Matrix Isolation Laser Raman Spectroscopy in Inorganic Chemistry

We report in this article the first Raman spectra of highly reactive inorganic molecules trapped in a low temperature matrix. The technique of matrix isolation infrared spectroscopy has been used for several years, and the need for reliable Raman data on comparable systems is obvious, in order to make reliable structural and vibrational assignments, for example.

It is now clear to us that the chief factors in the relatively slow progress in this field are the intricacies of the experimental procedures. These will be discussed in detail in a later publication. Because of the experimental difficulties, it seems unlikely that matrix isolation Raman spectroscopy will ever become a routine technique. We have now had sufficient success to convince us that the technique is practicable and that useful data can be obtained, provided the experiments are carried out under closely controlled conditions.

Here we report 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 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 Raman Spectrum of Selenium Dioxide Isolated in a Carbon Dioxide Matrix

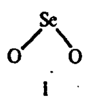
Raman (vapour)	Matrix Raman Monomer*	 Dimer†	 Trimer† and higher polymer	Raman (R.T. powder)
		1,002 s		
967 w‡ (ν_3)	967 mw (ν_3)			940 w
923 sp (ν_1)	933 s (ν_1)			908 mw
			900 msh	
			887 s	884 s
			710 w	
				704 mw
		660 m		
			592 m	594 s
			572 m	
		543 s		
			520 mw	521 mw
368 wp (ν_2)	382 mw (ν_2)			
		363 m		356 w
		352 m		
				299 w
				285 mw
				250 s
				195 m
				122 m

* 1% matrix deposited at 4.2 K.

† Observed by diffusion controlled experiments in the temperature range 30–90 K.

‡ This value is quoted from the vapour phase infrared as the corresponding band in the Raman was very weak.

Table 1 and Fig. 1 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 at 300° C (private communication from I. R. Beattie and J. Horder) (the bent triatomic[1] molecule I) and crystalline SeO_2 (ref. 2) (which has the well documented chain structure II).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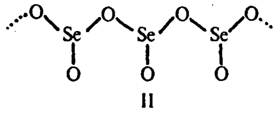
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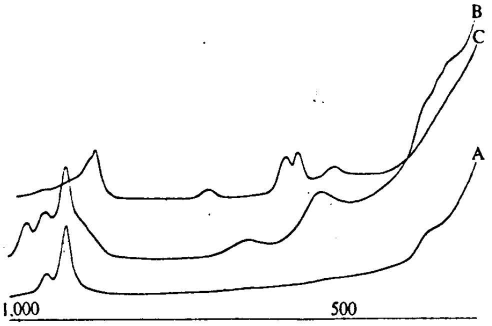


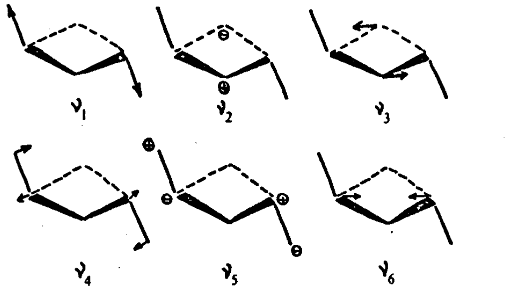
Fig. 1 *A*, The Raman spectrum of selenium dioxide monomer, isolated in a carbon dioxide matrix (M : A≃100 : 1) at 4.2 K. *B*, The Raman spectrum of matrix isolated selenium dioxide after diffusion at 50 K, showing both monomer and dimer bands. *C*, The Raman spectrum of matrix isolated selenium dioxide after diffusion at 50–90 K showing mainly polymer bands of $(SeO_2)_n$ where $n \geq 3$.

The results show unambiguously that pure SeO_2 monomer is isolated in the low temperature matrix, because the Raman spectrum is very similar to that of the vapour. Excellent spectra were obtained for concentrations of less than 1%. The symmetrical stretching and deformational 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 infrared data[3] and clearly identifies ν_2, the matrix frequency of which was previously in question.

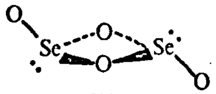
Spectacular changes in the Raman spectrum of the system occurred as the matrix was allowed to warm up. By measuring the spectrum at various matrix temperatures the progress and results of diffusion controlled reactions between SeO_2 monomers could be observed and the formation of the dimer $(SeO_2)_2$ and higher polymers could be detected (Figs. 1*B* and *C*).

Table 2 Vibrational Assignment of the Matrix Raman Spectrum of $(SeO_2)_2$

		Approximate description of mode
1,002 s	$\nu_1\ a_g$	νSeO_t
660 mw	$\nu_3\ b_g$	νSeO_b
543 s	$\nu_2\ a_g$	νSeO_b
363 mw	$\nu_5\ b_g$	δSeO_t
352 mw	$\nu_4\ a_g$	δSeO_t
not obs.	$\nu_6\ a_g$	$\nu SeSe$



Raman data for $(SeO_2)_2$ is shown in Table 2 and strongly 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 coordination around each selenium atom. Two structures seem likely (III) and IV).



III

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

IV

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

The matrix Raman spectrum of $(SeO_2)_2$ shows at least five bands which are most satisfactorily assigned to the vibrational modes of the *trans*-centrosymmetric double oxygen bridged structure III.

It is interesting to note that this structure would have been predicted on stereochemical and electrostatic grounds, because in III the lone-pair–lone-pair interactions and charge repulsion between the terminal oxygen atoms are minimized as compared with those in the *cis* structure IV.

As far as we know, Raman data for highly reactive species trapped at very low concentrations in rigid matrices have not been reported before. We emphasize our confidence that matrix isolation Raman spectroscopy is a viable technique, capable of giving valuable information on many chemically important systems. Following our initial successes, we have started a programme of "Matrix Raman Spectroscopy" of high temperature inorganic species and free radicals produced by microwave discharge and photolysis.

The cryostat used in these experiments was a commercially available liquid helium transfer system which is capable of holding and varying matrix temperatures from 4.2 to 300 K, thus allowing controlled diffusion experiments to be made in the matrix. For the production of a molecular beam of SeO_2 a molybdenum Knudsen cell was used with a 0.05 cm orifice diameter. The cell was heated by a tantalum-wound resistance furnace and the cell temperature measured with a chromel–alumel thermocouple situated at the base. Matrix Raman spectra were recorded on a Spex 1401 using 4,880 Å argon ion laser excitation.

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