

**Oxidative enhancement of the $c^{(3)}$ values of solutions of *cis*-
**Mo(CO)₄L₂ (L=PPh₃, AsPh₃, PPh₂Np) complexes as measured
by DFWM****

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Abstract

Detailed degenerate four wave mixing (DFWM) studies of four molybdenum complexes, *cis*-Mo(CO)₄(PPh₃)₂, *cis*-Mo(CO)₄(AsPh₃)₂, *cis*-Mo(CO)₄(PPh₂Np)₂ and *cis*-Mo(CO)₄(P(OPh)₃)₂ are reported in this paper. Upon exposure to air/oxygen, the $\chi^{(3)}$ values of solutions of the first three complexes increase dramatically with time. However, when excess free ligand is added to any of the solutions, no additional increase in the $\chi^{(3)}$ value is observed. Hence, it is possible to obtain solutions with high $\chi^{(3)}$ values by first oxidizing the solution and then adding excess ligand to stabilize the solution. Further, the increase in the $\chi^{(3)}$ values of the 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 $\chi^{(3)}$ values of the solutions. 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 (DFWM), third order nonlinearities, metal-organic complexes, 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 [1,2,3,4,5] because some of these have NLO responses that approach those of conjugated polymers [6,7,8,9,10,11,12]. The interest in these materials comes from the fact that low-lying metal to ligand or ligand to metal charge transfer states [13,14], not present in conjugated organic compounds, may allow for rapid movement of large quantities of charge [15,16]. 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 third order optical nonlinearities [5,17,18]. The large optical nonlinearities exhibited by these solutions 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 $\chi^{(3)}$ [5,19].

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 three complexes that are expected to have large γ values, *cis*-Mo(CO)₄(PPh₃)₂, *cis*-Mo(CO)₄(AsPh₃)₂ and *cis*-Mo(CO)₄(PPh₂Np)₂, and one complex, *cis*-Mo(CO)₄(P(OPh)₃)₂, that is not. Our results provide new understanding of the high optical nonlinearities of these complexes.

2. Materials Development

Reagent grade dichloromethane, tetrahydrofuran, and hexanes were purchased from Fisher Scientific and were used as received. The starting material, Mo(CO)₄(nbd), (nbd = norbornadiene), was prepared by literature procedures [20]. The ligands, PPh₃ and AsPh₃, were purchased from Aldrich Chemical Company, and were used as received. Complexes and solutions of the complexes were handled, synthesized, and recrystallized under a high-purity nitrogen atmosphere at all times. All complexes were stored in the dark and under nitrogen.

The purity of the materials studied was verified by elemental analysis performed at Atlantic Microlabs, Norcross, GA, and by ³¹P{¹H} NMR spectroscopy on a Bruker ARX-300 NMR spectrometer with a quad (¹H, ¹³C, ¹⁹F, ³¹P) 5mm probe. The ³¹P{¹H} NMR spectra were referenced to external 85% phosphoric acid and in all cases downfield was treated positive. Infrared spectra of dilute solutions of the complexes in KBr solution cells were run on a Bruker Vector 22 FT-IR spectrometer. The frequency range for all IR spectra was 2200-1800 cm⁻¹. Ultraviolet-visible spectra of dichloromethane solutions of the complexes with concentrations between 10⁻² to 10⁻³ mol/L were run on a Shimadzu UV-VIS-NIR Spectrophotometer (UV-

3101 PC). Dichloromethane was distilled from calcium hydride under high-purity nitrogen prior to use.

2-(Diphenylphosphino)naphthalene. A solution of 30.2 mL (48.3 mmol) of 1.6 M BuⁿLi in hexanes was diluted with 50 mL of tetrahydrofuran and this solution was added dropwise to a solution of 10.0 g (48.3 mmol) of 2-bromonaphthalene in 50 mL of tetrahydrofuran at -78 °C over a 90 min period. This mixture was maintained at a temperature of -78 °C for 1 h and then a solution of 10.1 g (45.9 mmol) of chlorodiphenylphosphine in 75 ml of tetrahydrofuran was added dropwise. This solution was stirred overnight at room temperature and then evaporated to dryness. The residue was extracted with dichloromethane, and the extract was evaporated to dryness to yield 11.01 g (77%) as a white powder. Recrystallization from dichloromethane-hexanes gave pure 2-(diphenylphosphino)naphthalene as white crystals. ³¹P{¹H} NMR (chloroform-*d*): δ -3.67 (s).

cis-Mo(CO)₄(PPh₃)₂. A mixture of 17.0 g (65.0 mmol) of triphenylphosphine and 9.75 g (32.5 mmol) of Mo(CO)₄(nbd) (nbd = norbornadiene) in 100 ml of hexanes was stirred for 2 h at room temperature. The pale brown precipitate was collected and then dissolved in 50 ml of a 1:1 dichloromethane-hexanes mixture. This solution was filtered through 25 g of silica gel and then the silica gel was washed with two 50 ml portions of a 1:1 dichloromethane-hexanes mixture. The filtrate and washes were combined and evaporated to dryness to yield 22.0 g of crude *cis*-Mo(CO)₄(PPh₃)₂ as a white powder. Two successive recrystallizations from dichloromethane-hexanes yielded 11.6 g (48.7%) analytically pure *cis*-Mo(CO)₄(PPh₃)₂ as pale yellow crystals. ν(CO) (dichloromethane): 2021, 1908, 1881 cm⁻¹. ³¹P{¹H} NMR

(chloroform-*d*): δ 39.34 (s). *Anal.* Calc. for $C_{40}H_{30}O_4P_2Mo$: C, 65.58; H, 4.13. Found: C, 65.72; H, 4.23 %.

cis- $Mo(CO)_4(AsPh_3)_2$. Using the above procedure, 0.263 g (0.877 mmol) of $Mo(CO)_4(nbd)$ and 0.537 g (1.75 mmol) of triphenylarsine yielded 0.593 g (82.5%) of *cis*- $Mo(CO)_4(AsPh_3)_2$ as pale yellow crystals. $\nu(CO)$ (dichloromethane): 2024, 1913, 1880 cm^{-1} . *Anal.* Calc. for $C_{40}H_{30}O_4As_2Mo$: C, 58.56; H, 3.69. Found: C, 58.32; H, 3.74 %.

cis- $Mo(CO)_4(PPh_2Np)_2$. Using the above procedure, 0.271 g (0.903 mmol) of $Mo(CO)_4(nbd)$ and 0.537 g (1.94 mmol) of 2-diphenylphosphinonaphthalene yielded 0.569 g (75.7%) of *cis*- $Mo(CO)_4(PPh_2Np)_2$ as pale yellow crystals. $\nu(CO)$ (dichloromethane): 2021, 1907, 1882 cm^{-1} . $^{31}P\{^1H\}$ NMR (chloroform-*d*): δ 39.51 (s). *Anal.* Calc. for $C_{48}H_{34}O_4P_2Mo$: C, 69.24; H, 4.12. Found: C, 69.28; H, 4.16 %.

cis- $Mo(CO)_4(P(OPh)_3)_2$. Using the above procedure, 2.20 g (7.33 mmol) of $Mo(CO)_4(nbd)$ and 4.60 ml (14.8 mmol) of triphenylphosphite yielded 3.13 g (52 %) of *cis*- $Mo(CO)_4(P(OPh)_3)_2$ as colorless crystals. $^{31}P\{^1H\}$ NMR (chloroform-*d*): δ 39.34 (s).

3. DFWM Measurements

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 second harmonic at 532 nm, with a temporal pulse width of 5 ns, and a repetition rate of 10 Hz. A single lens with a relatively long focal length (100 cm) is used to soft-focus all three beams at the sample,

and the beam spot diameter on the sample is about 2~3 mm. A syringe is used to inject the reference liquid into a 5 mm 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 (CS_2), a reference NLO material with a well-characterized $\chi^{(3)}$. The magnitude of $\chi^{(3)}$ for the NLO sample is given by [21]

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

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 6.8×10^{-13} esu is used as $\chi^{(3)}$ for CS_2 [22].

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, γ , 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

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

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

4. Results

Our previous studies have revealed that solutions of some $\text{Mo}(\text{CO})_{6-n}(\text{Ph}_2\text{PX})_n$ ($n = 1, 2$) complexes have high third-order optical nonlinearities. The highest third-order optical nonlinearity to date has been observed for solution of *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$. The nonlinearity of the solution was assumed to be entirely due to the dissolved *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$, and a γ value of 1.7×10^{-31} esu was calculated for the complex [17]. 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 the $\chi^{(3)}$ value of the *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$ solution increased dramatically with time (as shown in Fig. 2d). The $\chi^{(3)}$ value of the 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 γ value of the aged solution was calculated to be 1.8×10^{-31} esu. This value is in good agreement with the value from our previous study [17].

When we attempted to reproduce these results, we found that the rate of increase in the $\chi^{(3)}$ value of the solution 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 *cis*-Mo(CO)₄(PPh₃)₂ would be oxidation of the complex. Because the *cis*-Mo(CO)₄(PPh₃)₂ is coordinatively saturated, it is unlikely that this complex was being directly oxidized. However, oxidation could occur upon dissociation of a PPh₃ ligand. To test this possibility, we added excess PPh₃ ligand to dichloromethane solutions of *cis*-Mo(CO)₄(PPh₃)₂ that had been exposed to air for various periods of time. As shown in Fig. 2a, the effect of adding excess free ligand to 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 PPh₃ 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 was bubbled through a solution of *cis*-Mo(CO)₄(PPh₃)₂, a more rapid increase in the $\chi^{(3)}$ value was observed. The effect of oxygen exposure on the concentration dependence of the $\chi^{(3)}$ value is shown in Fig. 3. When the excess PPh₃ was added to the solution before it was exposed to oxygen, the γ value calculated from this concentration dependence, assuming that the $\chi^{(3)}$ was due to *cis*-Mo(CO)₄(PPh₃)₂, was 18×10^{-34} esu. However, when oxygen was bubbled through the solution for 15 minutes before the excess PPh₃ ligand was added, the resulting γ value was 270×10^{-34} esu.

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 absorption stopped when excess PPh₃ was 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.

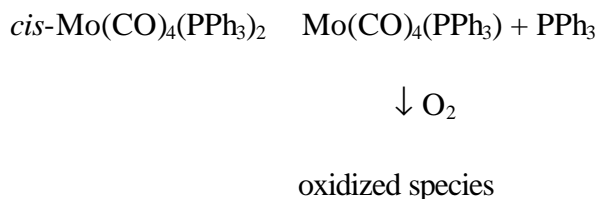
To determine whether the increase in the $\chi^{(3)}$ value is related to the nature of the ligands, we measured the time dependence of the $\chi^{(3)}$ values of dichloromethane solutions of *cis*-Mo(CO)₄(AsPh₃)₂, *cis*-Mo(CO)₄(PPh₂Np)₂ and *cis*-Mo(CO)₄(P(OPh)₃)₂ that had been exposed to air. As shown in Fig. 5 and Fig. 6, the $\chi^{(3)}$ values of dichloromethane solutions of *cis*-Mo(CO)₄(AsPh₃)₂ and of *cis*-Mo(CO)₄(PPh₂Np)₂ increased with time. The addition of excess ligand stopped this increase. In contrast, no increase was observed in the $\chi^{(3)}$ value of dichloromethane solution of *cis*-Mo(CO)₄(P(OPh)₃)₂ that had been exposed to air.

5. Discussion

Our preliminary studies had suggested that solutions of *cis*-Mo(CO)_{6-n}(PPh₂X)_n complexes could exhibit high $\chi^{(3)}$ values and that the $\chi^{(3)}$ value of the solution was strongly dependent upon the ligand present in the complex [5,19]. However, the more detailed findings in this paper now suggest that the $\chi^{(3)}$ values of all of the complexes are lower than originally reported, and no ligand dependence is observed (see Table 1).

The results described in this manuscript indicate that the high $\chi^{(3)}$ values observed for solutions of some *cis*-Mo(CO)_{6-n}(PPh₂X)_n complexes are due to oxidation of these complexes in solution. The oxidation appears to occur via dissociation of a phosphine ligand as shown in Scheme 1.

Scheme 1



Darensbourg and Kump [23,24] have reported that bulky phosphine ligands rapidly dissociate from *cis*-Mo(CO)₄L₂ complexes. Such dissociation would yield the monosubstituted Mo(CO)₄L complexes, which are coordinatively unsaturated and easily oxidized. Thus, solutions of complexes with bulky ligands such as *cis*-Mo(CO)₄(PPh₃)₂, *cis*-Mo(CO)₄(AsPh₃)₂ and *cis*-Mo(CO)₄(PPh₂Np)₂ exhibit high $\chi^{(3)}$ values when exposed to air/oxygen. In contrast, solutions of complexes with less bulky ligands, such as *cis*-Mo(CO)₄(P(OPh)₃)₂, which do not rapidly dissociate, do not exhibit higher $\chi^{(3)}$ values when exposed to air/oxygen.

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

The mechanism by which the oxidized species causes the increase in the $\chi^{(3)}$ value is unclear. The fact that the increase in the $\chi^{(3)}$ value of a solution parallels the increase in the linear absorption of the solution 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 [5,19]. To resolve this question, further experiments will be done using the Z-scan technique.

6. Conclusions

In this paper, we reported detailed degenerate four wave mixing (DFWM) studies of four molybdenum complexes. The effect of ligand dissociation and of the presence of oxygen on $\chi^{(3)}$ has been investigated. Our results indicate that the high γ value that we previously reported for *cis*-Mo(CO)₄(PPh₃)₂ is not due to this complex but rather to oxidation of the complex in solution. Stable solutions with high $\chi^{(3)}$ values can be prepared by first exposing solutions of *cis*-Mo(CO)₄L₂ (L = PPh₃, AsPh₃, PPh₂Np) complexes 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.

Acknowledgements

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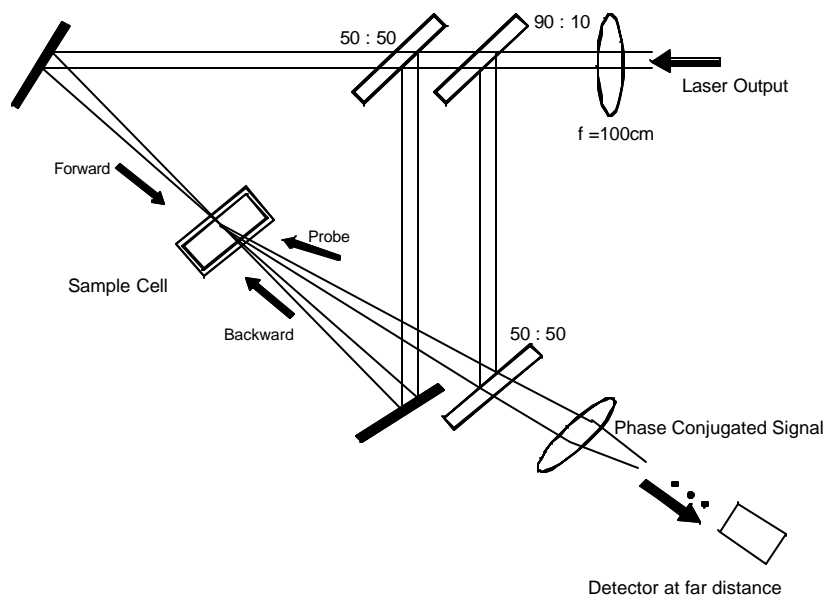


Fig. 1. DFWM experimental configuration. The ratio of pump beam to probe beam is 90:10.

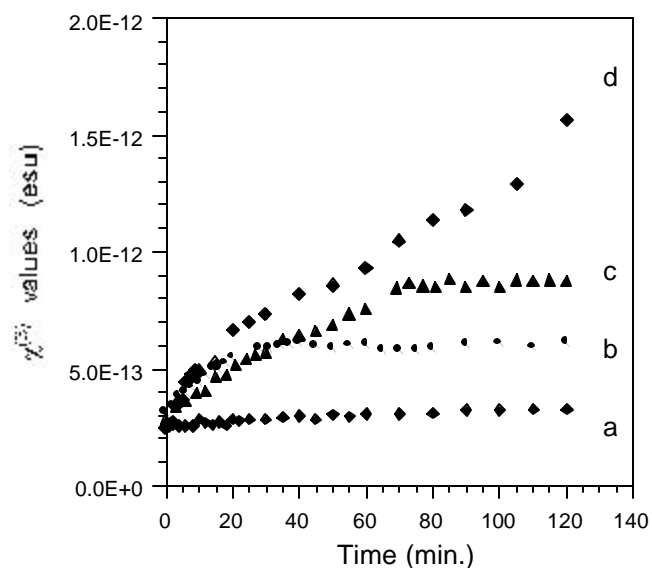


Fig. 2. $\chi^{(3)}$ values versus time for 8×10^{-3} mol/L dichloromethane solution of *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$. a) excess free ligand (1:1) added initially, b) ligand added 30 min. later, c) ligand added 70 min. later, d) without added ligand.

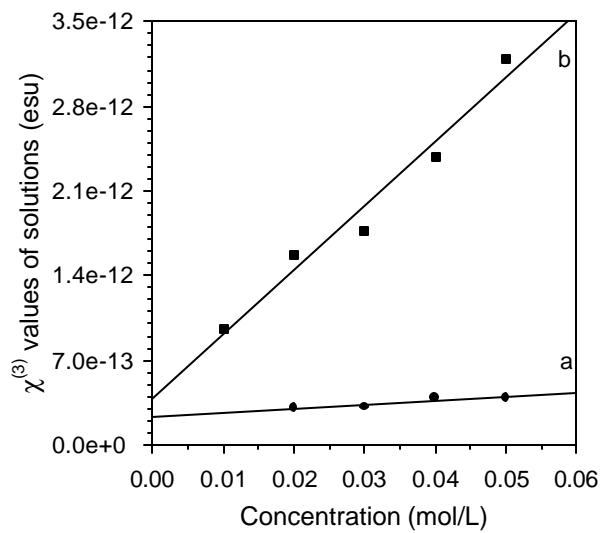


Fig. 3. $\chi^{(3)}$ values versus concentration for dichloromethane solution of *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_3)_2$. a) excess ligand (1:1) added initially, b) ligand added 15 min. after exposure to oxygen.

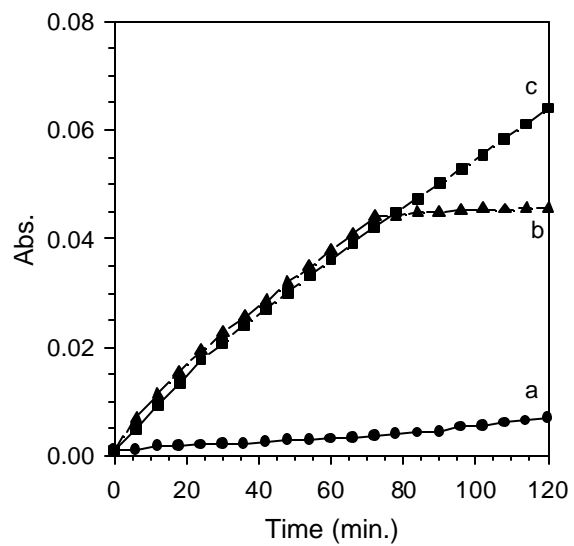


Fig. 4. Linear absorption changes at 532 nm for *cis*-Mo(CO)₄(PPh₃)₂ in 8×10⁻³ mol/L dichloromethane solution. a) excess free ligand (1:1) added initially, b) ligand added 70 min. later, c) without added ligand.

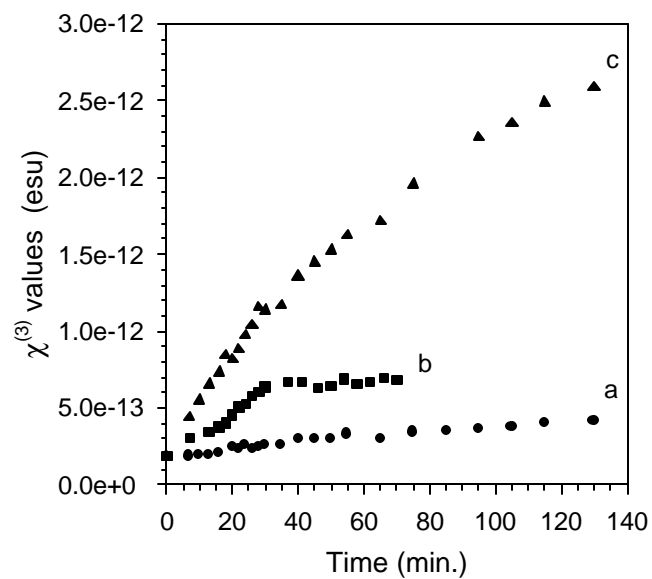


Fig. 5. $\chi^{(3)}$ values versus time for 5×10^{-3} mol/L dichloromethane solution of *cis*- $\text{Mo}(\text{CO})_4(\text{AsPh}_3)_2$. a) excess free ligand (1:1) added initially, b) ligand added 30 min. later, c) without added ligand.

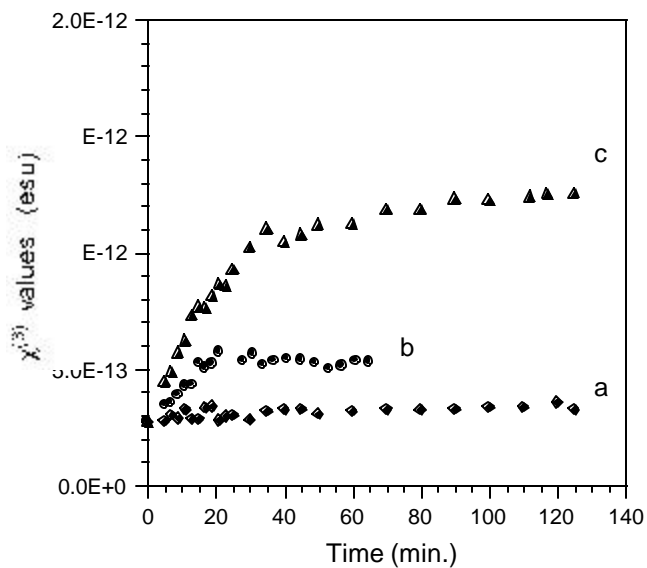


Fig. 6. $\chi^{(3)}$ values versus time for 1×10^{-2} mol/L dichloromethane solution of *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_2\text{Np})_2$. a) excess free ligand (1:1) added initially, b) ligand added 30 min. later, c) without added ligand.

Table 1 The $\chi^{(3)}$ values of dichloromethane solutions of four molybdenum complexes
(Concentration: 3×10^{-2} mol/L)

Complex	$\chi^{(3)}$ (esu)
<i>cis</i> -Mo(CO) ₄ (PPh ₃) ₂ (adding ligand initially)	3.8×10^{-13}
<i>cis</i> -Mo(CO) ₄ (AsPh ₃) ₂ (adding ligand initially)	4.2×10^{-13}
<i>cis</i> -Mo(CO) ₄ (PPh ₂ Np) ₂ (adding ligand initially)	4.2×10^{-13}
<i>cis</i> -Mo(CO) ₄ (P(OPh) ₃) ₂	3.9×10^{-13}