Significant contributions of Albrecht’s A term to non-resonant Raman scattering processes

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The Raman intensity can be well described by the famous Albrecht equation that consists of A and B terms. It is well known that the contribution from Albrecht’s A term can be neglected without loss of accuracy for far off-resonant Raman scattering processes. However, as demonstrated in this study, we have found that this widely accepted long-standing assumption fails drastically for totally symmetric vibration modes of molecules in general off-resonant Raman scattering. Perturbed first principles calculations for water molecule show that strong constructive interference between the A and B terms occurs for the Raman intensity of the symmetric O-H stretching mode, which can account for about 40% of the total intensity. Meanwhile, a minor destructive interference is found for the angle bending mode. The state to state mapping between the Albrecht’s theory and the perturbation theory allows us to verify the accuracy of the widely employed perturbation method for the dynamic/resonant Raman intensities. The model calculations rationalized from water molecule with the bending mode show that the perturbation method is a good approximation only when the absolute energy difference between the first excited state and the incident light is more than five times of the vibrational energy in ground state.

I. INTRODUCTION

Raman spectroscopy1 is one of the standard vibrational spectroscopic tools that has been extensively applied in different fields. The intensity of the Raman scattering can be generally treated by Albrecht’s Raman theory2, in which the polarizability is expanded into two terms, i.e., the famous Albrecht’s A and B terms2,3

\[ \alpha_{pq} = A_{pq} + B_{pq}, \]

where \( p \) and \( q \) represent Cartesian coordinates. If both initial and final electronic states belong to the ground state, they can be written as2,3

\[ A_{pq} = \frac{1}{\hbar} \sum_{r \neq g} \sum_{r' = 0} \frac{\langle v' | r' \rangle \langle v | r \rangle}{\omega_{r v'} - \omega} \]

\[ + \frac{1}{\hbar} \sum_{r \neq g} \sum_{r' = 0} \frac{\langle v' | r' \rangle \langle v | r \rangle}{\omega_{r v'} + \omega} \]

\[ B_{pq} = \frac{1}{\hbar} \sum_{r \neq g} \sum_{r' = 0} \frac{\langle v | r' \rangle \langle v' | r \rangle}{\omega_{r v'} - \omega} \]

\[ + \frac{1}{\hbar} \sum_{r \neq g} \sum_{r' = 0} \frac{\langle v | r' \rangle \langle v' | r \rangle}{\omega_{r v'} + \omega} \]

\[ + \frac{1}{\hbar} \sum_{r \neq g} \sum_{r' = 0} \frac{\langle v | r' \rangle \langle v' | r \rangle}{\omega_{r v'} - \omega} \]

\[ + \frac{1}{\hbar} \sum_{r \neq g} \sum_{r' = 0} \frac{\langle v | r' \rangle \langle v' | r \rangle}{\omega_{r v'} + \omega} \]

where \( \hbar \) is the reduced Planck’s constant, \( |e^g\rangle \) and \( |e^f\rangle \) are electronic ground and excited states, \( |v^g\rangle \) and \( |v^f\rangle \) are the initial and final vibrational states respectively, \( \omega_{r v'} \) is the frequency difference between \( |v^g\rangle \) and \( |v^f\rangle \), \( \lambda \) is the transition dipole moment between \( |e^g\rangle \) and \( |e^f\rangle \) at equilibrium geometry (\( Q_0 \)), \( p_{e^g v}^{k,0} \) is the derivative of \( p_{e^g v}^k \) with respect to specific normal mode \( Q_k \). Here we should emphasize that all modes could contribute as intermediate states in the Raman processes. In other words, \( |v^f\rangle \) represents all possible combination of all modes, i.e., \( |v^f\rangle = |v_1^f v_2^f \cdots v_N^f\rangle \), where \( N \) is the number of vibrational modes. In some cases, the denominator in Eq. 2 would be written in terms of vertical excitation energy \( \Delta E_{rg} \), which obeys the relationship \( \Delta E_{rg} = \hbar \omega_{r v'} + \lambda \). Here \( \lambda \) is the reorganization energy.4

The Albrecht’s theory is commonly used to study the resonant Raman scattering,3,6 although it is a general theory for all Raman processes. It is well known that, for strongly dipole-allowed transitions, A term is dominant in the resonant Raman spectra.5,6 It is noted that A term does not contribute to non totally symmetric modes.7 On the other hand, for weakly dipole-allowed transitions, both the A and B terms could significantly contribute to the Raman scattering of totally symmetric modes. In these cases, the relative magnitude of them could only be determined by quantum chemical calculations.8–11 It is also noted that the effects of higher-order terms were also discussed in recent studies.11

For non-resonant Raman scattering processes, we focus on the zero-frequency limit, i.e., the \( \omega \) is neglected.
In the traditional treatment of the Albrecht’s theory for non-resonant situations, it has been often assumed that \( \omega_{e^{r},e^{q},e^{s}} \approx \omega_{e^{r},e^{q},e^{s}} \). As a result, the denominator in Eq. 2 is independent of the vibrational state \( |\nu^{f}\rangle \). Therefore, the summation of \( \nu^{r} \) could be calculated prior. Because of the completeness of \( |\nu^{r}\rangle \) and orthonormality between \( |\nu^{i}\rangle \) and \( |\nu^{f}\rangle \), the prior summation will result in the \( A \) term only responsible for the Raleigh scattering and vanishing for non-resonant Raman scattering. However, this assumption is apparently too strong. If we only consider the fact that \( \Delta E_{rg} \gg \hbar \omega_{e^{r}} - \hbar \omega_{e^{r}} - \lambda \), in the framework of harmonic approximation and expanding the denominator by Taylor series, the component related to an arbitrary excited state \( |e^{r}\rangle \) in Eq. 2 can be rewritten as

\[
A_{pq}^{r} = \frac{2p_{e^{r}e^{q},e^{s}}^{0}}{\Delta E_{rg}} \langle \nu^{f}|\nu^{i}\rangle \\
+ \frac{p_{e^{r}e^{q},e^{s}}^{0}}{\Delta E_{rg}^{2}} \left[ (1 + v^{i} + v^{f}) \hbar \omega_{g}^{2} + 2 \lambda - \hbar \omega_{g}^{r} \right] \langle \nu^{f}|\nu^{i}\rangle \\
- \frac{2p_{e^{r}e^{q},e^{s}}^{0}}{\Delta E_{rg}^{2}} \sum_{v^{r}=0}^{\infty} \hbar \omega_{e^{r}} \omega_{e^{r}}^{r} \langle \nu^{f}|\nu^{i}\rangle \langle \nu^{r}|\nu^{i}\rangle \\
B_{pq}^{r} = \frac{2(k_{0}e^{r}e^{q},e^{s} + p_{e^{r}e^{q},e^{s}}^{0})}{\Delta E_{rg}} \langle \nu^{f}|Q_{k}|\nu^{i}\rangle \\
+ \mathcal{O} \left( -\hbar \omega_{e^{r}} - \hbar \omega_{e^{r}} - \lambda \right). \tag{3}
\]

Here we should emphasize the multimode nature of \( \omega^{g} \) and \( \omega^{r} \). For instance, we have the expression of \( \hbar \omega^{r} \omega^{r} = \sum_{k=1}^{N} \hbar \omega_{k}^{r} \omega_{k}^{r} \). The schematic drawings for a single vibrational mode of all definitions could be found in Fig. 1, where \( \omega_{k} \) and \( \omega_{k}^{r} \) are the vibrational frequencies related to \( |e^{g}\rangle \) and \( |e^{r}\rangle \), respectively. The summation \( A_{pq}^{r} \) over all \( |e^{r}\rangle \) would return to \( A_{pq} \). If we consider the Stokes shift for the fundamental frequency, i.e. \( v^{i} = 0 \) and \( v^{f} = 1 \), the first two terms in \( A_{pq}^{r} \) vanish due to the orthogonality of the vibrational wavefunctions in the ground state. However, the last term survives and should contribute to the non-resonant Raman intensity.

The finite difference method and coupled-perturbed method have also been used to compute the intensity of non-resonant Raman spectra by directly differentiating the electronic polarizabilities, i.e. \( \mathcal{E}^{3,16} \)

\[
\alpha_{pq}^{r} = \langle \nu^{f}|\alpha_{e^{r},pq}|\nu^{i}\rangle, \tag{4}
\]

where

\[
\alpha_{e^{r},pq} = \sum_{r \neq g} p_{e^{r}e^{q},e^{s}}^{0} \frac{\Delta E_{rg}}{\Delta E_{rg} + \hbar \omega_{e^{r}}^{r}}. \tag{5}
\]

As a result, the component related to state \( |e^{r}\rangle \) in Eq. 4 can be rewritten as

\[
\alpha_{pq}^{r} = \frac{2p_{e^{r}e^{q},e^{s}}^{0}}{\Delta E_{rg}} \langle \nu^{f}|\nu^{i}\rangle \\
- \frac{2p_{e^{r}e^{q},e^{s}}^{0}}{\Delta E_{rg}^{2}} \langle Q_{k}|v^{f}\rangle \langle v^{f}|Q_{k}|v^{i}\rangle \\
+ \frac{2(k_{0}e^{r}e^{q},e^{s} + p_{e^{r}e^{q},e^{s}}^{0})}{\Delta E_{rg}} \langle v^{f}|Q_{k}|v^{i}\rangle. \tag{6}
\]

FIG. 1. Schematic drawing of the single displaced harmonic model used to study the contribution of the \( A \) term to the Raman intensity. \( Q_{0} (\omega_{k}) \) and \( Q_{r} (\omega_{k}^{r}) \) are the equilibrium geometries (vibrational frequencies) of ground state \( |e^{g}\rangle \) and excited state \( |e^{r}\rangle \), respectively. All other symbols can be found in Eq. 3.

Again, the zero-frequency limit is also applied in Eq. 6 and the summation \( \alpha_{pq}^{r} \) would become \( \alpha_{pq} \). In both cases, the Raman cross section can be calculated from the polarizabilities in Eqs. 1 and 4.

In this work, we comprehensively investigate the relationship between Eqs. 6 and 3. Comparing Eqs. 6 and 3, we can immediately find that the \( B_{pq}^{r} \) term corresponds to the last term in \( \alpha_{pq}^{r} \). Thus, the focus of current study is the relationship for \( A \) term. We first address this issue in the model system and show that the \( A \) term indeed contributes to final results for non-resonant conditions. Then, the \( A \) term in time frame is briefly discussed. Finally, we take water monomer as a realistic example to show the importance of including the \( A \) term for final results.
II. MODEL SYSTEM

The first hint for the corresponding relationship for A term between Eqs. 6 and 3 can be found in the case of \( \partial \Delta E_{rg} / \partial Q_k = 0 \). If we consider that both potential energy surfaces (PESs) of \(| \epsilon^p \rangle \) and \(| \epsilon^r \rangle \) are harmonic, this case is equivalent to the situation that the displacement between the two PESs is 0 \( (\Delta Q = 0) \). We can immediately obtain that the second term in \( \alpha^r_{pq} \) is 0. On the other hand, because of the no shift in PESs, either \( \langle 1 | \nu^r \rangle \) or \( \langle v^r | 0 \rangle \) will be 0 due to the parity symmetry. As a result, the last \( A^r_r \) term is also 0 for Raman scattering. Hence, one could notice that the last term in \( A^r_r \) may correspond to the second term in \( \alpha^r_{pq} \). It is well known that the case can be realized in the non totally symmetric vibrations. For such kind of vibrations, there always exists at least one symmetric operator that makes the geometries of \( Q_0 \pm \delta Q_k \) to be identity and then \( \partial \Delta E_{rg} / \partial Q_k = 0 \). Thus, the reason of A term has no contribution to the non-resonant Raman intensity of non totally symmetric vibrations is the orthogonality of vibrational wavefunctions between ground and excited states rather than the orthogonality of two vibrational wavefunctions in the ground state. The former reason is exactly the same as that for the selection rule in resonant Raman processes. It is worth to note that this conclusion can also be generalized to resonant Raman intensities as well as general PESs (such as double well) of excited states.

To further confirm the corresponding relationship between the last term in \( A^r_r \) and the second term in \( \alpha^r_{pq} \), the condition of \( \partial \Delta E_{rg} / \partial Q_k \neq 0 \) should be enforced. In the framework of linear coupling model (LCM) where it assumes \( \omega_k = \omega_k' \), both terms can be calculated analytically and give the same result, i.e.,

\[
\frac{\sqrt{2\hbar \omega_k} \phi^0_{p} | \epsilon^r \rangle \epsilon^r_{e} | \epsilon^e_{e} \rangle \Delta Q}{\Delta E_{rg}^{2}}. \quad (7)
\]

When \( \Delta Q > 0 \), this result is equal to \( 2p_{\epsilon^r e} q^0_{e e} \omega_k \sqrt{S / \Delta E_{rg}^{2}} \), where \( S \) is the Huang-Rhys factor. We should emphasis that the current treatment is consistent with Ting’s work which could be traced back to Shorygin’s treatment in 1947. However, Ting’s work was restricted to the LCM scheme and the vibronic coupling (the B term) has not been included. Moreover, Ting’s algorithm was only widely applied in the two-state model and intrinsically pre-resonant conditions. In off-resonance conditions, Ting’s A term was usually considered to be very small and negligible.

When going beyond the LCM, with the help of the general sum rules for Franck-Condon integrals, we could obtain that the last term in \( A^r_r \) and the second term in \( \alpha^r_{pq} \) both equal to

\[
\frac{\sqrt{2\hbar \omega_k} \phi^0_{p} | \epsilon^r \rangle \epsilon^r_{e} | \epsilon^e_{e} \rangle \Delta Q}{\sqrt{\omega_k \Delta E_{rg}^{2}}}. \quad (8)
\]

We have further performed numerical calculations for more general condition of \( \partial \Delta E_{rg} / \partial Q_k = 0 \). The considered displaced harmonic model is shown in Fig. 1. For example, in the case of \( \omega_k = 1600 \text{ cm}^{-1}, \omega_k' = 1800 \text{ cm}^{-1} \), and \( \Delta Q_k = Q_r - Q_0 = 10 \text{ a.u.} \), both terms give the same value of 0.0055704918 in the unit of \( 2p_{\epsilon^r e} q^0_{e e} E_{av}^{(r)} / \hbar \Delta E_{rg}^{2} \).

The analytical and perfect numerical agreement not only confirm the equivalence of the two terms but also show that, for modes with \( \partial \Delta E_{rg} / \partial Q_k \neq 0 \), the A term can have non-zero contribution to the non-resonant Raman intensity. Note that, here the corresponding \( S \) is around 0.4, which is reasonable for realistic molecules. Because the \(| \epsilon^r \rangle \) is arbitrary in above discussions, a state to state relationship between Albrecht’s theory and perturbation method is thus established for non-resonant Raman spectrum. It is worth to mention that, in the original work of Albrecht, a similar relationship has also been discussed. However, it only focused on the case of near-resonance conditions (see Eq. 22 in Ref. 2).

III. TIME-DEPENDENT FRAME

Time-dependent frame of Raman theory has the advantage of avoiding the sum-over-states of \(| \nu^r \rangle \) in Albrecht’s theory. Instead, the dynamics of the wave packet given by the initial vibrational wave function times the corresponding electronic transition dipole on the excited states is involved. Mathematically, the equivalence of these two representations could be readily proven by a simple half-Fourier transform. In time frame, the “dynamic” and “static” terms are equivalent to the Albrecht’s A and B terms, respectively. Here, the “dynamic” term arises from wave packet propagation on the Born-Oppenheimer surfaces, while, the “static” term comes from the coordinate dependence of the electronic transition dipole. In other words, the first and second terms in the Taylor expansion of transition dipole, i.e.

\[
p_{\epsilon^r e} = p_{\epsilon^r e}^{0} + p_{\epsilon^r e} q_{e e} \]

associate with the “dynamic” and “static” terms, respectively.

In non-resonant conditions, the short time approximation holds. Thus, in the zero-frequency limit, the time average polarizability associated with \(| \epsilon^r \rangle \) could be calculated as

\[
\bar{\alpha}^r_{pq} = \frac{2\pi}{\hbar} \int_{0}^{T} \alpha^r_{pq}(s) ds, \quad (9)
\]

where the per-factor 2 arises from the zero-frequency limit, \( T = 2\pi / |E_{av} - E_{\epsilon^r e}| \), and

\[
\alpha^r_{pq}(s) = \int_{0}^{s} dt \exp \left( \frac{-iE_{\epsilon^r e} t}{\hbar} \right) \langle \phi_f | \exp (iH_r t/\hbar) | \phi_i \rangle. \quad (10)
\]

Here \( H_r \) is the vibrational Hamiltonian for \(| \epsilon^r \rangle \), the damping factor is omitted, \( \langle \phi_f | = \langle \nu^r | p_{\epsilon^r e}^{0}, \phi_i = q_{e e} | \nu^r \rangle \), and \( E_{av} \) is the average energy on \(| \epsilon^r \rangle \). If the assumption

\[
\langle \phi_f | H_r - E_{av} | \phi_i \rangle = 0 \quad (11)
\]
where $\Delta E = E_{av} - E_{exp}$. As a result, the “dynamic” term (the $A$ term) of the Stokes peaks at fundamental frequencies also vanishes in the time frame due to the orthogonality of the vibrational wavefunctions in the ground state. On the other hand, the “static” terms survive and its value in the first order of the ground state. On the other hand, the “static” terms at first principles level for non-resonant Raman intensities has been briefly touched,\textsuperscript{25,28} but magnitudes of both $A$ were no previous examples that have investigated the resonant Raman scattering factors were calculated by\textsuperscript{16,39}

$$S_k = 45a_k^2 + 7\gamma_k^2,$$

where

$$a_k = \frac{1}{3} \{ (\alpha_{xx})_k + (\alpha_{yy})_k + (\alpha_{zz})_k \}$$

$$\gamma_k^2 = \frac{1}{2} \{ (\alpha_{xx})_k - (\alpha_{yy})_k \}^2$$

$$+ (\alpha_{yy})_k - (\alpha_{zz})_k \}^2$$

$$+ (\alpha_{zz})_k - (\alpha_{xx})_k \}^2$$

$$+ 6 \{ (\alpha_{xy})_k^2 + (\alpha_{xz})_k^2 + (\alpha_{yz})_k^2 \},$$

Here the subscript “$k$” represents the individual vibrational mode. By using Eq. 6, we have calculated the scattering factors from three cases: only the $A$ term ($S_A$), only the $B$ term ($S_B$), and both $A$ and $B$ terms ($S_{\text{Tot}}$). With these scattering factors, the corresponding Raman intensities, i.e., $I_A$, $I_B$ and $I_{\text{Tot}}$, are calculated as\textsuperscript{3,16}

$$I = \sum_k \frac{\pi^2}{\nu_k^2} (\nu_m - \nu_k)^4$$

$$\times \frac{h}{8\pi^2 c \epsilon_0} \frac{1}{45} \frac{1}{1 - \exp \left( -h\nu_k / k_B T \right)},$$

where $\epsilon_0$ is the vacuum permittivity, $\nu_m$ and $\nu_k$ are the wave number of incident light and vibrational mode, respectively, $h$ is the Planck’s constant, $c$ is the speed of light, $k_B$ is the Boltzmann constant, and $T$ is the temperature. By definition, the interference contribution is calculated by $I_{\text{Tot}} - I_A - I_B$. For comparison, the analytical Raman scattering factors at the same density functional theory level were also computed.

All calculated scattering factors as well as experimental values\textsuperscript{40,41} are listed in Table I. As expected, the calculated $S_{\text{Tot}}$ are identical to the analytical results and in good agreement with the experimental values.\textsuperscript{15,40,41} Here a slight overestimation for $v_3$ should be attributed to the approximate exchange-correlation functionals, since, at the CASSCF(10,10) level with the same basis set used here, the calculated value (20.4 Å$^4$/amu) is in the range of experimental observation.\textsuperscript{42} For the $v_3$ mode

\begin{table}[h]
\centering
\caption{Calculated Raman scattering factors for water (in the unit of Å$^4$/amu) contain only the $A$ term ($A$), the $B$ term ($B$), or all terms (Tot.), as well as analytical results (Anal.). The experimental measurements (Expt.) extracted from Refs. 15, 40, and 41 also included for comparison.}
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
Mode & Symmetry & $A$ & $B$ & Tot. & Anal. & Expt. \\
\hline
$v_2$ & $A_1$ & 0.14 & 1.54 & 1.10 & 1.10 & 0.9±0.2 \\
v_1 & $A_1$ & 11.66 & 48.32 & 104.94 & 104.54 & 108±14 \\
v_3 & $B_2$ & 0.00 & 25.68 & 25.68 & 25.67 & 19.2±2.1 \\
\hline
\end{tabular}
\end{table}
that belongs to $B_2$ symmetry, the $A$ term does not contribute to the total intensity, consistent with the discussion mentioned above. For the $v_1$ and $v_2$ modes, on the other hand, the contribution of the $A$ term can no longer be neglected. For instance, the calculated $S_B$ of $v_1$ is less than half of the analytical value. It is interesting to note that $S_A$ can only account for about 10% of the analytical result and the summation of contributions from $S_A$ and $S_B$ terms can not provide the correct answer neither. On the other hand, a simple estimation shows that the value from $(\sqrt{S_A}+\sqrt{S_B})^2$ (107 Å$^3$/amu) can reproduce the analytical result nicely. It indicates that a strong constructive interference between the $A$ and $B$ terms does exit for the $v_1$ mode and covers almost 40% of the total intensity. A minor destructive interference is identified for the $v_2$ mode. In this case, the simple summation of $S_A$ and $S_B$ gives a value larger than the final one. Contributions from different terms for the Raman intensities are also displayed in Fig. 3, which emphasizes the importance of the interference for the relative intensity. Notice that the first excitation energy of water is around 7 eV, which obviously obeys the condition of $\omega_{e'p'1} \approx \omega_{e'1}$. But even though, the contribution of the $A$ term cannot be neglected. Overall, although the water monomer is a simple case, it is fully adequate to address our argument.

We notice that simple extension of Eq. 6 by replacing $\Delta E_{e'g}'$ and $\Delta E_{eg}$ with $2[\Delta E_{e'g}' \pm h(\omega + i\Gamma)]^2$ and $2[\Delta E_{eg} \pm h(\omega + i\Gamma)]$, respectively, was employed to calculate dynamic and resonant Raman$^{45}$ intensities. Here the damping factor $\Gamma$ represents the life time of the excited state. In addition, the same extension of the second term (the $A$ term, labeled as $A'_{pq}^r$ hereafter) in Eq. 6 has been used to explain the chemical enhancement of surface-enhanced Raman spectroscopy.$^{46,47}$ However, the accuracy of such extension is questionable because, near the resonant condition, the Taylor expansion for denominator in Eq. 2 may fail and thus $|v'| \langle v'|$ cannot be summed prior.$^{48}$

To verify the accuracy of this simplified extension of Eq. 6, we computed the relative error of $A'_{pq}^r$ respect to Eq. 2 at different energy of incident light for the model system shown in Fig. 1. The result is depicted in Fig. 4. Here all parameters were rationalized from the first excited state of water molecule with the bending mode in LCM. Specifically, $\Delta Q = 1.35$ a.u., $\omega_k = \omega_k = 1600$ cm$^{-1}$, and $\omega_{e'p'1} = 35 \omega_k$. Two $\Gamma$ of 100 and 800 cm$^{-1}$ were used. Around the resonant situation, different $\Gamma$ introduces different behaviour for the relative error. For instance, the maximum relative error for small $\Gamma$ is much larger than that for large $\Gamma$. For the specific case, the maximum relative errors are even larger than 1400% and 130% for small and large $\Gamma$, respectively. In the region of away from resonant condition, the identical behaviour for relative errors with different $\Gamma$ is observed in Fig. 4. Due to the uncertainty of experimental measurements as well as the limitation of the double harmonic approximation,$^{50}$ we used 15% as the threshold for the calculated $A'_{pq}^r$. According to the model calculations, we have found that $A'_{pq}^r$ is a good approximation when $|\omega_{e'p'1} - \omega| > 5 \omega_k$. We should emphasize that this value is mainly determined by $\Delta Q$ between two PESs. For example, when $\Delta Q = 10$ a.u., the range of accurate $A'_{pq}^r$ is $|\omega_{e'p'1} - \omega| > 10 \omega_k$. Apparently, when $\Delta Q = 0$, the parity symmetry will lead to zero $A$ term both in Eq. 2 and Eq. 6.
V. CONCLUSION

We have clearly shown that the contributions from the Albrecht’s A term are too large to be negligible for the non-resonant Raman intensities of totally symmetric fundamental vibrational modes, in contrast with the common wisdom of the field. The widely employed perturbation method is also found to be too crude for evaluating dynamic or resonant Raman spectra. Our findings are conceptually important for correctly understanding and modeling of Raman scattering processes under different conditions.

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1. C. V. Raman and K. S. Krishnan, Nature 121, 501 (1928).
2. A. C. Albrecht, J. Chem. Phys. 34, 1476 (1961).
3. D. A. Long, The Raman Effect: A Unified Treatment of the Theory of Raman Scattering by Molecules (Wiley, Chichester New York, 2002).
4. R. A. Marcus, J. Chem. Phys. 24, 966 (1956).
5. A. Myers Kelley, J. Phys. Chem. A 112, 11975 (2008).
6. D. W. Silverstein and L. Jensen, J. Chem. Phys. 136, 064110 (2012).
7. J. L. McHale, Molecular Spectroscopy, 1st ed. (Prentice Hall, Upper Saddle River, N.J, 1998).
8. E. Santoro, C. Cappelli, and V. Barone, J. Chem. Theory Comput. 7, 1824 (2011).
9. D. W. Silverstein and L. Jensen, J. Chem. Phys. 136, 064111 (2012).
10. H. Ma, J. Liu, and W. Liang, J. Chem. Theory Comput. 8, 4474 (2012).
11. F. Egidi, J. Bbloino, C. Cappelli, and V. Barone, J. Chem. Theory Comput. 10, 346 (2014).
12. E. Smith and G. Dent, Modern Raman Spectroscopy: A Practical Approach, 1st ed. (John Wiley & Sons, Ltd, Hoboken, N.J. 2005).
13. J. R. Lombardi and R. L. Birke, J. Phys. Chem. C 112, 5605 (2008).
14. G. John, C. B. Bacsakay, and N. S. Hush, Chem. Phys. 38, 319 (1979).
15. R. D. Amos, Chem. Phys. Lett. 124, 376 (1986).
16. J. Neugebauer, M. Reiner, C. Kind, and B. A. Hess, J. Comput. Chem. 23, 895 (2002).
17. F. Merzbacher, Quantum Mechanics, 2nd ed. (Wiley, New York, 1970).
18. S.-Y. Lee, J. Chem. Educ. 62, 561 (1985).
19. P. Macak, Y. Luo, and H. Ágren, Chem. Phys. Lett. 330, 447 (2000).
20. K. Huang and A. Rhys, Proc. R. Soc. Lond. A 204, 406 (1950).
21. C.-H. Ting, Spectrochim. Acta A 24, 1177 (1968).
22. P. Shorygin, Zh. Fiz. Khim. 12, 1125 (1947).
23. S.-Y. Lee and E. J. Heller, J. Chem. Phys. 71, 4777 (1979).
24. C. Castiglioni, M. Del Zoppo, and G. Zerbi, Phys. Rev. B 53, 13319 (1996).
25. C. Castiglioni, M. Del Zoppo, and G. Zerbi, Phys. Rev. B 56, 2275 (1997).
26. C.-C. Chou and B.-Y. Jin, Theor. Chem. Acc. 122, 313 (2009).
27. E. S. Yeung, M. Heiling, and G. J. Small, Spectrochim. Acta A 31, 1921 (1975).
28. M. Bishop and B. Kirtman, Phys. Rev. B 56, 2273 (1997).
29. A. J. Sadlej, Spectrochim. Acta A 26, 421 (1970), For facilitating obtaining current result, the vibrational Hamiltonian for $|e'$ would be rewritten as $\mathcal{H}_v = \frac{1}{2} (p_r^2 + \omega_n^2 Q_n^2 - \omega_n^2)$, where, in the ground state coordinate, the mass-weighted coordinate on $|e'$ could be expressed as $Q' = Q - \Delta Q$.
30. A. Alkauskas, J. L. Lyons, D. Steiau, and C. G. Van de Walle, Phys. Rev. Lett. 109, 267401 (2012).
31. E. J. Heller, Acc. Chem. Res. 14, 368 (1981).
32. E. J. Heller, R. Sundberg, and D. Tannor, J. Phys. Chem. 86, 1822 (1982).
33. D. J. Tannor and E. J. Heller, J. Chem. Phys. 77, 202 (1982).
34. Here the sign is consistent with Eq. 2 and the missed pre-factor $v/h$ in Ref. 23 is added.
35. I. Tang and A. C. Albrecht, in Raman Spectroscopy, edited by H. A. Szymanski (Springer US, 1970) pp. 33-68.
36. E. Cotton, Chemical Applications of Group Theory, 3rd ed. (Wiley, New York, 1990).
37. The used functional and basis set were B3LYP implemented in Gaussian 09 and Sadlej pVTZ, respectively.
38. B. Fornberg, Math. Comp. 51, 699 (1988).
39. K. Huang and A. Rhys, Proc. R. Soc. Lond. A 204, 406 (1950).