Vibrons in a disordered monolayer: Application to the determination of the infrared and sum frequency generation spectra of ¹²CO and ¹³CO isotopic mixtures adsorbed on NaCl(001)

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The internal dynamics of a disordered monolayer formed by a mixture of 12 CO and 13 CO isotopes is studied using a description in terms of vibron propagation and scattering by isotopic defects randomly distributed in the layer. The spectral densities connected to the infrared and sum frequency generation vibrational spectra of the disordered monolayer are expressed in terms of the average Green propagator of the vibrons using a generalized *t*-matrix approximation to describe the collision of vibrons with the distributed defects. Our model can interpret the experimental infrared spectra of CO monolayers adsorbed on NaCl(100) and explain the behavior of the linewidth with temperature and isotopic concentration. Differences in the infrared and sum frequency generation line shapes and intensities are discussed. Nonlinear spectroscopy experiments on this system should evidence these features. [S0163-1829(99)08043-1]

I. INTRODUCTION

The internal dynamics of admolecules has been extensively investigated using infrared spectroscopy¹ and, more frequency generation vibrational recently, sum spectroscopy.² Several aspects have been explored related to (i) the optical response of isolated species adsorbed on metals or dielectrics, (ii) the collective behavior of an assembly of admolecules on clean substrates, and (iii) the influence of point or extended defects on the structural and dynamical properties of the adspecies. The analysis of the vibrational spectrum provides information on the morphology of the substrate (surface periodicity, number and geometry of the adsorption sites, etc.) and the configuration of the adspecies (relative positions and orientations of the molecular axes, etc.) through the assignment of the signals, and on the relaxation processes (energy relaxation, fluctuations of motions, etc.) through the measurement of line shifts and linewidths. Importance was put on to the assignment of the peaks in the vibrational spectrum and to the analysis of the intensity, shift and width of these peaks as a function of external parameters such as temperature, adsorbate coverage, surface cleanliness etc. More specifically, the origin of the vibrational line shape was broadly classified into three categories,^{3,4} namely, lifetime, dephasing, and inhomogeneous broadenings. One of the challenge was to separate their relative contribution to the infrared bandwidth from experimental analyses or from theoretical arguments. A lot of papers^{1,3-13} on the infrared response of simple

A lot of papers^{1,3–13} on the infrared response of simple molecules were concerned with adsorption on metal surfaces, using CO as the test molecule. An electron-hole pair mechanism was clearly identified for the broadening of the peak connected to the stretching mode of CO adsorbed on Cu(100), for instance, Ref. 13, while dephasing process was rather invoked⁶ for the same adspecies on Ni(111), Pt(111), or Ru(100). Phonon-mediated decay of the lifetime of vibrational modes was shown to be efficient for lower frequency

modes,⁶ but in most cases the influence of inhomogeneous broadening was difficult to quantify.

On insulating surfaces,^{14–28} the competition between homogeneous and inhomogeneous broadening of the vibrational bands characteristic of physisorbed molecular species appeared more crucial in the lack of efficient relaxation population as observed for CO on metals. Indeed, it was established that the infrared peak width and shape depend strongly on the surface state and that accuracy could be improved significantly for the width measurement by reducing both surface defects of the ionic NaCl and MgO substrates and defects inside the adlayer. Generally, the measured broadening^{17,21} remains much smaller (≤ 1 cm⁻¹) than on metal surfaces, and the width can narrow below 0.1 cm⁻¹ in the most favorable situations.

Isotopic substitution of the adspecies can be an efficient tool for distinguishing among the various broadening processes and it has been extensively used on metal as well as on dielectric surfaces.^{3,5} The nature of the isotope effect, through mass change without affecting the interaction, was yet controversial since mass dependent linewidth changes are very small except for quantum species (H_2, D_2) and their detection requires high resolution spectroscopy. However, on ionic substrates, narrow peaks allowed isotopic effects to be resolved and clearly evidenced. The role of isotopic mixture of ¹²CO and ¹³CO on the dynamical coupling between adsorbate species has been analyzed by assuming a dipolar interaction model between the internal vibrations of the molecules adsorbed on copper surfaces.²⁹ The singular spectroscopic response of each isotope due to coupling interactions has also been used to study intensity transfers in the vibrational bands of species adsorbed close to steps on metal surfaces.⁵ The shift and shape of the vibrational bands of the CO isotopes adsorbed on NaCl(100) was studied independently by the groups of Ewing^{16,21} and Heidberg.²⁴ The influence of the isotopic mixture on the dipole-dipole coupling between the adspecies was discussed on the basis of Dis-

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selkampf *et al.*¹⁷ and Personn *et al.*²⁹ theoretical models. The former authors used simulation to calculate the peak frequency dispersion due to random distribution of the two isotopes without including the vibrational dephasing width, while the latters considered an ensemble of configurations of the isotopic mixture represented by an average molecule at each site.

A clear and complete account of the band shape observed in the frequency range of the two vibrational isotopic species as a function of temperature and molar fraction of the ¹²CO and ¹³CO isotopes was not given yet and experimental infrared spectra of the mixtures remained to be interpreted. The goal of this paper is to present a dynamical study of the vibron dynamics in a disordered molecular monolayer. The theoretical developments are based on a diagramatic expansion of the Green propagator describing the propagation and scattering by defects of the collective vibrations of the monolayer molecules. The disorder in the layer sites is considered within the *t*-matrix formalism which accounts for the collision of the vibrons at the defect sites, i.e., sites which are occupied by another isotope.

As it stands, the problem is very similar to the phonon propagation in disordered lattices,^{30–35} to the spin diffusion in random media,³⁶ or to the propagation of electrons in binary alloys.^{37–39} It can therefore be applied to several systems implying excitation transport (phonons, electrons, magons, etc.) in random media. Here, we limit our application to the vibron dynamics in isotopic mixtures but the method will be extended in a near future to the coadsorption of two molecular species, to the adsorption of molecules on different sites leading to the occurrence of several internal frequencies or to the adsorption of a pure monolayer on a surface with random defects.

The spectral density of the disordered monolayer is determined as a simple product of the average Green propagator describing the vibron dynamics and of a structure factor which depends on the nature of the spectroscopic probe. In addition the propagator accounts for the dephasing relaxation due the fluctuations of the external modes characterized by the phonons and librons of the monolayer and the substrate phonons. First, we calculate the infrared spectral density for the disordered monolayer CO on NaCl(100) which can be directly compared to the available experimental data. Then the spectral density connected to the infrared-visible sum frequency generation vibrational spectrum is evaluated and the similarities or the differences regarding the infrared peak intensity and shape when compared to linear spectroscopy data are analyzed in terms of temperature and molar fraction of isotopes.

In Sec. II, we present briefly the monolayer model, the total Hamiltonian and the vibron master equation already discussed in a previous paper for the pure monolayer.⁴⁰ Then, we introduce the ingredients that are required to include the disorder in the Green propagator and in the spectral density. An application to the IR and SFG responses of the vibrons in a disordered monolayer formed by a mixture of ¹²CO and ¹³CO molecules is developed in Sec. III and the calculation of the linewidth is performed for various impurity molar fractions. A discussion on the relative information given by the linear and nonlinear spectroscopies is made in Sec. IV.

II. THEORETICAL PART

A. The model

Let us consider a set of N diatomic molecules adsorbed on a well-organized ionic substrate. At completion, the molecules are assumed to form an ordered monolayer commensurate with the substrate. The periodicity of the whole system (layer + substrate) is characterized by the size of the unit cell containing n_c molecules which are not equivalently adsorbed on the substrate sites. Let l be the cell number and $s=1,\ldots,n_c$ the molecule number in the cell, the position $\mathbf{R}(ls)$ and the orientation $\mathbf{\Omega}(ls)$ of the (ls)th molecule is defined by the supervector $\mathbf{X}(ls) \equiv [\mathbf{R}(ls), \mathbf{\Omega}(ls)]$. In a similar way, the rth substrate atom belonging to the mth unit cell of the substrate in the *p*th plane (p=0) is the surface plane of the substrate) is defined by its position $\mathbf{x}(mpr)$. Each molecule behaves as an internal oscillator which is assumed to be harmonic and described by the coordinate Q(ls)around the equilibrium interatomic distance.

When the monolayer is formed by a single species of molecules labeled *a*, each molecule *a* is thus characterized by a harmonic frequency ω_a , and a reduced mass m_a connected to its internal vibration in gas phase. By contrast, when a second molecular species labeled *b* is added to the layer, new internal frequency ω_b and reduced mass m_b occur.

In order to limit the perturbation induced by the consideration of a second molecular species, we assume that molecules a and b are two isotopes such as ${}^{12}CO$ and ${}^{13}CO$. As a consequence, (i) the structural ordering of the initially single species monolayer is not destroyed by the presence of the isotopic defects since both the substrate-admolecule and molecule-molecule interactions are the same, (ii) the spatial distribution of the isotopic species a and b is random and monitored by the ratio of molar fraction p_a/p_b , and (iii) the difference in frequencies ω_a and ω_b are due only to the change of the isotope reduced masses m_a and m_b . We show in Fig. 1 a scheme of the perfect monolayer [Fig. 1(a)] and of a frozen configuration of the disordered monolayer [Fig. 1(b)]. The internal frequency ω_{ls} and the reduced mass m_{ls} of the molecule located on the (ls)th adsorption site are thus distributed randomly. They can take the values ω_a and m_a with a probability p_a for a molecule *a* in the (*ls*)th site or the values ω_b and m_b with a probability $p_b = 1 - p_a$ for an isotopic molecule b in the same site. In contrast, the stiffness $k_0 = m_{ls} \omega_{ls}^2$ of the internal vibration of the (*ls*)th admolecule is independent of its isotopic nature.

B. Hamiltonian and master equation for the vibrons

The Hamiltonian H for the whole system can be written in an improved way after the renormalization procedure was applied to the adspecies, as discussed in detail in Ref. 40. It is expressed as

$$H = H_I + H_E + \Delta H, \tag{1}$$

where H_I characterizes the internal dynamics of the admolecules and H_E the external dynamics of the system, i.e., the phonons and librons of the monolayer and the phonons of the substrate. The term ΔH denotes the coupling Hamiltonian between the internal vibrations and the external modes which is responsible for the relaxation processes.



FIG. 1. (a) Equilibrium structure of the pure CO monolayer adsorbed on NaCl(001). The unit cell of the bare NaCl surface is the square with size a_s whereas the unit cell of the system is the dark rectangle of size $(2a_s \times a_s)$. (b) A typical frozen configuration of a randomly disordered CO monolayer formed by the isotopic mixture of ¹²CO and ¹³CO molecules. Empty circles characterize the dominant isotope whereas full circles correspond to defect molecules.

The collective vibrations of the adlayer molecules are characterized by a self-term which describes the vibration of each isolated molecule at its adsorption site (renormalization) and by a quadratic contribution which represents the coupling between the admolecule vibrations. The Hamiltonian H_I is given as

$$H_{I} = \sum_{ls} \left[\frac{P^{2}(ls)}{2m_{ls}} + \frac{1}{2}m_{ls}\omega_{ls}^{2}Q^{2}(ls) \right]$$
$$+ \frac{1}{2} \sum_{ls} \sum_{l's'} \tilde{A} \binom{ll'}{ss'} Q(ls)Q(l's').$$
(2)

P(ls) is the conjugate momentum of the vibration coordinate Q(ls) and \tilde{A} the renomalized force constant between the internal vibrations of the (ls)th and (l's')th molecules which accounts for the molecule deformation by adsorption on the substrate.

The dynamics of the external modes is separated into three Hamiltonians which describe the translational and orientational motions of the adlayer H_M , the vibrational motions of the substrate ions H_S , and the coupling V_{MS} between the external motions of the monolayer and of the substrate. The total Hamiltonian of the external degrees of freedom is expressed as⁴⁰

$$H_{E} = \sum_{ls} H_{M}[\mathbf{X}(ls)] + \sum_{mpr} H_{S}[\mathbf{x}(mpr)] + \sum_{ls} \sum_{mpr} V_{MS}[\mathbf{X}(ls), \mathbf{x}(mpr)].$$
(3)

These motions are determined by solving the classical equations within the harmonic approximation for the substrate and using molecular dynamics simulation in a canonical ensemble for the adlayer in which all the molecules are assumed to be at their internal equilibrium.

The coupling Hamiltonian between internal and external degrees of freedom is limited to the linear and quadratic dependences on the internal modes while no limitation is imposed to the external motions which appear through the operators ΔA , as

$$\Delta H = \sum_{ls} \Delta A\binom{s}{l} Q(ls) + \frac{1}{2} \sum_{ls} \sum_{l's'} \Delta A\binom{ll'}{ss'} Q(ls)Q(l's').$$
(4)

The internal coordinate Q(ls) is then redefined in terms of local annihilation b_{ls} and creation b_{ls}^+ operators, as

$$Q(ls) = \sqrt{\frac{\hbar}{2m_{ls}\omega_{ls}}} (b_{ls} + b_{ls}^+).$$
(5)

In the next step, we determine a master equation which describes the time evolution of the Heisenberg representation of the annihilation $b_{ls}(t)$ [or creation $b_{ls}^+(t)$] operator of a vibrational excitation on the (ls)th admolecule, after averaging over the external motions. Let $B_{ls}(t) = \langle b_{ls}(t) \rangle_E$ be this average operator where $\langle \ldots \rangle_E$ means a trace over the external modes. The master equation obtained within the rotating wave approximation and the assumption of initial statistical decoupling between the vibrons and the external modes is expressed as⁴⁰

$$\frac{dB_{ls}(t)}{dt} + i\sum_{l's'} B_{l's'}(t) \left[D\binom{l'l}{s's} - iR\binom{l'l}{s's} \right] = \delta(t)b_{ls}(0),$$
(6)

where **D** is the dynamical matrix for the vibrons while **R** characterizes the relaxation matrix due to the coupling ΔH between the internal and external modes. Note that the relaxation matrix includes, in principle, population and phase relaxations of the vibrations over the low frequency modes (phonons and librons). However, as shown in Ref. 40, the population contribution is negligible with respect to the dephasing mechanism due to the fluctuations of the external modes and, therefore, **R** describes dephasing, only. The Dirac function in the right hand side of Eq. (6), corresponds to the initial statistical decoupling hypothesis between the systems *I* and *E*.

We define then a reduced field operator $\Phi_{ls}(t)$, expressed as

$$\Phi_{ls}(t) = \sqrt{\frac{\hbar}{2m_{ls}\omega_{ls}}} B_{ls}(t), \qquad (7)$$

which accounts for the mass and frequency of the molecule adsorbed at the (ls)th site. This allows us to write the quantities occurring in Eq. (6) in a reduced form, giving

$$\frac{1}{\omega_{ls}} \frac{d\Phi_{ls}(t)}{dt} + i \sum_{l's'} \Phi_{l's'}(t) \left[d \binom{l'l}{s's} - ir \binom{l'l}{s's} \right]$$
$$= \frac{\delta(t)}{\omega_{ls}} \Phi_{ls}(0). \tag{8}$$

The matrices \mathbf{d} and \mathbf{r} are written as

$$d\binom{l'l}{s's} = \delta_{ll'}\delta_{ss'} + \frac{\widetilde{A}\binom{ll'}{ss'}}{2k_0}, \qquad (9)$$

and

In Eq. (10), the term within brakets corresponds to the time correlation function of the reduced coupling operator which depends only on the external modes. This correlation function is determined from molecular dynamics simulation applied to the phonons and librons of the monolayer and from the knowledge of the phonon density of states for the substrate, as explained in Ref. 40.

The matrix **d** is a function of the force constant $\widetilde{\mathbf{A}}$ [Eq. (2)] reduced by the single valued stiffness k_0 of the internal vibrator which is independent of its isotopic nature. The expression of this matrix remains therefore the same whatever the isotopic molecule. In contrast, the reduced relaxation matrix **r** depends on the vibrational frequency ω_{ls} as shown in Eq. (10), although the correlation functions of the force constant matrix ΔA implied in the dephasing process are isotope independent. To be rigourous, the matrix \mathbf{r} is sensitive to the presence of isotopic impurities through the frequency change. But, in practice, the values of the elements of the matrix **r** are much smaller ($\sim 10^{-3}$) than the vibrational frequencies of the admolecules and we can therefore disregard this isotopic dependence. The Fourier-Laplace transform of Eq. (8) at the frequency ω_1 yields the matrix $\Lambda(\omega_1)$ expressed as

$$\Lambda\binom{l'l}{s's}, \omega_1 = \frac{\omega_1}{\omega_{ls}} \delta_{ll'} \delta_{ss'} - d\binom{l'l}{s's} + ir\binom{l'l}{s's}, \quad (11)$$

which characterizes the collective dynamics of the vibrons in the admonolayer coupled to a fluctuating bath represented by the external modes.

C. Infrared and sum frequency generation responses of the vibrons

The spectroscopic response of the collective internal vibrations of a monolayer formed by diatomic molecules is proportional to the real part of the spectral density $J(\omega_1)$ for

the infrared spectrum, and to the square modulus of $J(\omega_1)$ for the SFG spectrum. This latter quantity is itself a product of two contributions,⁴⁰

$$J(\omega_1) = \sum_{ls} \sum_{l's'} \Pi \begin{pmatrix} ll' \\ ss' \end{pmatrix} G \begin{pmatrix} l'l \\ s's \end{pmatrix}, \qquad (12)$$

where Π is a structure factor connected to the spectroscopic probe since it depends quadratically on the transition dipole components for the IR spectrum and on the product of the transition dipole and transition polarizability for the SFG spectrum. The values of these transition moments are either determined from *ab initio* calculations or obtained from the analysis of the infrared and Raman intensities of the gas molecule.

The Green tensor $\mathbf{G}(\omega_1)$ is the inverse of the complex matrix $\Lambda(\omega_1)$ defined in Eq. (11). It contains all the information on the vibron dynamics coupled to the external modes, i.e., including the dephasing relaxation mechanisms due to the bath fluctuations. Moreover, the matrix $\Lambda(\omega_1)$ is a random matrix modified by the presence of isotopic impurities in the monolayer which thus create a random disorder in the adsorbate.

However, the experimental determination of the spectral density $J(\omega_1)$ is measured over a macroscopic area of the layer, implying a very large number of admolecules and thus a large sampling of possible configurations for the defect distribution. Therefore, the spectral density can be considered as an average over the disorder of the Green propagator describing the vibron dynamics. More precisely, the G operator elements depend on the local surrounding around the (ls)th and (l's')th sites which differs from a site to another throughout the monolayer. The sum over the sites in Eq. (12)corresponds to a self-averaging quantity³⁵ which samples all the possible local environments. Hence this quantity can be calculated by fixing (ls) and (l's') and taking an average over the possible configurations. As a consequence, it is not necessary to know explicitly the Green propagator elements of vibrons but only their average values to determine the spectral density.

D. Average Green propagator of vibrons in a disordered monolayer

To evaluate the Green tensor of the vibrons, let us first consider a pure monolayer formed by single adspecies *a*. The dynamical behavior of the vibrons in such a perfect monolayer is described by the dynamical matrix $\Lambda_a(\omega_1)$ expressed as

$$\Lambda_a \begin{pmatrix} l'l\\ s's \end{pmatrix} = \frac{\omega_1}{\omega_a} \delta_{ll'} \delta_{ss'} - d \begin{pmatrix} l'l\\ s's \end{pmatrix} + ir \begin{pmatrix} l'l\\ s's \end{pmatrix}.$$
(13)

When molecular impurities are present in the monolayer, the general matrix $\Lambda(\omega_1)$ in Eq. (11) can be obtained by subtracting a perturbation matrix $\delta \Lambda(\omega_1)$ to the matrix $\Lambda_a(\omega_1)$ in Eq. (13). It is thus written as

$$\Lambda(\omega_1) = \Lambda_a(\omega_1) - \delta \Lambda(\omega_1). \tag{14}$$

The term in $\Lambda(\omega_1)$ which depends on the isotopic defects in a crucial way is the purely diagonal contribution of Eq. (11)

through ω_{ls}^{-1} . To determine the perturbation matrix $\delta \Lambda(\omega_1)$, let us define the random variable σ_{ls} which takes the value 1 (0) with probability $p_b(p_a)$ when the (*ls*)th site is occupied by a defect molecule b(a). The set of variables $\{\sigma_{ls}\}$ describes a particular configuration of the disordered monolayer, and for such a frozen configuration, the defect matrix $\delta \Lambda(\{\sigma_{ls}\}, \omega_1)$ is given as

$$\delta \mathbf{\Lambda}(\{\sigma_{ls}\}, \omega_1) = \sum_{ls} \left(\frac{\omega_1}{\omega_a} - \frac{\omega_1}{\omega_b} \right) \sigma_{ls} \mathbf{I}_{ls}$$
(15)
$$\equiv \sum_{ls} \delta \eta(\omega_1) \sigma_{ls} \mathbf{I}_{ls} ,$$

where \mathbf{I}_{ls} is the projector on the (*ls*)th site.

The inversion of the matrix $\Lambda(\omega_1)$ [Eq. (14)] using Eq. (15), leads to the Dyson equation for the vibron propagator in a given configuration of the disorder, as

$$\mathbf{G}(\{\sigma_{ls}\},\omega_{1}) = \mathbf{G}_{a}(\omega_{1}) + \sum_{ls} \mathbf{G}_{a}(\omega_{1}) \,\delta \eta(\omega_{1}) \sigma_{ls} \mathbf{I}_{ls} \mathbf{G}(\{\sigma_{ls}\},\omega_{1}),$$
(16)

where $\mathbf{G}_{a}(\omega_{1})$ is the Green propagator for the vibrons of the pure monolayer formed by molecules *a*. For instance, the projection of Eq. (16) on a given adsorption site $(l_{1}s_{1})$, yields an iterative expression of $\mathbf{G}(\{\sigma_{ls}\},\omega_{1})$ in terms of $\mathbf{G}_{a}(\omega_{1})$

$$\mathbf{G}(\{\sigma_{ls}\},\omega_{1}) = \mathbf{G}_{a}(\omega_{1}) + \sum_{ls} \mathbf{G}_{a}(\omega_{1})\mathbf{t}_{ls}\mathbf{G}_{a}(\omega_{1})\sigma_{ls}$$
$$+ \sum_{ls} \sum_{l's' \neq ls} \mathbf{G}_{a}(\omega_{1})\mathbf{t}_{ls}\mathbf{G}_{a}(\omega_{1})\mathbf{t}_{l's'}$$
$$\times \mathbf{G}_{a}(\omega_{1})\sigma_{ls}\sigma_{l's'} + \cdots, \qquad (17)$$

where \mathbf{t}_{ls} is the *t* matrix which describes the scattering process of the vibrons of the pure monolayer with adspecies *a* when an impurity *b* is located on the (*ls*)th site. We give in Appendix A the detailed algebraic manipulations that leads to the *t* matrix. It is then written as

$$\mathbf{t}_{ls}(\omega_1) = \frac{\delta \eta(\omega_1)}{1 - G_a(0;\omega_1)\delta \eta(\omega_1)} \mathbf{I}_{ls} \equiv t(\omega_1) \mathbf{I}_{ls}, \quad (18)$$

where $G_a(0;\omega_1)$ is the Green tensor for the pure monolayer determined at the defect site. In Eq. (17), two successive scatterings of the free propagator $\mathbf{G}_a(\omega_1)$ by the same isotopic defect are excluded since they have been already taken into account in the *t*-matrix expansion. Therefore we consider the modified Green propagator $\overline{\mathbf{G}}_a(\omega_1)$ which is defined as

$$\overline{\mathbf{G}}_{a}(\boldsymbol{\omega}_{1}) = \mathbf{G}_{a}(\boldsymbol{\omega}_{1}) - \boldsymbol{G}_{a}(0;\boldsymbol{\omega}_{1})\mathbf{1}.$$
(19)

By using Eq. (19) and after resumming the terms in the iteration, the sum of the various contributions in Eq. (17) gives the final expression of the vibron propagator for a given configuration of the disorder



FIG. 2. Diagramatic representation of Eq. (17) for a frozen configuration of the disordered monolayer. The dotted line corresponds to the Green propagator of the vibrons in the disordered monolayer whereas the full line represents the propagator of the vibrons in the pure monolayer (no defect). Each square characterizes a defect and corresponds to the scattering process of a vibron due to the presence of an isotopic defect.

$$\mathbf{G}(\{\boldsymbol{\sigma}_{ls}\},\boldsymbol{\omega}_{1}) = \mathbf{G}_{a}(\boldsymbol{\omega}_{1}) + \mathbf{G}_{a}(\boldsymbol{\omega}_{1})\mathbf{T}(\{\boldsymbol{\sigma}_{\ell s}\},\boldsymbol{\omega}_{1})$$
$$\times [\mathbf{1} - \overline{\mathbf{G}}_{a}(\boldsymbol{\omega}_{1})\mathbf{T}(\{\boldsymbol{\sigma}_{ls}\},\boldsymbol{\omega}_{1})]^{-1}\mathbf{G}_{a}(\boldsymbol{\omega}_{1}),$$
(20)

where the matrix $\mathbf{T}({\sigma_{ls}}, \omega_1)$ characterizes the disorder and is defined as

$$\mathbf{T}(\{\boldsymbol{\sigma}_{ls}\},\boldsymbol{\omega}_1) = \sum_{ls} \mathbf{t}_{ls}(\boldsymbol{\omega}_1) \boldsymbol{\sigma}_{ls}.$$
 (21)

Figure 2 shows a diagramatic representation of the propagator $\mathbf{G}(\{\sigma_{ls}\}, \omega_1)$ and the various paths that can be implied after scattering on defects.

Finally, the average Green propagator is expressed as

$$\langle \mathbf{G}(\boldsymbol{\omega}_1) \rangle_c = \sum_{\{\boldsymbol{\sigma}_{ls}=0,1\}} \mathbf{G}(\{\boldsymbol{\sigma}_{ls}\}, \boldsymbol{\omega}_1) f(\{\boldsymbol{\sigma}_{ls}\}), \qquad (22)$$

where the distribution function $f({\sigma_{ls}})$ of the random variables σ_{ls} is written as

$$f(\{\sigma_{ls}\}) = \prod_{ls} [p_a + \sigma_{ls}(p_b - p_a)].$$
(23)

Equation (22) represents the exact expression of the average Green propagator. It contains an average of products of random variables such as $\langle \sigma_{ls} \sigma_{l's'} \sigma_{l''s''} \cdots \rangle_c$ in the various terms of the Dyson series. However, a numerical calculation of this expression is very difficult due to the huge number of configurations associated with the disorder. Namely, when the monolayer exhibits *N* sites, there are 2^N possible configurations. To evaluate these averages, the random phase approximation³⁵ is applied which allows us to write

$$\langle \sigma_{l_1s_1}\sigma_{l_2s_2}\cdots\sigma_{l_Ms_M}\rangle_c \simeq \langle \sigma_{l_1s_1}\rangle_c \langle \sigma_{l_2s_2}\rangle_c\cdots \langle \sigma_{l_Ms_M}\rangle_c = p_b^M.$$
(24)

This leads to assume that the various matrices $\mathbf{t}_{ls}(\omega_1)$ are identical for every monolayer site and to express the average of the Green propagator in a simplified form (see Appendix B), as

$$\langle \mathbf{G}(\omega_1) \rangle_c = \mathbf{G}_a(\omega_1) + \mathbf{G}_a(\omega_1) \langle t(\omega_1) \rangle_c \times [1 - \overline{\mathbf{G}}_a(\omega_1) \langle t(\omega_1) \rangle_c]^{-1} \mathbf{G}_a(\omega_1).$$
 (25)

The resulting expression of the average *t* matrix is a simple *c* number which is function of the mass defect $\delta \eta(\omega_1)$, of the occupancy probability p_b and of the diagonal element of the Green function $G_a(0;\omega_1)$ for the pure monolayer, as

$$\langle t(\omega_1) \rangle_c = p_b \frac{\delta \eta(\omega_1)}{1 - G_a(0;\omega_1)\delta \eta(\omega_1)} = p_b t(\omega_1). \quad (26)$$

Finally the average vibron propagator in the isotopically disordered monolayer can be written in terms of the reduced dynamical and relaxation matrices of the pure monolayer corrected by a diagonal term which accounts for the disorder (see Appendix B), as

$$\langle \mathbf{G}(\omega_1) \rangle_c = \left[\left(\frac{\omega_1}{\omega_a} - \frac{p_b \delta \eta(\omega_1)}{1 - p_a G_a(0; \omega_1) \delta \eta(\omega_1)} \right) \mathbf{1} - \mathbf{d} + i \mathbf{r} \right]^{-1}.$$
(27)

This diagonal perturbation does not depend on the monolayer site and the inverse matrix of $\langle \mathbf{G}(\boldsymbol{\omega}_1) \rangle_c$ therefore appears to be an effective matrix which has the dynamical properties of a periodic monolayer. In other words, although the isotopic defects randomly distributed destroy the translational invariance of the dynamical matrix, the average over the various configurations of the disorder, within the random phase approximation, leads to the removing of this invariance. As a consequence, the wave vector \mathbf{q} connected to the vibrons in the perfect monolayer applies also to the disordered monolayer.

As shown in Eq. (12), the spectral density $J(\omega_1)$ is directly connected to the properties of the average propagator $\langle \mathbf{G}(\omega_1) \rangle_c$ [Eq. (27)], which is itself characterized by the **d** and **r** reduced matrices and by the diagonal defect contribution. This latter contribution is responsible for two different physical effects. First, the pole of this contribution leads to the occurrence of a localized frequency ω_L which is solution of the equation

$$G_a(0;\omega_1)\,\delta\eta(\omega_1) = \frac{1}{1-p_b}.\tag{28}$$

The frequency ω_L is close to the frequency of the isotope ω_b when p_b is sufficiently small. Hence, the corresponding spectral density will exhibit a peak at the frequency ω_L in the region of the defect frequency $\omega_b \neq \omega_a$. Second, since the diagonal defect contribution is complex through $G_a(0;\omega_1)$, it shifts and broadens the signals connected to the dominant species *a* which are characterized by the **d** and **r** matrices. This will result in inhomogeous effects due to the disorder in the infrared band of the pure monolayer.

E. Improvement of the disorder description

While Eqs. (22) and (20) are quite general, the expression given by Eq. (27) rests on the validity of the random phase approximation. Within this latter approximation, we assume that the scattering of the vibrons by a defect does not depend on the presence of the other defects. In other words, the successive scattering processes experienced by a vibron are not correlated and correspond simply to a product of single defect mechanisms. Such an assumption is valid for low defect molar fraction in the monolayer $(p_b \rightarrow 0)$ since, in this case, the defects are distributed randomly far apart from each other.³⁵

However, when p_b increases, the probability for finding configurations with nearest neighbor defects grows and the correlation of the scattering processes cannot be disregarded. To account for such a coupling between the defect induced vibron scatterings, we could substitute to Eq. (24), a cumulant expansion of the occupation variables σ_{ls} of the monolayer sites which would include correlations at each order of the expansion. For instance, a three defects scattering process would consist in changing the average $\langle \sigma_1 \sigma_2 \sigma_3 \rangle_{cc} = p_b^3$ in Eq. (24) by the cumulant average $\langle \sigma_1 \sigma_2 \sigma_3 \rangle_{cc} = p_b^3 + p_b^2 p_a \delta_{13}$, where δ is the Kronecker symbol.³⁵ Another approach could also be developed within the coherent potential approximation^{35,37} by describing the disordered monolayer as an effective two dimensional crystal having the translational invariance property.

Here, we use a third alternative for which we consider the possibility of forming defect aggregates in the monolayer, within the random phase approximation. Instead of the (2×1) unit cell characteristic of the pure monolayer, we define a larger cell whose sizes along X and Y are integer multiples of the former and which contains N_c adsorption sites (Fig. 1). This cell is periodically reproduced to describe the disordered layer. Inside this cell, there are 2^{N_c} possible configurations for arranging zero, one, two, ..., N_c isotopic impurities on the adsorption sites. Let L and S be the new cell number and site number, respectively. Equations (21) and (22) can then be rewritten using these new indices where \mathbf{t}_{LS} is now a $(N_c \times N_c)$ square random matrix connected to the defects inside each cell L and $\mathbf{G}_a(0)$ becomes a matrix having the dimension of the cell defect.

The route to determine the average propagator for the vibrons in the disordered monolayer is then similar to the previous model. The random phase approximation applies to the product of *t* matrices leading to a decorrelation of vibron scattering processes belonging to different cells *L*, whereas the corresponding scattering processes inside each cell are coupled. Equation (25) giving the resulting Green propagator for the disordered monolayer can be kept as it stands by considering now that $\overline{\mathbf{G}}_a$ and $\langle \mathbf{t}(\omega_1) \rangle_c$ are square matrices having the rank N_c of the cell. The condition for the occurrence of localized modes, as shown in the previous model [Eq. (28)], then becomes

$$\det[(1+\mathbf{I}_0\mathbf{G}_a\mathbf{I}_0\langle\mathbf{t}(\boldsymbol{\omega}_1)\rangle_c)^{-1}]=0, \qquad (29)$$

where I_0 is the projector over the origin cell L=0. The disorder gives rise to several localized modes which can be significantly shifted from the impurity frequency $\omega_L \approx \omega_b$, depending on the intensity of the coupling interaction between defects. Moreover, the disorder shifts and broadens the band of the pure monolayer around ω_a . The number and the intensity of the localized peaks is a function of the impurity concentration which favors more or less the formation of defect aggregates.

Such a procedure clearly improves the previous scheme of uncorrelated scattering processes when the molar fraction of defect isotope remains lower than 0.3. In fact, the size of the "extended" cell must be of the order of, or larger than, the

		$\omega(\mathrm{cm}^{-1})^{\mathrm{a}}$	FWHM (cm ⁻¹) ^a	$\omega(\mathrm{cm}^{-1})^{\mathrm{b}}$	FWHM (cm ⁻¹) ^b
¹² CO	$p_a = 0.99$	2156.4	0.13	2154.96	0.18
		2144.7	0.13	2148.71	0.17
	$p_a = 0.01$	2152.5	0.09	2150.47	0.17
¹³ CO	$p_{b} = 0.99$	2107.2	0.13	2107.20	0.18
		2096.5	0.13	2101.39	0.17
	$p_{b} = 0.01$	2104.7	0.09	2102.83	0.12

TABLE I. Calculated and experimental frequencies and widths of the CO monolayer peaks at 5 K.

^aCalculated values.

^bExperimental data taken from Ref. 21.

size of the aggregates formed by the impurities at a given molar fraction. When p_b is less than 0.3, the mean number of defects per aggregate is typically about 3 or 4, and the fluctuations of this number around its average value is negligible. Beyond this value, the fluctuations increase significantly with the concentration of defects and a convenient choice of the cell size becomes impossible.

III. APPLICATION TO THE IR AND SFG SPECTRA OF CO ISOTOPIC MIXTURES ADSORBED ON NACL(100)

A. Interactions and monolayer characteristics

The interaction potential between the CO molecules and the NaCl substrate, on one hand, and between CO molecules in the layer, on the other hand, is described by semiempirical forms including Lennard-Jones dispersion-repulsion terms and electrostatic contributions expanded up to the quadrupole moment. The expressions of the various terms and the values of the parameters, especially their vibrational dependence, are given in Ref. 40.

The minimization of the total interaction potential was shown to yield the (2×1) structure for CO with two inequivalently oriented molecules per unit cell, which is consistent with the geometry determined from elaborated potential expressions and inferred from the interpretation of the experimental spectra. The molecules form linear chains along the Na rows, their axes are tilted by about 45° from the normal to the surface and the projections of their axes on the surface plane are aligned along the Na rows forming parallel and antiparallel adjacent chains (Fig. 1). Molecular dynamics simulations performed at low temperature ($T \leq 30$ K) corroborate the stability of this phase and exhibit the occurrence of an orientational disorder of the molecular axes above 30 K, in close agreement with the observed signals in the infrared spectrum. In this orientationally disordered phase, the unit cell is that of the pure NaCl surface [i.e., a (1×1)] structure] instead of the well defined (2×1) cell at low temperature.

The isotopic mixture of ¹²CO and ¹³CO molecules does not change the interactions and the stable structures of the monolayer. Therefore, whatever the molar fraction of impurity molecules, the basic cell for the low temperature monolayer phase is the (2×1) geometry. However, the presence of isotopes at random sites implies the failure of the translational invariance leading *a priori* to an infinite unit cell for the disordered monolayer. In the following, the connection with the theoretical part (Sec. II) is introduced by denoting *a* and *b* the ¹²CO and ¹³CO molecules, respectively. The calculations are performed according to the improved model presented in Sec. II E and using a *t*-matrix expansion of the Green operator. We consider a (4×3) "extended" cell containing 12 adsorption sites and corresponding to 4096 possible configurations for arranging isotopic impurities in the cell. This cell is thus formed by 12 unit cells of the substrate. The dimension of the matrix $\mathbf{t}(\omega_1)$ is (12×12) and this allows us to distribute 0, 1, ..., up to 12 impurities in the cell.

B. p-polarization infrared spectrum of the monolayer

1. Pure ¹²CO and ¹³CO monolayers

The infrared spectrum of the CO monolayer is calculated from the real part of the spectral density given in Eq. (12). This density depends on two quantities. The structure factor characterizes the geometry of the photon beam and of the admolecules with respect to the surface whereas the Green tensor describes the dynamics of the layer and thus includes both frequency shifts and peak widths. Though an extension to the s-polarized spectrum is straightforward, we will assume that the photon beam is *p*-polarized, i.e., polarized perpendicular to the incident beam since the most intense signals are obtained with such an experimental setup. The calculated infrared spectrum for the pure monolayer at T ≤ 30 K exhibits two intense peaks, the relative intensities of which depend on the mutual orientation of the two admolecules in the (2×1) unit cell. The high frequency peak is 2.6 times more intense than the low frequency peak and the Davydov frequency splitting is equal to 12 cm^{-1} . These two quantities are the same for both isotopes (Table I). This latter result is consistent with the fact that the coupling between the two molecules in the unit cell depends on the forces and not on the masses.

The linewidth of the two peaks is the same (see Table II) and it is obtained as the sum of dephasing contributions which correspond to the elements of the relaxation matrix $\mathbf{r}(\omega_1)$. The diagonal elements characterize the influence on the vibron frequencies of the fluctuations of the external modes of the substrate (phonons) and of the adsorbate (phonons + librons). While the substrate contribution appears to remain small, the layer contribution becomes largely dominant as *T* rises. The nondiagonal elements describe the fluctuations of force constants between neighboring molecules. This contribution is generally small except at very

TABLE II. Calculated linewidth vs temperature of the pure CO monolayer peak and of the localized peak, at low defect molar fraction.

T (K)	$FWHM^{a} (cm^{-1})$	$FWHM^{b} (cm^{-1})$
5	0.13	0.09
25	0.28	0.24
55	0.40	0.36

^aPure monolayer.

^bIsolated impurity.

low temperature (T=5 K) where it is as large as the diagonal term.⁴⁰ Since we assume that the relaxation matrix is mass independent, once again the isotopic change does not modify the width of the infrared peaks assigned to the ¹²CO and ¹³CO pure layers.

2. ¹²CO/¹³CO mixtures

At very low molar fraction of defect isotope, the calculated *p*-polarization infrared spectrum at $T \le 30$ K of a slightly disordered monolayer exhibits still two peaks in the frequency range of the dominant isotope and a single peak in the range of the minor isotopic species. Since the results are similar when the role of ¹²CO and ¹³CO are reversed, let us, for instance, look at the spectral range of the ¹³CO frequencies.

For $p_b < 0.01$, this situation corresponds to a nearly perfect ¹²CO monolayer with single impurity molecules ¹³CO embedded in a ¹²CO layer. We obtain a slight blueshift of the single ¹³CO peak frequency centered at ω_L = 2104.7 cm⁻¹ when temperature rises from 5 to 55 K (Table I) and a concomitant broadening of the peak from 0.09 to 0.36 cm⁻¹ (Table II). The IR spectrum in the frequency range of the ¹³CO molecule is shown in Figs. 3(a) and 3(b) at T=25 K. Note for comparison that the spectrum of the nearly perfect ¹³CO layer ($p_b \approx 0.99$) displays two peaks splitted by 12 cm⁻¹ having approximately the same width which evolves from 0.13 cm⁻¹ at 5 K to 0.4 cm⁻¹ at 55 K (Fig. 4).

When the defect molar fraction increases up to $p_b = 0.3$, the single band in the frequency range of the defect species remains the most intense and it is slightly blue shifted by about 0.1 $\,\mathrm{cm}^{-1}$ with respect to the peak frequency obtained for the smallest molar fraction. At T=25 K (Fig. 5), the width varies from 0.53 to 1.06 cm^{-1} as the defect molar fraction increases from $p_b = 0.1$ to $p_b = 0.3$. However, several additional structures appear on both sides of this peak with two dominant peaks around 2100.0 and 2106.5 cm^{-1} which are assigned to the impurity ¹³CO dimers (Fig. 5). The frequencies of the dimers are not symmetric with respect to the single peak because there are two different dimer geometries in a (2×1) monolayer depending on the relative orientations of the two adjacent molecules which correspond to different force constant couplings. In addition, the two signals of each dimer are not *p*-infrared active due to the special symmetry of these dimers (colinear or antiparallel, see Fig. 1). As a result the signal of the antiparallel dimer is observed at higher frequency whereas the signal of the colinear dimer appears at lower frequency. Aside from the dimer structures, other less intense absorption signals lie in the frequency range [2097,2108.5 cm⁻¹]; they are assigned to larger aggregates of the isotopic defect (Fig. 5). Note that when the molar fraction of defect reaches 0.3, the single defect peak appears to be inhomogeneously broadened by other defect aggregates leading to a dissymmetric structured band broadened by about 2 cm⁻¹.

The corresponding IR spectrum of the dominant isotope ¹²CO when $p_a = 1 - p_b$ decreases from 1 to 0.7 is formed by the two previously mentioned peaks of the pure monolayer splitted by 12 cm⁻¹. The shape of these peaks becomes asymmetric when $p_b = 0.1$ and it appears to be structured at $p_b = 0.3$. In Fig. 6, we show the behavior of the high frequency mode of the spectrum of the ¹²CO monolayer with the defect molar fraction p_b . As p_b rises from 0.1 to 0.3, the total FWHM of this peak increases from 1.5 cm⁻¹ to 5.4 cm⁻¹ at T = 25 K. In addition, a second blueshifted peak occurs at 2162.0 cm⁻¹ for a high molar fraction of defects.

To understand the behavior of the line shift and width with the isotopic molar fraction p_b in terms of collective excitations, let us discuss the spectral response of the two isotopes. At small p_b value, one impurity molecule is surrounded statistically by the molecules of the dominant isotope. As a result, a single localized mode occurs at a frequency ω_L close to the vibrational frequency ω_h of the impurity whereas the infrared response of the dominant isotope looks similar to that of the pure monolayer with two ¹²CO molecules per unit cell. The width of the localized mode comes from the diagonal part of the relaxation matrix, only, since the dynamical coupling between a and b molecules tends to vanish when the frequency difference ω_a $-\omega_b$ is larger than the band width of the vibrons in the pure monolayer. We thus calculate a localized peak width that is always narrower than the width of the pure monolayer peaks for which both diagonal and non diagonal elements of the relaxation matrix contribute to the broadening (Table II). Furthermore, note that such a width difference depends also on temperature and is maximum at low temperature when the ratio between the non diagonal and diagonal relaxation terms is maximum.

When p_{h} increases, several localized modes appear which correspond to the formation of impurity aggregates (dimer, trimer, ...) leading to the occurrence of shifted and splitted signals in addition to the most intense peak connected to the single defect. The widths of these signals cannot be simply interpreted as it is the result of the relaxation matrix diagonalization. Similarly, the two infrared peaks of the dominant isotope tend to become wider and wider as p_h rises from 0.0 to 0.3. This behavior is due to the increasing influence of the defects which play the role of scattering centers for the vibrons. The collective motions of the internal vibrations are no longer pure eigenstates of the harmonic monolayer but they correspond to a superimposition of several eigenstates with different wave vectors q. This leads to the broadening of the vibron peaks due to spectroscopic activation of vibrons by the defect centers with frequencies that are shifted with respect to the frequencies of the vibrons at the center of the Brillouin zone (i.e., with $\mathbf{q} \neq 0$). In other words, the lifetime of the vibrons of the pure monolayer decreases as the molar fraction of impurities increases.



FIG. 3. Calculated IR and SFG spectra of the disordered monolayer in the frequency range of the ¹³CO impurity molecules. The spectra are drawn at T=25 K and for a low defect molar fraction p_b . Left hand side: *p*-polarized IR spectra for a molar fraction of ¹³CO molecules equal to $p_b=0.001$ and $p_b=0.01$. Right hand side: *ppp*-polarized SFG spectra for the same molar fractions of ¹³CO molecules.

This width has therefore an inhomogeneous nature and it is directly connected to the density of states (DOS) of the vibrons. As shown in Fig. 7, the DOS of the vibrons of a pure CO monolayer exhibits two peaks at 2162.0 cm⁻¹ and 2171.5 cm⁻¹. Since the CO monolayer is a two dimensional structure, the peak centered at 2162.0 cm⁻¹ corresponds to the well known logarithmic singularity.⁴¹ Moreover, the strong anisotropy of the force constants in the monolayer with a much larger coupling along the *Y* direction (Fig. 1) leads to a Van Hove singularity at the edge of the vibron band which characterizes a one-dimensional behavior of the vibrons in this direction. The resulting dissymmetry of the DOS leads to a dissymmetric line shape in the IR spectrum and to the occurrence of the second peak close to the logarithmic singularity of the DOS.

C. Infrared-visible sum frequency generation spectrum

The SFG vibrational spectrum for the CO monolayer depends on the polarization of the incident infrared and visible



FIG. 4. Calculated *p*-polarized IR spectrum of the CO monolayer at T=25 K and for a molar fraction in ¹³CO molecules equal to $p_b=0.99$.

beams and of the visible probe at the frequency sum. To be consistent with the previous section, we consider here the *ppp*-polarization spectrum where the visible and IR photons are polarized perpendicular to the beams. In the spectral density defined by Eq. (12), **G** appears to be the same as for the infrared spectrum while **II** contains the vibrational dependence of the dipole and polarizability tensors and the corresponding geometry of the experimental setup (angle of incidence of the beam equal to 45°). Another specificity of the spectroscopic probe which leads to differences in the spectral response of the monolayer is that the infrared spectrum is



FIG. 5. Behavior of the line shape of the *p*-polarized IR spectra in the frequency range of the ¹³CO molecules at T=25 K vs three typical values of the ¹³CO molar fraction.



FIG. 6. Behavior of the line shape of the *p* polarized IR high frequency peak in the frequency range of the dominant (¹²CO) species at T=25 K vs three typical values of the ¹³CO molar fraction.

proportional to the real part of the spectral density $J(\omega_1)$ whereas the SFG spectrum is proportional to the square modulus of $J(\omega_1)$. The consequence of these differences is threefold. First, it has been shown in Ref. 40 that the relative intensity of the two peaks in the pure monolayer spectrum is different for the infrared and SFG spectrum because the intensities are weighten by the square transition dipole in the former case and by the product of the transition dipole and polarizability in the latter case. This feature is also observed



FIG. 7. Density of states of the vibrons of the pure 12 CO monolayer. Note the two singularities at 2161 and 2172 cm⁻¹.



FIG. 8. Behavior of the line shape of the *ppp*-polarized SFG spectra in the frequency range of the ¹³CO impurities, at T = 25 K, vs three typical values of the ¹³CO molar fraction.

in the frequency range of the dominant species in the SFG spectrum. Then the two peaks broaden in the same way when the disorder increases to account for the vibron dispersion by scattering on defects. The broadening is identical to the infrared band broadening.

Second, in Fig. 8, the SFG spectrum in the frequency range of the impurity species exhibits the same feature as the IR one when the molar fraction of defects is larger than p_b = 0.1. The single peak, which corresponds to the localized mode, remains the most intense and several additional structures appear on each side of this peak characterizing the occurrence of impurity dimers, trimers, etc. However, the relative intensity of these additional signals when compared to the main peak intensity is different in the IR and SFG spectra. More precisely, the most intense peaks are enhanced in the nonlinear spectroscopy with respect to the less intense peaks, as the result of the square density dependence of the SFG spectrum.

Third, at low defect molar fraction $(p_b \le 0.01)$, the SFG response of the localized mode is very different from that of the infrared spectrum. Indeed the SFG signal corresponds to a single peak having a dispersive shape [Figs. 3(c) and 3(d)] whereas the IR peak is fully resonant [Figs. 3(a) and 3(b)]. Such a particular shape disappears when p_b increases beyond 0.1. To understand this feature, let us recall that the field detected at the sum frequency is the sum of the field emitted by the impurity molecules and by the dominant isotope. For an infrared frequency ω_1 close to the defect frequency ω_b , the nonlinear response of the impurities is resonant whereas the nonlinear response of the dominant species is not. The spectral density $J(\omega_1)$ is the sum of two contributions in the

SFG spectrum. The first term is a resonant term at the frequency ω_1 , denoted by $J_R(\omega_1)$, whereas the second term $J_{\rm NR}$ incorporates all the nonresonant contributions of the monolayer. Since the SFG spectrum is proportional to the square modulus of the spectral density, three contributions appear in the spectrum calculation. The first one, equal to $|J_{\rm NR}|^2$, is a pure background contribution nearly independent of ω_1 since the frequency difference $\omega_a - \omega_b$ is much larger than the vibron bandwidth of the pure monolayer. The second term, $|J_R(\omega_1)|^2$, is a pure resonant contribution corresponding to the response of single impurity molecules ¹³CO embedded in the ¹²CO layer. The last one, equal to $2 \operatorname{Re}[J_{NR}J_{R}(\omega_{1})]$, characterizes the interference between the resonant and nonresonant contributions and gives a dispersive shape to the SFG profile. When the number of impurities increases, i.e., when p_b is greater than 0.1, the weight of the pure resonant term increases with respect to the interference term and the dispersive profile of the SFG spectrum disappears leading to a peak shape similar to that of the IR spectrum.

IV. COMPARISON WITH EXPERIMENTAL DATA

Polarization infrared Fourier transform spectroscopy of the CO monolayer adsorbed on NaCl has been extensively studied with special emphasis brought to the influence of isotopic defect in Refs. 16, 21, and 24. In Table I, we give the experimental data determined by the group of Ewing^{21} at low temperature (T=5 K).

At low defect concentration, i.e., when the molar fraction of ¹³CO molecules is less than 0.01, the infrared spectrum in the frequency range of the impurity exhibits one peak centered at 2102.83 cm⁻¹ and with a FWHM equal to 0.12 cm^{-1} . This peak corresponds to the localized mode which occurs when a single ¹³CO molecule is embedded in a ¹²CO layer. By constrast, the pure ¹³CO monolayer leads to the occurrence of two peaks, centered at the frequencies 2107.20 and 2101.39 cm⁻¹ and having the same FWHM equal to 0.18 cm⁻¹. The width of the localized peak represents 67% of the width of the two peaks of the pure monolayer. Note that the experimental resolution (equal to 0.1 cm^{-1}) is close to the measured width and it probably leads to a significant uncertainty in the absolute determination of the width. In addition, another source of uncertainty occurs, due to the presence of surface defects. Therefore at T=5 K, the experimental width is probably overestimated by a factor that could range between 1.5 and 2 due to this additional inhomogeneous broadening.²¹ The comparison presented in Table I, shows that our calculations performed at the same temperature are in good agreement with the experimental data since the localized peak is blueshifted with respect to the high frequency peak of the pure monolayer and its width corresponds to 69% of the perfect monolayer one.

When the defect molar fraction increases, the experimental width¹⁶ of the single ¹³CO peak increases significantly since, at T=55 K and $p_b=0.2$, it is equal to 0.9 cm⁻¹ whereas the width of the pure monolayer is equal to 0.4 cm⁻¹. This latter width represents 45% of the width of the localized peak. At the same molar fraction and at 25 K, the calculated FWHM of the single peak is equal to 0.63 cm⁻¹ (Fig. 5) leading to the same ratio of 45% between the width of the pure monolayer and that of the localized peak.

From examination of Fig. 5, let us mention that a comparison with the experimental spectra becomes difficult when the isotope defect molar fraction increases. Indeed, the calculated spectrum does not display a single localized peak, but in addition a series of secondary signals occur due to the formation of impurity ¹³CO aggregates (dimers, trimers, etc.) in the ¹²CO monolayer. The aggregate peaks lying far apart from the single defect peak frequency could probably not be observed in experiments because they are much less intense. By contrast, the high frequency secondary peaks in the close neighborhood of the single defect peak could participate to the broadening, leading to a relatively wide dissymmetric signal (about 3 cm⁻¹) close to the ω_L frequency. Though the peak becomes effectively dissymmetric in the experimental spectrum, such a band structuring is apparently not observed. This can be due to either the experimental resolution which prevents the observation of this structure or to an overestimate of the calculated splittings of the peaks.

In the frequency range of the dominant isotope and when $p_a = 1 - p_b$ decreases from 1 to 0.2, the experimental spectrum is formed by the two peaks of the pure monolayer splitted by 6.25 cm⁻¹ at T=5 K (Table I). These peaks broaden smoothly from 0.4 to 1 cm^{-1} when the ¹³CO molar fraction rises from $p_b = 0.0$ to $p_b = 0.8$.¹⁶ In our calculations performed at T = 25 K, the width of these peaks increases considerably up to 5 cm⁻¹ as p_h increases from 0.0 to 0.3 as shown in Fig. 6. Such an overestimate of the calculated FWHM of the peaks for the dominant isotope may have two origins. First, the comparison between the theoretical and the experimental splittings of the two peaks of the pure monolayer, equal to 12 and 6.25 cm^{-1} , respectively, shows that we tend to overestimate the lateral force constants in the calculations, and therefore to spread out the signal connected to nonzero wave vector vibrons. Second, this can be due to a inadequate treatment of the influence of defects on the vibrons of the pure monolayer. Indeed, in our model, we assume that the scattering of the vibrons by a defect located in a given unit cell does not depend on the presence of defects inside another cell. Such an assumption is clearly valid for the vibrons which lie in the frequency range of the impurity since the internal vibrations are strongly localized near a defect. By contrast, the mean free path of the vibrons of the dominant species is limited by the dephasing process, only, and the correlation length in this frequency range should be much longer yielding the failure of our hypothesis at high defect molar fraction. Presently we are not able to discriminate between the two origins of discrepancy. Indeed, on one hand, the vibrational dependence of interaction potentials remains a source of inaccuracies which cannot be quantitatively estimated, even for simple molecules. On the other hand, a more accurate treatment of the high defect molar fraction model would require to change the present theoretical treatment of the defect distribution which is valid for reasonable molar fraction of defects, only. Finally, let us mention that, to our knowledge, this is the first a priori study of the spectral line behavior of a disordered monolayer since all the previous papers were concerned rather with the influence of defects on the integrated intensity and shift of the infrared signals of molecules adsorbed on metals²⁹ as well as on dielectrics.¹⁷

V. CONCLUSION

The generalized *t*-matrix model used in this paper allowed us to determine the infrared and SFG spectra of a disordered monolayer formed by a mixture of ¹²CO and ¹³CO isotopes. The Green propagator for the disordered monolayer dynamics has been determined from a master equation describing the propagation of collective vibrational excitations on the adsorbed molecules when the fluctuations of the low frequency (phonons and librons) modes tend to broaden homogeneously the infrared signal of vibrons.

The model is general, within the harmonic treatment of the vibrons, and leads to the calculation of the linear and nonlinear spectral densities for the isotopic mixture of admolecules. We have shown that the infrared resonances in the nonlinear SFG spectrum display differences when compared to the linear infrared adsorption peaks, especially at very low molar fraction of the isotope defect and, in a more general way, regarding the relative intensities of the localized peaks of the less abundant isotope in the mixture. The comparison of these results with the available linear infrared spectra show that we can account for most of the experimental features, though there remains quantitative differences in the inhomogeneous broadening calculations, probably due to the poor knowledge of accurate vibrational dependence of the interaction potentials. Further improvements of the theoretical treatment would require the consideration of vibrational anharmonicities^{42,43} and the extension of the statistical model to defect distribution close to the percolation transition.

APPENDIX A: GREEN PROPAGATOR FOR A SINGLE DEFECT PERTURBATION

Let us consider a pure monolayer formed by molecules *a* with one isotopic defect *b*, only, localized at the site (l_0s_0) . The dynamical matrix $\Lambda(\omega_1)$ is expressed as

$$\boldsymbol{\Lambda}(\boldsymbol{\omega}_1) = \boldsymbol{\Lambda}_a(\boldsymbol{\omega}_1) - \delta \boldsymbol{\eta}(\boldsymbol{\omega}_1) \mathbf{I}_{l_0 s_0}, \tag{A1}$$

where $\mathbf{I}_{l_0 s_0} = |l_0 s_0\rangle \langle l_0 s_0|$ is the projector on the impurity site. The Dyson equation leads to a Green propagator expressed as

$$\mathbf{G}(\boldsymbol{\omega}_1) = \mathbf{G}_a(\boldsymbol{\omega}_1) + \mathbf{G}_a(\boldsymbol{\omega}_1) \,\delta \,\eta(\boldsymbol{\omega}_1) \mathbf{I}_{l_0 s_0} \mathbf{G}(\boldsymbol{\omega}_1). \quad (A2)$$

When we apply the projector $I_{l_0s_0}$ to Eq. (A2), we obtain

$$\mathbf{I}_{l_0 s_0} \mathbf{G}(\omega_1) = \mathbf{I}_{l_0 s_0} [\mathbf{1} - \mathbf{I}_{l_0 s_0} \mathbf{G}_a(\omega_1) \mathbf{I}_{l_0 s_0} \delta \eta(\omega_1)]^{-1} \mathbf{G}_a(\omega_1).$$
(A3)

Inserting Eq. (A3) into Eq. (A2) gives the propagator $\mathbf{G}(\omega_1)$ as

$$\mathbf{G}(\boldsymbol{\omega}_1) = \mathbf{G}_a(\boldsymbol{\omega}_1) + \mathbf{G}_a(\boldsymbol{\omega}_1)\mathbf{t}_{l_0s_0}(\boldsymbol{\omega}_1)\mathbf{G}_a(\boldsymbol{\omega}_1), \quad (A4)$$

where $\mathbf{t}_{l_0 s_0}(\omega_1)$ is the single defect scattering *t* matrix defined as

$$\mathbf{t}_{l_0 s_0}(\omega_1) = \mathbf{I}_{l_0 s_0} \delta \eta(\omega_1) [\mathbf{1} - G_a(0; \omega_1) \delta \eta(\omega_1)]^{-1}$$
(A5)

$$=\mathbf{I}_{l_0s_0}t(\boldsymbol{\omega}_1),$$

where $G_a(0;\omega_1) = \mathbf{I}_{l_0 s_0} \mathbf{G}_a(\omega_1) \mathbf{I}_{l_0 s_0}$ is the projection of the Green propagator $\mathbf{G}_a(\omega_1)$ on the site containing the impurity. Extension to multiple defects scattering matrix can be obtained in a similar way, for a given configuration of the defects, by summing over the defect sites $(l_0 s_0)$.

APPENDIX B: GREEN PROPAGATOR IN RANDOM PHASE APPROXIMATION

From Eq. (17), the average Green propagator of the disordered monolayer is expressed as

$$\langle \mathbf{G}(\boldsymbol{\omega}_{1}) \rangle_{c} = \mathbf{G}_{a}(\boldsymbol{\omega}_{1}) + \sum_{ls} \mathbf{G}_{a}(\boldsymbol{\omega}_{1}) \mathbf{t}_{ls}(\boldsymbol{\omega}_{1}) \mathbf{G}_{a}(\boldsymbol{\omega}_{1}) \langle \boldsymbol{\sigma}_{ls} \rangle_{c}$$

$$+ \sum_{ls} \sum_{l's' \neq ls} \mathbf{G}_{a}(\boldsymbol{\omega}_{1}) \mathbf{t}_{ls}(\boldsymbol{\omega}_{1})$$

$$\times \mathbf{G}_{a}(\boldsymbol{\omega}_{1}) \mathbf{t}_{l's'}(\boldsymbol{\omega}_{1}) \mathbf{G}_{a}(\boldsymbol{\omega}_{1}) \langle \boldsymbol{\sigma}_{ls} \boldsymbol{\sigma}_{l's'} \rangle_{c} + \cdots$$
(B1)

Using the random phase approximation and the expression of the t matrix given in Eq. (A5), the average Green propagator is written as

$$\langle \mathbf{G}(\omega_1) \rangle_c = \mathbf{G}_a(\omega_1) + p_b \ t(\omega_1) \sum_{ls} \ \mathbf{G}_a(\omega_1) \mathbf{I}_{ls} \mathbf{G}_a(\omega_1)$$

$$+ p_b^2 t(\omega_1)^2 \sum_{ls} \sum_{l's'} \ \mathbf{G}_a(\omega_1) \mathbf{I}_{ls}$$

$$\times \overline{\mathbf{G}}_a(\omega_1) \mathbf{I}_{l's'} \mathbf{G}_a(\omega_1) + \cdots,$$
(B2)

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where $\overline{\mathbf{G}}_{a}(\omega_{1}) = \mathbf{G}_{a}(\omega_{1}) - G_{a}(0;\omega_{1})\mathbf{1}$. The closure relation applied to the total projector allows us to write $\Sigma_{ls}\mathbf{I}_{ls}=\mathbf{1}$. Therefore, an exact resummation procedure in Eq. (B2) leads to the expression for the average propagator as

$$\langle \mathbf{G}(\omega_1) \rangle_c = \mathbf{G}_a(\omega_1) + \mathbf{G}_a(\omega_1) \langle t(\omega_1) \rangle_c \times [\mathbf{1} - \overline{\mathbf{G}}_a(\omega_1) \langle t(\omega_1) \rangle_c]^{-1} \mathbf{G}_a(\omega_1), \quad (B3)$$

where $\langle t(\omega_1) \rangle_c = p_b t(\omega_1)$ is given by Eq. (26). From the expression of $\overline{\mathbf{G}}_a(\omega_1)$ we then obtain

$$\langle \mathbf{G}(\omega_1) \rangle_c = \mathbf{G}_a(\omega_1) + \mathbf{G}_a(\omega_1) \Sigma(\omega_1)$$

$$\times [\mathbf{1} - \mathbf{G}_a(\omega_1) \Sigma(\omega_1)]^{-1} \mathbf{G}_a(\omega_1) \qquad (B4)$$

or, in an equivalent way,

$$\langle \mathbf{G}(\boldsymbol{\omega}_1) \rangle_c = [\mathbf{G}_a^{-1}(\boldsymbol{\omega}_1) - \mathbf{1}\boldsymbol{\Sigma}(\boldsymbol{\omega}_1)]^{-1}$$

= $[\mathbf{\Lambda}_a(\boldsymbol{\omega}_1) - \mathbf{1}\boldsymbol{\Sigma}(\boldsymbol{\omega}_1)]^{-1},$ (B5)

where the defect influence is contained in the contribution

$$\Sigma(\omega_1) = \frac{\langle t(\omega_1) \rangle_c}{1 + G_a(0;\omega_1) \langle t(\omega_1) \rangle_c}.$$
 (B6)

From the expression of $\langle t(\omega_1) \rangle_c$, Eq. (B6) leads to Eq. (27).

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