

Antisymmetric Transition Polarizability Induced by Intermolecular Charge-Transfer Interactions

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Antisymmetric vibrational transition polarizability induced by intermolecular charge-transfer interactions is proposed and studied by using group theory, especially time-reversal symmetry, and Milliken's theory of charge-transfer complexes. The results show that under the Born–Oppenheimer (B–O) approximation, the antisymmetric transition polarizability of even-electron systems with real representation ground states is zero. But when a donor–acceptor complex is formed by the partial or complete transfer of an electron from donor to acceptor, the acceptor (donor) can have nonzero antisymmetric transition polarizability. Thus charge-transfer-induced antisymmetric light scattering from the interaction even-electron systems, especially charge-transfer complexes, can exist, which is characteristic of charge-transfer interaction and processes. The theoretical results are associated qualitatively with anomalous Raman polarization experiment of anthracene anion–Na⁺ ion complex and with the complexation enhancements of depolarization ratios of some substituted pyridine–Br₂ complexes. The connections of the charge-transfer-induced antisymmetric Raman tensors to sum-frequency vibrational spectroscopy (SFVS) in chiral solutions and in photoionization processes have been discussed.

1. Introduction

Antisymmetric matter tensors are important for linear magneto-optical and light scattering investigations,^{1,2} which are connected closely with the time-reversal symmetry.^{3,4} Antisymmetric Raman scattering for a molecule is characterized by the anomalous depolarization ratio that is conveniently expressed in terms of the rotational invariants of the transition polarizability component squares.⁵ The electronic, vibrational, and rotational antisymmetric transition polarizabilities, antisymmetric third rank hyperpolarizability, and vibronic effect, spin–orbital coupling, and rotational effect have been investigated.^{1–3,5–14} However, intermolecular interaction influences on the antisymmetric transition polarizabilities have not been studied yet, even though intermolecular interactions have prominent influences on the properties of the interacting systems^{15,16} and also on their polarizability and light scattering.¹⁷ In this paper, we attempt to study this problem.

We catalog intermolecular forces into two kinds: the non-charge-transfer electric interactions, such as electrostatic and dispersion forces, and the charge-transfer interactions. The non-charge-transfer interaction cannot directly induce any addition antisymmetric light scattering of even-electron systems, because in any system under a time-even electric field, time-odd phenomena such as antisymmetric polarizability cannot acquire a net observable amplitude, and there is no simple electric analogue of the Faraday effect.^{3,18} However, charge-transfer interaction can make an important contribution to antisymmetric light scattering from interacting even-electron systems. Its physical arguments are as follows. Under the Born–Oppenheimer (BO) approximation, the antisymmetric transition polarizabilities of even-electron systems in a real representation electronic state have been proved to be zero,^{9–11} which are applicable to most of molecules in nondegenerate ground states.

For odd-electron systems under the BO approximation, the antisymmetric transition polarizabilities can be nonzero due to time-reversal symmetry.^{3,7,10,11} Charge-transfer interaction makes even-electron systems become odd-electron states with certain probability due to the charge-transfer process in charge-transfer complexes,^{20,26a} which partially changes their time-reversal properties and induces the additional antisymmetric transition polarizabilities.

In this paper the effects of the charge-transfer interactions on antisymmetric light scattering from even-electron systems have been studied by using Mulliken's two-state resonant theory of donor–acceptor complexes^{20,21} and group theory, especially time-reversal arguments. In section 2, formulas of charge-transfer-induced antisymmetric transition polarizabilities at frequencies not far from and near the resonance to the charge-transfer absorption bands are given. The anthracene anion–Na⁺ ion system and some substituted pyridine–Br₂ complexes, as examples of charge-transfer complexes, have been qualitatively discussed in sections 3 and 4, respectively. The connections of the charge-transfer-induced antisymmetric Raman tensors to the SFVS in chiral solutions and in photoionization processes have been discussed in section 5.

Understanding and control of charge-transfer comprises one of the broadest and most active research areas of physical chemistry today.^{4,19} It is known¹⁹ that resonance Raman spectroscopy is an ideal probe to evaluate the parameters in the electron transfer if the optical equivalent of electron transfer can be observed. But there are some experimental limitations because optical electron-transfer bands are often of low intensity and convoluted with bands of higher intensity in the spectrum. The charge-transfer-induced antisymmetric Raman scattering can characterize a charge-transfer band in the spectrum and may be helpful for charge-transfer studies. On the other hand, for fundamental investigation of the Raman depolarization ratio, in addition to the contribution of the large-amplitude motion,²³

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the charge-transfer-induced antisymmetric scattering can be another origin of the depolarization ratios far higher than normal value for many hydrocarbons.²²

2. Theory

To study antisymmetric transition polarizabilities, their effective operators $\hat{\alpha}_{\rho\sigma}^A$ have been introduced^{3,7,10,11,33} and by using them the antisymmetric transition polarizability tensor can be written

$$(\alpha_{\rho\sigma}^A)_{mn} = \langle m | \hat{\alpha}_{\rho\sigma}^A | n \rangle \quad (1)$$

where $|m\rangle$ and $|n\rangle$ are the initial and final states, respectively. The effective antisymmetric transition polarizability operators, $\hat{\alpha}_{\rho\sigma}^A$, are time-odd and anti-Hermitian. On the basis of those properties, from eq 1 the time-reversal symmetry selection rule for antisymmetric Raman scattering has been deduced^{2,3,10,11}

$$\langle m | \hat{\alpha}_{\rho\sigma}^A | n \rangle = \langle \hat{K}m | \hat{\alpha}_{\rho\sigma}^A | \hat{K}n \rangle^* \quad (2)$$

where \hat{K} is the time-reversal operator. This important formula is due to Barron and Svendsen.⁷

On the basis of eqs 1 and 2 and the time-reversal arguments, it has been proved^{9–11} that for even-electron system with the ground state belonging to the real representation of a group, the imaginary part of the antisymmetric Raman transition polarizability is strictly zero; under the Born–Oppenheimer approximation, its real part is approximately zero, with a few exceptions, such as porphyrin compounds in resonance cases.¹¹

On the other hand, for an odd-electron system, a 2-fold Kramers-degenerate level associated with spin degeneracy, such as $|m\rangle$, $|\hat{K}m\rangle$ and $|n\rangle$, $|\hat{K}n\rangle$, provide a source of antisymmetric tensors in atoms and molecules.³ For an odd-electron system we have, by using eq 2 and $\hat{K}^2 = -1$,²⁵

$$\begin{aligned} \langle m | \hat{\alpha}_{\rho\sigma}^A | n \rangle &= \langle \hat{K}m | \hat{\alpha}_{\rho\sigma}^A | \hat{K}n \rangle^* = a \\ \langle m | \hat{\alpha}_{\rho\sigma}^A | \hat{K}n \rangle &= - \langle \hat{K}m | \hat{\alpha}_{\rho\sigma}^A | n \rangle^* = b \end{aligned} \quad (3)$$

Thus the antisymmetric Raman scattering intensity of an odd-electron system can be nonzero,^{10,7}

$$I_{\rho\sigma}^A \propto 2[|a|^2 + |b|^2] \quad (4)$$

For a charge-transfer complex, under the B–O approximation the wave functions can be written as

$$|m\rangle = |g\rangle|i\rangle \quad |n\rangle = |g\rangle|j\rangle$$

where $|g\rangle$ is the ground electronic state and i and j are the initial and final vibrational quantum numbers, respectively. Thus eq 1 becomes

$$(\alpha_{\rho\sigma}^A)_{gi,gj} = \langle i | \langle g | \hat{\alpha}_{\rho\sigma}^A | g \rangle | j \rangle \quad (5)$$

An intramolecular vibration of an acceptor in a weak charge-transfer complex is approximately independent of the donor in a complex. So is a donor. Hence to study the antisymmetric transition polarizability of the acceptor (or donor) in a charge-transfer complex, $\hat{\alpha}_{\rho\sigma}^A$, $|i\rangle$, and $|j\rangle$ in eq 5 refer to the investigated acceptor (or donor) in the complex. This approach has been often used to deal with a quantity of a subsystem as a part of the supersystem.^{26b,31}

The modern theory of charge-transfer complexes was first proposed and developed by Mulliken^{20,21} and was very suc-

cessful in explaining the origin of the charge-transfer absorption band and their stability. Mulliken's theory used a valence bond description (two-state resonant theory of donor–acceptor complexes). Although it is difficult to make quantitative calculation in contrast to the ab initio molecular orbital approaches, qualitative valence bond approaches have the great merit that they relate in a direct way the properties of the complex to some properties of the components, which is suitable for qualitative research in this paper. Mulliken wrote a very simple diatomic-like wave function for the ground and excited states of a charge-transfer complex,²⁰ for the ground states

$$\psi_g \equiv |g\rangle = C_0\psi_0(D,A) + C_1\psi_1(D^+,A^-) \quad (6)$$

and for the excited state

$$\psi_e \equiv |e\rangle = C_0^*\psi_1(D^+,A^-) - C_1^*\psi_0(D,A) \quad (7)$$

where D refers to the donor and A the acceptor. Equations 6 and 7 state very simply that the complex may be considered as a mixture of two states, a nonionic pair $\psi_0(D,A) \equiv \psi_0$ describing the nonbonding pair (nonbonded state) and an ionic pair $\psi_1(D^+,A^-) \equiv \psi_1$ (the dative state), which can be obtained by transferring one electron from the donor (D) to the acceptor (A). The extent to which electron transfer has occurred in the complex is measured by the ratio of the probabilities of dative and nonbond structures, in the ground state, that is, C_1^2/C_0^2 .

Now consider a charge-transfer complex with an even-electron acceptor A and donor D and after the charge transfer, A^- (or D^+) is an odd-electron system. Inserting eq 6 into eq 5, the antisymmetric transition polarizability of an even-electron acceptor in the complex is expressed as

$$\begin{aligned} (\alpha_{\rho\sigma}^A(A))_{gi,gj} &= \langle i | \{ C_0^2 \langle \psi_0 | \hat{\alpha}_{\rho\sigma}^A | \psi_0 \rangle + C_1^2 \langle \psi_1 | \hat{\alpha}_{\rho\sigma}^A | \psi_1 \rangle + \\ &C_0 C_1 [\langle \psi_0 | \hat{\alpha}_{\rho\sigma}^A | \psi_1 \rangle + \langle \psi_1 | \hat{\alpha}_{\rho\sigma}^A | \psi_0 \rangle] \} | j \rangle \end{aligned} \quad (8)$$

According to the foregoing conclusion on the antisymmetric transition polarizability for a even- or odd-electron system^{3,7,10,11} and eq 2, we have

$$\begin{aligned} \langle \psi_0 | \hat{\alpha}_{\rho\sigma}^A | \psi_0 \rangle &= 0 \\ \langle \psi_1 | \hat{\alpha}_{\rho\sigma}^A | \psi_1 \rangle &\neq 0 \\ \langle \psi_0 | \hat{\alpha}_{\rho\sigma}^A | \psi_1 \rangle &= \langle \psi_0 | \hat{\alpha}_{\rho\sigma}^A | \hat{K} \psi_1 \rangle^* \neq 0 \end{aligned} \quad (9)$$

thus the antisymmetric transition polarizability of the acceptor becomes

$$\begin{aligned} (\alpha_{\rho\sigma}^A(A))_{gi,gj} &= \langle i | \{ C_1^2 \langle \psi_1 | \hat{\alpha}_{\rho\sigma}^A | \psi_1 \rangle + C_0 C_1 [\langle \psi_0 | \hat{\alpha}_{\rho\sigma}^A | \psi_1 \rangle + \\ &\langle \psi_1 | \hat{\alpha}_{\rho\sigma}^A | \psi_0 \rangle] \} | j \rangle \end{aligned} \quad (10)$$

which is not zero. Thus the even-electron acceptor of charge-transfer complexes has nonzero antisymmetric transition polarizability when one electron charge of the donor is transferred in part or in whole to the acceptor of the complexes. For an even-electron donor similar results can be obtained. Hence a charge-transfer interaction can induce a nonzero addition antisymmetric transition polarizability from intermolecular charge-transfer interaction systems A and D. Two examples of charge-transfer complexes are discussed as follows in sections 3 and 4.

3. An⁻–Na⁺ Ion Complex

Aromatic hydrocarbons react with alkali metals in inert solvents such as tetrahydrofuran (THF) to form the mononega-

tive or dinegative ions.²⁷ Depending on the nature of the solvent, the alkali metal and temperature, these ions may be “free” or associated with the alkali ions to ion pairs.^{27,28,32} Fujimoto et al.^{29,30} presented the anomalous Raman polarization by measuring the polarization dispersion of a resonant depolarized line at 1466 cm⁻¹ (b_{1g} mode) of anthracene (An) anions excited near the first absorption band, which may be attributed to the charge-transfer band of the An⁻–Na⁺ complex.^{27–30} For this vibration at 1466 cm⁻¹ (b_{1g} mode) the depolarization ratio has been verified to increase beyond the normal maximum of 3/4, from 0.7 (at transparent wavelengths) to 1.15 (near the resonance), indicating the nonzero antisymmetric transition polarizabilities.²⁹ In their investigation the bulk of An²⁻ may probably be the associated species with Na⁺, i.e., the (Na⁺)₂–An²⁻ complex. For An⁻, it is coexistence of free and associated species, the An⁻–Na⁺ complex.³⁰ Now on the basis of the theory in section 2 we analyze the matter in three ways, i.e., time-reversal, spatial symmetry arguments, and depolarization ratio dispersion, as follows.

(i) First, on the basis of time-reversal arguments, it was proved^{7,10,11} and described in section 2 that under B–O approximation, the antisymmetric light scattering tensors of even-electron systems, such as An, An²⁻ is zero, but they can be nonzero for odd-electron systems such as An⁻. Thus the antisymmetric Raman scattering tensors are due to An⁻ or the An⁻–Na⁺ complex in the measurement of anomalous Raman polarization of anthracene anions.^{29,30} This agrees with Fujimoto et al.’s experimental fact that only in the An⁻–Na⁺ system was anomalous Raman polarization observed.²⁹

(ii) Second, on the basis of spatial symmetry arguments, we evaluate the antisymmetric transition polarizability of An⁻ in the An⁻–Na⁺ complex and compare it with the experiment results.^{29,30} Here we only consider the first term in eq 10, which may be dominant.

In resonance Raman scattering, the Albrecht *B* term (Herzberg–Teller resonance) is responsible for the Raman scattering by nontotally symmetric modes (here b_{1g} mode)^{5,7,24} and the antisymmetric transition polarizability can be written^{5,7}

$$(\alpha_{\rho\sigma}^A(A))_{gi,gj} = \frac{1}{h} \tilde{\nu} \left[\frac{\langle i_1 | j_1 \rangle \langle j_1 | Q | i_0 \rangle}{\tilde{\nu}_{eg} - \tilde{\nu} - i\Gamma_0} - \frac{\langle i_1 | Q | j_0 \rangle \langle j_0 | i_0 \rangle}{\tilde{\nu}_{eg} + \tilde{\nu}_Q - \tilde{\nu} - i\Gamma_1} \right] Z_{\rho\sigma}^A \quad (11)$$

and

$$Z_{\rho\sigma}^A = \sum_{g,e,k} \frac{1}{h\tilde{\nu}_{ek}} [(g|\mu_\rho|e)(e|h'_Q|k)(k|\mu_\sigma|g) - (g|\mu_\sigma|e)(e|h'_Q|k)(k|\mu_\rho|g)] \quad (12)$$

$$h'_Q \equiv \left(\frac{\partial \hat{H}}{\partial Q} \right)_0 \quad (13)$$

where for the sake of simplicity eq 11 includes only one resonant excited electronic state $|e\rangle$, which is vibronically coupled with one of other excited electronic states $|k\rangle$ through the vibrational mode Q . The suffixes 0 and 1 in eq 11 refer to the ground and first excited vibrational states in the ground electronic state $|g\rangle$ and the resonant excited electronic state $|e\rangle$, respectively, and they are due to the 0–0 and 0–1 vibronic transitions. In eq 12 the summation is made over all the degenerate components of the electronic states $|g\rangle$, $|e\rangle$, and $|k\rangle$, because they are 2-fold degenerate for odd-electron An⁻ anion in the complex.³⁴ As an example, we evaluate the antisymmetric transition polarizability component $(\alpha_{xy}^A(A))_{gi,gj}$ by eqs 11–13 as follows.

The anomalous polarization band at 1466 cm⁻¹ of An⁻ ions belongs to a nontotally symmetric modes $\Gamma_3(b_{1g})$ of double group D_{2h}^* ,³⁴ which was discussed in ref 29 by a single value group, and thus Fujimoto et al.’s analysis²⁹ apply to An and An²⁻ only but does not to a odd-electron system An⁻. Now we use the notions in ref 34 and apply a double group D_2^* to the An⁻ anion. On the basis of Fujimoto et al.’s identification of electron absorption spectra of An⁻,²⁹ all the group representations of the electronic states $|g\rangle$, $|e\rangle$, and $|k\rangle$, are Γ_5 , i.e., $|g\rangle = (\phi_{1/2}^5, \phi_{-1/2}^5)$, $|e\rangle = (\psi_{1/2}^5, \psi_{-1/2}^5)$, and $|k\rangle = (\Theta_{1/2}^5, \Theta_{-1/2}^5)$. The normal vibration coordinate Q and the dipole moments belong to the following representations, respectively, $Q \in \Gamma_3$, $\mu_x \in \Gamma_4$, and $\mu_y \in \Gamma_2$. Using the Wigner–Eckart theorem and the coupling coefficients³⁴ 20 matrix elements of Z_{xy}^A in eq 12 have been evaluated as follows:

$$\begin{aligned} \langle \phi_{-1/2}^5 | \mu_x | \psi_{1/2}^5 \rangle &= -ia & \langle \Theta_{-1/2}^5 | \mu_x | \phi_{1/2}^5 \rangle &= -ib \\ \langle \phi_{1/2}^5 | \mu_x | \psi_{-1/2}^5 \rangle &= -ia & \langle \Theta_{1/2}^5 | \mu_x | \phi_{-1/2}^5 \rangle &= -ib \\ \langle \phi_{1/2}^5 | \mu_y | \psi_{-1/2}^5 \rangle &= -a & \langle \Theta_{1/2}^5 | \mu_y | \phi_{-1/2}^5 \rangle &= -b \\ \langle \phi_{-1/2}^5 | \mu_y | \psi_{1/2}^5 \rangle &= a & \langle \Theta_{-1/2}^5 | \mu_y | \phi_{1/2}^5 \rangle &= b \\ \langle \psi_{-1/2}^5 | h'_Q | \Theta_{-1/2}^5 \rangle &= -ic & \langle \psi_{1/2}^5 | h'_Q | \Theta_{1/2}^5 \rangle &= ic \quad (14) \end{aligned}$$

and all the others of the matrix elements are zero, where a , b , and c symbolize the different reduced matrix elements. On the basis of eqs 14 and 12, the “state tensor” Z_{xy}^A for the Raman transition $|i\rangle|\phi_{1/2}^5\rangle \rightarrow |j\rangle|\phi_{1/2}^5\rangle$ is calculated

$$\begin{aligned} Z_{xy}^A(\phi_{1/2}^5 \rightarrow \phi_{1/2}^5) &= \frac{1}{h\tilde{\nu}_{ek}} \sum_{e,k} (e|h'_Q|k) [(\phi_{1/2}^5 | \mu_x | e) (k | \mu_y | \phi_{1/2}^5) - \\ & \quad (\phi_{1/2}^5 | \mu_y | e) (k | \mu_x | \phi_{1/2}^5)] \\ &= \frac{1}{h\tilde{\nu}_{ek}} \sum_k (\psi_{-1/2}^5 | h'_Q | k) [(\phi_{1/2}^5 | \mu_x | \psi_{-1/2}^5) \times \\ & \quad (k | \mu_y | \phi_{1/2}^5) - (\phi_{1/2}^5 | \mu_y | \psi_{-1/2}^5) (k | \mu_x | \phi_{1/2}^5)] \\ &= \frac{1}{h\tilde{\nu}_{ek}} (\psi_{-1/2}^5 | h'_Q | \Theta_{-1/2}^5) [(\phi_{1/2}^5 | \mu_x | \psi_{-1/2}^5) \times \\ & \quad (\Theta_{-1/2}^5 | \mu_y | \phi_{1/2}^5) - (\phi_{1/2}^5 | \mu_y | \psi_{-1/2}^5) (\Theta_{-1/2}^5 | \mu_x | \phi_{1/2}^5)] \\ &= \frac{1}{h\tilde{\nu}_{ek}} (-ic) [(-ia)(+b) - (-a)(-ib)] \\ &= \frac{2abc}{h\tilde{\nu}_{ek}} \quad (15) \end{aligned}$$

The other state tensors are calculated in the similar way

$$\begin{aligned} Z_{xy}^A(\phi_{1/2}^5 \rightarrow \phi_{-1/2}^5) &= 0 \\ Z_{xy}^A(\phi_{-1/2}^5 \rightarrow \phi_{-1/2}^5) &= -\frac{2abc}{h\tilde{\nu}_{ek}} \\ Z_{xy}^A(\phi_{-1/2}^5 \rightarrow \phi_{1/2}^5) &= 0 \quad (15') \end{aligned}$$

Thus the antisymmetric Raman scattering intensity I_{xy}^A of the vibration band at 1466 cm⁻¹ of An⁻ in An⁻–Na⁺ complex is not zero,

$$I_{xy}^A \propto \left(\frac{2|abc|}{h\tilde{\nu}_{ek}} \right)^2 \quad (16)$$

TABLE 1: Depolarization Ratio (ρ) of the ν_1 Band of Some Substituted Pyridines in the Free and in the Br_2 -Complexed Derivatives

	ρ_f free	ρ complex
2,4-diCH ₃ Py ^a	0.04	0.63
2-CH ₃ Py ^b	0.07	0.54
2-C ₂ H ₅ Py ^b	0.08	0.63

^a From ref 35. ^b From ref 36.

Therefore the theoretical results in this paper agree qualitatively with the experimental results of the $\text{An}^- - \text{Na}^+$ complex,^{29,30} which indicates that in addition to the vibronic effect the charge-transfer-induced antisymmetric transition polarizabilities may be essential to the anomalous Raman polarization observed in the $\text{An}^- - \text{Na}^+$ complex.^{29,30}

(iii) Third, consider the depolarization ratio dispersion of the anomalous Raman band of the $\text{An}^- - \text{Na}^+$ complex. From the frequency factor expression before $Z_{\rho\sigma}^A$ in eq 11, a far-reaching fundamental conclusion was drawn by Mortensen⁵ and Barron⁷ as follows. For the antisymmetric tensor component there is a destructive interference between the two terms due to the 0–0 and 0–1 vibronic transitions $\langle i_1 | j_1 \rangle \langle j_1 | Q | i_0 \rangle / \tilde{\nu}_{\text{eg}} - \tilde{\nu} - i\Gamma_0$ and $\langle i_1 | Q | j_0 \rangle \langle j_0 | i_0 \rangle / \tilde{\nu}_{\text{eg}} + \tilde{\nu}_Q - \tilde{\nu} - i\Gamma_1$. Thus, outside the resonance region, the destructive interference effectively kills the antisymmetric tensor components $Z_{\rho\sigma}^A$. This is the explanation for the fact that at transparent wavelength the depolarization ratio $\rho = 0.7$ of the $\text{An}^- - \text{Na}^+$ complex in Fujimoto et al.'s experiment²⁹ is normal.

On the whole, the theory in section 2 agrees qualitatively with Fujimoto et al.'s experimental results of the anomalous Raman depolarization of the $\text{An}^- - \text{Na}^+$ complex^{29,30} on the basis of the analysis of time-reversal, spatial symmetric selection rule, and the depolarization ratio dispersion.

4. Substituted Pyridine– Br_2 Complex

Charge-transfer complexes of substituted pyridine and Br_2 molecule have been extensively investigated for many years. Maes and Zeegers-Huyskens^{35,36} studied the depolarization ratio enhancement of the breathing ring vibration ν_1 of some substituted pyridine derivatives due to the complexation with Br_2 , which are shown in Table 1. The large depolarization ratio enhancement of 2,4-dimethylpyridine and others may include an important contribution from the charge-transfer-induced antisymmetric transition polarizabilities deduced in section 2. The vibration ν_1 of 2,4-dimethylpyridine belongs to the totally symmetric mode. Its Raman scattering intensity is described by Albrecht's A term (Franck–Condon term).^{5,7,24} In Franck–Condon resonance cases, Mortensen and Hassing deduced theoretically⁵ that without the antisymmetric components the depolarization ratio will have one of the values 0, 1/8, or 1/3, where 0, 1/8, and 1/3 are only possible in spatial 3-fold degenerate, double-degenerate, and nondegenerate excited electronic states, respectively, and with the assumption of the single excited-state resonance there will be no polarization dispersion for a given range of excitation frequencies.⁵ Thus in or not far from Franck–Condon resonance, without an antisymmetric Raman tensor, the maximum value of depolarization ratio ρ for a totally symmetric mode ν_1 in 2,4-dimethylpyridine– Br_2 complex is 1/3. Here the experiment value of the depolarization ratio ρ_{complex} of the ν_1 band in 2,4-dimethylpyridine– Br_2 complex is 0.63 and much larger than 1/3. The part over 1/3 should result from the contribution of the antisymmetric transition polarizability⁵

$$\rho = \frac{5\Sigma^1 + 3\Sigma^2}{10\Sigma^0 + 4\Sigma^2} = \frac{3\Sigma^2}{10\Sigma^0 + 4\Sigma^2} + \frac{5\Sigma^1}{10\Sigma^0 + 4\Sigma^2} \leq \frac{1}{3} + \frac{5\Sigma^1}{10\Sigma^0 + 4\Sigma^2} \quad (17)$$

where Σ^0 , Σ^2 , and Σ^1 are the trace, symmetric, and antisymmetric tensor invariants, respectively.⁵ Thus on the basis of theory in section 2 from the point of view of time reversal the charge-transfer-induced antisymmetric transition polarizabilities may make important contributions to the complexation enhancement of the depolarization ratio of the 2,4-diCH₃Py– Br_2 complex, even though further experimental measurements of the reversal coefficient are needed to confirm completely the theoretical results.^{5,6}

5. Discussion

Recently, it was demonstrated by Shen's group^{14,37,38} that sum-frequency vibrational spectroscopy (SFVS) in chiral solutions can yield the chiral vibrational spectra directly related to the molecular chiral structure. In particular, vibrational-electronic double resonance can enhance the chiral SFVS spectra strongly and makes SFVS as a novel probe of the molecular chirality much more attractive. It was theoretically proved^{14,37–40} that the strength of the vibrational bands in SFVS is proportional to the square of the corresponding antisymmetric Raman tensor (antisymmetric transition polarizability). Antisymmetric Raman scattering investigations have given a fundamental requirement for their observation;^{6–8,11} i.e., antisymmetric Raman tensors in the resonant Raman spectra arise when the Raman transition includes the degenerate electronic ground states or degenerate excited states with a small splittings due to some small perturbations,¹¹ such as vibronic-mixing-induced antisymmetric Raman tensors (for example, for the porphyrin-type complexes)⁶ and spin–orbit coupling-induced antisymmetry in the Raman tensors^{8,7} (for examples, for IrCl_6^{2-} and FeBr_4^- complexes). These results can be useful for the explanation of the SFVS in chiral solutions. In refs 37 and 38, both doubly resonant SFVS³⁷ and SFVS near electronic resonance³⁸ investigated a bulk solution of 1,1'-bi-2-naphthol (BN). The electronic absorption spectrum of BN consists of pairs of close lying bands, which result from the excitonic splitting of two degenerate transitions in the separated 2-naphthol monomers.⁴¹ This spectrum feature reminds us of the absorption spectra of metalloporphyrin.⁴² In the SFVS experiments of BN in refs 37 and 38, the sum frequency light at $\omega = \omega_1 + \omega_2$ is resonant to the exciton-splitting pair of close lying bands at 3.67 and 3.89 eV. Comparing the SFVS experiments^{37,38} with the polarization study of the resonant Raman spectra of porphyrins,⁶ BN and porphyrins show analogous qualitative features of the absorption spectra with the pair of close lying (or degeneracy) bands and the excited light in both of the SFVS and Raman experiments is resonant to the corresponding close lying bands, respectively. Thus, like porphyrin, BN can naturally show antisymmetric Raman tensors due to the vibronic interaction mechanism, which agrees with the foregoing fundamental requirement for antisymmetric Raman scattering tensor.^{6–8,11} This gives us a broad hint that in addition to the vibronic-induced antisymmetry, the spin–orbit coupling can also induce antisymmetric Raman tensors^{6–8} and thus can show the SFVS effects in some chiral solutions. Furthermore, section 2 has shown that on the basis of the Kramers degenerate states formed in the charge-transfer process and time-reversal arguments, antisymmetric Raman tensors can arise under resonance or near-resonance with

intermolecular charge-transfer transition. Hence charge-transfer-induced antisymmetric Raman tensors can also make contributions to the SFVS in some chiral solutions.

Usually, charge-transfer processes can be achieved chemically, electrochemically, or photochemically. In the photochemical processes, the system is excited by light photons to the excited electronic states that can accept or donate an electron with other compounds. In particular, photoionization is also a charge-transfer process. It is interesting to discuss whether the charge-transfer-induced antisymmetric Raman tensor can arise when the excited light is resonant with the potential energy surfaces leading to an electron ejection. Here the excited light is used for both resonance Raman scattering and photoionization processes. In the photoionization a neutral even-electron molecule M is photoionized and loses an electron and becomes an odd-electron ion M^+ . In this case, the resonant Raman scattering is determined by the initial $|i\rangle$, final $|f\rangle$ and intermediate $|a\rangle$ states. Where $|i\rangle$ is the ground state of the parent molecule M without spin-orbit coupling and $|f\rangle$ corresponds the ground state of the photoionized ion M^+ with an unpaired electron and spin-orbit interactions, they are different electronic states. Thus, due to the photoionization, this should be an electronic Raman scattering process. It is known⁴³ that there is a fundamental difference between vibrational Raman scattering and electronic Raman scattering in that the latter can be controlled by an asymmetric tensor including an antisymmetric one, even under nonresonance conditions. Hence on the basis of the time-reversal arguments³ and the results in section 2, we should say that in some cases asymmetric Raman tensors can arise when the excited light in Raman scattering experiment is resonant with potential energy surface leading to an electron ejection (photoionization process).

Finally, it should be noted that the spectrum selection rule of the time-reversal symmetry, like other selection rules, is necessary but not sufficient for nonzero antisymmetric Raman tensors. For an intermolecular charge-transfer complex, in addition to the formation of Kramers degenerate states due to the charge transfer, the strong spin-orbit coupling is essential for charge-transfer-induced antisymmetric Raman tensors. This is similar to the intramolecular charge-transfer complexes; for example, due to the spin-orbit coupling, all the Raman-active modes of IrCl_6^{2-} show anomalous polarization and important antisymmetric Raman tensors when excited in the $\text{Cl} \rightarrow \text{Ir}$ charge-transfer absorption envelope.⁸ Also, in some cases the vibronic interactions are needed⁴⁴ for the charge-transfer-induced antisymmetric Raman tensors; for example, in section 3 the anomalous Raman polarization in the $\text{An}^- - \text{Na}^+$ complex has been explained by using both time-reversal and vibronic coupling arguments.

6. Conclusion

In this paper the antisymmetric transition polarizabilities induced by intermolecular charge-transfer interactions are proposed and studied by using group theory, especially time-reversal symmetry and Mulliken's theory of charge-transfer complexes. The results show that under the Born-Oppenheimer approximation, the antisymmetric light scattering of even-electron systems with a nondegenerate ground state is zero. But when an electron is transferred, in part or in a whole, from the donor to the even-electron acceptor in charge-transfer complexes, the acceptor in the complex can have nonzero antisymmetric transition polarizability, and so do the donors. Thus charge-transfer-induced antisymmetric light scattering from

interacting even-electron systems, especially intermolecular charge-transfer complexes, can exist, which are characteristic of charge-transfer interactions and processes. The theoretical results are associated qualitatively with the anomalous Raman polarization experiment of the anthracene anion- Na^+ ion complex^{29,30} and with the complexation enhancements of depolarization ratio ρ for some substituted pyridine- Br_2 complexes.^{35,36} The connection of the charge-transfer-induced antisymmetric Raman tensors to the SFVS in chiral solutions and photoionization processes have been discussed.

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