

EXCITED STATES CALCULATION OF SOME ALKYL SULFIDES WITH TIME DEPENDENT DENSITY FUNCTIONAL THEORY****Zh. Yuanpeng¹, W. Haitao^{1*}, S. Chao¹, B. Yun¹, Zh. Jing¹, S. Hao²**

¹ State Key Laboratory of NBC Protection for Civilians, Beijing 102205, China; e-mail: dr_wht@163.com

² Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Jilin 130024, China

The excited states of mustard and related alkyl sulfides have been calculated using time dependent density functional theory. Among the seven commonly used density functionals, PBE0 exhibits the most accurate excited energy, while the Pearson-related coefficient of calculated energies and experimental peaks reaches 0.98. Boltzmann average analysis reveals that excited energies of different conformers are almost the same. The calculated excited states of mustard come to 5.56 and 6.00 eV, which are assigned as $n \rightarrow \sigma^*$ transition by the natural transition orbital visualization. Besides, sulfur ethers with C_{2v} symmetry show similar ultraviolet properties as mustard, whereas the excited states of simulated agents with the SCH_2CH_2Cl group differ from mustard.

Keywords: mustard, alkyl sulfide, excited states, time dependent density functional theory.

РАСЧЕТ ВОЗБУЖДЕННЫХ СОСТОЯНИЙ НЕКОТОРЫХ АЛКИЛСУЛЬФИДОВ МЕТОДОМ ЗАВИСЯЩЕЙ ОТ ВРЕМЕНИ ТЕОРИИ ФУНКЦИОНАЛА ПЛОТНОСТИ**Zh. Yuanpeng¹, W. Haitao^{1*}, S. Chao¹, B. Yun¹, Zh. Jing¹, S. Hao²**

УДК 539.194:623.459.452

¹ Государственная лаборатория защиты гражданского населения, 102205, Пекин, Китай; e-mail: dr_wht@163.com

² Институт химии функциональных материалов, Северо-восточный педагогический университет, 130024, Цзилнь, Китай

(Поступила 2 августа 2018)

Возбужденные состояния молекулы иприта (горчичного газа) и родственных алкилсульфидов рассчитаны методом зависящей от времени теории функционала плотности. Из семи обычно используемых функционалов плотности функционал PBE0 дает наиболее точные энергии возбуждения, причем коэффициент корреляции Пирсона между рассчитанными энергиями и экспериментальными пиками 0.98. Энергии возбуждения различных конформеров, найденные на основе Больцмановского распределения, практически одинаковы. Рассчитаны энергии первых возбужденных состояний иприта 5.56 и 6.00 эВ. По данным визуализации естественных орбиталей они отнесены к переходу $n \rightarrow \sigma^*$. Показано, что сернистые эфиры с симметрией C_{2v} проявляют в УФ области такие же свойства, как и иприт, тогда как возбужденные состояния модельных соединений с группой SCH_2CH_2Cl отличны от состояний иприта.

Ключевые слова: иприт, сернистый алкил, возбужденные состояния, зависящая от времени теория функционала плотности.

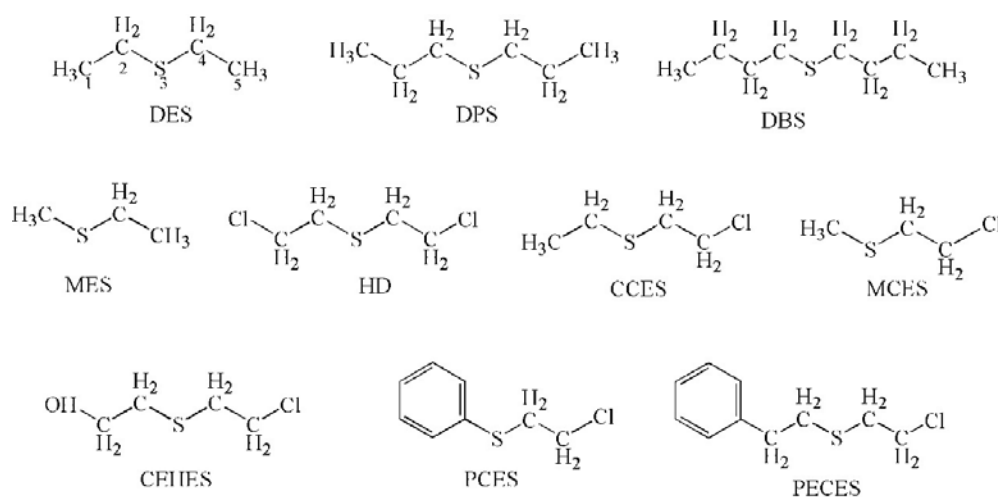
Introduction. Alkyl Sulfides are ubiquitous in the environmental atmosphere and can affect human health in many ways [1, 2]. One typical alkyl sulfide, namely Mustard (HD, $ClCH_2CH_2SCH_2CH_2Cl$), is used

** Full text is published in JAS V. 87, No. 3 (<http://springer.com/journal/10812>) and in electronic version of ZhPS V. 87, No. 3 (http://www.elibrary.ru/title_about.asp?id=7318; sales@elibrary.ru).

as a kind of nefarious synthetic chemical agent [3]. HD causes blisters on the skin, ocular injury, and respiratory disorders, and the effects may last several decades. It was first used in World War I and recently appeared in the Iran-Iraq conflict. A possible terrorist attack and the potential risk of unexpected exposure to abandoned HD after the war are unavoidable [4–6]. Therefore, the study of HD detection and destruction is of great importance.

So far there have been plenty of reports on UV spectra of HD and simulated agents. Rewick [7] measured the UV spectrum of HD in cyclohexane, and the absorption peak was at 6.05 eV. Vorontsov [4] studied the photocatalytic degradation of 2-phenethyl-2-chloroethyl sulfide (PECES), which showed the first absorption band centered at 4.81 eV and a stronger absorption centered at 5.39 eV in the liquid phase. Panayotov [8] reported the photocatalytic oxidation of 2-chloroethyl ethyl sulfide (CEES) on TiO₂-SiO₂ powders. However, the UV spectra of these sulfur compounds in the gas phase are rarely reported, which plays a crucial role in remote detection and natural degradation.

Herein we report calculations of HD excited states based on time dependent density functional theory (TDDFT). First, we carefully compared the excited states of five sulfur ethers calculated by seven popular TDDFT methods with the measured absorption signals, which are used to determine the most appropriate method. These sulfur ethers included diethyl sulfide (DES), methyl ethyl sulfide (MES), dipropyl sulfide (DPS), and dibutyl sulfide (DBS) [9, 10]. Then we studied the excited states of HD and its simulated agents, including 2-chloroethyl ethyl sulfide (CEES), methyl-2-chloroethyl sulfide (MCES), dichloroethyl hydroxyethyl sulfide (CEHES), phenyl chloroethyl sulfide (PCES), and phenyl chloroethyl sulfide (PECES) [11, 12]. Furthermore, we evaluated the spectral behavior of HD and its simulated agents. The molecular structures of sulfide compounds are as follows:



Methods. Time dependent density functional theory (TDDFT) is an effective tool for computing excited states [13]. With the development of computer science and quantum chemistry theory, the accuracy and efficiency of TDDFT are satisfactory [14–16]. It is a prior option for studying toxic compounds. In this work, we optimized the molecular structure using density functional theory. Then, the performance of seven density functionals, namely B3LYP, M06-2X, CAM-B3LYP, PBE0, BP86, BH&HLYP, and B97-2, was evaluated. The basis set was 6-311+g(d,p) with the calculation soft version Gaussian 09 [17].

Results and discussion. *Excited states of DES.* DES is a common chemical reagent. Its structure and properties have been studied in detail [9]. These sulfide molecules are flexible, and hence several conformers are likely to co-exist. To determine the conformers of DES, we scanned the potential energy surface (PES) of DES by rotating the dihedral angle of C1-C2-S3-C4 and C5-C4-S3-C2 from -270 to 90° with a resolution of 10° . As shown in Fig. 1, PES of DES has six minima marked as *a*, *b*, *b*₂, *b*₃, *b*₄, and *c*.

For each minimum point, the conformer was further optimized and followed by the TDDFT calculation. According to Boltzmann distribution law, the percentage of each conformer is determined by the energy, and then the macro-properties can be determined by the Boltzmann averaging. The Boltzmann distribution of DES is shown in Table 1. The conformer *c* has the lowest energy, and its content is 21.1%. Interestingly, the standard deviation of the excited energy is quite small, which means that these conformers show a small difference in the excited energy. Therefore, only one conformer is adopted for the rest of the calculation and analysis.

TABLE 1. Boltzmann Distribution of DES

| Minimum | E_i , a.u. | Boltzmann distribution, % | E_1 , eV | E_2 , eV | E_3 , eV |
|---------------------|--------------|---------------------------|------------|------------|------------|
| <i>a</i> | -556.3516 | 14 | 5.18 | 5.47 | 6.11 |
| <i>b</i> | -556.3518 | 16 | 5.31 | 5.55 | 6.12 |
| <i>b2</i> | -556.3518 | 16 | 5.31 | 5.55 | 6.12 |
| <i>b3</i> | -556.3518 | 16 | 5.31 | 5.55 | 6.12 |
| <i>b4</i> | -556.3518 | 16 | 5.31 | 5.55 | 6.12 |
| <i>c</i> | -556.3520 | 21 | 5.51 | 5.51 | 6.12 |
| Standard deviation | | | 0.106 | 0.033 | 0.004 |
| Boltzmann averaging | | | 5.28 | 5.47 | 6.06 |

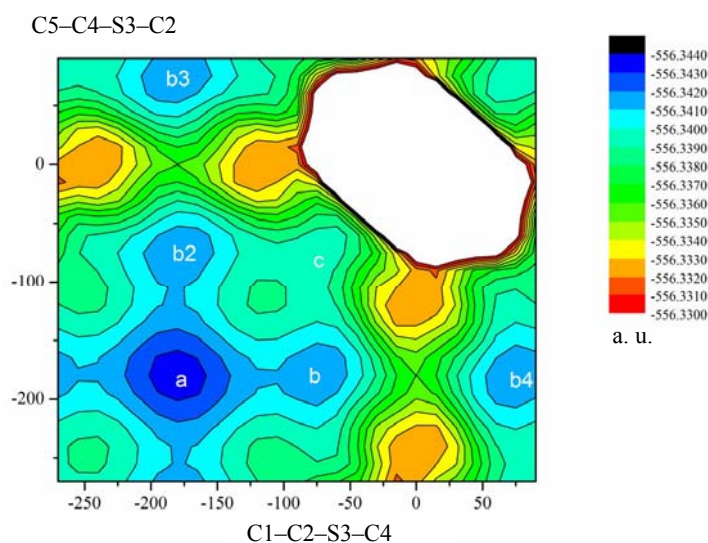


Fig. 1. PES of DES.

Williams [9] measured the UV-visible spectrum of DES and found that its peaks were at 5.58 and 6.11 eV. We compared our calculation excited states by TDDFT with Williams' experimental results, as shown in Table 2. The mean absolute error (MAE) of the calculation results is quite small; thus TDDFT methods can serve as a reliable way to calculate the excited states of DES. Among all TDDFT methods, PBE0/6-311+g(*d,p*) gives the smallest MAE, which indicates that PBE0 is the best method for calculating excited states of DES among candidates.

TABLE 2. Calculated Excited States of DES

| Method | $E_{\max 1}$, eV | $E_{\max 2}$, eV | MAE, eV |
|---------------------------------|-------------------|-------------------|---------|
| Williams' results | 5.58 | 6.08 | |
| B3LYP/6-311+g(<i>d,p</i>) | 5.24 | 5.83 | 0.29 |
| M06-2X/6-311+g(<i>d,p</i>) | 5.67 | 6.26 | 0.13 |
| CAM-B3LYP/6-311+g(<i>d,p</i>) | 5.76 | 6.36 | 0.23 |
| PBE0/6-311+g(<i>d,p</i>) | 5.47 | 6.11 | 0.07 |
| BP86/6-311+g(<i>d,p</i>) | 4.98 | 5.55 | 0.57 |
| BH&HLYP/6-311+g(<i>d,p</i>) | 5.92 | 6.53 | 0.40 |
| B97-2/6-311+g(<i>d,p</i>) | 5.43 | 6.05 | 0.09 |

Note. MAE is mean absolute error, $\text{MAE} = \sum_{i=1}^n |E_{\text{cal},i} - E_{\text{exp},i}| / n$, $n = 2$.

Excited states of MES, DPS, and DBS. For further testing the PBE0 method, we calculated the excited states of MES, DPS, and DBS. In fact, reduced sulfur compounds play a crucial role in the atmospheric sulfur cycling and have been the subject of intense laboratory study. The calculated excited states and previous experimental absorption bands are summarized and shown in Table 3. The MAE of these nine excited states is 0.11 eV. The correlation coefficient of the measured peaks and the calculated excited states is 0.98, as shown in Fig. 2. Thus, for the sulfur compounds tested, PBE0/6-311+g(*d,p*) works well in the calculation of excited states.

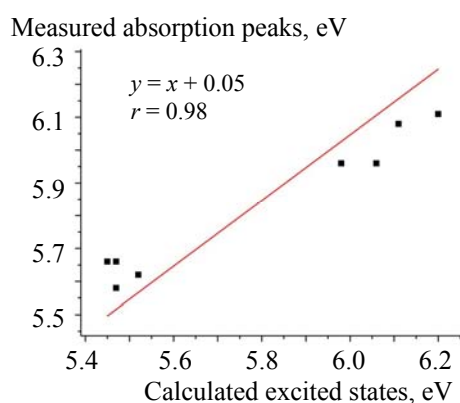


Fig. 2. Linear regression analysis of peak locations.

TABLE 3. Comparison of Calculated Excited States and Previously Measured Results

| Compound | $\lambda_{\max 1}$, eV | $\lambda_{\max 2}$, eV |
|----------|-------------------------|-------------------------|
| MES | 5.52 (5.62) | 6.20 (6.11) |
| DES | 5.47 (5.58) | 6.11 (6.08) |
| DPS | 5.47 (5.66) | 6.06 (5.96) |
| DBS | 5.45 (5.66) | 5.98 (5.96) |

Note. Data in brackets are experimental UV absorption peaks [9, 10].

Calculation of excited states of HD and simulated agents. Subsequently, calculations of the excited states and UV optical properties of HD, CEES, MCES, CEHES, PCES, and PECES were performed. These compounds are toxic because of the $\text{SCH}_2\text{CH}_2\text{Cl}$ group, which can alkylate proteins and other living components.

The corresponding calculation results are summarized in Table 4. As mentioned before, we analyzed the excited states of HD and simulated agents as some details should be clarified. Firstly, wavelengths presented in Table 4 are among the first three excited states of each compound. Secondly, the excited states with oscillator strengths (f) less than 0.00001 are ignored. Thirdly, each excited state corresponds to a combination of several transitions between MO pairs. The transitions presented in Table 4 are those contributing over 10% to the excited states.

TABLE 4. Excited States of HD and Related Sulfur Compounds

| Compound | E , eV | Transition | f |
|----------|----------|-------------------|---------|
| DES | 5.47 | HOMO→LUMO: 0.98 | 0.002 |
| | 6.11 | HOMO→LUMO+2: 0.95 | 0.0285 |
| MES | 5.25 | HOMO→LUMO: 0.78 | 0.00004 |
| | 5.52 | HOMO→LUMO+1: 0.85 | 0.0022 |
| | 6.20 | HOMO→LUMO+2: 0.86 | 0.0377 |
| DPS | 5.47 | HOMO→LUMO: 0.93 | 0.0032 |
| | 6.06 | HOMO→LUMO+2: 0.73 | 0.0375 |
| DBS | 5.45 | HOMO→LUMO: 0.91 | 0.0027 |
| | 5.98 | HOMO→LUMO+2: 0.72 | 0.0288 |
| HD | 5.56 | HOMO→LUMO: 0.98 | 0.006 |
| | 6.00 | HOMO→LUMO+2: 0.97 | 0.0121 |

Continue Table 4

| Compound | E , eV | Transition | f |
|----------|-------------------|---------------------|---------|
| CEES | 5.21 | HOMO→LUMO: 0.89 | 0.004 |
| | 5.62 | HOMO→LUMO+1: 0.96 | 0.0066 |
| | 5.97 | HOMO→LUMO+2: 0.91 | 0.0001 |
| MCES | 5.26 | HOMO→LUMO: 0.88 | 0.0007 |
| | 5.69 | HOMO→LUMO+1: 0.90 | 0.0082 |
| | 5.98 | HOMO→LUMO+2: 0.77 | 0.0003 |
| CEHES | 5.26 | HOMO→LUMO: 0.63 | 0.0003 |
| | 5.77 | HOMO→LUMO+1: 0.43 | 0.0125 |
| | | HOMO→LUMO+3: 0.34 | |
| | 5.86 | HOMO→LUMO: 0.28 | 0.0015 |
| | HOMO→LUMO+1: 0.36 | | |
| PCES | 4.65 | HOMO→LUMO: 0.96 | 0.0037 |
| | 5.14 | HOMO→LUMO+1: 0.94 | 0.0008 |
| | 5.38 | HOMO-2→LUMO: 0.49 | 0.0028 |
| | | HOMO-1→LUMO+1: 0.45 | |
| PECES | 5.12 | HOMO→LUMO: 0.65 | 0.00004 |
| | | HOMO→LUMO+1: 0.24 | |
| | 5.40 | HOMO-2→LUMO: 0.42 | 0.0005 |
| | | HOMO-1→LUMO+1: 0.53 | |
| | 5.55 | HOMO→LUMO+1: 0.97 | 0.0081 |

The first excited state of HD is 6.00 eV, which agrees with Rewick's measurement [7]. But the other calculated peak at 5.56 eV is not present in the measured UV spectrum. The two excited states may be shifted or broadened by the solvent, so that they cannot be distinguished. Based on the TDDFT calculation, the violet absorption of HD and related sulfur compounds is within the 5.17–6.20 eV range, which belongs to UV-C absorption. UV radiation in the UV-C (4.43–12.40 eV) region attenuates fast in the atmosphere. Therefore, the UV spectra of HD and stimulants are usually useless in the detection field. Interestingly, excited states of sulfur ethers coincide with those of HD. They have similar excited energies and absorption intensity, mainly near 5.51 and 6.05 eV. And the oscillator strength of their first excited states is zero. On the other hand, the excited states of the simulated agents are different. And the oscillator strength of their first excited states is above zero. It seems that the SCH₂CH₂Cl group does not make the simulated agents exhibit the same optical properties as HD, while the sulfur ethers that belong to the C_{2v} symmetry perform better.

The natural transition orbital (NTO) is useful in the transition assignment. The molecular orbitals involved in the first three excited states of the simulated agents and sulfur ethers are HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1, and LUMO+2, as visualized in Fig. 3. For HD and sulfur ethers, the transition of the second excited states is HOMO→LUMO. The unpaired electron of the S atom is excited to the antibonding orbital, which is the $n\rightarrow\sigma^*$ transition. In the third excited state, the unpaired electron of the S atom is excited further to a carbon chain. For CEES, MCES, and CEHES, their transition types are similar to HD, but their asymmetry affects the excited energy and oscillator strength. For PCES and PEHES, the electron transition is between the S atom and benzene ring. Groups at both ends show small impact on the excited transition, hence different conformers have similar excited states.

Compared to DES, the second excited states of CEES and HD display violet shifts of 6.27 and 3.77 eV, respectively, while the third excited states give red shifts of 4.57 and 3.71 eV. And the oscillator strength of CEES and HD is weaker. The Mulliken distribution analysis (Table 5) shows that the C1 atoms in CEES and HD have relatively lower electronegativity than the C1 atom in DES, and the HOMO→LUMO transition requires more energy. Thus, the second excited states of CEES and HD reveal blue-shifts. On the other hand, the C2 atoms in CEES and HD have relatively higher electronegativity than those of other compounds, which leads to red shifts of the third excited states. As for PCES and PECES, the first three excited states are red shifted by benzene rings.

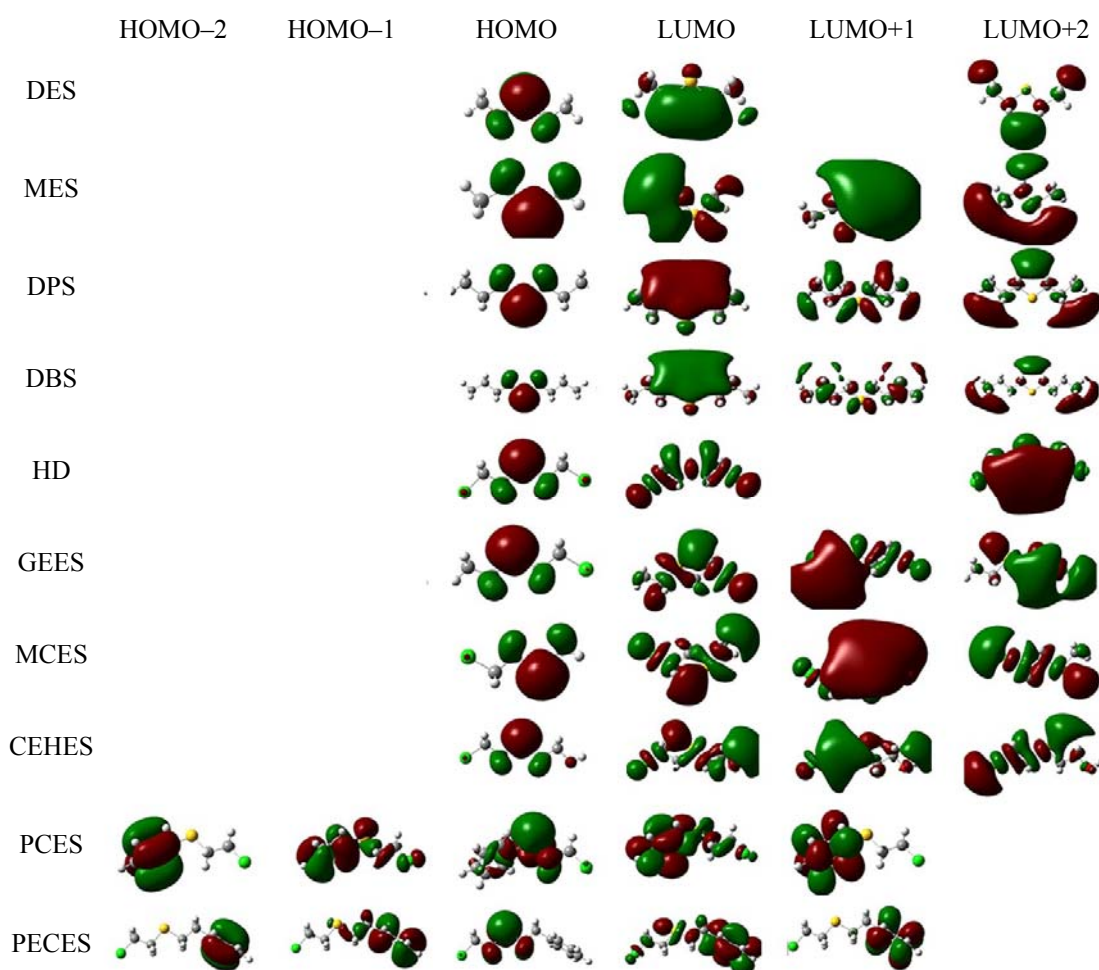


Fig. 3. Natural transition orbital of HD and alkyl sulfides.

TABLE 5. Mulliken Atomic Charges of DES, CEES, and HD

| Compound | C2' | C1' | S | C1 | C2 |
|----------|-------|-------|-------|-------|-------|
| DES | -0.80 | -0.07 | -0.09 | -0.07 | -0.80 |
| CEES | -0.84 | -0.12 | -0.18 | -0.01 | -0.92 |
| HD | -0.95 | -0.11 | -0.23 | -0.11 | -0.95 |

Conclusions. The excited states of HD and related sulfur compounds have been studied. The evaluation of seven widely used density functionals (B3LYP, M06-2X, CAM-B3LYP, PBE0, BP86, BH&HLYP, B97-2) demonstrates the accuracy and efficiency of TDDFT. Among the above density functionals, PBE0 is determined to be the best functional for studying sulfur containing compounds. The Boltzmann average analysis reveals that different conformers of DES have similar excited energies; thus, only one conformer for other sulfide compounds is calculated.

The TDDFT calculation reveals the excited state energies of HD to be 5.56 and 6.00 eV. Excited states of sulfur ethers (DES, MES, DPS, DBS) are similar to HD. In contrast, the simulated agents (CEES, MCES, CEHES, PCES, PECES) differ remarkably in the excited states, arising from molecular symmetry. By orbital visualization, we assign the second excited states of HD as the $n \rightarrow \sigma^*$ transition.

Acknowledgements. This work was financially supported by the Chinese National Natural Science Foundation (21177158, 21876202) and Special-Funded Program on National Key Scientific Instruments and Equipment Development (2013YQ060615).

REFERENCES

1. H. Wang, Y. Mu, *Front. Environ. Sci. Eng.*, **7**, 833–835 (2013).
2. H. Wang, Y. Zhang, Y. Mu, *Acta Phys. Chim. Sin.*, **24**, 945–950 (2008).
3. D. Noort, H. P. Benschop, R. M. Black, *Toxicol. Appl. Pharmacol.*, **184**, 116–126 (2002).
4. A. V. Vorontsov, A. A. Panchenko, E. N. Savinov, *Environ. Sci. Technol.*, **36**, 5261–5269 (2002).
5. P. K. Gutch, R. K. Srivastava, K. Sekhar, *J. Appl. Polym. Sci.*, **107**, 4109–4115 (2007).
6. S. Hanaoka, K. Nomura, T. Wada, *J. Chromatogr. A*, **1101**, 268–277 (2006).
7. R. T. Rewick, M. L. Schumacher, D. L. Haynes, *Appl. Spectrosc.*, **40**, 152–156 (1986).
8. D. A. Panayotov, D. K. Paul, J. T. Yates, *J. Phys. Chem. B*, **107**, 10571–10575 (2003).
9. M. B. Williams, P. Campuzano, D. D. Riemer, *J. Photochem. Photobiol. A*, **171**, 77–82 (2005).
10. S. P. Urbanski, R. E. Stickel, P. H. Wine, *J. Phys. Chem. A*, **102**, 10522–10529 (1998).
11. V. Kumar, M. P. Kaushik, *Synth. Commun.*, **36**, 2385–2388 (2006).
12. D. A. Jaeger, A. K. Zelenin, *Langmuir*, **15**, 7180–7185 (1999).
13. C. Adamo, D. Jacquemin, *Chem. Soc. Rev.*, **42**, 845–856 (2013).
14. E. I. Sanchez-Flores, R. Chavez-Calvillo, T. A. Keith, *J. Comput. Chem.*, **35**, 820–828 (2014).
15. N. Kungwan, F. Plasser, A. J. A. Aquino, *Phys. Chem. Chem. Phys.*, **14**, 9016–9025 (2012).
16. B. Champagne, M. Guillaume, F. Zutterman, *Chem. Phys. Lett.*, **425**, 105–109 (2006).
17. M. J. Frisch, G. W. Trucks, H. B. Schlegel, Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, 2010.