DOI: 10.1002/ejic.200600450

How Do the Different Defect Structures and Element Substitutions Affect the Nonlinear Optical Properties of Lacunary Keggin Polyoxometalates? A DFT Study

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Keywords: Polyoxometalates / Nonlinear optics / Lacunary species / Tungsten / Density functional theory

Systematic DFT calculations have been carried out on the lacunary α-Keggin polyoxometalate derivatives $[PW_{11}O_{39}]^{7-}$, $[XW_9O_{34}]^{n-}$ (X = Al^{III}, Si^{IV}, Ge^{IV}, P^{V}, As^{V}, and Sb^{V}), $[XW_9M_2O_{39}]^{n-}$, and $[XW_9M_3O_{40}]^{n-}$ (X = P^{V} and Si^{IV}, M = Mo^{VI}, V^{V}, Nb^{V}, and Ta^{V}) to investigate the geometric structure and element substitution effects on the molecular nonlinear optical response. Analysis of the computed static second-order polarizability (β_0) predicts that the molecular nonlinear optical activity of lacunary Keggin polyoxometalate derivatives can be modified by replacing the central heteroatom and the addenda metal atom. Substitution of the central Al atom or the addenda V atom causes significant enhancement in the molecular nonlinearity. Moreover, the β_0 values are substantially dependent on the defect structures. This class of inorganic complexes possesses remarkably large molecular optical nonlinearity, especially for the partial substitution complex $[SiW_9Nb_2O_{39}]^{10-}$ (**IIIc**), which has a computed β_0 value of 2071.0 a.u. Thus, lacunary Keggin polyoxometalates could become excellent candidates in the field of second-order NLO.

Introduction

Nonlinear optical (NLO) materials based on molecular compounds have continued to be of considerable current interest because they hold promise for potential applications in optical signal processing, switching, and telecommunications. Among inorganic nonlinear materials, borates, phosphates, and niobates (β-BaB_2O_4, LiB_3O_5, $Li_2B_4O_7$, $CsLiB_6O_{10}$, KH_2PO_4, $LiNbO_3$, etc.) have already been widely studied. However, compared with the organic and organometallic compounds that have been extensively examined for their NLO responses recently, NLO studies of inorganic materials are relatively rare even though inorganic compounds are robust and are available as large single crystals. They also possess a large transparency range, suffer very low optical losses, and offer a large variety of structures and a great diversity of electronic properties shaped by the metal-characterized core and therefore may comprise a promising family of NLO materials.

Among the various inorganic compounds, polyoxometalates (POMs) have generated substantial interest in recent years because of their unique structural variety and exciting properties in fields such as catalysis, medicine, materials science, etc.[1] The most representative POM is the well-known α-Keggin heteropolyanion $[XM_{12}O_{40}]^{n-}$ (denoted as α-XM_{12}; X = P^{V}, Si^{IV}, Ge^{IV}, etc.; M = Mo^{VI}, W^{VI}, or V^{V}). The structure of α-XM_{12} has overall T_d symmetry and consists of a central XO_4 tetrahedron that shares its oxygen atoms (O_a) with four M_3O_{13} groups. These M_3O_{13} groups, made of three edge-sharing octahedra, are linked together by corners. Lacunary α-Keggin polyanions (species with defect structures) are derived from α-XM_{12} by removing one MO_6 octahedron (α-XM_{11}, top series in Figure l) or by removing three MO_6 octahedra from different M_3O_{13} groups (A-α-XM_9, middle series in Figure l) or the same M_3O_{13} group (B-α-XM_9). In order to synthesize novel POMs with predicted structures, an approach widely used is to treat lacunary POM precursors with transition metal ions or organometallic fragments as lacunary structures possess a reactive nucleophilic polyoxygenated site. Different transition metal ions can partly or wholly fill these vacancies to give rise to compounds with magnetism or catalysts,[2] such as PW_9Fe_2Ni, PW_9Fe_3, or $PW_{11}Co$. The reactions of organometallic fragments with Keggin-type lacunary polyanions also give numerous novel compounds {e.g., open-type $[SiW_9O_{37}(SnR)_3]^{7-}$ and sandwich-type $[(SnR)_3(SiW_9O_{34})_2]^{7-}$}. Although the study of such lacunary polyanions is receiving considerable attention,[3] they need to be further investigated theoretically.

Murakami et al. have recently shown by the conventional powder second-harmonic generation (SHG) method that nanostructured materials made from lacunary POMs have larger NLO responses than KH_2PO_4. They also defined design criteria to obtain a large NLO response.[4] This experi-

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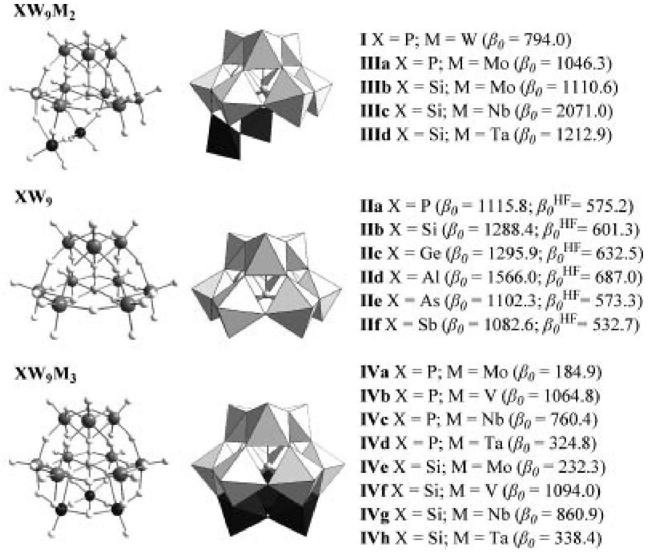

Figure 1. Ball-and-stick and polyhedral representations of the studied complexes. The values in brackets are the respective computed static second-order polarizability (a.u.).

mental result inspired us to further investigate the electronic and NLO properties of lacunary α-Keggin derivatives by a DFT method. In the past decade, DFT has been shown to be able to successfully predict the properties of molecules and materials, including the NLO properties.[5] The modeling of polyoxoanions has also made progress.[6] Recently, we have systematically investigated the bonding character, redox properties, protonation, stability, and NLO properties of $[X_2Mo_5O_{23}]^{6-}$, $[PTi_2W_{10}O_{40}]^{7-}$, $[Mo_6O_{17}R_2]^{2-}$, and $[H_{12}V_{13}O_{40}]^{3-}$ clusters by DFT.[7] Theoretical studies would be helpful in the rationalization of the observed properties and in the design of novel POM-based materials with functional properties by exploiting the unique electronic and structural characteristics of these complexes.

In this paper we present systematic DFT calculations on the static NLO responses of a series of lacunary α-Keggin polyanion derivatives, including C_s systems: $[PW_{11}O_{39}]^{7-}$, $[PW_9Mo_2O_{39}]^{7-}$, $[SiW_9Mo_2O_{39}]^{8-}$, $[SiW_9Nb_2O_{39}]^{10-}$, and $[SiW_9Ta_2O_{39}]^{10-}$; and C_{3v} systems: $[AlW_9O_{34}]^{11-}$, $[SiW_9O_{34}]^{10-}$, $[GeW_9O_{34}]^{10-}$, $[PW_9O_{34}]^{9-}$, $[AsW_9O_{34}]^{9-}$, $[SbW_9O_{34}]^{9-}$, $[PW_9V_3O_{40}]^{6-}$, $[SiW_9V_3O_{40}]^{7-}$, $[PW_9Nb_3O_{40}]^{6-}$, $[SiW_9Nb_3O_{40}]^{7-}$, $[PW_9Ta_3O_{40}]^{6-}$, $[SiW_9\ Ta_3O_{40}]^{7-}$, $[PW_9\ Mo_3O_{40}]^{3-}$, and $[SiW_9\ Mo_3O_{40}]^{4-}$. (Figure 1) The effects of geometric structure and element substitution on the molecular nonlinear response are analyzed and discussed in order to reveal the general rules governing the NLO properties of these polyanions.

Results and Discussion

Electronic Structures

The frontier molecular orbitals of all systems have a common character where the occupied orbitals formally delocalize over the p-oxygen orbitals, while the unoccupied d-

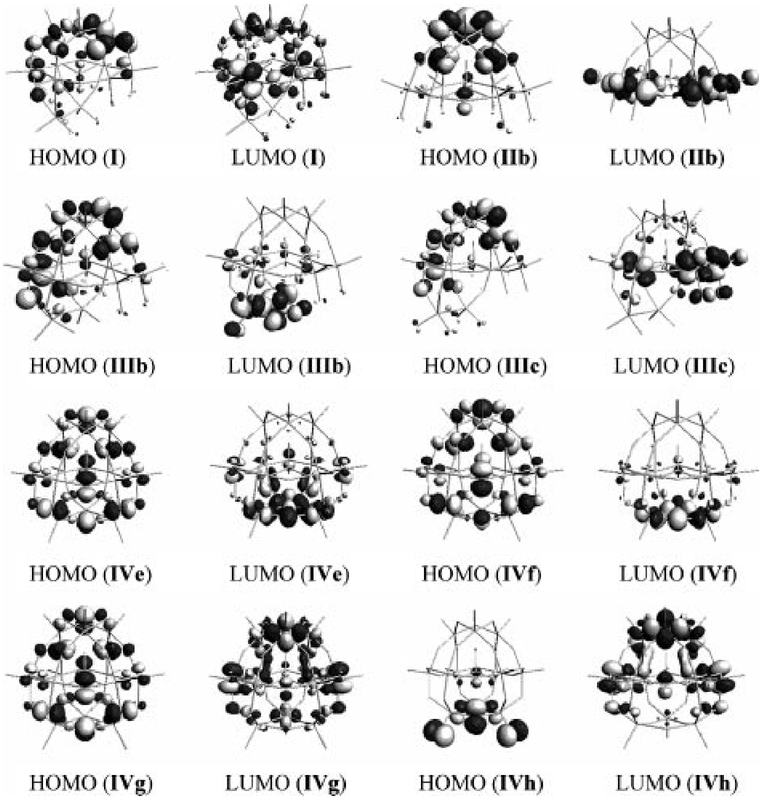

Figure 2. Frontier molecular orbitals of systems **I**, **IIb**, **IIIb**,**c**, and **IVe**–**h**.

metal orbitals delocalize over the addenda atoms.[6,7] This kind of charge transfer, namely O→M, must be responsible for the NLO properties of lacunary α-Keggin POM derivatives. The diagrams for the frontier molecular orbitals of eight representative systems (**I**, **IIb**, **IIIb**,**c**, and **IVe**–**h**) are displayed in Figure 2, from which several conclusions can be drawn:

(1) The frontier molecular orbitals of series **II** have similar character (Figure 2, **IIb**) in that the HOMOs formally delocalize over the bridge oxygen atoms that are away from the lacunary sites, which is similar to system **I**. The LUMOs delocalize mostly over the six tungsten atoms that are close to the lacunary sites and partially over the terminal oxygen atoms. In addition, the unoccupied W(d)–O(p) bands have an antibonding interaction in series **II**.

(2) The distribution of HOMOs in series **III** has a similar character to that of series **II**. However, when compared with series **II** the LUMOs in series **III** change significantly as it is the d-orbitals of the Mo atoms that contribute mainly to the LUMO of **IIIa**,**b** (Figure 2). When Mo atoms are substituted by Nb or Ta atoms (**IIIc** and **IIId**), the LUMOs mostly delocalize over the two tungsten atoms that are close to the lacunary sites (Figure 2).

(3) For trisubstituted systems (series **IV**), the HOMOs extensively delocalize over the p-oxygen orbitals, except for the Ta-substituted systems **IVd** and **IVh**, where the HOMOs almost delocalize over the bridge oxygen atom that links two tantalum atoms [O(TaTa)] and the terminal oxygen atom that links to tantalum atoms [O(Ta); Figure 2] The LUMOs of systems **IVa**,**b** and **IVe**,**f** are mainly concentrated on the three substituted addenda atoms (Figure 2), which shows that the d-orbitals of molybdenum and vanadium play an important role in the redox reactions of trisubstituted systems.[6b] However, the delocalization of LUMOs is obviously enhanced by Nb and Ta substitution (Figure 2, **IVg**,**h**).

Geometric Structure and Element Substitution Effects on *β*

In view of the molecular orbital character discussed above, we computed the static second-order polarizabilities (β_0) of the series of lacunary POM derivatives considered in this investigation by DFT. The static second-order polarizability is also termed the zero-frequency hyperpolarizability and is an estimate of the intrinsic molecular hyperpolarizability in the absence of any resonance effects. Geometric structure and element substitution effects were considered in a set of calculations by choosing mono- and trivacant Keggin derivatives and their mixed addenda species. The computed β_0 values of the studied complexes are given in Figure 1 (**I**, **IIa**–**c**, **IIIa**, and **IVa**). The results indicate some common trends, which are in agreement with the qualitative predictions of Murakami and co-workers on the NLO response of nanostructured materials made from lacunary POMs.[4] First, the trivacant Keggin complexes (**IIa**, **IIb**, and **IIc**) have larger β_0 values than the monovacant structure (**I**): all the β_0 values of **IIa**, **IIb**, and **IIc** are above 1100 a.u. whereas the present calculations predict the β_0 value of **I** to be just 794.0 a.u. Second, the replacement of the central heteroatom (X) slightly alters the β_0 values of **IIa**, **IIb**, and **IIc**, which increase as the heavy central atom changes in the order Ge ≥ Si > P; the difference between the β_0 values of **IIb** and **IIc** is relatively small. Third, partially substituting addenda metal atoms by molybdenum atoms (**IIIa**) causes significant enhancement in the molecular nonlinearity. As can be seen from Figure 1, the β_0 value of **IIIa** is much larger than that of **IVa**, the difference between the two systems exceeds 800 a.u., and this is confirmed by the frontier molecular orbital character (Figure 2 **IIIb** and **IVe**).

To shed further light on the second-order NLO properties of lacunary Keggin POM derivatives, more complexes (**IId**–**f**, **IIIb**–**d**, and **IVb**–**h**) were systematically calculated to understand the role of the central heteroatom (X) and addenda metal atom (M) in influencing the NLO response. The replacement of X in the trivacant complexes with five elements (Al, Si, P, As and Sb) results in different trends (Figure 3). The substitution by Al results in a larger effect than by Si, which, in turn, has a larger effect than P (**IId** > **IIb** > **IIa**); when X is one of the group 15 elements P, As, and Sb, the computed β_0 values indicate that the NLO response is **IIa** > **IIe** > **IIf**. As can be seen from two trends above, the magnitude of increase or decrease of β_0 with respect to the trivacant tungstates depends on both the atomic radius of the central heteroatom (Figure 3A) and its electronegativity (Figure 3B). When X is from the same row of the periodic table (e.g. the third row: Al, Si and P) the β_0 value is proportional to the atomic radius and is inversely proportional to the electronegativity; however, when X is from the same group (e.g. group 15: P, As, Sb) the opposite trend is observed: the β_0 value is proportional to the electronegativity and is inversely proportional to the atomic radius. From Figure 1, we also calculated the static second-order polarizabilities for series **II** employing the HF method (β_0^{HF}). According to the β_0^{HF} values, it can be seen that DFT and HF methods give consistent trends for the static second-order polarizabilities. However, the HF method underestimates the second-order polarizabilities of series **II** as there is no correlation consideration in the HF method, while the DFT methods used in this paper overestimate the β values. This is in accordance with the literature.[8] Therefore, it can also be concluded that DFT is a feasible method for the present POMs. Moreover, the central heteroatom substitution effects in series **III** and **IV** also obey the trends described above. Substitution by Si results in a larger effect than by P (**IIIb** > **IIIa**, **IVe** > **IVa**, **IVf** > **IVb**, **IVg** > **IVc**, and **IVh** > **IVd**). We believe that the sketch map in Figure 3 will be helpful in designing new NLO materials.

With regard to the role of the addenda metal atom, similar trends (Figure 3) can be seen from the calculated data (Figure 1: **IIIb**–**d** and **IVa**–**h**) obtained for series **III** and **IV**. Unfortunately, it is difficult to obtain a reasonable result for $[SiW_9V_2O_{39}]^{10-}$. The replacement of M with four elements (Mo, V, Nb, and Ta) significantly alters their β_0 values (Figure 1: **IIIc** > **IIId** > **IIIb**, **IVb** > **IVc** > **IVd** > **IVa**,

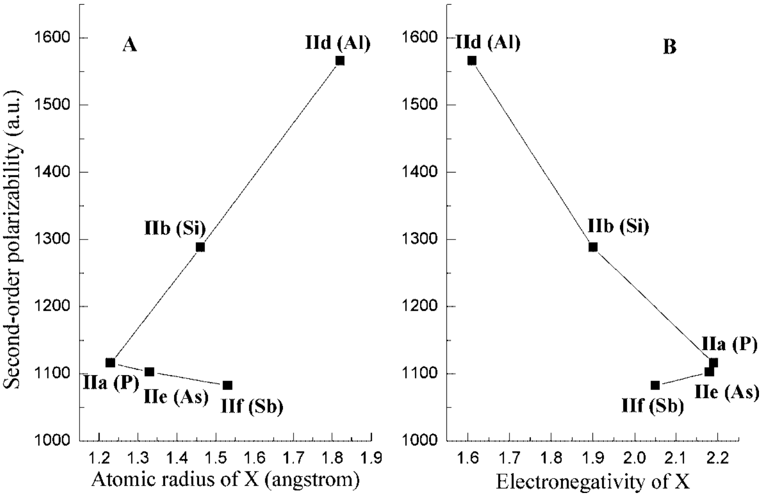

Figure 3. The second-order polarizabilities of trivacant complexes **IIa**–**f** as a function of the atomic radius (A) and electronegativity (B) of the central heteroatom (X).

and **IVf** > **IVg** > **IVh** > **IVe**), which increase as M changes in the order V > Nb > Ta > Mo. Thus, the computed β_0 values predict that the molecular nonlinear optical activity of lacunary Keggin POM derivatives can be fine-tuned by replacing the central heteroatom or the addenda metal atom. Substitution of the central Al atom or the addenda V atom causes a significant enhancement in the molecular nonlinearity. Furthermore, the defect structure plays a key role in increasing the β_0 value.

As can be seen from Figure 1, lacunary POMs have larger second-order polarizability coefficients, especially for the partially substituted complexes **IIIc**, whose computed β_0 value is even larger than that of the Au_{20} cluster with an equivalent molecular size. The present DFT calculations predict the β_0 value of system **IIIc** to be 2071.0 a.u., whereas the predicted second-order polarizability of Au_{20} is 1655.3 a.u.[9] All these complexes have high transparency in the visible area[4] therefore, in view of the merit of this class of inorganic complexes, they could be an excellent material for use in the second-order NLO field.

Conclusions

A series of lacunary α-Keggin POM derivatives have been systematically investigated for their molecular nonlinear response, including $[PW_{11}O_{39}]^{7-}$, $[XW_9O_{34}]^{n-}$ (X = Al^{III}, Si^{IV}, Ge^{IV}, P^{V}, As^{V}, and Sb^{V}), $[XW_9M_2O_{39}]^{n-}$, and $[XW_9M_3O_{40}]^{n-}$ (X = P^{V} and Si^{IV}; M = Mo^{VI}, V^{V}, Nb^{V}, and Ta^{V}). Geometric structure and element substitution effects on the molecular nonlinear response have been analyzed, and the computed β_0 values reveal the general rules to design a large nonlinearity: (i) the defect structured complex has a larger β value than a defect-free complex (series **IV**), especially for trivacant Keggin complexes (series **II**) and partially substituted complexes (series **III**); (ii) the β_0 value depends on both the atomic radius of the central heteroatom (X) and the addenda metal atom (M) and their electronegativity. When X and M are from the same row of the periodic table (X = Al, Si, and P; M = Nb and Mo) the β_0 value is proportional to the atomic radius and inversely proportional to the electronegativity, whereas when X and M are from the same group (X = P, As and Sb; M = V, Nb and Ta) the opposite trend is observed. This class of inorganic complexes possesses remarkably large static second-order polarizability, especially for $[SiW_9Nb_2O_{39}]^{10-}$ (**IIIc**), which has a computed β_0 value of 2071.0 a.u. The frontier molecular orbital character reveals that the main origin of the NLO properties of lacunary α-Keggin POMs derivatives is O→M charge transfer. It is hoped that the results presented in this paper will stimulate experimental research in the field of NLO properties involving lacunary Keggin POM derivatives.

Computational Details

The DFT calculations were carried out with the ADF2004.01 suite of programs.[10] The zero-order regular approximation (ZORA) was adopted in all the calculations to account for the scalar relativistic effects.[11] The generalized-gradient approximation (GGA) was employed in the geometry optimizations by using the Beck[12] and Perdew[13] (BP86) exchange-correlation (XC) functional. For the calculations, we made use of the standard ADF TZP basis set, which is a triple-ζ plus polarization STO basis set. The cores (O: 1s; Al, Si, P, V: 2p; Ge, As: 3p; Sb: 4p; Nb, Mo: 3d; Ta, W: 4d) were kept frozen. In calculations of the static second-order polarizability, the RESPONSE module[14] implemented in the ADF program was used based on the optimized geometries. The van Leeuwen–Baerends XC potential (LB94) was chosen for calculations of all the response properties.[15] The adiabatic local density approximation (ALDA) was applied for the evaluation of the first and second functional derivatives of the XC potential. Moreover, the value of the numerical integration parameter used to determine the precision of numerical integrals was 6.0. We also calculated the static second-order polarizabilities employing the Hartree–Fock (HF) method based on ab initio quantum chemistry with the GAUSSIAN03 program.[16] The basis set used for Al, Si, P, and O is the standard Gaussian basis set 6-31G(d) in which one set of d-polarization function is included. For 3d, 4d, and 5d transition metals, the LANL2DZ basis set[17] was used, in which the effective core potentials (ECPs) were adopted and mass-velocity, Darwin relativistic effects were incorporated.

Supporting Information (see footnote on the first page of this article): Cartesian coordinates of all systems (Tables S1–S19).

Acknowledgments

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China (projects 20373009 and 20573016) and the Science Foundation for Young Teachers of Northeast Normal University (20060307 and 111494017). We would also like to thank Yuhe Kan for computational support.

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Received: May 14, 2006