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Fluctuations in electronegativity and global hardness induced by molecular vibrations

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Abstract

A pair of novel molecular indices has been proved to contain important information on the coupling between atomic displacement and electronic properties based on the electron density function within the Density Functional Theory: the nuclear reactivity (Φ) and nuclear stiffness (**G**). Appropriate calculation procedure has been developed and their role in describing anharmonicity of diatomic molecules has been demonstrated. This present work provides analysis of this effect for small molecules, unveiling the role of symmetry of molecular vibrational modes in modifying the affinity of a molecule to intermolecular electron transfer. The indices have been found to be a crucial factor determining thermal fluctuations in the molecular energy derivatives: electronegativity (χ) and hardness (η). The fluctuations of hardness play a specific role, as they bring a molecule uniquely to a critical region ($\eta \cong 0$), when molecule becomes unstable to an electron exchange process, due to its excitation in a selected destructive vibrational mode.

Keywords: Electronegativity; Global hardness; Nuclear reactivity; Nuclear stiffness; Thermal effect

1. Introduction

Proposing possible tools for studies of chemical reactivity has been a challenging task to the Conceptual Density Functional Theory [1]. However, the progress in quantum chemical methods and their widespread use has reduced the need for a conceptual type description to problems beyond the scope of typical calculation procedures. Coupling between the molecular vibrations and the electron density has been recognized as a problem, where a conceptual type of analysis could reveal the possible role of vibrations in chemical reactivity [2,3]. A pair of indices has been introduced for atoms in molecules, in order to describe this effect using terms typical for the Density Functional Theory (DFT). Derivatives of electronegativity (negative chemical potential), and hardness over the nuclear deformation have been termed nuclear reactivity Φ and nuclear hardness G, respectively [4].

The $\mathbf{\Phi}_i$ and $\mathbf{G}_i$ atomic vectors are defined by means of the total electrostatic forces $\mathbf{F}_i^+$ and $\mathbf{F}_i^-$ acting on

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nuclei upon vertical ionization:

$$\mathbf{\Phi}_i = \frac{\partial \chi}{\partial \mathbf{Q}_i} \cong \frac{1}{2}(\mathbf{F}_i^+ - \mathbf{F}_i^-) \tag{1}$$

and

$$\mathbf{G}_i = \frac{\partial \eta}{\partial \mathbf{Q}_i} \cong -\frac{1}{2}(\mathbf{F}_i^+ + \mathbf{F}_i^-) \tag{2}$$

$\mathbf{F}_i^+$ and $\mathbf{F}_i^-$ are total electrostatic forces [5] acting on the i-th nucleus within the structure of molecular ions with a number of electrons increased $(N_0 + 1)$ and decreased $(N_0 - 1)$, respectively, while the structure of the molecular skeleton is kept unchanged; $\mathbf{Q}_i = \mathbf{R}_i - \mathbf{R}_{i,0}$ is the displacement vector of atom i from an equilibrium position $\mathbf{R}_{i,0}$; χ is the electronegativity (negative chemical potential) and η is the global hardness of the electronic system, as defined in the DFT [6].

2. Nuclear indices for normal vibrational modes

Let the indices Φ_α and G_α for a normal vibrational mode α be obtained by the projection of the atomic $\mathbf{\Phi}_i$ and $\mathbf{G}_i$ vectors onto the atomic displacements within this mode, $\mathbf{Q}_i^\alpha$

$$\Phi_\alpha \equiv \left|\sum_{i\in\alpha} \mathbf{\Phi}_i \mathbf{Q}_i^\alpha\right| \quad \text{and } G_\alpha \equiv \left|\sum_{i\in\alpha} \mathbf{G}_i \mathbf{Q}_i^\alpha\right| \tag{3}$$

The atomic displacements are conveniently available form normalized amplitudes of atoms within the normal mode, $\mathbf{l}_i^\alpha$ [7]:

$$\mathbf{l}_i^\alpha = \frac{\mathbf{Q}_i^\alpha}{\left[\sum_{i\in\alpha} (\mathbf{Q}_i^\alpha)^2\right]^{1/2}} \tag{4}$$

$\mathbf{Q}_i^\alpha$ and $\sum_{i\in\alpha}(\mathbf{Q}_i^\alpha)^2$ are actual and temperature (energy) dependent, while $\mathbf{l}_i^\alpha$ vectors are considered to be universal property of a molecule. Hence, the nuclear reactivity and nuclear stiffness indices for a normal mode α become:

$$\begin{aligned} \Phi_\alpha &= |\Phi_{\alpha,0}|\left[\sum_{i\in\alpha} (\mathbf{Q}_i^\alpha)^2\right]^{1/2} \\ \text{and } G_\alpha &= |G_{\alpha,0}|\left[\sum_{i\in\alpha} (\mathbf{Q}_i^\alpha)^2\right]^{1/2} \end{aligned} \tag{5}$$

where scalar quantities $\Phi_{\alpha,0}$ and $G_{\alpha,0}$ are:

$$\begin{aligned} \Phi_{\alpha,0} &= \frac{1}{2}\sum_{i\in\alpha} (\mathbf{F}_i^+ + \mathbf{F}_i^-)\mathbf{l}_i^\alpha \\ \text{and } G_{\alpha,0} &= -\frac{1}{2}\sum_{i\in\alpha} (\mathbf{F}_i^+ + \mathbf{F}_i^-)\mathbf{l}_i^\alpha \end{aligned} \tag{6}$$

If ionized states are nondegenerate then forces $\mathbf{F}_i$ are of molecular symmetry. However, atomic displacement vectors $\mathbf{l}_i^\alpha$ are not necessary totally symmetric. Φ_α and G_α, the sums of scalar products will be nonzero only if:

$$\Gamma_\gamma \times \Gamma_\alpha \supset \Gamma_\gamma \tag{7}$$

i.e. the irreducible representation Γ_γ is contained in the direct product of Γ_γ and Γ_α. Here the irreducible representation of the point group of $\mathbf{F}_i$ forces is Γ_γ, and αth normal mode transforms according to Γ_α [8].

When $\mathbf{\Phi}_i$ and $\mathbf{G}_i$ (Eqs. (1) and (2)) are symmetry adapted, only totally symmetric modes give nonzero effect. However, if degeneracy in either (+) or (−) ionized state occurs, forces are no longer of molecular symmetry since the Jahn–Teller effect occurs upon vertical ionization. The total electrostatic forces drive the molecule to the new global minimum by breaking the molecular symmetry. In such case, the nonzero values are obtained for other then totally symmetric modes which conform to the condition given by Eq. (7).

3. Thermal effects

The Φ_α and G_α indices are only determined for a particular vibrational state through $\sum_{i\in\alpha}(\mathbf{Q}_i^\alpha)^2$, Eq. (5). The net change in electronegativity (and hardness) due to deformation from equilibrium

Table 1
Predominant destructive vibrational modes identified by the values of calculated nuclear reactivity ($\Phi_{\alpha,0}$) and nuclear stiffness indices ($G_{\alpha,0}$). Vibrational modes have not been shown as destructive, when either $\Phi_{\alpha,0} < 0.1$, or $G_{\alpha,0} < 0.1$

Molecule	Vibrational mode		$\lvert\Phi_{\alpha,0}\rvert$ (eV/Å)	$\lvert G_{\alpha,0}\rvert$ (eV/Å)
	Symmetry	Frequency (cm^{-1})		
H_2O	A_1	1665	0.513	0.117
	A_1	3800	0.779	3.918
H_3O^+	A_1	783	1.404	1.131
	A_1	3584	0.918	5.840
H_2S	A_1	1226	0.990	0.906
	A_1	2692	1.904	2.572
H_2CO	A_1	1554	0.874	0.380
	A_1	1846	3.300	3.106
BCl_3	A_1'	869	4.155	4.252
BF_3	A_1'	472	2.155	1.312
BH_3	E'	1198	1.348	1.348
	A_1'	2553	0.835	2.258
	E'	2682	1.436	1.343
BH_4^+	E	1239	4.311	2.272
	E	1239	1.511	0.274
	A_1	2291	1.678	5.121
HOCl	A'	723	7.260	3.764
	A'	1272	0.202	0.272
	A'	3764	0.527	0.777
HOF	A'	998	13.400	7.93
	A'	1396	0.495	0.782
	A'	3736	0.870	1.296
HCN	S_g	2214	0.953	6.964
	S_g	3475	0.918	0.913
HCNO	S_g	1308	3.367	3.619
	S_g	2362	1.183	2.261
	S_g	3534	1.204	0.351
NH_3	A_1	1090	2.052	1.266
	A_1	3462	1.096	2.584
NH_4^+	E	1727	2.825	2.825
	E	1727	0.424	0.424
	A_1	3369	2.330	5.760
NH_2NH_2	A_g	940	3.709	2.391
	A_g	1262	1.628	1.004
	A_g	3419	0.873	1.874
CHCH	S_{gg}	2086	0.925	4.751
	S_{gg}	3537	0.953	0.919
CH_2CH_2	A_g	1389	0.428	1.102
	A_g	1715	3.589	0.250
	A_g	3160	2.115	1.861
CH_2F_2	A_1	1131	2.291	0.600
	A_1	1553	1.209	0.197
	A_1	3042	0.905	3.158
CH_3F	A_1	1191	1.072	1.211
	E	1219	0.255	0.255
	E	1219	0.147	0.137
	A_1	1632	0.191	0.786
	E	1660	0.394	0.384
	E	1660	0.676	0.676
	A_1	3196	0.905	1.485
	E	3343	0.334	0.351
	E	3343	0.587	0.587
CH_3Cl	A_1	719	5.396	4.993
	E	1035	0.131	0.131
	A_1	1398	0.160	0.239
	E	1495	1.104	1.373
	E	1495	0.233	0.233
	A_1	3088	3.995	4.685
	E	3192	0.222	0.223
	E	3192	0.418	0.160
CH_3NH_2	A'	859	1.389	0.658
	A'	1067	0.291	0.370
	A'	1183	1.056	0.905
	A'	2966	0.241	0.702
	A'	3072	0.372	0.193
	A'	3492	0.932	1.888
CH_3OH	A'	1095	0.297	0.622
	A'	1385	0.290	0.209
	A'	1527	0.118	0.287
	A'	2989	0.242	1.007
	A'	3122	0.301	0.118
CH_3NO_2	A'	672	0.952	0.394
	A'	944	1.478	0.351
	A'	1168	0.363	0.263
	A'	1436	2.864	4.829
	A'	3171	0.218	0.379
C_6H_6	E_{2g}	621	0.239	0.570
	A_{1g}	1020	0.316	1.501
	E_{2g}	1653	2.868	0.273
	A_{1g}	3210	0.240	0.038

Table 2
Calculated global hardness and electronegativity for molecules, and their zero-temperature fluctuations as given by Eqs. (8) and (9). In column 3, the vibrational lowering of the global hardness is shown (Eq. (13); $T \to 0$ K; $\times 10^3$)

Molecule	Global hardness η (eV)	$\sum_\alpha \Phi_{\alpha,0}^2/4k_\alpha^2(\hbar\omega_\alpha)$ ($\times 10^3$) (eV)	$\lvert\Delta\eta\rvert = \langle(\delta\eta)^2\rangle^{1/2}$ ($T \to 0$), (eV)	Electronegativity χ (eV)	$\lvert\Delta\eta\rvert = \langle(\delta\chi)^2\rangle^{1/2}$ ($T \to 0$), (eV)
H_2O	8.46	0.1345	0.2555	3.92	0.0709
H_3O^+	10.10	6.8973	0.4258	14.58	0.2003
H_2S	6.83	1.5271	0.2255	3.56	0.1868
H_2CO	6.42	0.4587	0.1240	4.31	0.1490
BF_3	12.45	0.1670	0.1359	5.37	0.1328
BCl_3	5.82	0.0830	0.0419	5.43	0.0689
BH_3	6.60	2.2650	0.2580	5.98	0.1979
BH_4^+	26.34	25.2756	0.5120	12.65	0.5497
HOCl	6.04	1.1540	0.1512	5.10	0.2718
HOF	7.76	1.6454	0.2770	4.88	0.4301
HCN	12.19	0.0398	0.2756	8.35	0.0692
HCNO	7.13	0.1948	0.1560	3.46	0.1522
NH_3	7.71	5.4185	0.2295	3.05	0.2468
NH_4^+	11.64	3.8953	0.4937	14.89	0.3256
NH_2NH_2	6.55	2.3168	0.2037	2.19	0.2365
CHCH	7.75	0.0460	0.2259	3.37	0.0730
CH_2CH_2	7.99	0.9636	0.1718	4.68	0.2525
CH_2F_2	9.01	0.9530	0.2318	3.59	0.1716
CH_3F	9.00	0.4804	0.1703	3.76	0.1273
CH_3Cl	7.31	5.4307	0.4672	3.96	0.4401
CH_3NH_2	7.02	5.3286	0.1968	2.46	0.2170
CH_3OH	7.59	0.1114	0.1219	3.06	0.0505
CH_3NO_2	7.23	0.4704	0.1516	5.40	0.1362
C_6H_6	5.65	0.5072	0.0891	3.37	0.1432

geometry by actual vibrations in all modes is:

$$|\Delta\chi| = \sum_i \left|\frac{\partial\chi}{\partial\mathbf{Q}_i}\mathbf{Q}_i\right| = \sum_i |\boldsymbol{\Phi}_i\mathbf{Q}_i| = \sum_i \left|\boldsymbol{\Phi}_i \sum_\alpha \mathbf{Q}_i^\alpha\right|$$

$$= \sum_\alpha \left|\sum_{i\in\alpha} \boldsymbol{\Phi}_i\mathbf{Q}_i^\alpha\right| = \sum_\alpha \Phi_\alpha \tag{8}$$

and

$$|\Delta\eta| = \sum_\alpha G_\alpha \tag{9}$$

From the experimental point of view, the average temperature effect is most important. The thermal average of the sum $\sum_{i\in\alpha}(\mathbf{Q}_i^\alpha)^2$ may be obtained for each normal mode within the harmonic approximation [9,10],

$$\left\langle \sum_{i\in\alpha} (Q_i^\alpha)^2 \right\rangle = \frac{\hbar\omega_\alpha}{2k_\alpha} \mathrm{ctgh}\frac{\hbar\omega_\alpha}{2k_\mathrm{B}T} \tag{10}$$

This result may be used directly in calculation of the thermal fluctuations of electronegativity and hardness. The average thermal fluctuations are:

$$\langle(\delta\chi)^2\rangle = \sum_\alpha \langle(\delta\Phi_\alpha)^2\rangle = \sum_\alpha \Phi_{\alpha,0}^2 \left\langle \sum_{i\in\alpha} (Q_i^\alpha)^2 \right\rangle \tag{11}$$

$$\langle(\delta\eta)^2\rangle = \sum_\alpha \langle(\delta G_\alpha)^2\rangle = \sum_\alpha G_{\alpha,0}^2 \left\langle \sum_{i\in\alpha} (Q_i^\alpha)^2 \right\rangle \tag{12}$$

At $T \to 0$, the results for $\Delta\chi$, $\Delta\eta$ and $\langle(\delta\eta)^2\rangle^{1/2}$, $\langle(\delta\chi)^2\rangle^{1/2}$ become identical, respectively.

4. Results

Calculations were performed using B3LYP method and 6-311 + G(3df, 3dp) basis set for GAUSSIAN 98 code [11]. Geometry was optimized for neutral molecule by a quasi Newton–Raphson

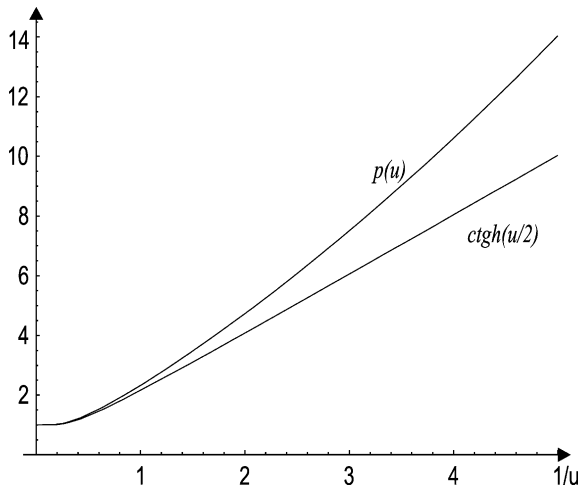

Fig. 1. The $p(u)$ function (Eq. (21)) as compared to the *ctgh* function; the difference between them is due to the estimated anharmonic effect ($u = \hbar\omega/k_B T$).

procedure [12,13]. Anion and cation energies and forces were calculated in neutral molecule geometry. Then frequencies were obtained. Anion and cation energies, forces, force constants and the normalized amplitudes of all atoms have been calculated for neutral molecule geometry. Results of calculations are collected in Tables 1 and 2. In Table 1, only the vibrational modes significant for a change in χ and η have been shown. The considerable differences between vibrations are first and striking feature of this result, inasmuch as they influence the electronegativity and/or global hardness of the system. From the results in Table 1, it is possible to identify the vibrational modes that play a particular destructive role; high values of nuclear reactivity ($\Phi_{\alpha,0}$) and nuclear stiffness indices ($G_{\alpha,0}$) parameters suggests, that these particular modes significantly modify the reactivity properties of a molecule.

The role of actual vibrational excitations in these destructive modes has been shown by calculating fluctuations of these values. At $T \rightarrow 0$ K, the function $ctgh(u/2) \rightarrow 1$, and the fluctuations reach their minimum level (Eqs. (10)–(12)). These zero limit values of $\Delta\chi$ and $\Delta\eta$ identical to the respective fluctuations have been calculated using Eqs. (8)–(10) and (5) and are shown in Table 2, column 4 and 6. At real temperature, this effect will increase considerably, as demonstrated by the properties of the *ctgh* function in Fig. 1.

5. Discussion

The Φ_α, and G_α indices provide information on the possible effect of vibrations on molecular electronegativity and hardness. However, the overall effect should be considered including two additional phenomena, as discussed in earlier work: (i) the effect of lowering the global hardness of a vibrating system as compared to a rigid one; (ii) the effect of anharmonicity [14]. Analysis of the first effect led to the conclusion, that due to the coupling between the deformation and the change in electron density, effective hardness of a vibrating system is lowered by $\Phi^2/2k$ for a simple harmonic oscillator. For a multi-atomic system, the same argument leads to an expression for the effective global hardness $\tilde{\eta}$:

$$\tilde{\eta} = \eta - \sum_\alpha \frac{\Phi_\alpha^2}{2k_\alpha}$$

$$= \eta - \sum_\alpha \frac{\Phi_{\alpha,0}^2}{4k_\alpha^2}(\hbar\omega_\alpha) ctgh \frac{\hbar\omega_\alpha}{2k_B T} \tag{13}$$

In order to estimate the role of this correction, corresponding sum has been calculated using the $\Phi_{\alpha,0}$ values (Eqs. (5) and (10)), for the $T \rightarrow 0$ limit in column 3 of Table 2. The correction is typically of the order of less than 0.001 eV. At real temperatures, the contributions increases with temperature according to the *ctgh* function for each mode, Fig. 1. For low frequency modes this contribution may reach considerable values even at moderate temperature limit ($1/u < 10$), however, as compared to the global hardness, the effect can hardly be significant, in thermal excitations. This mechanism of primary lowering applies to hardness only and has no effect on the electronegativity.

It has also been shown in previous work, that anharmonicity of an oscillator introduces additional effect on both electronegativity and hardness [14]. If the Morse potential is used as a convenient estimate of the energy of an anharmonic oscillator, the anharmonic effect must be added to the effect of mere vibration, it will modify the sum of amplitudes, $\sum_{i\in\alpha}(\mathbf{Q}_i^\alpha)^2$. To the first and only indicative approximation, substantiated by the arbitrary nature of the Morse formula, the thermal average of the amplitude of an anharmonic

oscillator may be roughly described as:

$$\langle \overline{Q}_\alpha \rangle = -\frac{1}{2a}\ln\left(1 - \frac{E_\alpha(T)}{D_e}\right) > 0 \qquad (14)$$

$$E_0 \leq E_\alpha(T) < D_e$$

(while it is '0' for a harmonic oscillator). In order to evaluate the upper limit of the anharmonic effect, the $E_\alpha(T)$ function for a vibrational mode α must contain both the thermal average of the energy as well as possible fluctuations thereof at temperature T

$$E(T) = \langle E \rangle + \langle (\delta E)^2 \rangle^{1/2} \qquad (15)$$

The first approximation for $\langle E \rangle$ and $\langle (\delta E)^2 \rangle$, justified at sufficiently low temperatures, is that for classical oscillator with frequency ω [10]

$$\langle E_{vib} \rangle = \frac{1}{2}\hbar\omega\frac{e^u + 1}{e^u - 1}$$

$$\text{and } \langle (\delta E_{vib})^2 \rangle = (\hbar\omega)^2 \frac{e^u}{(e^u - 1)^2} \qquad (16)$$

$$\text{where } u = \frac{\hbar\omega}{k_B T}$$

Then

$$E_\alpha(T) = \frac{1}{2}\hbar\omega_\alpha \frac{\exp(u_\alpha/2) + 1}{\exp(u_\alpha/2) - 1} \qquad (17)$$

Hence, the first approximation for the anharmonic nuclear reactivity and nuclear stiffness indices in a normal mode α becomes, roughly:

$$\Phi_\alpha = \Phi_{\alpha,0}\left[\left\langle \sum_{i\in\alpha} (Q_i^\alpha)^2 \right\rangle + \langle \overline{Q}_\alpha \rangle^2\right]^{1/2} \qquad (18)$$

$$G_\alpha = G_{\alpha,0}\left[\left\langle \sum_{i\in\alpha} (Q_i^\alpha)^2 \right\rangle + \langle \overline{Q}_\alpha \rangle^2\right]^{1/2} \qquad (19)$$

(The primary effect on the global hardness, Eq. (13) should also be corrected accordingly.)

Respective fluctuations become:

$$\langle (\delta\chi)^2 \rangle_{an} = \langle (\delta\chi)^2 \rangle + \sum_\alpha \Phi_{\alpha,0}^2 \langle \overline{Q}_\alpha \rangle^2$$

$$= \sum_\alpha \frac{\Phi_{\alpha,0}^2}{2k_\alpha}(\hbar\omega_\alpha)p(u_\alpha) \qquad (20)$$

$$\langle (\delta\eta)^2 \rangle_{an} = \langle (\delta\eta)^2 \rangle + \sum_\alpha G_{\alpha,0}^2 \langle \overline{Q}_\alpha \rangle^2$$

$$= \sum \frac{G_{\alpha,0}^2}{2k_\alpha}(\hbar\omega_\alpha)p(u_\alpha) \qquad (21)$$

The universal and temperature dependent $p(u)$ function is determined by the parameters of the oscillator, and at moderate values of $E_\alpha(T)$ function (Eq. (15)) can be approximated as:

$$p(u_\alpha) = ctgh(u_\alpha/2) + \frac{D_e - D_0}{2D_e}\left[\frac{\exp(u_\alpha/2) + 1}{\exp(u_\alpha/2) - 1}\right]^2 \qquad (22)$$

The second term is due to entirely to the anharmonic effect; D_0 and D_e are dissociation and minimum energies, respectively. Parameter $(D_e - D_0)/2D_e$ has been calculated from spectroscopic data for a set of diatomic molecules, as reported in Ref. [14]. It has been found to vary in rather narrow range from ca. 0.02 for HF, HCl, LiH, BH, F_2, to ca. 0.01–0.005 for Li_2, ClF, Cl_2, CO, CS, LiF. In order to show the possible role of the anharmonic effect, the universal $p(u_\alpha)$ function has been shown for $(D_e - D_0)/2D_e = 0.01$ in Fig. 1. The $p(u)$ function determines temperature dependence of fluctuations in electronegativity and hardness. The $p(u)$ function shows substantial anharmonic effect as compared to *ctgh* function. Anharmonic effect is reduced to the value of $(D_e - D_0)/2D_e$ parameter at $T \rightarrow 0$ temperature limit.

Vibrational excitation will significantly contribute to the fluctuations in electronegativity and hardness at real temperatures, as they will increase according to the $p(u)$ function, which is always larger than *ctgh* function even at moderate temperatures. Both harmonic and anharmonic effects lead to increase of fluctuations from their zero temperature limit as shown in Table 2. These values are relatively high as compared to χ and η (Table 2). When the temperature effect is added, fluctuations may get close to the critical limit, when $\delta X \cong X$. This may be especially important for the hardness, as decreasing global hardness of the electronic system brings it to less stability [15]. Pearson and Palke proved that the global hardness is at a maximum against any nontotally symmetric distortion of the molecule [16]. Hence, in molecules where such vibrations give $G_\alpha \neq 0$ (the Jahn–Teller effect), vibrations contribute to lowering the hardness only.

For totally symmetric modes, however, the practical effect of a reaction (changing the number of electron in a molecule) is facilitated by softening fluctuations only, others having no effect. It is then expected that large fluctuations in hardness for a particular vibrational mode of any molecule make it indeed a destructive one, indicating a most feasible reaction.

6. Conclusion

This work has led to several interesting results. First is a method of identification of destructive vibrational modes, which can now be made in a straightforward manner, using direct results of quantum chemical calculations. The mode may be destructive when $\Phi_\alpha \neq 0$ and $G_\alpha \neq 0$, hence when it may bring the lowering of global hardness. The role of electronegativity appears to be minor. Changing χ obviously modifies the effect of the reaction, however it is not possible to estimate this change in general terms; the effect is dependent on the nature of a second reacting species. The role of hardness is more important: identifying a mode with large Φ_α and G_α hints to this mode as to the destructive (softening) one.

The role of vibrational modes increases dramatically with temperature. Although the primary softening effect (Eq. (13)) could not play any major role, the effect of thermal fluctuations is substantial (Eqs. (11) and (12)). The increase with temperature may be particularly strong when modes identified as destructive are characterized by low frequencies (Eq. (10), $\hbar\omega/2k = \hbar/2\omega M$, M is reduced mass). Considering the values of hardness fluctuation $\Delta\eta$ given in Table 2, the magnitude of fluctuations would approach the critical region ($\Delta\eta \cong \eta \rightarrow \eta \cong 0$) in the temperature range ca. $k_B T \cong 5\hbar\omega$, which for a frequency mode 500 cm^{-1} would require temperatures as high as 3500 K, even for a molecule which shows considerable anharmonizm. Thermal excitations are then unlikely to bring a molecule close to the critical region.

Identifying the vibrational modes of a specifically destructive character opens a new chance to study reactivity of excited molecules, using radiation specifically chosen to match a selected vibrational mode. Such effects of coupling the vibrational modes with proton transfer reaction have been suggested [17]. Chemical effects of such reactions induced by the specific IR radiation are difficult to study, unless they lead to a chain of reactions that produce new stable products. Reactions of that type have indeed been observed, induced by the Near Infrared Radiation [18]. Applications of the results of this present work to quantitative predicting a destructive role of specific modes may be of great value for further studies of interactions and role of water in biological systems.

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