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Unified model of diffractive and multiphonon He atom scattering from adsorbates: Holstein renormalization of the interactions and the complete Debye-Waller factor

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We derive general expressions for the energy and lateral momentum resolved scattering spectrum describing collisions of beams of thermal energy He atoms with adsorbates on a flat substrate surface. Elastic and inelastic components of the projectile-adlayer interaction, of which the latter can be nonlinear in adsorbate displacements, are treated to all powers in the coupling constant g and with full account of the projectile recoil. The established formalism enables a combined treatment of elastic scattering (either diffuse or diffractive) and inelastic excitation of multiple phonons and overtones in the adlayer on an equivalent footing. For nonlinear vibrational coupling the distorted wave matrix elements of the interactions are Holstein-renormalized by zero point motion of adsorbates. In the case of scattering intensities calculated to lowest order in g this gives rise to a direct analog of the standard Glauber–van Hove Debye-Waller factor. The closed form solutions for the scattering spectra to all orders in g are characterized by a unified or complete Debye-Waller factor which embodies the effects discussed so far only separately in the literature: (i) attenuation of the scattered beam intensities due to zero point motion of adsorbates, and (ii) attenuation of the beam intensity in the elastic channel due to inelastic scattering from adlayer phonons and overtones. The complete Debye-Waller factor acquires a form of an exponentiated sum of Holstein-renormalized scattering intensities and acts to preserve the unitarity of the scattering spectrum in accord with the optical theorem. The developed model facilitates evaluation of the various approximate and limiting forms of the scattering spectra and the associated Debye-Waller factors characteristic of the different scattering regimes and different types of adlayer vibrational dynamics. Potential applications of the model are illustrated by estimating the effect of Holstein renormalization occurring in the unified Debye-Waller factor and scattering intensities for several prototype adlayer systems. [S0163-1829(99)02428-5]

I. INTRODUCTION

Despite the many efforts to formulate and unify the notion of the Debye-Waller factor (DWF) in atom-surface scattering theories, where it plays the role of an attenuation factor for the scattered beam intensities, its form has remained a matter of controversy. Already the earliest attempts in this direction encountered difficulties which were realized and clearly pinpointed.[1–6] Later approaches based either on a direct transposition of the Glauber-van Hove form of the DWF from quantum theory of neutron scattering by vibrating crystals, in which it appears as a reduction factor for the intensities of first order diffracted neutron beams due to zero point motion of the scattering centers,[7,8] or its reformulation taking into account the specific scattering conditions at surfaces,[9–11] have only confirmed such a state of affairs in the field. In the majority of these works the discussions of the DWF were concentrated on a more or less modified form of the original expression $\exp[-\Sigma_{\mathbf{q}}\langle\langle(\Delta\mathbf{k}\cdot\mathbf{u}_{\mathbf{q}})^2\rangle\rangle]$ typical of inelastic neutron scattering cross sections calculated in first order Born approximation. Here $\Delta\mathbf{k}$ is the change of the projectile particle momentum in the course of the collision, and $\langle\langle \ldots \rangle\rangle$ denotes thermal averaging of the squares of normal mode amplitudes $\mathbf{u}_{\mathbf{q}}$ describing the vibrations of ion cores in the crystal.

From the early stage of development of the theory of thermal energy atom-surface scattering attempts have been made to treat the diffractive and inelastic scattering on the same footing. A combined quantum treatment of diffractive and single-phonon He atom scattering (HAS) from clean surfaces has been developed in the distorted wave Born approximation[12–14] (DWBA). However, the Debye-Waller type of reduction of the scattered beam intensities is expected to be most prominent in collisions typified by multiple phonon exchange.[4,15–22] The theories aiming at taking into account multiphonon atom-surface scattering processes were often based on the trajectory approximation (TA) for description of the projectile particle motion,[23–26] particularly in the case of heavier projectiles and hyperthermal incident energies.[27] One of the standard quantities calculated in these approaches is the loss spectrum or the probability that an amount of energy and momentum is transferred from the projectile to quantized vibrations of the crystal. The normalization factor of such spectra, given by the weight of the elastic or no loss line, was found to exhibit the exponential form reminiscent of the DWF of neutron scattering theory. By analogy, this factor was also termed the DWF although no justification as to the same physical origin of the two quantities could be given at that stage. Later improvements over the results of the TA were achieved in the mean field[28] and wave packet[29] approaches which brought the expressions for the DWF closer to the ones derived in earlier quantum theories.[5,6]

Recently, a completely quantum treatment of the scattering intensities in inelastic multiphonon scattering of He atoms from statically flat surfaces has been developed.[30–32] This approach established the weight of the elastic peak in the exponential form, in a fashion analogous to the optical theorem. It has also been shown that in the limit of a classical motion of the projectile this exponential attenuation factor turns into the expression found earlier in the TA approaches. Due to this analogy it was also termed the DWF and its application to the calculation of intensities of elastically scattered thermal beams of noble gas atoms from statically flat surfaces[33,34] yielded a very good agreement with experimental results.[35,36] An additional analysis has shown that this type of the DWF has different origin relative to the one introduced in neutron scattering theory and that only in the limiting case of a classical particle motion the two expressions may coincide.[37] Obviously, this situation has given rise to a dilemma as to which form of the DWF to use in the discussions and interpretations of the atom-surface scattering data, whether only one of these, their product or some other more complex expression. The situation was additionally complicated by the difficulty to deconvolute the experimental multiphonon HAS spectra from metal surfaces and thereby identify the large DWF-induced reductions of the scattered beam intensities.[17–19]

The likely representatives of the systems in which the above mentioned Debye-Waller effects could be most conveniently studied are those in which a cross-over from a single to a multiphonon scattering regime can be easily traced and assessed. Such systems are provided by the adlayers of atoms or molecules adsorbed on metal surfaces as in very many cases they have been found to sustain low energy vibrational modes ($\hbar\omega\sim$ few meV) of which some may exhibit negligible dispersion. Their frequencies are usually detached from other modes of the system over the largest part of the surface Brillouin zone which makes their multiple excitation easily identifiable in the HAS time-of-flight (TOF) measurements. This has facilitated the studies of low energy dynamics of a number of adlayer systems in the single and multiphonon scattering regimes over the past two decades.[16,20,21,38–46]

Besides the Debye-Waller type of effects, the interest in the low energy modes stems also from the fact that they can be thermally activated already at very low temperatures which is of particular importance for the thermodynamical and structural properties of surfaces[47] and for the sliding friction.[48] However, due to the different structural properties of the various types of adlayers sustaining low energy modes, the theoretical interpretation of a variety of the corresponding HAS TOF spectra cannot be restricted only to the use of the formalism outlined in Ref. 32. This formalism proved successful in the interpretation of inelastic scattering from statically flat surfaces,[19–21,34,40,49] whereas in the case of adlayers of submonolayer coverage or isolated adsorbates the incoming beam is primarily scattered by the underlying substrate surface on top of which the array of vibrating adsorbates represents a perturbation for the distorted waves. In this situation the assumption of a statically flat surface underlying the HAS theory developed in Ref. 32 is no longer justified and a different approach is needed to describe the scattering event.

In this paper we present a unified theory of diffractive-elastic or diffuse-elastic and multiphonon-inelastic scattering of thermal energy He atoms from vibrating adsorbates and adlayers of submonolayer coverage. The theory encompasses combined aspects of the above mentioned two types of the DWF in a nontrivial fashion and allows one to retrieve each of them in special limits. The present work is focused on a general formulation of the theory of quantum scattering of He atoms from such adlayers and on the derivation of approximate expressions for the scattering spectra appropriate to the various scattering regimes. In the forthcoming papers we shall concentrate on the use of the developed formalism to interpret the experimental data obtained for some prototype adlayer systems studied by HAS. In Sec. II we formulate the projectile-adlayer interactions that are nonlinear in adsorbate displacements which then leads to Holstein renormalization of the scattering matrix elements. Thus formulated interactions are employed to set up a model Hamiltonian needed for the description of the dynamics of He atom scattering from adlayers. With the aid of these prerequisites we develop in Sec. III a formalism for calculation of the energy and parallel or lateral momentum resolved scattering spectrum. Here we introduce the notion of a complete or unified Debye-Waller factor which encompasses the aforementioned two aspects of the Debye-Waller effects originating from the Holstein renormalization of the scattering interaction and the total current conservation in the collision. By suitably separating the uncorrelated from the correlated phonon excitation processes we are able to identify the dominant contributions to the scattering spectra in the various regimes of HAS and define approximations in which they can be reliably calculated. We apply the developed formalism to obtain closed form solutions for the spectra pertinent to HAS from ordered submonolayers in Secs. IV and V and from disordered submonolayers and isolated adsorbates in Sec. VI. Finally, in Sec. VII we reiterate the basic assumptions and results of the developed theory and indicate the adlayer systems to which it can be readily applied by estimating the corresponding Holstein reductions of the scattering intensities and of the unified Debye-Waller factor. Formal derivations of some specific forms of the interaction matrix elements and of the general expression for the scattering spectrum based on the cumulant expansion are presented in Appendices.

II. FORMULATION OF THE PROJECTILE-SURFACE INTERACTION

We assume a flat substrate covered with adsorbates located in front of the physical surface of the substrate. Beams of thermal energy He atoms can excite vibrations localized within and typical of such adlayers, giving rise to specific, adsorbate-induced phonon structure in the experimental TOF spectra.

The unperturbed He atom motion in front of a clean flat substrate surface is governed by the projectile particle Hamiltonian

$$H_0^{\mathrm{part}}=\frac{\mathbf{p}^2}{2M}+U(z), \tag{1}$$

where the He atom radius vector $\mathbf{r}=(\boldsymbol{\rho},z)$ has the lateral or parallel to the surface component $\boldsymbol{\rho}$ and perpendicular to the surface component z, and $\mathbf{p}$ and M are the momentum operator and mass of the projectile, respectively. $U(z)$ is the laterally averaged static He atom-surface potential responsible for specular reflections of the projectile from the bare surface. Its repulsive component originates from the overlap of the electronic wave functions of the He atom and the surface, and hence is short ranged, whereas the attractive component follows asymptotically a long range van der Waals behavior $\propto -1/z^3$.

The wave functions diagonalizing (1) are written in the form of distorted waves

$$\langle \mathbf{r}|\mathbf{k}\rangle = \langle \boldsymbol{\rho}, z|\mathbf{K}, k_z\rangle = \frac{1}{\sqrt{L_z L_s^2}} \exp(i\mathbf{K}\boldsymbol{\rho})\chi_{k_z}(z). \tag{2}$$

Here $\hbar\mathbf{K}$ denotes the lateral momentum of the projectile which is a constant of motion in the absence of perturbations destroying translational invariance along the flat substrate surface. The quantum number k_z describes the perpendicular or normal to the surface motion of the atom in the potential $U(z)$ and $\hbar k_z$ has the meaning of the projectile perpendicular momentum far away from the surface. $\chi_{k_z}(z)$ is the corresponding nondegenerate solution of the one-dimensional Schrödinger equation. L_s and L_z are the lengths of the quantization box in the direction parallel and perpendicular to the surface, respectively. The continuum state wave functions (2) are equal up to an irrelevant phase factor to the unperturbed distorted wave scattering states[9,50,51] satisfying the box normalization condition

$$\langle \mathbf{k}'|\mathbf{k}\rangle = \delta_{\mathbf{k},\mathbf{k}'} . \tag{3}$$

The choice of this normalization proves convenient in later manipulations with the scattering matrix elements.

Two separate types of perturbations can affect the motion of He atoms described by the unperturbed wave functions (2). First, there is an interaction between He atoms and the dynamic corrugation of the substrate surface (substrate phonons) and, second, with atoms or molecules adsorbed on the surface. The two types of perturbations produce separate as well as interference (mixed) contributions to the scattering amplitudes. Quite generally, the separate contributions appear already in second order terms in the coupling constant whereas the mixed contributions appear first in fourth order terms in the coupling constant. Therefore, up to fourth order in the coupling constant the substrate and adsorbate induced modes can be studied separately as a superposition of the two dynamical structures in the scattering spectra. In the present study we shall concentrate on the systems in which the low energy vibrations of the substrate and adsorbates are nearly decoupled and well separated throughout the major part of the surface Brillouin zone (SBZ). The exception occurs in the long wavelength limit in which the frequencies of low energy adsorbate vibrations become degenerate with the continuum of substrate modes. However, even near the center of the SBZ one may consider the adsorbate induced modes as distinct modes with renormalized frequency and lifetime which are readily determined from the parameters of the system.[52] Hence, in the following we shall not consider the coupling of He atoms to the dynamic corrugation of the crystal surface but study only the interaction of the closed shell electronic structure of the He atom located at $\mathbf{r}$ with the adsorbates of the adlayer which can vibrate around their equilibrium positions at $\mathbf{r}_\mathbf{l} = (\boldsymbol{\rho}_\mathbf{l}, z_\mathbf{l})$. The effect of substrate phonons to lowest order in the coupling constant can be included in a rather straightforward fashion and some aspects of this problem were addressed in Ref. 53. We further invoke a common approximation of atom-surface scattering theory in which the total He atom-adlayer interaction potential $V(\mathbf{r})$ is represented by a pairwise sum of the potentials $v(\mathbf{r} - \mathbf{r}_\mathbf{l} - \mathbf{u}_\mathbf{l})$ describing the interaction of the scattered He atom with each single vibrating adsorbate.[54] This approximation is justified in the situation of submonolayer coverages and we obtain

$$V(\mathbf{r}) = \sum_{\mathbf{l}} v(\mathbf{r} - \mathbf{r}_\mathbf{l} - \mathbf{u}_\mathbf{l}) = \sum_{\mathbf{l}} v(\boldsymbol{\rho} - \boldsymbol{\rho}_\mathbf{l} - \mathbf{u}_{\mathbf{l}\parallel}, z - z_\mathbf{l} - \mathrm{u}_{\mathbf{l}\perp}), \tag{4}$$

where $\mathbf{u}_\mathbf{l} = (\mathbf{u}_{\mathbf{l}\parallel}, \mathrm{u}_{\mathbf{l}\perp})$ denotes the displacement of the $\mathbf{l}$th adsorbate as a whole from the equilibrium position. In the present formulation of the interaction we do not include the effect of intra-adsorbate vibrations, usually of much higher frequencies and hence inaccessible to HAS, which are measured, e.g., in EELS experiments. Their treatment requires the introduction of internal adsorbate vibrational degrees of freedom into the scattering potential, as was demonstrated in Ref. 55.

Assuming He atom wave functions given by Eq. (2) we obtain for the He atom-adlayer interaction matrix elements:

$$\langle \mathbf{K}', k_{z'}|V(\mathbf{r})|\mathbf{K}, k_z\rangle = \sum_{\mathbf{l}} e^{-i(\mathbf{K}'-\mathbf{K})(\boldsymbol{\rho}_\mathbf{l} + \mathbf{u}_{\mathbf{l}\parallel})} \times v(\mathbf{K}' - \mathbf{K}, k_z', k_z, \mathrm{u}_{\mathbf{l}\perp}), \tag{5}$$

where

$$v(\mathbf{K}' - \mathbf{K}, k_z', k_z, \mathrm{u}_{\mathbf{l}\perp}) = \frac{1}{L_z L_s^2} \int dz\, \chi^*_{k_z'}(z)\chi_{k_z}(z) \times \int d^2\boldsymbol{\rho}\, e^{-i(\mathbf{K}'-\mathbf{K})\boldsymbol{\rho}} v(\boldsymbol{\rho}, z - z_\mathbf{l} - \mathrm{u}_{\mathbf{l}\perp}). \tag{6}$$

Here the appearance of the adsorbate lateral coordinates $\boldsymbol{\rho}_\mathbf{l} + \mathbf{u}_{\mathbf{l}\parallel}$ in the exponent on the right-hand-side (RHS) of Eq. (5) is due to the translational invariance of the unperturbed particle wave functions along the surface.

Next we observe that for adsorbates whose centers lie outward the turning points z_t of the wave functions $\chi_{k_z}(z)$, i.e., $z_\mathbf{l} \geqslant z_t$, it would be appropriate to represent both the $\boldsymbol{\rho}$- and z-dependence of $v(\boldsymbol{\rho}, z - z_\mathbf{l} - \mathrm{u}_{\mathbf{l}\perp})$ through its Fourier transform (FT) $v_F(\mathbf{Q}, p)$. Defining

$$v(\boldsymbol{\rho}, z) = \int \frac{d^2\mathbf{Q}}{(2\pi)^2} \int_{-\infty}^{\infty} \frac{dp}{2\pi} e^{i\mathbf{Q}\boldsymbol{\rho}} e^{ipz} v_F(\mathbf{Q}, p), \tag{7}$$

we obtain

$$\langle \mathbf{K}',k_{z'}|V(\mathbf{r})|\mathbf{K},k_z\rangle=\frac{1}{L_zL_s^2}\sum_{\mathbf{l}} e^{-i(\mathbf{K}'-\mathbf{K})(\boldsymbol{\rho}_{\mathbf{l}}+\mathbf{u}_{\mathbf{l}\parallel})}\times\int_{-\infty}^{\infty}\frac{dp}{2\pi}e^{-ip(z_{\mathbf{l}}+\mathrm{u}_{\mathbf{l}\perp})}\times v_F(\mathbf{K}'-\mathbf{K},p)f_F(k_z',k_z,p), \quad (8)$$

where we have introduced the generalized FT-generated oscillator strength:

$$f_F(k_z',k_z,p)=\int_{-\infty}^{\infty}e^{ipz}\chi^*_{k_z'}(z)\chi_{k_z}(z)dz. \quad (9)$$

On the other hand, for small adsorbates whose centers may lie nearer to the surface than z_t, viz. $z_{\mathbf{l}}\leqslant z_t$, it may turn out more convenient to use the Laplace transform to represent the z-dependence of $v(\boldsymbol{\rho},z-z_{\mathbf{l}}-\mathrm{u}_{\mathbf{l}\perp})$ as this could provide faster convergence relative to the transformation coordinate p. This approach is briefly outlined in Appendix A.

Expressions (5)–(9) are quite general and valid for any type of adsorbate-He atom potential. One of their important and interesting properties, and thereby also of the He atom interactions with vibrating adlayers, can be recovered upon taking the thermal average over the vibrational modes in expression (5) which is assumed site-independent for adsorbates occupying equivalent adsorption sites. This yields

$$\langle \mathbf{K}',k_{z'}|\langle\langle V(\mathbf{r})\rangle\rangle|\mathbf{K},k_z\rangle=\frac{1}{L_s^2L_z}\sum_{\mathbf{l}} e^{-i(\mathbf{K}'-\mathbf{K})\boldsymbol{\rho}_{\mathbf{l}}}\int_{-\infty}^{\infty}\frac{dp}{2\pi}e^{-w(\mathbf{K}'-\mathbf{K},p)}\times v_F(\mathbf{K}'-\mathbf{K})f_F(k_z',k_z,p)e^{-ipz_{\mathbf{l}}}. \quad (10)$$

Here $\langle\langle\ \rangle\rangle$ denotes the thermal average and

$$e^{-w(\mathbf{K}'-\mathbf{K},p)}=\exp\left[-\frac{1}{2}\langle\langle[(\mathbf{K}'-\mathbf{K})\mathbf{u}_{\mathbf{l}\parallel}+p\mathrm{u}_{\mathbf{l}\perp}]^2\rangle\rangle\right], \quad (11)$$

where the exponential form of expression (11) follows from the Bloch-Glauber theorem. Its explicit form depends on the expansion of the displacements in terms of normal phonon modes of the system (see Secs. IV and VI below).

The occurrence of the exponential factor (11) arises from the local character of the interaction of the projectile atom with adsorbate displacements to all orders in the coupling constant. This factor has the appearance of the Holstein renormalization of the interaction matrix elements [presently $v_F(\mathbf{K}'-\mathbf{K},p)$] which is commonly encountered in the studies of boson fields perturbed by local potentials.[56–60] Its square plays the role of the standard Glauber-van Hove type of the Debye-Waller factor occurring in first order perturbation theories[7,8] which reduces the magnitude of the scattering intensities. Physically, this effect originates from zero point vibrations of the adlayer which act so as to smear out the scattering potential in the lateral and perpendicular directions. The explicit form of the contribution due to lateral vibrations arises from the translational invariance of the lateral component of the unperturbed projectile wave function. Perpendicular zero point vibrations smear out each p-component of the Fourier transform of the potential over the oscillatory part of the distorted waves and this gives rise to the appearance of the factor $p\mathrm{u}_{\mathbf{l}\perp}$ in the exponent on the RHS of Eq. (11). In both cases these renormalizations represent an off-the-energy-shell effect as they arise from virtual phonon exchange processes.[37]

III. SCATTERING SPECTRUM AND THE COMPLETE DEBYE-WALLER FACTOR

The derivation of the scattering spectrum is facilitated by writing the total Hamiltonian of the interacting scattering system in the form

$$H=H_0^{\mathrm{part}}+H_0^{\mathrm{ph}}+gV=H_0+gV, \quad (12)$$

and expressing the constituting terms in the second quantization. Thus

$$H_0^{\mathrm{part}}=\sum_{\mathbf{K},k_z}E_{\mathbf{K},k_z}c^\dagger_{\mathbf{K},k_z}c_{\mathbf{K},k_z}, \quad (13)$$

where $E_{\mathbf{K},k_z}=E_{\mathbf{k}}$ is the energy of the projectile particle whose motion is described by the distorted waves, Eq. (2), and $c^\dagger_{\mathbf{K},k_z}$ and $c_{\mathbf{K},k_z}$ denote, respectively, the creation and annihilation operators for the particle in the state denoted by quantum numbers $(\mathbf{K},k_z)$. H_0^{ph} is the Hamiltonian describing unperturbed vibrations in the adlayer which after the quantization of the adsorbate displacements gives the free phonon Hamiltonian in terms of the phonon field creation and annihilation operators $a^\dagger$ and a, respectively. Its particular form depends on the phonon quantum numbers, i.e., on whether the adlayer sustains localized or delocalized (propagating) modes. Hence, it will be explicitly written down in connection with the application of expression (12) to either ordered or disordered adlayers in Secs. IV and VI below. g is the coupling constant introduced for convenience and eventually set equal to unity. Making use of expression (5) we find for the interaction term

$$V=\sum_{\mathbf{l}}\sum_{\mathbf{K},\mathbf{K}',k_z,k_z'}e^{-i(\mathbf{K}'-\mathbf{K})(\boldsymbol{\rho}_{\mathbf{l}}+\mathbf{u}_{\mathbf{l}\parallel})}\times v(\mathbf{K}'-\mathbf{K},k_z',k_z,\mathrm{u}_{\mathbf{l}\perp})c^\dagger_{\mathbf{K}',k_z'}c_{\mathbf{K},k_z}, \quad (14)$$

where the scattering matrix elements are given by expression (6) and the adsorbate displacement operators $\mathbf{u}_{\mathbf{l}}$ are expressed as a linear function of the phonon field operators $a^\dagger$ and a explicitly defined in Secs. IV and VI.

Since the quantities $E_{\mathbf{K},k_z}$ and $\mathbf{K}$ fully specify the state $|\mathbf{K},k_z\rangle$, we can now define with the aid of Eq. (12) the angular resolved scattering spectrum by the relation

$$N_{\mathbf{k_i}}(\Delta E,\Delta\mathbf{K})=\lim_{t\to\infty}\langle\Psi(t)|\delta[\Delta E-(H_0^{\mathrm{part}}-E_i)]\times\delta[\hbar\Delta\mathbf{K}-(\hat{\mathbf{P}}-\hbar\mathbf{K_i})]|\Psi(t)\rangle, \quad (15)$$

where $\mathbf{k_i}=(\mathbf{K_i},k_{zi})$ are the quantum numbers describing the initial state of the projectile particle, $|\Psi(\infty)\rangle$ is the total wave function of the interacting system at $t\to\infty$ after the collision event has been completed and the particle scattered into the final state $|\mathbf{K_f},k_{zf}\rangle$. $\hat{\mathbf{P}}$ is the operator of the lateral momentum of the particle, and the changes of quantum numbers $\Delta\mathbf{K}$ and ΔE appearing in the arguments of the δ-functions on the RHS of Eq. (15) are given by $\Delta\mathbf{K}=\mathbf{K_f}-\mathbf{K_i}$ and $\Delta E=E_{\mathbf{k_f}}-E_{\mathbf{k_i}}=E_f-E_i$. With this convention used also in the terminology of the TOF spectra we have $\Delta E<0(>0)$ in the case of particle energy loss (gain).[50,51] Since E_i and the direction of $\mathbf{k_i}$ are fixed by experimental conditions the connection between ΔE and $\hbar\Delta\mathbf{K}$ through the conservation of total energy and lateral momentum in the collision leaves only ΔE and the final spherical polar scattering angles θ_f and φ_f as independent experimental observables. Taking into account the in-sagittal-plane scattering geometry in which the HAS TOF measurements are usually carried out, it can be shown that the scattering spectrum defined by Eq. (15) is directly proportional to the experimental spectrum.[19] Let us also note that for later convenience we have expressed in Eq. (15) the energy and lateral momentum transfer in terms of the particle rather than the phonon operators because in such a formulation we can retrieve the elastic diffraction and diffuse scattering effects explicitly from the elastic part of the spectrum for which $\Delta E=0$. This is in contrast to Ref. 32 in which the energy and lateral momentum transfer between the projectile and phonons of the statically flat surface were expressed in terms of the corresponding phonon operators.

A formal evaluation of expression (15) proceeds[32] by expressing the energy and momentum conserving δ-functions as Fourier transforms of exponentials of the operators H_0^{part} and $\hat{\mathbf{P}}$. This yields

$$\begin{aligned}N_{\mathbf{k_i}}(\Delta E,\Delta\mathbf{K})&=\int_{-\infty}^{\infty}\frac{d\tau}{2\pi\hbar}\int\frac{d^2\mathbf{R}}{(2\pi\hbar)^2}e^{(i/\hbar)[(\Delta E+E_i)\tau-\hbar(\Delta\mathbf{K}+\mathbf{K_i})\mathbf{R}]}\langle\Psi(\infty)|e^{-(i/\hbar)(H_0^{\mathrm{part}}\tau-\hat{\mathbf{P}}\mathbf{R})}|\Psi(\infty)\rangle\\&=\int_{-\infty}^{\infty}\frac{d\tau}{2\pi\hbar}\int\frac{d^2\mathbf{R}}{(2\pi\hbar)^2}e^{(i/\hbar)[(\Delta E+E_i)\tau-\hbar(\Delta\mathbf{K}+\mathbf{K_i})\mathbf{R}]}\langle i|S_I^\dagger e^{-(i/\hbar)(H_0^{\mathrm{part}}\tau-\hat{P}_xX-\hat{P}_yY)}S_I|i\rangle\\&=\int_{-\infty}^{\infty}\frac{d\tau}{2\pi\hbar}\int\frac{d^2\mathbf{R}}{(2\pi\hbar)^2}e^{(i/\hbar)[(\Delta E)\tau-\hbar(\Delta\mathbf{K})\mathbf{R}]}\langle i|e^{-(i/\hbar)(\mathcal{H}_0^{\mathrm{part}}\tau-\mathcal{P}_xX-\mathcal{P}_yY)}|i\rangle.\end{aligned}\tag{16}$$

Here $\mathbf{R}=(X,Y)$ is a two dimensional radiusvector parallel to the surface plane where the capital letters have been introduced to avoid confusion with the coordinates (x,y) of the particle, $|i\rangle$ is the initial noninteracting state of the scattering system at $t_0\rightarrow-\infty$ (implying also thermal averaging over the phonon states), S_I is defined in the interaction picture according to

$$S_I=\lim_{t\rightarrow\infty,t_0\rightarrow-\infty}U_I(t,t_0),\tag{17}$$

where

$$\begin{aligned}U_I(t,t_0)&=e^{(i/\hbar)H_0(t-t_0)}e^{-(i/\hbar)H(t-t_0)}\\&=e^{(i/\hbar)H_0t}e^{-(i/\hbar)H(t-t_0)}e^{-(i/\hbar)H_0t_0}\end{aligned}$$

is the evolution operator in the interaction representation,[61] and the canonically transformed operators appearing in the third line of Eq. (16) are defined by

$$\mathcal{H}_0^{\mathrm{part}}=S_I^\dagger H_0^{\mathrm{part}}S_I=H_0^{\mathrm{part}}+\mathcal{W}_H,\tag{18}$$

$$\mathcal{P}_x=S_I^\dagger\hat{P}_xS_I=\hat{P}_x+\mathcal{W}_x,\tag{19}$$

$$\mathcal{P}_y=S_I^\dagger\hat{P}_yS_I=\hat{P}_y+\mathcal{W}_y.\tag{20}$$

The last line of expression (16) defines the kernel $N(\tau,\mathbf{R})$ of the spatio-temporal Fourier transform as

$$N(\tau,\mathbf{R})=\langle i|e^{-(i/\hbar)(\mathcal{H}_0^{\mathrm{part}}\tau-\mathcal{P}_xX-\mathcal{P}_yY)}|i\rangle,\tag{21}$$

in which the initial state averages can be calculated by applying the cumulant expansion[32] (cf. Appendix B). This yields

$$\begin{aligned}N_{\mathbf{k_i}}(\Delta E,\Delta\mathbf{K})=&\int_{-\infty}^{\infty}\frac{d\tau}{2\pi\hbar}\int\frac{d^2\mathbf{R}}{(2\pi\hbar)^2}\\&\times e^{(i/\hbar)[(\Delta E)\tau-\hbar(\Delta\mathbf{K})\mathbf{R}]}\exp\left[\sum_{n=1}^{\infty}C_n(\tau,\mathbf{R})\right],\end{aligned}\tag{22}$$

where the explicit form of the cumulants $C_n(\tau,\mathbf{R})$ is given in Appendix B. Expression (22) is exact as no approximations have been employed in its derivation. The general properties of the thus obtained scattering spectrum and its connection and equivalence to the T-matrix scattering formalism have been discussed in detail in Ref. 32. Here we shall observe only one basic property of expression (22) which is important for further analyses of the scattering spectra. The terms in the exponentiated series in the integrand on the RHS of Eq. (22), which are all functions of the Holstein-renormalized matrix elements of the projectile-adsorbate interaction, can be separated into two subseries, one with the terms dependent and the other with the terms independent of the transformation variables τ and $\mathbf{R}$. The exponentiated sum of $(\tau,\mathbf{R})$-independent terms, which can be factorized out of the integral, gives the weight of the elastic line. This can easily be seen by expanding the remaining exponential function of the sum of $(\tau,\mathbf{R})$-dependent terms into a power series and carrying out the $(\tau,\mathbf{R})$-integrations, after which the no loss line is recognized as the term proportional to $\delta(\Delta E)\,\delta(\Delta\mathbf{K})$. Thereby the factorized $(\tau,\mathbf{R})$-independent exponential term preserves the unitarity of the scattering spectrum and hence can be identified with the complete Debye-Waller factor.

The infinite series of cumulants in the exponent on the RHS of Eq. (22) cannot be easily calculated except for very simple model systems and therefore some approximations in the evaluation of this expression must be introduced as, e.g., the truncation of the series. Due to the structure of expression (22) such a procedure does not violate the unitarity property of the scattering spectrum. In particular, the sum of the first two cumulants C_1 and C_2, which is proportional to g^2, describes only uncorrelated scattering processes whereas all other higher order ones give corrections to these basic processes in terms of the correlated scattering events. Thus, for instance, the probabilities of resonant processes in which the projectile is first elastically scattered by an adsorbate and then inelastically by another one by emitting or absorbing a phonon, or vice versa,[65] are correlated and proportional to g^4 and hence require the evaluation of the cumulants of the corresponding order.

It has been shown[32,63] that the terms describing uncorrelated phonon scattering processes give dominant contributions to the scattering matrix or the scattering spectrum for He atom incoming energies E_i up to ~ 100 meV. Hence, one can retain only these terms in the exponent on the RHS of Eq. (22) as the remainder gives a small correction to the cumulant sum. The spatio-temporal Fourier transform of such expression gives the scattering spectrum in the distorted wave exponentiated Born approximation (EBA):

$$N_{\mathbf{k_i}}^{\mathrm{EBA}}(\Delta E,\Delta\mathbf{K}) = \int_{-\infty}^{\infty} \frac{d\tau d^2\mathbf{R}}{(2\pi\hbar)^3} e^{(i/\hbar)[(\Delta E)\tau - \hbar(\Delta\mathbf{K})\mathbf{R}]} \times \exp[2W^{\mathrm{EBA}}(\tau,\mathbf{R}) - 2W^{\mathrm{EBA}}(0,0)], \tag{23}$$

where

$$2W^{\mathrm{EBA}}(\tau,\mathbf{R}) - 2W^{\mathrm{EBA}}(0,0) = C_1(\tau,\mathbf{R}) + C_2(\tau,\mathbf{R}). \tag{24}$$

To obtain the explicit expression for $2W^{\mathrm{EBA}}(\tau,\mathbf{R})$ one follows the procedure outlined in Appendix B to calculate $C_n(\tau,\mathbf{R})$ by taking cumulant averages of the products of interaction operators $(\mathcal{W}_H,\mathcal{W}_x,\mathcal{W}_y)$, with the latter calculated following Eqs. (18)–(20) and the procedure described in Sec. III B of Ref. 32. For the interaction given by Eq. (8) this yields

$$\begin{aligned} 2W^{\mathrm{EBA}}(\tau,\mathbf{R}) = {} & \sum_{\mathbf{K}',k_z'} e^{-(i/\hbar)[(E_{\mathbf{k}}'-E_{\mathbf{k_i}})\tau - \hbar(\mathbf{K}'-\mathbf{K_i})\mathbf{R}]} \frac{1}{(L_z L_s^2)^2} \sum_{\mathbf{l}',\mathbf{l}''} e^{i(\mathbf{K}'-\mathbf{K_i})(\boldsymbol{\rho}_{\mathbf{l}'}-\boldsymbol{\rho}_{\mathbf{l}''})} \int_{-\infty}^{\infty} \frac{dp'}{2\pi} e^{ip'z_{\mathbf{l}'}} e^{-w(\mathbf{K}'-\mathbf{K_i},p')} \\ & \times v_F^*(\mathbf{K}'-\mathbf{K_i},p') f_F^*(k_z',k_{zi},p') \int_{-\infty}^{\infty} \frac{dp''}{2\pi} e^{-ip''z_{\mathbf{l}''}} e^{-w(\mathbf{K}'-\mathbf{K_i},p'')} v_F(\mathbf{K}'-\mathbf{K_i},p'') f_F(k_z',k_{zi},p'') \\ & \times \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} dt'' e^{-(i/\hbar)(E_{\mathbf{k}'}-E_{\mathbf{k_i}})(t'-t'')} \\ & \times \exp\langle\langle[(\mathbf{K}'-\mathbf{K_i})\mathbf{u}_{\mathbf{l}'\parallel}(t') + p'\mathrm{u}_{\mathbf{l}'\perp}(t')][(\mathbf{K}'-\mathbf{K_i})\mathbf{u}_{\mathbf{l}''\parallel}(t'') + p''\mathrm{u}_{\mathbf{l}''\perp}(t'')]\rangle\rangle. \end{aligned} \tag{25}$$

$2W^{\mathrm{EBA}}(\tau,\mathbf{R})$ is the so-called EBA scattering or driving function whose time dependent part comprises exponentiated correlation function of lateral and normal adsorbate vibrations. The different form of the correlation function in the lateral and perpendicular directions reflects the break down of translational symmetry in the system due to the presence of the surface. The scattering function embodies two important features of the scattering event: (i) the projectile atom may interact simultaneously with more than one adsorbate in the adlayer in the course of the collision, and (ii) during this interaction the particle may be scattered elastically or inelastically, in the latter case by giving rise to either single or multiple (subsequent) phonon excitations, or to overtones (anharmonic vibrational transitions), or combinations of these.

In the EBA the exchange of energy and lateral momentum is automatically conserved in each interaction vertex (see Sec. IV). This property arises from the quantum character of both the particle and the phonon field and is preserved irrespective of the actual validity of the EBA. On the other hand, the EBA spectrum (23) does not on its own automatically imply conservation of the total energy and lateral momentum in a multiple scattering process. It is only in the range of the validity of the EBA, in which the correlations between subsequent phonon excitations in a sequence of the on-shell processes are very weak and therefore all $C_{n>2}(\tau,\mathbf{R})$ are negligible, that as a consequence ΔE and $\Delta\mathbf{K}$ satisfy the total energy and momentum conservation. Hence, in practical applications of expression (23) to multiple scattering one must first check the validity of the EBA in a particular collision regime (e.g., by following the prescriptions outlined in Refs. 30 and 32) and then calculate the EBA spectrum (23) for the values of ΔE and $\Delta\mathbf{K}$ obeying total energy and lateral momentum conservation, i.e., the values lying on the ‘‘scan curve.’’ Of course, the same also applies to the scattering spectra calculated in other approximations (classical trajectory, impulsive scattering, etc.) which are the special limits of the EBA (cf. Ref. 32 and Sec. V below).

Further evaluation of $2W^{\mathrm{EBA}}(\tau,\mathbf{R})$ requires a specification of the vibrational displacements $\mathbf{u_l}$ in terms of the phonon modes characteristic of the adlayer. However, an important remark can be made already at this point. As was noted in connection with expression (22), the quantity $\exp[-2W^{\mathrm{EBA}}(0,0)]=\exp[-2W^{\mathrm{EBA}}]$ on the RHS of Eq. (23), which is independent of τ and $\mathbf{R}$ and whose exponential appearance is independent of a particular form of the projectile-surface interaction, can be factorized out of the triple integral. After expanding $\exp[-2W^{\mathrm{EBA}}(\tau,\mathbf{R})]$ into a power series and carrying out the integrals we find that in the EBA the total weight N_0^{EBA} of the specular elastic peak is given in the form

$$N_{\mathrm{specular}}(\Delta E,\Delta\mathbf{K})=N_0^{\mathrm{EBA}}\delta(\Delta E)\,\delta(\Delta\mathbf{K})$$
$$=e^{-2W^{\mathrm{EBA}}}\delta(\Delta E)\,\delta(\Delta\mathbf{K}),\qquad(26)$$

which guarantees that the optical theorem is satisfied.[32] Hence, the factor $e^{-2W^{\mathrm{EBA}}}$ is identified with a quantal analog of the DWF obtained in the studies of scattering of classical particles by boson fields.[9] In the present quantal formulation such total DWF combines the features of (i) off-the-energy-shell Glauber-van Hove type of Debye-Waller factor arising from the Holstein renormalization of the interaction matrix elements in expression (25), and (ii) on-the-energy- and momentum-shell Debye-Waller factor discussed in Refs. 30–32,37 and 63 which according to Eq. (26) measures the total probability of finding the projectile in the entrance channel after the collision with the surface.

Quite generally, the open scattering channels can be classified as elastic $(\Delta E=0)$ and inelastic $(\Delta E\neq 0)$. According to Eq. (25) the total scattering function appears as a sum of the scattering functions from all channels. Hence, the developed formalism lends itself as particularly suitable for the description of HAS from adlayers in which both the elastic (diffuse or diffractive) and inelastic scattering effects are pronounced.

IV. SCATTERING FROM ORDERED ADLAYERS

Quite generally, the amplitude and phase of the modes over the neighboring adsorbates can be either coherent (propagating adlayer phonons) or incoherent (localized phonons) and the experimental data do not always allow discrimination between the two cases. However, in ordered superstructures with not too large nearest adsorbate-adsorbate distances the interadsorbate interactions are not totally absent. Thus, even weak interadsorbate forces would cause some correlation between vibrations of the neighboring adsorbates and hence give rise to a coherent lateral propagation of the vibrational modes in the adlayer. This causes dispersion of the adlayer modes, i.e., the dependence of their frequency on the lateral wave vector describing their propagation.[64] On the other hand, in the case of less dense and disordered adlayers the adsorbate vibrations may retain localized character. In this section we shall apply the formalism developed in Sec. III to elastic and inelastic scattering from ordered adlayers sustaining coherent vibrations and leave the problem of scattering from disordered adlayers and isolated adsorbates to Sec. VI.

The adsorbate displacements $\mathbf{u_l}=(\mathbf{u}_{\mathbf{l}\parallel},u_{\mathbf{l}\perp})$ in the case of coherent vibrations propagating in a periodic adlayer can be expanded in terms of normal phonon modes as:[50,51]

$$\mathbf{u_l}=(\mathbf{u}_{\mathbf{l}\parallel},u_{\mathbf{l}\perp})=\sum_{\mathbf{Q},j}\mathbf{e}(\mathbf{Q},j)\left(\frac{\hbar}{2M_aN_a\omega_{\mathbf{Q},j}}\right)^{1/2}$$
$$\times e^{i\mathbf{Q}\boldsymbol{\rho}_\mathbf{l}}(a_{\mathbf{Q},j}+a^\dagger_{-\mathbf{Q},j}),\qquad(27)$$

where $\mathbf{Q}$, j, $\hbar\omega_{\mathbf{Q},j}$ and $\mathbf{e}(\mathbf{Q},j)=[\mathbf{e}_\parallel(\mathbf{Q},j),e_\perp(\mathbf{Q},j)]=\mathbf{e}^*(-\mathbf{Q},j)$ denote the two dimensional wave vector, branch index, energy and polarization vector of a normal phonon mode, respectively, M_a is the adsorbate mass and the phonon mode creation and annihilation operators $a^\dagger_{\mathbf{Q},j}$ and $a_{\mathbf{Q},j}$, respectively, satisfy the commutation relations:

$$[a_{\mathbf{Q},j},a^\dagger_{\mathbf{Q}',j'}]=\delta_{\mathbf{Q},\mathbf{Q}'}\delta_{j,j'}.\qquad(28)$$

In terms of these operators the unperturbed phonon field Hamiltonian which determines the time dependence of $\mathbf{u_l}$ takes the form

$$H_0^{\mathrm{ph}}=\sum_{\mathbf{Q},j}\hbar\omega_{\mathbf{Q},j}a^\dagger_{\mathbf{Q},j}a_{\mathbf{Q},j}.\qquad(29)$$

Substitution of expansion (27) in expression (25) enables the full calculation of the scattering function pertinent to HAS from periodic adlayers.

A. Elastic diffractive scattering and the Debye-Waller factor

Elastic scattering processes are described by the term contained in $2W^{\mathrm{EBA}}(\tau,\mathbf{R})$, Eq. (25), which is obtained by expanding the exponentiated correlation function into a power series and retaining only the zeroth order term, i.e., unity. Then the summations over $\mathbf{l}'$ and $\mathbf{l}''$ can be carried out by recalling that for ordered overlayers

$$\sum_{\mathbf{l}}\exp[i(\mathbf{K_i}-K')\boldsymbol{\rho}_\mathbf{l}]=N_a\sum_{\mathbf{G}}\delta_{\mathbf{K}'-\mathbf{K_i},\mathbf{G}},\qquad(30)$$

where N_a is the number of adsorbates on the surface, i.e., per area L_s^2. Hence, in elastic scattering from ordered adlayers the lateral momentum is conserved up to the reciprocal adlayer lattice wave vector $\mathbf{G}$. Assumption of equivalent adsorption sites implies $z_\mathbf{l}=z_a$ and we find

$$2W^{\mathrm{EBA}}_{\mathrm{diffr}}(\tau,\mathbf{R})=\sum_{\mathbf{G}}e^{i\mathbf{GR}}\sum_{\mathbf{K}',k_z'}|\mathcal{V}^{k_z',k_{zi}}_{\mathbf{K}',\mathbf{K_i},\mathbf{G}}(0,z_a)|^2$$
$$=2W^{\mathrm{EBA}}_{\mathrm{diffr}}(0,\mathbf{R}),\qquad(31)$$

in which the on-the-energy and lateral-momentum-shell matrix elements describing diffraction are given by

$$\begin{aligned}\mathcal{V}^{k'_z,k_{zi}}_{\mathbf{K'},\mathbf{K_i},\mathbf{G}}(0,z_a)&=\delta_{\mathbf{K'},\mathbf{K_i}+\mathbf{G}}\frac{2\pi\delta(E_{\mathbf{k_i}}-E_{\mathbf{k'}})}{L_zA_a}\\&\quad\times\int_{-\infty}^{\infty}\frac{dp}{2\pi}e^{ipz_a}e^{-w(\mathbf{K'}-\mathbf{K_i},p)}\\&\quad\times v_F(\mathbf{K'}-\mathbf{K_i},p)f_F(k'_z,k_z,p)\\&=\delta_{\mathbf{K'},\mathbf{K_i}+\mathbf{G}}\delta_{\overline{k}_{zi}(0),k'_z}\Theta(\overline{k^2_{zi}}(0))\\&\quad\times\frac{\tilde{v}_F(\mathbf{K'}-\mathbf{K_i},k_{z'},k_{zi},z_a)}{A_a\hbar\sqrt{v_zv'_z}}.\end{aligned}\tag{32}$$

Here $v_z=\hbar k_z/M, A_a=L_s^2/N_a$ is the area of the surface unit cell of the superstructure, the requirement of energy conservation is expressed by using standard identities involving δ-functions[32] as

$$2\pi\delta(E_{\mathbf{k_i}}-E_{\mathbf{k'}})/L_z=\delta_{\overline{k}_{zi}(0),k'_z}\Theta(\overline{k^2_{zi}}(0))/(\hbar\sqrt{v_zv'_z}),\tag{33}$$

where

$$\overline{k^2_{zi}}(0)=\mathbf{K}_\mathbf{i}^2-\mathbf{K'}^2+k^2_{zi},\tag{34}$$

and the step function $\Theta(\overline{k^2_{zi}}(0))$ selects only the open scattering channels for which $\overline{k^2_{zi}}(0)>0$. Note in passing that the application of the latter condition to higher order cumulants, which describe correlated processes, would exclude the selective adsorption processes from the scattering spectrum and hence should not be implemented there. The pair interaction matrix element $\tilde{v}(\mathbf{K'}-\mathbf{K_i},k_{z'},k_{zi},z_a)$ can be expressed as

$$\begin{aligned}&\tilde{v}_F(\mathbf{K'}-\mathbf{K_i},k_{z'},k_{zi},z_a)\\&\quad=\int_{-\infty}^{\infty}dz\chi^*_{k'_z}(z)\chi_{k_{zi}}(z)\tilde{v}_F(\mathbf{K'}-\mathbf{K_i},z-z_a)\\&\quad=\int_{-\infty}^{\infty}dz\chi^*_{k'_z}(z)\chi_{k_{zi}}(z)\int_{-\infty}^{\infty}\frac{dp}{2\pi}e^{-ip(z-z_a)}\\&\qquad\times\tilde{v}_F(\mathbf{K'}-\mathbf{K_i},p),\end{aligned}\tag{35}$$

with

$$\tilde{v}_F(\mathbf{K'}-\mathbf{K_i},p)=e^{-w(\mathbf{K'}-\mathbf{K_i},p)}v_F(\mathbf{K'}-\mathbf{K_i},p).\tag{36}$$

The factor $\exp[-w(\mathbf{K'}-\mathbf{K},p)]$ multiplying $v_F(\mathbf{K'}-\mathbf{K},p)$ on the RHS of Eq. (36) is given by

$$e^{-w(\mathbf{K'}-\mathbf{K_i},p)}=\exp\left[-\frac{1}{2}\sum_{\mathbf{Q'},j'}\frac{\hbar|(\mathbf{K'}-\mathbf{K_i})\mathbf{e}_\parallel(\mathbf{Q'},j')+pe_\perp(\mathbf{Q'},j')|^2}{2M_aN_a\omega_{\mathbf{Q'},j'}}[2\overline{n}(\omega_{\mathbf{Q'},j'})+1]\right],\tag{37}$$

where $\mathbf{Q'}$ is restricted to the first SBZ of the adlayer. Hence, for coherent vibrations the Holstein renormalization factor associated with the Fourier transform of the interaction $v_F(\mathbf{K}-\mathbf{K'},p)$ defined in Eq. (7) is explicitly given by expression (37). Due to the Kronecker symbols $\delta_{\mathbf{K'},\mathbf{K_i}+\mathbf{G}}\delta_{\overline{k}_{zi}(0),k'_z}$ contained in expression (32) all the summations over the final wave vectors in Eq. (31) are easily carried out. Note that the diffraction amplitude $\mathcal{V}^{\overline{k}_{zi}(0),k_{zi}}_{\mathbf{K}+\mathbf{G},\mathbf{K_i}}(0,z_a)$ is a dimensionless quantity and that due to coherent scattering from an ordered overlayer one obtains $2W^{\mathrm{EBA}}_{\mathrm{diffr}}(0,\mathbf{R})\propto A_a^{-2}$ and all other quantization lengths and N_a factors cancel out. Thus obtained $2W^{\mathrm{EBA}}_{\mathrm{diffr}}(0,\mathbf{R})$ allows elastic scattering of the particles only into the diffraction channels of the $\mathbf{k}$-space, viz. the transitions $(\mathbf{K_i},k_{zi})\rightarrow[\mathbf{K_i}+\mathbf{G},\overline{k}_{zi}(0)]$ where $\overline{k}_{zi}(0)$ depends on $\mathbf{G}$ through Eqs. (30) and (34), and the probability of this process is given by $|\mathcal{V}^{\overline{k}_{zi}(0),k_{zi}}_{\mathbf{K_i}+\mathbf{G},\mathbf{K_i}}(0,z_a)|^2$. Diffraction processes give rise to a reduction of the intensity of the specularly reflected beam by a diffraction-induced Debye-Waller factor

$$e^{-2W^{\mathrm{EBA}}_{\mathrm{diffr}}}=\exp\left[-\sum_{\mathbf{G}}\left|\mathcal{V}^{\overline{k}_{zi}(0),k_{zi}}_{\mathbf{K_i}+\mathbf{G},\mathbf{K_i}}(0,z_a)\right|^2\right],\tag{38}$$

in accord with the optical theorem. The ''standard'' Glauber-van Hove Debye-Waller factor appears here in the scattering amplitude $\mathcal{V}^{\overline{k}_{zi}(0),k_{zi}}_{\mathbf{K_i}+\mathbf{G},\mathbf{K}}(0,z_a)$ through the Holstein renormalization of the Fourier transform of the pair interaction (36) in a fashion also discussed in Refs. 57, 58, and 60. It should be observed that the exponential form of this renormalization is a consequence of the specific symmetry of the unperturbed wave functions of the projectile and the interaction potential employed to calculate the matrix elements (5). On the other hand, the exponential form of the total DWF in Eq. (26), and thereby also in Eq. (38), is independent of the particularities of these quantities since it arises from general conservation laws. Hence, the complete DWF for diffractive scattering given by Eq. (38) combines two effects, the renormalization of the interaction matrix elements (36) due to elastic particle scattering by zero point vibrations of the adlayer, and the reduction of the intensity of the elastic specular beam due to the projectile diffractive scattering out of the entrance channel $(\mathbf{K_i},k_{zi})$.

B. Multiquantum inelastic scattering and the unified Debye-Waller factor

Expression (25) for the EBA scattering function contains all powers of the adsorbate displacement operators $\mathbf{ul}=(\mathbf{u}_{\mathbf{l}\parallel},\mathrm{u}_{\mathbf{l}\perp})$ and as such can generate two types of multiphonon processes upon expansion of the exponentiated correlation function into a power series in the displacements. The zeroth order term describes elastic diffraction effects discussed above. Multiphonon processes comprising subsequent phonon exchange in which only one phonon can be emitted or absorbed in an interaction vertex arise if besides the zeroth term, the next linear or first order term in the expansion of the exponentiated correlation function is retained in the scattering function (25). Then, due to the appearance of this term in the argument of the exponential function on the RHS of Eq. (23), it is repeated through expanding the latter function into a power series. Thus, an nth order term in this expansion generates phonon excitation processes with multiplicity of order n. In all diagrams representing these processes only a single phonon line can terminate in each interaction vertex (cf. Fig. 1a in Ref. 32). Alternatively, one can first expand $\exp[-2W^{\mathrm{EBA}}(\tau,\mathbf{R})]$ in Eq. (23) into a series in powers of $2W^{\mathrm{EBA}}(\tau,\mathbf{R})$ and keep only the zeroth and first order terms [the zeroth order term giving rise to the no loss line described by expression (26)], retain the correlation function in exponential form and treat it following the lines of Glauber–van Hove first order Born approximation approach.[53,71] This produces in the diagrammatic representation of $N(\tau,\mathbf{R})$ of Eq. (21) a class of diagrams with only two interaction vertices (each carrying a factor g) in which any number of phonon lines can terminate, but each such diagram appearing only once.[37] This type of interaction is nonlinear in displacements and hence can give rise to excitation of overtones. The diagrammatic representation of such correlation functions is shown in Fig. 1 of Ref. 37. However, this latter approximation leads to expressions for the scattering spectrum in which the unitarity is generally violated. Of course, combinations of the two types of the above described approaches are also possible.

The analyses of the T-matrix expansion for inelastic atom-surface scattering processes have shown[63] that multiphonon vertices arising from nonlinear coupling give rise to diagrams for the scattering matrix which for not too high incoming energies and substrate temperatures produce smaller contributions than the multiphonon diagrams of the same multiplicity but involving multiple single phonon vertices only. Hence, in the following we shall pursue the approach in which only the contributions leading to single phonon vertices are taken into consideration. The treatment of the complementary scattering regime in which the multiple phonon vertices were taken into account up to second order in the coupling constant g was presented in Ref. 53.

Expanding the exponentiated correlation function in expression (25), retaining the terms bilinear in the displacements and making use of the identity

$$\int \frac{dp}{2\pi} p e^{-ipz_a} = i\frac{\partial}{\partial z_a}\int \frac{dp}{2\pi} e^{-ipz_a} \tag{39}$$

we find the contribution to the scattering function which gives rise to subsequent one-phonon exchange processes (subscript 1 means single phonon vertices):

$$\begin{aligned}2W_{1\mathrm{coh}}^{\mathrm{EBA}}(\tau,\mathbf{R}) = {} & \sum_{\mathbf{K}',k_z'} e^{-(i/\hbar)[(E_{\mathbf{k}}'-E_{\mathbf{k_i}})\tau-\hbar(\mathbf{K}'-\mathbf{K_i})\mathbf{R}]}\frac{1}{(L_zL_s^2)^2}\sum_{\mathbf{l}',\mathbf{l}'} e^{i(\mathbf{K}'-\mathbf{K_i})(\boldsymbol{\rho}_{\mathbf{l}'}-\boldsymbol{\rho}_{\mathbf{l}''})}\\ & \times\frac{1}{\hbar^2}\int_{-\infty}^{\infty}dt'\int_{-\infty}^{\infty}dt'' e^{-(i/\hbar)(E_{\mathbf{k}'}-E_{\mathbf{k_i}})(t'-t'')}\\ & \times\langle\langle[(\mathbf{K}'-\mathbf{K_i})\cdot\mathbf{u}_{\mathbf{l}'\parallel}(t')-i\mathrm{u}_{\mathbf{l}'\perp}(t')(\partial/\partial z_{\mathbf{l}'})][(\mathbf{K}'-\mathbf{K_i})\cdot\mathbf{u}_{\mathbf{l}''\parallel}(t'')+i\mathrm{u}_{\mathbf{l}''\perp}(t'')(\partial/\partial z_{\mathbf{l}''})]\rangle\rangle\\ & \times\tilde{v}_F^{*}(\mathbf{K}'-\mathbf{K_i},k_z',k_{zi},z_{\mathbf{l}'})\tilde{v}_F(\mathbf{K}'-\mathbf{K_i},k_z',k_{zi},z_{\mathbf{l}''}).\end{aligned} \tag{40}$$

This is expressed in terms of the Holstein-renormalized interactions (35) and (36) and can be calculated once the polarization eigenvectors and eigenfrequencies of adsorbate vibrations are specified.

Substituting expression (27) into Eq. (40), carrying out summations over $(\mathbf{l}',\mathbf{l}'')$, which yield the lateral momentum conservation, and integrations over t' and t'', which yield the energy conservation, we obtain in the case of coherent vibrations

$$\begin{aligned}2W_{1\mathrm{coh}}^{\mathrm{EBA}}(\tau,\mathbf{R}) &= \sum_{\mathbf{K}',k_z'} e^{-(i/\hbar)[(E_{\mathbf{k}}'-E_{\mathbf{k_i}})\tau-\hbar(\mathbf{K}'-\mathbf{K_i})\mathbf{R}]}\sum_{\mathbf{Q},j}\sum_{\mathbf{G}}\{|\mathcal{F}_{\mathbf{K}',\mathbf{K_i},Q,j}^{k_z',k_{zi}}(+,z_a)|^2[\overline{n(}\omega_{\mathbf{Q},j})+1]+|\mathcal{F}_{\mathbf{K}',\mathbf{Ki},\mathbf{Q},j}^{k_z',k_{zi}}(-,z_a)|^2\overline{n(}\omega_{\mathbf{Q},j})\}\\ &= \sum_{\mathbf{Q},j}\sum_{\mathbf{G}}\{|\mathcal{F}_{\mathbf{K_i}-\mathbf{Q}-\mathbf{G},\mathbf{K_i},j}^{\overline{k}_{zi}(+),k_{zi}}(+,z_a)|^2[\overline{n(}\omega_{\mathbf{Q},j})+1]e^{i[\omega_{\mathbf{Q},j}\tau-(\mathbf{Q}+\mathbf{G})\mathbf{R}]}\\ &\quad +|\mathcal{F}_{\mathbf{K_i}+\mathbf{Q}+\mathbf{G},\mathbf{K_i},j}^{\overline{k}_{zi}(-),k_{zi}}(-,z_a)|^2\overline{n(}\omega_{\mathbf{Q},j})e^{-i[\omega_{\mathbf{Q},j}\tau-(\mathbf{Q}+\mathbf{G})\mathbf{R}]}.\end{aligned} \tag{41}$$

Here the force matrix elements $\mathcal{F}$ are defined by

$$\mathcal{F}_{\mathbf{K}',\mathbf{K_i},\mathbf{Q},j}^{k_z',k_{zi}}(\pm,z_a) = \left(\frac{\hbar}{2M_aN_a\omega_{\mathbf{Q},j}}\right)^{1/2}[(\mathbf{K}'-\mathbf{K_i})\cdot\mathbf{e}_{\parallel}(\mathbf{Q},j)+ie_{\perp}(\mathbf{Q},j)(\partial/\partial z_a)]\mathcal{V}_{\mathbf{K}',\mathbf{K_i},\mathbf{Q},j}^{k_z',k_{zi}}(\pm,z_a), \tag{42}$$

in which the inelastic counterpart of expression (32) is given by

$$\mathcal{V}^{k_z',k_{zi}}_{\mathbf{K}',\mathbf{K_i},Q,j}(\pm,z_a)=\delta_{\mathbf{K}'\pm\mathbf{Q}\pm\mathbf{G},\mathbf{K_i}}\delta_{\overline{k}_{zi}(\pm),k_z'}\Theta(\overline{k^2_{zi}}(\pm))\frac{\tilde{v}_F(\mathbf{K}'-\mathbf{K_i},k_{z'},k_{zi},z_a)}{A_a\hbar\sqrt{v_z v_z'}}. \tag{43}$$

In this expression the values of $\mathbf{K}'$ and $E_{\mathbf{k}}'$ are confined to the energy- and lateral-momentum-shell through the product $\delta_{\mathbf{K}'\pm\mathbf{Q}\pm\mathbf{G},\mathbf{K}_i}\delta_{\overline{k}_{zi}(\pm),k_z'}\Theta(\overline{k^2_{zi}}(\pm))$ in which the symbols $(+)$ and $(-)$ refer to one-phonon emission and absorption processes, respectively, and

$$\overline{k^2_{zi}}(\pm)=\mathbf{K_i}^2-\mathbf{K}'^2+k_{zi}^2\mp 2M\omega_{\mathbf{Q},j}/\hbar. \tag{44}$$

The condition $\overline{k^2_{zi}}(\pm)>0$ present in expression (43) automatically excludes the sticking processes for which the EBA-derived probabilities scale as g^2 but which are negligible for the studied systems.[66] Thus, the inelastic scattering matrix elements $\mathcal{F}^{k_z',k_{zi}}_{\mathbf{K}',\mathbf{K_i},\mathbf{Q},j}(\pm,z_a)$ conserve the lateral momentum and energy in each one-phonon interaction vertex but also embody the off-the-energy-shell features through the Holstein renormalization factor (37).

Expressions (37) and (41) are independent of N_a since the final summations over $\mathbf{K}'$ or $\mathbf{Q}$ when transformed into a two-dimensional integration introduce a factor $N_a A_a/(2\pi)^2$. Hence, expression (41) remains proportional to A_a^{-1} and not to A_a^{-2} as was the case with the analogous quantity in diffraction [cf. expression (31)]. Thus, larger unit cells of the superstructure act so as to reduce the amplitude of the scattering function for inelastic processes, and vice versa, but not to the extent as in the case of elastic diffraction processes. Note also the difference between the inelastic scattering probabilities of loss and gain processes in expression (41) which are associated with $[\overline{n}(\omega_{\mathbf{Q},j})+1]$ and $\overline{n}(\omega_{\mathbf{Q},j})$, respectively. These terms are different which is a manifestation of the recoil effects in both the energy and lateral momentum phase space.

Now, according to Eq. (23) the unified Debye-Waller factor due to inelastic scattering by coherent vibrations reads

$$e^{-2W^{\mathrm{EBA}}_{1\mathrm{coh}}}=\exp\Bigg[-\sum_{\mathbf{Q},j}\sum_{\mathbf{G}}\{|\mathcal{F}^{\overline{k}_{zi}(+),k_{zi}}_{\mathbf{K_i}-\mathbf{Q}-\mathbf{G},\mathbf{K_i},j}(+,z_a)|^2[\overline{n}(\omega_{\mathbf{Q},j})$$
$$+1]+|\mathcal{F}^{\overline{k}_{zi}(-),k_{zi}}_{\mathbf{K_i}+\mathbf{Q}+\mathbf{G},\mathbf{K_i},j}(-,z_a)|^2\overline{n}(\omega_{\mathbf{Q},j})\}\Bigg]. \tag{45}$$

The exponent on the RHS of Eq. (45) is integrated over all scattering channels and is therefore independent of N_a and scales as A_a^{-1}. In the limit of high temperature and large projectile incident energy it becomes effectively proportional to a product of the Holstein renormalization factor and Weare's parameter[67] $\alpha=(M/M_a)(E_i/k_B\Theta_D)(T/\Theta_D)$ which estimates the importance of multiphonon processes in atom-surface scattering (k_B is the Boltzman constant and the Debye temperature Θ_D should be identified with the average phonon energy at the adlayer zone edge). Moreover, inspection of the various formulas of the one-phonon scattering theory (cf. Ref. 50) enables us to identify the exponent on the RHS of Eq. (45) with the sum of one-phonon inelastic reflection coefficients $\tilde{R}^{\mathrm{DWBA}}_{fi}$ calculated in the DWBA and weighed by the Glauber–van Hove DWF which enters through the Holstein renormalization of the interaction (5), viz.

$$e^{-2W^{\mathrm{EBA}}_{1\mathrm{coh}}}=\exp\Bigg[-\sum_{f(\neq i)}\tilde{R}^{\mathrm{DWBA}}_{fi}\Bigg]. \tag{46}$$

This expression clearly demonstrates the relation between the EBA and the DWBA and the corresponding Debye-Waller factors.

Substitution of the sum of expressions (31) and (41) into Eq. (23) gives the momentum and energy resolved multiphonon scattering spectrum with the total DWF given by the product of expressions (38) and (45).

C. Mean energy transfer

An important property of the lateral momentum integrated spectrum is its first moment $\mu_1(T_s)$ or the mean energy transfer in the course of inelastic projectile scattering[49] from the surface at the temperature T_s. Starting from expression (22) it is easily shown that

$$\mu_1(T_s)=\int(\Delta E)(d\Delta E)\int d^2(\Delta\mathbf{K})N(\Delta E,\Delta\mathbf{K})$$
$$=i\frac{\partial}{\partial\tau}\sum_{n=1}^{\infty}C_n(\tau,\mathbf{R}=0)|_{\tau=0}. \tag{47}$$

This expression is exact. In the EBA we obtain

$$\mu_1^{\mathrm{EBA}}(T_s)=i\frac{\partial}{\partial\tau}2W(\tau,\mathbf{R}=0)|_{\tau=0}. \tag{48}$$

For coherent vibrations this takes the form

$$\mu^{\mathrm{EBA}}_{1\mathrm{coh}}(T_s)=\sum_{\mathbf{G}}\sum_{\mathbf{Q},j}(\hbar\omega_{\mathbf{Q},j})\{|\mathcal{F}^{\overline{k}_{zi}(+),k_{zi}}_{\mathbf{K_i}-\mathbf{Q}-\mathbf{G},\mathbf{K_i},j}(+,z_a)|^2$$
$$+[|\mathcal{F}^{\overline{k}_{zi}(+),k_{zi}}_{\mathbf{K_i}-\mathbf{Q}-\mathbf{G},\mathbf{K_i},j}(+,z_a)|^2$$
$$-|\mathcal{F}^{\overline{k}_{zi}(0),k_{zi}}_{\mathbf{K_i}+\mathbf{Q}+\mathbf{G},\mathbf{K_i},j}(-,z_a)|^2]\overline{n}(\omega_{\mathbf{Q},j})\}. \tag{49}$$

Note here the minus sign in the square bracket on the RHS of Eq. (49) which gives rise to a recoil induced temperature dependent contribution to $\mu^{\mathrm{EBA}}_{1\mathrm{coh}}(T_s)$. However, the total temperature dependence of $\mu_1^{\mathrm{EBA}}(T_s)$ comes both through the Holstein renormalization of the interaction matrix elements $\mathcal{F}$ by the factor e^{-w} and the recoil-induced term. It should also be pointed out that μ_1^{EBA} will provide a reliable estimate of the total energy transfer inasmuch as the corresponding EBA spectrum (23) reliably reproduces the exact scattering spectrum (22).

D. Mean energy transfer for fixed scattering geometry

In the majority of TOF experiments the scattered particles are detected in the sagittal plane with no change of the azimuth, i.e., $\varphi_i = \varphi_f$, and with $\theta_i + \theta_f = \theta_{\mathrm{SD}} = \mathrm{const}$ for a given apparatus. Additionally, during recording of each TOF spectrum the incident angle θ_i is kept fixed, which all determines $\Delta\mathbf{K}$ in the sagittal plane as a function of the energy transfer only, viz.

$$(\Delta\mathbf{K})_{\mathrm{sag}} = k_f \sin\theta_f - k_i \sin\theta_i = \Delta K(\Delta E), \tag{50}$$

where

$$k_f = \sqrt{\frac{2M(E_i + \Delta E)}{\hbar^2}}, \quad k_i = \sqrt{\frac{2ME_i}{\hbar^2}}. \tag{51}$$

This enables us to define the mean energy transfer for a particular TOF spectrum:

$$\mu_1(\varphi_i, \theta_i, T_s) = \frac{\int_{-\infty}^{\infty} \varepsilon N(\varepsilon, \Delta\mathbf{K}(\varepsilon)) d\varepsilon}{\int_{-\infty}^{\infty} N(\varepsilon, \Delta\mathbf{K}(\varepsilon)) d\varepsilon}, \quad \varepsilon = \Delta E. \tag{52}$$

Comparing the values obtained by applying expression (52) to the measured TOF spectra with the corresponding values calculated from the theoretical spectra enables yet another test of validity of the particular model employed in the description of the scattering event.[49,70]

Equations (41)–(52) represent the central results of this paper and demonstrate the essential features of the multiphonon scattering spectra and the corresponding unified DWF. The latter comprises the properties of analogous expressions which occurred as separate quantities in earlier theories. In the present theory we shall recover them as special limits (cf. Sec. V).

The fundamental difference between the above results and those for clean surfaces derived in Ref. 32 is in that the present approach allows for the static corrugation of the adlayer through ''embedding'' of the adsorbates into the distorted wave functions of the projectile. This effect combined with the multiphonon expansion leads in turn to the Holstein renormalization of the interaction matrix elements and their z_a-dependence, and the possibility of simultaneous occurrence of diffraction peaks and multiple and overtone excitations in the scattering spectra.

V. SPECIAL LIMITS OF THE SCATTERING SPECTRUM AND THE DEBYE-WALLER FACTOR

A. On-shell versus Glauber–van Hove Debye-Waller factor in single phonon scattering

The on-shell Debye-Waller factor compatible with the optical theorem was derived in Refs. 30–32 under the assumption of a simpler, i.e., linear projectile-phonon coupling. In the present approach this is equivalent to keeping only the terms quadratic in phonon displacement amplitudes in the expansion of the exponent of the complete DWF given by Eq. (45). Hence, we retrieve the on-shell DWF of Refs. 32 and 37 by neglecting the Holstein renormalization effect on the force matrix elements $\mathcal{F}$ in the exponent on the RHS of expression (45).

On the other hand, the appearance of the standard Glauber–van Hove DWF is retrieved under the assumption of first order DWBA or weak coupling (small g) but large vibrational amplitudes. In this case one retains in the expansion of the scattering spectrum only the terms which are zeroth order and quadratic in the coupling constant g. To this order the expression for the no-loss line is given by

$$N_0^{\mathrm{DWBA}}(\Delta E, \Delta\mathbf{K}) = (1 - 2W_{1\mathrm{coh}}^{\mathrm{EBA}})\,\delta(\Delta E)\,\delta(\Delta\mathbf{K}), \tag{53}$$

in which $(1 - 2W_{1\mathrm{coh}}^{\mathrm{EBA}})$ plays the role of the complete DWF up to second order in g with the Holstein-renormalized interaction matrix elements in $2W_{1\mathrm{coh}}^{\mathrm{EBA}}$. The analogy with the Glauber-van Hove DWF appears most clearly in the next term describing the inelastic one-phonon DWBA scattering probability. For coherent vibrations and to the same order in g this is given by

$$\begin{aligned} N_{1\mathrm{coh}}^{\mathrm{DWBA}}(\Delta E, \Delta\mathbf{K}) = \frac{N_a A_a}{(2\pi\hbar)^2} \sum_{\mathbf{Q},\mathbf{G},j} \{ & |\mathcal{F}_{\mathbf{K_i}+\Delta\mathbf{K},\mathbf{K_i},j}^{\overline{k}_{zi}(+),k_{zi}}(+, z_a)|^2 \\ & \times [\overline{n}(\omega_{\mathbf{Q},j}) + 1]\,\delta(\Delta E \\ & + \hbar\omega_{\mathbf{Q},j})\,\delta_{\Delta\mathbf{K},-\mathbf{Q}-\mathbf{G}} \\ & + |\mathcal{F}_{\mathbf{K_i}+\Delta\mathbf{K},\mathbf{K_i},j}^{\overline{k}_{zi}(-),k_{zi}}(-, z_a)|^2 \overline{n}(\omega_{\mathbf{Q},j}) \\ & \times \delta(\Delta E - \hbar\omega_{\mathbf{Q},j})\,\delta_{\Delta\mathbf{K},\mathbf{Q}+\mathbf{G}} \}, \end{aligned} \tag{54}$$

where the Glauber–van Hove DWF effect is contained in the Holstein-renormalized matrix elements $\mathcal{F}$ [cf. Eq. (42)]. Expressions analogous to expression (54) but without the Holstein renormalization have been extensively used as a point of departure in discussions of single phonon He atom scattering from surfaces.[50,51] As regards the DWF and the one-phonon excitation properties, they are distorted wave analogs of the standard Glauber–van Hove expression describing inelastic neutron scattering from crystal lattices. Energy conservation enters each of them through the factor $\delta_{\overline{k}_{zi}(\pm),k_z'}\Theta(\overline{k_{zi}^2}(\pm))$ present in $\mathcal{F}$ [cf. Eqs. (42) and (43)], which together with the lateral momentum conservation embodied in the Kronecker symbols $\delta_{\Delta\mathbf{K},\pm\mathbf{Q}\pm\mathbf{G}}$ defines the ''scan curve'' in standard TOF geometries.

B. Trajectory approximation in multiphonon scattering

Another frequently used approximation in the calculations of inelastic scattering spectra in the multiphonon regime is the so-called trajectory approximation (TA) for the projectile motion which is usually employed in the quasiclassical scattering regime. The conditions of validity for a passage from the description of the scattering event in terms of the quasiclassical scattering matrix elements to the description in terms of the projectile classical trajectory were discussed in Refs. 30 and 68 for short and long range projectile-surface interactions, respectively. However, as this also presents a difficult problem to solve if the classical projectile motion is subject to recoil, one further assumes the projectile particle motion on a *prescribed* and hence recoilless trajectory. The projectile motion then represents a time dependent perturbation on the phonon field and one may hope that the actual loss spectrum of the projectile can be calculated from conservation laws as the negative of the energy and lateral momentum gain of the phonon field. As this is an inherently inconsistent procedure the TA may represent a reasonable approximation in HAS from surfaces only under very restricted conditions.[30–32]

Expression (15) for the scattering spectrum proves inadequate as a starting point for the implementation of the TA because it is based on the projection of the *quantum states of the projectile* from the wave function of the collision system. In order to retrieve the TA expression for the inelastic scattering spectrum one has to revert to the projections using the phonon field operators H_0^{ph} and $\hat{\mathbf{P}}^{\mathrm{ph}}$ instead of H_0^{part} and $\hat{\mathbf{P}}$ in Eq. (15).[30–32] This is only feasible for flat surfaces for which the energy and momentum transfer to the phonon field is just the negative of the energy and momentum transfer to the projectile particle. Having done this one projects the desired final quantum states of the phonon field from the wave function of the system irrespective of whether the phonon field has been perturbed by a quantum or a classical perturbation. Thus, the application of the classical trajectory approximation to the projectile motion automatically rules out the possibility of calculating the diffraction and related effects.

To obtain the TA limit of the inelastic scattering spectrum (15) in which the operators H_0^{ph} and $\hat{\mathbf{P}}^{\mathrm{ph}}$ have been introduced one carries out the procedure completely analogous to the one described in Refs. 30–32. Here one has to take care to express all the summations in terms of phonon quantum numbers $(\mathbf{Q},j)$ and excitation frequencies $\omega_{\mathbf{Q},j}$. Then, the TA amounts to replacing the interaction matrix elements taken between the projectile states by their classical counterparts given by the Fourier transforms in the time variable of the classical force $\mathbf{F}(t)$ exerted on the adatoms by the particle moving along the classical trajectory $\mathbf{r}(t)$.[25,69] A detailed description of this procedure was given in Refs. 25, 31, and 32 and will not be further elaborated here. We shall only reiterate that the EBA is superior to both the DWBA and TA, moreover, it contains them as special limits and smoothly interpolates between the two.

C. Extreme multiphonon scattering regime

Another frequently encountered general limit of the scattering spectrum is reached in the extreme multiphonon regime in which $2W^{\mathrm{EBA}} \gg 1$, i.e., when the mean number of exchanged phonons is large.[9,31] In this case the major contribution to the Fourier transform in Eq. (23) comes from small values of the exponent $[2W^{\mathrm{EBA}}(\tau,\mathbf{R}) - 2W^{\mathrm{EBA}}]$ upon expanding it into a power series in τ and $\mathbf{R}$ and retaining only linear and quadratic terms. Collecting the leading contributions to this series we obtain

$$\lim_{2W^{\mathrm{EBA}} \gg 1} N(\Delta E, \Delta \mathbf{K}) = \frac{1}{(2\pi)^{3/2}\sigma_\omega \sigma_x \sigma_y} \times \exp\left[-\frac{(\Delta E - \mu_1(T_s))^2}{2\sigma_\omega^2} - \frac{(\hbar \Delta K_x)^2}{2\sigma_x^2} - \frac{(\hbar \Delta K_y)^2}{2\sigma_y^2} \right]. \quad (55)$$

Here $\mu_1(T_s)$ is given by Eq. (49), and in the case of coherent vibrations the temperature dependent spectral widths σ are given by

$$\sigma_\lambda^2(T_s) = \sum_{\mathbf{K}',k_z'} \sum_{\mathbf{G},\mathbf{Q},j} \lambda^2 \{ |\mathcal{F}^{k_z',k_{zi}}_{\mathbf{K}',\mathbf{K_i},Q,j}(+,z_a)|^2 \times [\overline{n}(\omega_{\mathbf{Q},j}) + 1] \delta_{\mathbf{K}'+\mathbf{Q}+\mathbf{G},\mathbf{K_i}} + |\mathcal{F}^{k_z',k_{zi}}_{\mathbf{K}',\mathbf{K_i},Q,j}(-,z_a)|^2 \overline{n}(\omega_{\mathbf{Q},j}) \delta_{\mathbf{K}'-\mathbf{Q}-\mathbf{G},\mathbf{K_i}} \}, \quad (56)$$

where λ stands for $\hbar\omega_{\mathbf{Q},j}$, $\hbar(\mathbf{K}'-\mathbf{K_i})_x$ or $\hbar(\mathbf{K}'-\mathbf{K_i})_y$. Expression (55) should represent a good approximation to expression (23) in the multiphonon limit in which ΔE and $\Delta\mathbf{K}$ are small and confined to the scan curve (i.e., connected through the total energy and lateral momentum conservation). Due to this, the maximum of the spectrum (55) will generally not coincide with μ_1, viz. it may occur either on the positive or negative energy transfers, depending on the scattering conditions. The intensity prefactor $[(2\pi)^{3/2}\sigma_\omega\sigma_x\sigma_y]^{-1}$ exhibits the temperature dependence which approaches $T_s^{-3/2}$ behavior in the high-T_s limit both for coherent and incoherent adsorbate vibrations. The detailed structure of the interaction matrix elements is here of no importance (e.g., pairwise interactions versus some different expressions) as long as the general structure of the scattering function (41) persists in that form. Note also that although expression (55) represents a limiting case of the momentum and energy resolved spectrum, the value of the mean energy transfer is here given by the momentum integrated expression $\mu_1(T_s)$, Eq. (49), and not by the corresponding $\mathbf{K}$-resolved quantity as one might expect. This is due to the uncertainty in energy and momentum fluctuation involved in the short-τ and small-$\mathbf{R}$ component of the response of the phonon system which is only relevant in deriving expression (55). The temperature dependence of $\mu_1(T_s)$ and $\sigma_\lambda(T_s)$ explicitly affects the position of the spectral maximum in the extreme multiphonon regime. In $\sigma_\lambda(T_s)$ this dependence is strong and analogous to that of the Debye-Waller exponent. On the other hand, in $\mu_1(T_s)$ it is weaker due to the structure of the recoil correction [cf. Eq. (49)]. As for relatively high incoming projectile energies the difference between the gain and loss values of the interaction matrix elements becomes very small, the temperature variation of $\mu_1(T_s)$ may then be dominantly determined by the Holstein renormalization of $|\mathcal{F}^{k_z',k_{zi}}_{\mathbf{K}',\mathbf{K_i},\mathbf{Q},j}(\pm,z_a)|^2$. However, the position of the spectral maximum of expression (55) may nevertheless be strongly temperature dependent as it also depends on σ_ω, σ_x and σ_y which are all strongly T_s dependent.

D. Scattering from adlayers sustaining Einstein modes

The multiquantum and Debye-Waller type of effects will manifest themselves most clearly in the case of excitation of adsorbate low energy vibrational modes which exhibit little or no dispersion. With incoming He atom energies exceeding several times the energies of such modes and for not too low substrate temperatures, one can clearly observe spectral peaks corresponding to multiple excitation of dispersionless modes both on the energy loss and gain sides in the TOF spectra of a number of systems.[17,20,21,41,49] Depending on the specificities of the systems studied, these modes can be associated either with lateral or perpendicular adsorbate motions.

A closed form solution for the scattering spectrum characteristic of an adlayer sustaining Einstein-like modes is obtained by separating the nondispersive branch j_0 of frequency ω_0 out of the sum in expression (41), giving

$$\exp[2W^{\mathrm{EBA}}_{1\mathrm{coh}}(\tau,\mathbf{R})-2W^{\mathrm{EBA}}_{1\mathrm{coh}}]=N^{\mathrm{Ein}}_{\mathbf{k_i},T_s}(\tau,\mathbf{R})N^{\mathrm{dis}}_{\mathbf{k_i},T_s}(\tau,\mathbf{R}), \tag{57}$$

where Ein and dis denote components comprising Einstein and all other dispersive modes, respectively. In the remainder of this subsection we shall for the sake of simplicity disregard $N^{\mathrm{dis}}_{\mathbf{k_i},T_s}(\tau,\mathbf{R})$ as its effect on the total scattering spectrum can be easily restored by a simple convolution procedure.[21,40] Denoting the single frequency of a set of Einstein oscillators by ω_0, the corresponding component of the scattering function (41) can be written in the form

$$\begin{aligned}2W^{\mathrm{Ein}}(\tau,\mathbf{R})={}&\mathcal{F}^2(\mathbf{R},+)[\overline{n}(\omega_0)+1]e^{-i\omega_0\tau}\\&+\mathcal{F}^2(\mathbf{R},-)\overline{n}(\omega_0)e^{i\omega_0\tau},\end{aligned} \tag{58}$$

where $\mathcal{F}^2(\mathbf{R},\pm)$ are obtained by carrying out the $(\mathbf{K}',\mathbf{Q},\mathbf{G},k_z')$ summations over the separated j_0th component of expression (41). Now, observing that $(\overline{n}+1)/\overline{n}=\exp(\hbar\omega_0/k_BT_s)$ and introducing the notation

$$\mathcal{F}^2(\mathbf{R},+)+\mathcal{F}^2(\mathbf{R},-)=\mathcal{M}(\mathbf{R}), \tag{59}$$

$$i[\mathcal{F}^2(\mathbf{R},+)-\mathcal{F}^2(\mathbf{R},-)]=\mathcal{N}(\mathbf{R}), \tag{60}$$

$$\theta(\tau)=(\omega_0\tau-i\hbar\omega_0/2k_BT_s), \tag{61}$$

and

$$\varphi(\mathbf{R})=\arctan[\mathcal{N}(\mathbf{R})/\mathcal{M}(\mathbf{R})]=\frac{i}{2}\ln\frac{\mathcal{F}^2(\mathbf{R},+)}{\mathcal{F}^2(\mathbf{R},-)}, \tag{62}$$

we may write

$$\begin{aligned}N^{\mathrm{Ein}}_{\mathbf{k_i},T_s}(\tau,\mathbf{R})={}&e^{-2W^0}\\&\times\exp\{\sqrt{\overline{n}(\overline{n}+1)[\mathcal{M}^2(\mathbf{R})+\mathcal{N}^2(\mathbf{R})]}\\&\times\cos[\theta(\tau)+\varphi(\mathbf{R})]\}\\={}&e^{-2W^0}\exp\{\sqrt{4\overline{n}(\overline{n}+1)\mathcal{F}^2(\mathbf{R},+)\mathcal{F}^2(\mathbf{R},-)}\\&\times\cos[\theta(\tau)+\varphi(\mathbf{R})]\},\end{aligned} \tag{63}$$

where

$$2W^0=2W^{\mathrm{Ein}}(\tau=0,\mathbf{R}=\mathbf{0})=(\overline{n}+1)\mathcal{F}^2(0,+)+\overline{n}\mathcal{F}^2(0,-). \tag{64}$$

Making use of the generating function expansion for the modified Bessel function of the first kind, $\exp(z\cos\alpha)=\Sigma_{l=-\infty}^{\infty}I_l(z)\exp(il\alpha)$, we find

$$N^{\mathrm{Ein}}_{\mathbf{k_i},T_s}(\tau,\mathbf{R})=e^{-2W^0}\sum_{l=-\infty}^{\infty}P_l(\mathbf{R})e^{-il\omega_0\tau}, \tag{65}$$

where

$$\begin{aligned}P_l(\mathbf{R})=\Bigg[&\left(\sqrt{\frac{(\overline{n}+1)\mathcal{F}^2(\mathbf{R},+)}{\overline{n}\mathcal{F}^2(\mathbf{R},-)}}\right)^l\\&\times I_l(\sqrt{4\overline{n}(\overline{n}+1)\mathcal{F}^2(\mathbf{R},+)\mathcal{F}^2(\mathbf{R},-)})\Bigg].\end{aligned} \tag{66}$$

This gives for the separated Einstein phonon component of the scattering spectrum

$$N^{\mathrm{Ein}}_{\mathbf{k_i},T_s}(\Delta E,\Delta\mathbf{K})=e^{-2W^0}\sum_{l=-\infty}^{\infty}N_l(\Delta\mathbf{K})\,\delta(\Delta E+l\hbar\omega_0), \tag{67}$$

where

$$N_l(\Delta\mathbf{K})=\int\frac{d^2\mathbf{R}}{(2\pi)^2}e^{-i(\Delta\mathbf{K})\mathbf{R}}P_l(\mathbf{R}). \tag{68}$$

The angular integrated scattering spectrum corresponding to expression (67) is obtained upon replacing $N_l(\Delta\mathbf{K})$ on the RHS of Eq. (67) by $P_l(\mathbf{R}=\mathbf{0})$. Accordingly, the DWF of such lateral momentum integrated spectrum[72] is given by $e^{-2W^0}P_0(\mathbf{R}=\mathbf{0})$ where $P_0(\mathbf{R}=0)\neq 1$ and both factors contain the contributions from all inelastic scattering channels.

Expressions (66) and (67) exhibit interesting structure. Expression (66) contains complex quantities $\mathcal{F}^2(\mathbf{R},+)$ and $\mathcal{F}^2(\mathbf{R},-)$ whose difference $-i\mathcal{N}(\mathbf{R})$ measures the recoil of the projectile in the one-phonon creation and annihilation events. Namely, in the limit of classical recoilless trajectory approximation one has $\mathcal{F}^2(\mathbf{R},+)=\mathcal{F}^2(\mathbf{R},-)$ and consequently $\mathcal{N}(\mathbf{R})=0$ and $\varphi(\mathbf{R})=0$. In this limit the angular integrated spectrum $N^{Ein}_{\mathbf{k_i},T_s}(\Delta E)$ is given by a generalized Poisson distribution [cf. Eq. (86) in Ref. 32] typical of the forced oscillator model applied to Einstein phonons. However, as is seen from expressions (66) and (67), the lateral momentum resolution and recoil effects destroy such a simple structure. The deviations of $N^{\mathrm{Ein}}_{\mathbf{k_i},T_s}(\Delta E)$ from the Poisson distribution grow larger as $\mathcal{N}(\mathbf{R})$ increases, i.e., as the quantum recoil effects become more important.

For finite T_s one generally has $N^{\mathrm{Ein}}_{\mathbf{k_i},T_s}(\Delta E=0,\Delta\mathbf{K}\neq 0)\neq 0$, meaning that due to coupling to the phonon heatbath a finite momentum transfer may occur also in nondiffractive elastic collisions. The spectral intensity of such off-specular elastic transitions in the $\Delta\mathbf{K}$ direction is given by $e^{-2W^0}N_0(\Delta\mathbf{K})$. In the limit of specular elastic transitions $(\Delta\mathbf{K}\rightarrow 0)$ this tends to $e^{-2W^0}P_0(\mathbf{R}\rightarrow\infty)\,\delta(\Delta\mathbf{K})$. The quantity $e^{-2W^0}P_0(\mathbf{R}\rightarrow\infty)$ may be identified with the DWF corresponding to the elastic specular peak. However, from definitions of $P_0(\mathbf{R})$, Eq. (66), and $\mathcal{F}^2(\mathbf{R},\pm)$ we can deduce that $P_0(\mathbf{R}\rightarrow\infty)\rightarrow 1$ because of the destructive interference effects in the argument of $P_0(\mathbf{R})$. Hence, the DWF corresponding to the elastic specular peak is again given by e^{-2W^0}.

The angular integrated or total mean energy transfer in the case of Einstein oscillators acquires in the EBA a simple form

$$\mu_1(T_s)=\frac{\sum_{l=-\infty}^{\infty}(l\hbar\omega_0)P_l(0)}{\sum_{l=-\infty}^{\infty}P_l(0)}$$
$$=\hbar\omega_0[\mathcal{F}^2(0,+)(\overline{n}+1)-\mathcal{F}^2(0,-)\overline{n}], \qquad (69)$$

because from the normalization of the spectrum it follows that $\Sigma_{l=-\infty}^{\infty}P_l(0)=e^{2W^0}$. Although expression (69) is reminiscent of the angular resolved mean energy transfer (52), the information contained in the two quantities is different and they may even bear different signs for the same scattering conditions.[70]

VI. SCATTERING FROM DISORDERED ADLAYERS

A different situation regarding the various terms in the expansion of expression (25) arises if the overlayer exhibits certain degree of internal disorder. Several situations concerning the structure of such overlayers are possible (cf. exhaustive discussions in Refs. 73 and 74) but here we shall focus on the case of lower coverages and temperatures when the island formation is precluded. In this case one may safely assume that interadsorbate distances are large enough (limit of isolated adsorbates) so as that their vibrations are uncorrelated or incoherent. Here we define an effective mean area $\langle A_a\rangle=L_s^2/N_a$ associated with each adsorbate where N_a is now the number of adsorbates on the surface. In the following we shall consider for simplicity only external translational vibrations of isolated adsorbates which are assumed to occupy equivalent adsorption sites.

We introduce the expansion of adsorbate displacements in terms of localized normal modes

$$\mathbf{u}_{\mathbf{l}}=\sum_{\sigma=1}^{3}\left(\frac{\hbar}{2M_a\omega_\sigma}\right)^{1/2}(\mathbf{e}_{\mathbf{l},\sigma}a_{\mathbf{l}},\sigma+\mathbf{e}^{*}_{\mathbf{l},\sigma}a^{\dagger}_{\mathbf{l},\sigma}), \qquad (70)$$

where $\omega_{\mathbf{l},\sigma}=\omega_\sigma$ and $\mathbf{e}_{\mathbf{l},\sigma}$ are the frequency and polarization vector of the σth normal mode associated with the adsorbate at site **l**, respectively, and the phonon field operators satisfy the commutation relations

$$[a_{\mathbf{l},\sigma},a^{\dagger}_{\mathbf{l}',\sigma'}]=\delta_{\mathbf{l},\mathbf{l}'}\delta_{\sigma,\sigma'}\,. \qquad (71)$$

For simplicity we shall also assume that these modes are decoupled from the phonon modes of the underlying substrate over almost the entire surface Brillouin zone which is practically fulfilled in the examples of adlayer systems discussed below. The corresponding unperturbed adsorbate phonon field Hamiltonian then takes the form

$$H_0^{\mathrm{ph}}=\sum_{\mathbf{l},\sigma}\hbar\omega_\sigma a^{\dagger}_{\mathbf{l},\sigma}a_{\mathbf{l},\sigma}\,. \qquad (72)$$

To carry out summations over adsorbates in expression (25) for the scattering function, i.e., over the pairs of randomly occupied adsorption sites $(\mathbf{l}',\mathbf{l}'')$, we assume configurational averaging based on the use of the joint probability $p_{\mathbf{l}',\mathbf{l}''}$ that the sites $\mathbf{l}'$ and $\mathbf{l}''$ are both occupied for a given overlayer coverage Θ. In the simplest independent site model this is given by[73,74]

$$p_{\mathbf{l}',\mathbf{l}''}=\Theta^2\left(1+\frac{1-\Theta}{\Theta}\delta_{\mathbf{l}',\mathbf{l}''}\right), \qquad (73)$$

where $\Theta=N_a/N_{\mathrm{site}}$ and N_{site} is the number of available equivalent adsorption sites on the substrate surface. The configurational averaging is then performed according to

$$\left\langle\sum_{\mathrm{occ.}\ \mathbf{l}',\mathbf{l}''}\right\rangle_{\mathrm{conf}}\rightarrow\sum_{\mathrm{all\ sites}\ \mathbf{l}',\mathbf{l}''}p_{\mathbf{l}',\mathbf{l}''}\,. \qquad (74)$$

This procedure yields for the two-dimensional structure factor:

$$\left\langle\sum_{\mathrm{occ.}\ \mathbf{l}',\mathbf{l}''}e^{i\mathbf{K}(\boldsymbol{\rho}_{\mathbf{l}'}-\boldsymbol{\rho}_{\mathbf{l}''})}\right\rangle_{\mathrm{conf}}=N_a^2\sum_{\mathbf{G}}\delta_{\mathbf{K},\mathbf{G}}+N_a\,, \qquad (75)$$

where **G** is a two-dimensional reciprocal lattice vector of the substrate surface lattice made of adsorption sites **l**, with the value $\mathbf{G}=0$ also included in the summation. After introducing such averages into the EBA expressions for the scattering function (25) the first term on the RHS of Eq. (75) gives rise to a coherent scattering contribution whose presence would reflect the existence of some long range order in the overlayer. This term leads to expression for the coherent elastic scattering component of the EBA scattering function analogous to the one discussed in Sec. IV but now with N_a and $\langle A_a\rangle$ acquiring the meaning defined at the beginning of this section. The second term leads to incoherent or diffuse scattering which according to expression (73) will give rise to a dominant contribution to the elastic component of the scattering function (25) in the low coverage limit $\Theta\ll 1$. Whereas both these terms contribute to elastic scattering component of the scattering function (25), only the $\mathbf{l}'=\mathbf{l}''$ or the diffuse term can contribute to its inelastic component due to the assumed local character of adsorbate modes expressed through commutation relations in Eq. (71).

Since the coherent scattering component of the EBA scattering function can be obtained by a trivial generalization of the formulas derived in the preceding sections by redefining the meanings of N_a and A_a, we shall concentrate in this section only on the incoherent scattering contribution. We first calculate zeroth order term in the expansion of the scattering function (25) which gives a contribution describing diffuse elastic scattering. Using Eq. (71) we find that the Holstein renormalization factor contained in $\mathcal{V}(\pm,z_a)$ is now, strictly speaking, **l**-dependent and reads

$$e^{-w_{\mathrm{loc}}(\mathbf{K}'-\mathbf{K}_{\mathbf{l}},p)}=\exp\left[-\frac{1}{2}\sum_{\sigma}\frac{\hbar|((\mathbf{K}'-\mathbf{K}_{\mathbf{l}}),p)\cdot\mathbf{e}_{\mathbf{l},\sigma}|^2}{2M_a\omega_\sigma}\right.$$
$$\left.\times[2\overline{n}(\omega_\sigma)+1]\right]. \qquad (76)$$

It should also be noted that the derived expressions for the Holstein renormalization factor e^{-w}, Eqs. (37) and (76), are functions of $(\mathbf{K}-\mathbf{K}')$, i.e., they are $\mathbf{K}'$-resolved quantities.

Hence, they will also appear as $\Delta\mathbf{K}$-resolved quantities in the inelastic scattering spectrum calculated in the DWBA, but not in the total DWF.

In order to make the calculations feasible we shall replace the $\mathbf{l}$-dependent exponent on the RHS of Eq. (76) by an ansatz which is obtained by taking a configurational average of the exponent by averaging over all directions of the polarization vectors $\mathbf{e}_{\mathbf{l},\sigma}$ of adsorbate normal vibrations:

$$|((\mathbf{K}'-\mathbf{K_i}),p)\cdot\mathbf{e}_{\mathbf{l},\sigma}|^2 \rightarrow \langle|((\mathbf{K}'-\mathbf{K_i}),p)\cdot\mathbf{e}_{\sigma}|^2\rangle_{\mathrm{conf}}. \quad (77)$$

The use of this ansatz makes expression (76) $\mathbf{l}$-independent and we may write

$$2W^{\mathrm{EBA}}_{\mathrm{diffuse}}(\tau,\mathbf{R}) = \frac{1}{N_a}\sum_{\mathbf{K}',k_z'} e^{i(\mathbf{K}'-\mathbf{K_i})\mathbf{R}}|\mathcal{V}^{k_z',k_{zi}}_{\mathbf{K}',\mathbf{K_i}}(0,z_a)|^2$$

$$= 2W^{\mathrm{EBA}}_{\mathrm{diffuse}}(0,\mathbf{R}). \quad (78)$$

This expression is again independent of N_a because integration over $d^2\mathbf{K}'$ introduces a factor $N_a\langle A_a\rangle$, but since $|\mathcal{V}|^2 \propto \langle A_a\rangle^{-2}$ expression (78) is now proportional to $\langle A_a\rangle^{-1}$ and not to the square of this quantity as in the case of coherent scattering contribution. Hence, the disordering of the adlayer has an effect on the scaling property of the diffuse elastic component of the scattering probability making it proportional to $\langle A_a\rangle^{-1}$.

The next term in the expansion of the scattering function characteristic of vibrating disordered adlayers takes the form

$$2W^{\mathrm{EBA}}_{1\mathrm{loc}}(\tau,\mathbf{R}) = \sum_{\mathbf{K}',k_z'} e^{i(\mathbf{K}'-\mathbf{K_i})\mathbf{R}}\frac{1}{N_a^2}$$

$$\times\sum_{\sigma}\{|\mathcal{F}^{k_z',k_{zi}}_{\mathbf{K}',\mathbf{K_i},\sigma}(+_{\mathrm{loc}},z_a)|^2[\overline{n}(\omega_\sigma)+1]e^{i\omega_\sigma\tau}$$

$$+|\mathcal{F}^{k_z',k_{zi}}_{\mathbf{K}',\mathbf{K_i},\sigma}(-_{\mathrm{loc}},z_a)|^2\overline{n}(\omega_\sigma)e^{-i\omega_\sigma\tau}\}, \quad (79)$$

in which the transition probabilities are given by

$$|\mathcal{F}^{k_z',k_{zi}}_{\mathbf{K}',\mathbf{K_i},\sigma}(\pm_{\mathrm{loc}},z_a)|^2$$

$$= \frac{\hbar}{2M_a\omega_\sigma}\sum_{\mathbf{l}}[(\hat{\mathbf{q}}\cdot\mathbf{e}_{\mathbf{l}\sigma})^*(\mathcal{V}^{k_z',k_{zi}}_{\mathbf{K}',\mathbf{K_i},\sigma}(\pm_{\mathrm{loc}},z_a))^*]$$

$$\times[(\hat{\mathbf{q}}\cdot\mathbf{e}_{\mathbf{l}\sigma})(\mathcal{V}^{k_z',k_{zi}}_{\mathbf{K}',\mathbf{K_i},\sigma}(\pm_{\mathrm{loc}},z_a))]. \quad (80)$$

Here $\mathcal{V}^{k_z',k_{zi}}_{\mathbf{K}',\mathbf{K_i},\sigma}(\pm_{\mathrm{loc}},z_a)$ is given by the on-the-energy-shell expression analogous to that on the RHS of Eq. (43) but without the factor $\delta_{\mathbf{K}'\pm\mathbf{Q}\pm\mathbf{G},\mathbf{K_i}}$, and the vector operator $\hat{\mathbf{q}}$ is defined by

$$\hat{\mathbf{q}} = ((\mathbf{K}'-\mathbf{K_i}),i(\partial/\partial z_a)), \quad (81)$$

and acts on $\mathcal{V}(\pm,z_a)$ whereas the complex conjugate $\hat{\mathbf{q}}^*$ acts on $\mathcal{V}^*(\pm,z_a)$. As the quantity $\mathcal{V}(\pm,z_a)$ in Eq. (80) is now proportional to $\langle A_a\rangle^{-1}$, expression (79) is again independent of N_a because the summations over $\mathbf{K}'$ and $\mathbf{l}$ bring around such a factor. It also scales as $\langle A_a\rangle^{-1}$, analogously to what has been found for expression (41). This means that a transition from incoherent localized to coherent delocalized vibrations, which may occur in an adlayer with the increase of coverage, does not introduce any changes in the scaling of inelastic scattering intensities with Θ (or $\langle A_a\rangle$) which would facilitate easy experimental resolution between the two types of vibrations.

The above assumption of configurational averaging and the therefrom obtained $\mathbf{l}$-independent Holstein factor (76) enable us to take such an average in the expression on the RHS of Eq. (80). This amounts to the replacement

$$\sum_{\mathbf{l}}(\hat{\mathbf{q}}\cdot\mathbf{e}_{\mathbf{l}\sigma})^*(\hat{\mathbf{q}}\cdot\mathbf{e}_{\mathbf{l}\sigma}) \rightarrow N_a\langle(\hat{\mathbf{q}}\cdot\mathbf{e}_\sigma)^*(\hat{\mathbf{q}}\cdot\mathbf{e}_\sigma)\rangle_{\mathrm{conf}}. \quad (82)$$

and such a procedure can be easily carried out in some special cases which are nevertheless of physical relevance. For instance, if the projectile coupling to perpendicular adsorbate vibrations is much stronger than to the lateral vibrations the effect of the latter may be neglected, whence

$$|\mathcal{F}^{k_z',k_{zi}}_{\mathbf{K}',\mathbf{K_i},\perp}(\pm_{\mathrm{loc}},z_a)|^2 = \frac{\hbar N_a}{2M_a\omega_\perp}\left|\frac{\partial}{\partial z_a}\mathcal{V}^{k_z',k_{zi}}_{\mathbf{K}',\mathbf{K_i},\perp}(\pm,z_a)\right|^2, \quad (83)$$

and the Holstein renormalization factor contained in the matrix elements $\mathcal{V}$ is given by

$$e^{-w_{\mathrm{loc}\perp}(\mathbf{K}'-\mathbf{K_i},p)} = \exp\left[-\left(\frac{1}{2}\right)\frac{\hbar p^2}{2M_a\omega_\perp}[2\overline{n}(\omega_\perp)+1]\right]. \quad (84)$$

Such a situation can be typical of noble gas adlayers at low coverage. On the other hand, if the adsorbate vibrations with polarization perpendicular to the surface exhibit much larger frequencies than the ones with lateral polarization, the projectile coupling to perpendicular vibrations may be neglected relative to the lateral ones. In this case

$$|\mathcal{F}^{k_z',k_{zi}}_{\mathbf{K}',\mathbf{K_i},\sigma\|}(\pm_{\mathrm{loc}},z_a)|^2 = \frac{\hbar(\mathbf{K}'-\mathbf{K_i})^2N_a}{4M_a\omega_{\sigma\|}}|\mathcal{V}^{k_z',k_{zi}}_{\mathbf{K}',\mathbf{K_i},\sigma\|}(\pm,z_a)|^2, \quad (85)$$

and the corresponding Holstein renormalization factor is given by

$$e^{-w_{\mathrm{loc}\|}(\mathbf{K}'-\mathbf{K_i},p)} = \exp\left[-\left(\frac{1}{2}\right)\sum_{\sigma\|}\frac{\hbar(\mathbf{K}'-\mathbf{K_i})^2}{4M_a\omega_{\sigma\|}}\right.$$

$$\left.\times[2\overline{n}(\omega_{\sigma\|})+1]\right]. \quad (86)$$

Expressions (85) and (86) are well suited for the description of excitation of the modes describing frustrated translations of Na atoms and CO molecules chemisorbed on metal surfaces.[42,43,45]

The incoherent vibration induced DWF is simply obtained by setting $\tau=0$ and $\mathbf{R}=0$ in Eq. (79). As for disordered adlayers both the elastic incoherent and inelastic terms in the scattering function describe diffuse scattering the magnitude of the corresponding total DWF calculated in the EBA will decrease exponentially with $\langle A_a\rangle^{-1}$, i.e., with the coverage.

In a similar fashion we obtain the expression for the mean energy transfer to localized vibrations:

$$\mu_{1\mathrm{loc}}^{\mathrm{EBA}}(T_s)=\frac{1}{N_a}\sum_{\mathbf{K}'}\sum_{k_z',\sigma}\hbar\omega_\sigma\{|\mathcal{F}_{\mathbf{K}',\mathbf{K_i},\sigma}^{k_z',k_{zi}}(+_{\mathrm{loc}},z_a)|^2 + [|\mathcal{F}_{\mathbf{K}',\mathbf{K_i},\sigma}^{k_z',k_{zi}}(+_{\mathrm{loc}},z_a)|^2 - |\mathcal{F}_{\mathbf{K}',\mathbf{K_i},\sigma}^{k_z',k_{zi}}(-_{\mathrm{loc}},z_a)|^2]\overline{n(\omega_\sigma)}\}. \tag{87}$$

As regards the DWBA limit of the inelastic scattering spectrum, we find for disordered overlayers and localized vibrations

$$N_{1\mathrm{loc}}^{\mathrm{DWBA}}(\Delta E,\Delta\mathbf{K})=\frac{\langle A_a\rangle}{(2\pi\hbar)^2 N_a}\sum_{k_z',\sigma}\times\{|\mathcal{F}_{\mathbf{K_i}+\mathbf{\Delta K},\mathbf{K_i},\sigma}^{k_z',k_{zi}}(+_{\mathrm{loc}},z_a)|^2 \times[\overline{n(\omega_\sigma)}+1]\delta(\Delta E+\hbar\omega_\sigma) + |\mathcal{F}_{\mathbf{K_i}+\mathbf{\Delta K},\mathbf{K_i},\sigma}^{k_z',k_{zi}}(-_{\mathrm{loc}},z_a)|^2\overline{n(\omega_\sigma)} \times\delta(\Delta E-\hbar\omega_\sigma)\}. \tag{88}$$

Finally, the scattering spectrum in the extreme multiphonon limit acquires the form identical to Eq. (55) with the first moment given by Eq. (87) and a set of σ_λ's which are derived in a fashion analogous to the one employed in obtaining the quantities typical of localized vibrations.

VII. APPLICATIONS OF THE DEVELOPED FORMALISM TO He ATOM SCATTERING FROM ADLAYERS

The formalism developed in the preceding sections should be best suited for applications to HAS from ordered or disordered adlayers in which the static projectile-surface interaction originates dominantly from a flat projectile-substrate potential defining the distorted waves, Eq. (2), and describing specular reflections. The distorted waves are then perturbed by the projectile coupling to adsorbates sticking out from the substrate surface which gives rise to combined diffractive or diffuse elastic and inelastic atom-surface scattering. This model can be applied to adlayer structures which are disordered and free from islands in the low coverage limit,[62] or ordered superstructures with interadsorbate distances large enough to cause that the dominant part of the incoming beam flux is scattered by the substrate surface. In all cases the adlayers should sustain either localized or delocalized low energy modes which could be efficiently excited in HAS experiments. As typical examples of the first class of systems one may consider noble gas and alkali atoms[42,43] or CO molecules[44] adsorbed on metals at low coverage and for low enough substrate temperatures to preclude any appreciable diffusion leading to island formation. A typical example of the second class of systems are the $(\sqrt{3}\times\sqrt{3})R30°$ adlayers of CO adsorbed on (111) surfaces of Rh[41] and Pt[45] in which the interadsorbate spacing is still much larger than the effective adsorbate radius. Close packed monolayers of heavier noble gas atoms (e.g., Xe) on metals would not fall into this category because they themselves represent a relatively flat reflecting surface, as evidenced by He diffraction measurements.[20,21,40] Hence inelastic HAS from such adlayers should be treated using the approach developed earlier.[20,21,32,40] The same may also apply to more densely packed ordered overlayers of CO molecules on Rh(111) and Pt(111) (see also below).

The importance of the effects which the present model predicts for HAS from adlayers can be illustrated by making a simple quantitative estimate of the Holstein renormalization of the interaction matrix elements (which are renormalized by the factor e^{-W}) or the one-phonon scattering probabilities (which are renormalized by the factor e^{-2W}) since they represent a prerequisite for calculating the scattering spectra and the complete DWF. The exhaustive calculations of the latter quantities will be left for a future publication.

We first consider Xe and Na atoms and CO molecules adsorbed at very low coverage on metal surfaces. These adsorbates act as isolated scattering centers for He beams. Xe atoms adsorbed on Cu(111) and Cu(001) exhibit a low energy mode ($\hbar\omega_S\sim 2.6$ meV) with the polarization vector perpendicular to the surface,[20] for isolated Xe atoms on Pt(111) one finds $\hbar\omega_S\sim 3.5$ meV,[46] whereas isolated Na atoms on Cu(001)[42,43] and CO molecules on Cu(001)[44] exhibit frustrated translation modes parallel to the surface with energies $\hbar\omega_{\mathrm{FT}}=5.6$ meV and $\hbar\omega_{\mathrm{FT}}=3.94$ meV, respectively.

In the case of disordered Xe submonolayers we employ Eq. (84) and observe that according to Eq. (9) the maximum contribution to Holstein renormalization comes from the values of p for which $p^2\simeq\beta^2+(\mathbf{K}'-\mathbf{K}'')^2$ where β is the effective range of the repulsive Xe-He pair interaction[75] and $(\mathbf{K}'-\mathbf{K}'')$ is the change of the projectile lateral momentum in a real one-phonon exchange process. From this we can estimate the magnitude of the Holstein renormalization factor in the scattering probabilities (the quantities $|\mathcal{V}|^2$ and $|\mathcal{F}|^2$ derived in Secs. IV and VI), for transitions in which the lateral momentum of magnitude $|\mathbf{K}'-\mathbf{K}''|$ has been exchanged in an interaction vertex. This is plotted in Fig. 1 as a function of $|\mathbf{K}'-\mathbf{K}''|$ and the surface temperature T_s. The plot shows that in the range of typical experimental parameters the reduction of the one-phonon scattering probabilities may be as large as $\sim$20%. This in turn means that higher multiquantum scattering intensities will be accordingly reduced, orientationally by a factor $(0.8)^n$ where n is the number of real phonons exchanged. Hence, the effect should most strongly manifest itself in the multiphonon scattering regime which has so far been routinely achieved in HAS from Xe overlayers.[20,46]

In the case of isolated Na and CO adsorbates on Cu(001), which exhibit low energy vibrations parallel to the surface[42–44] (degenerate frustrated translation modes), the Holstein effect is estimated by employing Eq. (86). Here we find that in a typical range of experimental parameters the reduction of the one-phonon scattering probability may be even more significant, mainly due to the larger intervals of experimentally accessible temperatures which are not limited by low adlayer desorption temperatures (see Figs. 2 and 3). This can strongly affect the intensities of higher multiquantum peaks and hence the present formalism should be employed in the studies of these systems as well.

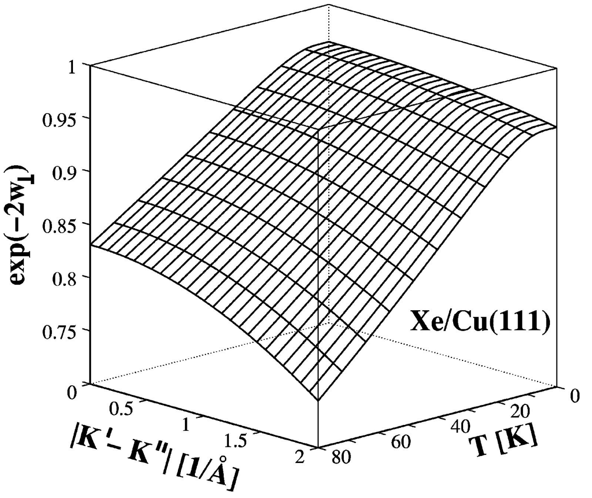

FIG. 1. Holstein renormalization factor $\exp(-2w_{\perp})$ of the one-phonon scattering probability pertinent to He atom scattering from isolated Xe atoms adsorbed on the Cu(111) surface plotted as a function of the lateral momentum exchange $|\mathbf{K}'-\mathbf{K}''|$ and substrate temperature T_s in the experimentally relevant intervals.

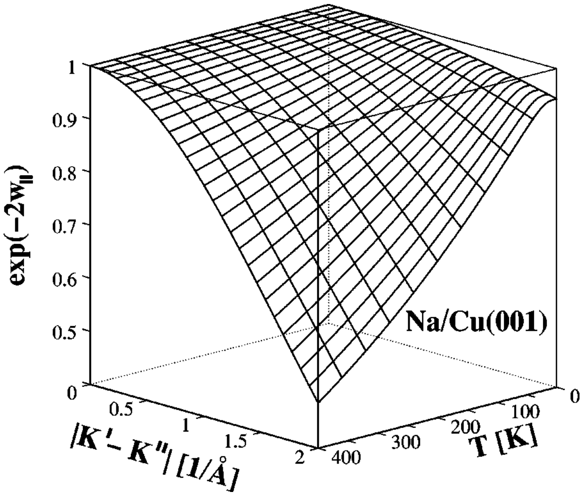

FIG. 3. Holstein renormalization factor $\exp(-2w_{\parallel})$ of the one-phonon scattering probability pertinent to He atom scattering from isolated Na atoms adsorbed on the Cu(001) surface plotted as a function of the lateral momentum exchange $|\mathbf{K}'-\mathbf{K}''|$ and substrate temperature T_s in the experimentally relevant intervals.

The final example pertains to HAS from ordered adlayers, i.e., the $(\sqrt{3}\times\sqrt{3})R30°$ superstructure of CO on Rh(111)[76] at the coverage $\Theta=\frac{1}{3}$. These adlayers exhibit dispersionless frustrated translation modes with $\hbar\omega_{\mathrm{FT}_x}=\hbar\omega_{\mathrm{FT}_y}=5.75$ meV which can be multiply excited in HAS.[41] Here the interadsorbate distances in the CO adlayer are large (~ 4.64 Å) relative to the distance of the closest approach of He atoms to an adsorbed CO molecule[77] (~ 2.12 Å), and hence the present formalism should be applicable. To estimate the Holstein effect in this case we apply Eqs. (37) and (86) with $\mathrm{e}_{\perp}(\mathbf{Q},j)=0$. Note that to obtain expression (86) the $\mathbf{Q}'$-summation was carried out over the virtual phonon modes, and not the ones giving rise to the change $(\mathbf{K}'-\mathbf{K}'')$ of the lateral momentum of the projectile. The Holstein reduction of the one-phonon exchange probabilities is illustrated in Fig. 4 and in the range of experimental parameters it reaches $\sim 20\%$. Hence, the present model should be also well suited for the studies of multiquantum excitations in HAS from $(\sqrt{3}\times\sqrt{3})R30°$ layers of CO on Rh(111) and, by analogy, also on the Pt(111) surface. On the other hand, in the case of a denser (2×2) CO superstructure on the same substrate[76] $(\Theta=\frac{3}{4})$, the interadsorbate distances are smaller and presumably this adlayer itself acts as a corrugated reflecting surface which defines the boundary conditions for distorted He atom wave functions. In this situation a different approach to obtain the wave functions describing diffractive scattering should be applied.[9,78]

Let us finally note that since the exponents in the expressions for the Holstein renormalization factor, Eqs. (37) and (76), are inversely proportional to the mode frequency, the

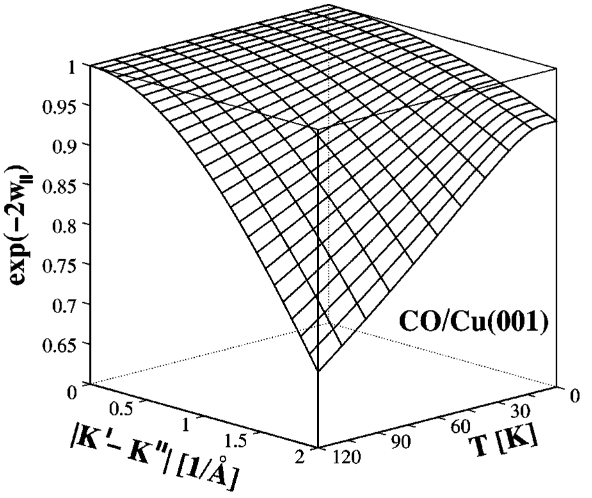

FIG. 2. Holstein renormalization factor $\exp(-2w_{\parallel})$ of the one-phonon scattering probability pertinent to He atom scattering from the isolated CO molecule adsorbed on the Cu(001) surface plotted as a function of the lateral momentum exchange $|\mathbf{K}'-\mathbf{K}''|$ and substrate temperature T_s in the experimentally relevant intervals.

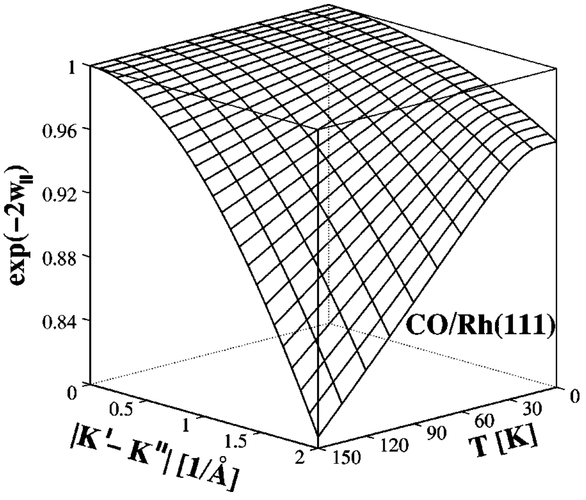

FIG. 4. Holstein renormalization factor $\exp(-2w_{\parallel})$ of the one-phonon scattering probability pertinent to He atom scattering from ordered $(\sqrt{3}\times\sqrt{3})R30°$ submonolayer of CO on the Rh(111) surface plotted as a function of the lateral momentum exchange $|\mathbf{K}'-\mathbf{K}''|$ and substrate temperature T_s in the experimentally relevant intervals.

largest reduction effect is expected for low energy modes. The existence of the mode degeneracy or of several low energy modes (including also the modes that cannot be singly excited in the first SBZ for the sagittal plane scattering geometry (e.g., shear horizontal modes) reduces the magnitude of the Holstein renormalization factor. Thus the role of the Holstein effect in HAS from adlayers sustaining more than one low energy mode is more pronounced. However, it should be pointed out that despite the Holstein reduction of the interaction matrix elements, the latter would still be generally larger for isolated adsorbates (e.g., Xe atoms) than for dense adlayers made of the same atoms. This is so because isolated adsorbates are embedded into the He atom distorted wave functions which makes their overlap with the projectile-adatom pair potential large. On the other hand, if a dense adlayer itself acts as the reflecting surface for He atom wave functions, their overlap with each adatom is significantly smaller, producing correspondingly smaller interaction matrix elements.

In conclusion, we have demonstrated that the theory developed in this work, which takes into account the interplay between diffraction or diffuse scattering and virtual and real phonon exchange processes, should prove indispensable in providing a full quantum mechanical description of multiple He atom scattering from the low energy modes characteristic of adlayers of submonolayer coverage on flat metal surfaces.

ACKNOWLEDGMENTS

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APPENDIX A: LAPLACE TRANSFORM OF PAIR POTENTIALS AND GENERALIZED OSCILLATOR STRENGTHS

In the case in which the z-coordinate of the centers of adsorbates lie closer to the surface than the classical turning points z_t of the projectile motion, i.e., $z_a < z_t$, the Laplace transform (LT) may prove more convenient in representing the pair potentials:

$$v(\boldsymbol{\rho},z)=\int \frac{d^2\mathbf{Q}}{(2\pi)^2} e^{i\mathbf{Q}\boldsymbol{\rho}} \int_0^\infty dp e^{-pz} v_L(\mathbf{Q},p). \tag{A1}$$

Using this representation the matrix elements of the projectile-adlayer interaction can be written in the form

$$\begin{aligned}\langle \mathbf{K}',k_{z'}|V(\mathbf{r})|\mathbf{K},k_z\rangle &= \frac{1}{L_z L_s^2} \sum_{\mathbf{l}} e^{-i(\mathbf{K}'-\mathbf{K})(\boldsymbol{\rho}_{\mathbf{l}}+\mathbf{u}_{\mathbf{l}\|})} \int_0^\infty dp e^{p(z_{\mathbf{l}}+\mathrm{u}_{\mathbf{l}\perp})} \\ &\quad \times v_L(\mathbf{K}'-\mathbf{K},p) f_L(k_z',k_z,p),\end{aligned} \tag{A2}$$

where the generalized LT generated oscillator strength is now defined by

$$f_L(k_z',k_z,p)=\int_{-\infty}^{\infty} e^{-pz} \chi_{k_z'}^*(z) \chi_{k_z}(z) dz. \tag{A3}$$

Thermal averaging then gives

$$\begin{aligned}\langle \mathbf{K}',k_{z'}|\langle\langle V(\mathbf{r})\rangle\rangle|\mathbf{K},k_z\rangle &= \frac{1}{L_z}\int_0^\infty dp e^{-w_L(\mathbf{K}'-\mathbf{K},p)} \\ &\quad \times v_L(\mathbf{K}'-\mathbf{K},p) f_L(k_z',k_z,p) \\ &\quad \times \frac{1}{L_s^2} \sum_{\mathbf{l}} e^{-i(\mathbf{K}'-\mathbf{K})\boldsymbol{\rho}_{\mathbf{l}}} e^{pz_{\mathbf{l}}}.\end{aligned} \tag{A4}$$

where the Holstein renormalization factor is now complex:

$$e^{-w_L(\mathbf{K}'-\mathbf{K},p)}=\exp\left[-\frac{1}{2}\langle\langle[(\mathbf{K}'-\mathbf{K})\mathbf{u}_{\mathbf{l}\|}+ip\mathrm{u}_{\mathbf{l}\perp}]^2\rangle\rangle\right], \tag{A5}$$

and the structure factor on the RHS of Eq. (A2) is correspondingly modified.

To understand expression (A4) for $z_{\mathbf{l}} \leqslant z_t$ we observe that here the perpendicular zero point vibrations of adsorbates, which take place in the steeply growing part of the distorted waves, bring the scattering centers closer to the projectile during the halfperiod of vibration. This, on the average, may give rise to an enhancement of the scattering probabilities derived with the interaction matrix elements renormalized through expression (A5).

Analogously, in the case in which Eq. (A2) is employed, the corresponding scattering function takes the form

$$\begin{aligned}2W_L^{\mathrm{EBA}}(\tau,\mathbf{R}) &= \sum_{\mathbf{K}',k_z'} e^{-i[(E_{\mathbf{k}'}-E_{\mathbf{k_i}})\tau-(\mathbf{K}'-\mathbf{K_i})\mathbf{R}]} \frac{1}{(L_z L_s^2)^2} \sum_{\mathbf{l}',\mathbf{l}''} e^{i(\mathbf{K}'-\mathbf{K_i})(\boldsymbol{\rho}_{\mathbf{l}'}-\boldsymbol{\rho}_{\mathbf{l}''})} \int_{-\infty}^{\infty} dp' e^{p' z_{\mathbf{l}'}} e^{-w_L^*(\mathbf{K}'-\mathbf{K_i},p')} \\ &\quad \times v_L^*(\mathbf{K}'-\mathbf{K_i},p') f_L^*(k_z',k_z,p') \int_{-\infty}^{\infty} dp'' e^{p'' z_{\mathbf{l}''}} e^{-w_L(\mathbf{K}'-\mathbf{K_i},p'')} v_L(\mathbf{K}'-\mathbf{K_i},p'') f_L(k_z',k_z,p'') \\ &\quad \times \frac{1}{\hbar^2} \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} dt'' e^{-i(E_{\mathbf{k}'}-E_{\mathbf{k_i}})(t'-t'')/\hbar} \\ &\quad \times \exp\langle\langle[(\mathbf{K}'-\mathbf{K_i})\mathbf{u}_{\mathbf{l}'\|}(t')-ip'\mathrm{u}_{\mathbf{l}'\perp}(t')][(\mathbf{K}'-\mathbf{K_i})\mathbf{u}_{\mathbf{l}''\|}(t'')+ip''\mathrm{u}_{\mathbf{l}''\perp}(t'')]\rangle\rangle.\end{aligned} \tag{A6}$$

The scattering amplitudes $\mathcal{F}(\pm, z_a)$ and other relevant quantities deriving thereof are obtained following the procedures employed in Sec. III with the Holstein-renormalized pair interaction matrix elements:

$$\tilde{v}_L(\mathbf{K}' - \mathbf{K_i}, p) = e^{-w_L(\mathbf{K}' - \mathbf{K_i}, p)} v_L(\mathbf{K}' - \mathbf{K_i}, p). \tag{A7}$$

APPENDIX B: CUMULANT EXPANSION OF THE SCATTERING SPECTRUM

According to a general theorem[79] the evolution operator of a quantum system can be expressed in the interaction representation in exponential form:

$$U_I(t,t_0) = e^{-iG(t,t_0)} = \exp\left[-i \sum_{n=1}^{\infty} G_n(t,t_0) \right], \tag{B1}$$

where $G(t,t_0)$ is a Hermitian operator which has a nested commutator expansion in powers of the coupling constant g:

$$G_1(t,t_0) = \frac{g}{\hbar} \int_{t_0}^{t} dt_1 V_I(t_1), \tag{B2}$$

$$G_2(t,t_0) = -\frac{i(g/\hbar)^2}{2} \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 [V_I(t_1), V_I(t_2)], \tag{B3}$$

$$\begin{aligned} G_3(t,t_0) = {} & \frac{(g/\hbar)^3}{4} \int_{t_0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \int_{t_0}^{t_2} dt_3 \\ & \times [V_I(t_1), [V_I(t_2), V_I(t_3)]] \\ & + \frac{(g/\hbar)^3}{12} \int_{t0}^{t} dt_1 \int_{t_0}^{t_1} dt_2 \int_{t_0}^{t_1} dt_3 \\ & \times [[V_I(t_1), V_I(t_2)], V_I(t_3)], \end{aligned} \tag{B4}$$

etc., where all other higher order terms in the coupling constant comprise higher order commutators $[.,[..,[\,....,.]]]$ of the particle-boson interaction operators:

$$V_I(t_j) = e^{(i/\hbar)H_0 t_j} V e^{-(i/\hbar)H_0 t_j}. \tag{B5}$$

Thus, according to Eqs. (17) and (B1) the S-matrix in the interaction picture can be written in a general form $S_I = e^{-iG}$ and the various canonically transformed operators in Eq. (16) can be calculated using the identity

$$S_I^\dagger A S_I = e^{iG} A e^{-iG} = \sum_{m=0}^{\infty} \frac{i^m}{m!} G^m[A], \tag{B6}$$

where $G^m[A]$ denotes mth order repeated commutator of G with an arbitrary operator A. This generates the terms in the exponent on the RHS of Eq. (16) which are expressed through the operators $(\mathcal{W}_H, \mathcal{W}_x, \mathcal{W}_y) = (\mathcal{W}_H, \boldsymbol{\mathcal{W}})$ defined by Eqs. (18)–(20).

Now, by writing the last line on the RHS of Eq. (16) in the form

$$\begin{aligned} N(\tau,\mathbf{R}) = {} & \langle i | \exp[-(i/\hbar)(H_0^{\mathrm{part}}\tau - \hat{\mathbf{P}}\mathbf{R})\lambda \\ & - (i/\hbar)(\mathcal{W}_H \tau - \boldsymbol{\mathcal{W}}\mathbf{R})\lambda] | i \rangle_{\lambda=1}, \end{aligned} \tag{B7}$$

where the parameter λ has been introduced for mathematical convenience, we can calculate $N(\tau,\mathbf{R})$ on noticing that the operator on the RHS of Eq. (B7) has the appearance of an evolution operator in which $(H_0^{\mathrm{part}}\tau - \hat{\mathbf{P}}\mathbf{R})$ is diagonal on $|i\rangle$. Hence, we can write in the interaction representation of the λ-space

$$\begin{aligned} N(\tau,\mathbf{R}) = {} & e^{-(i/\hbar)(E_i \tau - \hbar \mathbf{K_i} R)\lambda} \\ & \times \langle i | T_\lambda \exp\left[-(i/\hbar) \int_0^{\lambda} d\lambda' \mathcal{W}_I(\lambda') \right] | i \rangle_{\lambda=1}, \end{aligned} \tag{B8}$$

where

$$\begin{aligned} \mathcal{W}_I(\lambda') = {} & e^{(i/\hbar)(H_0^{\mathrm{part}}\tau - \hat{\mathbf{P}}\mathbf{R})\lambda'} [\mathcal{W}_H \tau \\ & - \boldsymbol{\mathcal{W}}\mathbf{R}] e^{-(i/\hbar)(H_0^{\mathrm{part}}\tau - \hat{\mathbf{P}}\mathbf{R})\lambda'}, \end{aligned} \tag{B9}$$

and T_λ is the ordering operator in the λ-space. Here it should be observed that the action of the transformation (B9) on all bilinear products of particle operators $c^\dagger_{\mathbf{K}',k_z'} c_{\mathbf{K},k_z}$ appearing in $[\mathcal{W}^H \tau - \boldsymbol{\mathcal{W}}\mathbf{R}]$ leads to expressions of the type

$$c^\dagger_{\mathbf{K}',k_z'} c_{\mathbf{K},k_z} e^{-(i/\hbar)[(E_{\mathbf{k}} - E_{\mathbf{k}'})\tau - \hbar(\mathbf{K} - \mathbf{K}')\mathbf{R}]\lambda'}. \tag{B10}$$

Now, applying the cumulant expansion to calculate the average on the RHS of Eq. (B8) and taking the Fourier transforms we find

$$\begin{aligned} N_{\mathbf{k_i}}(\Delta E, \Delta \mathbf{K}) = {} & \int_{-\infty}^{\infty} \frac{d\tau}{2\pi\hbar} \int \frac{d^2\mathbf{R}}{(2\pi\hbar)^2} e^{(i/\hbar)[(\Delta E)\tau - \hbar(\Delta \mathbf{K})\mathbf{R}]} \\ & \times \exp\left[\sum_{n=1}^{\infty} C_n(\tau,\mathbf{R}) \right], \end{aligned} \tag{B11}$$

with

$$\begin{aligned} C_n(\tau,\mathbf{R}) = {} & (-i/\hbar)^n \int_0^{\lambda=1} d\lambda_1 \ldots \\ & \times \int_0^{\lambda_{n-1}} d\lambda_n \langle i | \mathcal{W}_I(\lambda_1) \ldots \mathcal{W}_I(\lambda_n) | i \rangle_c, \end{aligned} \tag{B12}$$

in which the λ_j-dependence of bilinear products of particle operators in $\mathcal{W}_I(\lambda_j)$ is given by expression (B10) and the subscript c denotes the cumulant average.[80]

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