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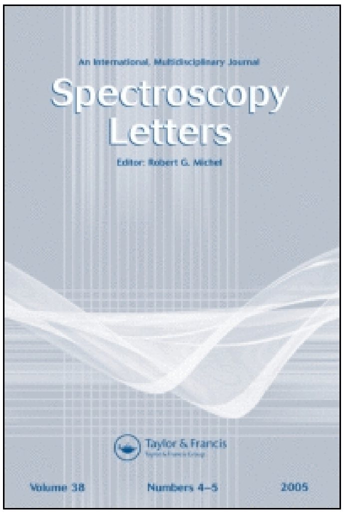

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AN OPTICAL PROBE DETECTION METHOD TO STUDY PHOTOLYSIS OF METHYLPYRIDINOCOBALOXIME IN AQUEOUS SOLUTION

Key words: optical probe detection, photolysis, methylpyridinocobaloxime

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Abstract: A novel optical probe detection method consisting of a laser heterodyne interferometer has been adapted to study photolysis of methylpyridinocobaloxime ($CH_3Co(DH)_2py$) aqueous solution in the temperature range 10 ~ 30 °C. The quantum yield and reaction volume change for the photolysis of anaerated $CH_3Co(DH)_2py$ solution at 355nm are determined to be 0.011 and 0.5 ml/mol, respectively. The resulting quantum yield is close to the value obtained by Schrauzer *et. al.* at 440nm, and the relatively small reaction volume change

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suggests that the contributions due to the conformational change of macrocyclic ligand and solvation effect accompanying Co-C bond cleavage are relatively unaffected.

INTRODUCTION

Acoustic waves are generated when the photoexcited molecules undergo a nonradiative relaxation process and transfer their excess energy to the solvent. Many different methods have been applied to detect photoacoustic (PA) signals. Piezoelectric transducers have widely been used as detectors for receiving the PA signals.[1] meanwhile, several optical detection techniques; such as the thermal lens,[2] the photothermal beam deflection[3] and the optical probe, have been developed successfully to replace conventional acoustic transducers. The use of these optical techniques for noncontact photoacoustic monitoring relies on detecting pulsed laser-induced refractive index change (Δn) of the sample solution by a continuous probe laser beam. The optical probe detection method is based on the perturbation of a nonabsorbed cw probe beam. This perturbation is caused by the nonuniform distribution of the refractive index in the sample due to the prior absorption of a pulsed excitation laser beam parallel to the probe beam. With high sensitivity and wide band, the optical probe method can directly provide the profiles of PA pressure waves, and expand the time scale of the investigations into micro- and millisecond range[5] and thus complement the related technique of laser-induced photoacoustic spectroscopy. This optical probe detection method differs significantly from the piezoelectric transducer method since there is no mechanical interaction with acoustic waves.[4a] The high sensitivity and stability of this method allow us to investigate fast photo-chemical reactions generated by the excitation laser beam.

After molecules absorb photons, the refractive index changes in the solution have various origins;[3] (a) heat release and subsequent thermal expansion (or contraction in some rare case), (b) structural volume changes or different

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solvations between the initial and final states at the particular time analyzed, leading to a density change, and (c) different optical absorbances of the ground state and the excited state or intermediates. The separation of these contributions can be obtained by changing experimental conditions. Thus, information about enthalpy, volume change of the photo-chemical reaction and lifetime of the intermediates in a wide time scale can be determined.

At present we study the photolysis of an organocobalt complex, methyl-pyridinocobaloxime ($CH_3Co(DH)_2py$), in anaerated aqueous solution in the temperature range of 10 to 30 °C by using the optical probe method. The quantum yield and the volume change for the reaction are reported.

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SAMPLE PREPARATION

$CH_3Co(DH)_2py$ is prepared according to the literature.[6] For the optical probe experiments, the absorbance of $CH_3Co(DH)_2py$ at 355nm is 0.2 ± 0.02 in neutral deionized water. $K_2Cr_2O_7$ (A.R) is used as a calorimetric reference.[1b]

THE OPTICAL PROBE SYSTEM

In the experimental optical probe system, a Q-switched Nd:YAG laser (Continuum NP70) operating at 10Hz, 355nm, pulse width 8ns, and 15μJ is used as an excitation source. The laser beam diameter is fixed by a 45μm pinhole, which determines the time resolution that equals to the travel time of the acoustic wave through the laser beam diameter, (about 30ns in the aqueous solutions). Temperature (10-30°C) is kept constant within ± 0.1°C using a thermostat and a thermoelement placed directly into the sample cell. Acoustic wave arises upon the absorption of this excitation laser beam with near Gaussian Spatial intensity distribution. The resulting distribution of the refractive index is detected by the probe beam oriented parallel to the excitation laser beam generated by a cw He-Ne laser at 632.8nm.

The diagram of the experimental setup is shown in Figure1. The employed optical probe is a Mach-Zehnder type of laser heterodyne interferometer (B. M. Industries, SH 120). The probe beam shifted in frequency by an acousto-optic Bragg cell ($f_B = 45$MHz) crosses the solution where the refractive index is changed by the acoustic wave, and is then reflected by a fixed mirror. The waveform (see Figure 2.) is an average of the signals from about 200 pulse excitations, and recorded by a digital oscilloscope (HP-54510B).

OPTICAL PROBE SIGNAL ANALYSIS

This method consists of a heterodyne interferometer for probing of the refractive index change proportional to the pressure of acoustic wave in the solution. The refractive index changes (Δn) arising in a liquid sample upon photo-excitation is composed of three contributions,

$$\Delta n = \frac{dn}{dT}\Delta T + \frac{dn}{d\rho}\Delta\rho_{vol} + \Delta n_{abs} \tag{1}$$

The first term of this equation represents the refractive index change due to the released heat, Q, and can be developed as in equation 2,

$$\frac{dn}{dT}\Delta T = \frac{dn}{d\rho}\frac{d\rho}{dT}\cdot\frac{Q}{C_p\rho V} = \frac{dn}{d\rho}\frac{d\ln\rho}{dT}\cdot\frac{Q}{C_p V} = -\frac{dn}{d\rho}\cdot\frac{\beta Q}{C_p V} \tag{2}$$

where ρ is the density of the solution, C_p is the heat capacity at constant pressure, and β is the thermal expansion coefficient for the solvent ($\beta = -(\partial \ln\rho/\partial T)_p$) which is significantly temperature-dependent in water between 0°C and room temperature.[7] The second term in equation 1 is due to different structural volumes or to the different solvations of the ground state and the intermediate analyzed in a particular time range. These effects will change the density $\Delta\rho_{vol}$ of the sample, thus calculated using equation 3

$$\Delta\rho_{vol} = -\rho\frac{\Delta V_r}{V} \tag{3}$$

where ΔV_r is structural volume change. This term is assumed to be temperature independent because of $\rho dn/d\rho = 0.326 \pm 0.001$ between 0°C and about 25°C.[8]

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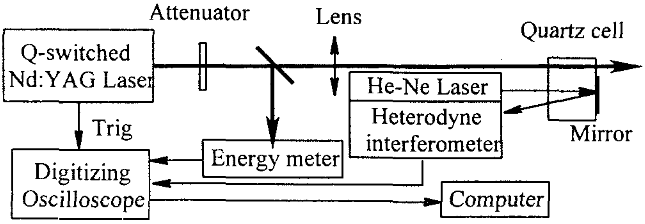

Figure 1. Schematic diagram of experimental setup for the optical probe

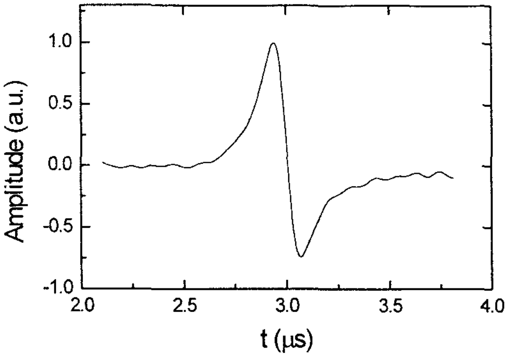

Figure 2. Photoacoustic spectroscopy signal for methylcobaloxime in neutral aqueous solution at 15°C

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The third term of equation 1 originates from different absorptions of the ground state and the excited state or the intermediates. Since the absorbance change ΔA at the monitoring wavelength is extremely small ($\Delta A_{623.8} < 10^{-4}$),[3] its contribution can be neglected.

In our experiment, the signal S of optical probe is proportional to Δn as follows

$$S = K\Delta n \tag{4}$$

Inserting equations 2 and 3 into eqution 1 and using equation 4, the amplitude of the optical probe signal is

$$S = K\left(-\frac{dn}{d\rho}\frac{\beta Q}{VC_p} - \frac{dn}{d\rho}\frac{\rho \Delta V_r}{V}\right) = K'\left(\frac{\beta Q}{\rho C_p} + \Delta V_r\right) \qquad (5)$$

where K and K' are system constants.

A calorimetric reference promptly releases to the medium all energy absorbed from the excitation laser pulse, i.e., the photon-to-heat conversion is unity and its relaxation process is faster than the resolution of the experiment. Fluorescence, structural volume change and absorbance change can be neglected. Therefore, the optical probe signal of calorimetric reference, R, is given by

$$R = K'\frac{\beta E_{h\nu}}{C_p \rho} \qquad (6)$$

The ratio ϕ of the signal amplitudes for the sample to the reference is,

$$\phi = \frac{S}{R} = \frac{Q}{E_{h\nu}} + \Delta V_r \cdot \frac{C_p \rho}{\beta E_{h\nu}} \qquad (7)$$

In the linear range of response to excitation energy, the amplitude of optical probe signal resulting from heat deposition is proportional to $\beta/C_p\rho$, where β greatly depends on temperature in aqueous solution, and closes to zero at 3.9°C. Based on equation 7, a plot of $\phi E_{h\nu}$ *vs* $C_p\rho/\beta$ will yield a line with a slope of ΔV_r and an intercept of Q. If we know the enthalpy change for the chemical reaction ΔH, the quantum yield, $\Phi = (E_{h\nu} - Q) / \Delta H$, and *vice versa*, and the reaction volume change per mole, $\Delta V_R = \Delta V_r / \Phi$, can be obtained.

RESULTS AND DISCUSSION

The relationship between signal and absorbed energy is linear within the range studied (Figure 3), which eliminate the possibility of multi-photon effect in solutions. The plot of $E_{h\nu}\phi$ vs $C_p\rho/\beta$ is present (Figure 4). The values of β, C_p and ρ at different temperatures are according to the literature.[8]

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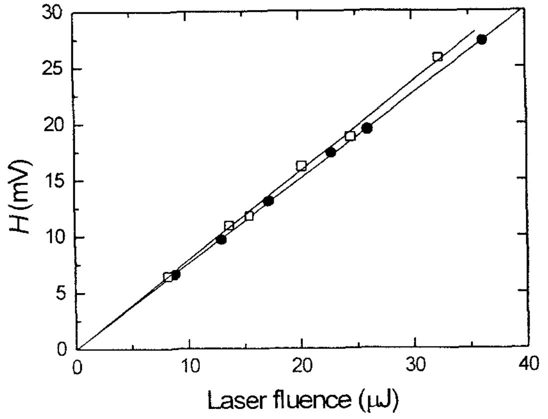

Figure 3. Photoacoustic signal amplitude H, as a function of the absorbed energy, at 15°C for $CH_3Co(DH)_2py$( ) and $K_2Cr_2O_7$ (•) in aqueous solution.

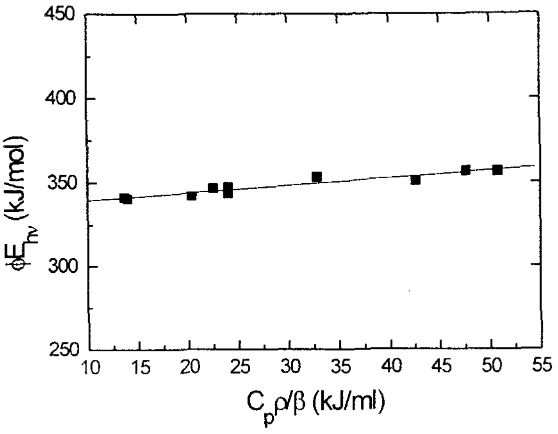

Figure 4. Plot of $E_{hv}\phi$ vs $C_p\rho/\beta$ for $CH_3Co(DH)_2py$ in neutral aqueous solution

$CH_3Co(DH)_2py$ is an organocobalt complex, similar to the natural coenzyme B_{12}, it has a σ-type cobalt-carbon bond which will be broken to produce a cobalt(II) and a methyl radical promptly in anaerobic photolysis.[9]

$$CH_3Co(DH)_2L \xrightarrow{h\nu} \cdot CH_3 + Co(DH)_2L \qquad (A)$$

$$L = H_2O,\ py,\ CH_3OH,\ etc$$

In general, the reaction enthalpy for homolytical process ($M - X \longrightarrow M + \bullet X$) can be used as the measurement of M-X bond strength.[10] For reaction A, the Co-CH_3 bond dissociation energy can be treated as the reaction enthalpy. Using the Co-CH_3 bond dissociation energy BDE(Co-C) = 138.4 kJ/mol,[11] and the values of Q and ΔV_r obtained by the intercept and the slope of linear plot at Fig. 4, the quantum yield for the photolysis of anaerated $CH_3Co(DH)_2py$ solution at 355nm, $\Phi = 0.011$ and reaction volume change $\Delta V_R = 0.5$ ml/mol, respectively, are obtained. The resulted quantum yield is close to the value obtained by Schrauzer *et. al.* at 440nm,[12] and the relatively small reaction volume change suggests that the contributions of the structural volume change of organocobalt complex and solvation effect accompanying Co-C bond cleavage are relatively unaffected.

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REFERENCES

1 (a) Peters K.S. and Snyder G.J., Science, 1988; 241: 1053-1057

(b) Braslavsky S.E. and Heibel G.E., Chem. Rev., 1992; 92: 1381-1410

(c) Luo L.B., Li G., Chen H.L., Fu S.W.and Zhang S.Y., J. Chem. Soc. Dalton Trans., 1998; 12: 2103-2107

2. Terazima M. and Hirota N., J. Chem. Phys., 1994; 100: 2481-2486
3. Schulenberg P.J., Gärtner W. and Braslavsky S.E., J. Phys. Chem, 1995; 99: 9617-9624
4. (a) Jia X., Quentin G. and Lassoued M., IEEE Trans. UFFC, 1993; 40: 67-69

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(b) Fu S.W., Wu Z., Gan C., Zhang S.Y., Zhang Z. and Chen H.L., Chin. Phys. Lett., 1996; 13: 313-316

5. Poston P.E. and Harris J.M., J. Am. Chem. Soc.,1990; 112: 644-650
6. Schrauzer G.N. and Windgassen R.J., J. Am. Chem. Soc., 1966; 88: 3738-3743
7. Weast R.C. (ed.), CRC Handbook of Chemistry and Physics, 70th ed., CRC Press, Boca Raton, FL, 1989-1990, F-4, F-5
8. Eisenberg H., J. Chem. Phys., 1965; 43: 3887-3892
9. Bakac A. and Espenson J.H., Inorg. Chem., 1989; 28: 3901-3904
10. Endicott J. F. and Ferraudi G. J., J. Am. Chem. Soc., 1977; 99: 243-245
11. Toscano P.J., Seligson A.L., Curran M.T., Skrobutt A.T. and Sonnenberger D.C., Inorg. Chem., 1989; 28: 166-168
12. Schrauzer G.N., Lee L.P. and Sibert J.W., J. Am. Chem. Soc., 1970; 92: 2997-3005

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