

# Dynamic and Spectroscopic Studies of Single Molecules Physisorbed on Graphite Substrates. 1. Theoretical Approach

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The homogeneous line shapes of the infrared spectrum of single small molecules adsorbed on a graphite substrate are determined by applying a renormalization technique to the Hamiltonian of the system. The absorption profile can be determined by using a cumulant series expansion theory to treat the dynamic couplings between the optical system (formed by the vibration–orientation modes of the molecule) and the bath modes (characterized by molecular translations and substrate phonons). The various causes of homogeneous broadening of the lines are studied, with emphasis on phase relaxations through orientation–phonon transfers.

## I. Introduction

To understand physical and chemical processes in the interstellar medium, i.e., the formation or dissociation of various molecular species, requires the analysis and interpretation of the observed spectra, which give information on the chemical composition and the physical conditions of the interstellar materials. In particular, observations in the cold regions of the interstellar medium have revealed the existence of interstellar clouds that contain high densities ( $n \gtrsim 10^3 \text{ cm}^{-3}$ ) of atoms and molecules and that have typical temperatures of about 10–20 K.

Infrared spectroscopy has been widely used to investigate surface phenomena, mainly to determine the adsorption characteristics of molecular species. Examination of the obtained infrared spectra gives information on the nature of the adsorption (physi- or chemisorption) by studying the modification of the molecular band frequencies and intensities due to the adsorption, with gas-phase values as reference values.

The present formalism is devoted to the calculation of the homogeneous width. It treats the problem of adsorbed species using theoretical models that have proven to be particularly efficient in treating the available experimental infrared spectra of molecules trapped in three-dimensional rare-gas crystals at low temperatures<sup>1–6</sup> and that were used in recent studies of the adsorption of some molecules on MgO and NaCl dielectric substrates<sup>7–9</sup> and of the ammonia molecule on the surface of an argon cluster at low temperatures.<sup>10</sup>

In these studies, detailed calculations of the potential energy surfaces have been developed to understand the statics and dynamics of the different degrees of freedom and their couplings.

A cumulant series expansion of the coupling operator describing the dynamic interactions between the adsorbate and the substrate is used; this requires a preliminary renormalization procedure for the adsorbate–substrate Hamiltonian. The renormalized optical Hamiltonian containing the vibrational and orientational modes of the molecule also includes the static influence of the substrate, while the renormalized bath Hamil-

tonian takes into account the low-frequency motions of the center of mass of the admolecule and the substrate phonon modes. The coupling Hamiltonian can then be considered as a small perturbative term.

Furthermore, when the vibrational energy levels of the admolecule are significantly higher than those associated with the orientational energy and the bath system, then the adiabatic approximation can be used, and the homogeneous widths of the vibration–orientation peaks are uniquely characterized by phase relaxation effects. This situation holds for the case of a graphite crystal with physisorbed molecules such as CO, CO<sub>2</sub>, NH<sub>3</sub>, and H<sub>2</sub>O.

In this paper, a theoretical investigation of a single molecule adsorbed on a graphite (0001) surface is performed to predict the infrared spectra in different spectral regions.

In section II, the total Hamiltonian for the adsorbate–substrate system and the interaction potential model used in these calculations are presented. The renormalization method to separate the different motions from each other is applied, and the frequency shifts of the vibrational modes and the orientational level schemes of the molecule are then calculated.

Finally, sections III and IV are devoted to a presentation of the formalism used for the construction of the infrared profile spectra and to a brief discussion of the model, with comments on improvements that could be made to take into account all of the coupling terms that affect the inhomogeneous widths of the line shapes.

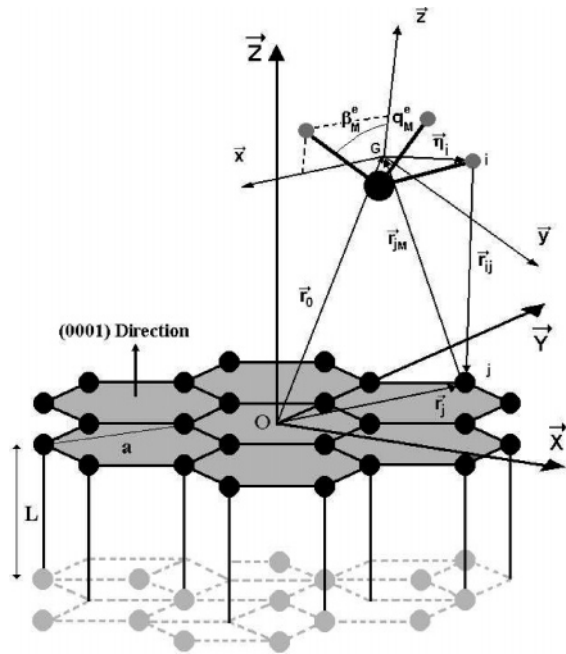
## II. Total Hamiltonian

The system formed by a single molecule adsorbed on a graphite (0001) surface can be described by the Hamiltonian

$$H = H_M + H_G + V_{MG} \quad (1)$$

where  $H_M$ ,  $H_G$ , and  $V_{MG}$  are, respectively, the Hamiltonian of the molecule in its gas-phase state, the Hamiltonian of the substrate in the absence of the molecule, and the interaction potential energy between the molecule and the substrate. The geometric characteristics of the admolecule–graphite system are defined in Figure 1.

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**Figure 1.** Geometrical characteristics of a molecule adsorbed on the (0001) graphite substrate.  $(X, Y, Z)$  and  $(x, y, z)$  represent the surface absolute frame and the molecular frame, respectively.  $L$  and  $a$  are the interlayer spacing and the distance between two next-nearest-neighbor carbon atoms of the graphite, and  $q_M^e$  and  $\beta_M^e$  define the equilibrium internal coordinates. Their numerical values will be given in paper 2 for the ammonia molecule case.

**A. Molecular Hamiltonian.** The Hamiltonian  $H_M$  of the isolated molecule can be written as a sum of three terms

$$H_M = H_{\text{vib}} + T_{\text{rot}} + T_{\text{trans}} \quad (2)$$

that describe the vibrational Hamiltonian and the rotational and translational kinetic energies.

The first term  $H_{\text{vib}}$  represents the internal vibrational Hamiltonian and is generally written in the form

$$H_{\text{vib}} = \sum_v \left[ \frac{P_v^2}{2\mu_v} + \frac{1}{2} k_v Q_v^2 + \sum_{v'v''} k_{vv'v''} Q_v Q_{v'} Q_{v''} + \sum_{v'v''v'''} k_{vv'v''v'''} Q_v Q_{v'} Q_{v''} Q_{v'''} + \dots \right] \quad (3)$$

where  $\mu_v$  and  $k_v$  are, respectively, the reduced mass and the harmonic force constant connected to the  $v$ th internal molecular vibrational mode, with associated normal coordinate  $Q_v$  and momentum  $P_v$ .  $k_{vv'v''}$ ,  $k_{vv'v''v'''} \dots$  are the anharmonic force constants describing the internal couplings between the vibrational modes.

The second term  $T_{\text{rot}}$  in eq 2 is the kinetic rotational operator for the isolated molecule. It is written in the general form

$$T_{\text{rot}} = \frac{L_x^2}{2I_x} + \frac{L_y^2}{2I_y} + \frac{L_z^2}{2I_z} \quad (4)$$

where  $I_\beta$  and  $L_\beta$  represent, respectively, the  $\beta$ th ( $\beta = x, y, z$ ) components of the moment of inertia and the angular momentum of the molecule in its associated frame  $(x, y, z)$ . However, to establish the molecular orientational degrees of freedom  $\Omega = (\varphi, \theta, \chi)$  (precession, nutation, and proper rotation angles) and the position vectors of the molecular center of mass and of the substrate atoms, an absolute frame  $(X, Y, Z)$  connected to the

surface of the graphite substrate is defined. In Figure 1, the geometric characteristics of the molecule–substrate system are presented. The corresponding rotational matrix transformation is given in Appendix A.<sup>11</sup>

In this frame, the components  $L_\beta$  of the angular momentum are expressed in terms of the orientational angles as

$$\begin{aligned} L_x &= -i\hbar \left\{ -\cos \varphi \cot \theta \frac{\partial}{\partial \varphi} - \sin \varphi \frac{\partial}{\partial \theta} + \frac{\cos \varphi}{\sin \theta} \frac{\partial}{\partial \chi} \right\} \\ L_y &= -i\hbar \left\{ -\sin \varphi \cot \theta \frac{\partial}{\partial \varphi} + \cos \varphi \frac{\partial}{\partial \theta} + \frac{\sin \varphi}{\sin \theta} \frac{\partial}{\partial \chi} \right\} \\ L_z &= -i\hbar \frac{\partial}{\partial \varphi} \end{aligned} \quad (5)$$

One should note that for diatomic molecules the proper rotation  $\chi$  motion does not exist.

Finally, the third term  $T_{\text{trans}}$  of eq 2 corresponds to the dynamic translational kinetic operator of the molecule in the absolute frame. It is written as

$$T_{\text{trans}} = \frac{\mathbf{P}_0^2}{2M_0} \quad (6)$$

where  $M_0$  and  $\mathbf{P}_0$  denote the mass and translational momentum operator of the molecule.

**B. Substrate Hamiltonian.** Within the harmonic approximation for the atomic vibrational motions of the graphite substrate, the Hamiltonian  $H_G$  in eq 1 has the general form

$$H_G = \frac{1}{2} \sum_{\lambda j} \left[ \frac{P_\lambda^2(j)}{M_j} + \sum_{\lambda' j'} \Phi_{\lambda\lambda'}(j, j') u_\lambda(j) u_{\lambda'}(j') \right] \quad (7)$$

where  $\lambda$  and  $\lambda'$  label the directions of the Cartesian coordinates in the absolute frame  $(X, Y, Z)$  and  $M_j$  and  $P_\lambda(j)$  are the mass and linear translational momentum in direction  $\lambda$  for the  $j$ th substrate atom.  $u_\lambda(j)$  and  $\Phi_{\lambda\lambda'}(j, j')$ , respectively, denote the  $\lambda$ th ( $\lambda = X, Y, Z$ ) component of the dynamic displacement of the  $j$ th atom around its equilibrium position and the harmonic force constant between the atoms  $j$  and  $j'$  in the directions  $\lambda$  and  $\lambda'$ .

**C. Interaction Potential Energy.** The interaction potential energy  $V_{\text{MG}}$  between the adsorbed molecule and the substrate can be written as the sum of three parts

$$V_{\text{MG}} = V_{\text{LJ}} + V_{\text{E}} + V_{\text{I}} \quad (8)$$

which are described in detail in the following sections.

**1. Quantum Contributions.** The first term  $V_{\text{LJ}}$  in eq 8 is generally treated by using semiempirical 12–6 Lennard-Jones (LJ) pairwise atom–atom potentials to describe the repulsion–dispersion contributions between each atom of the molecule and each carbon atom of the graphite substrate. However, it is widely known that carbon atoms in the graphite basal plane (0001) exhibit anisotropic polarizability effects that modify the spherical shape of these atoms.

To account for these anisotropies, Carlos and Cole<sup>12</sup> proposed a modified expression for  $V_{\text{LJ}}$ , of the form

$$V_{\text{LJ}} = \sum_j \sum_{i=1}^4 4\epsilon_{ij} \left\{ \left( \frac{\sigma_{ij}}{|\mathbf{r}_{ij}|} \right)^{12} \left[ 1 + \gamma_{\text{R}} \left( 1 - \frac{6}{5} \cos^2 \theta_{ij} \right) \right] - \left( \frac{\sigma_{ij}}{|\mathbf{r}_{ij}|} \right)^6 \left[ 1 + \gamma_{\text{A}} \left( 1 - \frac{3}{2} \cos^2 \theta_{ij} \right) \right] \right\} \quad (9)$$

In this equation,  $\mathbf{r}_{ij}$  is the distance vector between the  $i$ th atom of the molecule and the  $j$ th carbon atom of the graphite substrate, while  $\epsilon_{ij}$  and  $\sigma_{ij}$  are the mixed LJ potential parameters, obtained from the usual Lorentz–Berthelot combination rules  $\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}$  and  $2\sigma_{ij} = \sigma_i + \sigma_j$ . The two coefficients  $\gamma_R$  and  $\gamma_A$  specify the modifications to the repulsion and dispersion parts, respectively, and  $\theta_{ij}$  is the angle between the surface normal axis and the  $\mathbf{r}_{ij}$  vector.

2. *Electrostatic and Induction Contributions.* Vernov and Steele<sup>13</sup> noted that the bonds in the graphite crystal give rise to aspherical atomic charge distributions that are the source of multipole electrostatic fields with rapid spatial variations external to the graphite. To model this phenomenon, they represent the sources of the fields by axially symmetric quadrupole moment tensors  $\Theta^c$  at each carbon atom site. The elements of these latter tensors will be given in paper 2 of this series.

The quadrupole moment  $\Theta^c$  of the  $j$ th carbon atom produces the electrical potential

$$\Phi^j(\mathbf{r}_0) = \frac{1}{3}L_p \times \nabla \nabla \left( \frac{1}{|\mathbf{r}_j - \mathbf{r}_0|} \right) : \Theta^c \quad (10)$$

on the molecule at its center of mass position  $\mathbf{r}_0$ , while the multipole moments ( $\mu, \Theta, \dots$ ) of the molecule produce the potential

$$\Phi^M(\mathbf{r}_j) = L_p \times \nabla \left( \frac{1}{|\mathbf{r}_j - \mathbf{r}_0|} \right) \cdot \mu + \frac{1}{3}L_p \times \nabla \nabla \left( \frac{1}{|\mathbf{r}_j - \mathbf{r}_0|} \right) : \Theta + \dots \quad (11)$$

on the  $j$ th atom at position  $\mathbf{r}_j$ .

In eqs 10 and 11,  $L_p$  is a screening factor, equal to 1 for the surface plane and to  $2/(\epsilon + 1)$  for the internal planes ( $p \geq 2$ ), where  $\epsilon$  is the static dielectric constant of the graphite crystal.

The electrostatic and induction contributions to the interaction potential energy  $V_{MG}$  are

$$V_E = \sum_j \mu \cdot \nabla \Phi^j(\mathbf{r}_0) + \frac{1}{3} \sum_j \Theta : \nabla \nabla \Phi^j(\mathbf{r}_0) + \dots \quad (12)$$

$$V_I = -\frac{1}{2} \sum_j [\nabla \Phi^M(\mathbf{r}_j) : \alpha^c : \nabla \Phi^M(\mathbf{r}_j)] - \frac{1}{2} \sum_{j,j'} [\nabla \Phi^j(\mathbf{r}_0) : \alpha : \nabla \Phi^{j'}(\mathbf{r}_0)] \quad (13)$$

where  $\alpha$  and  $\alpha^c$  are the polarizability tensors of the molecule and of the graphite carbon atoms, respectively.

Figure 1 indicates how to describe the internal degrees of freedom of the molecule with respect to its frame ( $\mathbf{x}, \mathbf{y}, \mathbf{z}$ ) and the external degrees of freedom of the molecule and of the carbon atoms. The distance vector  $\mathbf{r}_{ij}$  in eq 9 can be expressed in terms of the position vectors  $\mathbf{r}_0(X, Y, Z)$  and  $\mathbf{r}_j$  of the molecular center of mass and of the  $j$ th atom with respect to the absolute frame and of the position vector  $\eta_i$  of the  $i$ th atom of the molecule with respect to its associated frame ( $\mathbf{x}, \mathbf{y}, \mathbf{z}$ )

$$\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_0 - \eta_i \quad (14)$$

Thus, to treat the influence of the surroundings on the molecular internal motions, the position vectors  $\eta_i$  of the atoms in the molecule, the molecular dipole moment vector  $\mu$ , and the quadrupole moment tensor  $\Theta$  can all be expressed in a series expansion with respect to the molecular frame in terms of the vibrational normal coordinates.

Taking only the first-order terms gives

$$\begin{aligned} \eta_i &= \eta_i^e + \sum_\nu \mathbf{a}_i^\nu Q_\nu \\ \mu &= \mu^e + \sum_\nu \mathbf{b}^\nu Q_\nu \\ \Theta &= \Theta^e + \sum_\nu \mathbf{c}^\nu Q_\nu \end{aligned} \quad (15)$$

In these expressions the superscript  $e$  refers to the equilibrium internal configuration of the molecule and  $\mathbf{a}^\nu$ ,  $\mathbf{b}^\nu$ , and  $\mathbf{c}^\nu$  are the first derivatives of  $\eta_i$ ,  $\mu$ , and  $\Theta$  with respect to the normal coordinate  $Q_\nu$  that describes the  $\nu$ th molecular vibrational mode with frequency  $\omega_\nu$ . Note that  $\mu^e$  and  $\Theta^e$  are the permanent multipole moments for the nonvibrating molecule.

**D. Separation of  $V_{MG}$  and Renormalized Hamiltonians.** From the above expressions, eqs 8–15, it is clear that the interaction potential energy  $V_{MG}$  depends on the molecular degrees of freedom (i.e., the internal vibrational coordinates  $Q_\nu$ , the external translational and orientational variables  $\mathbf{r}_0$ , and  $\Omega = (\varphi, \theta, \chi)$ ) and also on the position vectors  $\mathbf{r}_j$  of the substrate atoms,  $V_{MG} = V_{MG}(\{Q_\nu\}, \Omega, \mathbf{r}_0, \{\mathbf{r}_j\})$ .

However, it can be seen that the molecule and the substrate atoms move around their equilibrium positions  $\mathbf{r}_0^e$  and  $\mathbf{r}_j^e$ , so that it can be written

$$\mathbf{r}_j = \mathbf{r}_j^e + \mathbf{u}(j) \quad \mathbf{r}_0 = \mathbf{r}_0^e + \mathbf{u}(0) \quad (16)$$

where  $\mathbf{u}(0)$  and  $\mathbf{u}(j)$  denote the dynamic displacement vectors of the molecule and of the  $j$ th graphite atom from their equilibrium positions, respectively. The interaction potential energy  $V_{MG}$  becomes  $V_{MG}(\{Q_\nu\}, \Omega, \mathbf{u}(0), \mathbf{u}(\{j\}))$  and can be developed as a Taylor series expansion with respect to the variables  $Q$  and  $(\mathbf{u}(j) - \mathbf{u}(0))$ . One can write

$$V_{MG} = V_{MG}^e(\mathbf{r}_0) + V_{MG}^e(\Omega) + V_{MG}^e(\{Q_\nu\}) + V_{MG}^e(\mathbf{u}(0), \mathbf{u}(\{j\})) + \Delta V_{MG}(\{Q_\nu\}, \Omega, \mathbf{u}(0), \mathbf{u}(\{j\})) \quad (17)$$

In this expression,  $V_{MG}^e(\mathbf{r}_0)$  is the potential energy value for the molecule at position  $\mathbf{r}_0$  above the graphite surface. The three following terms in eq 17 describe the parts of the potential energy  $V_{MG}$  that depend, respectively, on the angular motions, internal vibrations, and translational motions. Note that the superscript  $e$  means a potential energy function where every coordinate except the one explicitly listed as an argument is fixed at its equilibrium value. The last term  $\Delta V_{MG}$  in eq 17 represents the dynamic coupling between all of the molecular and all of the graphite degrees of freedom and can be studied using a perturbation approach.

The total Hamiltonian of the system can then be written as

$$H = \tilde{H}_{\text{vib}} + \tilde{H}_{\text{orient}} + \tilde{H}_b + \Delta \tilde{H} \quad (18)$$

where  $\tilde{H}_{\text{vib}}$  and  $\tilde{H}_{\text{orient}}$  are, respectively, the renormalized Hamiltonians associated with the vibrational and orientational modes of the molecule and will be treated quantum mechanically. They are expressed as

$$\tilde{H}_{\text{vib}} = H_{\text{vib}} + V_{MG}^e(\{Q_\nu\}) \quad (19)$$

where

$$V_{\text{MG}}^e(\{Q_v\}) = \sum_v \frac{\partial V_{\text{MG}}}{\partial Q_v} Q_v + \frac{1}{2} \sum_{vv'} \frac{\partial^2 V_{\text{MG}}}{\partial Q_v \partial Q_{v'}} Q_v Q_{v'} + \dots \quad (20)$$

and

$$\tilde{H}_{\text{orient}} = T_{\text{rot}} + V_{\text{MG}}^e(\Omega) \quad (21)$$

Note that these modes represent the so-called “optically active system a”, which is involved in producing the near-infrared spectra. Its Hamiltonian  $\tilde{H}_a$  will be defined below.

In eq 18,  $\tilde{H}_b$  is the “bath b” renormalized Hamiltonian characterizing the molecule–substrate phonon modes and will be treated classically. It is written as

$$\tilde{H}_b = H_G + T_{\text{trans}} + V_{\text{MG}}^e(\mathbf{u}(0), \mathbf{u}(\{j\})) \quad (22)$$

where

$$V_{\text{MG}}^e(\mathbf{u}(0), \mathbf{u}(\{j\})) = \frac{1}{2} \sum_{jj'} [\nabla \nabla V_{\text{MG}}]_{\mathbf{r}_0^e, \mathbf{r}_j^e}(\mathbf{u}(\{j\}) - \mathbf{u}(0)) \times (\mathbf{u}(\{j'\}) - \mathbf{u}(0)) \quad (23)$$

This use of the harmonic approximation for the translational motions means that only the second-order terms in the series expansion must be considered.

Finally, the last part  $\Delta\tilde{H}$  of eq 18 characterizes the coupling Hamiltonian, which now represents only a small perturbation. It can be developed up to the second order with respect to the translation degrees of freedom

$$\begin{aligned} \Delta\tilde{H} = & \sum_j [\nabla V_{\text{MG}}(\Omega)]_{\mathbf{r}_0^e, \mathbf{r}_j^e}(\mathbf{u}(\{j\}) - \mathbf{u}(0)) + \\ & \frac{1}{2} \sum_{jj'} [\nabla \nabla V_{\text{MG}}(\Omega)]_{\mathbf{r}_0^e, \mathbf{r}_j^e}(\mathbf{u}(\{j\}) - \mathbf{u}(0)) \times \\ & (\mathbf{u}(\{j'\}) - \mathbf{u}(0)) + \sum_{\gamma} \sum_j \frac{\partial \nabla V_{\text{MG}}(\Omega)}{\partial Q_{\gamma}}(\mathbf{u}(\{j\}) - \mathbf{u}(0)) Q_{\gamma} + \dots \quad (24) \end{aligned}$$

The first two terms describe the dynamical coupling between the orientational motion and the phonon modes (vibrations of the substrate atoms + vibrations of the molecular center of mass) for the rigid molecule. This coupling will generate the orientational energy relaxation mechanisms. The remaining contributions are connected to the vibration–orientation–phonon coupling, which produces the vibrational energy relaxation mechanisms. However, since the present work is devoted to the determination of the infrared profile spectra of the molecule adsorbed on the graphite substrate, the adiabatic approximation can be used to separate the high-frequency vibrational modes of the molecule from the low-frequency external ones. Thus, only the orientation–phonon coupling part will be considered in the following treatments.

**E. Renormalized Bases. 1. Vibrational Modes.** To determine the eigenelements of the renormalized vibrational Hamiltonian  $\tilde{H}_{\text{vib}}$ , the eigenkets  $|v_1 \dots v_v\rangle$  associated with the anharmonic modes of the gas-phase molecular Hamiltonian  $H_{\text{vib}}$  need to be calculated. These eigenkets can themselves be expressed in a basis of harmonic eigenkets. It can be written that

$$|v_1 \dots v_v\rangle = \sum_{v'_1 \dots v'_v} \Gamma_v^{v'} |v'_1\rangle \dots |v'_v\rangle \quad (25)$$

where  $v$  and  $v'$  are the vibrational quantum numbers and the  $\Gamma$  values are the resulting coefficients from the first-order perturbation treatment.

Thus, the vibrational-dependent potential term  $V_{\text{MG}}^e(\{Q_v\})$  of  $\tilde{H}_{\text{vib}}$ , as given in eq 20, is generally a small perturbation that only gives frequency shifts and (possibly) splittings.

Let  $E_{v_v}$  and  $|\dots v_v \dots\rangle$  be the anharmonic eigenelements of the  $v$ th level associated with the  $v$ th vibrational mode; these are presumed to have been obtained previously. The frequency shift  $\Delta\omega_{vv'}$  of the vibrational transition  $|\dots v_v \dots\rangle \rightarrow |\dots v'_v \dots\rangle$  for the adsorbed molecule can be calculated from the equation

$$\Delta\omega_{vv'} = \hbar^{-1} [\langle \dots v'_v \dots | V_{\text{MG}}^e(\{Q_v\}) | \dots v'_v \dots \rangle - \langle \dots v_v \dots | V_{\text{MG}}^e(\{Q_v\}) | \dots v_v \dots \rangle] \quad (26)$$

in which all other modes remain in their fundamental states and  $\hbar$  is Planck's constant.

**2. Orientational Modes.** The Schrödinger equation associated with the orientational Hamiltonian  $\tilde{H}_{\text{orient}}$  is

$$\tilde{H}_{\text{orient}} |\widetilde{jmk}\rangle = E_{\widetilde{jmk}} |\widetilde{jmk}\rangle \quad (27)$$

where  $j$ ,  $m$ , and  $k$  are the angular, magnetic, and proper rotation quantum numbers connected to the nutation, precession, and proper rotation angles,  $\theta$ ,  $\varphi$ , and  $\chi$ . As has been noted previously, for diatomic molecules the proper rotation  $\chi$  motion does not exist, and so the quantum number  $k$  is not needed.

The techniques used for calculating the eigenenergies and eigenvectors for eq 27 depend fundamentally on the form and the magnitude of the potential energy surface  $V_{\text{MG}}^e(\Omega)$  experienced by the nonvibrating molecule at its adsorption site and in particular on the degree of perturbation of the molecular orientational motion due to the presence of the substrate. Several typical situations are described below.

(i) Moderately hindered angular motions. The calculations can be made on the basis of the eigenelements  $E_{JMK}$  and  $|JMK\rangle$  associated with the molecular free rotational motion. The eigenvectors  $|\widetilde{jmk}\rangle$  can be expressed as

$$|\widetilde{jmk}\rangle = \sum_{JMK} \Lambda_{JMK}^{jmk} |JMK\rangle \quad (28)$$

where  $\Lambda$  are the resulting coefficients (complex numbers) obtained by solving the secular eq 27.

(ii) Hindered angular motions. The molecule undergoes angular  $\theta$ ,  $\varphi$ , and  $\chi$  oscillations (librations) around the equilibrium values  $\theta^e$ ,  $\varphi^e$ , and  $\chi^e$ . The solutions are obtained using a basis of three-dimensional oscillator functions  $|n_{\theta} n_{\varphi} n_{\chi}\rangle$  (two-dimensional ones for diatomics) by writing

$$|\widetilde{jmk}\rangle = \sum_{n_{\theta} n_{\varphi} n_{\chi}} \Lambda_{n_{\theta} n_{\varphi} n_{\chi}}^{jmk} |n_{\theta} n_{\varphi} n_{\chi}\rangle \quad (29)$$

where  $\Lambda$  are the resulting coefficients (complex numbers) obtained by solving the secular eq 27.

(iii) Intermediate cases. The molecule undergoes angular  $\theta$  oscillations (librations) around its equilibrium value  $\theta^e$  and also angular  $\varphi$  or/and  $\chi$  motions that are either quasi-free or hindered. The solutions are obtained using mixed oscillator and free rotation basis functions.

Finally, matrix diagonalization gives the orientational level scheme and the transition matrix elements between the eigenvectors can then be calculated.

**3. Optical System.** As noted previously, the optically active system is formed by the vibration–orientation modes of the



molecule (absorber) and has the Hamiltonian

$$\tilde{H}_a = \tilde{H}_{\text{vib}} + \tilde{H}_{\text{orient}} \quad (30)$$

with associated eigenenergies  $E_{v\nu\overline{jmk}}$  and eigenvectors  $|\dots v\nu\overline{jmk}\rangle$ . However, using the Born–Oppenheimer approximation, which allows the separation of high-frequency vibrational modes from low-frequency orientational and phonon ones, the eigenvectors  $|\dots v\nu\overline{jmk}\rangle$  could be written as tensorial products  $|\dots v\nu\overline{jmk}\rangle \otimes |\overline{jmk}\rangle_{v\nu}$ , where the subscript  $v\nu$  of the orientational states indicates a weak static dependence on the vibrational state.

In effect, the potential energy surface  $V_{\text{MG}}^e(\Omega)$  experienced by the molecule and also its moments of inertia  $I$  (in eq 4) depend parametrically on the vibrational state, and therefore eq 27 must be solved for both the ground and excited states. As a consequence, the orientational level schemes exhibit some weak differences that can be neglected in this work.

**4. Translational Modes.** The solutions for the molecule–substrate phonon Hamiltonian  $\tilde{H}_b$  given in eq 22 are determined within the harmonic approximation by solving the dynamic equation

$$(\mathbf{D} - \mathbf{I}\omega^2)\mathbf{u} = 0 \quad (31)$$

of dimension  $3(N + 1)$ , where  $N$  is the number of substrate atoms. In this expression,  $\mathbf{D}$  is the square dynamic matrix of the molecule–substrate system,  $\mathbf{u}$  represents the column eigenvector associated with the eigenvalue  $\omega$ , and  $\mathbf{I}$  is the square unit matrix. The dynamical matrix  $\mathbf{D}$  can be partitioned as follows

$$\mathbf{D} = \begin{pmatrix} \mathbf{D}^0 & \Delta\mathbf{D}^{0G} \\ \Delta\mathbf{D}^{0G} & \mathbf{D}^G + \Delta\mathbf{D}^G \end{pmatrix} \quad (32)$$

In this equation,  $\mathbf{D}^0$  is the dynamical matrix for the center of mass motion of the molecule trapped in the potential well due to the static substrate, and  $\mathbf{D}^G$  is the dynamic matrix for the perfect substrate vibrations (without adsorbate).<sup>14–18</sup> The additional matrices  $\Delta\mathbf{D}^G$  and  $\Delta\mathbf{D}^{0G}$  represent, respectively, the static influence of the molecule on the substrate motions and the dynamic matrix coupling between the molecule and the substrate motion. In the following calculations, they will be treated as perturbations.

The solution of the dynamic equation (eq 31) is mainly made using Green’s function techniques. The Green’s function matrix  $\mathbf{G}$  of the system is defined as the inverse of the dynamical matrix  $\mathbf{D}$ , i.e.,  $\mathbf{G} = \mathbf{D}^{-1}$ . It contains all of the dynamic information on the bath motions and can be approximately expressed as

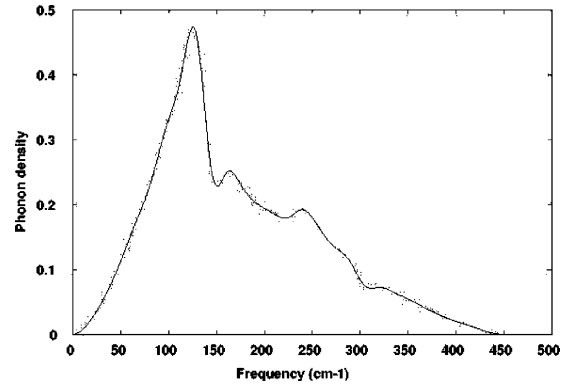
$$\mathbf{G} \simeq \mathbf{G}^{0G}[\mathbf{I} - (\Delta\mathbf{D}^G + \Delta\mathbf{D}^{0G})\mathbf{G}^{0G}] \quad (33)$$

with

$$\mathbf{G}^{0G} = \begin{pmatrix} \mathbf{D}^0 & 0 \\ 0 & \mathbf{D}^G \end{pmatrix}^{-1}$$

being the uncorrelated dynamical Green’s matrix for the admolecule and for the substrate (Appendix A).

While the  $(3 \times 3)$  matrix  $\mathbf{G}^0$ , which represents the molecular part of the Green’s matrix  $\mathbf{G}^{0G}$ , can easily be calculated in terms of its dynamical eigenvalue frequencies, the remaining  $(3N \times 3N)$  matrix  $\mathbf{G}^G$  tied to the substrate can be expressed in terms of its phonon density of states  $\omega^2 g(\omega^2)$  (Figure 2), as explained in Appendix B.



**Figure 2.** Phonon density of states  $\omega^2 g(\omega^2)$  of the (0001) graphite substrate.

It should be noted that, as for the orientational states, the molecular center of mass motion states depend parametrically on the molecular internal vibrational states.

### III. Infrared Absorption Spectra

**A. General.** The absorption coefficient associated with a number  $\mathcal{N}$  of optically active molecules per surface unit area is defined as the real part of the spectral density, i.e., the Fourier transform of the time-dependent autocorrelation function  $\phi(t)$

$$I(\omega) = \frac{4\pi\mathcal{N}\omega}{3hc} \text{Re} \int_0^\infty dt e^{i\omega t} \phi(t) \quad (34)$$

In this expression,  $\mu_A$  is the molecular dipole moment operator defined in the absolute frame,  $\rho(0)$  is the initial canonical density operator of the total system,  $\omega$  is the frequency variable (expressed in wavenumbers,  $\text{cm}^{-1}$ ), and  $c$  is the velocity of light. Finally, the  $\text{Tr}$  (Trace) symbol denotes the average over the initial conditions at time  $t = 0$  and over all of the possible evolutions of the system between times 0 and  $t$ .

In the Heisenberg representation, the time-dependent dipole moment operator  $\mu_A(t)$  of eq 34 can be expressed in the form

$$\mu_A(t) = e^{i\hbar^{-1}Ht} \mu_A(0) e^{-i\hbar^{-1}Ht} = e^{i\hbar^{-1}Lt} \mu_A(0) \quad (35)$$

where  $L$  is an operator defined in the Liouville space, the elements of which are the tensorial products of the Hilbert space vectors and their conjugates.<sup>19–21</sup> Note that in the Liouville space the calculations are performed using transition trajectories instead of the eigenelements of levels in the Hilbert space.  $L$  is the Liouville operator associated with the total Hamiltonian  $H$  of the system and is defined by the commutator

$$L\mu_A = [H, \mu_A] = (H\mu_A - \mu_A H) \quad (36)$$

It can be written as the sum

$$L = \tilde{L}_a + \tilde{L}_b + \Delta\tilde{L} \quad (37)$$

of the Liouville operators  $\tilde{L}_a$  and  $\tilde{L}_b$  associated with the optically active mode a (molecular vibration–orientation motions) and the bath phonons b (translation modes), respectively, and of the operator  $\Delta\tilde{L}$  describing the coupling between the a and b subsystems.

The Liouville space term  $e^{i\hbar^{-1}Lt}$  of eq 35 is written as

$$e^{i\hbar^{-1}Lt} = U_L(t) e^{i\hbar^{-1}\tilde{L}_b t} e^{i\hbar^{-1}\tilde{L}_a t} \quad (38)$$

where  $U_L(t) = e^{i\hbar^{-1}\int_0^t \Delta\tilde{L}(t')dt'}$  is the time evolution operator and where the coupling operator is

$$\Delta\tilde{L}(t') = e^{i\hbar^{-1}\tilde{L}_b t'} e^{i\hbar^{-1}\tilde{L}_a t'} \Delta\tilde{L}(0) \quad (39)$$

Let  $|i\rangle$ ,  $|f\rangle$ , ... and  $E_i$ ,  $E_f$ , ... be the eigenelements of the Hamiltonian  $\tilde{H}_a$  associated with the optically active mode considered, obtained by solving the appropriate Schrödinger equations. The eigenelements associated with the corresponding Liouville operator  $\tilde{L}_a$  are defined as the vectors  $|i,f\rangle = |i\rangle\langle f|$ , ... and the frequencies  $\omega_{if} = \hbar^{-1}(E_f - E_i)$ , ... characterizing the line transition  $i \rightarrow f$  (i for initial and f for final states).

The autocorrelation function of eq 34 cannot be calculated exactly; a numerical calculation involves several approximations, which are listed below.

(i) It is assumed that in the physisorption processes the induced dipole moment experienced by the molecule is small with respect to its permanent one ( $\mu_{\text{ind}} \ll \mu_{\text{per}}$ ) and that the total dipole moment does not depend on the bath (phonon) modes, i.e.,  $\mu \simeq \mu_{\text{per}}$ .

(ii) Because of the renormalization procedure, the coupling Hamiltonian  $\Delta\tilde{H}$  is small enough to justify an initial chaos hypothesis for the density operator between the renormalized optically active modes and the bath ones, so that  $\rho(0) \simeq \rho_a(0)\rho_b(0)$ , with  $\rho_a(0)$  and  $\rho_b(0)$  being diagonal in their respective active space and bath state spaces.

(iii) The spectral lines are assumed to be isolated from each other. This allows the application of the “linked cluster theorem”,<sup>22</sup> which involves calculating only the diagonal matrix elements of  $\langle U_L(t) \rangle_b$  in the Liouville basis of the  $\tilde{L}_a$  operator. Note that the broken brackets with the subscript b denotes an average over the bath modes.

Finally, under the above conditions the autocorrelation function  $\phi(t)$  can be written as

$$\begin{aligned} \phi(t) &= \text{Tr}_a[\rho_a(0)\mu_A(0)\langle U_L(t) \rangle_b e^{i\hbar^{-1}\tilde{L}_a t} \mu_A(0)] \\ &= \sum_{if} (\rho_a^i - \rho_a^f) \langle f|\mu_A|i \rangle \langle \langle if | \langle U_L(t) \rangle_b | if \rangle \rangle e^{-i(\omega_{if} + \Delta\omega_{if})t} \langle i|\mu_A|f \rangle \end{aligned} \quad (40)$$

where, to simplify the notation, the zero-time argument of the dipole moment operator has been omitted.  $\rho_a^i$  and  $\rho_a^f$  are the density factors of the initial and final states, respectively, and  $\Delta\omega$  is the vibrational frequency shift of the line transition defined above in eq 26.

In eq 40, it is evidently seen that all of the information on the line shape evolution is contained in the matrix element of the  $\langle U_L(t) \rangle_b$  average over the phonon bath states. Its evaluation can be performed using the well-known “cumulant series expansion theorem”<sup>23,24</sup> up to the second order with respect to  $\Delta\tilde{L}$ , giving

$$\begin{aligned} \langle \langle if | \langle U_L(t) \rangle_b | if \rangle \rangle &= \exp\{i\hbar^{-1} \int_0^t dt' \langle \langle if | \langle \Delta\tilde{L}(t') \rangle_b | if \rangle \rangle - \\ &\quad \hbar^{-2} \int_0^t dt' \int_0^{t'} dt'' \langle \langle \langle if | \langle \Delta\tilde{L}(t') \Delta\tilde{L}(t'') \rangle_b | if \rangle \rangle - \\ &\quad \langle \langle if | \langle \Delta\tilde{L}(t') \rangle_b | if \rangle \rangle \langle \langle if | \langle \Delta\tilde{L}(t'') \rangle_b | if \rangle \rangle \} \end{aligned} \quad (41)$$

Furthermore, the dynamic collisions between the molecule and the bath are taken to occur over infinitely short times, so that the impact approximation is valid and the line shapes have Lorentzian forms.

Finally, considering eqs 34, 40, and 41 and replacing the Liouville space matrix elements by Hilbert space ones, the absorption coefficient can be written as

$$I(\omega) = \frac{4\pi\omega}{3hc} \sum_{if} (\rho_a^i - \rho_a^f) |\langle i|\mu_A|f \rangle|^2 \text{Re} \int_0^\infty dt \exp\{i(\omega - \omega_{if} - \Delta\omega_{if})t\} \exp\{-i\Delta^{(1)}t\} \exp\{-i\Delta^{(2)}t\} \exp\{-\Gamma^{(2)}t\} \quad (42)$$

In this expression,  $\Delta^{(1)}$  is the dynamic frequency shift due to the first-order term in the cumulant series expansion of the time evolution operator, while  $\Delta^{(2)}$  and  $\Gamma^{(2)}$  are the dynamic frequency shift and broadening due to the second-order term, for the  $i \rightarrow f$  line transition. These can be written as

$$\Delta^{(1)} = \hbar^{-1} [\langle f | \langle \Delta\tilde{H} \rangle_b | f \rangle - \langle i | \langle \Delta\tilde{H} \rangle_b | i \rangle] \quad (43)$$

$$\Delta^{(2)} = \text{Im}[\hbar^{-2}(\Delta_i^{(2)} + \Delta_f^{(2)} + \Delta_{if}^{(2)})]$$

$$\Gamma^{(2)} = \text{Re}[\hbar^{-2}(\Delta_i^{(2)} + \Delta_f^{(2)} + \Delta_{if}^{(2)})] \quad (44)$$

where

$$\Delta_i^{(2)} = \int_0^\infty d\tau \sum_{i' \neq i} e^{i(\omega_{i'} - \omega_i)\tau} \langle i | \langle \Delta\tilde{H}(0) | i' \rangle \langle i' | \Delta\tilde{H}(\tau) \rangle_b | i \rangle \quad (45)$$

$$\Delta_f^{(2)} = \int_0^\infty d\tau \sum_{f' \neq f} e^{-i(\omega_f - \omega_{f'})\tau} \langle f | \langle \Delta\tilde{H}(\tau) | f' \rangle \langle f' | \Delta\tilde{H}(0) \rangle_b | f \rangle \quad (46)$$

and

$$\begin{aligned} \Delta_{if}^{(2)} &\simeq \int_0^\infty d\tau \langle i | \langle \Delta\tilde{H}(0) - \langle \Delta\tilde{H}(0) \rangle_b | i \rangle \langle i | \Delta\tilde{H}(\tau) - \\ &\quad \langle \Delta\tilde{H}(0) \rangle_b | f \rangle | i \rangle + \int_0^\infty d\tau \langle f | \langle \Delta\tilde{H}(0) - \langle \Delta\tilde{H}(0) \rangle_b | f \rangle \langle f | \Delta\tilde{H}(\tau) - \\ &\quad \langle \Delta\tilde{H}(0) \rangle_b | b \rangle | f \rangle - \int_0^\infty d\tau \langle i | \langle \Delta\tilde{H}(0) - \langle \Delta\tilde{H}(0) \rangle_b | i \rangle \langle f | \Delta\tilde{H}(\tau) - \\ &\quad \langle \Delta\tilde{H}(0) \rangle_b | b \rangle | f \rangle - \int_0^\infty d\tau \langle f | \langle \Delta\tilde{H}(0) - \langle \Delta\tilde{H}(0) \rangle_b | f \rangle \langle i | \Delta\tilde{H}(\tau) - \\ &\quad \langle \Delta\tilde{H}(0) \rangle_b | b \rangle | i \rangle \end{aligned} \quad (47)$$

are given in terms of the averages and time correlation functions of the orientation–translation (molecular center of mass motion + substrate atom vibrations) coupling Hamiltonian  $\Delta\tilde{H}$  over the bath states.

The two contributions given in eqs 45 and 46 characterize inelastic processes in the collision mechanism. They depend on the nondiagonal matrix elements describing the contamination of the considered initial and final optical states by other states through the phonon states. The  $\Delta_{if}^{(2)}$  of eq 47 describes elastic collisions only; it depends on the diagonal matrix elements, for the initial and final optical states, of the fluctuations of the coupling Hamiltonian  $\Delta\tilde{H}$  around its average value on the bath states.

**B. Average and Time Correlation Functions.** Within the adiabatic approximation, the time correlation functions and averages (eqs 44–47) can be calculated by separating the orientation–translation coupling Hamiltonian  $\Delta\tilde{H}$  into two parts  $\Delta\tilde{H}_1$  and  $\Delta\tilde{H}_2$ , which depend on the one- and two-phonon modes, respectively. One can write

$$\Delta\tilde{H}_1 = \sum_{\alpha j} \sum_{lpm} A_{\alpha}^{lpm}(\mathbf{r}_0, \mathbf{r}_j^e)(u_{\alpha}(j) - u_{\alpha}(0))D_{p,m}^l(\Omega) \quad (48)$$

$$\Delta\tilde{H}_2 = \sum_{\alpha j} \sum_{\gamma j'} \sum_{lpm}^{l \neq 0} A_{\alpha\gamma}^{lpm}(\mathbf{r}_0^e, \mathbf{r}_j^e)(u_\alpha(j) - u_\alpha(0))(u_\gamma(j') - u_\gamma(0))D_{p,m}^l(\Omega) \quad (49)$$

In these expressions, the  $A$  coefficients represent, respectively, the first- and second-order derivatives of the interaction potential energy  $V_{MG}$  with respect to the translational variables, and the  $D_{p,m}^l$  values are the usual rotational matrix elements (which become spherical harmonic ones for linear molecules).

The correlation functions and averages between two graphite carbon atoms, one graphite carbon atom and the molecule, or for the molecule only are generally given in terms of the Green's function matrix defined in eq 33 as

$$\langle u_\alpha(j, \tau) u_\gamma(j', 0) \rangle_b = -\frac{\hbar}{\pi} \int_{-\infty}^{+\infty} d\omega \frac{\text{sign}(\omega)}{1 - e^{-\beta\hbar\omega}} e^{-i\omega\tau} \text{Im } G_{\alpha\gamma}(j, j'; \omega^2 - i0) \quad (50)$$

and

$$\langle u_\alpha(j, 0) u_\gamma(j', 0) \rangle_b = -\frac{\hbar}{\pi} \int_0^{+\infty} d\omega \coth(\beta\hbar\omega/2) \text{Im } G_{\alpha\gamma}(j, j'; \omega^2 - i0) \quad (51)$$

where  $\text{Im}$  means the imaginary part of Green's matrix element  $G_{\alpha\gamma}$  and where  $j$  and/or  $j'$  take the value 0 for the molecule. The general expression for Green's matrix is given in Appendix B. In eqs 50 and 51,  $\hbar$  is Planck's constant, and  $\beta = (kT)^{-1}$ , where  $k$  is the Boltzmann constant and  $T$  is the temperature of the system.

One can note that the average of the one-phonon term  $\langle \Delta\tilde{H}_1 \rangle_b$  vanishes because of the harmonic description of the translational modes.

An estimate of the values for the averages and the time correlation functions can be made, with subsequent approximations yielding simplifications in the computation of the  $\Delta^{(1)}$ ,  $\Delta^{(2)}$ , and  $\Gamma^{(2)}$  terms in eqs 42 and 44. Moreover, it may be mentioned that these terms are composed of three contributions due to substrate phonon modes, to molecular center of mass modes, and to mixed modes.

Finally, it may be mentioned that the imaginary part of the  $G$  elements is simply written in terms of the phonon density of states  $\omega^2 g(\omega^2)$  for the substrate translational modes (Figure 2) together with a special molecular term  $\omega_k^2 \delta(\omega^2 - \omega_k^2)$  that describes possible resonance effects between the translational and orientational motions and that is described in detail in Appendix B.

**C. Near-Infrared Profile Spectrum.** Within this framework, the infrared profile for an isolated line transition  $|i\rangle = |v_v\rangle \otimes |jmk\rangle_{v_v} \rightarrow |f\rangle = |v'_v\rangle \otimes |j'm'k'\rangle_{v'_v}$  connected to the  $v$ th vibrational mode of the molecule is written in the Lorentzian form as

$$I_v(\omega) = \frac{8\pi^2 \mathcal{N}}{3hc} \omega \sum_{v, v'} |\langle v_v | Q_v | v'_v \rangle|^2 \sum_{jmkj'm'k'} \frac{e^{-\beta E_{vjm}} - e^{-\beta E_{v'j'm'k'}}}{Z} \frac{\left| \langle jmk | \frac{\partial \mu_A}{\partial Q_v} | j'm'k' \rangle \right|^2}{\Gamma^{(2)}} \frac{1}{(\omega - \omega_{vjm \rightarrow v'j'm'k'} - \Delta\omega_{vv'} - \Delta^{(1)} - \Delta^{(2)})^2 + (\Gamma^{(2)})^2} \quad (52)$$

In this equation, the broken brackets refer to vibrational transition elements of the normal coordinate  $Q_v$ , and to the orientational transition elements of the first derivative of the molecular dipole moment with respect to this coordinate.  $Z$  is the vibration-orientation canonical partition function, and  $\omega_{vjm \rightarrow v'j'm'k'} = \hbar^{-1}(E_{v'j'm'k'} - E_{vjm})$  is the frequency position of the line in the absence of the dynamic coupling between the optically active (vibration-orientation) system and the bath states.

Nevertheless, at low temperatures only a few orientational levels of the fundamental vibrational state are populated. Then the line transitions of interest are of type  $|0\rangle \otimes |jmk\rangle_0 \rightarrow |1_v\rangle \otimes |j'm'k'\rangle_{1_v}$ , and the  $e^{-\beta E_{v'j'm'k'}}$  term is very small and can be ignored.

Moreover, it may be noticed that when the dynamic coupling between the optically active modes and the bath states is disregarded then the dynamical lineshifts and line widths in eq 52 are ignored while the  $\Gamma^{(2)}/((\omega - \omega_{vjm \rightarrow v'j'm'k'} - \Delta\omega_{vv'} - \Delta^{(1)} - \Delta^{(2)})^2 + (\Gamma^{(2)})^2)$  term is replaced by the Dirac function  $\delta(\omega - \omega_{vjm \rightarrow v'j'm'k'} - \Delta\omega_{vv'})$ ; one then obtains the "bar spectrum".

**D. Far-Infrared Profile Spectrum.** In the far-infrared frequency region, only the line transitions between orientational levels  $|jmk\rangle \rightarrow |j'm'k'\rangle$  take place. The absorption coefficient of eq 52 becomes

$$I(\omega) = \frac{8\pi^2 \mathcal{N}}{3hc} \omega \sum_{jmkj'm'k'} \frac{e^{-\beta E_{jmk}} - e^{-\beta E_{j'm'k'}}}{Z} \frac{\Gamma^{(2)} |\langle jmk | \mu_A^e | j'm'k' \rangle|^2}{(\omega - \omega_{jmk \rightarrow j'm'k'} - \Delta^{(1)} - \Delta^{(2)})^2 + (\Gamma^{(2)})^2} \quad (53)$$

where the broken brackets refer to the orientational transition elements of the dipole moment operator  $\mu_A^e$ . In this case, the  $e^{-\beta E_{j'm'k'}}$  term cannot be considered as small.

#### IV. Discussion

The theoretical approach presented in this work is devoted to finding the profile spectrum associated with a  $v$ th vibrational mode for single small molecules adsorbed on perfect graphite (0001) substrates.

The first step in calculating the bar spectrum presents a pertinent test for this renormalization treatment of the Hamiltonian of the admolecule-substrate system. In effect, the calculated shape of the infrared spectrum is very sensitive to the details of the molecular motions on the surface, the calculation of which strongly depends on the quality and analysis of the potential energy model used to describe the interaction between the admolecule and the graphite substrate and also on the degree of convergence of the expansion of this potential in terms of the relevant coordinates. Moreover, the line width and line shift calculations require knowledge of the intensity of the coupling terms between the optical modes and the phonon states.

Nevertheless, the line widths result from a composition of homogeneous broadenings and inhomogeneous ones that are due to (i) vibrational energy relaxation mechanisms on the phonon modes, (ii) surface heterogeneities, and (iii) lateral interactions between the adsorbed molecule and possible nearby adsorbed species. These extra effects tend to give the line bands Gaussian forms rather than Lorentzian ones.

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## Appendix A: Rotational Matrix Transformation and Molecular Dipole Moment

The unitary matrix  $\mathbf{M}$  characterizing the transformation from the surface absolute frame  $(\mathbf{X}, \mathbf{Y}, \mathbf{Z})$  into the molecular one  $(\mathbf{x}, \mathbf{y}, \mathbf{z})$  through the Euler angles  $\varphi$ ,  $\theta$ , and  $\chi$  is given as<sup>11</sup>

$$\mathbf{M}(\varphi, \theta, \chi) = \begin{pmatrix} \cos \varphi \cos \theta \cos \chi - \sin \varphi \sin \chi & \sin \varphi \cos \theta \cos \chi + \cos \varphi \sin \chi & -\sin \theta \cos \chi \\ -\cos \varphi \cos \theta \sin \chi - \sin \varphi \cos \chi & -\sin \varphi \cos \theta \sin \chi + \cos \varphi \cos \chi & \sin \theta \sin \chi \\ \cos \varphi \sin \theta & \sin \varphi \sin \theta & \cos \theta \end{pmatrix} \quad (\text{A1})$$

Thus, the molecular dipole moment  $\mu_A$  and its first derivative  $\partial \mu_A / \partial Q_\nu$ , with respect to the normal coordinate  $Q_\nu$  of the  $\nu$ th vibrational mode, can be written in the absolute frame as

$$\begin{aligned} \mu_A &= \mathbf{M}^{-1}(\varphi, \theta, \chi) \mu \\ \frac{\partial \mu_A}{\partial Q_\nu} &= \mathbf{M}^{-1}(\varphi, \theta, \chi) \mathbf{b}^\nu \end{aligned} \quad (\text{A2})$$

where  $\mathbf{M}^{-1}$  is the inverse matrix of  $\mathbf{M}$ .  $\mu$  and  $\mathbf{b}^\nu = \partial \mu / \partial Q_\nu$  are the molecular dipole moment and its first derivative, with respect to  $Q_\nu$ , both expressed in the molecular frame (eq 15).

## Appendix B: Matrix Elements of Green's Tensor $\mathbf{G}$

Calculation of Green's matrix elements for the molecule–substrate system is a problem that cannot be treated rigorously. Nevertheless, analytical asymptotic expressions for the  $G_{\alpha\gamma}$  elements could be obtained using some assumptions and approximations<sup>15,18</sup> such as:

- (i) Only binary potential interactions are considered.
- (ii) Each atom of the substrate or the molecule interacts only with its first nearest neighbors.
- (iii) Green's matrix elements depend on the  $j$  and  $j'$  substrate atoms only through their index difference, i.e.,  $G_{\alpha\gamma}(jj'; \omega^2) = G_{\alpha\gamma}(j - j', 0; \omega^2)$ , and have numerical values that decrease rapidly with increasing distance between atoms. In effect, for two nearest-neighbor atoms,  $G_{\alpha\gamma}(jj'; \omega^2)$  represents less than 25% of the “self” Green's numerical value  $G_{\alpha\gamma}(jj; \omega^2)$ . For the calculations, only the self Green's functions can be considered (namely, the autocorrelation functions).

Note, however, that these nonself Green's functions are partly accounted for in the numerical calculations through the phonon density of states.

- (iv) Isotropy of the Green's function elements  $G_{\alpha\gamma}$  is assumed; this corresponds to neglecting the nondiagonal terms ( $\alpha \neq \gamma$ ).

- (v) The perturbation dynamic matrices  $\Delta \mathbf{D}^{0G}$  and  $\Delta \mathbf{D}^G$  are supposed to be negligibly small. Green's matrix  $\mathbf{G}$  of the molecule–substrate system can then be written as

$$\mathbf{G} \simeq \mathbf{G}^{0G} = \begin{pmatrix} \mathbf{G}^0 & 0 \\ 0 & \mathbf{G}^G \end{pmatrix}$$

where  $\mathbf{G}^0$  and  $\mathbf{G}^G$  are the Green's function matrices connected, respectively, to the translational dynamics of the molecule and due to the presence of the static substrate and the dynamics of the unperturbed substrate.

Finally, the Green's functions connected to the admolecule and to the substrate (for  $\alpha = X, Y, Z$ ) can be written as follows

$$1 + M_0 \omega^2 G_{\alpha\alpha}^0(0, 0; \omega^2 - i0) = -\frac{1}{3} \sum_{k=X,Y,Z} \omega_k^2 \left[ \text{PP} \left( \frac{1}{\omega^2 - \omega_k^2} \right) + i\pi \delta(\omega^2 - \omega_k^2) \right] \quad (\text{B1})$$

$$1 + M_j \omega^2 G_{\alpha\alpha}^G(jj; \omega^2 - i0) = -S(\omega^2) - i\pi \omega^2 g(\omega^2) \quad (\text{B2})$$

In these expressions, PP and  $\delta$  denote the principal part and the Dirac function. The function  $S(\omega^2)$  is expressed in terms of the phonon density  $\omega^2 g(\omega^2)$  as

$$S(\omega^2) = \text{PP} \int_0^\infty \frac{\omega'^2 g(\omega'^2)}{\omega^2 - \omega'^2} d\omega'^2 \quad (\text{B3})$$

- (vi) Finally, calculations of the averages and time correlation functions connected to the two-phonon process require an additional “Debye approximation” that is written as<sup>25</sup>

$$\begin{aligned} \langle u_\alpha(j, \tau) u_\beta(j', \tau) u_\alpha(j, 0) u_\beta(j', 0) \rangle_b &\simeq \\ 2 \langle u_\alpha(j, \tau) u_\alpha(j, 0) \rangle_b \langle u_\beta(j', \tau) u_\beta(j', 0) \rangle_b &+ \langle u_\alpha^2(j, 0) \rangle_b \langle u_\beta^2(j', 0) \rangle_b \end{aligned} \quad (\text{B4})$$

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