*

**

100080

SHG　　　　　　　　　　　SFG-VPS　　　　　　　　　　　　　　　　　　　.

.

.

A

A Simplified Formulation of Linear and
Nonlinear Spectroscopy of Ordered Molecular Systems [*]

Wang Hongfei [**]

State Key Laboratory of Molecular Reaction Dynamics　Center for Molecular Sciences
Institute of Chemistry　the Chinese Academy of Sciences　Beijing　100080

Abstract　A simplified formulation for treating the linear and nonlinear spectroscopy of ordered molecular systems is presented　in order to help experimentalists to have an explicit physical picture and quantitative tool on using linear and nonlinear spectroscopy to study molecules in ordered molecular systems. This formulation is expended from our recent quantitative orientational and polarization treatment on second-order nonlinear spectroscopic techniques in interface studies　namely　the Second Harmonic Generation　SHG　and Sum Frequency Generation-Vibrational Polarization Spectroscopy　SFG-VPS . The key to this formulation is to simplify the effective linear or nonlinear molecular susceptibility and construct the general orientational functional with a clear approach to calculate the orientational and intensity parameters from the experimental parameters　which determines the orientational and polarization behavior of the general orientational functional in a particular experimental configuration. Also discussed are the advantages of coherent spectroscopic techniques over incoherent ones for the accurate measurement of orientation and ordering of ordered molecular system.

Keywords　Linear and nonlinear spectroscopy　Second harmonic generation　Sum frequency generation vibrational spectroscopy　General orientational functional　Ordered molecular system

1   Introduction

Molecules in ordered media are not only useful for functional and photonics applications but also fundamental for understanding of molecular interactions and dynamics in the condensed media [1-4] . It is known that polarization spectroscopic methods are very useful for obtaining information on molecules in ordered media because the electric field with a chosen direction i. e. polarization interacts favorably with molecular dipole or transition dipole with certain orientations in a certain coordinate spaces. The ideas and many useful techniques of polarization spectroscopy have been treated in detail   and many examples were given in a few excellent textbooks or monographs [5 6] as well as review articles [7] . However   these efforts were focused mostly on absorption fluorescence and Raman spectroscopic applications   both linear and nonlinear in forms need to be reexamined.

Surface second harmonic generation SHG   and sum frequency generation SFG   vibrational spectroscopy have been developed and applied for studying molecules in ordered monolayers and films in the past two decades. The advancement in the theoretical treatment [8 9] and instrumental development [10] have made it a thriving subject of research towards studying of material and biological surfaces [11-15] . However the ability for the applications of SHG and SFG which depends on how well the quantitative molecular information could be extracted from the experimental data has not been fully employed and sometimes erroneous conclusions were reached because lack of such ability [16 17] . The very useful molecular information includes the knowledge on molecular ordering i. e. orientation orientational distribution and includes the knowledge on molecular structure and conformation from the measured spectroscopic details. Recently advances in this direction have made it possible for accurate and effective quantitative and orientational analysis with SHG and SFG [9 18 19] . These advances also provide a unique perspective for understanding and application of these aspects of linear and nonlinear spectroscopy.

In this short article I would briefly discuss the general ideas on treating the ordered molecular systems with linear and nonlinear spectroscopic methods   as well as the issues involved for quantitative orientational analysis. The basic idea and the take home message is the importance on constructing the general orientational functional which is in a very simple form and is the direct measure of the molecular order of the molecular system with interest. This orientational functional is derived through the explicit expression of the polarization vector which directly describes the interaction between the molecular susceptibilities and the interacting optical fields. The parameters of the orientational functional determine the behaviors of the orientational functional. It is further shown that these parameters are determined through experimental parameters and almost the known properties of the molecular system. Using the concepts developed here as a starting point many interesting phenomena in linear and nonlinear polarization spectroscopy could be described qualitatively and quantitative analysis could be explicitly implemented.

2   The effective linear and nonlinear susceptibilities and the general orientational functional

Spectroscopy measures the interactions between electromagnetic fields and molecular system. Through linear or nonlinear spectroscopy we are able to obtain information on molecular structure conformation and dynamics. Naturally the way in the application of linear and nonlinear spectroscopy lies in the way to obtain microscopic or molecular information from the macroscopic spectroscopic measurement. The ability to do so relies on the abilities for us to describe the macroscopic responses and to find out the relationship between the macroscopic responses and the microscopic or molecular properties. Therefore it is essential for us to address this problem with simple and explicit formulations.

Albrecht *et al*. seminally classified any given spectroscopy into either active Class I   or passive Class II [7] . As we can see below this categorization is very useful in order to distinguish and describe

processes such as fluorescence spectroscopy and Raman spectroscopy and Rayleigh scattering etc. According to Albrecht *et al.* in the active spectroscopies the principle even is a change of state population in the molecule. So obviously the well-known absorption and emission spectroscopies are active. While the passive spectroscopies come from the momentary exchange of energy between light and matter that induces a macroscopically electromagnetic polarization in the molecule and a new electromagnetic field signal is produced at the frequency of the oscillating polarization in the molecule. Obviously the scattering processes and coherent spontaneous processes all belong to this second category. In this paper we discuss only Class II spectroscopies for Class I spectroscopies have been extensively discussed in the literature [7].

It can be proven from electrodynamics that the amplitude A of an angular and polarization dependent dipolar radiation field at the far field from a dipole moment $\vec{\mu}$ is proportional to the projection of the second time derivative onto the direction of the unit vector $\vec{e}$ for that angle and polarization [20][21]

$$A \propto \vec{e} \cdot \frac{\partial^2 \vec{\mu}}{\partial t^2} \propto \vec{e} \cdot \ddot{\vec{\mu}} \qquad 1$$

The second proportional relationship in Equation 2 comes from the effectiveness of the slow-wave approximation which indicates that the oscillation of the radiation field is much faster than the changing of the molecular dipole itself [20][22].

In a perturbative molecular treatment of the interaction between light and matter an induced molecular dipole moment $\vec{\mu}$ can be expressed as

$$\vec{\mu} = \vec{\mu}^{1} + \vec{\mu}^{2} + \vec{\mu}^{3} + \vec{\mu}^{4} + \dots$$
$$= \beta^{1} \vec{E} + \beta^{2} \vec{E}\vec{E} + \beta^{3} \vec{E}\vec{E}\vec{E} +$$
$$\beta^{4} \vec{E}\vec{E}\vec{E}\vec{E} + \dots \qquad 2$$

where β^{i} represents the electrical polarizability tensor of molecule or atoms which is an $i+1$ rank tensor with 3^{i+1} elements to relate all the possible field vectors involved in this so-called $i+1$-wave-mixing processes $\vec{\mu}^{i}$ is the ith order induced polarization and $\vec{E}$ represents the interacting electric field of the light. The induced polarization $\vec{\mu}$ in turn generates electromagnetic radiations i. e. $\vec{\mu}^{i}$ terms are the source terms for

the generated electromagnetic radiations. The so-called linear process is produced by the term $\vec{\mu}^{1}$ and the rest of $\vec{\mu}^{i}$'s are responsible for the so-called higher-order nonlinear processes.

Therefore the radiation intensity of the ith order processes in the frequency space at the far field can be expressed as follows

$$I \propto A^2 \propto |\vec{e}_{i+1} \cdot \ddot{\vec{\mu}}^{i}|^2 \qquad 3$$

where $\vec{e}_{i+1}$ is the unit vector of the observation for the ith order dipolar radiation. It is thus clear from the simple expressions in equation 3 that the property $|\vec{e}_{i+1} \cdot \ddot{\vec{\mu}}^{i}|^2$ contains all the information for linear and nonlinear light-matter interactions and it is the starting point for understanding of molecular orientation with linear and nonlinear spectroscopic.

It is important to realize the fact that equation 2 only describes the instantaneous radiation of a single molecular dipole. Ensemble average has to be employed to treat the whole molecular system. The ensemble average for the coherent processes such as wave-mixing processes such as second-harmonic generation SHG and sum-frequency generation SFG coherent anti-stokes Raman spectroscopy CARS and incoherent processes such as fluorescence Rayleigh and hyper Rayleigh scattering HRS are different.

For coherent processes the total radiation intensity is the absolute square of the added field of the molecular system.

$$I_{coh} \propto |\vec{e}_{i+1} \cdot \ddot{\vec{\mu}}^{i}|^2$$
$$= |\vec{e}_{i+1} \cdot \beta^{i} \vec{e}_i \vec{e}_{i-1} \dots \vec{e}|^2$$
$$= \left| \vec{e}_{i+1} \cdot \left(\sum_{i \; i-1 \dots 1} \chi^{i} \; \vec{e}_i \vec{e}_{i-1} \dots \vec{e}_1 \right) \right|^2 \qquad 4$$

Where χ^{i} is the macroscopic ith order susceptibility defined in the expression of the polarisation $\vec{P}$ the total dipole in a unit volume.

$$\vec{P} = \vec{P}^{1} + \vec{P}^{2} + \vec{P}^{3} + \vec{P}^{4} + \dots$$
$$= \chi^{1} \vec{E} + \chi^{2} \vec{E}\vec{E} + \chi^{3} \vec{E}\vec{E}\vec{E} +$$
$$\chi^{4} \vec{E}\vec{E}\vec{E}\vec{E} + \dots \qquad 5$$

In the condensed phase all the properties regarding light-matter interactions including fields and polarizations have to be corrected with local field corrections [6][23]. Each field factor $\vec{e}$ in equation 4 and e-

quation 6 has to be replaced by $L_i \, \vec{e}_i$ where L_i is the tensorial field factors including Fresnel and local field correction factors.

Therefore equation 4 becomes the following equations respectively.

$$I_{coh} \propto |\chi_{eff}^{i}|^2$$
$$= |\; L_{i+1} \; \vec{e}_{i+1} \cdot$$
$$\left(\sum_{i\, i-1\, ...1} \chi^{i} \; L_i \; \vec{e}_i \; L_{i-1} \; \vec{e}_{i-1} \; ... \; L_1 \; \vec{e}_1 \right)|^2 \quad 6$$

It is important to realize that $|\chi_{eff}^{i}|^2$ contains all the information for the molecular system in the ith-order linear $i = 1$ or nonlinear $i \geq 2$ spectroscopy. As we have systematically demonstrated previously for the case of the second-order nonlinear processes i. e. Second Harmonic Generation SHG and Sum Frequency Generation SFG [9 18 19] χ_{eff}^{i} is the sum of all the possible terms of the point product of an observation vector $L_{i+1} \, \vec{e}_{i+1}$ and a polarization vector

$$\vec{P}^{i} = \chi^{i} \; L_i \; \vec{e}_i \; L_{i-1} \; \vec{e}_{i-1} \; ... \; L_1 \; \vec{e}_1$$

In a polarized spectroscopy experiment the field vectors of the incoming and outgoing light beams are controlled by the experimenter. Once these field vectors are fixed for a particular molecular system the tensorial Fresnel and local field factors are also fixed quantities. Therefore the linear or nonlinear spectroscopy experiment measures the radiation intensity at a certain frequency with a set of particular polarizations of the optical fields involved and it provides the information of the macroscopic susceptibility of the molecular system.

For an ordered molecular system certain macroscopic symmetry must exist. Therefore many of 3^{i+1} the elements of the $i + 1$ rank macroscopic tensor χ^{i} would vanish. This is also true for the $i + 1$ rank microscopic or molecular tensor β^{i} when the molecular is with certain symmetry. The nonvanishing macroscopic tensor elements $\chi_{IJK...}^{i}$ and the microscopic elements $\beta_{ijk...}^{i}$ are connected through

$$\chi_{IJK...}^{i} = N \times \sum_{ijk... = x'y'z'} R_{Ii}R_{Jj}R_{Kk}... \; \beta_{ijk...}^{i} \quad 7$$

where N is the number density of the molecule the summing term denotes the average over all the possible contributions from the molecular polarizability $\beta_{ijk...}^{i}$ to

$\chi_{IJK...}^{i}$. The operator denotes the orientational ensemble average over the Euler rotation matrix transformation elements $R_{A\lambda'}$ from the molecular coordination $x' \, y' \, z'$ to the laboratory coordination $x \, y \, z$ [23]. The transformation matrix R is defined as follows [25]

$$R = R_{A\lambda'} = \begin{pmatrix} R_{xx'} & R_{xy'} & R_{xz'} \\ R_{yx'} & R_{yy'} & R_{yz'} \\ R_{zx'} & R_{zy'} & R_{zz'} \end{pmatrix} \quad 8$$

in which

$$R_{xx'} = \cos\psi\cos\phi - \cos\theta\sin\phi\sin\psi$$
$$R_{xy'} = -\sin\psi\cos\phi - \cos\theta\sin\phi\cos\psi$$
$$R_{xz'} = \sin\theta\sin\phi$$
$$R_{yx'} = \cos\psi\sin\phi + \cos\theta\cos\phi\sin\psi$$
$$R_{yy'} = -\sin\psi\sin\phi + \cos\theta\cos\phi\cos\psi$$
$$R_{yz'} = -\sin\theta\cos\phi$$
$$R_{zx'} = \sin\theta\sin\psi$$
$$R_{zy'} = \sin\theta\cos\psi$$
$$R_{zz'} = \cos\theta$$

The Eular angles $\theta \, \phi \, \psi$ are defined as the following. $\theta \in 0 \, \pi$ is the angle between z and z' $\phi \in 0 \, 2\pi$ is the azimuthal angle about z axis of the laboratory coordinate system and $\psi \in 0 \, 2\pi$ is the azimuthal angle about z' axis of the molecular coordinates system [24].

The orientational ensemble average is defined as

$$\sum_{ijk... = x'y'z'} R_{Ii}R_{Jj}R_{Kk}... \; \beta_{ijk...}^{i}$$
$$= \sum_{ijk... = x'y'z'} \beta_{ijk...}^{i} \int \frac{R_{Ii}R_{Jj}R_{Kk}...e^{-U \theta \phi \psi /kT}\mathrm{d}\Omega}{\int e^{-U \theta \phi \psi /kT}\mathrm{d}\Omega} \quad 9$$

where $U \, \theta \, \phi \, \psi$ is the potential energy associated with different molecular orientation angles $\theta \, \phi \, \psi$ k in the exponential is the Boltzmann constant T is the system temperature and $\mathrm{d}\Omega = \sin\theta\mathrm{d}\theta\mathrm{d}\phi\mathrm{d}\psi$ is the integral element of the solid angle $\Omega \, \theta \, \phi \, \psi$.

Since $\beta_{ijk...}^{i}$ is an $i + 1$ order tensor which has 3^{i+1} tensorial elements the knowledge of $\beta_{ijk...}^{i}$ is very important for simplification of equation 9. Molecular symmetry would only allow some of the tensor elements of $\beta_{ijk...}^{i}$ be non-zero which would greatly simplify the problem. Sometimes such as under resonance conditions or far from resonance further simplification of equation 9 is possible because only one or a few ten-

sorial elements are dominant. Another way to simplify the problem is by knowing the ratios between the non-zero tensorial elements from measurements on degenerate or reduced order processes just as in SFG using the second-order tensorial elements ratio from the Raman depolarization measurement [18][23][25].

Usually in a ordered molecular system the Eular angle θ which is the angle between the molecular z axis and the laboratory Z axis and its distribution are interested. For most of the ordered molecular systems rotational isotropy would make the potential energy $U(\theta,\phi,\psi) = U(\theta)$. In such a case the integration over ϕ and ψ would be separated from the θ terms. If integrate ϕ and ψ over $(0,2\pi)$ all the terms with $\cos^{2n+1}\phi$, $\cos^{2n+1}\psi$, $\sin^{2n+1}\phi$ and $\sin^{2n+1}\psi$ would vanish with n = positive integer. With this approach $\chi_{IJK\dots}^{i}$ would be reduced into the following functional.

$$\chi_{IJK\dots}^{i} = N \times \sum_{j}^{i+1,i-1,i-3,\dots} a_j \times \cos^j\theta \qquad 10$$

In which i is the order of the process the smallest j is either 1 or 0 depending on whether i is an even or odd process respectively the coefficient a_{i+1} is a quantity with the same unit as $\beta_{ijk\dots}^{i}$. Therefore it is easy to show that

$$\chi_{eff}^{i} = N \times d \times \sum_{j}^{i+1,i-1,i-3,\dots} c_j \cos^j\theta$$
$$= N \times r(\theta) \qquad 11$$

and

$$I_{coh} \propto |\chi_{eff}^{i}|^2$$
$$= \left| N \times d \times \sum_{j}^{i+1,i-1,i-3,\dots} c_j \times \cos^j\theta \right|^2$$
$$= |N \times d \times r(\theta)|^2$$
$$= N^2 \times d^2 \times R(\theta) \qquad 12$$

in which $d = a_1$ or $d = a_0$ is called the intensity field factor $c_j = a_j/a_1$ or $c_j = a_j/a_0$ is called the jth general order parameter depending on whether i is even or odd respectively $R(\theta)$ and $r(\theta)$ can both be called the general orientational functional for the $(i+1)$th wave mixing processes or for the ith order linear or nonlinear processes.

Here are expressions for a few of typical coherent spectroscopic techniques. It is clear that for the coherent stimulate Raman process $i = 1$

$$R(\theta) = |1 + c_2 \times \cos^2\theta|^2 \qquad 13$$

while for SHG or SFG $i = 2$

$$R(\theta) = |\cos\theta + c_3 \times \cos^3\theta|^2 \qquad 14$$

while for CARS or other four-wave mixing processes $i = 3$

$$R(\theta) = |1 + c_2 \times \cos^2\theta + c_4 \times \cos^4\theta|^2 \qquad 15$$

and so on.

As we have shown in our previous works on SHG and SFG [9][18][19] the expressions for the coefficients c_j's could be directly derived for a particular processe using the experimental geometry parameters the proper Fresnel factors and the knowledge of the local field factors in the ordered film. With the known general orientational parameter c_j's the detailed behavior and the applications of thus constructed functional $R(\theta)$ in SHG and SFG was also explored extensively [9][18][19]. With explicit expressions such as equation 13 and 15 for other coherent nonlinear spectroscopic techniques their rich orientation dependent behavior could also be explored in similar ways.

It is worth mentioning that the higher the order of the coherent process the higher the order of the dependence of $R(\theta)$ on the order of $\cos\theta$. Therefore the ability of higher order nonlinear processes for probing sensitive orientational changes in the ordered molecular system should be an important feature of nonlinear spectroscopy. It is also important to realize that the null angle measurement for the zero signal intensity i.e. $R(\theta) = 0$ could be a very useful and accurate technique in coherent nonlinear spectroscopies such as SHG [9][26] SFG [19] and CARS [27].

Now let us look at the incoherent processes.

For the incoherent processes the total radiation intensity is the addition of the absolute square of the molecular radiation intensity.

$$I_{incoh} \propto |\vec{e}_{i+1} \cdot \vec{\mu}^{i}|^2$$
$$= |\vec{e}_{i+1} \cdot \beta^{i} \vec{e}_i \vec{e}_{i-1}\dots\vec{e}_1|^2 \qquad 16$$

By considering local field and Fresnel corrections we have

$$I_{incoh} \propto = |L_{i+1}\vec{e}_{i+1} \cdot \beta^{i} L_i \vec{e}_i \times L_{i-1}\vec{e}_{i-1}\dots L_1\vec{e}_1|^2 \qquad 17$$

Following the procedure for the coherent processes

of an ordered molecular system with $U(\theta, \phi, \psi) = U(\theta)$, one should have

$$I_{coh} \propto N \times G \times \sum_{j}^{i+1, i-1, i-3 \cdots} f_{2j} \times \cos^{2j}\theta$$
$$= N \times G \times K(\theta) \qquad\qquad 18$$

where G is the intensity parameter, f_{2j} could also be called the general orientational parameters and $K(\theta)$ the general orientational functional for the ith order incoherent spectroscopy. It is to be noted that normal Raman processes or Surface Enhanced Raman processes (SERS) ($i = 1$) would have their $K(\theta)$ as

$$K(\theta) = 1 + f_2 \cos^2\theta + f_4 \cos^4\theta \qquad 19$$

similar to the form for polarization fluorescence measurement of the immobile chromophores imbedded in an ordered molecular film [5, 28, 29].

From this formulation it seems that the incoherent processes could also be effective tools for probing molecular orientation and ordering in the ordered molecular system. But further examination can easily demonstrate the ineffectiveness of the incoherent processes.

Firstly, because of the incoherent nature, $K(\theta)$ doesn't have interference effect, so the modulation of $K(\theta)$ would always be much weaker than that of $R(\theta)$, which does show interference effect and contains phase information. Secondly, $K(\theta)$ could never actually go to zero, so it would never have the advantage of null angle measurement, which can generate very accurate and powerful information on molecular orientation in the ordered molecular system, thirdly, because there would not be able to have a very explicit expression for the G and f_{2j} parameters, due to the difficulties in performing ensemble average over the squared molecular quantities, it is not possible to have an effective treatment on the local field factors as with the coherent processes [30]. Even though in the literature, polarized absorption, fluorescence have been used extensively to probe the ordered molecular systems [5], only with very crude assumptions on the local field factors, which actually have significant effects on the results, and a calculation is possible. So it is fair to conclude here that those measurements are intrinsically qualitative other than quantitative.

Because Class I spectroscopies are intrinsically incoherent, their potential for measurement on molecular orientation and ordering of ordered molecular system is also limited. However, this is not to say that they can not probe other properties, such as spectra, dynamics of the ordered molecular system. On the other hand, Class I spectroscopies would be excellent tools for studies on photo-fragment alignment and reorientation in the gas phase [31-33], where the problem of local field factor does not exist, and the ensemble average also becomes simple. However, besides clear advantages for condensed phase studies, coherent spectroscopies of Class II may also have advantages in applications in the gas phase, since the signal is proportional to the square of molecular density in coherent processes, comparing to that proportional only to the molecular density in incoherent processes.

3   Conclusion

In this report, I have presented a general formulation of the linear and nonlinear spectroscopies for measurement of the molecular orientation and ordering of the ordered molecular system. I have formulated the general orientational functional for both the coherent and incoherent Class II spectroscopies. Such a formulation has been devised for SHG and SFG processes, and has shown important applications on probing molecular structure, spectroscopy, and phase transitions at various interfacial systems [9, 18, 19]. The generalization of this formulation to other spectroscopies would be useful with other coherent spectroscopic techniques, such as stimulated Raman, SHG, SFG, CARS, etc. in the foreseeable future.

The key to this formulation is to simplify the effective linear or nonlinear molecular susceptibility and construct the general orientational functional with a clear approach to calculate the orientational and intensity parameters from the experimental parameters which determines the orientational and polarization behavior of the general orientational functional in a particular experimental configuration. The usefulness and effectiveness of this approach have been demonstrated in previous works from my group [9, 18, 19]. A major conclusion in this report is that coherent spectroscopic

techniques should have many advantages on quantitative and accurate probing of molecular orientation and ordering of ordered molecular systems over the incoherent ones which are intrinsically qualitative rather than quantitative. These advantages originate from the facts that in coherent spectroscopies the treatment of the local field factor and the ensemble average can be simple and straightforward. The immediate future works following this line are expected for the detailed derivation of the general orientational parameters for specific coherent spectroscopic techniques and experiments the measurement or calculation of the necessary tensorial ratios which need to be used for quantitative treatment of particular molecular systems and exploring broad applications of the principles developed and to be developed.

References

1 Tredgold R H H. Order in Thin Organic Films Cambridge University Press 1994.

2 Roberts G. Langmuir-Blodgett Films Kluwar Academic Publishers 1990.

3 de Gennes P G Prost J. Physics of Liquid Crystal 2nd ed. Oxford University Press Oxford 1995.

4 Photonic Crystals Advances in Design Fabrication and Characterization edited by Busch K Lölkes S Wehrspohn R B Föll H. John Wiley & Sons 2004.

5 Michl J Thulstrup E W. Spectroscopy with Polarized Light VCH New York 1995.

6 Kliger D Lewis J Randall D. Polarized Light in Optics and Spectroscopy Academic Press 1990.

7 Kirkwood J Ulness D J Albrecht D C. *J. Phys. Chem. A* 2000 **104** 4167

8 Heinz T F. Nonlinear Surface Electromagnetic Phenomena Chap. 5 North-Holland New York 1991.

9 Rao Y Tao Y S Wang H F. *J. Chem. Phys.* 2003 **119** 5226

10 Richter L J Petralli-Mallow T P Stephenson J C. *Opt. Letts.* 1998 **23** 1594

11 Shen Y R. *Annu. Rev. Phys. Chem.* 1989 **40** 327

12 Eisenthal K B. *Chem. Rev.* 1996 **96** 1343

13 Corn R M Higgins D A. *Chem. Rev.* 1994 **94** 107

14 Miranda P B Shen Y R. *J. Phys. Chem. B* 1999 **103** 3292

15 Richmond G L. *Chem. Rev.* 2002 **102** 2693

16 Zhang T G Feng Z M Wong G K Ketterson J B. *Langmuir* 1996 **12** 2298

17 Tojima A Manaka T Iwamoto M. *J. Chem. Phys.* 2001 **115** 9010

18 Lu R Gan W Wu B H Chen H Wang H F. *J. Phys. Chem. B* 2004 **108** 7297

19 a . Lu R Gan W Wang H F. *Chin. Sci. Bull.* 2003 **48** 2183
    b . Lu R Gan W Wang H F. *Chin. Sci. Bull.* 2004 **49** 899

20 Born M Wolf E. Principles of Optics Electromagnetic Theory of Propagation Interference and Diffraction of Light 7th Edition Cambridge University Press 1999.

21 Jackson J D. Classical Electrodynamics Wiley Text Books 3rd edition 1998.

22 Boyd R W. Nonlinear Optics Academic Press 2nd edition 2002.

23 Zhuang X Miranda P B Kim D Shen Y R. *Phys. Rev. B* 1999 **59** 12632

24 Goldstein H. Classical Mechanics Addison-Wesley Publishing Company Inc. 1980. 147

25 Zhang D Gutow J Eisenthal K B. *J. Phys. Chem.* 1994 **98** 13729

26 Heinz T F Tom H W K Shen Y R. *Phys. Rev. A* 1983 **28** 1883

27 Saito Y Ishibashi T Hamaguchi H. *J. Raman. Spectrosc.* 2000 **31** 725

28 Edmiston P L Lee J E Wood L L Saavedra S S. *J. Phys. Chem.* 1996 **100** 775

29 Tronin A Strzalka J Chen X Dutton P L Blasie J K. *Langmuir* 2000 **16** 9878

30 Ye P X Shen Y R. *Phys. Rev. B* 1983 **28** 4288

31 Zare R N. Angular Momentum Understanding Spatial Aspects in Chemistry and Physics Wiley-Interscience 1st edition 1988.

32 Greene C H Zare R N. *Annu. Rev. Phys. Chem.* 1982 **33** 119

33 Cong S L Li Y M Yin H M Sun J L Han K L. *Chin. J. Chem. Phys.* 2002 **15** 198