Symmetry assignments of Raman scattering by F^+ and F centres in calcium oxide

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Abstract. Data on the Raman scattering of F and F^+ centres in CaO are recorded. Symmetry assignments of the Raman effect of F^+ centres are in agreement with the F^+ emission spectrum measurements of Hughes, Pells and Sonder. Furthermore, polarization results show that the frequency separation between T_{2g} and E_g modes is about 17 cm^{-1}. The vibrational modes of F centres are also discussed.

The properties of the F^+ centre (a single electron trapped at an oxygen vacancy) in irradiated and additively coloured calcium oxides have been investigated in great detail [1–3]. Both absorption and emission bands of the F^+ centre measured at low temperature possess well-resolved vibronic structures. These phonon-assisted sidebands are very similar, apart from the zero-phonon line, and range from 190 to 600 cm^{-1}. The main sideband peaks which occur at $\sim$202 and $\sim$302 cm^{-1} in both absorption and emission spectra have attracted a great deal of interest. The 202 cm^{-1} peak has the same form in both absorption and emission spectra. The $\sim$302 cm^{-1} peak is especially sharp in the emission spectrum, but is broadened in the absorption spectrum. On the basis of the perfect-lattice phonon density of states, Evans *et al* [1] have assigned the 202 cm^{-1} peak to the E_g mode, the 302 cm^{-1} peak to the T_{2g} mode, and a weak sideband at 360 cm^{-1} to the A_{1g} mode. However, on the basis of stress-induced dichroism in the emission spectrum of the F^+ centre, rather different symmetry assignments have been given by Hughes *et al* [2]. They suggest that the 202 cm^{-1} peak is due predominantly to the A_{1g} mode and that the 302 cm^{-1} peak is due to a composite of T_{2g} and E_g modes. The later assignment is consistent with Jahn–Teller coupling of the excited $^2T_{1u}$ state of the F^+ centre to both E_g and T_{2g} vibrational modes. The broadening mechanism of the 302 cm^{-1} peak in the absorption spectrum thus becomes clear because the absorption process samples the vibronic structure of the excited state.

Recently, Orera *et al* [4] have described the photoconversion between F and F^+ centres as due to the reversible process $H^- + e^- \leftrightarrow H^{2-}$, and Ke *et al* [5] have proposed a Jahn–Teller coupling of the ground $^1T_{1u}$ state of the H^{2-} centre to E_g mode lattice distortion alone. The difference between the Jahn–Teller coupling mechanisms of two such closely related defects in CaO motivated us to study the crystal lattice modes of the F^+ defects again. The technique that we have employed in this study is Raman spectroscopy, which probes a complete frequency spectrum of the modes interacting with the F and F^+ centres.

The experiments were performed using the 514.5 nm line from a Spectra Physics model 171 argon-ion laser as the exciting source, with an output power level of 500 mW. Light scattered at a right angle was collected by a Spex 1401 double monochromator and detected by a cooled RCA C31034 photomultiplier tube. The spectral slit width was 5 cm^{-1}. The polarization of the scattered beam was analysed by a Polaroid sheet placed in front of

the monochromator entrance slit. The samples were grown at The Oak Ridge National Laboratory by an arc-fusion method. Defects resulting from additively coloured CaO crystals at high temperatures and at high pressure of calcium vapours are primarily F centres. The F centre concentrations are of the order of 10^{17} cm^{-3}. The sample was cleaved along the principal axis to a size of $7 \times 7 \times 2$ mm^3. Data were taken at 300 K. Cooling to 80 K revealed no significant change in band structure or in the relative intensity of the main peaks.

In a pure CaO crystal, since every ion is at a centre of inversion symmetry, first-order Raman scattering is forbidden. The presence of vacancies destroys the translational symmetry of the lattice. The one-phonon spectrum thus becomes Raman active. The irreducible representations of the Raman-active lattice vibrations for F and F$^+$ centres in CaO with O$_h$ symmetry would comprise vibrational modes with symmetry A_{1g}, E_g, and T_{2g}.
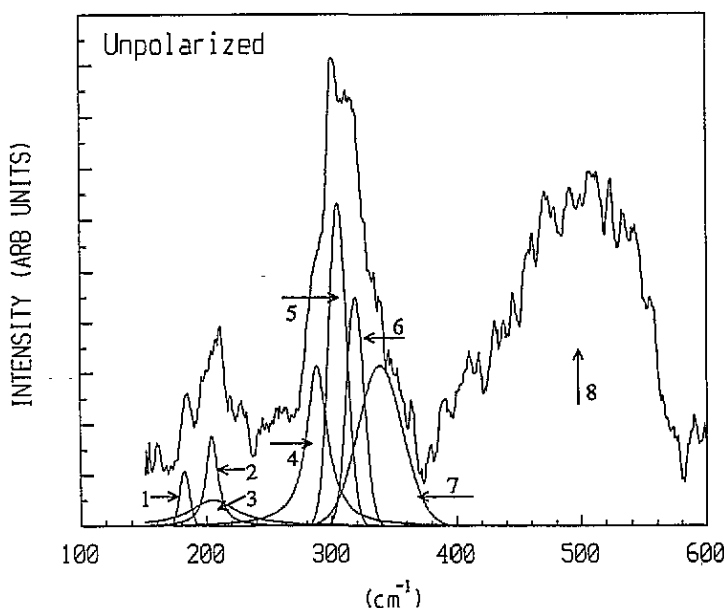

Figure 1. The unpolarized Raman spectrum of F and F$^+$ centres in CaO.

Figure 1 shows an unpolarized Raman spectrum, in which all the vibrational modes interacting with F and F$^+$ centres are recorded. The experimental overlapping bands are decomposed into eight individual peaks. The identification of peaks and their assignments (table 1) are based on previously reported data from the emission spectra measurements of Hughes *et al* [1], Henderson *et al* [3], and Saunderson *et al* [6]. The first peak at 185 cm^{-1} can be explained in two ways: (i) as belonging to a phonon band of F centres [3]; (ii) as due to the rotational transition [7] of Cu^{2+} in CaO. However, it seems reasonable to rule out the second possibility because we have not detected any epr signal due to substitutional Cu^{2+} ion in these CaO crystals. Furthermore, in the emission spectrum of the F centre band [3], phonon structures were observed at 196, 320 and 507 cm^{-1} and correspond in frequency to Raman peaks 1, 6 and 8. Hence, we attribute peaks 1, 6, and 8 to the lattice mode of F centres. Peaks 3 and 7 are close to the zone-boundary transverse acoustic peak

Table 1. Raman peak positions and assignments.

Peak	Raman (cm^{-1})	Emission sideband	Assignment	Reference
1	185	196 ± 20	F centre	[3]
2	203	202	F$^+$ centre	[1, 3]
3	206	200	Pure dos†	[6]
4	288	303 ± 15	F$^+$ centre	[1, 3]
5	305	303 ± 15	F$^+$ centre	[1, 3]
6	319	320 ± 20	F centre	[3]
7	340	330	Pure dos†	[6]
8	510	507 ± 50	F centre	[3]

† dos: density of states.

at 200 cm^{-1} and transverse optical peak at 330 cm^{-1} in the pure lattice density of states respectively [6].

Peaks 2, 4 and 5—of main interest—are associated with the F$^+$ lattice vibrational modes [1, 3]. The appearance of the 'shoulder' at half the height of the 302 cm^{-1} Raman peak indicates that this peak does not behave like a single mode, and we have decomposed it into peaks 4 and 5. To distinguish the symmetry mode of these vibrational peaks, three observation geometries are employed.

Table 2. Properties of Raman-active modes in O$_h$ symmetry.

Symmetry	System : Cubic, Class : m3m (Oh)		
Raman modes	Irreducible Representations		
	A$_{1g}$	E$_g$	T$_{2g}$
Porto	X(YY)Z	X(Y'X')Z	X(YX)Z
Raman tensor in x,y,z coord.	$\begin{bmatrix} a & o & o \\ o & a & o \\ o & o & a \end{bmatrix} \begin{bmatrix} b & o & o \\ o & b & o \\ o & o & -2b \end{bmatrix}$	$\begin{bmatrix} \sqrt{3}b & o & o \\ o & -\sqrt{3}b & o \\ o & o & o \end{bmatrix}$	$\begin{bmatrix} o & o & o \\ o & o & d \\ o & d & o \end{bmatrix} \begin{bmatrix} o & o & d \\ o & o & o \\ d & o & o \end{bmatrix} \begin{bmatrix} o & d & o \\ d & o & o \\ o & o & o \end{bmatrix}$
Axes transform in x',y',z coord	$\begin{bmatrix} a & o & o \\ o & a & o \\ o & o & a \end{bmatrix} \begin{bmatrix} b & o & o \\ o & b & o \\ o & o & -2b \end{bmatrix}$	$\begin{bmatrix} o & \sqrt{3}b & o \\ -\sqrt{3}b & o & o \\ o & o & o \end{bmatrix}$	$\begin{bmatrix} o & o & d \\ o & o & d \\ d & d & o \end{bmatrix} \begin{bmatrix} o & o & d \\ o & o & -d \\ d & -d & o \end{bmatrix} \begin{bmatrix} d & o & o \\ o & -d & o \\ o & o & o \end{bmatrix}$
Lattice Modes			

For convenience, the scattering geometries for observation and the irreducible representation with corresponding Raman tensors are listed in table 2. The laboratory coordinates are defined by the incident beam as the X axis and the scattered beam as the Z axis. The X' and Y' are crystal axes rotated by 45° about the Z axis. In Porto notation, the first letter in parentheses gives the direction of the incident electric field and the second letter gives the direction of the scattered electric field. Inspection of the Raman tensor verifies which type of mode—or combination thereof—is selected by the choices of crystal orientations and polarization of figures 2(a), (b) and (c).
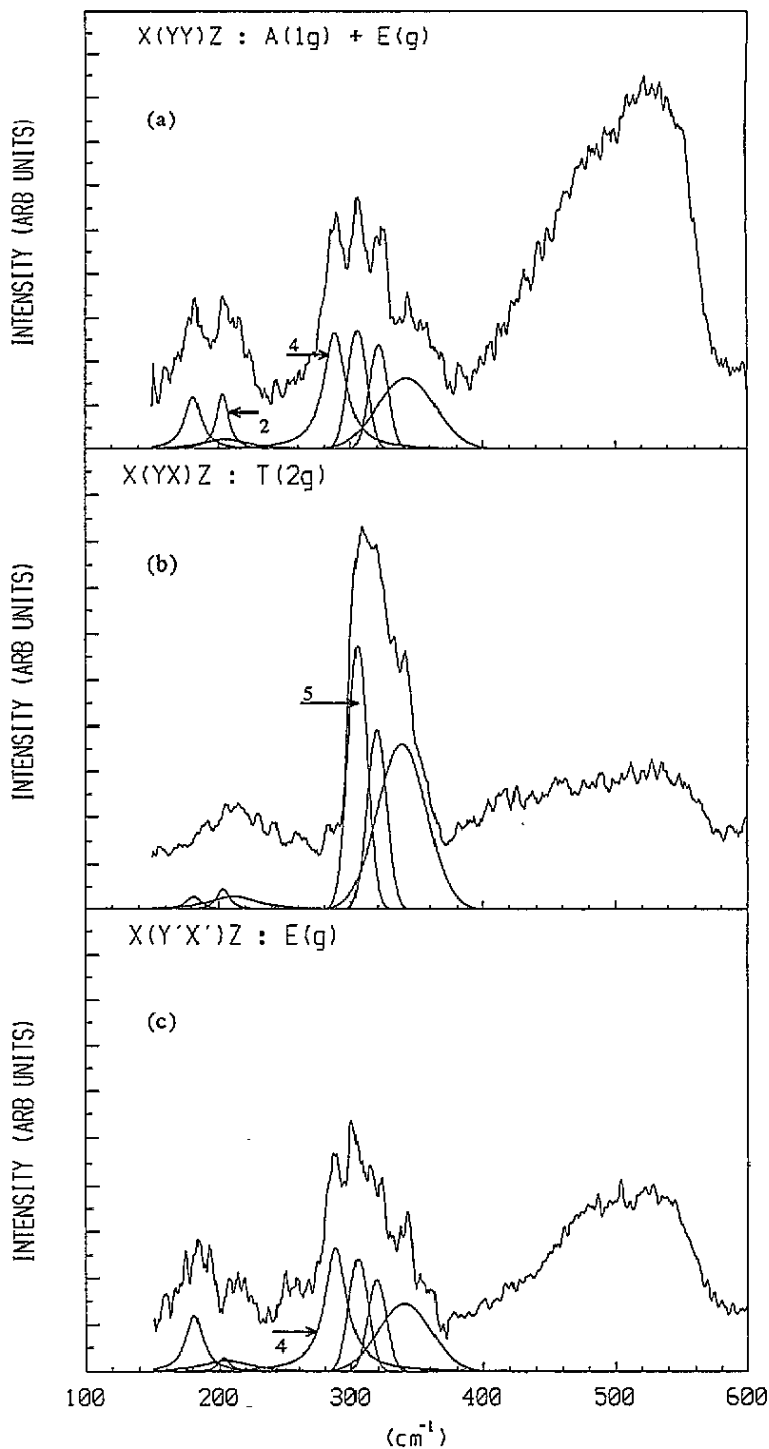
Figure 2. The polarization effect of F and F^+ centres in CaO: (a) polarized parallel to the laser light; (b) polarized perpendicular to the laser light; (c) polarized perpendicular to the laser light with the crystal rotated by 45° about the direction of observation.

Figure 2(a) displays an $A_{1g} + E_g$ spectrum, in which the incident and scattered electric field are parallel to each other, and both along the $\langle 100 \rangle$ crystal direction. In this orientation, the intensity of peak 5 is substantially decreased as compared to its intensity in the unpolarized spectrum, suggesting that peak 5 is of T_{2g} character. This assignment is further confirmed when the orientations are chosen to be $X(YX)Z$. Figure 2(b) displays solely a T_{2g} spectrum in which peaks 2 and 4 have been completely depolarized while peak 5 retains most of its intensity. The assignment of peak 5 located at 305 cm^{-1} to the T_{2g} mode has become essentially conclusive.

In figure 2(c), the orientations are $X(Y'X')Z$. It displays solely an E_g spectrum and distinguishes E_g (peak 4) from the coexistence of A_{1g} and E_g (peaks 2 and 4) in figure 2(a). Thus, we conclude that peak 4 located at 288 cm^{-1} is an E_g mode of vibration and peak 2 located at 203 cm^{-1} is an A_{1g} mode of vibration.

Our symmetry assignments of polarized Raman scattering by F$^+$ centres are consistent with the analysis of sidebands in the emission spectrum of the F$^+$ centre given by Hughes *et al* [2]. In addition, we have demonstrated that the mixture of $T_{2g} + E_g$ at ~302 cm^{-1} can be depolarized into a single T_{2g} or E_g mode. These two modes are separated by about 17 cm^{-1}.

For the F centre vibration bands at 185, 319 and 510 cm^{-1}, using polarization arguments as for the F$^+$ centres, we assign the broad band at 510 cm^{-1} to A_{1g}, that at 185 cm^{-1} to E_g, and that at 319 cm^{-1} to the T_{2g} mode of vibration. It is noteworthy [3] that the A_{1g} mode of a neutral F centre in both alkali oxides and halides has higher frequency than the T_{2g} and E_g modes, while an opposite trend is followed for the F$^+$ centre in CaO.

In conclusion, Raman spectra of F and F$^+$ centres in CaO have been recorded and assigned in detail. Our Raman data and symmetry assignments supplement previous investigations of the lattice dynamics of F and F$^+$ centres in the measurements of the emission spectra.

Acknowledgments

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