LMG 3 – Modelling the Nuclear Structure and Dynamics of Molecules in Different Environments

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In this poster, we showcase three collaboration projects of the past two years, in which our group led the theoretical developments. The theory focuses on the determination of the nuclear structure and dynamics of molecular crystals, adsorbed molecules and isolated molecules, in which a connection to experimental techniques that probe the electronic structure is also sought.

Nuclear Dynamics Accompanying	Tip-Enhanced Raman Scattering	Structure of Adsorbed and Iso-
Singlet Exciton Fission (SEF)	Spectra with Realistic Fields	lated Flexible Molecules
Ultrafast Processes in SEF	Single-Molecule TERS	Motivation

We studied the nuclear structure and dynamics involved in the SEF in pentacene single crystals [1]. We employed molecular dynamics simulations and real-time time-dependent density functional theory (RT-TDDFT), in addition to a structure factor analysis to identify the character of the low-frequency coherent motions which play a key role in the disintegration of the triplet pairs on ultrafast time scales.

Theory Modelling

Collaboration with H. Seiler (FHI-Berlin), H. Schwörer (MPSD Hamburg) and coworkers.



Figure 1: Experimental Data (a) Difference between the diffraction pattern at t = 1.5 ps after photoexcitation and prior to photoexcitation. (b) Changes in intensity as a function of delay for selected Bragg reflections. Inset shows the FFT spectrum of the oscillating residuals for $(0\overline{2}0)$.

Femtosecond electron diffraction on single-crystal pentacene (further experimental details in Ref. [1]) points to coherent motion after photoexcitation along the long-axis (Z) of the molecules.

^(b) 3.99 THz (C)

A high-resolution visualization of individual molecular vibrations in real space can be obtained by tip-enhanced Raman scattering (TERS) applied to single molecules [3]. Currently, methods commonly used to simulate TERS rely on a crude approximation of the local electric field. We derived a novel method to compute TERS spectra by combining TDDFT and Density Functional Perturbation Theory (DFPT) to calculate Raman cross sections with realistic local fields. We collaborate with F. Bonafé and H. Appel (MPSD) in this work.

Theory

Assuming a negligible charge overlap between the substrate and the tip, the total energy of the system, U_{tot} is

 $U_{\text{tot}}(\boldsymbol{E}^{f}) = U_{\text{tot}}^{0} - \int d\boldsymbol{r} \rho(\boldsymbol{r}) \boldsymbol{r} \boldsymbol{E}^{f} - \int d\boldsymbol{r} \rho(\boldsymbol{r}) \hat{\Phi}^{n}(\boldsymbol{r}, \boldsymbol{E}^{f}) \\ \approx U_{\text{tot}}^{0} - \int d\rho(\boldsymbol{r}) \Big[\boldsymbol{r} + \frac{\partial \hat{\Phi}^{n}(\boldsymbol{r}, \boldsymbol{E}^{f})}{\partial \boldsymbol{E}^{f}} \Big] \boldsymbol{E}^{f},$ (1)

where $\rho(r)$ is the charge density of the system, U_{tot}^0 is the total energy in absence of an external far field, E^f , $\hat{\Phi}^n$ is the Fourier Transform of Hartree potential generated by the interaction of E^f with the tip which gives rise to the local field. Only linear effects with respect to the far field are considered.

In this approach, we obtain $\hat{\Phi}^n$ from atomistic TDDFT calculations, and then evaluate Eq. 1 by Kohn-Sham DFPT with a numerical representation of $\hat{\Phi}^n$ in real space. We implemented this method in the FHI-aims code [4]. See also time-domain analysis of tip-induced local-fields in **THEO 3**. Finding the relevant structures of flexible molecules in different conditions can pose a substantial challenge. This task is of high importance for revealing structure-property relationships and for parametrizing multi-scale models that can treat self-assembly. Such studies require (i) accurate energetics for a system containing elements across the periodic table and where considerable charge rearrangement and chemical reactions can occur (ii) sampling and representing a large conformational space, and (iii) dealing with structure motifs that can only be represented by unit cells containing hundreds of atoms.

Description of GenSec package

GenSec [6] performs quasi-random global structure searches, with the ability to choose from internal molecular degrees of freedom and sample them with respect to specified fixed surroundings. Geometry optimizations (GO) are performed in connection with the Atomic Simulation Environment (ASE), which allows the use of various electronic structure packages. We have substantially accelerated the GO by designing approximate Hessian preconditioners for hybrid organic-inorganic systems.







Figure 2: Electron-phonon coupling and vibrational spectrum (a,b) Ehrenfest dynamics (RT-TDDFT, Octopus code [2], PBE+D3 functional) and (normalized) projection of atomic displacements on the crystal vibrational normal modes. Harmonic frequencies shown on the y axis. (c) Vibrational density of states (vDOS) from MD (AIREBO potential) on $3 \times 3 \times 2$ supercells. Projections onto the X, Y and Z axes (see sketch). Dashed lines correspond to carbon atoms only, solid lines to the molecular center of mass.

Molecular motion after singlet excitation (RT-TDDFT) shows motion predominantly along X and Y. However, long-range sliding motions along Z are present at equilibrium.



Figure 3: Phonon-phonon coupling 2D-vDOS correlation plots extracted from MD directly reveal phonon correlations. (a) 2D-vDOS correlation plot obtained based on the atomic motion projected on the X, Y, and Z molecular axes defined in Fig. 2.



Figure 4: Schematic representation of the simulation scheme. The atomistic tip is replaced by its field-induced Hartree potential, $\hat{\Phi}^n$, depicted by the red ellipsoids. $\hat{\Phi}^n$ produces the local-field that interacts with the substrate and generates the TERS signal.

An Efficient and Accurate Method



Figure 5: Preliminary Results: Simulated TERS spectra of isolated benzene molecule (LDA functional) for different tip-substrate distances. Local field obtained from linear-response TDDFT simulations on a pyramidal Ag tip structure.

Outlook

The new method inherits the high computational efficiency of DFPT and allows a realistic *ab initio* description of the tipinduced local-fields. It can also naturally incorporate chemical effects arising from the molecule-surface interaction, not available in previous approaches [5]. Work in progress for realistic systems aims to disentangle the impact on the TERS signal coming from chemical enhancements, form of the local-field, and quality of the electronic density response. **Figure 6:** a) Available degrees of freedom: torsion angles (up), position and orientation with respect to fixed frame (down); b) Workflow of GenSec package; c) Available schemes for preconditioning of GO.

Di-L-Alanine on Cu(110)



Figure 7: Energy hierarchy of di-L-alanine structures on the Cu(110) surface, obtained with GenSec (DFT-PBE+vdW) within the 1 eV relative energy range.

(a)



Calculation of 2D correlation spectra shows that motions along Z at around 1 THz correlate with modes along (X and Y) predominantly excited after photoexcitation (1 and 4 THz). Strong indication of phonon-phonon coupling.

Conclusions

We propose that electron-phonon with subsequent phononphonon coupling can explain the Bragg-peak oscillation observed in experiment. Low-frequency motions in the crystal have been shown to strongly impact excitonic transport. These results show that phonon-phonon coupling is necessary for a realistic description of atomic motion in soft crystals and for studying singlet-exciton fission.

References

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Figure 8: (a) Simulated STM image (DFT-PBE) of commensurate structure 7 together with unit cell represented with black dashed lines. (b) Comparison of simulated STM image with experimental STM from Ref. [7]

Outlook

Efficient *ab initio* structure search for adsorbed molecules allows an unbiased identification of deprotonated structures. The structures of peptides in different protonation states are under investigation in collaboration with experimental colleagues in DESY (A. Kotobi, S. Bari).







