

Imaging and Tuning Molecular Levels at the Surface of a Gated Graphene Device

Supporting Information

Alexander Riss^{1,∇,⊗,}, Sebastian Wickenburg^{1,2,⊗}, Liang Z. Tan^{1,2}, Hsin-Zon Tsai¹, Youngkyou Kim^{1,3}, Jiong Lu^{1,4,5}, Aaron J. Bradley¹, Miguel M. Ugeda¹, Kacey L. Meaker¹, Kenji Watanabe⁶, Takashi Taniguchi⁶, Alex Zettl^{1,2}, Felix R. Fischer^{2,7,8,*}, Steven G. Louie^{1,2}, Michael F. Crommie^{1,2,8,*}*

¹ Department of Physics, University of California, Berkeley, CA 94720, USA.

² Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA.

³ Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720, USA.

⁴ Graphene Research Centre, National University of Singapore, 6 Science Drive 2, Singapore 117546, Singapore

⁵ Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

⁶ Advanced Materials Laboratory, National Institute for Materials Science, 1-1 Namiki, Tsukuba, 305-0044, Japan.

⁷ Department of Chemistry, University of California, Berkeley, CA 94720, USA.

⁸ Kavli Energy NanoSciences Institute, University of California Berkeley and the Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA.

Table of Contents

- I. Calculation of Molecular LDOS Using Cumulant Expansion
- II. Fig. S1: Simulated spectral function for LUMO and LUMO+1 of CVB/graphene
- III. Fig. S2: DFT calculated LDOS maps of LUMO and LUMO+1 for CVB/graphene and free-standing CVB.

Calculation of Molecular Electronic LDOS in the Presence of Strong Electron-Phonon Coupling Utilizing the Cumulant Expansion

In order to understand the results of STM spectroscopy of molecular systems exhibiting strong electron-phonon coupling, we must be able to calculate the electronic local density of states (LDOS) or the spectral function under these conditions. Here we describe how we are able to calculate the LDOS for molecular adsorbates using density functional theory (DFT) together with the 1st order cumulant approximation for the electron-phonon coupling.

The electronic LDOS $\rho(\vec{r}, E)$ is related to the measured STM tunneling conductance by

$$\begin{aligned} \frac{dI}{dV} &\propto \rho(\vec{r}, E) \\ &= -2\text{Im}G(\vec{r}, \vec{r}; E) \end{aligned} \quad , \quad (\text{SI-1})$$

where G is the electronic Green's function for the combined electron and phonon system. G is obtained by solving the Hamiltonian

$$H = \sum_j E_j c_j^\dagger c_j + \sum_\nu \omega_\nu a_\nu^\dagger a_\nu + \sum_{ij\nu} M_{ij\nu} c_j^\dagger c_j (a_\nu^\dagger + a_\nu), \quad (\text{SI-2})$$

where c_j^\dagger , c_j are electron creation and annihilation operators and a_ν^\dagger , a_ν are phonon creation and annihilation operators. We will neglect the dependence on electron wavevector k , as well as phonon wavevector q . This is based on the observation that the electron and phonon bandwidths are both relatively small. We have also checked that the electron-phonon matrix elements do not change appreciably with wavevector.

In the following sections, we first describe how the quantities E_j , ω_ν , $M_{ij\nu}$ in Eq. SI-2 are calculated from DFT. With Eq. SI-2 fully parameterized, the cumulant approximation then provides a way to solve the strongly-coupled Hamiltonian in SI-2 to obtain the LDOS.

Calculation of electronic levels and phonon modes within density functional theory:

As a preliminary step for performing the cumulant approximation calculation for $G(\vec{r}, \vec{r}', E)$, we calculate the electronic orbital energies (E_j), phonon frequencies (ω_ν) and electron-phonon matrix elements ($M_{ij\nu}$) using standard DFT-based tools. These quantities serve as inputs to the cumulant approximation calculation (see Eq. SI-6 below).

Phonon frequencies and electron-phonon matrix elements are calculated within the density functional perturbation theory (DFPT) framework^{1,2}. Electronic orbital energies are first calculated within DFT, using the PBE exchange-correlation functional, and then corrected with the GW self-energy³⁻⁵ which accounts for electron-electron correlations not included in DFT for the quasiparticle energies. All calculations are performed for the combined CVB molecule+graphene system, with the inter-molecular lattice constant fixed at the experimental value of 1.13 nm.

Details of the cumulant approximation for G :

In systems with strong electron-phonon coupling, low-order perturbation theory for G can be improved by using the cumulant expansion^{6,7}. This expansion of the Green's function can be conveniently performed in the time domain:

$$G(t) = G_0(t) e^{(G_1(t)+G_2(t)+\dots) / G_0(t)}, \quad (\text{SI-3})$$

where the terms $G_n(t)$ contain the n^{th} power of the electron-phonon coupling, and $G_0(t)$ is the zeroth order Green's function. The 1st order cumulant approximation is as follows:

$$G(t) \approx G_0(t) e^{G_1(t) / G_0(t)} \quad (\text{SI-4})$$

which is known to give an exact solution to Eq. SI-2 when there is only a single electronic orbital⁷. Within this approximation, at $T=0$, the density of states for unoccupied electronic orbital j is written as

$$\rho_j(\omega) = 2\pi \sum_I \frac{1}{I!} e^{-\sum \lambda_{j,I}} \sum_{I_1 \dots I_I} \lambda_{j,I_1} \dots \lambda_{j,I_I} \delta(\omega - (E_j - \Delta_j) - (\Omega_{j,I_1} + \dots + \Omega_{j,I_I})) \quad (\text{SI-5})$$

Here, $I = (i, \nu)$ represents a composite index labeling an electronic orbital i and phonon mode ν , and the sum over I is understood to run over unoccupied electronic orbitals. In Eq. SI-5, the quantities

$$\begin{aligned}
\Delta_j &= \sum_I \frac{|M_{j,I}|^2}{\Omega_{j,I}} \\
\lambda_{j,I} &= \frac{|M_{j,I}|^2}{\Omega_{j,I}^2} \\
\Omega_{j,I} &= E_i + \omega_v - E_j
\end{aligned}
\tag{SI-6}$$

are calculated from the electronic orbital energies E_i , the phonon frequencies ω_v , and the electron-phonon matrix elements $M_{j,I}$, which are all obtained from first-principles calculations.

In this work we have computed Eq. SI-5 which corresponds to the experimental tunneling conductance, $\frac{dI}{dV}$, for a 2-fold degenerate LUMO and a non-degenerate LUMO+1. Our results include Gaussian broadening of δ -functions with a width of 0.07 eV, and are compared to the experiment in Fig. S1.

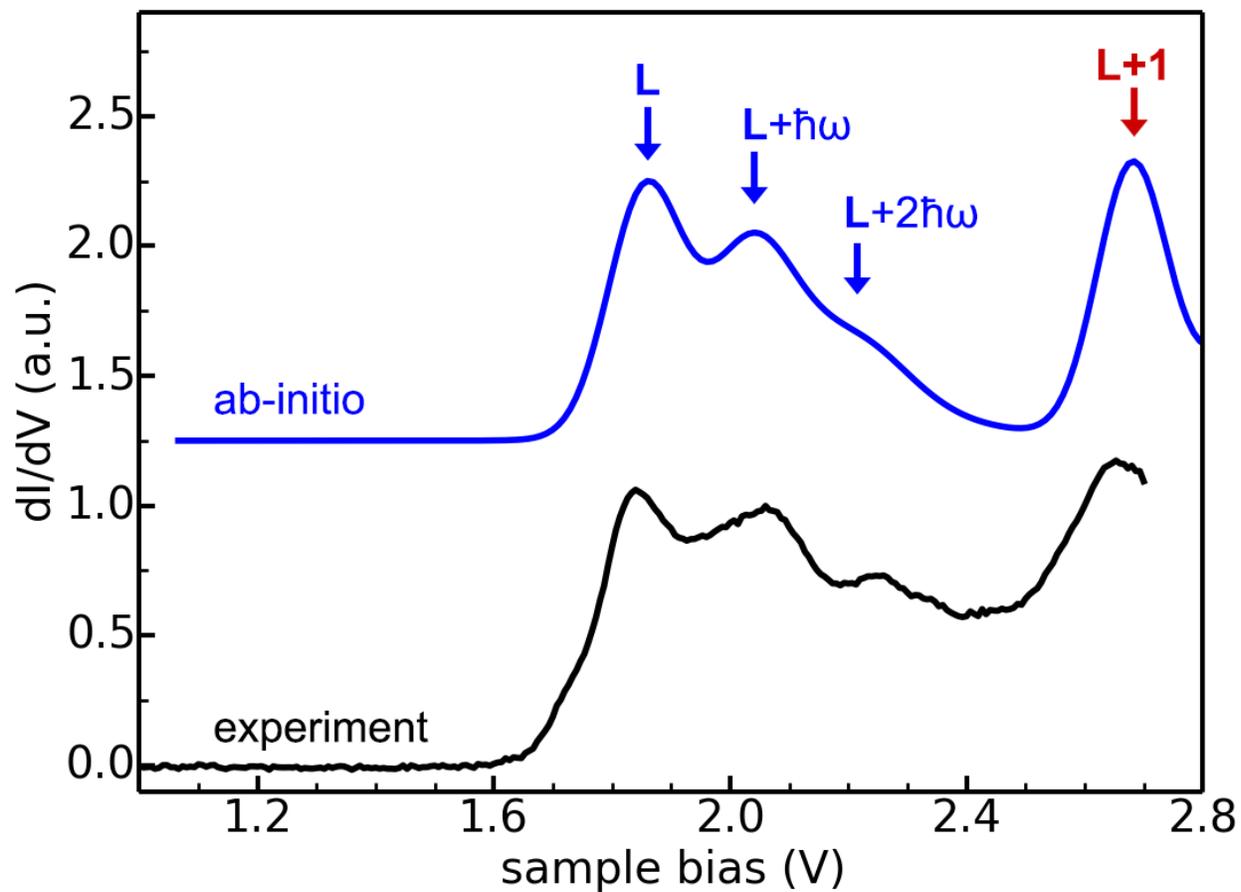


Figure S1: Simulated spectral function for the LUMO and LUMO+1 of CVB/graphene within the cumulant expansion framework (blue), and experimentally acquired dI/dV spectrum of CVB/graphene/BN (black). The dI/dV spectra show resonances associated with the LUMO (“L”), its vibronic excitations (“ $L+\hbar\omega$ ” and “ $L+2\hbar\omega$ ”), and the LUMO+1 (“L+1”).

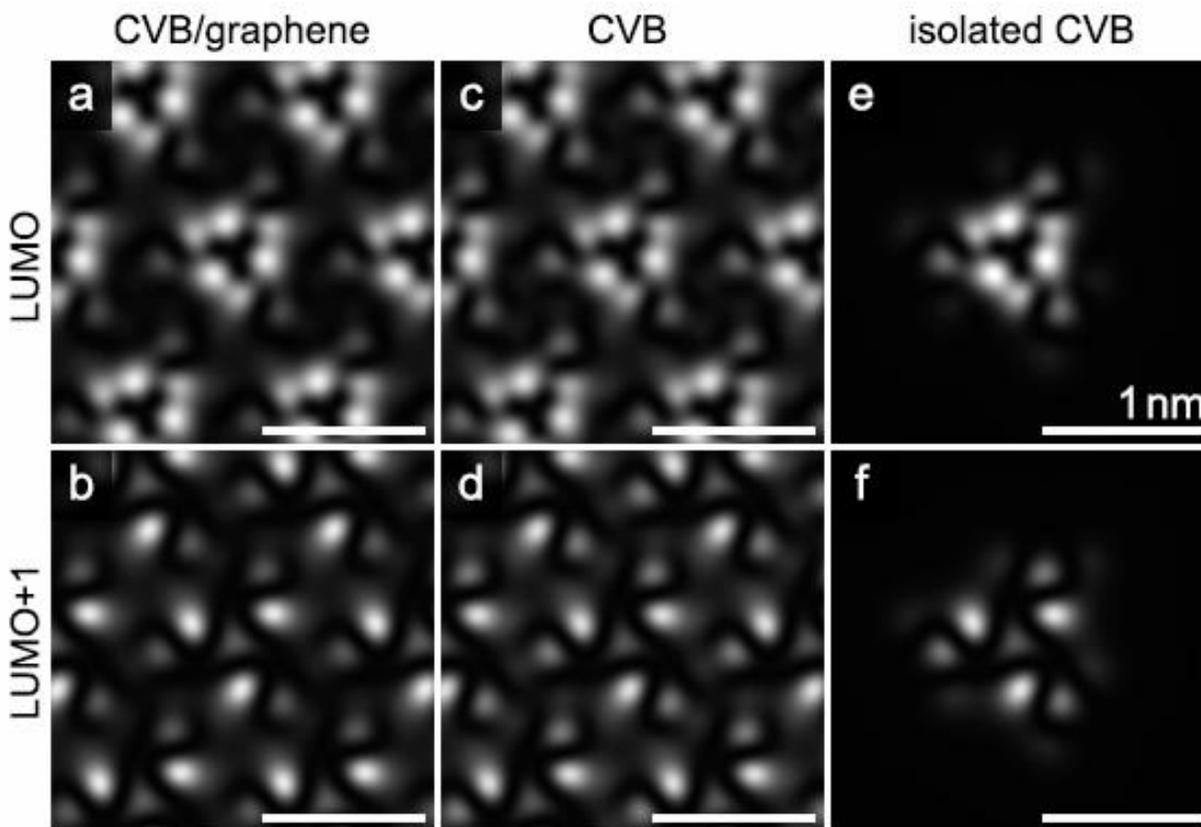


Figure S2: DFT calculated LDOS for **(a)** LUMO for CVB/graphene, **(b)** LUMO+1 for CVB/graphene, **(c)** LUMO for a free-standing CVB layer, **(d)** LUMO+1 for a free-standing CVB layer, **(e)** LUMO for an isolated free-standing CVB molecule, and **(f)** LUMO+1 for an isolated free-standing CVB molecule. In order to calculate the LDOS of the isolated molecules, the size of the supercell was increased by a factor of 4.

References

- (1) Baroni, S.; de Gironcoli, S.; Dal Corso, A.; Giannozzi, P. Phonons and Related Crystal Properties from Density-Functional Perturbation Theory. *Rev. Mod. Phys.* **2001**, *73*, 515–562.
- (2) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I.; *et al.* QUANTUM ESPRESSO: A Modular and Open-Source Software Project for Quantum Simulations of Materials. *J. Phys. Condens. Matter* **2009**, *21*, 395502.
- (3) Hybertsen, M.; Louie, S. First-Principles Theory of Quasiparticles: Calculation of Band Gaps in Semiconductors and Insulators. *Phys. Rev. Lett.* **1985**, *55*, 1418–1421.
- (4) Hybertsen, M. S.; Louie, S. G. Electron Correlation in Semiconductors and Insulators: Band Gaps and Quasiparticle Energies. *Phys. Rev. B* **1986**, *34*, 5390–5413.
- (5) Deslippe, J.; Samsonidze, G.; Strubbe, D. A.; Jain, M.; Cohen, M. L.; Louie, S. G. BerkeleyGW: A Massively Parallel Computer Package for the Calculation of the Quasiparticle and Optical Properties of Materials and Nanostructures. *Comput. Phys. Commun.* **2012**, *183*, 1269–1289.
- (6) Wingreen, N. S.; Jacobsen, K. W.; Wilkins, J. W. Inelastic Scattering in Resonant Tunneling. *Phys. Rev. B* **1989**, *40*, 11834–11850.
- (7) Mahan, G. D. *Many-Particle Physics*; Physics of Solids and Liquids; 3rd ed.; Springer, 2000.