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Electronic Supplementary Information for

Crossover in the inelastic electron tunneling spectra of conjugated molecules with direct Au-C links

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I. VIBRATIONAL MODES OF P2 AND P3

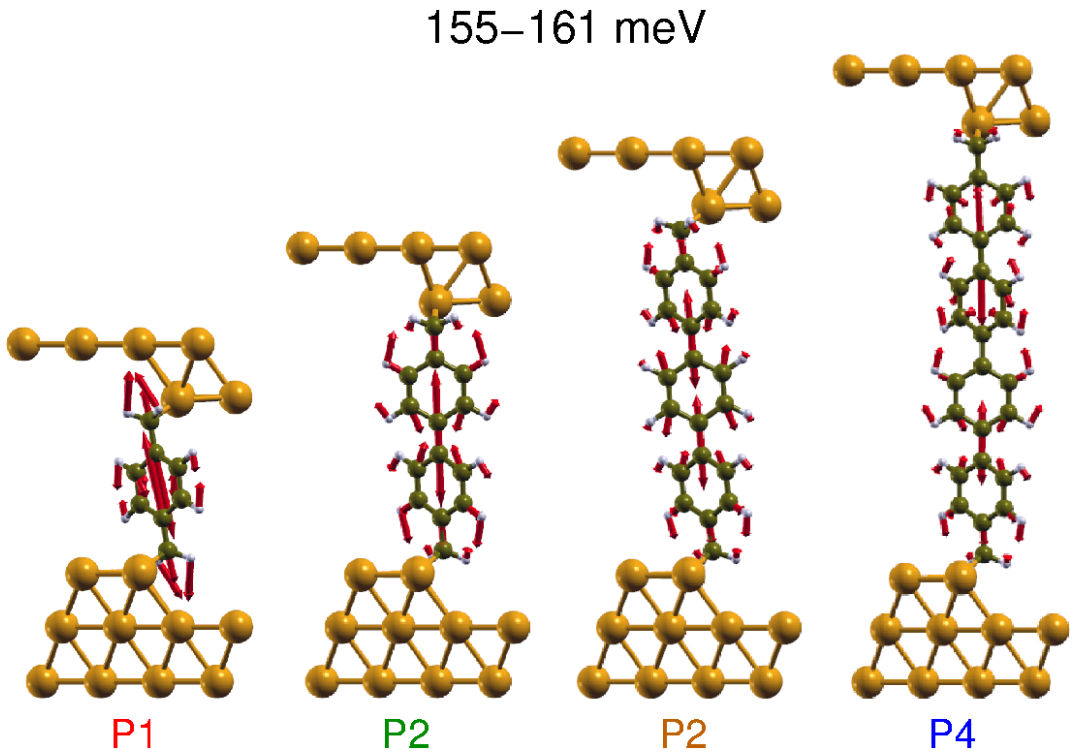


Figure S1: *Extra vibrational modes in the high energy region (155-161 meV) for P1 to P4.*

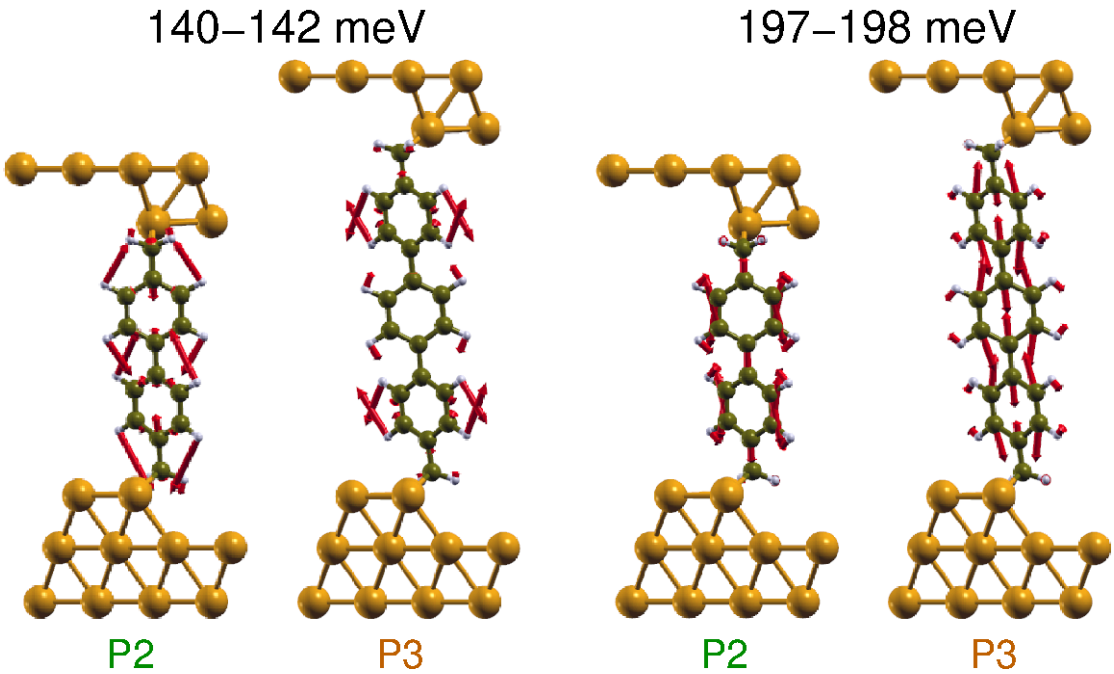


Figure S2: *Vibrational modes in the high energy region (140-142 and 197-198 meV) for P2 and P3.*

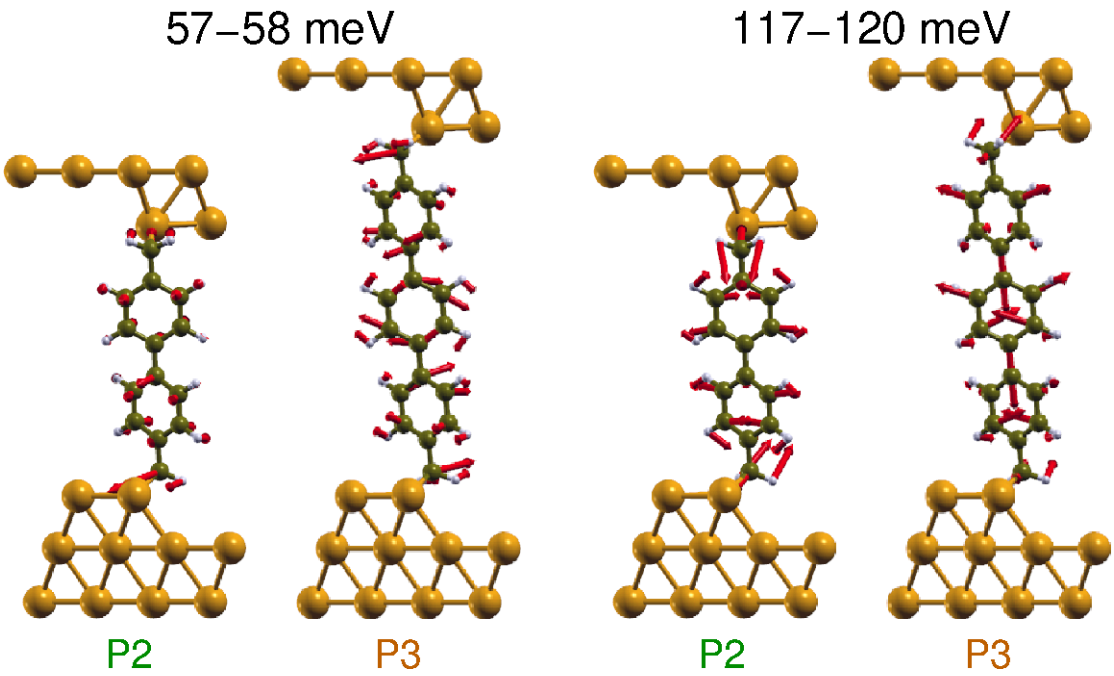


Figure S3: *Vibrational modes in the intermediate energy region (57-58 and 117-120 meV) for P2 and P3.*

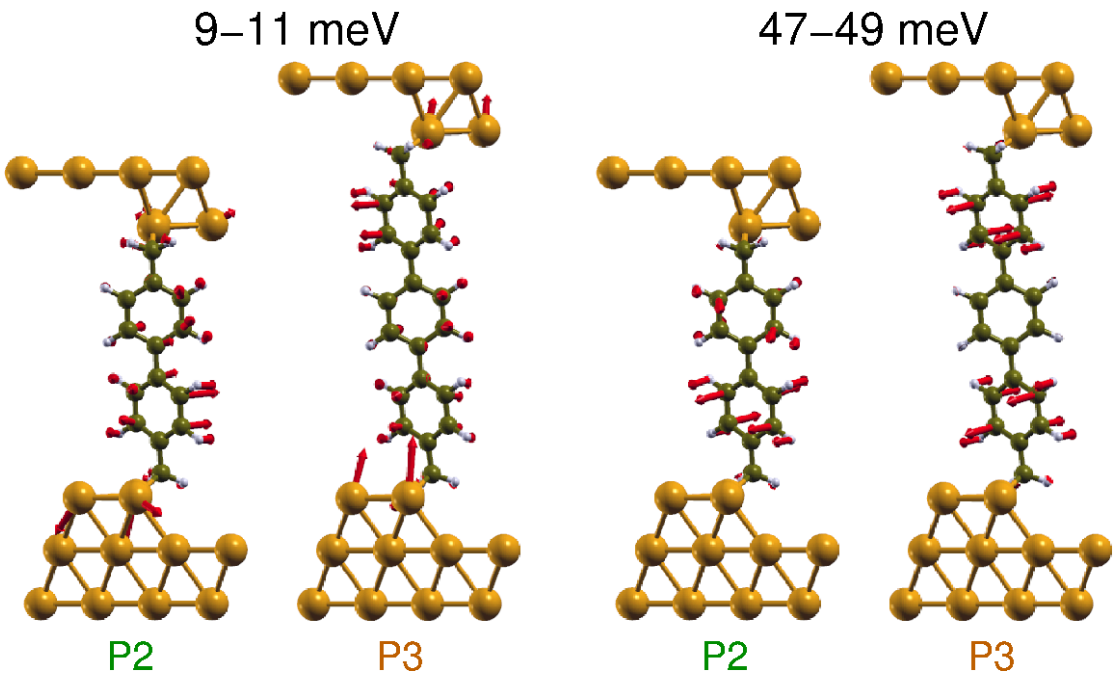


Figure S4: *Vibrational modes in the low energy region (9-11 and 47 -49meV) for P1 and P3.*

II. PROJECTION OF VIBRATIONAL MODES

To characterize the vibrational modes, we project each mode onto i) the plane formed by each benzene ring; ii) the direction perpendicular to each benzene ring, and iii) the Au-C bonds at each junction termination. The mode is defined by a normalized vector $\vec{U}$, which is an eigenstate of the dynamical matrix. For each benzene ring, we define a unitary vector normal to the plane of Carbon atoms $\hat{v}$. The out of plane component of the mode is given by the projection of the mode onto this vector $\hat{v}$,

$$U_{\mathrm{OP}} = \vec{U} \cdot \hat{v}. \tag{S1}$$

To find the in-plane component, we consider the plane formed by $\vec{U}$ and $\hat{v}$, and the plane of the benzene ring. The intersection between these two planes defines a line, and the in-plane component of the mode is given by its projection onto this line,

$$U_{\mathrm{IP}} = \left\| \hat{v} \times \left(\vec{U} \times \hat{v}^{\mathrm{T}} \right) \right\|. \tag{S2}$$

Finally, the component of the mode along the Au-C modes is given by the projection onto the unitary vector connecting these two atoms,

$$U_{\text{AuC}} = \vec{U} \cdot \hat{v}_{\text{AuC}}. \tag{S3}$$

To characterize the modes, we consider the components of the vibrational mode, as well as the size of the vibrational region. This takes into account the increasing number of atoms involved in the mode as more rings are added to the molecule. We define the following projections of the modes:

$$P_{\text{IP}} = \sum_i^{rings} |U_{\text{IP}}|^2 \cdot n_i, \tag{S4}$$

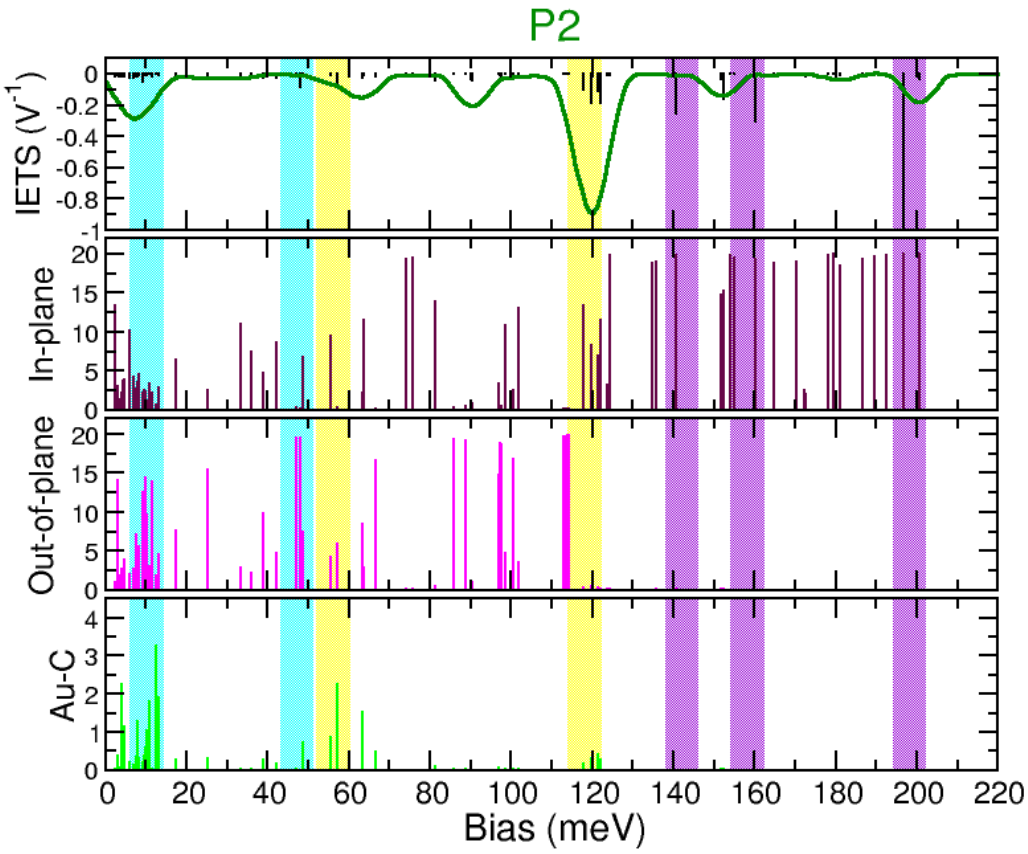
$$P_{\text{OP}} = \sum_i^{rings} |U_{\text{OP}}|^2 \cdot n_i, \tag{S5}$$

$$P_{\text{AuC}} = \sum_i^{rings} |U_{\text{AuC}}|^2 \cdot n_i. \tag{S6}$$

In each case, the square of the components are multiplied by the number of atoms n_i that make up each region (benzene rings or Au-C bonds), and the number of benzene units in each molecule is also taken into account. In the limit of a mode with a perfectly defined character (in plane, out of plane, of Au-C), the quantities P_{IP}, P_{OP}, and P_{AuC} would be equal to the number of atoms involved in the mode. The values of for P_{IP}, P_{OP} and P_{AuC} grow with the length of the molecule to reflect the increasing number of atoms involved in the mode. Values for P_{IP}, P_{OP} and P_{AuC} thus generated are given in Table 1 of the paper.

III. PROJECTIONS AND INELASTIC SIGNAL OF P2 AND P3

In Figures S5 and S6 we plot IETS signal, in plane, out of plane and Au-C projections for P2 and P3.



*F**igure S5:** Top panel, IETS signal with scattering rate for active vibrational modes for P2. Second, third, and fourth panels, in plane, out of plane, and Au-C projections, respectively. Shaded vertical bars highlight low (blue), medium (yellow), and high (magenta) energy regions.*

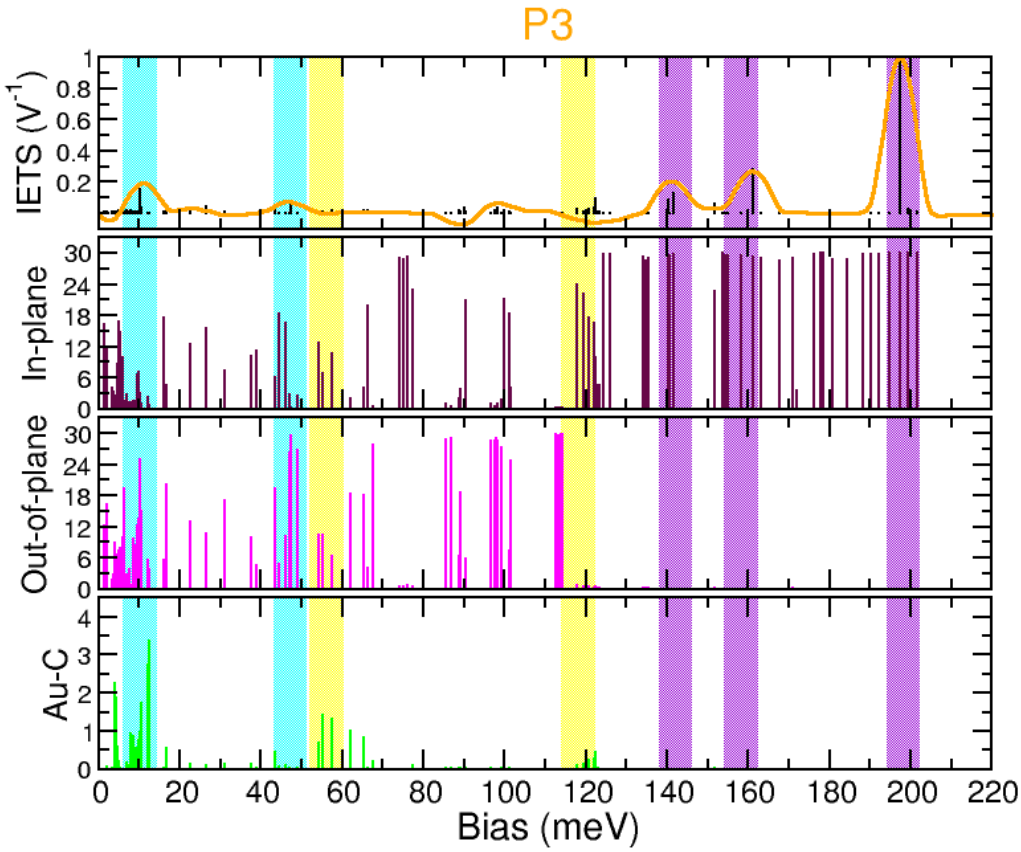


Figure S6: *Top panel, IETS signal with scattering rate for active vibrational modes for P3. Second, third, and fourth panels, in plane, out of plane, and Au-C projections, respectively. Shaded vertical bars highlight low (blue), medium (yellow), and high (magenta) energy regions.*

IV. DEPENDENCE ON TIP APEX

We also used single Au adatoms as electrode terminations and calculated the IETS for the shortest and longest molecules (P1 and P4). The calculated IETS for both tip choices are reported in Fig. S7. The inelastic spectra are very similar to those with trimer tips, showing that the energy of molecular vibrations at the junction and their intensity depend weakly on the choice of electrode apex for these systems. We also identified for adatom structures the modes discussed in the paper (Fig. S8). Therefore, we believe this shows that the trends reported and conclusions of the paper are not affected by the choice of electrode apex.

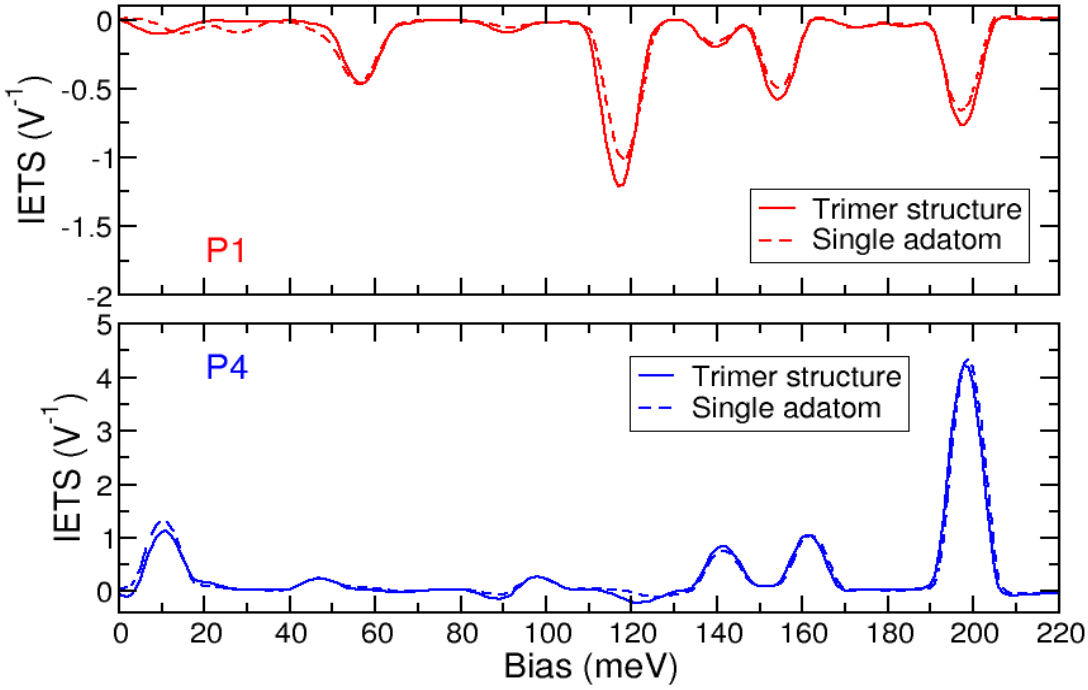


Figure S7: *Calculated IETS for P1 and P4 with different tip terminations.*

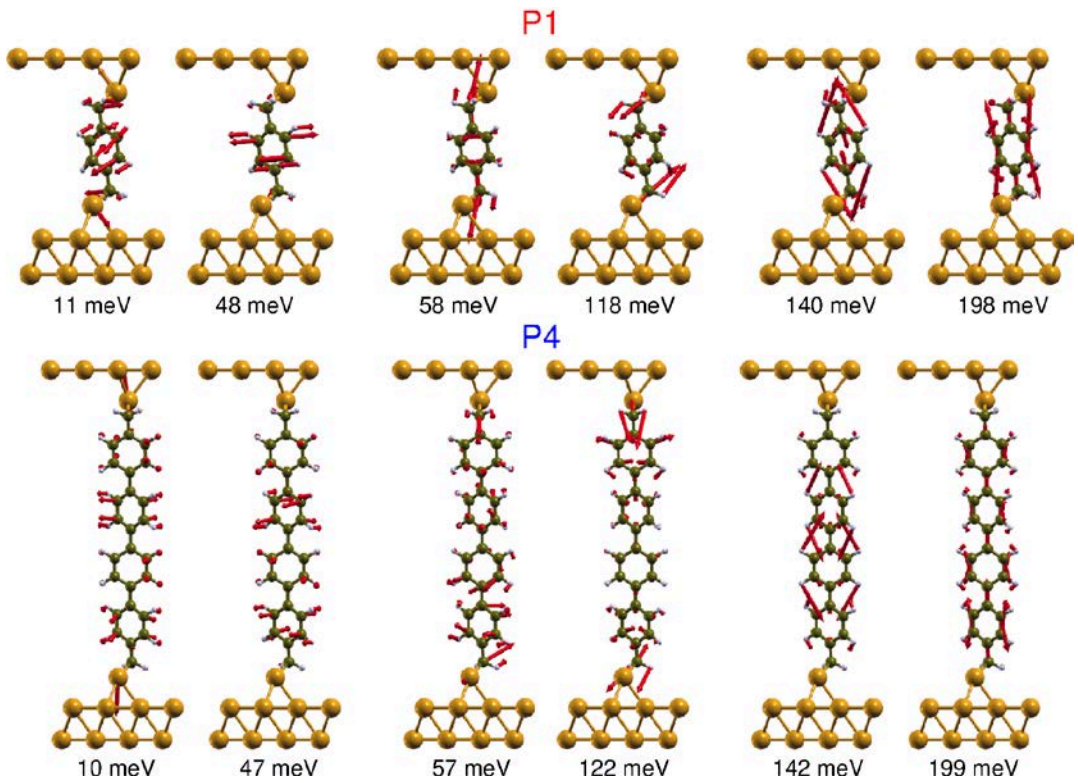


Figure S8: *Selected vibrational modes for the P1 (top) and P4 (bottom) junctions with adatom tip apices.*

V. INELASTIC SPECTRA FOR BOTH BIAS POLARITIES

Fig. S9 shows the calculated inelastic spectra for positive and negative bias polarities.

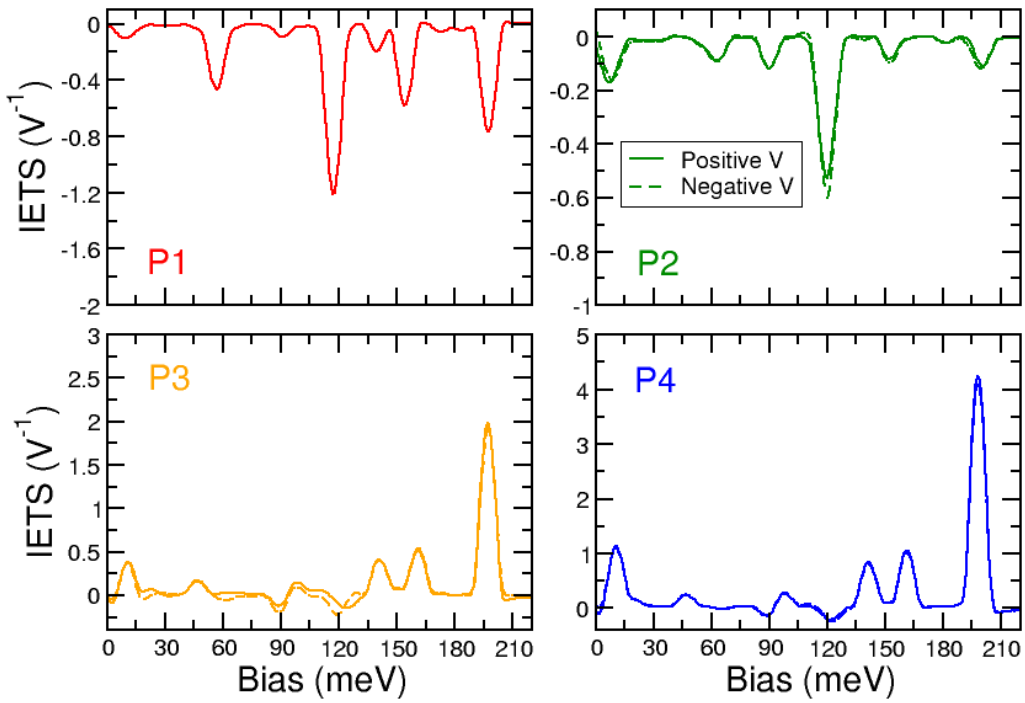


Figure S9: *Calculated inelastic spectra of P1-P4 for both bias polarities. For ease of comparison, the sign of the inelastic amplitude for negative bias voltages has been changed.*