Matrix Isolation Laser Raman Spectroscopy; the Raman Spectra and Structures of Selenium Dioxide Monomer and Dimer

By D. BOAL, G. BRIGGS, H. HÜBER, G. A. OZIN,* E. A. ROBINSON, and A. VANDER VOET

(*Lash Miller Chemical Laboratory and Erindale College, University of Toronto, Toronto, Ontario, Canada*)

Summary The Raman spectra and molecular structure of the selenium dioxide monomer and dimer are obtained by using the technique of "matrix isolation laser Raman spectroscopy."

THE technique of matrix isolation i.r. spectroscopy has been used successfully for several years. The need for reliable Raman data on comparable systems is obvious, but only four brief mentions of the matrix Raman technique, with little experimental detail and mostly involving stable compounds, can be referred to.[1] Matrix isolation Raman spectroscopy must be performed under closely controlled conditions, and almost every matrix has different scattering effects to laser light. Matrix preparation for Raman studies is more critical than for comparable i.r. experiments mainly because the Raman technique relies on specular reflection from the matrix rather than (as in i.r. studies) transmission through it. Thus the background scattering is extremely sensitive to the physical nature of the matrix, *i.e.*, whether opaque or transparent, amorphous or crystalline, glassy, *etc.* Background scattering may be reduced and the quality of the spectra considerably enhanced by experimenting with different types of matrix, produced by varying rates of deposition, temperature of the cold tip, matrix support materials, and by recording spectra with different angles of incidence of the laser beam on the matrix. Often, laser excitation near the Brewster angle (rather than 45°) or near grazing incidence can reduce the background scattering, which may allow closer approach to the exciting line, and also improve the signal to noise ratio.

We report here the Raman data for selenium dioxide monomers isolated in a carbon dioxide matrix at concentrations less than 1%. The investigation is part of a general study of the oxides of Group VI in the vapour and condensed states.

The cryostat used was a liquid helium transfer system (Air Products) capable of holding and varying matrix temperatures from 4·2 to 300 K thus allowing controlled diffusion experiments to be made in the matrix. The matrix preparation involved the vaporisation of selenium dioxide from a molybdenum Knudsen cell (0·05 cm diameter orifice, heated to 150 °C in a tantalum-wound resistance furnace) and co-condensation with the matrix gas onto a copper block at 4·2 K. The copper block (oxygen free, high conductivity copper) was screwed onto the end of the cryotip and thermal contact made with an indium gasket. The copper tip was a semicircular cylinder (3/4 in diameter with a polished rectangular face 1 × 3/4 in) and the matrix was deposited on the rectangular face during 3 h. The matrix thickness was estimated to be *ca.* 0·1 mm.

Matrix Raman spectra were recorded on a Spex 1401 spectrometer using 4880 Å argon ion laser excitation. Typical laser power levels used were 25—100 mW, and spectra were initially recorded at lower power levels which were gradually increased, using neutral density filters. Spectral slit widths were usually 2—5 cm^{-1}.

Selenium dioxide monomer formed at high temperature was trapped in the CO_2 matrix at 4·2 K and its diffusion-controlled reactions to form selenium dioxide polymers as the temperature of the matrix was carefully raised were observed by means of laser Raman spectroscopy.

Table 1 and the Figure show our spectra of matrix-isolated selenium dioxide before and after diffusion had been allowed to occur. Included in Table 1, for comparison, are the Raman spectra of gaseous SeO_2 monomer[2] [the bent triatomic molecule (I)][3] and crystalline SeO_2[4] which has the well documented chain structure (II).

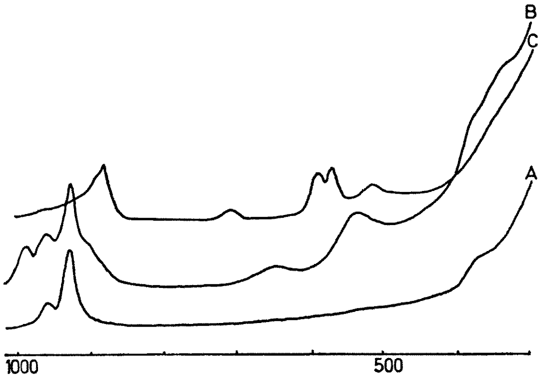


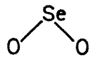
FIGURE. *The Raman spectrum of* A *selenium dioxide monomer, isolated in a carbon dioxide matrix* (M:A ≃ 100:1) *at* 4·2 K; B *matrix isolated selenium dioxide after diffusion at* 50 K, *showing both monomer and dimer bands*; C *matrix isolated selenium dioxide after diffusion at* 50—90 K *showing mainly polymer bands of* $(SeO_2)_n$ *where* $n \geqslant 3$.

TABLE 1

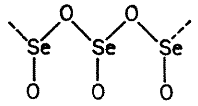
Raman spectrum of selenium dioxide isolated in a carbon dioxide matrix[a]

Raman (vapour)[2]	Matrix Raman Monomer	 Dimer[b]	 Trimer[b] and higher polymer	Raman (powder at R.T.)
		1002s		
967w[c] (ν_3)	967mw (ν_3)			940w
923sp (ν_1)	933s (ν_1)			908mw
			900msh	
			887s	884s
			710w	
				704mw
		660m		
			592m	594s
			572m	
		543s		
			520mw	521mw
368wp (ν_2)	382mw (ν_2)			
		363m		366w
		352m		
				299w
				285mw
				250s
				195m
				122m

[a] 1% matrix deposited at 4·2 K. [b] Observed by diffusion controlled experiments in the temperature range 30—90 K. [c] This value is quoted from the vapour phase i.r. as the corresponding band in the Raman was very weak.



(I)



(II)

The results show unambiguously that pure SeO_2 monomer is isolated in the low temperature matrix since the Raman spectrum is very similar to that of the vapour measured at 300 °C.[2] Excellent spectra were obtained for concentrations of less than 1%. The symmetrical stretching and deformation modes ν_1 and ν_2 show matrix shifts of 10 cm^{-1} and 14 cm^{-1}, respectively, from the similar frequencies in the vapour. Matrix isolation Raman data for SeO_2 monomer also support the reported matrix i.r. data[5] and clearly identify ν_2, the matrix frequency of which was previously in question.

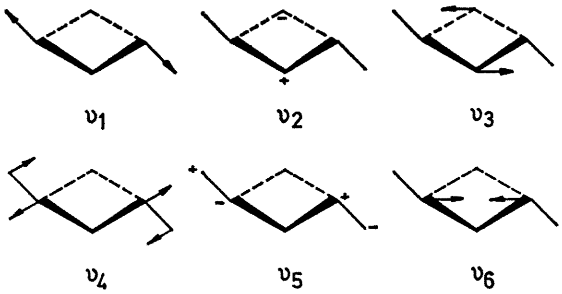
Spectacular changes in the Raman spectrum of the system occurred as the matrix was allowed to warm up. By measuring the spectrum at various matrix temperatures the progress and results of diffusion-controlled reactions between SeO_2 monomers were observed and the formation of the dimer $(SeO_2)_2$ and higher polymers were detected (Figure, B and C).

Raman data for $(SeO_2)_2$ shown in Table 2 favour a double oxygen bridged structure ($OSeO_2SeO$). The lone pair of electrons on selenium are likely to be stereochemically active in the dimer (as they are in the SeO_2 chain polymer) giving an essentially tetrahedral co-ordination around each selenium atom. Two structures seem likely, (III) and (IV). The matrix Raman spectrum of $(SeO_2)_2$ shows at least five bands which are best assigned to the vibrational modes of the *trans*-centrosymmetric double oxygen bridged structure (III).†

TABLE 2

Vibrational assignment of the matrix Raman spectrum of $(SeO_2)_2$

		Approximate description of mode
1002s	$\nu_1\ a_g$	νSeO_t
660mw	$\nu_3\ b_g$	νSeO_b
543s	$\nu_2\ a_g$	νSeO_b
363mw	$\nu_5\ b_g$	δSeO_t
352mw	$\nu_4\ a_g$	δSeO_t
Not obs.	$\nu_6\ a_g$	$\nu SeSe$

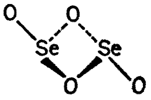


Schematic representation of the vibrational modes of $(SeO_2)_2$

---

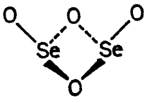
† Both the *number* and *frequencies* of the observed Raman active modes for $(SeO_2)_2$ support structure (III). For structure (IV), twelve Raman bands are predicted but only six for structure (III). We observe five Raman bands which strongly favours model (III). We are at present investigating the matrix Raman spectra of the series $(SO_2)_2$, $(SeO_2)_2$, and $(TeO_2)_2$ and are computing the frequencies of vibration of the various structures to provide additional evidence for our stereochemical assignments.

This structure would have been predicted on stereochemical and electrostatic grounds since in (III) the lone-pair–lone-pair interactions and charge repulsion between the terminal oxygen atoms are minimized, unlike those in the *cis* structure (IV).



(III)

C_{2h} symmetry
$\tau_{\text{vib}} = 4a_g + 2b_g + 2a_u + 4b_u$



(IV)

C_{2v} symmetry
$\tau_{\text{vib}} = 5a_1 + 2a_2 + 3b_1 + 2b_2$

As far as we are aware, this is the first Raman study of highly reactive species in rigid matrices. Work on the matrix Raman spectroscopy of high temperature inorganic species and free radicals produced by microwave discharge and photolysis is in progress.

We thank the National Research Council of Canada for financial support and Mr. W. Hughes for assistance with the handling of the liquid helium.

(*Received, January* 13*th*, 1971; *Com.* 061.)

---

[1] A. Cabana, A. Anderson, and R. Savoie, *J. Chem. Phys.*, 1965, **42**, 1122; P. A. Giguere, K. Herman, and X. Deglise, Paper J11, Abstracts of the Twenty-fifth Symposium on Molecular Structure and Spectroscopy, The Ohio State University, 1970; E. Nixon, *Raman Newsletter*, 1969; I. R. Beattie and R. Collis, *J. Chem. Soc.* (*A*), 1969, 2960.

[2] I. R. Beattie and J. Horder, personal communication.

[3] K. J. Palmer and W. Elliot, *J. Amer. Chem. Soc.*, 1938, **60**, 1852.

[4] J. D. McCullough, *J. Amer. Chem. Soc.*, 1937, **59**, 789.

[5] J. W. Hastie, R. Hauge, and J. L. Margrave, *J. Inorg. Nuclear Chem.*, 1969, **31**, 281.