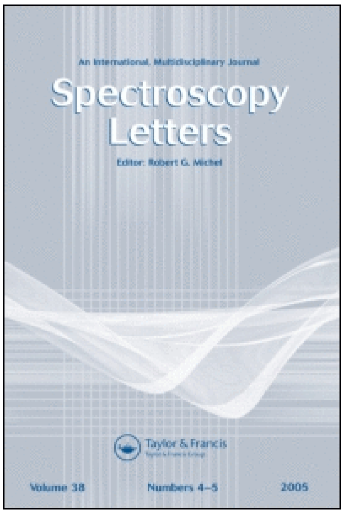

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RAMAN SPECTRA OF SELENIUM DIOXIDE AT HIGH PRESSURES

Key Words: Raman Spectra, High Pressures, Diamond Anvil Cells, Selenium Dioxide,

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ABSTRACT

Raman spectra of selenium dioxide at ambient temperature and at pressures up to 10 GPa are reported. There is no evidence of any structural phase transitions in this pressure range, and only minor perturbations of the electronic states are observed. Shifts of normal mode wavenumbers with pressure are used to deduce percentage changes in the principal force constants. Interchain interactions sharply increase with pressure, whereas the stronger interchain forces show smaller increases. The Se-O bonds in side branches slightly weaken as a result of charge transfer to neighbouring bonds. The effects of pressure and temperature on the spectra are briefly compared.

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INTRODUCTION

In a recent paper, the Raman spectra of solid selenium dioxide at ambient pressure and at temperatures between 15 and 295 K have been reported (1). All predicted Raman active fundamentals were observed for samples at low temperatures, and plausible assignments were proposed. Although no evidence was found for any solid state phase transitions, the dependence of peak wavenumbers on temperature showed some interesting trends which suggested that structural changes might occur when the crystal is subjected to high pressures. It is well known that at pressures of about 10 GPa (100 kbar), readily obtained in a diamond anvil cell, the changes in unit cell dimensions are typically an order of magnitude larger than those obtained by cooling the crystal from room temperature (295 K) to helium temperature (4 K).

We have therefore obtained the Raman spectra of SeO_2 at ambient temperature and at pressures up to 10 GPa and present the results in this communication. The aims are; to check for evidence of any structural phase transitions, to observe the dependence of the normal mode wavenumbers on pressure and hence obtain estimates of the changes in various force constants, to compare the effects of temperature and pressure changes on the spectra, and to investigate the stability of this crystal under the conditions of high pressures and high visible photon flux typically encountered in Raman experiments.

The structure of selenium dioxide has been determined by Stahl et al.(2), who confirmed and refined an earlier study by McCullough (3). The unit cell is tetragonal and contains eight formula units, with space group $P4_2/mbc$ (D_{4h}^{13}). Two views of the structure are shown in Fig 1. As seen, it consists of puckered chains along the z-axis with half of the oxygens (called “bridging”) equidistant between two selenium atoms and the other half (called “terminal”) strongly bonded only to single selenium atoms. The identity of the bent triatomic molecules which exist in the gas phase is partially retained in the crystal, but with considerable distortion of the bond lengths and angle, as discussed earlier (1). A group theoretical analysis predicts that 23 normal modes are Raman active (1,4). At ambient temperature and high pressures, however, Raman peaks will be broad, and overlap of adjacent features will occur, so that the full complement is not expected to be observed. In addition to our low temperature study (1), vibrational spectra of SeO_2 at ambient temperature and pressure have previously been reported, including Raman (4-6) and infrared studies (7). To the best of our knowledge, no previous spectroscopic study of selenium dioxide at high pressures has been published.

EXPERIMENTAL DETAILS

Selenium dioxide, a white crystalline powder, was purchased from Aldrich Chemicals and had a stated purity of 99.9%. In order to avoid hydration to selenious acid, samples were loaded into diamond anvil cells in an

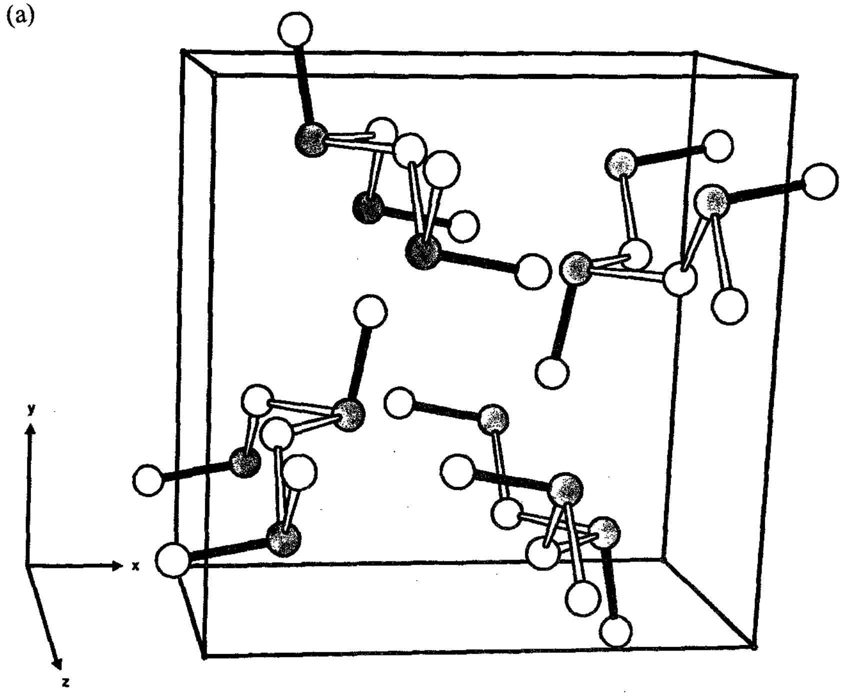

Fig.1: Structure of Selenium Dioxide. (Adapted from Ref 2).
(a) View along z-axis; (b) View along x-axis.
Shaded atoms are selenium; terminal oxygens are attached by filled bonds. The 4-fold axis is at the centre of the xy face.

atmosphere of dry nitrogen. These cells were of the piston cylinder type, fitted with specially selected low fluorescence diamonds and Inconel gaskets of thickness 0.25 mm. These were pre-indented by the diamonds to give an initial sample thickness of about 0.15 mm. and drilled to give a sample diameter of

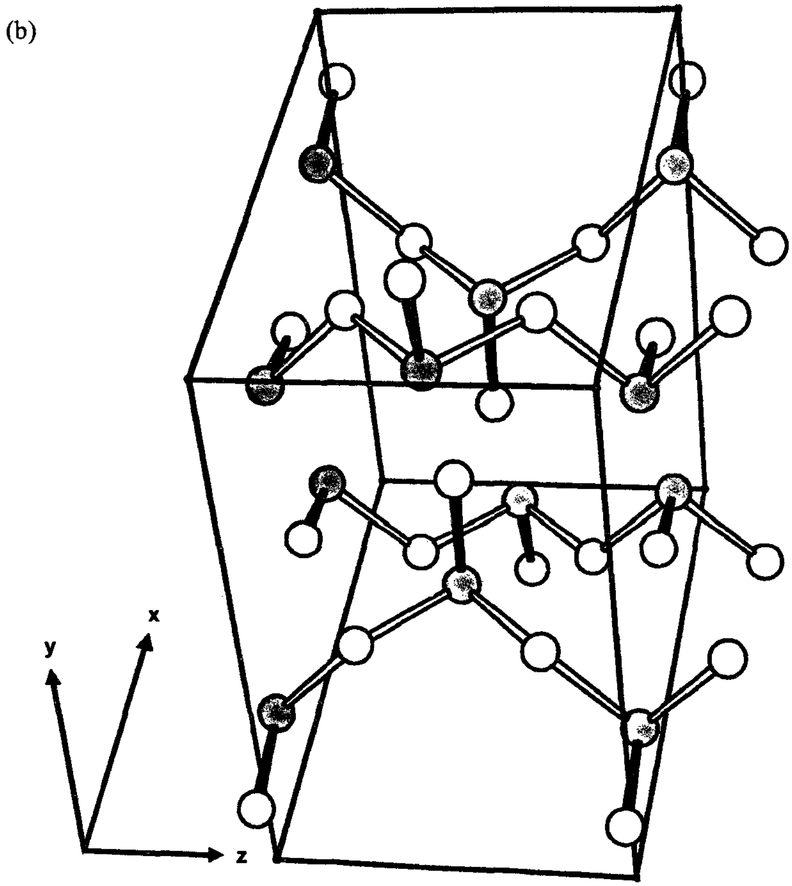

Fig. 1: Continued

0.25 mm. A few grains of ruby powder were included in the cell to allow in situ pressure measurements, using the well-known fluorescence technique (8).

Raman spectra were excited by an argon ion laser operating at 514.5 nm. and at powers up to 0.5 W. A back-scattering geometry was used, with radiation collected by a large aperture camera lens and focused on the entrance slit of a double monochromator. A photomultiplier with cooled photocathode was used as the detector and this was coupled to standard photon-counting electronics. Signals were processed by a personal computer which also controlled spectrometer scans. Spectra were recorded at a resolution of 2 cm^{-1}. Wavenumber calibration and resolution performance were checked by recording plasma lines from the laser. These could be suppressed if desired by introducing a spike filter.

Spectra were recorded always after increasing the pressure by small increments (about 0.5 GPa) to eliminate hysteresis effects. At the highest pressures, there was some evidence from the widths of the ruby fluorescence lines that pressure gradients were present in the sample, but these were minor and it is believed that quasi-hydrostatic conditions were maintained over the pressure range studied (0 to 10 GPa).

RESULTS

Raman spectra of solid SeO_2 at three selected pressures (low, medium, and high) are shown in Fig.2. Peak wavenumbers at these pressures are listed in Table 1. Wavenumbers are estimated to be accurate to +/- 1 cm^{-1} and pressures to +/- 0. 1 GPa. Also included in Table 1 are values from a single crystal study at ambient temperature and pressure (4) and from our recent low temperature work, together with tentative assignments (1). Plots of wavenumber versus pressure for 14 peaks which could be unambiguously

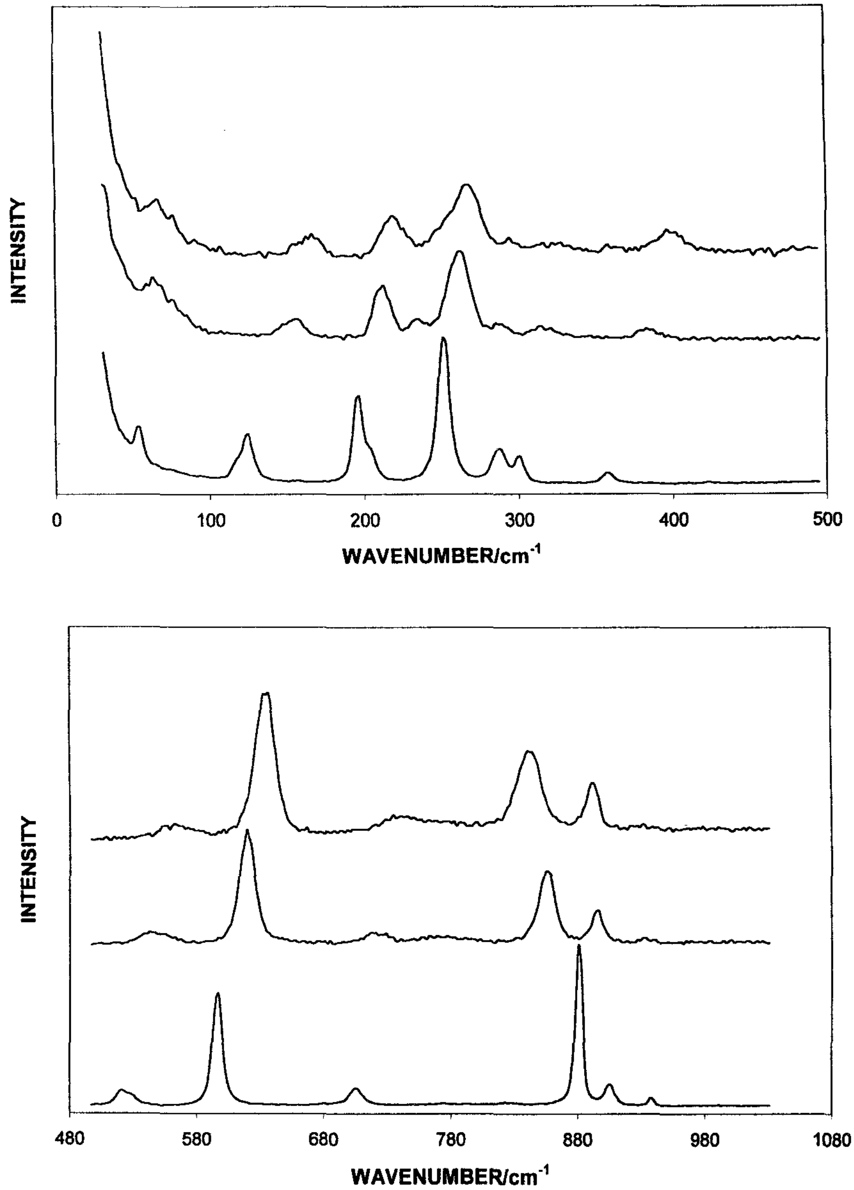

Fig 2: Raman Spectra of Selenium Dioxide at Selected Pressures.
(a) 20 - 500 cm^{-1} region; (b) 500 - 1030 cm^{-1} region.
Pressures: bottom curves, 0.32 GPa; middle curves, 5.58 GPa; top curves, 9.44 GPa.

Table 1

Raman Peak Wavenumbers (cm^{-1}) of Solid Selenium Dioxide

Ref (4)	Ref (1)	This Work			
295	15	295	295	295	**Temperature (K)**
0.0001	0	0.32	5.58	9.44	**Pressure (GPa)**
					Modes Ref (1)
48	49.5	—	—	—	Interchain translations
56	53.5	53.5	64	66	
59	60.5	—	—	—	
115	118	—	—	—	Chain deformations
—	101.5	—	—	—	
122	132	123.5	155.5	166	
197	197.5	197.5	212.5	219.5	O-Se-O bends (chain)
203	208	212	235	251.5	
253	252	251.5	262.5	267.5	
284	286	287	289.5	295	O-Se-O bends (branches)
288	289	—	—	—	
—	293	—	—	—	
301	300	299.5	316	325.5	
357	360	358	383.5	400	
523	523	522.5	547.5	564.5	Se-O streches (bridging oxygens)
531	533.5	—	—	—	
596	599.5	596	619.5	635.5	
—	617.5	—	—	—	
706	713.5	705.5	721	738.5	
871	866.5	—	—	—	Se-O streches (terminal oxygens)
886	879.5	880.5	856.5	843.5	
910	904.5	905	895.5	892	
940	936.5	937.5	932.5	930	

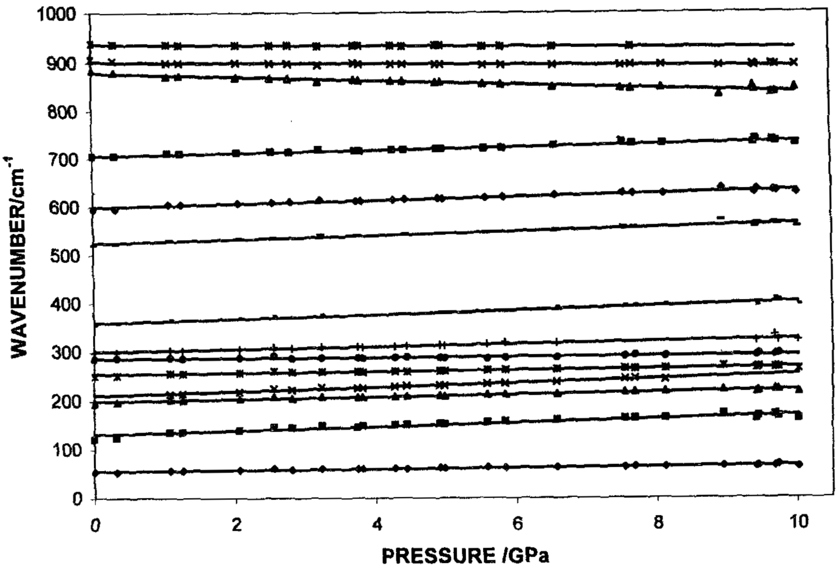

Fig.3: Plots of Peak Wavenumbers versus Pressure for Selenium Dioxide. See Table 2 for values of intercepts and slopes.

tracked through the pressure range 0 to 10 GPa are presented in Fig.3. These have been fitted to linear functions, the intercepts and slopes of which are given in Table 2.

DISCUSSION

There is no evidence from these Raman spectra of any solid state phase transition in SeO_2. The spectra evolve smoothly with no obvious discontinuities. The peaks generally broaden and have lower integrated intensities as the pressure increases. There are, however, some changes in relative intensities, as shown in Fig.2 (b). The peak near 880 cm^{-1} at ambient

Table 2

Linear Fits to Wavenumber versus Pressure Curves
(see figure 3)

Line #	Intercept (cm^{-1})	Slope (cm^{-1}/GPa)
1	55.9	1.11
2	130.6	3.99
3	198.8	2.31
4	210.9	4.28
5	253.9	1.43
6	285.9	0.72
7	300.7	2.61
8	359.9	4.26
9	524.7	4.05
10	599.5	3.53
11	705.9	3.03
12	878.8	-3.96
13	901.9	-0.97
14	937.6	-0.8

pressure is initially the strongest in the whole spectrum, about 10 times the intensity of its neighbour near 900 cm^{-1} and 1.5 times that of the peak near 600 cm^{-1}. At the highest pressure, the 600 cm^{-1} peak is the strongest, about twice the intensity of the 880 cm^{-1} peak, which in turn is now only about twice that of the 900 cm^{-1} peak.

There is a slight yellowing of the sample at the highest pressures as a result of perturbation of the electronic levels. Although this marginally reduces the intensity of the Raman signals because of absorption effects, there is no indication at these pressures that this will lead to break-up of the chains or to dissociation of the formula units.

The dependence of peak wavenumbers on pressure shows several interesting effects. As the pressure is increased, the weaker forces between chains will be most affected. The modes primarily dependent on these forces, interchain translations and chain deformations, appear in the 50 to 200 cm^{-1} region (1), and show appreciable increases in wavenumber. Over this pressure range, the average change is about 22.5% corresponding to an increase in these interchain force constants of about 45%. On the other hand, the stronger intrachain bonds will respond less to changes in pressure. The modes controlled by these forces, O-Se-O bends both in the chains and branches and the Se-O stretches in the chains, occur in the wavenumber range 250 to 750 cm^{-1}. These show an average increase in wavenumber of about 12.5%, corresponding to an increase in intrachain force constants of about 25% over this pressure range. The three peaks above 800 cm^{-1} correspond to stretching modes of the shorter Se-O bonds involving the terminal oxygen atoms in the chain branches. These peaks show a small decrease in wavenumber with increasing pressure of just over 2%, corresponding to a weakening of these bonds by about 4%. This behaviour results from a charge transfer from these bonds to neighbouring interchain bonds, as the chains are forced into closer proximity. It is interesting to speculate that if this trend continues at even higher pressures, cross-linkages between chains through these terminal oxygens will approach the strengths of the intrachain forces and lead to a structural phase transition.

It is also of interest to compare the effects of temperature and pressure on the Raman spectra of SeO_2. When the crystal is cooled from 295 to 15 K, the modes corresponding to interchain translations and chain deformations exhibit an average increase in wavenumber of 5.3% (1), compared to the 22.5% observed in this study when the pressure is increased to 10 GPa. Similarly, the intrachain modes increase on cooling by only 1.4% compared to 12.5% over this pressure range. Finally, the stretching modes involving the Se-O branches decrease by about 0.3% on cooling, compared to about 2% on compression. In all cases the pressure effects are greater, as expected, because of the much larger perturbations to the unit cell size. On the other hand, the low temperature spectra are much sharper and this allows many more features to be resolved.

In summary, the Raman spectra of SeO_2 indicate that no structural phase transitions occur in the pressure range 0 to 10 GPa and that the system is stable under the conditions of high pressures and high fluxes of visible photons. Estimates of percentage changes in principal force constants have been calculated and compared to those which occur on cooling the crystal. Future plans include an infrared study of selenium dioxide at high pressures. Because of the centrosymmetric structure, the infrared modes are distinct from those observed in the present Raman study and will provide complementary information on the vibrational properties of this interesting system.

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