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## Interstitial O isotope effects in silicon

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**Abstract.** The oxygen isotope shifts of the vibrational modes of interstitial oxygen in silicon, obtained from isotopically enriched silicon samples, are compared with the predictions of a calculation based on a bond-centred location of the O atom, as is obtained from first principles. This comparison confirms the existence of a Raman-active mode in which the O atom is weakly involved and of a resonance producing a broadening and a small shift of the  $^{17}\text{O}$  asymmetric mode.

### 1. Introduction

Most of the oxygen present in the bulk of as-grown silicon is in the form of an isolated O atom bonded to two nearest-neighbour Si atoms and this location is referred to as interstitial oxygen ( $\text{O}_i$ ). From a classical point of view, the Si–O–Si group is not linear and the apex angle is  $\sim 165^\circ$ . Quantum mechanically, the O atom is delocalized among six equivalent positions around the Si...Si axis. The energy barrier for this reorientation is small (about 1 meV for a path going through the axis and smaller for a rotating path [1]). Many detailed observations of the  $\text{O}_i$  absorption have been made, mainly near liquid helium temperature (LHeT) because the vibrational features are sharper and look more intense than at room temperature so that a better sensitivity is obtained [2]. Natural silicon is made up from  $^{28}\text{Si}$  (92.2%),  $^{29}\text{Si}$  (4.7%) and  $^{30}\text{Si}$  (3.1%) and, at LHeT, Si isotope shifts (ISs) of the vibrational lines can be observed. This, together with O isotope effects ( $^{16}\text{O}$  (99.76%),  $^{17}\text{O}$  (0.04%) and  $^{18}\text{O}$  (0.20%)), allows us to determine geometrical parameters of the  $\text{Si}_2\text{O}$  centre in the silicon crystal.

The vibrational absorption of  $\text{O}_i$  has been initially related to the modes of a  $\text{Si}_2\text{O}$  quasimolecule [3], but such a simple picture cannot account for the low-frequency motion. Features related to the  $^{28}\text{Si}_2^{16}\text{O}$  quasimolecule are the asymmetric mode  $\nu_3$  giving a strong absorption near  $1136\text{ cm}^{-1}$  (LHeT) and a mode at  $518\text{ cm}^{-1}$ . The dipole moment for this latter mode is oriented along the  $\text{C}_2$  axis of Si–O–Si [4, 5]. For this reason, the  $518\text{ cm}^{-1}$  line has been attributed up to now to a symmetric mode of Si–O–Si. A low-frequency line at  $29\text{ cm}^{-1}$ , observed only at low temperature, is ascribed to the delocalization of the O atom among equivalent configurations in the crystal about the Si...Si axis and it has often been identified with the other symmetric mode of  $\text{Si}_2^{16}\text{O}$ , with a frequency reduced by the

potential barrier [6]. A combination mode involving  $\nu_3$  and the low-frequency mode is also observed at  $1206\text{ cm}^{-1}$ . The full width at half peak (FWHP) of mode  $\nu_3$  and of the  $29\text{ cm}^{-1}$  mode are  $\sim 0.6$  and  $0.1\text{ cm}^{-1}$ , respectively [2, 7]. Except for the mode at  $518\text{ cm}^{-1}$ , all the features observed are isotope and also temperature dependent because excited levels are thermally populated above 10 K. Thus, new 'hot' lines appear in the spectrum when the temperature is raised, but below 10 K only the satellites corresponding to the other Si and O isotopes are observed.

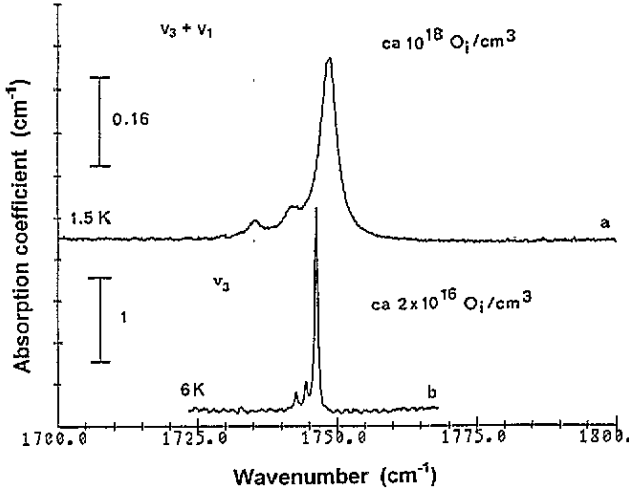


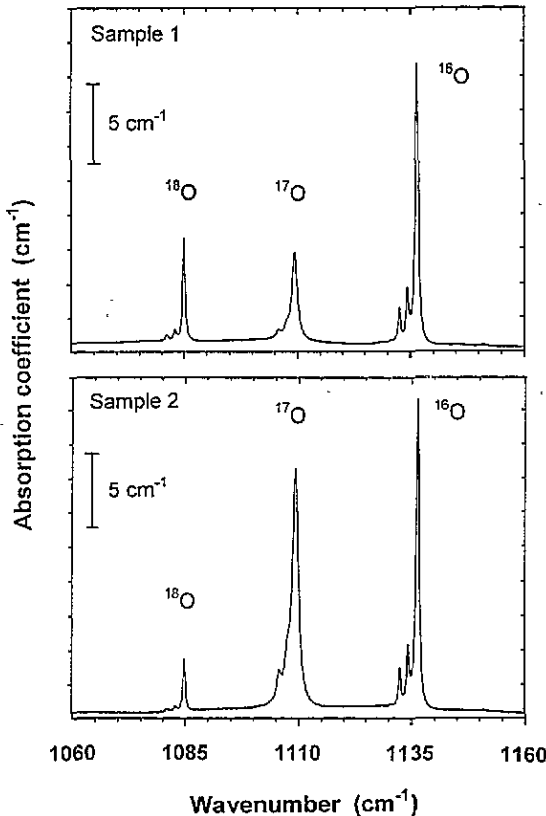
Figure 1. (a) Isotope shifts of  $^{28}\text{Si}^{16}\text{O}^{29}\text{Si}$  and  $^{28}\text{Si}^{16}\text{O}^{30}\text{Si}$  of the  $1748\text{ cm}^{-1}$  line, ascribed to the  $\nu_3 + \nu_1$  combination mode of  $\text{O}_i$ , compared with (b) the same shifts for the  $\nu_3$  mode, plotted with the same abscissa scale. The wavenumbers refer to (a). After [10].

A weak line at  $1748\text{ cm}^{-1}$  has also been related to  $\text{O}_i$  in silicon [8, 9]. Its intensity relative to  $\nu_3$  is only 0.015, but it displays the same temperature dependence. For this reason, it has been attributed to the combination of mode  $\nu_3$  with lattice phonon modes of silicon. However, the Si isotope shift (IS) of this line is about three times larger than the one of  $\nu_3$  [10] (figure 1). This point is difficult to reconcile with the isotope dependence of the two-phonon mode at  $613\text{ cm}^{-1}$  assumed to be the other component of the combination mode and it has been suggested that this component could be an as-yet unknown symmetric mode of  $\text{O}_i$  [1]. First-principles calculations have recently been performed on  $\text{O}_i$  in silicon that support the idea of a linear Si–O–Si quasimolecule [11]. Based on this, a calculation of the density of vibration modes associated with this centre predicts the existence of two modes in the  $500\text{--}600\text{ cm}^{-1}$  range instead of one. The one with the highest frequency is symmetric and only Raman active for a linear Si–O–Si bridge. This mode should be the one participating to the combination giving the  $1748\text{ cm}^{-1}$  line. A measurement of the O IS of this line is of interest to check the properties of this new mode predicted by these calculations. We present here data on silicon samples enriched with isotopes  $^{17}\text{O}$  and  $^{18}\text{O}$  which confirm this attribution and we try to determine whether this new mode could also explain other spectroscopic properties of  $\text{O}_i$  in silicon.

## 2. Results and discussion

### 2.1. Experimental details

Two float-zoned silicon samples enriched with  $^{17}\text{O}$  and  $^{18}\text{O}$  by diffusion near  $1400^\circ\text{C}$  were used. The diffusion was carried out for a typical duration of ten days in an IR chamber, where the walls of the quartz ampoule are maintained near  $900^\circ\text{C}$  [12, 13]. The concentration of  $^{17}\text{O}$  in In-doped sample 1, or  $[^{17}\text{O}](1)$ , is about  $1.2 \times 10^{17} \text{ cm}^{-3}$ . In sample 2,  $\text{O}_i$  is not homogeneously dispersed through the 2.5 mm thick sample. Taking the same thickness as for sample 1 (1.25 mm),  $[^{16}\text{O}](1)$ ,  $[^{18}\text{O}](1)$ ,  $[^{16}\text{O}](2)$ ,  $[^{17}\text{O}](2)$  and  $[^{18}\text{O}](2)$ , normalized to unity for  $[^{17}\text{O}](1)$ , are 1.8, 0.5, 1.7, 2.2 and 0.2, respectively. The measurement of the  $^{17}\text{O}$  and  $^{18}\text{O}$  isotopic replicas of the  $^{16}\text{O}$  lines has been performed at LHeT using a BOMEM DA3 Fourier transform spectrometer with spectral resolutions between 0.1 and  $0.3 \text{ cm}^{-1}$ . The LHeT spectra of  $\nu_3(\text{O})$  in the two samples is shown in figure 2. The experimental frequencies are given in tables 1 and 2.



**Figure 2.** LHeT absorption of the asymmetric mode  $\nu_3$  or  $A_{2u}$  of  $\text{O}_i$  for different O isotopes in silicon samples enriched with  $^{17}\text{O}$  and  $^{18}\text{O}$ . The characteristics of the samples are given in the text.

**Table 1.** Experimental frequencies ( $\text{cm}^{-1}$ ) at LHeT for transitions from the ground state associated with  $\text{Si}_2\text{O}$  in silicon for different O and Si isotopes. When relevant, they are labelled by the final state including the quantization of the 2D anharmonic excitation of the O atom or by the traditional labelling for an  $\text{XY}_2$  symmetrical molecule. The frequency of the  $^{29}\text{Si}_2\text{O}$  combination nearly coincides with that of  $^{28}\text{SiO}^{30}\text{Si}$  and it is 26 times less intense so it cannot be measured.

Si combination	Attribution	$^{16}\text{O}$	$^{17}\text{O}$	$^{18}\text{O}$
Quasi-independent of the Si mass	$ 0, \pm 1, 0\rangle$	29.3 [6]	28.2	27.2 [6]
$^{28}\text{Si}_2\text{O}$	$\nu_2$	517.8	517.8	517.8
$^{28}\text{Si}_2\text{O}$	$ 0, 0, 1\rangle$ or $\nu_3$	1136.4	1109.5 [10]	1085.0 [10]
$^{28}\text{SiO}^{29}\text{Si}$	"	1134.5	1107.6	1083.0
$^{28}\text{SiO}^{30}\text{Si}$	"	1132.7	1105.8	1081.2
$^{29}\text{SiO}^{30}\text{Si}$	"	1130.8	NM <sup>a</sup>	NM
$^{30}\text{Si}_2\text{O}$	"	1129.2	NM	NM
mainly $^{28}\text{Si}_2\text{O}$	$ 1, 0, 1\rangle$	1205.7 [10]	1176.7	1151.1

<sup>a</sup> NM, not measured (too weak).

**Table 2.** Experimental frequencies ( $\text{cm}^{-1}$ ) at LHeT of the high-frequency combination band of  $\text{O}_i$  in silicon for different O and Si isotopes.

Si combination	$^{16}\text{O}$	$^{17}\text{O}$	$^{18}\text{O}$
$^{28}\text{Si}_2\text{O}$	1748.6	1720.4	1696.0
$^{28}\text{SiO}^{29}\text{Si}$	1742.2	NM <sup>a</sup>	NM
$^{28}\text{SiO}^{30}\text{Si}$	1735.4	NM	NM

<sup>a</sup> NM, not measured (too weak).

## 2.2. Comparison with the calculations

First-principles calculations on an  $\text{Si}_3 \equiv \text{Si-O-Si} \equiv \text{Si}_3$  cluster [11] indicate that the interstitial O atom is dynamically located at a bond centre (BC) site and that the potential seen by the O atom in the direction perpendicular to the  $\text{Si} \dots \text{Si}$  axis is highly anharmonic. The relaxation of at least the first- and second-nearest neighbours of the O atom is shown to be essential, the final Si-O length being 1.56 Å. The symmetry of the centre is  $D_{3d}$ . Based on these results, a phonon calculation is performed for  $\text{O}_i$  in an infinite Si system. It uses the Born approximation for the vibrational potential and the cluster-Bethe lattice approximation for the infinite Si system [11]. The local densities of states (LDOSs) of the O atom and of the two nearest-neighbour Si atoms are shown in figure 3. In the O and Si LDOSs, a peak is shown at  $1150 \text{ cm}^{-1}$ , associated with an asymmetric  $A_{2u}$  stretch mode of the unit. It is identified with the  $\nu_3$  mode at  $1136 \text{ cm}^{-1}$ . The peak at  $517 \text{ cm}^{-1}$  in the Si LDOS corresponds to a doubly degenerate transverse motion ( $E_u$ ) of the Si atoms. The contribution at this frequency in the O LDOS is negligible. To remain consistent with the conventional spectroscopic notations, this mode should be labelled  $\nu_2$  [14]. The experimental asymmetric line shape of the  $518 \text{ cm}^{-1}$  mode is qualitatively reproduced in the calculated LDOS near  $517 \text{ cm}^{-1}$  [11]. The dipole moment associated with this mode is perpendicular to the  $\text{Si} \dots \text{Si}$  axis and this does not contradict the experimental results [4, 5]. The strongest peak in the Si LDOS is at  $594 \text{ cm}^{-1}$  and it corresponds to a symmetric stretch mode ( $A_{1g}$ ), or  $\nu_1$  in the conventional spectroscopic notation. Such a mode is only Raman active, but its combination with the  $A_{2u}$  mode is IR active and should be observed at  $1744 \text{ cm}^{-1}$ . Figure 4 shows the dynamical location of interstitial oxygen in silicon with the

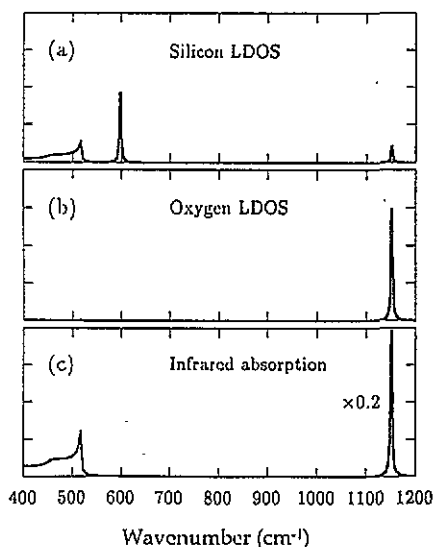


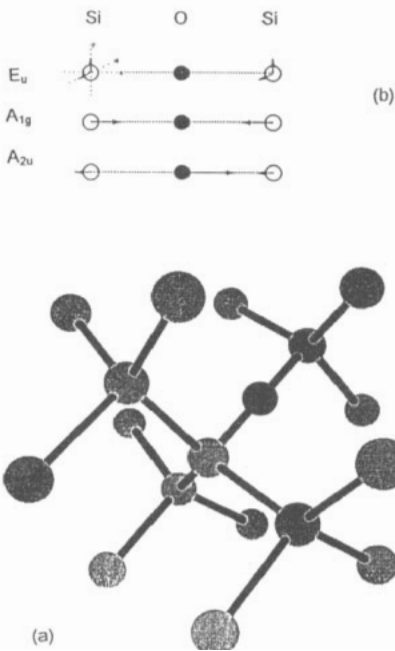
Figure 3. Vibration of the  $O_i$  centre. (a) Density of vibration modes projected on the Si atom neighbours to O. (b) Density of modes projected on the O atom. (c) Infrared absorption. LDOS stands for local density of states. From [11].

relative motions of the inner atoms for the different vibrational modes. For a slightly non-linear Si–O–Si structure (or in the presence of anharmonicity),  $\nu_1$  should become weakly IR active. This mode, however, has not been detected yet, possibly due to the fact that the frequency expected makes it resonant with the two-phonon IR absorption of silicon, peaking at  $613.6 \text{ cm}^{-1}$ . Si and O ISs have also been obtained in the above calculations and they are compared below with the experimental ones.

Table 3. Comparison between observed and calculated Si and O isotope shifts of  $O_i$  modes in silicon. The frequencies in parentheses are the ones calculated for  $^{28}\text{Si}_2^{16}\text{O}$ . The shifts ( $\text{cm}^{-1}$ ) are given with respect to  $^{28}\text{Si}_2^{16}\text{O}$ . The ones in parentheses are indirect determinations. The calculations are performed for a linear structure and non O-dependent shift is expected for the symmetric mode.

Combination	$A_{1g}$ or $\nu_1$ ( $596.3 \text{ cm}^{-1}$ )		$A_{2u}$ or $\nu_3$ ( $1150.3 \text{ cm}^{-1}$ )		$A_{1g} + A_{1u}$ ( $1746.6$ )	
	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.
$^{28}\text{Si}_2^{16}\text{O}^{29}\text{Si}$	(4.5)	5.0	1.9	2.3	6.4	(7.3)
$^{28}\text{Si}_2^{16}\text{O}^{30}\text{Si}$	(9.5)	9.7	3.7	4.5	13.2	(14.2)
$^{28}\text{Si}_2^{17}\text{O}$	(1.3)	0.0	26.9	26.0	28.2	(26.0)
$^{28}\text{Si}_2^{18}\text{O}$	(1.2)	0.0	51.4	49.7	52.6	(49.7)

Under the assumption, suggested by the calculations, that the  $1748 \text{ cm}^{-1}$  line is a combination of the  $A_{1g}$  and  $A_{2u}$  modes, or  $(\nu_1 + \nu_3)$ , of the linear  $^{28}\text{Si}-^{16}\text{O}-^{28}\text{Si}$  bridge, it is possible to derive from the experimental frequencies of  $\nu_3$  and of  $(\nu_1 + \nu_3)$  isotope-dependent frequencies of  $\nu_1$ . These 'measured' ISs of  $\nu_1$  are listed in table 3 with the experimental frequency  $\nu_1(^{28}\text{Si}_2^{16}\text{O})$  taken as  $612.2 \text{ cm}^{-1}$  and a FWHP of about  $3 \text{ cm}^{-1}$ . For a linear Si–O–Si bridge,  $\nu_1$  is expected to be independent of the O isotope in the



**Figure 4.** (a) Model of the dynamical bond-centered location of the interstitial O atom (dark grey) in the silicon lattice. (b) Relative displacements of the inner atoms for the different vibrational modes. The anharmonic low-frequency mode (not shown) is due to the two dimensional vibration of the O atom in the plane perpendicular to the Si–O–Si axis.

harmonic approximation. Experimentally, an O IS is obtained for this mode, but smaller than that of Si by a factor of about two, indicating a small contribution of the O atom to  $\nu_1$ , as a consequence of the anharmonicity of the potential. The large Si IS predicted by these calculations for this symmetric mode is also found experimentally and these two results confirm that the departure of Si–O–Si from a linear structure, if any, is small. The combination  $A_{1g} + E_u$  or  $\nu_1 + \nu_2$  is IR active, but the expected intensity, FWHP and location (near  $1129\text{ cm}^{-1}$ ) of this combination makes it difficult to detect because it is too close to the strong absorption of the  $\nu_3$  mode. These comparisons seem to show that, even if not detected directly, the symmetric mode near  $600\text{ cm}^{-1}$  predicted by the first-principles calculations exists.

### 2.3. The $^{17}\text{O}$ isotope effect

The experimental data of table 3 show an interesting result: the ‘experimental’ ISs for  $\nu_1$  are determined indirectly and it is found that the one for  $^{17}\text{O}$  is slightly *larger* than the one for  $^{18}\text{O}$  while a value smaller by a factor of about two is expected. This difference is beyond experimental error. Another puzzle related to  $^{17}\text{O}$  is the FWHP  $\sim 1.2\text{ cm}^{-1}$  (about 40 GHz) for the  $\nu_3$  components of this isotope, compared to  $\sim 0.6\text{ cm}^{-1}$  for  $^{16}\text{O}$  and  $^{18}\text{O}$  [2], as seen in figure 2. This broadening does not depend on the  $^{17}\text{O}$  concentration and it is not observed for the low-frequency mode at  $28.2\text{ cm}^{-1}$  [2]. Thus, the ground state is not broadened. This latter fact makes us think of an accidental effect like a resonance of  $\nu_3(^{17}\text{O})$  with another excitation as a possible explanation for the broadening. Accidental broadenings

due to phonon resonances are observed in the electronic spectra of shallow impurities in silicon [15, 16]. Such a resonance should also produce a small shift of  $\nu_3(^{17}\text{O})$  but would not shift  $(\nu_1 + \nu_3)(^{17}\text{O})$ . This resonance-induced shift is difficult to detect in the measured O IS of  $\nu_3$  because it is small compared to the mass-induced shift. However, it can result in an apparently anomalous IS of  $\nu_1(^{17}\text{O})$ , taken as the difference between  $(\nu_1 + \nu_3)$  and  $\nu_3$ , because the O IS is there much smaller. Considering for  $\nu_1(^{17}\text{O})$  a true IS of  $0.6 \text{ cm}^{-1}$ , about half the one for  $\nu_1(^{18}\text{O})$ , instead of the 'experimental' value of  $1.3 \text{ cm}^{-1}$ , one obtains 'corrected' values of  $611.6$  and  $1108.9 \text{ cm}^{-1}$  for  $\nu_1(^{17}\text{O})$  and  $\nu_3(^{17}\text{O})$ , respectively. Taking  $495 \text{ cm}^{-1}$  as an averaged IR value of the TO(L) phonon frequency in silicon at LHeT [17, 18], the frequency of the combination  $\nu_1(^{17}\text{O}) + \text{TO(L)}$  would be  $1107 \text{ cm}^{-1}$ , nearly resonant with  $\nu_3(^{17}\text{O})$ , but symmetry precludes such a resonance.  $^{17}\text{O}$  has a nuclear spin  $\frac{5}{2}$  while  $^{16}\text{O}$  and  $^{18}\text{O}$  have no nuclear spin. In principle, a broadening could result from the splitting of the  $\frac{5}{2}$  spin level of  $^{17}\text{O}$  by quadrupole interaction with an electric field gradient in the vibrational excited state. However, in order to explain the observed broadening for  $\nu_3(^{17}\text{O})$ , one would need a very large field gradient, about a hundred times larger than typically found for ground states in semiconductors. At present, we are unable to estimate such a large field gradient. An interesting check would be the experimental situation for  $^{17}\text{O}$  in germanium.

The combination mode of  $\nu_3$  with one quantum of the 2D low-frequency mode (2DLFM) is observed at  $1206 \text{ cm}^{-1}$  for  $^{16}\text{O}$  [2, 6]. Its FWHP is  $3 \text{ cm}^{-1}$  and no Si isotope satellite is resolved for this line. The O IS of this combination mode is the sum of that of  $\nu_3$  and of the 2DLFM. Using the observed frequencies of table 1, values of  $2.1$  and  $3.2 \text{ cm}^{-1}$  are derived for the  $^{17}\text{O}$  and  $^{18}\text{O}$  ISs of the 2DLFM, respectively. Here again, the  $^{17}\text{O}$  IS derived in this way is larger than expected. Taking for  $\nu_3(^{17}\text{O})$  the value corrected for the above-mentioned resonance ( $1108.9 \text{ cm}^{-1}$ ), the  $^{17}\text{O}$  IS reduces to  $1.5 \text{ cm}^{-1}$ , nearer the expected  $\sim 2/1$  ratio for  $^{18}\text{O}/^{17}\text{O}$  ISs. This point seems to confirm the existence of a small shift of  $\nu_3(^{17}\text{O})$  related to the unknown resonance. The observed and the corrected ISs are compared to table 4.

Table 4. Comparison of the experimental  $^{17}\text{O}$  and  $^{18}\text{O}$  isotope shifts ( $\text{cm}^{-1}$ ) of the  $\text{O}_i$ -related lines with respect to  $^{16}\text{O}$  at LHeT. The ones in parentheses are derived from the attribution of the line. Those for  $(^{17}\text{O})_{\text{cor}}$  are corrected for the resonance, on the assumption that the true shift of  $\nu_1$  is  $0.6 \text{ cm}^{-1}$  (value in square brackets).

Attribution of the line	$^{17}\text{O}$	$^{18}\text{O}$	$(^{17}\text{O})_{\text{cor}}$
$ 0, 0, 0\rangle \rightarrow  0, \pm 1, 0\rangle$	1.1	2.1	
$ 0, 0, 0\rangle \rightarrow  0, 0, 1\rangle$ or $\nu_3$	26.9	51.4	27.6
$ 0, 0, 0\rangle \rightarrow  1, 0, 1\rangle$	29.0	54.6	
$\nu_3 + \nu_1$	28.2	52.6	
$\nu_1$	(1.3)	(1.2)	[0.6]
$ 0, 0, 1\rangle \rightarrow  1, 0, 1\rangle$	(2.1)	(3.2)	1.5

#### 2.4. Comparison with *ab initio* calculations

An *ab initio* calculation of the vibrational modes of  $\text{O}_i$  in silicon using LDF has been reported [19] on a 87-atom cluster  $\text{OSi}_{44}\text{H}_{42}$  centred on the O atom at the midpoint of a bond. The local modes are calculated by evaluating the second derivatives of the energy with respect to the motion of the innermost Si-O-Si atoms. The highest two modes resulting of the diagonalization of the dynamical matrix are at  $1104$  and  $554 \text{ cm}^{-1}$  for  $^{28}\text{Si}^{16}\text{O}$ . The highest one describes the asymmetric stretching of the two Si-O bonds along  $\langle 111 \rangle$



axes. It is shifted by 6 and 53  $\text{cm}^{-1}$  for  $^{30}\text{Si}_2^{16}\text{O}$  and  $^{28}\text{Si}_2^{18}\text{O}$ , respectively. There is a clear correspondence between the value of 1104  $\text{cm}^{-1}$  and the experimental frequency for  $\nu_3$  in table 1; moreover, the isotope shifts agree qualitatively with the experimental ones (table 1). The mode at 554  $\text{cm}^{-1}$  is assimilated to the one observed at 518  $\text{cm}^{-1}$ . The calculation explains the absence of O isotope shift by the very small contribution of the O atom for this mode, but predicts large Si ISs ( $\sim 5 \text{ cm}^{-1}$  for  $^{28}\text{Si}^{16}\text{O}^{30}\text{Si}$ ). No Si IS has been observed for this line, whose FWHP is  $\sim 5 \text{ cm}^{-1}$  at LHeT. The first-principles calculations of [11] predict for the same isotopic combination an IS of 0.5  $\text{cm}^{-1}$ , which is below the experimental direction limit. There are two main differences between the two theoretical analyses. On the one hand, because of the breaking of the  $D_{3d}$  symmetry, the symmetric mode calculated at 554  $\text{cm}^{-1}$  in [19] is an admixture of the  $A_{1g}$  and  $E_u$  modes of [11]. On the other hand, the  $E_u$  mode actually involves many more atoms than the two Si atoms bonded to O because it is resonant in the continuum of the optical modes. This is the reason why it is not so sensitive to a change of mass of the nearest neighbours of the O atom.

### 3. Conclusion

From a comparison with experimental ISs of O and Si, it seems that the dynamics of the high-frequency modes of  $\text{O}_i$  in silicon can be explained by a new first-principles calculation taking into account quantum delocalization of the O atom around the BC location and assuming a  $D_{3d}$  symmetry for  $\text{O}_i$ . It leads to the reattribution of the  $\text{O}_i$  line at 518  $\text{cm}^{-1}$  ( $E_u$  mode instead of a symmetric mode) and to the prediction of the existence of a symmetric mode ( $A_{1g}$ ) which is only Raman active. It allows a correct evaluation of the Si IS of another  $\text{O}_i$  line attributed to a combination of this  $A_{1g}$  mode with the asymmetric  $A_{2u}$  mode. An indirect determination of the O IS of the  $A_{1g}$  mode gives evidence of a resonance-induced shift of the  $A_{2u}$  mode for  $^{17}\text{O}$ . The origin of this resonance, also responsible for the broadening of the mode, is not yet understood. The symmetry broken geometry corresponds to a location of the O atom at its potential minimum. A reasonable fit of the ISs of the asymmetric mode has previously been obtained in the harmonic approximation for this geometry by introducing an additional interaction parameter between Si–O–Si and the silicon matrix [10]. The description in terms of quantum delocalization of the O atom seems to better reflect reality for  $\text{O}_i$  in silicon and it should be preferred. For a  $D_{3d}$  symmetry, the first overtones of the three fundamental modes of  $\text{O}_i$  are not IR active. One line at 1013  $\text{cm}^{-1}$  has been previously attributed to the first overtone of the 518  $\text{cm}^{-1}$  mode [9]. For a  $D_{3d}$  symmetry of  $\text{O}_i$  and the above attributions, this point must be clearly reconsidered. Recently, a line at 1013  $\text{cm}^{-1}$  has been correlated with the presence of thermal donors [20], but the presence of thermal donors can be excluded for the samples investigated in [9]. The combination of the 518  $\text{cm}^{-1}$  mode with the TO(L) phonon of silicon would have a frequency of 1013  $\text{cm}^{-1}$ , but this combination should not be IR active.

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