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Citation: Chin. Phys. B, 2021, 30 (**6**): 063101. DOI: 10.1088/1674-1056/abea90
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Charge disturbance/excitation in the Raman virtual state revealed by ROA signal: A case study of pinane*

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(Received 20 December 2020; revised manuscript received 10 February 2021; accepted manuscript online 1 March 2021)

The Raman mode intensities are used to extract the bond polarizabilities which are the indication of the charge disturbance/excitation of the Raman virtual state. A classical formula based on the electric and magnetic dipolar coupling among the charges on the atoms is developed which relates the charges and vibrational amplitudes of the atoms in a normal mode to the Raman optical activity (ROA) mode signatures. By fitting with the experimental ROA signatures, we are able to elucidate the scaling parameter which relates the bond polarizability to the electric charge. The result shows that around 40% of the charges in pinane are involved in the Raman process under 532 nm laser excitation.

Keywords: Raman intensity, bond polarizabilities, Raman optical activity, handedness, pinane, electric charge

PACS: 31.15.ap, 33.20.Fb, 33.20.Tp, 52.38.Bv **DOI:** 10.1088/1674-1056/abea90

1. Introduction of the Raman virtual state

Raman effect is an inelastic two-photon process, in which the scattering photon is first absorbed by a molecule. The photon-perturbed molecule then relaxes and emits a secondary photon instantaneously. The photon-perturbed molecule, in general, may not be in its excited eigenstates. In such a case, we call it the non-resonant Raman process and the photon-perturbed molecule including its relaxation, the Raman excited virtual state, or simply the Raman virtual state.[1,2] Raman virtual state is just like a wave packet.

We note that the electronic information of the Raman virtual state is embedded in the Raman intensity. The charge distribution of the virtual state is reflected on the bond polarizabilities since they show how the excited/disturbed charges are among the bonds in a molecule during the Raman process. Then the issue is to retrieve the bond polarizabilities from the Raman mode intensities. This is demonstrated in the next section.

For a chiral molecule, its Raman mode intensities by the right and left circular polarized light excitations are different. This is called Raman optical activity (ROA).[3–9] The intensity difference is called the ROA signature. This offers an additional Raman information such as the steric structure, as is well recognized.[10] In this work, we will show that it even offers the information as to how many electrons are excited/disturbed in the Raman process.[11] This is realized through a classical interpretation of ROA along with the bond polarizability.[11,12] This is the goal of this work. We will demonstrate this idea through the case analysis of chiral pinane molecule.

2. Experimental details

The pinane sample was purchased from Alfa Aesar Company and used without further purification (endo and exo forms of 99%. For the analysis treated in this work, we will not differentiate these two forms). The sample was held in a micro quartz fluorescence sample cell. The ROA spectrum which covers from 700 cm^{-1} to 1800 cm^{-1} was taken by Biotool chiral Raman ROA spectrometer excited by 532 nm laser with a focused power of 400 mW. The scattered circular polarization (SCP) configuration was adopted. The spectral resolution is about 7 cm^{-1}. In the experiment, depolarized incident laser was used and the intensity difference in the right and left circularly polarized Raman scattered light was measured.

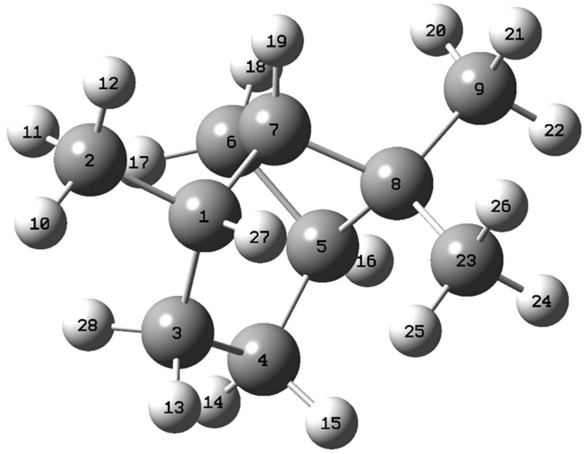


Fig. 1. The structure of pinane and the atomic numberings. The darker ones are the carbon atoms. The rest are the hydrogen atoms.

*Project supported by the National Natural Science Foundation of China (Grant No. 21872097) and Scientific Research Base Development Program of the Beijing Municipal Commission of Education.

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The Raman spectrum covering the C–H region was taken by Renishaw Invia Raman spectrometer with backward scattering. The excitation line was 532 nm from a semiconductor laser. The experimental details have been published before.[13,14] The structure of pinane is simulated by *ab initio* calculation at DFT B3LYP at the level of 6-311G* with Gaussian09W.[15] It is shown in Fig. 1.

3. The elucidation of bond polarizability

For elucidating the bond polarizabilities, we start from the Chantry formula[16] for the Raman intensity I_j of the j-th normal mode with wavenumber ν_j

$$I_j \propto I_0 (\nu_0 - \nu_j)^4 / \nu_j (\partial\alpha/\partial Q_j)^2 . \tag{1}$$

Here, I_0 is the intensity of the exciting laser with wavenumber ν_0, α is the electronic polarizability, and Q_j is the normal coordinate.

From Chantry's formula, we thus have[2]

$$\pm\sqrt{I_j} \propto \sqrt{I_0}\frac{(\nu_0 - \nu_j)^2}{\sqrt{\nu_j}} \sum L_{kj} (\partial\alpha/\partial S_k) \tag{2}$$

by transforming Q_j to the bond/symmetric coordinates S_k's through

$$S_k = \sum L_{kj} Q_j, \tag{3}$$

which can be obtained from the normal mode analysis.

By defining

$$a_{jk} = \frac{(\nu_0 - \nu_j)^2}{\sqrt{\nu_j}} L_{kj}, \tag{4}$$

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

$$\begin{bmatrix} P_1\sqrt{I_1} \\ P_2\sqrt{I_2} \\ \cdots \\ P_{3N-6}\sqrt{I_{3N-6}} \end{bmatrix} = [a_{jk}] \begin{bmatrix} \partial\alpha/\partial S_1 \\ \partial\alpha/\partial S_2 \\ \cdots \\ \partial\alpha/\partial S_{3N-6} \end{bmatrix}. \tag{5}$$

Here, the phase P_j is + or − which cannot be obtained from the experiment and needs determination.

The bond polarizabilities can be obtained 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 $(\partial\alpha/\partial S_k)$'s which are then checked with physical considerations to rule out the inadequate $\{P_j\}$ sets.

The Raman spectrum of pinane is shown in Fig. 2. We will first concentrate on the 11 C–C stretches since they are quite decoupled from the C–H motion. For this, we choose 11 Raman mode intensities whose normal coordinates are mostly due to the C–C stretches as marked by * in Fig. 1. Their relative values are listed in Table 1. By requiring the 11 C–C bond polarizabilities to be positive, we are left with multiple accepted phase sets, however, their relative magnitudes are quite consistent and only the represented one is shown in Table 3.[17]

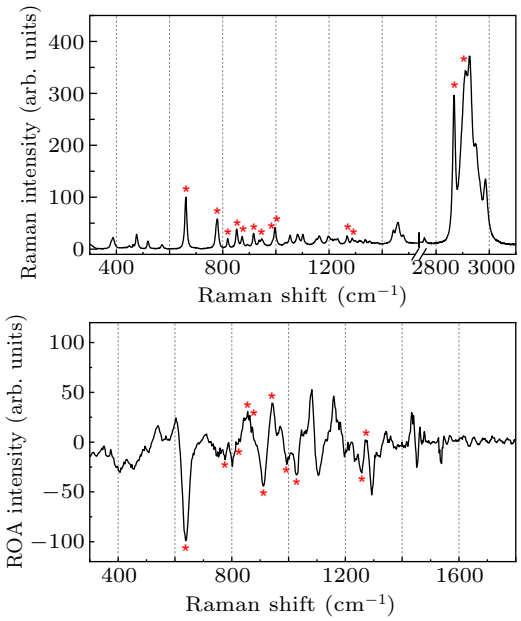


Fig. 2. The Raman and ROA spectra of pinane. * shows the modes whose intensities are employed for the analysis.

Table 1. The Raman mode shifts, relative intensities, and experimental, calculated ROA signatures by our algorithm. 0 means the signal is too small. See text for details.

Experimental Raman shift (cm^{-1})	Relative Raman intensity	Experimental ROA signature	Calculated ROA signature by our algorithm
2856–2905	1222.4		see Table 2
1299	6.3	0	–
1268	13.1	0	–
1000	30.8	–	–
997	9.4	–	–
937	12.6	+	+
917	13.3	–	–
873	10.9	+	+
853	49.7	+	+
819	31.9	–	–/+
779	10.4	0	+
661	100	–	+

Table 2. The calculated ROA signatures of the symmetric C–H stretching modes.

Calculated Raman shift (cm^{-1})	Calculated ROA signature by our algorithm
2905	+
2876	–
2871	–
2868	–
2863	–
2861	+
2858	–
2856	+

Table 3. The relative bond polarizabilities. That of C8–C23 is normalized to 10.

Bond	Bond polarizability
C1–C2	1.31
C1–C3	6.08
C1–C7	3.51
C3–C4	2.26
C4–C5	7.86
C5–C6	2.03
C5–C8	0.96
C6–C7	2.34
C7–C8	4.26
C8–C9	2.64
C8–C23	10
C–H	5.25

For the C–H stretch polarizability, we assume that the 18 C–H bonds are equivalent. This assumption is reasonable since they all protrude out toward molecular periphery. Considering the 8 symmetric C–H stretching modes, ranging from 2856 cm^{-1} to 2905 cm^{-1} and noting that the symmetric coordinates are of the following form with r denoting the C–H stretching coordinate:

$$S_{k\mathrm{C-H}} = \frac{1}{\sqrt{N_k}}\left(r_1 + r_2 + \cdots + r_{N_k}\right), \tag{6}$$

we can equate the following term deduced from the Chantry formula

$$\left(\nu_0 - \nu_j\right)^4 / \nu_j \left(\partial\alpha/\partial r_{\mathrm{C-H}}\right)^2 \sum_j \left(\sum_k \sqrt{N_k}\left(L^{\mathrm{T}}\right)_{jk}\right)^2 \tag{7}$$

to the mode intensity, which is

$$I_{\mathrm{C-H}} = \sum_j I_{j\mathrm{C-H}} \tag{8}$$

with j running over the 8 symmetric C–H modes (in the interval between 2856 cm^{-1} and 2905 cm^{-1}), to obtain the average $\partial\alpha/\partial r_{\mathrm{C-H}}$. In the calculation, the average Raman shift, 2880.5 cm^{-1} is taken for ν_j. The result is shown in Table 3.

4. Charge distribution of the Raman virtual state

As long as the bond polarizabilities are obtained, the charge distribution of the Raman virtual state can be obtained by the following consideration.[11]

We propose there is proportional constant t between the electron charge e and the bond polarizability $(\partial\alpha/\partial R_k)$, i.e., $e = t\,(\partial\alpha/\partial R_k)$. Note that the bond polarizabilities as shown in Table 3 are of relative magnitude. We first partition each bond polarizability evenly to the two atoms forming the bond. Then, all the polarizabilities on an atom are summed, scaled by parameter t and combined with its net charges in the ground state to form the net charge for the atom in the Raman virtual state. Since charges are concentrated on the bonds, this is the reason that only the symmetric stretching coordinates are adopted in this treatment.

When a molecule is in its ground state, there are charges distributing in between the atoms. This is the chemical bond. For convenience, one usually attributes the charges on a bond to the atoms which form the bond. This is the Mulliken charge e_j^0 (subscript j is for the atomic numbering). So, it is an effective charge. Since a molecule is neutral, the sum of all the Mulliken charges is zero, i.e., $\sum_j e_j^0 = 0$. In the Raman virtual state, the sum of the net charges on all the atoms is still zero. Our previous work[18] shows that close to the complete relaxation of the Raman excitation, the bond polarizabilities are very parallel to the bond electronic densities in the ground state which are calculated by all the occupied molecular orbitals (MO), i.e., all the electrons in a molecule. The implication is that all the electrons in a molecule contribute to the excited/perturbed charges in the Raman virtual state with equal probability. The electron number on the j-th atom in the ground state is $z_j = Z_j - e_j^0$ with Z_j the atomic number. Hence, in the virtual state, the excited charges contributed from the j-th atom is

$$t \cdot z_j \cdot \sum_l \partial\alpha/\partial R_l / N, \quad (t > 0), \tag{9}$$

where N is the total electron number in a molecule, i.e., $N = \sum_j Z_j = \sum_j z_j$. $\sum_l \partial\alpha/\partial R_l$ is the sum of all the bond polarizabilities. Since the distributions of the excited charges on the various bonds (as evidenced by the bond polarizabilities) are different and if we partition each bond polarizability evenly to the two atoms forming the bond, then the effective charge on the j-th atom is

$$e_j = e_j^0 + t \cdot z_j \cdot \sum_l \partial\alpha/\partial R_l / N - t \sum_{k_j} \partial\alpha/\partial R_{k_j,j}/2, \tag{10}$$

where k_j is the index for the bonds that are associated with the j-th atom. We note that $\sum_j z_j \sum_l \partial\alpha/\partial R_l / N = \sum_j \sum_{k_j} \partial\alpha/\partial R_{k_j,j}/2 = \sum_l \partial\alpha/\partial R_l$ and $\sum_j e_j^0 = 0$, hence $\sum_j e_j = 0$. This satisfies the condition that the net charge of the Raman virtual state is zero.

As to t, if we scale the bond polarizability to the unit of the elementary charge, then we have, $t\sum_l \partial\alpha/\partial R_l \le N$ or $t \le N/\sum_l \partial\alpha/\partial R_l$.

The Mulliken charges e_j^0 and z_j are shown in Table 4. From Table 3, we have $\sum_l \partial\alpha/\partial R_l = 137.75$. With $N = 78$, the total electron number of pinane, we have $t \le 0.566$.

Table 4. The Mulliken charges e_j^0, z_j, e_j, and $e_j - e_j^0$ for the designated t values. See text for details.

Atom	Mulliken charge e_j^0	z_j	e_j with $t = 0.218$ and 0.238		$e_j - e_j^0$ with $t = 0.218$ and 0.238	
C1	–0.470	6.470	0.261	0.328	0.731	0.798
C2	–0.905	6.905	–0.106	–0.033	0.799	0.872
C3	–0.276	6.276	0.087	0.120	0.363	0.396
C4	–1.057	7.057	–0.588	–0.545	0.469	0.512
C5	0.538	5.462	0.886	0.918	0.348	0.380
C6	–1.192	7.192	–0.044	0.061	1.148	1.253
C7	0.644	5.356	1.032	1.068	0.388	0.423
C8	0.458	5.542	0.645	0.662	0.187	0.204
C9	–0.784	6.784	–0.177	–0.121	0.607	0.663
C23	–0.972	6.972	–1.095	–1.106	–0.123	–0.134
H10	0.211	0.789	–0.057	–0.082	–0.269	–0.293
H11	0.226	0.774	–0.048	–0.073	–0.274	–0.300
H12	0.209	0.791	–0.058	–0.083	–0.268	–0.292
H13	0.224	0.776	–0.050	–0.075	–0.273	–0.298
H14	0.226	0.774	–0.049	–0.074	–0.274	–0.299
H15	0.242	0.758	–0.038	–0.064	–0.281	–0.306
H16	0.210	0.790	–0.058	–0.082	–0.268	–0.293
H17	0.229	0.771	–0.046	–0.071	–0.276	–0.301
H18	0.228	0.772	–0.047	–0.072	–0.275	–0.300
H19	0.199	0.801	–0.065	–0.089	–0.264	–0.288
H20	0.214	0.786	–0.055	–0.080	–0.270	–0.295
H21	0.219	0.781	–0.052	–0.077	–0.272	–0.297
H22	0.218	0.782	–0.053	–0.078	–0.271	–0.296
H24	0.222	0.778	–0.051	–0.076	–0.273	–0.298
H25	0.222	0.778	–0.051	–0.076	–0.273	–0.298
H26	0.225	0.775	–0.049	–0.074	–0.274	–0.299
H27	0.256	0.744	–0.030	–0.056	–0.286	–0.312
H28	0.235	0.765	–0.043	–0.068	–0.278	–0.303

5. A classical formula for the Raman mode signature

The Raman mode signature is defined as the sign of

$$\Delta \equiv (I^{\mathrm{R}} - I^{\mathrm{L}})/(I^{\mathrm{R}} + I^{\mathrm{L}}). \tag{11}$$

Here, I^{L} and I^{R} are the Raman mode intensities under left and right circularly polarized laser excitations, respectively. Of course, various geometric arrangements of ROA experimental setup can lead to different definitions for Δ and will reveal various aspects and properties of ROA. Since we only try to have a classical interpretation for ROA, these details will not be over-emphasized. We will compare the Δ sign by our classical algorithm, denoted by Δ_{cl}, with that from the experimental observation.

The physical picture of ROA mechanism is shown below. The j-th atom in a molecule with net charge e_j, under a normal mode vibration, will oscillate around its equilibrium position periodically. Its displacement $\Delta \boldsymbol{r}_j$ and the induced dipole $\boldsymbol{\mu}_j$ (i.e., $e_j \Delta \boldsymbol{r}_j$) are coincident in space. Meanwhile, the other i-th atom, with net charge e_i, will produce a magnetic moment $\boldsymbol{m}_{ij}$ on the j-atom, with a value of $\frac{1}{2}(e_i \boldsymbol{\upsilon}_i \times \boldsymbol{r}_{ij})$. Here, $\boldsymbol{r}_{ij}$ is the position vector from the i-th to the j-th atoms. $\boldsymbol{\upsilon}_i$ is the velocity of the i-th atom. The quanta expression for the intra-molecular interaction between the vibrationally induced electric and magnetic dipoles that is related to the ROA mechanism is[19]

$$\mathrm{Im}(\langle i|\boldsymbol{\mu}|f\rangle \ \langle f|\boldsymbol{m}|i\rangle).$$

Here, $|i\rangle$ and $|f\rangle$ are the initial and final states. Im shows the imaginary part of the electromagnetic interaction, for which $\boldsymbol{\mu}$ and $\boldsymbol{m}$ are out of phase by $\pi/2$. Hence, its classical expression is

$$\sum \boldsymbol{\mu} \cdot \boldsymbol{m}.$$

Specifically, for a normal mode, the term that determines its Δ_{cl} sign is

$$\sum_j \sum_i \boldsymbol{\mu}_{j\max} \cdot \boldsymbol{m}_{ij\mathrm{equ}}.$$

Here, $\boldsymbol{\mu}_{j\max}$ is the dipole when $\Delta \boldsymbol{r}_j$ reaches its maximum (denoted as $\Delta \boldsymbol{R}_j$). $\boldsymbol{m}_{ij\mathrm{equ}}$ is the magnetic moment induced by the motion of the charge on the i-th atom at the j-th atom when $\Delta \boldsymbol{r}_i = 0$ with maximal υ_i (note the phase difference of $\pi/2$ between $\boldsymbol{\mu}_{j\max}$ and $\boldsymbol{m}_{ij\mathrm{equ}}$). When $\Delta \boldsymbol{r}_i = 0$, υ_i is proportional to $\Delta \boldsymbol{R}_i$. As $\Delta \boldsymbol{r}_i = 0$, υ_i is proportional to $\Delta \boldsymbol{R}_i/\tau$. τ is the period of the normal mode. Hence, Δ_{cl} is determined by the sign of the following expression:[12]

$$\begin{aligned} &\sum_{ji} (e_j \Delta \boldsymbol{R}_j) \cdot (e_i \Delta \boldsymbol{R}_i \times \boldsymbol{r}_{ij}) \\ &= \sum_{ji} e_i e_j \boldsymbol{r}_{ij} \cdot (\Delta \boldsymbol{R}_j \times \Delta \boldsymbol{R}_i). \end{aligned} \tag{12}$$

Since $|\Delta \boldsymbol{R}_i|$ ($|\Delta \boldsymbol{R}_j|$) is much smaller than $|\boldsymbol{r}_{ij}|$, $\boldsymbol{r}_{ij}$ can take the value at the molecular equilibrium configuration which can be simply obtained by the quantum chemical calculation (or as simulated by the Gaussian package). Relative $\Delta \boldsymbol{R}_i$ ($\Delta \boldsymbol{R}_j$) can be obtained from the normal mode analysis (which is the output of the Gaussian package), if the force constants are known. As to the chirality of the above formula, we note that $\boldsymbol{r}_{ij} \cdot (\Delta \boldsymbol{R}_j \times \Delta \boldsymbol{R}_i)$ changes its sign as the coordinate system is shifted between the right-hand and the left ones as anticipated.

6. Results and discussion

Once the bond polarizabilities are known, by $e_j = e_j^0 + t \times z_j \cdot \sum_l \partial \alpha / \partial R_l / N - t \sum_{k_j} \partial \alpha / \partial R_{k_j,j} / 2$, the sign $\Delta_{\rm cl}$ of

$$\sum_{ji} e_i e_j \boldsymbol{r}_{ij} \cdot (\Delta \boldsymbol{R}_j \times \Delta \boldsymbol{R}_i)$$

can be obtained for each normal mode provided that $\boldsymbol{r}_{ij}$ and $\Delta \boldsymbol{R}_i$ are known. Note that t is between 0 and 0.566. In calculation, the step for t is 0.001. The result is that for t in [0.218, 0.238], the experimental Raman mode signatures for the 11 modes (among them, 3 are of very small ROA intensity) originating from the C–C stretches can be reproduced except 661 cm^{-1} (for 819 cm^{-1}, its t value meets at the margin at 0.238). These are shown in Table 1. The discrepancy of the 661 cm^{-1} mode may be due to that it has more bending components, that more mechanisms beyond the coupling between electric and magnetic dipolar moments, which is the foundation of our classical formula, are operative. This is evidenced by its huge ROA intensity due to multiple mechanisms. For the moment, there is no commercially available ROA instrument that can cover the C–H stretching region. The calculated/predicted Raman mode signatures for the C–H modes by our algorithm are tabulated in Table 2.

If $e_j - e_j^0$ is positive, then in the Raman process, charges are leaving from the j atom. Otherwise, charges are gained. Table 4 shows that all the H atoms and C23 gain charges during the Raman process. This is physically meaningful since the excited/disturbed charges tend to spread to the molecular periphery where most H atoms reside due to charge repulsion.

From the t range [0.218, 0.238], the electron numbers involved in the Raman process are readily calculated to be between 30.0 and 32.8. They correspond to that 38.5% or 42.1% of the total 78 electrons of pinane play their roles in the Raman process. Our unpublished result for β-pinene for this value is less than 50% which is not too different from the pinane case. These values are larger than the methyloxirane case,[11] 20%. One reason for this difference may be attributed to that the geometry of pinane molecule is closer to sphere than that of methyloxirane. Hence, charges of pinane are more easily excited/disturbed because of the steric effect.

For a careful study, we tried to obtain the Raman mode signatures simply by Mulliken charges e_j^0. The result is just not consistent. The consideration of the charge redistribution of the Raman virtual state is indispensable.

7. Concluding remarks

The ROA spectrum offers some additional information of the Raman process. The issue is how to extract this additional information. Besides the known stereo-chemical information embedded in the ROA spectrum, we address that, by combining with a classical ROA signature formula, the charge distribution in the Raman virtual state can be unfolded. The case study of pinane shows that about 40% of the electrons in pinane are involved in the Raman process. The difference, as compared with the methyloxirane case of 20%, is discussed from a molecular geometric viewpoint that pinane is more close to the spherical shape than methyloxirane.

Finally, we stress that our algorithm is rather universal provided that the target molecule is rigid enough. Though for the moment, only two molecules, methyloxirane and pinane, have been tested by our algorithm, we believe the conclusion, such as the percentage of excited charges involved in the Raman process should fall within the range as indicated.

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