ChemPubSoc Europe

DOI: 10.1002/chem.201806372

CHEMISTRY
A European Journal
Full Paper

Molecular Electride

Inorganic Molecular Electride Mg_4O_3: Structure, Bonding, and Nonlinear Optical Properties

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Abstract: Growing demands of material science and, in particular, in the field of nonlinear optics (NLO) encourage us to look for stable highly polarizable molecules with excess diffuse electrons. An unusual class of compounds called electrides comply with these requirements. Many attempts have been made, yet only few electrides have been synthesized as solids and none of them as molecular species. In this paper, a new theoretically designed molecular species with electride characteristics is reported. The idea of this molecular electride comes from the formation of electride-like features in the MgO crystal with defect F-centers. The geometry of the investigated molecule can be described as a Mg_4O_4 cube with one oxygen atom removed. In Mg_4O_3, two 3s electrons are pushed out from the inner area of the molecule forming a diffuse electride multicentered bond. Our calculations show that this electride-like cluster possesses a noticeably large first hyperpolarizability $\beta = 5733$ au. At the same time, a complete cube Mg_4O_4 and $Mg_4O_3^{2+}$ without electride electron pair have much smaller β: 0 au and 741 au, respectively. This fact indicates the decisive role of the electride electron pair in NLO properties. Additionally, vertical detachment energies of isomers (VDE), excitation energies ΔE, polarizabilities α, and IR spectra were calculated. These properties, including β, are supposed to be observable experimentally and can serve as indirect evidence of the stable molecular electride formation.

Introduction

Electrides are known as nontrivial compounds where electrons are localized in space distinct from atoms and they behave like anions. Such substances possess intriguing chemical and physical properties. For example, solid-state electrides with weakly bound interstitial electrons have already found plenty of applications as electron-emitting devices,[1,2] chemical reductants,[3] electron-injection layers in organic LEDs,[4,5] reversible hydrogen storage materials,[6] and secondary electron emitters in plasma display panels.[7] Furthermore, electrons localized in regions distinct from nuclear positions are more "flexible" and diffuse. Therefore, even weak electric fields cause pronounced polarization in electrides.

This indicates that these highly polarizable structures are very promising materials in the field of nonlinear optics (NLO). NLO materials attract significant interest because of their wide applications in optical communication, optical computing, dynamic image processing, and other laser devices.[8–16] Moreover, electrides are capable of boosting nitrogen dissociation, which, in turn, facilitates the process of ammonia synthesis.[6,17–21] The first hyperpolarizability is the factor that determines the presence of NLO properties in materials. As hyperpolarizabilities play decisive roles in the NLO properties, many experimental[22–25] and theoretical studies[26–31] of the first hyperpolarizability β of different materials were performed recently. To date, many attempts have been made to increase the hyperpolarizabilities of a wide variety of organic molecules.[9,31,32] Theoretical calculations show that structures with diffuse electrons have extremely high β.[34–37] For example, Li^+@calix[4]pyrrole(e^-)[36] has a value of β equal to 7326 au and TCNQ-Li_2[37] has $\beta = 19\,203$ au.

Despite many theoretical predictions, experimental attempts, existence of predictive models for electride formation,[38] and comprehensive reviews on theoretical descriptors of electrides,[39] only a few electride-like structures have been synthesized.[40–44] It is important to note that all these compounds are solids. In other words, although theoretical predictions of molecular electrides have been reported,[45–47] there are no experimental data on such species. Therefore, it is essential to continue theoretical investigations of molecular electrides to understand the nature of their formation and eventually find those that could be obtained experimentally. The current work presents the theoretical investigation of a stable neutral molecular electride-type structure Mg_4O_3 (Figure 1).

Our calculations show that this compound belongs to the C_{3v} point symmetry group and can be described as a Mg_4O_4

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https://doi.org/10.1002/chem.201806372.

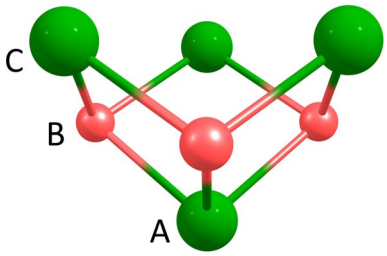

Figure 1. Structure of Mg_4O_3. Hereinafter magnesium atoms are green, oxygen atoms are red. R(A–B) = 1.98 Å, R(B–C) = 1.94 Å, ∠(A-B-C) = 85.9°.

cube with one oxygen atom removed. The idea of this molecule came from the MgO crystalline phase with F-defects.[48] It was recently shown that in this solid, an electride-like bond appears in the void in the shape of a five- or six-centered two-electron bond between Mg atoms upon the removal of one oxygen atom from the surface or from the bulk. This led us to guess that the isolated cluster Mg_4O_3 also could possess electride properties. In this article, we will show that the suggested structure is a global minimum (GM) and it has a diffuse electride bond localized in the position of the removed oxygen and, hence, has pronounced NLO properties, which will be described in terms of hyperpolarizability β.

Computational Methods

Isomers of Mg_4O_3 stoichiometry were obtained by using the Coalescence Kick global minimum search procedure[49] using the PBE0[50] functional and 6–311+G* basis set.[51] Coalescence Kick was designed to perform unbiased machine searches of global minimum out of large sets of initial structures. In the case of Mg_4O_3, we carried out a search out of 5000 initial geometries and then we selected the lowest lying isomers within 20.0 kcal mol^{-1} from the GM. After that, we reoptimized them at the more sophisticated PBE0/aug-cc-pVTZ[52] level of theory. Electronic property calculations of cations $Mg_4O_3^{1+}$ and $Mg_4O_3^{2+}$ were done using GM geometry. Relative energies of the lowest isomers were calculated at the CCSD(T)[53]/aug-cc-pVTZ//PBE0/aug-cc-pVTZ level of theory including zero-point energy (ZPE) correction. For single-point CCSD(T) calculations, ZPE values were taken from PBE0/aug-cc-pVTZ results. Additionally, the wave function stability was checked for GM and no instabilities were found. Single-point CASSCF(6,8)/aug-cc-pVTZ calculation was performed for the GM structure to check if the wave function has a multiconfigurational nature. We found that the Hartree–Fock configuration has 0.94 coefficient out of 1176 configurations. Thus, the wave function has single-reference character and our DFT results should be reliable. All calculations were performed with the Gaussian 09[54] software package.

The static polarizability matrix and the static first hyperpolarizability tensor of the Mg_4O_3 system were obtained by using the finite field method.[55] The total energy E of a system in the presence of a homogeneous electric field F can be expanded in Taylor's series according to Equations (1) and (2):

$$E(F) = E(0) + \partial E/\partial F|_{F=0} F + {}^1/_2(\partial^2 E/\partial F^2)|_{F=0} F^2 + {}^1/_6(\partial^3 E/\partial F^3)|_{F=0} F^3 + \ldots \quad (1)$$

in which

$$\mu_0 = \partial E/\partial F|_{F=0},\ \alpha = \partial^2 E/\partial F^2|_{F=0},\ \beta = \partial^3 E/\partial F^3|_{F=0} \quad (2)$$

and $E(0)$ is the total energy of a system without the electric field, μ_0 is the permanent dipole moment, α is the polarizability, β is the first hyperpolarizability also known as second-order NLO response. In the case of a static electric field, α and β are static (hyper)polarizabilities. The dipole moment of the system μ can be expanded as [Eq. (3)]:

$$\mu = -\partial E/\partial F = \mu_0 + \alpha F + {}^1/_2\beta F^2 + {}^1/_6\gamma F^3 + \ldots \quad (3)$$

and the average(isotropic) $<\alpha>$ is defined the following way [Eq. (4)]:

$$<\alpha> = {}^1/_3 \mathrm{Tr}(\alpha) = {}^1/_3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (4)$$

The static hyperpolarizability tensor $\beta_{ijk}(0;0,0)$ owing to Kleinman's symmetry can be described within just 10 components instead of 27 ones. Therefore, according to Equations (5–8):

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \quad (5)$$

$$\beta_y = \beta_{yyy} + \beta_{yzz} + \beta_{yxx} \quad (6)$$

$$\beta_z = \beta_{zzz} + \beta_{zxx} + \beta_{zyy} \quad (7)$$

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (8)$$

in which β_i and β_{tot} are the hyperpolarizability along ith direction and total hyperpolarizability, respectively. Chemical bonding analysis was carried out by using the adaptive natural density partitioning (AdNDP)[56,57] method, which is a natural bonding orbital (NBO)[58,59] method extension. To further verify the AdNDP analysis results, we performed calculations of electron localization function (ELF)[60] and Laplacian topology by using the Denstoolkit[61] and AIMALL[62] packages, respectively. Vertical electron detachment energies were calculated by using the time-dependent density functional theory (TD-DFT) method,[63] CCSD(T)/aug-cc-pVTZ, and outer valence green function (OVGF) method.[64–66]

Results and Discussion

Lowest isomers and geometry

Figure 2 represents the global minimum (GM) structure of C_{3v} symmetry and four lowest isomers. According to these calculations, the "quasi-cubic" C_{3v} structure with one oxygen atom removed is the global minimum. The C_{3v} structure is the lowest laying isomer with the difference between the next isomer of 9.3 kcal mol^{-1} and 6.0 kcal mol^{-1} at the PBE0 and CCSD(T) levels of theory, respectively. We also performed a Coalescence Kick search for the triplet state potential energy surface (PES) and, according to the calculations, the triplet GM (^3A) is 13.9 and 18.2 kcal mol^{-1} higher than the singlet GM at the DFT and CCSD(T) levels of theory, respectively. All the structures considered are local minima from the vibrational point of view.

Bonding analysis

We found that every oxygen atom holds four lone pairs with occupation number (ON) = 1.82–1.93 |e|, which corresponds to the formal atomic charge −2.00 |e|. As the 2p orbitals of

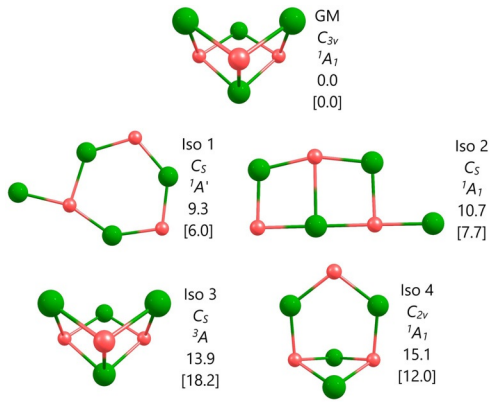

Figure 2. Global minimum and four lowest isomers of the Mg_4O_3 stoichiometry. The point symmetry groups and spectroscopic states are shown in italic. Values without brackets represent relative energies at the PBE0/aug-cc-pVTZ level of theory, whereas values in square brackets refer to the CCSD(T)/aug-cc-pVTZ//PBE0/aug-cc-pVTZ values.

oxygen atoms are filled now, two remaining 3s electrons of the magnesium atoms should be delocalized on magnesium atoms and be repelled by oxygen lone pairs out of the inner area. As we expected, the molecule has primarily ionic bonding, which is supported by the NBO charge values and occupation number values. According to NBO analysis, each oxygen atom possesses the charge of $-1.48|e|$ whereas on the Mg atom labeled 1 (Figure 3) $+1.35|e|$ is localized and the rest of the Mg atoms have $+1.03|e|$ charges.

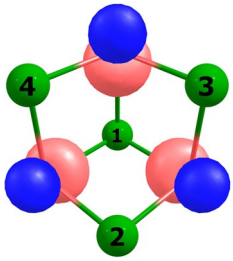

Figure 3. Oxygen p-electrons attracted from Mg, ON = 1.82 | e |.

According to the AdNDP analysis, the Mg_4O_3 molecule indeed has 12 valence lone pairs with occupation numbers (ON) $>1.82|e|$ and an electride-like 3c–2e diffuse bond with ON = 1.91 | e | (Figure 4). All this data indicates that electrons are substantially withdrawn from Mg atoms; however, one electron pair is located in the area of the removed oxygen atom and could be considered as a 3c–2e bond delocalized over three upper Mg atoms. Thus, this is indeed a molecular-like electride.

To support the results of the AdNDP study, we also performed QTAIM (quantum theory of atoms in molecules) analysis[67] and calculated electron localization functions (ELF).[60] In Figure 5, basins of Laplacian $\Delta\rho$ and ELF are depicted.

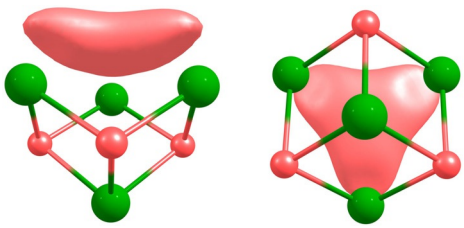

Figure 4. Mg_4O_3 diffuse electride-like doubly occupied orbital, ON = 1.91 | e |.

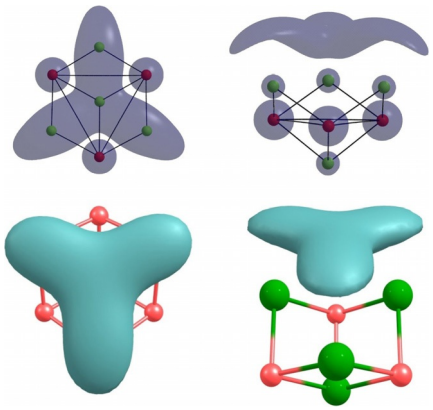

Figure 5. Top: Laplacian isosurface with contour value 0.00, inner area is <0. Bottom: ELF isosurface with contour value 0.89.

These basins are undoubtedly similar to the isosurface of the electride-like orbital recovered by the AdNDP analysis. We also plotted several planes dissecting the ELF basin in different ways (Figures S9–S10 in the Supporting Information). They are fully consistent with the 3D picture and provide quantitative evaluation of the ELF, which gives values in the position of the electride orbital reaching approximately 0.9. Taking into account that ELF = 1.0 means full possible localization, we consider our ELF analysis result as further solid evidence of the high occupancy of the electride orbital.

The electronic properties of Mg_4O_3

As the bonding nature of Mg_4O_3 is ionic and to some extent this structure might be considered as a "splinter" of the parental MgO crystalline phase, one should expect the recombination between freely interacting Mg_4O_3 species. Therefore, we guess that the structure could be synthesized, for example, under matrix isolation conditions or in a molecular beam. For the latter technique the electron spectrum is commonly used fingerprint, which could be matched with the theoretical one. Measurement of vertical detachment energies (VDE) is a common way of distinguishing a certain structure among others of given stoichiometry. In the present paper, we provide theoretical VDEs obtained by PBE0, CCSD(T), and OVGF methods within the aug-cc-pVTZ basis set (Table 1).

The results at all three levels of theory are in good agreement with each other. The vertical detachment energy (VDE) of the Mg_4O_3 electride-like structure is 5.5–5.6 eV, which indicates

Table 1. VDEs of five lowest isomers at different levels of theory.

Isomer	VDEs		
	PBE0 [eV]	CCSD(T) [eV]	OVGF [eV]
GM	5.58	5.57	5.49
Iso 1	6.10	6.14	6.14
Iso 2	6.11	6.17	6.18
Iso 3	4.95	4.74	4.88
Iso 4	5.48	5.60	5.48

that this doubly occupied electride-type orbital is relatively stable (Table 1).

It is known[31,32] that electrides as well as structures with diffuse electrons have comparatively low excitation energies ΔE. For example, Li@calix[4]pyrrole (where the Li atom donates the excess electron)[31] has $\Delta E = 1.98$ eV, whereas calix[4]pyrrole[31] has $\Delta E = 6.02$ eV. As for Mg_4O_3, TD-DFT revealed that it has $\Delta E = 2.06$ eV, whereas for the complete cubic structure of Mg_4O_4, $\Delta E = 3.39$ eV. ΔE values in Table 2 show that electrons in the electride-like orbital are responsible for the low ΔE. When the orbital is singly occupied in the $Mg_4O_3^{1+}$ cation, the alpha-electron in the orbital still has low ΔE although the usual beta-electron needs more energy for excitation.

Table 2. Electronic properties of M_4O_3 and related compounds.

Compound	Properties			
	ΔE [eV]	$<\alpha>$ [au]	β_{tot} [au]	$\beta_{tot}/<\alpha>$
Mg_4O_3	2.06	245.3	5733.5	23.0
Mg_4O_4	3.39	86.2	0.0	0.0
$Mg_4O_3^{1+}$	1.99[a] | 2.86[b]	129.9	65.5	0.5
$Mg_4O_3^{2+}$	2.64	61.3	743.9	12.0

[a] ΔE of electride α-electron. [b] ΔE of usual β-electron.

In the absence of the electride-like bond in the $Mg_4O_3^{2+}$ dication, ΔE is also higher than for Mg_4O_3.

Table 2 clearly displays that diffuse electrons have a significant effect on NLO properties. The value of the first hyperpolarizability $\beta = 5733.46$ au is much larger than the linear polarizability $\alpha = 245.27$ for Mg_4O_3. This fact means there is a clear second-order response to the electric field, which is direct evidence of pronounced NLO properties. When one or both diffuse electrons are removed ($Mg_4O_3^{1+}$ and $Mg_4O_3^{2+}$), β becomes significantly lower (65.55 and 743.87 au, respectively). Among all species provided in Table 1, the ratio $\beta_{tot}/<\alpha>$ is the highest for Mg_4O_3 with the doubly occupied diffuse orbital, which tremendously contributes to the NLO properties.

Conclusions

In this paper, we introduced a newly designed inorganic molecular electride, Mg_4O_3. The global minimum structure has C_{3v} symmetry structure, which can be considered as a cubic structure of Mg_4O_4 with one oxygen atom removed. AdNDP analysis revealed that 12 out of 13 electron lone pairs are localized on oxygen atoms, whereas the residual electron pair is pushed out of the inner area. That leads to the formation of a diffuse multicentered doubly occupied electride bond located over the area of the absent oxygen atom with substantially high ON = 1.91 | e |. This electride-like 3c–2e bond is similar to the multicentered 6c–2e and 5c–2e bonds located in F-centers in the MgO crystal.[38] Being an electride structure, Mg_4O_3 has a significant first hyperpolarizability value $\beta = 5733.46$ au, which is responsible for the nonlinear optical properties. We also showed that the diffuse electride orbital's contribution is crucial for NLO properties as ionized $Mg_4O_3^{1+}$ and $Mg_4O_3^{2+}$ species and the complete cube Mg_4O_4 possess appreciably lower values of β.

As was already pointed out, molecular electrides have not been obtained experimentally yet, so we also calculated the observable electronic properties such as excitation energies, VDEs, IR spectra (Figures S1–S8 in the Supporting Information), and linear polarizability α. We hope these results will encourage experimentalists and help them in further electride explorations. We believe theoretical study of such molecular electrides are of great importance as they have outstanding physical and chemical properties and may have a wide range of potential applications.

Acknowledgments

This project was supported by the National Science Foundation (CHE-1664379). The publication has been prepared with the support of the "RUDN University Program 5-100". The support and resources from the Center for High-Performance Computing at the University of Utah are gratefully acknowledged.

Conflict of interest

The authors declare no conflict of interest.

Keywords: chemical bonding · electrides · material design · molecular electride · nonlinear optics

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Manuscript received: December 23, 2018
Accepted manuscript online: February 2, 2019
Version of record online: March 14, 2019