

# Enhancement of the third-order susceptibility of *cis*-Mo(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> solution by oxygen in different solvents

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## ABSTRACT

Detailed degenerate four wave mixing (DFWM) studies of one molybdenum complex, *cis*-Mo(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) and tetrahydrofuran (THF) are reported in this paper. Upon exposure to air/oxygen, the of CH<sub>2</sub>Cl<sub>2</sub> and THF solutions of this complex increase dramatically with time. However, when excess free ligand is added to CH<sub>2</sub>Cl<sub>2</sub> solution of the complex, the increase in  $\chi^{(3)}$  values is stopped. Hence, it is possible to obtain a CH<sub>2</sub>Cl<sub>2</sub> solution with high  $\chi^{(3)}$  value by first oxidizing the solution and then adding excess ligand to stabilize the solution. For THF solution, due to the different mechanism causing the increase of  $\chi^{(3)}$  values, the increase in  $\chi^{(3)}$  values doesn't stop even though excess free ligand is added. Further, the increase in the  $\chi^{(3)}$  values of both the CH<sub>2</sub>Cl<sub>2</sub> and THF solutions parallels the increase in the linear absorption but it is unclear whether the increased linear absorption plays any role in the increase in the  $\chi^{(3)}$  value of the solution. This study also shows how degenerate four wave mixing can be used as a very sensitive technique to detect the chemical change in a solution when the third order optical nonlinearities of the reactant and product are very different.

**Keywords:** degenerate four wave mixing, third order nonlinearities, metal-organic complex, phosphine ligand dissociation, oxidation

## 1. INTRODUCTION

There are a large number of optical device applications that require nonlinear optical (NLO) materials with large intensity-induced changes in refractive index and absorption. Metal-organic complexes are an interesting class of NLO materials<sup>1,2,3,4,5</sup> because some of these have NLO responses that approach those of conjugated polymers.<sup>6,7,8,9,10,11,12</sup> The interest in these materials comes from the fact that low-lying metal to ligand or ligand to metal charge transfer states,<sup>13,14</sup> not present in conjugated organic compounds, may allow for rapid movement of large quantities of charge.<sup>15,16</sup> This could polarize the complex and enhance its non-resonant NLO response. However, many of the metal-organic complexes with the strongest NLO responses have absorption maxima near the wavelengths of interest. While this absorption may enhance the NLO response due to resonant mechanisms, the high transmission loss in these metal-organic complexes from this linear absorption makes them unsuitable for many optical device applications.

We have reported that solutions of  $\text{Mo}(\text{CO})_{6-n}(\text{Ph}_2\text{PX})_n$  complexes can exhibit strong optical nonlinearities.<sup>5,17,18</sup> The large optical nonlinearities exhibited by solutions of the  $\text{Mo}(\text{CO})_{6-n}(\text{Ph}_2\text{PX})_n$  complexes do not appear to be resonantly enhanced. The solutions have very little linear absorption in the visible spectrum, and preliminary Z-scan studies have demonstrated that the solutions have a positive  $\chi^{(3)}$ .<sup>5, 19</sup>

Our previous work did not provide any insight into the mechanism by which solutions of the  $\text{Mo}(\text{CO})_{6-n}(\text{Ph}_2\text{PX})_n$  ( $n = 1, 2$ ) complexes give rise to high optical nonlinearities. To better understand this, we have carried out detailed degenerate four wave mixing (DFWM) studies of one complex that is expected to have large  $\gamma$  values, *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$ . Our results provide new understanding of the high optical nonlinearities of these complexes.

## 2. EXPERIMENTAL

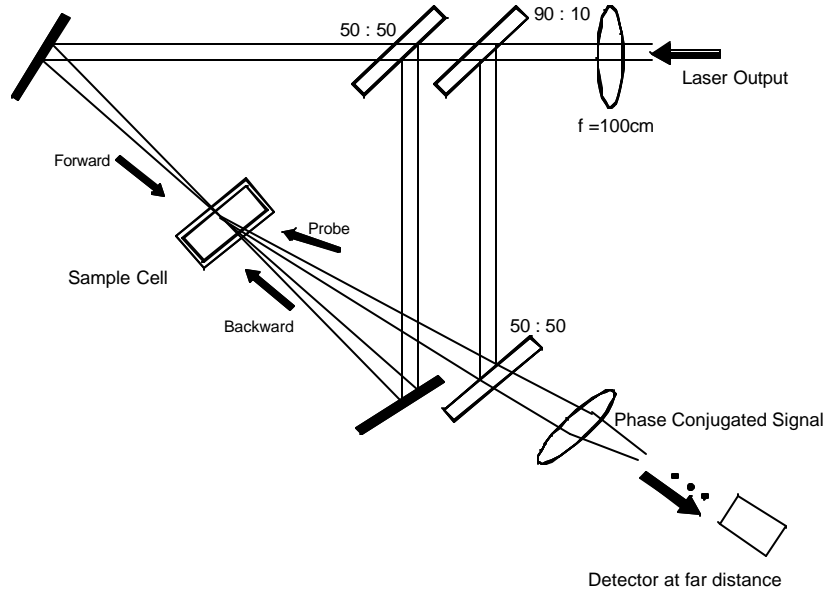
Solvents of reagent grade dichloromethane and tetrahydrofuran were purchased from Fisher Scientific, and were dried prior to use. Ultraviolet-visible spectra of dichloromethane and tetrahydrofuran solutions of the *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$  complex were run on a Shimadzu UV-VIS-NIR Spectrophotometer (UV-3101 PC).

The degenerate four-wave mixing (DFWM) apparatus is shown in Fig. 1. The light source of our experiment is a Q-switched Nd:YAG laser (Spectra Physics) running in the second harmonic at 532nm, with a temporal pulse width of 6ns, and a repetition rate of 10Hz. A single lens with a relatively long focal length (100cm) is used to soft-focus all three beams at the sample, and the beam spot diameter on the sample is about 2~3mm. The reference liquid is injected using a syringe into a 5mm spectrometric flow cell with Teflon tubing attached at both ends. After measurement of the phase conjugate signal, the reference liquid is drained, and the cell is rinsed with a constant flow of the solvent. The cell is then dried completely with nitrogen. The sample solution is injected into the cell, and the phase conjugate signal is again measured. The cell is drained, rinsed with solvent, and then dried with nitrogen before another reference measurement is performed.

The intensity of the phase conjugate signal,  $I_{sig}$ , for the NLO sample is compared to the phase conjugate intensity,  $I_{ref}$ , from carbon disulfide ( $\text{CS}_2$ ), a reference NLO material with a well-characterized  $\chi^{(3)}$ . The magnitude of  $\chi^{(3)}$  for the NLO sample is given by<sup>20</sup>

$$|\mathbf{c}^{(3)}|_{sample} = |\mathbf{c}^{(3)}|_{ref} \left( \frac{I_{sig}}{I_{ref}} \right)^{1/2} \left( \frac{n_{sample}}{n_{ref}} \right)^2 \left( \frac{L_{ref}}{L_{sample}} \right) \left( \frac{\mathbf{a}L}{e^{\left(\frac{-\mathbf{a}L}{2}\right)}(1 - e^{-\mathbf{a}L})} \right) \quad (1)$$

where  $n_{sample}$  and  $n_{ref}$  are the linear refractive indices of the sample and the reference liquid, respectively,  $\mathbf{a}$  is the linear absorption coefficient of the sample at the working wavelength, and  $L$  is the beam interaction length in the sample. A value of  $6.8 \times 10^{-13}$  esu is used as  $\chi^{(3)}$  for  $\text{CS}_2$ .<sup>21</sup>



**Fig. 1.** DFWM experimental configuration. The ratio of pump beam to probe beam is 90:10.

When a NLO material is taken up into solution, the concentration dependence of  $\chi^{(3)}$  for the solution can be used to determine the second-order hyperpolarizability,  $\gamma$ , of the solute. Assuming pairwise additivity and the validity of the Lorentz local field factor for the highly symmetric media, the concentration dependence of  $\chi^{(3)}$  can be related to the orientationally averaged hyperpolarizability by

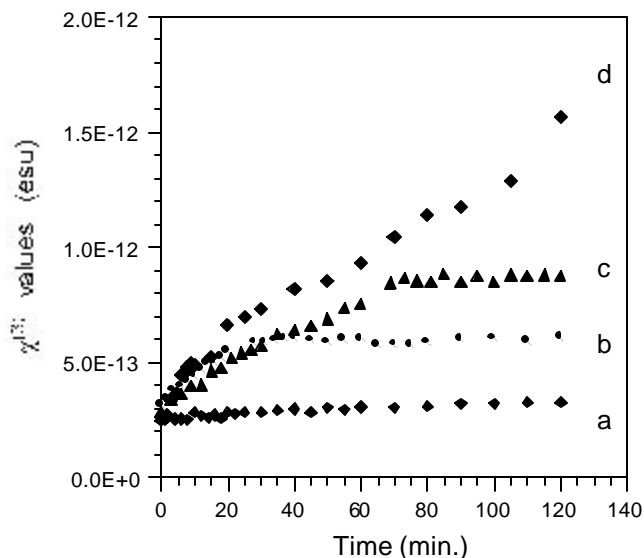
$$c_{solution}^{(3)} = f^4 (N_{solute} \mathbf{g}_{solute} + N_{solvent} \mathbf{g}_{solvent}) \quad (2)$$

where  $f$  is the Lorentz local field factor and  $N$  is the number density in molecules per ml.

### 3. RESULTS

Our previous studies of the  $\text{Mo}(\text{CO})_{6-n}(\text{Ph}_2\text{PX})_n$  ( $n = 1, 2$ ) complex have revealed that solutions of some of these complexes have high third-order nonlinearities. The highest third-order nonlinearities to date have been observed for *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$ . The nonlinearity of the solution was assumed to be entirely due to the *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$ , and thus a  $\gamma$  value of  $1.7 \times 10^{-31}$  esu was calculated for the complex.<sup>17</sup> To gain a better understanding of the mechanism that contributes to this high nonlinearity, an improved DFWM setup was used to study the optical nonlinearities of solutions of *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$  and some closely related complexes.

Our results were surprising in that we found that the  $\chi^{(3)}$  value of *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$  solutions increased dramatically with time (as shown in Fig. 2d). The  $\chi^{(3)}$  value of a dichloromethane solution of *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$  increased by about one order of magnitude over a period of seven hours. Using the assumption that the nonlinearity of the solution was entirely due to the *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$ , the  $\gamma$  value of the aged solution was calculated to be  $1.8 \times 10^{-31}$  esu. This value is in good agreement with the value from our previous study.<sup>17</sup>

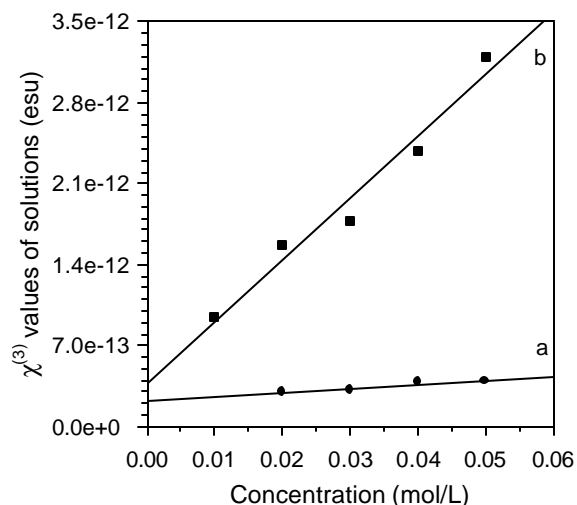


**Fig. 2.**  $\chi^{(3)}$  values versus time for  $8 \times 10^{-3}$  mol/L  $\text{CH}_2\text{Cl}_2$  solution of  $\text{cis-Mo}(\text{CO})_4(\text{PPh}_3)_2$ . a) excess free ligand (1:1) added initially, b) ligand added 30 min. later, c) ligand added 70 min. later, d) without added ligand.

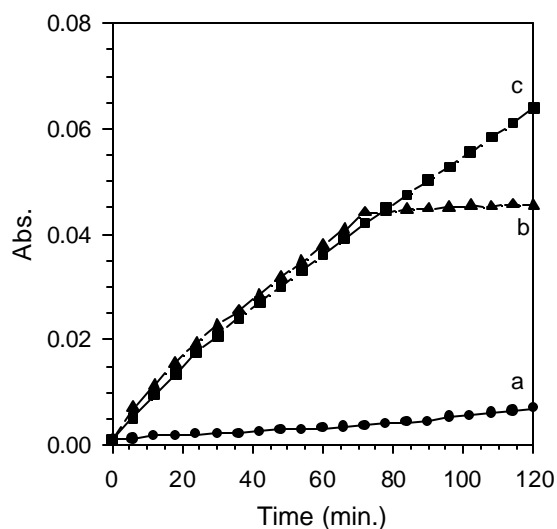
When we attempted to reproduce these results, we found that the rate of increase in the  $\chi^{(3)}$  value of the solutions was highly variable. This appeared to be due to exposure of the solutions to air as they were transferred to the DFWM apparatus. When care was taken to minimize exposure of the solutions to air, the rate of increase in the  $\chi^{(3)}$  value was greatly reduced.

The most likely effect of the introduction of air into a solution of  $\text{cis-Mo}(\text{CO})_4(\text{PPh}_3)_2$  would be oxidation of the complex. Because the  $\text{cis-Mo}(\text{CO})_4(\text{PPh}_3)_2$  is coordinatively saturated, it is unlikely that this complex was being directly oxidized. However, oxidation could occur upon dissociation of a  $\text{PPh}_3$  ligand. To test this possibility, we added excess  $\text{PPh}_3$  ligand to dichloromethane solutions of  $\text{cis-Mo}(\text{CO})_4(\text{PPh}_3)_2$  that had been exposed to air for various periods of time. As shown in Fig. 2a, the effect of adding excess free ligand in the solution before exposure to air greatly slowed the increase in the  $\chi^{(3)}$  value. Over a period of two hours, the  $\chi^{(3)}$  value increased only 20%. When excess  $\text{PPh}_3$  was added to the solution at some point after it had been exposed to air, no further increase in  $\chi^{(3)}$  was observed (Fig. 2b and Fig. 2c).

When oxygen is bubbled through a solution of  $\text{cis-Mo}(\text{CO})_4(\text{PPh}_3)_2$ , a more rapid increase in the  $\chi^{(3)}$  value is observed. The effect of oxygen exposure on the concentration dependence of the  $\chi^{(3)}$  value is shown in Fig. 3. When the excess  $\text{PPh}_3$  is added to the solution before it is exposed to oxygen, the  $\gamma$  value calculated from this concentration dependence, assuming that the  $\chi^{(3)}$  is due to  $\text{cis-Mo}(\text{CO})_4(\text{PPh}_3)_2$ , is  $18 \times 10^{-34}$  esu. However, when oxygen is bubbled through the solution for 15 minutes before the excess  $\text{PPh}_3$  ligand is added, the resulting  $\gamma$  value is  $270 \times 10^{-34}$  esu.

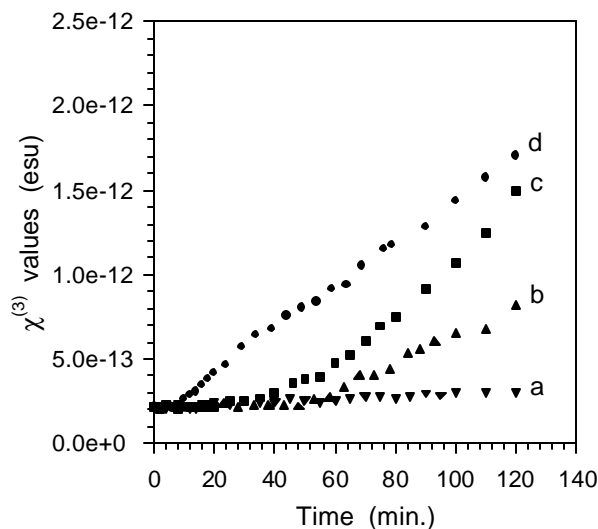


**Fig. 3.**  $\chi^{(3)}$  values versus concentration for  $\text{CH}_2\text{Cl}_2$  solution of  $\text{cis-Mo}(\text{CO})_4(\text{PPh}_3)_2$ . a) excess ligand (1:1) added initially, b) ligand added 15min. after exposure to oxygen.



**Fig. 4.** Linear absorption changes at 532 nm for  $\text{cis-Mo}(\text{CO})_4(\text{PPh}_3)_2$  in  $8 \times 10^{-3}$  mol/L  $\text{CH}_2\text{Cl}_2$  solution. a) excess free ligand (1:1) added initially, b) ligand added 70 min. later, c) without added ligand.

As oxidation of the solutions occurred, we observed a slight color change in the solution. This suggested that the linear absorption of the solution was changing. To determine whether this was indeed the case, we measured the change in linear absorption at 532nm. As shown in Fig. 4, the increase in the linear absorbance stops when excess  $\text{PPh}_3$  is added to the solution. By comparing Fig. 2 and Fig. 4, it becomes obvious that the increase in linear absorption and the increase in the  $\chi^{(3)}$  value are related.



**Fig. 5.**  $\chi^{(3)}$  values versus time for  $8 \times 10^{-3}$  mol/L THF solution of *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$ . a) degassed for 6 min., b) degassed for 4 min., c) ligand added initially and degassed for 2 min., d) exposure to air.

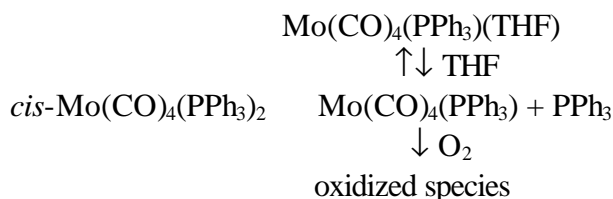
To determine whether the increase in the  $\chi^{(3)}$  value is related to the nature of the solvent, we measured the time dependence of the  $\chi^{(3)}$  values of tetrahydrofuran solutions of *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$  that had been exposed to air. As shown in Fig. 5, the  $\chi^{(3)}$  values of THF solutions of *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$  complex increase with time. However, the trend is quite different from that in dichloromethane. The curves show that the solutions are stable for variable periods of time according to the extent of degassing. When the solution was exposed to air, its  $\chi^{(3)}$  value was stable for about 8 min.. When the solutions were degassed for 2 min. and 4 min., the periods of stabilization were about 20 min. and 50 min. respectively. After these periods, the  $\chi^{(3)}$  values of the THF solutions of *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$  complex began to increase. In contrast to the behavior of the  $\text{CH}_2\text{Cl}_2$  solution, the addition of excess ligand to the THF solution didn't stop this increase (shown in Fig. 5c). However, when the solution was degassed for a relative long time, little increase in the  $\chi^{(3)}$  value of the solution is observed (Fig. 5a). In addition, the increase in the linear absorption at 532 nm in THF solution parallels the increase in the  $\chi^{(3)}$  values of THF solution.

#### 4. DISCUSSION

The results described in this manuscript indicate that the high  $\chi^{(3)}$  values observed for solution of the *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$  complex is due to oxidation of the complex in solution. The oxidation appears to occur via dissociation of a phosphine ligand as shown in Scheme 1. Darensbourg and Kump<sup>22,23</sup> have reported that bulky phosphine ligands rapidly dissociate from *cis*- $\text{Mo}(\text{CO})_4\text{L}_2$  complexes. Such dissociation would yield the monosubstituted  $\text{Mo}(\text{CO})_4\text{L}$  complex, which is coordinatively unsaturated and easily oxidized. Thus, solutions of complexes with bulky ligands such as *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$  exhibit high  $\chi^{(3)}$  values when exposed to air/oxygen. However, the mechanism of the increase in the  $\chi^{(3)}$  values is different in dichloromethane and THF. In THF solution, perhaps because the coordination of THF with the monosubstituted species competes with the

oxidation procedure, the increase in the  $\chi^{(3)}$  values does not begin immediately. In contrast, dichloromethane may not react as a coordinating ligand, thus oxidation will occur as soon as the monosubstituted species appears.

Scheme 1



The most interesting aspect of the results described in this paper is that a large increase in the  $\chi^{(3)}$  values of the solutions is observed even though only a small fraction of the complex has been oxidized. This suggests that the unidentified species causing the increases in the  $\chi^{(3)}$  values of the solutions may have very large  $\gamma$  values. Such complexes would be very interesting third order nonlinear optical materials.

The mechanism by which the oxidized species causes the increase is unclear. The fact that the increase in the  $\chi^{(3)}$  values of the solutions parallels the increase in the linear absorption of the solutions suggests that this could be an absorptive mechanism. However, our previous Z-scan experiments on solutions with high  $\chi^{(3)}$  values demonstrated that the primary mechanism was not absorptive.<sup>5,19</sup> To resolve this question, further experiments will be done using the Z-scan technique.

## 5. CONCLUSIONS

In this paper, we reported the detailed degenerate four wave mixing (DFWM) studies of *cis*- $\text{Mo(CO)}_4(\text{PPh}_3)_2$  complex in different solvents. The effect of ligand dissociation and of the presence of oxygen on  $\chi^{(3)}$  has been investigated. The results indicate that the high  $\gamma$  value that we have previously reported for *cis*- $\text{Mo(CO)}_4(\text{PPh}_3)_2$  is not due to this complex but rather to oxidation of the complex in solution. Stable dichloromethane solution with high  $\chi^{(3)}$  value can be prepared by first exposing solution of *cis*- $\text{Mo(CO)}_4(\text{PPh}_3)_2$  complex to air/oxygen and then adding excess ligand to the solution. Our study also demonstrates that degenerate four wave mixing can be used as a very sensitive technique to detect the chemical change in a solution when the third order optical nonlinearities of the reactant and product are very different.

## 6. ACKNOWLEDGEMENTS

This work was supported by Army Research Office Grant DAAH04-96-1-0400.

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