J. Phys. C: Solid State Phys., Vol. 9, 1976. Printed in Great Britain. © 1976

IR absorption spectrum of molecules trapped in matrices: I. The libron–phonon coupling in 1D

E Blaisten-Barojas† and M Allavena
Centre de Mécanique Ondulatoire Appliquée, 23 Rue du Maroc, 75019 Paris, France

Received 2 December 1975, in final form 12 April 1976

Abstract. Theoretical expressions are obtained for the infrared absorption coefficient of a one-dimensional monatomic lattice containing one diatomic substitutional impurity. The diatomic molecule interacts with the environment introducing high rotational barriers that reduce the molecular rotation to a libration coupled to the host-lattice vibrations (libron–phonon coupling). This is equivalent to the explicit consideration of static and dynamic interactions on the lineshape function. It is found that the absorption coefficient contains three main components associated with the pure vibration and libration spectra and with the combination spectrum of libration–vibration. These expressions are worked out in the harmonic and anharmonic approximation of the system Hamiltonian. Broadening of the absorption lines is obtained when the libration frequency falls inside the phonon band. The anharmonicities in the dynamical interaction (only third-order terms have been kept) give rise to an important temperature dependence of the shift and width of lines. Numerical results of the absorption coefficient of CO trapped in linear chains of Ne, Ar, Kr and Xe interacting via molecular-pair potentials are discussed. The near-infrared spectrum is qualitatively in agreement with the measured vibrational frequencies.

1. Introduction

Considerable effort in solid-state physics has been devoted to the investigation of the behaviour of solids due to impurities (Maradudin 1966a, b, Maradudin *et al* 1971). However, much less is known about the modifications that the crystal induces on the vibration–rotation spectrum of molecules isolated in matrices (Meyer 1971, Schnepp and Jacobi 1972). In recent years, there has been considerable interest in studying the optical absorption of inert crystals with molecular impurities in the near-infrared region, using various models and approximations (Milligan and Jacox 1972, Friedman and Kimel 1965, 1967, Mannheim and Friedman 1970). Most of the theoretical work has been restricted to the treatment of the so-called static approximation in which the defect is placed in a static crystalline field (Devonshire 1936, Flygare 1963, Girardet *et al* 1971, Girardet 1972). This seems somewhat incomplete, since in actual practice the introduction of a defect modifies the dynamics of the lattice (Dawber and Elliott 1963a, b, Elliott and Taylor 1964) as well as the motion of the impurities (Blaisten-Barojas 1974). Therefore it is of interest to investigate the infrared absorption in a crystal which contains

---

† Present address: Instituto de Física-Universidad Nacional Autónoma de México, Apartado, Postal 20-364, México 20, DF.

substitutional molecular impurities, taking into account the contribution of the dynamic field in addition to that of the static field.

The object of this paper is to point out the importance of the dynamical contributions to the broadening of IR absorption lines. Using the thermodynamic double-time Green functions (GF) defined by Zubarev (1960) and Kubo's (1957) formalism, expressions are obtained for the IR absorption coefficient (AC) of a simplified system. In § 2 we give a description of the system and write down its Hamiltonian and dipole moment operator. A simple one-dimensional model that we can usefully consider as first approach for a three-dimensional treatment is that of an isolated diatomic defect allowed to rotate, to vibrate and to translate along a linear chain of atoms. The orientational dependence of the interacting potential is supposed to introduce high rotational barriers leading to a molecular libration motion coupled to phonons, the libron–phonon coupling (LPC). This supposition is therefore opposite to the Friedman and Kimel (1965, 1967) rotation–translation coupling (RTC) in which the interaction between lattice and molecule is weak, allowing a perturbation treatment. The RTC model fails when the interactions are of the order of the spacing between rotational levels, as is generally the case with molecules with high moments of inertia. In spite of the simplicity of the model described in § 2, the reduction of rotation to libration changes the absorption spectrum completely and is one very important feature of the dynamical coupling. In three dimensions, instead of having one librational mode there will be at least two (projections of a top motion in two perpendicular planes), giving rise to a libration band. However, as the different libration modes have associated proper frequencies very close in value, this fine structure will certainly not be observed with the present experimental resolution (Dubost 1975, 1976). For this reason, an analysis of a one-dimensional model has the advantage of its mathematical simplicity, without losing physical insight into the real situation.

The model Hamiltonian may also be used in other contexts, for instance to obtain some information on the dielectric loss of polymers containing a group with a strong dipole moment (Work and Fujita 1966). Also, if the force constants joining the molecular impurity to atoms in the other two directions of space are small compared to the ones considered in the model, chain plus molecule may be seen as a longitudinal defect (Agrawal 1971). The operators involved in the anharmonic approximation of the LPC can be reinterpreted to describe the Jahn–Teller effect. Finally, in liquid solutions of non-polar solvents with polar solutes, one could think of this model as an indication of the coupling between longitudinal phonons in the liquid with the solute molecule in studying the IR absorption of that solution.

In §§ 3.1–3.4 we evaluate $G_\omega(M, M)$, the Fourier trasform of the GF of the dipole moment, solving the equations of motion (Zubarev 1960, Blaisten-Barojas and Allavena 1973) in the harmonic and anharmonic approximations of the LPC. The expression obtained for the AC, equation (15), is a superposition of four components, equations (18), (27), (32) and (34), which are simple functions of the frequency ω. A comparison is given of the results obtained in the static field and the contributions added by the dynamic field. The LPC in the harmonic approximation leads to shifts with respect to the static-field calculation and to widths of absorption lines almost independent of temperature. In § 3.2 we work out the influence on the lineshape function of anharmonic terms of the lower order in the LPC, obtaining a relevant temperature dependence of the AC at low temperatures. This fact is not evident *a priori*, even though it is known that a number of temperature-dependent effects can be explained on the basis that anharmonic terms in the potential energy of pure crystals induce transitions between the normal modes, which are now no longer stationary states of the system (Peierls 1955).

In §4 a numerical calculation is performed for carbon monoxide trapped in noble-gas chains. The analytical expression of the AC, equation (15), is parametrized with the parameters of a model intermolecular potential of Lennard–Jones type between pairs of noble-gas atoms and a modified diatomic potential (Sweet and Steele 1967) between the molecule and nearest-neighbours atoms. A qualitative agreement is obtained when a comparison of the theoretical results and the experimental measurements (Dubost 1975a, b) is carried out.

2. Model

The system consists of a linear chain containing atoms of mass m positioned at x_s and one heteronuclear diatomic molecule AB of mass $m_{AB} = m_A + m_B$ with centre of mass placed at $x_i \neq x_s$ and internuclear axis perpendicular to the chain, as seen in figure 1.

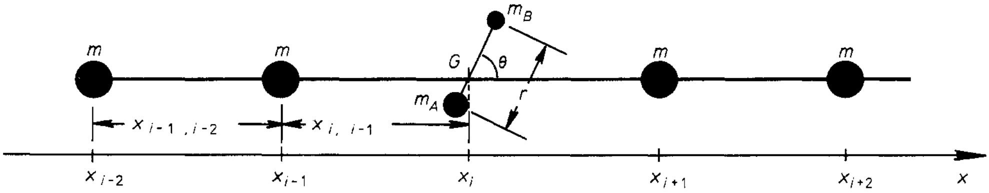

Figure 1. Instantaneous configuration of the system.

This impurity introduces three additional degrees of freedom when compared with a chain of $N + 1$ atoms. These are: (i) an internal molecular vibration along the internuclear axis; (ii) a rotation, characterized by an angle θ, in the plane containing the chain and the molecular axis; and (iii) a rotation perpendicular to the chain. This rotation perpendicular to the chain appears in the one-dimensional model, but not in a three-dimensional lattice. Besides, this degree of freedom is not coupled to the longitudinal translations. Hence we shall not consider it in this work.

The total motion of the molecule is thus composed of an internal vibration, a hindered rotation (or libration) and a translation. We assume the following:

(i) the internal vibration is coupled neither to the external modes (translations) nor to the planar rotation;

(ii) only nearest-neighbour interactions are taken into account;

(iii) the molecular centre of mass is constrained to displacements along the axis of the chain; and

(iv) the interaction between the molecule and its two nearest neighbours is strong enough to reduce the rotation of the molecule to a libration about an equilibrium configuration in which the diatomic molecule is perpendicular to the chain.

The kinetic energy of the system is

$$T = \sum_{\substack{s=1 \\ s \neq i}}^{N} \frac{p_s^2}{2m} + \frac{p^2}{2\mu} + \frac{p_i^2}{2m_{AB}} + \frac{p_\theta^2}{2I} \tag{1}$$

where p_s, p_i, p and p_θ are the conjugate momenta associated with coordinates x_s, x_i, r and θ, respectively. μ and I are the reduced mass and moment of inertia of the molecule, respectively.

Taking into account assumption (i), the potential energy is a superposition of two functions:

$$V = V_1(r) + V_2(x_{s,s-1}; x_{i+1,i}, x_{i,i-1}, \theta). \tag{2}$$

Here $V_1(r)$ stands for the intra-molecular potential energy while $V_2(x_{s,s-1}; x_{i+1,i}, x_{i,i-1}, \theta)$, the intermolecular potential, contains all the interactions existing between the particles of the system. These interactions depend on all the relative distances $x_{s,s-1} = x_s - x_{s-1}$ between the particles of mass m and on the molecular orientation θ, as well as on the relative distances between the centre of mass of the molecule and its neighbours in the chain, $x_{i+1,i}$ and $x_{i,i-1}$. By expanding (2) in a Taylor series about the configuration which minimizes V up to third-order terms containing only corrections of the type Δx_s^2 and by grouping the variables into two groups, (x_s, p_s, x_i, p_i) and (r, p, θ, p_θ), the system Hamiltonian $H = T + V$ may be written as:

$$H = H_\mathrm{C} + H_\mathrm{M} + H_\mathrm{CM} \tag{3}$$

where

$$H_\mathrm{C} = \sum_{\substack{s=1\\ s\neq i}}^{N} \frac{p_s^2}{2m} + \frac{p_i^2}{2m_{AB}} + \frac{g}{2} \sum_{\substack{s=1\\ s\neq i,\, i+1}}^{N} \Delta x_{s,s-1}^2 + \frac{g_{xx}}{2}(\Delta x_{i+1,i}^2 + \Delta x_{i,i-1}^2) \tag{4a}$$

$$H_\mathrm{M} = \frac{1}{2}\left(\frac{p^2}{\mu} + \kappa_1 \Delta r^2 + \frac{\kappa_2}{3}\Delta r^3\right) + \frac{1}{2}\left(\frac{p_\theta^2}{I} + g_{\theta\theta}\,\Delta\theta^2\right) \tag{4b}$$

$$\begin{aligned} H_\mathrm{CM} = {} & g_{\theta x}(\Delta x_{i+1,i} - \Delta x_{i,i-1})\,\Delta\theta + \tfrac{1}{2} g_{\theta xx}(\Delta x_{i+1,i}^2 - \Delta x_{i,i-1}^2)\,\Delta\theta \\ & + \tfrac{1}{2} g_{\theta\theta x}(\Delta x_{i+1,i} + \Delta x_{i,i-1})\,\Delta\theta^2 + \tfrac{1}{2} g_{\theta\theta\theta}\,\Delta\theta^3 \end{aligned} \tag{4c}$$

and where Δr, $\Delta x_{s,s-1}$ and $\Delta\theta$ are the instantaneous deviations with respect to the equilibrium positions r^0, $x_{s,s-1}^0$ and θ^0. The constants g and κ in the Taylor expansion are $g = (\partial^2 V/\partial x_{s,s-1}^2)_0$ $\forall s \neq i,\ i+1$, $g_{\theta\theta} = (\partial^2 V/\partial\theta^2)_0$, $g_{\theta\theta\theta} = (\partial^3 V/\partial\theta^3)_0 = 0$, $\kappa_1 = (\partial^2 V/\partial r^2)_0$ and $\kappa_2 = (\partial^3 V/\partial r^3)_0$, all other g constants being defined in table 1. Thus the system may be visualized as a monatomic chain with defects (H_C) interacting (H_CM) with a 'molecule' (H_M) represented by two independent oscillators: a vibrator and a librator with proper frequencies $\omega_\mathrm{V} = (\kappa_1/\mu)^{1/2}$ and $\omega_\mathrm{L} = (g_{\theta\theta}/I)^{1/2}$, respectively. The translational motion of the molecule as a whole (x_i, p_i) is therefore shared among H_C and H_CM. The splitting of the Hamiltonian is interesting because in H_M we have grouped that part of the system which is coupled to the external electromagnetic field. The static approximation is recovered when $H_\mathrm{C} = H_\mathrm{CM} = 0$.

It is convenient to rewrite H in terms of the normal coordinates of the unperturbed lattice expressed as combinations of phonon creation and annhilation operators b_k^+, b_k (Ziman 1960) and of b_L^+, b_L and b_V^+, b_V, associated with the creation and annihilation of a quantum of energy $\hbar\omega_\mathrm{L}$ or $\hbar\omega_\mathrm{V}$, respectively (Messiah 1965):

$$\begin{aligned} \varphi_k &= 2^{-1/2}(b_{-k}^+ + b_k); \qquad & \pi_k &= 2^{-1/2}(b_k^+ - b_{-k}) \\ \varphi_i &= 2^{-1/2}(b_i^+ + b_i); \qquad & \pi_i &= 2^{-1/2}(b_i^+ - b_i) \end{aligned} \tag{5}$$

where $i = \mathrm{L}$ or V, the allowed values of k are $2\pi\nu/(N+1)\mathrm{d}_0$, $\nu = 0, \pm 1, \ldots, \pm(N+1)/2$ and d_0 is the lattice spacing. These new operators satisfy boson commutation rules $[\varphi_\alpha, \pi_\beta] = \delta_{\alpha\beta}$, $[\varphi_\alpha, \varphi_\beta] = [\pi_\alpha, \pi_\beta] = 0$. The model Hamiltonian is therefore written as:

$$H_\mathrm{C} = \tfrac{1}{2}\sum_k \omega_k(\varphi_k\varphi_{-k} - \pi_k\pi_{-k}) + \lambda_1 \sum_{kk'} F_1(kk')\,\varphi_k\varphi_{k'} + \lambda_2 \sum_{kk'} F_2(kk')\,\pi_k\pi_{k'} \tag{6a}$$

Table 1. The constants g appearing in the Taylor expansion of the interaction potential, equation (2), are defined along with the constants λ_i and functions $F_i (i = 1, 2, \ldots, 5)$ appearing in the Hamiltonians (6). The following functions have been used: $f(k) = \omega_k^{-1}[1 - \exp(-ikd_0)]$, $\bar{f}(k) = \omega_k^{1/2}\exp(-ikx_i^0)$.

Constants		Functions
$g_{xx} = \left(\dfrac{\partial^2 V}{\partial x_{i+1,i}^{2}}\right)_0 = \left(\dfrac{\partial^2 V}{\partial x_{i,i-1}^{2}}\right)_0$	$\lambda_1 = \dfrac{g_{xx} - g}{2mc^2}$	$F_1(kk') = \dfrac{\bar{f}(k)\bar{f}(k')}{N+1}[f(k)f(k') + f(-k)f(-k')]$
	$\lambda_2 = \dfrac{m_{AB} - m}{2m_{AB}}$	$F_2(kk') = \dfrac{\bar{f}(-k)f(-k')}{N+1}$
$g_{\theta x} = \left(\dfrac{\partial^2 V}{\partial\theta\partial x_{i+1,i}}\right)_0 = -\left(\dfrac{\partial^2 V}{\partial\theta\partial x_{i,i-1}}\right)_0$	$\lambda_3 = \dfrac{-g_{\theta x}}{c^2(mI\omega_L)^{1/2}}$	$F_3(k) = \dfrac{\bar{f}(k)}{(N+1)^{1/2}}[f(k) + f(-k)]$
$g_{\theta xx} = \left(\dfrac{\partial^3 V}{\partial\theta\partial x_{i+1,i}^{2}}\right)_0 = -\left(\dfrac{\partial^3 V}{\partial\theta\partial x_{i,i-1}^{2}}\right)_0$	$\lambda_4 = \left(\dfrac{\hbar}{I\omega_L c^5}\right)^{1/2}\dfrac{g_{\theta xx}}{2m}$	$F_4(kk') = \dfrac{\bar{f}(k)\bar{f}(k')}{N+1}[f(k)f(k') - f(-k)f(-k')]$
$g_{\theta\theta x} = \left(\dfrac{\partial^3 V}{\partial\theta^2\partial x_{i+1,i}}\right)_0 = \left(\dfrac{\partial^3 V}{\partial\theta^2\partial x_{i,i-1}}\right)_0$	$\lambda_5 = -\left(\dfrac{\hbar}{mc^5}\right)\dfrac{g_{\theta\theta x}}{2I\omega_L}$	$F_5(k) = \dfrac{\bar{f}(k)}{(N+1)^{1/2}}[f(k) - f(-k)]$

$$H_{\mathrm{M}} = \tfrac{1}{2}\,\omega_{\mathrm{V}}(\varphi_{\mathrm{V}}^2 - \pi_{\mathrm{V}}^2) + \lambda_0\varphi_{\mathrm{V}}^3 + \tfrac{1}{2}\,\omega_{\mathrm{L}}(\varphi_{\mathrm{L}}^2 - \pi_{\mathrm{L}}^2) \qquad (6b)$$

$$H_{\mathrm{CM}} = \lambda_3 \sum_k F_3(k)\,\varphi_k\varphi_{\mathrm{L}} + \lambda_4 \sum_{kk'} F_4(kk')\,\varphi_k\varphi_{k'}\,\varphi_{\mathrm{L}} + \lambda_5 \sum_k F_5(k)\,\varphi_k\varphi_{\mathrm{L}}^2 \qquad (6c)$$

where $\omega_k = \omega_{\mathrm{c}}|\sin(kd_0/2)|$ are the normal mode frequencies, $\omega_{\mathrm{c}} = (4g/m)^{1/2}$ is the cutoff frequency, $\lambda_0 = (\mu^3\omega_{\mathrm{V}}^5 c^5/\hbar)^{-1/2}\,\kappa_2$. The λ_i and $F_i (i = 1, 2, \ldots, 5)$ are defined in table 1 and the system of units adopted is such that energy as well as frequencies are given in cm^{-1}. It is the interaction Hamiltonian, H_{CM}, which we shall refer to as the libron–phonon coupling (LPC). While the term in λ, on the right-hand side of equation (6*c*) denotes the LPC in the harmonic approximation, the last two terms stand for the anharmonic approximation of the interaction.

The dipole moment operator is obtained by following the same steps as for the Hamiltonian. Since the system is composed of N inert atoms and one heteronuclear molecule with permanent dipole moment $\boldsymbol{M}_{\mathrm{p}}(r)$, the impurity induces dipole moments on the atoms of the host chain. Because these induced dipole moments vary as $(x_{i,i+m})^{-3}$, $m = \pm 1, \pm 2, \ldots \pm N/2$, we neglect all of them except the two neighbours to the impurity, $\boldsymbol{M}_{\mathrm{ind}}(x_{i\pm 1,i})$. Also, as the dipole moment induced at the molecular site is of the same order as the far-neighbour dipoles, we shall neglect it as well. Therefore the total dipole moment is

$$\boldsymbol{M} \simeq \boldsymbol{M}_{\mathrm{p}}(r) + \boldsymbol{M}_{\mathrm{ind}}(x_{i+1,i}) + \boldsymbol{M}_{\mathrm{ind}}(x_{i-1,i}) \qquad (7)$$

and its instantaneous components parallel and perpendicular to the chain measured from the equilibrium configuration are

$$\begin{aligned} M_x &= M_{\mathrm{p}}(r)\cos(\pi/2 + \Delta\cos(\pi/2 + \Delta\theta)[1 - 2\alpha_{\mathrm{C}}(x_{i+1,i}{}^{-3} + x_{i,i-1}{}^{-3})] \\ M_y &= M_{\mathrm{p}}(r)\sin(\pi/2 + \Delta\theta)\,[1 + \alpha_{\mathrm{C}}\,(x_{i+1,i}{}^{-3} + x_{i,i-1}{}^{-3})] \end{aligned} \qquad (8)$$

where α_{C} is the polarizability of the host atoms. Supposing that $M_{\mathrm{p}}(r)$ varies linearly with Δr (Herzberg 1959),

$$M_{\mathrm{p}}(r) = M_0 + \left(\frac{\partial M_{\mathrm{p}}}{\partial r}\right)_0 \Delta r, \qquad (9)$$

expanding $M_{\mathrm{ind}}(x_{i\pm 1,i})$ in a phonon series (Born and Huang 1954) and keeping only terms linear in the atomic and angular displacements, we obtain, in terms of the operators given in (5):

$$\begin{aligned} M_x &= M_2\varphi_{\mathrm{L}} + M_3\,\varphi_{\mathrm{L}}\varphi_{\mathrm{V}} \\ M_y &= M_0(1 + 2\alpha_{\mathrm{C}}d_0^{-3}) + M_1\varphi_{\mathrm{V}} + M_4\sum_k F_5(k)\,\varphi_k \end{aligned} \qquad (10)$$

where

$$\begin{aligned} M_1 &= (\hbar/c\mu\omega_{\mathrm{V}})^{1/2}\,(\partial M_{\mathrm{p}}/\partial r)_0 \\ M_2 &= -\,M_0(\hbar/cI\omega_{\mathrm{L}})^{1/2}\,(1 + 4\alpha_{\mathrm{C}}d_0^{-3}) \\ M_3 &= -\,\hbar(\mu c^2\omega_{\mathrm{V}}\omega_{\mathrm{L}}I)^{-1/2}\,(\partial M_{\mathrm{p}}/\partial r)_0 \\ M_4 &= 3M_0\alpha_{\mathrm{C}}d_0^{-4}\,(\hbar/mc)^{1/2}. \end{aligned} \qquad (11)$$

When the polarizability of the host atoms is small, as in the case of noble-gas atoms, the contribution of the induced dipole moment in (7) is very small. Thus, all effects depending on M_4 will be considered as corrections to those arising from M_1, M_2 and M_3.

3. Green functions and the absorption coefficient

When the system described in §2 is placed in an external oscillating electric field $E(\omega)$, the AC of the impure crystal is given by (Landau and Lifshitz 1959, Bonch-Bruevich 1966):

$$\sigma(\omega) = -\Lambda\omega \sum_{vv'} E_v E^*_{v'}\, G''_\omega(M_v, M_{v'}) \qquad v, v' = x, y. \tag{12}$$

After integration over all possible orientations of the external field with respect to the axes of the chain, equation (12) reduces to

$$\sigma(\omega) = -\tfrac{2}{3}\Lambda\omega[G''_\omega(M_x, M_x) + 2G''_\omega(M_y, M_y)] \tag{13}$$

where Λ is a constant and $G''_\omega(M_v, M_{v'})$ stands for the imaginary part of the Fourier transform of the retarded double-time GF defined as (Zubarev 1960):

$$G(M_v(t), M_{v'}) = -\mathrm{i}\hbar^{-1}\theta(t)\langle[M_v(t), M_{v'}]\rangle. \tag{14}$$

Here the operators are in the interaction picture $M_v(t) = \exp(\mathrm{i}Ht/\hbar)\, M_v \exp(-\mathrm{i}Ht/\hbar)$ and the angular brackets denote the average over the canonical ensemble, $\langle\theta\rangle = \mathrm{Tr}[\exp(-H/k_\mathrm{B}T)\,\theta]/\mathrm{Tr}[\exp(-H/k_\mathrm{B}T)]$ (k_B is the Boltzmann constant and T is the temperature of the system).

Upon substitution of equations (10) into equation (13) we have the AC divided into four components:

$$\sigma(\omega) = \sigma_\mathrm{V}(\omega) + \sigma_\mathrm{L}(\omega) + \sigma_\mathrm{LV}(\omega) + \sigma_\mathrm{C}(\omega), \tag{15}$$

each one corresponding to one GF associated with a different operator φ_V, φ_L, $\varphi_\mathrm{L}\varphi_\mathrm{V}$ or φ_k:

$$\begin{aligned}
\sigma_\mathrm{V}\,(\omega) &= -\tfrac{4}{3}\Lambda M_1\omega\, G''_\omega(\varphi_\mathrm{V}, M_y)\\
\sigma_\mathrm{L}\,(\omega) &= -\tfrac{2}{3}\Lambda M_2\omega\, G''_\omega(\varphi_\mathrm{L}, M_x)\\
\sigma_\mathrm{LV}(\omega) &= -\tfrac{2}{3}\Lambda M_3\omega\, G''_\omega(\varphi_\mathrm{L}\varphi_\mathrm{V}, M_x)\\
\sigma_\mathrm{C}\,(\omega) &= -\tfrac{4}{3}\Lambda M_4\omega\, \mathrm{Im} \sum_k F_5(k)\, G_\omega(\varphi_k, M_y).
\end{aligned} \tag{16}$$

Every component in equation (15) gives rise to a different part of the spectrum, i.e. $\sigma_\mathrm{V}(\omega)$ and $\sigma_\mathrm{LV}(\omega)$ are associated with the pure vibration and with the libration–vibration spectrum, respectively. Both terms appear in the near-infrared where $\sigma_\mathrm{L}(\omega)$, associated with the pure libration spectrum, and $\sigma_\mathrm{C}(\omega)$, characterizing the activated spectrum of the chain, give contributions in the far-infrared.

In evaluating the four GF $G_\omega(\varphi_\mathrm{V}, M_y)$, $G_\omega(\varphi_\mathrm{L}, M_x)$, $G_\omega(\varphi_\mathrm{L}\varphi_\mathrm{V}, M_x)$ and $G_\omega(\varphi_k, M_y)$, we use the equation-of-motion method which has been described elsewhere (Zubarev 1960). In the harmonic approximation of the LPC, the generated set of equations of motion is closed; thus the GF obtained by this method are exact. The LPC anharmonic terms give rise to an open and infinite set of equations of motion. Therefore, only approximated GF can be obtained. The criterion used in this work (Tyablikov and Bonch-Bruevich 1962) is to close the set of equations by posing

$$G_\omega(\theta_l\theta_m\theta_n, M_v) \simeq \langle\theta_l\theta_m\rangle\, G_\omega(\theta_n, M_v) + \langle\theta_l\theta_n\rangle\, G_\omega(\theta_m, M_x) + \langle\theta_m\theta_n\rangle\, G_\omega(\theta_l, M_x) \tag{17}$$

where the operators $\theta_{l,m,n}$ can be either φ_i or $\pi_i (i = \pm k, \mathrm{L}, \mathrm{V})$. The average values are evaluated by means of the non-interacting Hamiltonian H^0, as indicated in the Appendix.

3.1. Vibration

As the internal vibration of the molecule is not coupled to the lattice, the calculation of

$G_\omega(\varphi_V, M_y)$ is straightforward (Blaisten-Barojas and Allavena 1973); the part of the AC associated with the pure vibration spectrum therefore becomes a delta-function:

$$\sigma_V(\omega) = \tfrac{4}{3}\pi\Lambda M_1^2 \omega_V \bar{\omega}_V^2\, \delta(\omega - \bar{\omega}_V) \tag{18}$$

where $\bar{\omega}_V$ is a modified vibration frequency defined as

$$\bar{\omega}_V = [\omega_V^2 + 90\,\lambda_0^2\,\langle\varphi_V\rangle\,\omega_V(\omega^2 - 4\omega_V^2)^{-1}]^{1/2}. \tag{19}$$

3.2. *Libration*

The analytic expression of $\sigma_L(\omega)$ implies the evaluation of $G_\omega(\varphi_L, M_x)$. The solution of the equation of motion for this GF leads to

$$\begin{aligned} G_\omega(\varphi_L, M_x) = \omega_L(\omega^2 - \omega_L^2)^{-1}\Big(M_2 &+ \lambda_3 \sum_k F_3(k)\, G_\omega(\varphi_k, M_x) \\ &+ \lambda_4 \sum_{kk'} F_4(kk')\, G_\omega(\varphi_k\varphi_{k'}, M_x) + \lambda_5 \sum_k F_5(k)\, G_\omega(\varphi_k\varphi_L, M_x)\Big). \end{aligned} \tag{20}$$

The harmonic approximation, $G_\omega^h(\varphi_L, M_x)$, is recovered when $\lambda_4 = \lambda_5 = 0$, while in the anharmonic approximation, all terms are kept in equation (20).

In the harmonic approximation, the result for $G_\omega^h(\varphi_L, M_x)$ is exact. In the anharmonic approximation, apart from the decoupling procedure used to truncate the infinite hierarchy of equations of motion, equation (17), an extra approximation has been considered. Namely, we have kept only terms up to second order in the coupling parameters λ_1 to λ_5 when calculating the last two summations in equation (20). This amounts to stating that the two-particle GF, $G_\omega(\varphi_k\varphi_{k'}, M_x)$ and $G_\omega(\varphi_k\varphi_L, M_x)$ are proportional to $G_\omega(\varphi_L, M_x)$ for each value of ω. The detailed calculation of all GF is given elsewhere (Blaisten-Barojas 1974), the final result being

$$G_\omega(\varphi_L, M_x) = M_2\omega_L[\omega^2 - \omega_L^2 - \Sigma_L(\omega)]^{-1} \tag{21}$$

where

$$\Sigma_L(\omega) = \Sigma_L^h(\omega) + T_L(\omega). \tag{22}$$

Since there are singularities on the real ω axis of the $\Sigma_L(\omega)$ function, as it stands, it is not completely defined. A prescription must then be given as to how to treat these singularities. We do this by giving ω a positive imaginary part $\omega \to \mathrm{Re}\omega + \mathrm{i}\epsilon, \epsilon \to 0$. We find, in terms of the reduced variables, $x = \omega_k/\omega_c$, $y = \omega/\omega_c$ and $I(y) = (N+1)^{-1}\,\Sigma_x x^2(x^2 - y^2)^{-1}$ that

$$\Sigma_L^h(\omega) \equiv \Sigma_L^h(\omega_c y) = -\,8\omega_L(\lambda_3/\omega_c)^2 \frac{1 + 2I(y)(y^2 - \lambda_2)}{1 + \zeta + 2I(y)[\zeta(y^2 - \lambda_2) - \lambda_2]} \tag{23}$$

and

$$\begin{aligned} T_L(\omega) &\equiv T_L(\omega_c y) \\ &= 2c_1 \int_0^1 \mathrm{d}x(1 - x^2)^{-1/2} \coth(\beta_c x)\, x\{x^2[I(y + x) + I(y - x)] \\ &\quad + (1 - 2x^2)[1 + (y + x)^2 I(y + x) + (y - x)^2 I(y - x)]\} \\ &\quad + c_2 y^{-1} \int_0^1 \mathrm{d}x\, B(x, y)\,[(x^2 - y_+^2)^{-1} - (x^2 - y_-^2)^{-1}] \end{aligned} \tag{24}$$

where $\zeta = 8\lambda_1/\omega_c^2$, $\beta_c = \hbar\omega_c/2k_BT$, $y_\pm = y \pm (\omega_L/\omega_c)$, $c_1 = 64\lambda_4^2\omega_L/\pi\omega_c^3$, $c_2 = 16\lambda_5^2/\pi\omega_c$ and

$$B(x, y) = \frac{\lambda_5 F_5(-k)[2\langle\varphi_k\varphi_{-k}\rangle\omega_c^{-1}\omega_L(y_+y_- + x^2) + \langle\varphi_L^2\rangle\, x(5y^2 - 3x^2 + 3\omega_L^2/\omega_c^2)]}{\omega_c(x^2 - y_+^2)(x^2 - y_-^2)} . \tag{25}$$

As $\Sigma_L(\omega)$ is a complex function, we can write

$$\Sigma_L(\omega) = \Sigma_L'(\omega) + i\Sigma_L''(\omega) \tag{26}$$

where $\Sigma_L'(\omega)$ and $\Sigma_L''(\omega)$ represent the real and imaginary parts of $\Sigma_L(\omega)$. From (21) and (26), the component of the AC associated with the pure libration spectrum can be immediately obtained as

$$\sigma_L(\omega) = \tfrac{2}{3}\Lambda M_2^2\omega_L \frac{\omega\Sigma_L''(\omega)}{(\omega^2 - \bar{\omega}_L^2)^2 + \Sigma_L''(\omega)^2} \tag{27}$$

with

$$\bar{\omega}_L = [\omega_L^2 + \Sigma_L'(\omega)]^{1/2}.$$

This expression contains the effect of the harmonic or anharmonic LPC (H_{CM}) on the spectrum, as well as that of the combined influence of the defects felt by the lattice because of the presence of the molecular impurity. The shape of $\sigma_L(\omega)$ will therefore depend upon the relative importance of three contributions, each one characterized by a λ parameter: force constant defect (λ_1), mass defect (λ_2) and harmonic (λ_3) or anharmonic (λ_4 and λ_5) coupling between libration and lattice modes. In the non-interacting case $\lambda_i = 0$, $i = 1, \ldots, 5$, for a molecule placed in a static field, the function $\delta_L(\omega)$ is a delta-function centred at ω_L, the pure libration frequency. Therefore, the dynamical contribution to the interacting potential is responsible for a frequency shift and a broadening of the libration line. The shift $\Delta_L = \bar{\omega}_L - \omega_L$ depends upon $\Sigma_L'(\omega)$ while the broadening, Γ_L, is proportional to $\Sigma_L''(\omega)$.

In the harmonic approximation, when the libration frequency ω_L falls outside the phonon band, near this pole the function $\Sigma_L^{h''}(\omega)$ is zero, in which case $\sigma_L(\omega)$ is a delta-function. But if $\omega_L < \omega_c$, then we can write the following explicit expressions:

$$\Sigma_L^{h'}(\omega) = -8\lambda_3^2\omega_L\omega_c^{-6}\gamma(\omega)\{\omega_c^4(1 + \zeta)(1 - 2\lambda_2) + [(1 + \zeta) + 2(1 - 2\lambda_2)]\,\omega^2 - 2\omega^4\}$$

$$\Sigma_L^{h''}(\omega) = -16\lambda_3^2\omega_L\omega_c^{-5}\,\gamma(\omega)\,\omega^3(\omega_c^2 - \omega^2)^{1/2} \tag{28}$$

where

$$\gamma(\omega) = \{\omega_c^4(1 + \zeta)^2(1 - 2\lambda_2)^2 + \omega_c^2(1 + \zeta)[2\zeta - (1 - \zeta)(1 - 4\lambda_2)]\,\omega^2 - 4\zeta\omega^4\}^{-1} \tag{29}$$

and where $I(y)$ in (23) has been evaluated as an integral over the continuous density of phonon states $\rho(x) = 2(N + 1)(\pi\omega_c)^{-1}(1 - x^2)^{-1/2}$. Equations (28) are simple functions of ω, whose evaluation is immediately obtained once the constants λ_1, λ_2 and λ_3 are known. If these values are such that $\Sigma_L^{h'}(\omega)$ and $\Sigma_L^{h''}(\omega)$ are slowly-varying functions of ω, then $\sigma_L^h(\omega)$ has a Lorentzian shape. But for different behaviours of these two functions, one may expect important deviations from a Lorentzian-function lineshape. In some cases, the line will present two maxima, one of which can be assigned to the broadened librational mode and the other to a resonance mode of the lattice. The resonance mode is only visible for very extreme values of the λ constants.

In the anharmonic approximation, the correction to the $\Sigma_L^h(\omega)$ function, $T_L(\omega)$, depends not only on the anharmonic LPC parameters λ_4 and λ_5, but also on the temperature. Therefore, the shift Δ_L and the linewidth Γ_L are temperature-dependent, broadenings being more sensitive than shifts to increases in temperature (Blaisten-Barojas 1974). When $\omega_L > 2\omega_c$, $\sigma_L(\omega)$ is a delta-function, and when $\omega_c < \omega_L \leqslant 2\omega_c$, the anharmonicities introduce a slowly-varying function of frequency, $T_L(\omega)$, giving rise to a Lorentizian lineshape. In the case $\omega_L \leqslant \omega_c$, the lineshape changes with respect to the harmonic approximation: (i) for temperatures below 4 K, the lineshape is very little modified; (ii) for increasing temperatures above 4 K, the line is broadened and loses height, tending to be confused with the background (Blaisten-Barojas and Allavena 1975). This is an indication that, for those temperatures, the LPC third-order anharmonic terms considered are not enough and the Taylor expansion of the potential energy, equation (2), should be carried out to higher-order terms in $\Delta\theta$. On the other hand, the fact that the height of the line decreases with increasing temperatures is because the possibility of energy transfer from the vibrator was excluded in the model. If a coupling of the vibrational motion of the molecule with either the molecular libration or with the phonons were considered, then new channels for energy transfer would be opened and the behaviour of the lineshape function would be modified (work is in progress in this direction). In spite of this limitation, at low temperatures the LPC is responsible for the librational relaxation, giving a value not far from the experimental measurement, as will be discussed in § 4.

3.3. Libration–vibration

The evaluation of $\sigma_{LV}(\omega)$ in equation (16) is more complicated than that of $\sigma_L(\omega)$ because the two-particle Green function $G_\omega(\varphi_L\varphi_V, M_x)$ connects vibration to libration operators through lattice operators. Only the harmonic approximation will be given here, since the details of this calculation have been worked out in length by Blaisten-Barojas (1974). The final result is:

$$G_\omega(\varphi_L\varphi_V, M_x) = \frac{N_{LV}(\omega)}{D_{LV}(\omega) - \Sigma_{LV}(\omega)} \tag{30}$$

where

$$\begin{aligned} N_{LV}(\omega) &= M_3\{Q_0(\omega) + 8\lambda_3^2\omega_L\omega_c^{-6}Q_2^{-1}(\omega)[\omega\langle\varphi_L^2\rangle Q_1(\omega) + (\omega_V\langle\varphi_L^2\rangle - \omega_L\langle\varphi_V^2\rangle)Q_3(\omega)]\} \\ D_{LV}(\omega) &= [\omega^2 - (\omega_V + \omega_L)^2][\omega^2 - (\omega_V - \omega_L)^2] \\ \Sigma_{LV}(\omega) &= 64\lambda_3^2\omega_L\omega_c^{-6}Q_2^{-1}(\omega)[Q_4(\omega) - Q_5(\omega)]. \end{aligned} \tag{31}$$

The average values $\langle\varphi_L^2\rangle$ and $\langle\varphi_V^2\rangle$ as well as the $Q_i(\omega)$ are given in the Appendix.

Separating the real and imaginary parts of $N_{LV}(\omega)$ and $\Sigma_{LV}(\omega)$:

$$N_{LV}(\omega) = N'_{LV}(\omega) + iN''_{LV}(\omega) \qquad \text{and} \qquad \Sigma_{LV}(\omega) = \Sigma'_{LV}(\omega) + i\Sigma''_{LV}(\omega),$$

the component of the AC associated with the combination spectrum is written as

$$\sigma_{LV}(\omega) = \frac{2\Lambda\omega}{3}\,\frac{N'_{LV}(\omega)\,\Sigma''_{LV}(\omega) + N''_{LV}(\omega)\,[D_{LV}(\omega) - \Sigma'_{LV}(\omega)]}{[D_{LV}(\omega) - \Sigma'_{LV}(\omega)]^2 + \Sigma''_{LV}(\omega)^2}. \tag{32}$$

The explicit expressions for the real and imaginary parts of $N_{LV}(\omega)$ and $\Sigma_{LV}(\omega)$ can be obtained after some algebraic work, but they may also be directly determined numerically by replacing ω by $\omega + i\epsilon$ in (31) and giving ϵ a value close to zero. The libration–vibration component of the AC, $\sigma_{LV}(\omega)$ gives rise to two shifted and broadened lines, one associated with a particle–particle process ($\omega_V + \omega_L$, absorption of two quanta, one associated with vibration and the other with libration) and the other to a particle–hole process ($\omega_V - \omega_L$, absorption of a vibration quantum and emission of a libration quantum). The profile of the two lines composing $\sigma_{LV}(\omega)$ is approximately that of $\sigma_L(\omega)$ and its mirror image from a point centred at $\bar{\omega}_V$. Therefore, we can say that the librational motion reflects the dynamical behaviour of impure lattices, even though the librational resonance interacts with the lattice resonance and exchange of energy occurs among them. The far-infrared spectrum is 'reflected' to the near-infrared region (Mannheim and Cohen 1971). On this reasoning, the correction to $\sigma_{LV}(\omega)$ due to anharmonicities in the LPC will be very much the same as those obtained explicitly for the pure libration component.

Because of the function $N_{LV}(\omega)$, equation (31), the two peaks of $\sigma_{LV}(\omega)$ are weighted by coefficients dependent on the initial population of the libration–vibration states. The shifts and broadenings of the lines are obtained with respect to the non-interacting case $H_{CM} = 0$ (molecule in a static field), in which

$$\sigma^0_{LV}(\omega) = \tfrac{1}{6}\pi\Lambda M_3[w_+\delta(\omega - \omega_V - \omega_L) + w_-\delta(\omega - \omega_V + \omega_L)] \tag{33}$$

where $w_+ = (\omega_V + \omega_L)(\langle\varphi^2_L\rangle + \langle\varphi^2_V\rangle)$ and $w_- = (\omega_V - \omega_L)(\langle\varphi^2_L\rangle - \langle\varphi^2_V\rangle)$. As expected, at $T = 0$, $w_- = 0$, and only one of the two lines in $\sigma^0_{LV}(\omega)$ will be present. This corresponds to the fact that, at $T = 0$, only the ground state of the librating–vibrating molecule is occupied.

3.4. Lattice modes

The induced part of the dipole moment, equation (7), gives rise to the activated infrared spectrum of the lattice, which is represented by $\sigma_C(\omega)$ in equation (15). In the harmonic approximation of the LPC, the final expression for this component of the total AC, associated with one-phonon processes, is (the detailed calculation can be found in Blaisten-Barojas (1974)):

$$\sigma_C(\omega) = \frac{8\Lambda\hbar}{mc\omega_c^2}\left(\frac{M_0\alpha_C}{3d_0^4}\right)^2 \frac{\omega^2(\omega_c^2 - \omega^2)^{1/2}}{(1+\zeta)^2\,\omega_c^2 - 4\zeta\omega^2} \qquad \text{if } \omega \leqslant \omega_c \tag{34}$$

and zero otherwise.

This component gives a broad feature that essentially modifies the tails of $\sigma_L(\omega)$ in the far-infrared region.

4. Numerical calculation: CO trapped in noble-gas chains

We discuss here one specific case in the harmonic approximation: carbon monoxide trapped in solid Ne, Ar, Kr or Xe. It is interesting to investigate this molecule because there has recently been some discussion regarding the experimental assignation of the monomeric absorption lines (Davies and Hallam 1972, Jiang *et al* 1975, Dubost and Abouaf-Marguin 1972, Dubost 1975a, b). Because the high-resolution near-infrared spectra of monomeric CO in four noble-gas matrices, reported by Dubost and summarized in table 2, were all recorded under the same experimental conditions, these measurements are suitable for comparison with theoretical results. Therefore we shall refer to Dubost's measurements in what follows.

We assume that the intermolecular potential in (2) is a superposition of model pair potentials

$$V_2(x_{s,s-1}; x_{i+1,i}, x_{i,i-1}, \theta) = \sum_{\substack{s=1 \\ s \neq i-1,i}}^{N} V_{\mathrm{aa}}(x_{s,s-1}) + V_{\mathrm{ma}}(x_{i+1,i}, x_{i,i-1}, \theta) \tag{35}$$

where any interaction among identical atoms not belonging to the impurity is of Lennard–Jones type:

$$V_{\mathrm{aa}}(x_{s,s-1}) = 4\varepsilon_{\mathrm{aa}}[(\sigma_{\mathrm{aa}}/x_{s,s-1})^{12} - (\sigma_{\mathrm{aa}}/x_{s,s-1})^6], \tag{36}$$

while the interaction between the molecule and the atoms in the chain is described by a modified diatomic potential (Sweet and Steele 1967, Blaisten-Barojas 1974):

$$V_{\mathrm{ma}}(x_{i+1,i}, x_{i,i-1}, \theta) = 2\varepsilon_{\mathrm{ma}} \sum_{j=1}^{4} [(\sigma_{\mathrm{ma}}/R_j)^{12} - (\sigma_{\mathrm{ma}}/R_j)^6]. \tag{37}$$

Here $\varepsilon_{\mathrm{ma}}$ and σ_{ma} are parameters and the R_j are the distances between any two non-bonded atoms (see figure 1):

$$\begin{aligned} R^2_{1,2} &= (x_{i+1,i})^2 + r^2_{A,B} \mp 2r_{A,B}\, x_{i+1,i} \cos\theta \\ R^2_{3,4} &= (x_{i,i-1})^2 + r^2_{B,A} \mp 2r_{B,A}\, x_{i,i-1} \cos\theta \end{aligned} \tag{38}$$

where $r_{A,B} = m_{B,A}\, r^0/m_{AB}$. The equilibrium configuration for the model potential (35) corresponds to $x^0_{s,s+1} = d_0$ (if $s \neq i-1, i$), $x^0_{i,i-1} = x^0_{i+1,i} = x_{\mathrm{ma}}$ and $\theta = 90°$.

Table 2. Vibrational frequencies measured by Dubost (1975a, b) and their assignment for monomeric CO trapped in noble-gas lattices.

	ν (cm^{-1})				Assignment
Matrix	Ne	Ar	Kr	Xe	
Strong	2136·4	——	——	——	Isolated CO in a large site
bands	2140·9	2138·6	2135·7	2133·2	Isolated librating CO ($\Delta n_{\mathrm{lib}} = 0$)($\nu_{\mathrm{r}}$)
Weak	2156·7	2150	2146	2143	Isolated librating CO ($\Delta n_{\mathrm{lib}} = 1$)
bands	2160·5	——	——	——	

By differentiating (35), the g and λ constants tabulated in table 1 are obtained immediately. The AC expression, equations (15), (18), (27), (32) and (34), is now parametrized by $\varepsilon_{\mathrm{aa}}$, σ_{aa}, $\varepsilon_{\mathrm{ma}}$ and σ_{ma}. In figure 2 we show the various contributions, represented by the λ constants, to the far-infrared component $\sigma_{\mathrm{L}}(\nu)$, $\nu = \omega/2\pi$. If $\lambda_1 = \lambda_2 = \lambda_3 = 0$, we obtain the static approximation and, as discussed in §3.2, the unperturbed librational absorption is a delta-function centred at the librational frequency $\omega_{\mathrm{L}} = 2\pi\nu_{\mathrm{L}}$. If the only perturbation is λ_3 (a perfect chain coupled to a harmonic librator figure 2(*a*)) then the delta-function is very slightly shifted and broadened ($\Delta_{\mathrm{L}} \approx -10^{-3}$ cm^{-1} and $\Gamma_{\mathrm{L}} \approx 10^{-4}$ cm^{-1}). If $\lambda_3 \neq 0$ and $m \neq m_{AB}$, but $\lambda_1 = 0$ (figure 2*b*), the line is almost the same as before, except that the shift is in the other direction. The case $\lambda_3 \neq 0$ but $\lambda_2 = 0$ is shown in figure 2(*c*). Here the shift and width of the absorption line are significant, being of the order of 0·2 cm^{-1}. The situation shown in (*d*) includes all the effects. This shows that in the expression for $\sigma_{\mathrm{L}}(\nu)$ there are cross terms in $\lambda_1\lambda_2$ which are very im-

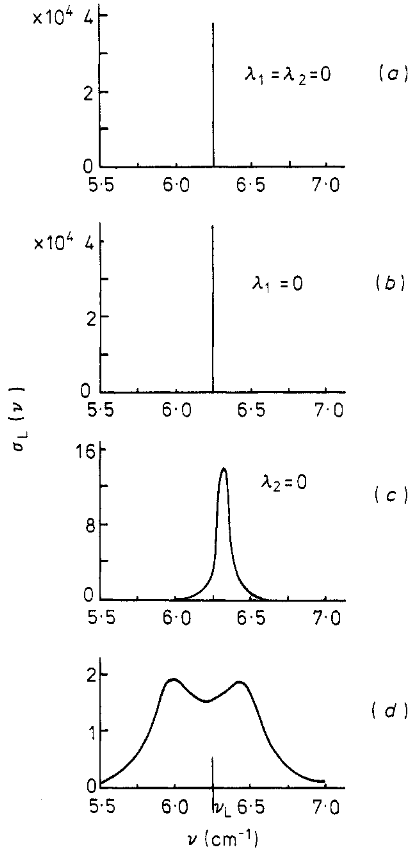

Figure 2. Contributions to $\sigma_L(\nu)$ of the force constant, the mass defects and the harmonic LPC, represented respectively by λ_1, λ_2 and λ_3. The calculation is performed for CO trapped in Ar, using the ε_{aa}, σ_{aa} values reported by Pollack (1964) for pure Ar, the molecular constants of CO given by Herzberg (1959) and setting $\varepsilon_{ma}/k_B = 10$ K, $\sigma_{ma} = 5$ Å. $\sigma_L(\nu)$ is given in units of $\kappa_L = 2M_2^2 \Lambda/3$.

portant, especially in making evident the possible existence of a resonance mode of the lattice.

In the far-infrared region we have also calculated (in § 3.4) a correction, $\sigma_C(\nu)$, resulting from induced dipole moments in the lattice. For CO–Ar, taking the same parameters as in the calculation shown in figure 2 and considering $\alpha_C = 1{\cdot}63 \times 10^{-24}$ cm^3 (Girardet and Robert 1971), this correction gives a background of 10^{-5}, in the same units as those used in figure 2(*d*).

In the near-infrared region we go a step further. From Dubost's measurements (Dubost and Abouaf-Marguin 1972, Dubost 1975a, b), the absorption lines of monomeric CO trapped in noble-gas matrices do not depend on the impurity concentration. This fact is verified because the relative intensity of the two lines is conserved with varying concentration. Nevertheless, there is a considerable increase in the widths of these lines when, at fixed concentration, the thickness of the sample is increased. One possible suggestion is that, in the crystallites composing the sample, there is formation of chain defects, each chain being of the type considered in this work. This amounts to saying that the force constants in the two dimensions of space different from the one considered here are negligible. Now, if these defects are formed following different axes of symmetry in each crystallite, then there will be an extra broadening of the inhomogeneous type, which we shall consider in a future publication. To make a qualitative comparison we try a fit with experimental results: we fix the values of $\varepsilon_{\mathrm{aa}}$ and σ_{aa} as those of a pure noble-gas solid (Pollack 1964) and fit $\varepsilon_{\mathrm{ma}}$ and σ_{ma} on one part of the spectrum, given in table 2. We expect from this fitting: (i) to see if the rest of the calculated lineshape function is in agreement with the measured spectrum profile; and (ii) to predict what will be the spectrum in the far-infrared region, for which there is no experimental evidence yet.

Taking into account the fact that we are not interested in obtaining the best values for $\varepsilon_{\mathrm{ma}}$ and σ_{ma} from a fit on the spectrum, but in seeing if the LPC is a good source of line broadening, we adjust only two points of the spectrum. The first one is to make the maximum of $\sigma_{\mathrm{V}}(\nu)$ coincide with the experimental assignment corresponding to $\Delta n_{\mathrm{lib}} = 0$. Therefore, the parameter fixed is ν_{V}, the molecular internal vibration frequency. The second point corresponds to the assignment $\Delta n_{\mathrm{lib}} = 1$. We fit the position of this line

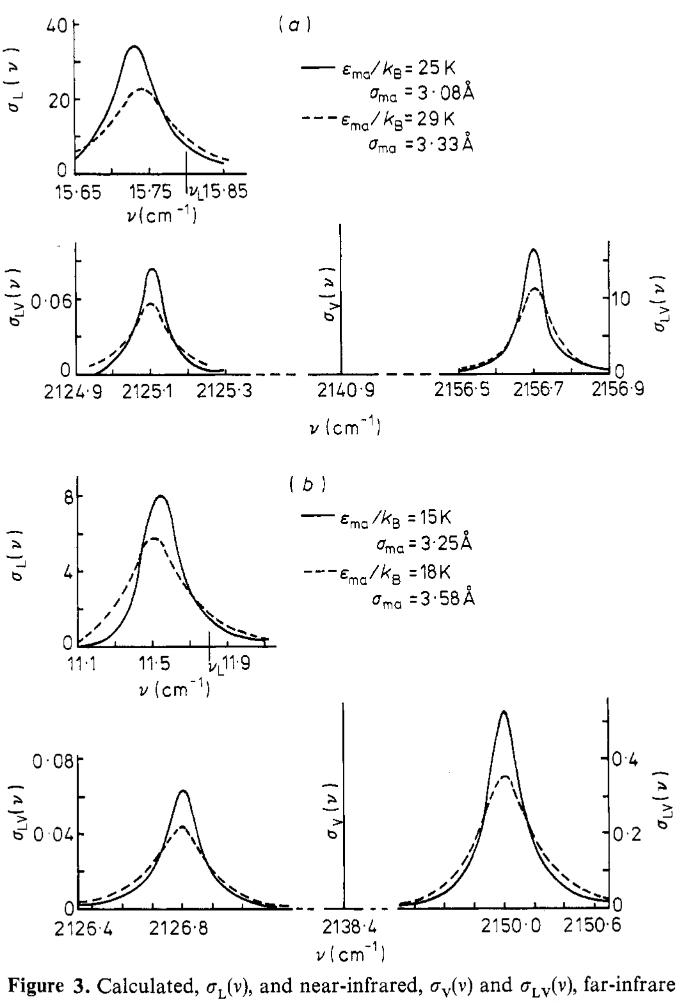

Figure 3. Calculated, $\sigma_{\mathrm{L}}(\nu)$, and near-infrared, $\sigma_{\mathrm{V}}(\nu)$ and $\sigma_{\mathrm{LV}}(\nu)$, far-infrared band profiles of CO trapped in (*a*) an Ne matrix and (*b*) an Ar matrix. The functions $\sigma_{\mathrm{L}}(\nu)$, $\sigma_{\mathrm{V}}(\nu)$ and $\sigma_{\mathrm{LV}}(\nu)$ are given in units of $\kappa_{\mathrm{L}} = \frac{2}{3}M_2^2\Lambda$, $\kappa_{\mathrm{V}} = \frac{4}{3}M_1^2\Lambda$ and $\kappa_{\mathrm{LV}} = \frac{2}{3}M_3^2\Lambda$, respectively. $\sigma_{\mathrm{V}}(\nu)$ is a delta-function and is not represented to scale.

with the higher-frequency maximum of $\sigma_{LV}(\nu)$, thus fixing values for the pair of parameters $(\varepsilon_{ma}, \sigma_{ma})$. Even though this poor fitting does not supply a unique pair $(\varepsilon_{ma}, \sigma_{ma})$, their influence on the lineshape function is not very strong and a qualitative comparison with experiment is possible. A family of pairs $(\varepsilon_{ma}, \sigma_{ma})$ such that x_{ma} varies in a region compatible with the van der Waals radii have been given elsewhere (Blaisten-Barojas 1974).

In figures 3 and 4 we have plotted the calculated line profiles for CO isolated in the four noble-gas matrices Ne, Ar, Kr and Xe for two pairs $(\varepsilon_{ma}, \sigma_{ma})$. For CO trapped in

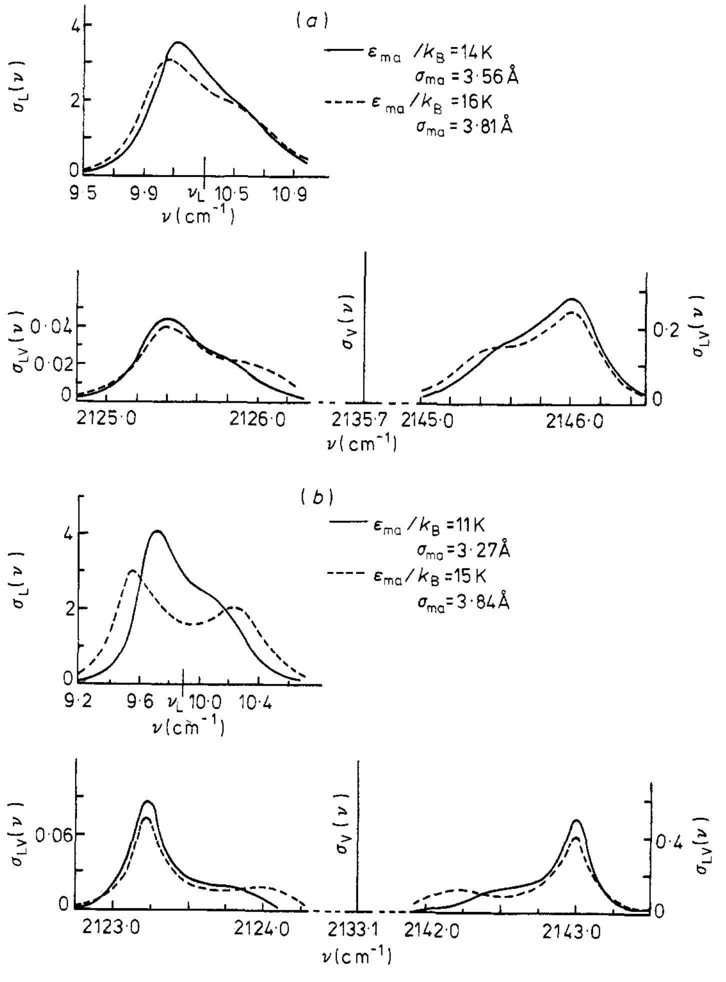

Figure 4. As figure 3 except for CO trapped in (*a*) a Kr matrix and (*b*) a Xe matrix.

Ne and Ar matrices, figures 3(*a*) and (*b*), the profile is almost Lorentzian except for an asymmetry in the tails. For CO isolated in Kr and Xe matrices, figures 4(*g*) and (*b*), the lineshape function in the far-infrared is very distorted, making evident some structure which we attribute to a resonance mode of the perturbed lattice. In the near-infrared region, this resonance mode is also evident in the structure of the two absorptions symmetrically placed with respect to the pure vibration line (a delta-function). This stresses the point mentioned in § 3.3 that the librational motion acts as a probe and can be used to study the dynamics of the lattice. It can be seen in figures 3 and 4 that $\varepsilon_{\mathrm{ma}}$ decreases as a function of the size of the host matrix atoms (Ne → Xe), while σ_{ma} and the linewidth increase. This is an indication that if the volume at the disposal of the trapped molecule increases, then the impurity is less strongly bound to its neighbours. As a consequence, the molecule librates with a smaller frequency, having more time to 'see' its translation, and therefore the LPC effect increases, giving rise to larger widths of the lines represented by $\sigma_{\mathrm{L}}(\nu)$ and $\sigma_{\mathrm{LV}}(\nu)$. The central line corresponding to $\sigma_{\mathrm{V}}(\nu)$ is not broadened because in the LPC model no interaction is allowed between the molecular internal vibration and the phonons or the librational motion. Lifting these restrictions would lead to broadening of the pure vibration line (Blaisten-Barojas and Allavena 1973).

The experimental data reported by Dubost and Abouaf-Marguin (1972) and Dubost (1975a, b) at 7 K show, in all cases, a narrow line ($\Delta v = 1$, $\Delta n_{\mathrm{lib}} = 0$) and a broader line at higher frequencies presenting a shoulder towards the side of the principal line ($\Delta v = 1$, $\Delta n_{\mathrm{lib}} = 1$). The widths of these two lines increase as a function of the size of the host atoms. When the experiments are performed at higher temperatures, 20 K to 40 K, there is evidence of a third line symmetrically placed with respect to the principal line towards its lower-frequency side. When comparing our results (figures 3 and 4) with these experiments, we find good qualitative agreement of the following features: (i) the width of the line corresponding to $\Delta v = 1$, $\Delta n_{\mathrm{lib}} = 1$, the high-frequency maximum of $\sigma_{\mathrm{LV}}(\nu)$, increases with the size of the host atoms; (ii) the shoulder observed experimentally can be explained by the presence of the lattice resonance mode; and (iii) the low-frequency maximum of $\sigma_{\mathrm{LV}}(\nu)$, on average ten times weaker than the high-frequency maximum, explains the third line, observed only with increasing temperature. This line should be assigned to the $\Delta v = 1$, $\Delta n_{\mathrm{lib}} = -1$ transition which is also broadened by the LPC influence and, as pointed out in § 3.3, is only present if $T \neq 0$.

To our knowledge there are no measurements of the far-infrared spectra of CO trapped in noble-gas crystals. Therefore, from this calculation, we predict that the LPC is also responsible for a broad absorption, $\sigma_{\mathrm{L}}(\nu)$, at a frequency lower than the phonon-band cut-off, representing the librational motion coupled to many infrared-active lattice normal modes. The lack of symmetry in the neighbourhood of the impurity site suggests that the far-infrared spectrum of this model will be closer to the pure CO crystal than to the pure noble-gas crystal. The important difference is that while in solid CO there is a band of librations (Ron and Schnepp 1967), in this case we have only one librational mode. For this reason there is no place for comparison with calculated resonance and localized modes of optically-activated phonons of noble-gas crystals containing impurities (Mannheim 1968, Mannheim and Cohen 1971, Cohen and Klein 1974).

5. Conclusion

This paper is devoted to an exhaustive analysis of the role that dynamical interactions play on the broadening of absorption lines. A one-dimensional model was the starting point to consider coupling between the quenched molecular rotation (libration) and phonons: the libron-phonon coupling (LPC). The AC was split into four components, equation (15). Three of them, $\sigma_{\mathrm{V}}(\omega)$, $\sigma_{\mathrm{L}}(\omega)$ and $\sigma_{\mathrm{LV}}(\omega)$ (equations (18), (27) and (32) in the harmonic approximation) are associated with the molecular permanent dipole moment and give by far the more important contributions to the AC. In the anharmonic approximation, we have worked out only a correction for $\sigma_{\mathrm{L}}(\omega)$, equations (22) and (24). The fourth component, $\sigma_C(\omega)$, equation (34), is due to the dipole moment induced in the lattice because of the molecular impurity present. As was pointed out in § 4, for the case of carbon monoxide isolated in an argon matrix, $\sigma_C(\omega)$ is approximately 10^{-5} times smaller than $\sigma_L(\omega)$. The pure vibration absorption, $\sigma_V(\omega)$, is a delta-function centred at the modified molecular vibration frequency $\bar{\omega}_V$. The function $\sigma_L(\omega)$ gives a broad absorption in the far-infrared resulting from the libration of the molecule. The width and shift of this line with respect to the static approximation (a delta-function centred at ω_L) are due to the LPC. As shown in § 4, figure 2, a resonance mode of the lattice may be infrared-activated by the molecular libration. The structure of the far-infrared absorption line is also evident in the medium-infrared, figures 3 and 4, in which $\sigma_{LV}(\omega)$ gives rise to two lines, corresponding to $\Delta v = 1, \Delta n_{\text{lib}} = \pm 1$. Anharmonicities are responsible for a lineshape function very sensitive to temperature changes.

When a comparison with experimental results is attempted, good qualitative agreement is obtained, as pointed out at the end of § 4. The analysis carried out in this section suggests that in the crystallites composing the samples there is formation of chain defects, and hence the one-dimensional model leaves several interesting problems still to be looked at. Among them, the most relevant are (i) to open new channels of energy exchange by introducing a correlation among the molecular internal vibration with the quenched rotation coupled to phonons, and (ii) to consider the statistical effect on the spectrum of impurities in slightly different environments.

We do not expect to study the dynamics of a real lattice with this one-dimensional model. Nevertheless, we can already conclude from the results of this paper that the dynamical interaction among particles of the system (LPC) in the calculation of the absorption coefficient is an appropriate and non-negligible source of line broadening.

Acknowledgments

One of the authors (EBB) would like to thank Professor S Fujita for many useful discussions, Professor R Peierls for his comments on the presentation of this work and Dr J Barojas for his suggestions regarding the computations involved in this study.

Appendix

The average values of the operators φ and π are approximated by the average values calculated with respect to a non-interacting Hamiltonian $H^0 = H^0_C + H^0_M$. Here H^0_C and H^0_M are, respectively, the Hamiltonians of a perfect chain (equation (6*a*) in which $\lambda_1 = \lambda_2 = 0$) and of two independent harmonic oscillators ($\lambda_0 = 0$). Therefore, the average value of an operator θ is given by

$$\langle\theta\rangle \simeq \mathrm{Tr}\,[\exp(-H^0/k_BT)\,\theta]/\mathrm{Tr}[\exp(-H^0/k_BT)]. \tag{A1}$$

We obtain that $\langle\varphi_V\rangle = \langle\varphi_L\rangle = \langle\varphi_k\rangle = 0$ and also

$$\begin{aligned}\langle\varphi_V^2\rangle &= -\langle\pi_V^2\rangle = \tfrac{1}{2}\coth(\hbar\omega_V/2k_BT)\\ \langle\varphi_L^2\rangle &= -\langle\pi_L^2\rangle = \tfrac{1}{2}\coth(\hbar\omega_L/2k_BT)\\ \langle\varphi_k\varphi_{k'}\rangle &= -\langle\pi_k\pi_{k'}\rangle = \tfrac{1}{2}\delta_{k-k'}\coth(\hbar\omega_k/2k_BT).\end{aligned} \tag{A2}$$

If for brevity we write $\omega_\pm = \omega \pm \omega_{\rm V}$, $I_\pm = I(\omega_\pm)$ and $R(\omega) = \omega_+ I_+ - \omega_- I_-$, then the six functions $Q_i(\omega)$, $i = 0, 1, \ldots, 5$, used in equation (37) are:

$$\begin{aligned}
Q_0(\omega) &= \langle\varphi_{\rm L}^2\rangle\, \omega_{\rm V}(\omega^2 - \omega_{\rm V}^2 + \omega_{\rm L}^2) + \langle\varphi_{\rm V}^2\rangle\, \omega_{\rm L}(\omega^2 + \omega_{\rm V}^2 - \omega_{\rm L}^2)\\
Q_1(\omega) &= R(\omega)\{[1 - 2\lambda_2(I_+ + I_-)]\,(\omega_+^2 I_+ - \omega_-^2 I_-)\\
&\qquad + 2\lambda_2 R(\omega)[4\omega I_+ I_-(1 + \lambda_2\zeta - \zeta\omega_+\omega_-/\omega_{\rm c}^2) - \zeta(\omega_+ I_+ + \omega_- I_-)]\}\\
Q_2(\omega) &= (\sqrt{2}/\omega_{\rm c}^2)R(\omega)\llbracket 1 + (16\lambda_1/\omega_{\rm c}^4)(\omega_{\rm c}^2 + \omega_+^2 I_+ + \omega_-^2 I_-) - 2\lambda_2(I_+ + I_-) + 4\lambda_2^2 I_+ I_-\\
&\qquad + (256\lambda_1^2/\omega_{\rm c}^8)\,[\tfrac{1}{4}\omega_{\rm c}^4 + \tfrac{1}{2}\omega_{\rm c}^2(\omega_+^2 I_+ + \omega_-^2 I_-) + \omega_+^2\omega_-^2 I_+ I_-]\\
&\qquad - (32\lambda_1\lambda_2/\omega_{\rm c}^4)\,[(\omega_+ I_+ + \omega_- I_-)^2 + \omega_{\rm c}^2(I_+ + I_-) + 2(\omega^2 + \omega_{\rm V}^2)\, I_+ I_-]\\
&\qquad - (512\lambda_1^2\lambda_2/\omega_{\rm c}^8)\,\{\tfrac{1}{4}\omega_{\rm c}^4(I_+ + I_-) + \tfrac{1}{2}\omega_{\rm c}^2[(\omega_+ I_+ + \omega_- I_-)^2 + 4\omega^2 I_+ I_-]\\
&\qquad + \omega_+\omega_- I_+ I_-[3\omega(\omega_+ I_+ + \omega_- I_-) + \omega_{\rm V} R(\omega)]\} + (64\lambda_1\lambda_2^2/\omega_{\rm c}^4)\\
&\qquad \times I_+ I_-[\omega_{\rm c}^2 + 2\omega(\omega_+ I_+ + \omega_- I_-)] + (512/\omega_{\rm c}^8)\, I_+ I_-\\
&\qquad \times \{\omega_{\rm c}^2(\tfrac{1}{2}\omega_{\rm c}^2 + \omega_+^2 I_+ + \omega_-^2 I_-) + \omega_+\omega_-\,[\tfrac{1}{2}\omega_{\rm c}^2(I_+ + I_-) + 4\omega^2 I_+ I_-]\}\rrbracket
\end{aligned}\tag{A3}$$

$$\begin{aligned}
Q_3(\omega) &= R(\omega)\,(\omega_{\rm c}^2 + \omega_+^2 I_+ + \omega_-^2 I_-) + 2\lambda_2\{(\omega_+^2 I_+ + \omega_-^2 I_-)\,(\omega_+ I_+^2 - \omega_- I_-^2)\\
&\qquad + R(\omega)\,[2I_+ I_-(2\omega_{\rm V}^2 - \omega^2) + \omega_{\rm c}^2(I_+ + I_-)]\} + 4\lambda_2^2 I_+ I_-\\
&\qquad \times \{2\omega_{\rm V} I_+ I_-\,[2(2\omega^2 - \omega_{\rm V}^2) - \omega_+^2 I_+^2 - \omega_-^2 I_-^2] - \omega_{\rm c}^2 R(\omega)\}\\
&\qquad - (8\lambda_1/\omega_{\rm c}^{\prime\prime})\, R(\omega)\,[\omega_{\rm c}^4 + 2\omega_{\rm c}^2\,(\omega_+^2 I_+ + \omega_-^2 I_-) + 4\omega_+^2\omega_-^2 I_+ I_-]\\
&\qquad + (16\lambda_1\lambda_2/\omega_{\rm c}^4)\,\llbracket\omega_{\rm c}^2[\omega_+ I_+^2(\omega_{\rm c}^2 + \omega_+^2 I_+) + \omega_-^3 I_-^3] + 2\omega_+\omega_- I_+ I_-\\
&\qquad \times \{\omega_{\rm V}[4\omega_+\omega_- I_+ I_- - 3(\omega_+ I_+ + \omega_- I_-)^2] - 3\omega(\omega_+^2 I_+^2 - \omega_-^2 I_-^2)\}\\
&\qquad + \omega_{\rm c}^2 I_+ I_-\,\{\omega_{\rm V}[2\omega_{\rm c}^2 + 5(\omega_+^2 I_+ + \omega_-^2 I_-)] - \omega(\omega_+^2 I_+ + 3\omega_-^2 I_-)\\
&\qquad + 2\omega_+\omega_-(\omega_- I_+ - \omega_- I_- - \omega_+ I_+) - \omega_{\rm c}^2\omega_-\}\rrbracket\\
&\qquad - (64\lambda_1\lambda_2^2/\omega_{\rm c}^4)\, I_+ I_-\,\llbracket\omega_{\rm c}^2[4\omega_{\rm V}\,(\omega^2 + \omega_{\rm V}^2)\, I_+ I_- + \omega_{\rm V}\omega_{\rm c}^2(I_+ + I_-)\\
&\qquad + \omega(\omega_{\rm c}^2 + 2\omega_+^2 I_+ + 2\omega_-^2 I_-)] + \omega_+\omega_-\{\omega_{\rm V} I_+ I_-[2\omega_{\rm c}^2 - 5\omega(\omega_+ I_+ + \omega_- I_-)\\
&\qquad + 3\omega_{\rm V} R(\omega)] - \omega_-^2 I_-^2(\omega I_+ + \omega_- I_-) + \omega_+ I_+^2(\omega I_- + \omega_+ I_+)\}\rrbracket\\
Q_4(\omega) &= -\,2\lambda_2^2\omega_+\omega_- I_+ I_-[\omega\omega_{\rm V} R(\omega)\,(I_+ - I_-)\\
&\qquad + (\zeta/\omega_{\rm c}^2)\,(\omega^2 + \omega_{\rm V}^2 - \omega_{\rm L}^2)\, I_+ I_-(\omega_{\rm c}^2\omega_{\rm V} + \omega_+^3 I_+ - \omega_-^3 I_-)]\\
Q_5(\omega) &= (\lambda_3^2\omega_{\rm L}/\omega_{\rm c}^4)\,\{\omega_{\rm c}^4[1 + 2\lambda_2\,(2\lambda_2 I_+ I_- - I_+ - I_-)]\\
&\qquad + 2\omega_{\rm c}^2[\omega_+^2 I_+ + \omega_-^2 I_- - 2\lambda_2\,(\omega_+^2 I_+^2 + \omega_-^2 I_-^2 + 4\omega_{\rm V}^2 I_+ I_-)]\\
&\qquad + 16\lambda_2 I_+ I_- R(\omega)\,[\omega_+\omega_-(\omega_{\rm V} + R(\omega)) + \lambda_2\omega_{\rm V}\omega_{\rm c}^2]\}.
\end{aligned}$$

References

Agrawal B K 1971 *Phys. Rev.* B 3 1843–56

Blaisten-Barojas E 1974 *Thesis* Paris VI, France

Blaisten-Barojas E and Allavena M 1973 *Int. J. Quant. Chem.* 7 195–213

—— 1975 *J. Chim. Phys.* 72 409–10

Bonch-Bruevich V L 1966 *Proc. Int. School of Physics 'Enrico Fermi' Course XXXIV* (New York: Academic Press) pp 331–78

Born M and Huang K 1954 *Dynamical Theory of Crystal Lattice* (London: Oxford UP) p 208

Cohen S S and Klein M L 1974 *J. Chem. Phys.* **61** 3210–6

Davies J B and Hallam H E 1972 *J. Chem. Soc. Faraday Trans.* II **68** 509–12

Dawber P G and Elliott R J 1963a *Proc. R. Soc.* **273**A 222–36

—— 1963b *Proc. Phys. Soc.* **81** 453–60

Devonshire A F 1936 *Proc. R. Soc.* A **153** 601–21

Dubost H 1975a *Thesis* Paris XI, France

—— 1976 *Chem. Phys.* **12** 139–51

Dubost H and Abouaf-Marguin L 1972 *Chem. Phys. Lett.* **17** 269–73

Elliott R J and Taylor D W 1964 *Proc. Phys. Soc.* **83** 189–97

Flygare W H 1963 *J. Chem. Phys.* **39** 2263–73

Friedman H and Kimel S 1965 *J. Chem. Phys.* **43** 3925–39

—— 1967 *J. Chem. Phys.* **47** 3589–605

Girardet C 1972 *Thesis* Besançon, France

Girardet C and Robert D 1971 *J. Molec. Struct.* **7** 31–44

Girardet C, Robert D and Galatry L 1971 *J. Chem. Phys.* **55** 5304–22

Herzberg G 1959 *Spectra of Diatomic Molecules* (New York: van Nostrand)

Jiang G J, Person W B and Brown K G 1975 *J. Chem. Phys.* **62** 1201–16

Kubo R 1957 *J. Phys. Soc. Japan* **12** 570–86

Landau L D and Lifshitz E M 1959 *Statistical Physics* (Oxford: Pergamon Press) p 391

Mannheim P D 1968 *Phys. Rev.* **165** 1011–8

Mannheim P D and Cohen S S 1971 *Phys. Rev.* B **4** 3748–56

Mannheim P D and Friedman H 1970 *Phys. Stat. Solidi* **39** 409–20

Maradudin A A 1966a *Solid St. Phys.* (New York: Academic Press) **18** 273–420

—— 1966b *Solid St. Phys.* (New York: Academic Press) **19** 1–134

Maradudin A A, Montroll E W and Weiss G V 1971 *Theory of Lattice Dynamics in the Harmonic Approximation* (New York: Academic Press)

Messiah A 1965 *Mécanique Quantique* (Paris: Dunod)

Meyer B 1971 *Low Temperature Spectroscopy* (New York: American Elsevier)

Milligan D and Jacox M E 1972 *MTP Int. Rev. Sci.: Spectrosc.* **3** 1–32

Peierls R E 1955 *Quantum Theory of Solids* (London: Oxford UP)

Pollack G L 1964 *Rev. Mod. Phys.* **36** 748–808

Ron A and Schnepp O 1967 *J. Chem. Phys.* **46** 3991–8

Schnepp O and Jacobi N 1972 *Adv. Chem. Phys.* **22** 205–313

Sweet J R and Steele W A 1967 *J. Chem. Phys.* **47** 3022–35

Tyablikov S V and Bonch-Bruevich V L 1962 *Adv, Phys.* **11** 317–47

Work R N and Fujita S 1966 *J. Chem. Phys.* **45** 3779–87

Ziman J M 1960 *Electrons and Phonons* (London: Oxford UP) p 30

Zubarev D N 1960 *Sov. Phys.–Usp.* **3** 320–45