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Kazuhiro Yabuuchi [a], Daisuke Kawamura [a], Makoto Inokuchi [a], Ichimin Shirotani [b], Junichi Hayashi [b], Kyuya Yakushi [c], Haruki Kawamura [d] & Hiroo Inokuchi [e]

[a] Faculty of Science and Engineering, Department of Materials Science and Environmental Engineering, Tokyo University of Science, Yamaguchi, Sanyo-Onoda, Yamaguchi, Japan

[b] Faculty of Engineering, Muroran Institute of Technology, Muroran, Hokkaido, Japan

[c] Institute for Molecular Science, Okazaki, Aichi, Japan

[d] School of Science, University of Hyogo, Kamigohri, Hyogo, Japan

[e] Japan Aerospace Exploration Agency, Tsukuba, Ibaraki, Japan

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Kazuhiro Yabuuchi
Daisuke Kawamura
Makoto Inokuchi
Faculty of Science and Engineering, Department of Materials Science and Environmental Engineering, Tokyo University of Science, Yamaguchi, Sanyo-Onoda, Yamaguchi, Japan

Ichimin Shirotani
Junichi Hayashi
Faculty of Engineering, Muroran Institute of Technology, Muroran, Hokkaido, Japan

Kyuya Yakushi
Institute for Molecular Science, Okazaki, Aichi, Japan

Haruki Kawamura
School of Science, University of Hyogo, Kamigohri, Hyogo, Japan

Hiroo Inokuchi
Japan Aerospace Exploration Agency, Tsukuba, Ibaraki, Japan

Raman spectra of bis(diphenylglyoximato)metal complexes $M(dpg)_2$ ($M = Pt$ and Ni) under high pressure have been studied. The $C=N$ stretching bands remarkably moved with increasing pressure. The relationship between the Raman shift and pressure is almost linear. The rates of increase in the Raman shift with pressure were determined. The platinum complex was more sensitive to pressure than the nickel complex, which is consistent with the pressure dependence of absorption

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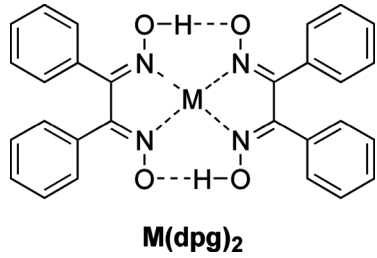
Address correspondence to Makoto Inokuchi, Faculty of Science and Engineering, Department of Materials Science and Environmental Engineering, Tokyo University of Science, Yamaguchi, Sanyo-Onoda, Yamaguchi 756-0884, Japan. E-mail: inokuchi@ed.yama.tus.ac.jp

spectra. The shear stress effect applied on the Pt(dpg)$_2$ thin film was quantitatively estimated by using the relationship between the Raman shift and pressure.

Keywords: bis(diphenyl glyoximato)metal complex; diamond anvil cell; hydrostatic pressure; pressure indicator; Raman spectroscopy; shear stress

INTRODUCTION

Stress is an important factor for studies in solid state physics and chemistry. Stress applied on solid materials is classified into normal and tangential stresses. The normal stress such as hydrostatic pressure has been used for material preparations and physical property measurements. In contrast, some reports concerning the shear stress for inorganic materials have been published [1,2]. A method to introduce the shear stress effect to materials science is still to be established. Therefore, we have focused our attention on the shear stress, aiming at applying the shear stress effect to materials science, particularly for organic materials and molecular crystals. We have developed the sapphire anvil cell to generate shear stress under high pressure. Using this anvil cell, we have studied the effect of shear stress. Firstly, we reported the shear stress effect on thin films of bis(diphenylglyoximato)metal complex M(dpg)$_2$ as shown in Figure 1 [3,4]. We also reported the preparation of TCNQ-TMPD charge transfer salt by shear stress [3]. Bis(1,2-dionedioximato)metal complexes including M(dpg)$_2$ have been known as pressure indicators which exhibit remarkable color changes depending on pressure [5–7]. In the course of our studies on the shear stress effect on M(dpg)$_2$ with the anvil cell, we have found that absorption and Raman spectra exhibit a remarkable move under shear stress as well as pressure [3,4]. We expected it would be possible to establish a method for the quantitative



M(dpg)$_2$

FIGURE 1 Molecular structure of M(dpg)$_2$ (M = Pt and Ni).

estimation of the shear stress effect as a unit of pressure by using the relationship between pressure and spectral shift.

In this paper, we describe Raman spectroscopic study of bis(diphenylglyoximato)metal complexes under high pressure, which is applicable to the quantitative estimation of the shear stress effect.

EXPERIMENTAL

Bis(diphenylglyoximato)metal complexes Pt(dpg)$_2$ and Ni(dpg)$_2$ were prepared by stirring a mixture of a hot ethanol solution of diphenylglyoxime (dpg) and an aqueous solution of K_2PtCl_4 and $NiCl_2{\cdot}6H_2O$, respectively. The resultant complexes were purified by recrystallization from *N*,*N*-dimethylformamide.

A clamped-type diamond anvil cell (DAC) made of BeCu 25 was used for the generation of hydrostatic pressure. Sapphires with 1.2 mm diameter culets were used as anvils instead of diamond and an Inconel gasket was used as a sample chamber (0.5 mm diameter and 0.3 mm thick). Thin films of M(dpg)$_2$ were formed by vacuum evaporation on the culet of sapphire anvils. A mixture of methanol and ethanol (4:1) was used as the pressure medium. Pressure was determined by the ruby fluorescence method [8].

Raman spectra were collected in backscattering geometry using a Renishaw Ramascope System 1000 equipped with an Olympus microscope. An excitation light from a diode laser was focused on a thin film on the culet through the microscope ($\lambda = 785$ nm, *ca.* 6 mW). The spectra were fitted with Lorentzian curves.

RESULTS AND DISCUSSION

We performed *in situ* microscopic observation and spectroscopic measurements of platinum complex Pt(dpg)$_2$ (Fig. 1) under hydrostatic pressure. Platinum ions in the square-planar d^8 complex are surrounded by four nitrogen atoms of two diphenylglyoxime anions. Pt(dpg)$_2$ thin films exhibited chromic behavior from red at ambient pressure through green to yellow with increasing pressure [5]. This color change is caused by the shift of metal-to-ligand charge-transfer transition and $5d_z^2 - 6p_z$ transition between platinum ions [5]. Figure 2(a) shows the Raman spectra of a Pt(dpg)$_2$ thin film under hydrostatic pressure. Two bands located at 1430 cm^{-1} and 1451 cm^{-1} at ambient pressure shift significantly with increasing pressure. These bands are attributed to C=N stretching. Figure 2(b) shows the relationship between these Raman shifts and pressure. For the

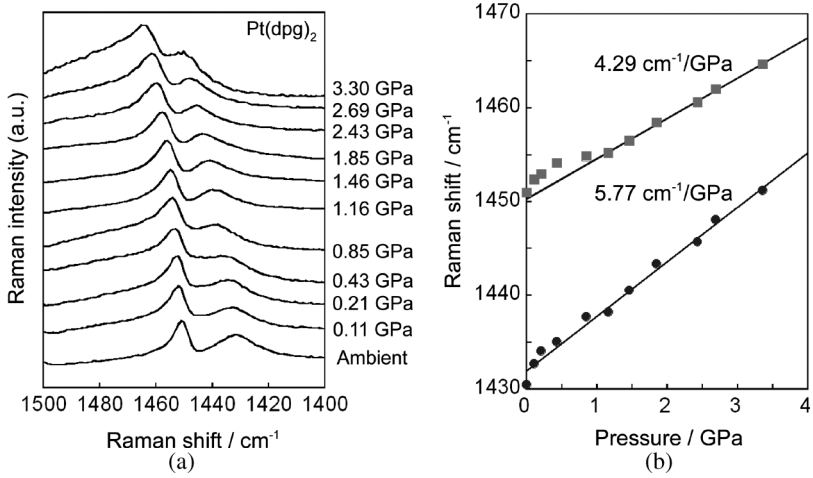


FIGURE 2 Raman spectra of $Pt(dpg)_2$ thin film under hydrostatic pressure (a) and the relationship between the pressure and the Raman shift (b).

pressure region above *ca*. 1 GPa the relationship is almost linear, and the rates of increase in the Raman shift are $5.77\,cm^{-1}$/GPa and $4.29\,cm^{-1}$/GPa, respectively. On the other hand, the relationship is not linear for the lower pressure region, though the wavenumbers of the bands increase monotonously. These relationships are used for the estimation of the shear stress effects.

For nickel complex $Ni(dpg)_2$, a similar Raman spectroscopic behavior was observed. The C=N bands at $1442\,cm^{-1}$ and $1461\,cm^{-1}$ shift to larger wavenumber with increasing pressure in a linear relationship. The rates of increase in the Raman shift are $3.12\,cm^{-1}$/GPa and $4.11\,cm^{-1}$/GPa, respectively. These values are rather smaller than those of $Pt(dpg)_2$, which means that $Pt(dpg)_2$ is more sensitive to pressure than $Ni(dpg)_2$. It is consistent with the previous study on the pressure dependence of absorption spectra of $Pt(dpg)_2$ and $Ni(dpg)_2$ [5], in which the shift of absorption bands of $Pt(dpg)_2$ is larger than that of $Ni(dpg)_2$. Possible explanations for the sensitiveness of platinum complexes are the degree of metal-to-ligand backdonation and the relative spatial extent of the outer *d* and *p* orbitals of Pt and Ni [9,10].

The results mentioned above indicate that the Raman shift of $M(dpg)_2$ can be used as a pressure gauge. Compared to the use of absorption spectra, Raman shift has the advantage that more precise and detailed evaluation of pressure would be possible. Moreover,

Raman bands of M(dpg)$_2$ under shear stress also exhibited significant move [3,4]. Assuming that the Raman bands under shear stress move in a similar manner to that under hydrostatic pressure, it would be also possible to evaluate the shear stress effects quantitatively by using the relationship between the Raman shift and pressure. With the relationship, the estimation of the shear stress effect on Pt(dpg)$_2$ thin films has been carried out. With our sapphire anvil cell, shear stress was generated by rotating the lower anvil under high pressure. Experimental details of application of the shear stress are described elsewhere [3,4]. The shear stress effect was estimated as a unit of pressure "GPa" by comparing the Raman bands under shear stress and under hydrostatic pressure. In the case of a Pt(dpg)$_2$ film with a thickness of 1800 Å, the initial pressure before the rotation was estimated to be 1.8 "GPa" at the outer part and 0.1 "GPa" at the center part of the anvil. Then the shear deformation was generated by 10° rotation and the estimated values increased to 2.4 "GPa" and 0.2 "GPa," respectively. The result indicates that the shear stress was applied more efficiently to the outer part than the center part. This behavior is almost consistent with the color change of Pt(dpg)$_2$ thin films. The estimation method described here would give us a useful scale for the shear stress effects, while shear stress is not identical with hydrostatic pressure.

REFERENCES

[1] Takasaka, S., Tsujimi, Y., & Yagi, T. (2002). *Phys. Rev.*, *B65*, 174102.
[2] Gogotsi, Y. G., Kailer, A., & Nickel, K. G. (1999). *Nature*, *401*, 663.
[3] Inokuchi, M., Nagaoka, A., Yamamoto, K., Shirotani, I., Hayashi, J., Yakushi, K., Kawamura, H., & Inokuchi, H. (2005). *Synth. Met.*, *152*, 421.
[4] Shirotani, I., Hayashi, J., Hirano, K., Kawamura, H., Inokuchi, M., & Inokuchi, H. (2003). *Proc. Japan Acad.*, *79*, *Ser. B*, 267.
[5] Shirotani, I., Inagaki, Y., Utsumi, W., & Yagi, T. (1991). *J. Mater. Chem.*, *1*, 1041.
[6] Shirotani, I., Konno, M., & Taniguchi, Y. (1989). *Synth. Met.*, *29*, F123.
[7] Shirotani, I., Suzuki, K., Suzuki, T., Yagi, T., & Tanaka, M. (1992). *Bull. Chem. Soc. Jpn.*, *65*, 1078.
[8] Piermarini, G. J., Block, S., Barnett, J. D., & Forman, R. A. (1975). *J. Appl. Phys.*, *46*, 2774.
[9] Tkacz, M. & Drickamer, H. G. (1986). *J. Chem. Phys.*, *85*, 1184.
[10] Burger, K., Ruff, I., & Ruff, E. (1965). *J. Inorg. Nucl. Chem.*, *27*, 179.