

# An Application of Green's Functions to the Study of the Vibration- Translation Coupling of Trapped Oscillators in a Linear Chain

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## Abstracts

The Green functions and Kubo linear-response theory are used to calculate the absorption coefficient of a collection of diatomic molecules embedded in a one-dimensional lattice. The effect of the environment is restricted to the coupling between the molecular internal vibration and lattice vibrations. For the molecular oscillators, both harmonic and anharmonic models are considered. The absorption line shape is expressed in closed form whether the molecular frequency falls outside or within the allowed phonon frequency range. In both cases a frequency shift is found. In the anharmonic case there is a broadening of the absorption lines. Expressions for the shift and line width are given.

Les fonctions de Green et la théorie de réponse linéaire de Kubo ont été employées pour calculer le coefficient d'absorption d'un ensemble de molécules diatomiques piégées dans un réseau unidimensionnel. L'effet du milieu est restreint au couplage entre la vibration moléculaire interne et les vibrations du réseau. Des modèles harmoniques et anharmoniques ont été considérés pour les oscillateurs moléculaires. La forme de la raie d'absorption est représentée par une expression analytique finie dans les deux cas où la fréquence moléculaire se trouve à l'intérieur ou à l'extérieur de la bande de fréquences permises des phonons. Dans le cas anharmonique il y a un élargissement des raies d'absorption. On donne des expressions pour le déplacement et la largeur de la raie.

Die Green'schen Funktionen und die Kubo'sche "linear response"-Theorie werden angewandt um den Absorptionskoeffizient einer Sammlung von zweiatomigen Molekülen zu berechnen, die in einem eindimensionalen Gitter eingebettet sind. Die Einwirkung der Umgebung wird zur Kopplung zwischen der internen Molekülschwingung und den Gitterschwingungen begrenzt. Für die Moleküloszillatoren werden sowohl harmonische als auch anharmonische Modelle betrachtet. Die Form der Absorptionslinie wird in geschlossener Form ausgedrückt, in den zwei Fällen wenn die Molekülfrequenz ausserhalb oder innerhalb des erlaubten Phononenfrequenzintervalls liegt. In beiden Fällen wird eine Frequenzverschiebung gefunden. Im anharmonischen Fall ergibt sich eine Erweiterung der Absorptionslinie. Ausdrücke für die Verschiebung und die Linienbreite werden gegeben.

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## 1. Introduction

The Kubo linear-response theory [1] and Green functions method [2, 3] have been widely used in solid state physics to study impurity or defect-induced effects on dynamical properties of crystals [4, 5]. However, these methods have not yet been applied to problems related to molecules isolated in a matrix where the effects of crystal environment on the molecular spectrum may be important [6]. The main goal of this paper is to apply the Green functions method to a one-dimensional model in order to derive an analytical expression for the molecular absorption coefficient. The model considers only a simple interaction between the molecules and their environment, i.e., a coupling between the internal vibration of each diatomic impurity and its quantized translation. Such a coupling is certainly not dominant in most of the cases found in matrix spectroscopy, but it can be a good starting point to further studies concerning matrix interaction with molecular motion. To carry out a comparison with experimental data, a more realistic situation should be studied, such as rotation-vibration-translation coupling in a three-dimensional lattice.

The simplest one-dimensional system is that of a collection of diatomic molecular defects embedded in a linear chain of atoms in which each particle interacts with its two nearest neighbors. We will discuss this model in Section 2 and write down the Hamiltonian of the system. In Section 3 we will calculate  $G(\omega)$ , the Fourier transform of the Green function for the dipole moment, by decoupling the infinite set of coupled equations of motion via a procedure already known [2, 3, 7]. Next  $G(\omega)$  is approximated as a form exact up to the second order in the coupling parameter. In Section 4 we will give expressions for the absorption coefficient, frequency shift and width of the molecular spectral lines. As it is expected, we find that the interaction between the molecular vibration and the phonon band leads to a broadening of the absorption lines only if the molecular frequency is within the phonon band or if the molecules are considered as anharmonic oscillators.

## 2. Model

The model consists of a linear chain containing  $n$  atoms of mass  $m$  and  $N$  diatomic impurities of mass  $m^A + m^B$ . Every impurity  $AB$  is an heteronuclear diatomic molecule with internuclear axes parallel to the chain. Thus, the total number of particles in the system is  $n + 2N$ . The lattice is divided into  $N + n$  unit cells of length  $a$ , each containing one site. The center of mass,  $X_\alpha^G$ , of the  $\alpha$ th molecule is at the site  $X_\alpha$ . Each atom can be specified by its motion in one cell, while every molecule introduces an additional degree of freedom within a given cell. Consequently, molecules  $AB$  have two motions: in one, the atoms  $A$  and  $B$  move in phase with one another, in the other they move out of phase. The molecular force constants are  $K$  and any two neighboring atoms  $m$ ,  $m$  and  $m^A$  or  $m$  and  $m^B$  are

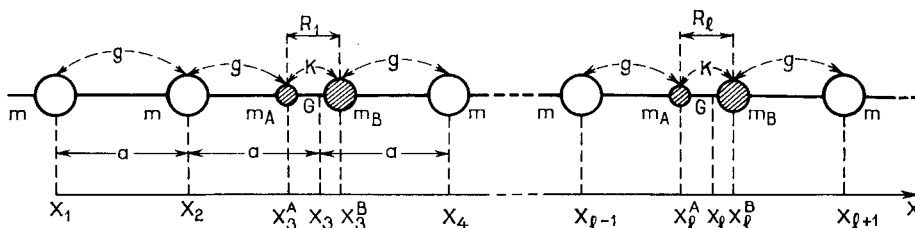


Figure 1. A schematic representation of the system. The various  $X_i$  are the equilibrium atomic positions,  $G$  is the molecular center of mass and  $R_\alpha$  the inter-nuclear distance of the  $\alpha$ -th molecule.  $a$  is the lattice spacing,  $K$  is the molecular force constant. Nearest neighbors interactions are pictured by  $g$ .

linked by force constants  $g$ . For simplicity, it is assumed that  $m = m^A + m^B$  and that all molecules are equally oriented and periodically distributed along the chain, as seen in Figure 1. The concentration of molecules,  $N/n$ , is low enough to neglect any direct interaction between them. We assume that the  $N$  molecules can be represented both by harmonic and anharmonic oscillators; the two cases will be considered.

We are interested in studying the infrared absorption spectrum of this system when it is placed in an external electromagnetic field. Hence, two operators will be necessary: the Hamiltonian and the dipole moment of the system. We suppose that only the molecules are active systems, so that the external field  $E(t)$  couples to the molecular dipole moment  $M$  and the whole system is perturbed by the coupling term  $-M \cdot E(t)$ .

In the first case (the molecules are harmonic oscillators) the Hamiltonian of the system before external perturbation, in the harmonic approximation and taking into account only nearest neighbors interactions, can be written as

$$(1) \quad H = \frac{1}{2} \sum_{i=1}^{n+2N} \left\{ \frac{p_i^2}{m_i} + g_i (x_{i+1} - x_i)^2 \right\}$$

where  $m_i$ ,  $x_i$  and  $p_i$  are the masses, displacements and moments of every individual particle, either atoms  $m$ ,  $m^A$  or  $m^B$ . The  $g_i$  are the force constants  $g$  or  $K$  according to the pair of particles involved.

It is readily verified that the introduction, in place of every pair of coordinates  $x_s^A, x_s^B$  of the  $s$ -th molecule, of two new coordinates  $x_s^G$  and  $R_s$

$$(2) \quad x_s^G = \frac{m^A x_s^A + m^B x_s^B}{m^A + m^B} \equiv x_s$$

$$R_s = x_s^B - x_s^A$$

will split the Hamiltonian (1) into three parts  $H_L$ ,  $H_M$  and  $V$ . Here the  $s$  is

associated with the  $s$ -th site in the lattice. The corresponding momenta are

$$(3) \quad \begin{aligned} p_s^G &= p_s^A + p_s^B \equiv p_s \\ P_s &= \mu_M \dot{R}_s \end{aligned}$$

where  $p^A = m^A \dot{x}^A$ ,  $p^B = m^B \dot{x}^B$  and  $\mu_M = m^A m^B / (m^A + m^B)$ .<sup>\*</sup> The resulting Hamiltonian can be written

$$H = H_L + H_M + V$$

where

$$(4) \quad \begin{aligned} H_L &= \frac{1}{2} \sum_{s=1}^{N'} \left\{ \frac{p_s^2}{m} + g(x_{s+1} - x_s)^2 \right\} \\ H_M &= \frac{1}{2} \sum_{\alpha=1}^N \left\{ \frac{P_\alpha^2}{\mu_M} + \bar{K} R_\alpha^2 \right\} \\ V &= -g / (m_A + m_B) \sum_{\alpha=1}^N R_\alpha \{ (x_\alpha - x_{\alpha-1}) m^B + (x_{\alpha+1} - x_\alpha) m^A \} \end{aligned}$$

with

$$\bar{K} = K + g \frac{m^A{}^2 + m^B{}^2}{(m^A + m^B)^2}$$

The term  $H_L$  represents the Hamiltonian of a linear chain of  $N' = n + N$  particles of mass  $m$ , because of the restriction  $m = m^A + m^B$ .  $H_M$  stands for the molecular Hamiltonian and represents an assembly of  $N$  independent and localized harmonic oscillators with force constants  $\bar{K}$ . As  $H_L$  depends only on lattice coordinates  $x$  and  $p$  and  $H_M$  depends only on molecular coordinates  $R$  and  $P$ , we associate their sum  $H_0 = H_L + H_M$  with a Hamiltonian of non-interacting particles. In that case the term  $V$  represents the interaction between these two systems showing that the molecules interact with each other only indirectly through their coupling to the lattice.

The assumptions  $m = m^A + m^B$  and that atoms  $m^A$  and  $m^B$  are linked to their nearest neighbors  $m$  by the same force constant  $g$  that links also two neighboring atoms  $m$ , are very restrictive. But it is of interest to simplify  $H_0$  as much as possible for two reasons. This simplification avoids the existence of localized or resonant modes. This fact reduces  $H_0$  to two independent systems instead of three or four as would appear according to the different situations  $m \gtrless m^A + m^B$  and/or  $g \gtrless g'$  (with  $g'$  the force constant linking atoms  $m$  to  $m^A$  or  $m^B$ ) [8]. Second, we

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<sup>\*</sup> The canonical variables  $x^A$  and  $x^B$  and their conjugated momenta  $p^A$  and  $p^B$  satisfy a set of commutations rules:  $[x^A, p^A] = [x^B, p^B] = i\hbar$  and  $[x^A, x^B] = [x^A, p^B] = [x^B, p^A] = [p^A, p^B] = 0$ . The transformation (2) preserves these rules, thus  $[x^G, R] = [x^G, P] = [R, p^G] = [p^G, P] = 0$  and  $[x^G, p^G] = [R, P] = i\hbar$ .

are primarily interested in studying the qualitative features of the pure phonon field on the internal vibration spectrum of the molecules.

It is convenient to write the terms  $H_L$  and  $V$  in Equation (4) using the transformation of the lattice coordinates  $x_s$  and  $p_s$  to normal coordinates expressed in terms of phonon creation and annihilation operators  $b_k^+$  and  $b_k$  [9]

$$(5) \quad \begin{aligned} x_s &= (1/2N'm)^{1/2} \sum_k \omega_k^{-1/2} (b_k + b_{-k}^+) e^{ikX_s} \\ p_s &= (m/2N')^{1/2} i \sum_k \omega_k^{1/2} (b_k^+ - b_{-k}) e^{-ikX_s} \end{aligned}$$

We take  $\hbar = 1$  throughout. The  $X_s$  are the equilibrium positions of lattice atoms,  $\omega_k = \omega_L |\sin \frac{1}{2}ka|^{1/2}$  are the normal mode frequencies,  $\omega_L = (4g/m)^{1/2}$  is the cutoff frequency,  $a$  is the lattice spacing and the allowed values of  $k$  are  $2\pi\nu/N'$  ( $\nu = 0, \pm 1, \pm 2, \dots, + N'/2$ ). The commutation rules for the new operators are

$$[b_k, b_{k'}^+] = \delta_{kk'}; \quad [b_k, b_{k'}] = [b_k^+, b_{k'}^+] = 0$$

Next we write the molecular Hamiltonian  $H_M$  as well as  $V$  in terms of dimensionless raising and lowering operators  $a_\alpha^+$  and  $a_\alpha$  defined as [10]

$$(6) \quad \begin{aligned} a_\alpha^+ &= (\mu_M \omega_M / 2)^{1/2} R_\alpha + i(2\mu_M \omega_M)^{-1/2} P_\alpha \\ a_\alpha &= (\mu_M \omega_M / 2)^{1/2} R_\alpha - i(2\mu_M \omega_M)^{-1/2} P_\alpha \end{aligned}$$

where  $\omega_M = (\bar{K}/\mu_M)^{1/2}$  is the molecular frequency. The operators  $a_\alpha^+$  and  $a_\alpha$  satisfy the commutation relations  $[a_\alpha, a_{\alpha'}^+] = \delta_{\alpha\alpha'}$ ,  $[a_\alpha^+, a_{\alpha'}^+] = [a_\alpha, a_{\alpha'}] = 0$ . In terms of these operators the Hamiltonian given in (4) may be written as

$$(7) \quad \begin{aligned} H_L &= \sum_k \omega_k (b_k^+ b_k + \frac{1}{2}) \\ H_M &= \sum_{\alpha=1}^N \omega_M (a_\alpha^+ a_\alpha + \frac{1}{2}) \\ V &= \frac{\lambda}{2} \sum_{\alpha=1}^N \sum_k f_\alpha(k) (b_k + b_{-k}^+) (a_\alpha + a_\alpha^+) \end{aligned}$$

where

$$\lambda = \frac{g}{m^A + m^B} (m\mu_M \omega_M)^{-1/2}$$

and

$$(8) \quad f_\alpha(k) = (N'\omega_k)^{-1/2} e^{ikX_\alpha} [m^A(1 - e^{ika}) - m^B(1 - e^{-ika})]$$

The  $X_\alpha$  are the equilibrium center of mass coordinates of the  $N$  molecules.

It is convenient to work with the related operators  $\varphi_k = (1/\sqrt{2})(b_k + b_{-k}^+)$ ,  $\pi_\alpha = (1/\sqrt{2})(b_k^+ - b_{-k})$ ,  $\varphi_\alpha = (1/\sqrt{2})(a_\alpha^+ + a_\alpha)$  and  $\pi_\alpha = (1/\sqrt{2})(a_\alpha^+ - a_\alpha)$  whose commutations rules are  $[\varphi_k, \pi_{k'}] = \delta_{kk'}$ ,  $[\varphi_k, \varphi_{k'}] = [\pi_k, \pi_{k'}] = 0$  and  $[\varphi_\alpha, \pi_{\alpha'}] = \delta_{\alpha\alpha'}$ ,  $[\varphi_\alpha, \varphi_{\alpha'}] = [\pi_\alpha, \pi_{\alpha'}] = 0$ . In terms of them the total Hamiltonian is given by

$$(9) \quad H = \frac{1}{2} \sum_k \omega_k (\varphi_k \varphi_{-k} - \pi_k \pi_{-k}) + \frac{\omega_M}{2} \sum_{\alpha=1}^N (\varphi_\alpha^2 - \pi_\alpha^2) + \lambda \sum_{\alpha=1}^N \sum_k f_\alpha(k) \varphi_k \varphi_\alpha$$

In the anharmonic case (the molecules are anharmonic oscillators) we only consider a cubic correction to the molecular Hamiltonian  $H_M$ , thus

$$(10) \quad H_M^A = \sum_{\alpha=1}^N \left[ \frac{1}{2} \left( \frac{P_\alpha^2}{\mu_M} + R R_\alpha^2 \right) + \frac{\zeta}{6} R_\alpha^3 \right]$$

where  $\zeta$  is the anharmonic constant. By using the operators  $\varphi_\alpha$  and  $\pi_\alpha$  already defined, the anharmonic Hamiltonian may be written as

$$(11) \quad H^A = H + \eta \sum_{\alpha=1}^N \varphi_\alpha^3$$

where

$$\eta = \frac{\zeta}{6} (\mu_M \omega_M)^{-3/2}$$

and  $H$  is given in (9).

The dipole moment operator of the system is obtained by following the same steps as for the Hamiltonian. Since the system is composed of  $n$  inert atoms and  $N$  molecules having a permanent dipole moment  $M$ , the total dipole moment is

$$(12) \quad M_T = \sum_{\alpha=1}^N M_\alpha = M_0 + M_1 \sum_{\alpha=1}^N R_\alpha$$

where we assume that the dipole moment varies linearly with  $R$ . Here,  $M_0$  is the dipole moment in the equilibrium position and  $M_1 = (\partial M_\alpha / \partial R)_0$ . Let  $M = M_T - M_0$  be the dipole moment referred to the equilibrium configuration, then

$$(13) \quad M = \gamma \sum_{\alpha=1}^N \varphi_\alpha$$

where

$$\gamma = M_1 (\mu_M \omega_M)^{-1/2}$$

### 3. Green's Functions and Absorption Coefficient

According to the Kubo linear-response theory [1], the rate at which a perturbation does work on the perturbed system is

$$(14) \quad W = \Lambda \sigma(\omega)$$

where  $\sigma(\omega)$  is the absorption line-shape function which we call absorption coefficient and  $\Lambda$  is a constant. When the perturbation is  $-M \cdot E(t)$ , where  $E(t) = E_0(e^{i\omega t} + e^{-i\omega t})$  is the applied electromagnetic field oscillating at a frequency satisfying the resonant condition  $\omega \approx \omega_M$ , the absorption coefficient is given by

$$(15) \quad \sigma(\omega) = \omega \int_{-\infty}^t dt' \langle [M(t), M(t')] \rangle$$

The operators in this relation are evaluated in the interaction picture:  $M(t) = e^{iHt} M e^{-iHt}$  with  $M$  as given in (13). Here, the Hamiltonian  $H$  is given in (9) for the harmonic case and includes the correction (11) in the anharmonic case. The brackets  $\langle \rangle$  represent the time-independent average value of an operator

$$(16) \quad \langle Op \rangle = Z^{-1} \text{Tr } e^{-\beta H} Op$$

where  $Z$  is the partition function,  $\beta = 1/k_B T$ ,  $k_B$  is the Boltzmann's constant and  $T$  is the temperature of the system.

The absorption coefficient as defined in (15) is the imaginary part of the Fourier transform of the dipole moment Green function [2]

$$(17) \quad \langle\langle M, M \rangle\rangle = -i\theta(t-t') \langle [M(t), M(t')] \rangle$$

where the step function  $\theta(t-t') = 1$  if  $t > t'$  and  $\theta(t-t') = 0$  if  $t < t'$ . Thus, in order to determine the absorption coefficient  $\sigma(\omega)$  one must calculate the frequency-dependent Green function

$$(18) \quad \langle\langle M, M \rangle\rangle_\omega = \int_{-\infty}^{\infty} dt e^{i\omega t} \langle\langle M, M \rangle\rangle$$

For any two operators  $A$  and  $B$ , the Green function satisfies the equation [2]

$$(19) \quad i \frac{d}{dt} \langle\langle A, B \rangle\rangle = \delta(t) \langle [A, B] \rangle + \langle\langle [A, H], B \rangle\rangle$$

By Fourier transforming this equation one obtains

$$(20) \quad \omega \langle\langle A, B \rangle\rangle_\omega = \langle [A, B] \rangle + \langle\langle [A, H], B \rangle\rangle_\omega$$

The last term is a new Green's function of higher order for which one can write a similar equation and generate a third function of still higher order. This process may be continued to give rise to an infinite hierarchy of equations. In order to solve this hierarchy of equations approximately, one breaks off the set some place to obtain a self-contained system of equations involving only lower-order Greens' functions. This is done by means of a decoupling procedure [7, 11].

In our case, by virtue of Equation (13) the Green function to be studied is

$$(21) \quad \langle\langle M, M \rangle\rangle_{\omega} = \gamma^2 \sum_{\alpha\alpha'} \langle\langle \varphi_{\alpha}, \varphi_{\alpha'} \rangle\rangle_{\omega}$$

Therefore we are interested in knowing the Green function of the molecular internuclear displacements.

#### A. Harmonic oscillator

Consider a system with Hamiltonian given as in Equation (9). Then, according to (20), the Green function of the molecular internuclear displacement is

$$(22) \quad \omega \langle\langle \varphi_{\alpha}, \varphi_{\alpha'} \rangle\rangle_{\omega} = -\omega_M \langle\langle \pi_{\alpha}, \varphi_{\alpha'} \rangle\rangle_{\omega}$$

The new function  $\langle\langle \pi_{\alpha}, \varphi_{\alpha'} \rangle\rangle_{\omega}$  gives rise to the following equations:

$$(23) \quad \begin{aligned} \omega \langle\langle \pi_{\alpha}, \varphi_{\alpha'} \rangle\rangle_{\omega} &= -\delta_{\alpha\alpha'} - \omega_M \langle\langle \varphi_{\alpha}, \varphi_{\alpha'} \rangle\rangle_{\omega} - \lambda \sum_k f_{\alpha}(k) \langle\langle \varphi_k, \varphi_{\alpha'} \rangle\rangle_{\omega} \\ \omega \langle\langle \varphi_k, \varphi_{\alpha'} \rangle\rangle_{\omega} &= -\omega_k \langle\langle \pi_{-k}, \varphi_{\alpha'} \rangle\rangle_{\omega} \\ \omega \langle\langle \pi_{-k}, \varphi_{\alpha'} \rangle\rangle_{\omega} &= -\omega_k \langle\langle \varphi_k, \varphi_{\alpha'} \rangle\rangle_{\omega} - \lambda \sum_{\beta} f_{\beta}(-k) \langle\langle \varphi_{\beta}, \varphi_{\alpha'} \rangle\rangle_{\omega} \end{aligned}$$

After some elementary algebra we obtain

$$(24) \quad \langle\langle \varphi_{\alpha}, \varphi_{\alpha'} \rangle\rangle_{\omega} = \Omega \left( \delta_{\alpha\alpha'} + \sum_{\beta} F_{\alpha\beta} \langle\langle \varphi_{\beta}, \varphi_{\alpha'} \rangle\rangle_{\omega} \right)$$

where

$$(25) \quad F_{\alpha\beta} = \lambda^2 \sum_k f_{\alpha}(k) f_{\beta}(-k) \frac{\omega_k}{\omega^2 - \omega_k^2} \equiv F_{\beta\alpha}$$

and

$$\Omega = \frac{\omega_M}{\omega^2 - \omega_M^2}$$

Equation (24) can be condensed into matrix form

$$(26) \quad \boldsymbol{\varphi} = \Omega(\mathbf{1} + \mathbf{F}\boldsymbol{\varphi})$$

and

$$(27) \quad \boldsymbol{\varphi} = \Omega(\mathbf{1} - \Omega\mathbf{F})^{-1}$$

Here  $\mathbf{1}$  is the unitary matrix and the elements of  $\mathbf{F}$  are given in (25).  $\boldsymbol{\varphi}$  is an  $N \times N$  symmetric matrix characteristic of the inhomogeneous set of equations obtained when Equation (23) is written for all pairs of molecules. This system



may be solved when the number of impurities is small. The  $N$  solutions yield a tight packet of frequencies near the initially degenerate molecular frequency  $\omega_M$ . This phonon induced process is a source of inhomogeneous broadening. However, for low concentration,  $N/n \leq \frac{1}{3}$ , the width of this band is very small because the  $F_{\alpha\beta}$  in Equation (25) is negligible except for the diagonal term  $F_{\alpha\alpha}$ . If we neglect the inhomogeneous broadening, the problem of  $N$  molecules reduces to that of one molecule. Thus,

$$(28) \quad \langle\langle \varphi_\alpha, \varphi_\alpha \rangle\rangle_\omega = \frac{\omega_M}{\omega^2 - \omega_M^2 - \omega_M F_{\alpha\alpha}}$$

To evaluate  $F_{\alpha\alpha}$  we integrate over the linear chain density of states

$$\mathcal{D}(\omega_k) = \frac{2N'}{\pi} (\omega_L^2 - \omega_k^2)^{-1/2}$$

if  $\omega_k < \omega_L$  and  $\mathcal{D}(\omega_k) = 0$  otherwise. Then

$$(29) \quad F_{\alpha\alpha} = F(\omega) + iM(\omega)$$

where

$$F(\omega) = P \int_0^{\omega_L} d\omega_k \mathcal{D}(\omega_k) F_{\alpha\alpha}$$

$P$  indicates the principal part of the integral and

$$(30) \quad M(\omega) = \frac{\pi}{\omega} \mathcal{D}(\omega) F_{\alpha\alpha}(\omega_k = \omega)$$

The integral  $F(\omega)$  has been evaluated numerically and several significant figures are given in Section 4. From Equation (27), the imaginary part of  $\langle\langle \varphi_\alpha, \varphi_\alpha \rangle\rangle_\omega$  is

$$(31) \quad \text{Im} \langle\langle \varphi_\alpha, \varphi_\alpha \rangle\rangle_\omega = \frac{\omega_M^2 M(\omega)}{(\omega^2 - \omega_M^2 - \omega_M F(\omega))^2 + (\omega_M M(\omega))^2}$$

Near the resonant frequency  $\omega \approx \omega_M$  two situations may be distinguished:  $\omega_M > \omega_L$  and  $\omega_M < \omega_L$ . In the first case  $M(\omega) = 0$  and  $F(\omega) \approx F(\omega_M)$ , thus

$$(32) \quad \text{Im} \langle\langle \varphi_\alpha, \varphi_\alpha \rangle\rangle_\omega = \pi \omega_M \delta(\omega^2 - \bar{\omega}_M^2)$$

where  $\bar{\omega}_M^2 = \omega_M^2 + \omega_M F(\omega_M)$ . Since  $F(\omega)$  is a positive quantity, the absorption frequency is shifted towards the high-frequency region. The absorption peak

has no broadening in this case. The second situation  $\omega_M < \omega_L$  is less frequent, but can be illustrated by several heavy diatomic molecules for which, however, no matrix experimental data are available. Other examples can be found in the infrared spectra of solid Ar doped with Kr or Xe [12] which exhibit an absorption band indicating the presence of an induced dipole moment presumably associated with the pair Ar-Kr or Ar-Xe. Such a pseudomolecule would oscillate at very low frequency and may constitute a physical example of this case. Let us call  $\bar{\omega}$  the frequency at which Equation (31) has a maximum value. Near this point the functions  $F(\omega)$  and  $M(\omega)$  vary slowly with  $\omega$ . Therefore, if we replace them by  $F \cong F(\bar{\omega})$  and  $\bar{M} \cong M(\bar{\omega})$ , Equation (31) has a Lorentzian shape:

$$(33) \quad \text{Im} \langle \langle \varphi_\alpha, \varphi_\alpha \rangle \rangle_\omega = \frac{\omega_M^2 \bar{M}}{(\omega^2 - \omega_M^2 - \omega_M \bar{F})^2 + \omega_M^2 \bar{M}^2}$$

The departure from a Lorentzian due to the fact that  $F(\omega)$  and  $M(\omega)$  are not strictly constants is very small and amounts to a 2 to 4 % discrepancy in the tails. Then, for all practical purposes the absorption coefficient is

$$(34) \quad \sigma(\omega) = \gamma^2 \omega \text{Im} \langle \langle \varphi_\alpha, \varphi_{\alpha'} \rangle \rangle_\omega$$

where  $\text{Im} \langle \langle \varphi_\alpha, \varphi_{\alpha'} \rangle \rangle_\omega$  is given in (32) or (33) according to the case. In the case  $\omega_M < \omega_L$  the Lorentzian-type function is modulated by  $\omega$  presenting, thus, an asymmetry which is more evident in the tails.

### B. Anharmonic oscillator

When the Hamiltonian (9) of the system includes the cubic correction given in (11), the starting Green's function for the displacements satisfies the same equation as in the harmonic case, i.e., Equation (22). But the function  $\langle \langle \pi_\alpha, \varphi_{\alpha'} \rangle \rangle_\omega$  gives rise to a different set of equations which is given in Appendix A. We obtain

$$(35) \quad \omega \langle \langle \pi_\alpha, \varphi_{\alpha'} \rangle \rangle_\omega = -\delta_{\alpha\alpha'} - \omega_M \langle \langle \varphi_\alpha, \varphi_{\alpha'} \rangle \rangle_\omega \\ - \lambda \sum_k f_\alpha(k) \langle \langle \varphi_k, \varphi_{\alpha'} \rangle \rangle_\omega - 3\eta \langle \langle \varphi_\alpha^2, \varphi_{\alpha'} \rangle \rangle_\omega$$

After substitution into Equation (22), we have

$$(36) \quad (\omega^2 - \omega_M^2) \langle \langle \varphi_\alpha, \varphi_{\alpha'} \rangle \rangle = \omega_M \left( \delta_{\alpha\alpha'} + \lambda \sum_k f_\alpha(k) \langle \langle \varphi_k, \varphi_{\alpha'} \rangle \rangle_\omega + 3\eta \langle \langle \varphi_\alpha^2, \varphi_{\alpha'} \rangle \rangle_\omega \right)$$

In order to find  $\langle \langle \varphi_\alpha^2, \varphi_{\alpha'} \rangle \rangle_\omega$  up to terms in  $\lambda^2$ , the systems of equations (A.1)–(A.3) must be solved in terms of several higher-order functions. These functions are afterwards written in terms of lower-order functions. This approximation which consists of pairing off all operators at one time [7] is equivalent to the Hartree-Fock self-consistent field approximation. In doing so, all third-order Green's

functions can be expressed in terms of first-order functions:

$$\begin{aligned}
 \langle\langle \pi_\alpha \varphi_\beta^2, \varphi_{\alpha'} \rangle\rangle_\omega &= \frac{1}{2}(2n_\beta + 1) \langle\langle \pi_\alpha, \varphi_{\alpha'} \rangle\rangle_\omega - \langle\langle \varphi_\beta, \varphi_{\alpha'} \rangle\rangle_\omega \delta_{\alpha\beta} \\
 \langle\langle \varphi_\alpha^2 \pi_\beta, \varphi_{\alpha'} \rangle\rangle_\omega &= \frac{1}{2}(2n_\alpha + 1) \langle\langle \pi_\beta, \varphi_{\alpha'} \rangle\rangle_\omega + \langle\langle \varphi_\alpha, \varphi_{\alpha'} \rangle\rangle_\omega \delta_{\alpha\beta} \\
 (37) \quad \langle\langle \varphi_\alpha^2 \varphi_\beta, \varphi_{\alpha'} \rangle\rangle_\omega &= (2n_\alpha + 1) \langle\langle \varphi_\alpha, \varphi_{\alpha'} \rangle\rangle_\omega \delta_{\alpha\beta} + \frac{1}{2} \langle\langle \varphi_\beta, \varphi_{\alpha'} \rangle\rangle_\omega \\
 \langle\langle \varphi_\alpha^2 \varphi_k, \varphi_{\alpha'} \rangle\rangle_\omega &= \frac{1}{2}(2n_\alpha + 1) \langle\langle \varphi_k, \varphi_{\alpha'} \rangle\rangle_\omega \\
 \langle\langle \varphi_\alpha^2 \pi_{-k}, \varphi_{\alpha'} \rangle\rangle_\omega &= \frac{1}{2}(2n_\alpha + 1) \langle\langle \pi_{-k}, \varphi_{\alpha'} \rangle\rangle_\omega
 \end{aligned}$$

where

$$n_\alpha = Z^{-1} \text{Tr} e^{-\beta H^A} a_\alpha^\dagger a_\alpha \approx (e^{\beta \omega_M} - 1)^{-1}$$

After substitution of the approximated functions into the sets (A.1)–(A.3) and by keeping only terms up to  $\lambda^2$  we obtain

$$(38) \quad D_\alpha \langle\langle \varphi_\alpha, \varphi_{\alpha'} \rangle\rangle_\omega = \omega_M \left( \delta_{\alpha\alpha'} + \sum_\beta F_{\alpha\beta}^A \langle\langle \varphi_\beta, \varphi_{\alpha'} \rangle\rangle_\omega \right)$$

where

$$\begin{aligned}
 (39) \quad D_\alpha &= \omega^2 - \omega_M^2 - \frac{45\eta^2 \omega_M^2 (2n_\alpha + 1)}{\omega^2 - 4\omega_M^2} - \frac{36\lambda^2 \eta^2 \omega_M^3 (2n_\alpha + 1)}{\omega^2 (\omega^2 - 4\omega_M^2)^2} \\
 &\times \sum_k \frac{f_\alpha(k) f_\alpha(-k) \omega_k (3\omega^4 + 6\omega^2 \omega_M^2 - 2\omega^2 \omega_k^2)}{(\omega^2 - \omega_M^2 - \omega_k^2)^2 - 4\omega_M^2 \omega_k^2} - \frac{9\lambda^2 \eta^2 \omega_M^3}{\omega^2 (\omega^2 - 4\omega_M^2)^2} \\
 &\times \sum_{k\beta} \frac{f_\alpha(k) f_\beta(-k) (2n_\beta + 1) (7\omega^4 + 25\omega^2 \omega_M^2 - 5\omega^2 \omega_k^2 - 4\omega_M^2 \omega_k^2 + 4\omega_M^4) \omega_k}{(\omega^2 - \omega_M^2 - \omega_k^2)^2 - 4\omega_M^2 \omega_k^2}
 \end{aligned}$$

and

$$\begin{aligned}
 (40) \quad F_{\alpha\beta}^A &= F_{\alpha\beta} + \frac{9\lambda^2 \eta^2 \omega_M^2 (2n_\alpha + 1)}{\omega^2 - 4\omega_M^2} \sum_k \frac{f_\alpha(k) f_\alpha(-k) \omega_k}{(\omega^2 - \omega_M^2 - \omega_k^2)^2 - 4\omega_M^2 \omega_k^2} \\
 &\times \left[ \frac{7\omega^2 - \omega_M^2 - 3\omega_k^2}{\omega^2 - \omega_k^2} + \frac{11\omega^4 + 11\omega^2 \omega_M^2 - 7\omega^2 \omega_k^2 + 4\omega_M^2 \omega_k^2 - 4\omega_M^4}{\omega^2 (\omega^2 - 4\omega_M^2)} \right]
 \end{aligned}$$

Just as in the harmonic case, Equation (38) can be condensed into matrix form

$$(41) \quad (\boldsymbol{\varphi})_{\alpha\alpha'} = \frac{\omega_M}{D_\alpha} (\mathbf{1} - \boldsymbol{\mathcal{F}}^A)^{-1}_{\alpha\alpha'}$$

where  $\mathcal{F}_{\alpha\alpha'}^A = \omega_M F_{\alpha\alpha'}^A / D_{\alpha'}$ . For one molecule the preceding equation reduces to

$$(42) \quad \langle\langle \varphi_\alpha, \varphi_\alpha \rangle\rangle_\omega = \frac{\omega_M}{K_\alpha} (\omega^2 - 4\omega_M^2)^2$$

where

$$(43) \quad \begin{aligned} K_\alpha = & (\omega^2 - 4\omega_M^2)[(\omega^4 - 5\omega^2\omega_M^2 + 4\omega_M^4 - 45\eta^2\omega_M^2(2n_\alpha + 1) \\ & - \omega_M(\omega^2 - 4\omega_M^2)F_{\alpha\alpha}] - 9\lambda^2\eta^2\omega_M^3(2n_\alpha + 1) \\ & \times \sum_k \frac{f_\alpha(k)f_\alpha(-k)\omega_k(37\omega^4 - 53\omega^2\omega_k^2 + 31\omega^2\omega_M^2 - 48\omega_k^2\omega_M^2 + 20\omega_k^4 + 4\omega_M^4)}{(\omega^2 - \omega_k^2)[(\omega^2 - \omega_M^2 - \omega_k^2)^2 - 4\omega_M^2\omega_k^2]} \end{aligned}$$

Once integrated over a continuous density of states  $K_\alpha$  can be separated into a real and an imaginary parts:

$$(44) \quad K_\alpha = K(\omega) + iM^A(\omega)$$

where

$$(45) \quad K(\omega) = P \int_0^{\omega_L} d\omega_k \mathcal{D}(\omega_k) K_\alpha$$

In the case  $\omega_M > \omega_L$ , the imaginary part of  $K_\alpha$  is

$$(46) \quad \begin{aligned} M^A(\omega) = & 9\pi\lambda^2\eta^2 \frac{\omega_M}{\omega} (2n_\alpha + 1) L(\omega - \omega_M) \\ & \times (\omega^3 + 7\omega^2\omega_M + 16\omega\omega_M^2 + 12\omega_M^3) \mathcal{D}(\omega - \omega_M) \end{aligned}$$

where

$$(47) \quad L(\omega - \omega_M) = \frac{(m^A - m^B)^2(1 - \cos k_- a) + m^A m^B(1 - \cos 2k_- a)}{\omega - \omega_M}$$

with

$$k_- = \frac{2}{a} \sin^{-1} \left( \frac{\omega - \omega_M}{\omega_L} \right)$$

When  $\omega_M < \omega_L$ , the function  $M^A(\omega)$  is given by

$$(48) \quad \begin{aligned} M^A(\omega) = & \pi\lambda^2 \left\{ -2\omega_M(\omega^2 - 4\omega_M^2)L(\omega)\mathcal{D}(\omega)[\omega^2 - 4\omega_M^2 + 18\eta^2(2n_\alpha + 1)] \right. \\ & \left. + 9\left(\frac{\eta^2}{\omega}\right)(2n_\alpha + 1)A(\omega) \right\} \end{aligned}$$

where

(49)

$$A(\omega) = \omega_M[(\omega^3 + 7\omega^2\omega_M + 16\omega\omega_M^2 + 12\omega_M^3)L(\omega - \omega_M)\mathcal{D}(\omega - \omega_M) \\ + (\omega^3 - 7\omega^2\omega_M + 16\omega\omega_M^2 - 12\omega_M^3)L(\omega + \omega_M)\mathcal{D}(\omega + \omega_M)]$$

Then, in both limits  $\omega_M \gtrless \omega_L$  the absorption coefficient is

$$(50) \quad \sigma(\omega) = \frac{\gamma^2 \omega_M \omega (\omega^2 - 4\omega_M^2)^2 M^A(\omega)}{(K(\omega))^2 + (M^A(\omega))^2}$$

with  $M^A(\omega)$  given by (46) or (48) according to the case.

#### 4. Results and Discussion

In the previous section expressions for the absorption coefficient have been given for both the harmonic case, Equation (34), and the anharmonic case, Equation (50). Expressions for the frequency shift between gas and matrix absorption lines and for the width of those lines can be also obtained. In the harmonic case the shift is

$$(51) \quad \Delta\omega = \bar{\omega} - \omega_M = \begin{cases} (\omega_M^2 + \omega_M F(\omega_M))^{1/2} - \omega_M & \text{if } \omega_M > \omega_L \\ (\omega_M^2 + \omega_M \bar{F})^{1/2} - \omega_M & \text{if } \omega_M < \omega_L \end{cases}$$

and the half-width is

$$(52) \quad \begin{aligned} \Gamma &= 0 & \text{if } \omega_M > \omega_L \\ &= \frac{\omega_M \bar{M}}{2} & \text{if } \omega_M < \omega_L \end{aligned}$$

In the anharmonic case the shift is  $\Delta\omega^A = \bar{\omega}^A - \omega_0$ . Here  $\bar{\omega}^A$  indicates the value in  $\omega$  where  $K(\omega) = 0$ , while  $\omega_0$  stands for the gas phase anharmonic frequency. The half-width is given by  $\Gamma^A = M^A(\omega)/2$ .

The shift and width for the harmonic and anharmonic cases have been computed numerically for several molecules. In Table II we give the anharmonic shift and width for HF, HCl, HBr, CO, and NO for which the harmonic shifts for these five molecules are not significant. Table I gives the noble-gas masses and the parameters  $g$  used to calculate the coupling constant  $\lambda$ . Also given are the cutoff frequencies  $\nu_L = \omega_L/2\pi$ . In order to fix the parameter  $\eta$ , the calculation for the anharmonic case has been carried out by putting  $\lambda = 0$ . Then  $\langle\langle\varphi_\alpha, \varphi_\alpha\rangle\rangle_\omega$

TABLE I. Masses, force constants and cutoff wave numbers of noble-gases used in this work[9].

	$m(\text{a.u.})$	$g \times 10^5 \text{ dyn/cm}^2$	$\omega_L(\text{cm}^{-1})$
Ne	20.2	0.27	290
Ar	39.9	0.61	320
Kr	83.8	0.70	240
Xe	131.3	0.87	210

<sup>a</sup> Parameters  $g$  are chosen large enough to obtain wide phonon bands so that the oscillation frequency of several heavy molecules fall inside.

TABLE II. Half-width and wave numbers of the  $0 \rightarrow 1$  vibrational transition of HF, HCl, HBr, CO and NO. Also given are the shifts  $\Delta\omega^A = \omega_{\text{matrix}}^A - \omega_{\text{gas}}^A$ . All values are given in wave numbers  $\nu(\text{cm}^{-1}) = \omega/2\pi c$ .

		$\nu_0$	$\Delta\nu^A$	$\Gamma^A$
HF	gas <sup>(a)</sup>	3958.38		
	Ne	3954.4	-4.0	16.5
	Ar	3948.7	-9.7	35.0
	Kr	3957.6	-0.8	50.0
	Xe	3962.4	4.0	56.0
HCl	gas <sup>(a)</sup>	2885.64		
	Ne	2880.1	-5.5	10.0
	Ar	2873.8	-11.8	21.5
	Kr	2875.2	-10.4	32.0
	Xe	2871.4	-14.2	48.5
HBr	gas <sup>(a)</sup>	2556.25		
	Ne	2550.5	-6.8	9.0
	Ar	2543.4	-12.9	21.5
	Kr	2544.5	-11.8	30.0
	Xe	2540.1	-16.2	42.0
CO	gas	2143.29		
	Ne	2143.2	-0.1	0.1
	Ar	2143.0	-0.3	0.1
	Kr	2142.8	-0.5	0.2
	Xe	2142.8	-0.5	0.2
NO	gas	1876.09		
	Ne	1876.0	-0.1	0.1
	Ar	1875.7	-0.4	0.2
	Kr	1875.7	-0.4	0.2
	Xe	1875.4	-0.7	0.2

<sup>(a)</sup> Reference [13].

TABLE III. Half-width and wave numbers of the  $0 \rightarrow 1$  vibrational translation of CsBr, HgBr and CsI for the pure and mass defect corrected harmonic case with  $\omega_M < \omega_L$ . Also given are the corresponding shifts  $\Delta\omega = \omega_{\text{matrix}} - \omega_{\text{gas}}$ . All values are given in wave numbers  $\nu(\text{cm}^{-1}) = \omega/2\pi c$

		$\nu_M$	$\Delta\nu$	$\Gamma$	$\nu_M^d$	$\Delta\nu^d$	$\Gamma^d$
CsBr	gas <sup>a</sup>	194.0					
	Ne	192.7	-1.3	9	191.3	-2.7	12
	Ar	192.2	-1.8	18	191.0	-3.0	22
	Kr	195.7	1.7	17	188.1	-6.9	18
	Xe	198.0	4.0	25	190.8	-3.2	20
HgBr	gas <sup>a</sup>	186.2					
	Ne	184.7	-1.5	8	181.0	-5.2	23
	Ar	183.9	-2.3	16	181.8	-4.4	28
	Kr	186.9	0.7	20	172.2	-14.0	22
	Xe	187.8	1.6	32	173.3	-12.9	32
CsI	gas <sup>a</sup>	126.9					
	Ne	140.0	13.1	7	140.0	13.1	7
	Ar	138.2	11.3	17	138.2	11.3	17
	Kr	142.1	15.2	18	142.1	15.2	18
	Xe	141.2	14.3	28	141.2	14.3	28

<sup>a</sup> Reference [13].

given in Equation (38) reduces to

$$(53) \quad \langle\langle\varphi_\alpha, \varphi_\alpha\rangle\rangle_\omega = \frac{\omega_M}{\omega^2 - \omega_M^2 - \frac{45\eta^2\omega_M^2(2n_\alpha + 1)}{\omega^2 - 4\omega_M^2}}$$

The value of  $\eta^2$  has been fitted to agree with the experimentally observed gas phase frequencies  $\omega_0$  [13], thus

$$(54) \quad \eta^2 = \frac{(\omega_0^2 - \omega_M^2)(\omega_0^2 - 4\omega_M^2)}{45\omega_M^2(2n_\alpha + 1)}$$

In Table III we give the harmonic frequency shifts and width of CsBr, CsI and HgBr. These molecules corresponding to the case  $\omega_M < \omega_L$  give broaden absorptions in contrast with the harmonic case where  $\omega_M > \omega_L$ . But these molecules are much heavier than the matrix host atoms; hence, there is an important correction caused by the mass defect that must to be included. In Appendix B the harmonic case with mass defect has been developed and the results are given in Table III. The absorptions are broaden by this correction and the widths  $\Gamma^d$  are also included in this table.

The Green function technique applied to the simple case of diatomic molecules coupled to the lattice modes of a linear chain shows that molecular anharmonicity and mass defect may give an important contribution to the broadening of absorption lines. Broadening always appears in the case  $\omega_M < \omega_L$ , even for the harmonic oscillator model. To give a more realistic model this treatment should be extended to three dimensions. In doing so, the effect, of vibration-translation coupling treated in this work could be included as a refinement of the rotation-translation model [6]. Work is in progress in this direction.

### Appendix A

In the anharmonic oscillator case the starting functions  $\langle\langle\varphi_\alpha, \varphi_{\alpha'}\rangle\rangle_\omega$  and  $\langle\langle\pi_\alpha, \varphi_{\alpha'}\rangle\rangle_\omega$  given in (22) and (35) respectively, give rise to the second-order function  $\langle\langle\varphi_\alpha^2, \varphi_{\alpha'}\rangle\rangle_\omega$ . To find this function a set of three equations must be solved in terms of third-order functions:

$$\begin{aligned}
 \omega\langle\langle\varphi_\alpha\varphi_\beta, \varphi_{\alpha'}\rangle\rangle_\omega &= -\omega_M\langle\langle\pi_\alpha\varphi_\beta, \varphi_{\alpha'}\rangle\rangle_\omega + \langle\langle\varphi_\alpha\pi_\beta, \varphi_{\alpha'}\rangle\rangle_\omega \\
 \omega\langle\langle\varphi_\alpha\pi_\beta, \varphi_{\alpha'}\rangle\rangle_\omega &= -\omega_M\langle\langle\pi_\alpha\pi_\beta, \varphi_{\alpha'}\rangle\rangle_\omega + \langle\langle\varphi_\alpha\varphi_\beta, \varphi_{\alpha'}\rangle\rangle_\omega \\
 &\quad - 3\eta\langle\langle\varphi_\alpha\varphi_\beta^2, \varphi_{\alpha'}\rangle\rangle_\omega - \lambda\sum_k f_\beta(k)\langle\langle\varphi_\alpha\varphi_k, \varphi_{\alpha'}\rangle\rangle_\omega \\
 (A.1) \quad \omega\langle\langle\pi_\alpha\pi_\beta, \varphi_{\alpha'}\rangle\rangle_\omega &= -\omega_M\langle\langle\pi_\alpha\varphi_\beta, \varphi_{\alpha'}\rangle\rangle_\omega + \langle\langle\varphi_\alpha\pi_\beta, \varphi_{\alpha'}\rangle\rangle_\omega \\
 &\quad - 3\eta\langle\langle\pi_\alpha\varphi_\beta^2, \varphi_{\alpha'}\rangle\rangle_\omega + \langle\langle\varphi_\alpha^2\pi_\beta, \varphi_{\alpha'}\rangle\rangle_\omega \\
 &\quad - \lambda\sum_k (f_\alpha(k)\langle\langle\pi_\beta\varphi_k, \varphi_{\alpha'}\rangle\rangle_\omega + f_\beta(k)\langle\langle\pi_\alpha\varphi_k, \varphi_{\alpha'}\rangle\rangle_\omega)
 \end{aligned}$$

As new second-order functions are still generated, two more sets of equations must be solved

$$\begin{aligned}
 \omega\langle\langle\varphi_\alpha\varphi_k, \varphi_{\alpha'}\rangle\rangle_\omega &= -\omega_M\langle\langle\pi_\alpha\varphi_k, \varphi_{\alpha'}\rangle\rangle_\omega - \omega_k\langle\langle\pi_{-k}\varphi_\alpha, \varphi_{\alpha'}\rangle\rangle_\omega \\
 \omega\langle\langle\pi_\alpha\varphi_k, \varphi_{\alpha'}\rangle\rangle_\omega &= -\omega_M\langle\langle\varphi_\alpha\varphi_k, \varphi_{\alpha'}\rangle\rangle_\omega - \omega_k\langle\langle\pi_\alpha\pi_{-k}, \varphi_{\alpha'}\rangle\rangle_\omega \\
 &\quad - 3\eta\langle\langle\varphi_\alpha^2\varphi_k, \varphi_{\alpha'}\rangle\rangle_\omega - \lambda\sum_{k'} f_\alpha(k')\langle\langle\varphi_k\varphi_{k'}, \varphi_{\alpha'}\rangle\rangle_\omega \\
 (A.2) \quad \omega\langle\langle\pi_{-k}\varphi_\alpha, \varphi_{\alpha'}\rangle\rangle_\omega &= -\omega_M\langle\langle\pi_\alpha\pi_{-k}, \varphi_{\alpha'}\rangle\rangle_\omega - \omega_k\langle\langle\varphi_k\varphi_{\alpha'}, \varphi_{\alpha'}\rangle\rangle_\omega \\
 &\quad - \lambda\sum_\beta f_\beta(-k)\langle\langle\varphi_\alpha\varphi_\beta, \varphi_{\alpha'}\rangle\rangle_\omega \\
 \omega\langle\langle\pi_\alpha\pi_{-k}, \varphi_{\alpha'}\rangle\rangle_\omega &= -\omega_M\langle\langle\varphi_\alpha\pi_{-k}, \varphi_{\alpha'}\rangle\rangle_\omega - \omega_k\langle\langle\varphi_k\pi_\alpha, \varphi_{\alpha'}\rangle\rangle_\omega - 3\eta\langle\langle\varphi_\alpha^2\pi_{-k}, \varphi_{\alpha'}\rangle\rangle_\omega \\
 &\quad - \lambda\left[\sum_{k'} f_\alpha(k')\langle\langle\varphi_{k'}\pi_{-k}, \varphi_{\alpha'}\rangle\rangle_\omega + \sum_\beta f_\beta(-k)\langle\langle\pi_\alpha\varphi_\beta, \varphi_{\alpha'}\rangle\rangle_\omega\right]
 \end{aligned}$$



and

$$\begin{aligned}
 \omega \langle \langle \varphi_{k'} \varphi_k, \varphi_{\alpha'} \rangle \rangle_{\omega} &= -\omega_{k'} \langle \langle \varphi_k \pi_{-k'}, \varphi_{\alpha'} \rangle \rangle_{\omega} - \omega_k \langle \langle \varphi_{k'} \pi_{-k}, \varphi_{\alpha'} \rangle \rangle_{\omega} \\
 \omega \langle \langle \varphi_k \pi_{-k'}, \varphi_{\alpha'} \rangle \rangle_{\omega} &= -\omega_k \langle \langle \pi_{-k'} \pi_{-k}, \varphi_{\alpha'} \rangle \rangle_{\omega} - \omega_{k'} \langle \langle \varphi_k \varphi_{k'}, \varphi_{\alpha'} \rangle \rangle_{\omega} \\
 &\quad - \lambda \sum_{\beta} f_{\beta}(-k') \langle \langle \varphi_{\beta} \varphi_k, \varphi_{\alpha'} \rangle \rangle_{\omega} \\
 \omega \langle \langle \varphi_{k'} \pi_{-k}, \varphi_{\alpha'} \rangle \rangle_{\omega} &= -\omega_k \langle \langle \pi_{-k'} \pi_{-k}, \varphi_{\alpha'} \rangle \rangle_{\omega} - \omega_{k'} \langle \langle \varphi_{k'} \varphi_k, \varphi_{\alpha'} \rangle \rangle_{\omega} \\
 (A.3) \quad &\quad - \lambda \sum_{\beta} f_{\beta}(-k) \langle \langle \varphi_{\beta} \varphi_{k'}, \varphi_{\alpha'} \rangle \rangle_{\omega} \\
 \omega \langle \langle \pi_{-k'} \pi_{-k}, \varphi_{\alpha'} \rangle \rangle_{\omega} &= -\omega_{k'} \langle \langle \varphi_{k'} \pi_{-k}, \varphi_{\alpha'} \rangle \rangle_{\omega} - \omega_k \langle \langle \varphi_k \pi_{-k'}, \varphi_{\alpha'} \rangle \rangle_{\omega} \\
 &\quad - \lambda \sum_{\beta} [f_{\beta}(-k') \langle \langle \varphi_{\beta} \pi_{-k}, \varphi_{\alpha'} \rangle \rangle_{\omega} \\
 &\quad + f_{\beta}(-k) \langle \langle \varphi_{\beta} \pi_{-k'}, \varphi_{\alpha'} \rangle \rangle_{\omega}]
 \end{aligned}$$

Next, all third-order functions are approximated as in (37) yielding the second-order functions in terms of the starting function.

## Appendix B

The Hamiltonian for the harmonic oscillator case given in Equation (4) needs to be corrected if the impurity mass is much higher than the host masses:

$$(A.4) \quad H^d = H + \sum_{\alpha=1}^N \frac{(m^A + m^B - m)}{2m^2} p_{\alpha}^2$$

The second term characterizes the correction due to the mass defect. After transformation to operators  $\varphi_k$ ,  $\pi_k$ ,  $\varphi_{\alpha}$  and  $\pi_{\alpha}$  the Hamiltonian (A.4) can be written as

$$(A.5) \quad H^d = H + \mathcal{K} \sum_{\alpha=1}^N \sum_{k,k'} U_{\alpha}(k, k') \pi_k \pi_{k'}$$

where

$$(A.6) \quad U(k, k') = U(-k, -k') = \frac{(\omega_k \omega_{k'})^{1/2}}{2N'} e^{-(k+k')X_{\alpha}}$$

Here the  $X_{\alpha}$  are the equilibrium molecular center of mass coordinates and  $\mathcal{K} = (m - m^A - m^B)/m$ .

The two starting Green's functions  $\langle \langle \varphi_{\alpha}, \varphi_{\alpha'} \rangle \rangle_{\omega}$  and  $\langle \langle \pi_{\alpha}, \varphi_{\alpha'} \rangle \rangle_{\omega}$  are the same as in the pure harmonic case, i.e., they are given in (22) and (23). But the function

$\langle\langle\varphi_k, \varphi_{\alpha'}\rangle\rangle_{\omega}$  originates a different set of equations whose solution leads to

$$(A.7) \quad \begin{aligned} (\omega^2 - \omega_k^2) \langle\langle\varphi_k, \varphi_{\alpha'}\rangle\rangle_{\omega} &= -2\mathcal{K} \sum_{\beta} \sum_{k'} U_{\beta}(k, -k') \omega_{k'} \langle\langle\varphi_{k'}, \varphi_{\alpha'}\rangle\rangle_{\omega} \\ &+ \lambda \sum_{\beta'} \left[ f_{\beta}(-k) \omega_k - 2\mathcal{K} \sum_{\beta'} \sum_{k'} f_{\beta}(k') U_{\beta'}(k, k') \right] \langle\langle\varphi_{\beta'}, \varphi_{\alpha'}\rangle\rangle_{\omega} \end{aligned}$$

Next we replace  $\langle\langle\varphi_{k'}, \varphi_{\alpha'}\rangle\rangle_{\omega}$  by the unperturbed function obtained from (23)

$$(A.8) \quad \langle\langle\varphi_{k'}, \varphi_{\alpha'}\rangle\rangle \approx \frac{\lambda \omega_{k'}}{\omega^2 - \omega_{k'}^2} \sum_{\beta} f_{\beta}(-k') \langle\langle\varphi_{\beta}, \varphi_{\alpha'}\rangle\rangle_{\omega}$$

When condensed into matrix form, Equation (22) can be written as

$$(A.9) \quad \boldsymbol{\varphi}^d = \Omega(\mathbf{1} - \Omega\mathcal{Z})^{-1}$$

where the matrix elements of  $\mathcal{Z}$  are

$$(A.10) \quad \mathcal{Z}_{\alpha\beta} = \lambda^2 \sum_k \frac{f_{\alpha}(k)}{\omega^2 - \omega_k^2} \left\{ f_{\beta}(-k) \omega_k - 2\mathcal{K} \omega^2 \sum_{k'} f_{\beta}(-k') \frac{U_{\beta'}(k, -k')}{\omega^2 - \omega_{k'}^2} \right\}$$

For one molecule, the previous result reduces to

$$(A.11) \quad \langle\langle\varphi_{\alpha}, \varphi_{\alpha}\rangle\rangle_{\omega} = \frac{\omega_M}{\omega^2 - \omega_M^2 - \omega_M F_{\alpha\alpha} + F_{\alpha\alpha}^d}$$

where

$$(A.12) \quad F_{\alpha\alpha}^d = \frac{\lambda^2 \mathcal{K} \omega_M \omega^2}{N'^2} (m_B - m_A)^2 \left[ \sum_k \frac{1 - \cos ka}{\omega^2 - \omega_k^2} \right]^2$$

Thus, the corrected absorption coefficient is

$$(A.13) \quad \sigma(\omega) = \frac{\gamma^2 \omega_M \omega [\omega_M M(\omega) - M^d(\omega)]}{[\omega^2 - \omega_M^2 - \omega_M F(\omega) + F^d(\omega)]^2 + [\omega_M M(\omega) - M^d(\omega)]^2}$$

where  $F^d(\omega)$  and  $M^d(\omega)$  are the real and imaginary parts of  $F_{\alpha\alpha}^d$ , once the integration over the continuous density of states has been carried out. A numerical application of the mass defect corrected shift and widths has been done for a group of three heavy molecules. The results for the shift

$$(A.14) \quad \Delta\omega^d = (\omega_M^2 + \omega_M F(\omega) - F^d(\omega))^{1/2} - \omega_M$$

and width  $\Gamma^d = \frac{1}{2}[\omega_M M(\omega) - M^d(\omega)]$  are given in Table III.

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