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Raman scattering intensities in α-quartz: A first-principles investigation

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Using a first-principles density functional approach, we calculate the first-order Raman intensities of α-quartz. The dynamical charge tensors, vibrational frequencies and eigenmodes, and polarizability tensors are obtained within a perturbational approach. We calculate Raman intensities by evaluating the variation of the polarizability tensors for finite displacements of the atoms. Calculated intensities agree well with experimental data, showing an average error of 13% for relative intensities. Using our first-principles results as reference, we critically examine simple models for the Raman activity. We first consider a bond polarizability model, for which the parameters are derived from our first-principles results for α-quartz. This model reproduces the first-principles intensities with an average error of 15%. In the attempt of reducing this error, we then introduce a model in which the symmetry of the first neighbor shell is accounted for in the most general way. For α-quartz, this model extends the bond polarizability model, which is recovered as a special case. The model, which fully accounts for the local symmetry, describes the first-principles results within an average error of 12%, marginally improving upon the bond polarizability model (15%). However, when these models with parameters derived for α-quartz are applied to a cristobalite polymorph, only the bond polarizability model shows good transferability properties. These results support the use of the bond polarizability model as a simple scheme for calculating Raman intensities in tetrahedrally bonded SiO_2 systems.

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I. INTRODUCTION

Raman spectroscopy is nowadays routinely used as a powerful experimental tool for the characterization of material properties.[1] Raman scattering consists of an inelastic process in which incoming photons are scattered by vibrational excitations. The simplicity of the experimental setup makes this technique one of the principal methods used in vibrational spectroscopy. In first-order Raman scattering processes, the shifts of the photon frequencies directly provide the vibrational frequencies of the scattering material. Additional information is contained in the intensities of the Raman lines, which characterize the vibrational eigenmodes and dielectric response of the material.

The interpretation of the positions and the intensities of Raman lines calls for accurate theoretical modeling. First-principles approaches have proved successful in the determination of vibrational properties both for isolated molecules[2] and crystalline solids.[3–5] However, while these approaches are nowadays routinely used for the determination of vibrational frequencies, their application to Raman activities has remained limited, mainly because of the demanding computational effort. Recently, the accuracy of density-functional approaches in reproducing Raman activities was examined, and a good agreement between theory and experiment was found for a set of small molecules.[6,7] A few successful applications of first-principles methods have also appeared for crystalline[8,9] or, more generally, for periodic systems.[10,11]

For modeling the Raman activities, theoretical investigations have frequently made recourse to empirical or semiempirical approaches, such as the bond polarizability model.[12,13] These models generally rely on a description of the dielectric response in terms of contributions of individual bonds, and their empirical parameters are obtained by considering experimental data of representative systems.

We address here the Raman activity in α-quartz. The motivation of studying α-quartz is twofold. First, this crystalline material presents a primitive cell with nine atoms giving rise to complex vibrational properties, including the occurrence of LO-TO splittings. Combined with the availability of detailed experimental data,[14] this material provides a nontrivial system for examining the accuracy of density functional theory in reproducing Raman activities. Second, the structure of α-quartz is composed of corner-sharing SiO_4 tetrahedra, which is common to a large class of SiO_2 polymorphs as well as to vitreous silica. Therefore, the understanding of the Raman activity in α-quartz might set a basis for the interpretation of Raman spectra of other SiO_2 materials.

Kleinman and Spitzer provided the first interpretation of measured Raman lines in α-quartz[15] using empirical force constants and the bond polarizability model.[16] With the advent of laser light sources, more accurate experimental data became available[14]. However, the theoretical scheme[17] which was subsequently used for analyzing these new data, did not differ substantially from that adopted by Kleinman and Spitzer. More recently, Gonze, Allan, and Teter calculated accurate vibrational properties of α-quartz within a perturbational density functional approach.[5] However, Raman intensities were not addressed.

In this work, we calculate Raman activities within the local density approximation (LDA) to density functional theory. This calculation requires several ingredients, such as the vibrational frequencies and eigenmodes, dynamical charge tensors, and dielectric tensors, which are all obtained by applying a linear response method.[3,4] Using our first-principles results as reference, we then test the accuracy of simple models for the calculation of Raman activities. In particular, we introduce a model that fully accounts for the symmetry of the nearest neighbor shell of each atom, and reduces to the bond polarizability model for a special choice of its parameters. Finally, the transferability of these simple models is investigated by considering their accuracy for a cristobalite polymorph, for which we also determine the Raman intensities by a direct first-principles calculation.

This paper is organized as follows. In Sec. II, we outline the theoretical formulation for the calculation of Raman activities. Section III is devoted to the study of α-quartz. Using a density functional approach, we obtain the structure, dielectric tensor, dynamical charge tensors, vibrational frequencies and eigenmodes, LO-TO splittings, and Raman activities. In Sec. IV, we focus on simple models for the calculation of the Raman activity. The parameters of these models are derived from our first-principles results obtained in Sec. III. In Sec. V, the transferability of the simple schemes is tested on a cristobalite polymorph. The conclusions are given in Sec. VI.

TABLE I. Structural parameters of α-quartz. Lattice cell parameters and bond lengths are given in Å , while internal cell parameters are in cell units.

	Theory		Experiment
	Present	Ref. 5	Ref. 29
a	4.870	4.814	4.916
c	5.346	5.321	5.405
u	0.471	0.461	0.470
x	0.415	0.410	0.413
y	0.265	0.281	0.267
z	0.121	0.108	0.119
Si-O	1.59		1.60
Si-O-Si	144.8°	139.1°	143.7°

II. THEORETICAL FORMULATION

Here we briefly outline the formulation that we used for the calculation of Raman activities. We only focus on first-order processes, which involve a single phonon excitation. The momentum conservation imposes that only phonons of wave vectors $\mathbf{q}$ close to the center of the Brillouin zone can be excited. In practice, adopting the dipole approximation, we only consider center-zone phonons $(\mathbf{q}=0)$ and account for the dependence on the direction of $\mathbf{q}$ resulting from the long-range nature of the Coulomb field in polar materials.[18,19]

Using a similar notation as Gonze and Lee,[20] we express the dynamical matrix for $\mathbf{q}\to\mathbf{0}$ as a sum of an analytical and a nonanalytical matrix:

$$\tilde{D}_{\alpha i,\beta j}(\mathbf{q}\to\mathbf{0})=\tilde{D}_{\alpha i,\beta j}(\mathbf{q}=\mathbf{0})+\tilde{D}^{NA}_{\alpha i,\beta j}(\mathbf{q}\to\mathbf{0}), \tag{1}$$

where the greek and latin indices run over the atoms in the primitive cell and the three Euclidean directions, respectively. The analytical part is given by

$$\tilde{D}_{\alpha i,\beta j}(\mathbf{q}=\mathbf{0})=\frac{1}{\sqrt{M_\alpha M_\beta}}\frac{\partial^2 E_{\mathrm{tot}}}{\partial r_{\alpha i}\partial r_{\beta j}}, \tag{2}$$

where E_{tot} is the total energy of the system and M_α are the masses of the atoms. The nonanalytical part depends on the direction of the momentum $\mathbf{q}$ exchanged with the radiation field:[18]

$$\tilde{D}^{NA}_{\alpha i,\beta j}(\mathbf{q}\to\mathbf{0})=\frac{1}{\sqrt{M_\alpha M_\beta}}\frac{4\pi}{\Omega}\frac{\left(\sum_k \mathbf{q}_k Z^*_{\alpha,ki}\right)\left(\sum_i \mathbf{q}_{k'} Z^*_{\beta,k'j}\right)}{\sum_{kk'} \mathbf{q}_k \epsilon^\infty_{kk'} \mathbf{q}_{k'}}, \tag{3}$$

where Ω is the volume of the primitive cell, ϵ^∞_{ij} the high-frequency dielectric tensor, and $Z^*_{\alpha,ij}$ the Born dynamical charge tensors defined as the induced polarization along the direction i by a unitary displacement of atom α in the direction j:[21]

$$Z^*_{\alpha,ij}=\frac{\partial^2 E_{\mathrm{tot}}}{\partial E_i \partial r_{\alpha j}}. \tag{4}$$

For a given direction of $\mathbf{q}$, the frequencies ω_n and corresponding normalized eigenmodes $v^n_{\alpha i}$ of the excited phonons are obtained by diagonalizing the dynamical matrix in Eq. (1). The atomic displacements $u^n_{\alpha i}$ associated with the mode n are then given by

$$u^n_{\alpha i}=\frac{1}{\sqrt{M_\alpha}}v^n_{\alpha i}. \tag{5}$$

We obtain transverse-optic (TO) and longitudinal-optic (LO) modes as follows.[20] For a given mode n of the analytical part of the dynamical matrix, we define the associated three-component mode effective charge vector:[20]

$$\bar{Z}^n_i=\sum_{\alpha i} Z^*_{\alpha,ij}u^n_{\alpha j}. \tag{6}$$

When $\mathbf{q}\cdot\bar{\mathbf{Z}}^n=0$, the eigenmode n of the analytical part is also an eigenmode with the same frequency of the full dynamical matrix, and is identified as a TO mode. In general, the LO modes are obtained from the full dynamical matrix by taking $\mathbf{q}\|\bar{\mathbf{Z}}^n$ for every $\bar{\mathbf{Z}}^n$. However, in practice, symmetry constraints often limit the number of different directions of $\bar{\mathbf{Z}}^n$.

In a Raman scattering process, an incoming photon of frequency ω_L and polarization $\mathbf{e}_L$ is scattered to an outgoing photon of frequency ω_S and polarization $\mathbf{e}_S$, either creating (Stokes process) or annihilating (anti-Stokes process) a pho-

TABLE II. Diagonal elements of the high-frequency dielectric tensor of α-quartz, parallel ($\epsilon_{\parallel}^{\infty}$) and perpendicular ($\epsilon_{\perp}^{\infty}$) to the optical axis.

	Theory		Experiment
	Present	Ref. 5	Ref. 30
$\epsilon_{\parallel}^{\infty}$	2.457	2.383	2.566
$\epsilon_{\perp}^{\infty}$	2.429	2.356	2.527

non of frequency ω_k. Because of energy conservation, $\omega_S = \omega_L \pm \omega_k$, where the minus (plus) sign applies to the (anti-)Stokes process. We consider here nonresonant Raman scattering processes which can be described in the Placzek approximation.[1,22] The power cross section of the Stokes process involving a phonon of eigenmode k reads (in esu units):[1,22]

$$\frac{d\sigma}{d\Omega} = |\mathbf{e}_S\cdot\mathbf{R}^k\cdot\mathbf{e}_L|^2 = \frac{\omega_S^4 V}{c^4}|\mathbf{e}_S\cdot\boldsymbol{\alpha}^k\cdot\mathbf{e}_L|^2\frac{\hbar}{2\omega_k}(n_k+1), \tag{7}$$

where V is the volume of the scattering sample, c is the speed of light, and n_k is the Boson factor,

$$n_k = \frac{1}{\exp(\hbar\omega_k/k_B T)-1}. \tag{8}$$

The second rank tensor $\mathbf{R}^k$ in Eq. (7) is referred to as the Raman tensor associated to the vibrational eigenmode k.[1] The Raman susceptibility $\boldsymbol{\alpha}^k$ is defined as:[1]

$$\alpha_{ij}^k = \sqrt{\Omega}\sum_{\alpha l}\frac{\partial\chi_{ij}}{\partial r_{\alpha l}}u_{\alpha l}^k, \tag{9}$$

where χ_{ij} is the electric polarizability tensor:

$$\chi_{ij} = \frac{\epsilon_{ij}^{\infty} - \delta_{ij}}{4\pi}. \tag{10}$$

In the case of an anti-Stokes process, the definition of ω_S changes and the factor (n_k+1) in Eq. (7) must be replaced by n_k. We note that the Raman susceptibility defined in Eq. (9) is independent of the volume of the adopted cell Ω, because $\partial\chi_{ij}/\partial r_{\alpha l}$ scales as the inverse of Ω.

TABLE III. Calculated Born charge tensors for silicon and oxygen atoms, compared to results of a previous calculation.[5] The charge tensors are given in atomic units.

Present			Ref. 5		
Silicon atom in $(u,0,0)$					
3.021	0.000	0.000	3.016	0.000	0.000
0.000	3.671	-0.224	0.000	3.633	-0.324
0.000	0.257	3.450	0.000	0.282	3.453
Oxygen atom in (x,y,z)					
-1.413	0.564	0.505	-1.326	0.480	0.298
0.519	-1.915	-0.615	0.429	-1.999	-0.679
0.447	-0.648	-1.715	0.222	-0.718	-1.726

TABLE IV. Vibrational frequencies of α-quartz at the Γ point. The frequencies are given in cm^{-1}.

Theory		Experiment [a]	
Present	Ref. 5	Refs. 30,32	Ref. 14
$A1$			
193.7	238.9	219	207
355.0	339.3	358	356
460.1	461.7	469	464
1123.3	1061.0	1082	1085
A_{2T}			
366.4	341.4	361.3	
489.3	493.4	499	
792.2	762.4	778	
1115.4	1056.5	1072	
A_{2L}			
391.4	365.7	385	
533.8	540.5	553	
815.0	784.7	791	
1272.6	1218	1230	
E_T			
120.9	133.3	133	128
257.3	261.3	269	265
390.0	377.6	393.5	394
448.0	443.8	452.5	450
703.3	690.8	698	697
809.6	791.7	799	795
1108.7	1045.0	1066	1072
1190.8	1128.1	1158	1162
E_L			
121.0	133.4	133	128
258.5	263.2	269	265
398.6	389.2	402	401
500.2	498.6	512	509
708.7	694.5	701	697
824.0	803.9	811.5	807
1185.7	1123.9	1155	1162
1270.6	1209.5	1227	1235

[a] The first set of experimental data were obtained in Ref. 5 by extrapolating to 0 K the measured frequencies in Refs. 30, 32.

III. RAMAN SCATTERING IN α-QUARTZ

A. Structure

The α-quartz structure is described by the space group D_3^4 ($P3_121$) and its hexagonal primitive cell contains three SiO_2 units.[23] The atomic positions in the primitive cell are identified by four internal cell parameters: u, x, y, and z. We obtained relaxed structural parameters of α-quartz within the local density approximation[24] to density functional theory.[25,26] The valence wave functions were expanded in a plane-wave basis set defined by an energy cutoff of 60 Ry, while the core-valence interactions were described by norm-conserving pseudopotentials for both Si [Ref. 27] and O atoms.[28] We sampled the Brillouin zone using a single special k point at $(\frac{1}{3},0,\frac{1}{4})$ in crystalline coordinates, which is

TABLE V. Calculated derivatives of the dielectric polarizability tensor with respect to displacements along the Cartesian axes for silicon and oxygen atoms. The derivatives are given in $(4\pi)^{-1}\cdot 10^{-2} \times$ Bohr^{-1}.

$\partial\chi_{ij}/\partial x$			$\partial\chi_{ij}/\partial y$			$\partial\chi_{ij}/\partial z$		
Si atom in $(u,0,0)$								
−0.29	−0.06	0.01	0.11	−0.99	2.12	0.50	4.61	2.40
−0.06	0.04	2.64	−0.99	0.56	0.06	4.61	0.76	−0.05
0.01	2.64	−0.57	2.12	0.06	0.28	2.40	−0.05	1.52
O atom in (x,y,z)								
−3.46	−0.54	1.57	−3.30	−0.46	0.20	3.11	−0.65	−2.55
−0.54	−2.38	−0.13	−0.46	−9.02	0.63	−0.64	2.50	−0.45
1.57	−0.13	−3.35	0.20	0.63	−4.21	−2.55	−0.45	6.55

sufficient for obtaining converged results.[5] Our calculated structural parameters are reported in Table I, where they are compared to experimental[29] and previous theoretical results.[5] The three sets of data are found to be in excellent agreement.

B. Dielectric tensor and Born charge tensors

Applying a linear response approach,[3,4] we calculated the high-frequency dielectric tensor and the Born charge tensors.[26] The dielectric tensor of α-quartz is diagonal and assumes different values for parallel and perpendicular directions to the optical axis (z axis). Our calculated results are reported in Table II, where they are compared with experimental data[30] and results from a previous density-functional calculation.[5] The three sets of data are in excellent agreement. A slight overestimation of the theoretical dielectric constants is usual in density functional approaches.[31]

In the structure of α-quartz all Si atoms and all O atoms are equivalent by symmetry. We therefore give in Table III only the Born charge tensors of specific Si and O atoms. For comparison, also the results obtained in Ref. 5 are reported in Table III. The agreement is very good. We attribute the small differences in the off-diagonal terms to the different structural parameters in the two calculations (see Table I).

C. Vibrational frequencies

We considered first the analytic part of the dynamical matrix at the Γ point. The eigenmodes transform according to the irreducible representations of the symmetry group D_3: the nondegenerate A_1 and A_2 and the doubly degenerate E. The representations A_2 and E are infrared active, while A_1 and E are Raman active.

To derive LO-TO splittings, we calculated the vector $\overline{\mathbf{Z}}^n$ belonging to each eigenmode n. For the A_1 modes, $\overline{\mathbf{Z}}^n = 0$. Hence, the A_1 do not depend on the direction of $\mathbf{q}$. For the A_2 modes, $\overline{\mathbf{Z}}^n$ is parallel to the z axis, resulting in different frequencies for LO and TO excitations. In Table IV, we report frequencies for A_{2T} and A_{2L} modes obtained by diagonalizing the full dynamical matrix with $\mathbf{q}$ orthogonal and parallel to the z axis, respectively. The doubly degenerate modes E are characterized by a couple of orthogonal vectors $\overline{\mathbf{Z}}^n$ spanning the xy plane. Thus a LO-TO splitting of the E modes occurs for $\mathbf{q}$ vectors orthogonal to the z axis, while the E modes remain degenerate at the E_T frequencies for $\mathbf{q}$ parallel to the z axis.

In Table IV, we compare our calculated frequencies[26] with results from another density-functional calculation[5] and with two sets of experimental data. The first set of experimental data corresponds to extrapolations to 0 K of frequencies measured in Refs. 30, 32, as detailed in Ref. 5. The second set of experimental data was obtained in Ref. 14 at room temperature. Overall, the agreement between the present theoretical values and experiment is very good, with errors generally smaller than 5%. The differences between the theoretical approaches should again be attributed to the different equilibrium structures.

D. Raman activities

The Raman susceptibility defined in Eq. (9) requires the derivatives of the polarizability tensor with respect to the atomic displacements. We calculated these derivatives by finite differences using polarizability tensors obtained by applying a density-functional linear response approach.[3,4,26] For every Cartesian direction, we used finite displacements of ±1 and ±2% of the unit cell parameter a to estimate the derivatives of the polarizability tensor.[8,10] We calculated derivatives of the polarizability tensor only for displacements of a single O and a single Si atom. The results are given in Table V. Note that the matricial norm of the O tensor in Table V is almost a factor of 3 larger than that of the Si tensor. The derivatives with respect to the displacements of the other atoms are determined by symmetry.

By symmetry, the Raman tensors assume a well-defined form. Following the notation of Loudon,[33] the Raman tensors of the A_1 modes are given by

$$\begin{pmatrix} a & & \\ & a & \\ & & b \end{pmatrix}, \qquad (11)$$

while those associated to $E(x)$ and $E(y)$ modes assume the forms

$$\begin{pmatrix} c & & \\ & -c & d \\ & d & \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} & -c & -d \\ -c & & \\ -d & & \end{pmatrix}, \tag{12}$$

respectively. For the modes $E(x)$ and $E(y)$, the associated charge vectors $\overline{\mathbf{Z}}^n$, defined in Eq. (6), are parallel to the x and y axes, respectively.

The Raman tensors depend on the direction of the wave vector $\mathbf{q}$. The calculation proceeds as follows. First, we diagonalized the full dynamical matrix whose nonanlytical term is determined by the direction of $\mathbf{q}$. The resulting eigenmodes, together with the calculated derivatives of the polarizability tensor, gave the Raman susceptibility in Eq. (9). The Raman tensors were then obtained from Eq. (7).

In order to compare with experimental data,[14] we took $\mathbf{q}$ parallel to the x axis. For this choice, three kind of modes are observed: A_1, E_T, and E_L. The forms of the Raman tensors associated to these modes are given in Eqs. (11) and (12). For this particular choice of $\mathbf{q}$, the E_T and E_L have the form of the $E(y)$ and $E(x)$ tensors, respectively. Calculated values of a^2, b^2, c^2, and d^2 characterizing the Raman tensors for the Stokes process are given in Table VI. Note that the experimental data are generally obtained at room temperature, whereas the theoretical results account for the temperature only through the statistical Boson factor.

The absolute intensities associated to the strongest A_1 mode (at about 466 cm^{-1}) were determined experimentally by Gorelik and Sushchinskii.[34] Using an argon laser ($\hbar\omega_L = 15308$ cm^{-1}), these reseachers measured a^2 and b^2 to be 0.2 and 0.3×10^{-7} sterad^{-1} cm^{-1},[1,34] in fair agreement with our calculated values of 0.39 and 0.37 $\times 10^{-7}$ sterad^{-1} cm^{-1}, respectively. In Table VI, we carried out a more detailed comparison between theory and experiment considering the more extensive set of Raman intensities measured by Masso, She, and Edwards.[14] However, because these authors only give relative intensities, we estimated the unknown scaling factor f by minimizing the relative error Δ, defined as

$$\Delta = \sqrt{\frac{\sum_n (I_n^{\text{theo}} - f I_n^{\text{expt}})^2}{\sum_n f^2 (I_n^{\text{expt}})^2}}, \tag{13}$$

where I^{theo} and I^{expt} are the theoretical and experimental intensities, respectively, and where the sum over n is over all entry in Table VI for which an experimental result is available. For the sake of comparison, the theoretical data in Table VI were rescaled by the factor of $1/f$.

Calculated and measured intensities show overall good agreement. The theory correctly describes the important difference in magnitude between the intensities of the A_1 and E modes. Among the A_1 modes, the lines at 193.7 and 460.1 cm^{-1} are found to be much stronger than those at 355.0 and 1123.3 cm^{-1}, in agreement with the experimental trend. However, the relative ordering of the intensities a^2 and b^2 is not always reproduced. Among the E modes, the line at 120.9 cm^{-1} stands out as the strongest and is well described by our theory. The quality of the comparison can be quantified by the error Δ in Eq. (13), which is found to be 13% for the optimal scaling factor.

TABLE VI. Theoretical Raman intensities for the Stokes process in α-quartz, obtained by first principles and within a bond polarizability model (BP), are compared to the experimental values of Ref. 14. The vibrational modes are identified by the theoretical frequencies (in cm^{-1}). The correspondence with the experimental modes is according to Table IV. The theoretical absolute intensities per unit volume can be obtained by multiplying the values in the table by ω_S^4 and $1/f = 2.368 \cdot 10^{-70}$ sterad^{-1} cm^{-1} s^4. The experimental data are only known on a relative scale.[14]

Mode	First principles		Model BP		Experiment	
A_1	a^2	b^2	a^2	b^2	a^2	b^2
193.7	601.5	693.7	592.4	876.5	484	619
355.0	60.4	33.3	7.4	13.4	38	55
460.1	898.7	864.3	946.7	740.0	906	1000
1123.3	3.7	28.3	8.1	46.0	2.3	31
E_T	c^2	d^2	c^2	d^2	c^2	d^2
120.9	117.9	68.2	103.3	23.7	125	62
257.3	1.6	22.6	13.4	6.8	<1	28
390.0	21.6	1.0	4.5	4.7	11	<1
448.0	0.3	19.1	0.2	16.5	<1	13
703.3	10.5	5.2	1.4	1.0	-	-
809.6	2.5	17.8	0.3	18.0	<1	14
1108.7	1.5	13.7	9.0	15.4	<1	2.7
1190.8	32.6	5.8	23.9	1.4	23	5.5
E_L	c^2	d^2	c^2	d^2	c^2	d^2
121.0	117.3	68.6	104.7	23.7	-	-
258.5	1.7	24.1	12.8	7.2	-	-
398.6	22.1	5.5	5.3	10.7	6	2
500.2	1.4	11.5	0.5	9.4	<1	10
708.7	9.7	5.2	0.8	1.1	-	-
824.0	3.2	24.7	1.0	24.0	<1	20
1185.7	25.2	11.2	13.1	5.2	-	-
1270.6	7.3	2.9	17.4	5.8	3.7	<1

It is interesting to observe that the values of c^2 and d^2 for the two components of a LO-TO doublet are different due to the electrooptic effect associated with the E vibrations.[14] In particular, we focus on the three LO-TO doublets identified by the theoretical frequencies at 390–399, 448–500, and 810–824 cm^{-1}, for which LO-TO ratios of intensities could be determined experimentally. For the ratio $d^2(\text{LO})/d^2(\text{TO})$ associated to the 448–500 and 810–824 doublets, we found 0.60 and 1.38 in good agreement with the measured values of 0.79 and 1.43, respectively. The agreement between theory and experiment is less good for the ratio $c^2(\text{LO})/c^2(\text{TO})$ of the 390–399 doublet, in which we calculated a value of 1.0 while a value of 0.55 was found experimentally.

TABLE VII. Parameters of the bond polarizability model derived for α-quartz (BP) and a cristobalite structure of space group $F\overline{4}d2$ (BPC). For the purpose of comparison, the parameters derived for the cristobalite structure are rescaled to account for the volume of the primitive cell of α-quartz. The values are given in $(4\pi)^{-1}\cdot 10^{-3}\times$ Bohr^{-1}.

Model	α	β	γ
BP	771	196	56
BPC	773	144	34

IV. SIMPLE MODELS

In order to extend the present results to other SiO$_2$ polymorphs composed of corner-sharing tetrahedra, we evaluate in this section the accuracy of simple model schemes. In our approach, we obtained the parameters of these simple models directly from the derivatives of the polarizability tensor $\partial\boldsymbol{\chi}/\partial\mathbf{r}$ calculated from first principles in Sec. III D.

A. Bond polarizability model

The bond polarizability model[12,13] has successfully been applied for the calculation of Raman intensities in a large variety of systems.[1] In this approach, the polarizability is modeled in terms of bond contributions:

$$\boldsymbol{\alpha}_{ij}=\frac{1}{3}(2\alpha_p+\alpha_l)\delta_{ij}+(\alpha_l-\alpha_p)\left(\frac{R_iR_j}{R^2}-\frac{1}{3}\delta_{ij}\right), \quad (14)$$

where $\mathbf{R}=\mathbf{R}_\beta-\mathbf{R}_\alpha$ is a vector which defines the direction and the distance of a pair of nearest neighbor atoms at sites $\mathbf{R}_\alpha$ and $\mathbf{R}_\beta$. The parameters α_l and α_p correspond to the longitudinal and perpendicular bond polarizability, respectively.

The bond polarizability model further assumes that the bond polarizabilities α_l and α_p only depend on the length of the bond. Thus the derivative of the bond polarizability with respect to the displacement of the atom β reads:

$$\frac{\partial\alpha_{ij}}{\partial R_{\beta k}}=\frac{1}{3}(2\alpha_p'+\alpha_l')\delta_{ij}\hat{R}_k+(\alpha_l'-\alpha_p')\left(\hat{R}_i\hat{R}_j-\frac{1}{3}\delta_{ij}\right)\hat{R}_k + \frac{(\alpha_l-\alpha_p)}{R}(\delta_{ik}\hat{R}_j+\delta_{jk}\hat{R}_i-2\hat{R}_i\hat{R}_j\hat{R}_k), \quad (15)$$

where $\hat{\mathbf{R}}$ is a unit vector along $\mathbf{R}$ and α_l' and α_p' are the derivatives of the bond polarizabilities with respect to the bond length. Therefore, when one type of bond occurs, the bond polarizability model is completely defined by three parameters:

$$\alpha=2\alpha_p'+\alpha_l', \quad \beta=\alpha_l'-\alpha_p', \quad \gamma=(\alpha_l-\alpha_p)/R. \quad (16)$$

We determined parameters of the bond polarizability model as follows. Adopting the standard tensorial norm, we minimized the deviations of the tensor $\partial\boldsymbol{\chi}/\partial\mathbf{r}$ with respect to our first principles results given in Table V. The parameters obtained in this way are given in Table VII. In the following, we refer to this specific bond polarizability model as to the BP model. The deviations of tensor, $\partial\boldsymbol{\chi}/\partial\mathbf{r}$ for Si and O atoms are 50% and 16%, respectively.

It is more significant to quantify the accuracy of the BP model on the basis of the Raman intensities. To this end, we used the same set of intensities as in Eq. (13). We first compared the intensities resulting from the BP model with those obtained by first principles, finding a relative deviation of 15%. This deviation is small, despite the rather large deviation found for the derivatives of the polarizability tensor, with respect to the displacements of Si atoms. This effect results from a combination of factors. The tensors in Table V are intrinsically larger for O than for Si atoms. The contributions of the O atoms to the Raman intensities are further enhanced by the larger number of O atoms in the unit cell and by their lighter atomic mass.

We also compared the intensities of the BP model with experimental data.[14] We calculated Δ, as in Eq. (13), with the same scaling factor f as obtained previously, finding $\Delta=25\%$. As expected, this value of Δ obtained within the BP model is worse than the corresponding value obtained by first principles (13%).

The parameters of the bond polarizability model are usually obtained by fitting the experimental intensities. Following this procedure, the parameters of the bond polarizability model remain indeterminate by a scaling factor, because the experimental intensities are only known on a relative scale. By minimizing Δ in Eq. (13), we found a deviation of 20%, independent of the scaling factor f. It is worth noting that this deviation is substantially larger than the deviation found for the first-principles intensities (13%).

B. Model dependent on local symmetry

In SiO$_2$ polymorphs composed of corner-sharing tetrahedra, the Si atoms are at the centers of tetrahedra while the O atoms are at their vertices. The Si-O bond length and O-Si-O angles generally do not deviate significantly from ~ 1.6 Å and the tetrahedral angle, respectively. The great variety of such polymorphs results from the flexibility of the Si-O-Si angle and the formation of different bonding networks.

In the attempt of improving upon the bond polarizability model, we introduce here a model for the tensor $\partial\boldsymbol{\chi}/\partial\mathbf{r}$, based on the ideal symmetry of the first neighbor shells. In the following, we refer to this model as the local symmetry (LS) model. In the case of Si atoms, we assumed the symmetry of the ideal tetrahedron (T_d), while we took the C_{2v} symmetry group for describing the environment of the O atoms. We express the derivatives of the polarizability tensor with respect to Si and O displacements, $\partial\boldsymbol{\chi}/\partial\mathbf{r}_{\mathrm{Si}}$ and $\partial\boldsymbol{\chi}/\partial\mathbf{r}_{\mathrm{O}}$, in terms of invariant tensors.[35] The third-order tensor $\partial\boldsymbol{\chi}/\partial\mathbf{r}$ transforms like a product of three polar vectors and is symmetric for exchanges of two of them.

By applying group theory, the form of the invariant tensors can be determined. For Si atoms a single invariant tensor is found, requiring the use of a single parameter for a full description. When the bonds of the Si atoms are oriented

TABLE VIII. Parameters of the local symmetry (LS) model obtained from first-principles results for α-quartz. The parameters are given in $(4\pi)^{-1}\cdot 10^{-2}\times$ Bohr^{-1}.

s	o_1	o_2	o_3	o_4	o_5
3.22	8.82	4.55	9.94	3.83	1.34

along the (1 1 1), $(\bar{1}\,\bar{1}\,1)$, $(\bar{1}\,1\,\bar{1})$ and $(1\,\bar{1}\,\bar{1})$ directions, the explicit form of the tensor $[(\partial\boldsymbol{\chi}/\partial x),(\partial\boldsymbol{\chi}/\partial y),(\partial\boldsymbol{\chi}/\partial z)]$ reads:

$$\left[\begin{pmatrix} & & \\ & & s \\ & s & \end{pmatrix},\begin{pmatrix} & & s \\ & & \\ s & & \end{pmatrix},\begin{pmatrix} & s & \\ s & & \\ & & \end{pmatrix}\right]. \tag{17}$$

In the case of O atoms, the lower symmetry allows as much as five different invariant tensors, and the full tensor thus remains indeterminate by five parameters. In order to obtain an explicit form, we located the O atom on the positive z axis and took the x axis along the segment connecting its Si neighbors. For this orientation, the tensor $\partial\boldsymbol{\chi}/\partial\mathbf{r}$ reads:

$$\left[\begin{pmatrix} & & o_4 \\ & & \\ o_4 & & \end{pmatrix},\begin{pmatrix} & & \\ & & o_5 \\ & o_5 & \end{pmatrix},\begin{pmatrix} o_1 & & \\ & o_2 & \\ & & o_3 \end{pmatrix}\right]. \tag{18}$$

For SiO_2 polymorphs composed of corner-sharing tetrahedra, the bond polarizability model results from the LS model as a special case. The following relations between the parameters hold:

$$s = 2\sqrt{3}(\beta - 2\gamma)/9,$$

$$o_1 = (\cos\theta)[\beta(3\sin^2\theta - 1) + \alpha - 6\gamma\sin^2\theta]/3,$$

$$o_2 = (\cos\theta)(\alpha - \beta)/3,$$

$$o_3 = (\cos\theta)[\beta(3\cos^2\theta - 1) + \alpha + 6\gamma]/3 - 2\gamma\cos^3\theta,$$

$$o_4 = (\cos\theta)[(\beta - 2\gamma)\sin^2\theta + \gamma],$$

$$o_5 = \gamma\cos\theta, \tag{19}$$

where 2θ is the Si-O-Si angle.

The free parameters of the LS model, in Eqs. (17) and (18), are obtained from our first-principles results in Table V by symmetrization. The values of these parameters are reported in Table VIII. The deviations of the LS model tensors, with respect to the tensors obtained by first principles, reflect the significance of the contributions of the global environment which do not satisfy the symmetry of the first-neighbor shell. In order to estimate these deviations, we adopted the standard tensorial norm and found a relative deviation of 50% and 12% for Si and O atoms, respectively. Because the BP model is a special case of the more general LS model, the latter necessarily provides a better description, as can be seen from the comparison in Table IX. However, despite the use of six parameters instead of three, the LS deviations only marginally improve upon the BP ones.

TABLE IX. Deviations $\Delta\partial\boldsymbol{\chi}/\partial\mathbf{r}$ for Si and O atoms with respect to the corresponding first-principles tensors of α-quartz, as found for the bond polarizability (BP) and local symmetry (LS) models using the standard tensorial norm. Deviations of the intensities ΔI with respect to first-principles and experimental results, determined using Eq. (13). The deviations are given in percent.

	BP	LS
with respect to first-principles		
$\Delta\partial\boldsymbol{\alpha}/\partial\mathbf{r}$(Si)	50	50
$\Delta\partial\boldsymbol{\alpha}/\partial\mathbf{r}$(O)	16	12
ΔI	15	12
with respect to experiment		
ΔI	25	23

This limited improvement is also evident when focusing on the intensities. The deviations of the LS and BP intensities do not differ significantly, neither when calculated with respect to the first-principles intensities nor to the experimental ones (Table VIII).

V. TRANSFERABILITY

In order to examine the transferability of the simple models, we consider here in detail another SiO_2 polymorph composed of corner-sharing tetrahedra. Because we were unable to find in the literature a polymorph other than α-quartz for which detailed experimental Raman activities were available, we chose to consider a cristobalite structure of space group $F\bar{4}d2$,[36,37] and to use Raman activities calculated from first principles as reference. This cristobalite structure offers the computational advantage of a unit cell containing just two formula units and the possibility of selecting the Si-O-Si angle by applying an appropriate tensile or compressive strain.[38] We fixed the cubic lattice parameter at $a = 6.97$ Å, and relaxed the internal degree of freedom. The electronic structure was described with the same technical parameters used for α-quartz. The Brillouin zone was sampled with two special k points at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{4})$ with respective weights of $\frac{1}{4}$ and $\frac{3}{4}$.[39]

We found a Si-O bond length of 1.58 Å and a Si-O-Si angle of 144.4° upon relaxation. We chose on purpose to work with a Si-O-Si angle close to that of α-quartz (143.7°), in order to avoid the consideration of additional parameters in our investigation of the transferability of the simple models.

The vibrational modes at the Γ point of the Brillouin zone belong to the irreducible representations of the D_{2d} group: the nondegenerate A_1, A_2, B_1, B_2 modes and the doubly degenerate E mode. The calculated vibrational frequencies are reported in Table X where they are ordered according to the symmetry of their eigenmodes. All the modes but those of A_2 symmetry are Raman active. Following the notation of Loudon,[33] the forms of the Raman tensors read

TABLE X. Transverse-optic vibrational frequencies at the Γ point and corresponding Raman intensities for a cristobalite structure of space group $F\overline{4}d2$.[36,37] Intensities obtained by first principles and by applying the bond polarizability model BP, originally derived for α-quartz, are compared. The absolute Raman intensities per unit volume can be obtained by multiplying the values in the table by ω_S^4 and by $1/f = 2.368 \cdot 10^{-70}$ sterad^{-1} cm^{-1} s^4.

Symmetry	Mode Frequency (cm^{-1})		Calculated intensity First-principles	BP
A_1	342.6	a^2	1501.6	1630.3
		b^2	1241.4	1001.0
A_2	1158.3	Raman inactive		
	359.8	Raman inactive		
B_1	1114.0	c^2	38.9	70.7
	445.9		24.5	13.9
B_2	779.2	d^2	4.2	5.3
	442.3		0.0	33.6
E	1144.0	e^2	5.6	16.8
	815.8		38.1	24.6
	474.4		0.8	1.5
	135.5		281.8	100.5

TABLE XI. Deviations $\Delta\partial\boldsymbol{\chi}/\partial\mathbf{r}$ and ΔI with respect to first-principles results for a cristobalite structure of space group $F\overline{4}d2$, as found for the local symmetry (LS) and bond polarizability (BP and BPC) models. The parameters of the BP and BPC models were derived for the α-quartz and cristobalite structures, respectively. The deviations were calculated, as in Table IX.

	LS	BP	BPC
$\Delta\partial\boldsymbol{\alpha}/\partial\mathbf{r}$(Si)	32	32	30
$\Delta\partial\boldsymbol{\alpha}/\partial\mathbf{r}$(O)	23	23	19
ΔI	25	16	10

$$\begin{pmatrix} a & & \\ & a & \\ & & b \end{pmatrix}, \quad \begin{pmatrix} c & & \\ & -c & \\ & & \end{pmatrix}, \quad \begin{pmatrix} & d & \\ d & & \\ & & \end{pmatrix}, \qquad (20)$$

for the nondegenerate modes A_1, B_1, and B_2, respectively, and

$$\begin{pmatrix} & & \\ & & e \\ & e & \end{pmatrix}, \quad \begin{pmatrix} & & e \\ & & \\ e & & \end{pmatrix}, \qquad (21)$$

for the doubly degenerate modes $E(x)$ and $E(y)$, as defined in the case of α-quartz. The calculated parameters for the Raman tensor of each mode are given in Table X. The A_1 mode at 342.6 cm^{-1} and the E mode at 135.5 cm^{-1} are the strongest Raman lines.

We used our first-principles results as a reference to test the transferability of the BP and LS models. Using the standard tensorial norm, we calculated the deviations $\Delta\partial\boldsymbol{\chi}/\partial\mathbf{r}$ with respect to the first-principles tensors. The accuracy of the BP and LS models were found to be similar, with deviations of 32% and 23% for Si and O atoms, respectively. In order to quantify the deviation with respect to the first-principles intensities, we calculated an average deviation ΔI, as in Eq. 13, using all the entries in Table X. We found a deviation of 16% and 25% for the BP and LS models, respectively. Table XI summarizes the results of these transferability tests. From Table XI, it clearly appears that the LS model, which depends on six parameters, does not bring any advantage with respect to the three-parameter BP model. The BP model reproduced the first-principles intensities of α-quartz and cristobalite with a similar deviation (15% and 16%, respectively). The intensities calculated with the BP model are shown in Table X, where they are compared with the first principles results. By comparison, the LS model reproduced the first-principles intensities of cristobalite with a deviation of 25%, substantially larger than the corresponding deviation found for α-quartz (12%).

We further examined the transferability of the bond polarizability model by extracting a new set of parameters α, β, and γ from the tensors $\partial\boldsymbol{\chi}/\partial\mathbf{r}$ calculated for the cristobalite structure. The parameters of this new bond polarizability model, which we refer to as the BPC model, are reported in Table VII, where they are rescaled to the volume of the primitive cell of α-quartz for permitting a comparison with the parameters of the BP model. The difference between the parameters α, β, and γ are smaller than 3% with respect to the size of the largest parameter α. We also added in Table XI the deviations $\Delta\partial\boldsymbol{\chi}/\partial\mathbf{r}$ and ΔI for the BPC model. This comparison shows that the BPC model, which corresponds to the optimal bond polarizability model for the cristobalite structure, only marginally improves upon the BP model originally derived for α-quartz. All these results provide additional evidence in support of the transferability of the bond polarizability model.

While the LS model slightly improves upon the BP model in describing the Raman intensities of α-quartz, it now clearly appears that this is achieved at the cost of degrading the transferability properties. We attribute the better transferability properties of the bond polarizability model to the validity of the underlying physical picture.

We only addressed here two structures with close Si-O-Si bond angles. It is of interest to extend the simple models to structures with different angles. In principle, the parameters of the simple models should be optimized for each angle separately. However, in the case of the bond polarizability model, this angular dependence follows from the physical picture on which the model is based [Eqs. 19].

VI. CONCLUSIONS

In the first part of our study, we calculated Raman intensities in α-quartz from first principles using a linear-response approach. Calculated and measured relative intensities were found to agree within an average error of 13%. This agreement is remarkable in consideration of the error of 20%

found for the bond polarizability model based on parameters which optimally fit the experimental intensities. In particular, this investigation provided us with the derivatives of the polarizability tensors with respect to the atomic displacements, which cannot be extracted from experiment in a trivial way.

In the second part of our work, we addressed the validity of simple models for the calculation of Raman intensities of SiO_2 polymorphs composed of corner-sharing tetrahedra. Using our first-principles results for α-quartz as reference, we derived a set of three parameters defining the bond polarizability model. This model described the first-principles intensities with an average error of about 15%. Searching for a more accurate model, we extended the bond polarizability model, introducing a six-parameter model that accounts in the most general way for the symmetry of the first-neighbor shell. Indeed, this new model improves upon the bond polarizability, slightly reducing the average error from 15% to 12%. However, this improvement is rather modest.

Furthermore, application to a cristobalite structure showed that the transferability properties of the new model are rather unsatisfactory. On the other hand, the bond polarizability model derived for α-quartz describes the cristobalite structure without loss of accuracy. Therefore, it appears that a full description of the symmetry of the first-neighbor shell does not lead to significant improvements, suggesting that the bond polarizability model already accounts for the relevant physical contributions. Simple schemes improving upon the bond polarizability model should necessarily go beyond a description of the first-neighbor shells. Overall, these considerations support the use of the bond polarizability model as a simple scheme for the calculation of Raman intensities in tetrahedrally bonded SiO_2 systems.

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