



# The asymmetry of the differential bond polarizabilities in the Raman optically active (+)-(R)-methyloxirane and L-alanine

Yan Fang<sup>a</sup>, Guozhen Wu<sup>a,\*</sup>, Peijie Wang<sup>b</sup>

<sup>a</sup>State Key Laboratory of Low-Dimensional Quantum Physics, Department of Physics, Tsinghua University, Beijing 100084, China

<sup>b</sup>The Beijing Key Laboratory for Nano-Photonics and Nano-Structure, Department of Physics, Capital Normal University, Beijing 100048, China

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## ABSTRACT

In this work, we demonstrate how an algorithm can be formulated to derive the bond polarizabilities from Raman intensities and how it can be extended to the elucidation of the so-called differential bond polarizabilities from the intensity difference,  $I_j^R - I_j^L$  which shows the variant responses to the right and left circularly polarized excitations, in the Raman optically active (ROA) systems. Both bond polarizabilities and differential bond polarizabilities are helpful for the interpretation of ROA spectra. We examined the systems of (+)-(R)-methyloxirane and L-alanine using this approach. There is evidence that the asymmetry of differential bond polarizabilities is rather complete in the sense that they are of opposite signs on the two sides along the methine C–H bond of which the disturbed charge density is the largest in Raman excitation. The physical implication is the opposite orientations of the vibrationally induced magnetic moments on the two opposite sides along the methine C–H bond.

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## 1. Introduction

The determination of the stereo-structural details, called chirality or handedness, of optically active molecules, including biological ones [1–4] plays a very important role in understanding their functions. Experimental methods such as Raman, Raman optical activity (ROA) spectroscopy and vibrational circular dichroism (VCD) enable us to obtain rich structural and electronic information [5–7] of these molecules. ROA is the measure of the differential Raman cross sections by the incident right and left circular polarizations of the exciting laser. Over the past three decades, ROA has emerged as a powerful spectroscopic technique for the chiral determination. It has been proven to be particularly useful in the aqueous environment [8–10] for proteins and nucleic acids. The method by the first principle [11] and the subsequent implementation of *ab initio* algorithm have resulted in more concrete interpretation of the experimental ROA spectra [12,13]. For the moment, considerable attention has been paid to methyloxirane because of its suitable size for a detailed theoretical ROA analysis [14–15]. The earlier computational work on methyloxirane includes, *ab initio*, coupled-cluster and density functional methods [16–18]. Alanine is another system of interest since it is the smallest chiral amino acid that can be treated as a model system [2,3,19,20]. A systematic exploration of its ROA intensity, in terms of its nuclear motions and their couplings, has also been addressed [21]. We further note that

ROA spectra using incident circular polarization (ICP) [21–23] and dual circular polarization (DCP) [24] as compared to the *ab initio* calculation have also been reported [21].

As known, Raman scattering is a two-photon process in which a molecule absorbs a photon first with the excitation (disturbance) of its electrons and then relaxes by emitting a second photon. During the process, there is the vibronic coupling between the electronic and the nuclear motions. The electronic excitation including its relaxation is called the Raman excited virtual state (non-resonance case) [25], for which the information of the vibronic coupling is embedded in the scattered intensity. We have developed an algorithm [26] to explore the electronic structure of the non-resonant virtual state from the spectral intensity. In this work, we will demonstrate how this analysis can be extended to ROA intensity, with the hope to obtain deeper information concerning the ROA phenomenon.

We have to stress that the electronic excitation in the non-resonant Raman case is not what generally recognized as in the transition between the eigenstates. The excitation in the virtual state is more or less an electronic disturbance in which the charge density distribution in the molecule changes upon excitation in the Raman process.

In the following, we will first briefly review our algorithm to elucidate the bond polarizabilities from Raman intensities. Then the extension of this algorithm to the case of ROA will be followed. With the experimental results and the normal mode analyses for (+)-(R)-methyloxirane and L-alanine, we are then ready for the elucidation of their bond polarizabilities and the so-called differential

\* Corresponding author.

E-mail address: [wgz-dmp@tsinghua.edu.cn](mailto:wgz-dmp@tsinghua.edu.cn) (G. Wu).

bond polarizabilities from the ROA intensities. The interpretations and discussions based on these quantities for the ROA process are then followed. Finally, a remark is concluded.

## 2. The algorithm to derive the bond polarizabilities from the Raman intensities

The algorithm for deriving the bond polarizabilities from the Raman intensities was proposed by Wu et al. [26]. It has been applied to several cases [27–29] and has revealed significant properties of the Raman virtual states. The essence of the Raman process is the vibronic coupling between the electrons and nuclei in a molecule. The vibronic coupling is parametrized by  $\partial\alpha/\partial\mathbf{Q}_j$ , which shows the response of the electronic charge to the nuclear motion.  $\alpha$  is the molecular electronic polarizability, which is a measure how loosely the charges thereof are bound to the nuclei and  $\mathbf{Q}_j$  is the nuclear normal coordinate.  $\alpha$  is also proportional to the amount of charges. For retrieving the bond electronic information of the virtual state, we have to derive  $\partial\alpha/\partial\mathbf{S}_k$  for the bond coordinate  $\mathbf{S}_k$  from  $\partial\alpha/\partial\mathbf{Q}_j$  if possible. For brevity,  $\partial\alpha/\partial\mathbf{S}_k$  will be called the bond (stretch/bend) polarizability. It is noted that the bond polarizability is an indication of the disturbed charge density during the Raman process.

The Raman intensity  $I_j$  of the  $j$ th normal mode with wavenumber  $\nu_j$  is related to  $\partial\alpha/\partial\mathbf{Q}_j$  through the formula by Chantry [30]:

$$I_j \sim I_0 \frac{(\nu_0 - \nu_j)^4}{\nu_j} (\partial\alpha/\partial\mathbf{Q}_j)^2.$$

Here,  $I_0$  is the intensity of the exciting laser with wavenumber  $\nu_0$ . The Raman intensity  $I_j$  can be obtained from the experimental Raman signals in the wavenumber domain. In fact, the treatment in the wavenumber domain can be extended to the temporal domain [31] if we Fourier transform  $I_j(\nu)$  in the wavenumber domain to the temporal domain and follow the procedures shown below analogously.

From Chantry's formula, we thus have

$$\pm\sqrt{I_j} \sim \sqrt{I_0} \frac{(\nu_0 - \nu_j)^2}{\sqrt{\nu_j}} \sum L_{kj}(\partial\alpha/\partial\mathbf{S}_k)$$

by transforming  $\mathbf{Q}_j$  to the bond coordinates  $\mathbf{S}_k$ s through:

$$\mathbf{S}_k = \sum L_{kj}\mathbf{Q}_j$$

which can be obtained from the normal mode analysis.

By defining

$$a_{jk} = \frac{(\nu_0 - \nu_j)^2}{\sqrt{\nu_j}} L_{kj}$$

we have the following matrix equation, if only relative intensities and bond polarizabilities are concerned:

$$\begin{pmatrix} P_1\sqrt{I_1} \\ P_2\sqrt{I_2} \\ \vdots \\ P_{3N-6}\sqrt{I_{3N-6}} \end{pmatrix} = [a_{jk}] \cdot \begin{pmatrix} \partial\alpha/\partial\mathbf{S}_1 \\ \partial\alpha/\partial\mathbf{S}_2 \\ \vdots \\ \partial\alpha/\partial\mathbf{S}_{3N-6} \end{pmatrix}.$$

Here, the phase  $P_j$  is + or – which cannot be obtained from the experiment and needs determination. In this formalism, only the relative magnitudes of the Raman intensities will be of concern. So are the relative bond polarizabilities.

The bond polarizabilities can be figured out if the above matrix equation is inverted and if the phases preceding the intensities can be determined. For the phase determination, various sets of  $\{P_j\}$  are

tried to obtain  $\partial\alpha/\partial\mathbf{S}_k$ 's which are then checked with physical considerations to rule out the inadequate  $\{P_j\}$  sets. In our previous study [28,29], it was found that quite often, a unique or a limited number of  $\{P_j\}$  sets can be figured out with physically significant  $\partial\alpha/\partial\mathbf{S}_k$ 's. In treatment, often the matrix equation can be reduced to accommodate only those mainly of stretching coordinates. This is because that the bond stretch polarizabilities are usually larger than those of the bending coordinates. Another reason is that the coupling between the stretching and bending coordinates is often small. Hence, the matrix equation is decoupled according to the stretching and bending spaces.

(Note: The reason that we have this phase problem is simply that since  $I_j \approx [\sum L_{kj}(\partial\alpha/\partial\mathbf{S}_k)]^2$ , from the intensity, we can only determine  $|\sum L_{kj}(\partial\alpha/\partial\mathbf{S}_k)|$  (the absolute value) but not its sign (phase). Hence, we just cannot simply determine  $(\partial\alpha/\partial\mathbf{S}_k)$  without the phases known from the intensities. This is quite analogous to the X-ray structural determination in which, one not only measures the diffracted spot intensities, but also has to nail down their phases in order to solve the structure.)

## 3. The algorithm to derive the differential bond polarizabilities

For the ROA experiment, we have  $I_j^R + I_j^L = I_j$  and  $I_j^R - I_j^L = \Delta I_j$  ( $R$  and  $L$  stand, respectively, for the right and left circularly polarized scatterings), i.e.,

$$I_j^R = (I_j + \Delta I_j)/2, \quad I_j^L = (I_j - \Delta I_j)/2$$

Furthermore, we have

$$\begin{bmatrix} \partial\Delta\alpha/\partial\mathbf{S}_1 \\ \partial\Delta\alpha/\partial\mathbf{S}_2 \\ \vdots \\ \partial\Delta\alpha/\partial\mathbf{S}_t \end{bmatrix} = [a_{jk}]^{-1} \begin{bmatrix} P_1 \left( \sqrt{I_1^R} - \sqrt{I_1^L} \right) \\ P_2 \left( \sqrt{I_2^R} - \sqrt{I_2^L} \right) \\ \vdots \\ P_t \left( \sqrt{I_t^R} - \sqrt{I_t^L} \right) \end{bmatrix}$$

Here,  $\Delta\alpha$  is defined formally as  $\alpha^R - \alpha^L$  by  $\partial\alpha^R/\partial\mathbf{S}_k - \partial\alpha^L/\partial\mathbf{S}_k$  which are related, respectively, to the intensities by the right and left circularly polarized scatterings.

Consider

$$\sqrt{2I_j^R} = \sqrt{I_j + \Delta I_j} = \sqrt{I_j} \left[ \sqrt{(1 + \Delta I_j/I_j)} \right] \approx \sqrt{I_j} [1 + \Delta I_j/2I_j],$$

$$\sqrt{2I_j^L} = \sqrt{I_j - \Delta I_j} = \sqrt{I_j} \left[ \sqrt{(1 - \Delta I_j/I_j)} \right] \approx \sqrt{I_j} [1 - \Delta I_j/2I_j]$$

with error  $< [\Delta I_j/I_j]^2/8$

then

$$\sqrt{I_j^R} - \sqrt{I_j^L} \approx \Delta I_j/\sqrt{I_j}$$

and

$$\begin{bmatrix} \partial\Delta\alpha/\partial\mathbf{S}_1 \\ \partial\Delta\alpha/\partial\mathbf{S}_2 \\ \vdots \\ \partial\Delta\alpha/\partial\mathbf{S}_t \end{bmatrix} = [a_{jk}]^{-1} \begin{bmatrix} P_1(\Delta I_1/\sqrt{I_1}) \\ P_2(\Delta I_2/\sqrt{I_2}) \\ \vdots \\ P_t(\Delta I_t/\sqrt{I_t}) \end{bmatrix}$$

Though  $I_j$  is much larger than  $\Delta I_j$  by an order of  $10^3$  to  $10^4$ , the relative magnitudes of  $I_j$ 's and  $\Delta I_j$ 's can be treated independently as not too small numbers. (For instance, they can be scaled to from 1 to 100 in most cases.) By this way,  $\Delta I_j/\sqrt{I_j}$  can be treated as not too small numbers.

In summary, once the bond polarizabilities were obtained from  $I_j$ 's, then together with the elucidated  $P_j$ 's and  $\Delta I_j$ 's which are obtained from the ROA experiment, relative  $\partial\Delta\alpha/\partial\mathbf{S}_k$  can be

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