

### C. Triatomic and 2-coordinate species

The far infrared spectra of H<sub>2</sub>O in noble gas matrices<sup>57</sup> and the infrared spectrum of D<sub>2</sub>O in a nitrogen matrix<sup>58</sup> indicate that both molecules rotate in these matrices. The intensity of the infrared bands due to the stretching modes of water in the polycrystalline solid was found to be about 30 times that of the vapour phase value and considerably higher than the liquid phase value<sup>59</sup>.

Solid H<sub>2</sub>S and D<sub>2</sub>S exist in three modifications. The Raman spectra<sup>60</sup> of the two higher temperature phases are consistent with their known disordered crystal structures. The Raman<sup>60</sup> and far infrared<sup>61</sup> spectra of the lowest temperature phase suggest a C<sub>1</sub> site symmetry. The infrared spectra of H<sub>2</sub>S and D<sub>2</sub>S in argon<sup>62</sup>, krypton<sup>62</sup>, and nitrogen<sup>63</sup> matrices have been reported, whilst the Raman frequency of the  $\nu_1(a_1)$  mode of H<sub>2</sub>S in the  $\beta$ -quinol clathrate is closer to the gas phase value than to the liquid or solid state values<sup>64</sup>.

The Raman bands<sup>64</sup> of crystalline SO<sub>2</sub> show a fine structure due to factor group splitting and to isotopic splitting. The infrared spectra of the various isotopic species of SO<sub>2</sub> trapped in krypton matrices have been observed<sup>65</sup>, and the Raman spectrum of the SO<sub>2</sub>/ $\beta$ -quinol clathrate has also been reported<sup>66</sup>.

The Raman spectrum of polycrystalline CO<sub>2</sub> has been reported<sup>66,67</sup>. Comparison of the infrared and Raman spectra of polycrystalline CS<sub>2</sub> shows no coincidences between the frequencies indicating that the centre of symmetry is preserved even in the crystalline state<sup>68</sup>. The infrared spectrum of polycrystalline carbonyl sulphide contains a broad, asymmetric  $\nu_3$  band. A study of the matrix-isolated molecule indicates that the asymmetry can be attributed to the different isotopic species of the molecule<sup>69</sup>. The Raman spectrum of polycrystalline nitrous oxide has been reported<sup>67</sup> and bands due to the various isotopic species have been observed in the infrared spectrum of the polycrystalline solid<sup>70</sup>.

The Raman<sup>71</sup> and far infrared<sup>72</sup> spectra of polycrystalline HCN and DCN show that the solid exists in two phases. The infrared spectra of HCN adsorbed on alkali halide films<sup>73</sup> and of the matrix isolated molecule<sup>74</sup> have been reported.

The gaseous phase Raman spectra of the dihalides of mercury(II) and zinc(II) and of the mixed mercury dihalides are consistent with a linear structure for the monomeric molecules<sup>75</sup>. The Raman spectrum<sup>75</sup> of gaseous "GaCl<sub>2</sub>" consists of bands due to GaCl and GaCl<sub>3</sub>, whilst in the liquid<sup>76</sup> and solid<sup>77</sup> states the Raman spectra of "GaCl<sub>2</sub>" are consistent with an ionic structure Ga<sup>+</sup>GaCl<sub>2</sub><sup>-</sup>.

The red to yellow phase transition of solid mercuric iodide above 126° has been followed by means of Raman spectroscopy<sup>78</sup>. There are marked differences between the spectra of non-molecular red HgI<sub>2</sub> and the molecular yellow phase (Fig. 2).

The gaseous phase Raman spectra<sup>79</sup> of GeCl<sub>2</sub>, TeCl<sub>2</sub>, SnCl<sub>2</sub>, PbCl<sub>2</sub> and PbBr<sub>2</sub> show that the monomeric species are non-linear in the gaseous phase. The solid state Raman spectrum of stannous chloride<sup>80</sup> differs considerably from the

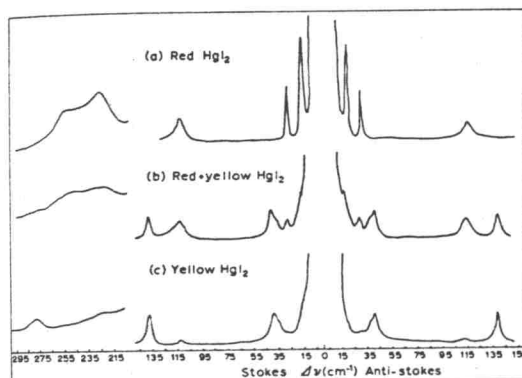


Fig. 2. (a) Raman spectrum of room-temperature red HgI<sub>2</sub>. (b) Raman spectrum of the red and yellow HgI<sub>2</sub> mixture at the point of incomplete phase conversion. (c) Raman spectrum of yellow HgI<sub>2</sub> just above the transition point. Residual trace of red HgI<sub>2</sub> is indicated. (Reproduced from A. J. Melveger, R. K. Khanna, B. R. Guscott and E. R. Lippincott, *Inorg. Chem.*, 7 (1968) 1650.)

gaseous state spectrum since the solid state structure consists of halogen-bridged SnCl<sub>2</sub> units.

The infrared spectra of a number of metal dihalide monomeric species isolated in noble gas matrices have been reported: the dichlorides of manganese, iron, cobalt and nickel<sup>81</sup>; the difluorides of cobalt, nickel and zinc<sup>82</sup>; the dihalides of cadmium and mercury<sup>83</sup>; the difluorides<sup>84,85</sup>, dichlorides<sup>86,87</sup>, dibromides<sup>86,87</sup> and di-iodides<sup>86</sup> of the alkaline earth elements.

Other triatomic species which have been studied spectroscopically are hydrated magnesium chloride and bromide<sup>88</sup>, the dihydrate of copper(II) dichloride<sup>89</sup>, solid ozone<sup>90</sup> at 10°K, matrix isolated<sup>91</sup> HOCl and HOBr, matrix isolated<sup>92</sup> CsOH and CsOD and matrix isolated<sup>93</sup> RbOH and NaOH.

The infrared spectrum of ammonium thiocyanate displays splittings of all the degenerate modes of the NH<sub>4</sub><sup>+</sup> and NCS<sup>-</sup> ions<sup>94</sup>. The infrared and Raman spectra of solid methyl mercury(II) thiocyanate contain no coincidences, suggesting that the unit cell is centrosymmetric<sup>95</sup>. The Raman spectrum of KSCN at room temperature displays the expected factor group splitting of the CN vibrational mode<sup>96</sup>. The IR spectra of gaseous and solid HNCS and DNCS have been reported (ref. 97). The shift in frequency of  $\nu(N-H)$  and  $\nu(N-D)$  upon solidification suggests a very short, strong hydrogen-bond.

The vibrational spectra of potassium<sup>98</sup> and caesium<sup>99</sup> azide are consistent