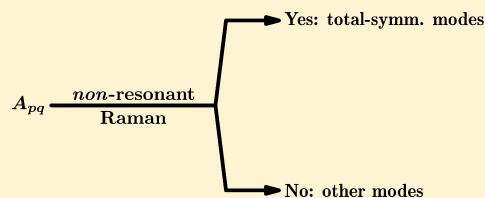


# Significant Contributions of the Albrecht's A Term to Nonresonant Raman Scattering Processes

Zu-Yong Gong,<sup>†,‡</sup> Guangjun Tian,<sup>‡</sup> Sai Duan,<sup>\*,‡</sup> and Yi Luo<sup>†,‡</sup><sup>†</sup>Hefei National Laboratory for Physical Science at the Microscale, Department of Chemical Physics, School of Chemistry and Materials Science, University of Science and Technology of China, Hefei, 230026 Anhui, People's Republic of China<sup>‡</sup>Department of Theoretical Chemistry and Biology, School of Biotechnology, Royal Institute of Technology, S-106 91 Stockholm, Sweden

**ABSTRACT:** The Raman intensity can be well described by the famous Albrecht's Raman theory that consists of A and B terms. It is well-known that the contribution from Albrecht's A term can be neglected without any 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 ~40% of the total intensity. Meanwhile, a minor destructive interference is found for the angle bending mode. The state-to-state mapping between Albrecht's theory and 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 greater than the vibrational energy in the ground state.



## 1. INTRODUCTION

Raman spectroscopy<sup>1</sup> 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 theory,<sup>2</sup> in which the polarizability is expanded into two terms, i.e., the famous Albrecht's A and B terms:<sup>2,3</sup>

$$\alpha_{pq} = A_{pq} + B_{pq} \quad (1)$$

where  $p$  and  $q$  represent Cartesian coordinates and the higher-order terms are neglected. Notice that, here, the  $B$  term consisted of the  $B$  and  $C$  terms in Albrecht's original definition for clarity.<sup>2,3</sup> If both initial and final electronic states belong to the ground state, they can be written as<sup>2,3</sup>

$$A_{pq} = \frac{1}{\hbar} \sum_{r \neq g} \sum_{v^r=0}^{\infty} \frac{p_{e^g e^r}^0 q_{e^r e^g}^0}{\omega_{e^r v^r: e^g v^i} - \omega} \langle v^f | v^r \rangle \langle v^r | v^i \rangle + \frac{1}{\hbar} \sum_{r \neq g} \sum_{v^r=0}^{\infty} \frac{p_{e^g e^r}^0 q_{e^r e^g}^0}{\omega_{e^r v^r: e^g v^f} + \omega} \langle v^f | v^r \rangle \langle v^r | v^i \rangle \quad (2a)$$

$$B_{pq} = \frac{1}{\hbar} \sum_{r \neq g} \sum_{v^r=0}^{\infty} \sum_k \frac{p_{e^g e^r}^{k,0} q_{e^r e^g}^0}{\omega_{e^r v^r: e^g v^i} - \omega} \langle v^f | Q_k | v^r \rangle \langle v^r | v^i \rangle + \frac{1}{\hbar} \sum_{r \neq g} \sum_{v^r=0}^{\infty} \sum_k \frac{p_{e^g e^r}^0 q_{e^r e^g}^{k,0}}{\omega_{e^r v^r: e^g v^f} + \omega} \langle v^f | Q_k | v^r \rangle \langle v^r | v^i \rangle + \frac{1}{\hbar} \sum_{r \neq g} \sum_{v^r=0}^{\infty} \sum_k \frac{p_{e^g e^r}^0 q_{e^r e^g}^{k,0}}{\omega_{e^r v^r: e^g v^i} - \omega} \langle v^f | v^r \rangle \langle v^r | Q_k | v^i \rangle + \frac{1}{\hbar} \sum_{r \neq g} \sum_{v^r=0}^{\infty} \sum_k \frac{p_{e^g e^r}^{k,0} q_{e^r e^g}^0}{\omega_{e^r v^r: e^g v^f} + \omega} \langle v^f | v^r \rangle \langle v^r | Q_k | v^i \rangle \quad (2b)$$

where  $\hbar$  is the reduced Planck's constant;  $|e^g\rangle$  and  $|e^r\rangle$  are the electronic ground and excited states, respectively;  $|v^i\rangle$  and  $|v^f\rangle$  are the initial and final vibrational states of  $|e^g\rangle$  associated with frequency  $\omega^g$ , respectively;  $|v^r\rangle$  is the vibrational state of  $|e^r\rangle$  associated with frequency  $\omega^r$ ;  $\omega$  is the frequency of the incident light;  $\omega_{e^r v^r: e^g v^i}$  is the frequency difference between  $|e^r\rangle |v^r\rangle$  and  $|e^g\rangle |v^i\rangle$ ;  $p_{e^g e^r}^0$  is the transition dipole moment between  $|e^g\rangle$  and  $|e^r\rangle$  at equilibrium geometry ( $Q_0$ ); and  $p_{e^g e^r}^{k,0}$  is the derivative of  $p_{e^g e^r}^0$  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,  $|v^r\rangle$  represents all possible combination of all modes, i.e.,  $|v^r\rangle = |v_1^r v_2^r \cdots v_N^r\rangle$ , where  $N$  is the number of vibrational modes. In some cases, the denominator in eqs 2 would be written in terms of vertical excitation energy  $\Delta E_{rg}$ , which obeys the relationship  $\Delta E_{rg} = \hbar\omega_{e^r: e^g} + \lambda$ . Here,  $\lambda$  is the reorganization energy.<sup>4</sup>

Albrecht's theory is commonly used to study the resonant Raman scattering,<sup>5</sup> although it is a general theory for all Raman processes.<sup>3</sup> It is well-known that, for strongly dipole-allowed transitions, A term is dominant in the resonant Raman spectra.<sup>5,6</sup> It is noted that the A term does not contribute to non-totally symmetric modes.<sup>7</sup> 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.<sup>8–16</sup> These calculations are based on the time-independent or time-dependent formalism, resulting in the frequency-dependent polarizabilities.

Received: August 7, 2015

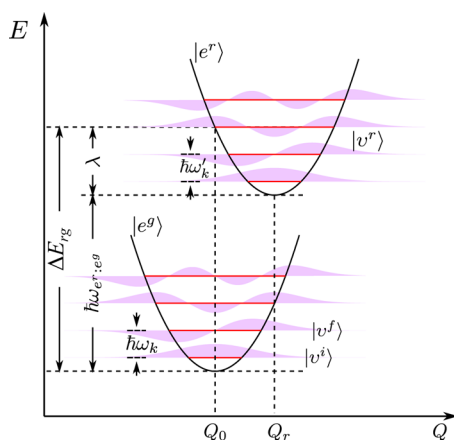
It is also noted that the effects of higher-order terms were also discussed in recent studies.<sup>16</sup>

For nonresonant Raman scattering processes, we focus on the zero-frequency limit, i.e., the parameter  $\omega$  is neglected. In the traditional treatment of Albrecht's theory for nonresonant situations, it has been often assumed that  $\omega_{e^r v^r; e^s v^s} \approx \omega_{e^r; e^s}$ .<sup>2</sup> As a result, the denominator in eqs 2 is independent of the vibrational state  $|v^r\rangle$ . Therefore, the summation of  $v^r$  could be calculated prior. Because of the completeness of  $|v^r\rangle$  and the orthonormality between  $|v^i\rangle$  and  $|v^f\rangle$ , the prior summation will result in the  $A$  term being only responsible for the Raleigh scattering and vanishing for nonresonant Raman scattering.<sup>2</sup> Nowadays, this argument has been widely accepted in the theory of nonresonant Raman scattering.<sup>3,7,17,18</sup> However, the assumption is apparently too strong. If we only consider the fact that  $\Delta E_{rg} \gg \hbar\omega_{v^r} - \hbar\omega_{v^i} - \lambda$ , 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 eqs 2 can be rewritten as

$$A_{pq}^r = \frac{2p_{e^s e^r}^0 q_{e^r e^s}^0}{\Delta E_{rg}} \langle v^f | v^i \rangle + \frac{p_{e^s e^r}^0 q_{e^r e^s}^0}{\Delta E_{rg}^2} [(1 + v^i + v^f) \hbar\omega^s + 2\lambda - \hbar\omega^r] \langle v^f | v^i \rangle - \frac{2p_{e^s e^r}^0 q_{e^r e^s}^0}{\Delta E_{rg}^2} \sum_{v^r=0}^{\infty} \hbar v^r \omega^r \langle v^f | v^r \rangle \langle v^r | v^i \rangle \quad (3a)$$

$$B_{pq}^r = \frac{2(p_{e^s e^r}^{k,0} q_{e^r e^s}^0 + p_{e^s e^r}^0 q_{e^r e^s}^{k,0})}{\Delta E_{rg}} \langle v^f | Q_k | v^i \rangle + O\left(\frac{\hbar\omega_{v^r} - \hbar\omega_{v^i} - \lambda}{\Delta E_{rg}}\right) \quad (3b)$$

where  $\lambda$  is the reorganization energy.<sup>4</sup> Here, we should emphasize the multimode nature of  $\omega^s$  and  $\omega^r$ . For instance, we have the expression of  $\hbar v^r \omega^r = \sum_{k=1}^N \hbar v_k^r \omega_k^r$ . The schematic drawings for a single vibrational mode of all definitions could be found in Figure 1, where  $\omega_k$  and  $\omega_k^r$  are the vibrational



**Figure 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  $|e^s\rangle$  and excited state  $|e^r\rangle$ , respectively. All other symbols can be found in eqs 3.

frequencies related to  $|e^s\rangle$  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, because of the orthogonality of the

vibrational wave functions in the ground state. However, the last term survives and should contribute to the nonresonant Raman intensity.

The finite difference method<sup>19</sup> and coupled-perturbed method<sup>20</sup> have also been used to compute the intensity of nonresonant Raman spectra by directly differentiating the electronic polarizabilities, i.e.,<sup>3,21</sup>

$$\alpha_{pq} = \langle v^f | \alpha_{e,pq} | v^i \rangle \quad (4)$$

where<sup>22</sup>

$$\alpha_{e,pq} = \sum_{r \neq g} \frac{p_{e^s e^r} q_{e^r e^s}}{\Delta E_{rg} \pm \hbar\omega} \quad (5)$$

Although  $\Delta E_{rg}$  does not explicitly include the vibrational energy, in principle, its derivative, with respect to  $Q_k$ , cannot be neglected, as illustrated in Figure 1. As a result, the component related to state  $|e^r\rangle$  in eq 4 can be rewritten as

$$\alpha_{pq}^r = \frac{2p_{e^s e^r}^0 q_{e^r e^s}^0}{\Delta E_{rg}} \langle v^f | v^i \rangle - \frac{2p_{e^s e^r}^0 q_{e^r e^s}^0}{\Delta E_{rg}^2} \frac{\partial \Delta E_{rg}}{\partial Q_k} \langle v^f | Q_k | v^i \rangle + \frac{2(p_{e^s e^r}^{k,0} q_{e^r e^s}^0 + p_{e^s e^r}^0 q_{e^r e^s}^{k,0})}{\Delta E_{rg}} \langle v^f | Q_k | v^i \rangle \quad (6)$$

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.<sup>21</sup>

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 the current study is the relationship for the  $A$  term. We first address this issue in the model system and show that the  $A$  term indeed contributes to the final results for nonresonant conditions. Then, the  $A$  term in time-dependent formalism is briefly discussed. Finally, we take water monomer as a realistic example to show the importance of including the  $A$  term for the final results.

## 2. 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  $|e^s\rangle$  and  $|e^r\rangle$  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  $\alpha_{pq}^r$  is 0. On the other hand, because no shift is observed in PESs, either  $\langle 1 | v^i \rangle$  or  $\langle v^f | 0 \rangle$  will be zero (0), because of the parity symmetry.<sup>7</sup> As a result, the last  $A_{pq}^r$  term is also 0 for Raman scattering. Hence, one could notice that the last term in  $A_{pq}^r$  may correspond to the second term in  $\alpha_{pq}^r$ . It is well-known that the case of  $\partial \Delta E_{rg} / \partial Q_k = 0$  can be realized in the non-totally symmetric vibrations.<sup>7</sup> For such types 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 why the  $A$  term has no contribution to the nonresonant Raman intensity of non-totally symmetric vibrations is the orthogonality of vibrational wave functions between ground and excited states rather than the orthogonality of two vibrational wave functions in the ground state. The former reason is exactly the same as that for the selection rule in resonant Raman processes.<sup>5,7,17</sup> Note that this conclusion can also be generalized to general PESs (such as double well<sup>23</sup>) of excited states.

To further confirm the corresponding relationship between the last term in  $A_{pq}^r$  and the second term in  $\alpha_{pq}^r$ , the condition of  $\partial\Delta E_{\text{rg}}/\partial Q_k \neq 0$  should be enforced. In the framework of the linear coupling model (LCM),<sup>24</sup> where it assumes  $\omega_k = \omega'_k$ , both terms can be calculated analytically and give the same result, i.e.,

$$\frac{\sqrt{2\hbar\omega_k^3} p_{e^s e^r}^0 q_{e^r e^s}^0 \Delta Q}{\Delta E_{\text{rg}}^2} \quad (7)$$

When  $\Delta Q > 0$ , this result equals to  $2p_{e^s e^r}^0 q_{e^r e^s}^0 \hbar\omega_k \sqrt{S}/\Delta E_{\text{rg}}^2$  where  $S$  is the Huang–Rhys factor.<sup>25</sup> We should emphasize that the current treatment is consistent with Ting's work,<sup>26</sup> which could be traced back to Shorygin's treatment<sup>27</sup> in 1947. However, Ting's work was restricted to the LCM scheme and the vibronic coupling (the  $B$  term) has not been included.<sup>28</sup> Moreover, Ting's algorithm was only widely applied in the two-state model<sup>29–31</sup> and intrinsically preresonant conditions.<sup>29,30,32</sup> Under off-resonance conditions, Ting's  $A$  term was usually considered to be very small and negligible.<sup>28,33</sup>

When going beyond the LCM, with the help of the general sum rules for Franck–Condon integrals,<sup>34</sup> we could obtain that the last term in  $A_{pq}^r$  and the second term in  $\alpha_{pq}^r$  both equal to

$$\frac{\sqrt{2\hbar}\omega_k'^2 p_{e^s e^r}^0 q_{e^r e^s}^0 \Delta Q}{\sqrt{\omega_k} \Delta E_{\text{rg}}^2} \quad (8)$$

We have further performed numerical calculations for the more general condition of  $\partial\Delta E_{\text{rg}}/\partial Q_k \neq 0$ . The considered displaced harmonic model is shown in Figure 1. For example, in the case of  $\omega_k = 1600 \text{ cm}^{-1}$ ,  $\omega'_k = 1800 \text{ cm}^{-1}$ , and  $\Delta Q_k = Q_r - Q_0 = 10 \text{ a. u.}$  (the dimensionless displacement is around 0.9), both terms give the same value of 0.0055704918 in the unit of  $2p_{e^s e^r}^0 q_{e^r e^s}^0 \hbar/\Delta E_{\text{rg}}^2$ . The analytical and perfect numerical agreement not only confirm the equivalence of the two terms but also show that, for modes with  $\partial\Delta E_{\text{rg}}/\partial Q_k \neq 0$ , the  $A$  term can have a nonzero contribution to the nonresonant Raman intensity. Note that, here, the corresponding  $S$  is  $\sim 0.4$ ,<sup>35</sup> which is reasonable for realistic molecules. Because the  $|e^r\rangle$  is arbitrary in above discussions, a state-to-state relationship between Albrecht's theory and the perturbation method is thus established for nonresonant Raman spectrum. It is worthwhile 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).

### 3. TIME-DEPENDENT FORMALISM

Time-dependent formalism of Raman theory has the advantage of avoiding the sum-over-states of  $|v^r\rangle$  in Albrecht's theory.<sup>23,28,36–38</sup> 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.<sup>28</sup> Mathematically, the equivalence of these two representations could be readily proven by a simple half-Fourier transform.<sup>28,36</sup> In time-dependent formalism, 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.<sup>28</sup> In other words, the first and second terms in the Taylor expansion of transition dipole, i.e.,  $p_{e^r e^s} = p_{e^r e^s}^0 + p_{e^r e^s}^{k0} Q_k$ , are associated with the terms “dynamic” and “static”, respectively.

In nonresonant conditions, the short time approximation holds. Thus, in the zero-frequency limit, the time-averaged polarizability associated with  $|e^r\rangle$  could be calculated as<sup>28,39</sup>

$$\bar{\alpha}_{pq}^r = -\frac{2i}{\hbar T} \int_0^T \alpha_{pq}^r(s) \text{d}s \quad (9)$$

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

$$\alpha_{pq}^r(s) = \int_0^s \text{d}t \exp\left(\frac{-iE_{e^r}t}{\hbar}\right) \langle \phi_j | \exp\left(\frac{i\mathcal{H}_r t}{\hbar}\right) | \phi_i \rangle \quad (10)$$

Here,  $\mathcal{H}_r$  is the vibrational Hamiltonian for  $|e^r\rangle$  (the damping factor is omitted),  $\langle \phi_j | = \langle v^j | p_{e^r e^s}^r$ ,  $| \phi_i \rangle = q_{e^r e^s}^i | v^i \rangle$ , and  $E_{\text{av}}$  is the average energy on  $|e^r\rangle$ . If the assumption<sup>28,40</sup>

$$\langle \phi_j | \mathcal{H}_r - E_{\text{av}} | \phi_i \rangle = 0 \quad (11)$$

is adopted, the “dynamic” term in eq 10 would be

$$\alpha_{pq}^{r,D}(s) = \int_0^s \text{d}t \exp\left(\frac{i\Delta E t}{\hbar}\right) p_{e^s e^r}^0 q_{e^r e^s}^0 \langle v^j | v^i \rangle \quad (12)$$

where  $\Delta E = E_{\text{av}} - E_{e^r}$ . As a result, the “dynamic” term (the  $A$  term) of the Stokes peaks at fundamental frequencies also vanishes in the time-dependent formalism, because of the orthogonality of the vibrational wave functions in the ground state. On the other hand, the “static” terms survives and its value in the first order of  $Q_k$  is exactly equal to  $B$  term in eqs 3 if we considered  $\Delta E = \Delta E_{\text{rg}}$  (see Appendix B in ref 28 for details). This conclusion is consistent with that presented in ref 28, where the emphasis for “far from resonance” is solely on the “static” term.

The reason for the vanishing of the “dynamic” term in non-resonance in the time-dependent formalism would be easily located as the assumption of eq 11, which is equivalent to the assumption of  $\omega_{e^r v^r, e^s v^s}^r \approx \omega_{e^r e^s}^r$  in the energy formalism. Both assumptions neglect the vibrational contributions in excited states. To obtain the correct result, in the time-dependent formalism, eq 9 should be calculated with the inclusion of vibrational contributions in  $\mathcal{H}_r$ , so that the contribution of the “dynamic” term (Albrecht's  $A$  term) will be included in the total intensity.

### 4. FIRST-PRINCIPLES EXAMPLE: WATER MONOMER

Although the contribution of  $A$  term for nonresonant Raman intensities has been briefly addressed,<sup>26–28</sup> its magnitude for realistic molecules was still controversial.<sup>30,33</sup> Therefore, a first-principles example is highly desirable to address this issue. To the best of our knowledge, there were no previous examples that have investigated the magnitudes of both  $A$  and  $B$  terms at the first-principles level for nonresonant Raman intensities. In the following, we take water molecule as a realistic example to fully examine the contribution of the  $A$  term. Water molecule has three vibrational modes,<sup>41</sup> which are  $\angle\text{H–O–H}$  bending ( $\nu_2$ ), symmetric O–H stretching ( $\nu_1$ ), and asymmetric O–H stretching modes ( $\nu_3$ ), respectively. The vibrational modes of water are depicted in Figure 2. All required excited states except core–hole excitations were calculated at time-dependent density functional theory level with the hybrid B3LYP functional and the Sadlej's pVTZ basis set as implemented in the Gaussian suite of programs.<sup>42</sup> As a result, 148 singly excited states were considered. The finite difference method<sup>43</sup> was used to calculate the derivatives in  $\alpha_{pq}^r$ . All calculated  $\alpha_{pq}^r$  were summed up over all singly excited

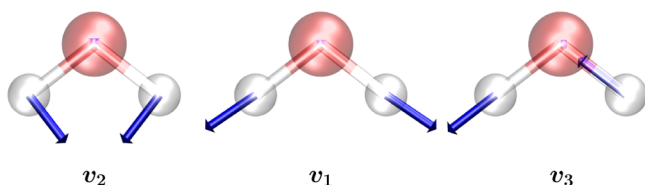


Figure 2. Three vibrational modes of the water molecule.

states to obtain  $\alpha_{pq}$  and finally Raman scattering factors were calculated using the expression<sup>21,44</sup>

$$S_k = 45a_k^2 + 7\gamma_k^2 \quad (13)$$

where

$$a_k = \frac{1}{3}\{(\alpha_{xx})_k + (\alpha_{yy})_k + (\alpha_{zz})_k\} \quad (14a)$$

$$\gamma_k^2 = \frac{1}{2}\{[(\alpha_{xx})_k - (\alpha_{yy})_k]^2 + [(\alpha_{yy})_k - (\alpha_{zz})_k]^2 + [(\alpha_{zz})_k - (\alpha_{xx})_k]^2 + 6[(\alpha_{xy})_k^2 + (\alpha_{xz})_k^2 + (\alpha_{yz})_k^2]\} \quad (14b)$$

Here, the subscript  $k$  represents the individual vibrational mode and the vibrational integral is not included. 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<sup>3,21</sup>

$$I = \sum_k \frac{\pi^2}{\epsilon_0^2} (\tilde{\nu}_{\text{in}} - \tilde{\nu}_k)^4 \frac{h}{8\pi^2 c \tilde{\nu}_k} \left( \frac{S_k}{45} \right) \left\{ \frac{1}{1 - \exp[-hc\tilde{\nu}_k/(k_B T)]} \right\} \quad (15)$$

where  $\epsilon_0$  is the vacuum permittivity;  $\tilde{\nu}_{\text{in}}$  and  $\tilde{\nu}_k$  are the wavenumber 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,<sup>45,46</sup> are listed in Table 1. As expected, the calculated

Table 1. Calculated Raman Scattering Factors for Water (in Units of  $\text{\AA}^4/\text{amu}$ ) Contain Only the A Term (A), the B Term (B), or All Terms (Tot), as Well as Analytical Results (Anal)

mode	symmetry	A	B	Tot	Anal	Expt <sup>a</sup>
$\nu_2$	$A_1$	0.14	1.54	1.10	1.10	$0.9 \pm 0.2$
$\nu_1$	$A_1$	11.66	48.32	104.94	104.54	$108 \pm 14$
$\nu_3$	$B_2$	0.00	25.68	25.68	25.67	$19.2 \pm 2.1$

<sup>a</sup>Experimental measurements extracted from refs 20, 45, and 46; these values are also included for comparison.

$S_{\text{Tot}}$  values are identical to the analytical results and in good agreement with the experimental values.<sup>20,45,46</sup> Here, a slight overestimation for  $\nu_3$  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 ( $20.4 \text{ \AA}^4/\text{amu}$ ) is in the range of experimental observation.<sup>47</sup> For the  $\nu_3$  mode that belongs to  $B_2$  symmetry, the A term does not contribute to the total intensity, which is consistent with the discussion mentioned above. For the  $\nu_1$  and  $\nu_2$  modes, on the other hand, the contribution of the A term can no longer be

neglected. For instance, the calculated  $S_B$  of  $\nu_1$  is less than half of the analytical value. It is interesting to note that  $S_A$  can only account for  $\sim 10\%$  of the analytical result and the summation of contributions from  $S_A$  and  $S_B$  terms cannot provide the correct answer neither. On the other hand, a simple estimation shows that the value from  $(S_A^{1/2} + S_B^{1/2})^2$  ( $107 \text{ \AA}^4/\text{amu}$ ) can reproduce the analytic result nicely. It indicates that a strong constructive interference between the A and B terms does exist for the  $\nu_1$  mode and covers  $\sim 40\%$  of the total intensity. A minor destructive interference is identified for the  $\nu_2$  mode. In this case, the simple summation of  $S_A$  and  $S_B$  terms gives a value larger than the final one. Contributions from different terms for the Raman intensities are also displayed in Figure 3, which emphasizes the

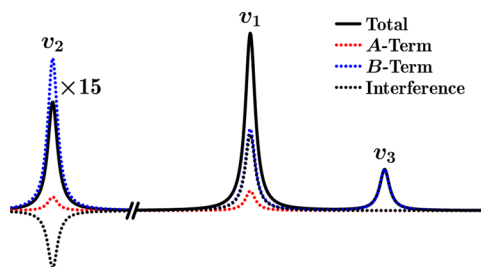


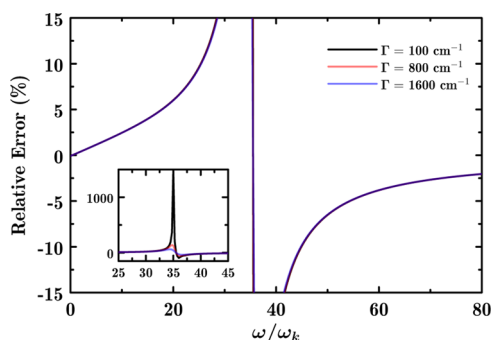
Figure 3. Calculated Raman intensities for water (black solid line). The contributions from the A term (red dotted line), the B term (blue dotted line), and the interference (black dotted line) are also shown. The incident light and temperature are set to be 514.5 nm and 400 K, followed by the experimental conditions,<sup>45,46</sup> respectively. All spectra have been broadened by Lorentzian function with a full width at half-maximum (fwhm) of  $10 \text{ cm}^{-1}$ .

importance of the interference for the relative intensity. Notice that the first excitation energy of water is  $\sim 7 \text{ eV}$ , which obviously obeys the condition of  $\omega_{e'v';e''v''} \approx \omega_{e';e''}$ . 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  $\Delta E_{\text{rg}}^2$  and  $\Delta E_{\text{rg}}$  with  $2[\Delta E_{\text{rg}} \pm \hbar(\omega + i\Gamma)]^2$  and  $2[\Delta E_{\text{rg}} \pm \hbar(\omega + i\Gamma)]$ , respectively,<sup>48</sup> was employed to calculate dynamic<sup>12</sup> and resonant Raman<sup>49</sup> intensities. Here, the damping factor  $\Gamma$  represents the lifetime of the excited state. In addition, the same extension of the second term (the A term, labeled as  $A_{pq}^{\text{rs}}$  hereafter) in eq 6 has been used to explain the chemical enhancement of surface-enhanced Raman spectroscopy.<sup>50–52</sup> However, the accuracy of such extension is questionable, because, near the resonant condition, the Taylor expansion for denominator in eqs 2 may fail and thus  $|v'\rangle\langle v'|$  cannot be summed prior.<sup>53</sup>

To verify the accuracy of this simplified extension of eq 6, we computed the relative error of  $A_{pq}^{\text{rs}}$  with respect to eqs 2, at different energies of incident light for the model system shown in Figure 1. The result is depicted in Figure 4. Here, all parameters were rationalized from the first excited state of water molecule with the bending mode in LCM (see caption for Figure 4 for details). Three typical  $\Gamma$  values were used, i.e., a small value of  $100 \text{ cm}^{-1}$  and large values of 800 and  $1600 \text{ cm}^{-1}$ .<sup>15,54</sup> Note that the large values of  $\Gamma$  correspond to the short-time approximation.<sup>55</sup> Around the resonant situation, different  $\Gamma$  values introduce different behavior for the relative error. For instance, the maximum relative error for the small  $\Gamma$  value is much larger than that for the two large  $\Gamma$  values. For the specific case, the maximum relative error is larger than 1400% for  $\Gamma = 100 \text{ cm}^{-1}$ , and the errors are larger than 130% and 60% for the two large  $\Gamma$ ,





**Figure 4.** Relative error of simply extended A term in eq 6, with respect to eqs 2, at different energies of incident light for the model in Figure 1. Here, all parameters are rationalized from the first excited state of water molecule with the bending mode in LCM. Specifically,  $\Delta Q = 1.35$  a.u.,  $\omega_k = \omega'_k = 1600$   $\text{cm}^{-1}$ , and  $\omega_{e',e} = 35 \omega_k$ . Three  $\Gamma$  values were used: 100, 800, and 1600  $\text{cm}^{-1}$ . Inset shows the incident light around the resonant situation.

respectively. In the region of away from resonant condition, the identical behavior for relative errors with different  $\Gamma$  is observed in Figure 4. Because of the uncertainty of experimental measurements, as well as the limitation of the double harmonic approximation,<sup>56</sup> we used 15% as the threshold for the calculated  $A_{pq}^{rs}$ . According to the model calculations, we have found that  $A_{pq}^{rs}$  is a good approximation when  $|\omega_{e',e} - \omega|$  is larger than  $5\omega_k$ . 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  $A_{pq}^{rs}$  is  $|\omega_{e',e} - \omega| > 10 \omega_k$ . Apparently, when  $\Delta Q = 0$ , the parity symmetry will lead to a zero A term both in eqs 2 and eq 6.

## 5. CONCLUSION

We have clearly shown that the contributions from the Albrecht's A term are too large to be negligible for the nonresonant 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.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: said@theochem.kth.se.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by the Ministry of Science and Technology of China (No. 2010CB923300), the "Strategic Priority Research Program" of the Chinese Academy of Sciences (Grant No. XDB01020200), the Natural Science Foundation of China (No. 21421063), and Swedish Research Council (VR). The Swedish National Infrastructure for Computing (SNIC) was acknowledged for computer time.

## REFERENCES

- (1) Raman, C. V.; Krishnan, K. S. A New Type of Secondary Radiation. *Nature* **1928**, *121*, 501–502.
- (2) Albrecht, A. C. On the Theory of Raman Intensities. *J. Chem. Phys.* **1961**, *34*, 1476–1484.

- (3) Long, D. A. *The Raman Effect: A Unified Treatment of the Theory of Raman Scattering by Molecules*; Wiley: Chichester, U.K., New York, 2002.
- (4) Marcus, R. A. On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I. *J. Chem. Phys.* **1956**, *24*, 966–978.
- (5) Myers Kelley, A. Resonance Raman and Resonance Hyper-Raman Intensities: Structure and Dynamics of Molecular Excited States in Solution. *J. Phys. Chem. A* **2008**, *112*, 11975–11991.
- (6) Silverstein, D. W.; Jensen, L. Vibronic Coupling Simulations for Linear and Nonlinear Optical Processes: Simulation Results. *J. Chem. Phys.* **2012**, *136*, 064110.
- (7) McHale, J. L. *Molecular Spectroscopy*, 1st Edition; Prentice Hall: Upper Saddle River, NJ, 1998.
- (8) Oddershede, J.; Svendsen, E. N. Dynamic Polarizabilities and Raman Intensities of CO, N<sub>2</sub>, HCl and Cl<sub>2</sub>. *Chem. Phys.* **1982**, *64*, 359–369.
- (9) van Gisbergen, S. J. A.; Snijders, J. G.; Baerends, E. J. Application of Time-Dependent Density Functional Response Theory to Raman Scattering. *Chem. Phys. Lett.* **1996**, *259*, 599–604.
- (10) Quinet, O.; Champagne, B. Time-Dependent Hartree-Fock Schemes for Analytical Evaluation of the Raman Intensities. *J. Chem. Phys.* **2001**, *115*, 6293–6299.
- (11) Smith, S. M.; Markevitch, A. N.; Romanov, D. A.; Li, X.; Levis, R. J.; Schlegel, H. B. Static and Dynamic Polarizabilities of Conjugated Molecules and Their Cations. *J. Phys. Chem. A* **2004**, *108*, 11063–11072.
- (12) Van Caillie, C.; Amos, R. D. Raman Intensities Using Time Dependent Density Functional Theory. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2123–2129.
- (13) Santoro, F.; Cappelli, C.; Barone, V. Effective Time-Independent Calculations of Vibrational Resonance Raman Spectra of Isolated and Solvated Molecules Including Duschinsky and Herzberg–Teller Effects. *J. Chem. Theory Comput.* **2011**, *7*, 1824–1839.
- (14) Silverstein, D. W.; Jensen, L. Vibronic Coupling Simulations for Linear and Nonlinear Optical Processes: Theory. *J. Chem. Phys.* **2012**, *136*, 064111.
- (15) Ma, H.; Liu, J.; Liang, W. Time-Dependent Approach to Resonance Raman Spectra Including Duschinsky Rotation and Herzberg-Teller Effects: Formalism and Its Realistic Applications. *J. Chem. Theory Comput.* **2012**, *8*, 4474–4482.
- (16) Egidi, F.; Bloino, J.; Cappelli, C.; Barone, V. A Robust and Effective Time-Independent Route to the Calculation of Resonance Raman Spectra of Large Molecules in Condensed Phases with the Inclusion of Duschinsky, Herzberg–Teller, Anharmonic, and Environmental Effects. *J. Chem. Theory Comput.* **2014**, *10*, 346–363.
- (17) Smith, E.; Dent, G. *Modern Raman Spectroscopy: A Practical Approach*, 1st Edition; John Wiley & Sons, Ltd.: Hoboken, NJ, 2005.
- (18) Lombardi, J. R.; Birke, R. L. A Unified Approach to Surface-Enhanced Raman Spectroscopy. *J. Phys. Chem. C* **2008**, *112*, 5605–5617.
- (19) John, I. G.; Bacskey, C. B.; Hush, N. S. Finite Field Method Calculations. V. Raman Scattering Activities and Infrared Absorption Intensities for H<sub>2</sub>O, D<sub>2</sub>O, CH<sub>4</sub> and CD<sub>4</sub>. *Chem. Phys.* **1979**, *38*, 319–328.
- (20) Amos, R. D. Calculation of Polarizability Derivatives Using Analytic Gradient Methods. *Chem. Phys. Lett.* **1986**, *124*, 376–381.
- (21) Neugebauer, J.; Reiher, M.; Kind, C.; Hess, B. A. Quantum Chemical Calculation of Vibrational Spectra of Large Molecules-Raman and IR Spectra for Buckminsterfullerene. *J. Comput. Chem.* **2002**, *23*, 895–910.
- (22) Merzbacher, E. *Quantum Mechanics*, 2nd Edition; Wiley: New York, 1970.
- (23) Lee, S.-Y. Potential Energy Surfaces and Effects on Electronic and Raman Spectra. *J. Chem. Educ.* **1985**, *62*, 561–566.
- (24) Macak, P.; Luo, Y.; Ågren, H. Simulations of Vibronic Profiles in Two-Photon Absorption. *Chem. Phys. Lett.* **2000**, *330*, 447–456.
- (25) Huang, K.; Rhys, A. Theory of Light Absorption and Non-Radiative Transitions in F-Centres. *Proc. R. Soc. London, Ser. A* **1950**, *204*, 406–423.

- (26) Ting, C.-H. Polarized Raman Spectra—I. Selection Rules. *Spectrochim. Acta A* **1968**, *24*, 1177–1189.
- (27) Shorygin, P. P. Intensity of Combination Scattering Lines and Structure of Organic Compounds. *Zh. Fiz. Khim.* **1947**, *12*, 1125–1134.
- (28) Lee, S.-Y.; Heller, E. J. Time-Dependent Theory of Raman Scattering. *J. Chem. Phys.* **1979**, *71*, 4777–4788.
- (29) Castiglioni, C.; Del Zoppo, M.; Zerbi, G. Molecular First Hyperpolarizability of Push–Pull Polyenes: Relationship Between Electronic and Vibrational Contribution by a Two-State Model. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *53*, 13319–13325.
- (30) Castiglioni, C.; Del Zoppo, M.; Zerbi, G. Reply to “Comment on ‘Molecular First Hyperpolarizability of Push–Pull Polyenes: Relationship Between Electronic and Vibrational Contribution by a Two-State Model’”. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1997**, *56*, 2275–2276.
- (31) Chou, C.-C.; Jin, B.-Y. Vibrational Contributions to Static Linear and Nonlinear Optical Coefficients: From Two-Level to Two-Band Systems. *Theor. Chem. Acc.* **2009**, *122*, 313–324.
- (32) Yeung, E. S.; Heiling, M.; Small, G. J. Pre-Resonance Raman Intensities. *Spectrochim. Acta, Part A* **1975**, *31*, 1921–1931.
- (33) Bishop, D. M.; Kirtman, B. Comment on “Molecular First Hyperpolarizability of Push–Pull Polyenes: Relationship Between Electronic and Vibrational Contribution by a Two-State Model”. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1997**, *56*, 2273–2274.
- (34) Sadlej, A. J. On the Sum Rules for Franck–Condon Integrals. *Spectrochim. Acta, Part A* **1970**, *26*, 421–423. To facilitate obtaining the current result, the vibrational Hamiltonian for  $|e'\rangle$  would be rewritten as  $\mathcal{H}_e' = \frac{1}{2}(p^2 + \omega_k'^2 Q'^2 - \hbar\omega_k')$ , where, in the ground-state coordinate, the mass-weighted coordinate on  $|e'\rangle$  could be expressed as  $Q' = Q - \Delta Q$ .
- (35) Alkauskas, A.; Lyons, J. L.; Steiauf, D.; Van de Walle, C. G. First-Principles Calculations of Luminescence Spectrum Line Shapes for Defects in Semiconductors: The Example of GaN and ZnO. *Phys. Rev. Lett.* **2012**, *109*, 267401.
- (36) Heller, E. J. The Semiclassical Way to Molecular Spectroscopy. *Acc. Chem. Res.* **1981**, *14*, 368–375.
- (37) Heller, E. J.; Sundberg, R.; Tannor, D. Simple Aspects of Raman Scattering. *J. Phys. Chem.* **1982**, *86*, 1822–1833.
- (38) Tannor, D. J.; Heller, E. J. Polyatomic Raman Scattering for General Harmonic Potentials. *J. Chem. Phys.* **1982**, *77*, 202–218.
- (39) Here, the sign is consistent with eqs 2 and the missed pre-factor  $1/\hbar$  in ref 28 is added.
- (40) Tang, J.; Albrecht, A. C. In *Raman Spectroscopy*; Szymanski, H. A., Ed.; Springer: New York, 1970; pp 33–68.
- (41) Cotton, F. *Chemical Applications of Group Theory*, 3rd Edition; Wiley: New York, 1990.
- (42) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09 Revision A.02*; Gaussian, Inc.: Wallingford, CT, 2009.
- (43) Fornberg, B. Generation of Finite Difference Formulas on Arbitrarily Spaced Grids. *Math. Comput.* **1988**, *51*, 699–760.
- (44) Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. *Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra*; Dover Publications: New York, 1980.
- (45) Murphy, W. F. The Ro-Vibrational Raman Spectrum of Water Vapour  $\nu_2$  and  $2\nu_2$ . *Mol. Phys.* **1977**, *33*, 1701–1714.
- (46) Murphy, W. F. The Rovibrational Raman Spectrum of Water Vapour  $\nu_1$  and  $\nu_3$ . *Mol. Phys.* **1978**, *36*, 727–732.
- (47) Neugebauer, J.; Reiher, M.; Hess, B. A. Coupled-Cluster Raman Intensities: Assessment and Comparison with Multiconfiguration and Density Functional Methods. *J. Chem. Phys.* **2002**, *117*, 8623–8633.
- (48) The opposite-sign convention for  $i\Gamma$  is adopted; see Chapter A18 in ref 3.
- (49) Rappoport, D.; Shim, S.; Aspuru-Guzik, A. Simplified Sum-Over-States Approach for Predicting Resonance Raman Spectra. Application to Nucleic Acid Bases. *J. Phys. Chem. Lett.* **2011**, *2*, 1254–1260.
- (50) Jensen, L.; Aikens, C. M.; Schatz, G. C. Electronic Structure Methods for Studying Surface-Enhanced Raman Scattering. *Chem. Soc. Rev.* **2008**, *37*, 1061–1073.
- (51) Morton, S. M.; Jensen, L. Understanding the Molecule-Surface Chemical Coupling in SERS. *J. Am. Chem. Soc.* **2009**, *131*, 4090–4098.
- (52) Zayak, A. T.; Hu, Y. S.; Choo, H.; Bokor, J.; Cabrini, S.; Schuck, P. J.; Neaton, J. B. Chemical Raman Enhancement of Organic Adsorbates on Metal Surfaces. *Phys. Rev. Lett.* **2011**, *106*, 083003.
- (53) Although the sum-over-states in eq 5 is circumvented, the implicit prior summation for the  $|b'\rangle\langle b'|$  is still included in the method in ref 12.
- (54) Zhao, L.; Jensen, L.; Schatz, G. C. Pyridine-Ag<sub>20</sub> Cluster: A Model System for Studying Surface-Enhanced Raman Scattering. *J. Am. Chem. Soc.* **2006**, *128*, 2911–2919.
- (55) Kane, K. A.; Jensen, L. Calculation of Absolute Resonance Raman Intensities: Vibronic Theory vs Short-Time Approximation. *J. Phys. Chem. C* **2010**, *114*, 5540–5546.
- (56) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*, 2nd Edition; Wiley–VCH Verlag GmbH: Weinheim, Germany, New York, 2001.