



Fig. 7. The gas-phase Raman spectrum of selenium tetrachloride vapour at 350 °C and a pressure of approximately 1 atm in the cell. (a) Parallel polarization and (b) crossed polarization measurements, showing the complete dissociation to selenium dichloride and chlorine. (Reproduced from G. A. Ozin and A. V. Voet, *Chem. Commun.*, (1970) 896.)

chloride³⁶⁶. Spectra have also been reported for such disubstituted compounds as *p*-dichlorobenzene³⁶⁷, guaiacol³⁶⁸, *p*-toluidine³⁶⁹, *o*- and *m*-toluic acid³⁷⁰, *o*- and *p*-tolunitrile³⁷¹, and a series of *o*-haloaryl compounds³⁷². The solid state spectra of iododurene³⁷³, tetrachloro- and pentachlorotoluene³⁷⁴, have also been reported.

The vibrational spectra of polycrystalline³⁷⁵⁻³⁷⁷ and of single crystals³⁷⁸ of naphthalene, naphthalene-*d*₈³⁷⁹, and of 1,5-dimethylnaphthalene³⁸⁰ have been reported. The infrared^{381,382} and Raman^{383,384} spectra of single crystals of anthracene and the infrared spectrum³⁸¹ of anthracene-*d*₁₀ have been reported. Other condensed aromatic molecules whose solid state spectra have been reported are pyrene³⁸⁵, perylene³⁸⁶, biphenyl^{387,388}, terphenyl³⁸⁹, quaterphenyl³⁹⁰, benzil³⁹¹, 9,10-anthraquinone³⁹², benzophenone³⁹³, fluorene³⁹⁴, acenaphthene (refs. 395-397), paracyclophane³⁹⁸, biphenylene³⁹⁹, triphenylene⁴⁰⁰, and carbazole⁴⁰¹.

(ii) Heterocyclic compounds

The infrared^{402,404} and Raman^{403,404} spectra of crystalline pyridine indicate the existence of two coexisting crystalline forms of symmetry D_{2h}^1 and D_{2h}^2 . The vibrational spectra of crystalline hydrogen-bonded pyridinium halides have been reported⁴⁰⁵. Crystalline pyrimidine⁴⁰⁶, pyrazine^{407,408}, phenazine⁴⁰⁹, quinoline (ref. 410), and imidazole^{411,412} have also been examined. Both cyanuric triazide⁴¹³ and cyanuric chloride⁴¹⁴ belong to the C_{3h}^2 space group.

The vibrational spectra of *p*-dioxane indicate the existence of two crystalline phases⁴¹⁵. The solid state vibrational spectra of ethylene oxide, ethylene sulphide, and trimethylene oxide have been examined⁴¹⁶. Crystalline state infrared spectra (refs. 417-419) of thiophene, furan and pyrrole exhibit bands due to the a_2 vibrational modes. These modes are IR inactive for the C_{2v} point group of the isolated

molecules, and the spectra are compatible with a C_{2v}^1 space group. Crystalline thietane exists in two crystalline phases⁴²⁰, and the infrared spectrum of crystalline *p*-dithiane has been reported⁴²¹.

(iii) Cycloalkanes

Polycrystalline cyclopropane has C_3 site symmetry and the space group is one of eight primitive D_{2h} groups^{422,423}. Cyclopentane exists in three crystalline modifications⁴²⁴⁻⁴²⁷ with the transition temperatures at 122 °K and 138 °K. Cyclohexane^{13,428,429} exists in two crystalline forms with a transition at 186 °K. The high temperature form has four molecules in the unit cell, whilst there are eight molecules in the unit cell of the low temperature form.

(iv) The Raman spectra of adsorbed species

The use of infrared spectroscopy for the study of adsorbed species has been well documented⁴³⁰ and will not be discussed in this review. During the period under review several publications appeared describing the use of Raman spectroscopy for the study of adsorbed species, and these will be discussed briefly.

Pershina and Raskin⁴³¹ studied the Raman spectra of several adsorbed species and found that the spectra could be classified into three groups:

(i) No changes were observed in the spectra of compounds such as benzene, naphthalene, and biphenyl on adsorption.

(ii) The spectra of compounds with a polar group (CH_3CN , $C_6H_5COCH_3$, CH_3NO_2) showed shifts of 10-15 cm^{-1} in the frequencies of the C-O, C=N and NO_2 groups on adsorption.

(iii) The spectra of $SbCl_3$, $SbBr_3$ and dichloroethane showed high shifts of all Raman bands on adsorption.

Pershina and Raskin concluded that the differences in the Raman spectra of the adsorbed species corresponded to the changes in the Raman spectra of the compounds during the liquid/crystal phase transition.

Using laser excitation, Hendra and Loader^{432a} have found that the spectra of adsorbed CCl_4 is similar to that of the liquid, while adsorbed Br_2 and CS_2 give frequencies similar to the gas phase values. The Raman spectrum of adsorbed *trans*-dichloroethylene does not contain any bands due to the Raman inactive modes, indicating that the adsorbed molecule retains its centre of symmetry.

The Raman spectrum of acetaldehyde adsorbed onto silica gel^{432b} shows none of the bands of liquid acetaldehyde, the carbonyl band being noticeably absent. The adsorbed spectrum closely resembles that of paraldehyde, and the data suggest that condensation of acetaldehyde has been catalysed at the surface, leaving a physically adsorbed cyclic product.

The Raman spectra⁴³³ of pyridine adsorbed onto alumina, titanium dioxide, magnesium oxide and silica gel have been used to distinguish between physical