ISSN 1674-1056
http://cpb.iphy.ac.cn
http://iopscience.iop.org/cpb
中国物理 B
Chinese Physics
中国物理
Chinese Physics B

# Scanning the energy dissipation process of energetic materials based on excited state relaxation and vibration-vibration coupling

Wen-Yan Wang(王文岩), Ning Sui(隋宁), Li-Quan Zhang(张里荃), Ying-Hui Wang(王英惠), Lin Wang(王琳), Quan Wang(王权), Jiao Wang(王娇), Zhi-Hui Kang(康智慧), Yan-Qiang Yang(杨延强), Qiang Zhou(周强), Han-Zhuang Zhang(张汉壮)

**Citation:**Chin. Phys. B . 2018, 27(10): 104205. **doi:** 10.1088/1674-1056/27/10/104205

Journal homepage: http://cpb.iphy.ac.cn; http://iopscience.iop.org/cpb

**What follows is a list of articles you may be interested in**

---

## Nonlinear spectral cleaning effect in cross-polarized wave generation

Linpeng Yu(於林鹏), Yi Xu(许毅), Fenxiang Wu(吴分翔), Xiaojun Yang(杨晓骏), Zongxin Zhang(张宗昕), Yuanfeng Wu(吴圆峰), Yuxin Leng(冷雨欣), Zhizhan Xu(徐至展)

Chin. Phys. B . 2018, 27(5): 054214. **doi:** 10.1088/1674-1056/27/5/054214

## Modulation and mechanism of ultrafast transient spectroscopy based on dimethylamino-carbaldehyde derivatives

Tong-xing Jin(金桐兴), Jun-yi Yang(杨俊义), Yu Fang(方宇), Yan-bing Han(韩艳兵), Ying-lin Song(宋瑛林)

Chin. Phys. B . 2018, 27(5): 054208. **doi:** 10.1088/1674-1056/27/5/054208

## Enhanced second harmonic generation in a two-dimensional optical micro-cavity

Jian-Jun Zhang(张建军), Hui-Fang Wang(王慧芳), Jun-Hua Hou(候俊华)

Chin. Phys. B . 2018, 27(3): 034207. **doi:** 10.1088/1674-1056/27/3/034207

## Analysis of detection limit to time-resolved coherent anti-Stokes Raman scattering nanoscopy

Liu Wei, Liu Shuang-Long, Chen Dan-Ni, Niu Han-Ben

Chin. Phys. B . 2014, 23(10): 104202. **doi:** 10.1088/1674-1056/23/10/104202

## Coherent coupling between vibrational modes of C–H bonds at different positions studied by femtosecond time-resolved coherent anti-Stokes Raman scattering

Du Xin,He Xing,Liu Yu-Qiang,Wang Ying-Hui,Yang Yan-Qiang

Chin. Phys. B . 2012, 21(3): 034210. **doi:** 10.1088/1674-1056/21/3/034210

---

# Scanning the energy dissipation process of energetic materials based on excited state relaxation and vibration–vibration coupling*

Wen-Yan Wang(王文岩)[1], Ning Sui(隋宁)[1], Li-Quan Zhang(张里荃)[1], Ying-Hui Wang(王英惠)[1,†], Lin Wang(王琳)[1], Quan Wang(王权)[1], Jiao Wang(王娇)[1], Zhi-Hui Kang(康智慧)[1], Yan-Qiang Yang(杨延强)[3], Qiang Zhou(周强)[2], and Han-Zhuang Zhang(张汉壮)[1,‡]

[1] *Femtosecond Laser Laboratory, Key Laboratory of Physics and Technology for Advanced Batteries (Ministry of Education), College of Physics, Jilin University, Changchun* 130012, *China*

[2] *State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun* 130012, *China*

[3] *National Key Laboratory of Shock Wave and Detonation Physics, Institute of Fluid Physics, China Academy of Engineering Physics, Mianyang* 621900, *China*

(Received 29 March 2018; revised manuscript received 21 June 2018; published online 27 September 2018)

The energy dissipation mechanism of energetic materials (EMs) is very important for keeping safety. We choose nitrobenzene as a model of EM and employ transient absorption (TA) spectroscopy and time-resolved coherent anti-stokes Raman scattering (CARS) to clarify its energy dissipation mechanism. The TA data confirms that the excited nitrobenzene spends about 16 ps finishing the twist intramolecular charge transfer from benzene to nitro group, and dissipates its energy through the rapid vibration relaxation in the initial excited state. And then the dynamics of vibrational modes (VMs) in the ground state of nitrobenzene, which are located at 682 $cm^{-1}$ ($\nu_1$), 854 $cm^{-1}$ ($\nu_2$), 1006 $cm^{-1}$ ($\nu_3$), and 1023 $cm^{-1}$ ($\nu_4$), is scanned by CARS. It exhibits that the excess energy of nitrobenzene on the ground state would further dissipate through intramolecular vibrational redistribution based on the vibrational cooling of $\nu_1$ and $\nu_2$ modes, $\nu_1$ and $\nu_4$ modes, and $\nu_3$ and $\nu_4$ modes. Moreover, the vibration–vibration coupling depends not only on the energy levels of VMs, but also on the spatial position of chemical bonds relative to the VM.

**Keywords:** energy dissipation, charge transfer, transient absorption, coherent anti-stokes Raman scattering (CARS)

**PACS:** 42.65.Sf, 42.65.Dr, 42.65.–k **DOI:** 10.1088/1674-1056/27/10/104205

## 1. Introduction

The interest in the energetic material has increased rapidly in the last three decades. It is one type of important functional materials and plays an important role in the fields of military affairs and civilian engineering.[1] Therefore, people have paid much attention to understand the reaction mechanism, so as to further employ the energetic materials. The previous report[2] shows that the macroscopic properties of energetic materials are much sensitive to the physical and chemical processes on the atomic or molecular scale and are also dependent on the excitation conditions. According to the special characteristics of energetic materials, the energy dissipation mechanism is very important to improve the safety and properties of energetic materials.[3] However, this process covers from femtosecond to nanosecond time scales and is much dependent on the relaxation of excited state and the damping oscillation of chemical bonds.[4] Besides the relaxation between the electronic states, the vibrational cooling and vibration–vibrational coupling also participate in the energy dissipation through intramolecular vibrational redistribution (IVR)[5] or multi-phonon up-pumping,[6] even though the energetic materials are located on the ground state. These complex dynamic processes would affect the excess energy redistribution in the energetic materials, which would induce the cleavage of the reaction bond and release chemical energy of energetic materials.[7] This finally affects the explosion rate and the reaction products. Therefore, it is very important to clarify the energy dissipation mechanism of energetic materials in detail. However, the most test technique for energetic materials could not offer the kinetic information, such as the relaxation of energy state or the vibrational cooling. Fortunately, transient absorption (TA) technique and the time-resolved coherent anti-Stokes Raman scattering (CARS) technique are two types of important ultrafast spectroscopy techniques. The former would offer the kinetic relaxation of materials in the excited state and the latter would clarify the vibration cooling and vibration–vibration coupling of chemical bonds. Therefore, we believe that the dissipation mechanism of energetic materials would be clarified by employing the TA and CARS. Among these energetic materials, the energetic materials with

*Project supported by the National Natural Science Foundation of China (Grant Nos. 21573094, 11274142, 11474131, 11574112, and 51502109), the National Found for Fostering Talents of Basic Science, China (Grant No. J1103202), the Science Challenging Program (Grant No. JCKY2016212A501), and China Scholarship Council (CSC) during a visit of Ning Sui (Grant No. 201706175038) to MPIA is also acknowledged.

†Corresponding author. E-mail: yinghui_wang@jlu.edu.cn

‡Corresponding author. E-mail: zhanghz@jlu.edu.cn

© 2018 Chinese Physical Society and IOP Publishing Ltd 

nitro unit are frequently used for a variety of applications.[8–10] So, we select nitrobenzene as a model object and discuss the energy dissipation mechanism of energetic materials by considering its energy dissipation between electronic states and that of vibrational modes together.

In this work, we study the energy dissipation process of nitrobenzene by employing transient absorption technique which detects the energy dissipation between electronic states, and time-resolved coherent anti-Stokes Raman scattering technique which tracks vibration relaxation dynamics among different vibrational modes in nitrobenzene. As a result, the relaxation between electronic states and the dynamics among vibrational energy levels are both disentangled in detail. Our results originated from TA and CARS would help us to understand the energy dissipation process of nitrobenzene at great length.

## 2. Experiment

Briefly, we employ a mode-lock Ti:sapphire femtosecond laser system (Coherent), which offers 2.6 mJ, 130-fs pulses at 800 nm with a repetition rate of 500 Hz. The output of the femtosecond laser beam is split into two parts by a beam splitter (9:1); the major one is frequency-doubled by a 1-mm thick beta barium borate (BBO) crystal to generate 400-nm pulses, which will be used as the pump pulse, while the minor one is focused into a 5-mm quartz cell filled with water to generate a white light continuum as the probe pulse. The excitation pulse (400 nm) is sent to a delay line and modulated by a synchronized optical chopper (Terahertz Technologies Inc., C-995) with a frequency of 250 Hz and used as the pump beam to excite the sample. The excitation spot is about 0.3 mm in diameter. The TA spectrum is carried out by a spectrometer (AvaSpec-2048×16). The time-resolved CARS system setup is shown in Fig. 1.[11,12] The laser pulse is split into three pulses by two beam splitters. Two of them with wave vectors $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$ act as pump light. The third one act as Stokes light with wave vector $\boldsymbol{k}_S$. The three beams are spatially focused into the sample in the folded box geometry. Herein, the pump ($\boldsymbol{k}_1$ and $\boldsymbol{k}_2$) and Stokes ($\boldsymbol{k}_S$) are coming from the noncollinear optical parametric amplifiers $NOPA_1$ and $NOPA_2$, and their wavelengths are 560 nm and 600 nm, respectively. Through adjusting the energy difference ($\Delta\nu$) between the pump and Stokes laser, the Raman transition from 600 $cm^{-1}$ to 1100 $cm^{-1}$ may be excited resonantly. Actually, the vibrational modes of nitrobenzene would be easily detected owing to the broad femtosecond pulse in frequency domain, which would cover multi-vibration modes simultaneously. The CARS spectrum is carried out by a spectrometer (AvaSpec-2048×16). The dynamic signal is obtained by a photomultiplier tube (Zolix, PMTH-S1-CR131) connected to the lock-in amplifier (SR830, DSP). The sample of nitrobenzene is produced by Beijing Chemical Works and the purity is 99.5%. Nitrobenzene is hold in a 1-mm quartz cuvette.

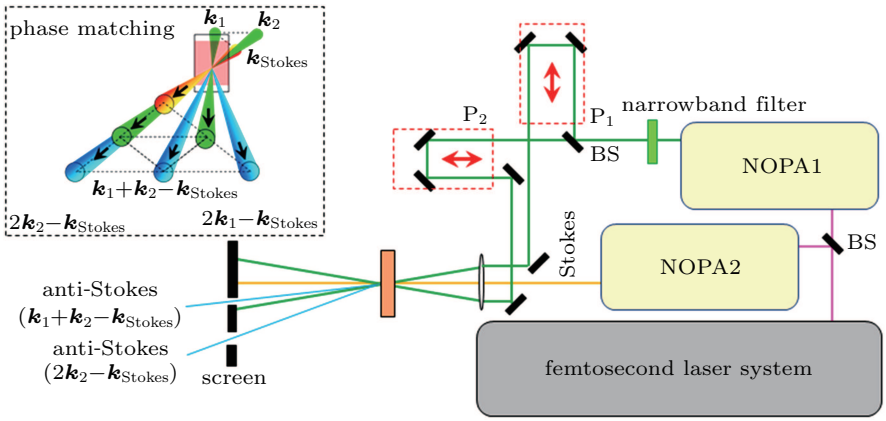



**Fig. 1.** (color online) Schematic diagram of the CARS system. BS: beam splitter (50% R:50% T). Inset: the BOXCARS configuration of CARS.

## 3. Results and discussion

The transient absorption (TA) is employed to probe the photo-excitation relaxation process of nitrobenzene. The nitrobenzene does not emit photons after photo-excitation, suggesting that the excited nitrobenzene would release its energy non-radiatively. Meanwhile, the excess energy originated from photo-excitation would heat up the nitrobenzene.[13] Figure 2(a) exhibits the time-dependent TA spectra, where a broad negative band appears in the TA spectra. This negative band is mainly located in the visible region and out of the absorption spectrum of nitrobenzene, implying that this spectral feature should be assigned to the excited state absorption (ESA). There is a rising behavior in the frequency domain from 590 nm to 700 nm, and then its amplitude gradually decreases after 40 ps. This dynamic behavior indicates that the ESA signal should be originated from the intermediate state.[14,15] The previous work has pointed out that this intermediate state should be assigned to the twisted intramolecu-

lar charge transfer (TICT) formation in excited states,[16,17] where the benzene (donor) and nitro (acceptor) group orbitals of the system exist in an orthogonal conformation in the excited state.[18] The rising spectral feature in TA spectra should correspond to the TICT process from the benzene to the nitro unit. Figures 2(b) and 2(c) present the TA curves of nitrobenzene at different wavelengths. The temporal trace at 670 nm exhibits that a rising component appears in the initial dynamic process with lifetime ($\tau_G$) of 16.1 ps, corresponding to the generation process of TICT after photo-excitation. And then this intensity monotonically decreases with time and its lifetime ($\tau_D$) is about 762 ps, which is used to describe the relaxation process of TICT. The dynamics at 475 nm display a monotonous relaxation process. To retrieve characteristic time constants, this dynamic curve is fitted by tri-exponential decay and the results are given in Fig. 2(b). $\tau_{VR}$ is about 690 fs, whose dynamic process is so rapid that it should be attributed to the vibration relaxation. $\tau_G$ and $\tau_D$ in Fig. 2(b) are about 15.2 ps and 751 ps, which should be assigned to the generation and relaxation lifetimes of TICT, respectively, owing to the similar lifetime.

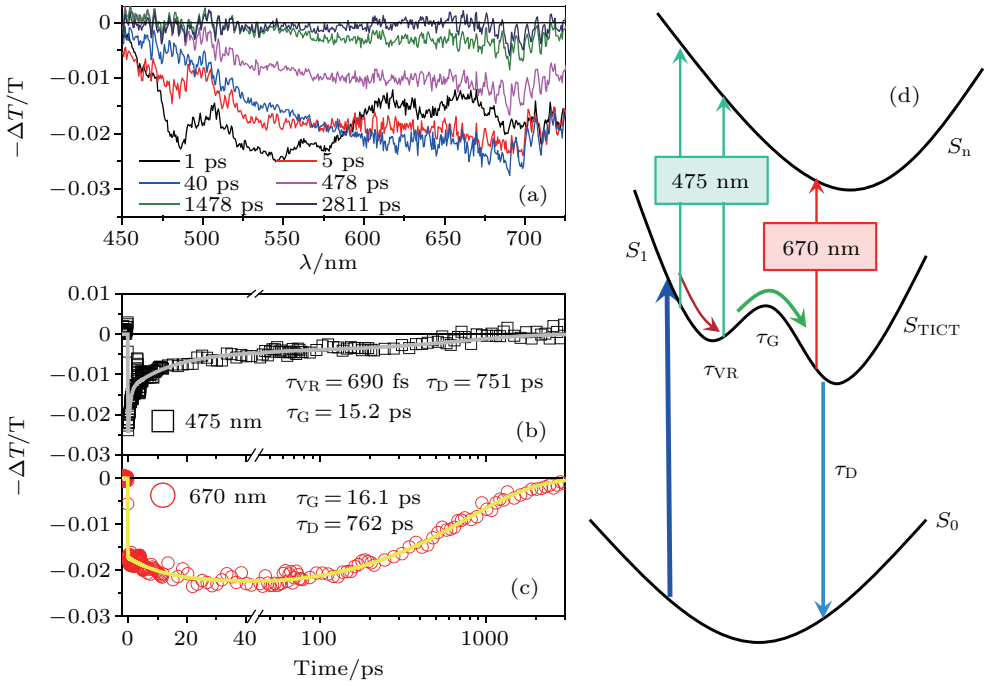



**Fig. 2.** (color online) (a) Time-dependent TA spectra of nitrobenzene, and the corresponding TA curves at (b) 475 nm and (c) 670 nm; (d) the corresponding energy dissipation mechanism among electronic states of nitrobenzene.

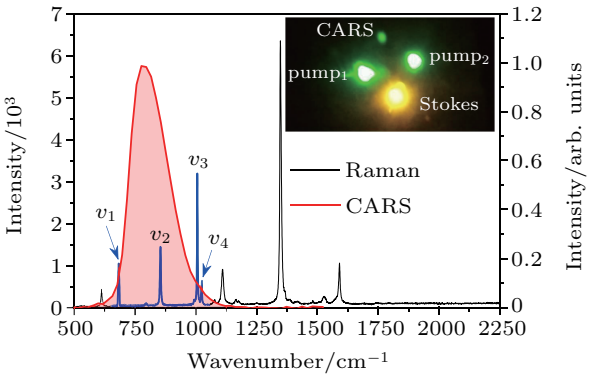



**Fig. 3.** (color online) Raman and CARS spectra of nitrobenzene. Note that the CARS signal (red line) overlaps with the four Raman peaks named $\nu_1$ (682 cm$^{-1}$), $\nu_2$ (854 cm$^{-1}$), $\nu_3$ (1006 cm$^{-1}$), and $\nu_4$ (1023 cm$^{-1}$). Inset: the picture of CARS signal.

After the excited nitrobenzene relaxes on the ground state, the excess energy on the ground state would further dissipate through the vibrational dynamic behaviors involving the IVR or the vibration–vibrational coupling (VC). Therefore, the time-resolved CARS is employed to track the vibrational dynamics. Figure 3 offers the Raman spectrum and the CARS signal of nitrobenzene, where the CARS signal covers about four Raman peaks named $\nu_1$, $\nu_2$, $\nu_3$, and $\nu_4$, which correspond to 682 cm$^{-1}$, 854 cm$^{-1}$, 1006 cm$^{-1}$, and 1023 cm$^{-1}$, respectively. The corresponding motion manners are summarized in Table 1. The real picture of CARS signal and other lasers is given in the inset of Fig. 3. The direction of CARS signal is different from that of other lasers, and the detection without background would be easily obtained.

**Table 1.** Theoretical and experimental values of Raman shift (in unit cm$^{-1}$) of nitrobenzene.[19]

| Modes | Theoretical value | Experimental value | Description |
|---|---|---|---|
| $\nu_1$ | 677 | 682 | C=C–C in-plane bend |
| $\nu_2$ | 843 | 854 | C=C–C in-plane bend |
| $\nu_3$ | 994 | 1006 | C=C–C trigonal bend |
| $\nu_4$ | 1015 | 1023 | C=C–H in-plane bend |

For a better understanding of the relationship of vibration modes appearing in CARS spectrum, figure 4(a) offers

the dynamic curve of total CARS signal in the direction of $\boldsymbol{k}_1+\boldsymbol{k}_2-\boldsymbol{k}_S$. Apparently, there is an obvious oscillation component signal originated from the vibration–vibration coupling, which is overlapped on the relaxation curve. Moreover, the amplitude of oscillation component decreases at the same time. In order to quantitatively analyze their components, we have to gradually extract these dynamic components from the relaxation curve of CARS signal. Note that the Gaussian curve is located near the zero time, which corresponds to the non-resonant electronic background.[20] This Gaussian component is related to the electron response to the electric filed component of light. Herein, the relaxation component follows an exponential relaxation behavior, which should correspond to the dephasing process of vibration modes. After the data fitting, it is found that the dephasing lifetime of these vibration modes is about 550 fs. The quantum beating signal appears in the relaxation curve of CARS signal as seen in Fig. 4(a), which is assigned to the coherent coupling of vibration modes originated from chemical bonds. In order to analyze this quantum beating signal, the corresponding oscillation component is extracted in Fig. 4(b). Apparently, its amplitude decreases with time, since the population in the vibrational modes would gradually decrease due to damping vibration originated from the inelastic collision with the surrounding nitrobenzene in the environment. Its lifetime is about 600 fs based on data analysis. And then, the oscillation component from 0.23 ps to 2.5 ps, which is originated from the vibration–vibration coupling, is confirmed by Fourier transform power spectra,[21] as shown in Fig. 4(c). There are three peaks at 15 $cm^{-1}$, 172 $cm^{-1}$, and 341 $cm^{-1}$ in the frequency domain. According to the Raman spectrum of nitrobenzene in the inset of Fig. 3, it is found that these values should correspond to the energy of $v_4-v_3$, $v_2-v_1$, and $v_4-v_1$, suggesting that the $v_4$ mode is coupled with $v_3$ mode, $v_2$ mode is coupled with $v_1$ mode, and $v_4$ mode is coupled with $v_1$ mode, respectively, which is summarized in Fig. 4(d). It means that the IVR would occur among these vibrational modes. According to the molecular structure of nitrobenzene, the vibration–vibration (V–V) coupling depends not only on the energy level but also on the spatial position of chemical bonds relative to the vibration mode. Moreover, the spatial position may play a distinctive role in the vibration–vibrational coupling in comparison with the energy level of the vibrational mode.

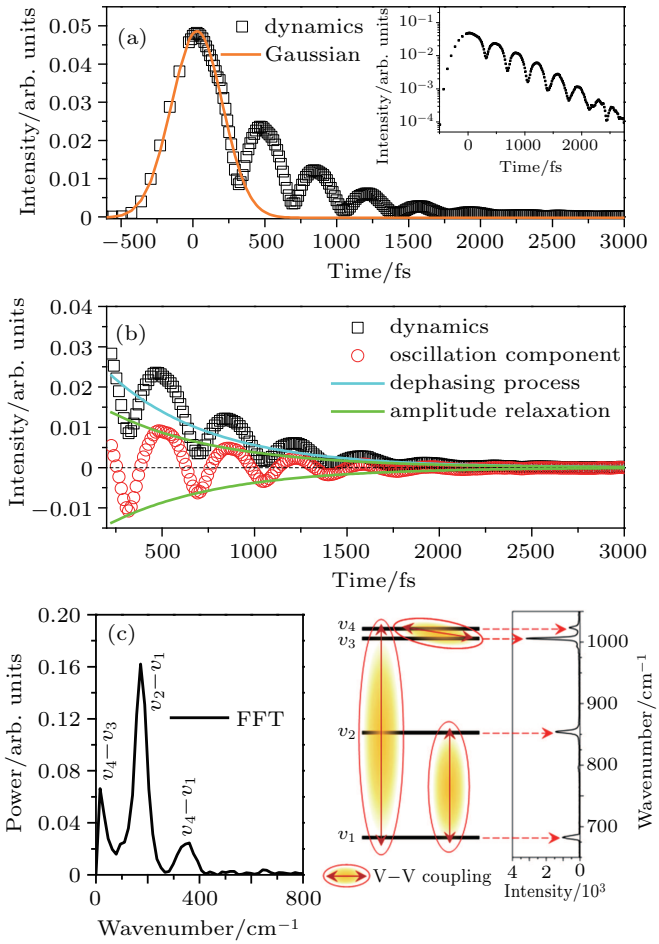



**Fig. 4.** (color online) (a) The dynamic curve containing the Gaussian curve (orange line); (b) the relaxation curve involving exponential decay curve (black square), oscillation signal (red circle), dephasing component (blue line), and the amplitude relaxation of oscillation signal (green line); (c) the result of the Fourier transformation of the oscillation component as shown in panels (b); (d) the coupling mechanism of $v_1$ (682 $cm^{-1}$), $v_2$ (854 $cm^{-1}$), $v_3$ (1006 $cm^{-1}$), and $v_4$ (1023 $cm^{-1}$) vibrational modes in the nitrobenzene. Inset: The total signal relaxation curve in logarithmic coordinate.

## 4. Conclusions

In summary, these data allow us to draw a detailed map of the relaxation pathways of excited nitrobenzene. It is found that the excited nitrobenzene has to spend about 16 ps carrying out structural twist to finish the intramolecular charge transfer from benzene to nitro group. Simultaneously, the excited nitrobenzene also dissipates its energy through the rapid vibration relaxation. After that, the nitrobenzene in the TICT state would relax to the ground state. Then, dynamics of vibrational modes in the ground state of nitrobenzene located at 682 $cm^{-1}$ ($v_1$), 854 $cm^{-1}$ ($v_2$), 1006 $cm^{-1}$ ($v_3$), and 1023 $cm^{-1}$ ($v_4$), is scanned by time-resolved CARS, which are all distributed on the benzene ring. Since the distance between the chemical bonds corresponding to these vibration modes is very close, the couplings of $v_4$ and $v_3$, $v_2$, and $v_1$, and $v_4$ and $v_1$ really exist, which would influence the intramolecular energy redistribution. The IVR process depends not only on the energy level but also on the spatial position of chemical bonds relative to the vibration mode.

## References

[1] Yu Z and Bernstein E R 2013 *J. Phys. Chem. A* **117** 1756
[2] Guo Y Q, Greenfield M, Bhattacharya A and Bernstein E R 2007 *J. Chem. Phys.* **127** 154301
[3] Zhurova E A, Tsirelson V G, Stash A I, Yakovlev M V and Pinkerton A A 2004 *J. Phys. Chem. B* **108** 20173

[4] Banerji N, Cowan S, Leclerc M, Vauthey E and Heeger A J 2010 *J. Am. Chem. Soc.* **132** 17459
[5] Boyarkin O V, Rizzo T R and Perry D S 1999 *J. Chem. Phys.* **110** 11346
[6] Dlott D D and Fayer M D 1990 *J. Chem. Phys.* **92** 3798
[7] Chen S, Tolbert W A and Dlott D D 1994 *J. Phys. Chem.* **98** 7759
[8] Zander M, Breymann U, Dreeskamp H and Koch E 1977 *Z. Naturforsch. A* **32** 1561
[9] Gerrard D L and Maddams W F 1976 *Appl. Spectrosc.* **30** 554
[10] Liu Q H, Wang Y H, Sui N, Wang Y T, Chi X C, Wang Q Q, Chen Y, Ji W Y, Zou L and Zhuang H Z 2016 *Sci. Rep.* **6** 29442
[11] Wang Y H, Peng Y J, He X, Song Y F and Yang Y Q 2009 *Chin. Phys. B* **18** 1463
[12] Namboodiri M, Kazemi M M, Khan T Z, Materny A and Kiefer J 2014 *J. Am. Chem. Soc.* **136** 6136
[13] Takezaki M, Hirota H and Terazima M 1998 *J. Chem. Phys.* **108** 4685
[14] Chi X C, Ni M C, Wang Y H, Sui N, Wang W Y, Lu R, Yang Y Q, Ji W Y and Zhang H Z 2017 *J. Photoch. Photobio. A* **346** 221
[15] Huang T H, Hou J Q, Kang Z H, Wang Y H, Lu R, Zhou H P, Zhao X, Ma Y G and Zhang H Z 2013 *J. Photoch. Photobio. A* **261** 41
[16] Sinha H K and Yates K 1990 *J. Chem. Phys.* **93** 7085
[17] Nagakura S, Kojima M and Maruyama Y 1964 *J. Mol. Spec.* **13** 174
[18] Retting W 1986 *Angew. Chem. Int. Ed.* **25** 971
[19] Zhu X M, Zhang S Q, Zheng X and Phillips D L 2005 *J. Phys. Chem. A* **109** 3086
[20] Yu G Y, Zeng Y Y, Guo W C, Wu H L, Zhu G B, Zheng Z Y, Zheng X X, Song Y F and Yang Y Q 2017 *J. Phys. Chem. A* **121** 2565
[21] Kano H and Hamaguchi H 2004 *Appl. Phys. Lett.* **85** 4298