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Research Article

Combined nonmetallic electronegativity equalization and point-dipole interaction model for the frequency-dependent polarizability

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A molecular mechanics model for the frequency-dependent polarizability is presented. It is a combination of a recent model for the frequency-dependence in a charge-dipole model [Nanotechnology 19, 025203, 2008] and a nonmetallic modification of the electronegativity equalization model rephrased as atom-atom charge-transfer terms [J. Chem. Phys. 131, 044101, 2009]. An accurate model for the frequency-dependent polarizability requires a more accurate partitioning into charge and dipole contributions than the static polarizability which has resulted in several modifications of the charge-transfer model. Results are presented for hydrocarbons including among others alkanes, polyenes and aromatic systems. Although their response to an electric field are quite different in terms of the importance of charge-transfer contributions, it is demonstrated that their frequency-dependent polarizabilities can be described with the same model and the same set of atom-type parameters.

Keywords: atomic charges; electronegativity equalization; point dipole; charge transfer

1. Introduction

The frequency-dependent polarizability gives the response at the microscopic level to a time-dependent electric field and is one of the fundamental properties in optics and in the construction of electric and optical devices on the molecular scale [1, 2]. To understand both the relation between structure and property and how a molecular material can be manipulated to optimize the property of interest, an understanding at the atomistic scale becomes a central issue. Here modeling and calculations play a prominent role. The frequency-dependent polarizability is in quantum chemistry obtained through response theory [3], and it is available in most general-purpose quantum-chemical program packages at different levels of theory. Quantum chemical calculations are, however, still expensive, although the efficiency is improved continuously, and is in most cases restricted to relatively small molecules in the gas phase.

    Force-field or molecular-mechanics models are on the other hand used in molecular dynamics simulations where the forces between thousands of atoms are calculated repeatedly [4]. Although the energy expression is much simpler than in

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quantum chemical calculations, it contains the essence of intermolecular interactions in particular for the electrostatics which in most cases is the most important energy contribution. Furthermore, electronic polarization has been included in force fields, for example by using atomic polarizabilities [5–7], charge equilibration schemes [8, 9], and charges-on-spring models [10–12].

In the point-dipole interaction (PDI) model [13–17], a set of native (in the sense that the atomic polarizabilities do not sum up to the molecular polarizability) atomic polarizabilities are used as atom-type parameters, and the molecular polarizabilities are obtained from solving a set of linear equations for a set of atomic polarizabilities interacting in an external electric field. The usefulness of the model has been improved by parametrization to quantum chemical data [18], and the inclusion of short-ranged damping of the interactions [18–22]. The model has been used extensively for the study of polarization in large systems such as carbon nanotubes and fullerenes [21, 23], boron nitride tubes [24] and proteins [25], and the model has been extended for example to optical rotation [26–29], hyperpolarizabilities [30–37], Raman intensities [38, 39], and in force fields[40, 41].

The PDI model has also been combined with the capacitance model [42–46] and with the electronegativity equalization model (EEM) [47–52]. Both the capacitance model and the EEM suffer from that it is in principal a metallic model, i.e. charge is allowed to flow freely in the molecule [45, 53], and modifications have been suggested to cure this problem [53–62]. In our contribution, we suggest a model that in the limits behaves as a metallic and a completely insulating model with a smooth transition dependent only on variations in bond lengths [61].

The inclusion of the frequency-dependence in a force-field model for the polarizability is a nontrivial task. It has been included in an Unsöld-type of approximation by regarding atom-type excitation frequencies [18, 23–25, 37], or a set of oscillators with Lorentzian band-shape associated with each atom [63–65]. In a recent work, [66] we associated the time-dependence of the atomic charges and the induced dipole moments with their respective kinetic energies and with bond currents. Solving the Lagrangian equations for the system leads to a relatively simple frequency-dependent modification of of the standard charge-dipole model. This model has subsequently been used for silver clusters and the interaction between molecules and silver clusters [67, 68].

In this work we combine our recent models for the frequency-dependence with the nonmetallic charge-transfer/point-dipole interaction (CT/PDI) model [61, 66]. Since the polarizability scales incorrectly with the size of the system for nonmetalic systems in the EEM model [58, 61], charge-transfer was in previus iteration of the model only applied for system based on sp^2 hybridized carbon. [66] Thus, different models was applied for sp^2 and sp^3 carbon. However here it is demonstrated that the frequency-dependence for the charge term is described in a more realistic way for molecular systems since, in contrast to metallic systems, its excitation energy is nonvanishing for nonmetallic systems. With computations, it is shown that the frequency-dependent polarizability of alkanes, polyenes, and aromatic systems can be described with the same set of atom-type parameters.

2.   Theory

2.1.   Frequency-dependence for a combined charge-transfer and point-dipole model

In this work two previous models [61, 66] are combined to give a nonmetallic electronegativity equalization and point-dipole interaction model for the frequency-

dependent polarizability. Each atom is associated with a time-dependent charge $q_I(t)$ and a time-dependent dipole moment $\mu_{I,\alpha}(t)$, so that the Lagrangian may be written as [66]

$$L = K^q + K^\mu - V \tag{1}$$

where K^q is the kinetic energy for the atomic charges, K^μ is the kinetic energy for the atomic dipole moments and V is the potential energy. For a system of N particles, the charge is rewritten in terms of charge-transfer variables $q_{IK}(t)$ as[53, 61]

$$q_I(t) = \sum_K^N L_{IK} q_{IK}(t) \ , \tag{2}$$

where L_{IK} is a topology matrix which is one if charge transfer is allowed between atoms I and K and zero otherwise. The time-derivative of the charge-transfer, $\dot{q}_{IK}$, is viewed as a current I_{IK} going from atom K to atom I. Thus, the kinetic energy K^q for the oscillation of charges is [66]

$$K^q = \frac{1}{2} \sum_{I,K>I}^N \left(c_I^q + c_K^q \right) R_{IK}^2 \left(\dot{q}_{IK} \right)^2 \tag{3}$$

where R_{IK} is the bond distance between atoms I and K, and c_I^q is an atom-type parameter. Here atomic units are used [1]. The kinetic energy K^μ for the oscillating atomic dipole moments is [66]

$$K^\mu = \frac{1}{2} \sum_I^N c_I^\mu \left(\dot{\mu}_I \right)^2 \tag{4}$$

where $\dot{\mu}_I$ is the time-derivative of μ_I and c_I^μ is an additional atom-type parameter.

With the extension that the atomic charges, atomic dipole moments and the external electric field can be time-dependent, the potential energy V in Eq. (1) is [61, 66]

$$V = V^{qq} + V^{q\mu} + V^{\mu\mu} \tag{5}$$

where V^{qq} is the charge-charge interaction, $V^{q\mu}$ is the charge-dipole interaction, and $V^{\mu\mu}$ is the dipole-dipole interaction energy, respectively. The starting point for V^{qq} is the standard electronegativity equalization model (EEM) [69, 70]

$$V^{qq} = \sum_I^N \left(\left(\chi_I^* + \varphi_I^{\text{ext}} \right) q_I + \frac{1}{2} \eta_I^* q_I^2 + \frac{1}{2} \sum_{J \neq I}^N q_I T_{IJ}^{(0)} q_J \right) \tag{6}$$

where χ_I^* is the atomic electronegativity, η_I^* is the atomic chemical hardness, φ_I^{ext} is the external electrostatic potential at atom I, $q_I T_{IJ}^{(0)} q_J$ is the Coulomb interaction,

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[1] In atomic units, $|e| = 1$, $\hbar = 1$, $m_e = 1$, $1/4\pi\epsilon_0 = 1$. The energy unit 1 hartree is given by $E_h = m_e e^4/(4\pi\epsilon_0\hbar)^2 \approx 4.36 \times 10^{-18}$ J, distance unit is 1 bohr given by $a_0 = 4\pi\epsilon_0/(m_e e^2) \approx 5.29 \times 10^{-11}$ m, frequency is given by $E_h/\hbar \approx 4.13 \times 10^{16}$ Hz and polarization is given by $a_0^3 \approx 0.15 \text{Å}^3$

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and in classical electrostatics $T_{IJ}^{(0)} = 1/R_{IJ}$ where R_{IJ} is the distance between atoms I and J. Furthermore, let $T_{II}^{(0)} = \eta_I^*$ and insert Eq. (2) into Eq. (6) to obtain[61]

$$V^{qq} = \sum_{I,J>I}^{N} \left(\chi_{IJ} + \varphi_{IJ}^{\text{ext}} \right) q_{IJ} + \frac{1}{2} \sum_{I,K>I,J,M>J}^{N} q_{IK} T_{IK,JM}^{(0)} q_{JM} \qquad (7)$$

where $\chi_{IJ} = \chi_I^* - \chi_J^*$, $\varphi_{IJ}^{\text{ext}} = \varphi_I^{\text{ext}} - \varphi_J^{\text{ext}}$ and $T_{IK,JM}^{(0)} = T_{IJ}^{(0)} - T_{KJ}^{(0)} - T_{IM}^{(0)} + T_{KM}^{(0)}$. The topology matrix elements L_{IK} in Eq. (2) are omitted here, but it is implied that only atom-pairs with $L_{IK} = 1$ are included in the summations. So far this is nothing but a reformulation of the EEM not changing the physics of the model. However, several modifications of the tensor $T_{IK,JM}^{(0)}$ are applied. Instead of point-charges for each atom, a Gaussian distribution is applied [21, 22]

$$\rho_I \left(r_i \right) = q_I \left(\frac{\Phi_I^*}{\pi} \right)^{\frac{3}{2}} e^{-\Phi_I^* r_i^2} \qquad (8)$$

where the width of the Gaussian, Φ_I^*, is an additional atom-type parameter of the model. Note that Eq. (8) is normalized so that the atomic charge is q_I. The interaction between two Gaussian charge distributions is approximated as[21]

$$V = \frac{q_I q_J}{\widetilde{R}_{IJ}} \qquad (9)$$

where $\widetilde{R}_{IJ}$ is a scaled distance given by[71]

$$\widetilde{R}_{IJ} = \sqrt{R_{IJ}^2 + \frac{\pi}{4a_{IJ}}} \qquad (10)$$

where

$$a_{IJ} = \frac{\Phi_I^* \Phi_J^*}{\Phi_I^* + \Phi_J^*} . \qquad (11)$$

Eq. (9) has the correct limiting behavior at $R_{IJ} \to 0$ and at $R_{IJ} \to \infty$. In earlier work the distances R_{IJ} was replaced by the scaled distances $\widetilde{R}_{IJ}$ also when considering the charge-dipole interaction $T_{IJ,\alpha}^{(1)}$ and the dipole-dipole interaction $T_{IJ,\alpha\beta}^{(2)}$. However, this damping model resulted in too small damping for the dipole-dipole interaction, and unphysically small Φ_I^*-parameters were needed to avoid a polarization catastrophe. Therefore $T_{IJ,\alpha}^{(1)}$ is here written as

$$T_{IJ,\alpha}^{(1)} = \frac{\partial T_{IJ}^{(0)}}{\partial R_{IJ,\alpha}} = -\frac{R_{IJ,\alpha}}{\widetilde{R}_{IJ}^3} \qquad (12)$$

and

$$T_{IJ,\alpha\beta}^{(2)} = \frac{\partial T_{IJ,\alpha}^{(1)}}{\partial R_{IJ,\beta}} = \frac{3R_{IJ,\alpha}R_{IJ,\beta}}{\widetilde{R}_{IJ}^5} - \frac{\delta_{\alpha\beta}}{\widetilde{R}_{IJ}^3} , \qquad (13)$$

where Greek subscripts, α, β, ..., denote one of the Cartesian coordinates, x, y or z, and the Einstein summation convention is used for repeated Greek subscripts. Still $T_{IJ,\alpha}^{(1)} \to 0$ when $R_{IJ} \to 0$, but the $T_{IJ,\alpha\beta}^{(2)}$ tensor in Eq. (13) is not traceless. Therefore care should be taken before expanding the model to quadrupole moments, where a traceless formalism is normally adoped.[72]

For the static polarizability to scale correctly with the size of the system both for metallic and nonmetallic systems, an energy for transporting charge through atoms have been added of the form [61]

$$\epsilon \eta_I^* q_{KI} q_{IM} \; ; \; K \neq M \tag{14}$$

where ϵ is a dimensionless quantity between 0 and 1. This term describes an energy cost for transporting charge from atom M through atom I to atom K. If $\epsilon = 0$, the system behaves metallically and if $\epsilon = 1$ the system behaves as an insulating system. The charge transport energy in Eq. (14) has been incorporated by modifying the chemical hardness terms in the potential energy V^{qq} as [61]

$$\frac{1}{2}\eta_I^* q_{KI} q_{IM} \to \frac{1}{2}\eta_I^* S_{IK}^{-\frac{1}{2}} S_{IM}^{-\frac{1}{2}} g_{I,KM} q_{KI} q_{IM} \tag{15}$$

where $g_{I,KM}$ is a function of the two distances R_{IK} and R_{IM}, and $g_{I,KM} = 1$ if $K = M$. For a two-atom system ($K = M$) this becomes $\eta_I \to \eta_I S_{IK}^{-1}$, where S_{IK} is the overlap between atoms I and K. Thus, $q_{IK} \propto S_{IK}$ and q_{IK} approaches zero when $R_{IK} \to \infty$. Furthermore if $S_{IK} = S_{IM}$, the following relation holds

$$\epsilon = 1 - g_{I,KM} \; . \tag{16}$$

Thus, $g_{I,KM}$ describes the resistance against charge-flow within the molecule. For some molecules included here, the previously used functional form of $g_{I,KM}$[61] gave a too drastic change in $g_{I,KM}$ with the bond length. For example, if $R_{IK} + R_{IM}$ is increased from 2.8 Å to 2.9 Å, ϵ increased from 0.05 to 0.4. This lead to problems describing molecules as stilbene where key junctions in the system with atypical bond lengths had a too high ϵ and thus a too low charge transfer. For this reason, $g_{I,KM}$ is here rewritten as

$$g_{I,KM} = (g_{0,I}^*)^2 g_{0,K}^* g_{0,J}^* H_{I,KM}(\Delta_{I,KM}) + (g_{1,I}^*)^2 g_{1,K}^* g_{1,J}^* (1 - H_{I,KM}(\Delta_{I,KM})) \tag{17}$$

where $g_{0,I}^*$ and $g_{1,I}^*$ are atom-type parameters. To ensure that $g_{I,KM}$ is between 0 and 1, these parameters must also be between 0 and 1. Furthermore, $H_{I,KM}$ is a smooth step function (dependent on atoms I, K and M) given as

$$H_{I,KM}(\Delta) = \frac{1}{2}\left(1 + \tanh(C_{I,KM}\Delta_{I,KM})\right) \tag{18}$$

where $C_{I,KM} = (C_I^*)^2 C_K^* C_M^*$ and C_I^* is an atom-type parameter. Furthermore,

$$\Delta_{I,KM} = R_{IK} + R_{IM} - 2R_I^* - R_K^* - R_M^* \tag{19}$$

where also R_I^* is an atom-type parameter. For carbon, $g_{0,I}^*$ describes ϵ for sp^3-carbon and $g_{1,I}^*$ describes ϵ for sp^2-carbon, respectively, and a smooth step function is added for the transition between the two cases. The R_I^* parameter govern where the transition between the two cases occurs, while C_I^* governs how steep the transition is.

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For double bonds and a system involving only carbon, ϵ is described by $\epsilon = 1 - (g_{1,C}^*)^4$. Since $0 \leq g_{1,I}^* \leq 1$ for all atoms, if replacing one carbon with another atom (not the central carbon),

$$1 - (g_{1,C}^*)^3 \leq \epsilon \leq 1 . \tag{20}$$

Thus, there exist a lower limit for the modified ϵ given by the parameters for pure carbon, but the connection could be made as nonmetallic as desired by setting $g_{1,K}^* = 0$. For simplicity, and to avoid a large amount of parameters for hydrogen that does not play any significant role, in this work $g_{I,KM}$ is set equal to $(g_{0,C}^*)^3 g_{0,H}^*$ (where $g_{0,C}^*$ is the parameter for carbon) when at least one of the atoms is a hydrogen atom. Thus Eq. (17) is used here only for carbon.

With the R_I^* parameters, S_{IK} is given as

$$S_{IK} = e^{-a_{IK}(R_{IK} - R_I^* - R_K^*)^2} \tag{21}$$

where a_{IK} is given by Eq. (11). $S_{IK} \approx 1$ when atoms I and K are within typical bonding distances, but for large R_{IK} it is an exponentially decaying function given by the overlap of two Gaussian distributions. Simplified, S_{IK} describes charge transfer between molecules, while $g_{I,KM}$ describes charge transfer within the molecule.

In earlier work, the out-of-plane polarizability for planar molecules tends to be too low, which has been compensated by low values of the Φ_I^*-parameters[61], or different atomic polarizabilities for the out-of-plane and in-plane components of the carbon atoms[52, 66]. One may modify the atomic polarizability parameter so that it depends on the chemical surroundings, for example as, [73]

$$\alpha_{I,\alpha\beta} = \alpha_I \left(\delta_{\alpha\beta} + x_I^* (1 - G_{I,\alpha\beta}) \right) \tag{22}$$

where α_I is an isotropic atomic polarizability and x_I^* is an additional atom-type parameter and $G_{I,\alpha\beta}$ is

$$G_{I,\alpha\beta} = \frac{3}{Tr(\Gamma_I)} \Gamma_{I,\alpha\beta} \tag{23}$$

where $\Gamma_{I,\alpha\beta}$ in this work is given as

$$\Gamma_{I,\alpha\beta} = \sum_{J \neq I}^{N} \alpha_J S_{IJ} \frac{R_{IJ,\alpha} R_{IJ,\beta}}{R_{IJ}^2} . \tag{24}$$

In Eq (24), $R_{IJ,\alpha} R_{IJ,\beta} / R_{IJ}^2$ gives the correct rotational properties of $\alpha_{I,\alpha\beta}$, S_{IJ} is an exponentially decaying function given by Eq. (21) to include a distance dependence, and the atom-type polarizability α_J serves as a measure of the size of the neighboring atom. The sum is restricted to atom-pairs where $L_{IJ} = 1$. For planar molecules, $R_{IJ,\alpha}$ is zero for $\alpha = z$. In this case, $\Gamma_{I,zz} = 0$, and Eq. (22) simplifies to

$$\alpha_{I,zz} = \alpha_I \left(1 + x_I^* \right) \tag{25}$$

for $\alpha = \beta = z$. Since the trace of $G_{I,\alpha\beta}$ is normalized to 3, the polarizability of the other components decreases. Thus the out-of-plane component of the polarizability

increases without increasing the in-plane components, which is the main purpose of introducing the anisotropic modification to the atomic polarizability. For the linear case, $G_{I,xx} = 3$, $G_{I,yy} = G_{I,zz} = 0$, and the xx-component of the atomic polarizability becomes

$$\alpha_{I,xx} = \alpha_I \left(1 - 2x_I^*\right) \tag{26}$$

To avoid the possibility of negative atomic polarizabilities, it is therefore required that $x_I^* < 0.5$. In this work, the PDI model is extended with this modification.

An exchange term according to our earlier work[61] is not included here. It has a relatively small impact on the molecular polarizability and a refined model for the exchange energy is developed elsewhere with argon as a model system[74].

Rewritten in terms of charge-transfer variables, the charge-dipole interaction energy, $V^{q\mu}$ is given by [61]

$$V^{q\mu} = \sum_{I,K,J}^{N} q_{IK} T_{IJ,\alpha}^{(1)} \mu_{J,\alpha} = \sum_{I,K>I,J}^{N} q_{IK} \left(T_{IJ,\alpha}^{(1)} - T_{KJ,\alpha}^{(1)}\right) \mu_{J,\alpha} \ . \tag{27}$$

The dipole-dipole interaction energy $V^{\mu\mu}$ is given by the point-dipole interaction (PDI) model [42]

$$V^{\mu\mu} = \frac{1}{2} \sum_{J}^{N} \mu_{J,\alpha} \left(\alpha_{J,\beta\alpha}\right)^{-1} \mu_{J,\beta} - \frac{1}{2} \sum_{J}^{N} \sum_{K \neq J}^{N} \mu_{J,\alpha} T_{JK,\alpha\beta}^{(2)} \mu_{K,\beta} - \sum_{J}^{N} E_{J,\alpha}^{\text{ext}} \mu_{J,\alpha} \tag{28}$$

where $\alpha_{J,\alpha\beta}$ is given by Eq. (22), $T_{IJ,\alpha\beta}^{(2)}$ is given in Eq. (13) and $E_{J,\alpha}^{\text{ext}}$ is an external electric field at atom J.

The Lagrangian equations to be solved are written as [66]

$$\frac{\partial}{\partial t} \left(\frac{\delta L}{\delta \dot{q}_{IK}}\right) - \frac{\delta L}{\delta q_{IK}} = 0 \quad ; \quad \frac{\partial}{\partial t} \left(\frac{\delta L}{\delta \dot{\mu}_{I,\alpha}}\right) - \frac{\delta L}{\delta \mu_{I,\alpha}} = 0 \tag{29}$$

If an external electric field and electrostatic potential at atom J with frequency ω is assumed,

$$E_{J,\alpha}^{\text{ext}} = E_{J,\alpha}^{(\omega)} \ Re \ e^{i\omega t} \quad ; \quad \varphi_{IJ}^{\text{ext}} = \varphi_{IJ}^{(\omega)} \ Re \ e^{i\omega t}, \tag{30}$$

and the charge transfer and atomic dipole moments also oscillate with the same frequency

$$q_{IK} = Re \ \left(q_{IK}^{(0)} + q_{IK}^{(\omega)} e^{i\omega t}\right) \quad ; \quad \mu_{I,\alpha} = Re \ \left(\mu_{I,\alpha}^{(0)} + \mu_{I,\alpha}^{(\omega)} e^{i\omega t}\right) \ . \tag{31}$$

where $q_{IK}^{(0)}$ and $\mu_{I,\alpha}^{(0)}$ are the static charge transfers and the static atomic dipole moments respectively. With these definitions, [66]

$$\frac{\partial}{\partial t} \left(\frac{\partial L}{\partial \dot{q}_{SP}}\right) = - \left(c_S^q + c_P^q\right) R_{SP}^2 \ \omega^2 \ Re \left(q_{SP}^{(\omega)} e^{i\omega t}\right) \ . \tag{32}$$

and for the dipole moments, [66]

$$\frac{\partial}{\partial t}\left(\frac{\partial L}{\partial \dot{\mu}_{I,\alpha}}\right) = \frac{\partial}{\partial t}\left(\frac{\partial K^\mu}{\partial \dot{\mu}_{I,\alpha}}\right) = -c_I^\mu \omega^2 Re\left(\mu_{I,\alpha}^{(\omega)}\, e^{i\omega t}\right) \tag{33}$$

The remaining terms of the Lagrangian in Eqs. (29) yield[61]

$$\frac{\partial L}{\partial q_{IK}} = -\frac{\partial V}{\partial q_{IK}} = -\sum_{J<M}^N T_{IK,JM}^{(0)} q_{JM} - \sum_J^N T_{IK,J,\alpha}^{(1)} \mu_{J,\alpha} - \left(\chi_{IK} + \varphi_{IK}^{\text{ext}}\right) \tag{34}$$

$$\frac{\partial L}{\partial \mu_{I,\alpha}} = -\frac{\partial V}{\partial \mu_{I,\alpha}} = -\sum_{J<M}^N T_{I,JM,\alpha}^{(1)} q_{JM} + \sum_J^N T_{IJ,\alpha\beta}^{(2)}\, \mu_{J,\beta} + E_{I,\alpha}^{\text{ext}} \tag{35}$$

where $T_{IK,J,\alpha}^{(1)} = T_{IJ,\alpha}^{(1)} - T_{KJ,\alpha}^{(1)}$, $T_{I,JM,\alpha}^{(1)} = -\left(T_{IJ,\alpha}^{(1)} - T_{IM,\alpha}^{(1)}\right)$ and $T_{II,\alpha\beta}^{(2)} = -(\alpha_{I,\beta\alpha})^{-1}$. Using Eqs. (31), the final Lagrangian equation can be divided into a field-independent part,

$$\sum_{J>M}^N T_{IK,JM}^{(0)} q_{JM}^{(0)} + \sum_J^N T_{IK,J,\alpha}^{(1)} \mu_{J,\alpha}^{(0)} = -\chi_{IK} \tag{36}$$

$$\sum_{J>M}^N T_{I,JM,\alpha}^{(1)} q_{JM}^{(0)} - \sum_J^N T_{IJ,\alpha\beta}^{(2)} \mu_{J,\beta}^{(0)} = 0 \tag{37}$$

and a field-dependent part

$$\sum_{J>M}^N T_{IK,JM}^{(0)} q_{JM}^{(\omega)} + \sum_J^N T_{IK,J,\alpha}^{(1)}\, \mu_{J,\alpha}^{(\omega)} - \omega^2 \left(c_I^q + c_K^q\right)\, R_{IK}^2 q_{IK}^{(\omega)} = -\varphi_{IK}^{(\omega)} \tag{38}$$

$$\sum_{J>M}^N T_{I,JM,\alpha}^{(1)} q_{JM}^{(\omega)} - \sum_J^N T_{IJ,\alpha\beta}^{(2)} \mu_{J,\beta}^{(\omega)} - \omega^2\, c_I^\mu \mu_{I,\alpha}^{(\omega)} = E_{I,\alpha}^{(\omega)} \tag{39}$$

It is noted that the terms $\omega^2 \left(c_I^q + c_K^q\right)\, R_{IK}^2 q_{IK}^{(\omega)}$ and $\omega^2\, c_I^\mu \mu_{I,\alpha}^{(\omega)}$ can be viewed as a frequency-dependent modification of a static model ($\omega = 0$). Dissipation may be introduced by replacing ω^2 with $\omega^2 - i\frac{1}{2}\left(\gamma_I^q + \gamma_K^q\right)\omega$ in Eq. (38) and with $\omega^2 - i\gamma_I^\mu \omega$ in Eq. (39), where γ_I^q and γ_I^μ are additional atom-type parameters. [66]

In matrix form the field-dependent equations, including non-zero dissipation, are given as

$$\left(\begin{pmatrix} T_{SP,JM}^{(0)} & T_{SP,K,\beta}^{(1)} \\ T_{I,JM,\alpha}^{(1)} & -T_{IK,\alpha\beta}^{(2)} \end{pmatrix} - \omega^2 \begin{pmatrix} \tau_{JM}\, \delta_{SJ}\delta_{PM} & 0 \\ 0 & c_K^\mu \left(1 - i\gamma_K^\mu/\omega\right) \delta_{IK}\delta_{\alpha\beta} \end{pmatrix}\right) \begin{pmatrix} q_{JM}^{(\omega)} \\ \mu_{K,\beta}^{(\omega)} \end{pmatrix} = \begin{pmatrix} -\varphi_{SP}^{(\omega)} \\ E_{I,\alpha}^{(\omega)} \end{pmatrix} \tag{40}$$

where $\tau_{JM} = \left(c_J^q + c_M^q\right) R_{JM}^2 \left(1 - i\left(\gamma_J^q + \gamma_M^q\right)/(2\omega)\right)$ and thus the modification to the static model is obtained by subtracting a diagonal matrix. If the wavelength λ is much larger than the size of the system/molecule, the external electric field may be regarded as homogeneous. In this case, $E_{I,\alpha}^{(\omega)} = E_\alpha^{(\omega)}$ and $\phi_{SP}^{(\omega)} = -\left(R_{S,\alpha} - R_{P,\alpha}\right) E_\alpha^{(\omega)}$. For a homogeneous electric field, $\partial q_{JM}^{(\omega)}/\partial E_\gamma^{(\omega)}$ and

$\partial \mu_{J,\alpha}^{(\omega)}/\partial E_\gamma^{(\omega)}$ are obtained by solving the following set of linear equations,

$$
\left(\begin{pmatrix} T_{SP,JM}^{(0)} & T_{SP,K,\beta}^{(1)} \\ T_{I,JM,\alpha}^{(1)} & -T_{IK,\alpha\beta}^{(2)} \end{pmatrix} - \omega^2 \begin{pmatrix} \tau_{JM} \ \delta_{SJ}\delta_{PM} & 0 \\ 0 & c_K^\mu \left(1 - i\gamma_K^\mu/\omega\right)\delta_{IK}\delta_{\alpha\beta} \end{pmatrix} \right) \begin{pmatrix} \partial q_{JM}^{(\omega)}/\partial E_\gamma^{(\omega)} \\ \partial \mu_{K,\beta}^{(\omega)}/\partial E_\gamma^{(\omega)} \end{pmatrix} = \begin{pmatrix} R_{SP,\gamma} \\ \delta_{\alpha\gamma} \end{pmatrix}
$$
(41)

The induced molecular dipole moment $\mu_\alpha^{\rm ind}$ oscillates with frequency ω and thus $\mu_\alpha^{(\omega)}$ may be defined as $\mu_\alpha^{\rm ind} = Re\left(\mu_\alpha^{(\omega)} e^{i\omega t}\right)$. With this definition, the molecular polarizability $\alpha_{\alpha\beta}^{\rm mol}(\omega)$ is given as

$$
\alpha_{\alpha\beta}^{\rm mol}(\omega) = \frac{\partial \mu_\alpha^{\rm ind}}{\partial E_\beta^{\rm ext}} = \frac{\partial \mu_\alpha^{(\omega)}}{\partial E_\beta^{(\omega)}} = \sum_{I,M}^N R_{I,\alpha}\frac{\partial q_{IM}^{(\omega)}}{\partial E_\beta^{(\omega)}} + \sum_I^N \frac{\partial \mu_{I,\alpha}^{(\omega)}}{\partial E_\beta^{(\omega)}}
$$

$$
= \sum_{I,M>I}^N R_{IM,\alpha}\frac{\partial q_{IM}^{(\omega)}}{\partial E_\beta^{(\omega)}} + \sum_I^N \frac{\partial \mu_{I,\alpha}^{(\omega)}}{\partial E_\beta^{(\omega)}}
$$
(42)

Solving Eq. (41) gives $\partial q_{IM}^{(\omega)}/\partial E_\beta^{(\omega)}$ and $\partial \mu_{I,\alpha}^{(\omega)}/\partial E_\beta^{(\omega)}$ and thus also the frequency-dependent polarizability $\alpha_{\alpha\beta}^{\rm mol}(\omega)$. If including the dissipation terms $i\gamma_I^q$ and $i\gamma_I^\mu$, the polarizability $\alpha_{\alpha\beta}^{(\omega)}$ becomes complex. In this case, the molecular induced dipole moment $\mu_\alpha^{\rm ind}$ is given by

$$
\mu_\alpha^{\rm ind} = E_\beta^{(\omega)} Re \ \alpha_{\beta\alpha}^{\rm mol} e^{i\omega t}.
$$
(43)

and the amplitude of the induced dipole moment is given by the amplitude of the polarizability.

2.2.   *The linear chain as a model system*

The static model has previously been analyzed analytically for a linear chain composed of identical atoms [61], which is here extended to the frequency-dependent polarizability. Let N be the number of atoms in the chain, η^* be the atomic chemical hardness, α be the atomic polarizability, let the distance between neighboring atoms be R_0, let $\epsilon = 1 - g(R_0, R_0)$ be a parameter of the model, c^q and c^μ be the parameters associated with K^q and K^μ, respectively. Dissipation is ignored for the moment. Furthermore, let the x-axis be along the linear chain, and $L_{IJ} = 1$ only if $J = I \pm 1$, such that only charge transfer between nearest neighbors is taken into account. In the case $N\epsilon \gg 1$, an equation of the form [61]

$$
N \begin{pmatrix} 2\epsilon\eta^* & 0 \\ 0 & \frac{1-4\zeta(3)R_0^{-3}\alpha}{\alpha} \end{pmatrix} \begin{pmatrix} < \partial q_{I,I+1}/\partial E_x > \\ < \partial \mu_{J,x}/\partial E_x > \end{pmatrix} = N \begin{pmatrix} R_0 \\ 1 \end{pmatrix}
$$
(44)

is obtained, where $\zeta(x)$ is the Riemann zeta function ($\zeta(3) \approx 1.202$, is also called Apéry's constant), $\langle \partial q_{I,I+1}/\partial E_x \rangle$ and $\langle \partial \mu_I/\partial E_x \rangle$ are the averages of $\partial q_{I,I+1}/\partial E_x$ and $\partial \mu_I/\partial E_x$, respectively. Here it is assumed that the electric field is uniform so that

$$
-\frac{d\varphi_{I,I+1}}{dE_x} = R_0 .
$$
(45)

For details about the approximations used to obtain Eq. (44), see the appendix in Ref. [61].

In the case of $\omega \neq 0$, Eq. (45) is a good approximation given that the wavelength, λ, is much larger than the length of the chain NR_0. The number of atoms N must be large so that $N\epsilon \gg 1$, but at the same time small so that $\lambda \gg NR_0$. Furthermore, Eq. (44) was obtained by setting $\omega = 0$ and taking the sum of all equations in Eq. (41). To obtain a similar equation for $\omega \neq 0$, all that is needed is adding the sum of all frequency-dependent terms to the static part. Since the frequency-dependence appears in the diagonal part of the matrix, the result becomes

$$N \begin{pmatrix} 2(\epsilon\eta^* - \omega^2 R_0^2 c_I^q) & 0 \\ 0 & \frac{1-4\zeta(3)R_0^{-3}\alpha}{\alpha} - \omega^2 c_J^\mu \end{pmatrix} \begin{pmatrix} \langle \partial q_{I,I+1}/\partial E_x \rangle \\ \langle \partial \mu_{J,x}/\partial E_x \rangle \end{pmatrix} = N \begin{pmatrix} R_0 \\ 1 \end{pmatrix} . \quad (46)$$

The frequency-dependent polarizability along the linear chain becomes

$$\begin{aligned} \alpha_{xx}^{\text{mol}}(\omega) &= N\left(R_0 \langle \partial q_{I,I+1}/\partial E_x \rangle + \langle \partial \mu_{J,x}/\partial E_x \rangle\right) \\ &= N\left(\frac{R_0^2}{2(\epsilon\eta^* - c^q\omega^2 R_0^2)} + \frac{\alpha}{1 - 4\zeta(3)R_0^{-3}\alpha - \omega^2\alpha c^\mu}\right) \end{aligned} \quad (47)$$

which has two poles, ω_1 and ω_2, one associated with charge-transfer at

$$\omega_1 = \sqrt{\frac{\epsilon\eta^*}{c^q R_0^2}} \quad (48)$$

and another associated with atomic point-dipoles at

$$\omega_2 = \sqrt{\frac{1}{c^\mu}\left(\frac{1}{\alpha} - \frac{4\zeta(3)}{R_0^3}\right)} . \quad (49)$$

The lowest of these two frequencies, ω_1 and ω_2, can be viewed as the first excitation energy. From Eq. (48), it is seen that the excitation energy decreases when ϵ becomes smaller, which is consistent with the interpretation that $\epsilon = 0$ corresponds to a metallic system. Furthermore, the poles of the frequency-dependent polarizability are dependent on a correct division of the polarizability into a charge-transfer part, $\langle \partial q_{I,I+1}/\partial E_\alpha \rangle$, and a point-dipole part, $\langle \partial \mu_I/\partial E_\alpha \rangle$.

Including non-zero dissipation, and using ω_1 and ω_2 given by Eqs. (48) and (49), the polarizability of the linear chain is

$$\alpha_{xx}^{\text{mol}}(\omega) = N\left(\frac{1}{2c^q(\omega_1^2 - \omega^2 + i\gamma^q\omega)} + \frac{1}{c^\mu(\omega_2^2 - \omega^2 + i\gamma^\mu\omega)}\right) \quad (50)$$

where it is understood that the amplitude of the polarisability α_{xx}, is real and given by the absolute value of this complex quantity. With dissipation, the polarizability is finite both at $\omega = \omega_1$ and $\omega = \omega_2$.

3. Calculations and parametrization

It is advantageous to use quantum chemical calculations for the parametrization of a molecular mechanics model since a consistent data set is obtained.[18] In principle, density functional theory (DFT) gives an improved description of molecular

properties over the Hartree-Fock approximation, but for polarizabilities of large systems many functionals present problems and several improvements have been suggested. [75–83] We therefore use current-DFT[84] with the AUG/ATZP[85, 86] basis set, which gives improved results for the polarizability for large systems. [87] If the frequency is too close to an excitation energy (pole in the polarization), DFT calculations are unreliable and such data points were removed from the data set. For the geometry optimization, the BLYP[88, 89] functional and the TZP[85] basis set were employed. It is noted that linear symmetry was used in the geometry optimization of the polyynes structures. The ADF software [90–92] was used for all DFT calculations.

To test the model, a parametrization has been carried out for a handful of molecules (see Table 1) and tested for all molecules in Table 2. Even though only the isotropic polarizabilities are presented in some cases, the full polarizability tensor was included in the parametrization. Furthermore, the error for each molecule and each component of the polarizability was divided by the isotropic polarization of the molecule, in an effort to keep all molecules in the training set equally important. For the frequency-dependent terms, the difference between the static and the polarization at the given frequency was considered in the parametrization.

In the notation of graphenes, we refer to one type of chains of aromatic rings as armchair structures, whereas the zigzag structures correspond to the acenes. The notation $g(N, M)$ refers to an aromatic system with N rings in the zigzag direction and M rings in the armchair direction (terminated with hydrogen at the ends, ie is finite single-sheet structures). The same set of parameters, given in Table 3, is used for all molecules. Since dissipation was not included in the DFT calculations, it is also excluded in the parametrization.

Table 1. Molecules in training set

Group	Molecules
Alkanes	ethane, propane, dodecane
Polyenes	ethene, $C_{18}H_{22}$
Acenes	benzene, octacene
Armchair	benzo[c]naphto[2,1-m]picene
Poly(p-phenylene vinylene)	1,4-dicinnamyl-benzene
Other systems	g(4,3)

Table 2. Molecules

Group	Molecules
Alkanes	ethane, propane, octane and dodecane
Polyenes	ethene, hexatriene, $C_{14}H_{16}$, $C_{18}H_{20}$ $C_{22}H_{24}$ and $C_{26}H_{28}$
Acenes	benzene, anthracene, pentacene, and octacene
Armchair	phenanthrene, chrysene, benzo[c]picene, benzo[c]naphto[2,1-m]picene
Poly(p-phenylene vinylene)	styrene, stilbene,1,4-dicinnamyl-benzene
Polyynes	ethyne, C_8H_2, $C_{16}H_2$, $C_{20}H_2$

Table 3. Atom-type parameters (au)

	α_I	x_I^*	Φ_I^*	$g_{0,I}^*$	$g_{1,I}^*$	C_I^*	R_I^*	η_I^*	c_I^q	c_I^μ
H	1.65	0.32	1.02	1.00	-	-	-	0.23	0.03	0.63
C	8.35	0.38	0.43	0.77	0.9957	4.13	1.41	1.03	0.61	0.59

The Φ_I^*-parameter used here is equivalent to a Gaussian distribution with a standard-deviation of about 1.1 Bohr, which is more reasonable than a Gaussian

with a standard-deviation of 2.6 Bohr obtained in earlier work. [61] Reasonable sizes for the Φ_I^* parameters are important when for example studying the inter-action between two molecules, where the function S_{IJ} is more important. The polarizability of carbon is within the expected range. It is noted that the model is sensitive to how close $g_{1,I}^*$ is to one, and it is therefore included with 4 digits here. To summarize, it is satisfying to have only one set of carbon parameters describing both sp^3 and sp^2-carbon atoms.

4.   Results

The polarizability of the alkane molecules, see Figure 1, is almost independent of the frequency. The out-of-plane component of the polyenes does not increase sig-nificantly with frequency, see Figure 2(a), while the in-plane component, defined as $\alpha_{in} = (\alpha_{xx} + \alpha_{yy})/2$, has a much stronger dependence on the frequency, espe-cially for the larger molecules (see Figure 2(b)). Thus for systems with a low ϵ as the polyenes, the critical frequency associated with charge transfer, examplified in Eq. (48), gives the dominating contribution to the frequency dependence of the polarizability. The isotropic polarizability of the alkanes and the out-of-plane com-ponent for the polyenes increase both about 4% from $\omega = 0$ to $\omega = 0.1$ hartree. Thus the charge transfer contribution for alkanes behave differently from the charge transfer terms of the polyenes.
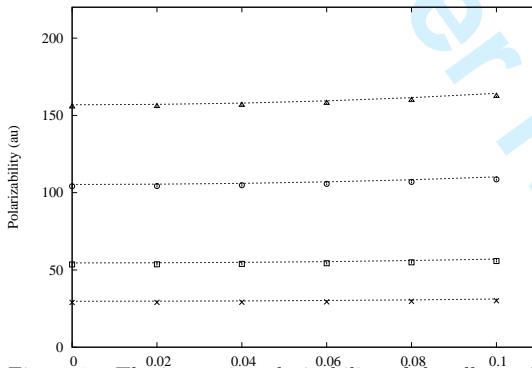
Figure 1.   The isotropic polarizability of the alkanes listed in Table 2 in order of increasing molecular size (from bottom to top), as a function of the frequency. The points represent c-DFT data while the lines represent the model.
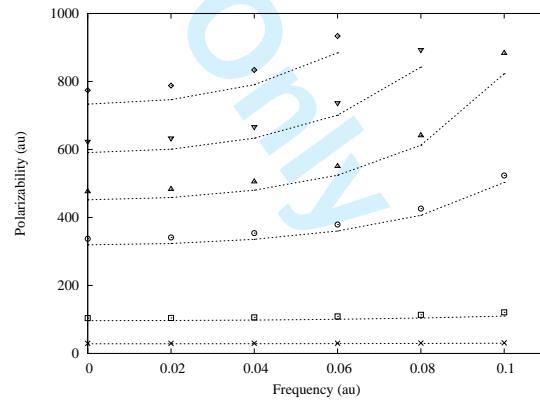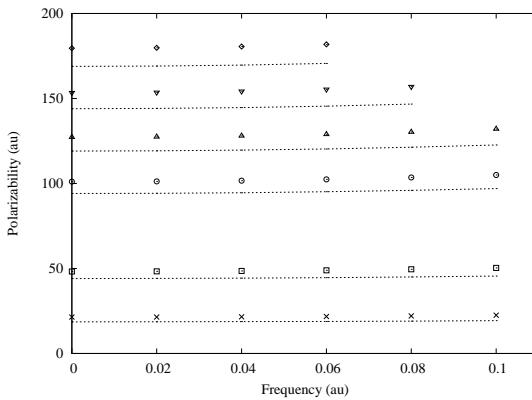
Figure 2.   The out-of plane (a) and in-plane (b) components of the polarizability of the polyenes listed in Table 2 in order of increasing molecular size (from bottom to top), as a function of the frequency. The points represent the c-DFT data while the lines represent the model.
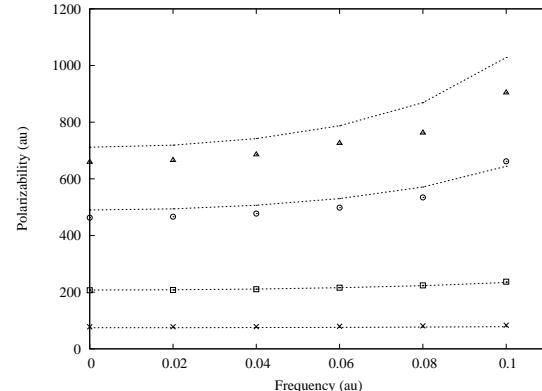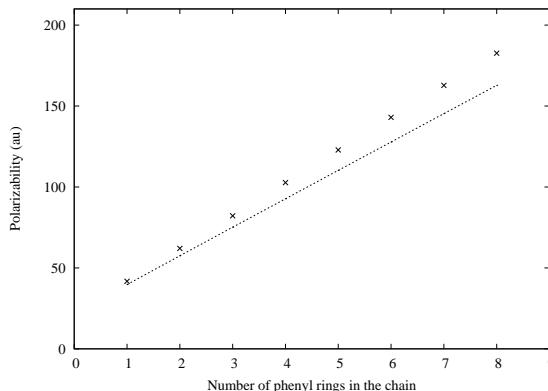
Figure 3. The out-of plane (a) and the in-plane (b) components of the polarizability of the acenes listed in Table 2. (a) the static polarizability as a function of the number of phenyl rings in the chain. (b) the polarizability in order of increasing molecular size (from bottom to top), as a function of the frequency. In both cases, the points represent the c-DFT data while the lines represent the model.
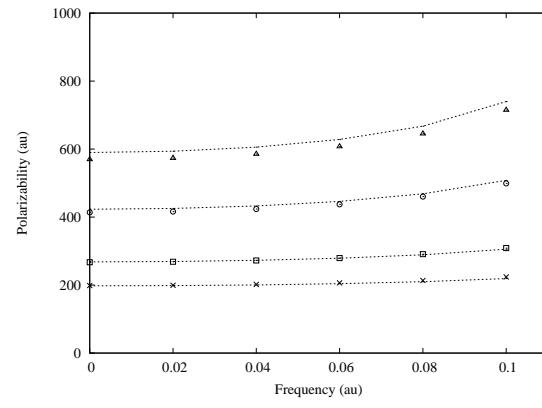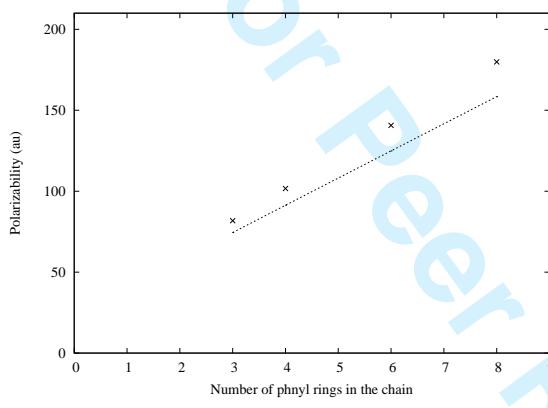
Figure 4. The out-of plane (a) and the in-plane (b) components of the polarizability of the armchair chain listed in Table 2. (a) static polarizability as a function of the number of phenylrings in the chain, (b) the polarizability in order of increasing molecular size (from bottom to top), as a function of the frequency. The points represent the c-DFT data while the lines represent the model.

The aromatic systems are presented in Figures 3, and 4. For the polyenes and the aromatic systems, the out-of plane components behave similarly for all systems and are more or less constant as a function of the frequency. Therefore only the static polarizability is shown in Figures 3(a) and 4(a). The out-of-plane contributions to the polarizability is adequately described for these systems.

Also the in-plane component behaves quantitatively similarly for these systems (polyenes, acenes and armchair structures). The static polarizability for these systems are larger than a corresponding alkane chain, and the increase in polarizability due to the frequency is higher. However, there are small differences within these systems, which appear both in the c-DFT data and in the data obtained from the model. The in-plane component of the polarizability of the polyenes increases more with length compared to the acenes (Figure 3(b)) which again has slightly higher polarizability than the armchair series (Figure 4(b)). The differences in polarizability can be explained by looking at the number of carbon atoms in the chain compared to the length of the chain. In Figure 4, the size of the chains are reported both with respect to number of carbon atoms and distance. It is noted that although the polyene $C_{18}H_{20}$ and octacene have a similar number of carbon atoms in the chain, the polyene is about 7% longer. Thus with the same electric field, the polyene feels a larger potential difference between its ends as compared to octacene. The same reasoning can be used to explain why octacene has a higher polarizability (both static and frequency-dependent) compared to benzo[c]naphto[2,1-m]picene.

Table 4.   Chain length

Name	Scaling[1]	#C[2]	Distance (Å)[3]
$C_{18}H_{20}$	1.85	18	21.7
octazene	1.34	17	19.7
benzo[c]naphto[2,1-m]picene	1.25	18	18.0

[1]c-DFT polarizability (in-plane component) at $\omega = 0.1$ divided by the corresponding static polarizability
[2]In the longest possible chain of carbon atoms
[3]Between the two carbon atoms with the largest separation

The latter is shorter in length but longer in terms of number of carbon atoms, both which according to the model should predict a lower polarizability. In addition, due to slightly different bond distances, octacene has a higher average ϵ along the chain compared to benzo[c]naphto[2,1-m]picene. For both polyenes and aromatic molecules, the sum of the two distances describing $g_{I,KM}$ and ϵ is usually about 2.8 Å. However, in a few cases where carbon is bonded to three other carbon atoms, this distance may increase to about 2.9 Å. In this case, ϵ increases to around 0.15 (see Figure 5), which is a factor 3 larger than the value for the polyene chains, and which lead to the revised form of $g_{I,KM}$ in Eq. (17). This is the case both for the acenes and in the armchair series, but for the acenes it has less impact on the total polarizability. For the acenes, ϵ becomes larger when connecting the two parallel carbon chains, and in this case the value of ϵ is of less importance. For the armchair series, ϵ becomes large for a few connections along the chain which have a larger impact.
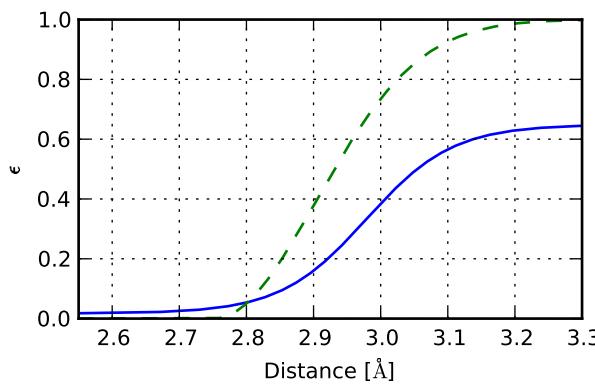
Figure 5. ϵ for carbon as a function of the sum of two bond lengths $(R_{IK} + R_{IM})$, — model and parameters used in this work, −− model and parameters used previously.[61] For sp^3 carbon the relevant distance is typically around 3.1 Å, while for sp^2-carbon it is typically about 2.8 Å, but can increase to about 2.9 Å in some situations. For sp-carbon the distance is about 2.6 Å.

In the poly(p-phenylene vinylene) systems, the key junctions between the benzene ring and the vinyl group has an $g_{I,KM}$ or ϵ described by bond lengths which sum to about 2.9 Å, so also in this case, the revised form of $g_{I,KM}$ in Eq. (17) lead to a dramatic improvement of the description of the polarizability along the chain. Thus these systems are now well described (see Figure 6). From Figure 5, it is also noted that ϵ for sp^3-carbon is lower than in our previous work.[61] In addition, both the hardness for hydrogen and and ϵ when one of the atoms is a hydrogen atom (given by $\epsilon = 1 - g_{0,C}^* {}^3 g_{0,H}^* \approx 0.46$) is less than in previous works.[61] In combination, these effects give a larger charge transfer contribution compared to previous work (for dodecane the charge transfer contribution is currently of the same order of magnitude as the point dipole terms).[61] However since the charge
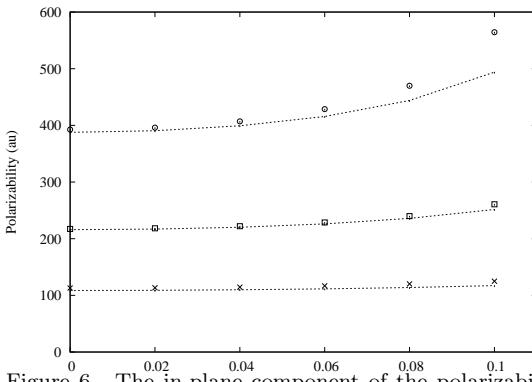
Figure 6.   The in-plane component of the polarizability of poly(p-phenylene vinylene) systems listed in Table 2, in order of increasing molecular size (from bottom to top), as a function of the frequency. The points represent the c-DFT data while the lines represent the model.

transfer term of the polarizability in a long linear chain is proportional to ϵ^{-1} (see Eq. (47)), the differences between the models are less critical for high values of ϵ.

To test an extreme case, the polarizability along linear polyyne chains (not included in the parametrization) are shown in Figure 7. For the longest chain at high frequencies, relatively large errors are noted. However, these errors are associated with a frequency close to the excitation energy, and small errors in the estimation of the excitation energy, approximately given by Eq. (49) for long chains, will have large impact on the result. For these systems ϵ approaches $1 - g_{I,C}^{*\,4}$ and is thus about 0.02 (see Figure 5), and since the model overestimates the frequency-dependent polarizability, this value is slightly too low. But, the shorter chains and the static polarizability for the larger systems are well described, which implies that the other parts of the model works fairly well, even for triple bonds. A better fit for the long polyyne chains would obviously have been obtained if one of them had been included in the training set. However, long polyyne chains are a special case and at this stage we prefer not to tweak the model to this particular case.
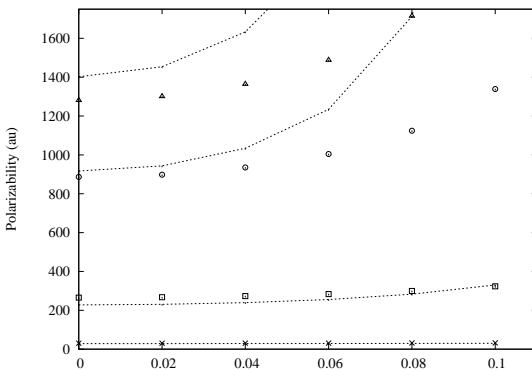
Figure 7.   The polarizability component along the polyyne chains (α_{xx}) listed in Table 2, in order of increasing molecular size (from bottom to top), as a function of the frequency. The points represent the c-DFT data while the lines represent the model.

In addition, the model was tested for both the static and frequency-dependent polarizability for a large set of carbon-hydrogen systems not included in the parametrization, and the results of this test is given in supplementary material. With the exception of a few cases with high frequency close to a critical frequency, the model predicts the polarizability within 5-10% error for all molecules and all polarizability components in the test. This shows that the parameters obtained studying simple systems are indeed transferable to other more complex molecules. One reason for obtaining good static polarizability for many different systems, with parameters obtained from a small training set is that the frequency-dependent polarizability is critically dependent on how the static polarizability is divided into

charge-transfer and point-dipole contributions.

5.   Conclusions

The differences between the c-DFT calculations and the model are in general small, and it is concluded that the presented model is capable of modeling the frequency-dependent polarizability for systems containing hydrogen and carbon. Investigating the frequency-dependent polarizability also helps in parametrize the static polarizability, since the frequency-dependent polarizability is highly dependent on how the static polarizability is divided into a charge-transfer part and a point-dipole part. It is demonstrated that parameters for the polarizability yielding good result for many different systems could be obtained using a small training set.

Acknowledgments

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Table 1: Polarizability in au

	ω	α_{xx}		α_{yy}		α_{zz}		α_{xy}		α_{xz}		α_{yz}	
		Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT
methane	0.00	16.46	17.23	16.46	17.23	16.46	17.23	0.00	0.00	0.00	0.00	-0.00	0.00
ethane	0.00	27.85	27.65	27.85	27.65	33.72	31.58	-0.00	0.00	-0.00	0.00	-0.00	0.00
ethane	0.02	27.88	27.69	27.88	27.69	33.82	31.63	-0.00	0.00	-0.00	0.00	-0.00	0.00
ethane	0.04	27.98	27.80	27.98	27.80	34.11	31.78	-0.00	0.00	-0.00	0.00	-0.00	0.00
ethane	0.06	28.16	28.01	28.16	28.01	34.61	32.04	-0.00	0.00	-0.00	0.00	-0.00	0.00
ethane	0.08	28.41	28.29	28.41	28.29	35.38	32.41	-0.00	0.00	-0.00	0.00	-0.00	0.00
ethane	0.10	28.74	28.68	28.74	28.68	36.46	32.90	-0.00	0.00	-0.00	0.00	-0.00	0.00
propane	0.00	46.24	45.28	38.06	38.01	41.92	40.27	0.00	0.00	-0.00	0.00	-0.00	0.00
propane	0.02	46.34	45.35	38.10	38.06	41.99	40.34	0.00	0.00	-0.00	0.00	-0.00	0.00
propane	0.04	46.64	45.57	38.24	38.23	42.22	40.52	0.00	0.00	-0.00	0.00	-0.00	0.00
propane	0.06	47.17	45.93	38.47	38.51	42.61	40.84	0.00	0.00	-0.00	0.00	-0.00	0.00
propane	0.08	47.95	46.46	38.80	38.92	43.19	41.30	0.00	0.00	-0.00	0.00	-0.00	0.00
propane	0.10	49.03	47.17	39.25	39.46	43.99	41.92	0.00	0.00	-0.00	0.00	-0.00	0.00
butane	0.00	62.31	61.24	53.38	51.27	48.05	48.16	-2.41	-1.43	-0.00	0.00	0.00	0.00
butane	0.02	62.44	61.34	53.47	51.35	48.11	48.23	-2.43	-1.44	0.00	0.00	-0.00	0.00
butane	0.04	62.86	61.64	53.76	51.59	48.27	48.44	-2.51	-1.45	0.00	0.00	-0.00	0.00
butane	0.06	63.59	62.15	54.24	52.01	48.56	48.80	-2.65	-1.47	0.00	0.00	-0.00	0.00
butane	0.08	64.66	62.88	54.95	52.61	48.97	49.32	-2.86	-1.50	-0.00	0.00	0.00	0.00
butane	0.10	66.14	63.86	55.93	53.42	49.52	50.01	-3.17	-1.55	0.00	0.00	-0.00	0.00
pentane	0.00	57.92	58.26	78.05	77.30	65.45	62.52	0.00	0.00	-0.00	0.00	0.00	0.00
hexane	0.00	82.65	79.18	89.08	88.76	67.74	68.36	-8.85	-9.22	-0.00	0.00	0.00	0.00
hexane	0.02	82.83	79.31	89.25	88.91	67.82	68.46	-8.89	-9.24	0.00	0.00	0.00	0.00
hexane	0.04	83.35	79.71	89.77	89.35	68.05	68.76	-9.03	-9.30	-0.00	0.00	-0.00	0.00
hexane	0.06	84.25	80.39	90.66	90.09	68.44	69.28	-9.28	-9.39	0.00	0.00	0.00	0.00
hexane	0.08	85.59	81.37	91.96	91.17	69.01	70.03	-9.63	-9.53	-0.00	0.00	-0.00	0.00
hexane	0.10	87.46	82.69	93.73	92.61	69.77	71.04	-10.13	-9.70	0.00	0.00	-0.00	0.00
heptane	0.00	77.53	78.31	111.68	111.37	88.50	84.57	-0.00	0.00	-0.00	0.00	-0.00	0.00
octane	0.00	129.23	128.80	99.62	95.36	87.30	88.26	-0.68	0.57	0.00	0.00	-0.00	0.00
octane	0.02	129.52	129.02	99.80	95.51	87.39	88.39	-0.70	0.57	0.00	0.00	-0.00	0.00
octane	0.04	130.40	129.68	100.32	95.98	87.68	88.79	-0.76	0.57	0.00	0.00	0.00	0.00
octane	0.06	131.90	130.82	101.22	96.77	88.18	89.45	-0.87	0.56	-0.00	0.00	-0.00	0.00
octane	0.08	134.11	132.45	102.54	97.93	88.90	90.42	-1.05	0.55	0.00	0.00	-0.00	0.00
octane	0.10	137.13	134.63	104.37	99.48	89.86	91.72	-1.31	0.54	-0.00	0.00	0.00	0.00
decane	0.00	164.02	164.05	122.57	117.49	106.78	108.13	0.39	1.75	-0.00	0.00	-0.00	0.00
dodecane	0.00	157.59	151.63	187.09	187.25	126.23	127.93	-22.51	-24.48	-0.00	0.00	0.00	0.00
dodecane	0.02	157.90	151.89	187.48	187.57	126.36	128.12	-22.60	-24.53	-0.00	0.00	0.00	0.00
dodecane	0.04	158.85	152.66	188.66	188.56	126.78	128.69	-22.88	-24.69	-0.00	0.00	0.00	0.00
dodecane	0.06	160.48	153.98	190.68	190.23	127.48	129.67	-23.37	-24.95	-0.00	0.00	0.00	0.00
dodecane	0.08	162.89	155.89	193.63	192.65	128.50	131.08	-24.08	-25.33	0.00	0.00	0.00	0.00
dodecane	0.10	166.23	158.47	197.65	195.89	129.88	132.98	-25.05	-25.82	0.00	0.00	0.00	0.00

Table 2: Polarizability in au

	ω	α_{xx}		α_{yy}		α_{zz}		α_{xy}		α_{xz}		α_{yz}	
		Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT
ethene	0.00	18.61	21.40	27.16	25.61	29.86	33.71	0.00	0.00	0.00	0.00	-0.00	0.00
ethene	0.02	18.64	21.44	27.19	25.65	29.94	33.79	0.00	0.00	0.00	0.00	-0.00	0.00
ethene	0.04	18.72	21.56	27.31	25.77	30.17	34.05	0.00	0.00	0.00	0.00	0.00	0.00
ethene	0.06	18.85	21.77	27.50	25.97	30.57	34.49	0.00	0.00	0.00	0.00	0.00	0.00
ethene	0.08	19.04	22.08	27.78	26.27	31.17	35.13	0.00	0.00	0.00	0.00	0.00	0.00
ethene	0.10	19.30	22.49	28.15	26.66	32.00	36.01	0.00	0.00	0.00	0.00	0.00	0.00
butadiene	0.00	63.12	75.70	50.98	48.86	31.47	34.83	-5.33	-9.01	0.00	0.00	0.00	0.00
butadiene	0.02	63.32	76.02	51.07	48.96	31.51	34.89	-5.38	-9.09	0.00	0.00	0.00	0.00
butadiene	0.04	63.94	76.99	51.35	49.27	31.64	35.06	-5.51	-9.33	0.00	0.00	0.00	0.00
butadiene	0.06	65.02	78.70	51.82	49.79	31.85	35.37	-5.75	-9.76	0.00	0.00	0.00	0.00
butadiene	0.08	66.63	81.31	52.52	50.57	32.15	35.81	-6.12	-10.42	0.00	0.00	0.00	0.00
butadiene	0.10	68.92	85.12	53.48	51.64	32.55	36.40	-6.65	-11.42	0.00	0.00	0.00	0.00
hexatriene	0.00	111.26	130.68	80.54	77.32	44.09	48.23	-21.03	-27.44	0.00	0.00	0.00	0.00
hexatriene	0.02	111.85	131.48	80.77	77.57	44.15	48.31	-21.28	-27.74	0.00	0.00	0.00	0.00
hexatriene	0.04	113.70	134.00	81.50	78.32	44.31	48.54	-22.06	-28.71	0.00	0.00	0.00	0.00
hexatriene	0.06	117.02	138.55	82.78	79.65	44.59	48.94	-23.47	-30.46	0.00	0.00	0.00	0.00
hexatriene	0.08	122.27	145.80	84.76	81.73	45.00	49.53	-25.74	-33.31	0.00	0.00	0.00	0.00
hexatriene	0.10	130.33	157.11	87.73	84.84	45.53	50.32	-29.33	-37.86	0.00	0.00	0.00	0.00
polyene(C_8H_{10})	0.00	169.89	195.34	116.58	112.68	56.63	61.53	-45.61	-54.79	0.00	0.00	0.00	0.00
polyene(C_8H_{10})	0.02	171.19	196.93	117.11	113.21	56.70	61.62	-46.28	-55.54	0.00	0.00	0.00	0.00
polyene(C_8H_{10})	0.04	175.30	201.93	118.77	114.86	56.91	61.91	-48.42	-57.90	0.00	0.00	0.00	0.00
polyene(C_8H_{10})	0.06	182.90	211.20	121.81	117.89	57.26	62.40	-52.41	-62.33	0.00	0.00	0.00	0.00
polyene(C_8H_{10})	0.08	195.56	226.61	126.79	122.84	57.77	63.11	-59.17	-69.80	0.00	0.00	0.00	0.00
polyene(C_8H_{10})	0.10	216.73	252.35	134.96	130.90	58.44	64.07	-70.72	-82.49	0.00	0.00	0.00	0.00
polyene($C_{10}H_{12}$)	0.00	238.62	269.78	155.69	150.72	69.14	74.72	-75.70	-87.18	0.00	0.00	0.00	0.00
polyene($C_{10}H_{12}$)	0.02	240.98	272.48	156.64	151.65	69.23	74.83	-77.01	-88.55	0.00	0.00	0.00	0.00
polyene($C_{10}H_{12}$)	0.04	248.52	281.08	159.67	154.59	69.48	75.17	-81.22	-92.96	0.00	0.00	0.00	0.00
polyene($C_{10}H_{12}$)	0.06	262.87	297.36	165.39	160.12	69.90	75.75	-89.29	-101.38	0.00	0.00	0.00	0.00
polyene($C_{10}H_{12}$)	0.08	287.89	325.53	175.22	169.57	70.51	76.59	-103.55	-116.15	0.00	0.00	0.00	0.00
polyene($C_{10}H_{12}$)	0.10	333.28	375.99	192.76	186.27	71.31	77.73	-129.82	-143.09	0.00	0.00	0.00	0.00
polyene($C_{14}H_{16}$)	0.00	394.93	438.47	241.95	236.08	94.12	101.07	148.32	165.27	0.00	0.00	0.00	0.00
polyene($C_{14}H_{16}$)	0.02	400.31	444.27	244.12	238.18	94.23	101.22	151.48	168.48	0.00	0.00	0.00	0.00
polyene($C_{14}H_{16}$)	0.04	417.80	463.07	251.15	244.99	94.56	101.67	161.80	178.93	0.00	0.00	0.00	0.00
polyene($C_{14}H_{16}$)	0.06	452.47	500.06	265.00	258.35	95.13	102.42	182.39	199.68	0.00	0.00	0.00	0.00
polyene($C_{14}H_{16}$)	0.08	517.79	568.94	290.81	283.17	95.93	103.52	221.54	238.85	0.00	0.00	0.00	0.00
polyene($C_{14}H_{16}$)	0.10	655.07	711.91	344.40	334.94	97.00	105.00	304.71	321.85	0.00	0.00	0.00	0.00

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Table 3: Polarizability in au

	ω	α_{xx}		α_{yy}		α_{zz}		α_{xy}		α_{xz}		α_{yz}	
		Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT
polyene($C_{18}H_{20}$)	0.00	566.92	623.95	334.75	329.15	119.05	127.26	231.12	254.72	0.00	0.00	0.00	0.00
polyene($C_{18}H_{20}$)	0.02	576.21	633.78	338.51	332.84	119.19	127.44	236.71	260.38	0.00	0.00	0.00	0.00
polyene($C_{18}H_{20}$)	0.04	606.84	666.07	350.85	344.97	119.61	127.99	255.19	279.05	0.00	0.00	0.00	0.00
polyene($C_{18}H_{20}$)	0.06	669.42	731.65	375.92	369.70	120.31	128.92	293.14	317.37	0.00	0.00	0.00	0.00
polyene($C_{18}H_{20}$)	0.08	794.53	862.65	425.62	419.73	121.32	130.26	369.59	395.33	0.00	0.00	0.00	0.00
polyene($C_{18}H_{20}$)	0.10	1093.44	1206.59	543.19	559.96	122.65	132.08	553.79	609.88	0.00	0.00	0.00	0.00
polyene($C_{22}H_{24}$)	0.00	747.80	819.05	431.54	427.42	143.97	153.38	319.99	351.61	0.00	0.00	0.00	0.00
polyene($C_{22}H_{24}$)	0.02	761.61	833.56	437.14	433.02	144.14	153.60	328.40	360.17	0.00	0.00	0.00	0.00
polyene($C_{22}H_{24}$)	0.04	807.57	880.82	455.71	452.07	144.64	154.25	356.45	389.46	0.00	0.00	0.00	0.00
polyene($C_{22}H_{24}$)	0.06	903.61	982.44	494.29	491.13	145.48	155.35	415.33	449.25	0.00	0.00	0.00	0.00
polyene($C_{22}H_{24}$)	0.08	1104.74	1203.62	574.47	582.61	146.69	156.95	539.42	587.08	0.00	0.00	0.00	0.00
polyene($C_{26}H_{28}$)	0.00	933.80	1020.57	529.95	527.99	168.88	179.56	411.72	452.05	0.00	0.00	0.00	0.00
polyene($C_{26}H_{28}$)	0.02	952.50	1040.20	537.53	535.71	169.07	179.81	423.18	463.81	0.00	0.00	0.00	0.00
polyene($C_{26}H_{28}$)	0.04	1015.14	1105.99	562.86	561.78	169.65	180.56	461.64	503.49	0.00	0.00	0.00	0.00
polyene($C_{26}H_{28}$)	0.06	1148.26	1247.82	616.40	619.56	170.64	181.84	543.74	590.70	0.00	0.00	0.00	0.00
benzene	0.00	73.85	77.67	73.85	77.67	39.10	41.74	0.00	0.00	0.00	0.00	0.00	0.00
benzene	0.02	73.99	77.88	73.99	77.88	39.15	41.80	0.00	0.00	0.00	0.00	0.00	0.00
benzene	0.04	74.40	78.50	74.40	78.50	39.28	41.99	0.00	0.00	0.00	0.00	0.00	0.00
benzene	0.06	75.11	79.57	75.11	79.57	39.50	42.30	0.00	0.00	0.00	0.00	0.00	0.00
benzene	0.08	76.14	81.16	76.14	81.16	39.82	42.76	0.00	0.00	0.00	0.00	0.00	0.00
benzene	0.10	77.54	83.37	77.54	83.37	40.24	43.38	0.00	0.00	0.00	0.00	0.00	0.00
anthracene	0.00	78.59	82.16	156.59	158.29	255.92	255.07	0.00	0.00	0.00	0.00	0.00	0.00
anthracene	0.02	78.67	82.26	156.88	158.76	257.29	256.48	0.00	0.00	0.00	0.00	0.00	0.00
anthracene	0.04	78.93	82.59	157.76	160.21	261.53	260.84	0.00	0.00	0.00	0.00	-0.00	0.00
anthracene	0.06	79.35	83.14	159.27	162.83	269.15	268.64	0.00	0.00	0.00	0.00	0.00	0.00
anthracene	0.08	79.96	83.95	161.52	167.08	281.18	280.88	0.00	0.00	0.00	0.00	0.00	0.00
anthracene	0.10	80.76	85.02	164.78	174.49	299.65	299.45	0.00	0.00	0.00	0.00	0.00	0.00
naphtalene	0.00	58.97	62.07	116.15	118.30	150.19	154.88	0.00	0.00	0.00	0.00	0.00	0.00
naphtalene	0.02	59.03	62.16	116.37	118.63	150.70	155.51	0.00	0.00	0.00	0.00	-0.00	0.00
naphtalene	0.04	59.23	62.41	117.03	119.64	152.26	157.44	0.00	0.00	0.00	0.00	-0.00	0.00
naphtalene	0.06	59.55	62.85	118.16	121.40	154.99	160.84	0.00	0.00	0.00	0.00	-0.00	0.00
naphtalene	0.08	60.02	63.49	119.83	124.07	159.12	166.02	0.00	0.00	0.00	0.00	0.00	0.00
naphtalene	0.10	60.63	64.34	122.20	127.95	165.06	173.53	0.00	0.00	0.00	0.00	0.00	0.00

Table 4: Polarizability in au

	ω	α_{xx}		α_{yy}		α_{zz}		α_{xy}		α_{xz}		α_{yz}	
		Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT
phenanthrene	0.00	78.20	81.77	227.56	229.09	165.19	168.13	0.00	0.00	0.00	0.00	-0.00	0.00
phenanthrene	0.02	78.28	81.88	228.55	230.20	165.53	168.64	0.00	0.00	0.00	0.00	-0.00	0.00
phenanthrene	0.04	78.53	82.21	231.64	233.65	166.58	170.22	0.00	0.00	0.00	0.00	-0.00	0.00
phenanthrene	0.06	78.95	82.77	237.17	239.83	168.38	173.01	0.00	0.00	0.00	0.00	-0.00	0.00
phenanthrene	0.08	79.55	83.58	245.93	249.52	171.05	177.27	0.00	0.00	0.00	0.00	-0.00	0.00
phenanthrene	0.10	80.34	84.67	259.67	264.27	174.90	183.57	0.00	0.00	0.00	0.00	-0.00	0.00
tetracene	0.04	397.56	383.96	197.91	199.65	98.53	103.24	0.00	0.00	0.00	0.00	0.00	0.00
tetracene	0.06	413.64	398.68	199.79	203.24	99.06	103.92	0.00	0.00	0.00	0.00	0.00	0.00
tetracene	0.08	439.99	422.46	202.61	209.57	99.81	104.89	0.00	0.00	0.00	0.00	0.00	0.00
tetracene	0.10	482.90	460.51	206.75	228.90	100.80	106.21	-0.00	0.00	0.00	0.00	0.00	0.00
pentacene	0.00	535.63	506.86	236.07	235.59	117.59	122.87	0.00	0.00	0.00	0.00	0.00	0.00
pentacene	0.02	540.42	511.03	236.49	236.30	117.71	123.03	0.00	0.00	0.00	0.00	0.00	0.00
pentacene	0.04	555.58	524.20	237.78	238.56	118.09	123.50	0.00	0.00	0.00	0.00	0.00	0.00
pentacene	0.06	583.94	548.59	240.02	242.77	118.71	124.29	0.00	0.00	0.00	0.00	0.00	0.00
pentacene	0.08	631.88	589.30	243.37	250.82	119.61	125.43	0.00	0.00	0.00	0.00	0.00	0.00
pentacene	0.10	714.25	660.25	248.39	273.75	120.78	126.97	0.00	0.00	0.00	0.00	0.00	0.00
heptacene	0.00	877.91	806.40	314.83	312.21	156.45	162.80	-0.00	0.00	0.00	0.00	0.00	0.00
heptacene	0.02	888.24	814.91	315.38	313.24	156.62	163.00	-0.00	0.00	0.00	0.00	0.00	0.00
heptacene	0.04	921.40	842.16	317.07	316.22	157.10	163.60	-0.00	0.00	0.00	0.00	0.00	0.00
heptacene	0.06	985.22	894.43	319.99	322.18	157.93	164.64	-0.00	0.00	0.00	0.00	0.00	0.00
heptacene	0.08	1098.90	988.94	324.37	337.51	159.10	166.13	-0.00	0.00	0.00	0.00	0.00	0.00
heptacene	0.10	1313.23	1123.95	330.99	348.18	160.65	168.12	-0.00	0.00	0.00	0.00	0.00	0.00

Table 5: Polarizability in au

	ω	α_{xx}		α_{yy}		α_{zz}		α_{xy}		α_{xz}		α_{yz}	
		Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT
hexacene	0.00	700.67	652.04	275.50	273.74	137.03	143.02	0.00	0.00	0.00	0.00	0.00	0.00
hexacene	0.02	707.99	658.20	275.99	274.56	137.18	143.20	0.00	0.00	0.00	0.00	0.00	0.00
hexacene	0.04	731.34	677.79	277.48	277.10	137.61	143.73	0.00	0.00	0.00	0.00	0.00	0.00
hexacene	0.06	775.69	714.70	280.06	281.81	138.33	144.64	0.00	0.00	0.00	0.00	0.00	0.00
hexacene	0.08	852.78	778.63	283.94	290.17	139.37	145.96	-0.00	0.00	0.00	0.00	0.00	0.00
hexacene	0.10	991.79	1017.47	289.78	306.46	140.73	147.72	-0.00	0.00	0.00	0.00	0.00	0.00
octacene	0.00	1064.45	967.60	354.08	351.30	175.86	182.66	-0.00	0.00	0.00	0.00	0.00	0.00
octacene	0.02	1078.19	978.77	354.70	352.52	176.04	182.88	-0.00	0.00	0.00	0.00	0.00	0.00
octacene	0.04	1122.55	1014.78	356.58	356.65	176.59	183.56	-0.00	0.00	0.00	0.00	0.00	0.00
octacene	0.06	1208.90	1085.06	359.82	367.13	177.52	184.71	-0.00	0.00	0.00	0.00	0.00	0.00
octacene	0.08	1366.05	1219.06	364.69	306.07	178.83	186.36	0.00	0.00	0.00	0.00	0.00	0.00
octacene	0.10	1674.59	1437.29	372.05	371.09	180.57	188.58	0.00	0.00	0.00	0.00	0.00	0.00
styrene	0.00	118.57	123.28	97.18	102.68	51.32	54.68	-10.08	-14.43	0.00	0.00	0.00	0.00
styrene	0.02	118.95	123.78	97.38	102.97	51.38	54.76	-10.17	-14.56	0.00	0.00	0.00	0.00
styrene	0.04	120.11	125.34	97.98	103.88	51.55	55.01	-10.45	-14.98	0.00	0.00	0.00	0.00
styrene	0.06	122.15	128.11	99.01	105.47	51.85	55.42	-10.96	-15.75	0.00	0.00	0.00	0.00
styrene	0.08	125.24	132.41	100.54	107.86	52.28	56.02	-11.74	-16.96	0.00	0.00	0.00	0.00
styrene	0.10	129.69	138.85	102.65	111.29	52.85	56.83	-12.89	-18.85	0.00	0.00	0.00	0.00
stilbene	0.00	203.95	210.23	225.39	224.13	83.25	87.77	58.95	57.62	0.00	0.00	0.00	0.00
stilbene	0.02	204.85	211.29	226.56	225.41	83.34	87.89	59.71	58.39	0.00	0.00	0.00	0.00
stilbene	0.04	207.65	214.61	230.23	229.41	83.61	88.25	62.13	60.81	0.00	0.00	0.00	0.00
stilbene	0.06	212.74	220.68	236.93	236.80	84.07	88.86	66.62	65.38	0.00	0.00	0.00	0.00
stilbene	0.08	220.95	230.59	247.82	249.10	84.72	89.75	74.12	73.23	0.00	0.00	0.00	0.00
stilbene	0.10	234.08	249.87	265.45	271.48	85.58	90.95	86.66	88.44	0.00	0.00	0.00	0.00
1,4-dicinnamyl-benzene	0.00	528.57	533.06	243.55	252.28	127.07	133.39	51.69	59.07	0.00	0.00	0.00	0.00
1,4-dicinnamyl-benzene	0.02	533.53	539.04	244.07	253.06	127.21	133.56	52.50	60.08	0.00	0.00	0.00	0.00
1,4-dicinnamyl-benzene	0.04	549.34	558.51	245.67	255.49	127.62	134.10	55.10	63.39	0.00	0.00	0.00	0.00
1,4-dicinnamyl-benzene	0.06	579.25	597.38	248.48	259.88	128.31	135.01	60.05	69.98	0.00	0.00	0.00	0.00
1,4-dicinnamyl-benzene	0.08	630.95	672.71	252.82	266.98	129.29	136.32	68.71	82.68	0.00	0.00	0.00	0.00
1,4-dicinnamyl-benzene	0.10	723.32	849.80	259.41	279.06	130.58	138.08	84.38	111.78	0.00	0.00	0.00	0.00
1,4-divinylbenzene	0.00	178.31	190.63	114.89	119.37	63.46	67.71	-13.41	-22.99	0.00	0.00	0.00	0.00
1,4-divinylbenzene	0.02	179.15	191.83	115.10	119.70	63.54	67.81	-13.55	-23.24	0.00	0.00	0.00	0.00
1,4-divinylbenzene	0.04	181.73	195.61	115.74	120.69	63.76	68.11	-13.99	-24.05	0.00	0.00	0.00	0.00
1,4-divinylbenzene	0.06	186.34	202.59	116.85	122.44	64.13	68.62	-14.78	-25.54	0.00	0.00	0.00	0.00
1,4-divinylbenzene	0.08	193.50	214.15	118.48	125.11	64.67	69.36	-16.01	-28.02	0.00	0.00	0.00	0.00
1,4-divinylbenzene	0.10	204.26	233.52	120.72	129.03	65.38	70.36	-17.90	-32.19	0.00	0.00	0.00	0.00

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Table 6: Polarizability in au

	ω	α_{xx}		α_{yy}		α_{zz}		α_{xy}		α_{xz}		α_{yz}	
		Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT
chrysene	0.00	208.01	212.08	325.26	322.35	97.29	101.64	20.28	20.81	0.00	0.00	0.00	0.00
chrysene	0.02	208.45	212.77	327.02	324.19	97.39	101.77	20.50	21.02	0.00	0.00	0.00	0.00
chrysene	0.04	209.78	214.90	332.52	329.96	97.70	102.16	21.18	21.68	0.00	0.00	0.00	0.00
chrysene	0.06	212.08	218.70	342.55	340.38	98.21	102.84	22.45	22.87	0.00	0.00	0.00	0.00
chrysene	0.08	215.52	224.69	358.94	357.06	98.95	103.82	24.53	24.76	0.00	0.00	0.00	0.00
chrysene	0.10	220.50	234.18	386.33	383.34	99.91	105.15	28.08	27.62	0.00	0.00	0.00	0.00
benzo[c]picene	0.00	524.12	508.53	318.08	318.98	135.29	140.66	84.42	74.21	0.00	0.00	0.00	0.00
benzo[c]picene	0.02	527.71	512.06	319.04	320.24	135.43	140.84	85.52	75.11	0.00	0.00	0.00	0.00
benzo[c]picene	0.04	539.04	523.16	322.01	324.17	135.84	141.39	89.03	77.96	0.00	0.00	0.00	0.00
benzo[c]picene	0.06	560.15	543.63	327.35	331.30	136.55	142.32	95.68	83.25	0.00	0.00	0.00	0.00
benzo[c]picene	0.08	595.98	577.58	335.90	342.95	137.54	143.67	107.26	92.06	0.00	0.00	0.00	0.00
benzo[c]picene	0.10	660.32	634.99	349.97	363.15	138.85	145.50	128.86	106.46	0.00	0.00	0.00	0.00
benzo[c]naphto[2,1-m]picene	0.00	694.55	667.06	480.61	472.43	173.19	179.88	189.36	165.87	0.00	0.00	0.00	0.00
benzo[c]naphto[2,1-m]picene	0.02	699.78	672.09	482.89	474.92	173.36	180.10	192.03	168.06	0.00	0.00	0.00	0.00
benzo[c]naphto[2,1-m]picene	0.04	716.41	688.02	490.09	482.78	173.89	180.79	200.58	175.02	0.00	0.00	0.00	0.00
benzo[c]naphto[2,1-m]picene	0.06	747.78	717.81	503.46	497.32	174.78	181.96	216.94	188.14	0.00	0.00	0.00	0.00
benzo[c]naphto[2,1-m]picene	0.08	802.29	768.69	526.17	521.82	176.04	183.67	246.06	210.59	0.00	0.00	0.00	0.00
benzo[c]naphto[2,1-m]picene	0.10	904.83	862.57	567.54	567.25	177.69	185.97	302.66	248.65	0.00	0.00	0.00	0.00
tetracene	0.00	386.00	373.30	196.47	197.15	98.12	102.71	0.00	0.00	0.00	0.00	0.00	0.00
tetracene	0.02	388.79	375.88	196.83	197.75	98.22	102.84	0.00	0.00	0.00	0.00	0.00	0.00

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Table 7: Polarizability in au

	ω	α_{xx}		α_{yy}		α_{zz}		α_{xy}		α_{xz}		α_{yz}	
		Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT
g(2,2)	0.00	249.08	257.69	200.20	199.56	85.64	88.99	-0.00	0.00	0.00	0.00	0.00	0.00
g(2,2)	0.02	250.06	259.12	200.70	200.26	85.73	89.10	-0.00	0.00	0.00	0.00	0.00	0.00
g(2,2)	0.04	253.07	263.63	202.23	202.39	86.00	89.45	-0.00	0.00	0.00	0.00	0.00	0.00
g(2,2)	0.06	258.40	271.94	204.89	206.17	86.46	90.03	-0.00	0.00	0.00	0.00	0.00	0.00
g(2,2)	0.08	266.60	285.88	208.95	212.02	87.10	90.88	-0.00	0.00	0.00	0.00	0.00	0.00
g(2,2)	0.10	278.80	310.60	215.13	220.80	87.96	92.02	-0.00	0.00	0.00	0.00	0.00	0.00
g(2,3)	0.00	111.56	115.26	332.67	330.18	307.87	310.92	0.00	0.00	0.00	0.00	-0.00	0.00
g(2,3)	0.02	111.67	115.40	334.00	332.01	308.90	312.37	0.00	0.00	0.00	0.00	-0.00	0.00
g(2,3)	0.04	112.01	116.56	338.11	348.70	312.05	325.18	0.00	0.00	0.00	0.00	-0.00	0.00
g(2,3)	0.06	112.59	116.56	345.48	348.70	317.60	325.18	0.00	0.00	0.00	0.00	-0.00	0.00
g(2,3)	0.08	113.41	117.62	357.20	368.01	326.14	338.68	0.00	0.00	0.00	0.00	0.00	0.00
g(2,3)	0.10	114.48	119.04	376.10	409.11	339.10	361.49	0.00	0.00	0.00	0.00	0.00	0.00
g(4,2)	0.00	565.70	562.28	346.03	349.57	138.19	142.92	31.01	45.53	0.00	0.00	0.00	0.00
g(4,2)	0.02	569.52	567.52	346.97	351.46	138.33	143.09	31.41	46.81	0.00	0.00	0.00	0.00
g(4,2)	0.04	581.49	584.86	349.85	357.74	138.75	143.61	32.65	51.40	0.00	0.00	0.00	0.00
g(4,2)	0.06	603.45	622.14	354.92	371.57	139.46	144.50	34.95	63.42	0.00	0.00	0.00	0.00
g(4,2)	0.08	639.55	737.47	362.77	418.95	140.47	145.77	38.74	119.57	0.00	0.00	0.00	0.00
g(4,2)	0.10	699.59	558.16	375.10	308.25	141.79	147.47	44.84	-43.88	0.00	0.00	0.00	0.00
g(6,2)	0.00	995.21	959.29	476.82	479.41	190.38	196.10	37.69	59.13	0.00	0.00	0.00	0.00
g(6,2)	0.02	1004.51	971.08	478.05	482.01	190.57	196.33	38.25	61.20	0.00	0.00	0.00	0.00
g(6,2)	0.04	1034.08	1012.41	481.82	491.42	191.13	197.03	40.04	69.93	0.00	0.00	0.00	0.00
g(8,2)	0.00	1491.21	1408.86	606.64	608.01	242.43	249.47	42.25	67.39	0.00	0.00	0.00	0.00
g(8,2)	0.02	1508.20	1429.00	608.15	611.49	242.66	249.76	42.94	70.11	0.00	0.00	0.00	0.00
g(8,2)	0.06	1667.71	1498.45	620.90	623.96	244.59	250.63	49.43	80.83	0.00	0.00	0.00	0.00
g(3,3)	0.00	144.51	149.07	433.14	432.79	495.22	489.85	0.00	0.00	0.00	0.00	-0.00	0.00
g(3,3)	0.02	144.66	149.25	434.76	435.74	497.59	492.94	0.00	0.00	0.00	0.00	-0.00	0.00
g(3,3)	0.04	145.09	149.78	439.81	445.56	504.99	502.74	0.00	0.00	0.00	0.00	-0.00	0.00
g(4,3)	0.00	177.27	182.47	531.58	529.83	719.27	697.34	0.00	0.00	0.00	0.00	0.00	0.00
g(4,3)	0.02	177.44	182.69	533.49	533.71	723.72	702.76	0.00	0.00	0.00	0.00	0.00	0.00
g(4,3)	0.04	177.96	183.32	539.42	547.12	737.67	720.17	0.00	0.00	0.00	0.00	0.00	0.00
g(6,3)	0.00	242.47	248.85	725.36	717.63	1251.52	1179.00	0.00	0.00	0.00	0.00	-0.00	0.00
g(6,3)	0.02	242.70	249.13	727.80	722.59	1262.16	1190.86	0.00	0.00	0.00	0.00	-0.00	0.00
g(8,3)	0.00	307.47	315.34	917.45	916.02	1867.67	1735.26	0.00	0.00	0.00	0.00	0.00	0.00
g(8,3)	0.02	307.76	315.69	920.41	926.18	1886.97	1756.40	0.00	0.00	0.00	0.00	0.00	0.00

Table 8: Polarizability in au

	ω	α_{xx}		α_{yy}		α_{zz}		α_{xy}		α_{xz}		α_{yz}	
		Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT
C_{60} fullerene	0.00	479.00	496.85	479.00	496.85	479.01	496.85	-0.00	0.00	0.00	0.00	-0.00	0.00
C_{60} fullerene	0.02	480.02	498.61	480.02	498.61	480.03	498.61	-0.00	0.00	0.00	0.00	-0.00	0.00
C_{60} fullerene	0.04	483.14	504.11	483.14	504.11	483.15	504.11	-0.00	0.00	0.00	0.00	-0.00	0.00
C_{60} fullerene	0.06	488.51	514.08	488.51	514.08	488.52	514.08	-0.00	0.00	0.00	0.00	-0.00	0.00
C_{60} fullerene	0.08	496.44	530.36	496.44	530.36	496.45	530.36	-0.00	0.00	-0.00	0.00	-0.00	0.00
C_{60} fullerene	0.10	507.45	558.66	507.45	558.66	507.46	558.73	-0.00	0.00	-0.00	0.00	-0.00	0.00
ethyne	0.00	16.97	19.01	16.97	19.01	28.10	30.47	0.00	0.00	0.00	0.00	0.00	0.00
ethyne	0.02	16.99	19.05	16.99	19.05	28.17	30.54	0.00	0.00	0.00	0.00	0.00	0.00
ethyne	0.04	17.07	19.16	17.07	19.16	28.38	30.74	0.00	0.00	0.00	0.00	0.00	0.00
ethyne	0.06	17.21	19.35	17.21	19.35	28.75	31.07	0.00	0.00	0.00	0.00	0.00	0.00
ethyne	0.08	17.41	19.62	17.41	19.62	29.27	31.56	0.00	0.00	0.00	0.00	0.00	0.00
ethyne	0.10	17.67	20.00	17.67	20.00	29.99	32.22	0.00	0.00	0.00	0.00	0.00	0.00
butadiyne	0.00	28.54	29.74	28.54	29.74	61.35	82.14	0.00	0.00	0.00	0.00	0.00	0.00
butadiyne	0.02	28.59	29.79	28.59	29.79	61.60	82.45	0.00	0.00	0.00	0.00	0.00	0.00
butadiyne	0.04	28.72	29.94	28.72	29.94	62.35	83.39	0.00	0.00	0.00	0.00	0.00	0.00
butadiyne	0.06	28.94	30.20	28.94	30.20	63.65	85.01	0.00	0.00	0.00	0.00	0.00	0.00
butadiyne	0.08	29.26	30.57	29.26	30.57	65.60	87.43	0.00	0.00	0.00	0.00	0.00	0.00
butadiyne	0.10	29.69	31.07	29.69	31.07	68.34	90.79	0.00	0.00	0.00	0.00	0.00	0.00
hexatriyne	0.00	39.86	40.18	39.86	40.18	127.55	160.57	0.00	0.00	0.00	0.00	0.00	0.00
hexatriyne	0.02	39.92	40.24	39.92	40.24	128.53	161.44	0.00	0.00	0.00	0.00	0.00	0.00
hexatriyne	0.04	40.10	40.43	40.10	40.43	131.59	164.10	0.00	0.00	0.00	0.00	0.00	0.00
hexatriyne	0.06	40.40	40.75	40.40	40.75	137.10	168.77	0.00	0.00	0.00	0.00	0.00	0.00
hexatriyne	0.08	40.83	41.22	40.83	41.22	145.84	175.86	0.00	0.00	0.00	0.00	0.00	0.00
hexatriyne	0.10	41.40	41.84	41.40	41.84	159.31	186.06	0.00	0.00	0.00	0.00	0.00	0.00
Polyyne(C_8H_2)	0.00	51.10	50.61	51.10	50.61	225.70	265.33	0.00	0.00	0.00	0.00	0.00	0.00
Polyyne(C_8H_2)	0.02	51.18	50.68	51.18	50.68	228.38	267.20	0.00	0.00	0.00	0.00	0.00	0.00
Polyyne(C_8H_2)	0.04	51.40	50.91	51.40	50.91	236.90	273.01	0.00	0.00	0.00	0.00	0.00	0.00
Polyyne(C_8H_2)	0.06	51.78	51.30	51.78	51.30	252.86	283.35	0.00	0.00	0.00	0.00	0.00	0.00
Polyyne(C_8H_2)	0.08	52.32	51.86	52.32	51.86	279.93	299.43	0.00	0.00	0.00	0.00	0.00	0.00
Polyyne(C_8H_2)	0.10	53.03	52.60	53.03	52.60	326.42	323.43	0.00	0.00	0.00	0.00	0.00	0.00
Polyyne($C_{16}H_2$)	0.00	95.87	92.44	95.87	92.44	913.12	886.72	0.00	0.00	0.00	0.00	0.00	0.00
Polyyne($C_{16}H_2$)	0.02	96.00	92.57	96.00	92.57	939.44	898.26	0.00	0.00	0.00	0.00	0.00	0.00
Polyyne($C_{16}H_2$)	0.04	96.41	92.96	96.41	92.95	1029.19	934.99	0.00	0.00	0.00	0.00	0.00	0.00
Polyyne($C_{16}H_2$)	0.06	97.09	93.61	97.09	93.61	1228.30	1004.32	0.00	0.00	0.00	0.00	0.00	0.00
Polyyne($C_{16}H_2$)	0.08	98.05	94.54	98.05	94.54	1702.52	1124.12	0.00	0.00	0.00	0.00	0.00	0.00
Polyyne($C_{16}H_2$)	0.10	99.33	95.79	99.33	95.79	3522.95	1338.92	0.00	0.00	0.00	0.00	0.00	0.00
Polyyne($C_{20}H_2$)	0.00	118.21	112.93	118.21	112.93	1397.70	1281.13	0.00	0.00	0.00	0.00	0.00	0.00

Table 9: Polarizability in au

	ω	α_{xx}		α_{yy}		α_{zz}		α_{xy}		α_{xz}		α_{yz}	
		Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT	Mod.	DFT
Polyyne($C_{20}H_2$)	0.02	118.38	113.08	118.38	113.08	1448.42	1300.87	0.00	0.00	0.00	0.00	0.00	0.00
Polyyne($C_{20}H_2$)	0.04	118.87	113.54	118.87	113.54	1627.18	1364.45	0.00	0.00	0.00	0.00	0.00	0.00
Polyyne($C_{20}H_2$)	0.06	119.70	114.33	119.70	114.33	2058.63	1488.10	0.00	0.00	0.00	0.00	0.00	0.00
Polyyne($C_{20}H_2$)	0.08	120.88	115.45	120.88	115.45	3333.97	1714.98	0.00	0.00	0.00	0.00	0.00	0.00
o-di(1-butadienylmethyl)-benzene	0.00	196.97	206.38	185.58	182.85	177.20	181.57	5.33	6.01	0.75	10.53	-0.44	2.82
p-hexyl-propyl-benzene	0.00	147.20	143.90	250.53	248.63	159.15	161.25	1.01	4.37	0.00	0.00	-0.00	0.00
trans-1.2-(3-vinylpropyl)-(butadienylmethyl)-ethene	0.00	136.18	136.41	166.33	172.95	152.09	155.78	-24.27	-21.57	-15.49	-23.01	8.46	9.73
trans-1-propyl-cis-methyl-decapentaene	0.00	156.92	160.54	352.59	360.44	162.20	158.66	101.43	103.14	8.46	14.05	28.59	36.57
2-naphtyl-1-butadienyl-methane	0.00	178.05	182.96	149.86	152.97	200.30	199.27	-5.49	-6.36	-45.86	-36.61	-0.21	1.43
1-octylbenzene	0.00	142.95	142.71	209.84	213.28	151.10	152.11	7.72	8.79	-8.17	-11.12	-16.75	-15.88
1-penthylbenzene	0.00	99.21	98.73	166.65	168.50	121.54	124.25	-4.77	-2.77	-0.00	0.00	0.00	0.00
6-pentyl-undecane	0.00	197.94	195.41	169.46	168.08	176.42	174.18	-12.98	-13.34	-15.73	-16.57	-13.63	-11.92
tetraphenyl	0.00	133.20	139.52	500.06	532.64	250.75	258.65	0.00	0.00	0.00	0.00	0.00	0.00
anti-1,3-dibutadienylpropane	0.00	204.66	229.01	111.98	109.89	112.67	110.85	-9.35	-5.63	-0.00	0.00	-0.00	0.00
1,7-gauche-3-methyl-nonane	0.00	116.03	114.52	132.09	129.42	137.89	135.85	2.30	2.05	-13.53	-12.43	-2.87	-2.08
6-gauche-2,3,4,5-tetramethylheptane	0.00	130.04	128.27	136.15	132.78	152.51	148.39	-4.28	-3.61	-4.21	-3.72	12.30	11.23
7-gauche-2,3,4-trimethylheptane	0.00	116.33	114.91	125.28	122.63	142.50	138.86	-5.25	-5.20	-3.73	-3.97	12.03	11.34
1-(m-ethylphenyl)-2-phenyl-propane	0.00	158.16	160.06	197.64	199.69	213.46	212.79	-4.28	-3.73	-7.86	-8.15	-0.20	2.78
1-phenyl-2-cyclohexyl-ethane	0.00	142.23	142.21	153.06	153.94	190.77	188.89	6.49	5.20	-31.98	-32.75	-4.97	-5.22
cis-1-methyl-decapentaene	0.00	134.01	127.37	306.50	331.53	79.67	84.14	41.76	43.55	0.00	0.00	-0.00	0.00
1,1-dimethyl-decapentaene	0.00	134.89	139.15	310.01	317.23	142.62	139.41	99.97	101.09	12.54	16.99	33.22	42.04