

TABLE 8

Raman and IR results for phases I, IV and II in the  $\text{HgCl}_2$  system [140]

Phase	Raman ( $\text{cm}^{-1}$ )	IR ( $\text{cm}^{-1}$ )
I (Ambient pressure)	383 (vvw)	370 (vs)
	315 (s, sp)	330 (vw)
	167 (vvw)	310 (w)
	126 (w)	100 (vs)
	74 (m)	75 (sh)
	43 (vw)	
	23 (m)	
	18 (s)	
IV (8.5 kbar)	386 (vvw)	370 (vs)
	316 (s, sp)	330 (w)
	170 (vvw)	310 (w)
	144 (w)	100 (vs)
	133 (w)	77 (sh)
	77 (m)	
	51 (w, sh)	
	41 (vvw)	
21 (m)		
II (30 kbar)	312 (vs)	369 (vs)
	178 (s)	100 (vs)
		72 (vs)

13 kbar red  $\text{HgI}_2$  converts to a yellow phase. Differences are observed in both the IR and Raman spectra of the two yellow phases. The high pressure phase has a more complex far IR spectrum than the high temperature phase, especially in the  $80 \text{ cm}^{-1}$  region. In the Raman spectrum the  $145 \text{ cm}^{-1}$  band in the high pressure phase has a shoulder, which is missing in the low temperature

TABLE 9

Raman frequencies ( $\text{cm}^{-1}$ ) for  $\text{HgBr}_2$  at various pressures (R.T.) [141]

Phase	Pressure (kbar)						
	0	6.3	18.8	23.3	31.6	35.7	49.5
	I	II	II	III	III	IV	IV
	186	185	184	191 184	191 184	179	176
	57	61	60	74 60	77 69	78.5	77
	40	38		50	49		
	17.5	22	24				
	15	17	18				

phase. The low temperature phase has Raman bands at 15 and 11.5  $\text{cm}^{-1}$ , which are missing in the pressure phase. Although the high pressure phase of  $\text{HgI}_2$  remains unknown, the vibrational spectrum resembles that of phase III of  $\text{HgBr}_2$ , and would thus appear to have a structure with a higher coordination number, consistent with consequences of increased pressure.

Studies of the effect of pressure on the  $\nu_{\text{HgCl}}$  vibration in  $\text{HgCl}_2 \cdot \text{dioxane}$  have been made [145]. This vibration shifts 18  $\text{cm}^{-1}$  towards lower energy, while modes of the organic ligand bands at 854, 614 and 290  $\text{cm}^{-1}$  are raised by ca. 5  $\text{cm}^{-1}$ .

### (2) Alkali metal cyanides

The various polymorphic phases of KCN and NaCN have been investigated using vibrational spectroscopy at high pressures [146]. Table 10 lists structural data for the polymorphs of KCN and NaCN. Raman frequencies are listed in Table 11 for KCN polymorphs at various pressures. The behavior of the cyanide vibration with pressure in KCN and NaCN is shown in Table 12. The Raman scattering of  $\text{K}[\text{Ag}(\text{CN})_2]$  has recently been measured to 18 kbar [146a]. Two high-pressure polymorphs were identified. A dramatic change in the pressure dependency of the CN stretching vibration was noted. The pressure of other internal and external modes was also determined.

### (3) Nitrates, carbonates

Infrared spectra of  $\text{KNO}_3$  have been obtained at pressures up to 40 kbar [147]. The pressure range of  $\text{KNO}_3$  (III) with a symmetry  $R3m$  ( $C_{3v}^5$ ) with  $z = 1$ , is very narrow and at 4 kbar and 38°C converts to  $\text{KNO}_3$  (IV). For this phase a new band was observed at 717  $\text{cm}^{-1}$ . The 825  $\text{cm}^{-1}$  absorption shifts to 831  $\text{cm}^{-1}$  and increases in intensity with pressure.  $\nu_3$  and  $\nu_1$  show a small shift to higher frequency, and a slight increase in intensity. The various combinations involving the  $\text{NO}_3^-$  vibration lose intensity with pressure. It was observed that  $\nu_1$  is more sensitive to pressure than  $\nu_4$ , and  $\nu_2$  is insensitive. The

TABLE 10

Structural data for the NaCN and KCN polymorphs [146]

Phase	Structure	Z
KCN	I Cubic, $F_{m3m}(O_h^5)$	4
	III Cubic, $P_{m3m}(O_h^1)$	1
	IV Monoclinic, $Cm(C_s^3)$	2
	V Orthorhombic, $I_{mmm}(D_{2h}^{25})$	2
	VI Orthorhombic, $P_{mnn}(D_{2h}^{13})$	2
	NaCN	I Isostructural with KCN I
II Isostructural with KCN V		
III Isostructural with KCN VI		