

Frequency Shifts Calculated at High Pressures (ϵ - ζ Transition) in Solid Oxygen

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The pressure dependences of the Raman and infrared frequencies are predicted using a relation derived from the Vinet equation of state, which uses the mode Grüneisen parameter (γ_T) for the ϵ - ζ transition in solid oxygen. For this calculation, the observed data for V - P and ν - P are taken from the literature. The Grüneisen parameter of the Raman vibron calculated by us increases with increasing pressure because the observed Raman frequencies of this vibron increase. For the infrared modes, γ_T exhibits a nearly symmetrical profile (ν_{FIR}) and λ -type behaviour (ν_{MIR}) for the δ - ϵ transition (in the ϵ phase) in solid oxygen. Our calculated frequencies for the Raman and infrared modes agree with the observed data, which indicates that the modified ν - P relation can be used to predict frequencies close to phase transitions in various molecular crystals.

topics: Vinet equation of state (EOS) (V - P relation), ν - P relation, mode Grüneisen parameter (γ_T), ϵ - ζ (δ - ϵ) transition

1. Introduction

The low-pressure phases α , β , and γ in solid oxygen (O_2) transform into high-pressure phases, namely the antiferromagnetic insulating δ - O_2 phase at 10 GPa, ϵ - O_2 , and a nonmagnetic, metallic molecular phase ζ - O_2 above 96 GPa [1, 2], respectively. At ambient pressure, solid oxygen is an antiferromagnetic insulator; it becomes a metal and superconductor under very high pressures [3]. The metallic ζ - O_2 phase is superconducting with a critical temperature of 0.6 K [4]. This phase starts at 96 GPa, and it coexists with the ϵ phase up to 110 GPa [5] as a first-order transition [6]. It has been stated that at 300 K and above 10 GPa, solid oxygen is stable in the ϵ phase [7]. Thus, at room temperature between 0 and 96 GPa, the insulator ϵ phase exists below 100 GPa, and above 96 GPa the crystalline structure of metallic ζ oxygen occurs [3, 7].

The temperature-pressure (T - P) phase diagram of oxygen has been determined experimentally and includes the low-pressure phases, as given in previous studies [1, 8–11]. As pointed out in the review paper [12], in the region of pressures up to 140 GPa, temperatures up to 1750 K, and magnetic fields

over 100 T, the existence of nine (α , β , γ , δ , ϵ , ζ , η , η' and θ) solid phases has been established in oxygen. For the low-pressure phases of oxygen, we have calculated the T - P phase diagram using mean-field theory in our previous study [13].

Regarding the physical properties of various low- and high-pressure phases of solid oxygen, a number of experimental and theoretical studies have been reported in the literature. Among them, the magnetic properties of condensed oxygen under high pressures and in strong magnetic fields [10, 14] have been studied. The magnetic field-temperature (H - T) phase diagram of solid oxygen has been obtained by measuring the adiabatic magnetocaloric effect (MCE) using pulsed magnetic fields [15, 16]. At ultrahigh magnetic fields, the physical properties of condensed oxygen have been studied [17]. Using experimental data [14], we have also analyzed the magnetic susceptibility of condensed oxygen under pressure and magnetic fields for the α - β , β - γ , and γ -liquid transitions [18, 19]. The magnetic collapse was discussed, and the structure factor of the ζ - O_2 phase was calculated [20].

Considering the physical properties of the insulator-metal (ϵ - ζ) transition in solid oxygen at high pressures, the structural transition from the ϵ to ζ phase has been observed in the range

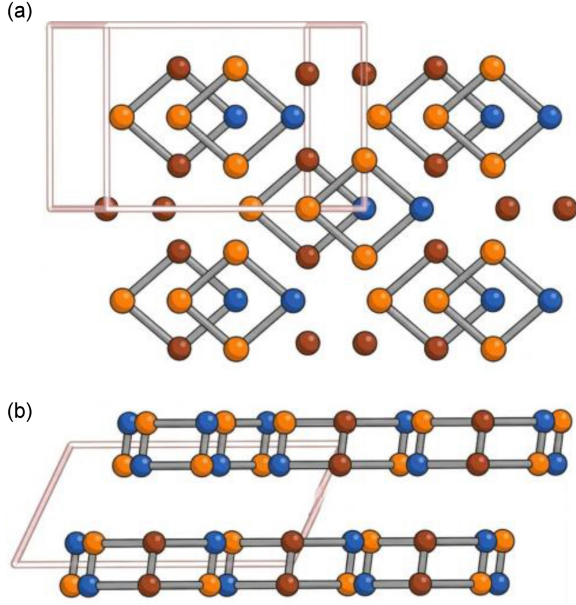


Fig. 1. Crystal structure of the ϵ phase of solid oxygen. The structure as viewed perpendicular to the (a) a - b plane and (b) a - c plane [22].

of 88–96 GPa [21]. The transition ϵ - ζ was first detected by absorption edge and reflectivity measurements [21]. The pressure dependence of the lattice constants has been measured [1, 5]. From a theoretical standpoint, density functional and many-body calculations for the insulator–metal transition have been performed [22]. The phase diagram of solid oxygen at terapascal pressures and very high temperatures has been calculated using *ab initio* density functional theory [23]. Also, the phase diagram of oxygen has been studied from 50 to 130 GPa and temperatures up to 1200 K using first-principles theory [24]. First-principles calculations for the ϵ - ζ transition have been reported in [25]. Recently, the structure of solid oxygen has been studied at pressures ranging from 50 to 140 GPa using molecular dynamics simulations for the ϵ - ζ transition [26]. Figure 1 shows the crystal unit cell of the ϵ phase with $C2/m$ symmetry of solid oxygen [22]. It has also been reported in the review paper [12].

Various techniques have been applied to spectroscopically investigate phase transitions in solid oxygen. Molecular excitations of ϵ -O₂ have been studied by Raman and infrared (IR) spectroscopy [21, 27]. The IR absorption properties of the ϵ (red) phase of solid oxygen [28], Raman vibron of the ϵ phase [1], and Raman vibrons in the α phase [29] have also been studied experimentally as a function of pressure. Near-IR measurements of the electronic transitions have been reported in [30, 31]. X-ray diffraction has been performed for the liquid–solid and solid–solid transitions of oxygen [32] and for ϵ -O₂ [33]. Optical properties of the δ -O₂ and ϵ -O₈ phases [34] and the metallic post- ζ phase [35–37]

under high pressure have been studied using density functional theory. In our previous work [38], we studied the pressure dependence of the Raman frequencies for two librins and one vibron by determining their mode Grüneisen parameters at constant temperatures for the low-pressure α -O₂ phase. Recently, the distinct vibrational characteristics of metallic ζ -O₂ from 85 to 225 GPa have been studied using Raman spectroscopy [39]. At high pressures, spin collapse in solid oxygen has been discussed [40].

Spectroscopically, the pressure dependence of the frequency of the Raman and IR modes can be predicted from V - P (volume–pressure) data in molecular crystals. Using the Vinet equation [41] in the P - V - T system, the frequency ν of the phonon modes can be calculated spectroscopically in the P - ν - T system. Since in our recent study [42], we developed the ν - P relation from the Vinet equation (V - P) and applied it to the cubic gauge nitrogen (cg-N), in this study we calculate the Raman frequencies of the vibron and the external mode for the high-pressure ϵ - ζ transition in solid oxygen. For this calculation of the Raman frequencies of the studied modes, we first fit the Vinet equation (V - P) to the observed data [7] in the ϵ phase and determine the mode Grüneisen parameters of these modes — as we did earlier for cg-N [42]. Using the corresponding ν - P relation [42], the Raman frequencies are calculated for the ϵ - ζ transition in solid oxygen. The Raman frequency data (ν - P) for the modes studied in [43] were used, and their pressure dependence was calculated through the ν - P relation, unlike in our earlier study [42], where $V(P)$ and $\nu(P)$ were considered quadratic functions. Our results indicate that the ν - P relation is also valid for solid oxygen (ϵ - ζ transition).

We present our calculations and results in Sect. 2. Discussion and conclusions are given in Sects 3 and 4, respectively.

2. Calculations and results

The vibrational frequencies (ν) depend on the crystal volume (V) through the Grüneisen parameter (γ). The temperature and pressure dependence of the vibrational frequency (ν_i) of mode i can be related to the dependence of the crystal volume V on T and P by determining the mode Grüneisen parameter (γ_i). Its definition is given as

$$\gamma_i = - \frac{V(T, P)}{\nu_i(T, P)} \frac{d\nu_i}{dV}. \quad (1)$$

The temperature dependence of γ_i (at constant pressure) can be defined as

$$\gamma_P(T) = - \frac{V(T)}{\nu(T)} \frac{(\partial\nu/\partial T)_P}{(\partial V/\partial T)_P} \quad (2)$$

and is called the isobaric mode Grüneisen parameter. In the particular case we are studying here, the isothermal mode Grüneisen parameter (γ_T), which

relates the frequency $\nu(P)$ to the crystal volume $V(P)$, can be defined as

$$\gamma_T(P) = -\frac{V(P)}{\nu(P)} \frac{(\partial\nu/\partial P)_T}{(\partial V/\partial P)_T}. \quad (3)$$

From (3), the pressure dependence of the vibrational mode frequency (ν_T) can be calculated as

$$\nu_T(P) = \nu_o \exp \left[-\gamma_T(P) \ln \left(\frac{V(P)}{V_o} \right) \right], \quad (4)$$

where ν_o and V_o define the mode frequency and the crystal volume, respectively, at ambient conditions ($P = 0$, $T = 295$ K).

In order to calculate the pressure dependence of the vibrational mode frequency with respect to the crystal volume (V_T) using the isothermal mode Grüneisen parameter (γ_T) according to (4), we can use the Vinet EOS (equation of state) in the V - P - T system.

Vinet EOS can be expressed as

$$P = 3 B_o \frac{(1-f_\nu)}{f_\nu^2} \exp \left[\frac{3}{2} (C_o - 1) (1-f_\nu) \right], \quad (5)$$

where $f_\nu = (V/V_o)^{1/3}$.

In the P - V - T system, V_o is the volume V at zero pressure ($P = 0$), B_o is the isothermal bulk modulus defined as $B_o = -V(P)(\partial P/\partial V)_T$, and C_o is its derivative, i.e., $B_o' = dB_o/dP$ at $P = 0$ [41].

In terms of spectroscopic parameters corresponding to the P - V - T system, the Vinet equation (5) can be reformulated for the P - ν - T system. Therefore, the pressure dependence of the frequency can be obtained as a P - ν relation corresponding to the P - V EOS (5), as previously studied for cubic gauge nitrogen (cg-N) [42].

To express the Vinet equation (5) spectroscopically in terms of the frequency and pressure (ν - P), one can use the isothermal mode Grüneisen parameter γ_T (3) to define the isothermal bulk modulus B_o as,

$$B_o = \gamma_T(P) \nu(P) \left(\frac{\partial P}{\partial \nu} \right)_T \quad (6)$$

and its pressure derivative (B_o') as

$$C_o = \frac{\partial}{\partial P} \left[\gamma_T(P) \nu(P) \left(\frac{\partial P}{\partial \nu} \right)_T \right], \quad (7)$$

both evaluated at $P = 0$, following our previous work [42]. Thus, with the definitions of B_o and C_o given by (6) and (7), respectively, together with the γ_T definition (see (3)), the Vinet EOS (5) can be expressed as

$$P = 3 B_o \left(\frac{1-u_\nu}{u_\nu^2} \right) \exp \left[\frac{3}{2} (C_o - 1) (1-u_\nu) \right], \quad (8)$$

where

$$u_\nu = \left(\frac{\nu}{\nu_o} \right)^{-\gamma_T/3} \quad (9)$$

is analogous to f_ν in (5) expressed in terms of the frequency ν_o at $P = 0$ with the isothermal mode Grüneisen parameter γ_T [42].

TABLE I

Values of the volume V_o (at $P = 0$), isothermal bulk modulus (B_o), and the derivative of B_o at $P = 0$ (C_o) with their uncertainties according to the Vinet EOS (5) for solid oxygen, using the observed data [7]. For this fitting procedure, the structure deviation (R^2) is also given.

	Solid oxygen	
	Vinet EOS (ϵ - ζ)	Vinet EOS (α - ϵ)
V_o [cm ³ /mol]	21.45	20.91
B_o [GPa]	1.80 ± 0.15	2.97
C_o	8.33 ± 0.19	7.78
R^2	0.998	—
Ref.	this study	[1]

In this study, we first used the Vinet EOS (5), which was fitted to the experimental data from [7] for volume versus pressure in the ϵ and ζ phases in solid oxygen. The experimental $V(P)$ data used in the fitting procedure were extracted from the plots in [7] using high-resolution digitization software. To account for both inherent experimental errors and potential systematic uncertainties introduced during the data extraction process, the standard deviations for all calculated parameters were strictly determined by regression analysis and are provided in Tables I and II. Then, the coefficients B_o and C_o were determined with their uncertainties and standard deviation (R^2), and V_o (i.e., volume at $P = 0$), see Table I. Figure 2 shows the Vinet EOS plot (V - P) according to (5), together with the observed data [7]. The Vinet EOS was also fitted to experimental data in the previous study [5]. However, it should be noted that our fitted values of B_o and of C_o ($= B_o'$) for the ϵ - ζ transition were compared with the values of the low-temperature α phase (α - ϵ transition), which were obtained using the Vinet EOS in the previous study [1] and are reported in Table I.

During the procedure of fitting the Vinet EOS, the zero-pressure unit cell volume V_o was kept fixed at 21.45 cm³/mol to prevent divergence of the fitting function. This specific value was chosen because it aligns well with the experimental zero-pressure volume reported in [1] and maximizes the correlation coefficient R^2 close to unity.

In order to calculate the pressure dependence on the frequency according to (8), we used experimental data for the Raman wavenumber shifts of the oxygen stretching mode (vibron) below and across the ϵ - ζ phase line at room temperature for polycrystalline O₂ [43]. Since (8) requires a constant or alternatively pressure dependence of the mode Grüneisen parameter (γ_T), we first determined γ_T of the vibron studied according to (3). By using the volume dependence on the pressure, $V(P)$, from experimental data [7], as well as the

TABLE II

Values of the isothermal mode Grüneisen parameter (γ_T), frequency ν_o (at $P = 0$), B_o (see (6)), and the derivative of B_o at $P = 0$ (C_o) with their uncertainties (see (7)) using the experimental data for the Raman vibron (polycrystalline) [43] and the infrared modes (ν_{FIR} and ν_{MIR}) [28] according to (8) for solid oxygen.

Solid oxygen	γ_T (average)	ν_o [cm^{-1}]	B_o [GPa]	C_o	R^2
Polycrystalline	0.35	1528.44 ± 11.96	180.63 ± 33.61	1.35 ± 0.65	0.998
ν_{FIR}	1.42	161.95	3.25 ± 0.113	7.60 ± 0.095	0.998
ν_{MIR}	0.017	1871.01	-23.45 ± 3.97	0.974 ± 0.002	0.934
		—	-31.66 ± 2.86	0.976 ± 0.001	0.938
		1491.53 ± 0.70	74.96 ± 3.63	-1.548 ± 0.06	0.994

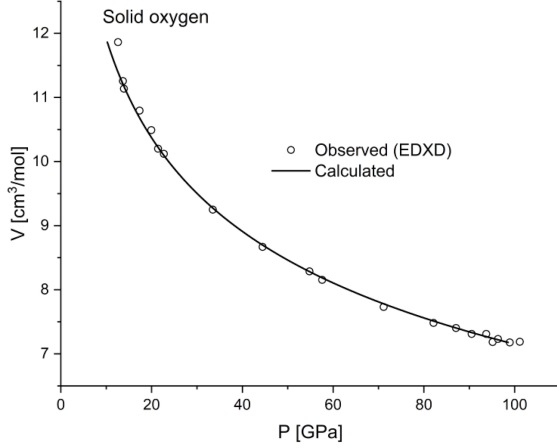


Fig. 2. Volume (V) calculated as a function of pressure (P) according to Vinet EOS (5) using the data observed for solid oxygen from [7].

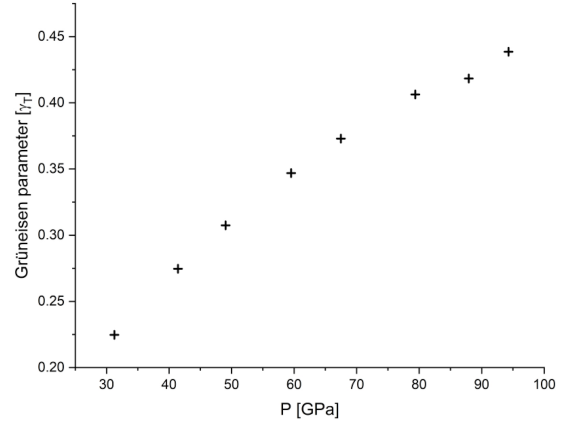


Fig. 3. The mode Grüneisen parameter (γ_T) calculated using (3) as a function of pressure at room temperature for the ϵ - ζ transition with respect to the observed V - P data [7] and the observed frequency data for the O_2 (polycrystalline) [43] (marked with +).

Raman wavenumber shifts of the vibron, $\nu(P)$ [43], the mode Grüneisen parameter γ_T was determined as a function of pressure, as plotted in Fig. 3.

The related research applied to polycrystalline solid oxygen was previously done in [43]. However, we will use (8) to predict the pressure dependence of the vibron frequencies of the polycrystalline O_2 . By considering the variation of γ_T from 0.22 to 0.44 in Fig. 3, we assume the average value of $\gamma_T = 0.35$ and then calculate the vibron frequencies as a function of pressure according to (8), as plotted in Fig. 4.

The pressure range from 30 to 100 GPa shown in this figure corresponds mainly to the ϵ phase. The transition from the insulator ϵ phase to the metal ζ phase occurs at ~ 96 GPa. In Fig. 4, we also show some vibron frequencies (ν) above ~ 100 GPa (observed by Goncharov et al. in [43]) in the metal ζ phase. Therefore, Fig. 4 presents our calculated ν values as a function of pressure, covering mainly the ϵ phase, the ϵ - ζ transition, and the ζ phase, together with the observed data [43]. The parameter values that were determined, along with their uncertainties (and R^2), when (8) was applied in the calculations to the polycrystalline O_2 system ($\gamma_T = 0.35$), are given in Table II.

We also tested the applicability of (8) to some other modes in the ϵ phase of solid oxygen near the ϵ - δ transition, using experimental data from [28]. The pressure dependence in the 10–63 GPa range of the new strong peak in the far infrared (FIR) region (i.e., ν_{FIR}) and of the mid-infrared (MIR) band (i.e., ν_{MIR}) in the O_2 fundamental vibration region [28] was studied at $T = 300$ K. We first calculated the pressure dependence of the mode Grüneisen parameter γ_T for both peak frequencies (i.e., ν_{FIR} and ν_{MIR}) by analyzing the Raman vibron according to (3) and with respect to the experimental V - P data [7]. The variation of γ_T with the pressure for the ν_{FIR} mode was unusual and varied from about 1.16 to 1.57, with its maximum value at about 33.7 GPa, as shown in Fig. 5. The frequencies of this mode were then evaluated using (8), with an average value of $\gamma_T = 1.42$ for the ν_{FIR} mode, and compared with the experimental data, as shown in Fig. 6.

In the case of the ν_{MIR} mode, since the peak frequencies rapidly decrease in phase ϵ to their minimum value and then increase smoothly with

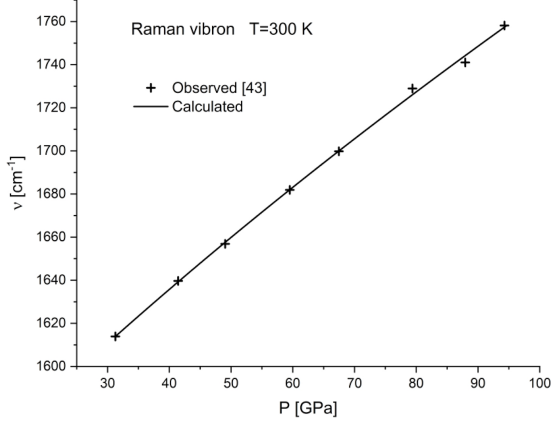


Fig. 4. The Raman vibron frequencies calculated as a function of pressure (at room temperature) according to (8) for the ϵ - ζ phase transition in solid oxygen. The symbol for this mode (+) indicated for the observed data from [43] is the same as given in Fig. 3.

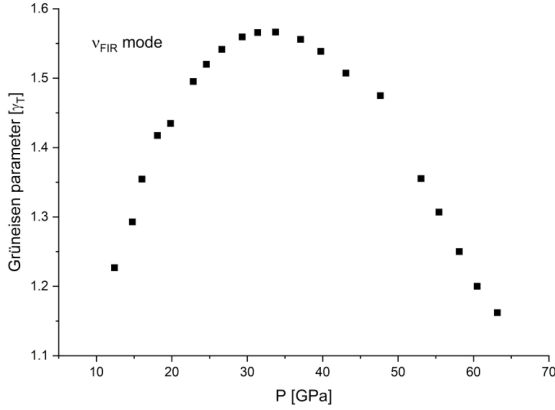


Fig. 5. Calculated Grüneisen parameter (γ_T) of the infrared mode of ν_{FIR} as a function of pressure according to (3) with respect to the observed V - P data [7] and the observed ν_{FIR} data [28] for the ϵ phase of solid oxygen.

increasing pressure, as observed experimentally [28], the Grüneisen parameter γ_T exhibits the λ -type behaviour with pressure (Fig. 7). The variation of γ_T with pressure was calculated using (3) and with respect to the V - P data [7] — in the same way as the calculation of the other modes studied here. In Fig. 7, the filled dots represent the calculated γ_T from the observed peak frequencies collected on the thin slab, and the open dots from the saturated absorption peak [28]. Finally, we calculated the pressure dependence of the peak frequencies of the ν_{MIR} mode using (8) and with respect to the observed data [28], as shown in Fig. 8. In this figure, the observed data are marked as follows: $\bullet$ — data collected on the thin slab; $\circ$ — data derived from the saturated absorption peak [28]; the same symbols for the mode Grüneisen parameter γ_T were used

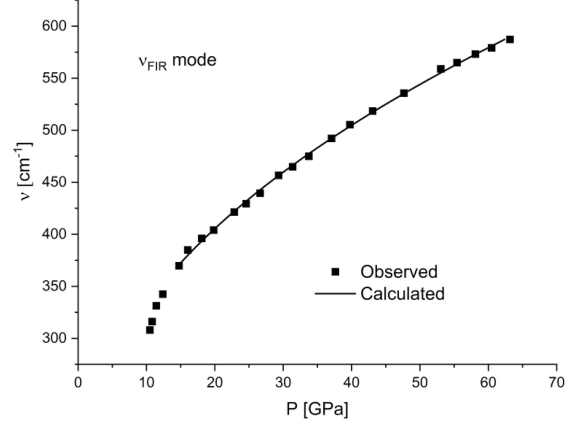


Fig. 6. The pressure dependence of the infrared frequency for the ν_{FIR} mode, which was calculated according to (8) for the ϵ phase of solid oxygen. The observed frequencies [28] are also shown in the figure.

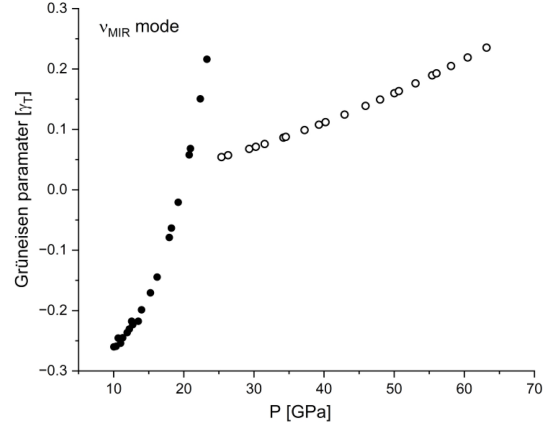


Fig. 7. Calculated Grüneisen parameter (γ_T) of the infrared mode of ν_{MIR} as a function of pressure according to (3) using the observed V - P data [7] and the observed ν_{MIR} data [28] for the ϵ phase of solid oxygen. Symbols used: solid dots ($\bullet$) — frequency data collected on the thin slab; open dots ($\circ$) — frequency data derived from the saturated absorption peak [28].

in Fig. 7. Values of the coefficients were determined when (8) was fitted to the experimental data [28]; they are given in Table II. We assume the average value of $\gamma_T = 0.017$ for the ν_{MIR} mode (Table II).

3. Discussion

We start from the Vinet EOS (5) for the pressure dependence of volume (V - P). Just as we modified the frequency-pressure (ν - P) relation (8) for cg-N in our previous study [42], in this study we predict the frequencies of some modes as a function of pressure for the ϵ - ζ transition in solid oxygen. Since

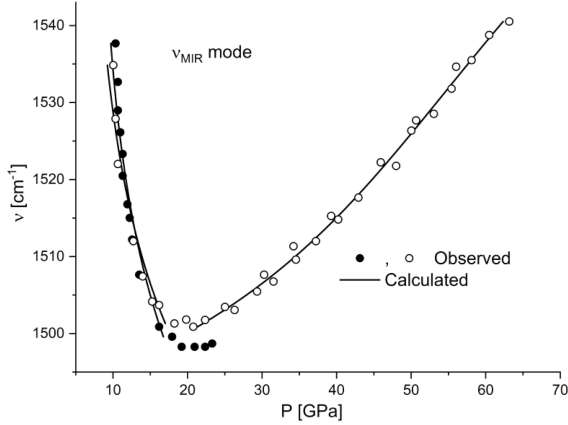


Fig. 8. Infrared frequency of the ν_{MIR} mode, which was calculated according to (8) as a function of pressure with respect to the observed data [28] with symbols as indicated in Fig. 7.

we were able to determine the coefficients B_o and C_o within the uncertainties in our V - P fitting of (5) to the observed data of Weck et al. [7] (Table I; see also Fig. 2), the obtained fit should be considered reliable. Note that the uncertainties we dealt with in the fit are relatively small ($B_o \cong 1.8$, varying from 1.7 to 2.0; $C_o \cong 8.0$, varying from 8.1 to 8.5). By fitting the observed data of Goncharov [43] for the Raman frequencies of the vibron (polycrystalline), the uncertainties in B_o (180.63 ± 33.61) and C_o (1.35 ± 0.65) were determined (Table II). Even though the uncertainty in C_o is comparatively large, the variation of the Raman vibron polycrystalline frequency (ν) with pressure should not be significantly affected (Fig. 4). To predict the Raman frequencies of the vibron using (8), we use the previously determined Grüneisen parameter γ_T , which increases smoothly as the pressure increases for the polycrystalline system, from ~ 0.23 to 0.44 (Fig. 3). This is consistent with the increase in the Raman frequency with pressure (see Fig. 4), which occurs as the volume decreases (see Fig. 2), according to the definition of γ_T given by (3). It has been indicated that the steady increase in the oxygen molecular stretching energy in the ϵ -O₂ phase gives rise to the discontinuous change in the frequency of this molecular stretching vibration (vibron) in the pressure range from 96 to 120 GPa [6, 8]. It was also indicated that there was no discontinuity of the vibron frequency at the semiconductor-metal transition at 96 GPa [6].

In contrast to the behaviour of the mode Grüneisen parameter (γ_T) for vibron (Fig. 3), the infrared modes ν_{FIR} and ν_{MIR} exhibit completely different behaviours in the ϵ phase (across the ϵ - ζ transition) of solid oxygen (Figs. 5 and 7). For the ν_{FIR} mode, γ_T with values between ~ 1.16 and ~ 1.57 (maximum value) shows a nearly symmetrical profile (Fig. 5), whereas γ_T for the

ν_{MIR} mode shows a cusp-like behaviour (Fig. 7), also taking negative values from -0.26 to ~ 0.22 as an internal mode.

As for the infrared frequencies of the ν_{FIR} mode, corresponding to increasing and decreasing γ_T by the maximum value (Fig. 5), this mode frequency increases with increasing pressure (Fig. 6) in accordance with (8) as the Raman (vibron) mode (Fig. 4), which also agrees with the experimental data. The behaviour of γ_T for the infrared mode ν_{MIR} is completely different from ν_{FIR} , which exhibits a λ -type behaviour (Fig. 7), as stated above. Correspondingly, as obtained experimentally [28], the frequency of this mode, which decreases to a minimum value at around 20 GPa and then increases, was calculated by means of (8). As seen in Fig. 8, the calculated frequencies agree with the experimental data. It was stated that the rapid increase in frequency of the ν_{FIR} mode up to 20 GPa (Fig. 6) and the opposite behaviour of the ν_{MIR} band (Fig. 8) can be explained by the charge density transfer, which gives rise to the formation of a new bond [28]. It should be noted that for the calculation of the Raman frequency (vibron) and the infrared frequencies (ν_{MIR} and ν_{FIR}) according to (8), we used the average (constant) values of the mode Grüneisen parameter (γ_T) given in Table II.

Taking into account the uncertainties in B_o and C_o for the IR modes (ν_{FIR} and ν_{MIR}) given in Table II, the calculated frequencies of ν_{FIR} (Fig. 6) and ν_{MIR} (Fig. 8) are in agreement with the observed data [28]. For the mode ν_{FIR} from our fitting procedure with values $B_o = 3.25 \pm 0.113$ and $C_o = 7.60 \pm 0.095$ (Table II), the uncertainties are relatively small. However, for the ν_{MIR} mode, whose value decreases to a minimum and then increases above about 20 GPa, as observed experimentally (Fig. 8), the uncertainties in the negative B_o , when ν_{MIR} decreases after two fits, are large (Table II). As ν_{MIR} increases (Fig. 8), the uncertainties in both B_o (positive) and C_o are reasonable (Table II). All this shows that with the uncertainties in the coefficients from our fitting procedure for the V - P relation (5) and the ν - P relation (8) (given in Tables I and II, respectively, along with the standard deviation R^2) on the basis of the observed data, our results are predictable with sufficient reliability.

Regarding the fitting procedure (P - ν) according to (8), since γ_T depends on pressure, the pressure functional form $P(\nu, \gamma_T)$ — depending on both ν and γ_T — required a surface fit that does not give a smooth curve of ν versus P . That is why the average value of γ_T was taken for the fit of the surface (ν - P) for the modes (Raman and infrared) studied here.

We found negative values of the Grüneisen parameter (γ_T) for the mid-infrared mode ν_{MIR} in the ϵ phase of solid oxygen over the pressure range of 10.34–19.21 GPa (see symbol ‘●’ in Fig. 7). Within this pressure range, γ_T varies from -0.26 to -0.02 ; then it becomes positive above about 20 GPa, with values ranging from 0.06 to 0.22 for pressures from

20.94 to 23.30 GPa, respectively (Fig. 7). This behaviour results from the unusual pressure dependence of the ν_{MIR} frequency observed in the thin-slab data of Gorelli et al. [28], where the frequency decreases to its minimum value at ~ 20 GPa and then increases with increasing pressure (see symbol ‘•’ in Fig. 7). This unusual behaviour of the ν_{MIR} mode leads to negative values of the Grüneisen parameter (γ_T) calculated according to (3) in this pressure region. On the other hand, the frequency data derived from the saturated absorption peak by Gorelli et al. [28] for the ν_{MIR} mode increase with increasing pressure (see symbol ‘o’ in Fig. 8). This is the expected behaviour of this mode above about 20 GPa. We have already found that the Grüneisen parameter γ_T increases with increasing pressure (above ~ 20 GPa) in Fig. 6 (see symbol ‘o’), as we calculated according to (3) in solid oxygen. From the experimental point of view, this result indicates that the pressure dependence of the mode frequency ν_{MIR} exhibits characteristic features for the frequency data collected on the thin slab, in comparison to that derived from the saturated absorption peak in solid oxygen.

Our approach for predicting the vibrational frequencies (Raman and IR) using the mode Grüneisen parameter γ_T according to the ν - P relation (see (8)), which in turn was derived from the Vinet EOS (see (5)), was applied in the present study to the ϵ - ζ transition at high pressures in solid oxygen. In our treatment, γ_T was taken as pressure-dependent, as shown in Figs. 3, 5, and 7, over the pressure ranges of 30–100 GPa (Fig. 3) and 10–90 GPa (Figs. 5 and 7). These studies were considered together with the pressure dependence of the volume and the Raman and IR frequencies in the ϵ phase in the pressure range of (~ 10 –90 GPa) and near the ϵ - ζ transition ($P_C \sim 96$ GPa) in solid oxygen. In the whole analysis, we used (8) to predict the pressure dependence of the vibrational (Raman and IR modes) frequencies in the high-pressure phase (ϵ phase), by taking the average values of the mode Grüneisen parameter γ_T (Table II). Therefore, (8) can be applied not only near the phase transition (ϵ - ζ), but also within the ϵ phase of solid oxygen. Regarding, in particular, the insulator–metal transition (i.e., ϵ - ζ transition) at high pressures ($P_C \cong 96$ GPa), the ν - P relation (8) can be applied to other molecular crystals that exhibit a similar type of transition (i.e., insulator–metal) as in the solid oxygen system at high pressures. For those molecular crystals, the pressure dependence of the vibrational frequencies $\nu(P)$ can be predicted by determining the mode Grüneisen parameter $\gamma_T(P)$ or assuming a constant γ_T from the volume dependence $V(P)$ by using (8). As we have established previously [42], polymeric solid nitrogen at high pressures (~ 110 GPa), which is cubic-phase nitrogen (cg-N), and similar structures such as solid H_2 , can be studied using the ν - P relation.

4. Conclusions

The Raman and infrared mode frequencies were calculated as a function of pressure (at room temperature) by means of the spectroscopically modified (ν - P) Vinet equation for the ϵ - ζ phase transition in solid oxygen. This was done by determining the mode Grüneisen parameters of the studied modes using observed data for pressure dependence of the volume and data from the literature for frequency.

Our results indicate that the spectroscopically modified ν - P relation satisfactorily predicts the observed Raman and infrared mode frequencies studied for the ϵ - ζ transition in solid oxygen. Apart from the cg-N and solid oxygen studied here, the ν - P relation can also be examined for some other molecular solids.

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