First-principles description of solid oxygen in the gigapascal pressure scale using the DFT+vdW+U approach

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We investigate the electronic and structural zero-temperature properties of the α phase of solid oxygen at pressures ranging from 0 to 6 GPa. Crystal and electronic structures have been characterized using a generalized gradient approximation combined with a semiempirical van der Waals dispersive interaction and a Hubbard U correction. Lattice parameters, volume-pressure relation, compressibility, dispersion curve, density of states, and phonon frequencies are studied under pressure and indicate a marked sensitivity with the considered electronic model. A systematic comparison of the various parameters permits one to determine an optimized scheme that reproduces the experimental behavior with pressure and represents a clear improvement with respect to previous simulations and phenomenological models.

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I. INTRODUCTION

Oxygen is particular and unique in many ways given its fundamental role in biology and geophysics. It is, indeed, the most abundant element in the earth's crust and the description and characterization of its complex phase diagram continues to stimulate both experimental and theoretical studies.

Oxygen is also the only elemental molecule which carries a magnetic moment due to the presence of two unpaired electrons on the upper π_{e}^{\star} molecular orbital (Fig. 1) which gives a ground state with S = 1 (Hund's rule) in the electronic triplet ground state ${}^{3}\Sigma_{\rho}^{-}$. From the first study by Perrier and Onnes [1] below the melting point of oxygen at around 54 K, experimental evidence has been provided that solid oxygen displays magnetic ordering. Among the documented low-temperature crystalline phases (denoted α , δ , and ϵ , see Fig. 2 the phase diagram without the external magnetic field, i.e., without the so called θ -O₂ nor η -O₂ and ζ -O₂ phases), the stable one at 24 K and ambient pressure (i.e., α -O₂ phase) has an antiferromagnetic long-range order [2]. At low temperature and/or high pressure, this ordering is disturbed and leads to various magnetic ground states which have been investigated recently by neutron scattering [3–6]. Numerical investigations using density functional theory (DFT) have essentially focused on high pressure phases [7-10] among which the characterization [9] of the ϵ -O₂ phase. The latter is thought to have a particular magnetic structure (a "plaquette"-like) in which spins display antiferromagnetic ordering over four oxygen molecules. Earlier work using empirical force fields [11] have attempted to describe the α phase but led to an unsuccessful modeling of the α - β transition, found at too small pressures. The structure of the α phase is well understood at ambient pressure, but the transition from α -O₂ to δ -O₂ has not been studied as part of a first-principles approach.

The aim of this work is precisely to improve the structural and electronic description of solid oxygen at low pressure by first-principles methods. In contrast with previous DFT calculations [7–10], the focus of the present contribution is, indeed, on the "low" pressure range, i.e., up to 10 GPa, where the stable magnetic phases α -O₂ and δ -O₂ are experimentally found. Regarding this region of the phase diagram, we are only aware of the classical model from work of Etters *et al.* using an empirical force fields [11], and DFT based approaches have not yet been considered, apart from exploring the structure of the magnetic-field-induced θ -O₂ phase [12].

At low pressure and low temperature (below 24 K at zero-pressure), the insulating α -O₂ phase crystallizes in a monoclinic structure (space group C2/m) with two O₂ molecules per unit cell (Fig. 3). These in-plane molecules have an antiferromagnetic coupling (Fig. 4) [2,3,13,14]. According to the choice of the monoclinic cell, there are two different sets of parameters *c* and β (see red vectors on Fig. 3) or *c'* and β' (see dashed blue lines in Fig. 3) to describe the monoclinic cell of α oxygen. We use in this paper the definition for which the monoclinic cell has the smallest monoclinic angle—Delone's rule [15]—i.e., *c* and β parameters. To compare our values with previous simulations [11,12] and experimental data [16–18] that sometimes use *c'* and β' , we will use volume conservation to link these parameters using

$$c\sin\beta = c'\sin\beta'.$$
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FIG. 1. Schematic molecular orbital diagram for the ${}^{3}\Sigma_{g}^{-}$ triplet ground state of O₂ molecule.

At fixed temperature and with increasing pressure from ambient conditions, an orthorhombic phase occurs (space group *Fmmm*) with also two O₂ molecules per unit cell. This transition from the monoclinic structure of the α phase to the orthorhombic structure (δ -O₂ phase) is characterized by a transition that manifests *e.g.* by a variation of the angle β^* from $\simeq 100^\circ$ to $\simeq 90^\circ$. Diffraction patterns during isothermal decompressions have revealed [17] that this δ - α transition occurs between 5.9 GPa and 5.3 GPa, albeit the exact experimental *locus* of the transition pressure [16,19,20] has not yet been established. Using Alkashi's relation, one can link this transition angle β^* to the other lattice characteristics by

$$c'\sin\beta' = \frac{1}{2}\mathcal{C}\sin\beta^{\star},\tag{2}$$



FIG. 2. Phase diagram of oxygen. Adapted from Ref. [9]. The present study focuses on α -oxygen found at low temperature between 0 and $\simeq 6$ GPa.



FIG. 3. Monoclinic structure of α -O₂. The dashed (blue) cell is equivalent to the monoclinic one defined by red lattice vectors.

where the lattice parameter C (see dotted green line on Fig. 3) is given by

$$C = \sqrt{a^2 + (2c')^2 - 4ac'\cos(180 - \beta')}.$$
 (3)

Neutron scattering experiments [3,4], furthermore, indicate that the cristallographic phase δ -O₂ has up to three different magnetic orders. The low-temperature commensurate (LTC) phase is the one originally suggested by Goncharenko *et al.* [5]. In the 2D space defined by (a, b), spins are in an antiferromagnetic (AFM) coupling, with a spin direction along the *b* axis, as suggested by Gorelli *et al.* [21] and Santoro *et al.* [22]. Between adjacent 2D spaces, spins are in a ferromagnetic (FM) coupling at low temperatures [3,5], which entails a doubling of the unit cell in the *c*-direction, compared to the α phase. Conversely, the high-temperature commensurate (HTC) phase differs from the LTC ones only by an AFM coupling between adjacent 2D spaces, i.e., for the monoclinic *c* lattice, equivalent (0; 0; 0) and (0; 0; *c*) molecules



FIG. 4. Magnetic configuration of monoclinic structure of α -O₂. The in-plane molecules are in an anti-ferromagnetic coupling, while the out-of-plane molecules are in a ferromagnetic configuration.

in HTC phase are not anymore in LTC phase. This HTC magnetic δ -O₂ phase is identical to the α -O₂ phase. Finally, the intermediate-temperature commensurate (ITC) phase is made up of FM and AFM alternation stacking along the *c* axis. This underscores the complexity of the magnetic ordering that is transformed in a rather subtle fashion with applied pressure.

To describe the low-pressure behavior of solid oxygen, it is very much desirable to assess a DFT scheme able to substantiate the electronic and magnetic characteristics and to improve the classical modeling [11]. This is the purpose of the present contributions that builds on the recent methodology [9] introduced for δ -O₂ and [12] for the investigation of θ -O₂. Our results indicate that the DFT simulations also must involve Hubbard and dispersive [van der Waals (vdW)] corrections to account for the complex electronic interactions at play at low pressure. Once such model parameters are fixed, we explore the phase transformation with increasing pressure, and obtain a transition pressure for the α - δ transformation that is now compatible with experiments. The electronic and vibrational properties are then investigated as a function of pressure.

The paper is organized as follows. In Sec. II we summarize the DFT+vdW-D2+U formalism we have used and a certain number of numerical considerations about our calculations. Then, we present and discuss our main results in Sec. III and compare them with other data. This permits to assess the parameters used for our model. We then describe in Sec. IV both electronic and vibrational properties with pressure. Finally, in Sec. V we summarize our findings and propose some conclusive remarks.

II. METHODS AND COMPUTATIONAL DETAILS

A. DFT framework

The use of DFT [23,24] has become a such general framework for bonding and structure studies in condensed matter. This theory involves the determination of one-electron Schrödinger equations—so called Kohn-Sham equations—in the presence of an effective one-electron self-consistent potential $V_{\text{eff}}(\mathbf{r})$, which stands for three contributions: (i) the Coulomb potential from the density $n(\mathbf{r})$, (ii) the external potential, and (iii) the functional derivative of the exchange-correlation (XC) density functional $E_{\text{XC}}[n(\mathbf{r})]$. In principle universal, the latter ones describe many-particle effects. According to this framework, an approximate density energy functional $E_{\text{DFT}}[n(\mathbf{r})]$ is obtained using the QUANTUM ESPRESSO (QE) suite [25–27].

The effect of electron correlations was complemented with GGA+U corrections and with long-range vdW corrections as shown hereafter—so that, at last, in our DFT+vdW-D2+U formalism, the total energy is then given by

$$E_{\text{DFT+disp+U}} = E_{\text{DFT}}[n(\mathbf{r})] + E_{\text{disp}} + E_{\text{U}}[\{n_{mm'}^{i\sigma}\}].$$
(4)

All properties were calculated using DFT as implemented in QE based on plane waves and periodic boundary conditions. The electron-ion interactions were treated using a projector augmented wave pseudopotential with six valence electrons. We used for the XC term a generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) functional [28]. Ultrasoft pseudopotentials [29] of Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ) type [30,31] are used without further modification to describe valence-core interactions, all scalar products between crystal and atomic pseudowave functions are intended to include the usual *S* matrix describing orthogonality in presence of charge augmentation [29].

The valence electron wave functions are expanded in a plane-wave basis set with a kinetic energy cutoff of 150 Ry and a charge density cutoff of 600 Ry are used to achieve pressure convergence within less than 5×10^{-2} GPa.

The crystal structure (C2/m) and the initial atomic positions were taken from the experimental data of Krupski et al. [32]. Both the lattice parameters and atomic coordinates for all the structure were obtained by performing variable-cell optimization at various values of pressure. A molecular AFM in-plane configuration was used to take into account the magnetization of the α phase. Vibrational zero-point motion, finite temperature effects and spin-orbit coupling are not included. The spin-orbit coupling matrix element between the triplet ${}^{3}\Sigma_{p}^{-}$ state and the singlet ${}^{1}\Sigma_{p}^{+}$ state has been widely studied [33–38] and published experimental and computational values vary between 150 to 180 cm^{-1} (around 20 meV), which is one to three orders of magnitude smaller than the dispersion energy and Hubbard energy. It should be noted that the absence of spin-orbit coupling avoids that the direction of the magnetization is coupled to the crystal lattice. As a result, the energy of the system is not affected by a global rotation of the magnetization, i.e., DFT calculations cannot predict the global direction of the magnetization, but only the relative orientation of the magnetization at different points in space.

Cell parameters and atomic positions were then fully optimized at different pressures until forces were smaller than 10^{-5} a.u. using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [39,40]. Results obtained with a denser 30-point grid did not change significantly the results: less than 0.1 mRy for the energy per molecule, less than $10^{-3} \text{ eV}/\text{\AA}$ for the forces on atoms and less than 0.5 kbar for the stress tensor.

Brillouin's zone (BZ) integration was carried out using *k*-point grids generated with the Monkhorst-Pack method [41]. The size of this grid is $4 \times 4 \times 4$ for the primitive cell of α -O₂ phase considered in this study (two O₂ molecules).

The DOS and Löwdin projected-DOS calculations were performed using a $8 \times 8 \times 8$ *q*-points mesh and a Gaussian broadening of 27.2 meV (2 mRy). Electronic integration in the self-consistent run before phonon calculations was performed on a $12 \times 12 \times 12$ Monkhorst-Pack *q*-points mesh. Finally, the vibrational properties at T = 0 K were calculated using DFPT in the linear response regime [42–44].

B. Dispersive forces scheme

To describe vdW interactions in the molecular crystals, we selected the semiempirical dispersion option called DFT-D2, developed by Grimme [45] and implemented into QE by Giannozzi *et al.* [25–27]. Added to the conventional DFT total energy, this long-range corrective term is given by

$$E_{\text{disp}} = -\frac{1}{2} \sum_{i,j} C_6^{ij} \left[\sum_{\boldsymbol{R}} |\boldsymbol{r}_{ij} + \boldsymbol{R}|^{-6} f_{\text{damp}}(|\boldsymbol{r}_{ij} + \boldsymbol{R}|) \right], \quad (5)$$

where $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ is the vector distance between two atoms, \mathbf{R} are the lattice vectors, and C_6^{ij} dispersion coefficients are computed for each atom pair ij by the geometric mean of atomic terms: $C_6^{ij} = \sqrt{C_6^i \cdot C_6^j}$. In Eq. (5), the external sum runs over the few atoms of the crystal unit cell, while the inner sum runs over the lattice parameters until the distance $|\mathbf{r}_{ij} + \mathbf{R}|$ becomes larger than 100 Å (convergence criterion). To avoid near-singularities for small lattice vectors, a damping function is used, which takes the following form:

$$f_{\text{damp}}(|\boldsymbol{r}_{ij} + \boldsymbol{R}|) = s_6 \left\{ 1 + \exp\left[-d\left(\frac{|\boldsymbol{r}_{ij} + \boldsymbol{R}|}{R_0} - 1\right)\right] \right\}^{-1},$$
(6)

where s_6 is a global functional-dependent scaling factor and d is a parameter that tunes the steepness of the damping function. According to Barone *et al.* [46], these parameters are set to $s_6 = 0.75$ and d = 20 (for PBE functional used here, see above). By default, the R_0 terms are a sum of atomic vdW radii of the atom pairs ($R_0 = R_0^i + R_0^j$).

We started our study by adopting the parameters proposed by Grimme [45,47], i.e., dispersion coefficient of $C_6 = 24.284 \text{ Ry } a_0^6$ and vdW radius of $R_0 = 2.536 a_0$.

C. GGA+U scheme

To describe the oxygen as an antiferromagnetic Mott-Hubbard insulator at low pressures, we introduce another correction by taking into account the strong intramolecular Coulomb repulsion within the π_g^* states (Fig. 1). In the DFT+U scheme, the DFT total energy $E_{\text{DFT}}[n(\mathbf{r})]$ is augmented by a corrective E_U term which favors Mott localization of electrons on atomic sites. Inspired by the Hubbard model [48], it was implemented into QE [49] using a simplified rotationally invariant formulation [50] as

$$E_{\rm U} = \sum_{i,\sigma} \frac{U^i}{2} \operatorname{Tr}[\boldsymbol{n}^{i\sigma} \left(\boldsymbol{1} - \boldsymbol{n}^{i\sigma}\right)],\tag{7}$$

where U^i is the spherically averaged onsite Coulomb repulsion parameter on atomic site *i* (here, applied on the 2p orbitals of oxygen) and the occupation matrices $\mathbf{n}^{i\sigma}$ are computed as

$$n_{mm'}^{i\sigma} = \sum_{k}^{N_{k}} \sum_{v}^{N_{occ}} f_{vk}^{\sigma} \langle \psi_{vk}^{\sigma} | \phi_{m'}^{i} \rangle \langle \phi_{m'}^{i} | \psi_{vk}^{\sigma} \rangle.$$
(8)

In Eq. (8), the first sum runs over the number of k points (N_k) in the first Brillouin zone, while the second one runs over the occupied states (N_{occ}) characterized by the electronic band index v. Indexes m and m' run over projections of the angular momentum manifolds that are subjected to the Hubbard correction on atoms i.

Furthermore, the ψ_{vk}^{σ} denote the oxygen valence electronic wave functions—i.e., Kohn-Sham states—matching to the (vk) state with a spin σ and for a f_{vk}^{σ} occupations according to the Fermi-Dirac distribution of their energy. Localized orbitals ϕ_m^i are the valence atomic orbitals with state index *m* (angular momentum component $|\ell m\rangle$) and centered on site *i*. Thus, projectors $|\phi_m^i\rangle\langle\phi_{m'}^i|$ are localized-level occupation matrices



FIG. 5. Evolution of the cell volume with pressure using regular DFT, compared to data from Etters' classical molecular dynamics simulations [11] and experiments from Akahama *et al.* [16] and Barrett *et al.* [52]. We also indicate the effect of an additional correction (+U or +vdW-D2) to the DFT (see text).

projecting on atomic pseudowave functions. Finally, the elements $n_{mm'}^{i\sigma}$ measure the occupation of localized orbitals.

In this paper, we have used the implementation by Giannozzi *et al.* [27] in QE of the density functional perturbation theory (DFPT) method from Timrov *et al.* [51] to calculate the *ab initio* onsite Coulomb repulsion parameters as introduced in Ref. [49] and neglecting intersite terms. Within the first-principles linear-response approach, the Hubbard interactions U^i associated to site *i* (for each inequivalent atom) are the elements of an effective interaction matrix, computed as the difference between bare χ_0 and screened χ inverse susceptibilities (i.e., noninteracting and interacting response matrices):

$$U^{i} = \left(\chi_{0}^{-1} - \chi^{-1}\right)_{ii}.$$
(9)

As for the BZ, the *q*-point grid used to obtain the effective interaction matrix was also of $4 \times 4 \times 4$.

III. RESULTS AND DISCUSSION

As a starting point, we represent the cell volume of α -O₂ (Fig. 5) and the transition angle β^* (Fig. 6) as a function of pressure for our results and other data from x-ray diffraction experiments (Akahama et al. [16]) and empirical simulations from Etters et al. [11]. When no corrections are considered, it can be noted from the V-P equation of state (Fig. 5) that the volume at low pressure is widely overestimated whereas at high pressure, simulations and experiments differ by 5-6%. Note that Kasamatsu *et al.* [12] studied α -O₂ using two different van der Waals density functionals (vdW-DF): the revised version of PBE (revPBE) and the Becke type (optB86b) exchanges, and in both cases, this led to an underestimate of the volume with $U = 0 \,\text{eV}$. Similarly, the application of the Hubbard correction alone (calculated value of $U = 6.0 \,\text{eV}$) overestimates the volume at low pressures, but considerably improves consistency between simulations and experiments



FIG. 6. Evolution of the transition angle β^* with pressure using regular DFT compared to data from classical molecular dynamics simulations [11] and from experiments [16,52]. We also indicate the effect of an additional correction (+U or +vdW-D2) to the DFT (see text).

at high pressures. Also note that with a vdW correction using default Grimme's values (see above), the volume is systematically underestimated.

On Fig. 6, the evolution of the transition angle β^* with pressure indicates a transition at around 1 GPa, that is even lower than the predicted one from Etters *et al.* [11] which itself is lower than the one measured in diffraction experiments [17]. Note that although the volume at low pressure is overestimated by our calculations, the transition angle is underestimated in comparison with the other represented data, and even more when vdW correction is used. However, one can see that the Hubbard term (U = 6.0 eV) enables to improve the zero-pressure value of this angle.

Obviously, the absence of corrections or even basic corrections (i.e., Grimme parameterized dispersive corrections or self-consistent Hubbard term) neither permit to describe correctly the pressure evolution α -O₂, nor to obtain the anticipated α - δ transition pressure.

A. Effect of the corrections

1. Hubbard correction

To get *ab initio* calculations closer to observations, we first examine the possible values of the Hubbard potential by imposing a set of vdW coefficients (R_0 ; C_6), the DFPT calculations providing a relationship between the fixed radius R_0 and the corresponding Hubbard potential U. Figure 7 represents for three selected pressures (0, 3, and 5) GPa, the calculated Hubbard potential U versus the vdW radius for different dispersion coefficients C_6 . Here, three possibilities are considered: (i) the default value proposed in the DFT-D2 scheme [45], i.e., $C_6 = 24.284 \text{ Ry a}_0^6$, (ii) the calculated atomic coefficient of Wu and Yang [53] (25.900 Ry a_0^6), which is in good agreement with that of Neumann and Perrin [54] (25.580 Ry a_0^6), and (iii) an



FIG. 7. DFPT determination of Hubbard potential U as a function of vdW radius R_0 . Horizontal dashed lines are the calculated Hubbard values without vdW correction.

arbitrary higher value of $30.112 \text{ Ry } a_0^6$ to check the trend of our simulations.

Results indicate that the higher the pressure, the greater the value of the potential U needed to obtain an α - δ transition at reasonable pressure value. Moreover, for the three selected pressures, the calculated Hubbard potential can be considered as independent of the value of C_6 coefficient, but is weakly correlated to the vdW radius, even at zero-pressure. The reason is as follows. Since the van der Waals radius of an atom is the radius of the corresponding hard sphere representing the closest approach distance to another atom, by increasing it, the electronic repulsions are also increasing for a given distance, due to the charge distributions overlap. Thus, one simply move the attractive effects of the vdW forces to a higher distance through the damping function. Indeed, we can note that for a given U correction, the distance between two neighboring molecules—given by the $\sqrt{a^2 + b^2}/2$ length (see Fig. 3 for the notations)—increases with the vdW radius. We conclude that the larger the R_0 , the less attractive the vdW forces.

However, this trend weakens by increasing pressure, which in essence brings molecules closer together and weakens the effect of nonlocal interactions, as seen for higher pressures (Fig. 7). Since the vdW radius dependence is still much smaller than the absolute value of Hubbard parameter at high pressures, we approximate the vdW-radius-dependent first-principles U by its value without vdW correction, i.e., the constants 7.8 eV or 8.3 eV for all oxygen atoms at all pressures (see dashed lines on Fig. 7). We will add another value 6.5 eV corresponding to vdW radius of $R_0 = 2.587 a_0$ at 0 GPa (see below) for comparison purposes.



FIG. 8. Effect of Hubbard potential on the α - δ transition— $R_0 = 2.587 a_0$ and $C_6 = 25.900 \text{ Ry } a_0^6$ —together with experimental data from Akahama *et al.* [16] and Barrett *et al.* [52] and classical MD from Etters *et al.* [11]. The gray zone represents the α - δ transition region determined from spectroscopic studies [17]. No δ -O₂ phase was observed [16] (see text).

Now, to fix the appropriate values of the vdW coefficients, we use the characteristics of the α - δ transition. Gorelli *et al.* [17] studied solid oxygen by x-ray scattering and concluded that the α - δ transition occurs when the angle β^* shifts from 96° to 90° . Figure 8 shows the effect of selected Hubbard potential on the optimized β^* angle calculated at different pressures. We also reproduce the experimental data from Akahama et al. [16] and the classical molecular dynamic (MD) simulation results from Etters et al. [11]. It is important to emphasize that Akahama *et al.* do not see any α - δ transition. With respect to the initial simulation containing no corrections at all (Fig. 6), plots on Fig. 8 now clearly indicates that (i) an incorporation of vdW-D2+U corrections leads to the presence of an α - δ transition and (ii) the value of the Hubbard potential directly influences the locus of the monoclinic to orthorhombic phase transition, the potential U obviously increasing the transition pressure, as also observed for the ζ - ϵ transition [55].

Between the three tested values of potentials, the two largest values reproduce a phase transition at high pressure, around 5.4 GPa, that is compatible with the anticipated transition pressure. Note that the obtained transition from classical MD [11] is around 2.3 GPa and Akahama's experiments [16] do not detect any α - δ transition, contrary to the evidence from x-ray, neutron and light scattering experiments [17,18]. This absence of the α - δ transition in Ref. [16] is probably due to a lack of kinetics at 19 K [4,17,56].

We can, thus, conclude that a U correction of typically 7 to 8 eV is needed to reproduce more accurately the α - δ phase transition. It is a rather high value compared to most of the literature values of transition metal systems, but our result is in



FIG. 9. Pressure dependence on the transition angle β^* at different dispersion coefficients C_6 —U = 8.3 eV and $R_0 = 2.587 a_0$ —together with Akahama's [16] and Barrett's [52] experiments.

good agreement with first-principles linear response calculations [55] which predicts a Hubbard value of \approx 9.6 eV around 20 GPa once coupled to a vdW-DF functional correction.

Moreover, the value of 8.3 eV may seem high compared with ones of 1.0 eV yielding the transition $\delta -\epsilon$ pressure and fitting experimental findings [9]. However, our value is not too high if we compare other studies [12] in which DFT+U in combination with van der Waals density functionals reported that $U_{\rm eff} = 5 \,\text{eV}$ (revPBE) and $U_{\rm eff} = 12 \,\text{eV}$ (optB86b) are needed for reproducing the experimental structure of the α -O₂ phase at ambient pressure.

2. Van der Waals correction

In contrast to U which was determined self-consistently as an intrinsic response of the material, the vdW parameters were chosen as the ones that fit more reasonably the experimental findings, that is, the structural parameters and the *locus* of the α - δ transition.

All the following results were obtained for a fixed Hubbard potential of 8.3 eV corresponding to the pressure closest to the observed α - δ transition pressure (as previously described). Figures 9 and 10 show the effect of the dispersion coefficient C_6 and the vdW radius R_0 on the transition angle β^* over the pressure range from 0 to 6 GPa, respectively. Experimental data [16] are also given as a reference.

Plots on Fig. 9 are obtained for a fixed value of vdW radius of $R_0 = 2.587 a_0$, while on Fig. 10, calculations ran with a selected value of $C_6 = 25.900 \text{ Ry } a_0^6$. It appears clearly that irrespective of the set of both parameters, our calculations predict a value of β^* that is always lower than the experiment one.

In both cases, these parameters influence the transition angle, as it is the case for the ζ - ϵ transition [55]. Indeed, the larger this dispersive coefficient, the more the α - δ transition pressure increases. We can note that the calculated value [53]



FIG. 10. Pressure dependence on the transition angle β^* at different vdW radii $R_0 - U = 8.3 \text{ eV}$ and $C_6 = 25.900 \text{ Ry a}_0^6$ - together with Akahama's [16] and Barrett's [52] experiments.

of $C_6 = 25.900 \text{ Ry } a_0^6$ gives a phase transition pressure rather close to the expected area [17] (see gray zone on Fig. 9). Conversely, the larger the vdW radius R_0 , the more the α - δ transition pressure decreases. One can see on Fig. 10 that Grimme's default value does not enable to reproduce the expected transition, no more than β^* values at low pressures. As a result, there seems to be some competition between these two vdW parameters: a more attractive vdW force (i.e., high C_6 value) permits to improve the phase transition pressure from the monoclinic to the orthorhombic structure, while a less attractive ones (i.e., high R_0 value) produces the same result.

Furthermore, a systematic inspection of the simulation results (not shown in this paper) on lattice parameters permits to state that regardless of the value of C_6 , simulations underestimate the *b* lattice and overestimate the *a* and *c* ones with respect to experimental data, while it is the opposite for the values of R_0 parameter (overestimate *b* and underestimate *a* and *c*). Our study reveals a certain dilemma as to the choice of the value of R_0 , since the greater the vdW radius, the closer the low-pressure description of lattice parameters is to the experimental data. So, a compromise was reached on the intermediate value of $R_0 = 2.587 a_0$.

More generally, it appears that the impact of the vdW dispersive term on the cell volume decreases with pressure, which seems to be consistent with the fact that under compression, the interatomic distances decrease so that the role of nonlocal interaction becomes smaller. However, we can also note that the bond length of the O_2 molecule decreases when C_6 increases. This behavior can be explained by the fact that C_6 is directly linked to the amplitude of the vdW correction, which becomes more attractive as this coefficient increases. As expected, vdW forces are less attractive for large values of R_0 , which can be detected from the dependence of the pressure on the molecular bond length.



FIG. 11. Pressure dependence of (a) the b/a ratio calculated from the lattice constants and (b) the transition angle β^* . For comparison, experimental values come from [16,52] (T = 19 K)—where only an α - ϵ transition is observed by Ref. [16] (see text)—and simulated data come from Ref. [11], for which the obtained α - δ transition is shown. Lines are guides for eyes.

Finally, based on the above semiempirical study of vdW parameters, we select $R_0 = 2.587 a_0$ and $C_6 = 25.900 \text{ Ry } a_0^6$ in the following. These values are higher than the default ones of Grimme [45] but have a certain legitimacy because they are physically acceptable: the first one does not exceed the Bondi's vdW oxygen radius [57] of 2.872 a_0 (1.52 Å) and the second one has been calculated [53].

B. Lattice parameters and phase transition

Figure 11(a) shows the pressure dependence of the b/aratio, which is about 0.64 for different temperatures at ambient pressure [13,16,32,52] [see dotted line Fig. 11(a)]. Such value results from the deformation of the frustrated triangular lattice of the in-plane lattice parameter which is b/a = $1/\sqrt{3} \approx 0.577$ in the basal plane of the β -O₂ phase due to the AFM interaction. In contrast to experiments [16] obtained at T = 19 K in the pressure range of stability from α -O₂ to ϵ -O₂ and MD force fields simulations [11], our calculations first present a decrease (not seen by Klotz [18] in the pressure range from 0 to 2 kbar) of this ratio until \approx 2 GPa then it increases with pressure and reaches a value of between 0.73 and less than 0.75 from 6 to 15 GPa. Furthermore, one can see a break in the slope of the b/a curve around 5.4 GPa, as as signature of the α - δ phase transition, which occurs at a much lower pressure in force fields simulations [11] [see arrow labeled " α - δ " on Fig. 11(a)].

Figure 11(b) shows the dependence of the transition angle β^{\star} (defined before, see notations on Fig. 3) with pressure. As mentioned above, the transition from the monoclinic α phase to the orthorhombic δ phase manifests by a sudden change of this angle. The dotted line Fig. 11(b) represents the limit angle $\beta^* = 90^\circ$. As experimentally measured [5,16,17], one can see that our calculated angle indeed approaches 90 $^{\circ}$ with increasing pressure. Moreover, the closer $(R_0; C_6; U)$ set of parameters describes rather well the *locus* of the α - δ transition approximately at 5.4 GPa. Again, previous MD simulations [11] underestimate the *locus* of this transition [at 2.3 GPa, see left arrow labeled " α - δ " on Fig. 11(b)]. However, at T =19K, the high-pressure x-ray-diffraction experiments [16] show a phase transition at 7.6 GPa [see right arrow labeled " $\alpha - \epsilon$ " on Fig. 11(b)] where $\alpha - O_2$ directly transforms into $\epsilon - O_2$ without any signature of the intermediate δ phase. However, one can note that although our calculations underestimate β^{\star} by less than 2% before the transition in comparison with experimental data, the pressure coefficient of β^* is well reproduced. Finally, the pressure dependence of the transition angle is not continuous up to 90° , as revealed by the experimental data [16]. So, we conclude, as previous simulations do [11], that the α - δ transition is likely to be first order [17,58]. Both plots on Fig. 11 reflect an α - δ phase transitions occurring between 5.3 and 5.9 GPa (see gray zones), in good agreement with experimental observations [17].

We also examined the different magnetic configurations of the δ -O₂ phase around 6 GPa at zero-temperature. It turns out that the LTC configuration is more stable than the HTC ones, which is in good agreement with experimental neutron scattering patterns [3,5] under pressure.

Figure 12 now shows the change of the cell volume as a function of pressure as compared to the experimental data [16,18] and to the classical MD simulations [11]. Although the volume of the α -O₂ shows an obvious reduction with pressure, it is clear that this is somewhat overestimated as compared to experiments. Indeed, the set of vdW parameters used to mimic the structures and properties of the α phase reduces the cell volume at 0 GPa. For comparison, with an initial compression to 1 GPa, the experimental volume reduces by around 16–17% of its initial value, whereas our calculated volume reduces by \approx 11% only. The underestimation of our calculated volume seems to be a general behavior for low pressures, up to 2 GPa.

The third-order Birch-Murnaghan (BM) isothermal equation of state (EOS) [59] allows to evaluate the cell volume $V_0 = V(0)$ at zero pressure, the bulk modulus B_0 and its pressure derivative B'_0 at zero pressure using a range of *P*-*V* data, which is given by

$$P(V) = \frac{3}{2} B_0 \left(\widetilde{V}^{\frac{7}{3}} - \widetilde{V}^{\frac{5}{3}} \right) \left(1 + \frac{3}{4} \left(B'_0 - 4 \right) \left[\widetilde{V}^{\frac{2}{3}} - 1 \right] \right), \quad (10)$$

where $\widetilde{V} = V_0/V$. All experimental and simulated (from the unit-cell volume) data were fitted by nonlinear least-squares using the EOS-fit program [60].



FIG. 12. Static-compression data for O₂ phases plotted as volume *versus* pressure. Calculated V(P) curve was fitted using third-order BM EOS (solid curve) in the range of stability of α phase. Experimental values come from Ref. [18] (solid circles), Ref. [16] (solid squares), and Ref. [52] (solid triangles). Simulated data (empty squares) come from Ref. [11]. Inset shows a zoom on the pressure range from 2 to 6 GPa.

Table I summarizes BM EOS—i.e., V_0 , B_0 , and its derivative B'_0 parameters—from our different simulations compared with experimental data [16,18], previous MD force fields simulations [11] and vdW-DF+U functionals [12] (retrieved data). As expected according to Fig. 12, our simulations underestimate by a factor of less than 10% the zeropressure volume. Moreover, the lower compressibility for pressures below 1 GPa is reflected in the bulk modulus, which is too high compared with experiments. Note that the bulk modulus extracted from experiments of Akahama *et al.* [16] is only of 3.3 GPa, whereas Kasamatsu *et al.* [12] established a value of ≈ 6 GPa. That being said, all simulations predict a much less compressible lattice than experiment.

Furthermore, one can note on Fig. 12 that no phase transition is visible within these volume-pressure plots. However,

TABLE I. Parameters (volume V_0 , bulk modulus B_0 and its initial pressure derivative B'_0) of the third-order BM isothermal EOS from experiments and theoretical calculations in the α -O₂ phase at ambient pressure. Only lines marked with the dagger symbol are the result of a fit.

Reference	V_0 (Å ³)	B ₀ (GPa)	B'_0
† This work	63.1	6.2	6.58
† Experiments [18]	67.5	3.1	(11.49)
† Experiments [16]	68.9	2.9	8.86
† Experiments [16,18]	67.5	3.3	9.16
Experiments [32]	69.1	3.6 ^a	_
† Classical MD [11]	68.6	4.0	5.21
vdW-DF-revPBE+U [12]	74.1	4.7	_
vdW-DF-optB86b+U [12]	69.7	4.4	—

^aCalculated from the isothermal compressibility value at 8 K.

Reference	$V(\text{\AA}^3)$	a (Å)	b (Å)	c' (Å)	d (Å)	β' (°)
This work	63.10	4.94	3.45	4.84	1.19	130
Experiments [32]	69.58	5.404	3.424	c = 4.252	1.207	$\beta = 117.82$
Experiments [14]	68.95	5.40	3.43	5.09	1.28	133
Experiments [61]	69.44	5.40	3.43	5.09	1.21	133
vdW-DF-revPBE+U (5 eV) [12]	73.92	5.35	3.60	5.01	1.25	130
vdW-DF-optB86b+U (12 eV) [12]	69.61	5.29	3.48	5.01	1.27	131
vdW-DF-SGC [62]	75.97	5.43	3.61	4.57		122
Force fields simulations [11]	69.36	5.36	3.45	5.06	1.21	132

TABLE II. Parameters of the monoclinic unit cell in the α -O₂ phase at ambient pressure. The *d* length stands for the intramolecular O₂ distance. See Fig. 3 for others notations.

the arrow (Fig. 12) pinpoints the *locus* of our previous α -O₂ to δ -O₂ lattice-parameter transition at \approx 5.4 GPa and the $\Delta V/V$ ratio at this pressure is apparently close to zero, as expected by experiments [17], for which the authors estimate this ratio to be less than 0.5% (due to the sensitivity of measurements).

Table II shows the lattice parameters of the α -O₂ phase (see Fig. 3 for notations) at zero-pressure obtained in our DFT+vdW-D2+U approach compared to x-ray [32] (used as input parameters for the variable-unit cell optimization procedure) and neutron diffraction [14] experiments and others simulations [11,12,61,62].

As mentioned above, the present simulation with the fixed set of DFT parameters has some difficulty reproducing very low pressure lattices, which is the result of our aim to describe an appropriate α - δ transition value. Indeed, at ambient pressure, the vdW-D2+U method underestimates by about 9.3% the cell volume of the experimentally reported value [32] while a scheme with a spin-dependence of GGA type [62] (vdW-DF-SGC, with two adjustable parameters) and vdW-DF-revPBE [12] (with one adjustable parameter) functionals overestimates by about 9.2% and 6.2%, respectively. With one adjustable parameter, the vdW-DF-optB86b functional seems to reproduce the cell volume rather well, as in other studies [11,61].

In all cases, simulations predict an AFM ground state, but they all fail to reproduce correctly the b/a ratio, except for certain simulations schemes [11,61]. Whatever the method, there is a general underestimation of the c' parameter and the angle β' . Note that both b/a and β' values are an indirect measure of the exchange interaction in the ab plane. We therefore conclude that this may be due to an insufficient description of the exchange interaction between the ab planes, which the approaches [11,61] do not have to describe explicitly. This shortcoming in the simulations apparently can explain the disagreement with experiment.

Finally, we note that the vdW-D2+U method leads to an improved agreement compared to vdW-DF+U functionals of the intramolecular O–O distance (denoted *d* in Table II). Indeed, compared with the experimental value of 1.21 Å, we find a bond length of 1.19 Å, that is an underestimate of only 1.6% for this work, while vdW-DF+U approaches overestimate it by 3.5 and 5.2%.

Figure 13 highlights an indirect method to detect a phase transition [63,64]. One introduces the effective strain g derived [65] from the assumption that the strain energy of a solid undergoing compression can be expressed as a Taylor series

in the finite Eulerian strain:

$$g = \frac{1}{2} \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right],$$
 (11)

which allows to define the normalized pressure for the Birch-Murnaghan EOS as [66]

$$G = \frac{P}{3g(1+2g)^{5/2}}.$$
 (12)

With this representation, the α - δ transition becomes evident at around $P \approx 3.7$ GPa from the V(P) data (upper horizontal dashed line on Fig. 13), lower than the expected pressure range [17] given by gray zone (Fig. 13). Given the lack of experimental data on V(P) from diffraction patterns at low temperatures [17], the gray zone is an indicative information only. This transition pressure is also lower than the transition obtained by the pressure-dependence of lattice parameters (b/a ratio and β^* angle) study in Fig. 11, represented by the upper arrow labeled " α - δ " (Fig. 13).



FIG. 13. Static-compression data for O_2 phases plotted as normalized stress *versus* effective strain (see text), compared with classical MD data [11].



FIG. 14. (a) Calculated band structure of α -O₂ at zero-pressure along the lines connecting points of high symmetry. (The dotted horizontal line marks a guide to the eye for the Fermi level.) (b) Plots of total density of states and its decomposition into 2*s* and 2*p* oxygen orbitals. Filled (empty) states have negative (positive) energies. The calculated band gap is about 3.9 eV.

Finally, monoclinic to orthorhombic phase transition occurs also at a lower pressure value with the MD force fields method [11] (see at the bottom of Fig. 13 the difference between dashed line and arrow which stands for the transition based on the evolution of the β^* angle).

IV. ELECTRONIC AND VIBRATIONAL PROPERTIES

A. Electronic structure

Figure 14(a) shows the electronic band structure established along high symmetry points of the Brillouin's zone (BZ) of the monoclinic α structure at 0 GPa. The valence bands at very low energies (below -26 eV) are not shown for the sake of clarity. One can see a rather flat band dispersion as calculated ones [8], unlike the δ -O₂ [7] (calculated at 10 GPa), ϵ -O₂ [67] (same pressure), or ϵ -O₂ [8] (at 13.7 GPa) band structures.

This calculated band structure reflects the electronic structure of α -O₂ (Fig. 1) with two highest valence bands and two lowest conduction bands, both of them derived from the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the two O₂ molecules defining the unit cell.

Our simulations displays an indirect band gap, corresponding to a transition between the HOMO located at the Γ point and the LUMO at the *D* point. A such indirect gap is also highlighted in ϵ -O₂ DFT-calculated band structure [67]. Our resulting value is of about 3.9 eV at zero-pressure. At ambient pressure, an other DFT simulations [8] performed on α phase gave also an indirect gap of 4.5 eV with the top of valence band located at the same high symmetry point.

Reference	Phase	Gap (eV)	Туре
This work	α -O ₂	3.9	indirect
DFT LSDA [8]	α -O ₂	4.5	indirect
vdW-DF-revPBE ^a [12]	α -O ₂	≈ 1.7	_
vdW-DF-SGC [68]	β -O ₂	≈ 1.7	indirect

TABLE III. Optical gap values at ambient pressure from different simulations.

^aRetrieved data ($U_{\rm eff} = 0 \, {\rm eV}$).

All other things being equal, the optical gap values of Table III sums up few band gap energy form different theoretical approaches.

The band structure with molecular levels is recognizable, except for σ_u^* , σ_g , and π_u orbitals which seem hybridized (unlike the δ phase [7] or the ϵ phase [8,67]). This behavior can be clearly seen on the projected DOS (PDOS) onto 2*s* and 2*p* orbitals of oxygen [Fig. 14(b)]. Note that the valence and the conduction bands have opposite spins while these have the same orbital character (i.e., π_g^* orbitals). The split between the valence and the conduction bands is due to the exchange interaction.

For three different pressures, Figure 15 shows the total electronic density of states (EDOS). Although, we do not



FIG. 15. Calculated total electronic density of states (EDOS) and inverse participation ratio (IPR) for different pressures (a–c) across the α - δ transition. Panel (c) shows the effect of the Hubbard correction at zero-pressure.

expect changes in the localization of Kohn-Sham orbitals accross the α - δ transition, we still decided to test this hypothesis by calculating the inverse participation ratio (IPR) [69–71]. This ratio permits to measure the degree of localized orbitals around specific bonds: a high value of IPR stands for a high degree of localization. It is commonly accepted that IPR tends toward 0 for a fully delocalized state (i.e., a conductor) and IPR tends toward 1 for a pure state. The IPR is defined by

$$IPR = \frac{\int |\psi(\mathbf{r})|^4 d\mathbf{r}}{\left(\int |\psi(\mathbf{r})|^2 d\mathbf{r}\right)^2}.$$
 (13)

In the setting of DFT calculations, oxygen electronic wave functions (i.e., Kohn-Sham states) can be written as a sum over the number of localized orbitals (N). With the same notations as before (and omitting the spin for more clarity), $\psi_{v\mathbf{k}} = \sum_{i=1}^{N} a_i \phi_i$. The IPR is thus defined as

$$IPR = \frac{\sum_{i=1}^{N} a_i^4}{\left(\sum_{i=1}^{N} a_i^2\right)^2},$$
(14)

where a_i is the coefficient of the *i*th localized orbitals of a given Kohn-Sham state. A Gaussian smearing (width of 2 mRy) was applied to determine the band occupations and electronic density of states.

With increasing pressure, the band gap of the α -O₂ and δ -O₂ phases decreases from 3.9 to 3.2 eV, as expected by the experiments in Refs. [19,72,73]. This behavior is consistent with the calculated band gap [67] of 200 meV in ϵ -O₂ at 10 GPa, which then becomes negative at high pressures when the conduction and valence bands lose their identity. As expected, no noticeable effect of localization with pressure of the Kohn-Sham orbitals can be seen on IPR plots in Fig. 15.

Moreover, Fig. 15(c) represents the effect of the Hubbard correction at 0 GPa and indicates that the DFT+U approach enables indeed to increase the energy band gap, which rises from 1.68 eV at U = 0 eV to 3.93 eV at U = 8.3 eV. The Hubbard correction shifts to lower energies the occupied states close to the Fermi level, while for the empty states, their position in energy with respect to the Fermi level is roughly identical to the calculation without correction.

A more detailed study of the Löwdin PDOS on oxygen orbitals (not shown) suggests that the bottom of the conduction band is mainly formed by the 2p(O) orbitals with a majority of spin down. These oxygen orbitals remain unchanged in energy due to the effect of the Hubbard potential. However, one can also note that the top of the valence band is mainly formed by the 2p(O) orbitals with a majority of spin up. Unlike the previous ones, these orbitals move down in energy under the effect of the U parameter. These observations are in agreement with DFT+U simulations [12] on the α phase.

Finally, we can note that the atomic magnetic moment also decreases with pressure from $0.99 \,\mu_{\rm B}/\text{atom}$ at 0 GPa to $0.93 \,\mu_{\rm B}/\text{atom}$ at 8 GPa. The magnetization of α -O₂ is almost the same as that of the free oxygen molecule, we can conclude that O₂ molecules in the α phase are far enough apart for the electrons to be localized. Indeed, without Hubbard correction, simulations give a value of $0.97 \,\mu_{\rm B}/\text{atom}$, compared to $0.6 \,\mu_{\rm B}/\text{atom}$ at 13.7 GPa and $0.1 \,\mu_{\rm B}/\text{atom}$ at 90.0 GPa [8].



FIG. 16. Calculated absorption edge at different pressures in solid oxygen, within DFT+vdW-D2+U scheme (crosses), compared to experimental data (squares and triangles) [19,73] (in β -O₂ at $T \approx 300$ K and ϵ -O₂). Circles are zero-temperature calculated data [8]. Squares data are fitted for extrapolation to zero-pressure (see text).

Figure 16 gives the dependence of the optical absorption gap *versus* pressure in solid oxygen. Squares [73] and triangles [19] represent experimental data obtained in the β -O₂ phase (300 K and 5.5 GPa) for two different crystalline orientations. To our knowledge, there is no experimental optical gap data reported at low pressure. To get a value at zero pressure, these experimental data were fitted using linear regression. Triangles are other retrieved data points [73] estimated from optical density curves [19] and circles are first-principles calculated data [8].

On another note, we compared the dependence of the band gap as a function of pressure. According to our simulations, we obtain a slope of about 0.08 eV/GPa, compared to slopes of 0.15 eV/GPa for $\delta \cdot \epsilon$ in Ref. [19] and 0.13 eV/GPa in Ref. [7]. In the pressure range from 13 to 50 GPa, the slope is about 0.05 eV/GPa for $\epsilon - O_2$ in Ref. [8].

Due the well-known band gap underestimation problem of conventional DFT, we assume that our calculated optical gap is smaller than the experimental value. However, optical absorption experiments at ambient pressure and low temperature will have to be carried out to determine the band gap and should help to clarify the level of agreement between experiments and simulations.

B. Phonons

Because of the fact that the intermolecular potential is affected severely by electronic properties, we now confront our vdW+U approach to vibrational spectroscopic data by

TABLE IV. Calculated phonon frequencies (in the center of the BZ) with their respective symmetry for different pressures. At 8 GPa, the crystal and magnetic structure of the δ phase gives other symmetry modes. Note that all these modes are Raman active, but only the in-phase vibration modes are experimentally observed.

Pressure (GPa)	Frequency (cm ⁻¹)	Symmetry	Vibration
	α -O ₂ : <i>C</i> 2/ <i>m</i> wi	th AFM structure	
0	86.65	B_g	in
	105.13	B_g	out
	155.61	A_g	in
	191.07	A_g	out
	1750.9	A_g	out
	1777.8	A_g	in
3	127.6	B_{g}	in
	156.4	B_g	out
	214.8	A_g	out
	229.5	A_g	in
	1749.7	A_g	out
	1812.5	A_g	in
5	167.3	B_g	in
	192.2	B_g	out
	247.6	A_g	out
	269.1	A_g	in
	1739.2	A_g	out
	1812.9	A_g	in
8	225.5	B_g	in
	244.7	B_g	out
	284.5	A_g	out
	318.2	A_g	in
	1709.4	A_g	out
	1799.5	A_g	in
	δ -O ₂ : <i>Fmmm</i> v	vith FM structure	
8	208.2	B_{3g}	in
	229.2	B_{3g}	out
	272.3	B_{1g}	out
	306.9	B_{1g}	in
	1728.5	A_g	out
	1818.8	A_g	in

calculating the phonon frequencies of the fully relaxed α -O₂ structure. Indeed, a spectroscopic study can highlight fine changes in the internal and external modes and are particularly relevant in the case of the α - δ transition.

With the selected (R_0 ; C_6 ; U) set of parameters (see above), our calculations produce for the α phase (C_{2h} space group, with two molecules per unit cell) nine optical modes, of which, at the center of the Brillouin zone, six would be Raman active and three infrared active according to the QE suite. Our calculations provide no information on peak intensity or magnons.

For different pressures, Table IV lists these 6 Raman modes, which are split into 4 librons at low frequencies and 2 vibrons at higher frequencies. Note that the simulations do not produce any imaginary modes—within the numerical limits of

the acoustic sum rule—i.e., it was confirmed that this structure is indeed stable in the AFM configuration.

Table IV also gives the A_g or B_g symmetry of the monoclinic AFM configuration, which is consistent with group theory of α -O₂ and the type of vibration of the molecules i.e., in-phase or out-of-phase refers to the relative motions of the two O₂ molecules in the unit cell—knowing that only the in-phase movements of atoms can be seen in experiments. Note that the lower visible frequency mode corresponds to the B_g symmetry and the higher one to the A_g symmetry, which is in line with experimental observations [74]. We additionally calculated vibrational modes for the LTC δ -O₂ phase (*Fmmm* space group and an FM configuration) at a pressure of 8 GPa. Note that to obtain the correct magnetic structure, we doubled the *c* lattice parameter of the orthorhombic structure, thus keeping two molecules per cell.

Our results can be compared with room-temperature Raman spectra of Akahama et al. [72] who studied solid oxygen up to the insulator-metal transition (until the ϵ -O₂ phase). At 20 GPa, their experiments show that there are three main bands: two low-frequency bands below 500 cm⁻¹ assigned as librons and a vibron mode with a frequency around 1590 cm⁻¹. Note that high-pressure Raman spectroscopy data [72] show a pressure-dependence of the Raman vibron frequency with a slope of around $2 \text{ cm}^{-1}/\text{GPa}$ throughout the pressure range of stability of ϵ -O₂, against $\approx 5 \text{ cm}^{-1}/\text{GPa}$ in α -O₂ according to our results, similar to the slope between α - δ transition range of $\approx 3 \text{ cm}^{-1}/\text{GPa}$ [75]. This behavior of the in-phase vibron Raman component whose frequency increases with pressure is most probably a hint for a phase transition. A complete study of the range of stability of δ -O₂ would allow us to verify this hypothesis.

Figure 17 shows the vibron [Fig. 17(a)] and libron [Fig. 17(b)] frequencies as a function of pressure across the α - δ transition (gray zone). We also retrieved the frequencies observed in Raman experiments from data at different temperatures:

(i) Meier *et al.* [76] at 6 K. Note that the authors could not see any significant difference between data at 6 K and 18 K,

(ii) Jodl et al. [75] and Klotz [18] at 10 K, and

(iii) Hochheimer et al. [77] at 25 K.

For a better comparison of the pressure-dependence, we shift on Fig. 17 our calculated libron frequencies by 50 cm^{-1} and vibron frequencies by 240 cm^{-1} . The choice of a constant offset for all phases is debatable, but it simplifies the reading of the figures. In addition, we also plot the low-frequency librons calculated by Ref. [11] [empty squares, Fig. 17(b)]. These classical MD simulations predict two low-frequency branches with respect to the crystallographic unit cell, while they produced two additional high-frequency branches by taking into account the magnetic unit cell. We remark that at very low pressures, three of these branches are degenerated.

As a result, the shifted frequencies of our in-phase vibrons are reasonably consistent with experiments. Moreover, the order of magnitude of our libron frequencies (shifted) are rather well simulated. However, our calculations overestimate the differences between frequencies at a given pressure, typically by 60 to 70% between the lowest and the highest frequency, and seem to increase with pressure. Therefore, one can see that our highest in-phase libron are in line



FIG. 17. Vibrational (a) and librational (b) frequencies of O_2 modes as a function of pressure across the α - δ transition, compared to experimental Raman data retrieved from Refs. [18,75–77] and classical MD simulations [11]. Note that our vibrational data are shifted for comparison (see text). The gray zone represents the α - δ transition region determined from spectroscopic studies [17]. The lower branch of vibron frequencies is not observed experimentally.

with experiments, while the lowest in-phase libron is systematically underestimated. Typically, temperature dependent Raman measurements suggest a split of around 32 cm^{-1} [74] or 34.5 cm^{-1} [78] (at ambient pressure and 13 K) and approximately 40 cm^{-1} [76], compared with around 69 cm^{-1} in our calculations (see the difference between in-phase modes in Table IV).

TABLE V. Raman active libron frequencies calculated at the Γ point (0; 0; 0) and calculated at the zone boundary along the *c* axis (0; 0; π/c) at 8 GPa according to the crystal and magnetic structure of the orthorhombic δ phase.

Frequency	(cm^{-1})	Vibration
at (0;0;0)	at (0;	$(0;\pi/c)$
_	54.7	in
_	114.8	in
_	123.4	in
_	196.3	out
208.2	212.7	in
229.2	218.1	out
_	227.4	out
_	262.8	in
272.3	271.8	out
306.9	309.4	in

Note that below the α - δ transition, experiments exhibit a change of the slope. This behavior seems to be reproduced to a certain extent at a pressure of 5 GPa and is consistent with our previous comment on the in-phase vibron Raman component.

At a last remark, the two lowest librons at zero-pressure are very close, but not degenerated as found in MD calculations [11] and *ab initio* approach with an empirical potential for long range dispersion coefficients [61]. However, we find different modes of vibration, compatible with the experiment [76].

To explain an additional experimental weak peak at around 90 cm^{-1} [18], we finally study the effect of the lattice structure along the *c* axis (doubling of the unit cell along *c* axis due to the HTC magnetic structure) on the librational modes at a pressure of 8 GPa. Note that this new peak can not be a magnon since it shifts with ¹⁸O isotopic substitution with the same coefficient than the phonons [18].

Table V compares these libron frequencies calculated along the *c* axis—at the $(0; 0; \pi/c)$ zone edge—to the previous Raman active ones in the center of the BZ. One can see that the simulations on the FM δ -O₂ phase produce modes below 120 cm⁻¹. By taking into account our (comparison) shift of 50 cm⁻¹, we found one possible mode at 73.4 cm⁻¹ (frequency of 123.4 cm⁻¹ in Table V), with an in-phase vibration.

V. SUMMARY AND CONCLUSION

We note that our DFT+vdW-D2+U method to reduce self-interactions is convenient but by no means unique, and other possibilities such as hybrid functional approximations could have been adopted. In addition, we assume to keeping Hubbard term constant in the range of stability of the α phase. However, this approach allows, even if at the approximate semiemperical vdW term, to describe the *locus* of the α - δ transition of solid oxygen. Indeed, while a plain GGA calculation would give the δ -O₂ as stable throughout the pressure range considered, we find that adding vdW and GGA+U corrections to the GGA correlation energy stabilizes the α -O₂ phase at ambient pressure. Within our approximations the *locus* of the α - δ transition takes place approximately at 5.4 GPa. According to the equation of state and other structural parameters, the agreement with experimental data is rather satisfactory, even though we have a better capability to reproduce volume and lattices from 2 GPa with our set of parameters.

The study of electronic properties of α -O₂ at ambient pressure reveals a flat band dispersion, in contrast to the others oxygen phases. Our simulations displays an indirect band of around 3.9 eV ambient pressure, which decreases with increasing pressure, as expected experimentally. Moreover, the localization of the Kohn-Sham orbitals using the IPR method shows that the Hubbard correction enables to increase significantly the energy band gap to a value compatible with extrapolation of experimental data at high pressure. This effect is all the more relevant as it does not affect the location of the orbitals. An experimental absorption study of solid oxygen at ambient pressure is needed to confirm these simulated values. As far as phonons are concerned, our model gives the right orders of magnitude and symmetry, in agreement with experimental data. Furthermore, the emergence of an additional Raman peak in the experimental patterns of δ -O₂ may be interpreted as a contribution of the BZ boundary effect due to the doubling of the *c* lattice parameter in the LTC magnetic phase. A complementary study of all δ -O₂ magnetic structures should verify our hypothesis.

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