Polarization Selectivity of Third-Order and Fifth-Order Raman Spectroscopies in Liquids and Solids†

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Received: June 18, 2007

Polarization selectivity of third-order and fifth-order Raman spectroscopies is examined for both isotropic liquids and periodic lattices. Our approach directly applies the symmetry property of the probed system to decompose the polarization tensor elements into independent components. The polarization selectivity predicted by symmetry analysis is rigorous and applicable to higher-order Raman spectroscopy. The different polarization selectivities of isotropic systems and periodic lattices can be used as a signature of the liquid−solid phase transition.

Introduction

Ultrafast multipulse time-resolved Raman spectroscopies[1−4] have been applied to extract dynamic and structural information in molecular systems.[5−20] In the $(2n + 1)$th-order Raman experiment, n pairs of ultrafast light pulses excite the system at times $t = 0$, t_1, $(t_1 + t_2)$, ..., and $(t_1 + t_2 + ... + t_{n-1})$. The Raman scattering intensity is detected at $t = (t_1 + t_2 + ... + t_{n-1} + t_n)$. The corresponding measurement is described by the $(2n + 1)$th-order response function $R^{(2n+1)}(t_n, t_{n-1}, ..., t_1)$ of the polarizability tensor Π. The time-resolved spectroscopies can select particular parts of $R^{(2n+1)}(t_n, t_{n-1}, ..., t_1)$ based on the phase-matching condition. The higher-order ($n \geq 2$) spectroscopies hold the promise of discriminating homogeneous and inhomogeneous line shape broadening, which are indistinguishable in the linear spectroscopy.[4]

As a $(2n + 2)$ rank tensor, the $(2n + 1)$th-order response function includes 3^{2n+2} tensor elements. On the basis of the spatial symmetry of the probed system, only a few of these 3^{2n+2} tensor elements are nonzero and distinct. In an isotropic system, the third-order response function has three distinct nonzero elements, $R^{(3)}_{zzzz}$, $R^{(3)}_{zzyy}$, and $R^{(3)}_{zyzy}$. It is also known that the polarizability tensor Π in isotropic systems can be separated into irreducible components, for example, $\Pi = \Pi_I + \Pi_D$ in isotropic systems, where Π_I is the isotropic part of Π and Π_D is the traceless part of Π. As a result, $R^{(2n+1)}$ can be expressed as a superposition of independent response functions induced by various combinations of irreducible parts of Π, for example, $R^{(3)}(t) = R^{(3)}_{\rm iso}(t) + R^{(3)}_{\rm aniso}(t)$ in isotropic systems, where $R^{(3)}_{\rm iso(aniso)}(t)$ is the product of two $\Pi_I(\Pi_D)$'s. Experimentally, we can choose particular angles (magic angles) to excite and probe the system so that these independent response functions are highly separable in spectroscopies. Theoretically, to study the polarization selectivity of a response function requires a complete understanding of the relationship between the distinct tensor elements such as $R^{(3)}_{zzzz(zzyy,zyzy)}(t)$ and the independent components such as $R^{(3)}_{\rm iso(aniso)}(t)$.

For isotropic systems, the polarization selectivity of the third- and fifth-order response functions has been examined by various approaches, such as the orientational diffusion model[5,6] and the instantaneous normal-mode approach.[10,11] However, these approaches invoke approximations which limit the validity of their conclusions. In refs 7 and 8, Cao and co-workers proposed a symmetry-based method to explicitly derive the Raman polarization selectivity for isotropic systems. The method employs the tensor properties of Π_I and Π_D and the geometric symmetry of the probed system without involving detailed angular averages or dynamic assumptions. The resulting polarization selectivity is rigorous and applicable to linear and nonlinear response functions and can be extended to nonisotropic systems. In fact, standard group theory explains the decomposition scheme of the polarizability tensor and the tensor invariance under various symmetry groups. A complete table on decomposing Π in lattice systems is presented in ref 21. We also note that in an earlier paper, Murry and Fourkas[9] explored the rotational invariance for isotropic systems and obtained useful relations for polarization tensors, which were later confirmed by instantaneous normal-modes simulations.[10,11] Further efforts along this line lead to another derivation of polarization selectivity of isotropic liquids.[22] In this paper, we will review the general method developed in refs 7 and 8 for isotropic liquids and extend it using group theory to study polarization selectivity in a particular example of periodic systems, the cubic lattice. To conclude, we summarize the procedure for deriving polarization selectivity and compare the general method with previous studies.

Isotropic Systems

Polarization selectivity in isotropic liquids was explicitly derived earlier in refs 7 and 8 using symmetry analysis and is included here as an illustration of our methods and for comparison with the selectivity for cubic lattices. In this section, we first present the angular average analysis of the third-order response, then the more general symmetry analysis for the third-order response, and finally, the symmetry analysis of the fifth-order response. In the next section, the same set of treatments are applied to cubic lattices.

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† Part of the "Sheng Hsien Lin Festschrift".

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10.1021/jp074716t CCC: $37.00

In classical mechanics, the $(2n + 1)$th-order response function is defined as

$$R^{(2n+1)}(t_n, t_{n-1}, ..., t_1) = (-1)^n \langle \{\Pi(t_1 + t_2 + ... + t_n), \{\Pi(t_1 + t_2 + ... + t_{n-1}), ... , \{\Pi(t_1), \Pi(0)\} ...\}\} \rangle \quad (1)$$

where $\{..., ...\}$ is the Poisson bracket. In the linear Raman measurement, the lowest-order (third-order) response function is usually expressed as $R^{(3)}(t) = -\beta \partial_t C(t)$, where β is the inverse temperature, and $C(t)$ is the time correlation function, $C(t) = \langle \mathbf{P}(t)\Pi(0)\rangle$. In isotropic systems, the polarizability tensor can decompose to

$$\Pi(\vec{r}) = \Pi_{\mathbf{I}} + \Pi_{\mathrm{D}} = h_{\mathrm{I}}(r)\mathbf{I} + h_{\mathrm{D}}(r)\mathbf{D} \quad (2)$$

where $\mathbf{I}$ is the identity matrix, $\mathbf{D}(\Omega) = 3\hat{r}\hat{r} - \mathbf{I}$ is a traceless matrix, $\hat{r} = \vec{r}/r$ is the unit vector along the direction of $\vec{r}$, and Ω is the solid angle. Although eq 2 is derived using the Drude model in ref 7, this general expression holds for all isotropic systems. In the continuum limit, the correlation function is given by

$$C(t) = \int \mathrm{d}\vec{r} \int \mathrm{d}\vec{r}\,' \bar{\Pi}(\vec{r})^{-}\Pi(\vec{r}\,')\mathrm{P}(\vec{r},t;\vec{r}\,',0) \quad (3)$$

For isotropic systems, the joint probability distribution function $P(\vec{r},t;\vec{r}\,',0)$ can be expanded using the spherical harmonics $Y_{lm}(\Omega)$ as

$$P(\vec{r},t;\vec{r}\,',0) = \left(\frac{1}{4\pi}\right) \sum_{l,m} P_l(\vec{r},t;\vec{r}\,',0) Y_{lm}(\Omega) Y^*_{lm}(\Omega') \quad (4)$$

Substituting eq 4 into eq 3 simplifies $C(t)$ to

$$C(t) = C_{\mathrm{iso}}(t)(\mathbf{II}) + C_{\mathrm{aniso}}(t) \sum_{m=-2}^{2} \times \frac{[\int \mathrm{d}\Omega Y_{2m}(\Omega)\mathbf{D}(\Omega)]\,[\int \mathrm{d}\Omega' Y^*_{2m}(\Omega')\mathbf{D}(\Omega')]}{4\pi} \quad (5)$$

where the two independent components are written as

$$C_{\mathrm{iso}}(t) = \int \mathrm{d}r \int \mathrm{d}r' h_{\mathrm{I}}(r) h_{\mathrm{I}}(r') P_0(r,t;r',0) \quad (6)$$

$$C_{\mathrm{aniso}}(t) = \int \mathrm{d}r \int \mathrm{d}r' h_{\mathrm{D}}(r) h_{\mathrm{D}}(r') P_2(r,t;r',0) \quad (7)$$

respectively. The three distinct elements of $R^{(3)}(t)$ are thus written as

$$\begin{cases} R^{(3)}_{zzzz}(t) = 4\partial_t C_{\mathrm{aniso}}(t)/5 + \partial_t C_{\mathrm{iso}}(t) \\ R^{(3)}_{zzyy}(t) = -2\partial_t C_{\mathrm{aniso}}(t)/5 + \partial_t C_{\mathrm{iso}}(t) \\ R^{(3)}_{zyzy}(t) = 3\partial_t C_{\mathrm{aniso}}(t)/5 \end{cases} \quad (8)$$

The above equations relate the distinct tensor elements $R^{(3)}_{zzzz(zzyy,zyzy)}(t)$ and the independent components $C_{\mathrm{iso(aniso)}}(t)$. In comparison with other approaches, this spherical harmonic expansion method generates polarization selectivity for $R^{(3)}(t)$ in a more rigorous manner, but the extension to higher-order response functions requires additional approximations, as shown in ref 8.

Since the most important information of polarization selectivity is the relative ratios of the independent components for various distinct tensor elements, the detailed calculation leading to eq 8 is unnecessary. Instead, these ratios can be directly obtained using the tensor properties of **I** and **D**. As shown in ref 7, the first step is to construct a general expression for $R^{(3)}(t)$ based on the orthogonality relation between **I** and **D**

$$R^{(3)}_{\mu_1\nu_1\mu_0\nu_0}(t) = R^{(3)}_{\mathrm{II},\mu_1\nu_1\mu_0\nu_0}(t) + R^{(3)}_{\mathrm{DD},\mu_1\nu_1\mu_0\nu_0}(t) = c_{\mathrm{II},\mu_1\nu_1\mu_0\nu_0} R^{(3)}_{\mathrm{II}}(t) + c_{\mathrm{DD},\mu_1\nu_1\mu_0\nu_0} R^{(3)}_{\mathrm{DD}}(t) \quad (9)$$

where $R^{(3)}_{\mathrm{II}}(t) \propto -\langle\{\Pi_{\mathrm{I}}(t), \Pi_{\mathrm{I}}(0)\}\rangle$ is the isotropic term (depolarized) and $R^{(3)}_{\mathrm{DD}}(t) \propto -\langle\{\Pi_{\mathrm{D}}(t), \Pi_{\mathrm{D}}(0)\}\rangle$ is the anisotropic term. All other terms, such as $R^{(3)}_{\mathrm{ID}}(t)$ and $R^{(3)}_{\mathrm{DI}}(t)$, are zero. Since all of the diagonal elements are the same and all the off-diagonal elements are zero for **I**, the coefficients of the isotropic component $R^{(3)}_{\mathrm{II}}(t)$ satisfy

$$c_{\mathrm{II},zzzz}:c_{\mathrm{II},zzyy}:c_{\mathrm{II},zyzy} = 1:1:0 \quad (10)$$

Since the **D** matrix is always traceless, $R^{(3)}_{\mathrm{DD},zzzz} + R^{(3)}_{\mathrm{DD},zzxx} + R^{(3)}_{\mathrm{DD},zzyy} = 0$, that is

$$c_{\mathrm{DD},zzzz}:c_{\mathrm{DD},zzyy} = 2:-1 \quad (11)$$

The rotational invariance for isotropic systems further requires $R^{(3)}_{zzzz} = R^{(3)}_{zzyy} + 2R^{(3)}_{zyzy}$, which together with eq 11, results in

$$c_{\mathrm{DD},zzzz}:c_{\mathrm{DD},zzyy}:c_{\mathrm{DD},zyzy} = 4:-2:3 \quad (12)$$

We thus obtain the same ratios for c_{II} and c_{DD} as those derived from the spherical harmonic expansion method, but without any assumptions.

To further demonstrate the symmetry-based method in examining the polarization selectivity, we evaluate the fifth-order response function in isotropic systems. Following ref 8, we identify 12 distinct nonzero tensor elements: $R^{(5)}_{zzzzzz}$, $R^{(5)}_{yyzzzz}$, $R^{(5)}_{zzyyzz}$, $R^{(5)}_{zzzzyy}$, $R^{(5)}_{zzyyxx}$, $R^{(5)}_{zzzyzy}$, $R^{(5)}_{zyzzzy}$, $R^{(5)}_{zyzyzz}$, $R^{(5)}_{zzxyxy}$, $R^{(5)}_{xyzzxy}$, $R^{(5)}_{xyxyzz}$,

TABLE 1: Decomposition of the Fifth-Order Raman Response Function in Isotropic Systems into Five Independent Components Derived in Ref 8[a]

	c_{III}	c_{IDD}	c_{DID}	c_{DDI}	c_{DDD}
$R^{(5)}_{zzzzzz}$	1	1	1	1	1
$R^{(5)}_{yyzzzz}$	1	1	$-1/2$	$-1/2$	$-1/2$
$R^{(5)}_{zzyyzz}$	1	$-1/2$	1	$-1/2$	$-1/2$
$R^{(5)}_{zzzzyy}$	1	$-1/2$	$-1/2$	1	$-1/2$
$R^{(5)}_{zzyyxx}$	1	$-1/2$	$-1/2$	$-1/2$	1
$R^{(5)}_{zzzyzy}$		3/4			$3/8 - a_1$
$R^{(5)}_{zzxyxy}$		3/4			$-3/4 + 2a_1$
$R^{(5)}_{zyzzzy}$			3/4		$3/8 - a_2$
$R^{(5)}_{xyzzxy}$			3/4		$-3/4 + 2a_2$
$R^{(5)}_{zyzyzz}$				3/4	$3/8 + a_1 + a_2$
$R^{(5)}_{xyxyzz}$				3/4	$-3/4 - 2a_1 - 2a_2$
$R^{(5)}_{zyyxxz}$					9/16

[a] The coefficient in each blank block is zero. Two variables a_1 and a_2 are zero for two-time Raman correlation functions but cannot be determined since the time reversal symmetry is not valid for nonlinear response functions. Notice that typos of Table 2 in ref 8 are corrected here.

and $R^{(5)}_{zxyxyz}$. Similar to eq 9, the fifth-order response function in the isotropic systems can be decomposed to

$$R^{(5)}_{\{\mu\nu\}}(t_2,t_1) = c_{\mathrm{III},\{\mu\nu\}}R^{(5)}_{\mathrm{III}}(t_2,t_1) + c_{\mathrm{IDD},\{\mu\nu\}}R^{(5)}_{\mathrm{IDD}}(t_2,t_1) + c_{\mathrm{DID},\{\mu\nu\}}R^{(5)}_{\mathrm{DID}}(t_2,t_1) + c_{\mathrm{DDI},\{\mu\nu\}}R^{(5)}_{\mathrm{DDI}}(t_2,t_1) + c_{\mathrm{DDD},\{\mu\nu\}}R^{(5)}_{\mathrm{DDD}}(t_2,t_1) \quad (13)$$

where $R^{(5)}_{\mathrm{ijk}}(t_2,t_1) \propto \langle\{\Pi_{\mathrm{i}}(t_1 + t_2), \{\Pi_{\mathrm{j}}(t_1), \Pi_{\mathrm{k}}(0)\}\}\rangle$ and $\{\mathrm{i, j, k}\} = \{\mathrm{I, D}\}$. We note that the orthogonality relation between **I** and **D** requires that all of the terms with only one Π_{D} are always zero. The rotational invariance for isotropic systems results in

$$Z_z : Z_{zy} : Z_{zyx} = 1:3:1 \quad (14)$$

where

$$\begin{cases} Z_z = R^{(5)}_{zzzzzz} \\ Z_{zy} = R^{(5)}_{yyzzzz} + R^{(5)}_{zzyyzz} + R^{(5)}_{zzzzyy} + 4[R^{(5)}_{zzzyzy} + R^{(5)}_{zyzzzy} + R^{(5)}_{zyzyzz}] \\ Z_{zyx} = R^{(5)}_{zzyyxx} + 2[R^{(5)}_{zzxyxy} + R^{(5)}_{xyzzxy} + R^{(5)}_{xyxyzz}] + 8R^{(5)}_{zxyxyz} \end{cases} \quad (15)$$

Using eq 14 and the tensor properties of **I** and **D**, we obtain the relative ratios for various c_{ijk}, as shown in Table 1. The derivation details of Table 1 can be found in ref 8; here, we will not repeat the derivation. Several typos in the original table in ref 8, for example, $c_{\mathrm{IDD},zzzyzy}$, are corrected in Table 1. From this table, we find that the ratios c_{III}, c_{IDD}, c_{DID}, and c_{DDI} can be directly obtained from the polarization selectivity of $R^{(3)}(t)$. For the ratios of c_{DDD}, two variables a_1 and a_2 cannot be determined since the time reversal symmetry is not valid for the response functions.

III. Cubic Lattices

In the previous section, we summarized the general method developed in refs 7 and 8 for analyzing polarization selectivity in isotropic systems. Recent studies of the time-resolved Raman spectroscopy in crystalline solids such as ice demonstrate interesting new phenomena.[23−25] The different polarization selectivities for isotropic systems and periodic lattices can serve as a signature for detecting and analyzing the liquid−solid phase transition. To analyze the data from solid systems, it would be desirable to use polarization selectivity to separate independent components. In this section, we extend the symmetry-based method to cubic lattices, a periodic system with the highest rotational symmetry.

Polarization selectivity is determined by the underlying geometric symmetry, which is, in general, described by the corresponding point group. For cubic lattices including classes T, T_h, O, T_d, and O_h, the active Raman modes are described by three irreducible representations, A, E, and T. Since the subscripts associated with A, E, and T for various cubic lattices do not affect our derivation, for convenience, we will ignore these subscripts. These three representations can be expressed as $\mathrm{A} \rightarrow n_x^2 + n_y^2 + n_z^2$, $\mathrm{E} \rightarrow \{n_x^2 + n_y^2 - 2n_z^2, \sqrt{3}(n_y^2 - n_x^2)\}$, and $\mathrm{T} \rightarrow \{n_yn_z, n_xn_z, n_xn_y\}$, where n_x, n_y, and n_z are the projections of the unit vector $\hat{r}$ along the x, y, and z axes, respectively. Using the spherical coordinates, we can define six orthogonal basis functions as

$$\begin{cases} e_{\mathrm{A}}(\Omega) = Y_{00}(\Omega) \\ e_{\mathrm{E}a}(\Omega) = -Y_{20}(\Omega) \\ e_{E\mathrm{b}}(\Omega) = -\dfrac{1}{\sqrt{2}}[Y_{22}(\Omega) + Y_{2\bar{2}}(\Omega)] \\ e_{\mathrm{T}a}(\Omega) = \dfrac{i}{\sqrt{2}}[Y_{21}(\Omega) + Y_{2\bar{2}}(\Omega)] \\ e_{\mathrm{T}b}(\Omega) = -\dfrac{1}{\sqrt{2}}[Y_{21}(\Omega) - Y_{2\bar{2}}(\Omega)] \\ e_{\mathrm{T}c}(\Omega) = -\dfrac{i}{\sqrt{2}}[Y_{22}(\Omega) - Y_{2\bar{2}}(\Omega)] \end{cases} \quad (16)$$

The polarizability tensor Π in the cubic lattices can thus be expressed as

$$\Pi(\vec{r}) = \sum_{ij} h_i(r)e_{ij}(\Omega)$$

where the coefficients $h_i(r)$ for degenerate basis functions are the same. Since the polarizability tensor Π is symmetric, that is, $\Pi_{\mu\nu} = \Pi_{\nu\mu}$, the six basis functions in eq 16 are adequate in describing Π. Assuming the spherical harmonic expansion for the joint probability distribution function $P(\vec{r},t;\vec{r}',0)$ in isotropic systems is still valid, we obtain the third-order Raman correlation function in cubic lattices as

$$C_{\mu_1\nu_1\mu_0\nu_0}(t) = C_{\mathrm{AA},\mu_1\nu_1\mu_0\nu_0}(t) + 2C_{\mathrm{EE},\mu_1\nu_1\mu_0\nu_0}(t) + C_{\mathrm{TT},\mu_1\nu_1\mu_0\nu_0}(t) \quad (17)$$

where

$$\begin{cases} C_{\mathrm{AA},\mu_1\nu_1\mu_0\nu_0}(t) = \dfrac{1}{4\pi}\int \mathrm{d}r \int \mathrm{d}r' h_{1,\mu_0\nu_0}(r)h_{1,\mu_1\nu_1}(r')P_0(r,t;r',0) \\ C_{\mathrm{EE},\mu_1\nu_1\mu_0\nu_0}(t) = \dfrac{1}{4\pi}\int \mathrm{d}r \int \mathrm{d}r' h_{2,\mu_0\nu_0}(r)h_{2,\mu_1\nu_1}(r')P_2(r,t;r',0) \\ C_{\mathrm{TT},\mu_1\nu_1\mu_0\nu_0}(t) = \dfrac{1}{4\pi}\int \mathrm{d}r \int \mathrm{d}r' h_{3,\mu_0\nu_0}(r)h_{3,\mu_1\nu_1}(r')P_2(r,t;r',0) \end{cases} \quad (18)$$

Although the third-order response function can be further evaluated using $R^{(3)}(t) = -\beta\partial_t C(t)$, we shall demonstrate that polarization selectivity can be derived much more easily without additional assumptions.

The method in ref 8 shows that the third-order response functions in cubic lattices include three distinct tensor elements,

TABLE 2: Decomposition of the Third-Order Raman Response Function in Cubic Lattices (D_6, C_{6v}, D_{3h}, D_{6h}) into Six Independent Components; the Coefficient in Each Blank Block Is Zero

	$c_{\mathrm{A}_{1a}\mathrm{A}_{1a}}$	$c_{\mathrm{E}_2\mathrm{E}_2}$	$c_{\mathrm{A}_{1a}\mathrm{A}_{1b}}$	$c_{\mathrm{A}_{1b}\mathrm{A}_{1a}}$	$c_{\mathrm{A}_{1b}\mathrm{A}_{1b}}$	$c_{\mathrm{E}_1\mathrm{E}_1}$
$R^{(3)}_{xxxx}$	1	1				
$R^{(3)}_{xxyy}$	1	−1				
$R^{(3)}_{xyxy}$		1				
$R^{(3)}_{xxzz}$			1			
$R^{(3)}_{zzxx}$				1		
$R^{(3)}_{zzzz}$					1	
$R^{(3)}_{xzxz}$						1

TABLE 3: Decomposition of the Fifth-Order Raman Response Function in Cubic Lattices (*T*, *T*$_h$, *O*, *T*$_d$, and *O*$_h$) into Twelve Independent Components; the Coefficient in Each Blank Block Is Zero

	c_{AAA}	c_{AEE}	c_{EAE}	c_{EEA}	c_{EEE}	c_{ATT}	c_{ETT}	c_{TAT}	c_{TET}	c_{TTA}	c_{TTE}	c_{TTT}
$R^{(5)}_{zzzzzz}$	1	1	1	1	1							
$R^{(5)}_{yyzzzz}$	1	1	−1/2	−1/2	−1/2							
$R^{(5)}_{zzyyzz}$	1	−1/2	1	−1/2	−1/2							
$R^{(5)}_{zzzzyy}$	1	−1/2	−1/2	1	−1/2							
$R^{(5)}_{zzyyxx}$	1	−1/2	−1/2	−1/2	1							
$R^{(5)}_{zzzyzy}$						1	−1/2					
$R^{(5)}_{zzxyxy}$						1	1					
$R^{(5)}_{zyzzzy}$								1	−1/2			
$R^{(5)}_{xyzzxy}$								1	1			
$R^{(5)}_{zyzyzz}$										1	−1/2	
$R^{(5)}_{xyxyzz}$										1	1	
$R^{(5)}_{zyyxxz}$												1

$R^{(3)}_{zzzz}$, $R^{(3)}_{zzyy}$, and $R^{(3)}_{zyzy}$. Similar to eq 2, the polarizability tensor in cubic lattices can be as general as $\Pi = \Pi_{\mathrm{A}} + \Pi_{\mathrm{E}} + \Pi_{\mathrm{T}}$, where Π_{A}, Π_{E}, and Π_{T} are irreducible tensor elements corresponding to the representations A, E, and T, respectively. Due to the orthogonality relations among Π_{A}, Π_{E}, and Π_{T}, the third-order response function can be expressed as

$$R^{(3)}_{\{\mu\nu\}}(t) = c_{\mathrm{AA},\{\mu\nu\}}R^{(3)}_{\mathrm{AA}}(t) + c_{\mathrm{EE},\{\mu\nu\}}R^{(3)}_{\mathrm{EE}}(t) + c_{\mathrm{TT},\{\mu\nu\}}R^{(3)}_{\mathrm{TT}}(t) \tag{19}$$

where $R^{(3)}_{\mathrm{ii}}(t) \propto -\langle\{\Pi_{\mathrm{i}}(t), \Pi_{\mathrm{i}}(0)\}\rangle$ and i = A, E, or T. As shown in ref 21, the irreducible polarizability tensors in cubic lattices satisfy the following conditions: Π_{A} is proportional to the identity tensor **I**, that is, $\Pi_{\mathrm{A},\mu\nu} \propto \delta_{\mu\nu}$; Π_{E} is a diagonal and traceless matrix, that is, $\Pi_{\mathrm{E},\mu\nu} = \Pi_{\mathrm{E},\mu\mu}\delta_{\mu\nu}$ and

$$\sum_{\mu}\Pi_{\mathrm{E},\mu\mu} = 0$$

and Π_{T} is an off-diagonal matrix, that is, $\Pi_{\mathrm{T},\mu\mu} = 0$. Similar to the general method for $R^{(3)}(t)$ in isotropic systems, we use the above tensor properties to evaluate the relative ratios for c_{AA}, c_{EE}, and c_{TT}. As a result, the distinct tensor elements of $R^{(3)}(t)$ in the cubic are decomposed into

$$\begin{cases} c_{\mathrm{AA},zzzz}{:}c_{\mathrm{AA},zzyy}{:}c_{\mathrm{AA},zyzy} = 1{:}1{:}0 \\ c_{\mathrm{EE},zzzz}{:}c_{\mathrm{EE},zzyy}{:}c_{\mathrm{EE},zyzy} = 1{:}-1/2{:}0 \\ c_{\mathrm{TT},zzzz}{:}c_{\mathrm{TT},zzyy}{:}c_{\mathrm{TT},zyzy} = 0{:}0{:}1 \end{cases} \tag{20}$$

The comparison between eqs 8 and 20 shows that Raman modes Π_{E} and Π_{T} in the cubic lattices become degenerate modes Π_{D} in isotropic systems due to rotational invariance.

Next, we proceed to study the fifth-order Raman response functions $R^{(5)}(t_2,t_1)$ in cubic lattices. Following the method in ref 8, we identify 12 distinct nonzero elements: $R^{(5)}_{zzzzzz}$, $R^{(5)}_{yyzzzz}$, $R^{(5)}_{zzyyzz}$, $R^{(5)}_{zzzzyy}$, $R^{(5)}_{zzzyzy}$, $R^{(5)}_{zzyyxx}$, $R^{(5)}_{zyzzzy}$, $R^{(5)}_{zyzyzz}$, $R^{(5)}_{zzxyxy}$, $R^{(5)}_{xyzzxy}$, $R^{(5)}_{xyxyzz}$, and $R^{(5)}_{zyyxxz}$. The decomposition of Π allows us to write $R^{(5)}(t_2,t_1)$ as

$$\begin{aligned} R^{(5)}_{\{\mu\nu\}}(t_2,t_1) = {} & c_{\mathrm{AAA},\{\mu\nu\}}R^{(5)}_{\mathrm{AAA}}(t_2,t_1) + c_{\mathrm{AEE},\{\mu\nu\}}R^{(5)}_{\mathrm{AEE}}(t_2,t_1) + \\ & c_{\mathrm{EAE},\{\mu\nu\}}R^{(5)}_{\mathrm{EAE}}(t_2,t_1) + c_{\mathrm{EEA},\{\mu\nu\}}R^{(5)}_{\mathrm{EEA}}(t_2,t_1) + \\ & c_{\mathrm{EEE},\{\mu\nu\}}R^{(5)}_{\mathrm{EEE}}(t_2,t_1) + c_{\mathrm{ATT},\{\mu\nu\}}R^{(5)}_{\mathrm{ATT}}(t_2,t_1) + \\ & c_{\mathrm{TAT},\{\mu\nu\}}R^{(5)}_{\mathrm{TAT}}(t_2,t_1) + c_{\mathrm{TTA},\{\mu\nu\}}R^{(5)}_{\mathrm{TTA}}(t_2,t_1) + \\ & c_{\mathrm{ETT},\{\mu\nu\}}R^{(5)}_{\mathrm{ETT}}(t_2,t_1) + c_{\mathrm{TET},\{\mu\nu\}}R^{(5)}_{\mathrm{TET}}(t_2,t_1) + \\ & c_{\mathrm{TTE},\{\mu\nu\}}R^{(5)}_{\mathrm{TTE}}(t_2,t_1) + c_{\mathrm{TTT},\{\mu\nu\}}R^{(5)}_{\mathrm{TTT}}(t_2,t_1) \end{aligned} \tag{21}$$

where all other terms, such as $R^{(5)}_{\mathrm{AAT}}(t_2,t_1)$, vanish due to the symmetry of the irreducible polarizability tensors. The tensor properties of Π_{A}, Π_{E}, and Π_{T} are used to obtain the complete relationship between the distinct nonzero tensor elements and the independent components of $R^{(5)}(t_2,t_1)$. For conciseness, here, we evaluate c_{EEE} as an example, and the ratios for other c_{ijk} ({i, j, k} = {A, E, T}) can be obtained similarly. Since all of the off-diagonal elements of Π_{E} are zero, the distinct elements with nonzero $R^{(5)}_{\mathrm{EEE}}(t_2,t_1)$ are $R^{(5)}_{zzzzzz}$, $R^{(5)}_{yyzzzz}$, $R^{(5)}_{zzyyzz}$, $R^{(5)}_{zzzzyy}$, and $R^{(5)}_{zzyyxx}$. The traceless property of Π_{E} requires $R^{(5)}_{xxzzzz} + R^{(5)}_{yyzzzz} + R^{(5)}_{zzzzzz} = 0$, yielding $c_{\mathrm{EEE},zzzzzz}{:}c_{\mathrm{EEE},yyzzzz} = 1{:}-1/2$. Similarly, we obtain the ratios between $c_{\mathrm{EEE},zzzzzz}$ and $c_{\mathrm{EEE},zyyzzz(zzzzyy)}$. The traceless property of Π_{E} also requires $R^{(5)}_{zzyyxx} + R^{(5)}_{zzyyyy} + R^{(5)}_{zzyyzz} = 0$, which, together with the above ratios, results in

$$c_{\mathrm{EEE},zzyyxx}{:}c_{\mathrm{EEE},zzzzzz}{:}c_{\mathrm{EEE},yyzzzz(zzyyxx,zzzzyy)} = 1{:}1{:}-1/2 \tag{22}$$

The relative ratios for all of the c_{ijk} are presented in Table 3. Due to the lose of spatial symmetry from isotropic systems to cubic lattices, more independent fifth-order Raman response functions appear in Table 3 than those in Table 1. For example, the degenerate $R^{(5)}_{\mathrm{DDD}}$ in isotropic systems becomes $R^{(5)}_{\mathrm{EEE}}$, $R^{(5)}_{\mathrm{EET}}$, $R^{(5)}_{\mathrm{ETE}}$, $R^{(5)}_{\mathrm{EET}}$, and $R^{(5)}_{\mathrm{TTT}}$ for different tensor elements. Independent components involving modes Π_{T} are easy to separate. For example, we can use $2R^{(5)}_{zzzyzy} + R^{(5)}_{zzxyxy}$ to extract independent component $R^{(5)}_{\mathrm{ATT}}$. As shown in the top left corner of Table 2, independent components involving only Π_{A} and Π_{E} are entangled and difficult to separate.

IV. Conclusion and Discussion

In this paper, we have studied the polarization selectivity of the response functions in isotropic systems and cubic lattices. Our procedure to decompose the $(2n + 1)$th-order Raman response function involves two steps. The first step is to extract the distinct tensor elements using the spatial symmetry of the system, as shown in ref 8. The second step is to decompose the polarizability tensor Π into the irreducible Raman active modes, $\Pi = \Pi_{\mathrm{I}} + \Pi_{\mathrm{D}}$, for the isotropic systems (whereas the decomposition for other anisotropic systems is presented in ref 21). These irreducible polarizability tensors are used to express $R^{(2n+1)}(t_n, t_{n-1}, ..., t_1)$ as the superposition of the independent response functions, for example, $R^{(3)}_{\{\mu\nu\}}(t) = c_{\mathrm{II},\{\mu\nu\}}R^{(3)}_{\mathrm{II}}(t) + c_{\mathrm{DD},\{\mu\nu\}}R^{(3)}_{\mathrm{DD}}(t)$ in isotropic systems. Extreme care should be taken in this step to avoid missing or overcounting the independent components, especially for higher-order response functions. For example, two distinct A-type Raman modes ($x^2 + y^2$, z^2) exist in the hexagonal lattices so that the third-order independent response function $R^{(3)}_{\mathrm{AA}}(t)$ exhibits four distinct components rather than three components in cubic lattices or two components in isotropic liquids.

Next, we use the tensor properties of the irreducible polarizability tensors to obtain the relative values of the coefficients for the independent response functions. For example, the traceless Π_{D} always provides $c_{...\mathrm{D}...,...zz...}:c_{...\mathrm{D}...,...yy...} = 1{:}-1/2$ in isotropic systems. To determine all of the coefficients, other symmetry operations may be invoked. For example, the rotational invariance requires $R^{(2n+1)}_{...xx...xx...} = R^{(2n+1)}_{...xx...yy...} + R^{(2n+1)}_{...xy...xy...} + R^{(2n+1)}_{...xy...yx...}$ in the isotropic systems, whereas the invariance over $2n\pi/3$ in the $x-y$ plane provides the same result in the trigonal and hexagonal lattices.

Compared with other approaches, our general method here demonstrates several advantages in studying the polarization selectivity in Raman spectroscopies. (i) Our approach is directly applicable to evaluate the response functions, while other approaches often use the evaluation of the correlation functions as an intermediate step. The transformation from the correlation functions to the response functions involves two difficulties. First, for each $(2n + 1)$th-order response function, the corresponding correlation functions include at least 2^{n-1} terms. Second, the additional stability matrix may prevent the explicit transformation from the response functions to the correlation functions. (ii) The symmetry-based method does not require any additional dynamic approximations, such as Brownian motions or a Taylor expansion of the polarizability $\Pi(t)$. (iii) The symmetry-based method avoids calculations of angular averages, which are always necessary in other approaches. The selectivity thus obtained is valid for all time scales, interaction potentials, and molecular structures.

Acknowledgment. This work is supported by the U.S. Army through the Institute of Soldier Nanotechnologies at MIT.

References and Notes

(1) Fleming, G. R. *Annu. Rev. Phys. Chem.* **1986**, *37*, 81.
(2) Mukamel, S. *Principles of Nonlinear Optical Spectrocopy*; Oxford University Press: New York, 1995.
(3) Mukamel, S. *Annu. Rev. Phys. Chem.* **2000**, *51*, 691.
(4) Tanimura, Y.; Mukamel, S. *J. Chem. Phys.* **1995**, *99*, 9496.
(5) Tokmakoff, A. *J. Chem. Phys.* **1996**, *105*, 1.
(6) Tokmakoff, A. *J. Chem. Phys.* **1996**, *105*, 13.
(7) Cao, J. S.; Wu, J. L.; Yang, S. L. *J. Chem. Phys.* **2002**, *116*, 3739.
(8) Cao, J. S.; Yang, S. L.; Wu, J. L. *J. Chem. Phys.* **2002**, *116*, 3760.
(9) Murry, R. L.; Fourkas, J. T. *J. Chem. Phys.* **1997**, *107*, 9726.
(10) Murry, R. L.; Fourkas, J. T.; Keyes, T. *J. Chem. Phys.* **1998**, *109*, 7913.
(11) Keyes, T.; Fourkas, J. T. *J. Chem. Phys.* **2000**, *112*, 287.
(12) Ma, A.; Stratt, R. M. *J. Chem. Phys.* **2002**, *116*, 4972.
(13) Ma, A.; Stratt, R. M. *J. Chem. Phys.* **2003**, *119*, 8500.
(14) Saito, S.; Ohmine, I. *J. Chem. Phys.* **1997**, *106*, 4889.
(15) Saito, S.; Ohmine, I. *J. Chem. Phys.* **2003**, *119*, 9073.
(16) Jansen, T.; Duppen, K.; Snijders, J. *Phys. Rev. B* **2003**, *67*, 134206.
(17) (a) Milne, C. J.; Li, Y. L.; Jansen, T.; Huang, L.; Miller, R. J. D. *J. Phys. Chem. B* **2006**, *110*, 19867. (b) Astinov, V.; Kubarych, K. J.; Milne, C. J.; Miller, R. J. D. Diffractive Optics Implementation of Six-Wave Mixing. *Opt. Lett.* **2006**, *25*, 853.
(18) Kubarych, K. J.; Milne, C. J.; Miller, R. J. D. *Int. Rev. Phys. Chem.* **2003**, *22*, 497.
(19) Kaufman, L. J.; Blank, D. A.; Fleming, G. R. *J. Chem. Phys.* **2001**, *114*, 2312.
(20) Kaufman, L. J.; Heo, J.; Ziegler, L.; Fleming, G. R. *Phys. Rev. Lett.* **2002**, *88*, 207402.
(21) Loudon, R. *Adv. Phys.* **1964**, *13*, 423.
(22) A similar derivation of polarization selectivity in isotropic liquids was obtained by Fourkas in a recent note.
(23) Nagata, Y.; Tanimura, Y. *J. Chem. Phys.* **2006**, *124*, 024508.
(24) Nagata, Y.; Hasegawa, T.; Tanimura, Y. *J. Chem. Phys.* **2006**, *124*, 194504.
(25) Saito, S.; Ohmine, I. *J. Chem. Phys.* **2006**, *125*, 084506.
(26) Butcher, P. N.; Cotter, D. *The Elements of Nonlinear Optics*; Cambridge University Press: New York, 1990.