Prediction of Large Second Harmonic Generation in the Metal-Oxide/Organic Hybrid Compound CuMoO$_3$(p2c)

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Abstract: Noncentrosymmetric hybrid framework (HF) materials are an important system in discovering new practical second-order nonlinear optical materials. We calculated the second harmonic generation (SHG) response of a noncentrosymmetric (NCS) organic–inorganic HF compound, CuMoO$_3$(p2c) (p2c = pyrazine-2-carboxylate) to find that it exhibits the largest SHG response among all known NCS HF materials with one-dimensional helical chains. Further atom response theory analysis revealed that the metal atoms Cu and Mo contribute much more strongly than do nonmetal atoms in determining the strength of the SHG response, which is a novel example in nonlinear optical materials known to date.

Keywords: nonlinear optical material; noncentrosymmetric; MOF; atom response theory; DFT calculation

1. Introduction

Nonlinear optical (NLO) crystals play a vital role in modern laser technologies and sciences due to their ability to convert the frequency of an incident laser beam through the second harmonic generation (SHG) process [1–5]. A noncentrosymmetric (NCS) arrangement of atoms is a prerequisite for the generation of non-zero second-order NLO properties in bulk materials. The search for new NCS structures with excellent SHG properties remains a hot scientific challenge. Although there exist a number of extensively studied and commercially available inorganic NLO crystals, there has been tremendous interest in finding new NLO materials in other systems such as organic molecular crystals, inorganic–organic hybrid nanocomposites, self-assembled chromophoric superlattices and inorganic–organic hybrid framework materials (including both nanoporous metal–organic frameworks (MOFs) and dense inorganic–organic frameworks (IOFs)) [6–10]. Hybrid framework materials are constructed by employing modular synthetic procedures with metal ions (i.e., Zn$^{2+}$, Cd$^{2+}$, Mn$^{2+}$, Ag$^+$, Cu$^+$) or inorganic nodes (i.e., metal-oxide, metal-fluoride, metal-chalcogenides and metal-halides) that are covalently and/or coordinately bonded to various organic linkers. Because of the advantages over conventional inorganic materials (e.g., structural tunability at a molecular level, chemical stability, and ease of synthesis on a large bulk scale), NCS hybrid framework materials are expected to form a new class of potentiality practical NLO materials [11–13].

Numerous hybrid framework materials have been reported to be SHG-active. According to the dimensionality of the coordination networks, they can be roughly classified...
into three groups: (a) three-dimensional (3D) networks (e.g., diamondoid, octupolar), (b) two-dimensional (2D) grid structures, and (c) one-dimensional (1D) chains (e.g., helical chains). Lin et al. suggested that 3D and 2D networks with a high degree of controllability and predictability are better platforms for the synthesis of NCS MOFs [6,8], and they reported a number of MOFs with a large SHG response, which includes Cd[3-(4-pyridyl)ethenyl]benzoate (4-py) [14] and other systems [15]. For hybrid framework materials, the molecular origin of SHG is believed to arise from the electronic asymmetry (push–pull effect or acceptor–donor effect) induced by the polarization of ligand electron density or the metal-to-ligand/ligand-to-metal charge transfer [6,9,10,16]. The alignment of NLO chromophores may be necessary for NCS hybrid framework materials to have a large SHG response. For example, Ye et al. obtained a zinc MOF based on a 2D square grid network, in which the ligands involve an aligned two-center acceptor–donor system, which displays a very strong SHG response \( I_{2\omega}^{\text{powder}} \) of 50 \( \times \) urea and 500 \( \times \) KH2PO4 (KDP, respectively) [16]. Yu et al. encapsulated a matching ordered organic dipolar chromophore in the pores of porous MOFs forming a highly NLO active anionic MOF (ZJU-28⊂DPASD, \( I_{2\omega}^{\text{powder}} \) of 18.3 \( \times \) SiO2 [17]. However, the NCS hybrid framework materials with 1D helical chains are not known to have large SHG responses, although it may be related to synthetic difficulty and unpredictability. Maggard et al. used short organic ligands to bridge polar or chiral inorganic basic building units (i.e., MoO2F4\(^{2-}\)) to obtain two isomorphous SHG-active NCS solids with helical chains [18,19], A(py2)(H2O)2MoO2F4 (A = Zn, Cd, pyz = pyrazine, \( I_{2\omega}^{\text{powder}} \) of \( \sim \)0.28–1 \( \times \)SiO2, P3\(_2\)1). Other examples with 1D helical chains include Cu(pzc)2AgReO4 (pzc = pyrazinecarboxylate, \( I_{2\omega}^{\text{powder}} \) of \( \sim \)0.5–0.7 \( \times \)SiO2, P4\(_{2}\)12) [20], [Zn(mpz)3]2[MoO2F4]2 (mpz = 3-methylpyrazole, \( I_{2\omega}^{\text{powder}} \) of \( \sim \)10 \( \times \)SiO2, Pna) [21], and [(S)-C5H4N2][(MoO3)3(SO4)]·H2O (\( I_{2\omega}^{\text{powder}} \) of \( \sim \)5 \( \times \)SiO2, Pna) [22]. The cancellation or the absence of a net dipole moment in these structures is usually considered to be responsible for their low SHG response [19]. Finding hybrid framework materials with 1D helical chains possessing a large SHG response remains a challenge. It should be pointed out that the SHG phenomenon, as a second-order polarization, involves both the occupied and the unoccupied states of a material, while the vector sum of the dipole moments of the groups within a unit cell, as a zero-order polarization, associated with only the occupied states. The non-zero vector sum of the dipole moments lead to a polar structure which guarantees the non-zero vector sum of the dipole moments lead to a polar structure which guarantees the presence of an NCS structure, which is a necessary condition for the occurrence of the SHG phenomenon, but it does not influence the magnitude of the second-order NLO properties. It is desirable to understand the SHG responses for the NCS hybrid framework compounds at the electronic and the atomic levels.

Recently, Luo et al. [23] reported a new NCS metal-oxide/organic hybrid compound CuMoO3(p2c) (p2c = pyrazine-2-carboxylate) with 1D helical chains. However, so far neither theoretical nor experimental work on the linear and the nonlinear optical properties of this compound has been reported. Based on our first-principles calculation, we found CuMoO3(p2c) exhibits a very strong SHG response with a static effective SHG value \( d_{\text{eff}}^{\text{static}} \) calculated to be 30.6 pm/V. This value is about 92.7 times that of KDP (-927 \( \times \)SiO2, 3.12 \( \times \)AgGaS2 (AGS)), which ranks the SHG response of CuMoO3(p2c) to be the highest among all the reported hybrid framework materials with 1D helical chains. Besides, our atom response theory (ART) analysis [24] shows that the SHG response of CuMoO3(p2c) originates largely from the states of the metal ions, Cu\(^{+}\) and Mo\(^{6+}\), i.e., approximately 56% of the total SHG response. Such a large contribution from metal ions also makes CuMoO3(p2c) a quite special example in NLO materials.

2. Materials and Methods
Computational Details

**VASP calculations.** The structural and the electronic properties of CuMoO3(p2c) were calculated within the framework of density functional theory (DFT) [25,26] by using the
Vienna ab-initio simulation package (VASP) [27–29] with the projector augmented wave (PAW) method [30]. The generalized gradient approximation (GGA) within the Perdew–Burke–Ernzerhof (PBE)-type exchange-correlation potentials [31] was used throughout this work. The employed PAW–PBE pseudopotentials [32] with 11 (3d104s1), 14 (4s24p64d5s1), 6 (2s22p4), 5 (2s22p4), 4 (2s22p2) and 1 (1s1) valence electrons for Cu, Mo, O, N, C, and H were used to describe the electron–ion interactions, respectively. The plane wave cutoff energy for the expansion of wave functions was set at 600 eV and the tetrahedron method with Blöchl corrections was used for integrations. The numerical integrations in the Brillouin zones were performed by utilizing 7 × 7 × 4 Monkhorst–Pack k-point mesh, which showed an excellent convergence of the energy differences (0.005 eV) and stress tensors (0.001 eV/Å). The quasi-Newton algorithm as implemented in the VASP code was used in all structural relaxations. In this work, both the cell volume and the atomic positions were all allowed to relax to minimize the internal forces. The optimized lattice parameters, \(a = 7.791 \) Å and \(c = 11.229 \) Å, are slightly overestimated with respect to the experimental, which were measured at room temperature as usual with the PBE functional. Details of the optimized structure and the agreement with the experimental values are given in Table S1 of the Supporting Information.

In our calculations for the linear and the nonlinear optical properties, we employed the sum over states (SOS) method [33–35] using the code we developed [24] based on the calculated electronic structures from the VASP optical module. The SOS formalism for second-order susceptibility was derived by Aversa and Sipe [33] and later modified by Rashkeev et al. [34,36] and Sharma et al. [35,37]. To gain insight into the origin of SHG response, the contributions \(A_\tau\) of the individual atoms \(\tau\) to a specific component, e.g., the largest, of the total SHG response tensor, were determined by performing atom response theory (ART) analysis [24,38] for the CuMoO\(_3\) (p2c) structure. Note that, the chirality may lead to higher-order interactions beyond the electric dipole approximation, for which one needs to use model studies instead of the first-principles method [39].

**Partial response functional (PRF) method.** The contribution of a certain occupied energy region between \(E_B\) and valence band maximum (VBM), \(\xi_V(E_B)\), to each SHG coefficient \(d_{ij} = \frac{1}{2}\chi^{(2)}_{ijk}\), \(i = 1, 2, 3, 4, 5, 6\) is determined by considering only those excitations from all occupied states between \(E_B\) and VBM to all the unoccupied states of the conduction bands (CBs) and the contribution, \(\delta\xi_V(E_B)\), of specific occupied states of energy \(E_B\) to each \(d_{ij}\) by the excitations from that energy to all unoccupied states of the CBs.

\[
\delta\xi_V(E_B) = -\frac{d\xi_V(E_B)}{dE_B}
\]  

Equation (1)

Similarly, the contribution, \(\xi_C(E_B)\), of a certain unoccupied region between the conduction band minimum (CBM) and \(E_B\) to each \(d_{ij}\) is determined by the excitations from all occupied states of the VBs only to all unoccupied states between CBM and \(E_B\), and the contribution, \(\delta\xi_C(E_B)\), of specific unoccupied states of energy \(E_B\) to each \(d_{ij}\) by the excitations from all occupied states of the VBs only to that energy.

\[
\delta\xi_C(E_B) = \frac{d\xi_C(E_B)}{dE_B}
\]  

Equation (2)

**Atom response theory (ART) analysis.** To evaluate the individual atom contributions to the SHG components, \(d_{ij}\), it is computationally more convenient to express the corresponding PRFs in terms of the band index \(I_B\), \(\xi_I(I_B)\), where the band index \(I_B\) runs from 1 to \(N_{tot}\) (i.e., the total number of band orbitals) with increasing energy \(E_B\), from \(E_{min}\) to \(E_{max}\). Here, \(\xi_V(I_B)\) and \(\xi_C(I_B)\) are denoted as \(\text{VB} \xi_j\) and \(\text{CB} \xi_j\), respectively, with \(I_B\) replaced by a subscript \(j\).
Suppose that a specific atom $\tau$ has $L$ atomic orbitals with a coefficient $^{VB}C_{L}^{k}j$ in the valence band $j$ at a wave vector $\vec{k}$. The total contribution $^{VB}A_{\tau}$ of an atom $\tau$ makes to the SHG coefficient from all the VB bands $j$ is written as

$$^{VB}A_{\tau} = \frac{\Omega}{(2\pi)^3} \int d\vec{k} \cdot \sum_{L,j}^{VB} \xi_j \left|^{VB}C_{L}^{k}j\right|^2$$

(3)

where $\Omega$ is the unit cell volume, $^{VB}\xi_j$ is the corresponding PRFs in terms of the band index $j$. Similarly, the total contribution $^{CB}A_{\tau}$ of an atom $\tau$ makes to the SHG coefficient from all the CB bands $j$ is written as

$$^{CB}A_{\tau} = \frac{\Omega}{(2\pi)^3} \int d\vec{k} \cdot \sum_{L,j}^{CB} \xi_j \left|^{CB}C_{L}^{k}j\right|^2$$

(4)

in which we assumed that the atom has $L$ atomic orbitals with coefficient $^{CB}C_{L}^{k}j$ in the conduction band $j$ at a wave vector $\vec{k}$. To calculate the actual contribution of each constituent atom in a unit cell to the total SHG response, one needs to consider the signs of $^{VB}\xi_j$ and $^{CB}\xi_j$.

The total contribution, $A_{\tau}$, each individual atom makes to the SHG response from both the VBs and the CBs (i.e., from all the bands) is given by

$$A_{\tau} = \frac{^{VB}A_{\tau} + ^{CB}A_{\tau}}{2}$$

(5)

where the factor of $1/2$ is applied to remove the double-counting of each excitation.

3. Results and Discussion

3.1. Structure

The Cu/Mo-oxide CuMoO$_3$(p2c) crystallizes in the NCS space group P3$_2$ (Figure 1 and Table S1). Within each unit cell, Cu and Mo atoms each have one crystallographically unique site, whereas the O, N, C, and H atoms occupy five, two, five and three independent crystallographic positions, respectively. All atoms are at special Wyckoff positions of $3a$. The Mo atoms are coordinated with five O atoms (O1, O3, O4, O4, O5) and one N1 atom, forming a distorted MoO$_5$N octahedron with Mo-O and Mo-N bond lengths around 1.92 and 2.37 Å, respectively. Neighbouring Mo-centered octahedra are connected by sharing the O4 atom with alternating short (1.82 Å) and long (2.12 Å) Mo-O4 bond distances as well as alternating small ($\angle$Mo-O4-Mo = 145.64$^\circ$) and large ($\angle$O4-Mo-O4 = 162.57$^\circ$) bond angles forming 1D zigzag -Mo-O-Mo- chains along the $c$-axis (Figure 1a). Besides, this zigzag chain propagates along the $3_2$ screw axis, that is, the MoO$_3$N octahedron could duplicate itself by rotating 120$^\circ$ within the $ab$ plane and gliding $2c/3$ along the $c$ axis. In addition, the Cu atoms form a distorted CuO$_3$N tetrahedron with the surrounding three O atoms (O2, O3, O5) and one N2 atom with the Cu-O and Cu-N distances of ~2.03 Å and ~1.99 Å, respectively. Each CuO$_3$N tetrahedra is corner shared with two neighbouring MoO$_3$N octahedra through the O3 and O5 atoms, forming the inorganic CuMoO$_3$ helical chains. Further, the N1 and O1 atoms from one p2c ligand simultaneously coordinate with the Mo atom, while the O2 and N2 atoms from two different p2c ligands connect the Cu atoms (Figure 1b). Thus, the 3D inorganic–organic hybrid network is constructed through the bridging p2c ligands. Note that, the Mo-O1 and the Cu-O2 distances (2.16 and 2.08 Å) connecting to the p2c ligands are slightly longer than the other Mo-O and Cu-O bonding lengths (1.86 and 2.01 Å) within each MoO$_3$N octahedra and CuO$_3$N tetrahedra, respectively. This fact reflects that the metal/ligand interaction is relatively weak compared with the interaction within the inorganic framework.
3.2. Electronic Structures

Our electronic calculations reveal that CuMoO$_3$(p2c) has a small indirect bandgap ($E_g$$_{\text{PBE}}$) of 0.743 eV, which is smaller than the experimentally measured ($E_g$$^{\text{exp}}$ = 1.32 eV). In computing optical properties, this deficiency of the DFT [26] is often corrected empirically by employing the scissor operation [40] in which the conduction bands (CBs) are shifted in energy to have the experimental bandgap [41,42]. The calculated density of states (DOS) and electronic band structure (Figures 2a and S1–S4) show that the top portion of valence bands (VBs) (−1.0 eV to $E_F$) is dominated by the Cu-3d orbitals, while the O-2p orbitals occupy the relatively lower energy range (−6.0 to −1.8 eV). The bottom part of the conduction bands (CBs) ($E_g$−7 eV) is primarily made up of the Mo-4d, C-2p, and N-2p states, while the antibonding states involving the 2p states of the O, C, N atoms are found in the energy range between 7 to 25 eV.

![Diagram](image_url)

**Figure 2.** (a) Calculated total DOS of CuMoO$_3$(p2c). (b) −pCOHP plots describing the average chemical bonding interactions. (c) $\zeta_V(E_B)$-vs-$E_B$ plot (left) and $\zeta_C(E_B)$-vs-$E_B$ plot (right) calculated for the largest SHG component $d_{11}$ of CuMoO$_3$(p2c). The values are in pm/V.
The crystal orbital Hamilton population (COHP) [43,44] analysis (Figure 2b) shows that the frontier orbital states (−4.4 eV to E_F) are described mainly by nonbonding states made up of Cu-3d and O-2p orbitals with a small mixture of weak Cu-O/N d-p antibonding states (Figure S2). Generally, these filled nonbonding and antibonding states near E_F are highly polarizable and hence are important for the optical properties. Besides, some O-2p and N-2p states make weak bonding interaction with Mo-4d and Cu-3d states as well as C-2p orbitals around −9.0 to −4.4 eV, leading to a dispersive orbitals feature. Strong Cu-O and Mo-O s-p bonding interaction can be found at around −18 eV. The covalent character of the C-O/N bonds is much stronger than that of the Mo-O/N and the Cu-O/N bonds (Figure 2b).

3.3. Optical Properties

Calculations of the refractive indices (n_o and n_e) as a function of wavelength (Figure 3) reveal that CuMoO_3(p2c) can meet the Type-I phase matching condition at λ = 1.88 μm, a value in the IR range. Besides, the calculated birefringence value Δn for CuMoO_3(p2c) is 0.21 at 1910 nm (Figure S5). Such a large birefringence reflects a strong optical anisotropy of CuMoO_3(p2c). The value of Δn in a uniaxial optical material is the difference between n_o and n_e, Δn = |n_o − n_e|. As n_o > n_e in CuMoO_3(p2c), it is a negative uniaxial crystal.

![Figure 3](image-url) Calculated refractive indices of the fundamental and second harmonic wavelengths for CuMoO_3(p2c). The pink point represents the meet of Type I phase-matching condition (n_e(2ω) = n_o(ω)) for negative uniaxial crystals.

Due to the point group of 3, the SHG tensor of CuMoO_3(p2c) has 13 non-zero components, in which 5 of them are independent, i.e., d_{11} = −d_{12} = −d_{22} = −d_{21} = −d_{16}, d_{31} = d_{32} = d_{24} = d_{15}, d_{14} = −d_{25} and d_{33}, as presented in Table S2. As the Kleinman symmetry, i.e., d_{14} = −d_{25} = 0, is not followed in CuMoO_3(p2c), it was not enforced in calculating the NLO properties in this work. The effective d_{eff}^{p}, an average SHG coefficient over all possible orientations of the powder crystals, is estimated from the formula derived by Kurtz-Perry [45] and Cyvin et al. [46] based on the calculated non-zero SHG tensors. The static effective SHG value of CuMoO_3(p2c) is calculated to be 30.6 pm/V, which is about 3.12 times that of commercial AGS (static d_{eff}^{AGS} = 9.8 pm/V) and 92.7 times that of KDP (static d_{eff}^{KDP} = 0.33 pm/V). At the wavelength of 1910 nm (~0.65 eV), the d_{eff}^{p} value of CuMoO_3(p2c) is predicted to be 121.35 pm/V, i.e., −8.20 × d_{eff}^{AGS} (d_{eff}^{AGS} = 14.8 pm/V at 1910 nm). We have tried to estimate the d_{eff} for large crystals using Midwinter et al.’s
method [47] and obtained a maximum value of ~168.7 pm/V at $\theta = 0^\circ$ and $\varphi = 45.0^\circ$ at $\omega = 1910$ nm, which is larger than the powder $d_{\text{eff}}^\text{p}$. Using the $d_{\text{eff}}$ and the refractive indices, one can get a much larger figure of merit value [48] $(FOM = d_{\text{eff}}^2 / (n(\omega)^2 n(2\omega)))$, ~2058.7 (pm/V)$^2$ than that 150 (pm/V)$^2$, of LiNbO$_3$, which suggests a great potential value of CuMoO$_3$(p2c)—though the large crystal has not yet been obtained. We also calculated the SHG responses for several NCS hybrid framework compounds with helical chains, as presented in Table S2, which also lists the available experimental SHG values. Clearly, Cu$_3$MoO$_3$(p2c) has the highest $d_{\text{eff}}^\text{p}$ value among all reported NCS hybrid framework materials with helical chains. This remarkably strong SHG response is larger than those found in the majority of hybrid framework materials reported to date. Only a few are exceptional: [Cd(L-N)$_3$]$_2$(H$_2$O)$_2$$_\text{powder}$ of 50 $\times$ urea) [49], Zn((E)-4-pv-v-3-bza)$_2$ ($I_{\text{powder}}^\text{2ω}$ of 1000 $\times$ α-SiO$_2$) [50], and [(CN$_4$-C$_6$H$_4$-C$_{12}$H$_7$N-C$_5$H$_4$N)$_2$Zn]-1.5H$_2$O ($I_{\text{powder}}^\text{2ω}$ of 50 $\times$ urea) [16]. Besides, the SHG response of CuMoO$_3$(p2c) is even larger than several newly reported inorganic IR-NLO crystals, e.g., Li[LiCs$_2$Cl] [Ga$_3$S$_4$] ($I_{\text{powder}}^{\text{2ω}}$ of 0.7 $\times$ AGS) [51], Ba$_2$SnS$_3$ ($I_{\text{powder}}^{\text{2ω}}$ of 1.1 $\times$ AGS) [52], Na$_2$MSn$_2$Se$_6$ (M = Zn/Cd) ($I_{\text{powder}}^{\text{2ω}}$ of 3 and 2.2 $\times$ AGS) [53], and 8-Ga$_2$Se$_3$ ($I_{\text{powder}}^{\text{2ω}}$ of 2.3 $\times$ AGS) [54]. These facts indicate that CuMoO$_3$(p2c) is a promising IR hybrid NLO crystal material.

3.4. Atom Response Theory Analyses

We investigate the origin of the SHG responses further by employing the ART analysis [24]. Shown in Figure 2c is the partial response functionals (PRFs), $\zeta_V(E_B)$ and $\zeta_C(E_B)$ as well as their derivatives (Figures 5e and 5f), $\delta\zeta_V(E_B)$ and $\delta\zeta_C(E_B)$, for CuMoO$_3$(p2c). The $\zeta_V(E_B)$ functional increases in magnitude with decreasing $E_B$ from $E_F$ to $-4.4$ eV indicating that the nonbonding Cu 3d and O 2p states are the dominating contributors to the SHG response in the VB part. From the rising amplitude of the $\zeta_V(E_B)$ functional, it is clear that the contribution from the Cu 3d states ($E_F$ to $-1.0$ eV) is greater than that from the O 2p states ($-1.8$ to $-4.4$ eV). This is so because the completely filled d orbitals of each Cu$^+$ (d$^{10}$) possess more electrons than the completely filled 2p orbitals of each O$^-$ (p$^6$). However, in the energy range of $-4.4$ to $-9.0$ eV where the C-O/N, Mo-O/N and Cu-O/N bonding interaction occurs, the functional shows small variation, showing that these bonding states contribute little to the SHG response. A dramatic change from the CB minimum to 7 eV and the steady increase at the higher energy range of the $\zeta_C(E_B)$ functional reveal the contribution from the unoccupied Mo 4d and C/O/N-2p states in the CB part.

The quantitative contribution of an individual atom $\tau$, $\tau\%$ (in %), to the strongest SHG coefficient $d_{11}$ for CuMoO$_3$(p2c) is obtained based on the PRFs. As presented in Tables 1 and S3, the $\tau\%$ of Cu (~11.7%) is nearly 1.7 times that of Mo (~7.0%) and 7.3 times that of O (~1.6%) and N (~1.2%). Besides, the $\tau\%$ value of C and H are negligibly small, <0.8%. These results reflect that the metal atoms Cu and Mo serve as the NLO-active centers at the atomic scale. Considering the number of atoms of each element in the unit cell, the total contributions of Cu, Mo, O, N, C, and H are 35.2, 20.9, 24.1, 7.4, 11.1, and 1.4%. Although the uneven stoichiometry effect is included, the metal atom Cu is still the leading contributor to the SHG response, while the contributions from the Mo and O atoms are comparable. This further reflects the important contribution from the metal atoms since the number of O in a unit cell is five times that of Cu and Mo. The relative atom contributions decrease in the order Cu >> Mo > O > N > C > H in the VB contributions (Table S3), and in the order Mo >> Cu > N > C > O > H in the CB contributions (Table S3). These findings show that the SHG of CuMoO$_3$(p2c) is governed largely by the occupied states of Cu 3d, Mo 4p, and O 2p, and by the unoccupied states of Mo 4d, Cu 3d, and N-2p. The metal atoms Cu and Mo contribute much more strongly than do the nonmetal atoms in determining the strength of the SHG response in CuMoO$_3$(p2c), which is quite special among the NLO materials known to date.
Table 1. Contributions of the atoms to the largest components of the SHG tensors $d_{11}$ of CuMoO$_3$(p2c). $N_A$ refers to the number of the atom type (on the same Wyckoff site) in a unit cell; $A_\tau$, $N_A A_\tau$, $VB A_\tau$, and $CB A_\tau$ refer to the contributions (in %) from a single atom, the total atoms of the same type, all VBs for a single atom, and all CBs for a single atom, respectively. $d_\tau$ denotes the actual value of the contribution (in pm/V) to the SHG for a single atom.

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<th>Atom</th>
<th>$N_A$</th>
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<th>$CB A_\tau$</th>
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</tbody>
</table>

According to the individual atomic contribution to the SHG response, the contribution of an atomic group can be calculated by summing the contributions of the center atom and those of its ligands. In this work, we partition the contribution of an anion (O$^{2-}$ and N$^{3-}$) equally to all the atomic groups it belongs to. The contribution of an atomic group can be calculated by summing the contributions of the center atom and those of its coordinated atoms [55]. Considering the coordination number for each O and N atom (2 and 3, respectively, Figure S8), the group CuO$_3$N can be rewritten as CuO$_{1/2}$O$_{3/2}$O$_{1/2}$N$_{1/3}$2/3. Therefore, the group contribution of CuO$_3$N to SHG response is calculated as follows,

$$\chi^{(2)}_{CuO_3N} = \chi^{(2)}_{Cu} + 1 \times \left( \chi^{(2)}_{O_2} / 2 \right) + 1 \times \left( \chi^{(2)}_{O_3} / 2 \right) + 1 \times \left( \chi^{(2)}_{O_5} / 2 \right) + 1 \times \left( \chi^{(2)}_{N_2} / 3 \right)$$  \hspace{1cm} (6)

The group with anion coordination numbers and the total group contributions for the largest SHG component $d_{11}$ of CuMoO$_3$(p2c) are given in Figure 4, which shows that the metal-centered group [CuO$_3$N] and [MoO$_3$N] contribute much more strongly to the SHG response than does the organic p2c ligand. That is, the total contribution of the inorganic part is ~79.1%, which far surpasses that of the organic part (i.e., ~20.9%). Our results reflect that the inorganic part contributes dominantly to the SHG response, while the organic part is important in the stabilization of the crystal structure of CuMoO$_3$(p2c). It is worth mentioning that we did not separately calculate the hyperpolarizability tensor $\beta_{ijk}$ by cutting out the ligand or groups from the structure of the compound. Such an approach will unavoidably lead to uncontrolled errors; thus, they are not used in our calculations.

Figure 4. The cause for the large second harmonic generation (SHG) of the metal-oxide/organic hybrid compound CuMoO$_3$(p2c) is shown to be the inorganic metal-cation-centered groups [CuO$_3$N] and [MoO$_3$N] rather than the organic nonmetal-cation-centered groups [C$_5$O$_2$N$_2$H$_3$].
4. Conclusions

Although a number of NCS HF materials with 3D and 2D frameworks have been reported with large SHG response, only low SHG intensities have been measured for HF materials with 1D helical chains. Our first-principles calculations predict that the recently synthesized CuMoO₃(p2c) exhibits the largest SHG response among all the NCS HF materials with 1D helical chains. Its static effective SHG response, 30.6 pm/V, is about 3.12 times greater than that of commercial AGS, and 92.7 times greater than that of KDP. This value also exceeds those of most NCS hybrid framework materials reported so far. Our ART analysis shows that the SHG of CuMoO₃(p2c) is determined largely by the occupied states composed of Cu 3d, Mo 4p, and O 2p, and by the unoccupied states composed of Mo 4d, Cu 3d, and N 2p. The metal atoms Cu and Mo contribute much more strongly than do the nonmetal atoms in determining the strength of the SHG response in CuMoO₃(p2c). The latter is quite special in the NLO materials known to date. Our work based on the quantitative calculations at the electronic and the atomic level reveals the importance of the contribution from metal atoms and the metal-centered inorganic groups for the SHG response of CuMoO₃(p2c).

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/sym14040824/s1, Figure S1: Calculated band structure for P3₂CuMoO₃(p2c). Figure S2: HOMO (M₁) and LUMO (A₁) for CuMoO₃(p2c). Figure S3: Calculated partial DOS for P3₂CuMoO₃(p2c). Figure S4: Calculated partial DOS of O and N atoms at independent crystallographic positions. Figure S5: Frequency-dependent refractive indices n (left) and birefringence Δn (right) of CuMoO₃(p2c). Figure S6: (a) δζ(E_B)-vs-E_B plot, and (b) δζ(E_B)-vs-E₂ plot calculated for the SHG coefficient d₁₁ of CuMoO₃(p2c). The values of the functions are in pm/V. Figure S7: Plots of (a) δζ(I_B)-vs-I_B, (b) δζ(I_B)-vs-I_B, (c) δζ(I_B)-vs-I_B and (d) δζ(I_B)-vs-I₅ calculated for the SHG coefficient d₁₁ of CuMoO₃(p2c). The values of the functions are in pm/V. Figure S8: Coordination environment for each inequivalent O and N atom of CuMoO₃(p2c). Table S1: The optimized crystal structure data for P3₂CuMoO₃(p2c). Table S2: Calculated SHG tensors d₃ and d₃eff for CuMoO₃(p2c) and several NCS HF compounds with helical chains. For the compounds with no available experimental band gap (E_g), the calculated E_g based on HSE06 with mixing parameter α = 0.3 is applied. The available experimental measured SHG responses are also presented. In this work, Kleinman symmetry is not enforced in calculating the NLO properties. Table S3: Contributions of the individual atoms to the SHG component d₃₁₁ of CuMoO₃(p2c). W_A refers to the number of the same type of atoms (on the same Wyckoff site) in a unit cell. Aₜ is the contribution (in %) from a single atom τ, and C_A from all atoms of the same type. Vₐ₂ₐ is the contribution in (%) the VBs, and Cₐ₂ₐ from the CBs. The contributions from the s, p, and d states of the atom τ to of Vₐ₂ₐ and Cₐ₂ₐ are also shown [56,57].


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**References**


