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Validity of the Minimum Polarizability Principle in Molecular Vibrations and Internal Rotations: An ab Initio SCF Study

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Molecular vibrations in ammonia (NH_3) and hydrogen sulfide (H_2S), and internal rotations in hydrogen peroxide (HOOH), hydrogen thioperoxide (HSOH), hydrogen persulfide (HSSH), and ethylene (C_2H_4) are studied using ab initio SCF methods at the Hartree−Fock level using a standard Pople 6-311G** basis set. Polarizability values are calculated using both Pople's and Sadlej's basis sets. Any nontotally symmetric distortion in bond length or bond angle along the vibrational symmetry coordinates of a molecule around its equilibrium geometry decreases the equilibrium hardness value and increases the equilibrium polarizability value. During rotational isomerization the minimum energy conformation corresponds to the maximum hardness and minimum polarizability values and the maximum energy conformation corresponds to the minimum hardness and maximum polarizability values. Density functional calculations confirm these observed trends. In general we have found that the conditions of maximum hardness and minimum polarizability complement the minimum energy criterion for molecular stability.

1. Introduction

Popular qualitative chemical concepts like electronegativity[1,2] (χ) and hardness (η)[3,4] are rigorously defined within density functional theory (DFT).[5,6] For an N-particle system with total energy E and external potential $v(\vec{r})$ they are defined as follows:[7,8]

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} \tag{1}$$

and

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

In eq 1 μ is the electronic chemical potential which is the Lagrange multiplier associated with the normalization constraint of DFT.[5,6]

These quantities are better appreciated through the related electronic structure principles. Sanderson's electronegativity equalization principle[9] states that "all the constituent atoms in a molecule have the same electronegativity value given by the geometric mean of the electronegativities of the pertinent isolated atoms". Pearson proposed two hardness-related principles, viz., the hard−soft acids and bases (HSAB) principle[3,4,8,9] and the maximum hardness principle (MHP).[4,10,11] While the former states[3,4,8] that "hard likes hard and soft likes soft", the statement[4,10] of the latter is "there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible".

Complete characterization of an N-particle wave function needs only N and $v(\vec{r})$. The response of the system is measured by χ and η when N is varied for a fixed $v(\vec{r})$. However, the polarizability (α) of the system may be used in understanding the behavior of the system for changing $v(\vec{r})$ at constant N. On the basis of an inverse relationship[12] between η and α, Chattaraj and Sengupta[13] have proposed a minimum polarizability principle (MPP) which states that "the natural direction of evolution of any system is toward a state of minimum polarizability". It has also been shown[14] that "a system is harder and less polarizable in its ground state than in any of its excited states".

In the present paper we verify whether the MPP is valid when a molecule undergoes vibration or internal rotation. For this purpose we compute various reactivity parameters, viz., χ, η, and α, using ab initio SCF methods in the context of molecular vibration and internal rotation. Symmetric and asymmetric distortions of ammonia and hydrogen sulfide along the directions specified by vibrational symmetry coordinates are taken from Pearson and Palke[15] and Chattaraj et al.,[16] respectively. The rotational isomerization of HOOH, HSOH, and HSSH is taken as given by Toro-Labbé and coworkers.[17] Along the torsional angle these molecules present the interesting feature of having a single well at the nonplanar gauche conformation with two energy barriers at the planar cis and trans conformations. We also test the validity of the MPP in the case of the rotation of planar ethylene[18] and in a few intermolecular double proton transfer reactions.[19]

2. Details of Computation

The chemical potential and the hardness are calculated as the following approximate versions of eqs 1 and 2:

$$\mu = \frac{1}{2}(\epsilon_L + \epsilon_H) \tag{3}$$

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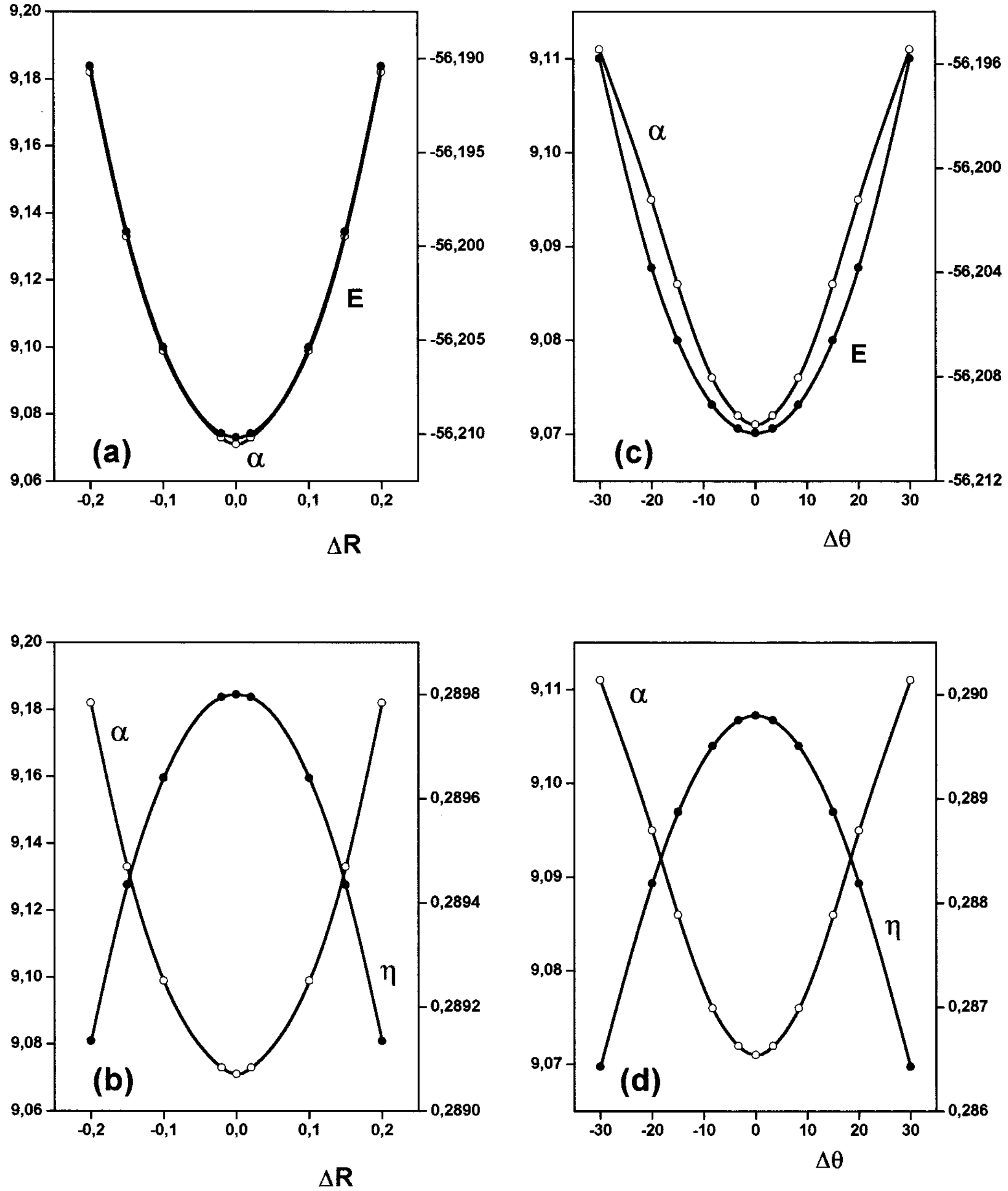

Figure 1. Asymmetric distortions of ammonia: (a) profiles of energy and polarizability and (b) profiles of hardness and polarizability for distortion in the N−H bond distance; (c) profiles of energy and polarizability and (d) profiles of hardness and polarizability for distortion in the HNH bond angle. All values are in atomic units; the left axis bears the polarizability values (open circles).

and

$$\eta = \frac{1}{2}(\epsilon_L - \epsilon_H) \tag{4}$$

where ϵ_L and ϵ_H are the lowest unoccupied and highest occupied molecular orbital energies, respectively. The energy, μ, and η were obtained through SCF ab initio calculations at the Hartree−Fock (HF) level with the Pople 6-311G** basis set using the Gaussian 94 package.[20] In addition to the calculations with the Pople basis set, the polarizability was calculated using the more adequate Sadlej basis set[21] that is designed to reproduce molecular electric properties, especially polarizabilities. These calculations were complemented with the use of the B3LYP model within the frame of DFT.[22]

3. Results and Discussion

Figures 1 and 2 depict the profiles of energy, hardness, and polarizability associated with the asymmetric distortions of E symmetry and the symmetric distortions of A_1 symmetry for ammonia,[15] respectively. In both figures parts a and b refer to the distortions in bond length (ΔR) while parts c and d refer to the distortions in bond angle ($\Delta\theta$). Unless otherwise specified all quantities are in atomic units. For the non totally symmetric distortions μ and electron−nuclear attraction potential (v_{en}) remain constant for small changes, in the Pearson−Palke sense.[15] However, neither of them remain constant for the totally symmetric distortions. In Figure 1a,c we see that the polarizability is minimum for the equilibrium configuration (energy is minimum) for the asymmetric stretching and bending modes, respectively. For these two modes the beautiful mirror-image relationship between α and η profiles is clearly manifested in Figure 1b,d demonstrating the simultaneous validity of the MHP and the MPP in the context of molecular vibration since the equilibrium configuration is associated with the largest η and the smallest α values. As analyzed by Pearson and Palke,[15] the hardness increases monotonically as the nuclei approach each

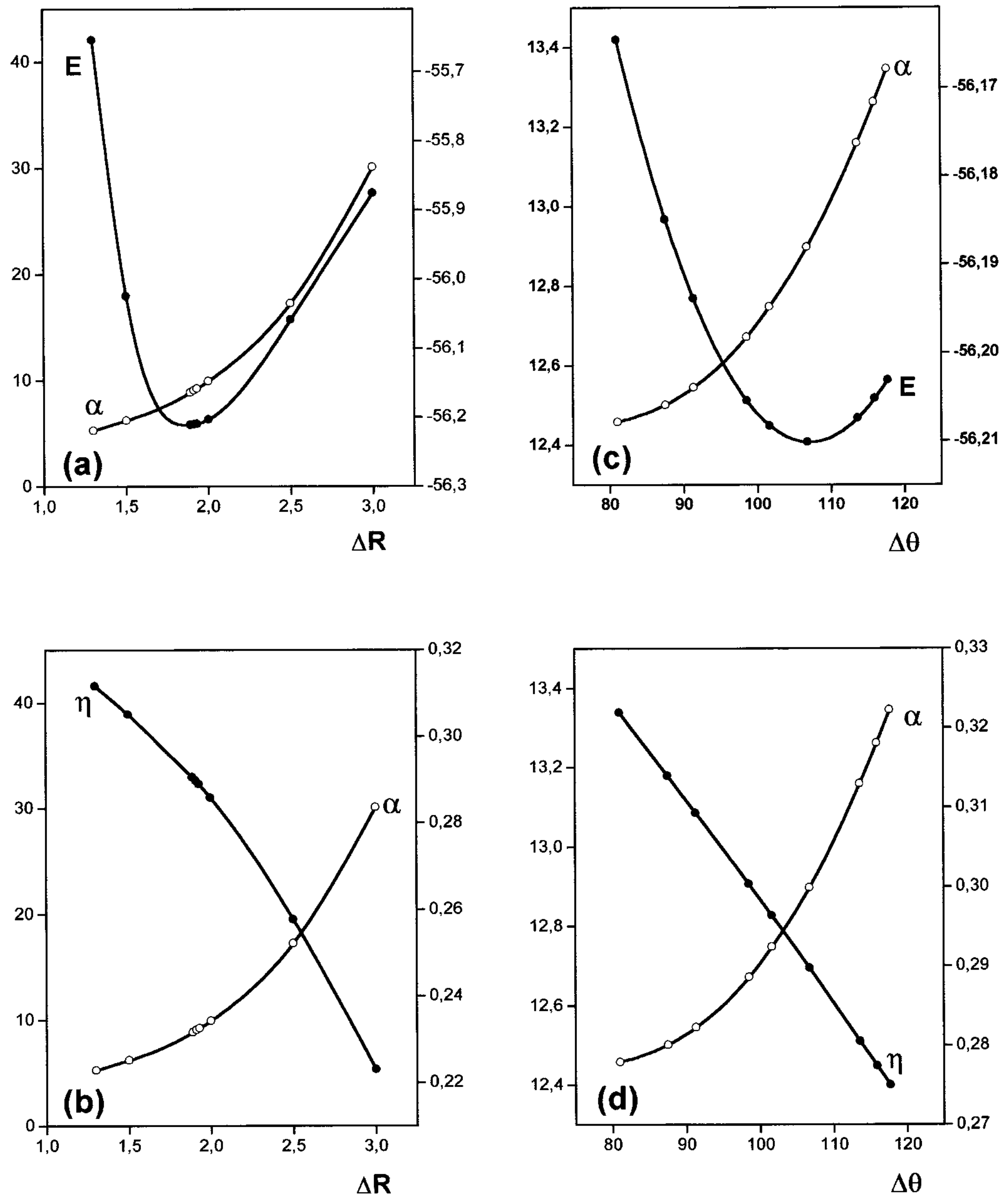

Figure 2. Symmetric distortions of ammonia: (a) profiles of energy and polarizability and (b) profiles of hardness and polarizability for distortion in the N−H bond distance; (c) profiles of energy and polarizability and (d) profiles of hardness and polarizability for distortion in the HNH bond angle. All values are in atomic units; the left axis bears the polarizability values (open circles).

other during the totally symmetric oscillation. In the present work (Figure 2a,c) it is shown that the polarizability also keeps on decreasing for such a distortion as the nuclei come closer to each other. An inverse relationship between α and η for the symmetric stretching and bending modes is transparent in parts b and d, respectively, of Figure 2. Calculation of polarizability using Pople's (α_{Pople}) and Sadlej's (α_{Sadlej}) basis sets shows the same qualitative trends for the asymmetric stretching in ammonia as is transparent in Figure 3a, which depicts the linear relationship between two sets of α values. In general the α_{Sadlej} values are larger than the α_{Pople} values. Since the α_{Pople} values do not reproduce the expected trend (decrease with an increase in HNH bond angle) for symmetric distortions of HNH bond angle in ammonia, in Figure 2c,d we present the α_{Sadlej} values. On the other hand, we have performed DFT/B3LYP calculations within the same scheme of Pople and Sadlej basis sets for energy, hardness, and polarizability. The results reproduce the same trends given in Figures 1 and 2. As an illustration of this observation, we display in Figure 3b the linear correspondence between the polarizability values for the asymmetric stretch of the Hartree−Fock and density functional calculations. We note that the DFT polarizability values are larger than the HF ones. This situation is encountered in all remaining normal modes of NH_3.

With the purpose of throwing more light on the applicability of these principles, we have performed similar calculations (HF and DFT) for the symmetric and asymmetric stretchings as well as the bending mode of H_2S. The results are quoted in Table 1. As for ammonia we find that the asymmetric distortions display opposite trends for α and η showing the simultaneous validity of the MHP and the MPP in the context of molecular vibration. In contrast to this for symmetric distortions neither α nor η is an extremum at the equilibrium geometry and both attain their extremum value when the atoms are closest.

Profiles of energy, hardness, and polarizability for the internal rotation of H_2O_2 are presented in Figure 4. It is clear (Figure

TABLE 1: Total Energy (*E*), Hardness (η), and Polarizability (α) Values Obtained through Hartree−Fock (DFT/B3LYP) Calculations for H_2S and Rotational Isomers of HSOH, HSSH, and C_2H_4 (All Values in au)

molecule	$-E$	η	α^a
H_2S			
asym stretch			
$\delta^b = 0.0$	398.701 237 (399.421 642)	0.258 (0.142)	23.715 (25.138)
$\delta = \pm 0.05$	398.698 494 (399.419 017)	0.256 (0.136)	23.749 (25.161)
$\delta = \pm 0.1$	398.690 108 (399.411 001)	0.252 (0.130)	23.850 (25.233)
$\delta = \pm 0.2$	398.654 109 (399.376 504)	0.243 (0.118)	24.257 (25.250)
sym stretch			
$\delta = -0.1$	398.688 228 (399.405 988)	0.265 (0.151)	22.125 (23.544)
$\delta = -0.05$	398.698 241 (399.417 162)	0.262 (0.147)	22.886 (24.315)
$\delta = 0.0$	398.701 237 (399.421 642)	0.258 (0.142)	23.715 (25.138)
$\delta = +0.05$	398.698 752 (399.420 927)	0.254 (0.136)	24.616 (26.014)
$\delta = +0.1$	398.692 011 (399.416 226)	0.250 (0.130)	25.594 (26.942)
HSH bending			
84.21	398.698 100 (399.419 734)	0.259 (0.137)	23.636 (25.029)
89.21	398.700 460 (399.421 378)	0.259 (0.139)	23.664 (25.073)
94.21[c]	398.701 237 (399.421 642)	0.258 (0.142)	23.715 (25.138)
99.21	398.700 465 (399.420 562)	0.257 (0.140)	23.786 (25.222)
104.21	398.698 189 (399.418 181)	0.256 (0.137)	23.879 (25.327)
cis-HSOH	473.531 796 (474.614 686)	0.232 (0.093)	26.860 (29.027)
gauche-HSOH	473.542 668 (474.626 130)	0.243 (0.110)	26.672 (28.799)
trans-HSOH	473.535 313 (474.618 957)	0.229 (0.093)	27.036 (29.164)
cis-HSSH	796.217 610 (797.619 719)	0.206 (0.082)	43.848 (45.779)
gauche-HSSH	796.230 201 (797.631 886)	0.234 (0.108)	43.194 (45.291)
trans-HSSH	796.221 192 (797.623 560)	0.206 (0.081)	43.980 (45.876)
planar-C_2H_4	78.054 725 (78.613 656)	0.273 (0.143)	27.276 (27.667)
90°-C_2H_4	77.882 949 (78.463 019)	0.150 (0.030)	35.111 (36.812)

[a] Calculated using the Sadlej basis set. [b] δ denotes the amount of distortion in Å. [c] Equilibrium value.

4a) that the polarizability curve more or less mimicks the corresponding energy curve as a function of the torsional angle (ω). The polarizability minimum is slightly shifted toward the right. A similar behavior was observed[17] for this molecule when E and η profiles were compared. Figure 4 demonstrates that the hardness and the polarizability (α_{Sadlej}) bear a mirror-image relationship. The α_{Pople} values keep on decreasing. It appears that Sadlej's basis set is more appropriate than Pople's one for the polarizability calculation whereas the latter works better for the calculation of energy and hardness. A maximum (minimum) in the hardness profile corresponds to a minimum (maximum) in the polarizability profile, a clear vindication of the validity of both the MHP and the MPP during molecular internal rotation. We have obtained the same trends from density functional calculations.

Further tests of the validity of the MHP and the MPP in the context of internal rotation were carried out by performing similar calculations on HSOH, HSSH, and ethylene. The energy, hardness, and polarizability values for the relevant isomers of these molecules are also quoted in Table 1. In all three cases we observe the same trends already described for hydrogen peroxide in that the stable conformations are associated with minimum values of α and maximum values of η. Moreover, we note in comparing HF with DFT calculations that in the present cases the validity of the MHP and the MPP is confirmed independent of the method of calculation.

The implication of the MPP during chemical reactions is being studied by us at present. However, it is worth to mention that results on different double proton transfer reactions are confirming the simultaneous validity of the MHP and the MPP.[19] As illustrative examples, in Table 2 we display values of energy, hardness, and polarizability for the fully optimized structures of reactants (R), products (P), and transition states (TS) of four double proton transfer reactions. The numbers were obtained through ab initio calculations at the Hartree−Fock level and using the standard 6-311G** basis set. Note that, in the first three reactions, reactants and products are the same species, the reaction is isoenergetic, and the TS is a planar symmetric structure. The fourth reaction is endoenergetic and the transition state, although planar, is not symmetric. In all cases the results show that the most favorable direction of evolution of these reactions is toward the state where the polarizability and energy are minima and the hardness is a maximum.

TABLE 2: Hartree−Fock 6-311G Values of Energy, Hardness, and Polarizability for the Stable Conformations and Transition States (TS) of Double Proton Transfer Reactions (All Values in au)**

reaction	$-E$	η	α
HCO−OH···HCO−OH			
R	377.664 112	0.320	30.958
TS	377.635 537	0.311	32.047
P	377.664 112	0.320	30.958
HCO−OH···HCS−SH			
R	1022.917 548	0.202	60.996
TS	1022.880 619	0.196	67.619
P	1022.917 548	0.202	60.996
HCS−SH···HCS−SH			
R	1668.176 971	0.197	88.614
TS	1668.117 387	0.184	106.245
P	1668.176 971	0.197	88.614
HCS−SH···HC(═O)−SH	1345.542 487	0.200	72.900
TS	1345.496 193	0.177	84.834
HCS−SH···HC(═S)−OH	1345.538 872	0.197	75.085

4. Concluding Remarks

Ab initio SCF studies on representative systems undergoing molecular vibrations, internal rotations, and chemical reactions have confirmed the validity of the maximum hardness and minimum polarizability principles for these processes. The molecule at the equilibrium geometry possesses the maximum hardness and the minimum polarizability values when compared with the corresponding values for any other geometry obtained through a non totally symmetric distortion. In internal rotation processes we have found that the most (least) stable isomer is associated with the maximum (minimum) hardness value and

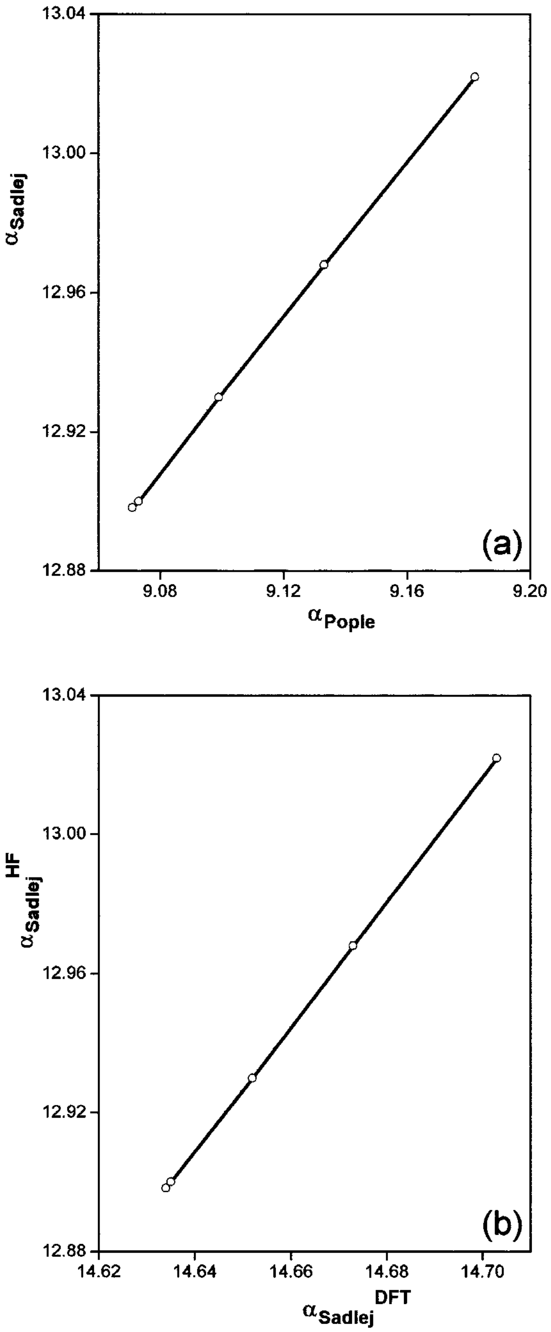

Figure 3. Asymmetric stretching of ammonia: (a) comparison of the Pople and Sadlej polarizabilities and (b) comparison of Hartree−Fock and DFT results.

the minimum (maximum) polarizability value. The double proton transfer reactions that we have reviewed in this paper tend to go in the direction that produces the less polarizable and hardest species.

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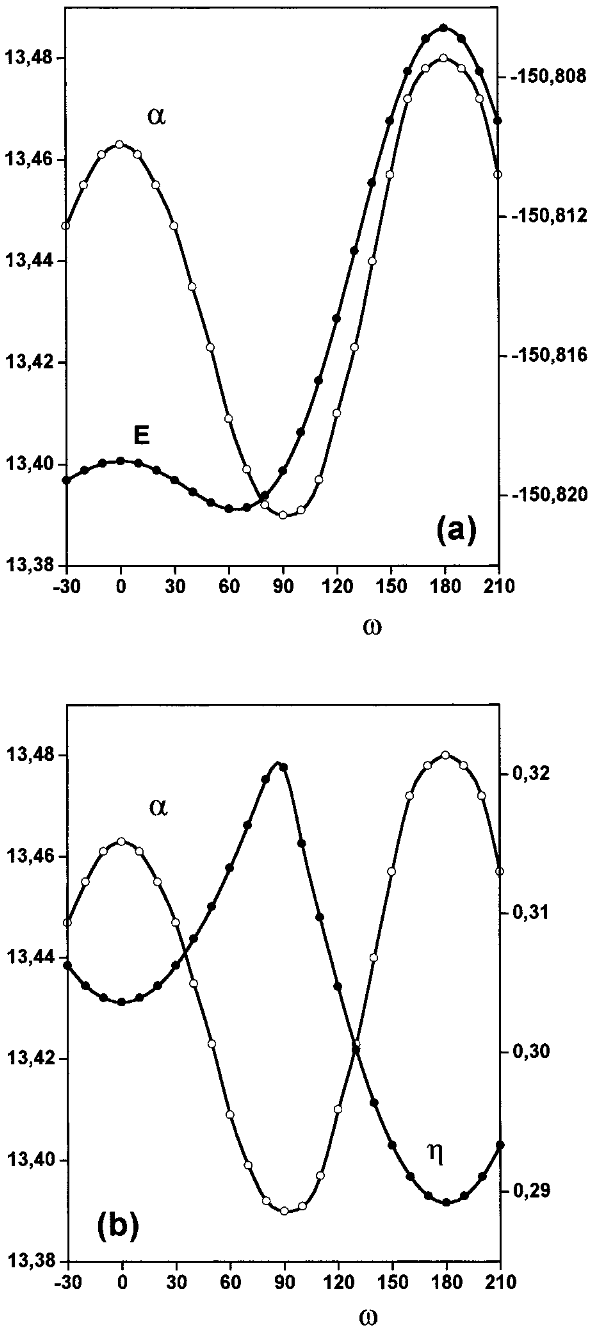

Figure 4. Internal rotation in H_2O_2: (a) profiles of energy and polarizability and (b) profiles of hardness and polarizability. All values are in atomic units; the left axis bears the polarizability values (open circles).

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