APPENDIX IIID-A

MOLECULAR LATTICE POINT CRYSTALS

Each molecule in a molecular lattice point crystal contributes $3n_a$ vibrational modes. In the text we pointed out how and why these modes could be divided between the optical and acoustical branches.

Optical Modes. There are $P_\ell = 3n_a - 5$ or $P_{n\ell} = 3n_a - 6$ optical modes per lattice point in linear and nonlinear molecule crystals, respectively. These modes are assumed to be *confined within the molecule* and to vibrate at a single fixed frequency. The property contributions of the internal, optical modes are to be predicted using the same relationships and characteristic temperatures as those used for vibration of gaseous molecules, see Table IIIC-1 and 2.

$$\bar{u}_{opt} = \bar{R}\sum_{p=1}^{P} \theta_{v,p}\left[\frac{1}{2} + \frac{1}{(e^{x_{v,p}}-1)}\right] \qquad \bar{c}_{v,opt} = \bar{R}\sum_{p=1}^{P} (x_{v,p})^2 \cdot \frac{e^{x_{v,p}}}{\left(e^{x_{v,p}}-1\right)^2} \qquad \text{(IIID-A1,A2)}$$

$$\bar{s}_{opt} = \bar{R}\left[\sum_{p=1} \frac{x_{v,p}}{(e^{x_{v,p}}-1)} - \ln(1-e^{x_{v,p}})\right] \qquad \text{where} \quad x_{v,p} = \frac{\theta_{v,p}}{T} \qquad \text{(IIID-A3)}$$

Acoustical Modes. There are 5 or 6 acoustical modes per lattice point in linear and nonlinear molecules, respectively. These modes are assumed to be distributed throughout the crystal as a whole. Their property contributions are to be predicted using the Debye continuum model. The characteristic temperatures are predicted by eqn. IIID-11b. Their respective property contributions are

$$\bar{u}_{\ell,\ell} = 5\bar{R}TD(x_{D,n}) \qquad \bar{u}_{\ell,n\ell} = 6\bar{R}TD(x_{D,n\ell}) \qquad \text{(IIID-A4a,b)}$$

$$\bar{c}_{v(\ell,\ell)} = 5\bar{R}\left[4D(x_{D,\ell}) - \frac{3x_{D,\ell}}{(e^{x_{D,\ell}}-1)}\right] \qquad \bar{c}_{v(\ell,n\ell)} = 6\bar{R}\left[4D(x_{D,n\ell}) - \frac{3x_{D,n\ell}}{(e^{x_{D,n\ell}}-1)}\right] \qquad \text{(IIID-A5a,b)}$$

$$\bar{s}_{\ell,\ell} = \frac{5}{3}\bar{R}\left[4D(x_{D,\ell}) - 3\ln(1-e^{-x_{D,\ell}})\right] \qquad \bar{s}_{\ell,n\ell} = 2\bar{R}\left[4D(x_{D,n\ell}) - 3\ln(1-e^{-x_{D,n\ell}})\right] \qquad \text{(IIID-A6a,b)}$$

$$\text{where} \quad x_{D,\ell} = \frac{\theta_{D,\ell}}{T} \qquad x_{D,n\ell} = \frac{\theta_{D,n\ell}}{T}$$

The total properties of the crystal are a linear superposition of optical and lattice properties.

$$\bar{u} = \bar{u}_{opt} + \bar{u}_\ell \qquad \bar{c}_v = \bar{c}_{v,opt} + \bar{c}_{v,\ell} \qquad \bar{s} = \bar{s}_{opt} + \bar{s}_\ell \qquad \text{(IIID-A7a,b,c)}$$

We illustrate the use of these relationships in the following problems.