

High-pressure effects on intramolecular electron transfer compounds

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2002 J. Phys.: Condens. Matter 14 10461

(<http://iopscience.iop.org/0953-8984/14/44/314>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 18/05/2010 at 15:21

Please note that [terms and conditions apply](#).

High-pressure effects on intramolecular electron transfer compounds

Liming He¹, Bo Zhong¹, Hong Li¹, Baowen Zhang², Yi Li^{2,3} and Guoqiang Yang^{1,3}

¹ Laboratory of Photochemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

² Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100101, China

Received 1 June 2002

Published 25 October 2002

Online at stacks.iop.org/JPhysCM/14/10461

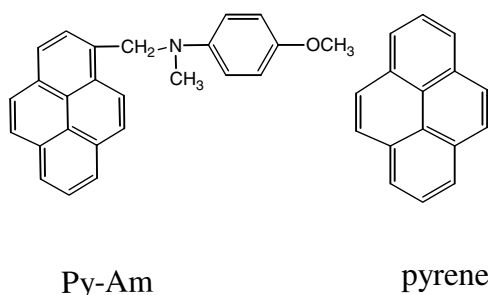
Abstract

We explore the effect of pressure on the fluorescence spectra of the intramolecular electron transfer compound *N*-(1-pyrenylmethyl), *N*-methyl-4-methoxyaniline (Py–Am) and its model version, with poly(methyl methacrylate) blended in, at high pressure up to 7 GPa. The emission properties of Py–Am and pyrene show distinct difference with the increase of pressure. This difference indicates the strength of the charge transfer interaction resulting from the adjusting of the conformation of Py–Am with increase of pressure. The relationship between the electronic state of the molecule and pressure is discussed.

1. Introduction

Charge transfer (CT) interaction provides an important and common way for energy relaxation to occur in excited state molecules [1–8]. This interaction, though determined by the intrinsic properties of donors and acceptors, is strongly influenced by environmental effects [9–13]. It has been reported that high pressure as a perturbing variable of the molecule environment can be a very useful tool for the study of electronic processes by altering the interaction between molecules in a continuous and controlled fashion. In this paper, we explore the effect of pressure on the fluorescence spectra of the intramolecular electron transfer compound *N*-(1-pyrenylmethyl), *N*-methyl-4-methoxyaniline (Py–Am) and its model version (pyrene; see scheme 1), with poly(methyl methacrylate) (PMMA) blended in, at high pressure up to 7 GPa, and discuss the relationship between the electronic state energetic level and pressure.

³ Authors to whom any correspondence should be addressed.



Scheme 1. The structure of the molecules.

2. Experiments

Py-Am was synthesized in our laboratory. Pyrene and PMMA (medium molecular weight) were purchased from Aldrich. The polymer was used without purification. Spectral grade chloroform was used as the solvent to dissolve the Py-Am, pyrene and PMMA.

The PMMA and Py-Am or pyrene were dissolved in chloroform. The solution was then poured into a glass dish to form a blended film after solvent evaporation at room temperature. Both of the films obtained (Py-Am or pyrene in PMMA-blended samples) were then put in a vacuum oven for a few days at 45 °C. Transparent and lightly coloured blend films (about 35 μm in thickness) were obtained. Under a microscope, the films are optically clear without any phase separation.

For absorption and fluorescence measurements a Merrill-Bassett diamond anvil cell (DAC) was used to generate high pressure. The hole diameter of the gasket used to hold the sample was about 300 μm with thickness of about 90 μm . A small chip of ruby was put in the hole to calibrate the pressure by measuring its fluorescence red-shift. Light mineral oil served as a pressure medium. For the emission measurement a CW He-Cd laser (325 nm, Omnichrom) was the excitation source. The fluorescence spectra were dispersed with a 0.3 m spectrometer and a photomultiplier tube (PMT) coupled to a 32-bit microprocessor-based data acquisition and spectrometer controller module (NCL Electronics Interface, Acton-Research Corporation) and a computer. For the absorption measurement a Xe lamp was as a light source and the light was dispersed with a 0.3 m spectrometer. Two optical fibres were connected to the DAC and their other ends were connected to a monochromator and the PMT, respectively. A NCL electronics interface and computer were used to record the spectra and control the system.

3. Results and discussion

In the Py-Am molecule, the electron donor is linked to the electron acceptor by a methylene ($-\text{CH}_2-$) group. As is well known, pressure can change the volume of the sample, and therefore can adjust the distance between atoms and molecules, which will influence the stereo-conformation of the molecule. So pressure may prompt CT interaction of the sample with PMMA blended in by tuning the relative positions of the two groups.

The absorption spectra of Py-Am at different pressures are presented in figure 1. The absorption spectra of Py-Am under pressure have two bands. With the increase of pressure, there are evident changes in the absorption centres of the two bands.

The effect of pressure on the emission of the sample with PMMA blended in is shown in figure 2. At 1 atm, there are two emission bands: one, at 23 000–26 000 cm^{-1} , is associated

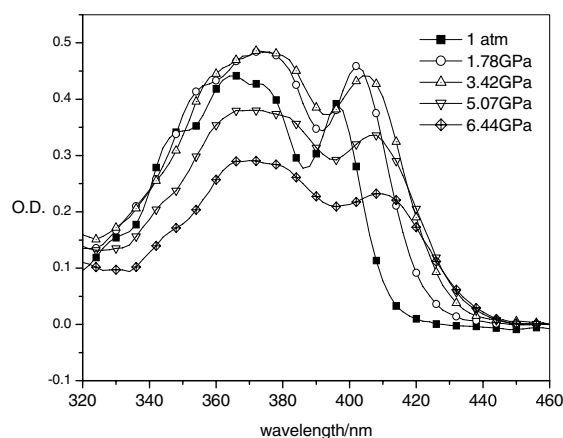


Figure 1. The absorption spectra of Py-Am at different pressures.

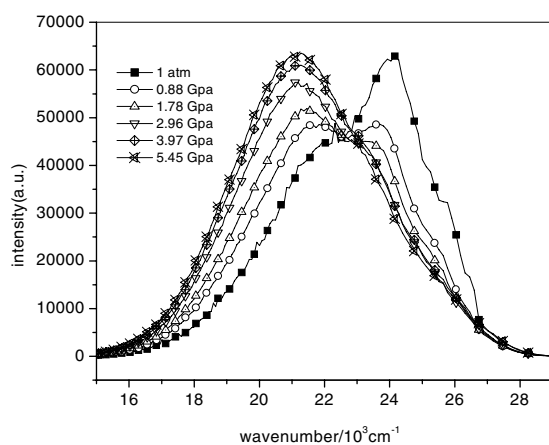


Figure 2. Fluorescence spectra of Py-Am at different pressures.

with the emission of the pyrenyl group in Py-Am molecule and is called the local band; and another one, at $22\,000\text{--}23\,000\text{ cm}^{-1}$, which is the CT band. With the increase of pressure, the intensity of the local band decreases and that of the CT band increases. This indicates that more and more CT interaction happens and less local emission can be observed when pressure is increasing.

The peak area of the fluorescence spectrum with subtracted absorption is in direct proportion to the fluorescence yield (Φ). To explore the relationship between pressure and fluorescence yield, the emission spectra at different pressures are fitted with two bands and two typical fitting spectra are shown in figures 3 and 4.

It can be seen in figures 3 and 4 that of the two bands, the one including two peaks at high wavenumber is the local emission band, while the other is the CT emission band. The sum of the normalized areas of the two peaks in the local band is calculated and, together with the normalized area of the CT band, is plotted against pressure, as shown in figure 5.

Figure 5 illustrates that before 2 GPa, the normalized area of the local band decreases sharply and then changes a little, while the area of the CT band increases at all pressures.

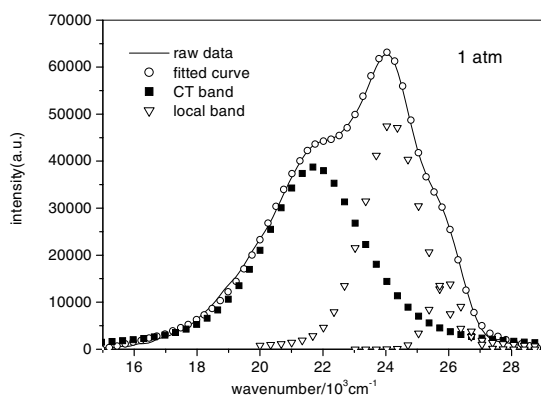


Figure 3. The fitting emission spectrum of Py-Am at 1 atm.

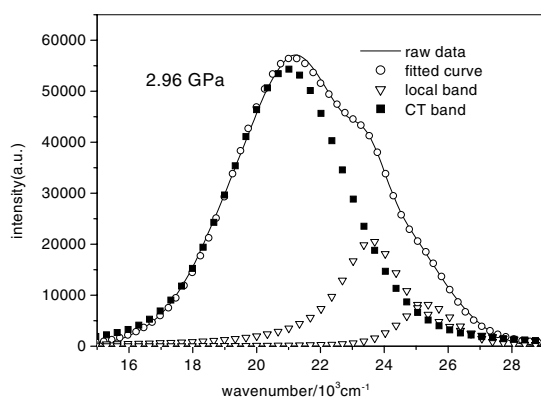


Figure 4. The fitting emission spectrum of Py-Am at 2.96 GPa.

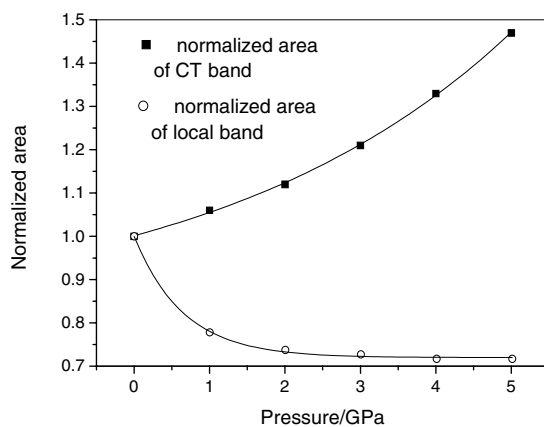


Figure 5. The normalized areas of the two bands at different pressures.

Figure 6 shows the normalized area of the emission spectra of the model compound pyrene with PMMA blended in at different pressures. It is evident that before 2 GPa the normalized area drops sharply but that it increases greatly after 2 GPa.

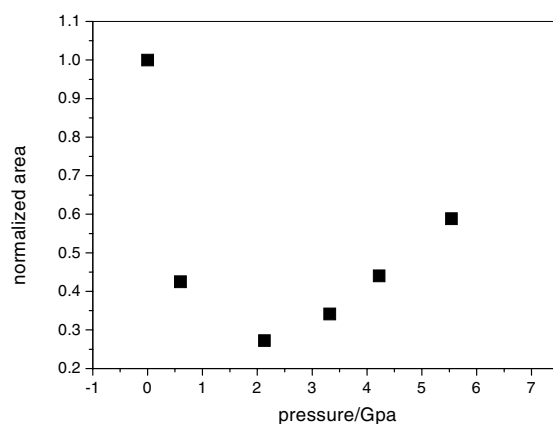
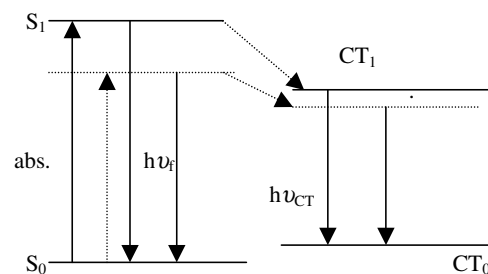


Figure 6. The normalized area (with absorption subtracted) of the model compound pyrene with PMMA blended in.



Scheme 2. Energy levels of electronic states of Py–Am at different pressure. —: the energy level at 1 atm; ·····: the energy level at high pressure.

Comparing figures 5 and 6, it is interesting to find that the normalized area of the local band and the emission of pyrene have opposite trends of change after 2 GPa. Considering our discussion in relation to figure 2, it is reasonable to presume that the CT interaction reduces the local emission of Py–Am, so the increase of the normalized area of pyrene is too small to see in figure 5, unlike that shown in figure 6.

According to the above discussion, a reasonable mechanism for the effect of pressure on the energetic level is as in scheme 2.

With increase of pressure, the energy gap between S_1 and CT is reduced because of the decrease of the distance between the electron donor and the electron acceptor. This will greatly favour the transition of the excited electron from its S_1 state to the CT state; thus the local emission decreases and CT emission increases.

4. Conclusions

The emission properties of Py–Am and pyrene with PMMA blended in show significant difference with the increase of pressure. This difference can be qualitatively explained in terms of the strength of the CT interaction resulting from the adjusting of the conformation of Py–Am with increase of pressure.

Acknowledgments

This work was supported by the Major State Basic Research Development Programme of China (grant no G2000078100) and the National Natural Science Foundation of China (no 20173066).

References

- [1] Föster Th and Kasper K 1955 *Z. Elektrochem.* **59** 977
- [2] Ferguson J 1958 *J. Chem. Phys.* **28** 765
- [3] Leonhardt H and Weller A 1963 *Ber. Bunsenges. Phys. Chem.* **67** 791
- [4] Beens H and Weller A 1968 *Acta Phys. Pol.* **34** 593
- [5] Rehm D and Weller A 1970 *Z. Phys. Chem. NF* **69** 183
- [6] Ottolenghi M 1973 *Acc. Chem. Res.* **6** 153
- [7] Mataga N and Ottolenghi M 1979 *Mol. Assoc.* **2** 1
- [8] Mataga N and Nakashima N 1975 *Spectrosc. Lett.* **8** 275
- [9] Mataga N, Okada T and Yamamoto N 1966 *Bull. Chem. Soc. Japan* **39** 2562
- [10] Okada T, Saito T, Mataga N, Sakata Y and Misumi S 1977 *Bull. Chem. Soc. Japan* **50** 331
- [11] Mataga N, Kaifu Y and Koizumi M 1955 *Bull. Chem. Soc. Japan* **28** 690
- [12] Knibbe H, Rollig K, Schafer F P and Weller A 1967 *J. Chem. Phys.* **47** 1184
- [13] Migita M, Okada R, Mataga N, Nakashima N, Yoshihara K, Sakata Y and Misumi S 1980 *Chem. Phys. Lett.* **72** 229
- [14] Okada T, Karaki I, Matsuzawa E, Mataga N, Sakata Y and Misumi S 1981 *J. Phys. Chem.* **85** 3957
- [15] Yang G, Li Y, White J O and Drickamer H G 1999 *J. Phys. Chem. B* **103** 5181
- [16] Luo Xiu-jin and Beddard G S 1982 *J. Chem. Soc. Faraday Trans. I* **78** 3467