

Vibrational optical activity of chiral carbon nanoclusters treated by a generalized π -electron method

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Cross sections of inelastic light scattering accompanied by vibronic excitation in large conjugated carbon structures is assessed at the π -electron level. Intensities of Raman and vibrational Raman optical activity (VROA) spectra of fullerenes are computed, relying on a single electron per atom. When considering only first neighbor terms in the Hamiltonian (a tight-binding (TB) type or Hückel-model), Raman intensities are captured remarkably well, based on comparison with frequency-dependent linear response of the self-consistent field (SCF) method. Resorting to π -electron levels when computing spectral intensities brings a beneficial reduction in computational cost as compared to linear response SCF. At difference with total intensities, the first neighbor TB model is found inadequate for giving the left and right circularly polarized components of the scattered light, especially when the molecular surface is highly curved. To step beyond first neighbor approximation, an effective π -electron Hamiltonian, including interaction of all sites is derived from the all-electron Fockian, in the spirit of the Bloch-equation. Chiroptical cross-sections computed by this novel π -electron method improve upon first-neighbor TB considerably, with no increase in computational cost. Computed VROA spectra of chiral fullerenes, such as C_{76} and C_{28} , are reported for the first time, both by conventional linear response SCF and effective π -electron models.

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I. INTRODUCTION

Chiral nanostructures are currently in the focus of nanoscience,^{1–4} including inherently chiral systems such as chiral fullerenes, single-walled carbon nanotubes (SWNT) and their derivatives.^{5,6} Although many applications using carbon nanostructures (CNS) require precise control over the molecular structure and properties, only recently has attention turned towards optical resolution of racemic mixtures of fullerene⁷ and SWNT⁸ samples. Enantiomer enrichment has been already achieved in a couple of studies, based on chiral recognition^{9–15} as well as by asymmetric synthesis.^{16–19}

For characterization of chiral structures, chiroptical spectroscopy is the standard tool. Chiroptical spectroscopy exists in many variants²⁰ still, only electronic circular dichroism (ECD)²¹ has been applied so far for chiral CNS (CCNS) characterization and derivatives thereof. Absolute configuration of chiral fullerenes has been determined based on ECD measurements of D_2 isomers of C_{76} ,^{16,22,23} C_{78} ,¹⁸ and C_{84} .^{18,19} Enantiomer assignment has been aided by ECD or optical rotatory dispersion computations at the semi-empirical level^{23,24} or by the application of time dependent density functional theory (TD-DFT).^{5,25–29} A limited number of studies have been performed on the SWNT ECD spectra by experiment^{8,11–15} and by theory.^{27,30–32} Induced optical activity of originally achiral molecules can be measured by magnetic circular dichroism (MCD).³³ The first theoretical MCD studies targeted π -electron systems.^{34,35} Interest in MCD spectra of fullerenes is vivid till our days.^{36,37}

Though no CCNS measurements have been reported yet, vibrational optical activity^{38,39} (VOA) is especially appealing for structural studies on chiral systems.⁴⁰ On one hand, VOA is a promising method—complementary to ECD^{41,42}—when aiming enantiomer identification. On the other hand, transition between vibrational states, e.g., VOA reveals much more structural information than ECD.

Of the two established forms of VOA—vibrational circular dichroism⁴³ (VCD) and vibrational Raman optical activity⁴⁴ (VROA or more simply ROA)—the present study focuses on the latter. Since Raman spectroscopy is a basic experimental tool for SWNT characterization,^{45,46} VROA has a special significance in the context of CCNS.

Increase in experimental spectroscopical interest together with the rapid development in CCNS sample preparation gives strong motivation for computational chiroptical CCNS studies. In fact, recent theoretical developments in describing VOA spectra is remarkable.⁴⁷ Current computational VROA studies mostly rely on linear response theory⁴⁸ based on the self-consistent-field (SCF) approximation (Hartree–Fock (HF) or Kohn–Sham (KS)). Incorporation of many-body effects in VROA intensity calculations is affordable only for small molecules and cannot be regarded well-spread.^{49–51} According to numerical experience,^{52–56} HF or KS linear response can be considered sufficient in most cases for reproducing experimental ROA spectra.

The two main steps of spectrum simulation are the calculation of (i) positions and (ii) intensities of spectral lines. Within the harmonic approximation, the first step of a Raman or ROA spectrum simulation is to obtain the

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vibrational normal modes, which involves calculation and full diagonalization of the Hessian of the molecular potential energy surface. For large clusters, this represents the computational bottleneck of modern ROA modeling.⁵⁷ Assuming non-resonant incident frequency, the second step necessitates calculation of geometrical derivatives of molecular polarizability tensors. These quantities are in principle third derivatives of the total energy. Still, VROA intensities can be computed based on the linear response of the wavefunction, exploiting the $2n + 1$ theorem.⁵⁸

To reduce the computational cost associated with Raman or ROA spectrum simulation, molecular symmetry can be efficiently exploited: e.g., line-group symmetry has been imposed⁵⁹ to assess three Raman active SWNT modes.⁶⁰ Simplification of the molecular energy expression is another way to keep the cost relatively low. For example, a quantum chemical force field developed for π -electron systems (QCFF/PI)⁶¹ has been shown to reproduce experimental C_{76} vibrational frequencies within a few cm^{-1} .⁶² Admittedly, the quality of QCFF/PI normal coordinates—which strongly influence scattering intensity—has not been assessed yet. For large molecules, it often helps to build ROA spectra using independent contributions of small parts of the molecule, cf. cartesian coordinate tensor transfer technique.^{63,64} Unfortunately, approaches based on the idea of segmentation are not suitable for CCNS, due to their indivisible delocalized π -electron system.

From the computational point of view, extended size of CNS is especially disadvantageous. State of the art *ab initio* ROA implementations^{57,65,66} are far from being applicable for systems accommodating hundreds of carbon atoms. Resorting to π -electrons is a straightforward way to cost-effectiveness in the case of conjugated systems. A properly parametrized, effective model can be highly useful for π -electron systems.^{23,62,67–77} Among π -electron models, the first-neighbor approximation (here called first-neighbor tight-binding (TB) or Hückel-model) represents the simplest approach. When applied in a broader sense, the TB approximation may refer to the application of a distance based cutoff. There are many variants of the TB model in this broader sense, ranging from π -electron, through all-valence to all-electron models.^{78,79} In particular, TB density functional theory (DFTB)⁸⁰ and its time-dependent extension (TD-DFTB)⁸¹ is a rapidly developing, low cost alternative for describing light-molecule interactions.⁸² It has been already applied for both fullerenes⁸³ and nanotubes.⁸⁴ Abbreviation TB is used for first-neighbor TB in this work. Distance based cutoff is not applied in the present study. To avoid confusion, the epithet “first-neighbor” precedes TB wherever space permits.

Applicability of effective models cannot be taken for granted in all circumstances. For instance, the first-neighbor approximation within the π -electron model fails to describe hybridization effects in highly curved CNS. Incorporating second and more distant neighbor terms has been shown to correct for this effect.⁶⁷ Our intentions with the present study are precisely to overcome such limitations of a simple π -electron model, when applied to CNS optical activity calculations. The goal is to assess the performance of a generalized

π -electron approximation in computing CNS VROA spectral intensities.

The study starts from the simplest possible π -electron model and gradually introduces improvements along two lines: (i) in the model Hamiltonian and (ii) in the calculation of property (electric/magnetic dipole and electric quadrupole) integrals. Among the effective Hamiltonians considered, the most complex one is a generalized π -electron model, derived from the molecular Fockian, following the idea of Bloch-equation^{85,86} or energy independent partitioning.⁸⁷

At each step of the theoretical improvement, performance of the model is compared to linear response SCF spectra. Focus is intentionally put on spectral cross-sections. Line positions are assumed to be the same when calculating intensities by either of the theoretical models. The B3LYP functional with polarized valence double or triple zeta basis set is adopted for computing harmonic normal modes. Chiral fullerenes are applied as test cases. In addition to ROA, Raman spectra are also reported to compare the reliability with VROA at the same level of theory. As Raman measurements are accessible, it also facilitates comparison with experiment. To the best of our knowledge, neither experimental nor calculated VROA spectra have been reported for chiral fullerenes yet.

II. MODEL HAMILTONIAN

A one-electron model is adopted throughout the study, given by the second-quantized expression

$$\hat{H} = \sum_{\mu\nu} h_{\mu\nu} \sum_{\sigma} \chi_{\mu\sigma}^{+} \chi_{\nu\sigma}^{-}, \quad (1)$$

assuming orthogonal atomic orbitals (AO), χ_{μ} . Symbols $\chi_{\mu\sigma}^{+}$ ($\chi_{\nu\sigma}^{-}$) refer to the associated creation (annihilation) operators with spin σ . Different levels of approximation affect the number of AO and the expression of one-electron integrals, $h_{\mu\nu}$. A π -electron model considers just one basis function per atom. In the first-neighbor TB approximation we take $h_{\mu\nu}$ nonzero only if atoms μ and ν are first neighbor, and the one-electron (hopping) integrals are expressed as

$$h_{\mu\nu}^{\text{TB}} = -h_0 e^{-\zeta R_{\mu\nu}}, \quad (2)$$

where $R_{\mu\nu}$ measures the distance between atoms μ and ν . Parameters $h_0 = 243.50486$ eV and $\zeta = 0.3074518$ Å⁻¹ are determined to match the experimental excitation energy of ethylene and poly-acetylene as described in Refs. 73 and 88. This parameter set was previously found successful in describing several spectroscopic properties of fullerene⁸⁸ and the electronic structure of fullerene polymers.⁷³ The field free excitation spectrum is an essential ingredient contributing to spectroscopic intensities, we therefore find this model sufficient for the purpose of this study. Reparametrization, focusing on chiral fullerenes and Raman/ROA spectral intensities could undoubtedly improve the first-neighbor TB results reported below, but this is out of our present scope.

Stepping beyond the first neighbor approximation, but staying with a one-electron Hamiltonian, we wish to see what can be best achieved by an all- π model. For this end hopping integrals between each atom are derived from more

sophisticated one-electron models, in the spirit of the Bloch-equation.^{67,85,86} As a starting point an SCF Fockian is taken, expressed in terms of the orbital energies, ϵ_p and the molecular orbitals (MO), ψ_p as

$$\hat{F} = \sum_p \epsilon_p \sum_\sigma \psi_{p\sigma}^+ \psi_{p\sigma}^-.$$

To select MO's constituting the π -electron system, a projector $\hat{P}^\pi$ is formulated as

$$\hat{P}^\pi = \sum'_\mu |\chi_\mu^\perp\rangle\langle\tilde{\chi}_\mu^\perp|,$$

where the prime on the sum indicates restriction to $2p$ AO's, oriented perpendicular to the molecular surface. Such AO's are overlapping, this is the reason for the appearance of reciprocal functions $\tilde{\chi}_\mu^\perp$, satisfying

$$\langle\tilde{\chi}_\mu^\perp|\chi_\nu^\perp\rangle = \delta_{\mu\nu}.$$

Among projected MO's

$$\psi'_p = \hat{P}^\pi \psi_p,$$

those having the largest norm are selected. Projected orbitals ψ'_p are orthonormalized among themselves by Löwdin's symmetrical procedure,⁸⁹ to give the set of (orthonormal) π -MO's

$$\psi_p^\pi = \sum'_q S_{qp}^{-1/2} \psi'_q.$$

Prime on the sum now indicates restriction to the selected projected MO's and $S^{-1/2}$ refers to the inverse square root of the overlap of functions ψ'_p . When constructing the effective π -Hamiltonian, orbital energies of the original Fockian are assigned to the π -MO's:

$$\hat{H}^{\text{all-}\pi} = \sum_p \epsilon_p \sum_\sigma (\psi_{p\sigma}^\pi)^+ (\psi_{p\sigma}^\pi)^-.$$

To conform with Eq. (1), it is practical to rewrite the all- π Hamiltonian in terms of the Löwdin-orthogonalized orbitals, denoted by

$$\chi_\mu^L = \sum'_\nu T_{\nu\mu}^{-1/2} \chi_\nu^\perp,$$

with T being the overlap matrix of the normally oriented $2p$ AO. In terms of χ_μ^L , operator $\hat{H}^{\text{all-}\pi}$ takes the form

$$\hat{H}^{\text{all-}\pi} = \sum_{\mu\nu} h_{\mu\nu}^{\text{all-}\pi} \sum_\sigma (\chi_{\mu\sigma}^L)^+ (\chi_{\nu\sigma}^L)^-, \quad (3)$$

with

$$h_{\mu\nu}^{\text{all-}\pi} = \sum_{pqr} \sum_{\lambda\kappa} T_{\mu\lambda}^{(1/2)} C_{\lambda q} S_{qp}^{-1/2} \epsilon_p S_{pr}^{-1/2} C_{\kappa r} T_{\kappa\nu}^{(1/2)}. \quad (4)$$

In the above, indices p, q, r run for the selected, π -projected MO's, indices λ, κ are restricted to perpendicular oriented $2p$ AO's, and $C_{\lambda q}$ are the expansion coefficients of π -projected MO's according to

$$\psi'_q = \sum_\lambda C_{\lambda q} \chi_\lambda^\perp.$$

Regarding the Hamiltonian, either the first-neighbor TB model, given by Eqs. (1) and (2) or the all- π model, given by Eqs. (3) and (4), is applied in the calculations below. To derive the all- π model, the *ab initio* Fockian is computed with minimal basis set.

The all- π model devised here is related to previous works by Szakács *et al.*,⁶⁷ Riberio and Macedo,⁹⁰ Popov,⁹¹ and Meyer *et al.*⁹² The latter study is particularly akin in the way of generating the model Hamiltonian. Similarly to the present all- π approach, Meyer *et al.* determine system-specific TB parameters from *ab initio* data, by projection to a small, optimized set of basis functions.

III. PROPERTY INTEGRALS

To pick up the most dominant effects, we apply the zero differential overlap (ZDO) approximation⁹³ when computing integrals of multipole moments responsible for electron-photon coupling.

At the ZDO level, the electric dipole integrals reduce to

$$\mathbf{d}_{\lambda\nu} = -\langle\chi_\lambda^\perp|\hat{\mathbf{r}}|\chi_\nu^\perp\rangle = -\delta_{\lambda\nu} \mathbf{R}^\lambda, \quad (5)$$

where $\hat{\mathbf{r}}$ is the position operator of the electron and $\mathbf{R}^\lambda$ is the position vector of nucleus λ . Following Linderberg and Seamans,⁹⁴ momentum integrals, necessary for the magnetic dipole, are derived based on the equation of motion (EOM)

$$\hat{\mathbf{p}} = -i[\hat{\mathbf{r}}, \hat{H}]. \quad (6)$$

At the ZDO level, this relation leads to

$$\mathbf{m}_{\lambda\nu} = \frac{1}{2}\langle\chi_\lambda^\perp|(\hat{\mathbf{r}} - \mathbf{G}) \times \hat{\mathbf{p}}|\chi_\nu^\perp\rangle = \frac{i}{2}h_{\lambda\nu}[(\mathbf{R}^\lambda - \mathbf{G}) \times \mathbf{R}^\nu], \quad (7)$$

for the magnetic dipole, with $\mathbf{G}$ denoting the gauge-origin. The third property needed for VROA intensities, is the electric quadrupole defined as

$$\hat{\theta}_{\alpha\beta} = -\frac{1}{2}\left(3\hat{r}_\alpha\hat{r}_\beta - \delta_{\alpha\beta}\sum_\gamma\hat{r}_\gamma^2\right),$$

with α, β, γ referring to Descartes-components. Matrix elements taken with $2p$ orbitals oriented normally to the surface are given by

$$\begin{aligned} (\theta_{\alpha\beta})_{\lambda\nu} &= \langle\chi_\lambda^\perp|\hat{\theta}_{\alpha\beta}|\chi_\nu^\perp\rangle \\ &= -\frac{1}{2}\delta_{\lambda\nu}\left(3R_\alpha^\lambda R_\beta^\lambda - \delta_{\alpha\beta}\sum_\gamma(R_\gamma^\lambda)^2 + I_{\alpha\beta}^\lambda\right), \end{aligned} \quad (8)$$

using the ZDO approximation. Term $I_{\alpha\beta}^\lambda$ is a quadratic function of the relative coordinate $\hat{\mathbf{p}}^\lambda = \hat{\mathbf{r}} - \mathbf{R}^\lambda$ according to

$$I_{\alpha\beta}^\lambda = \langle\chi_\lambda^\perp|3\rho_\alpha^\lambda\rho_\beta^\lambda - \delta_{\alpha\beta}\sum_\gamma(\rho_\gamma^\lambda)^2|\chi_\lambda^\perp\rangle.$$

The value of $I_{\alpha\beta}^\lambda$ depends on the orientation of the $2p$ orbitals with respect to the external field. It is calculated in an analytic manner, taking Slater $2p$ orbitals with exponent $\zeta = 1.625$.

Property integrals needed for VROA cross sections are given by Eqs. (5), (7), and (8) at the ZDO level. To test the

accuracy of the ZDO assumption, integrals computed with STO-6G orbitals are also applied below.

When calculating magnetic properties, gauge-invariance of observables has to be considered. Since the magnetic dipole integral Eq. (7) relies on the EOM of Eq. (6), gauge-invariance is ensured at the ZDO level. When applying integrals over STO-6G orbitals the EOM of Eq. (6) is not fulfilled. To achieve gauge-origin independence in such circumstances, one may recourse to a dipole velocity formulation⁹⁵ or integrals expressed with gauge-including atomic orbitals, also called London-orbitals.^{49,96} Both approaches are tested below. In addition, the gauge-dependent dipole length representation is also examined, with the gauge-origin fixed at the center of the positive charge.

IV. SPECTRAL INTENSITIES

The key quantities, determining the difference in the intensity of left and right circularly polarized component in the scattered light, are three transition polarizabilities. Their expression, within Placzek's approximation,⁹⁷ following from time-dependent linear response theory,⁵⁸ is listed here for the case of a one-electron model Hamiltonian, Eq. (1). The electric dipole-electric dipole tensor reads as

$$\begin{aligned}\alpha_{\alpha\beta} &= -\langle\langle d_\alpha, d_\beta \rangle\rangle_\omega \\ &= 2 \sum_i^{\text{occ}} \sum_a^{\text{virt}} \left(\frac{(d_\alpha)_{ia} (d_\beta)_{ai}}{\omega_{ai} - \omega} + \frac{(d_\beta)_{ia} (d_\alpha)_{ai}}{\omega_{ai} + \omega} \right),\end{aligned}\quad (9)$$

with ω standing for the energy of the incident light and indices i, a referring to occupied and virtual MO, respectively. Symbol ω_{ai} denotes the energy difference of orbitals a and i ,

$$\omega_{ai} = \varepsilon_a - \varepsilon_i.$$

The electric dipole-magnetic dipole tensor looks¹²⁶

$$\begin{aligned}G'_{\alpha\beta} &= -\text{Im}\langle\langle d_\alpha, m_\beta \rangle\rangle_\omega \\ &= 2 \sum_i^{\text{occ}} \sum_a^{\text{virt}} \text{Im} \left(\frac{(d_\alpha)_{ia} (m_\beta)_{ai}}{\omega_{ai} - \omega} + \frac{(m_\beta)_{ia} (d_\alpha)_{ai}}{\omega_{ai} + \omega} \right).\end{aligned}\quad (10)$$

Finally, the electric dipole-electric quadrupole tensor is given as

$$\begin{aligned}A_{\alpha,\beta\gamma} &= -\langle\langle d_\alpha, \theta_{\beta\gamma} \rangle\rangle_\omega \\ &= 2 \sum_i^{\text{occ}} \sum_a^{\text{virt}} \left(\frac{(d_\alpha)_{ia} (\theta_{\beta\gamma})_{ai}}{\omega_{ai} - \omega} + \frac{(\theta_{\beta\gamma})_{ia} (d_\alpha)_{ai}}{\omega_{ai} + \omega} \right).\end{aligned}\quad (11)$$

Notation $\langle\langle \cdot \rangle\rangle_\omega$ used above is a shorthand for frequency-dependent response functions.⁵⁸

Energy being absorbed in the vibrational degrees of freedom, spectral intensities are determined by derivatives of transition polarizabilities with respect to the normal coordinates, Q_p . Adopting the Herzberg-Teller expansion⁹⁷ up to first order, the so-called electron-phonon and phonon-photon coupling are both included. With the notation

$$\alpha_{\alpha\beta}^p = \left(\frac{\partial \alpha_{\alpha\beta}}{\partial Q_p} \right)_0, \quad (12)$$

for derivatives taken at the equilibrium geometry tensor invariants,⁹⁸ contributing to Raman and ROA cross sections, take the form

$$\begin{aligned}\beta(\alpha^p)^2 &= \frac{3}{2} \text{Tr}(\alpha^p \alpha^p) - \frac{1}{2} \text{Tr}(\alpha^p)^2, \\ \beta(G'^p)^2 &= \frac{3}{2} \text{Tr}(\alpha^p G'^p) - \frac{1}{2} \text{Tr}(\alpha^p) \text{Tr}(G'^p), \\ \beta(A^p)^2 &= \frac{\omega}{2} \sum_{\alpha\beta\gamma\delta} \alpha_{\alpha\beta}^p \epsilon_{\alpha\gamma\delta} A_{\gamma,\delta\beta}^p,\end{aligned}$$

where $\epsilon_{\alpha\gamma\delta}$ is the Levi-Civita symbol. Raman and ROA cross sections are computed for the experimentally favored backscattering arrangement, with unpolarized incident light:⁹⁹

$$\text{d}\sigma_u^{\text{Raman}}(180^\circ) = K [10 \text{Tr}(\alpha^p)^2 + 14 \beta(\alpha^p)^2], \quad (13)$$

$$\Delta \text{d}\sigma_u^{\text{ROA}}(180^\circ) = \frac{4K}{c} [12 \beta(G'^p)^2 + 4 \beta(A^p)^2], \quad (14)$$

where $K = (1/90)(\mu_0/(4\pi))^2(\omega - \omega_p)^3\omega$, μ_0 stands for the permeability of vacuum, c denotes the speed of light, and ω_p refers to the harmonic frequency associated with normal mode Q_p .

The rate-determining step of spectral cross section calculation, assuming the knowledge of the harmonic vibrational modes, is the evaluation of geometrical derivatives, Eq. (12). Property tensor derivatives of the type of Eq. (12) can be expressed as third derivatives of the energy.¹⁰⁰ With appropriate definition of intermediaries, calculation time of the most expensive terms scales with $N_\pi^2 N_{\text{mode}}$, where N_π is the number of π -orbitals (equal to the number of atoms) and N_{mode} is the number of vibrational degrees of freedom.

V. COMPUTATIONAL DETAILS AND DISCUSSION

Two chiral fullerene molecules are selected as test cases: C₇₆ and C₂₈, both having an isomer of D₂ symmetry. Being one of the most commonly studied chiral fullerene,^{16,22–27,62,101–103} D₂-C₇₆ is an excellent candidate for comparison between theoretical and prospective experimental ROA spectra. (The other, much less abundant, achiral T_d isomer of C₇₆¹⁰⁴ is not concerned in this study.)

The C₂₈ molecule, assumed to be the smallest synthesizable fullerene,^{105,106} represents a challenge for π -electron theories, due to its highly curved molecular surface.

As of yet, C₂₈ has been characterized only in its chemically stabilized derivatives, e.g., Ti@C₂₈.^{106,107} As confirmed by several theoretical studies,^{83,105–112} the most stable isomer of C₂₈ has a quintuplet ground state and a geometry of T_d symmetry, with four non-adjacent hexagons. The ground state of the less stable isomer, D₂-C₂₈ (characterized by two edge-sharing hexagon pairs) has a singlet ground state.^{83,110,112,113} Adopting the systematic fullerene numbering scheme,¹¹⁴ spectra presented below belong to the ^tA-D₂-C₇₆ and ^tC-D₂-C₂₈ configurations. (Symmetry, constitution, and configuration are not labeled for these are unambiguous.)

In lack of experimental ROA data, high level computations (exploiting symmetry) serve as reference for evaluating

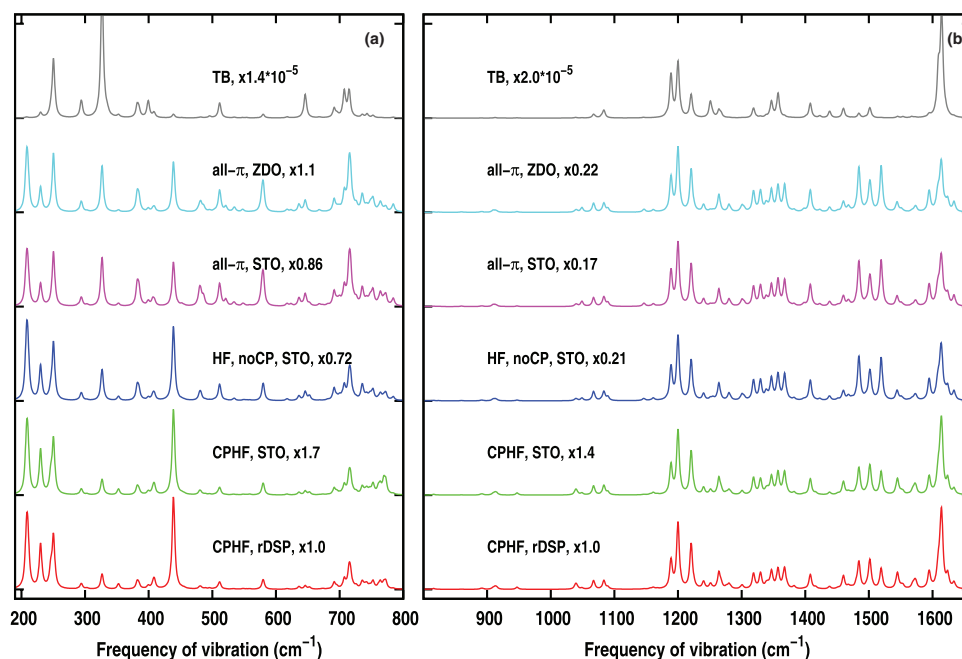


FIG. 1. Unpolarized backscattering Raman cross sections of C_{76} at 1064 nm. Spectra of panel (a) are normalized over the wavenumber interval $[0, 800] \text{ cm}^{-1}$, panel (b) over $[800, 1800] \text{ cm}^{-1}$. Relative scaling factors (RSF) are computed with respect to the “CPHF, rDSP” curve. See text for further notations.

the performance of π -electron theories. In the case of C_{28} this benchmark is provided by polarizability tensor derivatives computed by Hartree–Fock and by the B3LYP density functional, in aug(sp)-cc-pVDZ basis set.¹¹⁵ For C_{76} , HF and B3LYP references are found computationally attainable adopting the somewhat smaller rDSP basis set of Hug and Zuber.¹¹⁶ Both basis sets are well-suited for ROA computations.^{65,117,127}

Spectra reported below are computed using a common set of normal coordinates and harmonic frequencies. Equilibrium structures and vibrations of C_{76} are calculated at the B3LYP/6-31G* level, while for C_{28} the B3LYP functional with cc-pVTZ basis set is applied. In terms of vibrational frequencies, satisfactory agreement is found with recently reported experimental and theoretical data in case of both C_{76} ^{62,103} and C_{28} .⁸³

Electronic levels by the here described π -models and polarizability tensor derivatives are computed by a local implementation. In order to monitor a gradual improvement of theoretical approaches, tensor derivatives at the HF level are calculated both with and without orbital relaxation (OR). The OR effect is described by the coupled perturbed (CP) HF method.¹¹⁸ The results denoted as “HF, noCP” represent a step between all- π derivatives (where OR does not show up) and linear response SCF, with OR included. Neglect of OR in SCF response calculations is rare but not unprecedented.^{119–121} Analytical third derivatives of the energy¹⁰⁰ are implemented for the first-neighbor TB model. In all other cases polarizability tensors are computed as analytical second derivatives, according to Eqs. (9)–(11). Differentiation with respect to nuclear coordinates is computed numerically, adopting a step size of 10^{-3} a.u. in the finite difference formula.

In all depicted spectra Lorentzian line shapes are assumed with 5 cm^{-1} line width. Area below a Lorentz-shape

peak matches the cross section of Eq. (13) or (14), calculated for the given vibrational frequency. To make visual comparison easy, normalized spectra are plotted in Figs. 1–5. Adopting the notation $f(\omega)$ for a spectral curve, $f_n(\omega) = \mathcal{N}^{-1} f(\omega)$ are displayed, with

$$\mathcal{N}^2 = \langle f | f \rangle = \int_a^b f(\omega)^2 d\omega.$$

Values $a = 200 \text{ cm}^{-1}$ and $b = 1800 \text{ cm}^{-1}$ apply for the spectra displayed in a single panel. This interval is often split for a small and a large wavenumber range. Presentation of the small/large wavenumber range in separate panels allows to compare details that could remain imperceptible if plotted in the entire wavenumber interval. Relative scaling factors (RSFs)—i.e., $\mathcal{N}^{-1}/\mathcal{N}_{\text{ref}}^{-1}$ —are shown in figure labels, referenced by “ $\times \text{RSF}$.” As a numerical indicator of the similarity of spectra, overlap measures are also reported, computed as

$$\langle f_n | g_n \rangle = \int_a^b f_n(\omega) g_n(\omega) d\omega.$$

Neither fullerenes are transparent at the laser wavelength of 532 nm, applied most commonly in ROA experiments. The far-from-resonance approximation applied here necessitates the choice of an incident light of less energy. To allow comparison with a Raman experiment on C_{76} , these spectra are computed at 1064 nm laser wavelength, in spite of the fact, that both B3LYP and first-neighbor TB results are inappropriate due to strong resonance. Data are reported at an incident laser wavelength of 4256 nm also, to avoid the resonance region. Comparison of theoretical approaches is most relevant at this frequency.

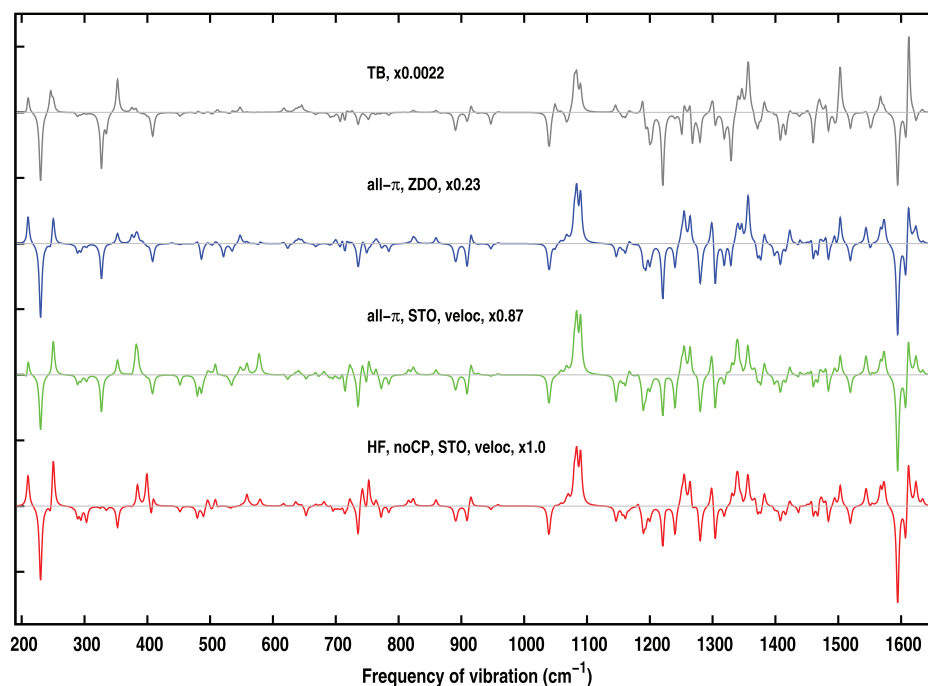


FIG. 2. Unpolarized backscattering ROA cross sections of C_{76} at 4256 nm. Values of RSF are computed with respect to the “HF, noCP, STO-6G” curve. See text for further notations.

A. Raman intensities of fullerenes

Raman spectra computed at 1064 nm for C_{76} are displayed in Fig. 1, split into two. A comparison between the experimental spectrum¹²² and the here computed CPHF/rDSP reference spectrum reveals a good agreement. The correct shape is well preserved through the introduction of systematic simplifications. The effect of the AO basis set size is

small (compare CPHF/rDSP and CPHF/STO-6G). The same holds for the CP effect (compare CPHF/rDSP and “HF, noCP, STO”) if inspecting Fig. 1. It is to be noted, however, that the RSF of panel (b) is roughly 3 times less than that of the RSF of panel (a) in the case of the “HF, noCP, STO” spectrum. This means that the relative weight of the small/large wavenumber range gets deteriorated when the CP effect is switched off.

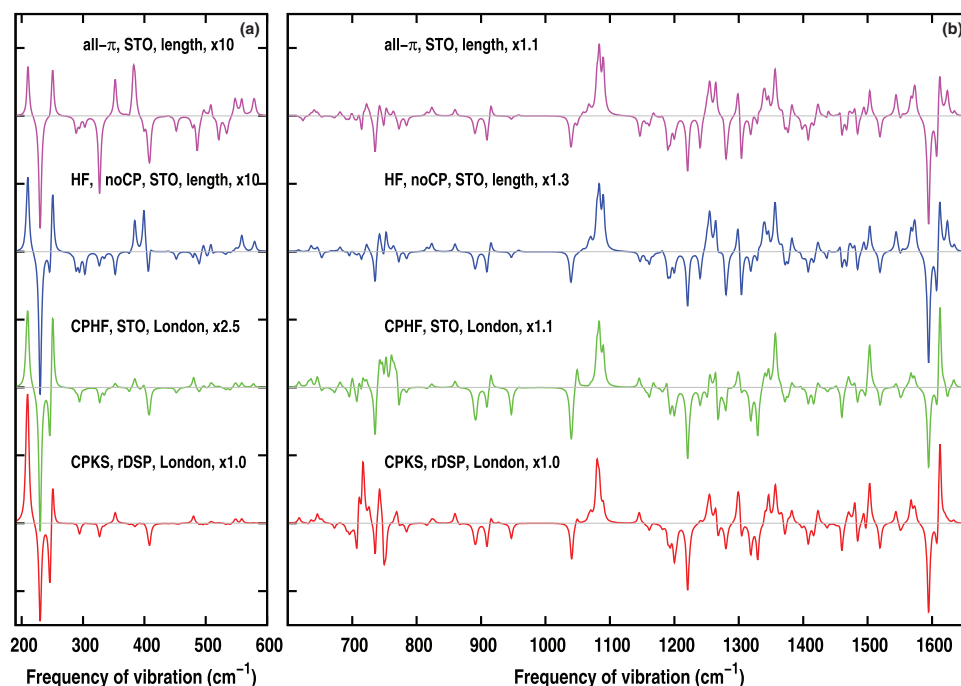


FIG. 3. Unpolarized backscattering ROA cross sections of C_{76} at 4256 nm. Spectra of panel (a) are normalized over the wavenumber interval $[0, 600] \text{ cm}^{-1}$, panel (b) over $[600, 1800] \text{ cm}^{-1}$. Values of RSF are computed with respect to the “CPKS/B3LYP/rDSP” curve. See text for further notations.

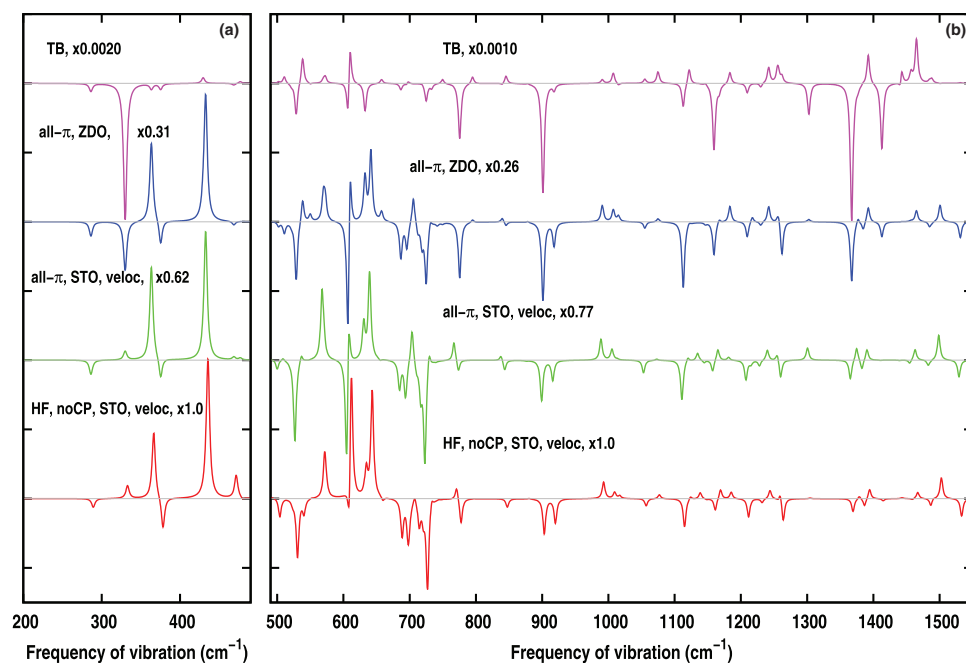


FIG. 4. Unpolarized backscattering ROA cross sections of C_{28} at 4256 nm. Spectra of panel (a) are normalized over the wavenumber interval $[0, 490] \text{ cm}^{-1}$, panel (b) over $[490, 1800] \text{ cm}^{-1}$. Values of RSF are computed with respect to the “HF, noCP, STO-6G” curve. See text for further notations.

Let us compare now π -electron spectra with the starting point of the derivation of all- π models: HF/STO-6G without orbital relaxation. As Fig. 1 demonstrates, all- π models show a great similarity with “HF, noCP, STO,” either when all multipole moment integrals are taken into account (“all- π , STO”) or when the ZDO approximation is utilized (“all- π , ZDO”). The first-neighbor TB result is shown only for completeness. (The HOMO-LUMO gap of the first-neighbor TB model is 43.4 mE_h , falling into the range of strong

resonance with the energy of the incident light, 42.8 mE_h at 1064 nm .)

Overlap measures are reported in Table I at 1064 nm as well as at 4256 nm , the latter being relevant for the first-neighbor TB model too. Overlaps obtained for the all- π models are very close to 1.0 (above 0.95) reflecting the success of the derivation of all- π models. The first-neighbor TB approximation falls just slightly behind, showing 0.90 overlap at 4256 nm .

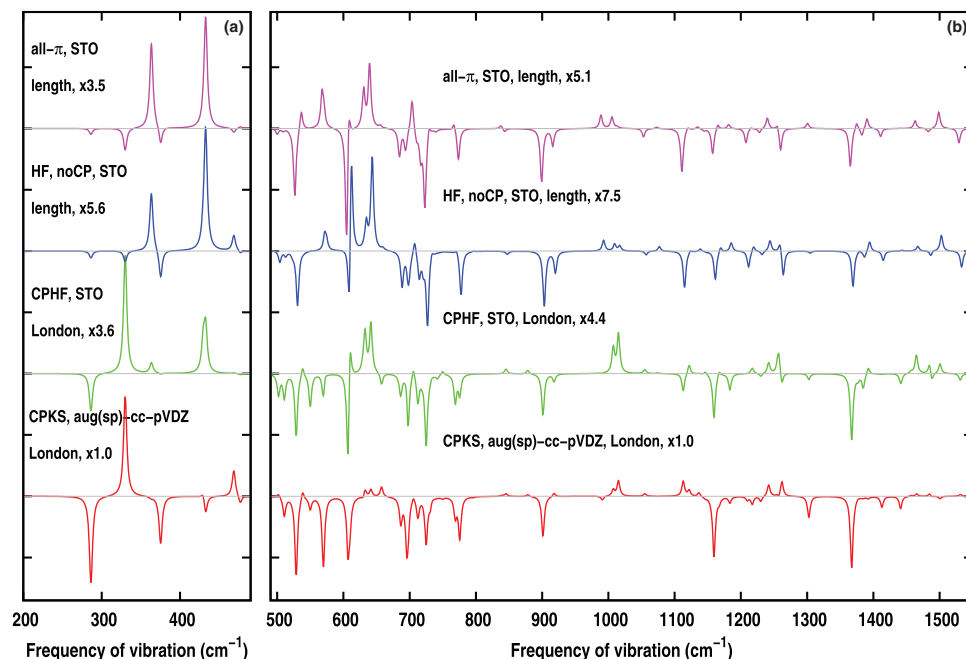


FIG. 5. Unpolarized backscattering ROA cross sections of C_{28} at 4256 nm. Spectra of panel (a) are normalized over the wavenumber interval $[0, 490] \text{ cm}^{-1}$, panel (b) over $[490, 1800] \text{ cm}^{-1}$. Values of RSF are computed with respect to the “CPKS/B3LYP/aug(sp)-cc-pVDZ” curve. See text for further notations.

TABLE I. Overlaps $\langle f_n | g_n \rangle$ of unpolarized Raman and ROA backscattering cross sections computed by various methods. Values in round brackets refer to less relevant data due to resonance with the incident light. For notations see text.

Spectroscopy: Raman, g_n : HF, noCP, STO-6G				
f_n	C_{76}		C_{28}	
	4256 nm	1064 nm	4256 nm	1064 nm
All- π , STO-6G	0.954	0.996	0.993	0.993
All- π , ZDO	0.964	0.997	0.996	0.996
First-neighbor TB	0.899	(0.790)	0.956	(0.763)
Spectroscopy: ROA, g_n : HF, noCP, velocity, STO-6G				
f_n	C_{76}		C_{28}	
	4256 nm	1064 nm	4256 nm	1064 nm
HF, noCP, length, STO-6G	0.980	0.994	0.978	0.940
All- π , velocity, STO-6G	0.925	0.991	0.950	0.943
All- π , ZDO	0.900	0.973	0.874	0.803
First-neighbor TB	0.657	(−0.127)	0.008	(−0.081)

Raman spectra for C_{28} are not reported, as they lead to conclusions in accordance with the case of C_{76} . Overlap values with the “HF, noCP, STO” Raman spectra for C_{28} , collected in Table I, support this statement. Similarity of π -electron models to “HF, noCP, STO” is even better than for C_{76} : the overlaps of all- π spectra are greater than 0.99 for both wavenumbers and the first-neighbor TB model results an overlap above 0.95 at 4256 nm.

While comparison with “HF, noCP, STO” characterizes the success of building an effective model, overlap computed with the reference spectrum serves for judging how good matching with experiments may be expected. The numbers reported in Table II are encouraging: overlaps with the reference at 1064 nm remain above 0.87 for all- π models.

TABLE II. Overlaps $\langle f_n | g_n \rangle$ of unpolarized Raman and ROA backscattering cross sections computed by various methods. Reference spectra g_n are as follow: CPKS/B3LYP/rDSP for C_{76} at 4256 nm, CPHF/rDSP for C_{76} at 1064 nm, CPKS/B3LYP/aug(sp)-cc-pVDZ for C_{28} at 4256 nm, CPHF/aug(sp)-cc-pVDZ for C_{28} at 1064 nm. Reference ROA spectra, g_n are computed with London-orbitals. Values in round brackets refer to less relevant data due to resonance with the incident light. For notations see text.

Spectroscopy: Raman				
f_n	C_{76}		C_{28}	
	4256 nm	1064 nm	4256 nm	1064 nm
CPHF, STO-6G	0.976	0.995	0.957	0.926
HF, noCP, STO-6G	0.721	0.913	0.884	0.897
All- π , STO-6G	0.494	0.882	0.840	0.872
All- π , ZDO	0.522	0.883	0.845	0.878
First-neighbor TB	0.405	(0.802)	0.768	(0.832)
Spectroscopy: ROA				
f_n	C_{76}		C_{28}	
	4256 nm	1064 nm	4256 nm	1064 nm
CPHF, London, STO-6G	0.862	0.991	0.714	0.792
HF, noCP, length, STO-6G	0.526	0.718	0.070	0.293
All- π , length, STO-6G	0.403	0.699	-4.0×10^{-5}	0.252
All- π , ZDO	0.449	0.742	-3.9×10^{-5}	0.324
First-neighbor TB	0.376	(−0.184)	−0.249	(−0.506)

Regarding Raman scattering, we can conclude that off-resonance HF spectra (without OR) of various fullerenes are very well reproduced by all- π models. As the basis set and CP effect is relatively small, spectra computed at the π -electron level compare well with the benchmark calculation as well as with experiment. The first-neighbor TB model performs similarly to all- π methods. In terms of overlap with the reference spectrum, first-neighbor TB is systematically but just slightly worse than all- π .

B. ROA intensities of fullerenes

Turning to ROA spectra, the case of C_{76} is plotted in Figs. 2 and 3, again split into two. Fig. 2 serves to monitor the performance of effective π -model construction. Though ROA spectra are generally more difficult to reproduce than Raman, Fig. 2 reveals that most of the information is again well preserved during the gradual simplification from “HF, noCP, STO” till “all- π , ZDO.” With STO-6G property integrals, the dipole velocity approach is adopted in Fig. 2, for this compares naturally with the parametrization of the ZDO integrals. Overlap of spectral curves with that of “HF, noCP, velocity, STO-6G” are collected in the bottom part of Table I. While the overlap of all- π models is again large – above 0.90 – first-neighbor TB is considerably poorer, giving 0.66. Inspection of Fig. 2 also reveals that the first-neighbor TB spectrum is less similar to “HF, noCP, velocity, STO-6G” than those of all- π .

Another point to note is the large overestimation of ROA cross sections by the first-neighbor TB model. This leads to the RSF on the order of 2×10^{-3} , indicated in Fig. 2. The reason behind is the small HOMO-LUMO gap of the first-neighbor TB eigenvalue spectrum compared to HF (43.4 mE_h vs. 231 mE_h). To prove this, first-neighbor TB virtual-occupied orbital energy differences have been blue shifted by 188 mE_h, resulting an RSF value of 0.17 – already falling in the acceptable range – and an overlap with “HF, noCP, velocity, STO-6G” increased to 0.76.

It is also interesting to observe the rough factor of 4 overestimation of spectral cross sections by the “all- π , ZDO” approach, cf. RSF values in Fig. 2. The source of this effect is not energy denominators but the application of ZDO property integrals.

Basis set and CP effect on ROA spectra can be studied in Fig. 3 for C_{76} . Compared with Raman spectra, we see more expressed changes in ROA. This is underlined by the overlap values reported for dipole length formulations in the bottom part of Table II. Overlap with the reference spectrum drops to roughly a half by the combined effect of elimination of orbital relaxation and resorting to minimal basis set. Similarly to Raman spectra, orbital relaxation is responsible for setting the relative intensities of small/large wavenumber ranges right, as reflected by the RSF values in Fig. 3.

The starting point of effective all- π model construction, “HF, noCP, STO” already compares poorly with the reference spectrum. For this reason neither of all- π models resemble much to the reference spectrum, as indicated by the overlap values in the bottom panel of Table II. Though the first-neighbor TB model is even worse in this respect, a

TABLE III. Absolute maxima of unpolarized Raman and ROA backscattering cross sections at 1064 nm, relative to the values of methyloxirane. Notation “method1/basis1//method2/basis2” refers to the computational level of structure optimization and normal modes analysis (method1/basis1) and Raman and ROA tensors (method2/basis2).

Molecule	Method	Raman	ROA
C ₂₈	B3LYP/cc-pVTZ//HF/aug(sp)-cc-pVDZ	98	5700
C ₇₆	B3LYP/6-31G**/B3LYP/3-21+G	38	1200
Hexahelicene (C ₂₆ H ₁₆)	B3LYP/cc-pVDZ//B3LYP/aug(sp)-cc-pVDZ	32	370
4,5-dimethyl-phenanthrene (C ₁₆ H ₁₄)	B3LYP/cc-pVTZ//B3LYP/aug-cc-pVDZ	7.9	57
α -pinene (C ₁₀ H ₁₆)	B3LYP/aug-cc-pVDZ//B3LYP/aug-cc-pVDZ	1.6	2.3
Methyloxirane (C ₃ H ₄ O)	B3LYP/aug-cc-pVDZ//B3LYP/aug-cc-pVDZ	1.0	1.0

better parametrized semi-empirical π -model may be capable to improve upon it. Spectral overlaps computed for the high wavenumber range ([800,1800] cm⁻¹) give a promising indication in this line: overlap of first-neighbor TB amounts only to 0.758 with “all- π , STO,” while it is much larger with *ab initio* spectra, 0.959 and 0.900 with CPHF/STO-6G and CPHF/rDSP, respectively. The same can be deduced by inspecting Figs. 2 and 3.

As for gauge-invariance, dipole length and velocity formulations give almost identical results, cf. overlap values in Table I.

Apart from the first-neighbor TB model – suffering from resonance – results obtained at 1064 nm lead to conclusions parallel with those drawn at 4256 nm. To support this statement, merely overlap values are included here at 1064 nm wavelength.

The case of C₂₈ is markedly different from C₇₆ if regarding the ROA spectrum. While the Raman spectrum is well captured by the first-neighbor TB model (cf. the overlaps 0.956 with “HF/STO-6G,” 0.871 with “CPHF/STO-6G,” and 0.768 with “B3LYP/aug(sp)-cc-pVDZ” at 4256 nm), ROA cross sections show hardly any similarity either to “HF, noCP, STO, veloc” (cf. Fig. 4) or to the reference in Fig. 5. This is a manifest curvature effect, reflected by the fact that all- π models – which include beyond first-neighbor interaction – are capable to reproduce “HF, noCP, STO-6G” spectra, cf. the overlap values in Table I. The need to introduce second and third neighbor interactions in π -electron models to describe carbon clusters with highly curved surface has been noted earlier also.⁶⁷ In fact, a remarkable success of the effective π -model construction is reflected both by Fig. 4 and Table I for C₂₈.

Looking at Fig. 5, the basis set and CP effect is found to be the biggest for C₂₈, in agreement with the Raman studies on C₂₈ by Witek *et al.*⁸³ While “CPHF/STO-6G” still shows similarity with the reference spectrum in the majority of the characteristic peak structure, switching the CP effect off diminishes the overlap to roughly 0.3. In accordance with this, there is hardly any relation between the “HF, noCP STO” curve and the reference in Fig. 5, except for the 680–900 cm⁻¹ range. The largest difference appears in the most dominant (small wavenumber range) of the spectrum, giving the reason for the exceedingly poor ROA overlaps reported in Table II for C₂₈.

Summarizing our ROA studies with π -electron methods, the all- π model is again found successful in reproducing pre-resonance HF spectra. In contrary to Raman, accuracy of ROA intensities by the first-neighbor TB model falls significantly behind all- π . While the all- π approach proves equally suitable to compute ROA cross-sections of carbon clusters with either low or high curvature, the first-neighbor approximation is applicable only in the former case. Neither basis set extension nor OR is taken into account in the present π -electron models. Both effects are expected to be more pronounced in ROA than in Raman, making it desirable to extend the π -electron models in this direction.

C. Fullerene optical activity (OA) compared to common chiral systems

Finally, we aim to estimate whether OA in the Raman scattered light of the above fullerenes is in effect measurable. For this end, comparative calculations have been carried out at the linear-response SCF level, on inherently chiral molecules and two common chiral organic compounds, with a center of asymmetry. We merely wish to assess the relative order of magnitude of spectral intensities. For this reason the effect of basis set, or the application of theories beyond SCF is not investigated, as they are expected to account to less than 50%.^{50,65}

Maxima of Raman and ROA cross sections collected in Table III are promising. Comparing hexahelicene or 4,5-dimethyl-phenanthrene with methyloxirane or α -pinene, maximal cross-sections increase by at least an order of magnitude. The investigated fullerenes, C₂₈ and C₇₆, exhibit an even more intensive VOA: there is another order of magnitude increase with respect to hexahelicene. This phenomenon is not present in the ECD spectra, the ECD band maximum of C₇₆ is ~ 320 M⁻¹ cm⁻¹,²³ while that of hexahelicene is ~ 250 M⁻¹ cm⁻¹.¹²³ It is a task of further studies to decide whether the increased intensity of the ROA signal of C₇₆, compared with inherently chiral structures, may be attributed to the small HOMO-LUMO gap or its doubly helical structure.^{16,101}

VI. CONCLUSION AND OUTLOOK

A simple, effective π -electron model has been developed to reproduce *ab initio* quality Raman and ROA spectral

cross-sections. Compared to all-electron models, such as HF or DFT a significant reduction has been achieved in computational time with only a minor loss in accuracy.

Being derived from the molecular Fockian, the present model is applicable to π -electron systems, built of atoms of any kind. Although systems containing exclusively carbon atoms are tested in the present study, the all- π model is expected to remain valid when heteroatoms also contribute to the π -system, since the derivation of the model is not specific to carbon. The validity of all- π spectra essentially relies on the fact that polarizabilities can be described well if accounting for π -electrons only. Curvature effects and long-range interaction between sites are taken into account.

The novel π -electron model reproduces HF minimal basis set spectral intensities remarkably well. Depending on the quality of the HF minimal basis set spectrum, this property may be either beneficial or disadvantageous. The present π -model is expected to be insufficient when basis set extension and/or orbital relaxation has a strong influence on spectral line intensities. This is known to be the case with several carbon clusters.¹²¹

In cases where minimal basis HF spectra are considered defective, an empirical model – tight-binding, all- π or SCF-type – parametrized to the experiment may have the possibility to capture both basis set and orbital relaxation effects. This in an encouraging way of development, regarding the fact that Raman and ROA spectra are recovered up to 70%–90% by the present tight-binding model, using only three external parameters (h_0 , ζ in Eq. (2) and the $2p$ Slater-exponent). Approaches of the TD-DFTB family⁸¹ are also expected to perform well for carbon clusters, though TD-DFTB ROA spectra have not been reported yet.

The success of the π -electron model in describing VROA spectra may render chiroptical spectroscopy of huge clusters, like nanotubes attainable by theoretical investigations in the future. In order to achieve comparability with prospective experiments, developments are needed to deal with resonance conditions.⁶⁶

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Reference ROA computations with the Gaussian 09 program package¹²⁴ were carried out using the supercomputing facility of the National Information Infrastructure Development Institute (NIIF). Input data for calculating Raman and ROA spectra at the π -electron level are produced by the GAMESS US program package¹²⁵ (Fockian integrals in STO-6G basis), the DALTON2011¹²⁸ program suite (electric dipole and quadrupole, magnetic dipole and electronic gradient integrals in STO-6G basis), and the Gaussian 09 program (equilibrium structures and normal modes).

- ²Y. Wang, J. Xu, Y. Wang, and H. Chen, *Chem. Soc. Rev.* **42**, 2930 (2013).
- ³D. B. Amabilino, *Chem. Soc. Rev.* **38**, 669 (2009).
- ⁴J. Zhang, M. T. Albelda, Y. Liu, and J. W. Canary, *Chirality* **17**, 404 (2005).
- ⁵F. Hidalgo and C. Noguez, *Phys. Status Solidi B* **247**, 1889 (2010).
- ⁶X.-Q. Chen, X.-Y. Liao, J.-G. Yu, F.-P. Jiao, and X.-Y. Jiang, *Nano* **08**, 1330002 (2013).
- ⁷Y. Shoji, K. Tashiro, and T. Aida, *J. Am. Chem. Soc.* **128**, 10690 (2006).
- ⁸X. Peng, N. Komatsu, S. Bhattacharya, T. Shimawaki, S. Aonuma, T. Kimura, and A. Osuka, *Nat. Nanotechnol.* **2**, 361 (2007).
- ⁹X. Peng, F. Wang, A. K. Bauri, A. F. M. M. Rahman, and N. Komatsu, *Chem. Lett.* **39**, 1022 (2010).
- ¹⁰E. M. Pérez and N. Martín, *Org. Biomol. Chem.* **10**, 3577 (2012).
- ¹¹F. Wang, K. Matsuda, A. F. M. M. Rahman, T. Kimura, and N. Komatsu, *Nanoscale* **3**, 4117 (2011).
- ¹²G. Liu, F. Wang, S. Chaunchaiyakul, Y. Saito, A. K. Bauri, T. Kimura, Y. Kuwahara, and N. Komatsu, *J. Am. Chem. Soc.* **135**, 4805 (2013).
- ¹³X. Peng, N. Komatsu, T. Kimura, and A. Osuka, *J. Am. Chem. Soc.* **129**, 15947 (2007).
- ¹⁴A. Green, M. Duch, and M. Hersam, *Nano Res.* **2**, 69 (2009).
- ¹⁵S. Ghosh, S. M. Bachilo, and R. B. Weisman, *Nat. Nanotechnol.* **5**, 443 (2010).
- ¹⁶J. M. Hawkins and A. Meyer, *Science* **260**, 1918 (1993).
- ¹⁷L. R. Whetten and F. Diederich, *Acc. Chem. Res.* **25**, 119 (1992).
- ¹⁸J. M. Hawkins, M. Nambu, and A. Meyer, *J. Am. Chem. Soc.* **116**, 7642 (1994).
- ¹⁹J. Crassous, J. Rivera, N. S. Fender, L. Shu, L. Echegoyen, C. Thilgen, A. Herrmann, and F. Diederich, *Angew. Chem. Int. Ed.* **38**, 1613 (1999).
- ²⁰*Comprehensive Chiroptical Spectroscopy*, edited by K. N. N. Berova, P. L. Polavarapu, and R. W. Woody (John Wiley & Sons, 2012).
- ²¹I. Warnke and F. Furche, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2**, 150 (2012).
- ²²R. Kessinger, J. Crassous, M. Rüttimann, L. Echegoyen, and F. Diederich, *Angew. Chem. Int. Ed.* **37**, 1919 (1998).
- ²³H. Goto, N. Harada, J. Crassous, and F. Diederich, *J. Chem. Soc., Perkin Trans. 2*, 1719–1724 (1998).
- ²⁴G. Orlandi, G. Poggi, and F. Zerbetto, *Chem. Phys. Lett.* **224**, 113 (1994).
- ²⁵P. L. Polavarapu, J. He, J. Crassous, and K. Ruud, *ChemPhysChem* **6**, 2535 (2005).
- ²⁶K. Yabana and G. Bertsch, *Phys. Rev. A* **60**, 1271 (1999).
- ²⁷F. Hidalgo, A. Sánchez-Castillo, and C. Noguez, *Phys. Rev. B* **79**, 075438 (2009).
- ²⁸F. Furche and R. Ahlrichs, *J. Am. Chem. Soc.* **124**, 3804 (2002).
- ²⁹A. Jiemchoorj and P. Norman, *J. Chem. Phys.* **128**, 234304 (2008).
- ³⁰G. G. Samsonidze, A. Grüneis, R. Saito, A. Jorio, A. G. Souza Filho, G. Dresselhaus, and M. S. Dresselhaus, *Phys. Rev. B* **69**, 205402 (2004).
- ³¹A. Sánchez-Castillo, C. E. Román-Velázquez, and C. Noguez, *Phys. Rev. B* **73**, 045401 (2006).
- ³²A. Sánchez-Castillo and C. Noguez, *J. Phys. Chem. C* **114**, 9640 (2010).
- ³³T. Kjaergaard, S. Coriani, and K. Ruud, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2**, 443 (2012).
- ³⁴J. Michl, *J. Am. Chem. Soc.* **100**, 6801 (1978).
- ³⁵J. Michl, *J. Am. Chem. Soc.* **100**, 6812 (1978).
- ³⁶P. Štěpánek, M. Straka, V. Andrushchenko, and P. Bouř, *J. Chem. Phys.* **138**, 151103 (2013).
- ³⁷T. Fahleson, J. Kauczor, P. Norman, and S. Coriani, *Mol. Phys.* **111**, 1401 (2013).
- ³⁸L. A. Nafie, *Vibrational Optical Activity: Principles and Applications* (John Wiley & Sons, 2011).
- ³⁹P. L. Polavarapu, *Vibrational Spectra: Principles and Applications with Emphasis on Optical Activity* (Elsevier, 1988).
- ⁴⁰L. D. Barron and A. D. Buckingham, *Chem. Phys. Lett.* **492**, 199 (2010).
- ⁴¹P. L. Polavarapu, *Chirality* **20**, 664 (2008).
- ⁴²P. L. Polavarapu, *Chirality* **24**, 909 (2012).
- ⁴³G. Magyarfalvi, G. Tarczay, and E. Vass, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **1**, 403 (2011).
- ⁴⁴L. A. Nafie, *Annu. Rev. Phys. Chem.* **48**, 357 (1997).
- ⁴⁵M. Dresselhaus, A. Jorio, and R. Saito, *Annu. Rev. Condens. Matter Phys.* **1**, 89 (2010).
- ⁴⁶M. Dresselhaus, G. Dresselhaus, R. Saito, and A. Jorio, *Phys. Rep.* **409**, 47 (2005).
- ⁴⁷K. Ruud and A. J. Thorvaldsen, *Chirality* **21**, 54 (2009).
- ⁴⁸T. Helgaker, S. Coriani, P. Jørgensen, K. Kristensen, J. Olsen, and K. Ruud, *Chem. Rev.* **112**, 543 (2012).

¹*Chirality at the Nanoscale, Nanoparticles, Surfaces, Materials and More*, edited by D. B. Amabilino (WILEY-VCH, Weinheim, 2009).

- ⁴⁹T. Helgaker, K. Ruud, K. L. Bak, P. Jørgensen, and J. Olsen, *Faraday Discuss.* **99**, 165 (1994).
- ⁵⁰T. D. Crawford and K. Ruud, *ChemPhysChem* **12**, 3442 (2011).
- ⁵¹M. Pecul and A. Rizzo, *Mol. Phys.* **101**, 2073 (2003).
- ⁵²M. Pecul and K. Ruud, *Int. J. Quantum Chem.* **104**, 816 (2005).
- ⁵³M. Pecul, *Chirality* **21**, 98 (2009).
- ⁵⁴P. L. Polavarapu, *Int. J. Quantum Chem.* **106**, 1809 (2006).
- ⁵⁵T. D. Crawford, *Theor. Chem. Acc.* **115**, 227 (2005).
- ⁵⁶J. Autschbach, *Chirality* **21**, 116 (2009).
- ⁵⁷A. J. Thorvaldsen, B. I. N. Gao, K. Ruud, M. Fedorovsky, G. Zuber, and W. Hug, *Chirality* **24**, 1018 (2012).
- ⁵⁸O. Christiansen, P. Jørgensen, and C. Hättig, *Int. J. Quantum Chem.* **68**, 1 (1998).
- ⁵⁹A. Ruzsnyák, J. Koltai, V. Zólyomi, and J. Kürti, *Phys. Status Solidi B* **246**, 2614 (2009).
- ⁶⁰J. Kürti, V. Zólyomi, M. Kertesz, and G. Sun, *New J. Phys.* **5**, 125 (2003).
- ⁶¹A. Warshel and M. Karplus, *J. Am. Chem. Soc.* **94**, 5612 (1972).
- ⁶²T. Jovanovic and D. Koruga, *Chem. Phys. Lett.* **577**, 68 (2013).
- ⁶³P. Bour, J. Sopkova, L. Bednarova, P. Malon, and T. A. Keiderling, *J. Comput. Chem.* **18**, 646 (1997).
- ⁶⁴N. S. Bieler, M. P. Haag, C. R. Jacob, and M. Reiher, *J. Chem. Theory Comput.* **7**, 1867 (2011).
- ⁶⁵J. R. Cheeseman and M. J. Frisch, *J. Chem. Theory Comput.* **7**, 3323 (2011).
- ⁶⁶L. Jensen, J. Autschbach, M. Krykunov, and G. C. Schatz, *J. Chem. Phys.* **127**, 134101 (2007).
- ⁶⁷P. Szakács, D. Mukherjee, S. Das, and P. R. Surján, *Phys. Rev. B* **77**, 103407 (2008).
- ⁶⁸M. Bennati, K. Németh, P. R. Surján, and M. Mehring, *J. Chem. Phys.* **105**, 4441 (1996).
- ⁶⁹P. R. Surján, K. Németh, M. Bennati, A. Grupp, and M. Mehring, *Chem. Phys. Lett.* **251**, 115 (1996).
- ⁷⁰P. R. Surján, *Appl. Phys. A* **64**, 315 (1997).
- ⁷¹P. R. Surján, K. Németh, and M. Kállay, *J. Mol. Struct. THEOCHEM* **398**, 293 (1997).
- ⁷²M. Kállay, K. Németh, and P. R. Surján, *J. Phys. Chem.* **102**, 1261 (1998).
- ⁷³P. R. Surján, A. Lázár, and M. Kállay, *Phys. Rev. B* **58**, 3490 (1998).
- ⁷⁴P. R. Surján, A. Lázár, and Á. Szabados, *Phys. Rev. A* **68**, 062503 (2003).
- ⁷⁵Á. Szabados, L. P. Bíró, and P. R. Surján, *Phys. Rev. B* **73**, 195404 (2006).
- ⁷⁶V. Zólyomi, J. Koltai, Á. Ruzsnyák, J. Kürti, Á. Gali, F. Simon, H. Kuzmany, Á. Szabados, and P. R. Surján, *Phys. Rev. B* **77**, 245403 (2008).
- ⁷⁷E. Richter and K. R. Subbaswamy, *Phys. Rev. Lett.* **79**, 2738 (1997).
- ⁷⁸C. M. Goringey, D. R. Bowler, and E. Hernandez, *Rep. Prog. Phys.* **60**, 1447 (1997).
- ⁷⁹A. P. Horsfield and A. M. Bratkovsky, *J. Phys. Condens. Matter* **12**, R1 (2000).
- ⁸⁰G. Seifert and J.-O. Joswig, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2**, 456 (2012).
- ⁸¹T. Niehaus, *J. Mol. Struct. THEOCHEM* **914**, 38 (2009).
- ⁸²V. Barone, I. Carnimeo, and G. Scalmani, *J. Chem. Theory Comput.* **9**, 2052 (2013).
- ⁸³H. A. Witek, S. Irle, G. Zheng, W. A. de Jong, and K. Morokuma, *J. Chem. Phys.* **125**, 214706 (2006).
- ⁸⁴V. Bezugly, H. Eckert, J. Kunstmann, F. Kemmerich, H. Meskine, and G. Cuniberti, *Phys. Rev. B* **87**, 245409 (2013).
- ⁸⁵I. Lindgren, *J. Phys. B: At. Mol. Phys.* **7**, 2441 (1974).
- ⁸⁶P. O. Löwdin, *Int. J. Quantum Chem.* **72**, 379 (1999).
- ⁸⁷D. Sinha, S. K. Mukhopadhyay, R. Chaudhuri, and D. Mukherjee, *Chem. Phys. Lett.* **154**, 544 (1989).
- ⁸⁸J. Kürti and P. R. Surján, *J. Math. Chem.* **10**, 313 (1992).
- ⁸⁹P.-O. Löwdin, *J. Chem. Phys.* **18**, 365 (1950).
- ⁹⁰A. N. Ribeiro and C. A. Macedo, *Eur. Phys. J. B* **74**, 527 (2010).
- ⁹¹V. N. Popov, *New J. Phys.* **6**, 17 (2004).
- ⁹²A. Urban, M. Reese, M. Mrovec, C. Elsässer, and B. Meyer, *Phys. Rev. B* **84**, 155119 (2011).
- ⁹³I. Fischer-Hjalmars, *Advances in Quantum Chemistry* (Academic Press, 1966), Vol. 2, pp. 25–46.
- ⁹⁴J. Linderberg and L. Seamans, *Int. J. Quantum Chem.* **8**, 925 (1974).
- ⁹⁵S. Lubert and M. Reiher, *Chem. Phys.* **346**, 212 (2008).
- ⁹⁶K. Ruud, T. Helgaker, and P. Bour, *J. Phys. Chem. A* **106**, 7448 (2002).
- ⁹⁷L. D. Barron, *Molecular Light Scattering and Optical Activity* (Cambridge University Press, 2004).
- ⁹⁸L. Hecht and L. A. Nafie, *Mol. Phys.* **72**, 441 (1991).
- ⁹⁹W. Hug, “Raman optical activity spectroscopy,” in *Handbook of Vibrational Spectroscopy* (John Wiley and Sons Ltd., Chichester, U.K., 2002), Vol. I, pp. 745–758.
- ¹⁰⁰V. Liégeois, K. Ruud, and B. Champagne, *J. Chem. Phys.* **127**, 204105 (2007).
- ¹⁰¹R. Ertl, I. Chao, F. Diederich, and L. R. Whetten, *Nature (London)* **353**, 149 (1991).
- ¹⁰²D. E. Manolopoulos, *J. Chem. Soc., Perkin Trans.* **87**, 2861 (1991).
- ¹⁰³T. Jovanovic, D. Koruga, B. Jovancevic, V. Vajs, and G. Devic, *Fullerenes, Nanotubes, Carbon Nanostruct.* **21**, 64 (2013).
- ¹⁰⁴I. E. Kareev, A. A. Popov, I. V. Kuvychko, N. B. Shustova, S. F. Lebedkin, V. P. Bubnov, O. P. Anderson, K. Seppelt, S. H. Strauss, and O. V. Boltalina, *J. Am. Chem. Soc.* **130**, 13471 (2008).
- ¹⁰⁵T. Guo, M. D. Diener, Y. Chai, M. J. Alford, R. E. Haufler, S. M. McClure, T. Ohno, J. H. Weaver, G. E. Scuseria, and R. E. Smalley, *Science* **257**, 1661 (1992).
- ¹⁰⁶P. W. Dunk, N. K. Kaiser, M. Mulet-Gas, A. Rodrigues-Forte, J. M. Poblet, H. Shinohara, C. L. Hendrickson, A. G. Marshall, and H. W. Kroto, *J. Am. Chem. Soc.* **134**, 9380 (2012).
- ¹⁰⁷B. Skwara, R. W. Góra, R. Zalesny, P. Lipkowski, W. Bartkowiak, H. Reis, M. G. Papadopoulos, J. M. Luis, and B. Kirtman, *J. Phys. Chem. A* **115**, 10370 (2011).
- ¹⁰⁸X. Lu and Z. Chen, *Chem. Rev.* **105**, 3643 (2005).
- ¹⁰⁹Y. N. Makurin, A. A. Sofronov, A. I. Gusev, and A. L. Ivanovsky, *Chem. Phys.* **270**, 293 (2001).
- ¹¹⁰B. Paulus, *Phys. Chem. Chem. Phys.* **5**, 3364 (2003).
- ¹¹¹N. Breda, R. A. Broglia, G. Colo, G. Onida, D. Provasi, and E. Vigezzi, *Phys. Rev. B* **62**, 130 (2000).
- ¹¹²S. Portmann, J. M. Galbraith, H. F. Schaefer, G. E. Scuseria, and H. P. Luthi, *Chem. Phys. Lett.* **301**, 98 (1999).
- ¹¹³E. Malolepsza, H. A. Witek, and S. Irle, *J. Phys. Chem. A* **111**, 6649 (2007).
- ¹¹⁴C. Thilgen and F. Diederich, *Chem. Rev.* **106**, 5049 (2006).
- ¹¹⁵R. A. Kendall, T. H. Dunning, and R. J. Harrison, *J. Chem. Phys.* **96**, 6796 (1992).
- ¹¹⁶G. Zuber and W. Hug, *J. Phys. Chem. A* **108**, 2108 (2004).
- ¹¹⁷M. Reiher, V. Liégeois, and K. Ruud, *J. Phys. Chem. A* **109**, 7567 (2005).
- ¹¹⁸R. McWeeny, *Methods of Molecular Quantum Mechanics* (Academic, London, 1989).
- ¹¹⁹P. Bouř, *Chem. Phys. Lett.* **288**, 363 (1998).
- ¹²⁰P. Bouř, *J. Comput. Chem.* **22**, 426 (2001).
- ¹²¹R. Demicheli, Y. Noel, P. D'Arco, M. Rerat, C. M. Zicovich-Wilson, and R. Dovesi, *J. Phys. Chem. C* **115**, 8876 (2011).
- ¹²²Y. Achiba, K. Kikuchi, M. Muccini, G. Orlandi, G. Ruani, C. Taliani, R. Zamboni, and F. Zerbetto, *J. Phys. Chem.* **98**, 7933 (1994).
- ¹²³Y. Nakai, T. Mori, and Y. Inoue, *J. Phys. Chem. A* **116**, 7372 (2012).
- ¹²⁴M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson *et al.*, Gaussian 09, Revision C.1, Gaussian Inc., Wallingford, CT, 2009.
- ¹²⁵M. S. Gordon and M. W. Schmidt, in *Theory and Applications of Computational Chemistry: The First Forty Years* (Elsevier, Amsterdam, 2005), pp. 1167–1189.
- ¹²⁶Note, that the sign of $G'_{\alpha\beta}$ as defined here is opposite with that of Ref. 97.
- ¹²⁷Note, that one set of diffuse d-type functions makes the difference between aug-cc-pVDZ and aug(sp)-cc-pVDZ. Moreover, the rDSP basis is identical to 3-21+G in our case, since hydrogen atoms are not present.
- ¹²⁸Dalton, a molecular electronic structure program, release dalton2011 (2011), see <http://daltonprogram.org/>.