attributable to the enhanced π-delocalization, which further supports the results of NMLO analysis.

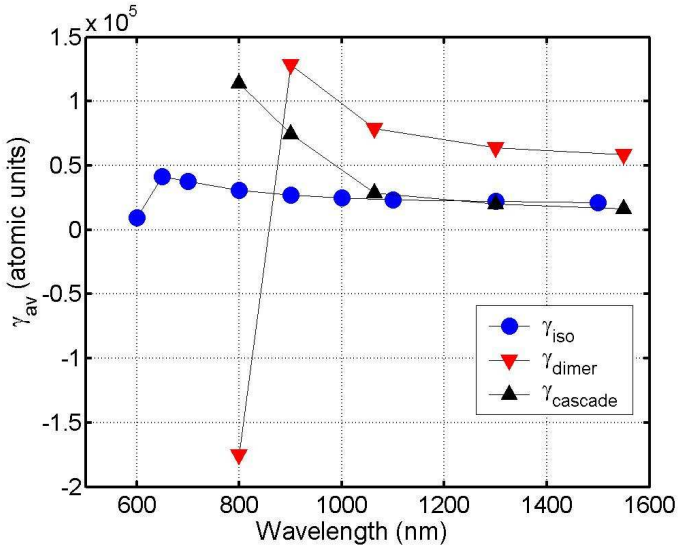

Fig. 5. Dispersion plots of γ_{av}.

It is worthwhile to also note that preliminary non-hybrid all-electron relativistic TDDFT computations on (*para*)nitroaniline molecules linked to a tetrahedral Au_{20} cluster delivered up to two orders of magnitude enhancement of the second hyperpolarizability. Although this enhancement is possibly overestimated in these computations, these results suggest that a combination of microscopic cascading with electromagnetic and chemical enhancement from a metal cluster has the potential to push $\chi^{(3)}$ to magnitudes far exceeding current limits. These computations are on-going; the results will be published elsewhere [27].

4. Conclusion

To conclude, we developed a simple phenomenological model of microscopic cascading based on local dipole-dipole interaction of neighboring molecules. A*b initio* computations of first and second hyperpolarizabilies of para-nitroaniline and dimers thereof substantiated the model and suggest a design protocol for obtaining materials with particularly large values of the real part of third-order nonlinearity. The most obvious way to increase the real part of the direct (as opposed to cascaded) contribution to the second polarizability, γ, is to use resonant enhancement. Unfortunately, the imaginary part will inevitably grow as one approaches one- or two-photon resonance of a molecule. Our design protocol allows for using molecules with a large real part of the first hyperpolarizability, β, to generate a large real part of second hyperpolarizability, γ, without introducing extra loss, because molecular resonances, in particular two-photon resonance, are not involved.

Acknowledgments

This work was supported by a seed grant from the Office of Vice President for Research at the University at Buffalo. The authors are grateful to Prof. Hans Ågren of KTH, Stockholm for valuable discussion. R. W. Boyd acknowledges support by a MURI grant from the U. S. Army Research Office (USARO). J. Autschbach acknowledges support from the National Science Foundation (NSF) (grant CHE 447321).

#124706- $15.00USD Received 25 Feb 2010; accepted 28 Mar 2010; published 9 Apr 2010