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REGULAR ARTICLE

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Variation of electrophilicity during molecular vibrations and internal rotations

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Abstract The interrelationships between global reactivity descriptors such as chemical hardness, chemical potential, polarizability and electrophilicity and associated electronic structure principles were investigated in detail by considering distortion along the normal coordinates from the equilibrium structure and internal rotation. The necessary conditions on the extremum of electrophilicity were probed along with other electronic structure principles associated with the global reactivity descriptors. It was observed that an extremum in electrophilicity is obtained where both chemical potential and chemical hardness attain their respective exiremal values in course of the molecular vibrations as well as internal rotations.

Keywords Electrophilicity · DFT · Reactivity descriptor · Vibration · Internal rotation

1 Introduction

Parr et al. [1] have proposed electrophilicity index (ω) as a global chemical reactivity descriptor of molecules and it is defined in terms of chemical potential (μ) and chemical hardness (η) of the molecular system as [2,3]

$$\omega = \frac{\mu^2}{2\eta}, \tag{1}$$

where the chemical hardness is defined for constant external potential $V(\vec{r})$ through the following equation

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{V(\vec{r})} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{V(\vec{r})}. \tag{2}$$

Using a finite difference method, a working equation for the calculation of chemical hardness can be given by

$$\eta = \frac{IP - EA}{2}, \tag{3}$$

where IP and EA are ionization potential (I) and electron affinity (A) of the atom or molecule, respectively. If $\in_{\text{HOMO}}$ and $\in_{\text{LUMO}}$ are the energies of the highest occupied and lowest unoccupied molecular orbitals respectively, then the above equation can be rewritten using Koopmans' theorem [3] as

$$\eta = \frac{\in_{\text{LUMO}} - \in_{\text{HOMO}}}{2}. \tag{4}$$

Various extremum principles, have been proposed [3] from time to time to effectively tackle different aspects of structure, properties, stability, reactivity, bonding, interactions and dynamics. The main objective in quantum chemistry is to obtain the stationary states using a variational principle for minimum energy. The stability of a system is directly related to its minimum energy configuration. In thermodynamics and information theory, a favorable situation is associated with the maximum values of macroscopic entropy and Shannon entropy, respectively. Equilibrium in any ensemble is defined in terms of the extremum values of the corresponding thermodynamic potentials. In order to augment these principles, the extremal behavior of different reactivity descriptors was considered to be important. Validation of the maximum hardness principle (MHP) [4] associated with atoms and molecules and their excited states were reported [5,6]. MHP compliments the minimum energy criterion for stability of atoms and molecules [4]. It is known that the polarizability is inversely proportional to the third power of hardness. Maximum hardness and minimum polarizability were related with greater stability of atoms and molecules [7,8]. Inverse relationship between chemical hardness and polarizability led to the minimum polarizability principle (MPP) by Chattaraj

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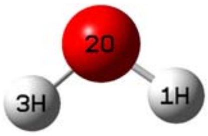
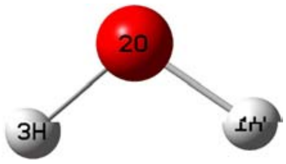
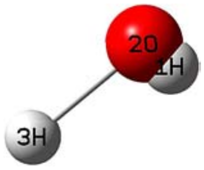
Table 1 Vibrational frequencies, corresponding molecular structures and geometrical parameters for equilibrium and various normal mode distortions of water

Distortion equilibrium	Frequency (cm^{-1})	Molecular structure	Molecular parameters			
			Bond length (Å)		Bond angle (°)	
			r_{1-2} r_{2-3}	0.968 0.968	$\angle_{3-2-1}$	103.976
ν1d	1735.15		r_{1-2} r_{2-3}	1.194 1.194	$\angle_{3-2-1}$	175.405
ν2ss	3777.17		r_{1-2} r_{2-3}	1.704 1.704	$\angle_{3-2-1}$	105.096
ν3as	3918.63		r_{1-2} r_{2-3}	0.311 1.674	$\angle_{3-2-1}$	109.876

d = H–O–H deformation, ss = O–H symmetric stretch, as = O–H asymmetric stretch

and coworkers [9]. Chattaraj et al. [10] have validated the MHP and MPP in molecular-excited states and recently they extended the HSAB principle to time dependent situations using time-dependent DFT and excited state DFT.

The electric dipole polarizability is a measure of the linear response of the electron density in the presence of an infinitesimal electric field F and it represents a second order variation in energy

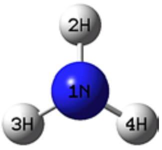
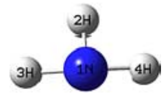
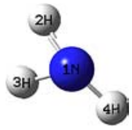
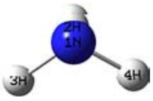
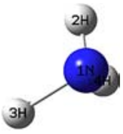
$$\alpha_{a,b} = -\left(\frac{\partial^2 E}{\partial F_a \partial F_b}\right)_{a,b=x,y,z} . \tag{5}$$

The polarizability α is calculated as the mean value as given in the following equation

$$\langle\alpha\rangle = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right) . \tag{6}$$

The electrophilicity index is intended to be the measure of energy lowering of the chemical species due to maximum electron flow from a donor environment. Earlier work by Maynard and coworkers [11–13] has provided strong quantitative support for the definition of electrophilicity by Parr and coworkers [1]. Since then, numerous reports on the application of electrophilicity index were made [13–16]. Recently, the variation of electrophilicity along the reaction path was investigated and various conditions for extremum of electrophilicity were analyzed [17]. A systematic study has also been undertaken to probe profiles of the chemical reactivity and selectivity indices during molecular vibration and rotation. During the last decade, several calculations were made to check the validity of MHP and MPP. It is very pertinent to mention the work of Pearson and Palke for the support of MHP [18]. Hartree–Fock calculations were made to derive numerical evidence for the support of MHP by considering changes in the hardness along various symmetric coordinates. It is interesting to note from the work that the changes in hardness are different for asymmetric and symmetric distortions. For non-totally symmetric distortion, both chemical potential and external potential are constant and hence hardness is maximum for equilibrium geometry. Whereas for symmetric distortion, neither μ nor η shows any sign of maximum or minimum near the equilibrium geometry. Torrent-Sucarrat et al. [19] have shown that there exist some molecules for which even in the case of non-totally symmetric vibrational modes, the generalized maximum hardness principle (GMHP) and minimum polarizability principle (GMPP) breakdown. Both Koopmans' theorem and ΔSCF method were used to calculate the hardness values. In contrary to common belief, they have found that both Koopmans' theorem and ΔSCF method results predict different trends when the values are calculated at HF level of treatment. The dependence of results on basis sets was also discussed. Recently, Blancafort et al [20] have investigated exceptions to the GMHP for nitrogen heterocycles, along non-totally symmetric vibrations. They have demonstrated that the exceptions to GMHP were caused by pseudo-Jahn-Teller (PJT) coupling between ground and excited states. The PJT effect increases the energy gap between the ground and excited states and thus increases the hardness. It is clear from the recent study on chemical reactions that, in principle, it is possible to look for a minimum electrophilicity principle (MEP) as a companion to MHP [17].

Table 2 Vibrational frequencies, corresponding molecular structures and geometrical parameters for equilibrium and various normal mode distortions of ammonia

Distortion equilibrium	Frequency (cm^{-1})	Molecular structure	Molecular parameters					
			Bond length (Å)		Bond angle (°)		Dihedral angle (°)	
			r_{1-2} r_{2-3} r_{3-4}	1.017 1.017 1.017	$\angle_{3-1-2}$ $\angle_{4-1-2}$	106.317 106.317	$D_{4-1-2-3}$	113.001
$\nu 1\tau$	1162.3		r_{1-2} r_{2-3} r_{3-4}	1.269 1.269 1.271	$\angle_{3-1-2}$ $\angle_{4-1-2}$	60.123 59.938	$D_{4-1-2-3}$	70.330
$\nu 2$d	1755.09		r_{1-2} r_{2-3} r_{3-4}	1.029 1.262 1.262	$\angle_{3-1-2}$ $\angle_{4-1-2}$	141.674 141.674	$D_{4-1-2-3}$	65.585
$\nu 3$d	1755.09		r_{1-2} r_{2-3} r_{3-4}	1.312 1.093 1.142	$\angle_{3-1-2}$ $\angle_{4-1-2}$	153.578 111.549	$D_{4-1-2-3}$	−41.087
$\nu 4ss$	3502.01		r_{1-2} r_{2-3} r_{3-4}	1.610 1.610 1.610	$\angle_{3-1-2}$ $\angle_{4-1-2}$	106.407 106.407	$D_{4-1-2-3}$	113.814
$\nu 5$as	3657.93		r_{1-2} r_{2-3} r_{3-4}	0.198 1.425 1.425	$\angle_{3-1-2}$ $\angle_{4-1-2}$	104.220 104.220	$D_{4-1-2-3}$	113.285
$\nu 6$as	3657.93		r_{1-2} r_{2-3} r_{3-4}	1.018 1.786 0.252	$\angle_{3-1-2}$ $\angle_{4-1-2}$	103.404 108.728	$D_{4-1-2-3}$	103.620

τ = torsion, d = H–N–H deformation, ss = N–H symmetric stretch, as = N–H asymmetric stretch

The primary objective of the present investigation is to study the nature of the electrophilicity profiles during molecular vibration and internal rotation vis-à-vis the validity of MHP and MPP and hence to extend the work of Chamorro et al [17] for chemical reactions to vibrations and internal rotations. To gain insight into the electronic structure principles and electrophilicity, distortions in the molecular geometry along normal mode of vibrations from the equilibrium position were considered. In addition to this, we analyze how internal rotations would influence the reactivity parameters by studying the variation of electrophilicity with rotational angles. The interrelationship between hardness, electrophilicity and polarizability was studied in detail.

2 Computational details

To investigate the variation of electrophilicity index during molecular vibration, water, ammonia and ethane molecules were used. Hydrogen peroxide and formamide molecular systems were considered for studying the variation of electrophilicity index during internal rotations. Various geometrical conformations of water, ammonia, formamide, hydrogen peroxide and ethane were optimized using MP2/6-31G* method. At the same level, frequency calculations have also been made. For each molecule, various global quantities were calculated at the equilibrium geometry and at molecular geometries distorted as per the displacement corresponding to the normal mode of vibration. For example, in the case of water molecule, global reactivity descriptors were calculated for equilibrium geometry and also for three different distorted geometries corresponding to the three different normal modes of vibrations. In rotational calculation, rotation through the bond O–O for hydrogen peroxide and C–N bond for formamide from −30° to 210° were carried out. All calculations are carried out using GAUSSIAN 98 package [21]. Using the Koopmans' theorem, [3] both ionization potential and electron affinity of various molecules in equilibrium geometry and also for different distorted positions were obtained.

Table 3 Vibrational frequencies, corresponding molecular structures and geometrical parameters for equilibrium and various normal mode distortions of ethane

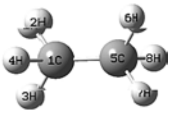
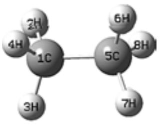
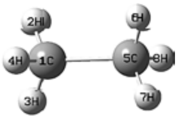
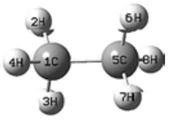
Distortion equilibrium	Frequency (cm^{-1})	Molecular structure	Molecular parameters					
			Bond length (Å)		Bond angle (°)		Dihedral angle (°)	
			r_{1-2}	1.093	$\angle_{3-1-2}$	107.694	$D_{4-1-2-3}$	115.890
			r_{1-3}	1.093	$\angle_{4-1-3}$	107.694	$D_{5-1-3-2}$	−122.054
			r_{1-4}	1.093	$\angle_{5-1-3}$	111.194	$D_{6-5-1-3}$	179.975
			r_{1-5}	1.526	$\angle_{6-5-1}$	111.194	$D_{7-5-1-3}$	−60.024
			r_{5-6}	1.093	$\angle_{7-5-1}$	111.194	$D_{8-5-1-3}$	59.975
			r_{5-7}	1.093	$\angle_{8-5-1}$	111.194		
			r_{5-8}	1.093				
$\nu 1\tau$	331.46		r_{1-2}	1.163	$\angle_{3-1-2}$	109.168	$D_{4-1-2-3}$	−118.993
			r_{1-3}	1.166	$\angle_{4-1-3}$	109.3623	$D_{5-1-3-2}$	120.451
			r_{1-4}	1.167	$\angle_{5-1-3}$	109.855	$D_{6-5-1-3}$	16.756
			r_{1-5}	1.526	$\angle_{6-5-1}$	109.855	$D_{7-5-1-3}$	136.825
			r_{5-6}	1.163	$\angle_{7-5-1}$	109.799	$D_{8-5-1-3}$	−103.542
			r_{5-7}	1.166	$\angle_{8-5-1}$	109.784		
			r_{5-8}	1.167				
$\nu 2$d	849.26		r_{1-2}	1.227	$\angle_{3-1-2}$	109.318	$D_{4-1-2-3}$	109.531
			r_{1-3}	1.163	$\angle_{4-1-3}$	105.144	$D_{5-1-3-2}$	−158.111
			r_{1-4}	1.142	$\angle_{5-1-3}$	117.593	$D_{6-5-1-3}$	−50.680
			r_{1-5}	1.528	$\angle_{6-5-1}$	95.481	$D_{7-5-1-3}$	76.740
			r_{5-6}	1.097	$\angle_{7-5-1}$	132.084	$D_{8-5-1-3}$	−155.091
			r_{5-7}	1.266	$\angle_{8-5-1}$	103.154		
			r_{5-8}	1.119				
$\nu 3$r	849.26		r_{1-2}	1.131	$\angle_{3-1-2}$	96.318	$D_{4-1-2-3}$	−115.433
			r_{1-3}	1.181	$\angle_{4-1-3}$	108.513	$D_{5-1-3-2}$	92.583
			r_{1-4}	1.208	$\angle_{5-1-3}$	103.814	$D_{6-5-1-3}$	62.281
			r_{1-5}	1.526	$\angle_{6-5-1}$	130.334	$D_{7-5-1-3}$	−151.855
			r_{5-6}	1.179	$\angle_{7-5-1}$	116.941	$D_{8-5-1-3}$	−49.486
			r_{5-7}	1.133	$\angle_{8-5-1}$	85.903		
			r_{5-8}	1.215				
$\nu 4$s	1049.43		r_{1-2}	1.103	$\angle_{3-1-2}$	104.484	$D_{4-1-2-3}$	108.874
			r_{1-3}	1.103	$\angle_{4-1-3}$	104.065	$D_{5-1-3-2}$	125.358
			r_{1-4}	1.107	$\angle_{5-1-3}$	114.355	$D_{6-5-1-3}$	179.975
			r_{1-5}	2.146	$\angle_{6-5-1}$	114.355	$D_{7-5-1-3}$	−59.607
			r_{5-6}	1.103	$\angle_{7-5-1}$	114.355	$D_{8-5-1-3}$	60.184
			r_{5-7}	1.103	$\angle_{8-5-1}$	114.277		
			r_{5-8}	1.107				
$\nu 5$r	1270.65		r_{1-2}	1.213	$\angle_{3-1-2}$	111.699	$D_{4-1-2-3}$	113.627
			r_{1-3}	1.204	$\angle_{4-1-3}$	88.459	$D_{5-1-3-2}$	−80.433
			r_{1-4}	1.157	$\angle_{5-1-3}$	100.180	$D_{6-5-1-3}$	−93.261
			r_{1-5}	1.552	$\angle_{6-5-1}$	80.863	$D_{7-5-1-3}$	21.682
			r_{5-6}	1.204	$\angle_{7-5-1}$	144.826	$D_{8-5-1-3}$	179.980
			r_{5-7}	1.213	$\angle_{8-5-1}$	100.185		
			r_{5-8}	1.156				
$\nu 6$r	1270.65		r_{1-2}	1.171	$\angle_{3-1-2}$	86.483	$D_{4-1-2-3}$	−113.885
			r_{1-3}	1.184	$\angle_{4-1-3}$	112.671	$D_{5-1-3-2}$	84.520
			r_{1-4}	1.215	$\angle_{5-1-3}$	94.216	$D_{6-5-1-3}$	93.905
			r_{1-5}	1.552	$\angle_{6-5-1}$	84.807	$D_{7-5-1-3}$	179.980
			r_{5-6}	1.184	$\angle_{7-5-1}$	94.212	$D_{8-5-1-3}$	−40.096
			r_{5-7}	1.171	$\angle_{8-5-1}$	147.935		
			r_{5-8}	1.213				
$\nu 7$d	1464.62		r_{1-2}	1.182	$\angle_{3-1-2}$	119.772	$D_{4-1-2-3}$	−169.188
			r_{1-3}	1.182	$\angle_{4-1-3}$	119.670	$D_{5-1-3-2}$	−84.575
			r_{1-4}	1.191	$\angle_{5-1-3}$	86.861	$D_{6-5-1-3}$	−179.941
			r_{1-5}	1.506	$\angle_{6-5-1}$	135.567	$D_{7-5-1-3}$	−60.037
			r_{5-6}	1.225	$\angle_{7-5-1}$	135.567	$D_{8-5-1-3}$	60.009
			r_{5-7}	1.225	$\angle_{8-5-1}$	135.860		
			r_{5-8}	1.219				
$\nu 8$d	1491.79		r_{1-2}	1.209	$\angle_{3-1-2}$	74.614	$D_{4-1-2-3}$	77.783
			r_{1-3}	1.209	$\angle_{4-1-3}$	74.480	$D_{5-1-3-2}$	140.884
			r_{1-4}	1.212	$\angle_{5-1-3}$	135.697	$D_{6-5-1-3}$	179.970
			r_{1-5}	1.306	$\angle_{6-5-1}$	135.697	$D_{7-5-1-3}$	−59.629
			r_{5-6}	1.209	$\angle_{7-5-1}$	135.697	$D_{8-5-1-3}$	60.170
			r_{5-7}	1.209	$\angle_{8-5-1}$	135.531		
			r_{5-8}	1.212				

Table 3 (Contd.)

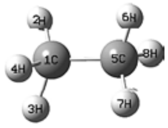
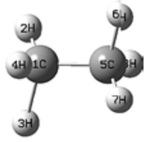
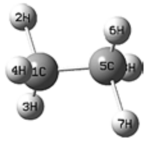
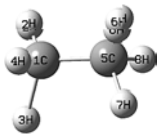
Distortion equilibrium	Frequency (cm^{-1})	Molecular structure	Molecular parameters					
			Bond length (Å)		Bond angle (°)		Dihedral angle (°)	
ν9d	1568.64		r_{1-2}	1.151	$\angle_{3-1-2}$	76.466	$D_{4-1-2-3}$	−148.965
			r_{1-3}	1.202	$\angle_{4-1-3}$	101.600	$D_{5-1-3-2}$	100.240
			r_{1-4}	1.160	$\angle_{5-1-3}$	122.572	$D_{6-5-1-3}$	96.193
			r_{1-5}	1.527	$\angle_{6-5-1}$	105.764	$D_{7-5-1-3}$	179.974
			r_{5-6}	1.202	$\angle_{7-5-1}$	122.570	$D_{8-5-1-3}$	−68.739
			r_{5-7}	1.151	$\angle_{8-5-1}$	100.648		
			r_{5-8}	1.160				
ν10d	1568.64		r_{1-2}	1.212	$\angle_{3-1-2}$	140.048	$D_{4-1-2-3}$	88.862
			r_{1-3}	1.115	$\angle_{4-1-3}$	124.164	$D_{5-1-3-2}$	131.824
			r_{1-4}	1.186	$\angle_{5-1-3}$	98.430	$D_{6-5-1-3}$	179.977
			r_{1-5}	1.527	$\angle_{6-5-1}$	98.429	$D_{7-5-1-3}$	−26.792
			r_{5-6}	1.115	$\angle_{7-5-1}$	111.675	$D_{8-5-1-3}$	44.073
			r_{5-7}	1.211	$\angle_{8-5-1}$	117.607		
			r_{5-8}	1.186				
ν11d	1572.78		r_{1-2}	1.108	$\angle_{3-1-2}$	141.369	$D_{4-1-2-3}$	−83.730
			r_{1-3}	1.230	$\angle_{4-1-3}$	122.134	$D_{5-1-3-2}$	−131.835
			r_{1-4}	1.186	$\angle_{5-1-3}$	99.624	$D_{6-5-1-3}$	80.080
			r_{1-5}	1.526	$\angle_{6-5-1}$	105.890	$D_{7-5-1-3}$	162.995
			r_{5-6}	1.224	$\angle_{7-5-1}$	121.997	$D_{8-5-1-3}$	−88.506
			r_{5-7}	1.142	$\angle_{8-5-1}$	101.642		
			r_{5-8}	1.165				
ν12d	1572.78		r_{1-2}	1.230	$\angle_{3-1-2}$	141.116	$D_{4-1-2-3}$	84.167
			r_{1-3}	1.111	$\angle_{4-1-3}$	122.888	$D_{5-1-3-2}$	131.992
			r_{1-4}	1.198	$\angle_{5-1-3}$	99.592	$D_{6-5-1-3}$	−163.527
			r_{1-5}	1.526	$\angle_{6-5-1}$	121.998	$D_{7-5-1-3}$	−80.606
			r_{5-6}	1.142	$\angle_{7-5-1}$	105.887	$D_{8-5-1-3}$	88.448
			r_{5-7}	1.224	$\angle_{8-5-1}$	101.609		
			r_{5-8}	1.169				
ν13ss	3111.29		r_{1-2}	1.513	$\angle_{3-1-2}$	106.489	$D_{4-1-2-3}$	113.271
			r_{1-3}	1.513	$\angle_{4-1-3}$	106.440	$D_{5-1-3-2}$	−123.347
			r_{1-4}	1.512	$\angle_{5-1-3}$	112.347	$D_{6-5-1-3}$	−60.036
			r_{1-5}	1.446	$\angle_{6-5-1}$	112.335	$D_{7-5-1-3}$	60.001
			r_{5-6}	1.513	$\angle_{7-5-1}$	112.335	$D_{8-5-1-3}$	179.982
			r_{5-7}	1.513	$\angle_{8-5-1}$	112.347		
			r_{5-8}	1.512				
ν14ss	3112.52		r_{1-2}	0.677	$\angle_{3-1-2}$	109.444	$D_{4-1-2-3}$	122.420
			r_{1-3}	0.677	$\angle_{4-1-3}$	110.774	$D_{5-1-3-2}$	−119.910
			r_{1-4}	0.772	$\angle_{5-1-3}$	109.431	$D_{6-5-1-3}$	179.912
			r_{1-5}	1.526	$\angle_{6-5-1}$	105.822	$D_{7-5-1-3}$	−60.050
			r_{5-6}	1.455	$\angle_{7-5-1}$	111.984	$D_{8-5-1-3}$	59.931
			r_{5-7}	1.509	$\angle_{8-5-1}$	111.996		
			r_{5-8}	1.509				
ν15as	3187.77		r_{1-2}	1.231	$\angle_{3-1-2}$	109.468	$D_{4-1-2-3}$	123.094
			r_{1-3}	0.490	$\angle_{4-1-3}$	111.867	$D_{5-1-3-2}$	−127.321
			r_{1-4}	1.568	$\angle_{5-1-3}$	119.143	$D_{6-5-1-3}$	179.942
			r_{1-5}	1.531	$\angle_{6-5-1}$	119.140	$D_{7-5-1-3}$	−52.803
			r_{5-6}	0.490	$\angle_{7-5-1}$	109.692	$D_{8-5-1-3}$	59.937
			r_{5-7}	1.231	$\angle_{8-5-1}$	106.605		
			r_{5-8}	1.558				
ν16as	3187.77		r_{1-2}	0.470	$\angle_{3-1-2}$	108.344	$D_{4-1-2-3}$	−112.836
			r_{1-3}	1.284	$\angle_{4-1-3}$	106.934	$D_{5-1-3-2}$	125.074
			r_{1-4}	1.517	$\angle_{5-1-3}$	119.269	$D_{6-5-1-3}$	55.114
			r_{1-5}	1.531	$\angle_{6-5-1}$	108.777	$D_{7-5-1-3}$	179.940
			r_{5-6}	1.284	$\angle_{7-5-1}$	119.270	$D_{8-5-1-3}$	−58.215
			r_{5-7}	0.470	$\angle_{8-5-1}$	107.513		
			r_{5-8}	1.517				
ν17as	3207.52		r_{1-2}	0.855	$\angle_{3-1-2}$	104.971	$D_{4-1-2-3}$	−116.190
			r_{1-3}	1.717	$\angle_{4-1-3}$	113.576	$D_{5-1-3-2}$	125.499
			r_{1-4}	0.795	$\angle_{5-1-3}$	109.467	$D_{6-5-1-3}$	−63.744
			r_{1-5}	1.526	$\angle_{6-5-1}$	114.538	$D_{7-5-1-3}$	59.189
			r_{5-6}	0.470	$\angle_{7-5-1}$	110.880	$D_{8-5-1-3}$	175.270
			r_{5-7}	1.333	$\angle_{8-5-1}$	110.701		
			r_{5-8}	1.485				

Table 3 (Contd.)

Distortion equilibrium	Frequency (cm^{-1})	Molecular structure	Molecular parameters					
			Bond length (Å)		Bond angle (°)		Dihedral angle (°)	
ν18as	3207.52		r_{1-2}	1.676	$\angle_{3-1-2}$	105.076	$D_{4-1-2-3}$	113.203
			r_{1-3}	1.002	$\angle_{4-1-3}$	111.245	$D_{5-1-3-2}$	−126.244
			r_{1-4}	0.598	$\angle_{5-1-3}$	113.153	$D_{6-5-1-3}$	−59.496
			r_{1-5}	1.526	$\angle_{6-5-1}$	111.013	$D_{7-5-1-3}$	65.056
			r_{5-6}	1.185	$\angle_{7-5-1}$	113.700	$D_{8-5-1-3}$	−175.750
			r_{5-7}	0.510	$\angle_{8-5-1}$	110.442		
			r_{5-8}	1.589				

τ = torsion, d = CH_3 deformation, s = C–C stretch, r = CH_3 rock, ss = C–H symmetric stretch, as = C–H asymmetric stretch

Table 4 Vibrational frequencies and other global reactivity descriptors for equilibrium and various distortion geometries of water

Distortion equilibrium	Frequency (cm^{-1})	Energy (Hartrees)	Chemical hardness (eV)	Chemical potential (eV)	Electrophilicity (eV)	Polarizability (a.u)
		−76.2	9.6	−3.93	0.81	5.04
ν1d	1735.15	−76.05	6.85	−4.74	1.64	6.90
ν2ss	3777.17	−75.94	6.32	−5.88	2.73	7.63
ν3as	3918.63	−72.53	6.91	−6.62	3.17	7.19

d = H–O–H deformation, ss = O–H symmetric stretch, as = O–H asymmetric stretch

3 Results and discussion

The frequency, molecular distortion in bond length and bond angle corresponding to the normal mode of vibration for water, ammonia, and ethane are given in Tables 1, 2 and 3 respectively. Table 4 shows, the results for water molecule in equilibrium geometry and also for three distorted geometries corresponding to the three normal modes of vibrations. It is clear from the results that a small displacement in the molecular geometry from the equilibrium position drastically influences various reactivity descriptors. It can be found from the results that hardness is maximum for the equilibrium geometry and displacements in all the three directions corresponding to the normal modes of vibration make the molecule less stable as authenticated by a decrease in hardness. Chemical potential is also a maximum for the equilibrium geometry. It is interesting to note that electrophilicity is minimum for the equilibrium geometry. Similar to electrophilicity, the mean polarizability is minimum for the geometry corresponding to equilibrium. It is possible to relate maximum hardness with minimum electrophilicity and polarizability values.

The extremum on the electrophilicity occurs at the points for which the following condition is satisfied

$$\frac{\partial \mu}{\partial x} = \frac{\mu}{2\eta}\left(\frac{\partial \eta}{\partial x}\right), \tag{7}$$

where x can be any reaction coordinate [17]. In the present work, we consider x to be a bond length (stretching), bond angle (bending) and dihedral angle (internal rotation) in a molecule. Since $\mu < 0$, $\eta > 0$ due to convexity in energy, the extremum of the electrophilicity occurs when the slopes of the variation of the chemical potential and the hardness are of opposite sign. According to the conditions for the extremum of electrophilicity obtained by Chamorro et al. [17] the extrema in chemical potential and chemical hardness ensure extremum in the electrophilicity index in the case of water molecule during molecular vibration, i.e. in the case of water molecule μ, η are maxima for the equilibrium geometry and hence ω is minimum for the corresponding geometry. It is evident from the previous investigation that Koopmans' theorem and ΔSCF methods provide different trends in the calculated values for hardness [19, 20]. In the calculation of both ionization potential and electron affinity, the validity of Koopmans' theorem was assumed. There are several limitations in the calculation of ionization potential and electron affinity using this approximation. Numerous theoretical investigations were carried out to predict reliable estimates of ionization potential and electron affinity using different theoretical methods of different theoretical rigor [22]. It is a general conviction that the ΔSCF methodology reliably yields I and A values when compared to the Koopmans' theorem. In order to probe how both calculations predict the trends discussed in the present investigation, calculations of I and A for water molecule were made using ΔSCF method as well by computing the total energies of cationic and anionic doublet species at the geometry of neutral system employing unrestricted formalism using MP2/6-31G* method. The neutral water molecule was treated using restricted formalism. From the energies, I and A were computed. From the ionization potential and electron affinity, electrophilicity for water molecule and three different normal modes were computed and the results are presented in Table 5. The comparison of the results obtained from Koopmans' theorem and ΔSCF clearly shows that the general trends are not significantly influenced by the method of calculations of global density functional descriptors.

The calculated global reactivity descriptors for ammonia are presented in Table 6. It is interesting to mention that distortion from the equilibrium geometry significantly

Table 5 Ionization potential (I), electron affinity (A) and electrophilicity for water molecule and its normal modes using ΔSCF method and Koopmans' theorem

Distortion equilibrium	Frequency (cm^{-1})	ΔSCF			Koopmans' theorem		
		I (Hartrees)	A (Hartrees)	ω (eV)	I (Hartrees)	A (Hartrees)	ω (eV)
		0.44613	−0.18766	0.72	0.49737	−0.20821	0.81
ν1d	1735.15	0.37136	−0.0615	1.51	0.42596	−0.07722	1.64
ν2ss	3777.17	0.41862	−0.03314	2.24	0.44831	−0.01648	2.73
ν3as	3918.63	0.44715	−0.00693	2.9	0.49739	−0.01056	3.17

Table 6 Vibrational frequencies and other global reactivity descriptors for equilibrium and various distortion geometries of ammonia

Distortion equilibrium	Frequency (cm^{-1})	Energy (Hartrees)	Chemical hardness (eV)	Chemical potential (eV)	Electrophilicity (eV)	Polarizability (a.u)
		−56.35	8.73	−2.76	0.44	8.025
$\nu1\tau$	1162.3	−56.18	8.37	−4.77	1.36	12.82
ν2d	1755.09	−56.14	6.93	−3.94	1.12	10.5
ν3d	1755.09	−56.16	6.4	−3.79	1.12	10.96
ν4ss	3502.01	−56.07	6.21	−4.88	1.92	19.57
ν5as	3657.93	−47.97	7.76	−4.82	1.5	10.56
ν6as	3657.93	−50.87	6.53	−5.21	2.08	9.939

τ = torsion, d = H–N–H deformation, ss = N–H symmetric stretch, as = N–H asymmetric stretch

Table 7 Vibrational frequencies and other global reactivity descriptors for equilibrium and various distortion geometries of ethane

Distortion equilibrium	Frequency (cm^{-1})	Energy (Hartrees)	Chemical Hardness (eV)	Chemical potential (eV)	Electrophilicity (eV)	Polarizability (a.u)
		−79.49	9.9	−3.32	0.56	22.43
$\nu1\tau$	331.46	−79.47	9.39	−3.27	0.57	24.39
ν2d	849.26	−79.42	8.72	−2.83	0.46	25.67
ν3r	849.26	−79.42	8.82	−3.04	0.52	25.66
ν4s	1049.43	−79.39	7.71	−3.19	0.66	28.1
ν5r	1270.65	−79.32	7.26	−2.25	0.35	25.54
ν6r	1270.65	−79.32	7.49	−2.65	0.47	25.52
ν7d	1464.62	−79.31	8.09	−2.92	0.53	26.65
ν8d	1491.79	−79.27	8.05	−2.41	0.36	28.81
ν9d	1568.64	−79.34	7.27	−2.42	0.4	25.54
ν10d	1568.64	−79.32	7.33	−2.14	0.31	25.05
ν11d	1572.78	−79.32	7.82	−2.43	0.38	25.13
ν12d	1572.78	−79.32	7.79	−2.44	0.38	25.23
ν13ss	3111.29	−79.16	7.24	−3.38	0.79	25.03
ν14ss	3112.52	−78.66	7.9	−3.74	0.88	25.51
ν15as	3187.77	−77.3	7.4	−3.1	0.65	26.04
ν16as	3187.77	−77.02	7.72	−3.25	0.69	26.13
ν17as	3207.52	−78	7.32	−3.69	0.93	25.07
ν18as	3207.52	−77.94	7.38	−3.75	0.95	24.63

τ = torsion, d = CH_3 deformation, s = C–C stretch, r = CH_3 rock, ss = C–H symmetric stretch, as = C–H asymmetric stretch

influences various reactivity descriptors and the trend similar to water in equilibrium geometry and also distorted arrangements were obtained. It is realizable from the numerical results that if both μ and η are maxima at any point along the internal coordinates, ω will be a minimum.

The calculated vibrational frequencies and chemical reactivity descriptors for ethane are depicted in Table 7. It can be observed from the results that there is no change in the minimum energy-maximum hardness-minimum polarizability relationships. However, equilibrium geometry does not correspond to minimum electrophilicity and deformations corresponding to the ν5r and ν8d have minimum electrophilicity. It is important to note that minimum energy-minimum electrophilicity conditions are not always true. This may be due to the extremum condition that the extremum (maximum or minimum) or constancy of omega is obtained when both μ and η are maximum/minimum/constant. In the cases of ethane, simultaneous existence of the extremum conditions for chemical potential and chemical hardness is not true for the equilibrium geometry and hence minimum energy-minimum electrophilicity condition is not valid. In this study, distortions corresponding to the vibrational frequencies associated with the normal mode of vibration were made. Since distortion is within the allowed vibrational mode, the validity of minimum energy-maximum hardness relationship can be observed. However, maximum hardness-

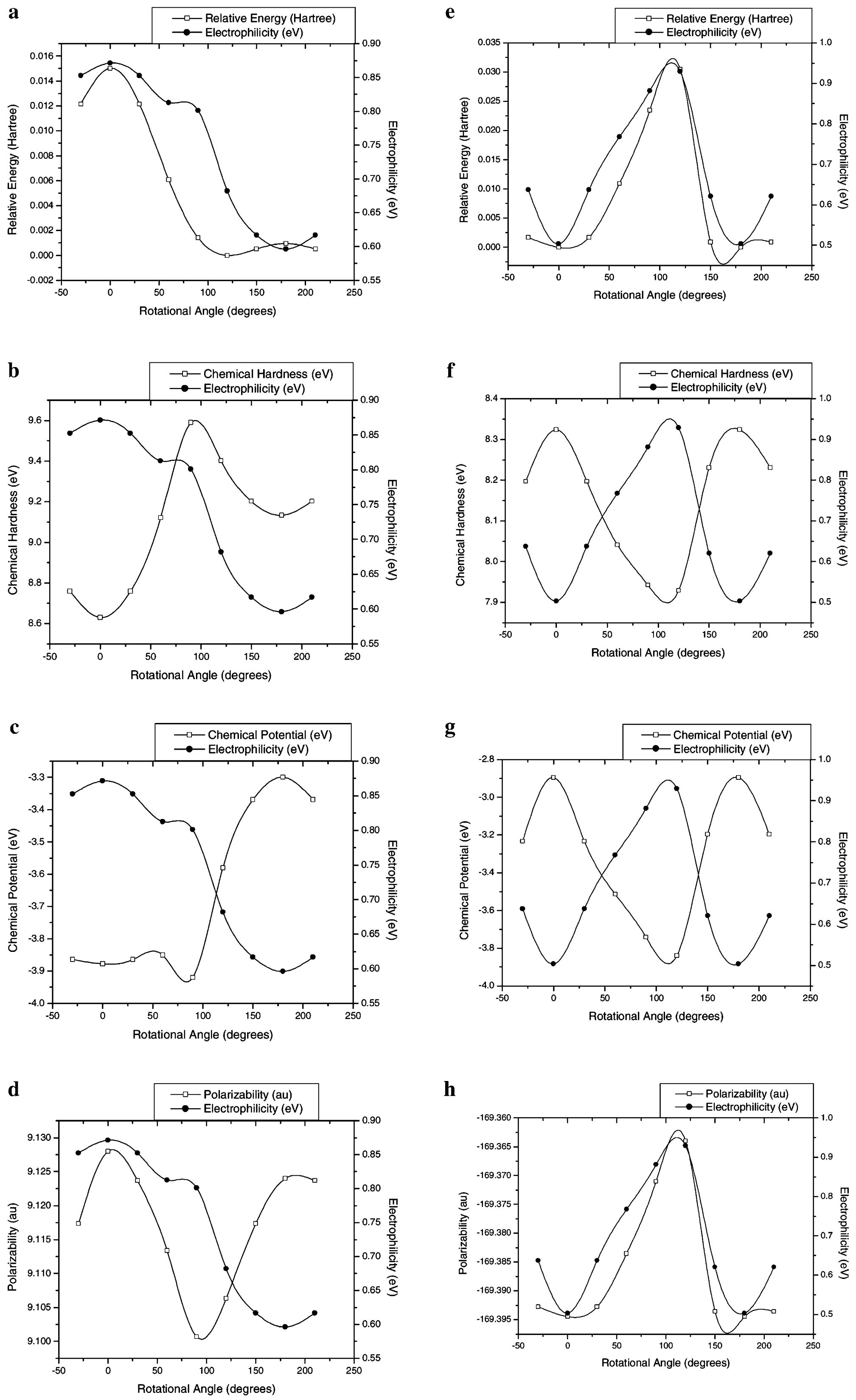


Fig. 1 Comparison of variation of global reactivity with electrophilicity for various rotational angles for HOOH (**a, b, c, d**) and formamide (**e, f, g, h**).

minimum electrophilicity condition is not satisfied in all the cases due to inherent changes in chemical hardness and chemical potential upon distortion along the normal coordinates and in accordance with the conditions for the extremum of electrophilicity.

The profiles of chemical reactivity indices during internal rotation for hydrogen peroxide and formamide are shown in Fig. 1. Profiles of formamide (Fig. 1e–h) reveal the validity of minimum energy-maximum hardness-minimum polarizability-minimum electrophilicity interrelationships governing the stability and reactivity of molecules. For various rotational conformations of formamide, the beautiful mirror image relationship between η and ω is clearly manifested in Fig. 1f and between μ and ω in Fig. 1g. On the other hand, the mimicking behavior between energy and electrophilicity is depicted in Fig. 1e and between polarizability and electrophilicity is in Fig. 1h. These results demonstrate the simultaneous validity of the MHP, MPP and MEP. However, such interesting interrelationship cannot be observed in the case of hydrogen peroxide. Although, minimum energy-maximum hardness (MHP) and minimum energy-minimum polarizability (MPP) relationships are valid for H_2O_2 molecule, the maximum hardness does not correspond to minimum electrophilicity because the extrema corresponding to μ do not coincide with those of η.

4 Conclusion

Ab initio studies on chosen molecular systems were used to probe the interrelationship between various global reactivity descriptors during molecular vibration and internal rotation. The electrophilicity profiles along various internal coordinates were calculated and compared with other global reactivity profiles. The conditions for minimum energy-maximum hardness-minimum polarizability-minimum electrophilicity were traced. It is observed from the numerical results that if η and μ are maxima at any point along the internal coordinates, the corresponding ω is minimum at that point. Similarly if η and μ are minima at any point, the corresponding ω is maximum. Although, in general, MHP and MPP are valid for changes along the internal coordinates, the validity of MEP cannot be generalized due to the necessary extremum conditions corresponding to ω.

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