CHIN. PHYS. LETT. Vol. 29, No. 8 (2012) 083301

Temporal Electronic Structures of Nonresonant Raman Excited Virtual States of P-Hydroxybenzoic Acid *

FANG Chao(房超)[1**], SUN Li-Feng(孙立凤)[1]

Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084

(Received 17 January 2012)

An algorithm is employed to calculate molecular bond polarizabilities of p-hydroxybenzoic acid, which supplies essential electronic information of the nonresonant Raman excited virtual states. The main dynamical behavior of the excited virtual states of p-hydroxybenzoic acid with 514.5 nm excitation is such that the Raman excited electrons tend to flow to the C–C connected with –OH and –COOH from the benzene ring because of the electronic repulsion effect. 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 de-excitation. Furthermore, the relaxation characteristic times of bond polarizabilities shows that the transport of electrons on –COOH is distinct.

PACS: 33.20.Fb, 36.20.Ng DOI: 10.1088/0256-307X/29/8/083301

There has been a great deal of information about the molecular electronic structures during the Raman process.[1–3] The main theme of this approach is to obtain the polarizability for each bond from the Raman intensity. The excitation (including its relaxation) is named as the virtual state because it is not an eigenstate and can not be well defined by the nuclear configuration.[4] 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. A distinctive approach based on the Raman intensity was adopted to evaluate the time-dependent bond polarizability (temporal bond polarizability), which is feasible to be applied to study the physical significance of the Raman process.[5] After applying this method to various molecular systems, it was found that the temporal Raman bond polarizability could map out the behavior of excited electrons in the Raman process and because all the results were derived from experimental data, this method can improve the reliability of the results.[6,7] In this way, the Raman excited virtual states in different molecular systems could be investigated thoroughly and a lot of detailed but important information has been obtained.[8,9] Previously, we have applied this approach to some cyclics such as ethylene thiourea,[10] 2-aminopyridine/3-aminopyridine,[11] methylviologen[12] and thiourea.[13] These results offer us some important characteristics of the temporal evolution of Raman virtual states. In this work, we take p-hydroxybenzoic acid with 514.5 nm excitation to deepen our search toward Raman excited states.

In order to obtain the temporal bond polarizabilities of a molecule, we should analyze 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 $\int I'_j(\nu)e^{i\nu t}d\nu = I_j(t)$. We note that for $t = 0$, this transformation reduces to $\int I'_j(\nu)d\nu = I_j(t = 0)$. Hence, the integrated Raman intensity over ν 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.[10–13]

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

$$I_j(t) \sim \frac{(\nu_0 - \nu_j)^4}{\nu_j}\Big(\frac{\partial\alpha(t)}{\partial Q_j}\Big)^2, \tag{1}$$

where ν_0 is the wavenumber of the pumping laser. When $t = 0$, we obtain

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

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

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

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

$$\pm\sqrt{I_j(t)} \approx \frac{(\nu_0 - \nu_j)^2}{\sqrt{\nu_j}}\sum L_{kj}\frac{\partial\alpha(t)}{\partial R_k}. \tag{4}$$

For convenience, $\partial\alpha(t)/\partial R_k$ is called the temporal bond polarizability. We can also rewrite the above

*Supported by the National Natural Science Foundation under Grant No 11104156.

**Corresponding author. Email: fangchao@tsinghua.edu.cn

© 2012 Chinese Physical Society and IOP Publishing Ltd

formula in matrix notation:

$$\begin{bmatrix} \partial\alpha(t)/\partial R_1 \\ \partial\alpha(t)/\partial R_2 \\ \vdots \\ \partial\alpha(t)/\partial R_{3N-6} \end{bmatrix} = [a_{jk}]^{-1} \begin{bmatrix} P_1\sqrt{I_1(t)} \\ P_2\sqrt{I_2(t)} \\ \vdots \\ P_{3N-6}\sqrt{I_{3N-6}(t)} \end{bmatrix}, \tag{5}$$

where $a_{jk} = (\nu_0 - \nu_j)^2 L_{kj}/\sqrt{\nu_j}$ and P_j is $+1$ or -1. Since the stretching bond polarizabilities offer significant physical interpretations, we mainly investigate the polarizabilities of the bond stretching coordinates. Furthermore, the coupling between the stretching and bending coordinates is generally weak and could be considered to be decoupled. Then the dimension of the above matrix equation will be reduced to the number of bonds in a molecule, which is resoluble through numerical calculation.

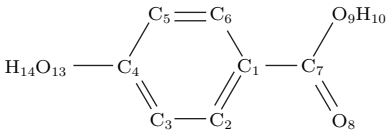

Fig. 1. The formal structure of p-hydroxybenzoic acid and its atomic numberings. All the atoms are in a plane.

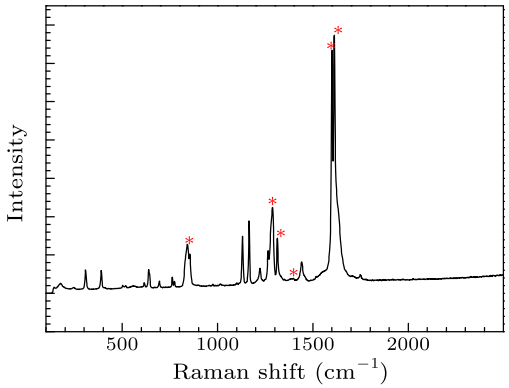

Fig. 2. The Raman spectra of p-hydroxybenzoic acid by 514.5 nm excitations. The asterisks show the peaks listed in Table 1 and are employed for the elucidation of the bond polarizabilities.

From the above analysis, 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. Here $[a_{jk}]^{-1}$ 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,[10–13] 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 this p-hydroxybenzoic acid case.

We also need the bond electronic densities ρ_k of the ground state to compare with the bond polarizabilities obtained from the Raman intensities and it could be calculated by the density functional theory (DFT) or other quantum chemistry methods with suitable basis sets, which should be selected in different systems. The formal structure of p-hydroxybenzoic acid and its atomic numberings (the configuration symmetry of p-hydroxybenzoic acid is C_s) are shown in Fig. 1. In the following theoretical calculation, we first used the RHF/6-31 G methods to optimize the structure in order to initiate its force constants and molecular structural parameters with reference to the literature.[17,18] These data are then employed to refine the force constants until the calculated normal mode wavenumbers are well fitted to the observed ones, which are obtained from the experimental Raman spectra.

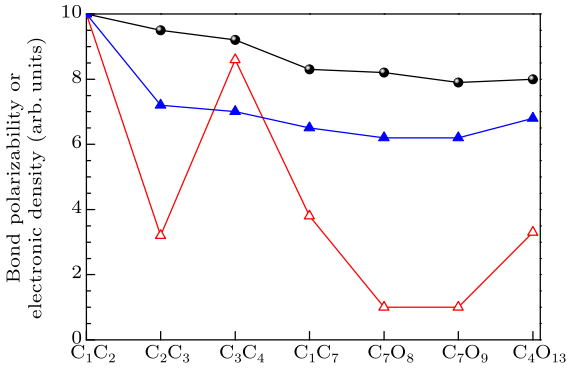

Fig. 3. The bond polarizabilities of p-hydroxybenzoic acid at the initial excitation moment (open triangle) and the final stage of Raman relaxation (closed triangle). The circles stand for the calculated bond electronic densities of the ground state. The values of C_1–C_2 bond are normalized to 10 for the initial excitation moment, the final stage of Raman relaxation and ground state, respectively.

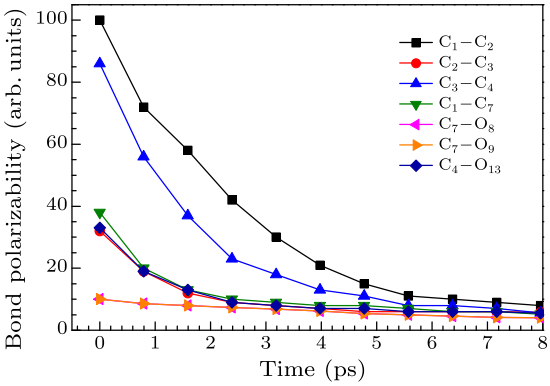

Fig. 4. The bond polarizabilities of p-hydroxybenzoic acid as a function of time with 514.5 nm excitations. The values for the C_1–C_2 bond at $t = 0$ are normalized to 100.

The Raman spectra of p-hydroxybenzoic acid were detected by a Renishaw RM-1000 microconfocal spectrophotometer equipped with a CCD detector. A 50× objective was used to perform a 180° backward scattering configuration. The excitations were 514.5 nm Ar^+ lines and the laser powers on the sample were

about 2.5 mW. The entrance-slit width was 30 μm and the integral time was 25 s. The p-hydroxybenzoic acid (powder) was purchased from Fluka (> 98% purity). The Raman spectra of p-hydroxybenzoic acid 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 together for the correction because of the different responses of the grating mirror and CCD detector in the various spectral ranges. The deconvolution will be 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%.

Because of the C_s symmetry, the following equivalence relation of the bonds in p-hydroxybenzoic acid molecule is tenable: C_1–C_2↔C_1–C_6, C_2–C_3↔C_5–C_6, C_3–C_4↔C_4–C_5, C_7–O_8↔C_7–O_9. As previously mentioned, we were concerned with only the backbone bond stretch polarizabilities, so we could only consider the 6 related normal modes of p-hydroxybenzoic acid and their observed, fitted wavenumbers, intensities and the main vibrational mode,[19–20] as listed in Table 1. For the 6 Raman intensities, we have $2^6 - 1$ possible phase combinations (note that $\{P_i\}$ is identical to $\{-P_i\}$) for the p-hydroxybenzoic acid molecule. The criterion for the phase choice is that: all the bond polarizabilities are of the same sign as time elapses and all the bond polarizabilities follow the monotonically decaying behavior as time elapses. With this criterion, there is only one phase solution, which is feasible to obtain the corresponding bond polarizabilities.

The bond polarizabilities of p-hydroxybenzoic acid at the initial excitation moment and the final stage of relaxation for 514.5 nm together with the calculated bond electronic densities of the ground state are shown in Fig. 3.

From these results, we can realize: (1) At the initial excitation moment with 514.5 nm excitations, the tendency of the bond polarizability of C_3–C_4 is different from the electronic densities of the ground state. This phenomenon is caused by the electronic repulsion effect and this effect on the bond C_3–C_4 is much greater than those on the bond C_1–C_7 and C_4–O_{13} because C_1–C_7 and C_4–O_{13} are in a much more crowded environment than the ones of C_3–C_4.[10–13] It is also shown in Fig. 3 that with 514.5 nm excitation, the bond polarizability magnitude of C_7–O_8 and C_7–O_9 are smaller than other bond polarizabilities and the polarizability magnitudes of C_2–C_3, C_1–C_7 and C_4–O_{13} are almost the same, which demonstrate that the flowing effects of excited state electrons are similar on these bonds with 514.5 nm excitation. (2) 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 with 514.5 nm excitations. This is in contrast with the situation at the very initial moment of the virtual state that the peripheral C_3–C_4 bonds possess larger polarizabilities. This demonstrates vividly the relaxation of the excited electrons from the peripheral bonds toward the inner skeletal bonds at the final stage of the evolution. The relaxation leads to the electronic distribution towards 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.

Table 1. The normal modes of A symmetry of C_s point group of p-hydroxybenzoic acid with their observed, fitted wavenumbers, intensities and main vibrational mode. The intensities of the modes at 1613 cm^{-1} are normalized to 100.

Raman shift (cm^{-1})		Intensity (514.5 nm excitation)	Vibrational mode
Expt	Fitted		
1613	1616	100	(CC) stretching of benzene
1600	1602	90	(CC) stretching of benzene
1389	1384	3	(COO–) symmetric stretching
1321	1325	27	(CC) stretching of benzene
1291	1292	35	(CO) stretching
846	845	30	(CCOO–) stretching

The bond polarizabilities with 514.5 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 C_1–C_7, C_2–C_3, C_3–C_4, C_1–C_2 and C_4–O_{13} decline fast for the 514.5 nm excitation and the bond polarizabilities of C_7–O_8 and C_7–O_9 decrease very slowly.

In most cases, the relaxation can be well followed by an exponential function in the form $Ae^{-t/t_c} + B$.[12,13] The relaxation characteristic times t_c of bond polarizabilities for two different excitations are listed 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 Table 2, it is found that the t_c for C_7–O_8 and C_7–O_9 are much larger than others, which demonstrates that the transfer of electrons in the peripheral bonds is complex and prolongs the relaxation time. Furthermore, it is realized that the characteris-

tic times of C_1–C_2 are much greater than C_2–C_3, C_3–C_4, C_1–C_7 and C_4–O_{13}, which demonstrates that the transfer of electrons of excited Raman virtual states are also obvious on this bond.

Table 2. The relaxation characteristic times t_c of bond polarizabilities with 514.5 nm excitations of p-hydroxybenzoic acid.

Bonds of p-hydroxybenzoic acid	C_1–C_2	C_2–C_3	C_3–C_4
t_c (ps)	2.57	1.14	1.66
Bonds of p-hydroxybenzoic acid	C_1–C_7	C_7–O_8 (C_7–O_9)	C_4–O_{13}
t_c (ps)	1.01	7.05	1.14

In summary, this work shows that the excited charges of Raman excited virtual states tend to flow to the molecular periphery and this conclusion is general for the electrons of excited Raman virtual states. Furthermore, it is found that the relaxation characteristic times of the bond polarizabilities of –COOH are plainly different from other ones, which is the evidence for the transfer of excited electrons between different function groups. From the above investigation, it is elucidated that the time-resolved bond polarizabilities are powerful methods for the investigation of Raman excited electrons.

References

[1] Nie S and Emory S R 1997 *Science* **275** 1102
[2] Lee S Y and Heller E J 1979 *J. Chem. Phys.* **71** 4777
[3] Raman C V 1928 *Ind. J. Phys.* **2** 387
[4] Wu G Z 1990 *J. Mol. Struct.* **79** 238
[5] Zhong F P and Wu G Z 1994 *J. Mol. Struct.* **324** 233
[6] Liu Z J and Wu G Z 2004 *Chem. Phys. Lett.* **389** 298
[7] Tian B G and Wu G Z 1987 *Spectrochim. Acta.* A **43** 65
[8] Fang C, Liu Z J and Wu G Z 2008 *J. Mol. Struct.* **885** 168
[9] Kiefer W 2008 *J. Raman Spectrosc.* **12** 1710
[10] Fang C and Wu G Z 2007 *J. Raman Spectrosc.* **38** 1416
[11] Fang C and Wu G Z 2008 *Spectrochim. Acta* A **71** 1588
[12] Fang C and Wu G Z 2009 *J. Raman Spectrosc.* **40** 308
[13] Fang C and Sun L F 2011 *Chin. Phys.* B **20** 043301
[14] Chantry G W 1971 *Polarizability Theory for the Raman Effect* (New York: Marcel Dekker)
[15] Wilson E B, Decius J C and Cross P C 1955 *Molecular Vibrations* (New York: McGraw-Hill)
[16] Otto A 1984 *Surface-Enhanced Raman Scattering: "Classical" and "Chemical Origin"* in *Light Scattering in Solid* Ⅳ ed Cardona M and Guntherodt G (New York: Springer-Verlag)
[17] Wu D and Fang Y 2003 *J. Colloid Interface Sci.* **265** 234
[18] Xu L L and Fang Y 2004 *J. Colloid Interface Sci.* **274** 122
[19] Wen R and Fang Y 2005 *J. Colloid Interface Sci.* **292** 469
[20] Cascaval D, Galaction A I and Turnea M 2009 *J. Mem. Sci.* **328** 228