Stiffness and Raman Intensity: a Conceptual and Computational DFT Study

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A DFT-based reactivity descriptor, the nuclear stiffness, is related to the Raman scattering intensity, which is experimentally accessible. The application of this new relationship obtained within certain approximations has been checked in two different sets of molecules. First, we study a favorable case, where the contribution of the anisotropy to the Raman intensity is zero (symmetric stretching mode in 15 tetrahedral molecules). Second, we consider a "worst" case scenario, where the anisotropy contribution can be expected to be important (stretching mode in 32 diatomic molecules). The numerical results clearly show a relationship between stiffness and Raman intensity reflecting the expected anisotropy influence.

I. Introduction

Within the context of Conceptual Density Functional Theory (DFT)[1−6] it has been possible to define a series of response properties describing the response of atomic or molecular systems to various types of perturbations typical for a chemical reaction: changes in external potential, $\nu(\vec{r})$ (mostly changes in the position of the nuclei), and in the number of electrons, N.

This approach leads to a natural way to a series of "reactivity descriptors" of the type $\partial^n E/\partial N^m \partial \nu^{m'}(\vec{r})$ with $n = m + m'$,[7] some of them showing direct correspondence with longstanding but sometimes rather vaguely defined chemical concepts such as electronegativity $(\partial E/\partial N)_\nu$, chemical hardness $(\partial^2 E/\partial N^2)_\nu$, which themselves can be related to experimentally accessible quantities such as the ionization energy and electron affinity. The most trivial case is the electron density, $\rho(\vec{r})$, being equal to $(\delta E/\delta \nu(\vec{r}))_N$, which, in the solid state, is measurable via X-ray diffraction experiments.[8]

The identification of higher derivatives with experimental accessible quantities becomes less evident. In recent studies some of the higher derivatives started to receive interest,[9] one of the examples being the nuclear Fukui function, $\vec{\phi}_\alpha$, defined by Cohen as the N-derivative of the force, $\vec{F}_\alpha$, on nucleus α at constant external potential, $(\partial \vec{F}_\alpha/\partial N)_\nu$.[10]

The nuclear Fukui functions received considerable interest in studies by the present authors[11,12] among others in view of its role in interpreting Jahn−Teller distortions.[11] The step forward to its N-derivatives was taken by Ordon and Komorowoski[13] leading to a third-order derivative of the type $\delta^3 E/\partial N^2 \delta \nu(\vec{r})$, where $\delta \nu(\vec{r})$ is identified as $d\vec{R}_\alpha$, a change in nuclear position. This vectorial quantity termed nuclear stiffness and denoted as $\vec{G}_\alpha$ was studied by Komorowoski and co-workers without however pointing out direct links with experimentally accessible quantities which might be used to gain more insight into its behavior, e.g., for similar molecules throughout the periodic table.

In the present contribution it is shown that within certain approximations the nuclear stiffness may be expected to correlate with the Raman scattering intensity[14] of certain modes of vibration, which in principle are experimentally accessible. Although the number of gas phase experimental data is not extremely high, these quantities are, in principle, accessible. Present day quantum chemical methods however also allow obtaining vibrational Raman intensities with reasonable accuracy (e.g., using DFT methods[15]) offering the possibility to test this relationship between stiffness and Raman intensity computationally at a uniform level of calculation.

In this study the relationship is derived in section II, paying particular attention to the approximations involved. Following the Computational Details in section III, results are presented and discussed for a case where the approximate relationship can be expected to be fulfilled to a high degree (symmetric stretching mode of tetrahedral molecules) and for a "worst" case scenario (stretching of diatomic molecules).

II. Theoretical Background

The hardness, η, is a measure of the resistance of a chemical species to change its electronic configuration.[16] Thus, the hardness is the second derivative of the energy with respect to the number of electrons, N, at a fixed external potential, $\nu(\vec{r})$:[17]

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

In contrast the first derivative of the energy with respect to the number of electrons is the chemical potential, μ, and measures the tendency of the electrons to escape from the considered system:[18]

$$\mu = \left(\frac{\partial E}{\partial N}\right)_\nu \tag{2}$$

Using the finite difference approximation and the Koopmans' theorem,[19] we arrive at the following operational equations of the hardness:

$$\eta_1 = I - A \tag{3}$$

and

$$\eta_2 = \epsilon_{\mathrm{LUMO}} - \epsilon_{\mathrm{HOMO}} \tag{4}$$

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where I and A are the first vertical ionization potential and electron affinity of the neutral molecule, respectively, while ϵ_{LUMO} and ϵ_{HOMO} are the energies of the lowest unoccupied molecular orbital and the highest occupied molecular orbital, respectively. The softness, S, is the inverse of the hardness:[16]

$$S = \frac{1}{\eta} \tag{5}$$

Connected to these global reactivity descriptors exists different reactivity principles, such as the hard−soft acid−base principle (HSAB),[20] the maximum hardness principle (MHP),[21] and the minimum polarizability principle (MPP).[22] The MHP affirms that, at a given temperature and external potential, molecular systems evolve to a state of maximum hardness. In contrast the MPP states that any system tends toward a state of minimum polarizability. The MPP is based on the MHP and the empirical inverse relationship between hardness and polarizability (α). Indeed, it has been proposed that softness and polarizability are correlated, the most convincing arguments[23−27] being given for a relationship between S and $\langle\alpha\rangle^{1/3}$.

$$S \propto \langle\alpha\rangle^{1/3} \tag{6}$$

where $\langle\alpha\rangle$ is one-third of the trace of the polarizablility tensor,

$$\langle\alpha\rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{7}$$

The MHP and the MPP have been applied to a number of different chemical processes (molecular vibrations, internal rotations, excited states, aromaticity, and chemical reactions) with numerous achievements[28] but also various described breakdowns.[29]

Changing the energy for the electronic force, $\vec{F}_\alpha$, in eqs 1 and 2, we obtain a new set of reactivity indexes that describes the response of the nuclei due to the changes in N. The nuclear Fukui function has been defined by Cohen and co-workers:[10]

$$\vec{\phi}_\alpha = \left(\frac{\partial \vec{F}_\alpha}{\partial N}\right)_\nu \tag{8}$$

and the nuclear stiffness by Ordon and Komorowski:[13]

$$\vec{G}_\alpha = -\left(\frac{\partial^2 \vec{F}_\alpha}{\partial N^2}\right)_\nu \tag{9}$$

Using a Maxwell relation, it is possible to express the nuclear Fukui function and the nuclear stiffness in function of the nuclear displacement, $\vec{R}_\alpha$:[30]

$$\vec{\phi}_\alpha = \left(\frac{\partial \vec{F}_\alpha}{\partial N}\right)_\nu = -\left(\frac{\partial^2 E}{\partial N \delta \vec{R}_\alpha}\right)_\nu = -\left(\frac{\delta \mu}{\delta \vec{R}_\alpha}\right)_N \tag{10}$$

and

$$\vec{G}_\alpha = -\left(\frac{\partial^2 \vec{F}_\alpha}{\partial N^2}\right)_\nu = \left(\frac{\partial^3 E}{\partial^2 N \delta \vec{R}_\alpha}\right)_\nu = \left(\frac{\delta \eta}{\delta \vec{R}_\alpha}\right)_N \tag{11}$$

The reported values of these properties have mainly been done in diatomic molecules[12,31] and some polyatomic molecules.[11,32] Now, from eq 11, using eq 5 and the relationship between the cube root of mean polarizability and softness (eq 6), one obtains

$$\vec{G}_\alpha = \left(\frac{\delta \eta}{\delta \vec{R}_\alpha}\right)_N = \left(\frac{\delta}{\delta \vec{R}_\alpha}\frac{1}{S}\right)_N \propto \left(\frac{\delta}{\delta \vec{R}_\alpha}\frac{1}{\langle\alpha\rangle^{1/3}}\right)_N = -\frac{1}{3\langle\alpha\rangle^{4/3}}\left(\frac{\delta \langle\alpha\rangle}{\delta \vec{R}_\alpha}\right)_N \tag{12}$$

In a diatomic molecule the natural choice of displacement coordinate is the internuclear distance, R, converting the stiffness from a vectorial to a scalar quantity. Using the chain rule, one finds that

$$G \propto -\frac{1}{3\langle\alpha\rangle^{4/3}}\left(\frac{\partial \langle\alpha\rangle}{\partial Q}\right)_N\left(\frac{\partial Q}{\partial R}\right)_N = -\frac{1}{3\langle\alpha\rangle^{4/3}}\sqrt{\mu}\left(\frac{\partial \langle\alpha\rangle}{\partial Q}\right)_N \tag{13}$$

with

$$Q = \sqrt{\mu} R \tag{14}$$

where μ is the reduced mass. The Raman scattering intensity corresponding to a fundamental vibration, ν, with associated normal coordinate, Q, is essentially governed by $\langle\alpha\rangle'$ and γ', the derivatives of the isotropic polarizability and the anisotropy with respect to the normal coordinate, respectively.

$$\langle\alpha\rangle' = \frac{1}{3}(\alpha'_{xx} + \alpha'_{yy} + \alpha'_{zz}) \tag{15}$$

and

$$\gamma' = \frac{1}{2}[(\alpha'_{xx} - \alpha'_{yy})^2 + (\alpha'_{yy} - \alpha'_{zz})^2 + (\alpha'_{zz} - \alpha'_{xx})^2] + 6(\alpha'^2_{xy} + \alpha'^2_{yz} + \alpha'^2_{xz}) \tag{16}$$

Assuming that γ' is negligible, the Raman scattering intensity is proportional to the square of the polarizability derivative

$$I \propto \langle\alpha'\rangle^2 = \left(\frac{\partial\langle\alpha\rangle}{\partial Q}\right)^2 \tag{17}$$

A comparison of eqs 13 and 17 leads to the following relationship:

$$\frac{|G|}{\sqrt{\mu}} \propto \frac{\sqrt{I}}{3\langle\alpha\rangle^{4/3}} \tag{18}$$

where $\sqrt{\mu}$ was moved to the left-hand side. Equation 18 connects the derivative of the polarizability with respect to the normal coordinates, governing the Raman intensity, with the stiffness.

It is worth noting that both "positive" and "negative" deviations from the equilibrium structure along nontotally symmetric vibrational modes yield molecular configurations that have unchanged values for properties such as E, μ, η, and $\langle\alpha\rangle$,[28a] transforming according to the totally symmetric irreducible representation of the molecular symmetry point group. Then, it follows that numerically $(\partial E/\partial Q) = (\partial \mu/\partial Q) = (\partial \eta/\partial Q) = (\partial\langle\alpha\rangle/\partial Q) = 0$ at the equilibrium geometry. Hence, for nontotally symmetric vibrational modes the stiffness is zero; therefore, these cases will obviously not be discussed further.

The aim of the present work is to study the applicability of these new relationships in two very different sets of molecules, the results of which have to be seen as a (positive) test of the relationships rather than a proof in the mathematical sense of the word. First, we study the most favorable case, where the contribution of the anisotropy to the intensity is zero. This is

TABLE 1: Properties for the Tetrahedral Molecules Studied in This Work; All Values Are Calculated at the B3LYP/aug-cc-pVTZ Level[a]

molecules	η_1[b]	η_2[b]	$\langle\alpha\rangle^{1/3}$[b]	$(\partial\eta_1/\partial S)$[b]	$(\partial\eta_2/\partial S)$[b]	$\lvert(\partial\eta_1/\partial Q)\rvert$[b]	I (Å^4/amu)	$\sqrt{I}/3\langle\alpha\rangle^{4/3}$ [b]
CH_4	0.541	0.387	2.572	−0.067	−0.055	0.067	227.282	0.410
CD_4	0.541	0.387	2.572	−0.067	−0.055	0.047	113.735	0.290
CF_4	0.614	0.458	2.693	−0.003	−0.003	0.001	8.753	0.067
CCl_4	0.397	0.248	4.152	−0.091	−0.098	0.015	22.662	0.019
CBr_4	0.320	0.183	4.682	−0.074	−0.073	0.008	18.132	0.011
SiH_4	0.477	0.346	3.180	−0.038	−0.037	0.038	396.476	0.232
SiD_4	0.477	0.346	3.180	−0.038	−0.037	0.027	198.391	0.164
SiF_4	0.584	0.427	2.852	−0.046	−0.069	0.011	9.765	0.056
$SiCl_4$	0.424	0.290	4.288	−0.074	−0.120	0.013	25.231	0.018
$SiBr_4$	0.355	0.226	4.830	−0.089	−0.098	0.010	19.490	0.010
GeH_4	0.463	0.331	3.294	−0.036	−0.043	0.036	449.907	0.214
GeD_4	0.463	0.331	3.294	−0.036	−0.043	0.025	225.126	0.152
GeF_4	0.554	0.362	3.030	−0.046	−0.069	0.011	16.990	0.058
$GeCl_4$	0.380	0.237	4.421	−0.115	−0.119	0.019	37.869	0.019
$GeBr_4$	0.318	0.186	4.957	−0.092	−0.091	0.010	27.567	0.010

[a] η_1, η_2, $\langle\alpha\rangle$, $(\partial\eta_1/\partial S)$, and $(\partial\eta_2/\partial S)$ are calculated using eqs 3, 4, 7, 20, and 21. [b] Atomic units.

the case of tetrahedral molecules XY_4, more precisely in their symmetric stretching mode, where the diagonal elements of the polarizablility tensor remain mutually equal and the off-diagonal elements remain zero upon stretching. Second, a simple "worst" case scenario was considered, where the anisotropy contribution can be expected to be very important, namely the stretching mode of diatomic molecules, where nonzero terms are appearing in the $(\alpha'_{ii} - \alpha'_{jj})^2$ contributions to γ'.

III. Computational Details

All calculations have been carried out with the GAUSSIAN 98 package[33] at the B3LYP level[34] using the aug-cc-pVTZ basis set.[35] All calculations of this work were also done using the Hartree−Fock instead of the B3LYP method with the same basis set yielding qualitatively the same results. The energy and gradient of the neutral, cationic, and anionic are always calculated using the most stable multiplicity. The cationic and anionic species have been evaluated at the geometry of the neutral systems. With N electrons all the systems are singlets, except the triplets O_2, S_2, Se_2, HN, and HP and the doublets HO, HS, HC, and HSi. The cationic species are doublet, with the exception of the singlets HO and HS and the triplets HC and HSi. Finally, the anionic species are always doublets, apart from the triplets HO and HS and the singlets HC and HSi. In this work, we evaluate the nuclear stiffness in three different ways:

$$G_0 = -\left(\frac{\partial^2 F}{\partial N^2}\right)_v = -\frac{F(N+1) + F(N-1) - 2F(N)}{1^2} = -F(N+1) - F(N-1) \quad (19)$$

$$G_1 = \left(\frac{\delta\eta_1}{\delta R}\right)_N = \frac{\eta_1(R+\delta R) - \eta_1(R-\delta R)}{2\delta R} \quad (20)$$

$$G_2 = \left(\frac{\delta\eta_2}{\delta R}\right)_N = \frac{\eta_2(R+\delta R) - \eta_2(R-\delta R)}{2\delta R} \quad (21)$$

where η_1 and η_2 are calculated using eqs 3 and 4, respectively. The numerical differentiation of η_1 and η_2 has been carried out performing displacements of the equilibrium geometry of $\pm(1, 2, 4, 8, 16, 32, 64, 128, 256, 512) \times 10^{-4}Q$, where Q is the normal mode studied. Then, the smallest magnitude displacement that produced a stable derivative has been selected using a Romberg method triangle.[36] In eq 19 the derivative of the energy with respect to the displacement is evaluated analytically, and the derivative with respect to the number of electrons, numerically; while in eqs 20 and 21 the derivatives are evaluated numerically. The problem of eq 1 is that it can only be strictly applied using an integer number of electrons ($\Delta N = \pm 1$).[37] In contrast, for the numerical differentiation with respect to the displacements it is possible to make the increments very small and to obtain numerical derivatives nearly as accurate as the analytical ones. Thus, the results obtained with eqs 19 and 20 are identical, and we only show the results for G_1 and G_2.

IV. Results and Discussion

In this section, we will study the "best" (symmetrical stretching of tetrahedral molecules) and the "worst" (stretching of diatomic molecules) conditions to evaluate the validity of the relationship between the Raman intensity and the stiffness.

(A) Tetrahedral Molecules. The tetrahedral molecules studied are CH_4, CD_4, CF_4, CCl_4, CBr_4, SiH_4, SiD_4, SiF_4, $SiCl_4$, $SiBr_4$, GeH_4, GeD_4, GeF_4, $GeCl_4$, and $GeBr_4$. In the case of the symmetric stretching of these molecules, the relationship that connects nuclear stiffness and Raman scattering intensity is slightly different from the diatomic case (eq 18). It can be written as

$$\left|\left(\frac{\partial\eta}{\partial Q}\right)\right| \propto \frac{\sqrt{I}}{3\langle\alpha\rangle^{4/3}} \quad (22)$$

where $Q = S\sqrt{m_Y}$, with S as the symmetry coordinate corresponding to the symmetric stretching and m_Y as the mass of the four equivalent atoms of the tetrahedral XY_4 molecules. Table 1 collects the values of the hardness using the two approximations (eqs 3 and 4), the cube root of mean polarizability, and the different factors entering eq 22. The derivative of the hardness with respect to the symmetric stretching has also been calculated using the two approximations of the hardness (eqs 20 and 21). It is worth noting that the results of $(\partial\eta_1/\partial S)$ and $(\partial\eta_2/\partial S)$ are always negative and very similar, more than η_1 and η_2. Thus one can be confident in the reliability of the stiffness results obtained. For the relationships between softness and polarizability and stiffness and Raman intensity, all the results of η, S, and G refer to the approximation of the hardness $I - A$, i.e., η_1, S_1, and G_1 (with the $\epsilon_{LUMO} - \epsilon_{HOMO}$ approximation the conclusions are the same).

As can be seen in Figure 1, a good correlation between S_1, the inverse of η_1, and $\langle\alpha\rangle^{1/3}$ is obtained. Taking into account that the anisotropy for the symmetric stretching of the tetrahedral

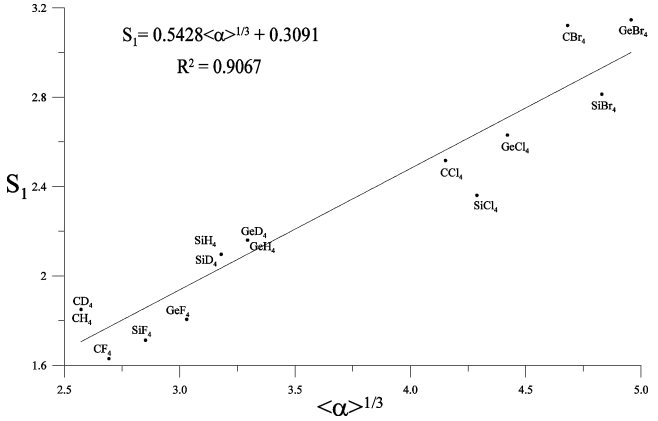

Figure 1. Correlation between the cube root of the mean polarizability and softness, $1/(I - A)$, for the tetrahedral molecules studied. All values are given in atomic units.

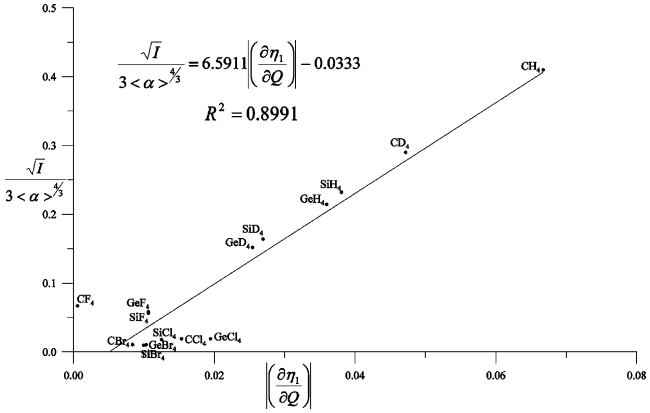

Figure 2. A representation of the relation $|(\partial\eta/\partial Q)| \propto \sqrt{I}/3\langle\alpha\rangle^{4/3}$ for the tetrahedral molecules studied. All values are given in atomic units.

molecules is zero, one can expect that we are in front of the "best" conditions to obtain an excellent correlation between stiffness and Raman intensity.

The fulfillment of the relationship of eq 22 is shown in Figure 2 and illustrates a tendency between these properties, although some molecules (CF_4, $GeCl_4$, and CCl_4) deviate.

The hardness is an important reactivity index, because it shows the resistance of a molecule to change its electronic cloud. A molecule or atom with a big value of hardness will be a species with a high resistance to offer/accept electrons to/from another system, and it will show a high affinity to interact with other hard molecules (HASB principle). A small hardness value implies an important tendency to offer and accept electrons and a likeness to interact with soft molecules. But during a chemical reaction, the molecules change their nuclear positions and their electronic density. Therefore it is interesting to study not only the hardness at the equilibrium geometry but also its derivative with respect to nuclear displacements, the stiffness.

A small value of stiffness involves that the hardness along the nuclear displacement is nearly constant, pointing out the system shows similar reactivity as in the equilibrium geometry (in the Koopmans' approximation, it implies that the HOMO and LUMO energies remain almost constant). This is the case of tetrahedral molecules with Y = H, D, and F showing large values for the hardness ($\eta_1 \geq 0.46$ and $\eta_2 \geq 0.33$) and relatively small absolute values of stiffness ($|\partial\eta/\partial S| \leq 0.070$). It is worth noting that the hardest system, CF_4, also presents the smallest

TABLE 2: Properties for the Diatomic Molecules Studied in This Work; All Values Are Calculated at the B3LYP/aug-cc-pVTZ Level[a]

molecules	η_1[b]	η_2[b]	$\langle\alpha\rangle^{1/3}$[b]	G_1[b]	G_2[b]	$\lvert G_1\rvert/\sqrt{\mu}$[b]	I (Å^4/amu)	$\sqrt{I}/3\,\langle\alpha\rangle^{4/3}$[b]	$45(\mathrm{d}\langle\alpha\rangle/\mathrm{d}Q)^2/I\cdot 0.01$[b]
HF	0.617	0.397	1.775	−0.101	−0.108	0.103	38.910	0.748	70.4
DF	0.617	0.397	1.775	−0.101	−0.108	0.075	20.449	0.543	70.4
HCl	0.485	0.311	2.599	−0.046	−0.086	0.046	89.919	0.248	64.3
HBr	0.445	0.277	2.902	−0.044	−0.095	0.044	119.727	0.184	63.1
H_2	0.646	0.449	1.770	−0.161	−0.149	0.227	162.337	1.545	91.1
D_2	0.646	0.449	1.770	−0.161	−0.149	0.161	81.231	1.093	91.1
HLi	0.289	0.145	3.104	−0.036	−0.030	0.039	648.232	0.326	88.0
HNa	0.261	0.127	3.548	−0.031	−0.027	0.031	732.092	0.203	77.8
HB singlet	0.343	0.144	2.861	0.005	0.013	0.006	250.735	0.281	10.3
HAl singlet	0.292	0.136	3.626	0.001	0.004	0.001	332.517	0.126	12.0
HN triplet	0.486	*c*	2.165	−0.026	*c*	0.027	93.760	0.525	50.8
HP triplet	0.333	*c*	3.062	−0.006	*c*	0.006	160.805	0.172	47.3
HO doublet	0.422	*c*	1.958	−0.040	*c*	0.041	60.823	0.631	64.2
HS doublet	0.299	*c*	2.833	−0.012	*c*	0.012	120.833	0.203	57.8
HC doublet	0.355	*c*	2.476	−0.014	*c*	0.015	147.235	0.384	13.3
HSi doublet	0.248	*c*	3.394	−0.002	*c*	0.002	208.284	0.130	30.9
F_2	0.563	0.265	2.020	−0.241	−0.268	0.078	9.821	0.224	56.0
Cl_2	0.380	0.178	3.146	−0.102	−0.116	0.024	16.087	0.049	64.5
Br_2	0.328	0.144	3.575	−0.079	−0.085	0.013	12.027	0.025	64.4
FCl	0.440	0.206	2.639	−0.114	−0.139	0.033	11.391	0.083	47.4
FBr	0.394	0.176	2.901	−0.093	−0.110	0.024	10.962	0.056	43.4
ClBr	0.351	0.158	3.367	−0.089	−0.098	0.018	15.070	0.036	63.5
Li_2	0.181	0.081	5.823	−0.015	−0.013	0.008	1948.747	0.046	74.4
Na_2	0.177	0.075	6.126	−0.015	−0.012	0.004	604.399	0.021	71.8
N_2	0.651	0.406	2.284	−0.193	−0.259	0.073	23.984	0.214	80.6
P_2	0.361	0.186	3.698	−0.113	−0.106	0.029	70.750	0.054	79.3
As_2	0.326	0.159	3.991	−0.096	−0.088	0.016	39.063	0.029	81.1
SO	0.265	0.047	2.880	0.007	0.001	0.002	18.400	0.074	31.4
CO	0.562	0.346	2.363	−0.035	−0.136	0.013	17.615	0.160	71.9
O_2 triplet	0.477	*c*	2.191	−0.003	*c*	0.001	17.035	0.213	64.6
S_2 triplet	0.299	*c*	3.458	−0.004	*c*	0.001	44.229	0.055	66.1
Se_2 triplet	0.271	*c*	3.852	−0.005	*c*	0.001	28.778	0.029	66.0

[a] η_1, η_2, $\langle\alpha\rangle$, G_1, and G_2 are calculated using eqs 3, 4, 7, 20, and 21. [b] Atomic units. [c] Not evaluated, because the ground state of this system is an open-shell system.

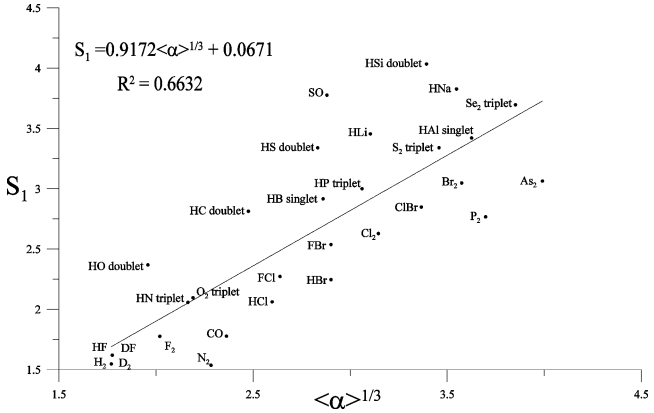

Figure 3. Correlation between the cube root of the mean polarizability and the softness, $1/(I-A)$, for the diatomic molecules studied, except Li_2 and Na_2 due their larger polarizabilities values. All values are given in atomic units.

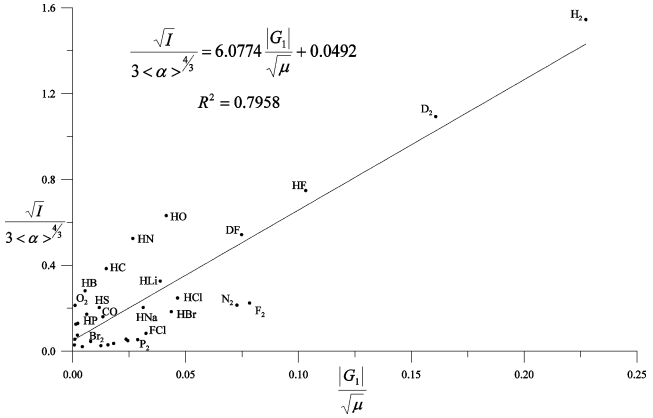

Figure 4. A representation of the relation $|G_1|/\sqrt{\mu} \propto \sqrt{I}/3\langle\alpha\rangle^{4/3}$ for the diatomic molecules studied. All values are given in atomic units.

stiffness value, indicating that its hardness will be nearly unchanged along the symmetric stretching. In contrast, the tetrahedral molecules with Y = Cl and Br are softer than the previous molecules at their equilibrium geometry, showing their huge predisposition to offer/accept electrons, and display bigger absolute values of stiffness, showing that this predisposition further will quickly increase upon symmetric stretching ($\partial\eta/\partial S < 0$).

(B) Diatomic Molecules. In the same way as Table 1, Table 2 contains all the required information to evaluate the relationships between cubic root of mean polarizability vs softness and Raman intensity vs stiffness of the diatomic molecules studied in this work. In contrast to the last section, there are some diatomic molecules for which the properties η_2 and G_2 are not evaluated, because their ground state is not a singlet, producing the problem of correctly defining the hardness using Koopmans' theorem. For the remaining molecules, the results of G_1 and G_2 are very similar, except for systems with a complicated electronic structure as N_2 and CO.

Although the existence of a tendency between softness and the cubic root of mean polarizability is clear (see Figure 3), the correlation $\langle\alpha\rangle^{1/3}$ vs S_1 is worse than the previous case. This fact is not quite surprising, taking into account the high similarity among the isotropic tetrahedral molecules and the diversity of anisotropic diatomic molecules that we are studying in this section (ionic systems vs covalent systems with single, double, and triple bonds).

The correlation between $|G_1|/\sqrt{\mu}$ with $\sqrt{I}/3\langle\alpha\rangle^{4/3}$ is also not excellent (see Figure 4). The anisotropy of the diatomic molecules and the worse correlation between $\langle\alpha\rangle^{1/3}$ and S_1 can be some of the reasons of the nontotal fulfilment of eq 18. Notwithstanding, it is possible to note a tendency between stiffness and Raman intensity, especially when looking at similar systems. For instance, the interhalogen diatomic molecules (F_2, Cl_2, Br_2, FCl, FBr, and ClBr) show an R^2 of 0.9964 between $|G_1|/\sqrt{\mu}$ and $\sqrt{I}/3\langle\alpha\rangle^{4/3}$. The subgroup of diatomic molecules containing a hydrogen atom plus an atom varying along a given period of the periodic table (HF, HO, HN, HC, and HB) displays an R^2 of 0.8159 for $|G_1|/\sqrt{\mu}$ vs $\sqrt{I}/3\ \langle\alpha\rangle^{4/3}\}$.

To analyze the effect of the anisotropy in the correlation between $|G_1|/\sqrt{\mu}$ with $\sqrt{I}/3\ \langle\alpha\rangle^{4/3}$, Table 2 includes the percentage of the isotropic contribution, $45(\mathrm{d}\langle\alpha\rangle/\mathrm{d}Q)^2$, to the Raman intensity. Figure 5 contains the plot of the isotropic contribution versus the total Raman intensity. As can been seen, the anisotropy contribution to the Raman intensity, $7\gamma'^2$,

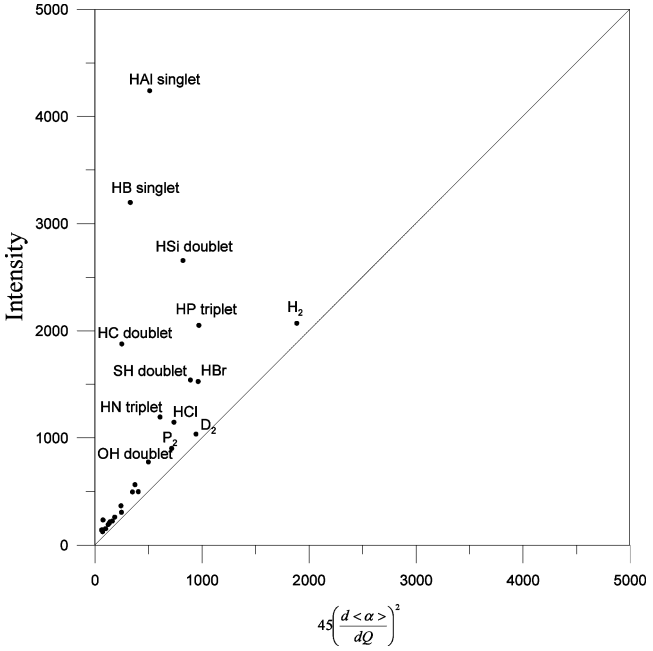

Figure 5. Calculated total Raman intensity versus its isotropic part for the diatomic molecules studied. The diagonal represents the situation with anisotropy contribution equal to zero. All values are given in atomic units.

becomes dominant in some molecules; e.g., the HB singlet and CH doublet the isotropic part only represents the 10.3 and 13.3, respectively, percentage to the Raman intensity. These systems also show a significant deviation in the general tendency depicted in Figure 4, although this result is not always true. For instance, N_2 and P_2 have a relatively small anisotropy contribution to the intensity (see Table 2) but display a notable deviation in Figure 4, which can be explained by the worse correlation between $\langle\alpha\rangle^{1/3}$ and S_1. In contrast, F_2 shows a considerable anisotropy contribution and a good fit in the tendency of Figure 3, resulting in a poor point in the correlation between $|G_1|/\sqrt{\mu}$ with $\sqrt{I}/3\langle\alpha\rangle^{4/3}$. In conclusion, it seems that a small anisotropy and a good correlation between $\langle\alpha\rangle^{1/3}$ and S are required to obtain good relationships in eq 22, and the breakdowns of these conditions are responsible for the dispersion of data points in both Figures 2 and 4.

V. Conclusions

An approximate scheme is presented to derive an expression that connects the stiffness, a third order derivative of the energy,

with an experimentally accessible quantity, the Raman scattering intensity. We test the applicability of this new equation in two representative sets of molecules. The numerical results confirm the expected relationship between these two properties, including their anisotropy influence. For systems where the contribution of the anisotropy to the intensity is zero (tetrahedral molecules), a good linear relationship shows up between the square root of the intensity and the stiffness. The results obtained with the diatomic molecules are, as expected, less clear-cut, as can be rationalized by the worse correlation between $\langle\alpha\rangle^{1/3}$ and S and the relatively important anisotropy contribution to the intensity shown by some of these molecules. It is worth noting that the latter relationships improve considerably when looking at similar systems (interhalogens diatomic molecules and hydrogen plus an atom varying along a given period of the periodic table).

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