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Manifestations of two-dimensional electron gas in molecular crystals

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A B S T R A C T

The existence of two-dimensional electron gas in molecular materials has not been reported or discussed. Intriguing properties of two-dimensional electron gas observed on interfaces of polar and nonpolar oxides spurred oxide electronics and advanced nanotechnology. Here we discover how an electrostatic instability occurs on polar surfaces of molecular crystals and explore its manifestations, chemical degradation of surfaces, charge separation, electrical conductivity, optical band-gap closure and surface metallization. A thin layer of polar surface of a dielectric molecular crystal becomes metallic due to interactions of polar molecules. Our findings are illustrated with two polymorphs of cyclotetramethylene-tetranitramine crystals, the polar δ-phase and nonpolar β-phase. Our theory offers an explanation to a relative stability of the β-phase versus the explosive reactivity of δ-phase and to the experimentally observed difference in conductivity of these crystals. We predict that the electrostatic instability takes place on all polar molecular materials.

1. Introduction

Two-dimensional electron gas observed on interfaces of polar and nonpolar oxide surfaces [1–3] led to revealing exotic phases of matter [4,5] that exhibit metal–insulator transitions [6,7], superconductivity [8,9] and its controllable on/off switching [10], large negative magnetoresistance [11], co-existence of superconducting and magnetic states [12], and giant thermoelectric effect [13]. Those unusual properties prompted the emerging field of oxide electronics [14] and opened new prospects in nanotechnology [15] among other intriguing opportunities. However, the existence and properties of two-dimensional gas in molecular materials have yet to be established. Here we discover an electrostatic instability that generates the two-dimensional electron gas state and takes place on polar surfaces in molecular crystals. A thin layer of polar surface of a wide band gap dielectric molecular crystal becomes metallic due to interactions of polar molecules. Among fundamental manifestations of this phenomenon, we theoretically explore chemical degradation of surfaces, charge separation, electrical conductivity, optical band-gap closure and surface metallization. We found that there is a dramatic difference in surface decomposition reactions of polar δ-phase and nonpolar β-phase polymorphs of molecular cyclotetramethylene-tetranitramine (HMX) crystals (Fig. 1). This difference is governed by excess or deficit of electrons, or surface conductivity, which explains a relative stability of the β-phase (Fig. 1a-c) and the high reactivity of the δ-phase (Fig. 1d-f). The polarization-induced separation of electrons and holes on δ-HMX creates the surface charge density of $7.9*10^{13}$ e/cm^2, corresponding to 0.458 electrons/molecule, which is similar to a typical charge carrier density at the oxide/oxide interfaces.

2. Computational approach

All molecular calculations in our study were carried out within the GAUSSIAN 09 [16] program suite. Density functional theory [17,18] (DFT) – based Heyd-Scuseria-Ernzerhof functional HSE06 [19] with 6–31+G(d,p) basis set was used to study the electronic structure of ground state equilibrium molecules. Optical absorption properties were explored with the time dependent DFT (TD HSE06) procedure [20,21].

Periodic solid-state calculations were performed using the GGA PBE functional and PAW pseudo-potentials [22] as implemented in the plane wave VASP code [23–25]. Details of calculations of ideal crystals of β- and δ-HMX are reported in [26,27].

The structure of ideal bulk crystal of the hexagonal δ-HMX (Fig. 1e) was investigated by constructing a supercell consisting of 6 molecules (168 atoms) with lattice parameters of a=b=8.18 and c=33.15 Å. In calculations of the ideal δ-HMX crystal with the $P6_1$ symmetry, we used 2×2×1 Monkhorst–Pack k-point mesh, and the kinetic energy cut-off was set to 600 eV (see ref. [26] for more details).

Electronic properties of the δ-HMX (001) surface were studied with the supercell model containing two symmetric lattice fragments each consisting of ten-molecule-thick (001) slabs (Fig. 2). Each ten-molecule fragment was cut out of the initially optimized hexagonal δ-HMX bulk supercell (Fig. 1e). Two crystalline pieces are placed in the supercell in such a way that one fragment in the slab represents a mirror reflection

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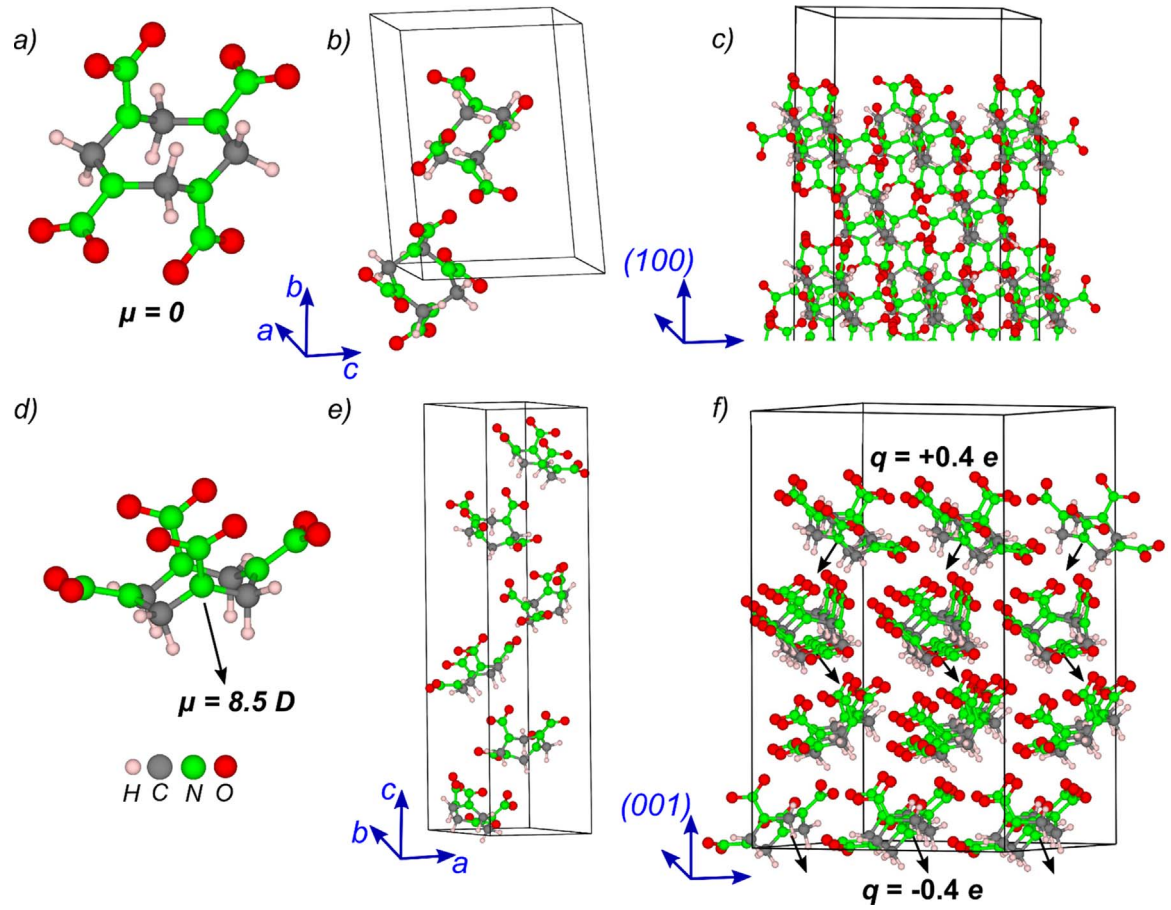

Fig. 1. The structure of a) β-HMX molecule, b) β-HMX crystal, c) nonpolar (100) β-HMX surface, d) δ-HMX molecule, e) δ-HMX crystal, and f) polar (001) δ-HMX surface.

of the other fragment. The resulting supercell slab has parameters of a=b=8.18 Å, c=132.27 Å and γ=120°. The vacuum layer of ~10 Å placed on top of the δ-HMX (001) surface was intended to minimize interactions between supercells in (001) direction and to ensure that electronic states of different slabs do not overlap. Such a 20-molecule (560-atom) supercell with zero total dipole moment was deliberately designed to remove an artificial electric field in the vacuum layer. The full optimization of the surface structure was carried out using Γ-point only and the kinetic energy cut-off of 520 eV. A single point calculation using 6×6×1 Monkhorst–Pack k-point mesh was then carried out to obtain accurate density of states.

Electronic properties of the β-HMX (100) surface (Fig. 1c) were studied with the supercell consisting of nine molecular layers cut out of the optimized bulk crystal in the (100) direction (Fig. S1 of Supplementary Information). The resulting supercell contained 18 molecules (504 atoms) and had lattice parameters of a=62.31 Å, b=11.41 Å, c=8.91 Å, α=β=γ=90°. The thickness of the vacuum layer placed on top of the β-HMX (100) surface was of ~10 Å. The full optimization of the surface structure was carried out using Γ-point only and the kinetic energy cut-off of 520 eV. A single point calculation using 6×6×1 Monkhorst–Pack k-point mesh was then carried out.

To correct significantly underestimated band gap energies, obtained from GGA PBE, a self-consistent single point calculation for each configuration was performed with the hybrid HSE06 functional at the Γ-point only and the kinetic energy cut-off set to 520 eV. A series of test calculations shows that such an approach yields reasonable band gap energies (See discussion in Supplemntary Information). In simulating optical absorption spectrum, we plotted the frequency-dependent imaginary part of the dielectric functions of ideal crystals and surfaces of β- and δ-HMX [28].

Bader charges were analyzed by using Bader Charge Analysis code [29–31]. Coordinates of all structures employed in this study are collected in Supplemntary Information.

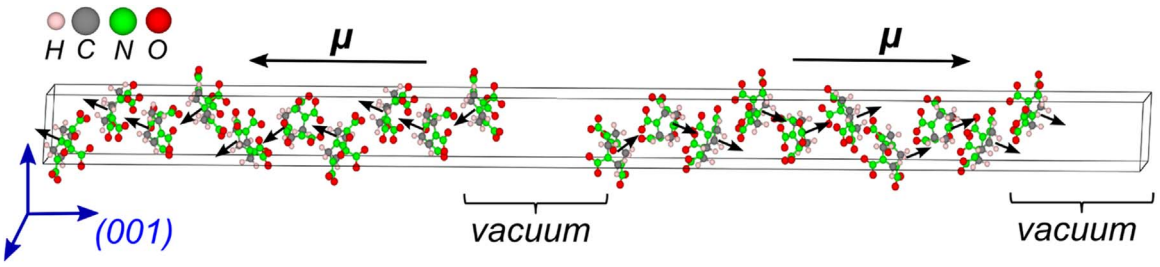

Fig. 2. The slab model of the ten-molecule-layer δ-HMX (001) surface supercell. The model with two mirrored molecular crystal images separated by the vacuum layer is chosen to compensate for the dipole moment and to eliminate the electrostatic field.

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