Non-linear optical properties of the mixed-metal mixed-chalcogen clusters $[Fe_2(CO)_6\{\mu\text{-}SeC(Ph)=C(Se)\}\{(OEt)C=Cr(CO)_5\}]$ and $[Fe_2(CO)_6Se_2\{\mu\text{-}(CO)_3Cr(\eta^5\text{-}C_5H(CH_2Ph)(Ph)(OEt))\}]$

Reji Philip [a,1], G. Ravindra Kumar [a,*], P. Mathur [b], S. Ghosh [b]

[a] *Tata Institute of Fundamental Research, Colaba, Bombay 400 005, India*
[b] *Department of Chemistry, Indian Institute of Technology, Bombay 400 076, India*

Abstract

We report studies of the third-order optical non-linearity of the newly synthesized butterfly-shaped mixed-metal mixed-chalcogen clusters $[Fe_2(CO)_6\{\mu\text{-}SeC(Ph)=C(Se)\}\{(OEt)C=Cr(CO)_5\}]$ and $[Fe_2(CO)_6Se_2\{\mu\text{-}(CO)_3Cr(\eta^5\text{-}C_5H(CH_2Ph)(Ph)(OEt))\}]$ using 532 nm, 6 ns laser pulses. Their effective non-linear absorption coefficient and non-linear index intensity coefficient are measured by the *z*-scan technique from which the corresponding cubic hyperpolarizabilities are evaluated. The obtained values indicate a high non-linearity comparable to some of the best values reported previously for cluster compounds. Both compounds show strong optical limiting, and the second compound exhibits non-linear scattering. Their photostability is superior to many of the previously reported highly non-linear clusters.

---

1. Introduction

Non-linear optics (NLO) is one of the few research areas where great interest has been shown in recent years, owing to the richness of various novel phenomena unraveled by this exciting field of study. Some of its applications include harmonic generation, frequency up/down conversion, electro-optic modulation, parametric amplification, high-speed optical gating and optical limiting [1,2]. Several NLO materials have been developed over the years. For example, Garito and Wu [3] have reported absorptive optical bistability in silicon naphthalocyanine oligomer (SINC) thin films and Cahill [4] has described NLO waveguides made from transition metal–ruthenium dye complexes. The current status of optical limiting and the variety of limiters being used have been discussed in detail by Bogess and Tutt [5] and, in two recent papers, Nalwa [6] and Long [7] have reviewed the importance of organometallic materials to NLO.

Recently it has been found that transition-metal–chalcogenide clusters possess large NLO properties due to their cage/nest-like structures which favour a large field-induced electron delocalization. Following early reports [8,9], several clusters were studied which yielded high values of the non-linearity parameters [10–15]. A special advantage of metal–chalcogenide clusters is that, in a sense, they possess the combined strength of organic polymers and semiconductors. On the one hand, metal–chalcogenide clusters contain many heavy atoms resembling semiconductors, thereby introducing more sublevels into the energy continuum in comparison to organic molecules with the same number of skeletal atoms. This leads to more allowed electronic transitions, and hence an enhanced non-linearity. On the other hand, both the skeletal and terminal elements of the chalcogenide clusters can be altered and/or removed as in organic molecules so that an optimization of the NLO properties can be realized through structural manipulation. These characteristics of chalcogenide clusters make them attractive candidates for NLO experimentation.

As part of our efforts to synthesize cluster compounds suitable for NLO applications, we recently observed that the homo- and mixed-chalcogenide compounds $Fe_2(CO)_6(\mu\text{-}EE')$ (where $E \neq E'$ and $E,E' = S,Se,Te$) readily add to the activated triple bond of alkynyl carbene complexes of the Fischer-type $(CO)_5M{=}C(OEt)C{\equiv}CPh$ (where M = Cr or W). The metal–carbene fragment $Fe_2(CO)_6\{\mu\text{-}SeC(Ph){=}C(Se)[(OEt)C{=}Cr(CO)_5]\}$ (compound I), a synthetically useful function which remains intact in the trimetallic adduct, offers many interesting possibilities of chemical modification of the organic appendage to the cluster. The structure of compound I can be described as an Fe_2EE' tetrahedral butterfly core containing the alkynyl Fischer carbene as a bridge between the two wingtip chalcogens with three terminally bonded carbonyl groups on each Fe atom. When a tetrahydrofuran (THF) solution containing compound I is heated under reflux in an argon atmosphere for 2.5 h, formation of a new red-coloured complex $[Fe_2(CO)_6Se_2\{\mu\text{-}(CO)_3Cr(\eta^5\text{-}C_5H(CH_2Ph)(Ph)(OEt))\}]$ (compound II) is observed, which is isolated from the reaction medium by chromatography using silica gel TLC plates. Its structure can best be described as consisting of a $CO_3Cr\{(\eta^5\text{-}C_5H(CH_2Ph)(Ph)(OEt))\}$ moiety attached to the Se atoms of the open butterfly unit of $Fe_2(CO)_6(\mu\text{-}Se)_2$. The absorption spectra of these compounds dissolved in *n*-hexane are shown in Fig. 1. Details of their synthesis, spectroscopic data and structure determination have been published elsewhere [16–18].

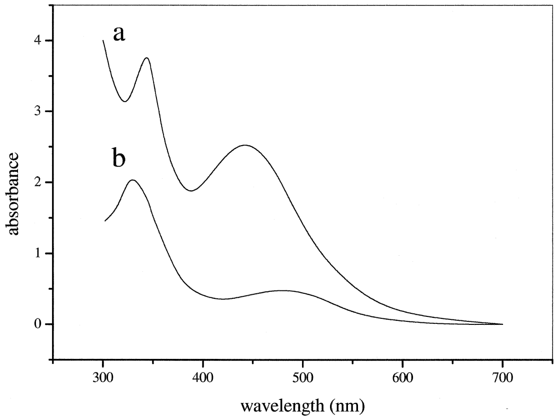

Fig. 1. Visible spectra of the compounds taken in a 1 cm cuvette (a) compound I at 1.6×10^{-4} mol/lt, (b) compound II at 1.1×10^{-4} mol/lt.

In this Letter, we report the measurement of the NLO parameters of these compounds, carried out using the *z*-scan [19] technique. The second harmonic output of a Q-switched Nd:YAG laser (532 nm, 6 ns, 5 Hz plane polarized pulses) is used to excite sample solutions prepared in *n*-hexane. At 532 nm, the absorption cross-sections of compounds I and II are found to be 1.9×10^{-17} cm^2 and 9.4×10^{-18} cm^2, respectively. The pure solvent does not show any non-linearity at the light intensities used ($\leqslant 230$ MW cm^{-2} at the focus, where the beam spot size is 28 μm). Solution concentrations are adjusted to give a linear optical transmission of approximately 70% at the excitation wavelength. We have calculated the *effective* values of the non-linear absorption coefficient (β_{eff}) and non-linear index intensity coefficient (γ_{eff}) of these compounds, from which the corresponding cubic hyperpolarizabilities $\langle\gamma\rangle_{eff}$ are determined. These values are compared with those reported in literature for other clusters of different geometries. In addition, the optical limiting performance as well as the photostability of these compounds also has been examined.

2. Results and discussion

It is well known that in media with inversion symmetry the lowest non-linearity is of the third order and that the real and imaginary parts of the

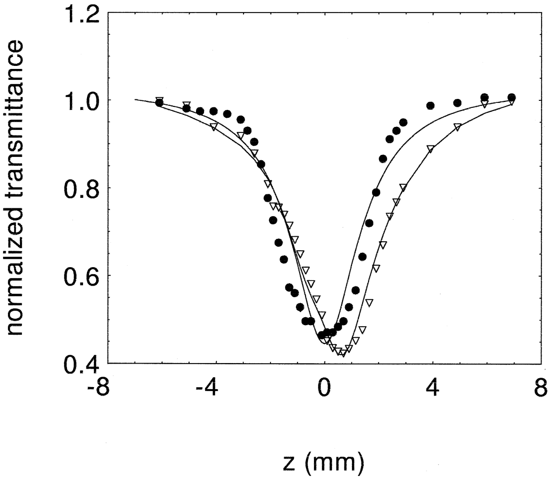

Fig. 2. *z*-Scan of compound I. Filled circles: open-aperture data; triangles: closed-aperture data. Solid curves are the best numerical fits.

third-order non-linear susceptibility $\chi^{(3)}(-\omega; \omega, \omega, -\omega)$ correspond to the intensity-dependent refractive index and two-photon absorption in the medium, respectively. In the presence of a strong light field, the modified absorption coefficient α and refractive index n are given by $\alpha = \alpha_0 + \beta I$ and $n = n_0 + \gamma I$ where α_0 (m^{-1}) and n_0 are the linear absorption coefficient and linear refractive index, respectively, I ($\mathrm{W\,m}^{-2}$) is the incident light intensity, β ($\mathrm{m\,W}^{-1}$) is the two-photon absorption coefficient and γ ($\mathrm{m}^2\,\mathrm{W}^{-1}$) is the non-linear index intensity coefficient.

The above equations are valid for instantaneous non-linear polarization involving virtual or bound intermediate excited states of a normally transparent sample. However, for clusters with moderate absorption at the excitation wavelength, the heavy atoms can facilitate intersystem crossing via spin–orbital coupling leading to non-linear losses by reverse saturable absorption (RSA) [13]. This effect is seen in other systems as well, including C_{60} and phthalocyanines where RSA is the major contributor to optical limiting [20–22]. The above equations can be modified to accommodate RSA while retaining the convenient formalism developed for describing the instantaneous non-linearity, by defining a set of *effective* non-linear parameters β_{eff}, γ_{eff} and $\chi^{(3)}_{\mathrm{eff}}$ [20]. The modified absorption coefficient can now be written as $\alpha = \alpha_0 + \beta_{\mathrm{eff}}\,\mathrm{I}$ where β_{eff} is an *effective* value for the non-linear absorption coefficient, given by $\beta_{\mathrm{eff}} = [\mathrm{S}_0]\alpha_0\alpha_{\mathrm{T}}$, where $[\mathrm{S}_0]$ is the ground state population and α_{T} is the triplet state absorption coefficient. Since the triplet population is intensity dependent, β_{eff} also becomes intensity dependent unlike β. Similarly, the equation for the modified refractive index becomes $n = n_0 + \gamma_{\mathrm{eff}}\,\mathrm{I}$ where γ_{eff} is an *effective* value for the non-linear index intensity coefficient. When RSA is dominant γ_{eff} is proportional to the product $n_0 n_{\mathrm{T}}$, where n_{T} is the triplet state linear refractive index. Obviously γ_{eff} is also intensity dependent unlike γ. The quantities of interest, β_{eff} and γ_{eff}, can be measured by the *z*-scan experiment.

Fig. 2 shows the open- and closed-aperture *z*-scans obtained for compound I at a concentration of 4.5×10^{-4} mol/dm^3. Fig. 3 depicts those obtained for compound II, at a concentration of 1.5×10^{-3} mol/dm^3. Filled circles denote open-aperture data whereas triangles represent closed-aperture data. The solid curves are the best numerical fits obtained using the *z*-scan transmission equations for a cubic non-linearity, and the good agreement between theory and experiment reveals that the non-linearity is mainly of third order. However, it may be noted that the experimental points are slightly steeper than the best theoretical fits at the base of the curves. In addition, the peak and valley of the closed-aperture

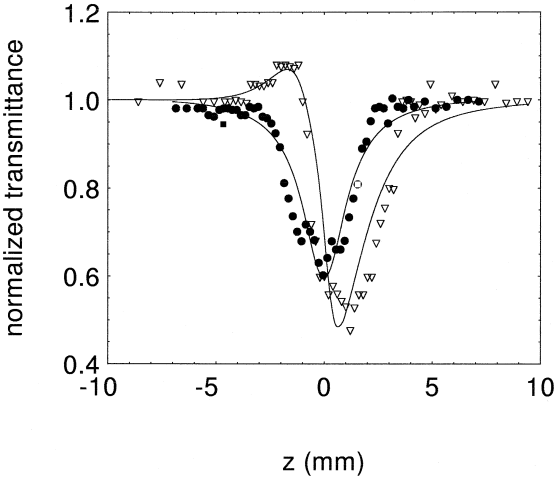

Fig. 3. *z*-Scan of compound II. Filled circles: open-aperture data; triangles: closed-aperture data. Solid curves are the best numerical fits.

scan are not exactly equidistant from the $z = 0$ point in Fig. 3. Both these features are indicative of the weak presence of higher-order non-linearities in addition to third-order processes in the media [19]. Furthermore, it may be observed that the experimental points show more ‘scatter’ in Fig. 3. This is in fact due to the presence of non-linear light scattering [23,24] in compound II at higher intensities, which could be clearly observed in the far field. Interestingly, compound I, from which compound II was derived, did not show any such scattering. From the numerical fits, values of $\beta_{\text{eff}} = 6.8 \times 10^{-10}$ m W^{-1} and $\gamma_{\text{eff}} = -5.3 \times 10^{-17}$ m^2 W^{-1} are obtained for compound I, and $\beta_{\text{eff}} = 5.5 \times 10^{-10}$ m W^{-1} and $\gamma_{\text{eff}} = -6.3 \times 10^{-17}$ m^2 W^{-1} for compound II. The negative signs in the γ_{eff} values show that both compounds have a self-defocusing-type non-linearity.

Figs. 4 and 5 give the optical limiting performance of the samples at concentrations corresponding to linear transmittances not less than 70%. The transmittance defined here is the ratio of the transmitted energy to the incident energy. It can be seen that the limiting threshold (incident fluence at which the solution transmittance falls to 50% of the linear transmittance) for both samples is around 1 J cm^{-2}. This value is better than that of the benchmark optical limiter C_{60} which has a limiting threshold of 1.6 J cm^{-2} in toluene at a linear transmittance of 62% [25].

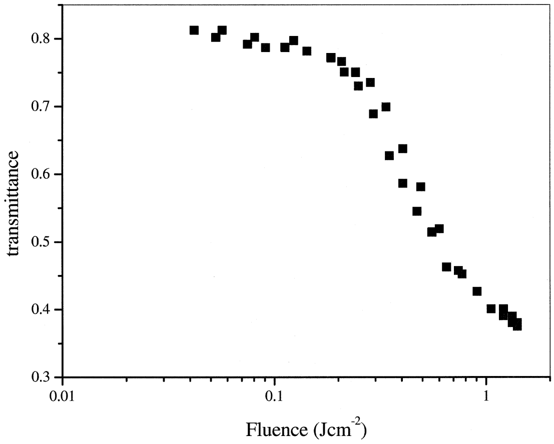

Fig. 4. Optical limiting behaviour of compound I. Limiting threshold is approximately 1 J cm^{-2}.

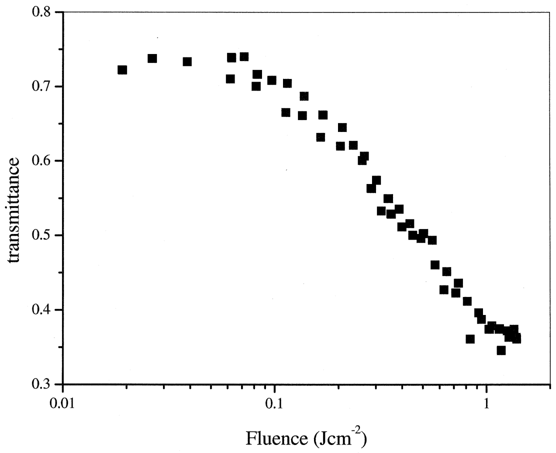

Fig. 5. Optical limiting behaviour of compound II. Limiting threshold is approximately 1 J cm^{-2}.

The cubic hyperpolarizability values calculated from β_{eff} and γ_{eff} are found to be 8.5×10^{-29} esu for compound I and 2.1×10^{-29} esu for compound II, respectively. These may be compared with some of the best values reported recently for different clusters of various geometries at 532 nm: 1.6×10^{-28} esu for a half-open cubane-like $[WOS_3(CuBr)_3(\mu_2\text{-}Br)]^{3-}$ [12], 2.8×10^{-29} esu for another half-open cubane-like $[Et_4N]_3[WOS_3(CuI)_3(\mu_2\text{-}I)] \cdot H_2O$ [11], 4.8×10^{-29} esu for a nest-shaped $[MoOS_3(CuNCS)]^{2-}$ [13], 9.0×10^{-29} esu for a butterfly-shaped $[WOS_3Cu_2(PPh_3)_4]$ [10], 3.3×10^{-32} esu for *trans*-$[Mo(CO)_4(PPh_3)_2]$ and 1.7×10^{-31} esu for *cis*-$[Mo(CO)_4(PPh_3)_2]$ [14]. Obviously, the present compounds can be classified among the best non-linear clusters reported so far in literature.

It is important to note here that many of the previously investigated highly non-linear clusters possessing intact structures are nevertheless prone to fast photodegradation, necessitating low input energies and very low pulse repetition rates (< 1 Hz) to ensure stability. Obviously, this will impose severe constraints on their utility as practical optical limiters. For example, in cubane-like structures the cage skeletons have great strength due to the $\mu 3$ bridging mode of the constituent metals and chalcogens. However, photo-induced damage still occurs with 1–2 Hz laser pulses above a fluence of 3 J cm^{-2} due to the light-induced terminal ligand substitution by the solvent [8,9]. It is suggested that this weakness can be overcome by incorporating the clusters into polymer hosts, but the obvious penalty is that they will lack healing capability after a chance photodamage. However, we found that the currently investigated compounds are quite photostable in liquid form. For instance, the linear absorbance at 532 nm of a dilute 1 mm thick solution of compound I in *n*-hexane remained the same even after a continuous irradiation by 5 Hz laser pulses at a fluence of 9 J cm^{-2} for 1 h. Compound II showed such stability upto a fluence of 5 J cm^{-2}, and when the fluence was increased to 9 J cm^{-2}, its linear absorbance in fact increased by 14%. It appears that this behaviour of compound II is either due to a photochemical change, or is probably related to the large non-linear scattering exhibited by this cluster at high fluences. More studies are required to further understand the mechanism in this sample.

No definite methodology is available at present to calculate and quantitatively correlate the NLO properties of a given cluster to its structural ramifications. In general, the optical limiting capability is found to increase with the incorporation of more heavy atoms due to an enhanced intersystem crossing rate, and substitution at skeletal positions is found to have a stronger influence than substitution at terminal positions [8,9]. Furthermore, in transition metal clusters containing many ionizable low-valence IB elements and chalcogenides, apart from intersystem crossing the process of ionization and germinate recombination can also populate the triplet levels [11]. Polar solvents can enhance such processes as compared to non-polar solvents. In fact according to an empirical classification, butterfly-shaped clusters exhibit strong non-linear refraction, cubane-like show strong non-linear absorption, nest-shaped and twin nest-shaped show strong non-linear absorption and self-defocusing, and hexagonal prism clusters are strongly limiting [26]. However, there are notable exceptions to this rule, as in the case of the compounds $[WOS_3Cu_3I(py)_5]$ and $[MoOS_3Cu_3I(py)_5]$ which possess similar molecular structures but have opposite non-linear refractive properties. In fact by mixing them together, the non-linearity can be continuously altered from a self-focusing to self-defocusing type [27]. Likewise, even though the present clusters can be included in the butterfly-shaped category, our results show that they have a stronger non-linear absorption in comparison to their refractive non-linearity.

3. Conclusions

We have calculated the non-linear optical parameters of the recently synthesized, butterfly-shaped clusters $[Fe_2(CO)_6\{\mu\text{-}SeC(Ph)=C(Se)\}\{(OEt)C=Cr(CO)_5\}]$ and $[Fe_2(CO)_6Se_2\text{-}\{\mu\text{-}(CO)_3Cr(\eta^5\text{-}C_5H(CH_2Ph)(Ph)(OEt)\}]$, and investigated their optical limiting performance. The cubic hyperpolarizabilities obtained are comparable to the best values reported to date for cluster compounds. Their optical limiting thresholds are found to be better than that of C_{60}. RSA is believed to be the major cause of their non-linear absorption and optical limiting, even though non-linear light scattering also plays a role in compound II. The photostability of these compounds, particularly that of compound I, is found to be much better than that of several reported clusters, thereby making them more suitable for practical optical limiting applications.

Acknowledgements

We acknowledge useful discussions with Sudeep Banerjee. R.P. wishes to thank the management of Sacred Heart College, Thevara, Cochin, for the grant of a study leave.

References

[1] J.L. Bredas, R.R. Chance (Eds.), Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics, Kluwer Academic Publ., Dordrecht, 1990.
[2] S.R. Marder, J.E. Sohn, G.D. Stucky (Eds.), Materials for Nonlinear Optics: Chemical Perspectives, ACS Symposium series 455, American Chemical Society, 1990.
[3] A.F. Garito, J.W. Wu, SPIE Proc. 1147 (1989) 2.
[4] P.A. Cahill, Mater. Res. Soc. Proc. 109 (1988) 319.
[5] L.W. Tutt, T.F. Boggess, Prog. Quantum Electr. 17 (1993) 299.
[6] H.S. Nalwa, Appl. Organomet. Chem. 5 (1991) 349.
[7] N.J. Long, Angew. Chem. Int. Ed. Engl. 34 (1995) 21.
[8] S. Shi, W. Ji, J.P. Lang, X.Q. Xin, J. Phys. Chem. 98 (1994) 3570.

[9] S. Shi, W. Ji, S.H. Tang, J.P. Lang, X.Q. Xin, J. Am. Chem. Soc. 116 (1994) 3615.

[10] S. Shi, H.W. Hou, X.Q. Xin, J. Phys. Chem. 99 (1995) 4050.

[11] W. Ji, H.J. Du, S.H. Tang, S. Shi, J. Opt. Soc. Am. B 12 (1995) 876.

[12] Z.R. Chen, H.W. Hou, X.Q. Xin, K.B. Yu, S. Shi, J. Phys. Chem. 99 (1995) 8717.

[13] S. Shi, W. Ji, W. Xie, T.C. Chong, H.C. Zeng, J.P. Lang, X.Q. Xin, Mater. Chem. Phys. 39 (1995) 298.

[14] T. Zhai, C.M. Lawson, D.C. Gale, G.M. Gray, Opt. Mater. 4 (1995) 455.

[15] S. Banerjee, G. Ravindra Kumar, P. Mathur, P. Sekar, Chem. Commun., 1997, p. 299.

[16] P. Mathur, S. Ghosh, A. Sarkar, C.V.V. Satyanarayana, A.L. Rheingold, L.M. Liable-Sands, Organometallics 16 (1997) 3536.

[17] P. Mathur, S. Ghosh, A. Sarkar, C.V.V. Satyanarayana, V.G. Puranik, Organometallics 16 (1997) 4392.

[18] P. Mathur, S. Ghosh, A. Sarkar, A.L. Rheingold, I.A. Guzei, Organometallics 17 (1998) 770.

[19] M. Sheik-Bahae, A.A. Said, T.H. Wei, D.J. Hagan, E.W. Van Stryland, IEEE J. Quantum Electron. 26 (1990) 760.

[20] S. Couris, E. Koudoumas, A.A. Ruth, S. Leach, J. Phys. B. At. Mol. Opt. Phys. 28 (1995) 4537.

[21] J.W. Perry, L.R. Khundkar, D.R. Coulter, D. Alvarez Jr., S.R. Marder, T.H. Wei, M.J. Sence, E.W. Van Stryland, D.J. Hagan, in: J. Messier (Ed.), Organic Molecules for Nonlinear Optics and Photonics, Kluwer Academic Publ., 1991.

[22] C. Li, L. Zhang, M. Yang, H. Wang, Y. Wang, Phys. Rev. A 49 (1994) 1149.

[23] B.L. Justus, A.J. Campillo, A.L. Huston, Opt. Lett. 19 (1994) 673.

[24] V. Joudrier, P. Bourdon, F. Hache, C. Flytzanis, Appl. Phys. B 67 (1998) 627.

[25] A. McLean, R.L. Sutherland, M.C. Brant, D.M. Brandelik, P.A. Fleitz, T. Pottenger, Opt. Lett. 18 (1993) 858.

[26] H. Hongwei, L. Bin, X. Xinquan, Y. Kaibei, G. Pin, J. Wei, S. Shi, J. Chem. Soc. Faraday Trans. 92 (1996) 2343.

[27] P. Ge, S.H. Tang, W. Ji, S. Shi, H.W. Hou, D.L. Long, X.Q. Xin, S.F. Lu, Q.J. Wu, J. Phys. Chem. B 101 (1997) 27.