A Gas-phase Raman Study of the Dissociation of Selenium Tetrachloride and the Vibrational Spectrum and Molecular Structure of Selenium Dichloride

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Summary Selenium tetrachloride is shown by gas-phase laser Raman spectroscopy to be fully dissociated in the vapour to selenium dichloride and chlorine, the vibrational spectrum of gaseous selenium dichloride being entirely consistent with that expected for a non-linear triatomic molecule.

HIGH-TEMPERATURE gas-phase laser Raman spectroscopy is rapidly becoming a powerful technique for studying the molecular constitution and structure of inorganic vapours.[1] We report here how the vibrational spectrum and molecular structure of the selenium dichloride molecule $SeCl_2$, which is stable only in the vapour state and not in the liquid or solid states, can be obtained by investigating the Raman spectrum of the dissociation products of gaseous selenium tetrachloride, under the isothermal equilibrium conditions of a gas-phase Raman experiment. Vibrational-spectroscopic data were not previously available for selenium dichloride.

It is well known from vapour density[2] and electron diffraction[3] measurements† that selenium tetrachloride is fully dissociated in the vapour phase, where the vapour density is constant in the temperature range 190—600°. This implies that the $SeCl_2$ formed in the gas-phase dissociation reaction

$$SeCl_4 \rightleftharpoons SeCl_2 + Cl_2$$

must be a very stable entity. However, in the liquid and solid states, selenium dichloride appears to go over to Se_2Cl_2 or $SeCl_4$.

The Raman spectrum of gaseous selenium tetrachloride‡ was recorded in an all-glass cell in the temperature range 190—400°, using 5145Å argon ion laser excitation. The Raman spectrum showed four lines (Table, Figure) of which three were observed to be polarised. The spectrum showed very little change with increasing temperature up to 400°.

The gas-phase Raman spectrum of selenium tetrachloride vapour at 350°

Observed		Assignment	
545 mbr	(pol)[a]	ν Cl–Cl	
415 s	(pol)	ν SeCl	ν_1
377 wsh	(dep)	ν SeCl	ν_3
153 m	(pol)	δ SeCl	ν_2

[a] The spectral slit width was not sufficiently narrow to resolve the splitting of this band resulting from ^{35}Cl and ^{37}Cl isotopes.

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† Only the selenium–chlorine internuclear distance was reported for $SeCl_2$ and not the interbond angle.[3]

‡ Selenium tetrachloride was prepared under anhydrous conditions by standard literature methods and purified further by repeated vacuum sublimation.

Gas-phase Raman spectra were recorded using a Spex model 1401 Raman spectrometer and a Carson model 500 argon ion laser with a power output of 2 w at either 5145Å or 4880Å.

Cell and furnace designs for recording high-temperature gas-phase Raman spectra were similar to those described previously.[1c]

No resonance fluorescence effects were observed which could be attributed to diatomic selenium.[4] This confirmed that the selenium tetrachloride sample was free of traces of elemental selenium from the preparation and purification procedure and that selenium was not produced in the dissociation reaction of $SeCl_4$.

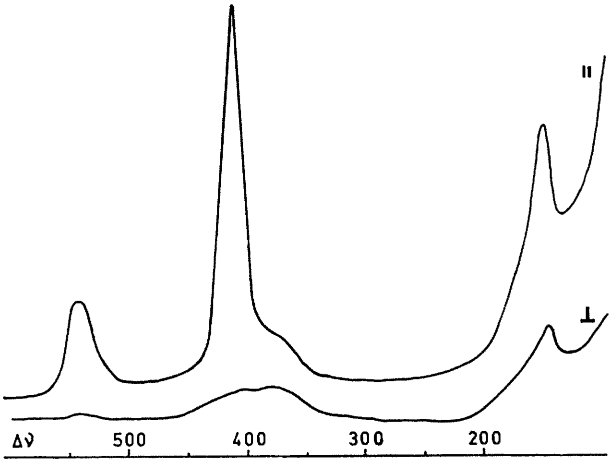

FIGURE. *The gas-phase Raman spectrum of selenium tetrachloride vapour at* 350° *and a pressure of approximately* 1 *atm. in the cell*; (a) *parallel polarisation and* (b) *crossed polarisation measurements, showing the complete dissociation to selenium dichloride and chlorine.*

The polarised line at 545 cm^{-1} can be satisfactorily assigned to the stretching mode of diatomic chlorine. The remaining lines were observed at 415 (pol), 153 (pol), and 377 (dep) cm^{-1} and are assigned to the vibrational modes of selenium dichloride (Table).

For a linear triatomic molecule MX_2 only one polarised Raman-active stretching mode is expected, whereas for a non-linear MX_2 molecule, three Raman-active modes are expected of which two (a high-frequency stretching mode and a low-frequency deformational mode) should be polarised. Thus the gas-phase Raman data for $SeCl_2$ unambiguously prove that the molecule is non-linear.

The polarised lines of $SeCl_2$ at 415 and 153 cm^{-1} may be compared with the observed gas-phase Raman frequencies for non-linear $SnCl_2$[5] at 352 (pol) and 120 (pol) cm^{-1}, respectively.[6]

We thank the National Research Council of Canada for financial support.

(*Received, February 27th*, 1970; *Com.* 289.)

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