Modeling Intermolecular Effects on Nonlinear Optical Properties of Transition-Metal Complexes. An Effective Core Potential Study

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An initial effort to study the nonlinear optical (NLO) properties of interacting transition-metal−oxo complexes is presented and studied by effective core potential approaches. Osmium tetroxide is used for this study. Favorable intermolecular interaction effects, even within this weak interaction regime, that yield enhancements in NLO properties have been found. Interaction effects increase α (polarizability) up to 6% and γ (second hyperpolarizability) up to 100% relative to the isolated monomer result for OsO_4. The magnitude of the interaction (hyper)polarizabilities, and indeed even the sign, is found to be quite sensitive to the relative orientation of the osmium tetroxide monomers.

INTRODUCTION

Nonlinear optical (NLO) properties are of interest wherever the interaction of light and matter is important, e.g., optical computing or laser and fiber optical materials.[2] Inorganic crystals, such as lithium niobate ($LiNbO_3$), barium titanate ($BaTiO_3$), and potassium dihydrogen phosphate (KH_2PO_4),[3] are the first and still belong to the most important NLO materials in application. Computational studies of inorganic solids have been reported.[4] For example, Harrison and co-workers have published a series of papers on the nonlinear optical properties of potassium titanyl phosphate using molecular models.[4] There has also been recent interest, experimental and computational, in the nonlinear optical properties of metal−organic species.[5]

In the present paper we seek to investigate the effect of intermolecular interactions, with respect to both the energetics and relative orientation of the interacting monomers, on the polarizability and hyperpolarizability of a prototypical transition-metal (TM) complex. The interactions being considered are in a considerably weaker regime than those expected in an ionic solid. However, calculations by Chen and Kurtz for model organic polymers showed that even weak intermolecular interactions between neutral species can significantly attenuate NLO properties for some molecular orientations.[6] Hence, we sought to extend this research to an inorganic species. Osmium tetroxide was chosen for study since previous work[7] from our lab focused on the NLO properties of the monomer, particularly with respect to the development of reliable (yet computationally efficient) basis sets for inorganic TM complexes. Cundari et al. reported in previous papers that a reliable and efficient basis set for NLO property calculations for transition-metal oxides was found to be a good energy basis set (for the main group ligands) augmented by several extra very diffuse s, p, and d orbital functions to sufficiently and accurately describe the induced polarization of electrons.[7] NLO property calculations were found to be less sensitive to modifications of the TM basis set, a result consistent with their high formal oxidation states in the complexes studied.[7] Furthermore, OsO_4 is a prototypical, neutral metalate whose experimental geometry and polarizability (Os−O = 1.712 Å; α = 55.1 au) are known.[8]

COMPUTATIONAL METHODS

In this study, $(OsO_4)_2$ dimers are fixed to six different orientations, Figure 1, with a variable intermolecular distance indicated by the separation distance between the two Os atoms. The RHF/SBK(d) optimized geometry is utilized for each OsO_4 monomer.[7] A test RHF/SBK(d) geometry optimization of corner-to-corner oriented $(OsO_4)_2$ with an Os•••Os distance fixed at 6.0 Å results in only a 0.001 Å increase in the Os−O bond length versus that in the monomer. The corresponding effects of the geometric distortion on energy and (hyper)polarizabilities are all less than 1%. Thus, geometry optimization is not performed for the different $(OsO_4)_2$ conformations depicted in Figure 1.

A supermolecule approach[6] is applied to calculate the intermolecular interaction effects in $(OsO_4)_2$ dimer models. For a dimer, interaction properties (ΔP) are defined as

$$\Delta P(R) = P(R)_{dimer} - 2P_{monomer} \tag{1}$$

and the relative properties (P_{rel}) are defined as

$$P_{rel}(R) = P(R)_{dimer}/2P_{monomer} \tag{2}$$

where R is the separation distance between the two Os atoms.

For NLO property calculations, polarizabilities (α) and the second hyperpolarizabilities (γ) are calculated at the RHF level using the TDHF[9] method. All calculations are done with the GAMESS program.[10] The reported $\langle\alpha\rangle$ and $\langle\gamma\rangle$ results are the static field (dc) isotropic average values defined respectively by

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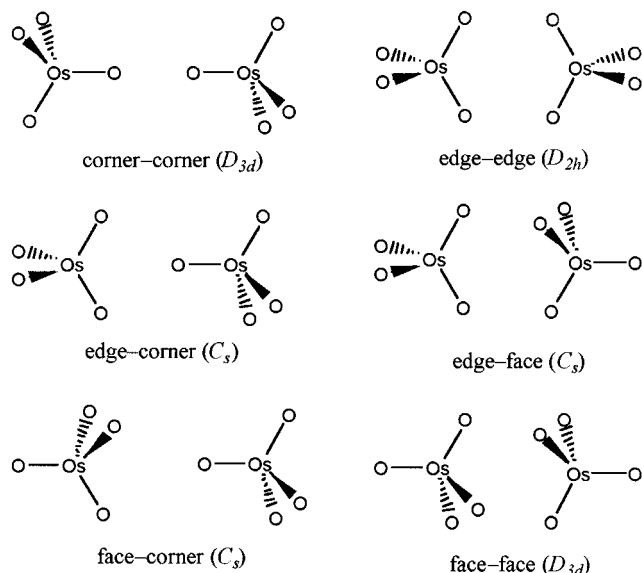
Figure 1. Osmium tetroxide dimers with the specified point group symmetry in six different orientations. The local symmetry of each OsO_4 unit is T_d.

$$\langle \alpha \rangle = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \qquad (3)$$

and

$$\langle \gamma \rangle = [\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})]/5 \quad (4)$$

The first hyperpolarizability (β) is excluded as it is zero by symmetry for some of the dimers.

Reliable calculation of NLO properties requires more careful attention to SCF convergence than typical electronic structure calculations.[11] Hence, the following GAMESS options were employed:[10] ICUT = 20 (integrals less than 10^{-20} are ignored; default, ICUT = 9), ITOL = 30 (products of primitives whose preexponential factor is less than 10^{-30} are skipped; default, ITOL = 20), INTTYP = HONDO (HONDO/Rys integrals used for all integral evaluations, slightly more accurate but slower than the default, INTTYP = POPLE), and NCONV = 10 (convergence is reached when the absolute value of the density change between two consecutive SCF cycles is less than 10^{-10}; default, NCONV = 10^{-5}).

Given the size of the dimers involving two TMs as heavy as osmium, an ECP/VBS scheme is the only feasible computational approach. On the basis of a previous comprehensive study of basis set effects on NLO properties of TM metalates, $[MO_4]^{q-}$,[7a] the standard SBK[12] and the compact SBK + ELP-pdd′ [13] basis sets are employed for osmium and oxygen, respectively, to calculate the interacting NLO properties of $(OsO_4)_2$ dimers. The latter is the SBK[12] basis set for oxygen augmented with a set of diffuse s ($\zeta = 0.06$), diffuse p ($\zeta = 0.05$), and polarization d ($\zeta = 0.13$) functions extracted from Dykstra's electrical properties (ELPs) basis.[14] Our previous research suggests that NLO properties are much less sensitive to the TM basis set, a result consistent with the high formal oxidation state of the TM. Details about the competence of these basis sets and the ECPs for NLO calculations of inorganic TM complexes can be found elsewhere.[7a] Results regarding $(OsO_4)_2$ dimers are given in Tables 1−5.

Table 1. Results for Isolated OsO_4^a

energy (au)	−152.8736
α (au)	44.8
γ (au)	2394

[a] Results were obtained at the RHF level without counterpoise correction for the BSSE. Basis set: Os, SBK; O, SBK + ELP-pdd′.

RESULTS AND DISCUSSION

1. Interaction Energies. Figure 2 shows the interaction energies for the systems studied, calculated from the data in Tables 1 and 2 by eq 1. For each orientation of dimers, conformers with R shorter than the minimal R shown in the figure are excluded, because the resulting interaction energies are all over 50 kcal/mol and outside the regime of interest− weakly interacting dimer systems. For all orientations, calculated energies with no counterpoise correction (NCP; solid lines) for the basis set superposition error (BSSE)[15] show both repulsive (at shorter R) and attractive (at longer R) features. A lowest point is seen for each NCP energy curve, indicating a preferred separation distance for each orientation. Overall, as indicated by the comparison of the most negative interaction energies, the three configurations of $(OsO_4)_2$ with an oxo of a monomer (corner of a tetrahedron) directly pointing at the other monomer (A, B, and C of Figure 2) are more favorable than the other three orientations (D, E, and F of Figure 2), and the corner-to-corner (A) orientation at R = 6.0 Å and face-to-corner (C) orientation at R = 4.75 Å seem to be the two preferred configurations.

For these supermolecule models of dimer systems, the BSSE is assessed by the counterpoise correction (CP).[16] It is found that the BSSE has a big impact on the energetics of $(OsO_4)_2$ dimer systems. Figure 2 also shows the counterpoise-corrected (dashed lines) interaction energies of all systems calculated from the data in Tables 2 and 5. It is seen that CP energy shapes change dramatically in comparison with the NCP trends. The CP energies become purely repulsive and are positive at all separation distances. Such a large magnitude of the BSSE should be correlated with the nature of the specific basis set, SBK + ELP-pdd′,[14] used in the calculations. This efficient NLO basis set is generated from the SBK basis by augmenting with diffuse s, p, and d orbital functions.[7a] The incompleteness of the basis sets used in most calculations and the overlap of the orbitals of the two moieties in a dimer are considered to be the two main origins of the BSSE.[15] Thus, the BSSE is most important for calculations employing intermediate-sized basis sets with nonlocalized, diffuse functions that have inherently more overlap with adjacent atomic sites, particularly in the calculation of weak interaction energies.[15]

The magnitude of the BSSE shown in Figure 2 may also be partly due to the inherent errors in employing the counterpoise correction. The CP correction tends to overestimate the BSSE, and thus the BSSE is difficult to calculate accurately.[15] Thus, the "correctly" calculated interaction energies fall most likely somewhere between the NCP and CP lines. For all dimer systems, both CP and NCP interaction energies are ≤10 kcal/mol for R ≥ 5 Å, indicating the weakly interacting nature of the monomers in $(OsO_4)_2$.

2. Polarizabilities. The interaction polarizabilities ($\Delta \alpha$) of $(OsO_4)_2$ are calculated from the data in Tables 1 and 3.
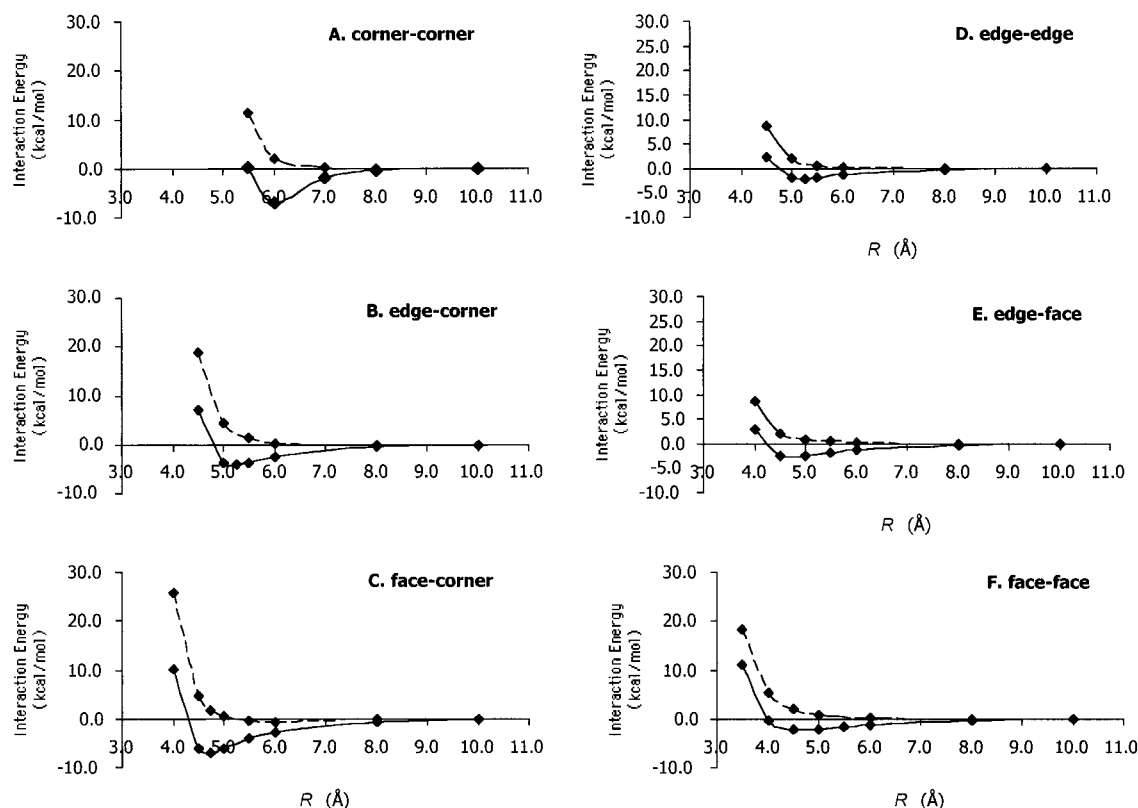
Figure 2. Interaction energy of $(OsO_4)_2$ dimers in six different orientations. Dashed lines are CP results. Solid lines are NCP results.

Table 2. $(OsO_4)_2$ Energies (au)[a]

Os⋯Os distance (Å)	corner−corner	edge−corner	face−corner	edge−edge	edge−face	face−face
3.50						−305.7295
4.00			−305.7308		−305.7427	−305.7477
4.50		−305.7358	−305.7570	−305.7434	−305.7509	−305.7507
4.75			−305.7580			
5.00		−305.7529	−305.7569	−305.7503	−305.7512	−305.7504
5.25		−305.7536		−305.7505		
5.50	−305.7466	−305.7530	−305.7536	−305.7500	−305.7502	−305.7498
6.00	−305.7583	−305.7510	−305.7514	−305.7490	−305.7493	−305.7493
7.00	−305.7503					
8.00	−305.7477	−305.7479	−305.7480	−305.7478	−305.7478	−305.7477
10.00	−305.7474	−305.7473	−305.7474	−305.7472	−305.7472	−305.747

[a] Results are obtained at the RHF level. Basis set: Os, SBK; O, SBK + ELP-pdd′.
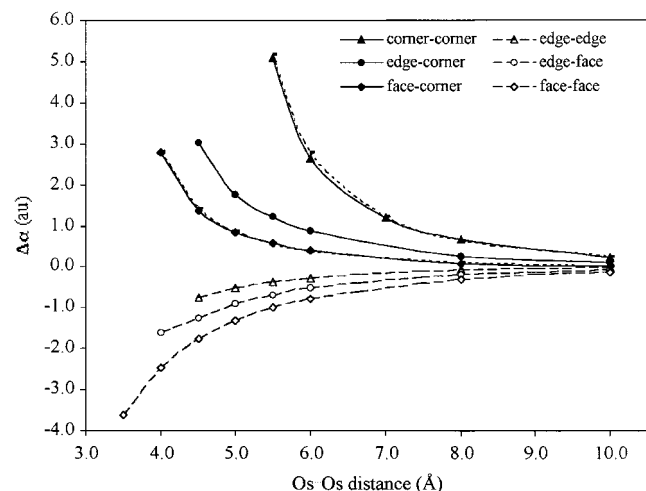
Table 3. $(OsO_4)_2$ Polarizabilities (au)[a]

Os⋯Os distance (Å)	corner−corner	edge−corner	face−corner	edge−edge	edge−face	face−face
3.50						85.9
4.00			92.3		87.9	87.0
4.50		92.5	90.9	88.8	88.3	87.7
5.00		91.3	90.4	89.0	88.6	88.2
5.50	94.6	90.7	90.1	89.2	88.8	88.5
6.00	92.2	90.4	89.9	89.2	89.0	88.7
7.00	90.7					
8.00	90.2	89.8	89.6	89.4	89.3	89.2
10.00	89.7	89.6	89.5	89.5	89.4	89.4

[a] Results are obtained at the RHF level. Basis set: Os, SBK; O, SBK + ELP-pdd′.

Results are illustrated in Figure 3. The interaction effects fall into two categories—positive and negative. For the three orientations with a corner (i.e., an oxo ligand) of an OsO_4 monomer pointing at the other monomer, the intermolecular interactions have a positive effect and thus increase α. For the other three dimer orientations, the intermolecular interactions are negative and thus decrease α. The dimer conformation with minimal "contact" between the two monomers, i.e., corner-to-corner, yields the biggest increment in α (~5 au at $R = 5.5$ Å). In contrast, the dimer orientation with the maximal contact between the two monomers, face-to-face, results in the biggest attenuation in α (~4 au at $R = 3.5$ Å). Overall, intermolecular interactions tend to be more favorable (increasing α) in dimers when the interacting surface between the two monomers becomes smaller. It is seen that positive interactions increase the α value per OsO_4 monomer (α_{rel}, calculated from the data in Tables 1 and 3 by eq 2) up to 6% at $R = 5.5$ Å versus the isolated OsO_4 result, while the negative interactions diminish α_{rel} by as much as 4% at $R = 3.5$ Å.

For two orientations, corner-to-corner and face-to-corner, the interaction α (Δα) is also calculated with the counterpoise correction to assess the BSSE on the Δα results, Table 5

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Figure 3. Interaction polarizabilities of $(OsO_4)_2$ dimers in six different orientations. The dashed lines overlapping with the solid lines for corner−corner and face−corner results correspond to the counterpoise-corrected results for these two cases.
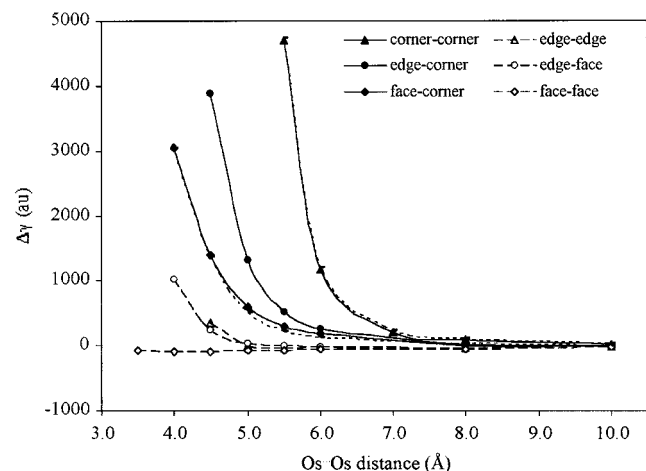
Figure 4. Interaction second hyperpolarizabilities of $(OsO_4)_2$ dimers in six different orientations. The dashed lines overlapping with the solid lines for corner−corner and face−corner results correspond to the counterpoise-corrected results for these two cases.

and Figure 3. In light of the results for dimer interaction energies, it is surprising to find that the BSSE is very small and negligible for calculation of $\Delta\alpha$. The CP and NCP $\Delta\alpha$ results are seen to almost overlap each other, Figure 3.

3. Second Hyperpolarizabilities. Figure 4 shows the interaction second hyperpolarizabilities ($\Delta\gamma$) calculated from the data in Tables 1 and 4 by eq 1. Overall, intermolecular interactions have stronger effects on γ than on α. Unlike α, the interaction effects on γ are mainly positive (except for some very small negative values for some orientations at longer R). As was the case for α, configurations with less contact between the two monomers are more desirable in terms of increasing γ. The most favorable corner-to-corner configuration increases γ up to 5000 au at $R = 5.5$ Å. The enhancement in the γ value per OsO_4 monomer (γ_{rel}, calculated from the data in Tables 1 and 4 by eq 2) is up to 100% relative to the isolated OsO_4 result. Figure 4 also shows that the enhancement in γ attenuates quickly with increased R and hence weaker interaction. For some dimer orientations, such as face-to-face, the interaction effects are almost negligible. As for α, the BSSE for γ is assessed for two

Table 4. $(OsO_4)_2$ Second Hyperpolarizabilities (au)[a]

Os⋯Os distance (Å)	corner− corner	edge− corner	face− corner	edge− edge	edge− face	face− face
3.50						4709
4.00		7844			5815	4702
4.50		8679	6189	5144	5040	4704
5.00		6103	5385	4784	4832	4714
5.50	9488	5306	5094	4751	4789	4721
6.00	5960	5046	4971	4773	4777	4731
7.00	4999					
8.00	4886	4810	4788	4745	4743	4734
10.00	4800	4799	4787	4781	4774	4764

[a] Results are obtained at the RHF level. Basis set: Os, SBK; O, SBK + ELP-pdd′.

Table 5. Counterpoise-Corrected Results for OsO_4 (au)

Os⋯Os distance (Å)	energies		polarizabilities		second hyperpolarizabilities	
	corner− corner	face− corner	corner− coner	face− corner	corner− corner	face− corner
4.0		−152.8858		44.7		2400.4
4.5		−152.8822		44.7		2409.6
4.75		−152.8803				
5.0		−152.8788		44.7		2429.6
5.5	−152.8824	−152.8766	44.7	44.8	2378.3	2432.1
6.0	−152.8807	−152.8751	44.7	44.8	2372.2	2421.6
7.0	−152.8753		44.7		2381.2	
8.0	−152.8739	−152.8739	44.8	44.8	2384.6	2370.7
10.0	−152.8737	−152.8737	44.8	44.8	2379.8	2387.8

[a] Results are obtained at the RHF level. Basis set: Os, SBK; O, SBK + ELP-pdd′. Calculations are done for OsO_4 in the presence of the total basis set for $(OsO_4)_2$ in the specific orientations.

orientations, corner-to-corner and face-to-corner, and found to be very small and negligible, Figure 4.

CONCLUSIONS

ECP approaches are applied in the study of NLO properties of dimers of inorganic TM complexes. Several interesting results have been obtained, the most significant of which are summarized here. Intermolecular interactions that give rise to an enhancement in NLO properties have been found in osmium tetroxide dimers despite the fact that monomer−monomer interactions are in an energetic regime that is weak. The enhancement is found to be quite sensitive to the relative orientation of the monomer units, and generally the enhancement is greater (for both α and γ) as the contact surface between the two tetrahedral molecules is diminished. Interestingly, unlike the effects observed for organic polyene chains,[6] positive interaction effects (i.e., enhancement of the response) are identified in specific $(OsO_4)_2$ orientations, while they are always negative in the organic polymer systems studied by Chen and Kurtz. More work is clearly needed to see whether such a generalization is applicable to other families of organic and inorganic compounds. Interaction effects have been found to reduce α_{rel} up to 15% and γ_{rel} up to 70% relative to the isolated monomer result for organic polyene systems.[6] In contrast, in dimers of osmium tetroxide, interaction effects increase α_{rel} up to 6% and γ_{rel} up to 100% relative to the isolated monomer result for OsO_4.

The results are obtained from dimer conformers in some fixed and arbitrary orientations, and a "real" osmium tetroxide solution could approximate a mixture or average

of these conformations. Thus, the average and more likely effect of intermolecular interactions will be more moderate than the extreme effects shown in Figures 3 and 4. Specifically for the dimer of osmium tetroxide, intermolecular interaction is not expected to be very large, as OsO_4 is a nonpolar, spherical molecule. To obtain further features in regard to the intermolecular interaction effects on NLO properties of inorganic systems, more different and prototypical dimers and even oligomers should be modeled and calculated.

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