Resonant Raman spectra of diindenoperylene thin films


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Resonant and preresonant Raman spectra obtained on diindenoperylene (DIP) thin films are interpreted with calculations of the deformation of a relaxed excited molecule with density functional theory (DFT). The comparison of excited state geometries based on time-dependent DFT or on a constrained DFT scheme with observed absorption spectra of dissolved DIP reveals that the deformation pattern deduced from constrained DFT is more reliable. Most observed Raman peaks can be assigned to calculated $A_2$-symmetric breathing modes of DIP or their combinations. As the position of one of the laser lines used falls into a highly structured absorption band, we have carefully analyzed the Raman excitation profile arising from the frequency dependence of the dielectric tensor. This procedure gives Raman cross sections in good agreement with the observed relative intensities, both in the fully resonant and in the preresonant case. © 2011 American Institute of Physics. [doi:10.1063/1.3514709]

I. INTRODUCTION

Due to various device applications ranging from light emitting diodes over photovoltaic cells to organic field effect transistors, organic semiconducting thin films have attracted significant attention. An important prerequisite for device applications are molecular films with reproducible morphology, depending however on various growth parameters like the reactivity of the substrates, growth temperature, and deposition rate. For crystalline organic materials, microscopic interpretations of charge transport and optical properties rely heavily on the previous knowledge of the arrangement of the molecules in the crystal unit cell, as determined, e.g., by x-ray diffraction.

Diindenoperylene (DIP), synthesized as early as in 1937, has received renewed attention due to relatively high charge carrier mobilities, well defined ordering of thin films, the existence of two polymorphs, and interesting growth properties. From a comparison of thin films with these polymorphs, it turned out that the thin film phase corresponds to a substrate-stabilized high-temperature phase. In a recent investigation of the optical response of dissolved DIP and crystalline thin films, we have shown that the vibronic progression of the dissolved chromophore is modified in the solid, revealing the formation of Frenkel excitons and their interference with charge transfer (CT) states. Nevertheless, even in the crystalline phase, the largest parameters involved in the calculated shape of the optical response arise from the deformation of a DIP molecule in its relaxed excited geometry.

Preresonant and resonant Raman spectroscopy in the region of a strong dipole-allowed transition gives detailed information on the projection of the deformation of a molecule in its relaxed excited geometry onto internal vibrations. Therefore, Raman spectra are complementary to optical absorption and photoluminescence (PL), where elongations of internal vibrations in an excited molecule give rise to pronounced vibronic progressions together with a Stokes shift between the average excitation and de-excitation energies. After the Raman process, the molecule returns to an excited vibrational level in its electronic ground state, so that in principle, the Raman modes coincide with the vibronic sidebands observed in fluorescence. However, only under favorable conditions like single molecules embedded in droplets of superfluid helium or in Shpol’skii matrices, the vibronic features of the fluorescence or fluorescence excitation spectra can be observed with high resolution, whereas the optical spectra of chromophores dissolved in typical solvents suffer from a large broadening arising from fluctuations of the surrounding solvent molecules. Hence, sidebands of individual vibrational modes cannot be resolved because they merge into broad Gaussian bands. For these reasons, Raman spectroscopy is the method of choice for an investigation of the coupling between optical excitations and internal vibrations of a molecule. Together with calculations based on density functional theory (DFT), a microscopic assignment of the observed features to specific internal vibrations can be obtained.

In Sec. II, we present the theoretical background of resonant and preresonant Raman spectra. Section III is devoted to the experimental results obtained on DIP films which are interpreted in Sec. IV with density functional calculations of the deformation of a DIP molecule in its relaxed excited geometry. Deviations between different resonance conditions are
analyzed in Sec. V. The main achievements of the present work are summarized in Sec. VI.

II. THEORETICAL BACKGROUND

A. Deformation of an excited molecule

The geometry of a molecule depends on its electronic configuration, so that the electronic ground state and the lowest excited state after a HOMO–LUMO transition correspond to slightly different shapes. From a projection of the respective deformation onto the vibrational eigenvectors, the reorganization energy \( \lambda \) on the ground or excited state potential surface can be decomposed into contributions of different vibrational modes according to

\[
\lambda = \sum_k S_k \hbar \omega_k,
\]

where \( \omega_k \) is the vibrational frequency and \( S_k \) the Huang–Rhys factor of mode \( k \). Density functional calculations addressing these quantities will be discussed in Sec. IV.

B. Raman cross sections

The present work concentrates on the dominating Raman cross sections arising from breathing modes, so that all except for the lowest modes have energies well above thermal energy at room temperature. Therefore, in the following, we shall present the equations underlying Raman spectroscopy under the assumption that all breathing modes are in the vibrational ground state, and known correction factors at finite temperature will be added in the final equations. At zero temperature, the differential cross section of the Stokes Raman temperature will be added in the final equations. At zero temperature, the differential cross section of the Stokes Raman cross section can be expressed as

\[
\frac{d\sigma(\omega_L, \omega_k)}{d\Omega} = \sum_f \frac{\omega_L \omega_k^3}{16\pi^2 \hbar^2 e^4} \frac{\left| \sum_m \left( \frac{\langle f|\mathbf{e}_s \cdot \hat{\mu}|m\rangle\langle m|\mathbf{e}_L \cdot \hat{\mu}|i\rangle}{\omega_m - \omega_i - \omega_L - i\gamma} + \frac{\langle f|\mathbf{e}_s \cdot \hat{\mu}|m\rangle\langle m|\mathbf{e}_L \cdot \hat{\mu}|i\rangle}{\omega_m - \omega_i + \omega_L + i\gamma} \right|^2}{\omega_m - \omega_i - \omega_L - i\gamma}
\]

where \( \omega_L \) and \( \omega_k \) are the incident and scattered frequencies, and \( \mathbf{e}_s \) and \( \mathbf{e}_L \) the corresponding polarization vectors. The initial state \( |i\rangle \) is the lowest vibrational level in the electronic ground state, and the final state \( |f\rangle \) may contain excited vibrational levels in the electronic ground state where, in the following, we shall concentrate on excitations containing only a single vibrational quantum of an arbitrary internal breathing mode. The intermediate state \( |m\rangle \) is a vibrational level of the excited state coupled by the dipole operator \( \hat{\mu} \) to the electronic ground state.

Equation (2) can be evaluated most easily if the excited state potential of a molecule consists of a sum over displaced harmonic oscillators for all symmetry-conserving internal modes. Under the additional assumption of vanishing Dushinsky rotations, a transition dipole independent of the nuclear geometry, and the same vibrational frequencies on both potential energy surfaces involved, the matrix elements for excitation of a single vibration \( \hbar \omega_k \) factorize into contributions of different internal modes,

\[
\langle m|\hat{\mu}|i\rangle = \mu_{ex}\langle m_{k}^{(e)}|\delta_{k}^{(e)}\prod_{j \neq k} \langle m_{j}^{(e)}|\delta_{j}^{(e)}\rangle,
\]

\[
\langle f|\hat{\mu}|m\rangle = \mu_{ex}\langle 1_{k}^{(e)}|\delta_{k}^{(e)}\prod_{j \neq k} \langle 0_{j}^{(e)}|\delta_{j}^{(e)}\rangle,
\]

with the abbreviation \( \mu_{ex} = |\langle e|\hat{\mu}|g\rangle | \) for the transition dipole, and similarly for its adjoint. The superscript \( e \) stands for the excited state, and \( g \) for the ground state, and \( |m_{e}^{(e)}\rangle \) denotes the vibrational level \( m \) of mode \( k \) in the excited potential. The Franck–Condon factors \( \langle m_{j}^{(e)}|\delta_{j}^{(e)}\rangle \) can be obtained from the Poisson progression over the transition probabilities involved in absorption,

\[
P(|0_{e}^{(e)}\rangle \rightarrow |m_{j}^{(e)}\rangle) = \left| \langle m_{j}^{(e)}|0_{e}^{(e)}\rangle \right|^2 = e^{-S_{j}^{(e)} m_{j}^{(e)}!\left[ m_{j}^{(e)}! \right]}. (5)
\]

where the Huang–Rhys factor \( S_{j} \) of each mode can be deduced from its contribution \( S_{j}\hbar \omega_{j} \) to the reorganization energy \( \lambda \). In Eqs. (2)–(4), each mode \( j \neq k \) returning to its lowest vibrational level after the scattering process gives a matrix element coinciding with the normalized transition probability observed in absorption according to Eq. (5). The product of the Franck–Condon factors of the vibrational mode \( k \) excited by the scattering process can be calculated as

\[
\langle 1_{k}^{(e)}|\delta_{k}^{(e)}|m_{k}^{(e)}|0_{e}^{(e)}\rangle
\]

\[
eq e^{-S_{k}^{(e)} m_{k}^{(e)}!\left[ m_{k}^{(e)}! \right]}. (6)
\]

C. Preresonant Raman spectra

A compact evaluation of the sum over intermediate states in Eq. (2) can only be obtained in the preresonant case. Replacing all modes except for the mode \( k \) by a detuning \( \delta \) with respect to the laser frequency \( \omega_{L} \),

\[
\delta = \omega_{00} + \sum_{j \neq k} \omega_{j} - \omega_{L},
\]

the resonance denominator can be expanded into a Taylor series,

\[
\frac{1}{\omega_{m} - \omega_{i} - \omega_{L} - i\gamma} = \frac{1}{\delta + \frac{m_{k}^{(e)}\omega_{k}}{\delta} - i\gamma} \approx \frac{1}{\delta} \left( 1 - \frac{m_{k}^{(e)}\omega_{k}}{\delta} \right).
\]

Inserting this Taylor series expansion and the expression (6) into the sum in Eq. (2), the lowest order gives a vanishing contribution, but the first order results in

\[
- \frac{1}{\delta^2} \sum_{m_{k}^{(e)}} m_{k}^{(e)} \omega_{k} \left| 1_{k}^{(e)} \right| \left| m_{k}^{(e)} \right| \frac{\left| 0_{e}^{(e)} \right|}{\delta^2} = \sqrt{\sum_{k} \omega_{k} \delta^2}.
\]
Taking an average over the detunings, $\langle 1/\delta^2 \rangle$, the absolute square of the sum in Eq. (2) gives the following Raman cross section
\[
\frac{d\sigma(\omega_L)}{d\Omega} \propto \frac{\omega_L \omega_s^3}{16\pi^2\hbar^2c^3} \langle e_l \cdot \hat{\mu}_{\text{ex}} \rangle^2 \times \langle e_L \cdot \hat{\mu}_{\text{ex}} \rangle^2 \left(\frac{1}{\delta^2}\right),
\]
where in the average $\langle 1/\delta^2 \rangle$ each vibrational level in the excited state contributes according to the product of the transition probabilities defined in Eq. (5). The fact that the cross section is proportional to $\langle 1/\delta^2 \rangle^2$ gives a direct measure of the large resonance enhancement of the Raman signal when the detuning from full resonance is decreased. At finite temperature, the cross section for Stokes Raman scattering increases due to the thermal occupation of each mode,
\[
\frac{d\sigma(\omega_L)}{d\Omega} \propto S_k \omega_s^2 \left[1 + n_{1h}(\hbar\omega_k, k_B T)\right] \left(\frac{1}{\delta^2}\right)^2.
\]

### D. Resonant Raman spectra

In the fully resonant case, the Taylor series expansion in Eq. (8) cannot be used, so that the resulting cross section will differ from the compact result in Eq. (11). The analytical derivation summarized in Sec. II B relies on the assumption of independent molecules, with an excited state potential consisting of displaced harmonic oscillators for internal breathing modes which can easily be parameterized. Albeit, in the crystalline phase, the optical response of a single molecule is modified by transfer of optical excitations between neighboring sites and by the interference between neutral excitations and inter-molecular CT states, so that the Hamiltonian for the excited electronic state does not factorize into independent internal modes. Instead, the transfer of neutral excitations between different sites and the coupling to CT states is formulated in terms of an effective internal vibration, with energy and effective Huang–Rhys factor corresponding to the vibronic progression observed for dissolved DIP molecules.

Therefore, at the present stage, it is not possible to provide an excited state Hamiltonian allowing to determine the vibrational levels $|m\rangle$ required in Eq. (2).

In cases where a suitable Hamiltonian for the excited state is not known in sufficient detail, it was demonstrated that the so-called transformed theory can be used to derive resonance profiles of Raman spectra from the polarizability. The basic ingredients can be motivated from the transformation of the resonant part of the cross section in Eq. (2) into the time domain, neglecting the off-resonant part altogether. This allows to express the cross section for Stokes Raman scattering in the form
\[
\frac{d\sigma(\omega_L)}{d\Omega} \propto S_k \left[1 + n_{1h}(\hbar\omega_k, k_B T)\right] |\Phi(\omega_L) - \Phi(\omega_s)|^2,
\]
where $\Phi$ is the resonant part of the complex polarizability, $n_{1h}$ the thermal occupation of the vibrational mode $k$ excited by Raman scattering, and the scattered frequency $\omega_s$ is redshifted by the frequency $\omega_s, \omega_s = \omega_L - \omega_k$.

The polarizability $\Phi$ can be obtained from the resonant part of the complex dielectric tensor, multiplied from both sides with the polarization vectors $e_L$ or $e_s$ of incident and scattered light, respectively:
\[
\Phi(\omega_L) = e_s \cdot \hat{\epsilon}(\omega_L) \cdot e_L, \quad \Phi(\omega_s) = e_s \cdot \hat{\epsilon}(\omega_s) \cdot e_L.
\]

Transform theory of Raman cross sections was applied successfully to molecules with a rather structured absorption lineshape, so that the difference between the polarizabilities at the laser frequency $\omega_L$ and at the frequency of the scattered light $\omega_s$ results in strongly modulated Raman excitation profiles. In the opposite limit of broad unmodulated absorption bands, transform theory according to Eq. (12) correctly predicts structureless Raman excitation profiles resembling the absorption lineshape. In these cases, the difference between the polarizabilities in Eq. (12) can be replaced to leading order by the derivative at the midpoint between $\omega_L$ and $\omega_s$,
\[
\Phi(\omega_L) - \Phi(\omega_s) \approx \omega_s \frac{|\Phi'(\omega_L + \omega_s/2)|}{\sqrt{\omega_s^2 - (\omega_L - \omega_s)^2}},
\]
where the difference between incident and scattered frequencies has been expressed by the frequency of the excited vibration, $\omega_k = \omega_L - \omega_s$. Inserting this approximation into the Raman cross section, one finds
\[
\frac{d\sigma(\omega)}{d\Omega} \propto S_k \left[1 + n_{1h}(\hbar\omega_k, k_B T)\right] \left|\Phi'(\omega_L - \omega_k/2)\right|^2.
\]

In the preresonant case, the polarizability is dominated by the real part, with a functional form corresponding to a dispersive Lorentzian. In this approximation, the derivative $\Phi'$ depends on the detuning $\delta = \omega_{res} - (\omega_L - \omega_k/2)$ with respect to full resonance as
\[
\Phi'(\omega_L - \omega_k/2) \propto \frac{1}{\delta^2},
\]
so that a dependence on Huang–Rhys factor and detuning like in Eq. (11) is recovered. In cases involving smooth structureless absorption bands with a full width at half maximum (FWHM) much larger than the frequency $\omega_k$ of the vibrational mode, even at resonance the Raman cross section is essentially proportional to
\[
\frac{d\sigma(\omega_L)}{d\Omega} \propto S_k \left[1 + n_{1h}(\hbar\omega_k, k_B T)\right],
\]
with a further dependence on the mode $k$ introduced only via the weakly frequency-dependent derivative of the polarizability in the form $|\Phi'(\omega_L - \omega_k/2)|^2$.

As discussed below, DIP has a highly structured absorption band with several vibronic sublevels of the Frenkel exciton arising from the strong HOMO-LUMO excitation of each molecule. Therefore, for preresonant excitation at $\lambda = 632.8$ nm (1.96 eV), Eqs. (11) and (18) remain a valid approximation, whereas for resonant excitation at $\lambda = 532.1$ nm
(2.33 eV), the refined analysis according to Eq. (12) has to be taken into account.

E. Sum frequencies

Treating two different modes $k \neq l$ explicitly, the detuning according to Eq. (7) is generalized to

$$\delta = \omega_{kl} + \sum_{j \neq k, j \neq l} m_{j}^{(e)} \omega_{j} - \omega_{L}. \quad (19)$$

Raman scattering involving simultaneous excitation of the modes at $\omega_{k}$ and $\omega_{l}$ via the intermediate state at $\epsilon = m_{k}^{(e)} \omega_{k} + m_{l}^{(e)} \omega_{l}$ is governed by the product of the respective matrix elements $\langle 1_{k}^{(e)} | m_{k}^{(e)} | 0_{k}^{(e)} \rangle$ and $\langle 1_{l}^{(e)} | m_{l}^{(e)} | 0_{l}^{(e)} \rangle$ according to Eq. (6) and a Taylor expansion of $1/\omega_{m} - \omega_{i} - \omega_{L} - i \gamma$ analogous to Eq. (8):

$$\frac{1}{\omega_{m} - \omega_{i} - \omega_{L} - i \gamma} \approx \frac{1}{\delta + \epsilon + i \frac{\epsilon}{\delta}}. \quad (20)$$

The second order term contains a contribution

$$\frac{1}{\delta} \left[ 1 - \frac{2m_{k}^{(e)} m_{l}^{(e)} \omega_{k} \omega_{l}}{\delta^{2}} + \ldots \right] \quad (21)$$

Based on similar algebra as in Eq. (9) for the first order Raman scattering, one finds

$$2 \sqrt{S_{L} S_{g} \omega_{k} \omega_{l}} \quad (22)$$

for the respective term, and the Raman cross section generalizing Eq. (10) becomes

$$\frac{d\sigma_{(\omega_{kl})}}{d\Omega} = \frac{\omega_{1} \omega_{2}}{16\pi^{2} c^{2}} \left( \epsilon_{L} \cdot \hat{\mu}_{cg} \right)^{2} \times \left( \epsilon_{L} \cdot \hat{\mu}_{cg} \right)^{2} \frac{2}{\delta^{3}} \quad (23)$$

At finite temperatures, the cross sections for Stokes scattering from sum frequencies $\omega_{k} + \omega_{l}$ have to be corrected by $[1 + n_{th}(\hbar \omega_{k}, \hbar \omega_{l}, k_{B} T)] + [1 + n_{th}(\hbar \omega_{k}, k_{B} T)]$, and frequency differences like $\omega_{k} - \omega_{l}$ by $[1 + n_{th}(\hbar \omega_{k}, k_{B} T)] m_{th}(\hbar \omega_{l}, k_{B} T)$. Due to the steeper dependence on the detuning according to $(1/\delta^{3})^{2}$, second order Raman scattering under resonant conditions is expected to be much weaker than first order scattering. Under full resonance, the assumptions underlying the series expansion in Eq. (21) are no more valid, and a closed analytical expression cannot be obtained. To leading order, Raman cross sections at the sum or difference frequency of two modes $\omega_{k}$ and $\omega_{l}$ remain proportional to the product of the respective Huang–Rhys factors, or $S_{k} S_{l}$.

III. EXPERIMENTAL

A. Film preparation

A clean Au(111) surface was prepared by a very gentle and brief Ar$^{+}$ ion bombardment (500 V), followed by annealing in UHV at approximately $T = 900$ K. On this substrate held at room temperature, thin films of diindenoperylene (DIP) were prepared by organic molecular beam deposition (OMBD) in UHV using strictly controlled evaporation conditions (evaporation rate 3 Å/min). During growth the deposition rate was monitored using a quartz microbalance, and after DIP deposition the nominal thickness of about 4 nm was cross-checked by using the attenuation of the x-ray photoemission signal from the gold substrate.

For the DIP films grown on SiO$_{2}$, a 1 mm thick oxidized Si(100) wafer served as a substrate. The DIP films were grown by OMBD under UHV conditions at a base pressure of $2 \times 10^{-10}$ mbar with the substrate held at a temperature of $T = 400$ K. The growth rate of about 2 Å/min was monitored via a water-cooled quartz-crystal microbalance. For these growth conditions the crystalline structure is well ordered along the surface normal, corresponding to the $\beta$ phase.

B. Film structure

As discussed elsewhere in more detail, for DIP films grown on SiO$_{2}$ substrates held above room temperature, the molecules adsorb with the long axis tilted by about $\theta = 17^\circ$ against the substrate normal. The crystallites have a random azimuthal orientation, so that after averaging over the crystallites in the illuminated area, the largest component of the dielectric tensor coincides with the substrate normal, whereas the two in-plane components are equal and much smaller in size.

Scanning tunneling microscopy of DIP monolayers on gold has determined that DIP adsorbs with the molecular plane parallel to the substrate surface. In thicker DIP films, each type of substrate defines a specific structure with a fraction of lying-down molecules ($\lambda$ phase) and standing molecules ($\sigma$ phase), with a predominance of the $\lambda$ phase on polycrystalline gold and of the $\sigma$ phase on nonmetallic substrates. More specifically, complementary investigations of DIP films on polycrystalline gold performed with x-ray scattering and transmission electron microscopy indicate that in at least 74% of the film volume, the long axis of DIP remains parallel to the substrate. On the other hand, for film thicknesses above 1 nm, x-ray absorption spectroscopy yields an average tilting angle between the molecular normal and the substrate normal in the range between 40 and 50°. Recent highly resolved photoemission electron microscopy investigations on thin films of DIP deposited on Au(111) single crystals have revealed that, although the first monolayer of DIP is adsorbed with the molecular plane parallel to the substrate, the structure of subsequent layers is a compromise between intermolecular interactions and substrate–molecule interactions. As a consequence, the molecules arrange themselves in a herringbone fashion as in the bulk $\beta$ phase, but with the longest lattice vector $c$ of the crystal unit cell parallel to the substrate plane.

In the context of Raman spectroscopy close to resonant with the HOMO–LUMO transition, this film structure defines a preferential orientation of the HOMO–LUMO transition dipoles along the long molecular axes parallel to the
substrate surface. This indicates that the shape of the dielectric function for light polarization parallel to the substrate surface corresponds to the largest element of the dielectric tensor observed for DIP films grown on oxidized silicon, where this largest optical response occurred for electric field along the substrate surface. This indicates that the shape of the dielectric function for light polarization parallel to the substrate surface corresponds to the largest element of the dielectric tensor observed for DIP films grown on oxidized silicon, where this largest optical response occurred for electric field along the substrate surface. This indicates that the shape of the dielectric function for light polarization parallel to the substrate surface corresponds to the largest element of the dielectric tensor observed for DIP films grown on oxidized silicon, where this largest optical response occurred for electric field along the substrate surface.

C. Optical instrumentation and data analysis

Raman spectra of freshly prepared samples were measured ex situ in back-scattering geometry using a confocal Raman spectrometer (LabRam HR 800, Horiba Jobin Yvon) equipped with a frequency-doubled Nd:YAG laser (532.1 nm), a He-Ne laser (632.8 nm), and a CCD detector. The laser beam was focused onto the samples by a 100-fold magnifying microscope objective (NA=0.9) leading to a spot size of about 1 μm in diameter. The spectral resolution was about 2 cm⁻¹. In order to prevent radiation damage, a reduced laser power (<1 mW) was used. The polarization-dependent Raman spectra collected in crossed (I∥) and parallel (I∥) polarization configuration with respect to the incident laser light did not reveal substantial differences, so that the following discussion will be restricted to spectra obtained for parallel polarization. The analysis of the spectra was performed using the Levenberg–Marquardt algorithm for fitting the Raman profiles together with a frequency-dependent background, as implemented in the GNUPLot software package.

D. Resonant Raman spectra for DIP on Au

Figure 1(a) shows resonant Raman spectra recorded ex situ with a laser at 532.1 nm (2.33 eV) from a freshly prepared DIP film on Au(111). The spectra reveal a strong PL background dominated by a broad Lorentzian band centered at 1620 cm⁻¹ below the laser line, or 2.13 eV on an absolute energy scale, and a rising tail of PL bands at lower energies. Both parts of the background resemble PL features of DIP observed earlier. For simplicity, fluctuations of the smooth background of unknown origin were fitted to a very few very broad Lorentzians. The various sharp Raman modes were fitted to Lorentzians with FWHM between 2.5 and 27 cm⁻¹.

The Raman spectra before and after subtracting the PL background are shown in Fig. 1(a), and the positions and intensities of the most prominent Raman bands are summarized in Table I. The spectra visualized in Fig. 1(a) are normalized to the height of the largest scattering cross section at 1285 cm⁻¹. For this specific mode, the splitting into a dominating cross section at 1285 cm⁻¹ and a much smaller contribution at 1289 cm⁻¹ was analyzed in detail, and the sum of these two cross sections was used for the normalization of the measured intensities in Table I.

Out of the 24 \(A_g\) breathing modes of a rectangular DIP molecule, 20 occur in the region covered by the measured Raman spectra. The most intense among the observed Raman modes correspond to the out-of-plane component of the dielectric tensor of DIP in panels b, c, and d.
E. Resonant Raman spectra for DIP on Au

The resonance Raman spectrum for Au has a cross-section of about 0.001 at 221 cm$^{-1}$ and is suppressed by several orders of magnitude. Due to the steep dependence of the Raman cross sections on the detuning according to Eqs. (10) and (11), the intensity of the Raman signal is reduced as well. Figure 1(b) presents the resonant Raman spectra obtained at this wavelength. The sharp Raman lines are superimposed to a fluctuating background dominated by a broad band about 0.1 eV below the laser line. In this energy region, several broad PL bands from DIP have been observed, but the background in Fig. 1(b) does not coincide with the respective energies, so that no assignment to specific PL features can be made. Instead, the broad band at about 800 cm$^{-1}$ below the laser line corresponding to an energy of about 1.86 eV might reveal PL from the gold substrate.29 Below 400 cm$^{-1}$, the background becomes even more structured, so that the cross section of the lowest breathing mode at 221 cm$^{-1}$ could not be analyzed in detail. As no other prominent features are expected in this region, it has been excluded from Fig. 1(b) and Table I.

A comparison of the resonant and the preresonant Raman spectra in Figs. 1(a) and 1(b) reveals that the same breathing modes dominate the spectra. Nevertheless, there are also pronounced differences: First, a rather strong Raman feature at 1420 cm$^{-1}$ could only be observed under resonant excitation at 532.1 nm, second, the splitting of two breathing modes into the pairs at 1285 and 1291 cm$^{-1}$ and at 1383 and 1397 cm$^{-1}$ could not be resolved off-resonantly, and third, all Raman peaks assigned to sum frequencies or difference frequencies do not contribute significantly under off-resonant excitation.

F. Raman spectra for DIP on SiO$_2$

In the following, the discussion of Raman spectra obtained from 30 nm thick DIP film grown on SiO$_2$ will be restricted to the region 1200–1650 cm$^{-1}$ contributing to the progression over an effective internal vibration at about 170 meV (1371 cm$^{-1}$) observed in solution spectra.8 Resonant Raman spectra obtained from these thicker DIP films are shown in Fig. 1(c). With respect to the spectra in Fig. 1(a) obtained at the same laser energy of 2.33 eV, the PL background is about 3.5 times more prominent, indicating a larger PL yield arising from a better crystallinity of the thicker DIP films and a smaller influence of PL quenching at the substrate/DIP interface. The strongest Raman features tabulated in Table II coincide with the vibrational modes contributing to the DIP films on gold, and they can again be assigned to $A_g$ breathing of the free molecule.

Preresonant Raman spectra obtained at a laser energy of 1.96 eV are shown in Fig. 1(d). The oscillatory features of the background are modeled by a sum of broad Lorentzians, so that a fit of the narrow cross sections arising from the breathing modes can be presented separately.

As shown in Table II, both the resonant Raman spectra in Fig. 1(c) and the preresonant Raman spectra in Fig. 1(d) can be assigned to the $A_g$ breathing modes with the largest calculated Huang–Rhys factors. Deviations from the Raman cross sections expected according to Eqs. (11) and (17) remain much smaller than for the DIP film grown on a gold substrate. Therefore, we conclude that Raman spectra from DIP...
TABLE II. Positions of the Raman peaks observed on 30 nm thick DIP films grown on SiO₂ for excitation at λ = 532.1 nm (2.33 eV) and λ = 632.8 nm (1.96 eV), together with the calculated breathing modes and their Huang–Rhys factors S obtained with a constrained DFT scheme (nHOMO = nLUMO = 1) at the B3LYP/TZVP level discussed in Sec. IV C. The calculated mode frequencies scaled by a factor of 0.973 and Huang–Rhys factors scaled by 1/0.973, keeping the reorganization energy of each mode constant.

<table>
<thead>
<tr>
<th>Mode (cm⁻¹)</th>
<th>Int.</th>
<th>λ = 532.1 nm</th>
<th>Int.</th>
<th>Mode (cm⁻¹)</th>
<th>S</th>
<th>S(ho)²</th>
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<tr>
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<td>1285</td>
<td>0.760</td>
<td>1277</td>
<td>0.371</td>
<td>1.000</td>
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<tr>
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<td>0.315</td>
<td>1321</td>
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<tr>
<td>1397</td>
<td>0.430</td>
<td>1397</td>
<td>0.711</td>
<td>1387</td>
<td>0.137</td>
<td>0.436</td>
</tr>
<tr>
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<td>0.344</td>
<td>1458</td>
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<td>1447</td>
<td>0.142</td>
<td>0.491</td>
</tr>
<tr>
<td>1471</td>
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<td>0.020</td>
</tr>
<tr>
<td>1611</td>
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<td>1611</td>
<td>0.677</td>
<td>1594</td>
<td>0.024</td>
<td>0.100</td>
</tr>
</tbody>
</table>

films on weakly reactive substrates like SiO₂ or TiO₂ follow the behavior expected for a free molecule rather closely.

IV. ELECTRONIC TRANSITIONS AND DEFORMATION OF EXCITED MOLECULE

Earlier investigations confirm that DFT gives accurate results for the ground state properties of polycyclic hydrocarbons, including very large molecules like terpylene. Furthermore, calculations of the lowest electronic excitations with time-dependent DFT (TD-DFT) have revealed a reasonable agreement with the observed transition energies. In TD-DFT calculations based on the B3LYP hybrid functional, systematic deviations arising from the DFT and Hartree–Fock weights in this functional compensate to a large extent, so that the resulting transition energies are particularly reliable. Nevertheless, due to the wrong asymptotics of the exchange-correlation functional, TD-DFT produces systematic deviations in specific cases. As an example, the ordering of \(^1L_a\) and \(^1L_b\) transitions may differ from the observed spectra, but in our case where a single dipolar transition of DIP dominates the optical response within the energy range of interest, such shortcomings are hardly relevant.

In all the DFT and TD-DFT calculations presented below, we have used the B3LYP hybrid functional, as implemented in the TURBOMOLE 5.9 program package. Our variational basis has triple-ζ quality with polarized basis functions (TZVP, [5s3p1d][11s6p1d]).

A. Electronic transitions

The geometry of DIP has been optimized with B3LYP/TZVP, and the vertical transition energies have been computed with TD-DFT using the same functional and variational basis set. The lowest dipole-active transitions resulting from this method are tabulated in Table III, revealing that there are no strong transitions within about 1.8 eV above the HOMO–LUMO transition at 2.35 eV. Therefore, Raman spectra excited with laser lines below 2.5 eV are dominated by the resonant or prereesonant enhancement of the HOMO–LUMO transition, so that the deformation pattern in the relaxed excited geometry associated to this transition will determine the relative cross sections of different breathing modes.

B. Relaxed excited geometry

As the lowest transition obtained with TD-DFT involves mainly HOMO and LUMO, a constrained calculation of the excited geometry using fixed occupations nHOMO = nLUMO = 1 can be compared with a TD-DFT optimization of the relaxed excited geometry. The deformation patterns resulting from both approaches have a similar shape, but from a previous analysis of the absorption of dissolved DIP chromophores and other perylene compounds, it was found that the deformation obtained with the constrained scheme is quantitatively more reliable: TD-DFT gives a too small deformation of the relaxed excited geometry. In Fig. 2, we compare the deformation obtained under the constraint nHOMO = nLUMO = 1 with the frontier orbitals. The elongation of the various bonds in DIP follows a simple rule: in cases where a bonding lobe of the HOMO is replaced by a repulsive node of the LUMO, the bond length increases, and bonds where a repulsive node of the HOMO is replaced by a bonding lobe of the LUMO react with a shortening of the respective interatomic distance. The increased strength of bonds along the long axis of the molecule results in a shortening along this direction, whereas the additional nodes of the LUMO roughly parallel to the long axis result in an increase in the width of the excited molecule along its short axis.

C. Elongation of breathing modes

The calculated deformation of an excited DIP molecule is projected onto the vibrational eigenvectors of the \(A_x\) breathing modes, defining in turn the respective Huang–Rhys factors. A weighted average of the strong Raman modes above 900 cm⁻¹ defines a progression over consecutive subbands of
an effective vibrational mode as observed in the optical response of dissolved molecules. Based on a constrained DFT scheme with $n_{\text{HOMO}} = n_{\text{LUMO}} = 1$, the sum over the Huang–Rhys factors for modes above 900 cm$^{-1}$ gives an effective Huang–Rhys factor $S_{\text{eff}} = \sum S_k = 0.93$ for an effective mode $\hbar\omega_{\text{eff}} = \sum_k S_k \hbar\omega_k = 1371$ cm$^{-1} = 170$ meV, in good agreement with the observed vibronic bands of dissolved DIP with $S_{\text{eff}} = 0.87$. A TD-DFT calculation of the relaxed excited geometry significantly underestimates the deformation, resulting in an effective Huang–Rhys factor of only $S_{\text{eff}} = 0.64$, well below the value observed for dissolved DIP.

Out of the 20 calculated breathing modes within the frequency range covered by the experimental Raman spectra, 11 can be assigned to observed features, including nine modes with substantial Huang–Rhys factors above 0.05. Using a common scaling factor of 0.973 for all calculated mode frequencies recommended for the B3LYP functional, the average deviation between calculated and measured modes is $-9$ cm$^{-1}$, or $-0.8\%$. For the specific case of DIP, this residual deviation reveals that a scaling factor of 0.981 accounting for the influence of anharmonicities would be the best choice, so that the average deviation would vanish, and the average absolute deviation would be reduced to 4 cm$^{-1}$.

D. Comparison between measured and calculated cross sections

The Stokes Raman cross sections of DIP on Au will first be analyzed in terms of Eqs. (11) and (18) (compare the last column in Table I). Among the strongest Raman cross sections observed in the preresonant case (calculated) at 1286 (1277), 1397 (1387), 1435 (1421), 1458 (1447), and 1610 cm$^{-1}$.

FIG. 3. Elongation patterns of the six breathing modes with the largest calculated Huang–Rhys factors, with observed and calculated positions. The calculated values are given in parentheses, corresponding to B3LYP/TZVP frequencies scaled by a factor of 0.973.
(1592) cm$^{-1}$, four follow the trends of the calculated Huang–Rhys factors, whereas the mode at 1397 (1387) cm$^{-1}$ is nearly three times stronger than expected. This rather large deviation might be related to a resonance condition between this breathing mode and the second harmonics of a breathing mode at 697 cm$^{-1}$. Moreover, substantial cross sections at 221 (215), 534 (529), and 631 (626) cm$^{-1}$ correspond to rather large calculated Huang–Rhys factors. The absence of significant Raman cross sections in the vicinity of several further calculated breathing modes is easily understood from their very small Huang–Rhys factors. The mode pair observed at 1458 and 1471 cm$^{-1}$ seems to arise from a Davydov splitting of the calculated breathing mode at 1447 cm$^{-1}$ due to the two basis molecules in the crystal unit cell.

The good agreement between measured and calculated Raman intensities demonstrates that DFT-based deformation patterns in the relaxed excited geometry give a quantitatively meaningful measure for the expected Raman cross sections. However, a few exceptions are worth mentioning: first, the modes at 1397 (1387) cm$^{-1}$ and at 1097 (1089) cm$^{-1}$ give much larger cross sections than expected, and second, two substantial cross sections at 1420 and 1579 cm$^{-1}$ observed only under resonant conditions at 532.1 nm cannot be assigned to any breathing modes or their combinations. Instead, from a comparison with modes of different representations, the one at 1420 cm$^{-1}$ is a candidate for a second order process involving a dipole-active $B_{3u}$ out-of-plane mode with a calculated position of 703 cm$^{-1}$, and the one at 1579 cm$^{-1}$ for a second order process based on a $B_{2u}$ out-of-plane mode with a calculated position of 789 cm$^{-1}$. Clearly, these two Raman cross sections cannot be quantified within the theoretical framework summarized in Sec. II. Furthermore, a calculated breathing mode at 1584 cm$^{-1}$ with still relatively large Huang–Rhys factor is not observed. The Raman peak measured under resonant excitation at 1579 cm$^{-1}$ cannot be assigned to this breathing mode because the off-resonant spectra do not show any narrow structure in this region, revealing that the calculated Huang–Rhys factor must be too large.

The Raman modes of DIP films grown on SiO$_2$ summarized in Table II coincide with the respective modes of thinner DIP films on gold in Table I. They show a closer correspondence with the Raman cross sections expected according to Eqs. (11) and (18), including especially the mode pair at 1388 and 1397 cm$^{-1}$. Together with the complete absence of substantial cross sections which cannot be assigned to $A_1$ breathing modes, this indicates that the DIP films grown on SiO$_2$ preserve the spectroscopic properties of a free molecule more closely. A comparison of the two types of DIP films suggests that some of the peculiarities of specific vibrational modes in the DIP films on polycrystalline gold may arise from a modified behavior of molecules in contact to the metal substrate and from a different film structure.

V. RAMAN EXCITATION PROFILES OF DIP ON GOLD

A. Breathing modes

In the following, the polarization function $\Phi$ has to be replaced by the in-plane component of the dielectric tensor.

From the structure of the DIP films on gold summarized in Sec. III B, this in-plane component can be related to the large out-of-plane component of the dielectric tensor observed for DIP films grown on SiO$_2$ substrates, so that the polarizability function $\Phi$ will be chosen accordingly.

Ignoring all the other ingredients of Eq. (12), the following discussion of the Raman excitation profiles will concentrate on the absolute square of the difference of polarizabilities,

$$\big| \Phi(\omega_L) - \Phi(\omega_s) \big|^2.$$  

(24)

Based on the known shape of $\Phi$, Eq. (24) can easily be evaluated for each Raman shift $\omega_L - \omega_s$. As shown in Fig. 4, for small values of $\omega_L - \omega_s$ the difference $|\Phi(\omega_L) - \Phi(\omega_s)|$ is linear in $\omega_L - \omega_s$, so that its square $|\Phi(\omega_L) - \Phi(\omega_s)|^2$ starts proportional to a parabola $(\omega_L - \omega_s)^2$ as in the simplified Raman cross section according to Eq. (11). For pre-resonant excitation, the function $|\Phi(\omega_L) - \Phi(\omega_s)|^2$ drops monotonously with respect to the parabolic reference, reaching a value of about 41% for the highest breathing mode observed at 1610 cm$^{-1}$. Under resonant excitation at 532.1 nm, the polarizability $\Phi(\omega_L)$ at the laser frequency falls into the valley between the Gaussian subbands of the dielectric function at $E_{00} = 2.25$ eV and at $E_{01} = 2.42$ eV, whereas the polarizability $\Phi(\omega_s)$ is sampled across the $E_{00}$ resonance. Therefore, for small arguments $\omega_L - \omega_s$, the difference $|\Phi(\omega_L) - \Phi(\omega_s)|$ starts steeper than linear and $|\Phi(\omega_L) - \Phi(\omega_s)|^2$ steeper than the parabolic approximation, but as soon as $\hbar \omega_s$ drops below $E_{00}$ at a Raman shift of about 600 cm$^{-1}$, the ratio $|\Phi(\omega_L) - \Phi(\omega_s)|^2/(\omega_L - \omega_s)^2$ falls to values far below one, down to only 9% for the highest observed Raman mode at 1610 cm$^{-1}$.

The deviations of the observed Raman cross sections from $S(h\omega_0)^2$ as tabulated in Table I can be interpreted with the Raman excitation profiles in Fig. 4. Under pre-resonant excitation at 632.8 nm, the high frequency region between 1285 and 1610 cm$^{-1}$ is only weakly affected.
because the ratio \(|\Phi(\omega_L) - \Phi(\omega_i)|^2 / (\omega_L - \omega_i)^2\) drops only from 47% down to 41%. Nevertheless, as this ratio rises to 66% at 632 cm\(^{-1}\) and 70% at 534 cm\(^{-1}\), these low frequency modes will be enhanced with respect to the reference mode at 1285 cm\(^{-1}\), as observed. Under resonant excitation at 532.1 nm, at 1285 cm\(^{-1}\) the ratio \(|\Phi(\omega_L) - \Phi(\omega_i)|^2 / (\omega_L - \omega_i)^2\) has dropped to only 18%, so that the modes at 632 cm\(^{-1}\) and below seem to be particularly enhanced. More precisely, for Raman modes at low frequencies, the parabolic approximation to \(|\Phi(\omega_L) - \Phi(\omega_i)|^2\) still remains reasonable, whereas for the reference mode at 1285 cm\(^{-1}\) the value of this function is much smaller, so that the respective cross section is strongly reduced, as observed. Residual deviations between observed and calculated Raman cross sections may be associated to modified optical properties in the first few monolayers, as observed recently for the growth of different molecular semiconductors even on nonreactive substrates.\(^{47}\)

B. Sums and differences of breathing modes

Even under resonant excitation at 532.1 nm, the Raman cross sections at sums \(\omega_k + \omega_l\) and differences \(\omega_k - \omega_l\) of two breathing modes at \(\omega_k\) and \(\omega_l\) remain much smaller than the first order scattering of each mode contributing. For pairs of Raman peaks involving the same breathing modes, like the ones at 754 cm\(^{-1}\) and 313 cm\(^{-1}\) interpreted as \(\omega_k \pm \omega_l = 534 \pm 221\) cm\(^{-1}\), the intensities should scale as \([1 + n_{\text{th}}(\omega_k, k_B T)] [1 + n_{\text{th}}(\omega_l, k_B T)]\) and \([1 + n_{\text{th}}(\omega_k, k_B T)] n_{\text{th}}(\omega_l, k_B T)\). Based on the thermal occupation \(n_{\text{th}}(\omega_k, k_B T) = 0.53\) for the lowest breathing mode at 221 cm\(^{-1}\), the ratio between the cross sections at the sum and difference frequencies should be about 2.9, in reasonable agreement with the observed ratio of 2.1. Also for the two Raman peaks at 854 and 411 cm\(^{-1}\), an interpretation as \(631 \pm 221\) cm\(^{-1}\) should give the same intensity ratio of 2.9, but the agreement with the observed ratio of 5.6 seems somewhat less convincing. Presumably, such deviations can be related to more complicated but unknown resonance profiles for sums and differences of strongly elongated breathing modes.

VI. CONCLUSION

In the present work, experimental Raman spectra obtained on thin DIP films deposited on gold or SiO\(_2\) were interpreted with DFT-based calculations of the deformation of a single DIP molecule in its relaxed excited geometry. From a comparison with the vibronic subbands of the absorption spectra determined on dissolved DIP molecules, the results from the constrained DFT calculation turned out to be more reliable, so that they have been used throughout the present analysis of resonant and preresonant Raman spectra. Due to the strongly modulated dielectric function of DIP thin films, for a quantitative comparison of the observed Raman signals of breathing modes at low and high frequencies, it was necessary to calculate the Raman resonance profiles directly from the frequency-dependent dielectric response. This analysis has provided some quantitative insight into the apparent resonant enhancement of the cross sections arising for breathing modes at moderately high frequencies with respect to the strongly elongated high frequency modes in the region between 1286 and 1610 cm\(^{-1}\). As expected, simpler approximations for the calculated Raman cross sections have remained more reliable for preresonant excitation. A few of the observed structures in resonantly enhanced Raman spectra have remained assigned to sums or differences of strongly elongated breathing modes. Under preresonant excitation, the respective mode combinations have remained below the detection limit because their intensities drop with a higher inverse power of the detuning. In relatively thick DIP films grown on SiO\(_2\), the expected spectroscopic signature of an excited molecule was followed more closely with respect to the much thinner DIP films deposited on gold. On the other hand, the specific structure of DIP on gold favored Raman signals from combinations of breathing modes, a feature which could not be observed in the thicker DIP film on silicon oxide with its larger and differently oriented crystallites. Therefore, the different structures of both types of samples have allowed us to reveal several complementary aspects of the respective Raman spectra.

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42The deformation in the relaxed excited geometry as displayed in Fig. 2 of Ref. 8 was misrepresented for several atoms, including especially the indeno groups. Nevertheless, the projection schemes underlying the tables in the present work and the interpretation of the solution spectra in Ref. 8 are both correct. Moreover, Ref. 8 contained a sign error of the hole transfer $t_h$ required in the Frenkel–CT exciton model. The correction of this error improves the agreement between model calculation and measured spectra and leaves the conclusions of Ref. 8 unaffected (compare Table XII and Sec. VIII.F of Ref. 9 for details).