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Theory of vibrational, rotational, and phonon inelastic collisions of a triatomic molecule by a crystal surface. I. A quantum-mechanical treatment of the scattering dynamics

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Based on time-independent scattering theory, we present a systematic formulation of triatomic-molecule–crystalline-surface scattering dynamics including the vibrational states of the solid (phonons) and the vibrational and rotational states of the molecular projectile. The vibrational and rotational motions of the triatomic molecule are treated by separating out the motion of the center of mass of the molecule in a manner that is suitable for treating the surface collisions with a molecular projectile. This method can be essentially applied to a general polyatomic projectile case. From the translational invariance of the full Hamiltonian, we employ the total (projectile+phonon) momentum representation parallel to the surface to derive the properties of the total scattering wave function of the triatomic-molecule–crystalline-surface system, a representation of the simultaneous phonon and vibrational-rotational transition potential matrix, and the characteristics of the independent physical solutions for a given energy and momentum of the system. The scattering equation in differential and integral forms as well as the related Green functions are also obtained. In particular, the explicit configurational expression of the Green function of the molecule-surface system presented here, including phonons and vibrations and rotations, is quite different from those of conventional scattering theory where the collision partners are spatially localized. Several important versions of the integral expressions of the scattering and transition matrices that are useful for introducing approximation schemes are also presented. The time-reversal invariance and microscopic reversibility of the triatom-surface scattering are discussed. The equations relating the incoming and outgoing scattering wave functions, which are satisfied in the present molecule-surface system and are important in the transition-matrix scheme, are also obtained. Further, the relation between the scattering matrix elements that describes the microscopic reversibility in the present scattering system is presented. Since phonon annihilation and creation are mutually time-reversed phenomena, this relation of microscopic reversibility can be tested by experiment. From the present formulation, some specific theoretical schemes for simultaneous diffraction and phonon or vibrational-rotational transitions, a bound-state resonance inelastic-scattering method for phonon-mediated and rotation-mediated selective adsorption and desorption, and a method of obtaining quantal physisorption probabilities are derived in the following paper. These results are suitable for the triatomic-molecular-projectile case—quite realistic compared to what has been employed so far, and at the same time capable of yielding effective *ab initio* calculations.

I. INTRODUCTION

Collision between gas-phase atoms or molecules and surfaces in the thermal-energy range is important in understanding the nature of the energy transfer between the gas and surface. The energy-transfer processes include the transfer of translational or internal energy of the projectile to the surface phonons, accommodation of these energies, and transfer of the energy from one site on the surface to the other sites. A complete knowledge of these processes is essential in the reactions taking place near or on the surface and in the heterogeneous catalysis.[1–6]

Study of the scattering of atoms and molecules by a surface is also useful in determining the characteristics of the adiabatic gas-phase–surface interaction potential for a clean or adsorbate-covered crystalline surface including alkali halides, metals, and semiconductors. The information of the (gas-phase–surface) potential is necessary in the adsorption-desorption calculations. *Ab initio* calculations of gas-phase–surface potentials that take into account the surface ionic or atomic motion are extremely difficult and almost nonexistent. Even the computation of the gas-phase–rigid-surface potential which is not sufficient for the above practical application is a very complex task. Therefore, the determination of the potentials eventually depends on the theoretical results of the scattering dynamics. Employing collision dynamics, one can compute the elastic and inelastic scattering intensities from a certain set of possible potentials and the results are compared with experiments. A potential which yields the best agreement with measurements of the intensities can then be selected. Therefore, it is highly desirable to develop accurate collision dynamics.

There has been considerable theoretical activity with respect to the study of gas-surface collisions, such as the quasiclassical[7,8] and classical trajectory approaches,[9–12] the stochastic trajectory method with the generalized Langevin equation,[13–16] the quantum-mechanical

Cabrera-Celli-Goodman-Manson (CCGM) theory for elastic diffractive scattering,[17,18] the semiclassical S-matrix method,[19,20] the diffractional sudden-approximation method,[21] the diffractive eikonal approximation,[22-25] the wave-packet calculation,[26] the bound-state resonance (selective adsorption) for elastic diffraction,[27,28] the inclusion of the Debye-Waller-type factor in the elastic scattering probability to take into account the inelastic effect,[29] the local optical potential model,[30] the nonlocal energy-dependent self-energy scheme,[31] and quantum-mechanical close-coupling calculations for the selective-adsorption study of elastic diffraction,[32-35] etc.

Experimental measurements have been made of phonon inelastic scattering for a variety of atom or molecule-surface systems with improved time-of-flight techniques and resonances.[1,2,4,6,36-41] The quantum-mechanical phonon inelastic calculations have been carried out employing distorted-wave Born approximation (DWBA),[41-46] semiclassical schemes,[47] the impulsive-collision or sudden-approximation method,[48,49] the optical model,[50] higher-order phonon processes with a "golden rule" approach,[51] improved DWBA with the inclusion of corrugation,[52] and the unitary one-phonon approximation.[53] Inclusion of the phonon degrees of freedom in the gas-phase–surface collision is important as manifested in the temperature effects of diffractive and inelastic scattering intensities.

The bound-state-resonance method derived from the elastic-diffractive-resonance method[27] and based on the eikonal approximation with hard corrugated walls has been theoretically studied for inelastic scattering as well.[54] Extension of the quantum-mechanical close-coupling calculations, which is in principle the most realistic theoretical approach, to the cases where the phonon degrees of freedom are included is very difficult due to the extremely large number of phonons states involved. An attempt to carry out the close-coupling calculations in the phonon inelastic scattering employing a discretization method was only partly successful.[55] The close-coupling approach is not useful for the practical computations in phonon transition diffractive scattering, but it serves as a starting point to develop further a scattering formulation and to introduce approximations. It should be pointed out that there are some general formulations of gas-surface scattering,[44,56] but they are again based on a simple model Hamiltonian or interaction potential.

All of the theoretical works previously mentioned are concerned with collisions between atoms or diatomic molecules and a surface. Interactions of the polyatomic molecules, in particular, triatomic molecules with surfaces, are of much importance since the dynamics and mechanisms of the triatomic molecular collision and reaction processes with surfaces have many practical applications. Among all the processes, inelastic triatomic-molecule–surface scattering is the simplest one. This process involves the energy transfer among translational, vibrational, rotational, and phonon degrees of freedom and provides essential knowledge for understanding catalysis and complex reactions on the surface. Further, the rotational degrees of freedom are found to affect the physisorption. Experimental measurements on the angular distribution of triatomic molecules such as CO_2, N_2O, NO_2 scattered from clean or adsorbate-covered surfaces were performed for the purpose of studying energy transfer between surface vibrations (surface phonons) and the rotation of the projectile.[57] Laser-detection techniques or time-of-flight methods were used to determine the final-state distribution of the molecules scattered from the surface.

Theoretical studies on the triatomic-molecule–surface collisions are mainly confined to the semiclassical trajectory calculations. There exists an effective-mass theory[58] on the polyatom-surface scattering where the inelastic scattering problem is treated within the first order in the distorted-wave expansion. The first-order distorted-wave method can yield reasonably good results for one-phonon processes but it is not suitable for interpreting the experimental measurements on, for example, selective adsorption (resonance) or multiphonon transitions. Moreover, most of the theoretical work on atom or molecule-surface collisions previously mentioned are based on time-dependent scattering theory. It is necessary to develop a realistic quantum-mechanical formulation of the triatomic-molecule–nonrigid-surface collision dynamics and an *ab initio* theoretical scheme that can be adopted to a flexible input potential based on the time-independent scattering theory. This would enable us to assess the precise nature of the triatomic-molecule–surface interaction potential and interpret the experimental measurements on resonances, etc. Such a formulation exists for the simple case of atom-surface collision. However, its applicabilities are limited because the atomic projectile was employed in the formulation. It is desirable to extend the formulation to the triatomic-molecule–surface-collision case. We find that the task is not straightforward.

In the present work, we extend our previous work[59] for the atom-surface scattering to develop a systematic quantum-mechanical formulation of the triatomic-molecule–crystal-surface scattering dynamics that takes into account the internal degrees of freedom of the projectile (vibration and rotation), diffraction, phonons, and the resonances. Our work uses time-dependent scattering theory in contrast to most of the theoretical works previously mentioned where time-dependent theory was employed for the atom or diatom–surface system. The total (projectile+phonon) momentum representation parallel to the surface obtained from the translational symmetry is employed in our formulation, analogous to the total angular momentum representation obtained from the rotational symmetry used in gas-phase scattering.[60] The vibrational and rotational motions of the molecule are properly treated for the collision dynamics with the center-of-mass motion separated out. This method can be basically applied to the general polyatomic projectile case. The formulation turns out to be somewhat different from the cases such as, e.g., atom or molecule–molecule system, where collision partners are spatially localized. From the formulation, specific theoretical schemes suitable for the triatomic molecular projectile are also derived. They are more realistic, systematic and at the same time amenable to *ab initio* computation compared to some theoretical schemes employed so far. The present formulation and theoretical schemes can be applied to both clean and adsorbate-covered crystalline surfaces as long as the adsorbates form ordered overlayers such that two-dimensional periodicity of the crystal surface exists. In practice, there are no perfect two-dimensional translational symmetries, but small deviation from the symmetry can always be treated as a perturbation from the present case.

In the next section, we first derive the properties of the total scattering wave function of the triatomic-molecule–crystal-surface system with the internal (vibration and rotation) degrees of freedom of the projectile and phonons in the solid. Then we present a representation of the phonon and internal-state transition potential with translational symmetry, the coupled differential equations, and independent physical solutions for given energy and momentum. Triatomic vibrational-rotational wave functions appropriate for the collisions and the (triatomic) molecule-surface interaction potential matrix are discussed in Sec. III. Various versions of the integral equations, explicit expressions of Green functions of the molecule-surface system with phonons and vibrations and rotations, and corresponding integral representation of the scattering and transition matrices are presented in Sec. IV. These are necessary for obtaining approximate, realistic computational schemes for higher-order DWBA, multiphonon processes, and a coupled-channel transition-matrix method (see the following paper). In Sec. V, the time-reversal invariance and microscopic reversibility in the triatomic-molecule–crystal-surface system are discussed. A summary is provided in the last section. As applications of the present formulation, we will present in the following paper specific theoretical schemes for simultaneous phonon and vibrational-rotational transitions suitable for the (triatomic) molecular projectile, the bound-state resonance scattering approach for phonon- and rotation-mediated selective adsorption and desorption, and a method of obtaining quantum-mechanical physisorption probabilities.

II. INELASTIC-SCATTERING DYNAMICS OF A TRIATOMIC-MOLECULE–SURFACE SYSTEM

We first briefly review some attributes of the phonons in the presence of a crystal surface for the purpose of explaining the relevant notations adopted in the present work for the triatomic-molecule–nonrigid-crystal-surface scattering. We consider only the cases where the two-dimensional translational symmetry exists. Thus, the following formulations are applied to both clean and adsorbate-covered surfaces that form periodic overlayers in such a way that the solid surfaces have the same periodicity. More specifically, we assume that the surface layer and the substrates have a common periodicity regardless of whether the surfaces have the structures of relaxation or reconstruction.

The displacement $\mathbf{u}^a(\mathbf{R}_\mathbf{G})$ with $a = li$ from the equilibrium position of the ith basis atom of the $\mathbf{G}$th two-dimensional unit cell in the lth layer is written in the form

$$\mathbf{u}^a(\mathbf{R}_\mathbf{G},t)=\mathrm{Re}[\boldsymbol{\varepsilon}_s^a(\mathbf{Q})e^{i[\mathbf{Q}\cdot\mathbf{R}_\mathbf{G}-\omega_s(\mathbf{Q})t]}]$$

in the classical picture. Here $\mathbf{R}_\mathbf{G}$ is the two-dimensional direct lattice vector parallel to the surface with $\mathbf{G}$ being the corresponding two-dimensional reciprocal lattice vector, that is, $\mathbf{R}_\mathbf{G}=g_1\mathbf{A}_1+g_2\mathbf{A}_2$, $\mathbf{G}=g_1\mathbf{B}_1+g_2\mathbf{B}_2$ with $\mathbf{A}_i$'s, $\mathbf{B}_i$'s being the two-dimensional direct and reciprocal primitive lattice vectors satisfying $\mathbf{A}_i\cdot\mathbf{B}_j=2\pi\delta_{i,j}$ and g_i's being integers. Thus, if $\mathbf{G}'=g_1'\mathbf{B}_1+g_2'\mathbf{B}_2$, then $\mathbf{G}'\cdot\mathbf{R}_\mathbf{G}=2\pi m$ with m an integer. $\mathbf{Q}$ denotes a single-phonon momentum parallel to the surface; $\hbar\omega_s(\mathbf{Q})$ and $\boldsymbol{\varepsilon}_s^a(\mathbf{Q})$ are the phonon energy and polarization, respectively, with s denoting the phonon modes. Thus, s includes the perpendicular component of the momentum for the bulk phonon case, and the Rayleigh modes, etc., for the surface phonon case. The classical equation of motion is transformed into an algebraic eigenvalue equation through the unitary transformation $\mathbf{R}_\mathbf{G}\rightarrow\mathbf{Q}$.

The two-dimensional Born–von Karman boundary condition with the boundary determined by the number of two-dimensional unit cells on the surface, $N=N_1N_2$, is employed. Then, we can write

$$\frac{1}{N}\sum_{\mathbf{G}}e^{i\mathbf{Q}\cdot\mathbf{R}_\mathbf{G}}=\delta_{\mathbf{Q},0},\quad \frac{1}{N}\sum_{\mathbf{Q}}e^{i\mathbf{Q}\cdot\mathbf{R}_\mathbf{G}}=\delta_{\mathbf{G},0}\ ,$$

when the $\mathbf{Q}$'s lie in the first two-dimensional Brillouin zone. It should be noted that

$$\frac{1}{A}\int_{\mathrm{uc}}d\mathbf{R}e^{i\mathbf{G}\cdot\mathbf{R}}=\delta_{\mathbf{G},0}\ ,$$

where $\int_{\mathrm{uc}}$ denotes the integration over the two-dimensional unit cell and A is the area of the cell.

The polarization and the eigenvalue relations, $\boldsymbol{\varepsilon}_s^{a*}(\mathbf{Q})=\boldsymbol{\varepsilon}_s^a(-\mathbf{Q})$ and $\omega_s(\mathbf{Q})=\omega_s(-\mathbf{Q})$, are obtained from the properties of the dynamic matrix. In addition, we have the orthogonality and completeness relations

$$\sum_a M^a\boldsymbol{\varepsilon}_s^{a*}(\mathbf{Q})\cdot\boldsymbol{\varepsilon}_{s'}^a(\mathbf{Q})=\delta_{s,s'}\ ,$$

$$\sum_s[\boldsymbol{\varepsilon}_s^{a*}(\mathbf{Q})]_i[\boldsymbol{\varepsilon}_s^{a'}(\mathbf{Q})]_{i'}=\frac{1}{M^a}\delta_{a,a'}\delta_{i,i'}$$

with the subscripts i and i' being the Cartesian components, and M^a being the mass of the ith basis ion in the lth layer.

The interaction potential V between the triatomic molecular projectile and the crystal surface is a function of all the $\mathbf{u}^a(\mathbf{R}_\mathbf{G})$'s and $\mathbf{r}_A$, $\mathbf{r}_B$, and $\mathbf{r}_C$, the position vectors of A, B, and C atoms with respect to a fixed origin O. These three position vectors can be transformed into another set of three vectors, $\mathbf{r}$, $\mathbf{S}$, and $\mathbf{s}$, where $\mathbf{r}$ is the position vector of the center of mass of the triatomic molecule from the origin O, and $\mathbf{S},\mathbf{s}$ are any two independent internal relative vectors of the triatomic system as shown in Fig. 1. Specific choices of $\mathbf{S}$ and $\mathbf{s}$ will be discussed later. It is sufficient to note here that the rotational and vibrational wave functions of the molecule are described by the six variables associated with the internal vectors $\mathbf{S}$ and $\mathbf{s}$. Therefore, V may be written as

$$V=V(\mathbf{r},\mathbf{S},\mathbf{s},\mathbf{u}^a(\mathbf{R}_\mathbf{G}))\qquad(1)$$

including all a and $\mathbf{G}$. Since V essentially depends on the relative vectors between the projectiles and the ions in the solid, it is invariant under the transformations $\mathbf{r}\rightarrow\mathbf{r}+\mathbf{R}_{G_0}$, $\mathbf{S}\rightarrow\mathbf{S}$, $\mathbf{s}\rightarrow\mathbf{s}$, and $\mathbf{u}^a(\mathbf{R}_G)\rightarrow\mathbf{u}^a(\mathbf{R}_G-\mathbf{R}_{G_0})$. Note that $\mathbf{R}_G-\mathbf{R}_{G_0}=\mathbf{R}_{G-G_0}$.

The crystal Hamiltonian is given by

$$H_{\mathrm{cr}}=H_{\mathrm{cr}}(\mathbf{p}^a(\mathbf{R}_G),\mathbf{u}^a(\mathbf{R}_G))$$

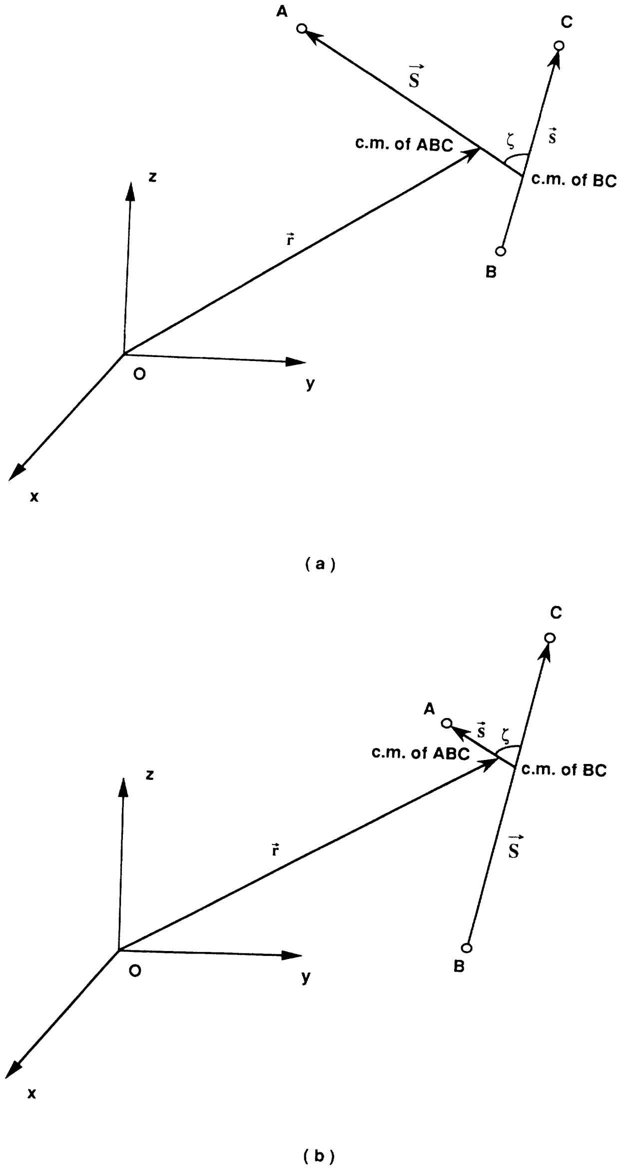

FIG. 1. Scattering geometry of the triatomic-molecule–surface system. The (x,y,z) is the space-fixed coordinate system with the x,y plane being the plane of the crystal surface. The z axis is chosen to be the outward normal to the crystal surface, and $\mathbf{r}$ is the position of the center of mass of the triatomic molecule ABC; (a) nonlinear molecule; $\mathbf{S}$ and $\mathbf{s}$ are the relative vectors from the center of mass of diatom BC to atom A and from B to C, respectively and ζ is the angle between $\mathbf{S}$ and $\mathbf{s}$; (b) linear molecule; $\mathbf{S}$ and $\mathbf{s}$ are the relative vectors from atom B to atom C and from the center of mass of diatom BC to atom A, respectively and ζ is the angle between $\mathbf{S}$ and $\mathbf{s}$.

with

$$\mathbf{p}^a(\mathbf{R}_G)=M^a\frac{d}{dt}\mathbf{u}^a(\mathbf{R}_G)\ .$$

It is also invariant under $\mathbf{R}_G\rightarrow\mathbf{R}_G-\mathbf{R}_{G_0}$ in $\mathbf{p}^a(\mathbf{R}_G)$ and $\mathbf{u}^a(\mathbf{R}_G)$. Using the creation and annihilation operators $a^\dagger_{\mathbf{Q},s},a_{\mathbf{Q},s}$ of a single phonon with momentum $\mathbf{Q}$ and mode s, we obtain the second-quantization formalism. These operators satisfy the boson commutation relations $[a_{\mathbf{Q},s},a^\dagger_{\mathbf{Q}',s'}]=\delta_{\mathbf{Q},\mathbf{Q}'}\delta_{s,s'}$. The $\mathbf{u}^a(\mathbf{R}_G)$ and $\mathbf{p}^a(\mathbf{R}_G)$ are now Hermitian operators,

$$\begin{aligned}\mathbf{u}^a(\mathbf{R}_G)&=\frac{1}{\sqrt{N}}\sum_{\mathbf{Q},s}\left[\frac{\hbar}{2\omega_s(\mathbf{Q})}\right]^{1/2}(a_{\mathbf{Q},s}+a^\dagger_{-\mathbf{Q},s})\\&\quad\times\boldsymbol{\varepsilon}^a_s(\mathbf{Q})e^{i\mathbf{Q}\cdot\mathbf{R}_G}\ ,\\\mathbf{p}^a(\mathbf{R}_G)&=\frac{-i}{\sqrt{N}}\sum_{\mathbf{Q},s}M^a\left[\frac{\hbar\omega_s(\mathbf{Q})}{2}\right]^{1/2}(a_{\mathbf{Q},s}-a^\dagger_{-\mathbf{Q},s})\\&\quad\times\boldsymbol{\varepsilon}^a_s(\mathbf{Q})e^{i\mathbf{Q}\cdot\mathbf{R}_G}\ .\end{aligned}\qquad(2)$$

The Cartesian components of these operators satisfy the canonical commutation relations

$$[[\mathbf{u}^a(\mathbf{R}_G)]_i,[\mathbf{p}^{a'}(\mathbf{R}_{G'})]_{i'}]=i\hbar\delta_{i,i'}\delta_{a,a'}\delta_{G,G'}\ .$$

The operators $\mathbf{u}^a(\mathbf{R}_G,t)$ and $\mathbf{p}^a(\mathbf{R}_G,t)$ in the interaction picture (Dirac picture) are obtained from the replacements

$$a_{\mathbf{Q},s}\rightarrow a_{\mathbf{Q},s}e^{-i\omega_s(\mathbf{Q})t}\ ,\quad a^\dagger_{\mathbf{Q},s}\rightarrow a^\dagger_{\mathbf{Q},s}e^{i\omega_s(\mathbf{Q})t}\ ,$$

in Eq. (2). Then $\mathbf{u}^a(\mathbf{R}_G)=\mathbf{u}^a(\mathbf{R}_G,0)$, $\mathbf{p}^a(\mathbf{R}_G)=\mathbf{p}^a(\mathbf{R}_G,0)$ are the operators in the Schrödinger picture and one sees that

$$\mathbf{p}^a(\mathbf{R}_G,t)=M^a\frac{d}{dt}\mathbf{u}^a(\mathbf{R}_G,t)\ .$$

The phonon state $|\phi_n\rangle$ is specified by a set $n=\{n_{\mathbf{Q},s}\}$ of the occupation numbers $n_{\mathbf{Q},s}$ with $\mathbf{Q}$ and s being the momentum and mode, respectively. The crystal Hamiltonian diagonal in this representation and corresponding total phonon energy are given, respectively, by

$$\begin{aligned}H_{\mathrm{cr}}&=\sum_{\mathbf{Q},s}\hbar\omega_s(\mathbf{Q})(a^\dagger_{\mathbf{Q},s}a_{\mathbf{Q},s}+\tfrac{1}{2})\ ,\\\mathcal{E}_n&=\sum_{\mathbf{Q},s}\hbar\omega_s(\mathbf{Q})(n_{\mathbf{Q},s}+\tfrac{1}{2})\ .\end{aligned}\qquad(3)$$

We thus have $H_{\mathrm{cr}}|\phi_n\rangle=\mathcal{E}_n|\phi_n\rangle$. The phonon states are orthonormalized such that $\langle\phi_n|\phi_{n'}\rangle=\delta_{n,n'}$. The potential V becomes a second-quantized operator through Eq. (2) as well.

The center-of-mass momentum operator of the projectile (which is also the total linear momentum of the projectile) and parallel phonon momentum operator are, respectively, given by

$$\mathbf{p}=\frac{\hbar}{i}\nabla_r,\quad \mathcal{K}_{\mathrm{cr}}=\sum_{\mathbf{Q},s}\mathbf{Q}a^\dagger_{\mathbf{Q},s}a_{\mathbf{Q},s}\ .$$

Thus $\mathcal{K}_{\mathrm{cr}}|\phi_n\rangle=\mathbf{Q}_n|\phi_n\rangle$ with $\mathbf{Q}_n=\sum_{\mathbf{Q},s}\mathbf{Q}n_{\mathbf{Q},s}$. One sees that

$$\mathbf{r}+\mathbf{R}_{\mathbf{G}_0}=e^{(i/\hbar)\mathbf{p}\cdot\mathbf{R}_{\mathbf{G}_0}}\mathbf{r}e^{-(i/\hbar)\mathbf{p}\cdot\mathbf{R}_{\mathbf{G}_0}},$$
$$\mathbf{u}^a(\mathbf{R}_\mathbf{G}-R_{\mathbf{G}_0})=e^{i\mathcal{K}_{\mathrm{cr}}\cdot\mathbf{R}_{\mathbf{G}_0}}\mathbf{u}^a(\mathbf{R}_\mathbf{G})e^{-i\mathcal{K}_{\mathrm{cr}}\cdot\mathbf{R}_{\mathbf{G}_0}}, \tag{4}$$
$$\mathbf{p}^a(\mathbf{R}_\mathbf{G}-R_{\mathbf{G}_0})=e^{i\mathcal{K}_{\mathrm{cr}}\cdot\mathbf{R}_{\mathbf{G}_0}}\mathbf{p}^a(\mathbf{R}_\mathbf{G})e^{-i\mathcal{K}_{\mathrm{cr}}\cdot\mathbf{R}_{\mathbf{G}_0}}.$$

We also have

$$e^{i\mathcal{K}_{\mathrm{cr}}\cdot\mathbf{R}_\mathbf{G}}H_{\mathrm{cr}}e^{-i\mathcal{K}_{\mathrm{cr}}\cdot\mathbf{R}_\mathbf{G}}=H_{\mathrm{cr}}. \tag{5}$$

Using these translation operators, we have the invariance of V previously mentioned,

$$\begin{aligned}e^{(i/\hbar)\mathbf{P}\cdot\mathbf{R}_{\mathbf{G}_0}}e^{i\mathcal{K}_{\mathrm{cr}}\cdot\mathbf{R}_{\mathbf{G}_0}}V(\mathbf{r},\mathbf{S},\mathbf{s},\mathbf{u}^a(\mathbf{R}_\mathbf{G}))e^{-i\mathcal{K}_{\mathrm{cr}}\cdot\mathbf{R}_{\mathbf{G}_0}}e^{-(i/\hbar)\mathbf{P}\cdot\mathbf{R}_{\mathbf{G}_0}}&=V(\mathbf{r}+\mathbf{R}_{\mathbf{G}_0},\mathbf{S},\mathbf{s},\mathbf{u}^a(\mathbf{R}_\mathbf{G}-\mathbf{R}_{\mathbf{G}_0}))\\&=V(\mathbf{r},\mathbf{S},\mathbf{s},\mathbf{u}^a(\mathbf{R}_\mathbf{G})).\end{aligned} \tag{6}$$

The operator $\mathbf{P}=(\hbar/i)\nabla_R$ is the projection of $\mathbf{p}$ onto the surface, and $\mathbf{R}$ the projection of $\mathbf{r}$ onto the surface. Note that $\mathbf{p}\cdot\mathbf{R}_\mathbf{G}=\mathbf{P}\cdot\mathbf{R}_\mathbf{G}$. The total Hamiltonian H of the whole system is given by

$$H=H_0+V,\quad H_0=-\frac{\hbar^2}{2M}\nabla_r^2+H_{\mathrm{mol}}+H_{\mathrm{cr}},$$

M being the sum of M_A, M_B, and M_C, i.e., the masses of atoms A, B, and C, respectively. If $\mathbf{S}$ is chosen to be the relative position vector from the center of mass of atom B and C to atom A, and $\mathbf{s}$ the relative position vector from B to C as in Fig. 1(a), then the molecular Hamiltonian is given by

$$H_{\mathrm{mol}}=-\frac{\hbar^2}{2\mu_{A,BC}}\nabla_S^2-\frac{\hbar^2}{2\mu_{BC}}\nabla_s^2+V_{\mathrm{mol}}(\mathbf{S},\mathbf{s}), \tag{7}$$

with

$$\frac{1}{\mu_{A,BC}}=\frac{1}{M_A}+\frac{1}{M_B+M_C},\quad \frac{1}{\mu_{BC}}=\frac{1}{M_B}+\frac{1}{M_C},$$

and V_{mol} is the molecular potential of an ABC system. Equations (5)–(7) then yield

$$U_G H U_G^\dagger=H \tag{8}$$

for all $\mathbf{G}$, where

$$U_G=e^{(i/\hbar)\mathbf{P}\cdot\mathbf{R}_\mathbf{G}}e^{i\mathcal{K}_{\mathrm{cr}}\cdot\mathbf{R}_\mathbf{G}}. \tag{9}$$

Since $[\mathbf{P},\mathcal{K}_{\mathrm{cr}}]=0$, $U_G=e^{i\mathcal{K}\cdot\mathbf{R}_\mathbf{G}}$ with $\mathcal{K}=\mathbf{P}/\hbar+\mathcal{K}_{\mathrm{cr}}$.

From the translational invariance previously discussed we study the properties of the scattering wave function. We use $\mathbf{k}_i$, α_i, and n_i to denote the initial momentum of the projectile, the initial internal (vibrational-rotational) state of the molecule ABC, and the initial phonon state of the crystal surface, respectively. The total energy of the system and the total momentum parallel to the surface are given, respectively, by

$$E=\frac{\hbar^2\mathbf{k}_i^2}{2M}+E_{\alpha_i}+\mathcal{E}_{n_i},\quad \mathbf{K}=\mathbf{K}_i+\mathbf{Q}_{n_i}, \tag{10}$$

where $\mathbf{K}_i$ is the projection of $\mathbf{k}_i$ onto the surface and E_{α_i} is the internal vibrational and rotational energy of the ABC molecule. $\mathbf{K}$ is a good quantum number up to $\mathbf{G}$ as seen From Eq. (8). We define the perpendicular wave number from

$$k_{\alpha n\mathbf{G}}^2=\frac{2M}{\hbar^2}(E-E_\alpha-\mathcal{E}_n)-(\mathbf{K}-\mathbf{Q}_n+\mathbf{G})^2.$$

We also define outgoing or incoming free-particle wave functions of the molecular-surface system from

$$\begin{aligned}\varphi_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}^{(\pm)}(\mathbf{r},\mathbf{S},\mathbf{s})=e^{\pm ik_{\alpha_i n_i \mathbf{G}_i}z}\Phi_{\alpha_i}(\mathbf{S},\mathbf{s})|\phi_{n_i}\rangle\\ \times e^{i(\mathbf{K}-\mathbf{Q}_{n_i}+\mathbf{G}_i)\cdot\mathbf{R}},\end{aligned}$$

where $\Phi_{\alpha_i}(\mathbf{S},\mathbf{s})$ is the molecular vibrational and rotational wave function with $H_{\mathrm{mol}}\Phi_\alpha=E_\alpha\Phi_\alpha$ and $\langle\Phi_\alpha|\Phi_{\alpha'}\rangle=\delta_{\alpha,\alpha'}$. More details of the molecular wave function will be discussed in Sec. III. The total scattering wave function of the system $\psi_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}^{(\pm)}(\mathbf{r},\mathbf{S},\mathbf{s})$ with outgoing or incoming asymptotic boundary condition satisfies the following differential form of Lippmann-Schwinger equation:[61]

$$(E-H\pm i\epsilon)\psi_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}^{(\pm)}(\mathbf{r},\mathbf{S},\mathbf{s})=\pm i\epsilon\varphi_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}^{(\mp)}(\mathbf{r},\mathbf{S},\mathbf{s}). \tag{11}$$

In Eq. (11) $\epsilon>0$ with the understanding $\epsilon\rightarrow 0$ and $\psi_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}^{(\pm)}(\mathbf{r},\mathbf{S},\mathbf{s})$ is not simply the spatial wave function. $\varphi_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}^{(+)}$ for $\mathbf{G}_i=0$ is equal to $e^{i\mathbf{k}_i\cdot\mathbf{r}}\Phi_{\alpha_i}|\phi_{n_i}\rangle$ and thus $\psi_{\mathbf{K},\alpha_i n_i 0}^{(+)}$ corresponds to the well-known physical solution. Equation (11) is different from that of the ordinary scattering theory where the collision partners are spatially localized. Proof of the equation will be omitted here. Its validity will be seen in the subsequent discussions. Applying the operator U_G to both sides of Eq. (11) and using Eq. (8), we have

$$\begin{aligned}(E-H\pm i\epsilon)&U_G\psi_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}^{(\pm)}(\mathbf{r},\mathbf{S},\mathbf{s})\\&=\pm i\epsilon e^{i\mathbf{K}\cdot\mathbf{R}_\mathbf{G}}\varphi_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}^{(\mp)}(\mathbf{r},\mathbf{S},\mathbf{s}).\end{aligned} \tag{12}$$

If the solution of Eq. (11) is unique, then Eq. (12) results in

$$\begin{aligned}e^{i\mathbf{K}\cdot\mathbf{R}_\mathbf{G}}\psi_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}^{(\pm)}(\mathbf{r},\mathbf{S},\mathbf{s})&=U_G\psi_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}^{(\pm)}(\mathbf{r},\mathbf{S},\mathbf{s})\\&=e^{i\mathcal{K}_{\mathrm{cr}}\cdot\mathbf{R}_\mathbf{G}}\psi_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}^{(\pm)}(\mathbf{r}+\mathbf{R}_\mathbf{G},\mathbf{S},\mathbf{s}),\end{aligned} \tag{13}$$

which shows that the wave function $\psi_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}^{(\pm)}$ is the eigenfunction of the translation operator U_G with the eigenvalue $e^{i\mathbf{K}\cdot\mathbf{R}_G}$ for arbitrary **G**. Expanding the total wave function in terms of the basis states $|\phi_n\rangle$,

$$\psi^{(\pm)}_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}(\mathbf{r},\mathbf{S},\mathbf{s}) = \sum_n f^{(\pm)}_{n,\mathbf{K}\alpha_i n_i \mathbf{G}_i}(\mathbf{r},\mathbf{S},\mathbf{s})|\phi_n\rangle \;, \tag{14}$$

and using Eq. (13), we have

$$f^{(\pm)}_{n,\mathbf{K}\alpha_i n_i \mathbf{G}_i}(\mathbf{r}+\mathbf{R}_\mathbf{G},\mathbf{S},\mathbf{s}) = e^{i(\mathbf{K}-\mathbf{Q}_n)\cdot\mathbf{R}_\mathbf{G}} f^{(\pm)}_{n,\mathbf{K}\alpha_i n_i \mathbf{G}_i}(\mathbf{r},\mathbf{S},\mathbf{s}) \;. \tag{15}$$

Therefore, $f^{(\pm)}_{n,\mathbf{K}\alpha_i n_i \mathbf{G}_i}$ is a product of $e^{i(\mathbf{K}-\mathbf{Q}_n)\cdot\mathbf{R}}$ and a wave function that has the two-dimensional periodicity with respect to **r**. The latter can be further expanded in terms of the molecular wave functions Φ_α. Thus we have the expression

$$\psi^{(\pm)}_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}(\mathbf{r},\mathbf{S},\mathbf{s}) = \sum_{\alpha n \mathbf{G}} \psi^{(\pm)}_{\alpha n \mathbf{G},\alpha_i n_i \mathbf{G}_i}(z)\Phi_\alpha(\mathbf{S},\mathbf{s})|\phi_n\rangle \times e^{i(\mathbf{K}-\mathbf{Q}_n+\mathbf{G})\cdot\mathbf{R}} \;. \tag{16}$$

Here the subscripts $(\alpha_i n_i \mathbf{G}_i)$ correspond to the initial condition, $\alpha=\alpha_i$, $n=n_i$, $\mathbf{G}=\mathbf{G}_i$. We choose the unit vector $\hat{\mathbf{z}}$ to be the outward normal to the crystal surface. The position vector of the center of mass is given by $\mathbf{r}=z\hat{\mathbf{z}}+\mathbf{R}$ with $\hat{\mathbf{z}}\cdot\mathbf{R}=0$. The total wave function $\psi^{(\pm)}_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}$ is a linear combination of the phonon states $|\phi_n\rangle$ with *c*-number coefficient functions. Thus $\psi^{(\pm)\dagger}_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}$ can be written as

$$\psi^{(\pm)\dagger}_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}(\mathbf{r},\mathbf{S},\mathbf{s}) = \sum_{\alpha n \mathbf{G}} \psi^{(\pm)*}_{\alpha n \mathbf{G},\alpha_i n_i \mathbf{G}_i}(z)\Phi^*_\alpha(\mathbf{S},\mathbf{s}) \times \langle\phi_n| e^{-i(\mathbf{K}-\mathbf{Q}_n+\mathbf{G})\cdot\mathbf{R}} \;. \tag{17}$$

The total interaction potential of the triatomic-molecule–crystal-surface system is then expressed as

$$\begin{aligned} V &= V(\mathbf{r},\mathbf{S},\mathbf{s},\mathbf{u}^a(\mathbf{R}_\mathbf{G})) \\ &= \sum_{nn'} |\phi_n\rangle V_{n,n'}(\mathbf{r},\mathbf{S},\mathbf{s})\langle\phi_{n'}| \;, \end{aligned} \tag{18}$$

where $V_{n,n'}(\mathbf{r},\mathbf{S},\mathbf{s}) = \langle\phi_n|V|\phi_{n'}\rangle$. Applying the translational invariance, Eq. (6), to V, we have

$$V_{n,n'}(\mathbf{r}+\mathbf{R}_\mathbf{G},\mathbf{S},\mathbf{s}) = e^{i(\mathbf{Q}_{n'}-\mathbf{Q}_n)\cdot\mathbf{R}_\mathbf{G}} V_{n,n'}(\mathbf{r},\mathbf{S},\mathbf{s}) \;. \tag{19}$$

Therefore, $V_{n,n'}$ is a product of $e^{i(\mathbf{Q}_{n'}-\mathbf{Q}_n)\cdot\mathbf{R}}$ and a wave function that has two-dimensional periodicity with respect to **r**, and thus we have the following representation for the interaction potential of the molecule–crystal-surface system:

$$\begin{aligned} V &= \sum_{nn'\mathbf{G}} |\phi_n\rangle V^\mathbf{G}_{n,n'}(z,\mathbf{S},\mathbf{s})\langle\phi_{n'}| e^{i(\mathbf{Q}_{n'}-\mathbf{Q}_n+\mathbf{G})\cdot\mathbf{R}} \\ &= \sum_{\substack{nn'\mathbf{G} \\ \alpha\alpha'}} |\Phi_\alpha\rangle|\phi_n\rangle V^\mathbf{G}_{\alpha n,\alpha' n'}(z)\langle\phi_{n'}|\langle\Phi_{\alpha'}| e^{i(\mathbf{Q}_{n'}-\mathbf{Q}_n+\mathbf{G})\cdot\mathbf{R}} \;. \end{aligned} \tag{20}$$

Here,

$$\begin{aligned} V^\mathbf{G}_{\alpha n,\alpha' n'}(z) &= \langle\Phi_\alpha|V^\mathbf{G}_{n,n'}(z,\mathbf{S},\mathbf{s})|\Phi_{\alpha'}\rangle \\ &= \int\int d\mathbf{S}\, d\mathbf{s}\,\Phi^*_\alpha(\mathbf{S},\mathbf{s})V^\mathbf{G}_{n,n'}(z,\mathbf{S},\mathbf{s})\Phi_{\alpha'}(\mathbf{S},\mathbf{s}) \;. \end{aligned}$$

Since the displacement vector $\mathbf{u}^a(\mathbf{R}_\mathbf{G})$ is a Hermitian operator and V is a real function of **r**, **S**, **s**, and $\mathbf{u}^a(\mathbf{R}_\mathbf{G})$, V is Hermitian too, i.e., $V^\dagger=V$. From this property we can show that

$$\begin{aligned} V^\mathbf{G}_{n,n'}(z,\mathbf{S},\mathbf{s}) &= V^{-\mathbf{G}*}_{n',n}(z,\mathbf{S},\mathbf{s}) \;, \\ V^\mathbf{G}_{\alpha n,\alpha' n'}(z) &= V^{-\mathbf{G}*}_{\alpha' n',\alpha n}(z) \;. \end{aligned} \tag{21}$$

The initial momentum of the center of mass of the projectile is given by

$$\mathbf{k}_i = -k_{iz}\hat{\mathbf{z}}+\mathbf{K}_i = -k_{\alpha_i n_i 0}\hat{\mathbf{z}}+(\mathbf{K}-\mathbf{Q}_{n_i}) \;,$$

with $k_{iz}=k_{\alpha_i n_i 0}>0$. Equation (12) implies both Schrödinger equation

$$H\psi^{(\pm)}_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}(\mathbf{r},\mathbf{S},\mathbf{s}) = E\psi^{(\pm)}_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}(\mathbf{r},\mathbf{S},\mathbf{s}) \tag{22}$$

and the asymptotic boundary condition

$$\begin{aligned} &\psi^{(\pm)}_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}(\mathbf{r},\mathbf{S},\mathbf{s}) \\ &\quad\sim \varphi^{(\mp)}_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}(\mathbf{r},\mathbf{S},\mathbf{s}) \\ &\qquad + (\text{outgoing or incoming scattered wave}) \;. \end{aligned} \tag{23}$$

The notation $\sim$ is used to indicate the asymptotic behavior as z goes to infinity. Substituting Eq. (16) into Eq. (22) and using the orthogonalities, $\langle\phi_n|\phi_{n'}\rangle=\delta_{n,n'}$ and $\langle\Phi_\alpha|\Phi_{\alpha'}\rangle=\delta_{\alpha,\alpha'}$, we have a coupled differential equation (CDE),

$$\left[\frac{d^2}{dz^2}+k^2_{\alpha n \mathbf{G}}\right]\psi^{(\pm)}_{\alpha n \mathbf{G},\alpha_i n_i \mathbf{G}_i}(z) = \frac{2M}{\hbar^2}\sum_{\alpha' n' \mathbf{G}'} V^{\mathbf{G}-\mathbf{G}'}_{\alpha n,\alpha' n'}(z)\psi^{(\pm)}_{\alpha' n' \mathbf{G}',\alpha_i n_i \mathbf{G}_i}(z) \;. \tag{24}$$

The orthogonality

$$\frac{1}{L^2}\int d\mathbf{R}\, e^{i(\mathbf{K}_1-\mathbf{K}_2)\cdot\mathbf{R}} = \delta_{\mathbf{K}_1,\mathbf{K}_2}$$

with the $\mathbf{K}_i$'s being the vectors parallel to the surface and consistent with the (two-dimensional) Born–von Karman boundary condition, and L^2, the area of the surface within the boundary, were also employed to obtain Eq. (24). The open channels are the $(\alpha n\mathbf{G})$'s satisfying $k^2_{\alpha n \mathbf{G}}>0$ with $k_{\alpha n \mathbf{G}}>0$. The closed channels are the $(\alpha n\mathbf{G})$'s satisfying $k^2_{\alpha n \mathbf{G}}<0$. For a closed channel it is convenient to write $\kappa^2_{\alpha n \mathbf{G}}=-k^2_{\alpha n \mathbf{G}}$ with $\kappa_{\alpha n \mathbf{G}}>0$. The initial channel $(\alpha_i n_i \mathbf{G}_i)$ is an open channel by definition. For practical purposes, we define z_0 as the smallest z coordinate where the potential $V^0_{\alpha n,\alpha n}(z)$ for $z\le z_0$ is very large compared to the vertical component of the incident energy of the molecule. Therefore, the wave functions cannot penetrate beyond z_0 and we can write $\psi^{(\pm)}_{\alpha n \mathbf{G},\alpha_i n_i \mathbf{G}_i}(z_0)=0$. The asymptotic boundary condition of the total wave function [Eq. (23)] yields the condition of vertical component,

$$\psi^{(\pm)}_{\alpha n\mathbf{G},\alpha_i n_i \mathbf{G}_i}(z) \sim \left[\frac{k_{\alpha_i n_i \mathbf{G}_i}}{k_{\alpha n\mathbf{G}}}\right]^{1/2} \Big(e^{\mp i k_{\alpha n\mathbf{G}} z}\delta_{\alpha,\alpha_i}\delta_{n,n_i}\delta_{\mathbf{G},\mathbf{G}_i} - S^{(\pm)}_{\alpha n\mathbf{G},\alpha_i n_i \mathbf{G}_i} e^{\pm i k_{\alpha n\mathbf{G}} z}\Big) , \tag{25}$$

for open channels and

$$\psi^{(\pm)}_{\alpha n\mathbf{G},\alpha_i n_i \mathbf{G}_i}(z) \sim -\left[\frac{k_{\alpha_i n_i \mathbf{G}_i}}{\kappa_{\alpha n\mathbf{G}}}\right]^{1/2} \bar{S}^{(\pm)}_{\alpha n\mathbf{G},\alpha_i n_i \mathbf{G}_i} e^{-\kappa_{\alpha n\mathbf{G}} z} \tag{26}$$

for closed channels. Here $S^{(\pm)}$ is the scattering matrix (S matrix).

We have defined the scattering wave function $\psi^{(\pm)}_{\mathbf{K},\alpha' n' \mathbf{G}'}(\mathbf{r},\mathbf{S},\mathbf{s})$ with an arbitrary initial condition ($\alpha' n' \mathbf{G}'$) *for given total energy E and parallel momentum* **K**. Matrix elements of the scattering matrix $S^{(\pm)}$ are defined only for the open channels of columns and rows and satisfy the following unitary conditions:

$$\begin{aligned} &\sum_{\alpha'' n'' \mathbf{G}''} S^{(\pm)}_{\alpha n\mathbf{G},\alpha'' n'' \mathbf{G}''} S^{(\pm)*}_{\alpha' n' \mathbf{G}',\alpha'' n'' \mathbf{G}''} = \delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{\mathbf{G},\mathbf{G}'} , \\ &\sum_{\alpha'' n'' \mathbf{G}''} S^{(\pm)}_{\alpha'' n'' \mathbf{G}'',\alpha n\mathbf{G}} S^{(\pm)*}_{\alpha'' n'' \mathbf{G}'',\alpha' n' \mathbf{G}'} = \delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{\mathbf{G},\mathbf{G}'} , \end{aligned} \tag{27}$$

for a given total energy E and momentum **K**. For a given E and **K**, the scattering wave functions $\psi^{(\pm)}_{\mathbf{K},\alpha' n' \mathbf{G}'}(\mathbf{r},\mathbf{S},\mathbf{s})$ are the eigenfunctions of the translation operator U_G for arbitrary initial conditions $\alpha' n' \mathbf{G}'$ with the same eigenvalue $e^{i\mathbf{K}\cdot\mathbf{R}_\mathrm{G}}$. More specifically, these eigenfunctions for different $\alpha' n' \mathbf{G}'$ are independent and span the eigenspace determined by the simultaneous eigenvalues E and $e^{i\mathbf{K}\cdot\mathbf{R}_\mathrm{G}}$ of the operators H and U_G. The total parallel momentum **K** is analogous to the total angular momentum **J** in the gas-phase scattering[62] where the rotational symmetry exists. The S matrix and the component functions are also functions of **K**. If we express the **K** dependence explicitly by

$$\begin{aligned} &\psi^{(\pm)}_{\alpha n\mathbf{G},\alpha' n' \mathbf{G}'}(z) = \psi_{\alpha n\mathbf{G},\alpha' n' \mathbf{G}'}(z;\mathbf{K}) , \\ &S^{(\pm)}_{\alpha n\mathbf{G},\alpha' n' \mathbf{G}'} = S^{(\pm)}_{\alpha n\mathbf{G},\alpha' n' \mathbf{G}'}(\mathbf{K}) , \end{aligned} \tag{28}$$

then one can show that

$$\begin{aligned} &S^{(\pm)}_{\alpha n\mathbf{G},\alpha' n' \mathbf{G}'}(\mathbf{K}) = S^{(\pm)}_{\alpha n\mathbf{G}-\mathbf{G}_0,\alpha' n' \mathbf{G}'-\mathbf{G}_0}(\mathbf{K}+\mathbf{G}_0) , \\ &\psi^{(\pm)}_{\alpha n\mathbf{G},\alpha' n' \mathbf{G}'}(z;\mathbf{K}) = \psi^{(\pm)}_{\alpha n\mathbf{G}-\mathbf{G}_0,\alpha' n' \mathbf{G}'-\mathbf{G}_0}(z;\mathbf{K}+\mathbf{G}_0) , \\ &\psi^{(\pm)}_{\mathbf{K},\alpha' n' \mathbf{G}'}(\mathbf{r},\mathbf{S},\mathbf{s}) = \psi^{(\pm)}_{\mathbf{K}+\mathbf{G}_0,\alpha' n' \mathbf{G}'-\mathbf{G}_0}(\mathbf{r},\mathbf{S},\mathbf{s}) , \end{aligned} \tag{29}$$

using the CDE and the asymptotic boundary condition of the component functions.

The CDE is not quite useful for obtaining the numerical solutions, but it is used to further develop the scattering formulation and introduce approximation schemes as discussed later. In what follows, $V(\mathbf{r},\mathbf{S},\mathbf{s})$ will be used to denote the full interaction potential $V(\mathbf{r},\mathbf{S},\mathbf{s},\mathbf{u}^a(\mathbf{R}_\mathrm{G}))$ unless specified further.

III. MOLECULAR WAVE FUNCTIONS AND POTENTIAL MATRIX ELEMENTS

In this section, we discuss the triatomic-molecular vibrational and rotational wave functions and the potential matrix elements of molecular-surface interaction for the simultaneous vibrational, rotational, and phonon transitions. This is necessary for the present molecule–nonrigid-surface scattering study. The vibrational and rotational wave functions and the corresponding energies are obtained from the eigenvalue equation,

$$H_\mathrm{mol}(\mathbf{S},\mathbf{s})\Phi_\alpha(\mathbf{S},\mathbf{s}) = E_\alpha \Phi_\alpha(\mathbf{S},\mathbf{s}) . \tag{30}$$

If **S** is chosen to be the relative vector from the center of mass of diatom BC to atom A, and **s** the relative vector from B to C as in Fig. 1(a), then

$$H_\mathrm{mol}(\mathbf{S},\mathbf{s}) = -\frac{\hbar^2}{2\mu_{A,BC}}\nabla^2_S - \frac{\hbar^2}{2\mu_{BC}}\nabla^2_s + V_\mathrm{mol}(S,s,\cos\zeta) , \tag{31}$$

with $\cos\zeta = \hat{\mathbf{S}}\cdot\hat{\mathbf{s}}$. If atoms B and C are of the same species, then **S** is the symmetry axis. Rotational wave functions of the molecule are described by the three Euler angles $(\Omega) = (\varphi,\theta,\chi)$ for a rotation from the (x,y,z) space-fixed coordinate system to the (x',y',z') body-fixed coordinate system of the molecule defined from

$$\hat{\mathbf{z}}' = \hat{\mathbf{S}}, \quad \hat{\mathbf{x}}' = \hat{\mathbf{S}}\times(\hat{\mathbf{s}}\times\hat{\mathbf{S}})/\sin\zeta, \quad \hat{\mathbf{y}}' = \hat{\mathbf{z}}'\times\hat{\mathbf{x}}' . \tag{32}$$

The x' axis lies in the plane determined by the vectors **S** and **s**. The vibrational wave functions are described by the normal modes derived from the three variables $S,s,\cos\zeta$.

Equation (30) can be solved employing the simultaneous eigenfunction of the square of the total angular momentum $\mathbf{J}^2$ and its projection J_z onto the z axis, since $[H_\mathrm{mol},\mathbf{J}]=0$. Here, $\mathbf{J} = \boldsymbol{l} + \mathbf{j}$, $\boldsymbol{l} = (1/i)\mathbf{S}\times\nabla_S$, $\mathbf{j} = (1/i)\mathbf{s}\times\nabla_s$. In terms of space fixed coordinates

$$\Phi_\alpha(\mathbf{S},\mathbf{s}) = \Phi^{JM}(\mathbf{S},\mathbf{s}) = \sum_{lj} G^J_{lj}(S,s)\mathcal{Y}^{JM}_{lj}(\hat{\mathbf{S}},\hat{\mathbf{s}})$$

with

$$\mathcal{Y}^{JM}_{lj}(\hat{\mathbf{S}},\hat{\mathbf{s}}) = \sum_{m_1 m_2} \langle l m_1 j m_2 | JM \rangle Y_{l m_1}(\hat{\mathbf{S}}) Y_{j m_2}(\hat{\mathbf{s}}) .$$

Here, $Y_{lm}(\hat{\mathbf{S}}) = Y_{lm}(\theta_S,\varphi_S)$, e.g., are the spherical harmonics. As usual, J, l, and j denote the eigenvalues $J(J+1)$, $l(l+1)$, and $j(j+1)$ of the operators $\mathbf{J}^2$, $\boldsymbol{l}^2$, and $\mathbf{j}^2$, respectively, and M is the eigenvalue of J_z. The same wave function can also be expressed in terms of the body-fixed variables as

$$\begin{aligned} \Phi^{JM}(\mathbf{S},\mathbf{s}) &= \sum_K F^J_K(S,s,\cos\zeta)\bar{D}^{J*}_{MK}(\Omega) \\ &= \sqrt{2\pi}\sum_{Kj} F^J_{Kj}(S,s) Y_{jK}(\zeta,0)\bar{D}^{J*}_{MK}(\Omega) . \end{aligned}$$

Here

$$\bar{D}^J_{MK}(\Omega) = \left[\frac{2J+1}{8\pi^2}\right]^{1/2} D^J_{MK}(\Omega)$$

where $D^J_{MK}(\Omega)$ being the well-known rotation matrix and K the eigenvalue of the projection $J_{z'}$ of $\mathbf{J}$ onto the z' axis. The asterisk denotes the complex conjugation. It can be shown that

$$G^J_{lj}(S,s)=\sum_K U^{Jj}_{lK}F^J_{Kj}(S,s) \ ,$$

$$F^J_{Kj}(S,s)=\sum_l U^{Jj}_{lK}G^J_{lj}(S,s) \ ,$$

$$\sum_l U^{Jj}_{lK}U^{Jj}_{lK'}=\delta_{K,K'}, \quad \sum_K U^{Jj}_{lK}U^{Jj}_{l'K}=\delta_{l,l'} \ ,$$

using the relation between $\mathcal{Y}^{JM}_{lj}$ and $Y_{jK}\bar{D}^{\,J}_{MK}$. Here

$$U^{Jj}_{lK}=\left[\frac{2l+1}{2J+1}\right]^{1/2}\langle l0jK|JK\rangle \ .$$

It is convenient to employ body-fixed variables for the separation of vibration and rotation, since V_{mol} is described in terms of S,s,ζ. In what follows, we use the notations

$$\tau=S,s,\cos\zeta, \quad d\tau=S^2dS\,s^2ds\,\sin\zeta\,d\zeta \ .$$

The τ are the variables related to the vibrational degrees of freedom. Since the coupling between different K's are small, we use the following vibrational and rotational basis functions:

$$\Phi(\mathbf{S},\mathbf{s})=F^J_K(\tau)\bar{D}^{\,J*}_{MK}(\Omega) \ . \tag{33}$$

Employing the standard techniques of rigid rotor with $l^2=(\mathbf{J}-\mathbf{j})^2$ in suitable body-fixed frame, we obtain

$$\langle \bar{D}^{\,J*}_{MK}|l^2|\bar{D}^{\,J'*}_{M'K'}\rangle=\int d\Omega\,\bar{D}^{\,J}_{MK}(\Omega)l^2\bar{D}^{\,J'*}_{M'K'}(\Omega)$$
$$=\delta_{J,J'}\delta_{M,M'}[\delta_{K,K'}A^J_K(\cos\zeta)-\delta_{K,K'+1}B^{J+}_K(\cos\zeta)+\delta_{K,K'-1}B^{J-}_K(\cos\zeta)] \ , \tag{34}$$

where

$$d\Omega=\sin\theta\ d\theta\,d\varphi\,d\chi, \quad A^J_K(\cos\zeta)=\mathbf{j}^2+J(J+1)-2K^2 \ ,$$

$$B^{J\pm}_K(\cos\zeta)=\sqrt{(J\pm K)(J\mp K+1)}\left[\frac{\partial}{\partial\zeta}\mp(K\mp1)\cot\zeta\right] \ , \tag{35}$$

$$\mathbf{j}^2=-\frac{1}{\sin\zeta}\frac{\partial}{\partial\zeta}\sin\zeta\frac{\partial}{\partial\zeta}+\frac{K^2}{\sin^2\zeta} \ .$$

Note that $d\mathbf{S}\,d\mathbf{s}=d\tau\,d\Omega$. Using Eq. (34), the molecular Hamiltonian matrix is given by

$$\langle \bar{D}^{\,J*}_{MK}|H_{\mathrm{mol}}|\bar{D}^{\,J'*}_{M'K'}\rangle=\delta_{J,J'}\delta_{M,M'}[\delta_{K,K'}H^J_K(\tau)+H^{cJ}_{K,K'}(\tau)] \ , \tag{36}$$

which divides the diagonal from the nondiagonal part. Here,

$$H^J_K(\tau)=-\frac{\hbar^2}{2\mu_{A,BC}}\frac{1}{S^2}\frac{\partial}{\partial S}S^2\frac{\partial}{\partial S}+\frac{\hbar^2}{2\mu_{A,BC}}\frac{A^J_K(\cos\zeta)}{S^2}-\frac{\hbar^2}{2\mu_{BC}}\frac{1}{s^2}\frac{\partial}{\partial s}s^2\frac{\partial}{\partial s}+\frac{\hbar^2}{2\mu_{BC}}\frac{\mathbf{j}^2}{s^2}+V_{\mathrm{mol}}(\tau) \ ,$$
$$H^{cJ}_{K,K'}(\tau)=\frac{\hbar^2}{2\mu_{A,BC}S^2}[\delta_{K,K'-1}B^{J-}_K(\cos\zeta)-\delta_{K,K'+1}B^{J+}_K(\cos\zeta)] \ . \tag{37}$$

The nondiagonal part $H^{cJ}_{K,K'}$ of the Hamiltonian is basically the Coriolis coupling term and in general is small. If we neglect this term, the eigenvalue equation,

$$H^J_K(\tau)F^J_{K\beta}(\tau)=E^J_{K\beta}F^J_{K\beta}(\tau) \ , \tag{38}$$

for the vibrational wave function yields the molecular vibrational and rotational wave function

$$\Phi_\alpha(\mathbf{S},\mathbf{s})=F^J_{K\beta}(\tau)\bar{D}^{\,J*}_{MK}(\Omega) \tag{39}$$

for the solution of Eq. (30) with $E_\alpha=E^J_{K\beta}$. Thus $\alpha=(JMK\beta)$ in this case. Although the vibrational and rotational energy $E^J_{K\beta}$ is independent of M, we denote it by E_α. We note that the J and K dependence in $F^J_{K\beta}$ are negligible and β indicates a suitable normal mode. In order to solve Eq. (38), the molecular potential $V_{\mathrm{mol}}(S,s,\cos\zeta)$ is usually approximated up to the quadratic order in the displacements from the equilibrium position S_0,s_0,ζ_0, and the normal modes of the small oscillation should be computed by carrying out the transformation from S,s,ζ to certain normal coordinates q_1,q_2,q_3. For a linear molecule ABC where displacement of B from its equilibrium position is small from the linear axis AC, the vector $\mathbf{S}$ is chosen to be the interatomic vector from A to C, and $\mathbf{s}$ the vector from the center of mass of AC to B. The K is then the rotational projection quantum number onto the linear axis AC [see Fig. 1(b)]. For example in CO_2, B is the carbon atom.

Let $H^J_{K,K'}(\tau)$ be the expression inside square brackets in Eq. (36). Then

$$H^J_{K,K'}(\tau)=(-1)^{K+K'}H^J_{-K,-K'}(\tau) \ . \tag{40}$$

This is a consequence of the parity conservation $H_{\mathrm{mol}}(\mathbf{S},\mathbf{s})=H_{\mathrm{mol}}(-\mathbf{S},-\mathbf{s})$. One sees that Eq. (40) is also satisfied for both the diagonal and nondiagonal parts separately and, in particular, $H^J_K=H^J_{-K}$. Therefore, $E^J_{K\beta}=E^J_{-K\beta}$ and $F^J_{K\beta}=F^J_{-K\beta}$. The basis functions $D^{Jp}_{MK}(\Omega)$ of the parity eigenfunction are defined from

$$D^{Jp}_{MK}(\Omega)=\sum_{K'=-J}^{J}C^{J,pK}_{K'}\bar{D}^{\,J*}_{MK'}(\Omega) \ , \tag{41}$$

with

$$C^{J,pK}_{K'}=N_K(\delta_{K,K'}+(-1)^{J+K+p}\delta_{K,-K'})$$

for $J\geq K\geq 0$. Here $p=0$ corresponds to the $(+)$ parity and $p=1$ indicates the $(-)$ parity. $N_K=1/\sqrt{2}$ for $K>0$

and $N_K=\frac{1}{2}$ for $K=0$. It is understood that $(-1)^J=(-1)^p$ for the $K=0$ case. If $\mathcal{P}$ is the parity operator defined as $\mathcal{P}f(\mathbf{S},\mathbf{s})=f(-\mathbf{S},-\mathbf{s})$, then $\mathcal{P}D^{Jp}_{MK}=(-1)^p D^{Jp}_{MK}$. Neglecting the nondiagonal term $H^{cJ}_{K,K'}$ (Coriolis coupling term), we see that the molecular wave function

$$\Phi_\alpha(\mathbf{S},\mathbf{s})=\Phi^{JMp}_{K\beta}(\mathbf{S},\mathbf{s})=F^J_{K\beta}(\tau)D^{Jp}_{MK}(\Omega) \tag{42}$$

for $K\geq 0$ again satisfies Eq. (30) with $E_\alpha=E^J_{K\beta}$. This is from the relations $H^J_K=H^J_{-K}$, $E^J_{K\beta}=E^J_{-K\beta}$, and $F^J_{K\beta}=F^J_{-K\beta}$. In Eq. (42), $\alpha=(JMpK\beta)$ with $K\geq 0$.

Including the Coriolis coupling term, the eigenvalue K of $J_{z'}$ is no longer a good quantum number in the molecular system. In order to obtain numerical solutions of Eq. (30), the following linear combination of the wave functions that are associated with the diagonal part of the molecular Hamiltonian could be made:

$$\Phi^{JMp}_\gamma(\mathbf{S},\mathbf{s})=\sum_{K\beta} U^{Jp,\gamma}_{K\beta}\Phi^{JMp}_{K\beta}(\mathbf{S},\mathbf{s}) \tag{43}$$

with $K\geq 0$. Then, the equation

$$H_{\text{mol}}(\mathbf{S},\mathbf{s})\Phi^{JMp}_\gamma(\mathbf{S},\mathbf{s})=E^{Jp}_\gamma\Phi^{JMp}_\gamma(\mathbf{S},\mathbf{s}) \tag{44}$$

yields an algebraic eigenvalue equation

$$\sum_{K'\beta'} H^{Jp}_{K\beta,K'\beta'}U^{Jp,\gamma}_{K'\beta'}=E^{Jp}_\gamma U^{Jp,\gamma}_{K\beta} . \tag{45}$$

Here,

$$\begin{aligned} H^{Jp}_{K\beta,K'\beta'} &= \langle \Phi^{JMp}_{K\beta}|H_{\text{mol}}|\Phi^{JMp}_{K'\beta'}\rangle \\ &= E^J_{K\beta}\delta_{K,K'}\delta_{\beta,\beta'}+2N_K N_{K'}[H^{cJ}_{K\beta,K'\beta'}+(-1)^{J+K+p}H^{cJ}_{-K\beta,K'\beta'}] , \end{aligned} \tag{46}$$

with

$$H^{cJ}_{K\beta,K'\beta'}=\int d\tau F^{J*}_{K\beta}(\tau)H^{cJ}_{K,K'}(\tau)F^J_{K'\beta'}(\tau) . \tag{47}$$

In practice, the Coriolis coupling term is small and thus $U^{Jp,\gamma}_{K\beta}\simeq\delta_{\gamma,K\beta}$. In order words, the molecular wave function Φ^{JMp}_γ has in general a dominant component $K\beta$.

Assuming that the bth atom is in the gas phase, the molecular–bth-atom interaction potential is of the form

$$V^a=V^a(\mathbf{S},\mathbf{s},\mathbf{r}_{mb}) , \tag{48}$$

where the $\mathbf{r}_{mb}$ is the relative vector from the bth atom to the center of mass of the molecule with $b=li\mathbf{G}$, $a=li$. The potential given by Eq. (48) is rotationally invariant in the sense that simultaneous rotations of $\mathbf{S}$, $\mathbf{s}$, and $\mathbf{r}_{mb}$ yield the same value. The expression for the molecule–bth-atom interaction potential, where the bth atom is in the solid is of the same form as in Eq. (48) except that the empirical parameters should be adjusted from those in the gas phase to the ones suitable to the solid phase. We adopt the pairwise molecule-atom (with suitably adjusted parameters for the solid) potential summed over all the atoms in the solid to represent the molecule-surface interaction potential, i.e.,

$$\begin{aligned} V &= \sum_b V^a(\mathbf{S},\mathbf{s},\mathbf{r}_{mb}) , \\ &= \sum_{\mathbf{G},a} V^a(\mathbf{S},\mathbf{s},\mathbf{r}-\mathbf{R}_\mathbf{G}-\mathbf{r}_a-\mathbf{u}^a(\mathbf{R}_\mathbf{G})) . \end{aligned} \tag{49}$$

The vector $\mathbf{R}_\mathbf{G}+\mathbf{r}_a$ denotes the equilibrium position of the ith basis ion in the $\mathbf{G}$th two-dimensional unit cell of the lth layer ($a=li$). From the Fourier decomposition

$$V^a(\mathbf{S},\mathbf{s},\mathbf{r}_{mb})=\frac{1}{L^3}\sum_\mathbf{k} V^a_\mathbf{k}(\mathbf{S},\mathbf{s})e^{i\mathbf{k}\cdot\mathbf{r}_{mb}} \tag{50}$$

and the operator representation of $\mathbf{u}^a(\mathbf{R}_\mathbf{G})$, we have

$$V^\mathbf{G}_{\alpha n,\alpha' n'}(z)=\frac{1}{L^3}\sum_{\mathbf{G}'a\mathbf{k}_z}(V^a_{\mathbf{k}_\mathbf{G}})_{\alpha,\alpha'}\exp\{i[k_z z+(\mathbf{Q}_n-\mathbf{Q}_{n'})\cdot\mathbf{R}_{\mathbf{G}'}-\mathbf{k}_\mathbf{G}\cdot\mathbf{r}_a]\}\prod_{\mathbf{Q},s}\langle n_{\mathbf{Q},s}|\exp(-\delta a^\dagger_{\mathbf{Q},s}+\delta^* a_{\mathbf{Q},s})|n'_{\mathbf{Q},s}\rangle , \tag{51}$$

where

$$(V^a_{\mathbf{k}_\mathbf{G}})_{\alpha,\alpha'}=\int\int d\mathbf{S}\,d\mathbf{s}\,\Phi^*_\alpha(\mathbf{S},\mathbf{s})V^a_{\mathbf{k}_\mathbf{G}}(\mathbf{S},\mathbf{s})\Phi_{\alpha'}(\mathbf{S},\mathbf{s}) ,$$

$$\mathbf{k}_\mathbf{G}=k_z\hat{\mathbf{z}}+\mathbf{G}+\mathbf{Q}_{n'}-\mathbf{Q}_n,\quad \delta=i\left[\frac{\hbar}{2N\omega_s(\mathbf{Q})}\right]^{1/2}\mathbf{k}_\mathbf{G}\cdot\varepsilon^{a*}_s(\mathbf{Q})e^{-i\mathbf{Q}\cdot\mathbf{R}_{\mathbf{G}'}} .$$

It should be noted that the rotational invariance gives $V^a_\mathbf{k}(\mathbf{S},\mathbf{s})=V^a_{\mathbf{k}'}(\mathbf{S}',\mathbf{s}')$ with the primes indicating the vectors obtained from an arbitrary rotation. If we make the expansion

$$V^a_{\mathbf{k}_\mathbf{G}}(\mathbf{S},\mathbf{s})=\sum_{J''M''K''}V^{a,J''M''K''}_{\mathbf{k}_\mathbf{G}}(\tau)D^{J''*}_{M''K''}(\Omega) , \tag{52}$$

then from the rotational invariance, $V^{a,J''M''K''}_\mathbf{k}$ is of the form

$$V^{a,J''M''K''}_\mathbf{k}(\tau)=(-1)^{M''}V^{a,J''K''}(\tau,k)Y_{J''-M''}(\hat{\mathbf{k}}) .$$

When $\alpha=(JMK\beta)$, $\alpha'=(J'M'K'\beta')$,

$$(V^{a}_{\mathbf{k}_{\mathrm{G}}})_{\alpha,\alpha'}=(V^{a}_{\mathbf{k}_{\mathrm{G}}})_{JMK\beta,J'M'K'\beta'}$$

$$=\sqrt{(2J+1)(2J'+1)}\sum_{J''M''K''}\frac{(-1)^{M'+K'}}{2J''+1}\langle JMJ'-M'|J''M''\rangle\langle JKJ'-K'|J''K''\rangle(V^{a,J''M''K''}_{\mathbf{k}_{\mathrm{G}}})_{JK\beta,J'K'\beta'}\ . \tag{53}$$

Here

$$(V^{a,J''M''K''}_{\mathbf{k}_{\mathrm{G}}})_{JK\beta,J'K'\beta'}=\int d\tau\, F^{J*}_{K\beta}(\tau)V^{a,J''M''K''}_{\mathbf{k}_{\mathrm{G}}}(\tau)F^{J'}_{K'\beta'}(\tau)\ . \tag{54}$$

When $\alpha=(JMpK\beta)$, $\alpha'=(J'M'p'K'\beta')$ for $K,K'\geq 0$,

$$(V^{a}_{\mathbf{k}_{\mathrm{G}}})_{\alpha,\alpha'}=(V^{a}_{\mathbf{k}_{\mathrm{G}}})_{JMpK\beta,J'M'p'K'\beta'}$$

$$=\sum_{\bar{K}\bar{K}'}C^{J,pK}_{\bar{K}}(V^{a}_{\mathbf{k}_{\mathrm{G}}})_{JM\bar{K}\beta,J'M'\bar{K}'\beta'}C^{J',p'K'}_{\bar{K}'}\ . \tag{55}$$

Finally, if $\alpha=(JMp\gamma)$, $\alpha=(J'M'p'\gamma')$, then

$$(V^{a}_{\mathbf{k}_{\mathrm{G}}})_{\alpha,\alpha'}=\sum_{K\beta,K'\beta'}U^{Jp,\gamma}_{K\beta}(V^{a}_{\mathbf{k}_{\mathrm{G}}})_{JMpK\beta,J'M'p'K'\beta'}U^{J'p',\gamma'}_{K'\beta'}\ . \tag{56}$$

We consider here the potential matrix elements of either the phonon elastic scattering $(n=n')$ or the single-phonon transitions. An extension of the present method to the multiphonon transition potential matrix is straightforward. In the following, we employ a scheme that is different from the others for obtaining the matrix elements. Applying the Baker-Hausdorf theorem to the phonon creation and annihilation operators and using the fact that $|\delta|^2\sim O(1/N)\ll 1$, the matrix element of the interaction potential for the phonon elastic but vibrational-rotational inelastic scattering ($n=n'$ case, i.e., $n_{\mathbf{Q},s}=n'_{\mathbf{Q},s}$ for all $\mathbf{Q},s$) is obtained as

$$V^{\mathrm{G}}_{\alpha n,\alpha' n'}(z)\simeq\frac{N}{L^3}\sum_{ak_z}(V^{a}_{\mathbf{k}_{\mathrm{G}}})_{\alpha,\alpha'}e^{i(k_z z-\mathbf{k}_{\mathrm{G}}\cdot\mathbf{r}_a)}e^{-W_a(\mathbf{k}_{\mathrm{G}})} \tag{57}$$

with

$$W_a(\mathbf{k}_{\mathrm{G}})=\sum_{\mathbf{Q},s}(n_{\mathbf{Q},s}+\tfrac{1}{2})|\delta|^2$$

$$=\frac{1}{2N}\sum_{\mathbf{Q},s}\frac{(n_{\mathbf{Q},s}+\frac{1}{2})\hbar}{\omega_s(\mathbf{Q})}|\mathbf{k}_{\mathrm{G}}\cdot\boldsymbol{\varepsilon}^{a*}_{s}(\mathbf{Q})|^2\ , \tag{58}$$

and $k_{\mathrm{G}}=k_z\hat{\mathbf{z}}+\mathbf{G}$. The simultaneous phonon, vibrational, and rotational elastic scattering is described as $n=n'$, $\alpha=\alpha'$. The matrix element is given by Eq. (57) with $\alpha=\alpha'$. Assuming that the gas-phase and the surface have the same temperatures, the thermal average of the potential which will be used later is defined from

$$v(\mathbf{r})=\langle V\rangle=\frac{\sum\limits_{\alpha,n}\langle\Phi_\alpha,\phi_n|V|\Phi_\alpha,\phi_n\rangle e^{-(E_\alpha+\mathcal{E}_n)/kT}}{\sum\limits_{\alpha,n}e^{-(E_\alpha+\mathcal{E}_n)/kT}}\ . \tag{59}$$

From

$$v(\mathbf{r})=\sum_{\mathbf{G}}v_{\mathbf{G}}(z)e^{i\mathbf{G}\cdot\mathbf{R}}$$

with $v^{*}_{\mathbf{G}}(z)=v_{-\mathbf{G}}(z)$, we have

$$v_{\mathbf{G}}(z)=\frac{\sum\limits_{\alpha,n}V^{\mathbf{G}}_{\alpha n,\alpha n}(z)e^{-(E_\alpha+\mathcal{E}_n)/kT}}{\sum\limits_{\alpha,n}e^{-(E_\alpha+\mathcal{E}_n)/kT}}\ . \tag{60}$$

With approximation $|\delta|^2\ll 1$, $v_{\mathbf{G}}(z)$ is given by Eq. (57) with $(V^{a}_{\mathbf{k}_{\mathrm{G}}})_{\alpha,\alpha'}$ being replaced by $\langle V^{a}_{\mathbf{k}_{\mathrm{G}}}\rangle$ and $W_a(\mathbf{k}_{\mathrm{G}})$ being replaced by $\overline{W}_a(\mathbf{k}_{\mathrm{G}})$, which is again given by Eq. (58) with $n_{\mathbf{Q},s}$ being replaced by $\bar{n}_{\mathbf{Q},s}=1/(e^{\hbar\omega_s(\mathbf{Q})/kT}-1)$, the thermally averaged phonon occupation number. Here,

$$\langle V^{a}_{\mathbf{k}_{\mathrm{G}}}\rangle=\frac{\sum\limits_{\alpha}(V^{a}_{\mathbf{k}_{\mathrm{G}}})_{\alpha,\alpha}e^{-E_\alpha/kT}}{\sum\limits_{\alpha}e^{-E_\alpha/kT}} \tag{61}$$

and $e^{-2\overline{W}_a(\mathbf{k}_{\mathrm{G}})}$ is the Debye-Waller factor.

The matrix element for one-phonon emission having $(\mathbf{Q},s)$ mode is obtained in a similar manner. Therefore, when $n_{\mathbf{Q}'s'}-n'_{\mathbf{Q}'s'}=\delta_{\mathbf{Q},\mathbf{Q}'}\delta_{s,s'}$ for all $(\mathbf{Q}'s')$,

$$V^{\mathrm{G}}_{\alpha n,\alpha' n'}(z)\simeq-\frac{i}{L^3}\left[\frac{\hbar N n_{\mathbf{Q},s}}{2\omega_s(\mathbf{Q})}\right]^{1/2}\sum_{ak_z}\mathbf{k}_{\mathrm{G}}\cdot\boldsymbol{\varepsilon}^{a*}_{s}(\mathbf{Q})(V^{a}_{\mathbf{k}_{\mathrm{G}}})_{\alpha,\alpha'}e^{i(k_z z-\mathbf{k}_{\mathrm{G}}\cdot\mathbf{r}_a)}e^{-W_a(\mathbf{k}_{\mathrm{G}})} \tag{62}$$

with $\mathbf{k}_{\mathrm{G}}=k_z\hat{\mathbf{z}}+\mathbf{G}-\mathbf{Q}$. For the one-phonon annihilation in $(\mathbf{Q},s)$ mode, i.e., for the case $n_{\mathbf{Q}'s'}-n'_{\mathbf{Q}'s'}=-\delta_{\mathbf{Q},\mathbf{Q}'}\delta_{s,s'}$, the expression of the matrix element can be inferred from Eq. (62) using the Hermitian property $V^{\mathrm{G}}_{n,n'}(\mathbf{S},\mathbf{s})=V^{-\mathrm{G}*}_{n',n}(\mathbf{S},\mathbf{s})$. This property is obtained from the relation $V^{a}_{\mathbf{k}}(\mathbf{S},\mathbf{s})=V^{a*}_{-\mathbf{k}}(\mathbf{S},\mathbf{s})$ using the fact that $V^{a}(\mathbf{S},\mathbf{s},\mathbf{r}_{mb})$ is a real function of its arguments.

Thermal average of the molecular states results in the $J''=M''=K''=0$ component, that is, the spherically symmetric component of the molecule-surface interaction potential. This is seen as follows. Since the molecular vibrational and rotational energy E_α with $\alpha=(JMpK\beta)$, for example, is independent of M, we get

$$\sum_{\alpha}(V^{a}_{\mathbf{k}_{\mathbf{G}}})_{\alpha,\alpha}e^{-E_{\alpha}/kT}=\sum_{JpK\beta}e^{-E^{J}_{K\beta}/kT}\sum_{M}(V^{a}_{\mathbf{k}_{\mathbf{G}}})_{\alpha,\alpha}\,.$$

From the relation

$$\sum_{M}(-1)^{M}\langle JMJ-M|J''M''\rangle=(-1)^{J}\sqrt{2J+1}\delta_{J'',0}\delta_{M'',0}\,,$$

we have

$$\sum_{M}(V^{a}_{\mathbf{k}_{\mathbf{G}}})_{\alpha,\alpha}=(2J+1)\sum_{\bar{K}}|C^{J,pK}_{\bar{K}}|^{2}(V^{a,000}_{\mathbf{k}_{\mathbf{G}}})_{J\bar{K}\beta,J\bar{K}\beta}$$

$$\simeq(2J+1)(V^{a,000}_{\mathbf{k}_{\mathbf{G}}})_{\beta,\beta}$$

since the J,K dependences in vibrational wave functions are insignificant.

IV. INTEGRAL EQUATION AND SCATTERING MATRIX

For the thermally averaged potential $v(\mathbf{r})$, one might use a certain molecule–rigid-surface potential. The components of $v(\mathbf{r})$ are given by

$$v^{\mathbf{G}}_{\alpha n,\alpha' n'}(z)=v_{\mathbf{G}}(z)\delta_{\alpha,\alpha'}\delta_{n,n'}\,.$$

The criterion for selecting the potential is to make the quantity $|V^{\mathbf{G}}_{\alpha n,\alpha n}(z)-v_{\mathbf{G}}(z)|$ as small as possible for a certain range of the (αn)'s of interest. Using the potential $v_0(z)$ and $v(\mathbf{r})$, we present various Green functions, integral equations, and the scattering matrix formulations for the molecule-surface system in the following.

A. Distorted-wave Green-function approach

Employing the laterally averaged potential $v_0(z)$, the CDE is transformed into

$$\left[\frac{d^2}{dz^2}+k^{2}_{\alpha n\mathbf{G}}-\frac{2M}{\hbar^2}v_0(z)\right]\psi^{(\pm)}_{\alpha n\mathbf{G},\alpha_i n_i\mathbf{G}_i}(z)=\frac{2M}{\hbar^2}\sum_{\alpha' n'\mathbf{G}'}\tilde{V}^{\mathbf{G}-\mathbf{G}'}_{\alpha n,\alpha' n'}(z)\psi^{(\pm)}_{\alpha' n'\mathbf{G}',\alpha_i n_i\mathbf{G}_i}(z)\,, \tag{63}$$

where

$$\tilde{V}^{\mathbf{G}-\mathbf{G}'}_{\alpha n,\alpha' n'}(z)=V^{\mathbf{G}-\mathbf{G}'}_{\alpha n,\alpha' n'}(z)-v_0(z)\delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{\mathbf{G}-\mathbf{G}',0}\,.$$

The number of coupled channels is determined from that of the $(\alpha n\mathbf{G})$'s. The inclusion of a tremendously large number of phonon states n which are the collections $\{n_{\mathbf{Q},s}\}$ of the occupation numbers and many closed channels makes the numerical integration of the CDE an unmanageably complex task. Therefore, the CDE is not useful for obtaining numerical solutions. Transforming the CDE to an integral equation which does not require as many fine mesh points of the integration as those of the CDE, the scattering problem is tractable with a certain limited choice of the phonon states. This integral equation is solved by iteration and enables us to obtain the numerical solutions effectively. In what follows, the integral equation method is described. The CDE of Eq. (63) is transformed into a coupled integral equation

$$\psi^{(\pm)}_{\alpha n\mathbf{G},\alpha_i n_i\mathbf{G}_i}(z)=\chi^{0(\pm)}_{\alpha n\mathbf{G},\alpha_i n_i\mathbf{G}_i}(z)+\frac{2M}{\hbar^2}\sum_{\alpha' n'\mathbf{G}'}\int_{z_0}^{\infty}dz'\,\mathcal{G}^{0(\pm)}_{\alpha n\mathbf{G}}(z,z')\tilde{V}^{\mathbf{G}-\mathbf{G}'}_{\alpha n,\alpha' n'}(z')\psi_{\alpha' n'\mathbf{G}',\alpha_i n_i\mathbf{G}_i}(z') \tag{64}$$

with

$$\chi^{0(\pm)}_{\alpha n\mathbf{G},\alpha_i n_i\mathbf{G}_i}(z)=\delta_{\alpha,\alpha_i}\delta_{n,n_i}\delta_{\mathbf{G},\mathbf{G}_i}\chi^{0(\pm)}_{\alpha n\mathbf{G}}(z),\quad \mathcal{G}^{0(\pm)}_{\alpha n\mathbf{G}}(z,z')=\chi^{0(\pm)}_{\alpha n\mathbf{G}}(z_<)\eta^{0(\pm)}_{\alpha n\mathbf{G}}(z_>)\,, \tag{65}$$

where $z_< =\min(z,z')$ and $z_> =\max(z,z')$. The $\chi^{0(\pm)}_{\alpha n\mathbf{G}}$ and $\eta^{0(\pm)}_{\alpha n\mathbf{G}}$ satisfy

$$\left[\frac{d^2}{dz^2}+k^{2}_{\alpha n\mathbf{G}}-\frac{2M}{\hbar^2}v_0(z)\right]\begin{bmatrix}\chi^{0(\pm)}_{\alpha n\mathbf{G}}(z)\\ \eta^{0(\pm)}_{\alpha n\mathbf{G}}(z)\end{bmatrix}=0 \tag{66}$$

with $\chi^{0(\pm)}_{\alpha n\mathbf{G}}(z_0)=0$. They also satisfy the following asymptotic boundary conditions:

$$\chi^{0(\pm)}_{\alpha n\mathbf{G}}(z)\sim\begin{cases}e^{\mp ik_{\alpha n\mathbf{G}}z}-s^{(\pm)}_{\alpha n\mathbf{G}}e^{\pm ik_{\alpha n\mathbf{G}}z} & \text{(open channel)}\,,\\ e^{\kappa_{\alpha n\mathbf{G}}z}-\bar{s}_{\alpha n\mathbf{G}}e^{-\kappa_{\alpha n\mathbf{G}}z} & \text{(closed channel)}\,,\end{cases} \tag{67}$$

$$\eta^{0(\pm)}_{\alpha n\mathbf{G}}(z)\sim\begin{cases}\dfrac{\pm 1}{2ik_{\alpha n\mathbf{G}}}e^{\pm ik_{\alpha n\mathbf{G}}z} & \text{(open channel)}\,,\\ \dfrac{-1}{2\kappa_{\alpha n\mathbf{G}}}e^{-\kappa_{\alpha n\mathbf{G}}z} & \text{(closed channel)}\,,\end{cases} \tag{68}$$

with $s^{(\pm)}_{\alpha n\mathbf{G}}=e^{\pm 2i\delta_{\alpha n\mathbf{G}}}$. Here $\delta_{\alpha n\mathbf{G}}$ is the phase shift from the potential $v_0(z)$. Although $k_{\alpha n\mathbf{G}}$, $\chi^{0(\pm)}_{\alpha n\mathbf{G}}(z)$, and $\delta_{\alpha n\mathbf{G}}$ are independent of M, the eigenvalue of J_z, we will keep the notations as they are. From Eqs. (64)–(68), we have the S matrix

$$S^{(\pm)}_{\alpha n\mathbf{G},\alpha_i n_i\mathbf{G}_i}=\delta_{\alpha,\alpha_i}\delta_{n,n_i}\delta_{\mathbf{G},\mathbf{G}_i}s^{(\pm)}_{\alpha n\mathbf{G}}+C^{(\pm)}_{\alpha n\mathbf{G},\alpha_i n_i\mathbf{G}_i}\sum_{\alpha' n'\mathbf{G}'}\int_{z_0}^{\infty}dz'\chi^{(\mp)*}_{\alpha n\mathbf{G}}(z')\tilde{V}^{\mathbf{G}-\mathbf{G}'}_{\alpha n,\alpha' n'}(z')\psi^{(\pm)}_{\alpha' n'\mathbf{G}',\alpha_i n_i\mathbf{G}_i}(z') \tag{69}$$

with

$$C^{(\pm)}_{\alpha n\mathbf{G},\alpha_i n_i\mathbf{G}_i}=\frac{\pm iM}{\hbar^2(k_{\alpha n\mathbf{G}}k_{\alpha_i n_i\mathbf{G}_i})^{1/2}}$$

$\chi^{0(+)}_{\alpha n\mathbf{G}}(z)$, $\mathcal{G}^{0(+)}_{\alpha n\mathbf{G}}(z,z')$, and $s^{(+)}_{\alpha n\mathbf{G}}$ are complex conjugates of $\chi^{0(-)}_{\alpha n\mathbf{G}}(z)$, $\mathcal{G}^{0(-)}_{\alpha n\mathbf{G}}(z,z')$, and $s^{(-)}_{\alpha n\mathbf{G}}$, respectively.

We define the distorted wave functions for arbitrary initial conditions $(\alpha' n'\mathbf{G}')$ as

$$\begin{aligned}\chi^{0(\pm)}_{\mathbf{K},\alpha' n'\mathbf{G}'}(\mathbf{r},\mathbf{S},\mathbf{s})&=\sum_{\alpha n\mathbf{G}}\chi^{0(\pm)}_{\alpha n\mathbf{G},\alpha' n'\mathbf{G}'}(z)\Phi_\alpha(\mathbf{S},\mathbf{s})|\phi_n\rangle e^{i(\mathbf{K}-\mathbf{Q}_n+\mathbf{G})\cdot\mathbf{R}}\\&=\chi^{0(\pm)}_{\alpha' n'\mathbf{G}'}(z)\Phi_{\alpha'}(\mathbf{S},\mathbf{s})|\phi_{n'}\rangle e^{i(\mathbf{K}-\mathbf{Q}_{n'}+\mathbf{G}')\cdot\mathbf{R}}\ .\end{aligned} \tag{70}$$

The $\chi^{0(\pm)}_{\mathbf{K},\alpha' n'\mathbf{G}'}$ are distorted wave functions from the potential $v_0(z)$, that is, the eigenfunctions of the Hamiltonian

$$H^0=-\frac{\hbar^2}{2M}\nabla_r^2+H_{\text{mol}}+H_{\text{cr}}+v_0(z)\ . \tag{71}$$

More specifically, we have the following Lippmann-Schwinger equation:

$$(E-H^0\pm i\epsilon)\chi^{0(\pm)}_{\mathbf{K},\alpha n\mathbf{G}}(\mathbf{r},\mathbf{S},\mathbf{s})=\pm i\epsilon\varphi^{(\mp)}_{\mathbf{K},\alpha n\mathbf{G}}(\mathbf{r},\mathbf{S},\mathbf{s})\ . \tag{72}$$

Employing the orthogonality relations and Eqs. (17) and (70), we rewrite Eq. (69) as

$$S^{(\pm)}_{\alpha n\mathbf{G},\alpha_i n_i\mathbf{G}_i}=\delta_{\alpha,\alpha_i}\delta_{n,n_i}\delta_{\mathbf{G},\mathbf{G}_i}s^{(\pm)}_{\alpha n\mathbf{G}}+\frac{C^{(\pm)}_{\alpha n\mathbf{G},\alpha_i n_i\mathbf{G}_i}}{L^2}\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,\chi^{0(\mp)\dagger}_{\mathbf{K},\alpha n\mathbf{G}}(\mathbf{r},\mathbf{S},\mathbf{s})\tilde{V}(\mathbf{r},\mathbf{S},\mathbf{s})\psi^{(\pm)}_{\mathbf{K},\alpha_i n_i\mathbf{G}_i}(\mathbf{r},\mathbf{S},\mathbf{s}) \tag{73}$$

with $\tilde{V}(\mathbf{r},\mathbf{S},\mathbf{s})=V(\mathbf{r},\mathbf{S},\mathbf{s})-v_0(z)$.

Defining the Green-function components as

$$\mathcal{G}^{0(\pm)}_{\alpha n\mathbf{G},\alpha' n'\mathbf{G}'}(z,z')=\delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{\mathbf{G},\mathbf{G}'}\mathcal{G}^{0(\pm)}_{\alpha n\mathbf{G}}(z,z')\ , \tag{74}$$

we obtain the following Green operators:

$$\begin{aligned}\mathcal{G}^{0(\pm)}_{\mathbf{K}}(\mathbf{r},\mathbf{S},\mathbf{s};\mathbf{r}',\mathbf{S}',\mathbf{s}')&=\sum_{\substack{\alpha n\mathbf{G}\\ \alpha' n'\mathbf{G}'}}\langle\mathbf{R},\mathbf{S},\mathbf{s}|\alpha n\mathbf{G}\rangle\mathcal{G}^{0(\pm)}_{\alpha n\mathbf{G},\alpha' n'\mathbf{G}'}(z,z')\langle\alpha' n'\mathbf{G}'|\mathbf{R}',\mathbf{S}',\mathbf{s}'\rangle\\&=\frac{1}{L^2}\sum_{\alpha n\mathbf{G}}\Phi_\alpha(\mathbf{S},\mathbf{s})|\phi_n\rangle\langle\phi_n|\Phi^*_\alpha(\mathbf{S}',\mathbf{s}')\mathcal{G}^{0(\pm)}_{\alpha n\mathbf{G}}(z,z')e^{i(\mathbf{K}-\mathbf{Q}_n+\mathbf{G})\cdot(\mathbf{R}-\mathbf{R}')}\ .\end{aligned} \tag{75a}$$

The following orthonormal basis functions for a given $\mathbf{K}$:

$$\langle\mathbf{R},\mathbf{S},\mathbf{s}|\alpha n\mathbf{G}\rangle\equiv\Psi_{\alpha n\mathbf{G}}(\mathbf{R},\mathbf{S},\mathbf{s})\equiv\frac{1}{L}\Phi_\alpha(\mathbf{S},\mathbf{s})|\phi_n\rangle e^{i(\mathbf{K}-\mathbf{Q}_n+\mathbf{G})\cdot\mathbf{R}} \tag{75b}$$

were used. Note that $\langle\alpha n\mathbf{G}|\alpha' n'\mathbf{G}'\rangle=\delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{\mathbf{G},\mathbf{G}'}$. The Green operators satisfy

$$\mathcal{G}^{0(\pm)\dagger}_{\mathbf{K}}(\mathbf{r},\mathbf{S},\mathbf{s};\mathbf{r}',\mathbf{S}',\mathbf{s}')=\mathcal{G}^{0(\mp)}_{\mathbf{K}}(\mathbf{r}',\mathbf{S}',\mathbf{s}';\mathbf{r},\mathbf{S},\mathbf{s})\ .$$

It is seen that

$$\mathcal{G}^{0(\pm)}_{\alpha n\mathbf{G},\alpha' n'\mathbf{G}'}(z,z')=\frac{\hbar^2}{2M}\left\langle\alpha n\mathbf{G}\left|\frac{1}{E-H^0\pm i\epsilon}\right|\alpha' n'\mathbf{G}'\right\rangle\ .$$

Using Eqs. (17), (70), and (75) with the orthogonality relations mentioned before, we rewrite Eq. (64) as

$$\psi^{(\pm)}_{\mathbf{K},\alpha_i n_i\mathbf{G}_i}(\mathbf{r},\mathbf{S},\mathbf{s})=\chi^{0(\pm)}_{\mathbf{K},\alpha_i n_i\mathbf{G}_i}(\mathbf{r},\mathbf{S},\mathbf{s})+\frac{2M}{\hbar^2}\int d\mathbf{r}'d\mathbf{S}'d\mathbf{s}'\mathcal{G}^{0(\pm)}_{\mathbf{K}}(\mathbf{r},\mathbf{S},\mathbf{s};\mathbf{r}',\mathbf{S}',\mathbf{s}')\tilde{V}(\mathbf{r}',\mathbf{S}',\mathbf{s}')\psi^{(\pm)}_{\mathbf{K},\alpha_i n_i\mathbf{G}_i}(\mathbf{r}',\mathbf{S}',\mathbf{s}')\ . \tag{76}$$

For $(\alpha n\mathbf{G})\neq(\alpha_i n_i 0)$, we define the transition matrix (T matrix) as

$$T_{\alpha n\mathbf{G},\alpha_i n_i 0}=\frac{1}{L^3}\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,\chi^{0(-)\dagger}_{\mathbf{K},\alpha n\mathbf{G}}(\mathbf{r},\mathbf{S},\mathbf{s})\tilde{V}(\mathbf{r},\mathbf{S},\mathbf{s})\psi^{(+)}_{\mathbf{K},\alpha_i n_i 0}(\mathbf{r},\mathbf{S},\mathbf{s})\ . \tag{77}$$

Then from Eq. (73), we have

$$T_{\alpha n\mathbf{G},\alpha_i n_i 0}=(C^{(+)}_{\alpha n\mathbf{G},\alpha_i n_i 0}L)^{-1}S^{(+)}_{\alpha n\mathbf{G},\alpha_i n_i 0} \; . \tag{78}$$

Equations (77) and (78) also define the off-shell T or S matrix when $\chi^{(-)}$ and $\psi^{(+)}$ are the solutions corresponding to different total energies E. Including the $(\alpha n\mathbf{G})=(\alpha_i n_i 0)$ case in general, Eq. (78) gives the definition of the T matrix for the molecule-surface scattering.

The vibrational-rotational and phonon transition diffraction coefficient $(\alpha_i n_i \neq \alpha_f n_f)$ is given by

$$\frac{d^2\sigma}{d\Omega_{\mathbf{k}_f} dE_f^p}=\left[\frac{ML^3}{2\pi\hbar^2}\right]^2 \frac{k_f}{k_i}\sum_{n_f}\langle \delta(\mathcal{E}_f-\mathcal{E}_i+\hbar\omega)|T_{\alpha_f n_f \mathbf{G}_f,\alpha_i n_i 0}|^2\rangle \; , \tag{79}$$

where the bracket denotes the thermal average over the initial phonon states n_i, i.e.,

$$\langle O_{n_i}\rangle \equiv \frac{\sum_{n_i} Q_{n_i} e^{-\mathcal{E}_{n_i}/kT}}{\sum_{n_i} e^{-\mathcal{E}_{n_i}/kT}} \; .$$

As we see from Eq. (79), the energy is conserved with

$$\hbar\omega=E_f^p+E_{\alpha_f}-E_i^p-E_{\alpha_i}, \quad E_f^p=\frac{\hbar^2 k_f^2}{2M}, \quad E_i^p=\frac{\hbar^2 k_i^2}{2M} \; .$$

Here, $\mathbf{k}_f=\mathbf{K}_f+\hat{\mathbf{z}}k_{fz}$ is the final scattered molecular momentum, with $\mathbf{K}_f$ being the projection of $\mathbf{k}_f$ onto the surface and given by $\mathbf{K}_f=\mathbf{K}_i+\mathbf{Q}_{n_i}-\mathbf{Q}_{n_f}+\mathbf{G}_f=\mathbf{K}-\mathbf{Q}_{n_f}+\mathbf{G}_f$. Conservation of the total parallel momentum has already been taken into account in the T matrix. The vibrational-rotational and phonon transition diffraction coefficient can be written using Eq. (78) as

$$\frac{d^2\sigma}{d\Omega_{\mathbf{k}_f} dE_f^p}=\left[\frac{L^2}{2\pi}\right]^2 \frac{k_f}{k_i}\sum_{n_f}\langle \delta(\mathcal{E}_f-\mathcal{E}_i+\hbar\omega)k_{\alpha_f n_f \mathbf{G}_f}k_{\alpha_i n_i 0}|S^{(+)}_{\alpha_f n_f \mathbf{G}_f,\alpha_i n_i 0}|^2\rangle \; . \tag{80}$$

B. Diffractive-wave Green-function method

In this subsection, we study the diffractive wave function from the thermally averaged potential $v(\mathbf{r})$. The $\chi^{(\pm)}_{\mathbf{K},\alpha' n' \mathbf{G}'}$ are the diffractive wave functions from $v(\mathbf{r})$ with outgoing and incoming boundary conditions. The Hamiltonian H^v for the potential $v(\mathbf{r})$ and corresponding Lippmann-Schwinger equation are, respectively, given by

$$\begin{gathered} H^v=-\frac{\hbar^2}{2M}\nabla_r^2+H_{\mathrm{mol}}+H_{\mathrm{cr}}+v(\mathbf{r}) \; , \\ (E-H^v\pm i\epsilon)\chi^{(\pm)}_{\mathbf{K},\alpha' n' \mathbf{G}'}(\mathbf{r},\mathbf{S},\mathbf{s})=\pm i\epsilon\varphi^{(\mp)}_{\mathbf{K},\alpha' n' \mathbf{G}'}(\mathbf{r},\mathbf{S},\mathbf{s}) \; . \end{gathered} \tag{81}$$

This equation is different from what was expected from the conventional scattering theory, where the collision partners are spatially localized. The relations between the incoming and outgoing waves will be discussed in the next section. Expanding the wave function as

$$\chi^{(\pm)}_{\mathbf{K},\alpha' n' \mathbf{G}'}(\mathbf{r},\mathbf{S},\mathbf{s})=\sum_{\alpha n\mathbf{G}}\chi^{(\pm)}_{\alpha n\mathbf{G},\alpha' n' \mathbf{G}'}(z)\Phi_\alpha(\mathbf{S},\mathbf{s})|\phi_n\rangle e^{i(\mathbf{K}-\mathbf{Q}_n+\mathbf{G})\cdot\mathbf{R}} \; ,$$

we can see that

$$\chi^{(\pm)}_{\alpha n\mathbf{G},\alpha' n' \mathbf{G}'}(z)=\delta_{n,n'}\delta_{\alpha,\alpha'}\chi^{(\pm)}_{\alpha n\mathbf{G},\mathbf{G}'}(z) \tag{82}$$

and Eq. (81) results in a CDE and asymptotic boundary condition for the open and closed channels as

$$\left[\frac{d^2}{dz^2}+k^2_{\alpha n\mathbf{G}}-\frac{2M}{\hbar^2}v_0(z)\right]\chi^{(\pm)}_{\alpha n\mathbf{G},\mathbf{G}'}(z)=\frac{2M}{\hbar^2}\sum_{\mathbf{G}''}\tilde{v}_{\mathbf{G}-\mathbf{G}''}(z)\chi^{(\pm)}_{\alpha n\mathbf{G}'',\mathbf{G}'}(z) \tag{83}$$

and

$$\chi^{(\pm)}_{\alpha n\mathbf{G},\mathbf{G}'}(z)\sim\left[\frac{k_{\alpha n\mathbf{G}'}}{k_{\alpha n\mathbf{G}}}\right]^{1/2}(e^{\mp ik_{\alpha n\mathbf{G}}z}\delta_{\mathbf{G},\mathbf{G}'}-\mathcal{S}^{(\pm)}_{\alpha n\mathbf{G},\alpha n\mathbf{G}'}e^{\pm ik_{\alpha n\mathbf{G}}z}) \; , \tag{84a}$$

$$\chi^{(\pm)}_{\alpha n\mathbf{G},\mathbf{G}'}(z) \sim \left[\frac{k_{\alpha n\mathbf{G}'}}{\kappa_{\alpha n\mathbf{G}}}\right]^{1/2} \bar{\mathcal{S}}^{(\pm)}_{\alpha n\mathbf{G},\alpha n\mathbf{G}'} e^{-\kappa_{\alpha n\mathbf{G}} z} \; . \tag{84b}$$

Here, $\tilde{v}_{\mathbf{G}-\mathbf{G}'}(z)=v_{\mathbf{G}-\mathbf{G}'}(z)-v_0(z)\delta_{\mathbf{G},\mathbf{G}'}$. The integral equation for the diffractive wave functions and the integral expression of the phonon and molecular elastic ($n=n'$, $\alpha=\alpha'$) diffractive scattering matrix $\mathcal{S}^{(\pm)}$ can be written as

$$\chi^{(\pm)}_{\alpha n\mathbf{G},\mathbf{G}'}(z)=\delta_{\mathbf{G},\mathbf{G}'}\chi^{0(\pm)}_{\alpha n\mathbf{G}}(z)+\frac{2M}{\hbar^2}\sum_{\mathbf{G}''}\int dz'\,\mathcal{G}^{0(\pm)}_{\alpha n\mathbf{G}}(z,z')\tilde{v}_{\mathbf{G}-\mathbf{G}''}(z')\chi^{(\pm)}_{\alpha n\mathbf{G}'',\mathbf{G}'}(z') \; , \tag{85}$$

$$\mathcal{S}^{(\pm)}_{\alpha n\mathbf{G},\alpha n\mathbf{G}'}=\delta_{\mathbf{G},\mathbf{G}'}s^{(\pm)}_{\alpha n\mathbf{G}}+C^{(\pm)}_{\alpha n\mathbf{G},\alpha n\mathbf{G}'}\sum_{\mathbf{G}''}\int dz\,\chi^{0(\mp)*}_{\alpha n\mathbf{G}}(z)\tilde{v}_{\mathbf{G}-\mathbf{G}''}(z)\chi^{(\pm)}_{\alpha n\mathbf{G}'',\mathbf{G}'}(z) \; . \tag{86}$$

In what follows, a matrix $A_{\alpha n\mathbf{G},\alpha' n'\mathbf{G}'}(z,z')$ will be denoted as $[A]$. Here, $(\alpha n\mathbf{G}z)$ and $(\alpha' n'\mathbf{G}'z')$ are regarded as the row and the column indices, respectively, with z,z' being continuous variables. With these definitions, matrix multiplication then takes the following form:

$$([A][B])_{\alpha n\mathbf{G},\alpha' n'\mathbf{G}'}(z,z')=\sum_{\alpha'' n''\mathbf{G}''}\int dz''\,A_{\alpha n\mathbf{G},\alpha'' n''\mathbf{G}''}(z,z'')B_{\alpha'' n''\mathbf{G}'',\alpha' n'\mathbf{G}'}(z'',z') \; ,$$

and the Hermitian conjugation is expressed as

$$[A]^{\dagger}_{\alpha n\mathbf{G},\alpha' n'\mathbf{G}'}(z,z')=A^{*}_{\alpha' n'\mathbf{G}',\alpha n\mathbf{G}}(z',z) \; .$$

We define the following matrices for bracket notation as

$$\begin{aligned} 1_{\alpha n\mathbf{G},\alpha' n'\mathbf{G}'}(z,z') &= \delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{\mathbf{G},\mathbf{G}'}\delta(z-z') \; , \\ L^{0(\pm)}_{\alpha n\mathbf{G},\alpha' n'\mathbf{G}'}(z,z') &= \frac{2M}{\hbar^2}\langle \alpha n\mathbf{G}|E-H^0\pm i\epsilon|\alpha' n'\mathbf{G}'\rangle \\ &= \left[\frac{d^2}{dz^2}+k^2_{\alpha n\mathbf{G}}-\frac{2M}{\hbar^2}v_0(z)\pm i\epsilon\right]\delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{\mathbf{G},\mathbf{G}'}\delta(z-z') \; . \end{aligned} \tag{87}$$

The Green-function matrices $[\mathcal{G}^{0(\pm)}]$ corresponding to $[L^{0(\pm)}]$ have already been obtained in Eq. (74). It is seen that $[L^{0(\pm)}]^{\dagger}=[L^{0(\mp)}]$, $[\mathcal{G}^{0(\pm)}]^{\dagger}=[\mathcal{G}^{0(\mp)}]$. Here the Hermitian conjugate is the same as the complex conjugate. Furthermore,

$$[L^{0(\pm)}][\mathcal{G}^{0(\pm)}]=[\mathcal{G}^{0(\pm)}][L^{0(\pm)}]=[1] \; .$$

The component wave function $\psi^{(+)}_{\alpha n\mathbf{G},\alpha' n'\mathbf{G}'}(z)$, $\chi^{0(+)}_{\alpha n\mathbf{G},\alpha' n'\mathbf{G}'}(z)$, $\chi^{(+)}_{\alpha n\mathbf{G},\alpha' n'\mathbf{G}'}(z)$, etc., are regarded as the elements of column matrices $[\psi^{(+)}_{\alpha' n'\mathbf{G}'}(z)]$, $[\chi^{0(+)}_{\alpha' n'\mathbf{G}'}(z)]$, $[\chi^{(+)}_{\alpha' n'\mathbf{G}'}(z)]$, etc. We also define a column matrix $[\varphi^{(\mp)}_{\alpha' n'\mathbf{G}'}(z)]$ with the elements

$$\varphi^{(\mp)}_{\alpha n\mathbf{G},\alpha' n'\mathbf{G}'}(z)=e^{\mp ik_{\alpha n\mathbf{G}}z}\delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{\mathbf{G},\mathbf{G}'} \; .$$

Note that

$$\varphi^{(\pm)}_{\mathbf{K},\alpha' n'\mathbf{G}'}(\mathbf{r},\mathbf{S},\mathbf{s})=\sum_{\alpha n\mathbf{G}}\varphi^{(\pm)}_{\alpha n\mathbf{G},\alpha' n'\mathbf{G}'}(z)\Phi_{\alpha}(\mathbf{S},\mathbf{s})|\phi_n\rangle e^{i(\mathbf{K}-\mathbf{Q}_n+\mathbf{G})\cdot\mathbf{R}} \; .$$

By iteration, Eq. (85) is rewritten in the following form:

$$[\chi^{(\pm)}_{\alpha' n'\mathbf{G}'}]=[\chi^{0(\pm)}_{\alpha' n'\mathbf{G}'}]+\frac{2M}{\hbar^2}[\mathcal{G}^{0(\pm)}][\tilde{v}][\chi^{(\pm)}_{\alpha' n'\mathbf{G}'}]=\left[[1]+\frac{2M}{\hbar^2}[\mathcal{G}^{(\pm)}][\tilde{v}]\right][\chi^{0(\pm)}_{\alpha' n'\mathbf{G}'}] \tag{88}$$

with

$$\begin{aligned} \tilde{v}_{\alpha n\mathbf{G},\alpha' n'\mathbf{G}'}(z,z') &= (v_{\mathbf{G}-\mathbf{G}'}(z)-v_0(z)\delta_{\mathbf{G},\mathbf{G}'})\delta_{\alpha,\alpha'}\delta_{n,n'}\delta(z-z') \; , \\ [\mathcal{G}^{(\pm)}] &= [\mathcal{G}^{0(\pm)}]+\frac{2M}{\hbar^2}[\mathcal{G}^{0(\pm)}][\tilde{v}][\mathcal{G}^{(\pm)}]=[\mathcal{G}^{0(\pm)}]+\frac{2M}{\hbar^2}[\mathcal{G}^{(\pm)}][\tilde{v}][\mathcal{G}^{0(\pm)}] \; . \end{aligned} \tag{89}$$

We have $[\tilde{v}]^{\dagger}=[\tilde{v}]$ and thus $[\mathcal{G}^{(\pm)}]^{\dagger}=[\mathcal{G}^{(\mp)}]$. The $[\tilde{v}]$ is block diagonal and so is $[\mathcal{G}^{(\pm)}]$, that is,

$$\mathcal{G}^{(\pm)}_{\alpha n\mathbf{G},\alpha' n'\mathbf{G}'}(z,z')=\delta_{\alpha,\alpha'}\delta_{n,n'}\mathcal{G}^{(\pm)}_{\alpha n\mathbf{G},\mathbf{G}'}(z,z') \; .$$

The Green-function matrix $[\mathcal{G}^{(\pm)}]$ is useful for obtaining the approximation scheme, in particular, the coupled-channel transition-matrix element to be discussed in the following paper.

Employing the following matrices:

$$\bar{V}_{\alpha n\mathbf{G},\alpha' n'\mathbf{G}'}(z,z')=(V^{\mathbf{G}-\mathbf{G}'}_{\alpha n,\alpha' n'}(z)-v_{\mathbf{G}-\mathbf{G}'}(z)\delta_{\alpha,\alpha'}\delta_{n,n'})\delta(z-z') \ , \tag{90}$$

$$\begin{aligned}L^{(\pm)}_{\alpha n\mathbf{G},\alpha' n'\mathbf{G}'}(z,z')&=\frac{2M}{\hbar^2}\langle \alpha n\mathbf{G}|E-H^{v}\pm i\epsilon|\alpha' n'\mathbf{G}'\rangle\\ &=\left[\left(\frac{d^2}{dz^2}+k^2_{\alpha n\mathbf{G}}\pm i\epsilon\right)\delta_{\mathbf{G},\mathbf{G}'}-\frac{2M}{\hbar^2}v_{\mathbf{G}-\mathbf{G}'}(z)\right]\delta_{\alpha,\alpha'}\delta_{n,n'}\delta(z-z') \ ,\end{aligned} \tag{91}$$

we obtain the matrix forms of differential Lippmann-Schwinger equations, Eqs. (72) and (81), as

$$[L^{0(\pm)}][\chi^{0(\pm)}_{\alpha' n'\mathbf{G}'}]=\pm i\epsilon[\varphi^{(\mp)}_{\alpha' n'\mathbf{G}'}], \quad [L^{(\pm)}][\chi^{(\pm)}_{\alpha' n'\mathbf{G}'}]=\pm i\epsilon[\varphi^{(\mp)}_{\alpha' n'\mathbf{G}'}] \tag{92}$$

and likewise the matrix form of differential Lippmann-Schwinger equation of the total wave function in terms of $[L^{(+)}]$, $[\bar{V}]$, $[\psi^{(\pm)}]$, and $[\varphi^{(\mp)}]$. Note that $[\bar{V}]^{\dagger}=[\bar{V}]$. Using Eq. (89) and the relation $[L^{(\pm)}]-[L^{0(\pm)}]=-(2M/\hbar^2)[\bar{v}]$, we obtain

$$[L^{(\pm)}][\mathcal{G}^{(\pm)}]=[\mathcal{G}^{(\pm)}][L^{(\pm)}]=[1] \ . \tag{93}$$

The matrix form of the differential Lippmann-Schwinger equation of the total wave function is then transformed into a matrix form of integral equation,

$$[\psi^{(\pm)}_{\alpha_i n_i 0}]=[\chi^{(\pm)}_{\alpha_i n_i 0}]+\frac{2M}{\hbar^2}[\mathcal{G}^{(\pm)}][\bar{V}][\psi^{(\pm)}_{\alpha_i n_i 0}] \ , \tag{94}$$

by multiplying $[\mathcal{G}^{(\pm)}]$ to the former. From Eq. (89), we have the asymptotic behavior

$$([\mathcal{G}^{(\pm)}][\bar{V}][\psi^{(\pm)}_{\alpha_i n_i 0}])_{\alpha' n'\mathbf{G}'}(z)\sim\frac{\pm 1}{2ik_{\alpha' n'\mathbf{G}'}}e^{\pm ik_{\alpha' n'\mathbf{G}'}z}[\chi^{(\mp)}_{\alpha' n'\mathbf{G}'}]^{\dagger}[\bar{V}][\psi^{(\pm)}_{\alpha_i n_i 0}] \ . \tag{95}$$

From Eqs. (25), (94), and (95), we obtain the following integral expression of the S matrix:

$$S^{(\pm)}_{\alpha_f n_f\mathbf{G}_f,\alpha_i n_i 0}=\delta_{\alpha_f,\alpha_i}\delta_{n_f,n_i}\mathcal{S}^{(\pm)}_{\alpha_f n_f\mathbf{G}_f,\alpha_f n_f 0}+C^{(\pm)}_{\alpha_f n_f\mathbf{G}_f,\alpha_i n_i 0}[\chi^{(\mp)}_{\alpha_f n_f\mathbf{G}_f}]^{\dagger}[\bar{V}][\psi^{(\pm)}_{\alpha_i n_i 0}] \tag{96}$$

with

$$\bar{V}^{\mathbf{G}''-\mathbf{G}'}_{\alpha_f n_f,\alpha' n'}(z)=V^{\mathbf{G}''-\mathbf{G}'}_{\alpha_f n_f,\alpha' n'}(z)-v_{\mathbf{G}''-\mathbf{G}'}(z)\delta_{\alpha_f,\alpha'}\delta_{n_f,n'} \ .$$

Equation (29) is also satisfied by $\chi^{(\pm)}_{\mathbf{K},\alpha' n'\mathbf{G}'}$, $\chi^{(\pm)}_{\alpha n\mathbf{G},\alpha' n'\mathbf{G}'}$, and $\mathcal{S}^{(\pm)}_{\alpha n\mathbf{G},\alpha' n'\mathbf{G}'}$ as functions of **K**, **G**, and **G**′. Equation (96) can be rewritten as

$$S^{(\pm)}_{\alpha_f n_f\mathbf{G}_f,\alpha_i n_i 0}=\delta_{\alpha_f,\alpha_i}\delta_{n_f,n_i}\mathcal{S}^{(\pm)}_{\alpha_f n_f\mathbf{G}_f,\alpha_f n_f 0}+\frac{C^{(\pm)}_{\alpha_f n_f\mathbf{G}_f,\alpha_i n_i 0}}{L^2}\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,\chi^{(\mp),\dagger}_{\mathbf{K},\alpha_f n_f\mathbf{G}_f}(\mathbf{r},\mathbf{S},\mathbf{s})\bar{V}(\mathbf{r},\mathbf{S},\mathbf{s})\psi^{(\pm)}_{\mathbf{K},\alpha_i n_i 0}(\mathbf{r},\mathbf{S},\mathbf{s}) \ , \tag{97}$$

with

$$\bar{V}(\mathbf{r},\mathbf{S},\mathbf{s})=V(\mathbf{r},\mathbf{S},\mathbf{s})-v(\mathbf{r})=\sum_{nn'\mathbf{G}}|\phi_n\rangle\bar{V}^{\mathbf{G}}_{n,n'}(z,\mathbf{S},\mathbf{s})\langle\phi_{n'}|e^{i(\mathbf{Q}_{n'}-\mathbf{Q}_n+\mathbf{G})\cdot\mathbf{R}} \ .$$

The first term in Eq. (96) or (97) is the phonon and molecular elastic diffractive S matrix from $v(\mathbf{r})$. The phonon transition ($n_f\neq n_i$) matrix $T_{\alpha_f n_f\mathbf{G}_f,\alpha_i n_i 0}$ is given by the integral expression of Eq. (97) for $S^{(+)}$ multiplied by $(C^{(+)}L)^{-1}$ as seen from the relation between the S and T matrices given by Eq. (78). We write the Green operator $\mathcal{G}^{(\pm)}_{\mathbf{K}}$ as follows:

$$\mathcal{G}^{(\pm)}_{\mathbf{K}}(\mathbf{r},\mathbf{S},\mathbf{s};\mathbf{r}',\mathbf{S}',\mathbf{s}')=\sum_{\substack{\alpha n\mathbf{G}\\ \alpha' n'\mathbf{G}'}}\langle\mathbf{r},\mathbf{S},\mathbf{s}|\alpha n\mathbf{G}\rangle\mathcal{G}^{(\pm)}_{\alpha n\mathbf{G},\alpha' n'\mathbf{G}'}(z,z')\langle\alpha' n'\mathbf{G}'|\mathbf{r}'\mathbf{S}'\mathbf{s}'\rangle \ . \tag{98}$$

It is seen that $\mathcal{G}^{(\pm)\dagger}_{\mathbf{K}}(\mathbf{r},\mathbf{S},\mathbf{s};\mathbf{r}',\mathbf{S}',\mathbf{s}')=\mathcal{G}^{(\mp)}_{\mathbf{K}}(\mathbf{r}',S',\mathbf{s}';\mathbf{r},\mathbf{S},\mathbf{s})$. Equation (94) can be written as an integral equation with the help of the orthogonality relation of the basis function

$$\psi^{(\pm)}_{\mathbf{K},\alpha_i n_i 0}(\mathbf{r},\mathbf{S},\mathbf{s})=\chi^{(\pm)}_{\mathbf{K},\alpha_i n_i 0}(\mathbf{r},\mathbf{S},\mathbf{s})+\frac{2M}{\hbar^2}\int d\mathbf{r}'d\mathbf{S}'d\mathbf{s}'\mathcal{G}^{(\pm)}_{\mathbf{K}}(\mathbf{r},\mathbf{S},\mathbf{s};\mathbf{r}',\mathbf{S}',\mathbf{s}')\bar{V}(\mathbf{r}',\mathbf{S}',\mathbf{s}')\psi^{(\pm)}_{\mathbf{K},\alpha_i n_i 0}(\mathbf{r}',\mathbf{S}',\mathbf{s}') \ . \tag{99}$$

In the same manner as before, one can see that for any division of the full potential $V=V^1+V^2$,

$$S^{(\pm)}_{\alpha_f n_f\mathbf{G}_f,\alpha_i n_i 0}=\mathcal{S}^{1,(\pm)}_{\alpha_f n_f\mathbf{G}_f,\alpha_i n_i 0}+C^{(\pm)}_{\alpha_f n_f\mathbf{G}_f,\alpha_i n_i 0}[\chi^{1,(\mp)}_{\alpha_f n_f\mathbf{G}_f}]^{\dagger}[V^2][\psi^{(\pm)}_{\alpha_i n_i 0}] \ . \tag{100}$$

Here, $\mathcal{S}^{1,(\pm)}$ and $\chi^{1,(\mp)}$ are the scattering matrix and wave function from the Lippmann-Schwinger equation for V^1. Equations (73), (97), and (100) are the two-potential method of S matrix theory in a molecule-surface system. The first terms in these equations cannot be expressed as matrix elements of V^1 between *plane wave* and $\chi^{1,(\pm)}$ in contrast to the conventional scattering theory.

V. THE TIME-REVERSAL INVARIANCE AND MICROSCOPIC REVERSIBILITY FOR TRIATOMIC-MOLECULE–SURFACE SYSTEM

For each phonon state $|\phi_n\rangle$, there exists a unique (phonon) state $|\phi_{\tilde{n}}\rangle$ such that $\tilde{n}_{\mathbf{Q},s}=n_{-\mathbf{Q},s}$. Thus $\mathbf{Q}_{\tilde{n}}=-\mathbf{Q}_n$ and $\tilde{\tilde{n}}=n$. The time-reversal operator $\mathcal{T}=\mathcal{U}\mathcal{C}$ of the present (spinless) molecule-surface system is defined such that $\mathcal{C}$ is the complex-conjugate operation of c numbers of $\mathcal{U}|\phi_n\rangle=|\phi_{\tilde{n}}\rangle$ for any n. In other words,

$$\mathcal{T}\left[\sum_n \chi_n(\mathbf{r},\mathbf{S},\mathbf{s})|\phi_n\rangle\right]=\sum_n \chi_n^*(\mathbf{r},\mathbf{S},\mathbf{s})|\phi_{\tilde{n}}\rangle$$

with the $\chi_n(\mathbf{r},\mathbf{S},\mathbf{s})$'s being the c-number functions. The operator $\mathcal{U}$ is then unitary and $\mathcal{T}$ is antiunitary with $\mathcal{T}^{-1}=\mathcal{T}$. Obviously $\mathcal{T}v(\mathbf{r})\mathcal{T}^{-1}=v(\mathbf{r})$ since $v(\mathbf{r})$ is real and diagonal with respect to the molecular and phonon states α,n. In this section, we consider the molecular states with a definite parity. Therefore, $\alpha=(JMpK\beta)$ or $\alpha=(JMp\gamma)$. The molecular state $-\alpha$ is used to denote $-\alpha=(J-MpK\beta)$ or $(J-Mp\gamma)$ for the α previously given. The time-reversal invariance of $v(\mathbf{r})$ mentioned before is then equivalent to

$$v_{\mathbf{G}}(z)\delta_{\alpha,\alpha'}\delta_{n,n'}=\epsilon_\alpha\epsilon_{\alpha'}v^*_{-\mathbf{G}}(z)\delta_{-\alpha,-\alpha'}\delta_{\tilde{n},\tilde{n}'}\ . \tag{101}$$

Here, the phase factors $\epsilon_\alpha=(-1)^{J+M+p}$, $\epsilon_{\alpha'}=(-1)^{J'+M'+p'}$ are introduced to make Eq. (101) consistent with the general expression of invariance discussed later, although $\epsilon_\alpha\epsilon_{\alpha'}$ becomes 1 because of $\delta_{\alpha,\alpha'}$. This equation can also be obtained from the Hermiticity $v_{\mathbf{G}}(z)=v^*_{-\mathbf{G}}(z)$. Several physical quantities depend on the total parallel momentum $\mathbf{K}$. To show such dependence explicitly, we will sometime use the notation $\chi^{(\pm)}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}(z;\mathbf{K})$, $k^2_{\alpha n\mathbf{G}}(\mathbf{K})$, etc., as we did before. Since $\chi^{(+)}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}(z;\mathbf{K})$ and $\chi^{(-)}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}(z;\mathbf{K})$ satisfy the CDE of Eq. (83) but have different boundary conditions given by Eq. (84), we obtain

$$\begin{aligned}\chi^{(\pm)}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}(z;\mathbf{K})&=\epsilon_\alpha\epsilon_{\alpha'}\chi^{(\mp)*}_{-\alpha\tilde{n}-\mathbf{G},-\alpha'\tilde{n}'-\mathbf{G}'}(z;-\mathbf{K})\ ,\\ \mathcal{S}^{(\pm)}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}(\mathbf{K})&=\epsilon_\alpha\epsilon_{\alpha'}\mathcal{S}^{(\mp)*}_{-\alpha\tilde{n}-\mathbf{G},-\alpha'\tilde{n}'-\mathbf{G}'}(-\mathbf{K})\ ,\end{aligned} \tag{102}$$

using Eq. (101) and the relation $k^2_{\alpha n\mathbf{G}}(\mathbf{K})=k^2_{-\alpha\tilde{n}-\mathbf{G}}(-\mathbf{K})$. When $\alpha=(JMpK\beta)$ or $\alpha=(JMp\gamma)$, we have $\Phi^*_\alpha(\mathbf{S},\mathbf{s})=\epsilon_\alpha\Phi_{-\alpha}(\mathbf{S},\mathbf{s})$ since the $U^{Jp,\gamma}_{K\beta}$'s are real. Thus, we obtain

$$\begin{aligned}\mathcal{T}\chi^{(\pm)}_{\mathbf{K},\alpha'n'\mathbf{G}'}(\mathbf{r},\mathbf{S},\mathbf{s})&=\epsilon_{\alpha'}\chi^{(\mp)}_{-\mathbf{K},-\alpha'\tilde{n}'-\mathbf{G}'}(\mathbf{r},\mathbf{S},\mathbf{s})\ ,\\ \mathcal{T}\varphi^{(\pm)}_{\mathbf{K},\alpha'n'\mathbf{G}'}(\mathbf{r},\mathbf{S},\mathbf{s})&=\epsilon_{\alpha'}\varphi^{(\mp)}_{-\mathbf{K},-\alpha'\tilde{n}'-\mathbf{G}'}(\mathbf{r},\mathbf{S},\mathbf{s})\ ,\\ \mathcal{T}\chi^{0(\pm)}_{\mathbf{K},\alpha'n'\mathbf{G}'}(\mathbf{r},\mathbf{S},\mathbf{s})&=\epsilon_{\alpha'}\chi^{0(\mp)}_{-\mathbf{K},-\alpha'\tilde{n}'-\mathbf{G}'}(\mathbf{r},\mathbf{S},\mathbf{s})\ .\end{aligned}$$

From Eq. (101) and using Eq. (89) or (93), we can show that

$$\mathcal{G}^{(\pm)}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}(z,z';\mathbf{K})=\epsilon_\alpha\epsilon_{\alpha'}\mathcal{G}^{(\pm)}_{-\alpha'\tilde{n}'-\mathbf{G}',-\alpha\tilde{n}-\mathbf{G}}(z',z;-\mathbf{K})\ .$$

This relation results in the equation

$$\mathcal{T}\mathcal{G}^{(\pm)}_{\mathbf{K}}(\mathbf{r},\mathbf{S},\mathbf{s};\mathbf{r}',\mathbf{S}',\mathbf{s}')\mathcal{T}^{-1}=\mathcal{G}^{(\mp)}_{-\mathbf{K}}(\mathbf{r},\mathbf{S},\mathbf{s};\mathbf{r}',\mathbf{S}',\mathbf{s}')\ .$$

The same relation holds for $\mathcal{G}^{0(\pm)}_{\mathbf{K}}(\mathbf{r},\mathbf{S},\mathbf{s};\mathbf{r}',\mathbf{S}',\mathbf{s}')$. So far the factor $\epsilon_\alpha\epsilon_{\alpha'}$ is redundant since it becomes 1 due to the fact that the relevant quantities are zero for $\alpha\neq\alpha'$. In what follows the factor has its own right since the relevant quantities are not zero for $\alpha\neq\alpha'$. We can show that

$$\mathcal{U}a_{\mathbf{Q},s}\mathcal{U}^{-1}=a_{-\mathbf{Q},s},\quad \mathcal{U}a^\dagger_{\mathbf{Q},s}\mathcal{U}^{-1}=a^\dagger_{-\mathbf{Q},s}\ .$$

Therefore,

$$\begin{aligned}&\mathcal{T}\mathbf{u}^a(\mathbf{R}_\mathbf{G})\mathcal{T}^{-1}=\mathbf{u}^a(\mathbf{R}_\mathbf{G}),\quad \mathcal{T}\mathbf{p}^a(\mathbf{R}_\mathbf{G})\mathcal{T}^{-1}=-\mathbf{p}^a(\mathbf{R}_\mathbf{G})\ ,\\ &\mathcal{T}H_{\mathrm{cr}}\mathcal{T}^{-1}=H_{\mathrm{cr}},\quad \mathcal{T}\mathbf{P}\mathcal{T}^{-1}=-\mathbf{P}\ ,\\ &\mathcal{T}\mathcal{K}_{\mathrm{cr}}\mathcal{T}^{-1}=-\mathcal{K}_{\mathrm{cr}},\quad \mathcal{T}\mathcal{K}\mathcal{T}^{-1}=-\mathcal{K}\ ,\\ &\mathcal{T}H_{\mathrm{mol}}\mathcal{T}^{-1}=H_{\mathrm{mol}},\quad \mathcal{T}H^v\mathcal{T}^{-1}=H^v\ .\end{aligned} \tag{103}$$

Since the molecule-surface potential $V=V(\mathbf{r},\mathbf{S},\mathbf{s},\mathbf{u}^a(\mathbf{R}_\mathbf{G}))$ is Hermitian, the Fourier components in Eq. (50) satisfy $V^{a*}_{\mathbf{k}}=V^a_{-\mathbf{k}}$. In other words, V is a real function of $\mathbf{u}^a(\mathbf{R}_\mathbf{G})$. Thus, from Eq. (103), we also have

$$\mathcal{T}V\mathcal{T}^{-1}=V,\quad \mathcal{T}H\mathcal{T}^{-1}=H\ .$$

The time-reversal invariance of V is seen to be equivalent to

$$\begin{aligned}V^{\mathbf{G}}_{n,n'}(z,\mathbf{S},\mathbf{s})&=V^{-\mathbf{G}*}_{\tilde{n},\tilde{n}'}(z,\mathbf{S},\mathbf{s})\ ,\\ V^{\mathbf{G}}_{\alpha n,\alpha'n'}(z)&=\epsilon_\alpha\epsilon_{\alpha'}V^{-\mathbf{G}*}_{-\alpha\tilde{n},-\alpha'\tilde{n}'}(z)\ .\end{aligned} \tag{104}$$

Employing the same method as before with Eq. (104), we obtain

$$\begin{aligned}\psi^{(\pm)}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}(z;\mathbf{K})&=\epsilon_\alpha\epsilon_{\alpha'}\psi^{(\mp)*}_{-\alpha\tilde{n}-\mathbf{G},-\alpha'\tilde{n}'-\mathbf{G}'}(z;-\mathbf{K})\ ,\\ S^{(\pm)}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}(\mathbf{K})&=\epsilon_\alpha\epsilon_{\alpha'}S^{(\mp)*}_{-\alpha\tilde{n}-\mathbf{G},-\alpha'\tilde{n}'-\mathbf{G}'}(-\mathbf{K})\ .\end{aligned}$$

Therefore,

$$\mathcal{T}\psi^{(\pm)}_{\mathbf{K},\alpha'n'\mathbf{G}'}(\mathbf{r},\mathbf{S},\mathbf{s})=\epsilon_{\alpha'}\psi^{(\mp)}_{-\mathbf{K},-\alpha'\tilde{n}'-\mathbf{G}'}(\mathbf{r},\mathbf{S},\mathbf{s})\ .$$

It is thus seen that differential or integral equations satisfied by wave functions of incoming boundary conditions having superscripts $(-)$ in Eqs. (11), (72), (76), (81), and (99) are obtained from those satisfied by the wave functions of outgoing boundary conditions having superscripts $(+)$ by operating $\mathcal{T}$ with subsequent replacement $(-\mathbf{K},-\alpha_i\tilde{n}_i-\mathbf{G}_i)\rightarrow(\mathbf{K},\alpha_i n_i\mathbf{G}_i)$ and vice versa. The relations between the incoming and outgoing wave functions obtained in this section are not trivial. These equations are different from those of the ordinary scattering theory where the collision partners are spatially localized. Equation (99) is expressed in matrix form as

$$[\psi^{(\pm)}_{\alpha'n'\mathbf{G}'}]=[\chi^{(\pm)}_{\alpha'n'\mathbf{G}'}]+\frac{2M}{\hbar^2}[\mathcal{G}^{(\pm)}][\bar{V}][\psi^{(\pm)}_{\alpha'n'\mathbf{G}'}]$$

$$=\left\{[1]+\frac{2M}{\hbar^2}[\mathcal{G}^{t(\pm)}][\bar{V}]\right\}[\chi^{(\pm)}_{\alpha'n'\mathbf{G}'}]\ , \qquad (105)$$

where

$$[\mathcal{G}^{t(\pm)}]=[\mathcal{G}^{(\pm)}]+\frac{2M}{\hbar^2}[\mathcal{G}^{(\pm)}][\bar{V}][\mathcal{G}^{t(\pm)}]$$

$$=[\mathcal{G}^{(\pm)}]+\frac{2M}{\hbar^2}[\mathcal{G}^{t(\pm)}][\bar{V}][\mathcal{G}^{(\pm)}]\ . \qquad (106)$$

Equation (76) can be rewritten as

$$[\psi^{(\pm)}_{\alpha'n'\mathbf{G}'}]=[\chi^{0(\pm)}_{\alpha'n'\mathbf{G}'}]+\frac{2M}{\hbar^2}[\mathcal{G}^{0(\pm)}][\tilde{V}][\psi^{(\pm)}_{\alpha'n'\mathbf{G}'}]$$

$$=\left\{[1]+\frac{2M}{\hbar^2}[\mathcal{G}^{t(\pm)}][\tilde{V}]\right\}[\chi^{0(\pm)}_{\alpha'n'\mathbf{G}'}]\ , \qquad (107)$$

with

$$[\mathcal{G}^{t(\pm)}]=[\mathcal{G}^{0(\pm)}]+\frac{2M}{\hbar^2}[\mathcal{G}^{0(\pm)}][\tilde{V}][\mathcal{G}^{t(\pm)}]$$

$$=[\mathcal{G}^{0(\pm)}]+\frac{2M}{\hbar^2}[\mathcal{G}^{t(\pm)}][\tilde{V}][\mathcal{G}^{0(\pm)}]\ . \qquad (108)$$

One sees that the same Green function $[\mathcal{G}^{t(\pm)}]$ is expressed in different forms, Eqs. (106) and (108). Note further that $[\mathcal{G}^{t(\pm)}]^\dagger=[\mathcal{G}^{t(\mp)}]$. Defining

$$L^{t(\pm)}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}(z,z')=\frac{2M}{\hbar^2}\langle \alpha n\mathbf{G}|E-H\pm i\epsilon|\alpha'n'\mathbf{G}'\rangle$$

$$=\left[\left\{\frac{d^2}{dz^2}+k^2_{\alpha n\mathbf{G}}\pm i\epsilon\right\}\delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{\mathbf{G},\mathbf{G}'}-\frac{2M}{\hbar^2}V^{\mathbf{G}}_{\alpha n,\alpha'n'}(z)\right]\delta(z-z')\ .$$

and employing the same method as before, we have

$$[L^{t(\pm)}][\mathcal{G}^{t(\pm)}]=[\mathcal{G}^{t(\pm)}][L^{t(\pm)}]=[1] \qquad (109)$$

and thus

$$\mathcal{G}^{t(\pm)}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}(z,z')=\frac{\hbar^2}{2M}\left\langle \alpha n\mathbf{G}\left|\frac{1}{E-H\pm i\epsilon}\right|\alpha'n'\mathbf{G}'\right\rangle\ .$$

We can also show that

$$\mathcal{G}^{t(\pm)}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}(z,z';\mathbf{K})=\epsilon_\alpha\epsilon_{\alpha'}\mathcal{G}^{t(\pm)}_{-\alpha'\tilde{n}'-\mathbf{G}',-\alpha\tilde{n}-\mathbf{G}}(z',z;-\mathbf{K})\ . \qquad (110)$$

Equation (110) is equivalent to

$$\mathcal{T}\mathcal{G}^{t(\pm)}_{\mathbf{K}}(\mathbf{r},\mathbf{S},\mathbf{s};\mathbf{r}',\mathbf{S}',\mathbf{s}')\mathcal{T}^{-1}=\mathcal{G}^{t(\mp)}_{-\mathbf{K}}(\mathbf{r},\mathbf{S},\mathbf{s};\mathbf{r}',\mathbf{S}',\mathbf{s}')\ .$$

The Green operators $\mathcal{G}^{t(\pm)}_{\mathbf{K}}(\mathbf{r},\mathbf{S},\mathbf{s};\mathbf{r}',\mathbf{S}',\mathbf{s}')$ were defined as before from $\mathcal{G}^{t(\pm)}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}$. These $\mathcal{G}^{t(\pm)}$'s are the Green functions of the full Hamiltonian H. It can be seen easily from Eqs. (105) and (106) that

$$\frac{1}{L^2}\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,\chi^{(-)\dagger}_{\mathbf{K},\alpha_b n_b\mathbf{G}_b}(\mathbf{r},\mathbf{S},\mathbf{s})\bar{V}(\mathbf{r},\mathbf{S},\mathbf{s})\psi^{(+)}_{\mathbf{K},\alpha_a n_a\mathbf{G}_a}(\mathbf{r},\mathbf{S},\mathbf{s})=\frac{1}{L^2}\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,\psi^{(-)\dagger}_{\mathbf{K},\alpha_b n_b\mathbf{G}_b}(\mathbf{r},\mathbf{S},\mathbf{s})\bar{V}(\mathbf{r},\mathbf{S},\mathbf{s})\chi^{(+)}_{\mathbf{K},\alpha_a n_a\mathbf{G}_a}(\mathbf{r},\mathbf{S},\mathbf{s})\ . \qquad (111)$$

From Eqs. (107) and (108), we also have

$$T_{ba}\equiv\frac{1}{L^3}\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,\chi^{0(-)\dagger}_{\mathbf{K},\alpha_b n_b\mathbf{G}_b}(\mathbf{r},\mathbf{S},\mathbf{s})\tilde{V}(\mathbf{r},\mathbf{S},\mathbf{s})\psi^{(+)}_{\mathbf{K},\alpha_a n_a\mathbf{G}_a}(\mathbf{r},\mathbf{S},\mathbf{s})$$

$$=\frac{1}{L^3}\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,\psi^{(-)\dagger}_{\mathbf{K},\alpha_b n_b\mathbf{G}_b}(\mathbf{r},\mathbf{S},\mathbf{s})\tilde{V}(\mathbf{r},\mathbf{S},\mathbf{s})\chi^{0(+)}_{\mathbf{K},\alpha_a n_a\mathbf{G}_a}(\mathbf{r},\mathbf{S},\mathbf{s})\ . \qquad (112)$$

Substituting the time-reversal invariance $\mathcal{T}\tilde{V}(\mathbf{r},\mathbf{S},\mathbf{s})\mathcal{T}^{-1}=\tilde{V}(\mathbf{r},\mathbf{S},\mathbf{s})$ into the first line of Eq. (112), we obtain

$$T_{ba}\equiv\frac{1}{L^3}\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}[\mathcal{T}\psi^{(+)}_{\mathbf{K},\alpha_a n_a\mathbf{G}_a}(\mathbf{r},\mathbf{S},\mathbf{s})]^\dagger\tilde{V}(\mathbf{r},\mathbf{S},\mathbf{s})\mathcal{T}\chi^{0(-)}_{\mathbf{K},\alpha_b n_b\mathbf{G}_b}(\mathbf{r},\mathbf{S},\mathbf{s})$$

$$=\epsilon_{\alpha_a}\epsilon_{\alpha_b}\frac{1}{L^3}\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,\psi^{(-)\dagger}_{-\mathbf{K},-\alpha_a\tilde{n}_a-\mathbf{G}_a}(\mathbf{r},\mathbf{S},\mathbf{s})\tilde{V}(\mathbf{r},\mathbf{S},\mathbf{s})\chi^{0(+)}_{-\mathbf{K},-\alpha_b\tilde{n}_b-\mathbf{G}_b}(\mathbf{r},\mathbf{S},\mathbf{s})\ . \qquad (113)$$

Equations (112) and (113) with $s^{(+)}_{\alpha n \mathbf{G}}(\mathbf{K}) = s^{(+)}_{-\alpha \tilde{n} - \mathbf{G}}(-\mathbf{K})$ result in

$$S^{(+)}_{\alpha_b n_b \mathbf{G}_b, \alpha_a n_a \mathbf{G}_a}(\mathbf{K}) = \epsilon_{\alpha_a} \epsilon_{\alpha_b} S^{(+)}_{-\alpha_a \tilde{n}_a - \mathbf{G}_a, -\alpha_b \tilde{n}_b - \mathbf{G}_b}(-\mathbf{K}) . \quad (114)$$

This is the statement of the microscopic reversibility. We consider now the reflection cases ($\mathbf{G}_a = \mathbf{G}_b = 0$) for simplicity. The probability that a molecule with, e.g., $(J_a M_a p_a \gamma_a)$ and parallel momentum $\mathbf{K}_a$ collides with the surface and is scattered with $(J_b M_b p_b \gamma_b)$ and $\mathbf{K}_b$ with the creation of a single phonon in mode $(\mathbf{Q}, s)$ is the same as the probability that the molecule is incident with $(J_b - M_b p_b \gamma_b)$ and parallel momentum $-\mathbf{K}_b$ and scattered with $(J_a - M_a p_a \gamma_a)$ and $-\mathbf{K}_a$ with the annihilation of a single phonon having $(-\mathbf{Q}, s)$. The reversibility could be tested by a measurement. For the atom-surface system, the fact that the half-collision processes, adsorption and desorption, are related to each other through the microscopic reversibility has been observed.[37]

VI. SUMMARY AND DISCUSSIONS

We have developed a systematic (quantum-mechanical) formulation of the triatomic-molecule–crystalline-surface scattering dynamics that takes into account the vibrational and rotational states of the projectile, diffraction, and phonons in the solid by extending the previous work on the atom-surface scattering.[59] The vibrational and rotational motions of the triatomic molecule are treated by separating out the center of mass of the molecule, which can be applied to general polyatomic molecules scattered by a surface. The present formulation is derived based on the time-independent scattering theory, in contrast to most other work on atom or diatom-surface scattering where time-dependent theory was employed. With the translational symmetry of (triatomic) molecule-surface system, total (projectile+phonon) momentum representation parallel to the surface was employed in the formulation, which is analogous to the total angular momentum representation of the gas-phase scattering where rotational symmetry exists. This representation greatly simplifies the triatom-surface scattering formulation. We presented here the properties of the total scattering wave function of the triatomic-molecule–crystalline-surface system with the inclusion of phonons in the solid and vibrations and rotations of the projectile, a representation of the simultaneous phonon and internal (vibrational-rotational) state transition potential matrix, the coupled differential equation, and independent physical solutions for given energy and momentum. These are all obtained based on the translational invariance of the total Hamiltonian. The coupled differential equation serves as a basis to further develop scattering formulations and to introduce approximation schemes, although it is not useful in practice for computing the wave function and scattering amplitudes because of the very large number of phonon and vibrational-rotational states involved.

The scattering equations of the system in differential and integral forms as well as the related Green functions were also obtained. They are not the same as those from the ordinary scattering theory where the collision partners are spatially localized. In particular, explicit configuration expressions of the Green function of the molecule-surface system presented here including phonons and vibrations and rotations are quite different from those of the conventional collision theory. Several important versions of the integral expressions of the scattering and transition matrix are presented. They are useful for obtaining realistic computational approximation schemes, e.g., higher-order DWBA and multiphonon processes, as we shall see in the following paper.

The time-reversal invariance and the microscopic reversibility of the triatomic-molecule–surface scattering have also been discussed. The equations between the incoming and outgoing scattering wave functions that are important in the T matrix schemes were also obtained. One notices that these nontrivial equations and the scattering equation in differential form [see, e.g., Eq. (11)] are different from those of the ordinary scattering theory. We have further obtained the relation between the scattering matrix elements describing the microscopic reversibility in the present triatomic-molecule–surface system. Our results have shown that the phonon annihilation and creation are mutually time-reversed phenomena which can be tested by experiments.

The *ab initio* results on the gas phase, in particular, triatomic-molecule–surface interaction potential are nonexistent as mentioned before. One aim of the triatomic-molecule–surface-collision study is to obtain the precise nature of the interaction potential for other applications. The theoretical scattering dynamics is employed to assist the determination of an accurate potential by comparing the computational results with the experiments. Therefore, an accurate collision dynamics is desirable. We have developed a formulation of the triatomic-molecule–surface scattering dynamics that can be used for obtaining an *ab initio* calculational scheme and a realistic approximation method, and at the same time can be adopted to a general input potential. Thus our formulation presented here and the calculation schemes to be derived in the following paper should be useful for extracting information regarding the gas-surface potential and for interpreting the experiments.

Based on the present formulation, we present in the following paper, specific theoretical schemes for simultaneous diffraction, phonon, and vibrational-rotational transitions suitable for the triatomic molecular projectile, the bound-state-resonance scattering approach for phonon- and rotation-mediated selective adsorption and desorption, and a method of obtaining the physisorption probability.

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