Study of Absorption and Fluorescence Spectra of Iodomethane Molecules by Solvent Effect

F Yao, N Ning, J H Li, Y Wang, Y J Zhai and W H Fang*

Key Laboratory of Nanohotonics and Biophotonics of Jilin Province, School of Scie nce, Changchun University of Science and Technology, Changchun 130022, China

Corresponding author and e-mail: W H Fang, whfang@cust.edu.cn

Abstract. The absorption spectra and fluorescence spectra and their haracteristics of iodomethane (CH₃I) excited by ultraviolet light were analyzed experimentally. It was found that methyl iodide had a good absorption of 280-375 nm ultraviolet light and obvious fluorescence was emitted at 280-320 nm ultraviolet light excitation; CH₃I-toluene mixed solutions with different ratio on volume were excited at the light with the wavelength of 300nm. It was found that the fluorescence intensity gradually increased with the increase of toluene volume ratio and a basic linear relationship was shown. We also measured the fluorescence spectra of the CH₃I-ethanol mixed solutions at different wavelengths of ultraviolet light, and variation of the fluorescence intensity of the CH₃I-ethanol solutions with different mixing ratio is also different. In additional, we are giving the mathematical expression of the fluorescence peak position of the mixed solution. This give some reference significance of the solvent effect and the study of CH₃I molecular dynamics by the spectrum.

1. Introduction

In the industrial field, CH₃I is an important downstream industrial product of coal chemical industry. It is also a precursor of many methylation reactions [1, 2]. CH₃I is a typical molecular theoretical and experimental model in the laboratory, which plays an important role in the kinetics of photolysis [3, 4] and thermal cracking. However, CH₃I is easily decomposed by heat and can produce toxic iodide flue gas, which can be absorbed by respiratory tract, digestive tract and skin, so it is very important for quantitative analysis. At present, the quantitative analysis by gas chromatography [5] is an analytical method widely used in analytical laboratories. This method determines the content of the components to be measured in a sample. Standard samples are also useful for spectrophotometric analysis of trace amounts of CH₃I. Based on the molecular fluorescence spectrum analysis (MFS)[6] is the use of certain substances produced by ultraviolet or visible light irradiation after can reflect the material characteristics of the fluorescence, and carries on the qualitative and quantitative analysis, is widely used and the promising a spectrum analysis technology. Using this technique, we studied the corresponding absorption and fluorescence spectra [7, 8, 9] of CH₃I. The results showed that CH₃I [9] can emit strong fluorescence under the excitation of 280-320 nm UV light. The fluorescence characteristics were characterized in this paper.

2. Experimental device and experimental method

2.1. A subsection experimental device

The absorption spectrum of this experiment is based on the Gary 5000 UV-Vis-NIR spectrophotometer, light source: xenon lamp, mercury lamp, among which the mercury lamp is used for wavelength calibration to ensure the accuracy of the instrument for long-term use of the wavelength, and the three light sources are automatically switched. Monochromator: Heteropoly Littorow monochromator, dual monochromator design. Detectors: High-sensitivity photomultipliers and semiconductor-cooled PbS. The fluorescence spectrum was measured using a Gary Eclipse fluorescence spectrophotometer with a horizontal light source: a flashing xenon lamp with a pulse width at half maximum of less than 2 microseconds, a power relative to 75 kW when continuously illuminated, and a Cheney-Turner monochromator, ultra low Stray light.

2.2. Reagents

The CH_3I , toluene and ethanol used in the test were all manufactured by AKCO Reagents. In the experiment, CH_3I was separately mixed with toluene and ethanol as solvents, and the corresponding concentrations were formulated according to the volume ratio.

2.3. Test methods

When measuring the absorption spectrum of CH_3I , toluene is used as a reference. When the absorption spectrum of a CH_3I -ethanol mixed solution is measured, ethanol is used as a reference. When the absorption spectrum of the CH_3I -toluene mixed solution is measured, toluene is used as a reference. When measuring the fluorescence spectrum of CH_3I , the width of the slit is 20 nm, and a group of excitation light of a control group is selected according to the absorption band, followed by excitation, and the spectrum is collected.

3. Experimental results

3.1. Absorption spectrum experiment

In this experiment, we used the different volume ratio of CH₃I mixed solution to scan the whole spectrum to get the absorption spectrum.



Figure 1. Absorption spectra of pure CH₃I and mixed solutions of CH₃I-toluene at different volume ratios.

Figure 1 shows that in the spring, CH_3I absorbs ultraviolet light from 280 to 375 nm, its absorbance reaches a maximum at 337 nm, and there is almost no absorption after 375 nm, and the absorption band width is 298 to 344 nm in luminosity. The process of rapid decline after reaching the maximum.



Figure 2. Absorption spectra of pure CH₃I and mixed solutions of CH₃I-ethanol at different volume ratios.

Comparing the absorption spectra of the CH_3I -toluene mixed solution, only four control groups were given in this experiment. It can be seen from the figure 2 that the ethanol solution has less influence on the absorption spectrum of CH_3I . The absorption peak of the mixed solution shifts blue as the volume ratio of ethanol solvent increases.

3.2. Fluorescence spectroscopic experiment of CH3I and its mixed solution

3.2.1. CH_3I fluorescence spectrum experiment. We use 280-375 nm UV light as the excitation light, and once every 10 nm [10]. The fluorescence spectrum is found at 280-320 nm UV. As Figure 3 shows that under the UV excitation light of 300nm, the fluorescence intensity of CH_3I is the strongest.



Figure 3. Fluorescence spectra of CH₃I solution under different excitation light.

3.2.2. Fluorescence spectra of CH_3I -ethanol solutions at different volume ratios. Under certain wavelengths of UV excitation, CH_3I and ethanol exhibit fluorescence characteristics. Mix the two at different volume ratios, and excite them with different wavelengths of UV light to find out which kind of excitation, and which kind of fluorescence ratio is the best. Figures 4(a) to (e) show the fluorescence spectra of CH3I-ethanol solutions $V_1:V_2$ in volume ratios of 1:9, 3:7, 5:5, 7:3, and 9:1 respectively, excited by ultraviolet light.



(b)







(e)

Figure 4. Fluorescence spectra of CH₃I -ethanol solutions with different volume ratio under different excitation light: (a) V1: V2 = 9:1; (b) V1: V2 = 7:3; (c) V1: V2 = 5:5; (d) V1: V2 = 3:7; (e) V1: V2 = 1:9.

It can be seen from Figure 4. that with the increase of the volume ratio of ethanol solvent, the fluorescence peak intensity of the mixed solution increases. When the volume ratio V1:V2 is 5:5 respectively, the fluorescence intensity is the strongest under the excitation light of 290 nm. In other the fluorescence intensity was the strongest under the excitation light of 300 nm.

3.2.3. Fluorescence spectra of methyl iodide-toluene solution at different volume ratios. Under different solvents, the fluorescence spectrum of CH_3I mixed solution is also one of the topics we discuss. Figure 5 (a) to (e) respectively show the fluorescence spectra of CH_3I -toluene solutions in volume ratios of 9:1, 7:3, 5:5, 3:7 and 1:9, excited by ultraviolet light.











Figure 5. Fluorescence spectra of CH₃I-toluene solutions with different volume ratio under different excitation light: (a) V1: V3 = 9:1; (b) V1: V3 = 7:3; (c) V1: V3 = 5:5; (d) V1: V3 = 3:7; (e) V1: V3 = 1:9.

It can also be seen from Figure 5. when the mixing ratio of 9:1, the fluorescence intensity is the strongest under the irradiation of light with 300 nm.

In order to better demonstrate the effect of different volume ratio of mixed solution on the fluorescence intensity and the position change corresponding to the strongest peak of fluorescence, we chose 300nm excitation light to act on CH_3I -toluene mixed solution to obtain the curve of concentration and fluorescence intensity change. Figure 6 shows, 10% in the figure refers to V1:V3=1:9, and so on.





From Figure 6 show as the volume ratio of solvent increases, the fluorescence intensity gradually increases. When the volume ratio of CH_3I -toluene mixed solution is V1:V3=1:9, the fluorescence intensity is the strongest, which is almost the volume ratio V1:V3 = 2 times at 9:1.

(e)

When the CH₃I-toluene mixed solution was irradiated with 300 nm excitation light, the curve showing the change of the peak intensity of the fluorescence with respect to the volume ratio was shown in Figure 7.



Figure 7. Fluorescence peak position diagram of mixed solution of different concentrations of CH₃I and toluene at 300 nm excitation light.

From the above figure, it can be seen that with the increase of the volume ratio of the solvent, the strongest fluorescence peaks are red-shifted and have a linear relationship.

Under UV excitation, the corresponding fluorescence position of the mixed solution with the change of the volume fraction of CH₃I is shown in Table 1.

Iodomethane Volume fraction/%	280nm	290nm	300nm	310nm	320nm
10	360	363	361	365	364
30	366	366	366	371	368
50	369	371	370	373	375
70	373	375	372	375	377
90	375	377	373	377	380

Table 1. Changes of the position of the strongest fluorescence peak of the CH₃I-toluene mixed solution with concentration and excitation wavelength.

4. Discussion and analysis

The relative intensity of the fluorescence from the excitation of the UV light after 320 nm is relatively weak, it is almost not reflected in the superimposed image, so it is not drawn in this figure. Because the wavelength corresponding to the maximum absorption intensity is close to the absorption cutoff wavelength; the electron absorbs the photons and can return to the ground state without radiation.

Spectrum, found that at a certain wavelength, there is the following mathematical relationship between the fluorescence peak position $\lambda = \lambda_1 \cdot C_1 + \lambda_2 \cdot C_2$

 λ :the fluorescence position of the mixed solution; λ_I :the CH₃I fluorescence position; λ_2 :the position of the ethanol fluorescence; C_I :the volume fraction of CH₃I; C_2 :the volume fraction of ethanol in the mixed solution.

5. Conclusions

In this paper, the UV absorption spectra and fluorescence spectra of CH_3I solution were studied, and the fluorescence spectra of different concentrations of CH_3I solution, different volume ratio of mixed CH_3I -ethanol solution and CH_3I -toluene solution were compared. Concluded the fluorescence intensity of the CH_3I -toluene solution is the strongest under the excitation light of 300 nm. This provides adequate preparation for subsequent solvent effects and studies of enhanced stimulated Raman scattering of CH_3I .

Acknowledgment

This work is supported by the "111" Project of China (D17017), the National Natural Science Foundation of China (21703017, 11604024), the Advance Recearch Project of Weapon and Equipment (6140414020102), the Developing Project of Science and Technology of Jilin Province (20180519017JH), Nanophotonics and Biophotonics Key Laboratory of Jilin Province (20140622009J), and the Project of Education Department of Jilin Province (JJKH20170611KJ, JJKH20181101KJ, and JJKH20181106KJ). Science Foundation for Young Scientists of Changchun University of science and technology (XQNJJ-2016-14).

References

- [1] Nakajima S, Takaya H and Nakamura M 2017 Iron-catalyzed methylation of arylboron compounds with iodomethane J. Chemistry Letters 46 (5) 711
- [2] Li Y, Sun Y and Wang R 2014 The steam by-product of cyclohexanone is utilized J. *Chenmical Intermediate* (10) 57-60
- [3] Shao L 2014 Photodissociation dynamics of NO2 and CH3I with femosecond pump-probe technique D. Jilin University
- [4] Jiang B and Xie D Q 2012 Theoretical studies for photodissociation dynamics of small molecules *J. progress in chemistry* **24(06)** 1120-1128
- [5] Hu D D 2017 Study on method of reducing errors in gas chromatographic analysis J. Engineering Technology (3) 00319-00320
- [6] Zhang Z W,Xinshun J and Cao G Q 2008 Molecular fluorescence spectroscopy and its engineering applications *J.physics bulletin* (09) 56-57
- [7] Wang Y J and Song Z F 1995 Spectral Analysis and Chromatogram Analysis Beijing University Press
- [8] Wei Y J, Li N and Qin S J 2004 Fluorescence spectra and fluorescence quantum yield of sulfosalicylic acid *Spectroscopy and Spectral Analysis* **24(6)** 647
- [9] Wang S, Fang W, Li T, Li F, Sun C and et al 2016 An insight into liquid water networks through hydrogen bonding halide anion: Stimulated Raman scattering J.Journal of Applied Physics 119(16) 163104
- [10] Xu H, Zhu T, Shi A M and Gu ED 2008 Study of 1-butanol absorption and fluorescence spectra induced by UV-light *J. Spectroscopy and Spectral Analysis* **28(1)** 178-182