Raman Spectroscopy

An Intensity Approach

（拉曼谱学）

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Preface

I began to recognize the importance of studying Raman intensity as I encountered surface enhanced Raman scattering (SERS) back to 1980's. SERS is a surface phenomenon that as a molecule, especially the nitrogen containing molecule, is adsorbed on the metal surface, in particular the silver electrode, its Raman cross section can be amplified up to a million fold. More interesting is that the Raman mode intensities of the adsorbed molecule are applied voltage dependent. The question then in my mind was: what is the physical picture behind this Raman intensity variation? In order to solve this issue, we therefore established an algorithm to retrieve the so-called bond polarizabilities from the Raman mode intensities in a systematic way. This leads to a nice harvest, showing that this approach is an adequate direction, albeit the algorithm is semi-classical. This attracted much of my intention in 1980's.

During that time, I also thought of the fields of Raman optical activity (ROA) and phase transition. These two fields involve Raman intensity variation as well. In particular, ROA shows that for a chiral molecule under right and left circularly polarized light scatterings, its respective Raman intensities are different, though the difference is very small, only 10^{-3} to 10^{-4} of its Raman intensity. The differential Raman intensity is called the ROA spectrum.

Our work on the phase transitions of the systems with very low degree of doping (ranging from 10^{-2} to 10^{-4}) seemed to be a success. The rate of mode intensity variation as a function of temperature shows a power law. The exponent of the power law is very sensitive to the doping degree and bears the information of the doping effects. Among the doping effects, the self-similarity by doping which is characterized by the scaling factor, $d/\sqrt{M}$, with d the separation between the doping ions and M their mass is most impressive.

However, our work on ROA turned out to be a maze, but not a loss. I hence was acquainted with the idea of ROA and proposed a classical formula for predicting the ROA mode signatures①. Though with this formula, the prediction was not so successful due to the reason that, at that time, we did not have a clear picture concerning the Raman excited virtual state from the retrieved bond polarizabilities.

A clear picture of the Raman excited virtual state sparked us in 2006 when we noticed that the bond polarizabilities retrieved from Raman mode intensities were definitely in variation with the bond electronic densities in the ground state②. This hints that bond polarizabilities bear the information of the excited/disturbed charges during the Raman process, i. e., the electronic structure of the Raman virtual state! With this breakthrough, we immediately came into the detailed study on the Raman virtual state and extended the bond polarizability algorithm to retrieve the differential bond polarizabilities from ROA mode intensities. All these offered us vivid pictures of the Raman and ROA processes. Though they are classical pictures, just because they are classical, they can provide comprehensive pictures of the Raman virtual state and the phenomena in ROA, which were not known or neglected before. Furthermore, our classical formula for ROA which was developed in 1998, turns out to be a success after its re-interpretation by the bond polarizability. Another byproduct of this work is that we showed, probably for the first time to the best of our knowledge, that there are about 20% electrons in a molecule that are involved in the Raman process③. The 14 years' waiting (from 1998 to 2012) is really worthwhile to me!

My bias is that, at least in the field of molecular physics or molecular spectroscopy, quantum treatment is often a requisite, but not an absolute necessity. Classical or semi-classical treatment is in ge-

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① Ma S, Wu G. Chinese Phys. Letters, 1998, 15: 753

② See Fig. 4. 3 of Chapter 4 and Wang H, Wu G. Chem. Phys. Letters, 2006, 421: 460

③ Fang Y, Wu G, Wang P. Spectrochimica Acta, 2012, A88: 216

neral simpler and easier though numerically may not be so accurate. However, it can still offer clear and concrete physical picture which is very beneficial for our tangible feeling and understanding of the physics under study. We have to admit that quantal language like wave function is often too abstract and farther beyond our daily conceptual ability than the classical language.

This book summarizes the highlights of our work on the bond polarizability approach to the Raman intensity analysis. The topics covered include surface enhanced Raman scattering, Raman excited virtual state and ROA. The first chapter briefly introduces the Raman effect in a succinct and clear way. Chapter 2 deals with the normal mode analysis which is a basic tool for our work. Chapter 3 introduces our proposed algorithm for the Raman intensity analysis. Chapter 4 heavily introduces the physical picture of Raman virtual states. Chapter 5 presents our work that leads to a comprehensive idea about the Raman virtual states. Chapter 6 demonstrates how this bond polarizability algorithm is extended to ROA intensity analysis. Chapters 7 and 8 offer our works on ROA, showing many findings on ROA mechanism that were not known or neglected before. Chapter 9 introduces our proposed classical treatment on ROA which, as combined with the results from the bond polarizability analysis, leads to a comprehensive physical picture of the Raman process. In particular, this classical treatment unifies ROA and VCD (vibrational circular dichroism) on equal footing. In this book, in each section, there are *Comments* which summarize the key ideas and their evaluation. This will help the readers to capture the core ideas of the presentations in a logical and sequential way. In Appendix B, a summary of our publications are listed including those on phase transitions which are not covered in this book. This may be convenient to the readers, if needed.

Indeed, few monographs on Raman effect are written from the viewpoint of Raman intensity in a systematic way as this book is. I hope our works will convince the readers that many Raman and ROA features not known or neglected before can be retrieved by this intensity approach. I also hope the readers can appreciate these novel viewpoints on Raman and ROA, albeit polarizability for Raman is an old idea which has already been exploited deeply by many researchers since its discovery in 1928 and when computer simulation for Raman and ROA is becoming a daily experience nowadays.

Finally, I have to mention that these works bear the efforts of my former graduate students at the Institute of Chemistry, Chinese Academy of Sciences and Physics Department of Tsinghua University who have engaged in these studies during the past years. Also, I thank Professors P. J. Wang and H. X. Shen for their cooperation with me on the ROA work. Over the past nearly 30 years, the grant support by the China National Science Foundation and that by the State Key Laboratory of Low-dimensional Quantum Physics of the Department of Physics, Tsinghua University are greatly acknowledged.

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On the 6th of April, 2015
At Physics Department,
Tsinghua University, Beijing

Contents

Chapter 1

Raman effect

1.1 Basics: the Raman virtual state

Raman effect was discovered by C. V. Raman in 1928[1-3]. It is an inelastic two-photon process, in which the scattering photon is first absorbed by the scatterer, for instance a molecule (in the followings, we will specify the scatterer to molecule without loss of generality). The photon-perturbed molecule is excited/disturbed and then relaxes and emits a secondary photon instantaneously. What excited/disturbed in the photon-perturbed molecule is its charges/electrons(from the ground state). During this process, the energy of the excited/disturbed charges may exchange with the molecular internal quanta, such as vibration through the so-called vibronic(vibration-electronic) coupling, so that the energy of the emitted photon may be different from the scattering photon. This energy difference is called the Raman shift. Raman shift is expressed in wavenumber (cm^{-1}, wavenumber multiplied by the velocity of light, 3×10^{10} cm/sec, gives the actual frequency). Raman shift gives the information of the molecular internal motion. For molecular vibration, Raman shift gives its frequency which is related to the molecular structure (geometry and atomic masses) and bond strengths. In fact, this information can also be obtained from other effects, such as infrared absorption. Hence, we know that the Raman shift is not the core information that we can obtain from the Raman effect.

The real core information lies in the Raman intensity which offers the dynamics of the photon-perturbed molecule. The photon-perturbed molecule, in general, may not be in its excited eigenstates. In such case, we call it the non-resonant the Raman process and the photon-perturbed molecule including its relaxation, the Raman excited virtual state, or simply the Raman virtual state. However, we have to stress that the Raman virtual state is a real physical entity, not just by our imagination. The word *virtual* should not be exaggerated to imply a physical meaning. The Raman virtual state is like a wave packet.

It is a common daily experience that in a pan full of water, there can be standing waves which are shaped by the pan. When a pebble is thrown into the pan, the water inside will be splashed above or even out of the pan in a random way. Similarly, when a molecule(the pan) absorbs a light quantum(the pebble), its electronic distribution(the water)will be disturbed. The disturbed(excited)electronic distribution in such an excitation is, in general, not stationary(the splashing water) or non-resonant and does not correspond to an eigenstate (the standing wave). We know that the eigenstates are governed by the molecular nuclei and can be accurately predicted by Schroedinger equation (just as that the patterns of the standing waves are defined by the pan boundary)while the non-stationary excitation including its relaxation, called virtual state, is not well defined by the nuclei and is hard to figure out though not impossible. This is the physical concept of the Raman virtual state. Just like that we cannot say that the splashing water is not a physical reality due to it is not a standing wave, we cannot say that the Raman virtual state is not a real physical entity due to that it is simply not an eigenstate or resonant one!

Back to the core issue: how to retrieve the information of the Raman virtual state from the Raman intensity? This is the central issue for the Raman study and the core topic we will cover in this book.

Before going to the issue of Raman intensity study, we will first introduce briefly the classical and quantum mechanical treatments of the Raman effect. If the readers are familiar with them, these sections may be skipped, except the ***Comments*** in Section 1. 3.

Comments

If Raman excitation is to an eigenstate, we call the process resonant. In general, this is not the case, then the process is called non-resonant. In such case, no doubt that the electrons are disturbed and the molecule is in the so-called Raman virtual state. Hence, the virtual state is a physical reality, albeit the molecule is not in an eigenstate. Do not try to interpret the phenomenon from the vocabulary—*virtual*. It is only a word, a nomenclature for the phenomenon, not a deduction based on any physical considerations.

1. 2 The classical treatment

As a molecule is hit by the visible light(called the scattering light), the nuclear motion(vibration)will not be disturbed since its frequency is much less than that of the light. However, the electrons will be disturbed by the light. This disturbance of electrons by the external light is described by the electronic polarizability, which is a measure how easily the electrons can be affected by the light. As the electrons are more tightly bound to the nuclei and harder to be disturbed by the light, the electronic polarizability is smaller, otherwise, it is larger. The dimension of the electronic polarizability is volume. Its physical significance is the space occupied by the electrons. It is also proportional to the amount of electron numbers(charges). Since the electronic distribution of a molecule(or the molecular configuration/shape)is, in general, not spherical, the electronic polarizability is direction dependent, or a tensor. However, for the convenient elucidation of its physical significance, we will not go that far but simply consider it as a scalar in this book as we will pay more attention to the electronic polarizability of a bond. This will not affect the retrieval of the physical concepts of the topics concerned. For convenience, electronic polarizability is often shortened as polarizability.

Suppose the electric field of the scattering light with angular frequency ω is

$$\varepsilon = \varepsilon_0 \mathrm{e}^{\mathrm{i}\omega t}$$

and the vibration is described by the normal mode(at least, in the low excitation)coordinate Q_k with frequency ω_k, as

$$\begin{aligned} Q_k &= Q_k^0 \cos\omega_k t \\ &= Q_k^0 [e^{i\omega_k t} + e^{-i\omega_k t}]/2 \end{aligned}$$

in which Q_k^0 is the coordinate at equilibrium.

The electronic polarizability α will depend on Q_k. By expanding α in terms of Q_k:

$$\alpha = \alpha^0 + \sum_k (\partial\alpha/\partial Q_k)_0 Q_k \cdots$$

then under the influence of the scattering light, the induced electric dipole μ, which is responsible for the emitted light, is

$$\begin{aligned} \mu &= \alpha\varepsilon \\ &= \left[\alpha^0 + \sum_k (\partial\alpha/\partial Q_k)_0 Q_k^0 \frac{1}{2}(e^{i\omega_k t} + e^{-i\omega_k t})\right]\varepsilon_0 e^{i\omega t} \\ &= \alpha^0 \varepsilon_0 e^{i\omega t} + \frac{1}{2}\sum_k (\partial\alpha/\partial Q_k)_0 Q_k^0 \varepsilon_0 [e^{i(\omega+\omega_k)t} + e^{i(\omega\omega_k)t}] \end{aligned}$$

With μ containing $e^{i\omega t}$, $e^{i(\omega+\omega_k)t}$ and $e^{i(\omega-\omega_k)t}$. This shows that the scattered light possesses frequencies $\omega \pm \omega_k$ besides ω. Its spectrum looks like that shown in Fig. 1. 1. The line with frequency ω is the Rayleigh line. Its intensity is related to α^0. The lines with frequencies $\omega \pm \omega_k$ are the Raman lines. The one with $\omega - \omega_k$ is the Stokes line and that with $\omega + \omega_k$ is the anti-Stokes line. Pictorially, the former can be considered as that the energy of one vibrational quantum is absorbed from the scattering light by the molecule while the latter as that one vibrational quantum is transferred to the scattered light from the molecule. The energy radiated by the dipole is proportional to the fourth power of its angular frequency. Hence, their intensity ratio is (no other factors will be considered for the time being):

$$\frac{I_{\text{Stokes}}}{I_{\text{antiStokes}}} = \frac{(\omega - \omega_k)^4 N_{V_k=0}}{(\omega + \omega_k)^4 N_{V_k=1}}$$

Here, N_{V_k} is the molecular population with vibrational quantum number V_k. Though $(\omega - \omega_k)^4 < (\omega + \omega_k)^4$, the population of the ground state is much larger due to the Boltzmann distribution:

$$N_{V_k=0} \gg N_{V_k=1}$$

Hence, the Stokes line is stronger than the anti-Stokes line.

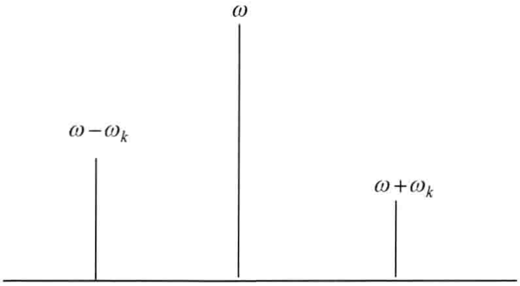

Fig. 1.1 Rayleigh and Raman lines. Those with $\omega-\omega_k$ and $\omega+\omega_k$ are the Stokes and anti-Stokes lines, respectively.

α^0 is the static polarizability. It is the polarizability when the molecular motion is frozen. It shows roughly the molecular dimension. $(\partial\alpha/\partial Q_k)_0$ shows the vibronic coupling between the electronic and nuclear motions——the changing of the electronic space as the nuclei move during vibration. The Raman intensity is proportional to $(\partial\alpha/\partial Q_k)_0^2$. We stress again that the Raman intensity bears the information of the vibronic coupling which is the core physical parameter in the Raman process, while the Raman shift just does not play this core role.

Comments

Classical treatment can nicely show up the Raman shifts and that Raman is due to the vibronic coupling whose information is embedded in the intensity.

1.3 The quantal treatment

Quantum mechanical treatment was proposed by Albrecht[4]. Here, we only offer the result of the quantal treatment, instead of its detailed derivation. In quantum mechanics, a physical process is expressed in terms of the probability of the transition from the initial state $|I\rangle$ to the final state $|F\rangle$ via H' mechanism as $\langle F|H'|I\rangle$ in Dirac's notation. (Analogously, in Schroedinger's notation, it is the integral of the wave functions of the initial and final states with the operator H'). The quantum mechanical expression of the polarizability for the Raman process from state a to state b(like from the vibrational ground state to the excited state in the Stokes process) is:

$$(\alpha_{\rho\sigma})_{ab} = \frac{1}{\hbar}\left\{\sum_{n\neq a}\frac{\langle a_0 \mid \mu_\sigma \mid n_0\rangle\langle n_0 \mid \mu_\rho \mid b_0\rangle}{\omega_{an}+\omega} + \sum_{m\neq b}\frac{\langle a_0 \mid \mu_\rho \mid m_0\rangle\langle m_0 \mid \mu_\sigma \mid b_0\rangle}{\omega_{bm}-\omega}\right\}$$

Here, $(E_i - E_j)/\hbar = \omega_{ij}$ is the angular frequency corresponding to the energy difference between the transition states. $|n_0\rangle$ and $|m_0\rangle$ are the intermediate excited states. The Raman process is the superposition of all the paths that each starts and ends in the same initial and final states but proceeds through all possibly allowed intermediate excited states. μ_ρ and μ_σ are the polarization operators of the photons involved in the two photon process of the Raman scattering. The appearance of $\omega_{an}+\omega$ (note that ω_{an} is negative by definition) in the denominators shows that as the energy of the light quantum is very close to the energy differences of these levels, that is when $\omega_{an}+\omega \approx 0$, the scattering probability will be much larger. This is the resonance effect. Otherwise, if the energy differences of the molecular levels and the energy of the light quantum are very large, then very small the scattering probability will be. When $E_a > E_b$, the process is the anti-Stokes scattering. When $E_a < E_b$, the process is the Stokes scattering. From the viewpoint of symmetry, μ_σ and μ_ρ are of symmetry x, y or z. Hence, $\alpha_{\rho\sigma}$ is of symmetry xx, yy, zz, xy, xz, yz.

Comments

Since the Raman virtual state is not an eigenstate, in the quantal treatment, it is expressed in terms of the complete eigenstates $\{|n_i\rangle\}$ as:

$$\text{Raman virtual state} = \sum c_i \mid n_i\rangle$$

This is shown in Fig. 1. 2, pictorially. However, we cannot deny its physical entity just because it is not an eigenstate. This expression of