107.2	108.3	108.1	108.2
5 7 1 2	110.0	110.6	109.8	109.1	109.1	109.8	109.8	109.4	110.0	108.3
6 8 1 2	109.4	109.7	109.7	109.1	109.5	109.6	109.7	109.9	109.6	109.5
7 10 2 1	109.1	109.6	109.7	109.1	109.4	109.6	109.7	109.4	109.7	108.9
8 9 2 1	109.8	110.0	109.8	109.1	109.6	109.8	109.8	109.9	110.6	108.6
Dihedral angles**										
1 3 1 2 4	61.6	57.1	60.3	180.0	179.9	-180.0	60.3	177.4	57.1	66.3
2 5 3 1 2	-164.9	73.8	-80.7	-180.0	-175.7	70.4	-80.7	67.1	-43.5	-175.9
3 6 4 2 1	-51.2	-43.4	-80.7	180.0	72.2	-70.4	-80.7	67.1	73.9	58.7
4 7 1 2 4	-178.2	-178.9	178.3	59.4	58.9	62.9	178.2	59.8	175.7	-172.8
5 8 1 2 4	-57.9	-58.8	-62.5	-59.4	-59.7	-55.5	-62.6	-58.5	-65.5	-55.0
6 10 2 1 3	-61.2	-65.6	-62.5	59.4	62.5	55.5	-62.6	59.8	-58.8	-51.3
7 9 2 1 3	179.9	175.7	178.3	-59.4	-55.9	-62.9	178.2	-58.5	-178.9	-169.2
Relative energies**										
HF	0.00	2.96	3.77	6.22	7.75	8.74	3.77	9.89	2.96	13.08
MP2	0.00	1.71	3.84	11.21	11.92	12.03	3.84	12.69	1.71	15.03
	Conformers				RFC Values for (O- -H)					
	EG1				0.08					
	EG2 (EG9)				0.08					
	EG3 (EG7)				0.01					

* After optimization EG7 goes to EG3 and EG9 goes to EG2 conformer.

** Bond lengths in Angstrom(Å), bond angles and dihedral angles in Degree(°), relative energies in kJ/mole and RFC values in mdyn/Å.

4. Conclusions

The equivalent complete basis sets in VIC are defined in such a way that the intramolecular H-bond(s) is/are part of at least one set of VIC. As a result, their RFCs could be used as a measure of bond strength interaction. In 1,2-ethanediol, the RFC values indicate that the IMHB is extremely weak to be of any significance as predicted earlier.

Supplementary Information

Cartesian coordinates, internal coordinates, harmonic frequencies, local coordinates, and the normal modes in terms of cartesian displacement coordinates are given for oxalic acid and 1,4-butanediol with and without hydrogen bonding as supplementary material (tables S1–S4).

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References

1. Majumder M and Manogaran S 2013 *J. Chem. Sci.* **125** 9
2. Decius J C 1963 *J. Chem. Phys.* **38** 241
3. Cyvin S J 1968 In *Molecular Vibrations and Mean Square Amplitudes* (Amsterdam: Elsevier)
4. Jones L H and Swanson B I 1976 *Acc. Chem. Res.* **9** 128
5. Brandhorst K and Grunenberg J 2008 *Chem. Soc. Rev.* **37** 1558 and references therein
6. Madhav M V and Manogaran S 2009 *J. Chem. Phys.* **131** 174112
7. Jones L H 1970 *Proc. Int. Conf. Coord. Chem.* 13th [as given in Ref. 8]
8. Swanson B I 1976 *J. Am. Chem. Soc.* **98** 3067
9. Baker J and Pulay P 2006 *J. Am. Chem. Soc.* **128** 11324
10. Baker J 2006 *J. Chem. Phys.* **125** 014103
11. Halgren T A 1990 *J. Am. Chem. Soc.* **112** 4714
12. Pulay P, Fogarasi G, Pang F and Boggs J E 1979 *J. Am. Chem. Soc.* **101** 2550
13. Tan B T, Demaison J and Rudolph H D 1979 *J. Mol. Spectrosc.* **76** 104

14. Mallinson P D and Nemes L 1976 *J. Mol. Spectrosc.* **59** 470
15. Hollenstein H and Gunthard Hs H 1980 *J. Mol. Spectrosc.* **84** 457
16. Ozkabak A G and Goodman L 1987 *J. Chem. Phys.* **87** 2564
17. Pulay P Fogarasi G and Boggs J E 1981 *J. Chem. Phys.* **74** 3999
18. Torii H and Tasumi M 1995 *J. Mol. Struct.* **352/353** 465
19. Gaussian 09, Revision D.01, Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Scalmani G, Barone V, Mennucci B, Petersson G A, Nakatsuji H, Caricato M, X Li, Hratchian H P, Izmaylov A F, Bloino J, Zheng G, Sonnenberg J L, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery, Jr. J A, Peralta J E, Ogliaro F, Bearpark M, Heyd J J, Brothers E, Kudin K N, Staroverov V N, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant J C, Iyengar S S, Tomasi J, Cossi M, Rega N, Millam J M, Klene M, Knox J E, Cross J B, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann R E, Yazyev O, Austin A J, Cammi R, Pomelli C, Ochterski J W, Martin R L, Morokuma K, Zakrzewski V G, Voth G A, Salvador P, Dannenberg J J, Dapprich S, Daniels A D, Farkas Ö, Foresman J B, Ortiz J V, Cioslowski J and Fox D J, Gaussian, Inc. Wallingford CT, 2009
20. McIntosh D F and Peterson M R, 1989 Program UMAT, QCPE576, University of Indiana, Bloomington, IN47405
21. Fogarasi G and Pulay P 1985 In *Vibrational Spectra and Structure* J R Durig (Ed.) Vol. 14 (Amsterdam: Elsevier) p. 193
22. Yeh T S, Chang Y P and Su T M 1994 *J. Phys. Chem.* **98** 8921
23. Cramer C J and Truhlar D G 1994 *J. Am. Chem. Soc.* **116** 3892
24. Trindle C, Crum P and Douglass K 2003 *J. Phys. Chem.* **107A** 6236
25. Chopra D, Guru Row T N, Arunan E and Klein R A 2010 *J. Mol. Struct.* **964** 126
26. Petterson K A, Stein R S, Drake M D and Roberts J D 2005 *Magn. Reson. Chem.* **43** 225