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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}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 (O_i). From a classical point of view, the Si–O–Si group is not linear and the apex angle is $\sim 165°$. 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 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}Si (92.2%), ^{29}Si (4.7%) and ^{30}Si (3.1%) and, at LHeT, Si isotope shifts (ISs) of the vibrational lines can be observed. This, together with O isotope effects (^{16}O (99.76%), ^{17}O (0.04%) and ^{18}O (0.20%)), allows us to determine geometrical parameters of the Si_2O centre in the silicon crystal.

The vibrational absorption of O_i has been initially related to the modes of a Si_2O quasimolecule [3], but such a simple picture cannot account for the low-frequency motion. Features related to the $^{28}Si_2{}^{16}O$ quasimolecule are the asymmetric mode ν_3 giving a strong absorption near 1136 cm^{-1} (LHeT) and a mode at 518 cm^{-1}. The dipole moment for this latter mode is oriented along the C_2 axis of Si–O–Si [4, 5]. For this reason, the 518 cm^{-1} line has been attributed up to now to a symmetric mode of Si–O–Si. A low-frequency line at 29 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 $Si_2{}^{16}O$, with a frequency reduced by the

potential barrier [6]. A combination mode involving ν_3 and the low-frequency mode is also observed at 1206 cm^{-1}. The full width at half peak (FWHP) of mode ν_3 and of the 29 cm^{-1} mode are $\sim$ 0.6 and 0.1 cm^{-1}, respectively [2, 7]. Except for the mode at 518 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.

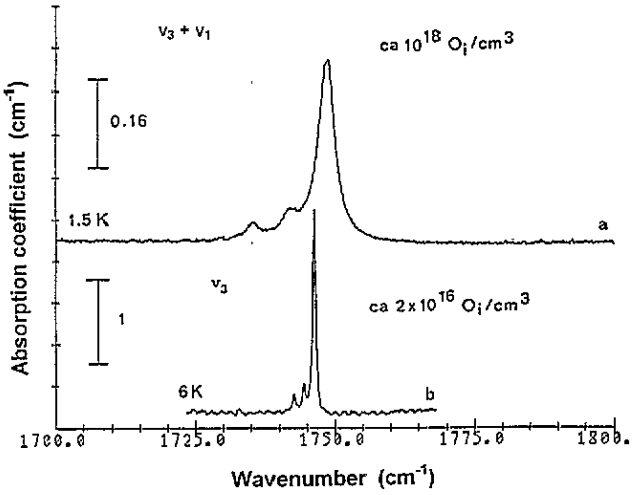

Figure 1. (a) Isotope shifts of $^{28}Si^{16}O^{29}Si$ and $^{28}Si^{16}O^{30}Si$ of the 1748 cm^{-1} line, ascribed to the $\nu_3 + \nu_1$ combination mode of O_i, compared with (b) the same shifts for the ν_3 mode, plotted with the same abscissa scale. The wavenumbers refer to (a). After [10].

A weak line at 1748 cm^{-1} has also been related to O_i in silicon [8, 9]. Its intensity relative to ν_3 is only 0.015, but it displays the same temperature dependence. For this reason, it has been attributed to the combination of mode ν_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 ν_3 [10] (figure 1). This point is difficult to reconcile with the isotope dependence of the two-phonon mode at 613 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 O_i [1]. First-principles calculations have recently been performed on 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 500–600 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 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}O and ^{18}O which confirm this attribution and we try to determine whether this new mode could also explain other spectroscopic properties of O_i in silicon.

2. Results and discussion

2.1. Experimental details

Two float-zoned silicon samples enriched with ^{17}O and ^{18}O by diffusion near 1400 °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 °C [12, 13]. The concentration of ^{17}O in In-doped sample 1, or [^{17}O](1), is about 1.2×10^{17} cm^{-3}. In sample 2, 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}O](1), [^{18}O](1), [^{16}O](2), [^{17}O](2) and [^{18}O](2), normalized to unity for [^{17}O](1), are 1.8, 0.5, 1.7, 2.2 and 0.2, respectively. The measurement of the ^{17}O and ^{18}O isotopic replicas of the ^{16}O lines has been performed at LHeT using a BOMEM DA3 Fourier transform spectrometer with spectral resolutions between 0.1 and 0.3 cm^{-1}. The LHeT spectra of ν_3(O) in the two samples is shown in figure 2. The experimental frequencies are given in tables 1 and 2.

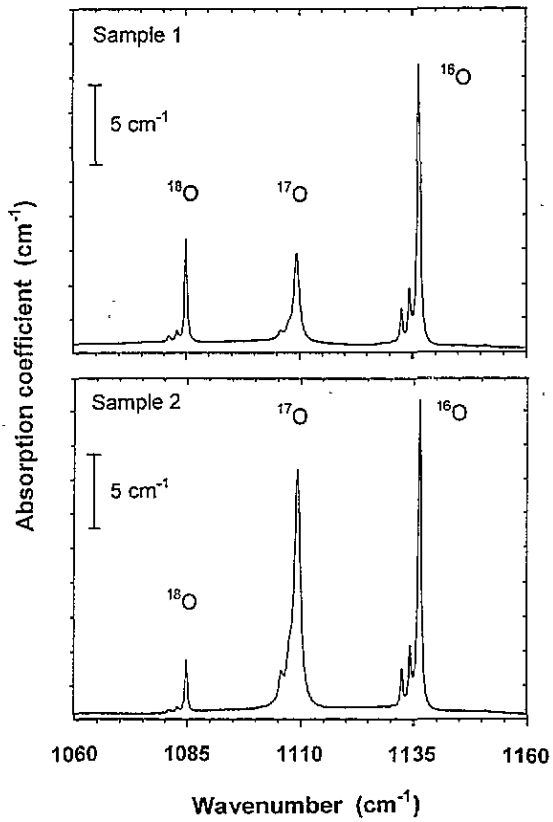

Figure 2. LHeT absorption of the asymmetric mode ν_3 or A_{2u} of O_i for different O isotopes in silicon samples enriched with ^{17}O and ^{18}O. The characteristics of the samples are given in the text.

Table 1. Experimental frequencies (cm^{-1}) at LHeT for transitions from the ground state associated with Si_2O 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 XY_2 symmetrical molecule. The frequency of the $^{29}Si_2O$ combination nearly coincides with that of $^{28}SiO^{30}Si$ and it is 26 times less intense so it cannot be measured.

Si combination	Attribution	^{16}O	^{17}O	^{18}O
Quasi-independent of the Si mass	$\|0, \pm1, 0\rangle$	29.3 [6]	28.2	27.2 [6]
$^{28}Si_2O$	ν_2	517.8	517.8	517.8
$^{28}Si_2O$	$\|0, 0, 1\rangle$ or ν_3	1136.4	1109.5 [10]	1085.0 [10]
$^{28}SiO^{29}Si$	"	1134.5	1107.6	1083.0
$^{28}SiO^{30}Si$	"	1132.7	1105.8	1081.2
$^{29}SiO^{30}Si$	"	1130.8	NM[a]	NM
$^{30}Si_2O$	"	1129.2	NM	NM
mainly $^{28}Si_2O$	$\|1, 0, 1\rangle$	1205.7 [10]	1176.7	1151.1

[a] NM, not measured (too weak).

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

Si combination	^{16}O	^{17}O	^{18}O
$^{28}Si_2O$	1748.6	1720.4	1696.0
$^{28}SiO^{29}Si$	1742.2	NM[a]	NM
$^{28}SiO^{30}Si$	1735.4	NM	NM

[a] NM, not measured (too weak).

2.2. *Comparison with the calculations*

First-principles calculations on an $Si_3 \equiv$ Si–O–Si $\equiv Si_3$ 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 Si...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 ångströms. The symmetry of the centre is D_{3d}. Based on these results, a phonon calculation is performed for 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 cm^{-1}, associated with an asymmetric A_{2u} stretch mode of the unit. It is identified with the ν_3 mode at 1136 cm^{-1}. The peak at 517 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 ν_2 [14]. The experimental asymmetric line shape of the 518 cm^{-1} mode is qualitatively reproduced in the calculated LDOS near 517 cm^{-1} [11]. The dipole moment associated with this mode is perpendicular to the Si...Si axis and this does not contradict the experimental results [4, 5]. The strongest peak in the Si LDOS is at 594 cm^{-1} and it corresponds to a symmetric stretch mode (A_{1g}), or ν_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 cm^{-1}. Figure 4 shows the dynamical location of interstitial oxygen in silicon with the

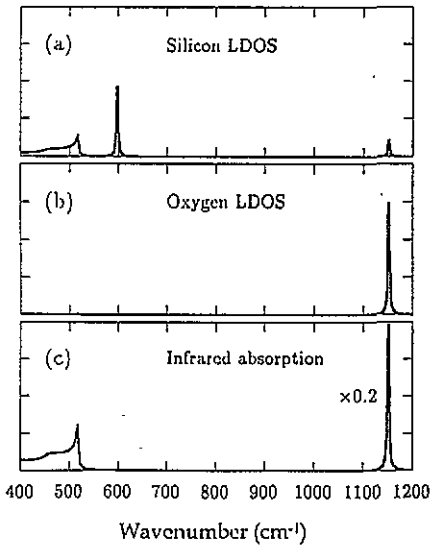

Figure 3. Vibration of the O_i centre. (a) Density of vibration modes projected on the Si atom neighbours to O. (b) Density of modes projected on the O atom. (c) Infrared absorption. LDOS stands for local density of states. From [11].

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), ν_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 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 $^{28}Si_2{}^{16}O$. The shifts (cm^{-1}) are given with respect to $^{28}Si_2{}^{16}O$. 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.

	A_{1g} or ν_1 (596.3 cm^{-1})		A_{2u} or ν_3 (1150.3 cm^{-1})		$A_{1g} + A_{1u}$ (1746.6)	
Combination	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.
$^{28}Si^{16}O^{29}Si$	(4.5)	5.0	1.9	2.3	6.4	(7.3)
$^{28}Si^{16}O^{30}Si$	(9.5)	9.7	3.7	4.5	13.2	(14.2)
$^{28}Si_2{}^{17}O$	(1.3)	0.0	26.9	26.0	28.2	(26.0)
$^{28}Si_2{}^{18}O$	(1.2)	0.0	51.4	49.7	52.6	(49.7)

Under the assumption, suggested by the calculations, that the 1748 cm^{-1} line is a combination of the A_{1g} and A_{2u} modes, or $(\nu_1 + \nu_3)$, of the linear ^{28}Si–^{16}O–^{28}Si bridge, it is possible to derive from the experimental frequencies of ν_3 and of $(\nu_1 + \nu_3)$ isotope-dependent frequencies of ν_1. These 'measured' ISs of ν_1 are listed in table 3 with the experimental frequency $\nu_1(^{28}Si_2{}^{16}O)$ taken as 612.2 cm^{-1} and a FWHP of about 3 cm^{-1}. For a linear Si–O–Si bridge, ν_1 is expected to be independent of the O isotope in the

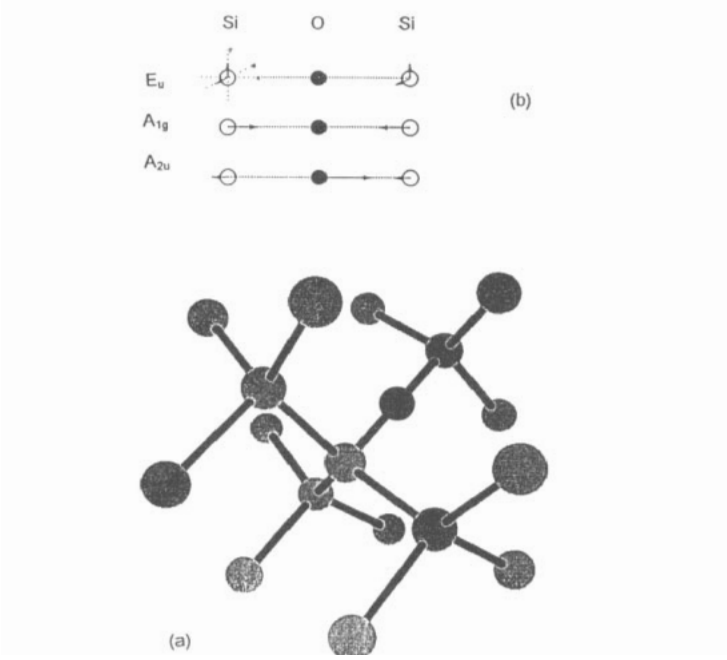

Figure 4. (a) Model of the dynamical bond-centred location of the interstitial O atom (dark grey) in the silicon lattice. (b) Relative displacements of the inner atoms for the different vibrational modes. The anharmonic low-frequency mode (not shown) is due to the two dimensional vibration of the O atom 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 ν_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 cm^{-1}) of this combination makes it difficult to detect because it is too close to the strong absorption of the ν_3 mode. These comparisons seem to show that, even if not detected directly, the symmetric mode near 600 cm^{-1} predicted by the first-principles calculations exists.

2.3. *The ^{17}O isotope effect*

The experimental data of table 3 show an interesting result: the 'experimental' ISs for ν_1 are determined indirectly and it is found that the one for ^{17}O is slightly *larger* than the one for ^{18}O while a value smaller by a factor of about two is expected. This difference is beyond experimental error. Another puzzle related to ^{17}O is the FWHP ~ 1.2 cm^{-1} (about 40 GHz) fo the ν_3 components of this isotope, compared to ~ 0.6 cm^{-1} for ^{16}O and ^{18}O [2], as seen in figure 2. This broadening does not depend on the ^{17}O concentration and it is not observed for the low-frequency mode at 28.2 cm^{-1} [2]. Thus, the ground state is not broadened. This latter fact makes us think of an accidental effect like a resonance of $\nu_3(^{17}O)$ 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 $\nu_3(^{17}O)$ but would not shift $(\nu_1 + \nu_3)(^{17}O)$. This resonance-induced shift is difficult to detect in the measured O IS of ν_3 because it is small compared to the mass-induced shift. However, it can result in an apparently anomalous IS of $\nu_1(^{17}O)$, taken as the difference between $(\nu_1 + \nu_3)$ and ν_3, because the O IS is there much smaller. Considering for $\nu_1(^{17}O)$ a true IS of 0.6 cm^{-1}, about half the one for $\nu_1(^{18}O)$, instead of the 'experimental' value of 1.3 cm^{-1}, one obtains 'corrected' values of 611.6 and 1108.9 cm^{-1} for $\nu_1(^{17}O)$ and $\nu_3(^{17}O)$, respectively. Taking 495 cm^{-1} as an averaged IR value of the TO(L) phonon frequency in silicon at LHeT [17, 18], the frequency of the combination $\nu_1(^{17}O)$+TO(L) would be 1107 cm^{-1}, nearly resonant with $\nu_3(^{17}O)$, but symmetry precludes such a resonance. ^{17}O has a nuclear spin $\frac{5}{2}$ while ^{16}O and ^{18}O have no nuclear spin. In principle, a broadening could result from the splitting of the $\frac{5}{2}$ spin level of ^{17}O by quadrupole interaction with an electric field gradient in the vibrational excited state. However, in order to explain the observed broadening for $\nu_3(^{17}O)$, 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}O in germanium.

The combination mode of ν_3 with one quantum of the 2D low-frequency mode (2DLFM) is observed at 1206 cm^{-1} for ^{16}O [2, 6]. Its FWHP is 3 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 ν_3 and of the 2DLFM. Using the observed frequencies of table 1, values of 2.1 and 3.2 cm^{-1} are derived for the ^{17}O and ^{18}O ISs of the 2DLFM, respectively. Here again, the ^{17}O IS derived in this way is larger than expected. Taking for $\nu_3(^{17}O)$ the value corrected for the above-mentioned resonance (1108.9 cm^{-1}), the ^{17}O IS reduces to 1.5 cm^{-1}, nearer the expected $\sim 2/1$ ratio for $^{18}O/^{17}O$ ISs. This point seems to confirm the existence of a small shift of $\nu_3(^{17}O)$ related to the unknown resonance. The observed and the corrected ISs are compared to table 4.

Table 4. Comparison of the experimental ^{17}O and ^{18}O isotope shifts (cm^{-1}) of the O_i-related lines with respect to ^{16}O at LHeT. The ones in parentheses are derived from the attribution of the line. Those for $(^{17}O)_{cor}$ are corrected for the resonance, on the assumption that the true shift of ν_1 is 0.6 cm^{-1} (value in square brackets).

Attribution of the line	^{17}O	^{18}O	$(^{17}O)_{corr}$
$\|0,0,0\rangle \rightarrow \|0,\pm 1,0\rangle$	1.1	2.1	
$\|0,0,0\rangle \rightarrow \|0,0,1\rangle$ or ν_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	
ν_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 O_i in silicon using LDF has been reported [19] on a 87-atom cluster $OSi_{44}H_{42}$ 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 cm^{-1} for $^{28}Si^{16}O$. 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 cm^{-1} for $^{30}Si_2{}^{16}O$ and $^{28}Si_2{}^{18}O$, respectively. There is a clear correspondence between the value of 1104 cm^{-1} and the experimental frequency for ν_3 in table 1; moreover, the isotope shifts agree qualitatively with the experimental ones (table 1). The mode at 554 cm^{-1} is assimilated to the one observed at 518 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 (~ 5 cm^{-1} for $^{28}Si^{16}O^{30}Si$). No Si IS has been observed for this line, whose FWHP is ~ 5 cm^{-1} at LHeT. The first-principles calculations of [11] predict for the same isotopic combination an IS of 0.5 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 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 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 O_i. It leads to the reattribution of the O_i line at 518 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 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}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 O_i in silicon and it should be preferred. For a D_{3d} symmetry, the first overtones of the three fundamental modes of O_i are not IR active. One line at 1013 cm^{-1} has been previously attributed to the first overtone of the 518 cm^{-1} mode [9]. For a D_{3d} symmetry of O_i and the above attributions, this point must be clearly reconsidered. Recently, a line at 1013 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 cm^{-1} mode with the TO(L) phonon of silicon would have a frequency of 1013 cm^{-1}, but this combination should not be IR active.

Acknowledgments

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