# The evaluation of temporal electronic structures of nonresonant Raman excited virtual state of thiourea*

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An algorithm has been introduced to calculate molecular bond polarizabilities of thiourea, which supply essential electronic information about the nonresonant Raman excited virtual states. The main dynamical behaviour of the excited virtual states of thiourea is that the Raman excited electrons tend to flow to the N–H bonds and C–N bonds from the S–C bonds because of the electronic repulsion effect. The difference in Raman excited electron relaxation time of thiourea under 514.5-nm and 325-nm excitations has been observed, which quantitatively shows that the Raman scattering process is dependent on the wavelength of the pumping laser. Finally, the distribution of the electrons at the final stage of relaxation is given out through the comparison between the bond electronic densities of the ground states and the bond polarizabilities after deexcitation.

**Keywords:** Raman intensity, electronic relaxation, bond polarizability, virtual state, thiourea

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## 1. Introduction

Raman scattering[1,2] is a two-photon exchange process and when the electrons are excited to the intermediate state, the excitation may exchange its energy with the nuclear motion and then relax to new ground states with a photon emission. The excitation (including its relaxation) is called a "virtual state" because it is not an eigenstate and cannot be well defined by the nuclear configuration. However, the Raman excited virtual state is real in the sense that there is electronic disturbance by the absorption/emission of light quantum in the scattering process. The electronic structure of the virtual state evolves with time and contains much information about the interaction between the nuclei and the photons. Lee and Heller[3] established a time-dependent theory of Raman scattering, which gives a way to study the virtual state. This theory is based on the idea of wave packet evolution on the excited surface. However, the representation and generalization of this theory in certain molecular systems meet some difficulty because it is very hard to obtain an analytical expression for the Raman cross section. Alternatively, a different approach based on the Raman intensity was adopted to evaluate the time-dependent bond polarizability (temporal bond polarizability), which can be applied to study the physical significance of the Raman process.[4−6] Furthermore, this temporal bond polarizability approach was also used in studying the mechanism of surface enhanced Raman scattering (SERS).[7,8] After applying this method to various molecular systems, it is found that the temporal Raman bond polarizability could map out the behaviour of excited electrons in the Raman process and because all of the results were derived from experiments, this method improved the reliability of the results. In this way, the Raman excited virtual states in different molecular systems could be investigated thoroughly and a lot of detail and important information has been obtained.[9]

In previous studies, we applied this approach to some cyclics, such as ethylene thiourea,[10] 2-aminopyridine/3-aminopyridine[11] and methylviologen.[12] These results offered us some important characteristics of the Raman virtual states temporal evolution. However, the features of Raman excited virtual states of a chain compound have not been studied and it is obvious that the temporal Raman bond polarizability approach could be extended to this kind of compound. In this work, we took thiourea under the 514.5-nm and 325-nm excitations as a case study in order to deepen our search toward chain molecules.

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The choice of thiourea is to confirm the properties of Raman excited virtual states in a simple but typical symmetrical chain molecule.

In the following sections, the algorithm for retrieving the temporal bond polarizabilities is given briefly first. Then, the temporal bond polarizabilities of thiourea are calculated through the Raman intensities from experimental and physical pictures are interpreted. Finally, a concluding remark is offered.

## 2. Retrieval of the temporal bond polarizabilities from the Raman intensities

In order to obtain the temporal bond polarizabilities of a molecule, we should analyse the spectral intensity in the temporal domain $I_j(t)$ (index $j$ is for the normal mode), which is related to the wavenumber domain $I'_j(\nu)$, through the Fourier transform as $\int I'_j(\nu)\,\mathrm{e}^{\mathrm{i}\nu t}\mathrm{d}\nu = I_j(t)$. We note that for $t = 0$, this transformation reduces to $\int I'_j(\nu)\mathrm{d}\nu = I_j(t = 0)$. Hence, the integrated Raman intensity over $\nu$ is just the temporal intensity at $t = 0$. In the Fourier transformation, the central wavenumber of $I'_j(\nu)$ is reset to 0 and it could be demonstrated that this trick is reasonable and available.[13]

The temporal Raman intensity $I_j(t)$ of the $j$-th normal mode with Raman shift $\nu_j$ is related to the electronic polarizability derivative with respect to its normal coordinate $Q_j$ through:[14,15]

$$I_j(t) \sim \frac{(\nu_0 - \nu_j)^4}{\nu_j}(\partial\alpha(t)/\partial Q_j)^2,$$

where $\nu_0$ is the wavenumber of the pumping laser. When $t = 0$, we obtain

$$I_j(t = 0) \approx \frac{(\nu_0 - \nu_j)^4}{\nu_j}(\partial\alpha(t = 0)/\partial Q_j)^2.$$

By transforming $Q_j$s to the internal coordinates $R_k$s through

$$R_k = \sum L_{kj}Q_j,$$

which can be obtained from the normal mode analysis,[16] we have

$$\pm\sqrt{I_j(t)} \approx \frac{(\nu_0 - \nu_j)^2}{\sqrt{\nu_j}}\sum L_{kj}(\partial\alpha(t)/\partial R_k).$$

For convenience, $\partial\alpha(t)/\partial R_k$ is called the temporal bond polarizability.

We can also re-write the above formula in a matrix notation as follows:

$$\begin{bmatrix} \partial\alpha(t)/\partial R_1 \\ \partial\alpha(t)/\partial R_2 \\ \vdots \\ \partial\alpha(t)/\partial R_{3N-6} \end{bmatrix} = [a_{jk}]^{-1} \begin{bmatrix} P_1\sqrt{I_1(t)} \\ P_2\sqrt{I_2(t)} \\ \vdots \\ P_{3N-6}\sqrt{I_{3N-6}(t)} \end{bmatrix},$$

where

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

and $P_j$ is $+1$ or $-1$.

Since the stretching bond polarizabilities offer significant physical interpretations, we will mainly investigate the polarizabilities of bond stretching coordinates. Furthermore, the coupling between the stretching and bending coordinates is generally weak and could be considered as decoupled. Then the dimension of the above matrix equation will be reduced to the number of bonds in a molecule, which is soluble through numerical calculation.

From the above analyses, it is clear that $\partial\alpha(t)/\partial R_k$ could be obtained if $[a_{jk}]^{-1}$ matrix, $I_j(t)$s and a $\{P_j\}$ set are known. $[a_{jk}]^{-1}$ can be derived from the normal mode analysis. $I_j(t)$s can be obtained from the Fourier transform of the Raman profiles. Then, various sets of $\{P_j\}$ can be modified to obtain the solution $\partial\alpha/\partial R_k$s, which are then checked with physical considerations to rule out the inadequate $\{P_j\}$ sets. In our previous studies,[4,5] we found that a unique or a limited number of phase sets can be figured out with physically significant $\partial\alpha/\partial R_k$s in most cases. We will show later how to solve this problem for the thiourea case.

We also need the bond electronic densities $\rho_k$ of the ground state to compare with the bond polarizabilities obtained from the Raman intensities and it could be calculated by density functional theory (DFT) or other quantum chemistry methods with suitable basis sets, which should be selected in different systems.

## 3. The case study of thiourea

The formal structure of thiourea and its atomic numberings (the configuration symmetry of thiourea is $C_{2V}$) are shown in Fig. 1. In the following theoretical calculation, we first used the RHF/6-31G methods to optimize the structure in order to initiate its force constants and molecular structural parameters with

reference to the literature.[6] These data were then employed to refine the force constants until the calculated normal mode wavenumbers were well fitted to the observed ones, which were obtained from the experimental Raman spectra.

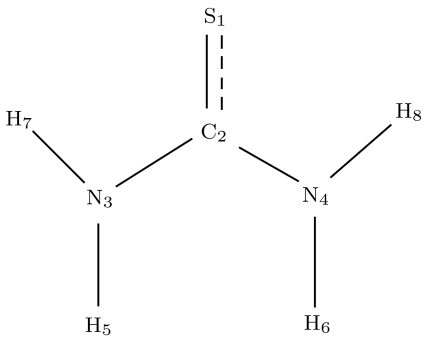



**Fig. 1.** The formal structure of thiourea and its atomic numberings. All of the atoms are in a plane.

The Raman spectra of thiourea were detected by the Renishaw RM-1000 microconfocal spectrophotometer equipped with a CCD detector. A 50x objective was used to perform a 180° backward scattering configuration. The excitations were 514.5-nm $Ar^+$ and 325-nm He–Cd lines. The laser powers on the sample were about 3 mW for 514.5 nm and 1 mW for 325 nm, respectively. The entrance-slit width was 25 $\mu$m and the integral time was 20 s. Thiourea (powder) was purchased from Fluka (> 98% purity).

The Raman spectra of thiourea by these excitations are shown in Fig. 2. For a careful relative intensity measurement, the polarizations of the Raman signals were considered. These signals were taken separately and then combined for the correction because of the different responses of the grating mirror and CCD detector in the various spectral ranges. The deconvolution was taken to resolve the profile into Gaussian components if there is spectral profile overlapping. This process will lead to the intensities obtained with an uncertainty less than 20%.

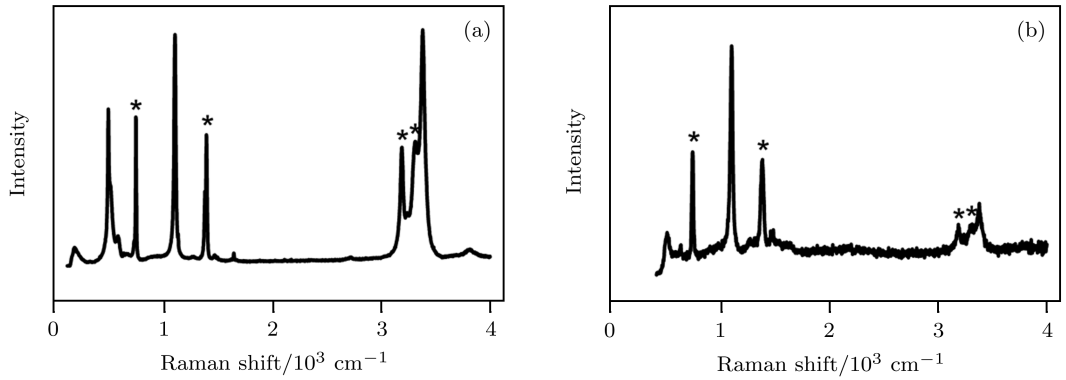



**Fig. 2.** The Raman spectra of thiourea by (a) 514.5 nm and (b) 325 nm excitations. The symbol $*$ shows that the peaks in Table 1 are employed for the elucidation of the bond polarizabilities.

Because of $C_{2V}$ symmetry, the following equivalence relation of the bonds in thiourea molecule is tenable,

$$\mathrm{C_2}\text{–}\mathrm{N_3} \Leftrightarrow \mathrm{C_2}\text{–}\mathrm{N_4}; \quad \mathrm{N_3}\text{–}\mathrm{H_7} \Leftrightarrow \mathrm{N_4}\text{–}\mathrm{H_8};$$
$$\mathrm{N_3}\text{–}\mathrm{H_5} \Leftrightarrow \mathrm{N_4}\text{–}\mathrm{H_6}.$$

As previously mentioned, we considered only the bond stretch polarizabilities. For thiourea, 4 non-equivalent bond stretches (due to symmetry) need to elucidate their bond polarizabilities. So we could only consider the four related normal modes (a type of symmetrical representation of $C_{2V}$ point group) of thiourea and their observed, fitted wavenumbers, intensities and the main potential energy distributions are listed in Table 1. These four intensities (marked by $*$ in Fig. 2, and the intensities of the modes at 3307 $\mathrm{cm^{-1}}$ are normalized to 100) are used to elucidate the bond polarizabilities and our labor in solving this phase problem is reduced greatly by this process. For the four Raman intensities, we have $2^4-1$ possible phase combinations (note that $\{P_i\}$ is identical to $\{-P_i\}$) for the thiourea molecule. The criterion for the phase choice is that all of the bond polarizabilities are of the same sign as time elapses and all of the bond polarizabilities follow the monotonically decaying behaviour as time elapses. With this criterion, there is only one phase solution, which is feasible to obtain the corresponding bond polarizabilities.

**Table 1.** The normal modes of A symmetry of $C_{2V}$ point group of thiourea with their observed, fitted wavenumbers, intensities and main potential energy distributions. The intensities of the modes at 3307 $cm^{-1}$ are normalized to 100. $\nu_s$ stands for symmetrical bond stretch. $\delta$ stands for the in-plane bending motions.

| Raman shift/$cm^{-1}$ | | intensity | | potential energy distribution/% |
|---|---|---|---|---|
| exp. | fitted | 514.5 nm | 325.0 nm | |
| 734 | 735 | 24 | 60 | $v(S_1–C_2)(69.2), \delta(N_3–C_2–N_4)(21.5)$ |
| 1385 | 1383 | 24 | 70 | $v_s(C_2–N_3, C_2–N_4)(50.2), v(S_1–C_2)(20.3), \delta(N_3–C_2–N_4)(25.2)$ |
| 3187 | 3182 | 80 | 126 | $(v_s(N_3–H_7, N_4–H_8) + v_s(N_3–H_5, N_4–H_6))(99.4)$ |
| 3307 | 3311 | 100 | 100 | $(v_s(N_3–H_7, N_4–H_8) - v_s(N_3–H_5, N_4–H_6))(99.2)$ |

# 4. Results and discussion

The bond polarizabilities of thiourea at the initial excitation moment and the final stage of relaxation for both 514.5 nm and 325 nm excitations, together with the calculated bond electronic densities of the ground state, are shown in Fig. 3. From these results, it is clear that:

(i) At the initial excitation moment by 514.5-nm and 325-nm excitations, the tendency of the bond polarizabilities of $N_3$–$H_5$ ($N_4$–$H_6$) and $N_3$–$H_7$ ($N_4$–$H_8$) are obviously different from the electronic densities of the ground state. The bond polarizabilities of $N_3$–$H_7$ ($N_4$–$H_8$) are enhanced greatly and the magnitude of enhancement is larger under 514.5-nm excitation than the one under 325-nm excitation. This phenomenon is caused by the electronic repulsion effect and this effect on the bond $N_3$–$H_5$ ($N_4$–$H_6$) is much greater than the one on the bond $N_3$–$H_7$ ($N_4$–$H_8$) because $N_3$–$H_5$ ($N_4$–$H_6$) is in a much more crowded environment (it is closer to the bonds $C_2$–$N_3$ ($C_2$–$N_4$)) than the ones of $N_3$–$H_5$ ($N_4$–$H_6$). It is elucidated that under the Raman excitation, the excited electrons tend to flow to the molecular peripheral due to the electronic repulsion and it is more obvious under the 514.5-nm excitation. It is also shown in Fig. 3 that under the 514.5-nm excitation, the bond polarizability magnitude of $S_1$–$C_2$ is larger than the one of $C_2$–$N_3$ or $C_2$–$N_4$ and the polarizability magnitudes of $S_1$–$C_2$, $C_2$–$N_3$ and $C_2$–$N_4$ are almost the same, which demonstrate that the flowing effects of excited state electrons are different in 514.5-nm and 325-nm excitations. It is also confirmed in our previous studies.[10,11]

(ii) As shown in Fig. 3, when the final stage of relaxation is approached, the relative magnitudes of the bond polarizabilities are approaching the bond electronic densities of the ground state by the quantum chemical calculation for both 514.5-nm and 325-nm excitations. This is in contrast with the situation at the very initial moment of the virtual state that the peripheral $N_3$–$H_7$ and $N_4$–$H_8$ bonds possess larger polarizabilities. This demonstrates vividly the relaxation of the excited electrons from the peripheral N–H bonds toward the inner skeletal C–N bonds at the final stage of the evolution. The relaxation leads the electronic distribution toward that of the ground state. In this way, we can observe the (relative) bond electronic densities of the molecular ground state via the Raman spectra.

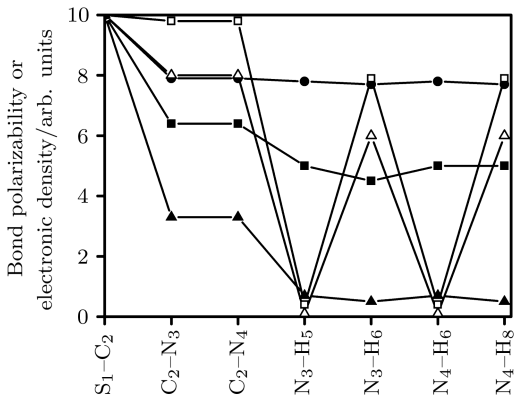



**Fig. 3.** The bond polarizabilities of thiourea at the initial excitation moment (Δ and □ for 514.5-nm and 325-nm excitations, respectively) and the final stage of Raman relaxation (▲ and ■ for 514.5-nm and 325-nm excitations, respectively). Symbol • is for the calculated bond electronic densities of the ground state. The values of $S_1$–$C_2$ bond are normalized to 10.

The bond polarizabilities under 514.5-nm and 325-nm excitations as a function of time, which shows the relaxation of the Raman excited virtual states, are shown in Fig. 4. As time evolves, the bond polarizabilities of $N_3$–$H_7$ ($N_4$–$H_8$), $C_2$–$N_3$ ($C_2$–$N_4$) and $S_1$–$C_2$ decline fast for the 514.5-nm excitation and the bond polarizabilities of $N_3$–$H_5$ ($N_4$–$H_6$) decrease very slowly. For the 325-nm excitation, the decay behaviours of the bond polarizabilities are almost the same with the one in 514.5-nm excitation (Fig. 4). It is noted that the relaxation of the temporal bond po-

larizabilities are in the ranges around 8 ps and 5 ps, respectively, by the 514.5-nm and 325-nm excitations, as shown in Fig. 4. These time durations show roughly the lifetimes of the Raman virtual states under the 514.5-nm and 325-nm excitations. This ratio of 8:5 is roughly proportional to the wavelength ratio of the excitations. That is, the lifetime is proportional to the wavelength of the pumping light. This confirms that the Raman excited states are not stationary eigenstates. Hence, it is correct to call these states *virtual*.

In most cases, the relaxation can be closely followed by an exponential function with the form: $A\,\mathrm{e}^{-t/t_c} + B$.[7] The relaxation characteristic times $t_c$ of bond polarizabilities for two different excitations are shown in Table 2. The relaxation characteristic times of the bond polarizabilities are the important parameters from the viewpoint of this temporal bond polarizability study. From the data in this table, it was found that the $t_c$ for $N_3$–$H_7$ ($N_4$–$H_8$) is much larger than $N_3$–$H_5$ ($N_4$–$H_6$) in both 514.5 nm and 325 nm, which demonstrates that the transfer of electrons in the peripheral bonds is complex and prolongs the relaxation time. Furthermore, it is found that the characteristic times of 514.5 nm excitation are much greater than the ones of 325 nm excitation, which demonstrates that the lifetime of Raman excited virtual states of 514.5 nm excitation is longer than the case of 325 nm excitation.

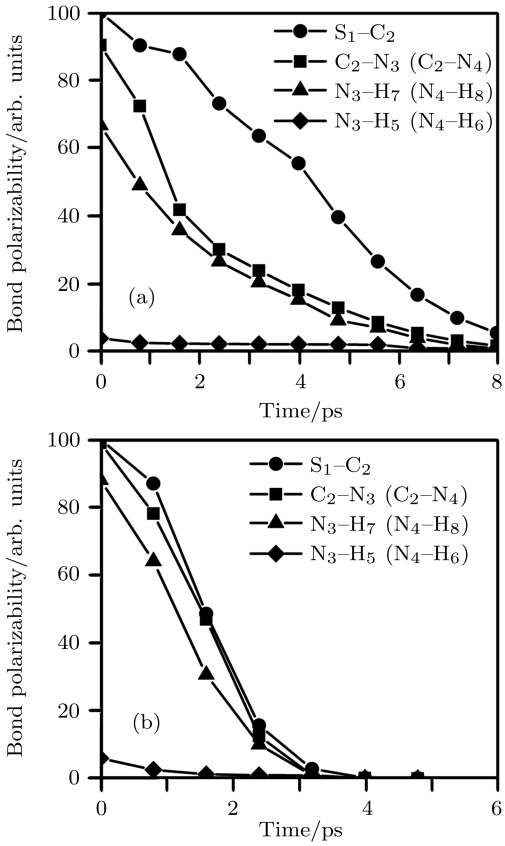



**Fig. 4.** The bond polarizabilities of thiourea as a function of time under (a) 514.5 nm and (b) 325 nm excitations. The values for $S_1$–$C_2$ bond at $t = 0$ are normalized to 100.

**Table 2.** The relaxation characteristic times $t_c$ of bond polarizabilities for 514.5 nm and 325 nm excitations of thiourea. The unit of $t_c$ is picosecond (ps).

| | $S_1$–$C_2$/ps | $C_2$–$N_3$ ($C_2$–$N_4$)/ps | $N_3$–$H_7$ ($N_4$–$H_8$)/ps | $N_3$–$H_5$ ($N_4$–$H_6$)/ps |
|---|---|---|---|---|
| 514.5 nm | 3.01 | 2.16 | 2.39 | 1.24 |
| 325 nm | 2.06 | 1.98 | 1.90 | 1.04 |

## 5. Concluding remarks

In this paper, we have demonstrated the relaxation of the bond polarizabilities for thiourea as the case study. We assert that the excited charges tend to flow to the molecular periphery. The relaxations mostly obey the exponential decaying process and the relaxation is faster for the peripheral N–H. Furthermore, it is shown that the Raman excited virtual state in the thiourea molecule is dependent on the pumping wavelength. This offers us a realm for the exploration of the nonresonant Raman excited states not only in cyclics but also in chain molecules via the Raman intensities, and the conclusion is similar.

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