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# Electronic and vibrational first hyperpolarizabilities of polymethineimine oligomers

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## Abstract

The longitudinal static electronic and vibrational first hyperpolarizabilities of nonplanar *trans-cisoïd* polymethineimine oligomers of increasing size have been evaluated at the Hartree–Fock 6-31G level and with the double harmonic approximation. It turns out that the vibrational static first hyperpolarizability per unit cell is very large and still increases linearly with chain length for oligomers containing fifteen unit cells, whereas its electronic counterpart tends to saturate. The vibrational component also contributes substantially to the dc-Pockels and Optical Rectification processes but not to the second harmonic generation phenomenon. The analysis of the vibrational first hyperpolarizability shows that the vibrational normal modes contributing the most have frequencies larger than $1000 \text{ cm}^{-1}$ and involve variations of the bond length alternation along the chain backbone. The effects of electron correlation on the static electronic first hyperpolarizability are also addressed. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Related to the design of new compounds in nonlinear optical (NLO) applications [1,2], the computation of the hyperpolarizabilities of π-conjugated polymers such as polyacetylene (PA), polydiacetylene (PDA), polyyne (PY) and polythiophene (PTh) remains a field of high interest. Quantum chemistry highlights the physical underlying phenomena of the interactions between light and matter, and also determines the meaningful structure-property relationships. Ab initio Hartree–Fock evaluations of both static electronic and vibrational hyperpolarizabilities are available for various interesting polymers [3–5], while results taking into account the effects of the surroundings [6,7], the influence of including electron correlation [8,9], or the frequency-dispersion [10] of the electronic contribution have already appeared for typical systems.

In addition to the electronic contribution to (hyper)-polarizabilities ($\alpha^e$, $\beta^e$, and $\gamma^e$), a vibrational counterpart ($\alpha^v$, $\beta^v$, and $\gamma^v$) also exists [11,12], which involves nuclear relaxation ($\alpha^r$, $\beta^r$, and $\gamma^r$) and

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curvature ($\alpha^c$, $\beta^c$, and $\gamma^c$) contributions. The former originates from field-induced nuclear relaxation effects whereas the latter comes from the field-dependence of the vibrational energy. Until now, with the exception of small systems [13,14] or very recent investigations [15,16], vibrational hyperpolarizability calculations have usually been carried out within the double harmonic oscillator approximation. These studies [3–5,15–17] have shown that in the static limit as well as many NLO processes, these vibrational contributions are at least of the same order of magnitude as their electronic counterpart.

Among the polymeric/oligomeric structures, polymethineimine (PMI) chains have recently attracted a renewed interest. PMI, like PA, presents a bond alternating structure built from single (C–N) and double (C=N) bonds. The only reported experimental works concern the synthesis of oligomers and their reduced spectroscopic characterization [18,19]. In the last five years, several theoretical works have addressed the influence of the chain conformation upon the vibrational frequencies [20], the XPS spectra [21], and the electronic first hyperpolarizabilities [22–24]. For the latter issue, the evolution with a chain length of $\beta^e$ as well as its large amplitude with respect to common D/A systems has been related to the combination of asymmetry and $\pi$-electron delocalization. The sensitivity of its electronic properties, ($\mu$,$\alpha$,...) with respect to geometrical changes, makes PMI also a candidate for large vibrational hyperpolarizabilities. This has recently been confirmed for its vibrational second hyperpolarizability, for which the anharmonic contribution can be very large [16].

This paper aims at addressing the amplitude of the longitudinal dominant component, $\beta_L^v$, as a function of the chain length in comparison with its electronic counterpart, and also aims at characterizing the contributing vibrational normal modes. These results and their interpretation are given in Section 3, after a brief summary of the methods and techniques.

## 2. Methodological and computational aspects

The first hyperpolarizability ($\beta$) is the second-order response of the dipole moment with respect to the external electric fields:

$$\mu_\zeta(\omega_\sigma) = \mu_\zeta^0 \delta_{\omega,0} + \sum_\eta \alpha_{\zeta\eta}(-\omega_\sigma; \omega_1) E_\eta(\omega_1)$$

$$+ \tfrac{1}{2} K^{(2)} \sum_{\eta\xi} \beta_{\zeta\eta\xi}(-\omega_\sigma; \omega_1, \omega_2) E_\eta(\omega_1) E_\xi(\omega_2) + \cdots$$

$$(1)$$

where $\omega_\sigma = \sum_i \omega_i$ and the summations are running over the field indices $\eta$ and $\xi$, associated with the Cartesian coordinates. $K^{(2)}$ is such that $\beta$ for different NLO processes converge towards the same static value. When addressing the effects of external electric fields on matter, it is common to resort to the clamped nucleus (CN) approximation, which assumes that the fields act sequentially on the electronic and nuclear motions [25]. Adopting the CN scheme leads, therefore, to the distinction between an electronic, including the zero-point vibrational average (ZPVA), and a pure vibrational hyperpolarizability contribution. In that approximation, the nuclei are fixed in position, which means that the vibronic states reduce to electronic states and the vibronic energy denominators become electronic energy denominators. Several approximate schemes to evaluate the SOS/CN electronic and vibrational responses are available. For a question of computational feasibility, most of our study has been achieved at the Hartree–Fock level; the inclusion of electron correlation effects being considered only for $\beta^e$ of small PMI oligomers.

The Coupled-Perturbed Hartree–Fock (CPHF) [26–30] procedure is probably the most common procedure for computing ab initio the static electronic (hyper)polarizabilities. In this approach, a term representing the interaction between the external static electric field and the molecular dipole is added to the Fock matrix. Its effects upon the density matrix are obtained by expanding the CPHF equation as a power series in the field amplitude and by solving it self-consistently order-by-order. The successive density matrix derivatives are used to evaluate the electronic (hyper)polarizabilities. This procedure self-consistently includes the field-induced electron reorganization effects through the average Coulomb and Pauli potentials: it is a fully relaxed SCF approach. In order to evaluate the importance of the electron correlation corrections on $\beta$, we use the second-order Møller–Plesset scheme and a numerical

finite field technique, which consists of the evaluation of the energies calculated for electric fields of different amplitudes. Details about the strategy to evaluate the MP2 $\beta^e$ values can be found in Ref. [24].

At the double harmonic oscillator level of approximation [31–33] the static vibrational first hyperpolarizability tensor elements read

$$\beta^v_{\zeta\eta\xi}(-\omega_\sigma; \omega_1, \omega_2) = [\mu\alpha]^{0,0}$$

$$= \tfrac{1}{2} \sum P_{-\sigma,1,2} \sum_a \frac{\left(\frac{\partial \mu^e_\zeta}{\partial Q_a}\right)_0 \left(\frac{\partial \alpha^e_{\eta\xi}}{\partial Q_a}\right)_0}{(\omega_a^2 - \omega_\sigma^2)} \qquad (2)$$

where superscript 0,0 indicates that no electrical or mechanical anharmonicity is included, $\sum P_{-\sigma,1,2}$ is a summation over the six permutations of the pairs $(-\omega_\sigma, \zeta)$, $(\omega_1, \eta)$, and $(\omega_2, \xi)$. $Q_a$ is the normal coordinate of the vibrational motion with circular frequency $\omega_a = 2\pi v_a$, and the subscript 0 indicates the equilibrium nuclear configuration. As shown by Eq. 2, $\beta^v$ is determined by the importance of the simultaneous IR and Raman activities. Furthermore, $\beta^v$ can be decomposed into the contributions of the different vibrational normal modes that provide information concerning the speed of the response: the higher the frequency, the faster the process.

The $\beta^e$ and $\beta^v$ calculations have been performed on the RHF/6-31G fully-optimized structures. A tight convergence threshold on the residual forces has been adopted to meet a satisfactory accuracy in computing the $(\partial P/\partial Q_a)_0$ values. When comparing $\beta^e$ and $\beta^v$, it is important to highlight their different behaviors with respect to frequency dispersion. On the one hand, the $\beta^e$ variation with the frequency obeys the relation [34],

$$\beta^e_{\zeta\eta\xi}(-\omega_\sigma; \omega_1, \omega_2)/\beta^e_{\zeta\eta\xi}(0) = 1 + A\omega_L^2 + B\omega_L^4 + \cdots \qquad (3)$$

where $\omega_L^2 = \omega_\sigma^2 + \omega_1^2 + \omega_2^2$. For the diagonal and average quantities, $A$ is a parameter that depends upon the molecule but not upon the NLO process. $B$ depends upon both the NLO process and the molecule. On the other hand, the frequency-dependence of $\beta^v$ is highlighted by adopting the infinite optical frequency approximation [35], which relies on the fact that the optical frequencies are at least one order of magnitude larger than the vibrational ones. For any diagonal

tensor component of $\beta^v$ such as the longitudinal one, one obtains:

$$\beta^v_L(-\omega; \omega, 0)_{\omega\to\infty} = \beta^v_L(0; \omega, -\omega)_{\omega\to\infty} = \tfrac{1}{3}[\mu\alpha]^{0,0}_{L;\omega=0} \qquad (4)$$

$$\beta^v_L(-2\omega; \omega, \omega)_{\omega\to\infty} = 0 \qquad (5)$$

In other words, $\beta^v$ decreases with the frequency. For SHG $\beta^v_L$ is negligible, whereas for the dc-Pockels (dc-P) and optical rectification (OR) processes, it amounts to 1/3 of the static quantity. Similar relations can also be written for isotropically averaged quantities. These totally different frequency-dependences of the electronic and vibrational phenomena have obviously to be accounted for in optimizing the responses as a function of the NLO process.

The $\beta^e$ and all the quantities necessary to evaluate Eq. (2) have been computed with GAUSSIAN94 [36] by following our usual scheme [13–15]. Throughout this paper, we use the 6-31G basis set, which has often been used with success, to evaluate both the electronic and vibrational contributions to NLO properties of increasingly large systems. Indeed, in sufficiently large oligomers, the 6-31G basis set provides a sufficient accuracy in the longitudinal direction, due to the cooperative effect of the gaussians in adjacent unit cells. In addition, we have performed test calculations with larger basis sets ($X = $ 6-311G$^{**}$, cc-pVDZ and aug-cc-pVDZ) on small oligomers. In all the cases, the $\beta$(6-31G)/($\beta$($X$)) ratios tend towards a constant, with respect to chain length, which is similar for electronic and vibrational counterparts. This confirms the (at least qualitative) validity of the 6-31G basis set for the present evaluation.

## 3. Results and discussion

We have sampled the different conformers of increasingly large PMI chains and have found that the structure that relaxes from the planar *trans–cisoïd* (TC) conformer possesses the lowest energy. This is in agreement with the study of Del Nero et al. [37], which shows that the planar structures are unstable with respect to out-of-plane distortions. For the octamer, we have calculated at the MP2/6-31G level that the all-*trans* form is about 3 kcal/mole of unit cells higher in energy than the nonplanar TC structure. In
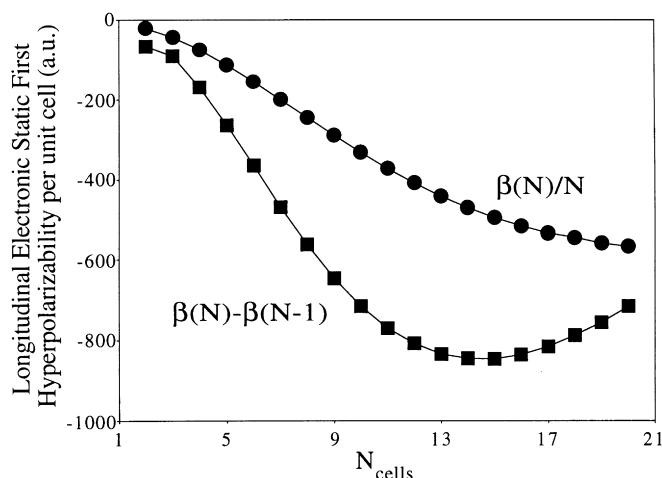
Fig. 1. Evolution with chain length of the electronic first hyperpolarizability per unit cell. 1 a.u. of $\beta = 3.2064 \times 10^{-53}$ C$^3$ m$^3$ J$^{-2}$.

this regard, it is also interesting to mention the vibrational frequency study of Hirata and Iwata [20], which concludes that the conformation of the PMI synthesized and characterized by Wöhrle [18,19], is not all-*trans*. A helical conformation has been shown to be almost as stable as the TC one, indicating that the crystal packing effect could substantially modulate their relative stability. For the TC nonplanar structures, the unit cell parameters evolve slightly with chain length and from the H–(CH=N)$_{16}$–H chain, the 'polymeric' parameters can be estimated as

$R_{C-N} = 1.375$ Å; $R_{C=N} = 1.278$ Å; $R_{C-H} = 1.075$ Å; $\alpha_{N-C-H} = 114.7°$ and $\alpha_{C=N-C} = 122.0°$.

Fig. 1 displays the evolution with chain length of $\beta_L^e$ per unit cell for oligomers ranging between $N = 1$ and $N = 20$. These quantities are either represented by the ratio between $\beta_L^e(N)$ and the number of unit cells or by the variation of $\beta_L^e$ when going from a system with $N - 1$ unit cells to a system with $N$ unit cells, $\Delta\beta_L^e(N) = \beta_L^e(N) - \beta_L^e(N - 1)$. The latter expression removes most of the chain end effects and is better suited, in general, for extrapolating to the infinite
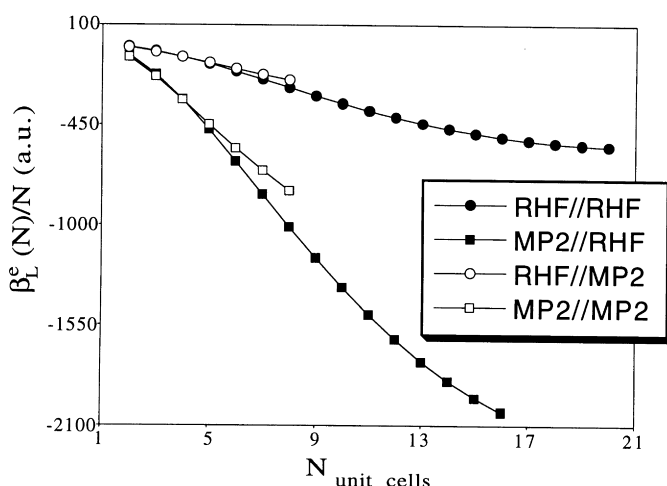


Fig. 2. Electron correlation effects upon the first hyperpolarizability. The A//B notation means that method A is used to evaluate the hyperpolarizability of structures optimized at the B level.
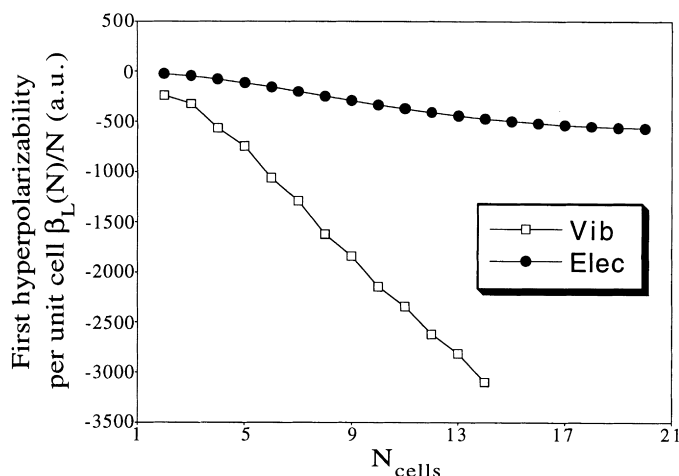
Fig. 3. Longitudinal first hyperpolarizability per unit cell (in a.u.) of increasingly large PMI chains.

chain limit [22]. Since both functions converge towards the same asymptotic limit, it is possible to give a rough estimate of $\Delta\beta_L^e(\infty)$ of $-600 \pm 100$ a.u. (in this orientation, the dipole moment has a negative sign for all oligomer sizes).

Fig. 2 compares the full RHF values with $\beta_L^e$ per unit cell obtained by including electron correlation effects for either the geometry optimization, or for the $\beta_L^e$ calculation, or for both. The full MP2 treatment (MP2//MP2) provides values that are roughly three times larger than the full RHF one for medium chain length. This increase mainly originates from the method for computing $\beta_L^e$. Similarly, for the all-trans PMI, considering the HF geometry, the impact of the MP2 scheme on $\beta_L^e$ is a five times multiplication [24]. The small effect upon $\beta_L^e$ due to the method used to optimize the geometry can be

related to the small variation of Bond Length Alternation (BLA): for the decamer, BLA increases from 0.103 Å at the RHF level to 0.105 Å at the MP2 level.

In Fig. 3, we compare the RHF/6-31G electronic and vibrational first hyperpolarizabilities of increasingly large PMI chains. For the oligomers up to $N = 16$, $\beta_L^v(N)/N$ increase nearly linearly with chain length and do not show any leveling off, which contrasts with $\beta_L^e(N)/N$ and hinders any extrapolation to the infinite system limit. Furthermore, one clearly notices that $\beta_L^v(N)/N$ is much larger than $\beta_L^e(N)/N$.

Similarly, to other π-conjugated systems [17], only a few modes significantly contribute to the vibrational hyperpolarizability. The frequencies and relative contributions of four normal modes dominating $\beta_{L;\omega=0}^v$ in large PMI chains are given in Table 1. The first

Table 1
The RHF/6-31G vibrational frequencies $(cm^{-1})$ and relative contributions (in %) to $[\mu\alpha]_L^{0,0}$; $\omega = 0$ of the most contributing modes for increasingly large PMI chains

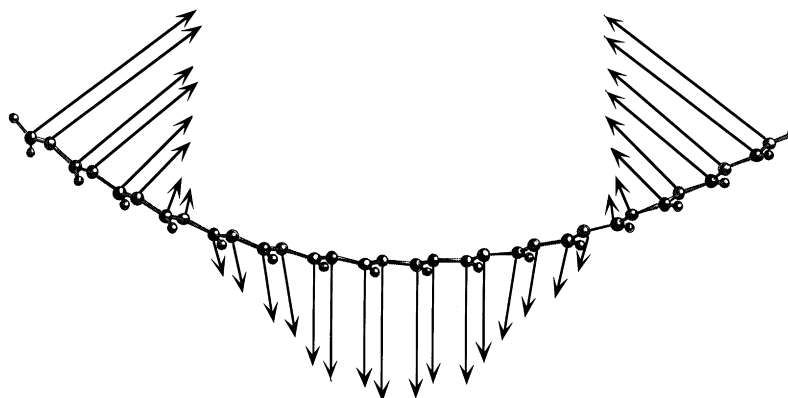| PAM-2 | | | Torsion | | ECC-a | | ECC-b | |
|---|---|---|---|---|---|---|---|---|
| $N_{cells}$ | $\omega$ $(cm^{-1})$ | % | $\omega$ $(cm^{-1})$ | % | $\omega$ $(cm^{-1})$ | % | $\omega$ $(cm^{-1})$ | % |
| 9 | 19.0 | −13.6 | 325.2 | – | 1086.3 | 18.0 | 1682.5 | 66.6 |
| 10 | 15.4 | −16.4 | 323.0 | – | 1083.2 | 19.9 | 1665.8 | 65.5 |
| 11 | 12.7 | −20.1 | 321.8 | 1.7 | 1080.2 | 22.4 | 1650.9 | 66.2 |
| 12 | 10.6 | −22.4 | 320.7 | 4.1 | 1077.2 | 23.8 | 1637.7 | 65.3 |
| 13 | 8.9 | −24.0 | 319.9 | 7.0 | 1074.3 | 25.6 | 1625.8 | 64.9 |
| 14 | 7.6 | −23.6 | 319.2 | 9.4 | 1071.5 | 26.3 | 1615.3 | 61.7 |
| 15 | 6.6 | −22.3 | 318.7 | 11.3 | 1068.8 | 26.8 | 1605.9 | 58.8 |
| 16 | 5.8 | −18.2 | 318.3 | 12.2 | 1066.3 | 26.9 | 1597.7 | 53.7 |

Fig. 4. Displacements of the heavy atoms during the PAM-2 in the hexadecamer.

vibrational species (Fig. 4) consists of perpendicular motions, which along the chain axis, present two sign reversals in the cartesian displacements. This collective mode has been called PAM-2 by analogy with the TAMs and LAMs previously identified in PA, PDA or PSi [3,4,15]. The PAM-2's negative relative contribution to $\beta_L^v$ is due to the same signs of $(\partial\mu_L/\partial Q^{PAM-2})_0$ and $(\partial\alpha_L/\partial Q^{PAM-2})_0$. In the largest PMI chains, these derivatives and the IR related vibrational frequencies tend to zero, but the corresponding contribution is still around 18% for the chains containing sixteen unit cells.

Several torsion modes are seen in the 300–350 cm$^{-1}$ zone and the one that contributes the most presents a frequency converging to 318 cm$^{-1}$ at large chain length. These modes are characterized by out-of-phase perpendicular displacements of nitrogen and hydrogen atoms, leading to a distortion of the chain as shown in Fig. 5.

The relative contribution of this mode is still increasing for the longest system we have studied.

Like for $\gamma^v$ in many $\pi$-conjugated compounds, most of the $\beta^v$ contribution originates from vibrational normal modes that involve motions of the backbone associated with changes in the BLA. Out-of-phase or in-phase H-wagging motions (Fig. 6) are added to these BLA or ECC (Effective Conjugate Coordinate) components. In PMI chains, there are two such modes that combine both large IR and Raman activities and make important contributions to $[\mu\alpha]_L^{0,0}$. For the lowest frequency mode, the carbon and attached hydrogen atoms are moving in phase whereas the second ECC-like mode corresponds to an out-of-phase combination of the carbon and hydrogen motions. The evolution of the relative weights of these two normal modes strongly differs: while for the first mode it seems to saturate towards an upper bound
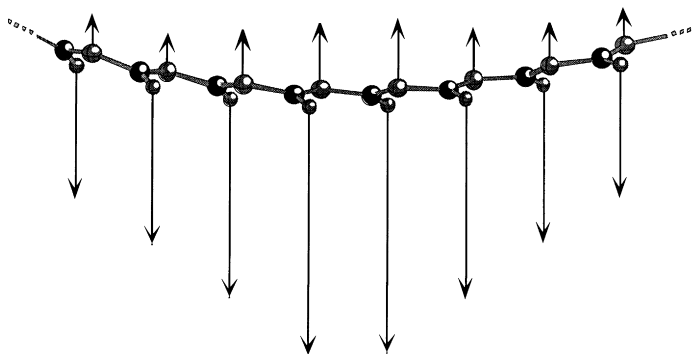


Fig. 5. Perpendicular motions of N and H atoms during the 318 cm$^{-1}$ torsion mode. Carbon atoms remain fixed during this motion.
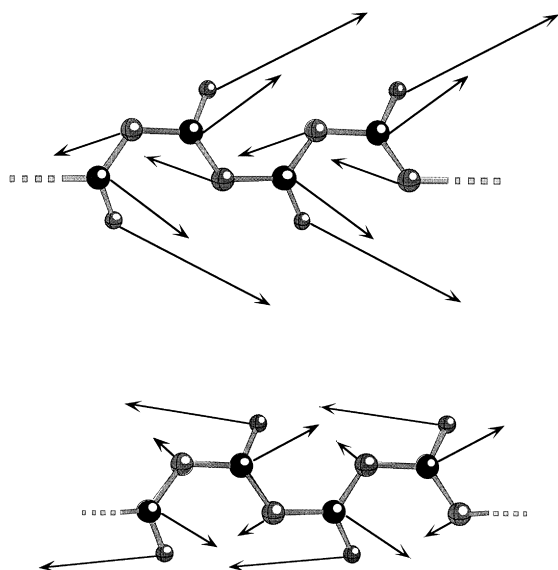
Fig. 6. Atomic displacements in the central unit cells corresponding to the ECC/H-wagging modes with in-phase (top) and out-of-phase (bottom) motion of carbon and hydrogen atoms.

value of 27% of the total $[\mu\alpha]_{\mathrm{L}}^{0,0}$, the second mode has a larger contribution, which decreases for the longest chains. In both cases, the circular frequencies of the vibrational species do not show saturation, even for the largest systems.

This study has shown that nonplanar TC PMI chains present a substantial first hyperpolarizability due to a very large vibrational contribution. This vibrational contribution is still increasing supralinearly with chain length for the largest oligomer ($N = 16$) we have considered. Moreover, since the most contributing modes have frequencies larger than 1000 cm$^{-1}$, it is expected that the corresponding vibrational response will only be one or two order of magnitude slower than its electronic counterpart.

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