I. EFFECTIVE PHONON HAMILTONIAN IN PRESENCE OF ELECTRON-PHONON COUPLING

We begin with a Hamiltonian containing an electron part $\hat{H}_e$, a phonon part $\hat{H}_{ph}$, and an electron-phonon coupling term $\hat{H}_{e-ph}$,

$$\hat{H}_{tot} = \hat{H}_e + \hat{H}_{ph} + \hat{H}_{e-ph}, \tag{1}$$

with each part described below. We project the electron part into the eletronic eigenstates $|n\rangle$, with $n = 0$ indicating the electronic ground state,

$$\hat{H}_e = \sum_n E_n \hat{c}_n^\dagger \hat{c}_n. \tag{2}$$

Evidently $\sum_n \langle \hat{c}_n^\dagger \hat{c}_n \rangle = 1$. The phonon part is,

$$\hat{H}_{ph} = \sum_j \hbar\omega_j \hat{a}_j^\dagger \hat{a}_j \tag{3}$$

For the electron-phonon interaction, we keep only the $\mathbf{q} = 0$ part of the Frölich Hamiltonian, to simplify the requirement for momentum conservation. This approximation converges to the full Frölich Hamiltonian when the size of the supercell is increased. In addition, the interaction term also contains a correction due to the phonon frequency differences between the electronic states $|n\rangle$ and the ground state. The interaction Hamiltonian is,

$$H_{e-ph} = \sum_j g_{0j} \hat{c}_0^\dagger \hat{c}_0 \left(\hat{a}_j^\dagger + \hat{a}_j \right) + \sum_{n>0,j} \hat{c}_n^\dagger \hat{c}_n \left[g_{nj} \left(\hat{a}_j^\dagger + \hat{a}_j \right) + \hbar\delta\omega_{nj} \hat{a}_j^\dagger \hat{a}_j \right]. \tag{4}$$

When one approximates the wave functions as the Born-Oppenheimer form, $|\Psi\rangle = |\psi_{\mathbf{R}}(\mathbf{r})\rangle |X(\mathbf{R})\rangle$, where $|\psi\rangle$ is the electron wave function and $|X\rangle$ is the phonon wave function, the electron-phonon coupling term should not be thrown away in the separation process. Instead, the coupling is treated in the mean-field manner, leading to an effective phonon Hamiltonian that depends on the electronic state. If the electronic state is $|0\rangle$, the effective phonon Hamiltonian is,

$$\hat{H}_{ph}^0 = \langle 0|\hat{H}_{tot}|0\rangle - E_0 = \sum_j \hbar\omega_j \hat{a}_j^\dagger \hat{a}_j + \sum_j g_{0j} \left(\hat{a}_j^\dagger + \hat{a}_j \right) \tag{5}$$

If the electronic state is $|n\rangle$, the effective phonon Hamiltonian is,

$$\hat{H}_{ph}^n = \langle n|\hat{H}_{tot}|n\rangle - E_n = \sum_j \hbar\omega_{nj} \hat{a}_j^\dagger \hat{a}_j + \sum_j g_{nj} \left(\hat{a}_j^\dagger + \hat{a}_j \right) \tag{6}$$

where $\omega_{nj} = \omega_j + \delta\omega_{nj}$. Using the canonical coordinates,

$$\hat{q}_j = \sqrt{\frac{\hbar}{2\omega_j}} \left(\hat{a}_j^\dagger + \hat{a}_j \right), \tag{7}$$

we can express the phonon Hamiltonians as,

$$\hat{H}_{ph}^0 = \sum_j \frac{1}{2}\hat{p}_j^2 + \frac{1}{2}\omega_j^2 \left(q_j + \frac{g_{0j}}{\omega_j}\sqrt{\frac{2}{\hbar\omega_j}} \right)^2 - \frac{g_{0j}^2}{\hbar\omega_j}, \tag{8}$$

$$\hat{H}_{ph}^n = \sum_j \frac{1}{2}\hat{p}_j^2 + \frac{1}{2}\omega_{nj}^2 \left(q_j + \frac{g_{nj}}{\omega_{nj}^2}\sqrt{\frac{2\omega_j}{\hbar}} \right)^2 - \frac{g_{nj}^2\omega_j}{\hbar\omega_{nj}^2}. \tag{9}$$

The g^2 terms are the polaron binding energy [**?**] and will be neglected. The equilibrium positions are displaced due to electron-phonon coupling. These displacements are independent of the number of phonons and are already reflected in the equilibrium atomic positions of a self-consistent first-principles calculation. Therefore, the change in the equilibrium position between electronic states $|0\rangle$ and $|n\rangle$,

$$\delta q_{nj} = \frac{g_{0j}}{\omega_j}\sqrt{\frac{2}{\hbar\omega_j}} - \frac{g_{nj}}{\omega_{nj}^2}\sqrt{\frac{2\omega_j}{\hbar}}, \tag{10}$$

can be computed by comparing the equilibrium atomic positions between the electronic ground state $|0\rangle$ and the electronic excited state $|n\rangle$ calculated from first-principles. Redefining the origin of the q_j for the electronic ground state, we can write $\hat{H}_{ph}^0$ and $\hat{H}_{ph}^i$ as,

$$\hat{H_{ph}^0} = \sum_{j=1}^{M} \left(\frac{\hat{p}_j^2}{2} + \frac{1}{2}\omega_j^2 q_j^2 \right), \tag{11}$$

and

$$\hat{H}_{ph}^n = \sum_{j=1}^{M} \left[\frac{\hat{p}_j^2}{2} + \frac{1}{2}\omega_{nj}^2 (q_j - \delta q_{nj})^2 \right]. \tag{12}$$

The eigenstates of the phonon Hamiltons relevant to the Raman process are,

$$\hat{H}_{ph}^0 |X_{i,f}\rangle = \Theta_{i,f} |X_{i,f}\rangle, \tag{13}$$

where i and f indicate the initial and the final states, respectively, and,

$$\hat{H}_{ph}^n |X_a\rangle = \Theta_a |X_a\rangle, \tag{14}$$

where a indicates an intermediate state.

II. PERTURBATION THEORY DERIVATION OF RAMAN INTENSITY

The electron-radiation interaction involving two photon frequencies in the interaction picture is,

$$\hat{H}_{e-r}(t) = \sum_n \left(\beta_{1n} \hat{b}_1 \hat{c}_0 \hat{c}_n^\dagger e^{-i\nu_1 t} + \beta_{1n}^* \hat{b}_1^\dagger \hat{c}_0^\dagger \hat{c}_n e^{i\nu_1 t} + \beta_{2n} \hat{b}_2 \hat{c}_0 \hat{c}_n^\dagger e^{-i\nu_2 t} + \beta_{2n}^* \hat{b}_2^\dagger \hat{c}_0^\dagger \hat{c}_n e^{i\nu_2 t} \right). \quad (15)$$

where $\hat{b}_1^\dagger, \hat{b}_1, \hat{b}_2^\dagger, \hat{b}_2$ denote the creation and annihilation operators of each photon mode respectively. Applying the second-order time-dependent perturbation theory, in which the external field is turned on gradually with the factor $e^{\epsilon t}$ with an infinitesimal ϵ, the Raman scattering intensity is expressed as,

$$I(E_L) = \lim_{\epsilon \to 0} \frac{1}{\hbar^4} \frac{d}{dt} \left| \langle \Psi_f | \int_{-\infty}^{t} dt' V_I(t') e^{\epsilon t'} \int_{-\infty}^{t'} dt'' V_I(t'') e^{\epsilon t''} | \Psi_i \rangle \right|^2 \quad (16)$$

where $E_L = \hbar\nu_1$,

$$V_I(t) = e^{i\frac{\hat{H}_{tot}}{\hbar}t} \hat{H}_{e-r}(t) e^{-i\frac{\hat{H}_{tot}}{\hbar}t}$$

and $\Psi_{i,f}$ are the total wave functions,

$$|\Psi_i\rangle = |0\rangle|X_i\rangle, \qquad |\Psi_f\rangle = |0\rangle|X_f\rangle. \quad (17)$$

Expand Eq. (16) as,

$$I(E_L) = \lim_{\epsilon \to 0} \frac{1}{\hbar^4} \frac{d}{dt} \left| \langle \Psi_f | \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' e^{i\frac{\hat{H}_{tot}}{\hbar}t'} \hat{H}_{e-r}(t') e^{i\frac{\hat{H}_{tot}}{\hbar}(t''-t')} \hat{H}_{e-r}(t'') e^{-i\frac{\hat{H}_{tot}}{\hbar}t''} e^{\epsilon(t'+t'')} | \Psi_i \rangle \right|^2. \quad (18)$$

The intensity expression above includes several scattering processes, each of which has a unique combination of photon emission and absorption. However, only the process that conserves the total energy is nonzero, which is the absorption of a photon with frequency ν_1 and the emission of another photon with frequency ν_2,

$$I(E_L) = \lim_{\epsilon \to 0} \frac{1}{\hbar^4} \frac{d}{dt} \left| \langle \Psi_f | \int_{-\infty}^{t} dt' \int_{-\infty}^{t'} dt'' e^{i\frac{\hat{H}_{tot}}{\hbar}t'} \hat{H}^{(2)}_{e-r}(t') e^{i\frac{\hat{H}_{tot}}{\hbar}(t''-t')} \hat{H}^{(1)}_{e-r}(t'') e^{-i\frac{\hat{H}_{tot}}{\hbar}t''} e^{\epsilon(t'+t'')} | \Psi_i \rangle \right|^2, \quad (19)$$

where,

$$H^{(1)}_{e-r}(t) = \sum_n \beta_{1n} \hat{b}_1 \hat{c}_0 \hat{c}_n^\dagger e^{-i\nu_1 t} \qquad H^{(2)}_{e-r}(t) = \sum_n \beta_{2n}^* \hat{b}_2^\dagger \hat{c}_0^\dagger \hat{c}_n e^{i\nu_2 t} \quad (20)$$

Using,

$$\hat{H}^{(1)}_{e-r}(t'')e^{-i\frac{\hat{H}_{tot}}{\hbar}t''}|0\rangle|X_i\rangle = \sum_n \beta_{1n}e^{-i\nu_1 t''-i\frac{E_0}{\hbar}t''}|n\rangle e^{-i\frac{\hat{H}^0_{ph}}{\hbar}t''}|X_i\rangle$$

$$e^{i\frac{\hat{H}_{tot}}{\hbar}t'}\hat{H}^{(2)}_{e-r}(t')e^{i\frac{\hat{H}_{tot}}{\hbar}(t''-t')}|n\rangle|X_i\rangle = \sum_n \beta^*_{2n}e^{\frac{iE_n+\gamma}{\hbar}(t''-t')+\frac{E_0}{\hbar}t'+i\nu_2 t'}|n\rangle e^{i\frac{\hat{H}^0_{ph}}{\hbar}t'}e^{i\frac{\hat{H}^n_{ph}}{\hbar}(t''-t')}|X_i\rangle$$

where γ is introduced to represent the lifetime of the electronic state $|n\rangle$. The electron-radiation coupling constants in Eq. 15 are expanded as,

$$\beta_{1n}\beta^*_{2n} = \beta^0_{1n}\beta^{0*}_{2n} + \frac{\partial\beta_{1n}\beta^*_{2n}}{\partial\vec{q}}\cdot(\vec{q}-\vec{q_0}), \tag{21}$$

where $\vec{q}$ and $\vec{q_0}$ are the general coordinates of the atomic positions for the current configuration and at equilibrium, respectively, and $\beta^0_{1n,2n} = \beta_{1n,2n}(\vec{q_0})$. Taking the inner product of the above two expressions, we find the total intensity as,

$$I(E_L) = \lim_{\epsilon\to 0}\frac{1}{\hbar^4}\frac{d}{dt}\left|\sum_n\int_{-\infty}^{t}dt'\int_{-\infty}^{t'}dt''K_n(t',t'')e^{i\frac{E_n-E_0-\hbar\nu_1}{\hbar}t''+i\frac{-E_n+E_0+\hbar\nu_2}{\hbar}t'+\frac{\gamma}{\hbar}(t''-t')+\epsilon(t'+t'')}\right|^2, \tag{22}$$

with the kernal function,

$$\begin{aligned}K_n(t',t'') \equiv\ & \beta^0_{1n}\beta^{0*}_{2n}\langle X_f|e^{i\frac{\hat{H}^0_{ph}}{\hbar}t'}e^{i\frac{\hat{H}^n_{ph}}{\hbar}(t''-t')}e^{-i\frac{\hat{H}^0_{ph}}{\hbar}t''}|X_i\rangle \\ &+ \frac{\partial\beta_{1n}\beta^*_{2n}}{\partial\vec{q}}\cdot\langle X_f|(\vec{q}-\vec{q_0})e^{i\frac{\hat{H}^0_{ph}}{\hbar}t'}e^{i\frac{\hat{H}^n_{ph}}{\hbar}(t''-t')}e^{-i\frac{\hat{H}^0_{ph}}{\hbar}t''}|X_i\rangle.\end{aligned} \tag{23}$$

The kernal function describes a physical process in which the phonon system initially moves on the ground state potential energy surface (PES), then jumps to the PES of an excited electronic state, and finally jumps back to the groud state PES. The kernel function can be simplified by inserting intermediate phonon states X_a,

$$\begin{aligned}K_n(t,t') &= \left[\beta^0_{1n}\beta^{0*}_{2n}\langle X_f| + \frac{\partial\beta_{1n}\beta^*_{2n}}{\partial\vec{q}}\cdot\langle X_f|(\vec{q}-\vec{q_0})\right]e^{i\frac{\hat{H}^0_{ph}}{\hbar}t}e^{i\frac{\hat{H}^n_{ph}}{\hbar}(t'-t)}\sum_a|X_a\rangle\langle X_a|e^{-i\frac{\hat{H}^0_{ph}}{\hbar}t'}|X_i\rangle \\ &= \sum_a K_{na}e^{i\frac{\Theta_a-\Theta_i}{\hbar}t'+i\frac{\Theta_f-\Theta_a}{\hbar}t},\end{aligned} \tag{24}$$

where

$$K_{na} = \left[\beta^0_{1n}\beta^{0*}_{2n}\langle X_f|X_a\rangle + \frac{\partial\beta_{1n}\beta^*_{2n}}{\partial\vec{q}}\cdot\langle X_f|(\vec{q}-\vec{q_0})|X_a\rangle\right]\langle X_a|X_i\rangle \tag{25}$$

and $\Theta_{i,a,f}$ are the phonon energies of the initial, intermediate and final states, respectively.

Integrating over all the time variables yields the Raman intensity due to the electronic excited state $|n\rangle$ as,

$$\begin{aligned} I_n(E_L) &= \lim_{\epsilon\to 0}\frac{1}{\hbar^2}\frac{d}{dt}\sum_{i,f}\left|\int_{-\infty}^{t}dt'\sum_a \frac{e^{i\frac{\hbar\nu_2-\hbar\nu_1+\Theta_f-\Theta_i}{\hbar}t'+\epsilon t'}K_{na}}{i(E_n-E_0+\Theta_a-\Theta_i-\hbar\nu_1-i\gamma-i\epsilon\hbar)}\right|^2 \\ &= \lim_{\epsilon\to 0}\frac{2\epsilon}{\left[E_s+(\Theta_f-\Theta_i)\right]^2+\epsilon^2\hbar^2}\sum_{i,f}\left|\sum_a\frac{K_{na}}{E_L+E_0-E_n-(\Theta_a-\Theta_i)+i\gamma}\right|^2 \\ &= \frac{2\pi}{\hbar}\sum_{i,f}\left|\sum_a\frac{K_{na}}{E_L+E_0-E_n-(\Theta_a-\Theta_i)+i\gamma}\right|^2\delta[E_s+(\Theta_f-\Theta_i)], \end{aligned} \tag{26}$$

where $E_s=\hbar\nu_2+\Theta_f-E_L-\Theta_i$.

III. RESONANT RAMAN INTENSITY

The resonant condition is $E_L+E_0-E_n\approx 0$. In this case we can neglect the linear term of $(\vec{q}-\vec{q}_0)$ so that

$$K_{na}=\beta_{1n}^0\beta_{2n}^{0*}\langle X_f|X_a\rangle\langle X_a|X_i\rangle. \tag{27}$$

The intensity contribution due to the excited state $|n\rangle$ is,

$$I_n(E_L)=\kappa'\sum_{i,f}\left|\sum_a\frac{\langle X_f|X_a\rangle\langle X_a|X_i\rangle}{E_L+E_0-E_n-(\Theta_a-\Theta_i)+i\gamma}\right|^2 e^{-\beta\Theta_i}\delta[E_s+(\Theta_f-\Theta_i)], \tag{28}$$

where $\kappa'=2\pi|\beta_{1n}\beta_{2n}|^2/\left(\hbar\sum_i e^{-\beta\Theta_i}\right)$, and the thermally averaging over the initial phonon states is taken. This is equivalent to Eq. (2) in the main text. Note that this derivation provides a rigorous justification for nonzero inner products $\langle X_f|X_a\rangle$ and $\langle X_a|X_i\rangle$. That these inner products should be nonzero can also be argued on the basis of the Franck-Condon principle.

IV. NON-RESONANT RAMAN INTENSITY

For non-resonant Raman, laser energy is far away from the the excited electronic states, which means $\Theta\ll|E_L+E_0-E_n|$. Under such a condition, the phonon energy term on the denominator of the I_n, can be neglected, making it independent of a. Because the initial and final phonon states are orthogonal to each other,

$$\sum_a\langle X_f|X_a\rangle\langle X_a|X_i\rangle=\langle X_f|X_i\rangle=0, \tag{29}$$

we find,

$$\sum_a K_{na} = \frac{\partial \beta_{1n}\beta_{2n}^*}{\partial \vec{q}} \cdot \langle X_f|\vec{q}|X_i\rangle. \tag{30}$$

The Raman intensity becomes,

$$I_n(E_L) = \kappa' \sum_{i,f} \left| \frac{\partial \ln(\beta_{1n}\beta_{2n}^*)}{\partial \vec{q}} \cdot \frac{\langle X_f|\vec{q}|X_i\rangle}{E_L + E_0 - E_n + i\gamma} \right|^2 \delta[E_s + (\Theta_f - \Theta_i)]. \tag{31}$$

The matrix element is nonzero only when $n_{fj} = n_{ij} \pm 1$ or $n_{fj} = n_{ij}$, where n_j is the occupation number of the jth phonon mode. This expression is consistent with the existing theory of non-resonant Raman scattering.

V. COMPUTATIONAL FORMALISM FOR RESONANT RAMAN INTENSITY

Here we provide the detailed steps from Eq. (2) to Eq. (4) in the paper. First, we rewrite the terms in Eq. (28) without the δ-function as,

$$I'_n(E_L) = \sum_{a,a'} e^{-\beta\Theta_i} \frac{\langle X_f|X_a\rangle\langle X_a|X_i\rangle}{E_L + \Theta_i - \Theta_a - E_a + i\gamma} \times \frac{\langle X_i|X_{a'}\rangle\langle X_{a'}|X_f\rangle}{E_L + \Theta_i - \Theta_{a'} - E_{a'} - i\gamma}. \tag{32}$$

Next, we replace the troublesome denominator with a more manageable time-domain integration. Because there are two denominators, we used two-dimensional integration,

$$\begin{aligned} I'_n(E_L) = \sum_{a,a'} e^{-\beta\Theta_i} \int_0^\infty dx \langle X_f|X_a\rangle\langle X_a|X_i\rangle e^{\frac{-\gamma + iE_L - iE_a}{\hbar}x} e^{\frac{i(\Theta_i - \Theta_a)}{\hbar}x} \\ \times \int_0^\infty dy \langle X_i|X_{a'}\rangle\langle X_{a'}|X_f\rangle e^{\frac{-\gamma - iE_L + iE_{a'}}{\hbar}y} e^{\frac{i(\Theta_{a'} - \Theta_i)}{\hbar}y}. \end{aligned} \tag{33}$$

With the help of the effective phonon Hamiltonians, the exponential factors in Eq. (35) are converted into operators,

$$\begin{aligned} I'_n(E_L) = \int_0^\infty dx \int_0^\infty dy e^{\frac{-\gamma + iE_L - iE_a}{\hbar}x} e^{\frac{-\gamma - iE_L + iE_{a'}}{\hbar}y} \\ \times \quad \sum_{i,f} \sum_a \langle X_f|e^{-\frac{ix}{\hbar}\hat{H}^n_{ph}}|X_a\rangle\langle X_a|e^{\frac{ix}{\hbar}\hat{H}^0_{ph}}|X_i\rangle \sum_{a'} \langle X_i|e^{-\frac{iy}{\hbar}\hat{H}^0_{ph} - \beta\hat{H}^0_{ph}}|X_{a'}\rangle\langle X_{a'}|e^{\frac{iy}{\hbar}\hat{H}^n_{ph}}|X_f\rangle \end{aligned}$$

Now we go back and take care of the δ-function part, which represents the energy conservation condition. By applying Fourier transform theory,

$$\delta(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} dt, \tag{34}$$

Eq. (28) can be written as a time-domain integration,

$$I_n(E_L) = \frac{\kappa'}{2\pi} \sum_{i,f} \int_{-\infty}^{\infty} e^{\frac{i}{\hbar}E_s t} e^{\frac{i}{\hbar}(\Theta_f - \Theta_i)t} I'_n(E_L) dt. \tag{35}$$

The exponential containing phonon energies is again absorbed into the inner produts as operators, and the total intensity becomes a triple-integration,

$$I_n(E_L) = \frac{\kappa'}{2\pi} \int_{-\infty}^{\infty} dt \int_0^{\infty} dx \int_0^{\infty} T(x,y,t) e^{\frac{i}{\hbar}E_s t} e^{\frac{-\gamma + iE_L - iE_a}{\hbar}x} e^{\frac{-\gamma - iE_L + iE_{a'}}{\hbar}y} dy, \tag{36}$$

where $T(x,y,t)$ is defined as,

$$\begin{aligned} T(x,y,t) &\equiv \sum_{i,f} \sum_{aa'} \langle X_f | e^{\frac{it}{\hbar}\hat{H}^0_{ph}} e^{-\frac{ix}{\hbar}\hat{H}^n_{ph}} |X_a\rangle\langle X_a| e^{\frac{ix-it-iy}{\hbar}\hat{H}^0_{ph}} |X_i\rangle\langle X_i| e^{-\beta\hat{H}^0_{ph}} |X_{a'}\rangle\langle X_{a'}| e^{\frac{iy}{\hbar}\hat{H}^n_{ph}} |X_f\rangle \\ &= \mathrm{Tr}\left(e^{\frac{iy}{\hbar}\hat{H}^n_{ph}} e^{\frac{it}{\hbar}\hat{H}^0_{ph}} e^{-\frac{ix}{\hbar}\hat{H}^n_{ph}} e^{\frac{ix-iy-it-\beta\hbar}{\hbar}\hat{H}^0_{ph}} \right). \end{aligned} \tag{37}$$

where we used the completeness of the phonon eigenstates,

$$\sum |X\rangle\langle X| = \hat{I}. \tag{38}$$

The effective phonon Hamiltonian is a sum over Hamiltonians of individual phonon modes,

$$\hat{H}^0_{ph} = \sum_{j=1}^{M} \hat{H}_j \qquad \hat{H}_j = \frac{1}{2}\hat{p}_j^2 + \frac{1}{2}\omega_j^2 q_j^2$$

$$\hat{H}^n_{ph} = \sum_{j=1}^{M} \hat{H}'_j \qquad \hat{H}'_j = \frac{1}{2}\hat{p_j}^2 + \frac{1}{2}{\omega_{nj}}^2 (q_j - \delta q_{nj})^2. \tag{39}$$

The following commutation rules hold:

$$[\hat{H}_i, \hat{H}'_j] = 0 \quad [\hat{H}_i, \hat{H}_j] = 0 \quad [\hat{H}'_i, \hat{H}'_j] = 0. \tag{40}$$

The integrand function can be separated as a product of the individual phonon modes,

$$T(x,y,t) = \prod_{j=1}^{M} \mathrm{Tr}(e^{\frac{iy}{\hbar}\hat{H}'_j} e^{\frac{it}{\hbar}\hat{H}_j} e^{-\frac{ix}{\hbar}\hat{H}'_j} e^{\frac{ix-iy-it-\beta\hbar}{\hbar}\hat{H}_j}). \tag{41}$$

If we assume that the frequency changes $\delta\omega_{nj}$ are small, we can expand the above expression to first order in $\delta\omega_{nj}$,

$$T(x,y,t) \approx \prod_{j=1}^{M} \mathrm{Tr}(e^{\frac{iy'}{\hbar}\hat{H}_{1j}} e^{\frac{it}{\hbar}\hat{H}_j} e^{-\frac{ix'}{\hbar}\hat{H}_{1j}} e^{\frac{ix-iy-it-\beta\hbar}{\hbar}\hat{H}_j}), \tag{42}$$

where

$$x' = \frac{\omega_{nj}}{\omega_j} x, \qquad y' = \frac{\omega_{nj}}{\omega_j} y, \tag{43}$$

and

$$\hat{H}_{nj} = \frac{1}{2}\hat{p_j}^2 + \frac{1}{2}\omega_j^2 (q_j - \delta q_{nj})^2. \tag{44}$$

Projecting the operators in Eq. (39) into the basis of the canonical coordinates, $\mathbf{q}$, the matrix product and the trace operation are turned into integrations,

$$\begin{aligned} T(x,y,t) &\approx Tr(e^{\frac{i(y'-x')}{\hbar}\hat{H}_{1j}} e^{\frac{ix'}{\hbar}\hat{H}_{nj}} e^{\frac{it}{\hbar}\hat{H}_j} e^{-\frac{ix'}{\hbar}\hat{H}_{nj}} e^{\frac{ix-iy-it-\beta\hbar}{\hbar}\hat{H}_j}) \\ &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dq dq' dq'' \langle q|e^{\frac{i(y'-x')}{\hbar}\hat{H}_{nj}}|q'\rangle\langle q'|e^{\frac{ix'}{\hbar}\hat{H}_{nj}} e^{\frac{it}{\hbar}\hat{H}_j} e^{-\frac{ix'}{\hbar}\hat{H}_{nj}}|q''\rangle\langle q''|e^{\frac{ix-iy-it-\beta\hbar}{\hbar}\hat{H}_j}|q\rangle. \end{aligned} \tag{45}$$

The general form of these matrix elements of quantum harmonic oscillators is evaluated from a Feynman path-integral formula,

$$\langle q_1|e^{-\frac{i}{\hbar}\hat{H}_0 t_0}|q_2\rangle = \left[\frac{\omega_0}{2\pi i\hbar\sin(\omega_0 t_0)}\right]^{\frac{1}{2}} \exp\left[\frac{i}{\hbar}\frac{\omega_0}{2}\frac{(q_1^2+q_2^2)\cos(\omega_0 t_0) - 2q_1 q_2}{\sin(\omega_0 t_0)}\right], \tag{46}$$

where $\hat{H}_0$ is the Hamiltonian of a quantum Harmonic oscillator,

$$\hat{H}_0 = \frac{\hat{p}^2}{2} + \frac{1}{2}\omega_0^2 q^2. \tag{47}$$

$T(x,y,t)$ is evaluated using several Gaussian integrals,

$$T(x,y,t) = \prod_{j=1}^{M} \frac{e^{\frac{1}{2}(i\delta\omega_{nj}x - i\delta\omega_{nj}y + \beta\hbar\omega_j)}}{e^{(i\delta\omega_{nj}x - i\delta\omega_{nj}y + \beta\hbar\omega_j)} - 1} e^{iS_j F_j(x,y,t)}, \tag{48}$$

where S_j is defined as[**?**],

$$S_j = \frac{\omega_j^2}{2\hbar}\delta q_j^2 \tag{49}$$

and the function F_j is,

$$\begin{aligned} F_j(x,y,t) \equiv & -\sin(\omega_j y' + \omega_j t) + \sin(\omega_j x' - \omega_j t) + \sin(\omega_j t) \\ & + \sin(\omega_j y') - \sin(\omega_j x') - \sin(\omega_j x' - \omega_j y' - \omega t) \\ & - \frac{\sin(\omega_j x' - \omega_j y' - \omega_j x + \omega_j y - i\hbar\omega_j\beta)}{\cos(\omega_j x' - \omega_j y' - \omega_j x + \omega_j y - i\hbar\omega_j\beta) - 1} \times [2 - \cos(\omega_j x') - \cos(\omega_j y') \\ & - \cos(\omega_j t) - \cos(\omega_j x' - \omega_j y' - \omega_j t) + \cos(\omega_j y' + \omega_j t) + \cos(\omega_j x' - \omega_j t)]. \end{aligned} \tag{50}$$

TABLE I. Zero momentum phonon modes of MoS_2/WS_2 heterostructure. Wave numbers are in unit of cm^{-1}.

Mode		Degen.	Mo	W	S_{Mo1}	S_{Mo2}	S_{W1}	S_{W2}
23.0		2	x, y	$-x, -y$	x, y	x, y	$-x, -y$	$-x, -y$
35.4		1	z	$-z$	z	z	$-z$	$-z$
288.9		2	0	0	x, y	$-x, -y$	0	0
298.8		2	0	0	0	0	x, y	$-x, -y$
358.9	E_{2g}	2	0	x, y	0	0	$-x, -y$	$-x, -y$
389.8	E_{2g}	2	x, y	0	$-x, -y$	$-x, -y$	0	0
410.8	A_{1g}	1	0	0	z	$-z$	0	0
420.7	A_{1g}	1	0	0	0	0	z	$-z$
440.9		1	0	z	0	0	$-z$	$-z$
475.0		1	z	0	$-z$	$-z$	0	0

VI. GROUND-STATE PHONON MODES

In the table below, we list all zero-momentum ($\mathbf{q} = 0$) phonon modes of a MoS_2/WS_2 heterostructure, their frequencies and eigenvector components. The S atoms are inequivalent due to their bonding to different Mo and W atoms and are labeled with corresponding subscripts. These phonon modes can be grouped to in-layer modes, with atoms moving within the xy plane, and inter-layer modes, with atoms moving along the z direction.

VII. ATOMIC DISPLACEMENTS OF EXCITED STATES

The next table lists the maximum and average atomic displacements of the S atoms for the four excited electronic states at energies $E_a = 1.598$ eV, $E_a = 1.756$ eV, $E_a = 2.096$ eV, and $E_a = 2.118$ eV.

TABLE II. Maxium and average atomic displacements of the S atoms in 10^{-3} Å

	Maximum				Average			
E_a (eV)	S_{Mo1}	S_{Mo2}	S_{W1}	S_{W2}	S_{Mo1}	S_{Mo2}	S_{W1}	S_{W2}
1.598	−8.6	13	−7.4	4.4	0.54	−0.27	0.06	−0.29
1.756	5.0	12	−7.4	−4.0	0.5	−0.45	0.02	−0.18
2.096	−6.0	9.8	−4.7	−3.2	0.33	−0.13	0.4	0.13
2.118	−7.9	11	−5.9	−1.9	0.35	−0.45	0.46	−0.17