

Tables 15–19 list some ionic lattice frequencies [167]. Most of the frequencies for the transverse optical lattice modes ( $\nu_{\text{TO}}$ ) in ionic salts are found below  $300 \text{ cm}^{-1}$ . The capability of measuring vibrational spectra in the far-IR region under pressure allowed study of these vibrations for the first time in this manner. The longitudinal mode ( $\nu_{\text{LO}}$ ) is more difficult to study in the IR. It is not normally observed at  $90^\circ$  incident radiation. Berreman [168] observed the longitudinal mode for a thin film of LiF with an oblique incident radiation, and longitudinal optical modes of the silver halides have been studied by a similar technique [171]. The longitudinal modes can be observed with a diamond cell and highly converging oblique radiation arriving from the beam condenser. They appear as shoulders on the main, intense transverse vibrational bands, and are not easily studied with pressure in the IR, for they are less pressure sensitive than the transverse modes and, because of the high-frequency shift of the  $\nu_{\text{TO}}$  band, become lost in the  $\nu_{\text{TO}}$  envelope. In more covalent solids  $\nu_{\text{TO}}$  approaches  $\nu_{\text{LO}}$ , and in a homopolar covalent crystal,  $\nu_{\text{TO}}$  may equal  $\nu_{\text{LO}}$ . In this instance, a very broad absorption is observed, which shows very little frequency shift with pressure.

Figure 10 shows a comparison of several  $\nu_{\text{TO}}$  frequencies with pressure. The  $\nu_{\text{LO}}$  pressure dependence for NaF is shown in Fig. 11. In this system the separation between  $\nu_{\text{LO}}$  and  $\nu_{\text{TO}}$  is sufficiently large to make possible a determination of the pressure dependence of both optical modes.

In general, ionic lattice vibrations shift toward higher frequencies with increasing pressure, although red shifts can be observed. The shifts at pressures of up to 50 kbar may be considerable; however, not all ionic lattice vibrations show dramatic shifts, since the compressibility of the solid is involved. The relationship between the change in frequency with pressure for simple cubic ionic solids, where the three crystallographic axes are equal, is given in eqn.

$$(1) \quad \gamma\chi\nu = (\partial\nu/\partial p)_T \quad (1)$$

where  $\gamma$  is the Grüneisen parameter,  $\chi$  is the isothermal compressibility of the

TABLE 15  
Lattice vibrations for alkali halides<sup>a</sup>

Halide	$\nu_{\text{TO}}$ ( $\text{cm}^{-1}$ )	Halide	$\nu_{\text{TO}}$ ( $\text{cm}^{-1}$ )	Halide	$\nu_{\text{TO}}$ ( $\text{cm}^{-1}$ )
LiF	307	NaI	117	RbCl	118
LiCl	191	KF	190	RbBr	88
LiBr	159	KCl	141	RbI	77
NaF	246	KBr	113	CsCl <sup>b</sup>	99
NaCl	164	KI	98	CsBr <sup>b</sup>	74
NaBr	134	RbF	156	CsI <sup>b</sup>	62

<sup>a</sup> Ref. 169. <sup>b</sup> Ref. 170.

TABLE 16

Lattice vibrations for several other ionic crystals<sup>a</sup>

	$\nu_{TO}$ (cm <sup>-1</sup> )	$\nu_{LO}$ (cm <sup>-1</sup> )
TlCl	63	158
TlBr	43	101
AgCl	106	196
AgBr	79	138
MgO	401	718
NiO	401	580
CoO	349	546
MnO	262	552

<sup>a</sup> IR data from S.S. Mitra, AFCRL-69-0468, Air Force Cambridge Research Labs., Oct. 1969.

TABLE 17

Lattice vibrations for II-VI compounds<sup>a</sup>

	$\nu_{TO}$ (cm <sup>-1</sup> )	$\nu_{LO}$ (cm <sup>-1</sup> )
ZnO	(  ) 377 (⊥) 406	575 589
ZnS	278	350
ZnSe	205	253
ZnTe	179	206
CdS	239	306
CdSe	170	211
CdTe	125	151

<sup>a</sup> IR data from S.S. Mitra, AFCRL-69-0468, Air Force Cambridge Research Labs., Oct. 1969.

TABLE 18

Lattice vibrations for III-V compounds<sup>a</sup>

	$\nu_{TO}$ (cm <sup>-1</sup> )	$\nu_{LO}$ (cm <sup>-1</sup> )
InSb	185	197
InAs	219	243
InP	304	345
GaSb	231	240
GaAs	269	292
GaP	367	403
AlSb	319	340
AlP	440	501
AlN	667	916
BP	820	834
BN	1056	1304

<sup>a</sup> From S.S. Mitra, AFCRL-69-0468, Air Force Cambridge Research Labs., Oct. 1969.