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**CHEMICAL  
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# Vibrational polarizability and hyperpolarizability of *p*-nitroaniline

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## Abstract

Within the double harmonic oscillator approximation scheme based on an RHF/6-31G electronic structure, the vibrational contributions to the polarizability, and first and second hyperpolarizability tensors of *p*-nitroaniline have been evaluated for different optical processes by adopting the infinite frequency or enhanced approximation. The static vibrational longitudinal first hyperpolarizability reaches 1352 au whereas the corresponding electronic counterpart is 1264 au. The  $[\alpha^2]^{0,0}$  and  $[\mu\beta]^{0,0}$  contributions to the vibrational longitudinal second hyperpolarizability are, in the static limit, equal to 44750 and 61112 au, respectively, in comparison with the 70874 au electronic value. These vibrational contributions remain important when considering the different dynamic optical processes with the exception of second- and third-harmonic generation. The main contributions to both the first and second vibrational hyperpolarizabilities are due to vibrational normal modes which describe the oscillation between aromatic-like and quinoid-like structures.

## 1. Introduction

The evaluation of the polarizabilities ( $\alpha$ ), and first and second hyperpolarizabilities ( $\beta$  and  $\gamma$ ) by using quantum chemical procedures is a field of intense research because it is related to the design of new compounds for non-linear optical (NLO) applications and to the understanding of the interaction between electromagnetic fields and matter [1–4]. Recently, attention has been given to the vibrational contributions to these properties. These vibrational components originate from the coupling between the electronic and the nuclear motions. In this way, the application of an external electric field to a system induces distortions of the nuclear, in addition to the

electronic, motions which lead to vibrational contributions to the (hyper)polarizabilities ( $\alpha^\nu$ ,  $\beta^\nu$  and  $\gamma^\nu$ ) [5,6].

Bishop and Kirtman [7] have provided general sum-over-modes (SOM) expressions for the dynamic and static vibrational polarizabilities and hyperpolarizabilities in terms of force constants and derivatives with respect to the normal coordinates of the electronic dipole moment, polarizability and first hyperpolarizability. This general perturbation approach which enables successive improvements by considering higher and higher orders in both the mechanical and electrical anharmonicities, has been followed to calculate the dynamic and static  $\alpha^\nu$ ,  $\beta^\nu$  and  $\gamma^\nu$  of small and medium-size molecules with and without considering the effects of including electron correlation [7–10]. Duran and co-workers [11,12] have designed a geometry relaxation procedure to account for both the relaxation and curvature contributions to

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the (hyper)polarizabilities; the curvature contribution being related to the field-dependent vibrational frequencies whereas the other term originates from the field-induced nuclear relaxation. The correspondence between the perturbation and finite field relaxation approaches has been discussed by Martí and Bishop [13]. Another version of this finite field relaxation approach has been worked out by Handy and co-workers [14]. The drawback of these finite field relaxation procedures is their restriction to the evaluation of the static field responses. Recently, Bishop et al. [15] derived a simple method for calculating approximate static and dynamic vibrational hyperpolarizabilities which consists in the determination of electrical properties in the presence of a static field with and without geometry optimization. Within this approach only the infinite frequency or enhanced contributions [16] are kept, i.e. those obtained by taking the limit  $\omega \rightarrow \infty$  or those which through a cancellation of the frequencies contain no optical frequency in the denominator. This finite field relaxation version of the infinite frequency approximation has been explored for  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{HF}$  and  $\text{CO}_2$  [10] and turns out to be a satisfactory approximation for NLO vibrational dynamic second hyperpolarizabilities.

Zerbi and co-workers have tackled conjugated molecules which present a potential interest for NLO applications [17–19]. From their dual approach based on theoretically or experimentally determined spectroscopic quantities, it turned out, for the molecules they have studied, that the ratio between the electronic and vibrational static hyperpolarizabilities is close to unity. As a consequence, Zerbi and co-workers assumed that both the electronic and vibrational contributions to  $\beta$  and  $\gamma$  are two independent measures of the same physical quantity. In a recent work, on the basis of static calculations of the electronic properties of distorted oligomers, Kirtman et al. [20] evaluated the vibrational contributions of some normal modes to the static and dynamic second hyperpolarizabilities of polyacetylene (PA), polyyne (PY), polysilane (PS) and polyethylene chains. They pointed out an interesting mode in PA and PY which is associated with the effective conjugation coordinate (ECC). This ECC motion has been shown to be the primary source of the resulting  $[\alpha^2]^{0,0}$  term in the vibrational second hyperpolarizability and of ma-

jor significance with respect to the electronic counterpart.

In the present study, we evaluate the vibrational contributions to the (hyper)polarizabilities of a prototype push–pull conjugated molecule, *p*-nitroaniline (*p*-NA). Many theoretical studies have already considered the frequency dependence, electron correlation and basis set effects on the electronic components of its (hyper)polarizabilities [21–24]. In particular Sim et al. [23] have demonstrated that the inclusion of electron correlation within the second-order Møller–Plesset perturbation scheme leads to 60% and 100% increases for the longitudinal components of  $\beta^e$  and  $\gamma^e$ , respectively. However, even when scaling these correlated results to incorporate the frequency dispersion effects, the computed  $\beta^e$  and  $\gamma^e$  values remain considerably smaller than the experimentally determined values. Recently, self-consistent reaction field studies of the solvent dependence of  $\beta^e$  [25,26] demonstrate that the solvent effects can account for a part of the discrepancy between theory and experiment. In this study we show that the vibrational contributions bring into play other substantial contributions to these electronic estimates in the case of specific NLO processes. To our knowledge, these vibrational contributions have only been addressed by Zerbi et al. [19] in the case of the static first hyperpolarizability. The following Section describes the method used as well as the computational procedure. Section 3 presents the (hyper)polarizability components, discusses their importance with respect to their electronic counterparts in the case of different optical processes and describes the most important modes. Finally, we give our conclusions in Section 4.

## 2. Methodology and computational procedure

The application of an external electrical field  $E$  on a molecule creates electronic and nuclear reorganizations driven by the search for the maximum stabilization energy. These polarization effects can be characterized, for any molecular moment, by the constant coefficients of a Taylor series in the amplitudes of the monochromatic components of the ap-

plied electrical field. In the case of the electric dipole moment

$$\begin{aligned}\mu_{\zeta}(\omega_{\sigma}) &= \mu_{\zeta}^0 + \sum_{\eta} \alpha_{\zeta\eta}(-\omega_{\sigma}; \omega_1) E_{\eta}(\omega_1) \\ &+ \frac{1}{2} K^{(2)} \sum_{\eta\xi} \beta_{\zeta\eta\xi}(-\omega_{\sigma}; \omega_1, \omega_2) \\ &\times E_{\eta}(\omega_1) E_{\xi}(\omega_2) \\ &+ \frac{1}{6} K^{(3)} \sum_{\eta} \gamma_{\zeta\eta\xi\chi}(-\omega_{\sigma}; \omega_1, \omega_2, \omega_3) \\ &\times E_{\eta}(\omega_1) E_{\xi}(\omega_2) E_{\chi}(\omega_3) + \dots, \quad (1)\end{aligned}$$

where the subscripts  $\zeta, \eta, \dots$  correspond to the Cartesian molecular axis,  $\omega_{\sigma} = \sum_i \omega_i$ ,  $\mu_{\zeta}^0$  is one of the components of the permanent dipole moment,  $\alpha_{\zeta\eta}(-\omega_{\sigma}; \omega_1)$ ,  $\beta_{\zeta\eta\xi}(-\omega_{\sigma}; \omega_1, \omega_2)$  and  $\gamma_{\zeta\eta\xi\chi}(-\omega_{\sigma}; \omega_1, \omega_2, \omega_3)$  are the linear polarizability, first and second hyperpolarizability tensor components, respectively associated with various optical processes.  $K^{(2)}$  and  $K^{(3)}$  are process-dependent factors which ensure that all quantities converge to the same static limit [27]. The frequency-dependent (hyper)polarizabilities are expressed as a summation over vibronic states which are written as a product of an electronic and a vibrational function. By assuming a larger separation between the electronic than the vibrational levels, the distinction between the pure vibrational expressions from those containing electronic quantities leads to the separation of the different electric responses into a pure vibrational component and a zero-point vibrationally averaged (ZPVA) quantity. In this investigation we have adopted the double harmonic oscillator approximation [7] to evaluate  $\alpha^v$ ,  $\beta^v$  and  $\gamma^v$ , which means that the variation of the dipole moment, polarizability and first hyperpolarizability are considered to be linear in the normal coordinates  $Q_a$  and that the vibrational potential is limited to the term quadratic in  $Q_a$ . Consequently, the ZPVA correction is zero. The frequency dependence is described by invoking the enhanced [16] or infinite frequency [15] approximation. Therefore, since the optical frequency values are considered much larger than the normal mode vibrational frequencies, the dynamic NLO responses are assumed to be constant for a given optical process, irrespective of the associated optical frequencies. The charge transfer character of *p*-NA makes the axial or longi-

tudinal components to the (hyper)polarizability tensors, by far, the dominant contribution. Within the scheme we have adopted, these  $\alpha_L^v$ ,  $\beta_L^v$  and  $\gamma_L^v$  quantities are given by the following SOM expressions,

$$\begin{aligned}\alpha_L^v(-\omega_{\sigma}; \omega_1) &= [\mu^2]^{0,0} \\ &= F^{(1)} \sum_a \left( \frac{\partial \mu_L^e}{\partial Q_a} \right)_0 \left( \frac{\partial \mu_L^e}{\partial Q_a} \right)_0 / \omega_a^2, \quad (2)\end{aligned}$$

$$\begin{aligned}\beta_L^v(-\omega_{\sigma}; \omega_1, \omega_2) &= [\mu\alpha]^{0,0} \\ &= F^{(2)3} \sum_a \left( \frac{\partial \mu_L^e}{\partial Q_a} \right)_0 \left( \frac{\partial \alpha_L^e}{\partial Q_a} \right)_0 / \omega_a^2, \quad (3)\end{aligned}$$

$$\begin{aligned}\gamma_L^v(-\omega_{\sigma}; \omega_1, \omega_2, \omega_3) &= [\alpha^2]^{0,0} + [\mu\beta]^{0,0} \\ &= F^{(3a)3} \sum_a \left( \frac{\partial \alpha_L^e}{\partial Q_a} \right)_0 \left( \frac{\partial \alpha_L^e}{\partial Q_a} \right)_0 / \omega_a^2 \\ &+ F^{(3b)4} \sum_a \left( \frac{\partial \mu_L^e}{\partial Q_a} \right)_0 \left( \frac{\partial \beta_L^e}{\partial Q_a} \right)_0 / \omega_a^2, \quad (4)\end{aligned}$$

where  $\omega_a = 2\pi\nu_a$  is the circular frequency associated with  $Q_a$ , the  $F^{(i)}$  factors, listed in Table 1,

Table 1

Infinite optical frequency factors determining the magnitude of different SOM contributions to the diagonal elements of the double harmonic oscillator vibrational (hyper)polarizability tensors. SHG and THG stand for second- and third-harmonic generation whereas IDRI means intensity-dependent refractive index

Optical processes		Factors	
polarizability		$F^{(1)}$	
static	$\alpha(0;0)$	1	
dynamic	$\alpha(-\omega; \omega)$	0	
first hyperpolarizability		$F^{(2)}$	
static	$\beta(0;0,0)$	1	
dc-Pockels	$\beta(-\omega; \omega, 0)$	1/3	
SHG	$\beta(-2\omega; \omega, \omega)$	0	
second hyperpolarizability		$F^{(3a)}$	$F^{(3b)}$
static	$\gamma(0;0,0,0)$	1	1
dc-Kerr	$\gamma(-\omega; \omega, 0, 0)$	1/3	1/2
IDRI	$\gamma(-\omega; \omega, -\omega, \omega)$	2/3	0
dc-SHG	$\gamma(-2\omega; \omega, \omega, 0)$	0	1/4
THG	$\gamma(-3\omega; \omega, \omega, \omega)$	0	0

depend upon the optical process and the  $^{0,0}$  superscript denotes the zeroth order in both the electrical and mechanical anharmonicities. The corresponding expressions for the other tensor components are slightly more involved and can be deduced from the original works of Bishop and Kirtman [7]. In addition to the longitudinal tensor components we also present numerical results for the experimentally meaningful quantities. These are the scalar components of  $\alpha$  and  $\gamma$  given by their isotropic average

$$\bar{\alpha} = \frac{1}{3} \alpha_{\zeta\zeta}, \quad (5)$$

$$\bar{\gamma} = \frac{1}{15} (\gamma_{\zeta\zeta\eta\eta} + \gamma_{\zeta\eta\eta\zeta} + \gamma_{\zeta\eta\zeta\eta}), \quad (6)$$

where Einstein summation over the subscripts  $\zeta, \eta$  ( $= x, y, z$ ) is assumed, and the vector component of the  $\beta$  tensor in the direction of the permanent dipole moment  $\mu^0$  which defines the molecular  $z$ -axis,

$$\beta_{\text{vec}} = \frac{1}{3} (\beta_{z\zeta\zeta} + \beta_{\zeta z\zeta} + \beta_{\zeta\zeta z}) = \frac{5}{3} \beta_{\parallel}, \quad (7)$$

where  $\beta_{\parallel}$  is the experimentalist definition of  $\beta_{\text{vec}}$ .

From its CPHF procedure, GAUSSIAN94 [28] provides directly the vibrational frequencies and the derivatives with respect to the normal coordinate of the dipole moment and polarizability. These quantities being sensitive to geometrical structure a tight convergence threshold has been utilized with the residual forces set at  $1.5 \times 10^{-5} E_h/a_0$  or  $E_h/\text{rad}$  ( $1.0 E_h/a_0 = 1.0 \text{ au}$  of strength  $= 8.23873 \times 10^{-8} \text{ N}$ ). The derivatives of the  $\beta$  tensor<sup>2</sup> with respect to the normal coordinate have been carried out with the finite distortion procedure. For each vibrational normal mode, different fractions of the normal coordinate have been successively added to the equilibrium geometry and the  $\beta$  tensor is computed. A finite difference formula is then applied with one Romberg's type iteration [29] to remove higher-order derivative contaminations. A good accuracy has been met by using a normal coordinate distortion amplitude of  $\pm 0.025$  and  $\pm 0.05 \text{ \AA}$ . This has been verified by comparing the static  $[\mu^2]^{0,0}$  and  $[\alpha^2]^{0,0}$  terms originating from both the analytical CPHF and numerical finite distortion procedures; the difference

being  $1.0 \text{ au}$  for  $[\alpha^2]^{0,0}$  and less than  $10^{-3} \text{ au}$  for  $[\mu^2]^{0,0}$ . In order to make the comparison with the electronic counterpart on the basis of the same geometrical structure the static  $\alpha^e$ ,  $\beta^e$  and  $\gamma^e$  tensor components of  $p$ -NA have been evaluated at the coupled Hartree–Fock level by using the HONDO 95.3 program [30]. The adequacy of the split-valence 6-31G atomic basis set [31] for computing the  $\alpha^e$  and  $\gamma^e$  of polyacetylene chains [32] as well as the  $\beta^e$  of push–pull systems [24] determined our choice of the 6-31G basis set. This choice has further been validated by the good agreement between these electronic 6-31G values and other results computed with more extended basis sets [21–24].

### 3. Results and discussion

The equilibrium geometry of  $p$ -NA after complete geometry optimization at the RHF/6-31G level is planar and belongs to the  $C_{2v}$  point group. As detailed in Fig. 1 the optimized geometrical parameters are in good agreement with the X-ray crystallographic data of Trueblood et al. [33] and the theoretical values computed by Daniel and Dupuis [21,22] who employed a more extended atomic basis set. It is, however, relevant to mention that, experimentally,  $p$ -NA is slightly non-planar. Knowing that the CC bond length of benzene is  $1.388 \text{ \AA}$  at the same RHF/6-31G level, it is natural that the  $\pi$ -donor  $\text{NH}_2$  group modifies more the bond alternation pattern than its homologous acceptor.

Tables 2–5 list the longitudinal as well as average or vector vibrational components to the (hyper)polarizabilities of  $p$ -NA. The electronic counterparts are also given for the sake of comparison with both static and dynamic vibrational values obtained at the double harmonic level of approximation by invoking the infinite optical frequency approximation.

In the static case, the  $\alpha^v/\alpha^e$  ratio reaches 0.18 and 0.35 for the longitudinal and average components, respectively. Such ratios lie in between the  $\alpha_L^v/\alpha_L^e$  ratios associated with other conjugated systems. Indeed, for PA and PS chains treated at the same level of approximation, the ratios tend for the infinite chain limit towards 0.08 [34] and 0.54 [35], respectively. At optical frequencies,  $\alpha^v$  tends to

<sup>2</sup> As a caution for GAUSSIAN users, the sign convention for  $\mu$  and  $\beta$  is inconsistent. The  $\beta$  values have therefore been multiplied by  $-1$ .

Table 2

RHF/6-31G [ $\mu^2$ ] $^{0,0}$  contribution to the longitudinal and average vibrational polarizability of *p*-NA in au (1.0 au of polarizability =  $1.6488 \times 10^{-41}$  C $^2$  m $^2$  J $^{-1}$  = 0.14818 Å $^3$ ). For comparison,  $\alpha_L^e(0;0) = 118.714$  au and  $\bar{\alpha}^e(0;0) = 76.133$  au

	$\alpha_L^v(0;0)$	$\bar{\alpha}^v(0;0)$
[ $\mu^2$ ] $^{0,0}$	20.933	26.899

wards zero and therefore, is of little importance. Nevertheless, it is interesting to note that  $\alpha^v(0;0)$  can be considered as the difference between the total  $\alpha(0;0)$  and the zero optical frequency limit of  $\alpha(-\omega; \omega)$  [16].

When considering the static first hyperpolarizability, the vibrational/electronic ratios are larger than unity (1.07 and 1.26 for the longitudinal and vector components, respectively). Although the static quantities are experimentally meaningless and the second harmonic generation (SHG) contribution is tending to zero, the vibrational contribution to the dc-Pockels phenomena remains, according to the enhanced [ $\mu\alpha$ ] $^{0,0}$  term, equal to 1/3 of the corresponding static value. The frequency dispersion for this NLO process being reduced (following Karna et al. [22], for a 1.06  $\mu$ m wavelength, the dc-Pockels/static ratios are 1.10 and 1.12 for the longitudinal and vector  $\beta$  terms, respectively), one can infer that the vibrational contribution attains 30% of its electronic counterpart. At the RHF/3-21G level, Del Zoppo et al. [19] obtained, in the static limit, a similar  $\beta_L^v/\beta_L^e$  ratio (1.12).

The vibrational modulation of  $\gamma$  is more important than for the corresponding  $\alpha$  and  $\beta$ . In the static limit, the [ $\alpha^2$ ] $^{0,0}/\gamma^e(0;0,0,0)$  and [ $\mu\beta$ ] $^{0,0}/\gamma^e(0;0,0,0)$  ratios are 0.63 and 0.86 for

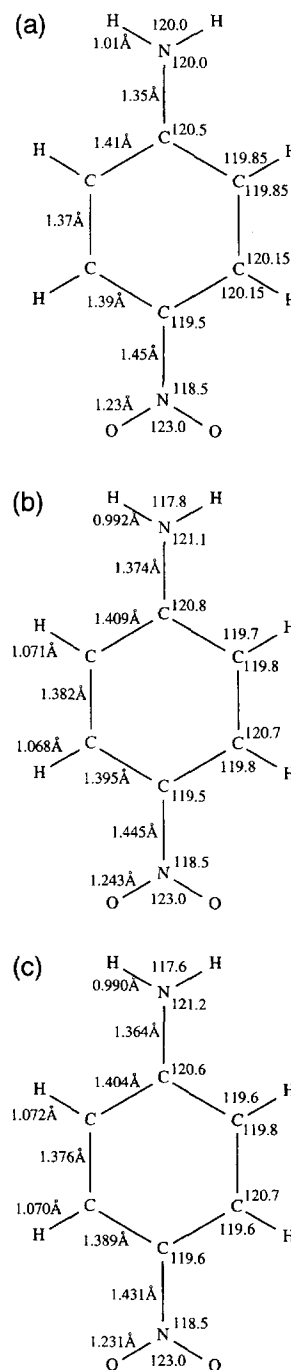


Fig. 1. Geometrical parameters of *p*-NA in Å and ° for the bond length and bond angle values, respectively. (a) Experiment [33], (b) [21,22], (c) this work.

Table 3

RHF/6-31G [ $\mu\alpha$ ] $^{0,0}$  contribution to the longitudinal and vector components of the static and dc-Pockels vibrational first hyperpolarizabilities of *p*-NA in au (1.0 au of first hyperpolarizability =  $3.2063 \times 10^{-53}$  C $^3$  m $^3$  J $^{-2}$  =  $8.641 \times 10^{-33}$  esu). For the dynamic values, the infinite optical frequency approximation is adopted. The corresponding electronic contributions are 1262.8 and 1043.1 au, for  $\beta_L^e(0;0,0)$  and  $\beta_{vec}^e(0;0,0)$ , respectively

$\beta_L^v(0;0,0)$	$\beta_L^v(-\omega; \omega, 0)$	$\beta_{vec}^v(0;0,0)$	$\beta_{vec}^v(-\omega; \omega, 0)$
1351.6	450.5	1312.6	437.5

Table 4

RHF/6-31G [ $\alpha^2$ ] $^{0,0}$  and [ $\mu\beta$ ] $^{0,0}$  components as well as the total longitudinal vibrational second hyperpolarizability of *p*-NA as a function of the NLO process. All the values are given in au (1.0 au of second hyperpolarizability =  $6.2354 \times 10^{-65} \text{ C}^4 \text{ m}^4 \text{ J}^{-3} = 5.0367 \times 10^{-40} \text{ esu}$ ). For the dynamic values, the infinite optical frequency approximation is adopted. For comparison,  $\gamma_L^e(0;0,0,0) = 70873 \text{ au}$

	$\gamma_L^{\text{vib}}(0;0,0,0)$	$\gamma_L^{\text{vib}}(-\omega; \omega, 0, 0)$	$\gamma_L^{\text{vib}}(-\omega; \omega, -\omega, \omega)$	$\gamma_L^{\text{vib}}(-2\omega; \omega, \omega, 0)$
$[\alpha^2]^{0,0}$	44750	14917	29833	0
$[\mu\beta]^{0,0}$	61112	30556	0	15278
$[\alpha^2]^{0,0} + [\mu\beta]^{0,0}$	105862	45473	29833	15278

the longitudinal component whereas they are equal to 0.91 and 0.43 for the average values, respectively. Therefore, the total double harmonic oscillator contributions attain 149 and 134% of the associated CHF  $\gamma^e(0;0,0,0)$ . With the exception of the intensity-dependent refractive index (IDRI) case where

optical frequencies can cancel each other, the amplitude of these vibrational contributions decreases with the number of optical frequencies in the process until reaching zero for the third-harmonic generation (THG), provided that the infinite optical frequency approximation is used. In order to address the impor-

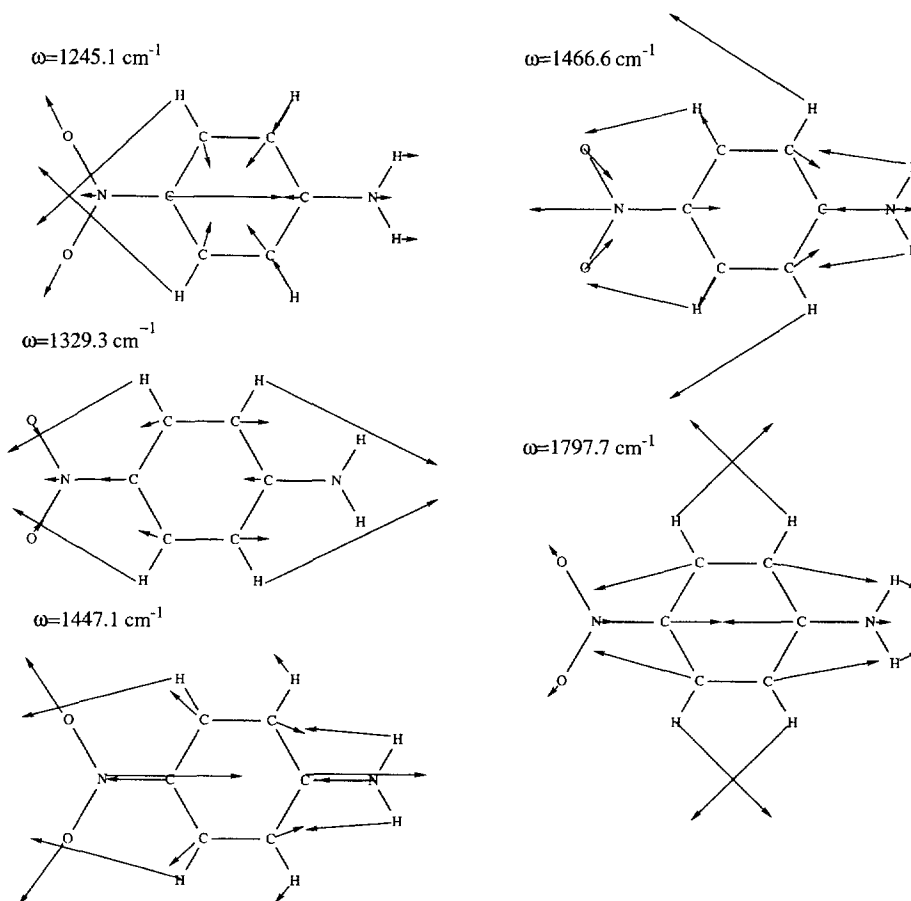


Fig. 2. Schematic drawing of the in-plane Cartesian displacements of the vibrational normal mode of *p*-NA that contribute most to the different vibrational responses.

Table 5

RHF/6-31G [ $\alpha^2$ ] $^{0,0}$  and [ $\mu\beta$ ] $^{0,0}$  components as well as the total average vibrational second hyperpolarizability of *p*-NA as a function of the NLO process. All the values are given in au. The infinite optical frequency approximation is adopted for computing the dynamic responses. For comparison,  $\bar{\gamma}^e(0; 0, 0, 0) = 13269$  au

	$\bar{\gamma}^{\text{vib}}(0; 0, 0, 0)$	$\bar{\gamma}^{\text{vib}}(-\omega; \omega, 0, 0)$	$\bar{\gamma}^{\text{vib}}(-\omega; \omega, -\omega, \omega)$	$\bar{\gamma}^{\text{vib}}(-2\omega; \omega, \omega, 0)$
[ $\alpha^2$ ] $^{0,0}$	12044	4015	7752	0
[ $\mu\beta$ ] $^{0,0}$	5650	2825	0	1413
[ $\alpha^2$ ] $^{0,0}$ + [ $\mu\beta$ ] $^{0,0}$	17694	6840	7752	1413

tance of the vibrational contribution with respect to the electronic quantity for various NLO processes, we have scaled our  $\gamma^e(0; 0, 0, 0)$  values according to the frequency dispersion study due to Karna et al. [22]. For a wavelength of 1.06  $\mu\text{m}$  (corresponding to an energy of 1.17 eV or 0.0430 au), the dc-Kerr/static, IDRI/static, dc-SHG/static and THG/static  $\gamma^e$  ratios are equal to 1.14, 1.31, 1.51 and 2.57 for the longitudinal component whereas they are, for the average value, equal to 1.12, 1.27, 1.43 and 2.45, respectively. As a consequence, at this optical frequency and by invoking the enhanced approximation in the double harmonic oscillator approach for computing the  $\gamma^v$ , the  $\gamma_L^v/\gamma_L^e$  ratio is equal to 0.56, 0.32, 0.14 and 0.0 for the dc-Kerr, IDRI, dc-SHG and THG, whereas the  $\bar{\gamma}^v/\bar{\gamma}^e$  ratio is equal to 0.46, 0.46, 0.07 and 0.0, respectively.

Table 6

RHF/6-31G  $A_1$  normal mode vibrational frequency (in  $\text{cm}^{-1}$ ) and their associated double harmonic oscillator vibrational contributions to the static longitudinal (hyper)polarizabilities (in au)

$\omega$	[ $\mu^2$ ] $^{0,0}$	[ $\mu\alpha$ ] $^{0,0}$	[ $\alpha^2$ ] $^{0,0}$	[ $\mu\beta$ ] $^{0,0}$
400.3	0.082	7.7	242	-1042
699.7	1.761	-10.7	22	-2102
889.5	0.068	1.7	14	-583
931.0	0.416	-42.9	1474	-1249
1120.8	0.088	11.6	513	676
1245.2	1.823	171.1	5350	6955
1329.3	1.879	75.8	1018	4866
1447.1	9.170	764.3	21234	39523
1466.6	0.600	104.1	6015	6106
1691.7	0.676	-31.7	496	-2167
1797.7	2.740	236.8	6787	8422
1852.7	1.399	45.3	488	1033
3375.6	0.030	-3.1	107	-16
3428.5	0.008	-1.0	41	55
3863.2	0.192	23.4	948	635
Total	20.933	1351.6	44750	61112

In Table 6 are listed the vibrational normal mode contributions to the longitudinal (hyper)polarizabilities of *p*-NA. This molecule belongs to the  $C_{2v}$  point group and only the  $A_1$  modes contribute to the diagonal tensor components, i.e. those associated with the axial or longitudinal direction. The 1447.1  $\text{cm}^{-1}$  mode is, by far, the largest contribution to all vibrational quantities. Indeed, it contributes to 44, 57, 47 and 65% of [ $\mu^2$ ] $^{0,0}$ , [ $\mu\alpha$ ] $^{0,0}$ , [ $\alpha^2$ ] $^{0,0}$  and [ $\mu\beta$ ] $^{0,0}$ , respectively. The normal mode having a 1797.7  $\text{cm}^{-1}$  frequency is also contributing to more than 10% of the static vibrational longitudinal polarizability whereas it contributes to 18% of [ $\mu\alpha$ ] $^{0,0}$ . Other interesting modes for [ $\mu\alpha$ ] $^{0,0}$  have frequencies of 1245.2 and 1466.6  $\text{cm}^{-1}$ . These 1245.2, 1466.6 and 1797.7  $\text{cm}^{-1}$  modes also bring a substantial contribution to [ $\alpha^2$ ] $^{0,0}$  and [ $\mu\beta$ ] $^{0,0}$ , the 1329.3  $\text{cm}^{-1}$  mode contributing significantly to [ $\mu\beta$ ] $^{0,0}$  only. These principal vibrational normal modes are sketched in Fig. 2. As expected, each of these modes partially describes the oscillation of *p*-NA between a more aromatic-like and a more quinoid-like structure; in some cases, these motions are restricted to some parts of the molecule (the benzene ring or the extremities). Though at the RHF/3-21G level [19] the vibrational normal mode and their respective contributions differ, the same general pattern is reproduced: electron delocalization and charge transfer phenomena are strongly influenced by the bond length alternation pattern along the chain and as a consequence, lead to large derivatives of  $\mu^e$ ,  $\alpha^e$  and  $\beta^e$  with respect to the corresponding normal coordinates.

#### 4. Conclusion

In this investigation of *p*-NA, we have demonstrated that, in addition to the electronic response,



the vibrational response is also a critical quantity to tune in order to enhance the NLO responses. Consequently, as for its electronic counterpart, it is important to determine which chemical species are associated with the largest NLO responses and which chemical substitutions enhance these vibrational effects. In the specific case of  $\gamma$  this design of new vibrational NLO materials relies, at least, on two quantities,  $[\alpha^2]^{0,0}$  and  $[\mu\beta]^{0,0}$ , which, in principle, can present completely different behaviour with respect to chemical modifications.

Our RHF/6-31G study, carried out within the double harmonic oscillator approximation, could certainly be improved by exploring the basis set variations and the electron correlation effects on these vibrational (hyper)polarizabilities. Anharmonicity corrections also deserve to be considered and particularly, for  $\gamma$ , the  $[\mu^2\alpha]^{1,0}$ ,  $[\mu^2\alpha]^{0,1}$ ,  $[\mu^4]^{2,0}$  and  $[\mu^4]^{1,1}$  terms as it appears from the recent infinite frequency investigation of Bishop and Dalskov [10] that they are important. These corrections are nevertheless limited to the static ( $[\mu^2\alpha]$  and  $[\mu^4]$ ) and dc-Kerr ( $[\mu^2\alpha]$ ) second hyperpolarizabilities. Finally, the effects of the surroundings which modulate the charge transfer and thus the benzoid/quinoid character of such push–pull systems also need to be addressed for the vibrational contributions. Since these considerations (basis sets, electron correlation, solvent effects) have been shown to be of importance for the electronic (hyper)polarizabilities of *p*-NA, they are expected to modulate substantially the vibrational components too. Research along these lines is in progress.

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