PHYSICAL REVIEW B VOLUME 42, NUMBER 7 1 SEPTEMBER 1990

Theory of vibrational, rotational, and phonon inelastic collisions of a triatomic molecule by a crystal surface. II. Approximate methods and applications to resonance and adsorption

B. H. Choi, Z. B. Güvenç,* and N. L. Liu

Department of Physics, University of California, Riverside, Riverside, California 92521

(Received 17 August 1989; revised manuscript received 1 February 1990)

Realistic theoretical approximation schemes for the calculation of phonon and vibrational-rotational (triatomic) molecule–crystal-surface inelastic scattering were derived from the formulation in the preceding paper. These schemes can be adopted to a flexible input potential and are at the same time capable of yielding effective *ab initio* computation. An iterative coupled-integral-equation method thus obtained is much more tractable than its counterpart of the coupled differential equation when phonons in the solid and vibrations and rotations of the molecular projectile are taken into account. This approach is further useful for the triatomic projectile case where multiphonon transitions become more probable compared to the light atom and/or diatom projectile, since it yields calculational procedures of DWBA of any higher orders as a byproduct. A rotationally impulsive integral-equation scheme appropriate for the triatomic molecular projectile (and basically applicable to the polyatomic case) with simplification of the rotational states of the molecule in the calculational procedures is also derived from this method. For the purpose of studying direct (nonresonant) inelastic scattering of the simultaneous diffraction, phonon, and vibrational-rotational transitions, angular, velocity, and vibrational-rotational state distribution of the scattered molecule, a coupled-diffractive-channel transition-matrix (CDCTM) method and a coupled-molecular-state transition-matrix (CMSTM) method with an exponential unitarization scheme are obtained. The former may be used when the corrugation of the molecule–crystal-surface interaction potential is significant as in nonmetallic crystals and the latter could be used when the dependence on the internal coordinates of the molecule or the anisotropy is considerably large in the interaction potential. As an application of the present scattering formulation, a bound-state resonance scattering method for a (triatomic) molecule-surface system is presented within the framework of a Feshbach-type internal excitation approach. Our emphasis here is on a systematic and unified treatment of the mediations of the diffraction, phonon, and vibration-rotation in selective adsorption and desorption, which are analogous to compound nucleus theory in nuclear reaction studies. The present method describes such trapping-desorption processes for inelastic (indirect) resonance scattering. Our method is adoptable again to arbitrary input potentials, and even with inclusion of phonons and vibrations and rotations, it yields efficient *ab initio* calculational procedures from which the resonance energies, the energy shift, width function, line shapes, and the intensities of the simultaneous diffraction, phonon, and vibrational-rotational transitions can be obtained. Among other effective calculational schemes, we discuss a method where the bound-state resonance scattering amplitude is computed from our explicit expressions with simplified wave functions. They are obtained as products of the spatial wave function generated from the elastic diffraction potential and vibrational-rotational and phonon states. The nonresonant potential scattering amplitude is obtained within open channels from, e.g., a coupled-diffractive-channel transition-matrix approach. Finally, a method of obtaining the quantal trapping or physisorption probabilities of the molecule, which deals with a half-collision process, is presented as another application of our scattering formulation.

I. INTRODUCTION

In the preceding paper,[1] which will be referred to here as paper I, we have developed a systematic formulation of the triatomic-molecule–crystal-surface scattering dynamics including the vibrational states of the atoms or ions in the solid (phonon) and vibrational-rotational states of the projectile. The triatomic projectile case has more applicabilities than its atom or diatom counterpart. The formulation is based on the total (projectile+phonon) momentum representation parallel to the surface using time-independent scattering theory. The scattering equation in differential and integral forms as well as the corresponding Green's functions were obtained. It is desirable to have theoretical schemes that are realistic and at the same time amenable to practical *ab initio* calculation for the interpretation of the experimental measurements on the simultaneous vibration-rotation (mainly rotation) and phonon inelastic scattering, the energy transfers between translations, vibrations, rotations, and phonons, and angular, velocity, and rotational state distributions of the scattered molecules, and rotation- and phonon-mediated resonances (selective adsorption and desorption).[2] In this paper, we obtain such theoretical schemes suitable for the triatomic-molecular-projectile case (which can be essentially applied to the general polyatomic case) based on the formulation in paper I.

An iterative coupled integral equation is derived from the distorted-wave Green function with phonons and vibrations and rotations of the triatom. It is much more tractable than the corresponding coupled differential equation (CDE) and capable of yielding an efficient *ab initio* calculational scheme when suitable truncation of the phonon states is made. The CDE could be replaced by this equation in the future when phonons and vibrations and rotations are included. Compared to atom or diatomic molecular projectile, phonon transition probabilities are large for the triatomic or polyatomic molecule case. Moreover, multiphonon inelastic scattering and the participation of bulk phonons become probable in addition to the elastic and single-Rayleigh-phonon inelastic scattering.[2] The present iterative integral approach is further useful for studying multiphonon processes since it yields calculational procedures of any higher-order DWBA. From iterative coupled integral equations, we derive a rotationally impulsive iterative equation method that is appropriate for the triatomic-molecular-projectile case and basically can be applied to the general polyatomic case again. This method reduces the complexity of the calculation arising from the rotational states of the triatomic molecule.

Simultaneous rotation and phonon inelastic scattering was experimentally studied.[2,3] Employing laser-induced fluorescence,[4] multiphonon ionization,[5] infrared (IR) excitation with bolometric detection,[6] and IR emission,[7,8] the vibrational and rotational state distributions of the scattered molecules have been measured. An experiment on vibrationally inelastic scattering for a triatom-surface system was also performed with IR spectroscopy.[7] Based on these state selective detection methods with angular and velocity distributions of the scattered molecules,[9] the energy transfers among translations, vibrations, rotations and phonons are investigated. Angular distribution is used to separate direct scattering from indirect trapping-desorption (Feshbach-type resonance) inelastic scattering.

Depending on the incident angles or energies, direct or indirect (resonance) processes are dominant. We develop in this paper theoretical schemes for the simultaneous diffraction, vibration-rotation and phonon transitions with direct inelastic-scattering processes: the coupled-diffractive-channel transition-matrix method (CDCTM) and coupled-molecular-state transition-matrix method (CMSTM) incorporated with an exponential unitarization scheme. The former may be used when corrugation of the molecule-surface potential is significant. The coupling between the reciprocal lattice points due to the molecule-surface interaction is taken into account in the incident and the scattered wave functions of the projectile. When the dependence of the molecule-surface potential on the internal coordinates of the projectile is significant, in particular, when the anisotropy of the potential is considerably large, the latter method could be employed. The dynamic coupling between the vibrational-rotational states of the projectile through the interaction potential is included in the incident and scattered wave functions. The two theoretical schemes might be used for studying angular, velocity, and vibrational-rotational state distributions of the scattered molecule and energy transfers among vibrations and rotations and phonons.

The experimental measurements have been carried out on the phonon or rotational transition resonance scattering for the molecule-surface system with improved time-of-flight techniques and resolutions.[2] The selective adsorption of the molecule mediated by phonon,[10] diffraction, or rotation[11] was observed from the angular distribution measurements. The lifetime of such temporarily bound state of the molecule on the surface or the width of the resonance depends on the (selective) adsorption and desorption probability upon transition of the phonon, rotation, or vibration. Theoretical methods describing such resonance phenomena have been developed based on the simple-potential model with impulsive or sudden approximation, optical-potential model,[12] and hard corrugated wall model[13] with eikonal approximation derived from the elastic-diffractive-resonance scattering case.[14] These methods could give reasonable results for certain cases, but are somewhat phenomenological and the applications are limited since the potentials employed are not flexible. Again *ab initio* computational schemes of the lifetime, theoretical intensities, and line shapes of such diffraction-, phonon-, and rotation-mediated resonance processes, which can be adopted to a general (triatomic) molecule-surface input potential, are desired as noted in paper I for the interpretation of the measurements so that it can be applied to the assessment of the precise nature of the potential.

The selective adsorption with diffraction, phonon, or vibration-rotation assistance results from the effect of the closed channels at the energies where the molecular projectile is temporarily bound to the surface. The coupling between the closed channel and open diffraction (or reflection) channel results in the resonance scattering. In other words, the projectile is temporarily trapped to the surface and after a certain lifetime it is desorbed again from the surface upon transition of phonon, rotation, and vibration. This is basically the (indirect) trapping-desorption inelastic scattering in contrast to the direct inelastic collisions and also analogous to the compound nucleus theory in the nuclear reaction study. It is consistent with the principle of the Feshbach-type approach.[15] For the atom or diatom–surface elastic diffraction case, close-coupling studies[16,17] have been quite useful for describing the selective-adsorption phenomena. It was also useful for studying rotation-mediated selective adsorption of the diatom-surface scattering case.[18] Computations, however, are complex due to the large number of closed channels included. When phonons and vibrations and rotations are taken into account, the close-coupling calculations are almost impossible. For these reasons, the Feshbach-type approach which describes the trapping-desorption scattering is most suitable for *ab initio* theoretical study of the phonon- and vibration-rotation-mediated bound-state resonance scattering (selective adsorption and desorption). Nevertheless, there exists no such systematic treatments for molecule-surface scattering, although the method was suggested in the atom-surface diffraction case[19] with the hard corrugated potential model.

Therefore, we present the phonon-, and vibration-rotation-assisted bound-state resonance scattering method suitable for the triatomic-molecule–surface system within the framework of the Feshbach approach based on our formulation in paper I. Some approximation schemes for computations are also described. Compared with the other related theoretical works including those with the Feshbach approach, whereas they have their own merits, our method is adoptable to an arbitrary molecule-surface interaction potential, takes into account simultaneous diffraction, vibration-rotation, and phonon mediations in a systematic and unified manner, and describes the trapping-desorption mechanism explicitly. The present method is *ab initio* in nature and yields an effective calculational scheme (see Sec. III for more details).

As another application of the present triatomic-molecule–surface scattering dynamics, we present a method of obtaining the quantum-mechanical physisorption or trapping probabilities. This phenomenon arises mainly from the long-range attractive (van der Waals) potential and can be described basically by the half-collision processes. Most of these quantities have so far been computed employing the classical stochastic trajectory method with the generalized Langevin equation[20] or (the one-dimensional) semiclassical method with the harmonic oscillator.[21] The classical stochastic trajectory or semiclassical approaches may be efficient but have somewhat limited applicabilities due to the quantum-mechanical effects (e.g., tunneling) that are important in the thermal energy range.

In the next section, the approximate theoretical schemes for the calculation of the simultaneous phonon, vibrational-rotational inelastic scattering suitable for the triatomic-molecular-projectile case are derived from the formulations presented in paper I. The phonon- and vibration-rotation-mediated bound-state resonance scattering method is presented in Sec. III within the framework of the Feshbach approach. A method of obtaining the quantum-mechanical trapping or physisorption probabilities is presented in Sec. IV. In the last section, the present work is summarized. An exponential unitarization scheme of the transition-matrix method of molecule-surface scattering is described in the Appendix. Some numerical results obtained from the theoretical schemes presented in this paper will be reported in later publications. Equation (*n*) of paper I will be indicated as Eq. I (*n*). We will use the same notations as in paper I unless specified otherwise.

II. APPROXIMATION SCHEMES FOR TRIATOMIC-MOLECULE–SURFACE INELASTIC-SCATTERING THEORY

Many computations of the atom-surface phonon inelastic scattering have been developed based on the simple distorted-wave Born approximation (DWBA). For the present triatomic-molecule–surface vibrational-rotational, phonon inelastic scattering case, this approximation is given by

$$\begin{aligned} \psi^{(+)}_{\mathbf{K},\alpha_i n_i 0}(\mathbf{r},\mathbf{S},\mathbf{s}) &\simeq \chi^{0(+)}_{\mathbf{K},\alpha_i n_i 0}(\mathbf{r},\mathbf{S},\mathbf{s}) \;, \\ \chi^{0(-)}_{\mathbf{K},\alpha n \mathbf{G}}(\mathbf{r},\mathbf{S},\mathbf{s}) &\simeq \chi^{0(-)}_{\mathbf{K},\alpha n 0}(\mathbf{r},\mathbf{S},\mathbf{s})\delta_{\mathbf{G},0} \end{aligned} \tag{1}$$

in Eqs. I (76) and I (73) of the integral expressions of T and S matrices, respectively, obtained from the distorted-wave Green function. The normalization condition of the S matrix elements, which is a special case of the unitarity condition of the matrix, is usually taken into account in this approximation. The normalization of the S matrix is not sufficient to obtain reliable values of the matrix elements. Therefore, we present a unitarized DWBA S-matrix method in the Appendix. In any case, the diffraction effect to the vibrational-rotational and phonon inelastic scattering cannot be studied with DWBA, because the wave functions given by Eq. (1) are distorted only from $v_0(z)$ which does not contain any diffraction part. The corrugation of the potential is significant in the interaction between the gas phase and nonmetallic crystalline surface or adsorbate covered surface. Therefore, the inclusion of the diffractive part in the scattering wave function should be important. Furthermore, the dynamic coupling of the internal (vibrational-rotational) states of the projectile should be included when the anisotropy of the interaction potential is significant. Higher-order distorted-wave effect should be more important in the collision processes of the triatomic-molecule–surface case than the light atom or diatom projectile case. In this section, we intend to develop more realistic theoretical schemes than DWBA as previously mentioned which are suitable for the triatomic-molecule–surface system in treating the vibrational-rotational and phonon inelastic scattering.

A. Iterative coupled-integral-equation method

The inclusion of a tremendously large number of phonon and vibrational-rotational states, in particular, those states from the many closed channels makes the integration of the coupled differential equation (CDE) an unmanageably complex task as mentioned before. The iterative coupled-integral-equation approach, to be discussed later, does not require as many fine mesh points of integration as those of the CDE and is tractable with a certain limited choice of the phonon states. The following iterative integral equation is derived from the integral equation given by I(64) obtained from the distorted-wave Green function

$$\chi^{k+1(+)}_{\alpha n\mathbf{G},\alpha_i n_i 0}(z) = \chi^{0(+)}_{\alpha n\mathbf{G},\alpha_i n_i 0}(z) + \frac{2M}{\hbar^2}\sum_{\alpha' n' \mathbf{G}'}\int_{z_0}^{\infty} dz'\, \mathcal{G}^{0(+)}_{\alpha n\mathbf{G}}(z,z')\tilde{V}^{\,\mathbf{G}-\mathbf{G}'}_{\alpha n,\alpha' n'}(z')\chi^{k(+)}_{\alpha' n' \mathbf{G}',\alpha_i n_i 0}(z') \quad (k=0,1,2,\ldots)\;. \tag{2}$$

It is seen from the preceding that $\chi^{k(+)}(z)$ is the kth-order approximate wave function for $\psi^{(+)}(z)$. Since

$|V^{\mathbf{G}-\mathbf{G}'}_{\alpha n,\alpha' n'}(z)| \ll |V^{0}_{\alpha n,\alpha n}(z)|$ for $(\alpha n\mathbf{G}) \neq (\alpha' n'\mathbf{G}')$ and $v_0(z)$ is chosen such that

$$|v_0(z)| \gg |V^{0}_{\alpha n,\alpha n}(z) - v_0(z)| ,$$

the convergence of the iteration should be relatively fast. The kth-order (distorted-wave) S matrix $S^{k(+)}_{\alpha n\mathbf{G},\alpha_i n_i 0}$ is obtained from

$$S^{k(+)}_{\alpha n\mathbf{G},\alpha_i n_i 0} = \delta_{\alpha,\alpha_i}\delta_{n,n_i}\delta_{\mathbf{G},0}s^{(+)}_{\alpha n\mathbf{G}} + C^{(+)}_{\alpha n\mathbf{G},\alpha_i n_i 0}\sum_{\alpha' n'\mathbf{G}'}\int_{z_0}^{\infty} dz\, \chi^{0(-)*}_{\alpha n\mathbf{G}}(z)\tilde{V}^{\mathbf{G}-\mathbf{G}'}_{\alpha n,\alpha' n'}(z)\chi^{k-1(+)}_{\alpha' n'\mathbf{G}',\alpha_i n_i 0}(z) \tag{3}$$

with $k = 0,1,2,\ldots$. In the limit as k goes to infinity, $S^{k(+)}_{\alpha n\mathbf{G},\alpha_i n_i 0}$ approaches the exact S matrix $S^{(+)}_{\alpha n\mathbf{G},\alpha_i n_i 0}$. Many closed channels can be included in the present iterative method without affecting numerical accuracy. This is different from the CDE case where instability of the numerical solution is known to arise from the closed channels. Therefore, realistic results could be obtained for the vibrational-rotational and phonon inelastic resonance scattering as well using the present iterative method. In a practical computation, $n \rightarrow n'$ in Eq. (2) is to be limited to the elastic scattering or the one-phonon creation or annihilation, that is, to the cases where the number $\sum_{\mathbf{Q},s}|n_{\mathbf{Q},s} - n'_{\mathbf{Q},s}|$ is 0 or 1. One method of truncating the phonon states $|\phi_n\rangle$ is to consider the collections $\{n_{\mathbf{Q},s}\}$ of the occupation numbers such that $\sum_{\mathbf{Q},s}|n_{\mathbf{Q},s} - n^{0}_{\mathbf{Q},s}| \leq m$ where m could be 2 or 3. Here $n^{0}_{\mathbf{Q},s}$ is a certain fixed occupation number, which, for instance, may be chosen to be the closest integer to $\bar{n}_{\mathbf{Q},s}$, the thermally averaged phonon number. Many pairs of the phonon states in the truncated set are connected through higher-order processes due to the restrictions on n and n' in Eq. (2). Thermal averages over the initial phonon states for the intensities thus obtained may be made using the normalization of the (thermal) distributions within the truncated set. The higher-order distorted waves can be efficiently computed with the present method as intermediate steps. At the same time the multiphonon transition intensities are obtained since the higher-order effects of the potential $\tilde{V}$ is conveniently taken into consideration in the method. Multiphonon transition becomes more probable for the triatom-surface collision compared to the light atom or diatom case. Therefore, the present method is certainly useful for the case with triatomic (or polyatomic) projectile. It should be pointed out that when the Rayleigh surface phonon mode and the laterally averaged part $V^{0}_{\alpha,\alpha'}(z)$ of the stationary interaction potential are dominant, one could further approximate Eqs. I (57) and I (62) of the phonon elastic and one-phonon emission potential matrix elements with vibrational-rotational transition ($\alpha \rightarrow \alpha'$) by

$$\begin{aligned} V^{\mathbf{G}}_{\alpha n,\alpha' n}(z) &\simeq e^{-W}V^{0}_{\alpha,\alpha'}(z)\delta_{\mathbf{G},0} , \\ V^{\mathbf{G}}_{\alpha n,\alpha' n'}(z) &\simeq -\left[\frac{\hbar n_{\mathbf{Q},R}}{2N\omega_R(\mathbf{Q})}\right]^{1/2}\varepsilon_{R_z}(\mathbf{Q}) \\ &\quad\times\left[\frac{d}{dz}V^{0}_{\alpha,\alpha'}(z)\right]e^{-W}\delta_{\mathbf{G},0} . \end{aligned} \tag{4}$$

The subscript R denotes the Rayleigh mode, ε_{R_z} is the z component of the polarization, and e^{-2W} is the phenomenological Debye-Waller factor.

For computational purposes, $\sum_{\mathbf{Q}}$ may be replaced by $(L/2\pi)^2\int d\mathbf{Q}$ and $\delta_{\mathbf{Q},\mathbf{Q}'}$ by $(2\pi/L)^2\delta(\mathbf{Q}-\mathbf{Q}')$, noting that the $\mathbf{Q}$'s are consistent with the two-dimensional Born–von Karman boundary condition.

One can obtain alternative expressions of the iterative processes employing a complete set of the eigenfunctions of H^0. The continuum eigenfunctions $\chi^{0(+)}_{\mathbf{K},\alpha n\mathbf{G}}$ were normalized such that

$$\begin{aligned} \langle\chi^{0(+)}_{\mathbf{K}',\alpha' n'\mathbf{G}'}(E')|\chi^{0(+)}_{\mathbf{K},\alpha n\mathbf{G}}(E)\rangle &= \int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,\chi^{0(+)\dagger}_{\mathbf{K}',\alpha' n'\mathbf{G}'}(\mathbf{r},\mathbf{S},\mathbf{s};E')\chi^{0(+)}_{\mathbf{K},\alpha n\mathbf{G}}(\mathbf{r},\mathbf{S},\mathbf{s};E) \\ &= \left[\frac{2\pi L^2\hbar^2}{M}\right]k_{\alpha n\mathbf{G}}\delta_{\mathbf{K},\mathbf{K}'}\delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{\mathbf{G},\mathbf{G}'}\delta(E'-E) \end{aligned}$$

with E' and E being the total energies. Strictly speaking, $\delta_{\mathbf{K},\mathbf{K}'}\delta_{\mathbf{G},\mathbf{G}'}$ on the right-hand side of this equation is true only when the $\mathbf{K}$'s lie in the first (two-dimensional) Brillouin zone. This can always be satisfied since $\mathbf{Q}_n$ and $\mathbf{Q}_n+\mathbf{G}$ have the same physical properties for the phonons [see Eq. I (70)]. Excluding the bound state for simplicity, we have the approximate closure property

$$\left[\frac{M}{2\pi L^2\hbar^2}\right]\sum_{\mathbf{K}\alpha n\mathbf{G}}\int dE\, k^{-1}_{\alpha n\mathbf{G}}|\chi^{0(+)}_{\mathbf{K},\alpha n\mathbf{G}}(E)\rangle\langle\chi^{0(+)}_{\mathbf{K},\alpha n\mathbf{G}}(E)| \simeq 1 .$$

From Eqs. I (76) and I (73), we then obtain

$$\left[\frac{M}{2\pi L^2\hbar^2}\right]\langle \chi^{0(+)}_{\mathbf{K},\alpha',n'\mathbf{G}'}(E')|\chi^{k+1(+)}_{\mathbf{K},\alpha_i n_i 0}(E)\rangle$$

$$=k_{\alpha n\mathbf{G}}\delta_{\alpha'\alpha_i}\delta_{n',n_i}\delta_{\mathbf{G}',0}\delta(E'-E)+\left[\frac{M}{2\pi L^2\hbar^2}\right]^2\left[P\frac{1}{E-E'}-\pi i\delta(E-E')\right]$$

$$\times\sum_{\alpha''n''\mathbf{G}''}\int dE''k''^{-1}_{\alpha''n''\mathbf{G}''}\langle \chi^{0(+)}_{\mathbf{K},\alpha'n'\mathbf{G}'}(E')|\tilde{V}|\chi^{0(+)}_{\mathbf{K},\alpha''n''\mathbf{G}''}(E'')\rangle\langle \chi^{0(+)}_{\mathbf{K},\alpha''n''\mathbf{G}''}(E'')|\chi^{k(+)}_{\mathbf{K},\alpha_i n_i 0}(E)\rangle ,$$

$$S^{k(+)}_{\alpha n\mathbf{G},\alpha_i n_i 0}=\delta_{\alpha,\alpha_i}\delta_{n,n_i}\delta_{\mathbf{G},0}s^{(+)}_{\alpha n\mathbf{G}}$$

$$+\frac{C^{(+)}_{\alpha n\mathbf{G},\alpha_i n_i 0}}{L^2}\left[\frac{M}{2\pi L^2\hbar^2}\right]\sum_{\alpha'n'\mathbf{G}'}\int dE'k'^{-1}_{\alpha'n'\mathbf{G}'}\langle \chi^{0(-)}_{\mathbf{K},\alpha n\mathbf{G}}(E)|\tilde{V}|\chi^{0(+)}_{\mathbf{K},\alpha'n'\mathbf{G}'}(E')\rangle\langle \chi^{0(+)}_{\mathbf{K},\alpha'n'\mathbf{G}'}(E')|\chi^{k-1(+)}_{\mathbf{K},\alpha_i n_i 0}(E)\rangle$$

corresponding to Eqs. (2) and (3). Here

$$k''^2_{\alpha n\mathbf{G}}=\frac{2M}{\hbar^2}(E''-E_\alpha-\mathscr{E}_n)-(\mathbf{K}-\mathbf{Q}_n+\mathbf{G})^2 ,$$

$$\langle \chi^{0(\pm)}_{\mathbf{K},\alpha n\mathbf{G}}(E)|\tilde{V}|\chi^{0(+)}_{\mathbf{K},\alpha'n'\mathbf{G}'}(E')\rangle=L^2\int_{z_0}^{\infty}dz\,\chi^{0(\pm)*}_{\alpha n\mathbf{G}}(z;E)\tilde{V}^{\mathbf{G}-\mathbf{G}'}_{\alpha n,\alpha'n'}(z)\chi^{0(+)}_{\alpha'n'\mathbf{G}'}(z;E') .$$

It should be pointed out, however, that the preceding methods are more complex than those given by Eqs. (2) and (3) for practical purposes, since the eigenfunctions of H^0 should be computed for all energies E.

B. Rotationally impulsive iterative integral equation

Inclusion of a large number of rotational states specified by the quantum numbers J,M,K would make the computation of the iterative coupled-integral-equation method quite complex. Therefore, we present in the following a rotationally impulsive integral-equation approach. In the molecular Hamiltonian given by I (31), the rotational energy operators $\hbar^2 l^2/2\mu_{A,BC}$ and $\hbar^2\mathbf{j}^2/2\mu_{BC}$ with $l=(1/i)(\mathbf{S}\times\nabla_S)$, $\mathbf{j}=(1/i)(\mathbf{s}\times\nabla_s)$ are neglected. Thus we can approximate $H_{\text{mol}}(\mathbf{S},\mathbf{s})$ by

$$H_{\text{mol}}(\mathbf{S},\mathbf{s})\simeq-\frac{\hbar^2}{2\mu_{A,BC}}\frac{1}{S^2}\frac{\partial}{\partial S}\left[S^2\frac{\partial}{\partial S}\right]$$

$$-\frac{\hbar^2}{2\mu_{BC}}\frac{1}{s^2}\frac{\partial}{\partial s}\left[s^2\frac{\partial}{\partial s}\right]$$

$$+V_{\text{mol}}(S,s,\cos\zeta)\equiv\tilde{H}_{\text{mol}}(S,s,\cos\zeta) .$$

The vibrational wave functions F_β satisfying the eigenvalue equation

$$\tilde{H}_{\text{mol}}(S,s,\cos\zeta)F_\beta(S,s,\cos\zeta)=E_\beta F_\beta(S,s,\cos\zeta)$$

constitute a complete set. E_β is the normal-mode vibrational energy. The total Hamiltonian of the triatomic-molecule–surface system is then approximated as

$$\tilde{H}=-\frac{\hbar^2}{2M}\nabla_r^2+\tilde{H}_{\text{mol}}+H_{\text{cr}}+V .$$

$\tilde{H}$ is a function of the phonon operators $\mathbf{p}^a(\mathbf{R}_\mathbf{G}),\mathbf{u}^a(\mathbf{R}_\mathbf{G})$ and the variables $\mathbf{r},\tau,\Omega$, where $(\tau)=(S,s,\cos\zeta)$ and $\Omega=(\varphi,\theta,\chi)$. Note that $\tilde{H}$ does not contain any differential operators with respect to the Euler angles Ω. Therefore, we need to solve the following Lippmann-Schwinger equation:

$$[E-\tilde{H}(\mathbf{r},\tau,\Omega)+i\epsilon]\psi^{(+)}_{\mathbf{K},\beta_i n_i 0}(\mathbf{r},\tau,\Omega)$$

$$=i\epsilon e^{i\mathbf{k}_i\cdot\mathbf{r}}F_{\beta_i}(\tau)|\phi_{n_i}\rangle \quad (5)$$

with Ω as parameters. More specifically, we solve the equation for all fixed Ω's. For this purpose, we set [**K** is given by Eq. I (10)]

$$\psi^{(+)}_{\mathbf{K},\beta_i n_i 0}(\mathbf{r},\tau,\Omega)=\sum_{\beta n\mathbf{G}}\psi^{(+)}_{\beta n\mathbf{G},\beta_i n_i 0}(z,\Omega)F_\beta(\tau)|\phi_n\rangle$$

$$\times e^{i(\mathbf{K}-\mathbf{Q}_n+\mathbf{G})\cdot\mathbf{R}} .$$

Equation (5) results in a CDE with the asymptotic boundary condition

$$\psi^{(+)}_{\beta n\mathbf{G},\beta_i n_i 0}(z,\Omega)\sim\left[\frac{k_{\beta_i n_i 0}}{k_{\beta n\mathbf{G}}}\right]^{1/2}[e^{-ik_{\beta n\mathbf{G}}z}\delta_{\beta,\beta_i}\delta_{n,n_i}\delta_{\mathbf{G},0}-S^{(+)}_{\beta n\mathbf{G},\beta_i n_i 0}(\Omega)e^{ik_{\beta n\mathbf{G}}z}] . \quad (6)$$

Here

$$k^2_{\beta n\mathbf{G}}=\frac{2M}{\hbar^2}(E-E_\beta-\mathscr{E}_n)-(\mathbf{K}-\mathbf{Q}_n+\mathbf{G})^2 .$$

Employing the distorted-wave Green function $\mathcal{G}^{0(+)}(z,z')$ defined in Eqs. I (65) to I (68), the CDE can be transformed into the integral-equation form

$$\psi^{(+)}_{\beta n\mathbf{G},\beta_i n_i 0}(z,\Omega)=\chi^{0(+)}_{\beta n\mathbf{G},\beta_i n_i 0}(z)+\frac{2M}{\hbar^2}\sum_{\beta' n'\mathbf{G}'}\int_{z_0}^{\infty}dz'\,\mathcal{G}^{0(+)}_{\beta n\mathbf{G}}(z,z')\tilde{V}^{\mathbf{G}-\mathbf{G}'}_{\beta n,\beta' n'}(z',\Omega)\psi^{(+)}_{\beta' n'\mathbf{G}',\beta_i n_i 0}(z',\Omega)\ , \tag{7}$$

where

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

$$V^{\mathbf{G}}_{\beta n,\beta' n'}(z,\Omega)=\int d\tau\, F_\beta(\tau)U^{\mathbf{G}}_{n,n'}(z,\tau,\Omega)F_{\beta'}(\tau)\ ,$$

$$U^{\mathbf{G}}_{n,n'}(z,\tau,\Omega)=V^{\mathbf{G}}_{n,n'}(z,\mathbf{S},\mathbf{s})\quad(d\tau=S^2dS\,s^2ds\,\sin\zeta\,d\zeta)\ .$$

Therefore, we have

$$S^{(+)}_{\beta n\mathbf{G},\beta_i n_i 0}(\Omega)=\delta_{\beta,\beta_i}\delta_{n,n_i}\delta_{\mathbf{G},0}s^{(+)}_{\beta n\mathbf{G}}+G^{(+)}_{\beta n\mathbf{G},\beta_i n_i 0}\sum_{\beta' n'\mathbf{G}'}\int_{z_0}^{\infty}dz'\,\chi^{0(-)*}_{\beta n\mathbf{G}}(z')\tilde{V}^{\mathbf{G}-\mathbf{G}'}_{\beta n,\beta' n'}(z',\Omega)\psi^{(+)}_{\beta' n'\mathbf{G}',\beta_i n_i 0}(z',\Omega) \tag{8}$$

from Eq. (6). $C^{(+)}$ is defined as in paper I. The vibrational and rotational states α and α_i are used to denote $\alpha=JMpK\beta$, $\alpha_i=J_iM_ip_iK_i\beta_i$. The corresponding wave function is, e.g., given by

$$\Phi_\alpha(\mathbf{S},\mathbf{s})=F_\beta(\tau)D^{Jp}_{MK}(\Omega)\ .$$

The rotation-parity eigenfunction $D^{Jp}_{MK}(\Omega)$ was defined in Eq. I (41). The rotationally impulsive S matrix for the vibrational-rotational transition from α_i to α is then computed from

$$S^{(+)}_{\alpha n\mathbf{G},\alpha_i n_i 0}=\int d\Omega\, D^{Jp*}_{MK}(\Omega)S^{(+)}_{\beta n\mathbf{G},\beta_i n_i 0}(\Omega)D^{J_ip_i}_{M_iK_i}(\Omega)\quad(d\Omega=d\varphi\, d\chi\,\sin\theta\, d\theta)\ .$$

From Eqs. (7) and (8), we have an iterative integral equation

$$\chi^{k+1(+)}_{\beta n\mathbf{G},\beta_i n_i 0}(z,\Omega)=\chi^{0(+)}_{\beta n\mathbf{G},\beta_i n_i 0}(z)+\frac{2M}{\hbar^2}\sum_{\beta' n'\mathbf{G}'}\int_{z_0}^{\infty}dz'\,\mathcal{G}^{0(+)}_{\beta n\mathbf{G}}(z,z')\tilde{V}^{\mathbf{G}-\mathbf{G}'}_{\beta n,\beta' n'}(z',\Omega)\chi^{k(+)}_{\beta' n'\mathbf{G}',\beta_i n_i 0}(z',\Omega) \tag{9}$$

for $k=0,1,2,\ldots$, and

$$S^{k(+)}_{\beta n\mathbf{G},\beta_i n_i 0}(\Omega)=\delta_{\beta,\beta_i}\delta_{n,n_i}\delta_{\mathbf{G},0}s^{(+)}_{\beta n\mathbf{G}}+C^{(+)}_{\beta n\mathbf{G},\beta_i n_i 0}\sum_{\beta' n'\mathbf{G}'}\int_{z_0}^{\infty}dz'\,\chi^{0(-)*}_{\beta n\mathbf{G}}(z')\tilde{V}^{\mathbf{G}-\mathbf{G}'}_{\beta n,\beta' n'}(z',\Omega)\chi^{k-1(+)}_{\beta' n'\mathbf{G}',\beta_i n_i 0}(z',\Omega) \tag{10}$$

for $k=1,2,\ldots$. The kth-order impulsive S matrix for the vibrational-rotational transition from α_i to α is then calculated from

$$S^{k(+)}_{\alpha n\mathbf{G},\alpha_i n_i 0}=\int d\Omega\, D^{Jp*}_{MK}(\Omega)S^{k(+)}_{\beta n\mathbf{G},\beta_i n_i 0}(\Omega)D^{J_ip_i}_{M_iK_i}(\Omega)\ . \tag{11}$$

We solve the iterative integral equation for each parameter Ω. Approximation for the inclusion of the phonon states is made in the same manner as in Sec. II A. The present iterative integral-equation method substantially reduces the complexity due to the rotational states of the triatomic molecule.

C. Coupled-diffractive-channel transition-matrix method

In this subsection, we discuss a method where the corrugation effect of the molecule-surface interaction potential is included in the distorted wave when the corrugation is sufficiently large in the (triatomic-) molecule–(nonmetallic) crystal surface. Substituting the approximation

$$\psi^{(+)}_{\mathbf{K},\alpha_i n_i 0}(\mathbf{r},\mathbf{S},\mathbf{s})\simeq\chi^{(+)}_{\mathbf{K},\alpha_i n_i 0}(\mathbf{r},\mathbf{S},\mathbf{s})\ ,$$

or equivalently,

$$\psi^{(+)}_{\alpha n\mathbf{G},\alpha_i n_i 0}(z)\simeq\chi^{(+)}_{\alpha n\mathbf{G},\alpha_i n_i 0}(z)$$

$$=\delta_{\alpha,\alpha_i}\delta_{n,n_i}\chi^{(+)}_{\alpha n\mathbf{G},0}(z)$$

into Eq. I (97) of the integral expression of the S matrix obtained from the diffraction-wave Green function, the diffraction, vibrational-rotational and phonon transition $(\alpha_f n_f\mathbf{G}_f\neq\alpha_i n_i 0)$ matrix is given by

$$\begin{aligned}T_{\alpha_f n_f\mathbf{G}_f,\alpha_i n_i 0}&=\frac{1}{L^3}\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,\chi^{(-)\dagger}_{\mathbf{K},\alpha_f n_f\mathbf{G}_f}(\mathbf{r},\mathbf{S},\mathbf{s})\bar{V}(\mathbf{r},\mathbf{S},\mathbf{s})\chi^{(+)}_{\mathbf{K},\alpha_i n_i 0}(\mathbf{r},\mathbf{S},\mathbf{s})\\&=\frac{1}{L}\sum_{\mathbf{G}'\mathbf{G}}\int_{z_0}^{\infty}dz\,\chi^{(-)*}_{\alpha_f n_f\mathbf{G}',\mathbf{G}_f}(z)\bar{V}^{\mathbf{G}}_{\alpha_f n_f,\alpha_i n_i}(z)\chi^{(+)}_{\alpha_i n_i\mathbf{G}'-\mathbf{G},0}(z)\ .\end{aligned} \tag{12}$$

In the present approach, the coupling between the reciprocal lattice points due to the molecule-surface interaction is taken into account in the incident and scattered wave functions. In other words, the initial- and the final-wave functions of the projectile contain diffractive distortions that arise from the periodic part (or the corrugation) of the potential. This is the coupled-diffractive-channel transition-matrix method (CDCTM). It should be suitable to describe the effect of the diffraction on the simultaneous vibrational-rotational and phonon inelastic scattering. From the expression of the potential matrix elements given by Eq. I (62), we obtain the diffractive intensity of the present approximation for the (simultaneous) one-phonon emission and vibrational-rotational transition. From the energy and momentum conservation, $\chi^{(-)}_{\alpha_f n_f \mathbf{G},\mathbf{G}_f}(z)$ and $\chi^{(+)}_{\alpha_i n_i \mathbf{G},0}(z)$ satisfy the same CDE given by Eq. I (83) with the (same) total energy

$$E=E_i^p+E_{\alpha_i}+\mathcal{E}_{n_i}=E_f^p+E_{\alpha_f}+\mathcal{E}_{n_f}$$

and the (same) parallel momentum

$$\mathbf{K}=\mathbf{K}_i+\mathbf{Q}_{n_i}=\mathbf{K}_f+\mathbf{Q}_{n_f}-\mathbf{G}_f$$

but different boundary conditions given by Eq. I (114). For simplicity, the diffractive potential $v(\mathbf{r})$ is chosen to be independent of the initial and final vibrational-rotational and phonon states, $\alpha_i n_i$ and $\alpha_f n_f$. Then, for a given energy and phonon momentum transfers, $\hbar\omega$ and $\hbar\mathbf{Q}$, and incident energy E_i^p, the dependence of the elastic diffractive wave functions $\chi^{(\pm)}_{\alpha n\mathbf{G}',\mathbf{G}}(z)$ on α_i, α_f, n_i, n_f, E, and $\mathbf{K}$ is replaced by those on E_i^p, $\mathbf{K}_i$, $\hbar\omega$, and $\hbar\mathbf{Q}$. Denoting the wave functions by $\chi^{(\pm)}_{\mathbf{G}',\mathbf{G}}(z)$ in that case, we carry out the thermal average analytically and obtain the diffractive intensity for the (simultaneous) one-phonon emission and vibrational-rotational transition as

$$\frac{d^2\sigma}{d\Omega_{\mathbf{k}_f}dE_f^p}=\frac{M^2}{8\pi^2\hbar^4}\left[\frac{N}{L^2}\right]\frac{k_f}{k_i}\sum_s\frac{\bar{n}_{\mathbf{Q},s}+1}{\omega_s(\mathbf{Q})}\delta(\omega_s(\mathbf{Q})+\omega)$$
$$\times\left|\sum_{\mathbf{G}'\mathbf{G}}\int_{z_0}^{\infty}dz\,\chi^{(-)*}_{\mathbf{G}',\mathbf{G}_f}(z)\chi^{(+)}_{\mathbf{G}'-\mathbf{G},0}(z)\right.$$
$$\left.\times\sum_{ak_z}[\mathbf{k}_\mathbf{G}\cdot\boldsymbol{\varepsilon}_s^{\alpha *}(\mathbf{Q})](V^a_{\mathbf{k}_\mathbf{G}})_{\alpha_f,\alpha_i}\exp[i(k_z z-\mathbf{k}_\mathbf{G}\cdot\mathbf{r}_a)-\overline{W}_a(\mathbf{k}_\mathbf{G})]\right|^2 . \qquad (13)$$

Here, $\hbar\omega=E_f^p+E_{\alpha_f}-E_i^p-E_{\alpha_i}$ is the energy transfer of the projectile, the brackets $\langle\ \rangle$ denote the thermal average over the initial phonon states, $\mathbf{k}_\mathbf{G}=k_z\hat{\mathbf{z}}+\mathbf{G}-\mathbf{Q}$, $\bar{n}_{\mathbf{Q},s}$ is the thermal average of the phonon occupation number for the mode $(\mathbf{Q},s)$. The polarization and energy dispersion, $\boldsymbol{\varepsilon}_s^a(\mathbf{Q})$ and $\omega_s(\mathbf{Q})$, of the single phonon are computed from diagonalization of the dynamic matrix in a semi-infinite slab model or using the Green-function technique.

D. Coupled-molecular-state transition-matrix method

If the molecular-surface interaction potential $V(\mathbf{r},\mathbf{S},\mathbf{s})$ depends significantly on the internal coordinates $\mathbf{S},\mathbf{s}$ of the molecule or the anisotropy of the potential is significant, the dynamic distortion of the vibrational-rotational states of the projectile should be included in the (approximate) scattering wave functions. More specifically, the effect of the dynamic coupling between the internal (vibrational-rotational) states of the projectile through the interaction potential should reflect the scattering wave function. For this purpose, we consider the potential $v^m(z,\mathbf{S},\mathbf{s})$ by laterally averaging $V(\mathbf{r},\mathbf{S},\mathbf{s})$ over $\mathbf{R}$ and then thermally averaging over the phonon states. The $v^m(z,\mathbf{S},\mathbf{s})$ is basically a molecule–flat- and rigid-surface interaction potential. The $\chi^{m(\pm)}_{\mathbf{K},\alpha' n'\mathbf{G}'}(\mathbf{r},\mathbf{S},\mathbf{s})$ are the outgoing and incoming scattering wave functions distorted from the potential $v^m(z,\mathbf{S},\mathbf{s})$. That is, the dynamic distortion of the molecular internal states, denoted by the superscript m, is included in the wave functions as mentioned before. Note that m is not an integer. The Hamiltonian H^m and corresponding Lippmann-Schwinger equation are, respectively, given by

$$H^m=-\frac{\hbar^2}{2M}\nabla_r^2+H_{\mathrm{mol}}+H_{\mathrm{cr}}+v^m(z,\mathbf{S},\mathbf{s}) ,$$

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

Expanding the wave function as

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

we have

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

and $\chi^{m(\pm)}_{\alpha n\mathbf{G},\alpha'}(z)$ satisfies a CDE and the boundary condition

$$\chi^{m(\pm)}_{\alpha n\mathbf{G},\alpha'}(z)\sim\left[\frac{k_{\alpha' n\mathbf{G}}}{k_{\alpha n\mathbf{G}}}\right]^{1/2}(e^{\mp ik_{\alpha n\mathbf{G}}z}\delta_{\alpha,\alpha'}$$
$$-\mathcal{S}^{m(\pm)}_{\alpha n\mathbf{G},\alpha' n\mathbf{G}}e^{\pm ik_{\alpha n\mathbf{G}}z}) \qquad (14a)$$

for an open channel, and

$$\chi^{m(\pm)}_{\alpha n\mathbf{G},\alpha'}(z) \sim -\left[\frac{k_{\alpha' n\mathbf{G}}}{\kappa_{\alpha n\mathbf{G}}}\right]^{1/2} \bar{\mathcal{S}}^{m(\pm)}_{\alpha n\mathbf{G},\alpha' n\mathbf{G}} e^{-\kappa_{\alpha n\mathbf{G}} z} \tag{14b}$$

for a closed channel. The $\mathcal{S}^{m(\pm)}$ is the vibrational-rotational transition scattering matrix for the molecule–flat-surface collision. The column matrix $[\chi^{m(\pm)}_{\alpha' n' \mathbf{G}'}]$ is defined to have elements $\chi^{m(\pm)}_{\alpha n\mathbf{G},\alpha' n' \mathbf{G}'}(z)$. Then, we have

$$\begin{aligned}[\chi^{m(\pm)}_{\alpha' n' 0}] &= [\chi^{0(\pm)}_{\alpha' n' 0}] + \frac{2M}{\hbar^2}[\mathcal{G}^{0(\pm)}][\tilde{v}^{\,m}][\chi^{m(\pm)}_{\alpha' n' 0}] \\ &= \left[[1] + \frac{2M}{\hbar^2}[\mathcal{G}^{m(\pm)}][\tilde{v}^{\,m}] \right][\chi^{0(\pm)}_{\alpha' n' 0}]\end{aligned} \tag{15}$$

with

$$\begin{aligned}\tilde{v}^{\,m}_{\alpha n\mathbf{G},\alpha' n' \mathbf{G}'}(z,z') &= \tilde{v}^{\,m}_{\alpha,\alpha'}(z)\delta_{n,n'}\delta_{\mathbf{G},\mathbf{G}'}\delta(z-z') , \\ [\mathcal{G}^{m(\pm)}] &= [\mathcal{G}^{0(\pm)}] + \frac{2M}{\hbar^2}[\mathcal{G}^{0(\pm)}][\tilde{v}^{\,m}][\mathcal{G}^{m(\pm)}] \\ &= [\mathcal{G}^{0(\pm)}] + \frac{2M}{\hbar^2}[\mathcal{G}^{m(\pm)}][\tilde{v}^{\,m}][\mathcal{G}^{0(\pm)}] .\end{aligned} \tag{16}$$

Here $\tilde{v}^{\,m}_{\alpha,\alpha'}(z) = v^{m}_{\alpha,\alpha'}(z) - v_0(z)\delta_{\alpha,\alpha'}$ with $v^{m}_{\alpha,\alpha'}(z)$ the matrix element of $v^{m}(\mathbf{r},\mathbf{S},\mathbf{s})$ between the molecular states α and α'. $[\mathcal{G}^{m(\pm)}]^{\dagger} = [\mathcal{G}^{m(\mp)}]$ since $[\tilde{v}^{\,m}]^{\dagger} = [\tilde{v}^{\,m}]$. Since $[\tilde{v}^{\,m}]$ is in a block diagonal form, $[\mathcal{G}^{m(\pm)}]$ is also block diagonal, that is,

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

We define the Green operator as

$$\mathcal{G}^{m(\pm)}_{\mathbf{K}}(\mathbf{r},\mathbf{S},\mathbf{s};\mathbf{r}',\mathbf{S}',\mathbf{s}') = \sum_{\substack{\alpha n\mathbf{G} \\ \alpha' n' \mathbf{G}'}} \langle \mathbf{R},\mathbf{S},\mathbf{s} | \alpha n\mathbf{G}\rangle \mathcal{G}^{m(\pm)}_{\alpha n\mathbf{G},\alpha' n' \mathbf{G}'}(z,z') \langle \alpha' n' \mathbf{G}' | \mathbf{R}',\mathbf{S}',\mathbf{s}'\rangle , \tag{17}$$

where $\langle \mathbf{R},\mathbf{S},\mathbf{s} | \alpha n\mathbf{G}\rangle$ was defined in Eq. I (75b). It is seen that

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

Employing the Green operator and a similar method as in Sec. IV B of paper I, we obtain

$$\begin{aligned}\psi^{(\pm)}_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}(\mathbf{r},\mathbf{S},\mathbf{s}) &= \chi^{m(\pm)}_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}(\mathbf{r},\mathbf{S},\mathbf{s}) + \frac{2M}{\hbar^2}\int d\mathbf{r}' d\mathbf{S}' d\mathbf{s}' \, \mathcal{G}^{m(\pm)}_{\mathbf{K}}(\mathbf{r},\mathbf{S},\mathbf{s};\mathbf{r}',\mathbf{S}',\mathbf{s}') \bar{V}^{\,m}(\mathbf{r}',\mathbf{S}',\mathbf{s}') \psi^{(\pm)}_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}(\mathbf{r}',\mathbf{S}',\mathbf{s}') , \\ S^{(\pm)}_{\alpha_f n_f \mathbf{G}_f,\alpha_i n_i \mathbf{G}_i} &= \delta_{\mathbf{G}_f,\mathbf{G}_i}\delta_{n_f,n_i}\mathcal{S}^{m(\pm)}_{\alpha_f n_i \mathbf{G}_i,\alpha_i n_i \mathbf{G}_i} + \frac{C^{(\pm)}_{\alpha_f n_f \mathbf{G}_f,\alpha_i n_i \mathbf{G}_i}}{L^2}\int d\mathbf{r}\, d\mathbf{S}\, d\mathbf{s}\, \chi^{m(\mp)\dagger}_{\mathbf{K},\alpha_f n_f \mathbf{G}_f}(\mathbf{r},\mathbf{S},\mathbf{s}) \bar{V}^{\,m}(\mathbf{r},\mathbf{S},\mathbf{s}) \psi^{(\pm)}_{\mathbf{K},\alpha_i n_i \mathbf{G}_i}(\mathbf{r},\mathbf{S},\mathbf{s})\end{aligned} \tag{18}$$

with

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

Making the approximation

$$\psi^{(+)}_{\mathbf{K},\alpha_i n_i 0}(\mathbf{r},\mathbf{S},\mathbf{s}) \simeq \chi^{m(+)}_{\mathbf{K},\alpha_i n_i 0}(\mathbf{r},\mathbf{S},\mathbf{s})$$

in Eq. (18), we have the simultaneous diffraction, phonon and vibrational-rotational transition matrix ($\mathbf{G}_f \neq 0$, $n_f \neq n_i$, $\alpha_f \neq \alpha_i$) as

$$T_{\alpha_f n_f \mathbf{G}_f,\alpha_i n_i 0} = \frac{1}{L}\sum_{\alpha\alpha'}\int dz \, \chi^{m(-)*}_{\alpha n_f \mathbf{G}_f,\alpha_f}(z) \bar{V}^{\,m,\mathbf{G}_f}_{\alpha n_f,\alpha' n_i}(z) \chi^{m(+)}_{\alpha' n_i 0,\alpha_i}(z) \tag{19}$$

with

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

This is the coupled-molecular-state transition-matrix method (CMSTM). As previously mentioned, the dynamic distortion of the vibrational-rotational states of the projectile due to the molecule-surface interaction has been taken into account in the incident and scattered wave functions in Eq. (19). $\chi^{m(-)}_{\alpha n_f \mathbf{G}_f,\alpha_f}(z)$ and $\chi^{m(+)}_{\alpha' n_i 0,\alpha_i}(z)$ are solutions to the same CDE with the (same) total energy and parallel momentum

$$E = E^{p}_{i} + E_{\alpha_i} + \mathcal{E}_{n_i} = E^{p}_{f} + E_{\alpha_f} + \mathcal{E}_{n_f}, \quad \mathbf{K} = \mathbf{K}_i + \mathbf{Q}_{n_i} = \mathbf{K}_f + \mathbf{Q}_{n_f} - \mathbf{G}_f ,$$

but satisfy the incoming and the outgoing boundary conditions, respectively. As long as the potential $v^{m}(z,\mathbf{S},\mathbf{s})$ is chosen to be independent of the initial and final states, the dependence of the wave functions $\chi^{m(\pm)}$ on n_i, n_f, $\mathbf{K}$ and E can be replaced by those on E^{p}_{i}, $\mathbf{K}_i$, $\hbar\omega$, and $\hbar\mathbf{Q}$. Doing this and denoting the wave functions by $\chi^{m(\pm)}_{\alpha\mathbf{G},\alpha'}(z)$, we carry out a thermal average over the initial phonon states. The resulting expression of the diffractive intensity derived from the present method for the simultaneous vibrational-rotational transition $\alpha_i \rightarrow \alpha_f$ and one-phonon emission is given by the following expression:

$$\frac{d^2\sigma}{d\Omega_{\mathbf{k}_f} dE_f^p} = \frac{M^2}{8\pi^2\hbar^4} \left(\frac{N}{L^2} \right) \frac{k_f}{k_i} \sum_s \frac{\bar{n}_{\mathbf{Q},s}+1}{\omega_s(\mathbf{Q})} \delta(\omega_s(\mathbf{Q})+\omega)$$

$$\times \left| \sum_{\alpha\alpha'} \int_{z_0}^{\infty} dz\, \chi^{m(-)*}_{\alpha\mathbf{G}_f,\alpha_f}(z) \chi^{m(+)}_{\alpha'0,\alpha_i}(z) \right.$$

$$\left. \times \sum_{ak_z} [\mathbf{k}_{\mathbf{G}_f} \cdot \boldsymbol{\varepsilon}_s^{a*}(\mathbf{Q})] (V^a_{\mathbf{k}_{\mathbf{G}_f}})_{\alpha,\alpha'} \exp[i(k_z z - \mathbf{k}_{\mathbf{G}_f} \cdot \mathbf{r}_a) - \overline{W}_a(\mathbf{k}_{\mathbf{G}_f})] \right|^2 . \qquad (20)$$

Here the energy transfer of the projectile is again given by $\hbar\omega = E_f^p + E_{\alpha_f} - E_i^p - E_{\alpha_i}$. The computational procedure developed for the coupled-channel T-matrix approximation of gas-phase reactive collisions[22] will be quite useful for the present method of molecule-surface scattering. The S matrices obtained from DWBA, CDCTM, or CMSTM are, in general, not unitary. A simple normalization condition for the S matrix is not sufficient. We will briefly discuss the unitarized schemes for these approximations in the Appendix. The CDCTM and CMSTM methods of the molecule-surface scattering could be best suited for studying the (nonresonant) direct process of the simultaneous diffraction, phonon and vibrational-rotational transitions, angular and velocity distribution of the scattered molecule, and the energy transfers among translation, phonons and vibrations and rotations. A theoretical method for the (indirect) resonance processes will be presented in the following section.

III. BOUND-STATE RESONANCE SCATTERING METHOD FOR SELECTIVE ADSORPTION

The selective adsorption and desorption phenomena arise from the effects of the closed channels at the energies where the molecule is temporarily bound to the surface. Here the closed channels are defined to be the $(\alpha n\mathbf{G})$'s with $k^2_{\alpha n\mathbf{G}} < 0$ for the molecule-surface scattering with the inclusion of the phonon degrees of freedom. The open channels correspond to $k^2_{\alpha n\mathbf{G}} > 0$. The selective adsorption and desorption are basically resonance scatterings originated from coupling between closed channels and open diffraction (or reflection) channels. They are indirect scattering processes where the molecular projectile is temporarily trapped to the surface. After a certain lifetime elapses, the molecule is desorbed again upon transition of the phonons and vibrations and rotations. This is analogous to the compound nucleus theory in the nuclear reaction. The CDE describing such scattering includes a large number of closed channels. It becomes a quite complex numerical problem to solve the CDE. When the phonons are taken into account, the close-coupling calculations are almost impossible. Therefore, a Feshbach-type approach should be quite efficient for the resonance scattering, in particular, when the phonons and vibrations and rotations are included. The S matrix derived from the Feshbach-type approach describes the trapping-desorption mechanism [see Eq. (34)]. Nevertheless, no systematic treatments exist for the molecule-surface scattering case. In what follows, we briefly outline the Feshbach approach modified for the present purpose. Specific application to the molecule-surface scattering will be made subsequently.

Based on whether we are dealing with the open $(\alpha n\mathbf{G})$'s or the closed ones, the basis states are divided into two groups, the open and the closed states. This division depends on the total energy E, but we fix the division in a certain range of E such that most of the channels in the former group are the open channels and those in the latter group are the closed ones. We will simply call "open" and "closed" channels which belong to the former and latter groups, respectively, unless specified further. The corresponding projection operators will be denoted by P_o and P_c, respectively. Thus, $P_o^2 = P_o$, $P_c^2 = P_c$, $P_c P_o = P_o P_c = 0$, $P_o + P_c = 1$. The total molecule-surface scattering wave function $\psi_i^{(+)}$ determined by the initial condition i in $\phi_i^{(-)}$ satisfies the Lippmann-Schwinger equation

$$(E - H + i\epsilon)\psi_i^{(+)} = i\epsilon\phi_i^{(-)} . \qquad (21)$$

Multiplying both sides of Eq. (31) by P_o and P_c, we have

$$(E - H_{oo} + i\epsilon)\psi_{io}^{(+)} = i\epsilon\phi_i^{(-)} + H_{oc}\psi_{ic}^{(+)} , \qquad (22)$$

$$(E - H_{cc} + i\epsilon)\psi_{ic}^{(+)} = H_{co}\psi_{io}^{(+)} , \qquad (23)$$

where

$$H_{oo} = P_o H P_o, \quad H_{cc} = P_c H P_c, \quad H_{oc} = P_o H P_c ,$$

$$H_{co} = P_c H P_o, \quad \psi_{io}^{(+)} = P_o \psi_i^{(+)}, \quad \psi_{ic}^{(+)} = P_c \psi_i^{(+)} .$$

To obtain Eqs. (22) and (23), the relations $P_o\phi_i^{(-)} = \phi_i^{(-)}$ and $P_c\phi_i^{(-)} = 0$ were used. If we solve Eq. (23) for $\psi_{ic}^{(+)}$ and substitute it into Eq. (22), we obtain the Lippmann-Schwinger equation for the open-channel component $\psi_{io}^{(+)}$ of the total wave function,

$$(E - H_{\text{eff}} + i\epsilon)\psi_{io}^{(+)} = i\epsilon\phi_i^{(-)} . \qquad (24)$$

Here H_{eff} is the effective Hamiltonian given by

$$H_{\text{eff}} = H_{oo} + W_{oo}$$

with

$$W_{oo} = H_{oc}\mathcal{G}^{(+)c}H_{co}, \quad \mathcal{G}^{(+)c} = \frac{1}{E - H_{cc} + i\epsilon} .$$

It is in general difficult to obtain a realistic solution of Eq. (24) for a nonlocal potential unless a phenomenological (local) optical potential is introduced. Therefore, we employ a slightly different approach. If one defines the wave functions $\chi_i^{(\pm)o}$ from

$$(E-H_{oo}\pm i\epsilon)\chi_i^{(\pm)o}=\pm i\epsilon\phi_i^{(\mp)}\ , \tag{25a}$$

then Eq. (22) can be rewritten as

$$(E-H_{oo}+i\epsilon)\psi_{io}^{(+)}=(E-H_{oo}+i\epsilon)\chi_i^{(+)o}+H_{oc}\psi_{ic}^{(+)}\ . \tag{25b}$$

We solve Eq. (25b) for $\psi_{io}^{(+)}$ and substitute it into Eq. (23). This yields $\psi_{ic}^{(+)}$ in terms of $\chi_i^{(+)o}$. Substituting the resulting $\psi_{ic}^{(+)}$ into Eq. (25b) again, we have

$$\psi_{i0}^{(+)}=\chi_i^{(+)o}+\mathcal{G}^{(+)o}H_{oc}\frac{1}{E-H_{cc}-W_{cc}+i\epsilon}H_{co}\chi_i^{(+)o}\ , \tag{26a}$$

where

$$\mathcal{G}^{(+)o}=\frac{1}{E-H_{oo}+i\epsilon},\quad +W_{cc}=H_{co}\mathcal{G}^{(+)o}H_{oc}\ . \tag{26b}$$

Equation (25a) holds only for the atom or molecule–surface scattering case. The wave function $\chi_i^{(-)o}$ is needed to obtain the S matrix from Eq. (26a). All scattering information is contained in Eq. (26a), since $\psi_{io}^{(+)}$ has the same asymptotic boundary conditions as that of $\psi_i^{(+)}$, the full wave function. This equation contains the essence of the Feshbach method for our purpose. The spectrum of the Hamiltonian H_{cc} may include both the discrete and continuum energies. Only the discrete states are considered here because the discrete eigenvalues from the bound states of H_{cc} are important in resonance scattering.

In the following, the above formalism is applied to the molecule-surface resonance collision with the inclusion of the phonon degree of freedom. As seen in the subsequent discussions, it is best suited for the simultaneous molecular and phonon inelastic resonance scattering. The present approach is adoptable to an arbitrary molecule-surface interaction potential, treats diffraction, vibration-rotation, and phonon mediations in resonance systematically, describes the explicit trapping-desorption mechanism, and results in an effective calculational procedure, while it is *ab initio* in character. The H is the full Hamiltonian given previously by

$$H=-\frac{\hbar^2}{2M}\nabla_\tau^2+H_{\text{cr}}+H_{\text{mol}}+V(\mathbf{r},\mathbf{S},\mathbf{s})\ .$$

The wave function $\psi^{(+)}$ and $\chi^{(\pm)o}$ are expanded as

$$\psi_{\mathbf{K},\alpha'n'0}^{(+)}(\mathbf{r},\mathbf{S},\mathbf{s})=\sum_{\alpha n\mathbf{G}}\psi_{\alpha n\mathbf{G},\alpha'n'0}^{(+)}(z)\Phi_\alpha(\mathbf{S},\mathbf{s})|\phi_n\rangle e^{i(\mathbf{K}-\mathbf{Q}_n+\mathbf{G})\cdot\mathbf{R}}\ , \tag{27}$$

$$\chi_{\mathbf{K},\alpha'n'\mathbf{G}'}^{(\pm)o}(\mathbf{r},\mathbf{S},\mathbf{s})=\sum_{\alpha n\mathbf{G}}{}'\,\chi_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}^{(\pm)o}(z)\Phi_\alpha(\mathbf{S},\mathbf{s})|\phi_n\rangle e^{i(\mathbf{K}-\mathbf{Q}_n+\mathbf{G})\cdot\mathbf{R}}\ , \tag{28}$$

with $\mathbf{K}=\mathbf{K}_i+\mathbf{Q}_{n_i}$ being the total parallel momentum of the system. The $\sum'$ denotes the summation over the open $(\alpha n\mathbf{G})$'s. Replacing $\sum$ by $\sum'$ in Eq. (27), we have the open-channel component of $\psi_{\mathbf{K},\alpha'n'0}^{(+)}(\mathbf{r},\mathbf{S},\mathbf{s})$. The asymptotic boundary condition of the wave functions (for the open channels with $k_{\alpha n\mathbf{G}}^2>0$) are

$$\begin{aligned}\psi_{\alpha n\mathbf{G},\alpha'n'0}^{(+)}(z)&\sim\left[\frac{k_{\alpha'n'0}}{k_{\alpha n\mathbf{G}}}\right]^{1/2}(e^{-ik_{\alpha n\mathbf{G}}z}\delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{\mathbf{G},0}-S_{\alpha n\mathbf{G},\alpha'n'0}^{(+)}e^{ik_{\alpha n\mathbf{G}}z})\ ,\\ \chi_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}^{(\pm)o}(z)&\sim\left[\frac{k_{\alpha'n'\mathbf{G}'}}{k_{\alpha n\mathbf{G}}}\right]^{1/2}(e^{\mp ik_{\alpha n\mathbf{G}}z}\delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{\mathbf{G},\mathbf{G}'}-\mathcal{S}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}^{(\pm)o}e^{\pm ik_{\alpha n\mathbf{G}}z})\ .\end{aligned} \tag{29}$$

The wave function $\chi^{(\pm)o}$ and the scattering matrix $\mathcal{S}^{(\pm)o}$ could be obtained from the integral-equation method presented in Sec. II in the subspace of the open $(\alpha n\mathbf{G})$'s and within the subset of the phonon states mentioned there. However, as previously mentioned, computation of $\psi_{\alpha n\mathbf{G},\alpha'n'0}^{(+)}(z)$ with the CDE is quite complex since many closed $(\alpha n\mathbf{G})$'s are involved for the resonance scattering. Elimination of the closed channels results in a complicated coupled integro-differential equation due to the nonlocal potential as seen in Eq. (24). Therefore, the present approach presented later based on Eq. (26a) should be efficient.

By setting the ith bound eigenfunction $g_{\mathbf{K}}^i(\mathbf{r},\mathbf{S},\mathbf{s})$ of the Hamiltonian H_{cc} for a given $\mathbf{K}$ with eigenvalue $E_{\mathbf{K}}^i$ in the following form:

$$g_{\mathbf{K}}^i(\mathbf{r},\mathbf{S},\mathbf{s})=\frac{1}{L}\sum_{\alpha n\mathbf{G}}g_{\alpha n\mathbf{G}}^i(z)\Phi_\alpha(\mathbf{S},\mathbf{s})|\phi_n\rangle\times e^{i(\mathbf{K}-\mathbf{Q}_n+\mathbf{G})\cdot\mathbf{R}}\ , \tag{30}$$

we obtain the eigenvalue equation

$$\left[\frac{d^2}{dz^2}-\kappa_{\alpha n\mathbf{G},i}^2\right]g_{\alpha n\mathbf{G}}^i(z)=\frac{2M}{\hbar^2}\sum_{\alpha'n'\mathbf{G}'}V_{\alpha n,\alpha'n'}^{\mathbf{G}-\mathbf{G}'}(z)g_{\alpha'n\mathbf{G}'}^i(z) \tag{31}$$

with

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

For convenience, we normalize the eigenfunctions as

$$\sum_{\alpha n\mathbf{G}} \int dz\, g^{i*}_{\alpha n\mathbf{G}}(z) g^{i'}_{\alpha n\mathbf{G}}(z) = \delta_{i,i'} \ .$$

In Eqs. (30) and (31), the $(\alpha n\mathbf{G})$'s are limited to the closed ones. Some truncated set of such $(\alpha n\mathbf{G})$'s may be used in practical calculations. Since we are interested in the bound eigenfunctions, $\kappa^2_{\alpha n\mathbf{G},i} > 0$ for all $(\alpha n\mathbf{G})$'s. The differential eigenvalue equation given by Eq. (31) is in general not tractable. If $g^i_{\alpha n\mathbf{G}}(z)$ is expanded in terms of a complete set of certain known basis functions $\{f_m(z)\}$ which satisfy

$$\left[-\frac{\hbar^2}{2M}\frac{d^2}{dz^2} + u(z) \right] f_m(z) = E_m f_m(z) \ ,$$

$$\int dz\, f^*_m(z) f_{m'}(z) = \delta_{m,m'} \ ,$$

then Eq. (31) becomes an algebraic eigenvalue equation which can be solved without difficulty. More specifically, employing the following expansion:

$$g^i_{\alpha n\mathbf{G}}(z) = \sum_m C^i_{\alpha n\mathbf{G}m} f_m(z) \ ,$$

Eq. (31) is transformed into an algebraic eigenvalue equation

$$\sum_{\alpha' n' \mathbf{G}' m'} H_{\alpha n\mathbf{G}m,\alpha' n' \mathbf{G}' m'} C^i_{\alpha' n' \mathbf{G}' m'} = E^i_{\mathbf{K}} C^i_{\alpha n\mathbf{G}m} \ , \tag{32}$$

where

$$H_{\alpha n\mathbf{G}m,\alpha' n' \mathbf{G}' m'} = \left[E_m + E_\alpha + \mathscr{E}_n + \frac{\hbar^2}{2M}(\mathbf{K} - \mathbf{Q}_n + \mathbf{G})^2 \right] \times \delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{\mathbf{G},\mathbf{G}'}\delta_{m,m'} + (V_{\alpha n\mathbf{G}m,\alpha' n' \mathbf{G}' m'} - u_{m,m'}\delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{\mathbf{G},\mathbf{G}'}) \ ,$$

$$V_{\alpha n\mathbf{G}m,\alpha' n' \mathbf{G}' m'} = \int dz\, f^*_m(z) V^{\mathbf{G}-\mathbf{G}'}_{\alpha n,\alpha' n'}(z) f_{m'}(z) \ .$$

It should be recalled here that, since

$$|V^{\mathbf{G}-\mathbf{G}'}_{\alpha n,\alpha' n'}(z)| \ll |V^0_{\alpha n,\alpha n}(z)| \simeq |v_0(z)|$$

for $(\alpha n\mathbf{G}) \neq (\alpha' n' \mathbf{G}')$, the potential $u(z)$ may be chosen to be, e.g.,

$$u(z) = v_0(z_c) + \tfrac{1}{2} v''_0(z_c)(z - z_c)^2$$

in order to achieve fast convergence of the eigenvalue. Here z_c is the point such that $v'_0(z_c) = 0$. It should also be noted that not all eigenvalues of Eq. (32) are those of Eq. (31). By letting the number of basis functions $f_m(z)$ increase, a suitable convergence test should be applied to determine the proper eigenvalues. In practice, the diagonalization of the matrix $(H_{\alpha n\mathbf{G}m,\alpha' n' \mathbf{G}' m'})$ in Eq. (32) could be made in the subset of the phonon states as discussed in Sec. II for the computational efficiency.

The Green function components are

$$\mathcal{G}^{(+)o}_{\alpha n\mathbf{G},\alpha' n' \mathbf{G}'}(z,z') = \left\langle \alpha n\mathbf{G} \left| \frac{1}{E - H_{oo} + i\epsilon} \right| \alpha' n' \mathbf{G}' \right\rangle$$

with

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

Here the $(\alpha n\mathbf{G})$'s are all open channels. It is seen that

$$[\nabla^2_r, P_o] = [\nabla^2_r, P_c] = 0$$

from the representation

$$P_o = \sum_{\alpha n\mathbf{G}}{}' |\alpha n\mathbf{G}\rangle\langle \alpha n\mathbf{G}|, \quad P_c = 1 - P_o$$

with $|\alpha n\mathbf{G}\rangle$ given above and $\sum'$ denoting the summation over the open $(\alpha n\mathbf{G})$'s. Thus

$$H_{oc} = P_o V P_c, \quad H_{co} = P_c V P_o \ .$$

Using the Green-function components and Eq. (26b), the energy shift and width function matrix $\Delta + i\Gamma$ is computed from

$$\begin{aligned} (\Delta + i\Gamma)_{i,i'} &= \langle g^i_{\mathbf{K}} | W_{cc} | g^{i'}_{\mathbf{K}} \rangle \\ &= \sum_{\substack{\alpha n\mathbf{G} \\ \alpha' n' \mathbf{G}'}} \int\int dz\, dz' \langle g^i_{\mathbf{K}} | V | \alpha n\mathbf{G} \rangle \mathcal{G}^{(+)o}_{\alpha n\mathbf{G},\alpha' n' \mathbf{G}'}(z,z') \langle \alpha' n' \mathbf{G}' | V | g^{i'}_{\mathbf{K}} \rangle \ . \end{aligned} \tag{33}$$

Note that in Eq. (33), matrix elements are evaluated by integrating over **R**,**S**,**s** only and thus

$$\langle g^i_{\mathbf{K}} | V | \alpha n\mathbf{G} \rangle = \sum_{\alpha'' n'' \mathbf{G}''} g^{i*}_{\alpha'' n'' \mathbf{G}''}(z) V^{\mathbf{G}''-\mathbf{G}}_{\alpha'' n'',\alpha n}(z) \ ,$$

$$\langle \alpha' n' \mathbf{G}' | V | g^{i'}_{\mathbf{K}} \rangle = \sum_{\alpha''' n''' \mathbf{G}'''} V^{\mathbf{G}'-\mathbf{G}'''}_{\alpha' n',\alpha''' n'''}(z') g^{i'}_{\alpha''' n''' \mathbf{G}'''}(z') \ .$$

It should be recalled here that $(\alpha''\mathbf{G}'')$ and $(\alpha'''\mathbf{G}''')$ belong to the closed channels, but $(\alpha\mathbf{G})$ and $(\alpha'\mathbf{G}')$ belong to the open channels. From Eq. (26a), the diffractive resonance scattering matrix for the simultaneous vibrational-rotational and phonon transition is given by

$$S^{(+)}_{\alpha_f n_f \mathbf{G}_f,\alpha_i n_i 0} = \mathscr{S}^{(+)o}_{\alpha_f n_f \mathbf{G}_f,\alpha_i n_i 0} + \frac{C^{(+)}_{\alpha_f n_f \mathbf{G}_f,\alpha_i n_i 0}}{L^2} \sum_{ii'} \langle \chi^{(-)o}_{\mathbf{K},\alpha_f n_f \mathbf{G}_f} | V | g^i_{\mathbf{K}} \rangle \left[\frac{1}{(E - E_{\mathbf{K}}) - (\Delta + i\Gamma)} \right]_{ii'} \langle g^{i'}_{\mathbf{K}} | V | \chi^{(+)o}_{\mathbf{K},\alpha_i n_i 0} \rangle \ , \tag{34}$$

where, e.g.,

$$\begin{aligned}\langle \chi^{(-)o}_{\mathbf{K},\alpha_f n_f \mathbf{G}_f} | V | g^i_{\mathbf{K}} \rangle &= \int d\mathbf{r}\, d\mathbf{S}\, d\mathbf{s}\, \chi^{(-)o*}_{\mathbf{K},\alpha_f n_f \mathbf{G}_f}(\mathbf{r},\mathbf{S},\mathbf{s}) V(\mathbf{r},\mathbf{S},\mathbf{s}) g^i_{\mathbf{K}}(\mathbf{r},\mathbf{S},\mathbf{s}) \\ &= L \sum_{\substack{\alpha n \mathbf{G} \\ \alpha' n' \mathbf{G}'}} \int dz\, \chi^{(-)o*}_{\alpha n \mathbf{G},\alpha_f n_f \mathbf{G}_f}(z) V^{\mathbf{G}-\mathbf{G}'}_{\alpha n,\alpha' n'}(z) g^i_{\alpha' n' \mathbf{G}'}(z) \ .\end{aligned}$$

The matrix $(E - E_{\mathbf{K}})$ is defined from

$$(E - E_{\mathbf{K}})_{ii'} = (E - E^i_{\mathbf{K}})\delta_{ii'} \ ,$$

and $(1/A)_{ii'} \equiv (A^{-1})_{ii'}$. The $\mathcal{S}^{(+)o}_{\alpha_f n_f \mathbf{G}_f,\alpha_i n_i 0}$ is the nonresonant potential scattering matrix contained in $\chi^{(+)o}_{\alpha_f n_f \mathbf{G}_f,\alpha_i n_i 0}(z)$. The bound-state resonance scattering amplitude is the second term in Eq. (34). The second matrix element of V represents a trapping and the first one indicates a desorption. The i'th and ith bound states are connected through a propagator.

We discuss some approximation schemes which are used in practical computations. Since $|V^{\mathbf{G}-\mathbf{G}'}_{\alpha n,\alpha' n'}(z)| \ll |V^0_{\alpha n,\alpha n}(z)|$ for $(\alpha n \mathbf{G}) \neq (\alpha' n' \mathbf{G}')$ and $|v_0(z) - V^0_{\alpha n,\alpha n}(z)| \ll |v_0(z)|$, the Hamiltonian H^0 derived from $v_0(z)$ could be used to obtain the Green function, and bound and continuum eigenfunctions. Then

$$\begin{aligned}&\mathcal{G}^{(+)o}_{\alpha n \mathbf{G},\alpha' n' \mathbf{G}'}(z,z') \simeq \delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{\mathbf{G},\mathbf{G}'} \frac{2M}{\hbar^2} \mathcal{G}^{o(+)}_{\alpha n \mathbf{G}}(z,z') \ , \\ &g^i_{\alpha n \mathbf{G}}(z) \simeq \delta_{\alpha,\alpha^i}\delta_{n,n^i}\delta_{\mathbf{G},\mathbf{G}^i} g^i_{\alpha^i n^i \mathbf{G}^i}(z) \ , \\ &\chi^{(\pm)o}_{\alpha n \mathbf{G},\alpha' n' \mathbf{G}'}(z) \simeq \delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{\mathbf{G},\mathbf{G}'} \chi^{0(+)}_{\alpha n \mathbf{G}}(z)\end{aligned}$$

from Sec. IV of paper I. Here, $(\alpha^i n^i \mathbf{G}^i)$ is some $(\alpha n \mathbf{G})$ determined from the eigenfunction index i (cf. next section). Thus

$$(\Delta + i\Gamma)_{i,i'} \simeq \frac{2M}{\hbar^2} \sum_{\alpha n \mathbf{G}} \int\int dz\, dz' g^{i*}_{\alpha^i n^i \mathbf{G}^i}(z) V^{\mathbf{G}^i-\mathbf{G}}_{\alpha^i n^i,\alpha n}(z) \mathcal{G}^{0(+)}_{\alpha n \mathbf{G}}(z,z') V^{\mathbf{G}-\mathbf{G}^{i'}}_{\alpha n,\alpha^{i'} n^{i'}}(z') g^{i'}_{\alpha^{i'} n^{i'} \mathbf{G}^{i'}}(z') \ . \tag{35}$$

The $\mathcal{S}^{(+)o}_{\alpha_f n_f \mathbf{G}_f,\alpha_i n_i 0}$ may be evaluated from the simple DWBA. However, we retain the full potential V in the matrix elements in Eqs. (33) and (34). Since the truncations of channels $(\alpha n \mathbf{G})$ within each group are inevitable, we have $P_o + P_c \simeq 1$. For evaluating $\chi^{(\pm)o}_{\mathbf{K},\alpha' n' \mathbf{G}'}(\mathbf{r},\mathbf{S},\mathbf{s})$, $g^i_{\mathbf{K}}(\mathbf{r},\mathbf{S},\mathbf{s})$, and $\mathcal{S}^{(+)o}_{\alpha_f n_f \mathbf{G}_f,\alpha_i n_i 0}$, more refined approximation than the preceding may be used. We could employ, e.g., the Hamiltonian H^v derived from $v(\mathbf{r})$ for that purpose and note that $|v_{\mathbf{G}}(z) - V^{\mathbf{G}}_{\alpha n,\alpha n}(z)| \ll |v_{\mathbf{G}}(z)|$. Since this is basically the approximation

$$V^{\mathbf{G}}_{\alpha n,\alpha' n'}(z) \simeq \delta_{\alpha,\alpha'}\delta_{n,n'} v_{\mathbf{G}}(z)$$

for computing the bound and continuum eigenfunctions, they are obtained as simple products of the continuum or bound spatial eigenfunctions of the stationary diffractive potential and molecule-phonon wave functions within the open or closed channels. The $\mathcal{S}^{(+)o}_{\alpha_f n_f \mathbf{G}_f,\alpha_i n_i 0}$ may be computed from the CDCTM approach employing the scattering wave function $\chi^{(\pm)o}_{\mathbf{K},\alpha' n' \mathbf{G}'}(\mathbf{r},\mathbf{S},\mathbf{s})$ thus obtained within the open channels. Alternatively one may employ the Hamiltonian H^m for $\mathcal{S}^{(+)o}$, and $\chi^{(\pm)o}$ from the CMSTM within the open channels when the anisotropy of the potential is large.

The preceding approximations make the present bound-state resonance (Feshbach-type) approach quite efficient when the molecular internal states and phonons are included.

An alternative expression of the energy shift and width function is given by

$$(\Delta + i\Gamma)_{i,i'} = \left[\frac{M}{2\pi L^2 \hbar^2}\right] \sum_{\alpha n \mathbf{G}} \int dE' k'^{-1}_{\alpha n \mathbf{G}} \left[P \frac{1}{E - E'} - \pi i \delta(E - E')\right] \langle g^i_{\mathbf{K}} | V | \chi^{(+)o}_{\mathbf{K},\alpha n \mathbf{G}}(E') \rangle \langle \chi^{(+)o}_{\mathbf{K},\alpha n \mathbf{G}}(E') | V | g^{i'}_{\mathbf{K}} \rangle \tag{36}$$

using the continuum eigenfunctions $\chi^{(\pm)o}_{\mathbf{K},\alpha n \mathbf{G}}(\mathbf{r},\mathbf{S},\mathbf{s};E)$ of H_{oo}. This equation was obtained from the normalization and closure property of the (continuum) eigenfunctions of H_{oo}:

$$\begin{aligned}&\langle \chi^{(+)o}_{\mathbf{K},\alpha n \mathbf{G}}(E) | \chi^{(+)o}_{\mathbf{K}',\alpha' n' \mathbf{G}'}(E') \rangle = \left[\frac{2\pi L^2 \hbar^2}{M}\right] k_{\alpha n \mathbf{G}} \delta_{\mathbf{K},\mathbf{K}'}\delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{\mathbf{G},\mathbf{G}'}\delta(E - E') \ , \\ &\left[\frac{M}{2\pi L^2 \hbar^2}\right] \sum_{\mathbf{K}\alpha n \mathbf{G}} \int dE\, k^{-1}_{\alpha n \mathbf{G}} |\chi^{(+)o}_{\mathbf{K},\alpha n \mathbf{G}}(E)\rangle \langle \chi^{(+)o}_{\mathbf{K},\alpha n \mathbf{G}}(E)| \simeq 1\end{aligned}$$

with the bound eigenfunctions being neglected for simplicity. The summation $\sum_{\mathbf{K}}$ is over the first (two-dimensional) Brillouin zone. Conservation of the total parallel momentum $\mathbf{K}$ (up to $\mathbf{G}$) was also used. The total energy E or E' dependence in $\chi^{(+)o}_{\mathbf{K},\alpha n \mathbf{G}}$ is explicitly indicated. The matrix element of $V(\mathbf{r},\mathbf{S},\mathbf{s})$, e.g., is given by

$$\langle g^{i}_{\mathbf{K}}|V|\chi^{(+)o}_{\mathbf{K},\alpha n\mathbf{G}}(E)\rangle = \int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,g^{i*}_{\mathbf{K}}(\mathbf{r},\mathbf{S},\mathbf{s})V(\mathbf{r},\mathbf{S},\mathbf{s})\chi^{(+)o}_{\mathbf{K},\alpha n\mathbf{G}}(\mathbf{r},\mathbf{S},\mathbf{s};E)$$
$$= L\sum_{\substack{\alpha' n'\mathbf{G}' \\ \alpha'' n''\mathbf{G}''}} \int dz\, g^{i*}_{\alpha' n'\mathbf{G}'}(z)V^{\mathbf{G}'-\mathbf{G}''}_{\alpha' n',\alpha'' n''}(z)\chi^{(+)o}_{\alpha'' n''\mathbf{G}'',\alpha n\mathbf{G}}(z;E)\ .$$

Since the wave functions need to be evaluated for all energies E', Eq. (36) is more complex than Eq. (33).

It should be recalled here that the relation between S and T matrix elements is given by Eq. I (78). The simultaneous molecular and phonon transition resonance diffraction coefficient is given by Eq. I (80) with the present S matrix element of Eq. (34). The selective adsorption and desorption processes upon transition of the phonons and molecular internal states are basically contained in Eq. (34). Therefore, the present method is best suited for investigating the diffraction, phonon, and rotational mediations in resonance scattering (selective adsorption and desorption). The theoretical intensities and line shapes of the phonon-, vibration-rotation-assisted resonance can be computed with the present scheme.

IV. ADSORPTION RATES

When molecules collide with a crystalline surface in the thermal energy range, some of them are adsorbed to the surface whereas others are scattered out. The adsorption takes place with or without dissociation of the molecule. In this section, we discuss the adsorption rates of the molecular projectile in the absence of any dissociation using reasonable approximations. We are mainly concerned with physisorption or trapping rather than chemisorption or sticking. In general the long-range attractive behavior of the adiabatic molecule-surface interaction potential, i.e., van der Waals force, is important in the physisorption or trapping processes. The adsorption rate (or probability) refers to the physisorption or trapping rate in this section unless specified further. This rate is basically the transition rate between the incident wave and bound wave function of the molecule to the surface. The incident molecule is adsorbed to the surface by transferring sufficiently large energy to it so that the molecule does not have the perpendicular component of the kinetic energy to be scattered out. The molecular projectile is caught by the thermally averaged potential $\mathcal{V}(\mathbf{r},\mathbf{S},\mathbf{s})$. Adsorption rate is generally given by a semiempirical function of the coverage ratio θ of the adsorbates with the initial and final adsorption rates corresponding to $\theta=0$ and 1, respectively. The central quantities to be evaluated are thus the adsorption rates for the $\theta=0$ case for which it is easy to carry out measurements on the rates. But the following theoretical scheme can also be applied to the $\theta\neq 0$ case (partial or whole coverage) as long as the adsorbates form ordered overlayers such that the two-dimensional periodicity of the crystalline surface exists.

We assume that $|\mathcal{V}^{\mathbf{G}-\mathbf{G}'}_{\alpha,\alpha'}(z)| \ll |\mathcal{V}^{0}_{\alpha,\alpha}(z)|$ for $(\alpha,\mathbf{G})\neq(\alpha',\mathbf{G}')$ and $|\mathcal{V}^{0}_{\alpha,\alpha}(z)-v_0(z)| \ll |v_0(z)|$, where $v_0(z)$ is obtained by suitably averaging $\mathcal{V}^{0}_{\alpha,\alpha}(z)$ over the molecular states α. However, this assumption is not essential in our scheme of obtaining adsorption rates because it is used only for conveniently indexing the bound-state eigenvalues and eigenfunctions.

We begin our discussion with the simple Hamiltonian H^0 given before,

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

This is a molecule–flat-surface Hamiltonian. The jth bound eigenfunction $g_j^0(z)$ and the eigenvalue E_j^0 of the z coordinate are obtained from

$$\left[-\frac{\hbar^2}{2M}\frac{d^2}{dz^2} + v_0(z)\right] g_j^0(z) = E_j^0 g_j^0(z)$$

with $E_j^0<0$, $\int dz\, g_j^{0*}(z)g_{j'}^0(z)=\delta_{j,j'}$. The total bound-state wave function of the molecule–flat-surface system can be written as

$$g^0_{\mathbf{K},\alpha n\mathbf{G}j}(\mathbf{r},\mathbf{S},\mathbf{s}) = \frac{1}{L}g_j^0(z)\Phi_\alpha(\mathbf{S},\mathbf{s})|\phi_n\rangle e^{i(\mathbf{K}-\mathbf{Q}_n+\mathbf{G})\cdot\mathbf{R}}$$

with $\mathbf{K}$ being the total parallel momentum of the system (mod$\mathbf{G}$). The wave functions satisfy

$$H^0 g^0_{\mathbf{K},\alpha n\mathbf{G}j}(\mathbf{r},\mathbf{S},\mathbf{s}) = E^0_{\mathbf{K},\alpha n\mathbf{G}j}\, g^0_{\mathbf{K},\alpha n\mathbf{G}j}(\mathbf{r},\mathbf{S},\mathbf{s})\ , \tag{37}$$

$$\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,g^{0\dagger}_{\mathbf{K},\alpha n\mathbf{G}j}(\mathbf{r},\mathbf{S},\mathbf{s})g^0_{\mathbf{K}',\alpha' n'\mathbf{G}'j'}(\mathbf{r},\mathbf{S},\mathbf{s}) = \delta_{\mathbf{K},\mathbf{K}'}\delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{\mathbf{G},\mathbf{G}'}\delta_{j,j'}\ , \tag{38}$$

with

$$E^0_{\mathbf{K},\alpha n\mathbf{G}j} = E_j^0 + E_\alpha + \mathcal{E}_n + \frac{\hbar^2}{2M}(\mathbf{K}-\mathbf{Q}_n+\mathbf{G})^2\ .$$

Equation (38) of the orthogonality holds when the $\mathbf{K}$'s lie again in the first (two-dimensional) Brillouin zone. This is always possible by redefining the $\mathbf{Q}_n$'s (as a function of n) up to $\mathbf{G}$ without affecting the physical consequences. Note that $E_j^0<0$ for the bound state. By a suitable superposition of states with different $\mathbf{K}$'s, the bound-state wave functions can be localized in the $\mathbf{R}$ coordinates.

Thermally averaging the total molecular-surface interaction potential over the phonon states, we obtain the molecule–rigid-surface potential $\mathcal{V}(\mathbf{r},\mathbf{S},\mathbf{s})$. Using $\mathcal{V}(\mathbf{r},\mathbf{S},\mathbf{s})$, the bound-state wave function and eigenvalues are generally obtained and indexed in the manner described in Sec. III without restriction to the closed $(\alpha n\mathbf{G})$'s here. But based on the assumption previously mentioned, we discuss a suitable indexing scheme of the wave functions and eigenvalues for the potential. We define the molecule-surface Hamiltonian H^r as

$$H^r = -\frac{\hbar^2}{2M}\nabla_r^2 + H_{\mathrm{mol}} + \mathcal{V}(\mathbf{r},\mathbf{S},\mathbf{s}) + H_{\mathrm{cr}}\ ,$$

where h^r is an approximate Hamiltonian in the sense that no coupling between the projectile and the phonons is included. The superscript r refers to the molecule–*rigid*-surface interaction in the Hamiltonian. The corresponding (bound-state) eigenvalue equation for a given **K**,

$$H^r g^r_{\mathbf{K},\alpha n\mathbf{G}j}(\mathbf{r},\mathbf{S},\mathbf{s})=E_{\mathbf{K},\alpha n\mathbf{G}j}\,g^r_{\mathbf{K},\alpha n\mathbf{G}j}(\mathbf{r},\mathbf{S},\mathbf{s})\ , \tag{39a}$$

can be solved without difficulty by setting

$$g^r_{K,\alpha'n'\mathbf{G}'j'}(\mathbf{r},\mathbf{S},\mathbf{s})=\frac{1}{L}\sum_{\alpha\mathbf{G}}g^r_{\alpha\mathbf{G},\alpha'\mathbf{G}'j'}(z)\Phi_\alpha(\mathbf{S},\mathbf{s})|\phi_{n'}\rangle\times e^{i(\mathbf{K}-\mathbf{Q}_{n'}+\mathbf{G})\cdot\mathbf{R}} \tag{39b}$$

with the following equivalent expressions of the orthogonality condition:

$$\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,g^{r\dagger}_{\mathbf{K},\alpha n\mathbf{G}j}(\mathbf{r},\mathbf{S},\mathbf{s})g^r_{\mathbf{K}',\alpha'n'\mathbf{G}'j'}(\mathbf{r},\mathbf{S},\mathbf{s})=\delta_{\mathbf{K},\mathbf{K}'}\delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{\mathbf{G},\mathbf{G}'}\delta_{j,j'}\ ,$$

$$\sum_{\alpha\mathbf{G}}\int dz\,g^{r*}_{\alpha\mathbf{G},\alpha'\mathbf{G}'j'}(z)g^r_{\alpha\mathbf{G},\alpha''\mathbf{G}''j''}(z)=\delta_{\alpha',\alpha''}\delta_{\mathbf{G}',\mathbf{G}''}\delta_{j',j''}\ . \tag{39c}$$

Note that $g^r(\mathbf{r},\mathbf{S},\mathbf{s})$ is the product of the spatial wave function and the phonon wave function $|\phi_{n'}\rangle$. If we set

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

then the second term on the right-hand side of the above equation is much smaller than the first in our assumption. The subscripts $(\alpha n\mathbf{G}j)$ or $(\alpha'n'\mathbf{G}'j')$ in Eqs. (39a)–(39c) are the indices suitable for the present potential, with the property that as $\mathcal{V}(\mathbf{r},\mathbf{S},\mathbf{s})\rightarrow v_0(z)$, or equivalently, as $\tilde{\mathcal{V}}^{\mathbf{G}}_{\alpha,\alpha'}(z)\rightarrow 0$,

$$E_{\mathbf{K},\alpha'n'\mathbf{G}'j'}\rightarrow E^0_{\mathbf{K},\alpha'n'\mathbf{G}'j'}\ ,$$

$$g^r_{\mathbf{K},\alpha'n'\mathbf{G}'j'}(\mathbf{r},\mathbf{S},\mathbf{s})\rightarrow g^0_{\mathbf{K},\alpha'n'\mathbf{G}'j'}(\mathbf{r},\mathbf{S},\mathbf{s})\ .$$

The latter is equivalent to

$$g^r_{\alpha\mathbf{G},\alpha'\mathbf{G}'j'}(z)\rightarrow g^0_{j'}(z)\delta_{\alpha,\alpha'}\delta_{\mathbf{G},\mathbf{G}'}\ .$$

Other indexing scheme of the eigenfunctions and eigenvalues rather than the present $(\alpha'n'\mathbf{G}'j')$'s may be used in general cases as indicated by the superscripts i or i' in the bound-state eigenvalues or eigenfunctions in the previous section. But under the present assumption that

$$|\mathcal{V}(\mathbf{r},\mathbf{S},\mathbf{s})-v_0(z)|\ll|v_0(z)|\ ,$$

the number of eigenfunctions of H^r for a given **K** is basically the same as that of the indices $(\alpha'n'\mathbf{G}'j')$. The latter yield the number of the eigenfunctions of H^0 and are convenient for keeping track of the eigenvalues when $\mathcal{V}(\mathbf{r},\mathbf{S},\mathbf{s})\rightarrow v_0(z)$. As usual, Eqs. (39a) and (39b) result in the differential eigenvalue equation

$$\left[\frac{d^2}{dz^2}-\kappa^2_{\alpha\mathbf{G},\alpha'\mathbf{G}'j'}\right]g^r_{\alpha\mathbf{G},\alpha'\mathbf{G}'j'}(z)=\frac{2M}{\hbar^2}\sum_{\alpha''\mathbf{G}''}\mathcal{V}^{\mathbf{G}-\mathbf{G}''}_{\alpha,\alpha''}(z)g^r_{\alpha''\mathbf{G}'',\alpha'\mathbf{G}'j'}(z)$$

with

$$\kappa^2_{\alpha\mathbf{G},\alpha'\mathbf{G}'j'}=(\mathbf{K}_p+\mathbf{G})^2-\frac{2M}{\hbar^2}(E_{\mathbf{K}_p,\alpha'\mathbf{G}'j'}-E_\alpha)\ ,$$

$$\mathbf{K}=\mathbf{K}_p+\mathbf{Q}_{n'},\quad E_{\mathbf{K},\alpha'n'\mathbf{G}'j'}=E_{\mathbf{K}_p,\alpha'\mathbf{G}'j'}+\mathcal{E}_{n'}\ .$$

This is essentially the same as Eq. (31) if the following replacements:

$$g^r_{\alpha\mathbf{G},\alpha'\mathbf{G}'j'}(z)\delta_{n,n'}\rightarrow g^{i'}_{\alpha n\mathbf{G}}(z)\ ,$$

$$\kappa^2_{\alpha\mathbf{G},\alpha'\mathbf{G}'j'}\rightarrow\kappa^2_{\alpha n\mathbf{G},i'}\ ,$$

$$E_{\mathbf{K},\alpha'n'\mathbf{G}'j'}\rightarrow E^{i'}_{\mathbf{K}}$$

are made. Note that the present equation is solved without any restriction to $(\alpha\mathbf{G})$'s in contrast to Eq. (31). Expanding $g^r_{\alpha\mathbf{G},\alpha'\mathbf{G}'j'}(z)$ in terms of the basis functions $\{f_m(z)\}$ with coefficients $C_{\alpha\mathbf{G}m,\alpha'\mathbf{G}'j'}$, we obtain basically the same algebraic eigenvalue equation given by Eq. (32) with suitable replacements. This algebraic equation is efficient in obtaining numerical results. Note that

$$E_{\mathbf{K},\alpha'n'\mathbf{G}'j'}=E_{\mathbf{K}+\mathbf{G}_0,\alpha'n'\mathbf{G}'-\mathbf{G}_0j'}\ ,$$

$$g^r_{\mathbf{K},\alpha'n'\mathbf{G}'j'}(\mathbf{r},\mathbf{S},\mathbf{s})=g^r_{\mathbf{K}+\mathbf{G}_0,\alpha'n'\mathbf{G}'-\mathbf{G}_0j'}(\mathbf{r},\mathbf{S},\mathbf{s})\ ,$$

$$g^r_{\alpha\mathbf{G},\alpha'\mathbf{G}'j'}(z;\mathbf{K})=g^r_{\alpha\mathbf{G}-\mathbf{G}_0,\alpha'\mathbf{G}'-\mathbf{G}_0j'}(z;\mathbf{K}+\mathbf{G}_0)\ .$$

If other indexing scheme of the eigenfunctions and eigenvalues rather than the present $(\alpha'n'\mathbf{G}'j')$ is used, then the preceding equation should read as for any index i, there exists an i' satisfying

$$E^i_{\mathbf{K}}=E^{i'}_{\mathbf{K}+\mathbf{G}_0}\ ,$$

$$g^i_{\mathbf{K}}(\mathbf{r},\mathbf{S},\mathbf{s})=g^{i'}_{\mathbf{K}+\mathbf{G}_0}(\mathbf{r},\mathbf{S},\mathbf{s})\ ,$$

$$g^i_{\alpha\mathbf{G}}(z;\mathbf{K})=g^{i'}_{\alpha\mathbf{G}-\mathbf{G}_0}(z;\mathbf{K}+\mathbf{G}_0)\ .$$

If the index scheme is based on the ascending order of the eigenvalues, we have $i=i'$. Therefore, this is basically the band structure of the eigenvalue and eigenfunction of the adsorbed molecule due to the corrugation.

The scattering wave function $\chi^{r(\pm)}_{\mathbf{K},\alpha_in_i0}(\mathbf{r},\mathbf{S},\mathbf{s})$ is defined from

$$(E-H^r\pm i\epsilon)\chi^{r(\pm)}_{\mathbf{K},\alpha_in_i0}(\mathbf{r},\mathbf{S},\mathbf{s})=\pm i\epsilon\varphi^{(\mp)}_{\mathbf{K},\alpha_in_i0}(\mathbf{r},\mathbf{S},\mathbf{s})\ .$$

The coupled differential equation, asymptotic boundary condition, and coupled integral equation satisfied by the wave function can be inferred from Eqs. I (25), I (63), and I (64). The dependence of the wave function and scattering matrix on the initial phonon state n_i is due to the total-energy representation employed here. If $\chi^{r(+)}_{\mathbf{K},i}(\mathbf{r},\mathbf{S},\mathbf{s})$ is the incident wave function, then the adsorption transition amplitude is given by

$$C^a_{f,i}=\frac{1}{L^{3/2}}\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,g^{r\dagger}_{\mathbf{K},f}(\mathbf{r},\mathbf{S},\mathbf{s})U(\infty,-\infty)\times\chi^{r(+)}_{\mathbf{K},i}(\mathbf{r},\mathbf{S},\mathbf{s}) \tag{40}$$

with $f=\alpha_fn_f\mathbf{G}_f$, $i=\alpha_in_i0$. The initial and final states satisfy

$$H^r\chi^{r(+)}_{\mathbf{K},i}=E_i\chi^{r(+)}_{\mathbf{K},i},\quad H^rg^r_{\mathbf{K},f}=E_fg^r_{\mathbf{K},f} \tag{41}$$

with their respective energies given by E_i and E_f. The $U(\infty,-\infty)$ is the time evolution or S operator in the interaction picture. Using the following formal definition:

$$U(0,\mp\infty)=\lim_{t\to\mp\infty}U(0,t)=\Omega_\pm\ , \tag{42}$$

S is given by

$$S=U(\infty,-\infty)=U^\dagger(0,\infty)U(0,-\infty)=\Omega_-^\dagger\Omega_+\ . \tag{43}$$

Here

$$U(0,t)=e^{(i/\hbar)Ht}e^{-(i/\hbar)H^r t}$$

with H being the full Hamiltonian. Thus

$$\begin{aligned}S&=\lim_{t\to+\infty}U^\dagger(0,t)U(0,-t)\\&=1+\int_0^\infty dt\,\frac{d}{dt}[U^\dagger(0,t)U(0,-t)]\ .\end{aligned} \tag{44}$$

Employing Eqs. (41) and (44) with $H-H^r=V-\mathcal{V}\equiv\mathcal{U}$, we obtain

$$\begin{aligned}C^a_{f,i}=\frac{1}{L^{3/2}}\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,g^{r\dagger}_{\mathbf{K},f}(\mathbf{r},\mathbf{S},\mathbf{s})\\ \times[1-2\pi i\delta(E_f-E_i)T_{\mathcal{U}}]\chi^{r(+)}_{\mathbf{K},i}(\mathbf{r},\mathbf{S},\mathbf{s})\end{aligned} \tag{45}$$

from Eq. (40), where

$$T_{\mathcal{U}}=\mathcal{U}+\mathcal{U}\mathcal{G}_r^{(+)}\mathcal{U}+\cdots=\mathcal{U}+T_{\mathcal{U}}\mathcal{G}_r^{(+)}\mathcal{U}=\mathcal{U}+\mathcal{U}\mathcal{G}_r^{(+)}T_{\mathcal{U}}$$

with

$$\mathcal{G}_r^{(+)}=\frac{1}{E-H^r+i\epsilon}\ .$$

Since

$$\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,g^{r\dagger}_{\mathbf{K},f}(\mathbf{r},\mathbf{S},\mathbf{s})\chi^{r(+)}_{\mathbf{K},i}(\mathbf{r},\mathbf{S},\mathbf{s})=0\ ,$$

$$T_{\mathcal{U}}\chi^{r(+)}_{\mathbf{K},i}=\mathcal{U}\psi^{(+)}_{\mathbf{K},i}\ ,$$

we have

$$C^a_{f,i}=-2\pi i\delta(E_f-E_i)T^a_{f,i}(\mathbf{K},E) \tag{46}$$

with

$$\begin{aligned}T^a_{f,i}(\mathbf{K},E)=\frac{1}{L^{3/2}}\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,g^{r\dagger}_{\mathbf{K},f}(\mathbf{r},\mathbf{S},\mathbf{s})\\ \times\mathcal{U}(\mathbf{r},\mathbf{S},\mathbf{s})\psi^{(+)}_{\mathbf{K},i}(\mathbf{r},\mathbf{S},\mathbf{s})\ .\end{aligned} \tag{47}$$

Here $g^{r\dagger}_{\mathbf{K},f}$ and $\psi^{(+)}_{\mathbf{K},i}$ have the same total energy $E=E_i$. The $\mathbf{K}=\mathbf{K}_i+\mathbf{Q}_{n_i}=\mathbf{K}_p+\mathbf{Q}_{n_f}$ is the total parallel momentum of the system up to $\mathbf{G}$. The conservation of the total parallel momentum (up to $\mathbf{G}$) has already been taken into account. The total adsorption rate is then computed from

$$\begin{aligned}R_a&=\frac{2\pi}{\hbar}\sum_f\delta(E_f-E_i)|T^a_{f,i}(\mathbf{K},E)|^2\\&=\frac{2\pi}{\hbar}\rho(E)|T^a_{f,i}(\mathbf{K},E)|^2\ ,\end{aligned} \tag{48}$$

for given $\mathbf{K}$, E, and $\alpha_i n_i$. Note that $i=\alpha_i n_i 0$, and $\rho(E)$ is the number of the adsorbed states per unit energy interval, i.e., the density of the bound states.

As previously mentioned, some other projectiles are scattered out without adsorbing to the surface. Since we do not consider here dissociation or bond-breaking processes of the molecule, we discuss only the scattering rates in the following. The scattering transition amplitude is

$$\begin{aligned}C^s_{f,i}&=\frac{1}{L^3}\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,\chi^{r(-)\dagger}_{\mathbf{K},f}(\mathbf{r},\mathbf{S},\mathbf{s})U(\infty,-\infty)\\&\quad\times\chi^{r(+)}_{\mathbf{K},i}(\mathbf{r},\mathbf{S},\mathbf{s})\\&=\frac{1}{L^3}\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,\psi^{(-)\dagger}_{\mathbf{K},f}(\mathbf{r},\mathbf{S},\mathbf{s})\psi^{(+)}_{\mathbf{K},i}(\mathbf{r},\mathbf{S},\mathbf{s})\ .\end{aligned} \tag{49}$$

Here $f=\alpha_f n_f\mathbf{G}_f$, $i=\alpha_i n_i 0$ and

$$H^r\chi^{r(-)}_{\mathbf{K},f}=E_f\chi^{r(-)}_{\mathbf{K},f},\quad H^r\chi^{r(+)}_{\mathbf{K},i}=E_i\chi^{r(+)}_{\mathbf{K},i}\ ,$$

$$H\psi^{(-)}_{\mathbf{K},f}=E_f\psi^{(-)}_{\mathbf{K},f},\quad H\psi^{(+)}_{\mathbf{K},i}=E_i\psi^{(+)}_{\mathbf{K},i}\ ,$$

with respective incoming or outgoing boundary conditions. The second equality of Eq. (49) is obtained from Eqs. (42) and (43). The parallel momenta, $\mathbf{K}_i$ and $\mathbf{K}_f$, of the incident and scattered molecules are given by $\mathbf{K}_i=\mathbf{K}-\mathbf{Q}_{n_i}$ and $\mathbf{K}_f=\mathbf{K}-\mathbf{Q}_{n_f}+\mathbf{G}_f$, respectively. With the same techniques as adopted before, we obtain

$$\begin{aligned}C^s_{f,i}&=\frac{1}{L^3}\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,\chi^{r(-)\dagger}_{\mathbf{K},f}(\mathbf{r},\mathbf{S},\mathbf{s})(1-2\pi i\delta(E_f-E_i)T_{\mathcal{U}})\chi^{r(+)}_{\mathbf{K},i}(\mathbf{r},\mathbf{S},\mathbf{s})\\&=-2\pi i\delta(E_f-E)T_{f,i}(\mathbf{K},E)=-2\pi\left[\frac{\hbar^2}{ML}\right]\sqrt{k_f k_i}\,\delta(E_f-E)S^{(+)}_{f,i}(\mathbf{K},E)\end{aligned} \tag{50}$$

with $E=E_i$. The $T_{f,i}(\mathbf{K},E)$ and $S^{(+)}_{f,i}(\mathbf{K},E)$ are the similar transition and scattering matrices as discussed in Sec. IV of paper I. It should be noted that

$$\begin{aligned}&\frac{1}{L^3}\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,\chi^{r(\pm)\dagger}_{\mathbf{K},f}(\mathbf{r},\mathbf{S},\mathbf{s})\chi^{r(\pm)}_{\mathbf{K},i}(\mathbf{r},\mathbf{S},\mathbf{s})=2\pi\left[\frac{\hbar^2}{ML}\right]\sqrt{k_f k_i}\,\delta(E_f-E)\delta_{\alpha_f,\alpha_i}\delta_{n_f,n_i}\delta_{\mathbf{G}_f,0}\ ,\\&\frac{1}{L^3}\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,\chi^{r(-)\dagger}_{\mathbf{K},f}(\mathbf{r},\mathbf{S},\mathbf{s})\chi^{r(+)}_{\mathbf{K},i}(\mathbf{r},\mathbf{S},\mathbf{s})=-2\pi\left[\frac{\hbar^2}{ML}\right]\sqrt{k_f k_i}\,\delta(E_f-E)\delta_{n_f,n_i}\mathcal{S}^{r(+)}_{\alpha_f n_i\mathbf{G}_f,\alpha_i n_i 0}(\mathbf{K},E)\end{aligned} \tag{51}$$

with $\mathcal{S}^{r(+)}$ representing the scattering matrix from $\mathcal{V}$ contained in the asymptotic boundary condition of $\chi^{r(+)}$. Further note the minus sign on the right-hand side of the second equation. This indicates that the scattering theory being studied here is different from the conventional scattering theory where the target is spatially localized. Equation (50) thus can be rewritten as

$$C^{s}_{f,i} = -2\pi\delta(E_f - E)\left[\left|\frac{\hbar^2}{ML}\right|\sqrt{k_f k_i}\,\delta_{n_f,n_i}\mathcal{S}^{r(+)}_{\alpha_f n_i \mathbf{G}_f,\alpha_i n_i 0}(\mathbf{K},E) + \frac{i}{L^3}\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,\chi^{r(-)\dagger}_{\mathbf{K},f}(\mathbf{r},\mathbf{S},\mathbf{s})\mathcal{U}(\mathbf{r},\mathbf{S},\mathbf{s})\psi^{(+)}_{\mathbf{K},i}(\mathbf{r},\mathbf{S},\mathbf{s})\right] . \tag{52}$$

Here, $\chi^{r(-)}_{\mathbf{K},f}$ and $\psi^{(+)}_{\mathbf{K},i}$ have the same total energy E. For given $\alpha_i n_i \mathbf{K}$ and E, the total scattering rate is given by (after δ-function manipulation)

$$R_s = \frac{ML}{\hbar^3}\sum_{\alpha_f n_f \mathbf{G}_f}\left[\frac{2M}{\hbar^2}(E - E_{\alpha_f} - \mathcal{E}_{n_f}) - (\mathbf{K} - \mathbf{Q}_{n_f})^2\right]^{-1/2} |T_{f,i}(\mathbf{K},E)|^2 . \tag{53}$$

The adsorption and scattering rates should be thermally averaged over n_i using a surface temperature T_s. It should be noted that, in the average procedure, $\mathbf{K}$ and E are not kept fixed because

$$\mathbf{K} = \mathbf{K}_i + \mathbf{Q}_{n_i}, \quad E = E_i = E^p_i + E_{\alpha_i} + \mathcal{E}_{n_i}$$

with

$$E^p_i = \frac{\hbar^2}{2M}k_i^2 = \frac{\hbar^2}{2M}(k_{iz}^2 + K_i^2) .$$

Further thermal averages over E^p_i and α_i could be made employing the translational and vibrational-rotational temperatures of the gas, T_t and T_{vr}, respectively. We also carry out the average over the incident direction, that is, over $\hat{\mathbf{k}}_i$. Denoting the averaged quantities by $\langle\ \rangle$, we obtain the total adsorption and scattering rates as follows:

$$\mathcal{R}_a = \langle R_a \rangle = \mathcal{R}_a(T_s, T_t, T_{vr}) ,$$
$$\mathcal{R}_s = \langle R \rangle = \mathcal{R}_s(T_s, T_t, T_{vr}) . \tag{54}$$

These quantities can be measured experimentally and are important in surface studies. If the average over $\hat{\mathbf{k}}_i$ were omitted, we would have more detailed rates as functions of the incident angles. In a practical computation of the adsorption and scattering rates, we could make the approximation $\psi^{(+)}_{\mathbf{K},i}(\mathbf{r},\mathbf{S},\mathbf{s}) \simeq \chi^{r(+)}_{\mathbf{K},i}(\mathbf{r},\mathbf{S},\mathbf{s})$ in Eqs. (47) and (52).

V. SUMMARY AND DISCUSSIONS

We have obtained realistic theoretical approximation schemes for the calculation of the phonon and vibrational-rotational inelastic triatomic-molecule–surface scattering based on the formulation in paper I. An iterative coupled integral equation derived from the distorted-wave Green function with the inclusion of phonons in the solid and vibrations and rotations of the triatom is much more tractable than its counterpart of the coupled differential equation. Our method is capable of yielding an efficient *ab initio* computational scheme when a suitable truncation of the phonon states as discussed in Sec. II is made. For the molecule-surface scattering study including phonons and vibrations and rotations, the coupled differential equation should be replaced by the iterative integral equation. Considering the fact that multiphonon transitions become more probable for a triatomic (or polyatomic) projectile than the light atom or diatom projectile case, the present iterative-integral-equation approach is also useful for studying these transitions since it yields calculational procedures of DWBA of any higher orders as a byproduct. A rotationally impulsive integral-equation scheme, which is appropriate for the triatomic molecular projectile and is essentially applicable to a general polyatomic case, is also obtained from the present method. The complexity of the calculation resulting from the rotational states of the triatomic molecule is simplified in our approach.

Employing proper Green functions, we have obtained theoretical approaches for the simultaneous diffraction, phonon and vibrational-rotational transitions of the (nonresonant) direct inelastic-scattering processes, CDCTM and CMSTM, with an exponential unitarization scheme (see the Appendix). The CDCTM may be used when corrugation of the molecule-surface potential is significant. The coupling between the reciprocal lattice points due to the molecule-surface interaction is taken into account in the incident and scattered wave functions of the molecular projectile. The CMSTM could be employed when the dependence of the molecule-surface potential on the internal coordinates of the projectile or the anisotropy of the potential is considerably large. The dynamic coupling between the internal (vibrational-rotational) states of the projectile is included in the incident and scattered wave functions of the molecule. These two theoretical schemes may be used for studying the angular, velocity, and vibrational-rotational state distribution of the scattered molecule and energy transfers among translation, vibrations and rotations, and phonons. Our method results in both the diagonal (elastic reflection) and nondiagonal (simultaneous diffraction, phonon, vibrational-rotational transition) elements in the S matrix.

As an application of the present scattering formulation, we have presented the bound-state resonance scattering method of the (triatomic) molecule-surface system within the framework of the Feshbach approach for the purpose of studying the diffraction-, phonon-, and rotational-mediated selective adsorption and desorption. The (indirect) resonance scattering results from coupling between the closed channels and open diffraction (or reflection) channels. In other words, the projectile is temporarily trapped to the surface. After a certain lifetime elapses, it is desorbed again upon transition of phonons, rotations, and vibrations. Thus, the resonance scattering is basically the trapping-desorption scattering in contrast to the direct collision processes (the bound-state resonance is analogous to the compound nucleus model in the nuclear reaction theory). Selective adsorption or desorption upon creation and/or annihilation of phonons or rotational transitions has been observed in some experiments. The theoretical methods developed for the interpretation of such processes are generally not *ab initio* in character, but rather are either phenomenological or limited to certain potentials. The close-coupling calculation becomes very complex due to the closed channels when phonons, rotations, and vibrations are included. Therefore, the Feshbach-type approach which describes the trapping-desorption scattering mechanism should be most appropriate for theoretical study of the phonon-, rotation-, and vibration-mediated bound-state resonance scattering (selective adsorption).

We have presented explicit expressions of the scattering matrix and (*ab initio*) calculational procedures from which the resonances energies (with band structure due to corrugation), the shift and width function of the energies, and resonance line shape and intensities of the simultaneous phonon, vibrational-rotational transition, and diffraction can be obtained. Some realistic approximation schemes of the phonon and vibrational-rotational transition resonance scattering method which are effective for computations are also discussed. Especially included is a scheme where the bound-state resonance scattering amplitude is computed from the expression given in Eq. (34) with simplified wave functions. These wave functions are obtained as products of the spatial wave function generated from the elastic diffraction potential and that of the phonon and vibrational-rotational states. The nonresonant potential scattering amplitude in the scheme is computed from CDCTM (or CMSTM) approach *within the open channels.* Compared to the other related theoretical works mentioned in Sec. I including those with Feshbach approach, while they have certain merits, the present method is adoptable to an arbitrary molecule-surface input potential, treats simultaneous diffraction, vibration-rotation, and phonon mediations in resonance in a systematic and unified manner, and includes a transparent description of the trapping-desorption mechanism. It should be pointed out here again that our method is *ab initio* in nature and yields efficient calculational schemes.

Finally, a method of obtaining the quantum-mechanical trapping or physisorption probabilities of the triatomic molecular projectile to the surface (without any dissociation processes) was presented as another application of our scattering formulation. As previously mentioned, most computations of the physisorption or trapping probabilities were made by using classical stochastic trajectory with a generalized Langevin equation or semiclassical scheme where the band structure (due to corrugation) of the adsorbed atom and the diffraction part of the incident wave were neglected. In the present method, the approximation $\psi^{(+)} \simeq \chi^{r(+)}$ may be used in practice for the computation between the transition amplitudes expressed in Eqs. (47) and (52) for the trapping or physisorption and scattering probabilities, respectively.

In paper I and this paper, we have developed a systematic formulation of the triatomic-molecule–crystal-surface scattering in the thermal energy range and obtained theoretical schemes that are realistic and at the same time amenable to efficient calculations. These schemes are more *ab initio* in nature to a certain extent compared to the other theoretical methods employed so far. Further, the present treatment of rotations and vibrations of the projectile (in paper I and this paper) can be basically applied to a general polyatomic case. Some numerical results obtained from the theoretical schemes presented in this paper will be reported in later publications.

As previously mentioned, one purpose of the present scattering formulation is to obtain realistic theoretical approaches for the interpretation of the experimental measurements on the phonon and vibrational-rotational inelastic resonance scattering with the best available potentials. Another aim is to obtain the theoretical methods that can be used to determine the precise nature of the adiabatic- (triatomic-) molecule–surface potential using the experimental information. Since the interplay between the experiment, the potential, and the theoretical scattering dynamics is important and the computational results on the potential are nonexistent, obviously an accurate scattering dynamics is essential. We hope that the present formulation and the theoretical schemes would serve such a purpose.

ACKNOWLEDGMENTS

We thank the Universitywide Energy Research Group at the University of California for partial support of this work. One of us (Z. B. G.) would like to thank the Turkish Government for partial support of this research.

APPENDIX

The unitarity conditions of the S matrix for given $\mathbf{K}$ and E were discussed in Eq. I (27) in Sec. II, paper I. Since the simple normalization condition $\sum_{\alpha n \mathbf{G}} |S^{(+)}_{\alpha n \mathbf{G},\alpha' n' \mathbf{G}'}|^2 = 1$ is not sufficient for the unitarization for the approximate S matrices, we apply in this appendix the exponential unitarization scheme employed in other fields of the scattering study[23] to the S matrices obtained from the DWBA, e.g., CDCTM method of Sec. II.

In DWBA, the S matrix is given by

$$S^{(+)}_{\alpha n \mathbf{G},\alpha' n' \mathbf{G}'} \simeq \delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{\mathbf{G},\mathbf{G}'} e^{2i\delta_{\alpha n \mathbf{G}}} + \frac{C^{(+)}_{\alpha n \mathbf{G},\alpha' n' \mathbf{G}'}}{L^2} \langle \chi^{0(-)}_{\mathbf{K},\alpha n \mathbf{G}} | \tilde{V} | \chi^{0(+)}_{\mathbf{K},\alpha' n' \mathbf{G}'} \rangle \qquad (\mathrm{A1})$$

from Eq. I(73), where

$$\langle \chi^{0(-)}_{\mathbf{K},\alpha n\mathbf{G}}|\tilde{V}|\chi^{0(+)}_{\mathbf{K},\alpha'n'\mathbf{G}'}\rangle=\int d\mathbf{r}\,d\mathbf{S}\,d\mathbf{s}\,\chi^{0(-)\dagger}_{\mathbf{K},\alpha n\mathbf{G}}(\mathbf{r},\mathbf{S},\mathbf{s})\times\tilde{V}(\mathbf{r},\mathbf{S},\mathbf{s})\chi^{0(+)}_{\mathbf{K},\alpha'n'\mathbf{G}'}(\mathbf{r},\mathbf{S},\mathbf{s})\ .$$

Defining the S matrix as $S^{(+)}=(S^{(+)}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'})$, we rewrite Eq. (A1) as

$$S^{(+)}\simeq e^{i\Delta}(1+iT^{DW})e^{i\Delta} \tag{A2}$$

with

$$T^{DW}=(T^{DW}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'})\ ,$$

$$T^{DW}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}=-i\frac{C^{(+)}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}}{L^2}e^{-i\delta_{\alpha n\mathbf{G}}}\times\langle \chi^{0(-)}_{\mathbf{K},\alpha n\mathbf{G}}|\tilde{V}|\chi^{0(+)}_{\mathbf{K},\alpha'n'\mathbf{G}'}\rangle e^{-i\delta_{\alpha'n'\mathbf{G}'}}\ ,$$

$$\Delta=(\Delta_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'})=(\delta_{\alpha n\mathbf{G}}\delta_{\alpha,\alpha'}\delta_{n,n'}\delta_{\mathbf{G},\mathbf{G}'})\ .$$

The T^{DW} is seen to be Hermitian, i.e., $T^{DW*}_{\alpha'n'\mathbf{G}',\alpha n\mathbf{G}}=T^{DW}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}$. Equation (A2) then yields a unitarized S matrix as

$$S^{(+)}=e^{i\Delta}e^{iT^{DW}}e^{i\Delta}\ . \tag{A3}$$

The S matrix given by Eq. (A3) is unitary, since T^{DW} is Hermitian.

The CDCTM S matrix can be inferred from Eq. (12) as

$$S^{(+)}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}\simeq\mathcal{S}^{(+)}_{\alpha n\mathbf{G},\alpha n\mathbf{G}'}\delta_{\alpha,\alpha'}\delta_{n,n'}+\frac{C^{(+)}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}}{L^2}\langle \chi^{(-)}_{\mathbf{K},\alpha n\mathbf{G}}|\bar{V}|\chi^{(+)}_{\mathbf{K},\alpha'n'\mathbf{G}'}\rangle\ . \tag{A4}$$

Since $\mathcal{S}^{(+)}_{\alpha n\mathbf{G},\alpha n\mathbf{G}'}$ is the exact S matrix elements obtained from the stationary diffractive potential $v(\mathbf{r})$, the matrix $\mathcal{S}^{(+)}_{\alpha n}=(\mathcal{S}^{(+)}_{\alpha n\mathbf{G},\alpha n\mathbf{G}'})$ is unitary. Therefore, one can determine the Hermitian matrix $\mathcal{T}^{cc}_{\alpha n}=(\mathcal{T}^{\alpha n}_{\mathbf{G},\mathbf{G}'})$ such that

$$\mathcal{S}^{(+)}_{\alpha n}=e^{i\Delta_{\alpha n}}e^{i\mathcal{T}^{cc}_{\alpha n}}e^{i\Delta_{\alpha n}}$$

with $\Delta_{\alpha n}=(\delta_{\alpha n\mathbf{G}}\delta_{\mathbf{G},\mathbf{G}'})$. Since $|v_0(z)|>>|v_{\mathbf{G}}(z)|$ for $\mathbf{G}\neq 0$, $\mathcal{S}^{(+)}_{\alpha n}\simeq e^{2i\Delta_{\alpha n}}$, that is, $\mathcal{T}^{cc}_{\alpha n}\simeq 0$.

Equation (A4) can be written as

$$S^{(+)}\simeq e^{i\Delta}(1+i\mathcal{T}^{cc}+i\bar{T}^{cc})e^{i\Delta} \tag{A5}$$

with $\mathcal{T}^{cc}=(\mathcal{T}^{\alpha n}_{\mathbf{G},\mathbf{G}'}\delta_{\alpha,\alpha'}\delta_{n,n'})$. The matrix $\bar{T}^{cc}$ is defined from the expression $\bar{T}^{cc}=(\bar{T}^{cc}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'})$, where

$$\bar{T}^{cc}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}=-i\frac{C^{(+)}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}}{L^2}e^{-i\delta_{\alpha n\mathbf{G}}}\times\langle \chi^{(-)}_{\mathbf{K},\alpha n\mathbf{G}}|\bar{V}|\chi^{(+)}_{\mathbf{K},\alpha'n'\mathbf{G}'}\rangle e^{-i\delta_{\alpha'n'\mathbf{G}'}}\ ,$$

For the same reasons as discussed previously, $\bar{T}^{cc}$ is close to a Hermitian matrix. Therefore,

$$\begin{aligned}&\bar{T}^{cc}\simeq\tfrac{1}{2}[\bar{T}^{cc}+(\bar{T}^{cc})^\dagger]\equiv\tilde{T}^{cc}\ ,\\&S^{(+)}\simeq e^{i\Delta}[1+i(\mathcal{T}^{cc}+\tilde{T}^{cc})]e^{i\Delta}\ .\end{aligned} \tag{A6}$$

Equation (A6) results in a unitarized S matrix

$$S^{(+)}=e^{i\Delta}e^{iT^{cc}}e^{i\Delta} \tag{A7}$$

with

$$T^{cc}=\mathcal{T}^{cc}+\tilde{T}^{cc}\ .$$

We introduce a further approximation within the present exponential unitarization method of the CDCTM S matrix for practical computation. Since only the transitions $(\alpha_i n_i 0)\rightarrow(\alpha n\mathbf{G})$ are of interest, the off-diagonal elements of T^{cc} that do not involve $(\alpha_i n_i 0)$ are neglected. More specifically, we set $T^{cc}_{\alpha n\mathbf{G},\alpha'n'\mathbf{G}'}=0$ when $(\alpha n\mathbf{G})\neq(\alpha'n'\mathbf{G}')$ *and* $(\alpha'n'\mathbf{G}')\neq(\alpha_i n_i 0)$, *and* $(\alpha n\mathbf{G})\neq(\alpha_i n_i 0)$, and all other matrix elements of T^{cc} are computed as described above. The T^{cc} thus obtained is again Hermitian and the unitarized S matrix is obtained from Eq. (A7). The unitarized scheme in the present approximation is basically equivalent to the case where the transitions containing no initial channel $(\alpha_i n_i 0)$ are neglected in the first order. This scheme is computationally efficient. The unitarization scheme for the CMSTM S matrix can be easily inferred from the preceding discussions.

---

[*] Present address: Argonne National Laboratory, 9700 South Cass Avenue, CHM/200, Argonne, Illinois 60437

[1] B. H. Choi, Z. B. Güvenç, and N. L. Liu, preceding paper, Phys. Rev. B **41**, 3887 (1990).

[2] J. A. Barker and D. J. Auerbach, Surf. Sci. Rep. **4**, 1 (1985), and references therein.

[3] For diatomic-molecule-projectile case, see, e.g., G. Brusdeylins and J. P. Toennies, Surf. Sci. **126**, 647 (1983).

[4] F. Frankel, J. Hager, W. Krieger, W. Walther, C. T. Cambell, G. Ertl, H. Knipers, and K. Segner, Phys. Rev. Lett. **46**, 152 (1982); A. W. Kleyn, A. C. Luntz, and D. J. Auerbach, *ibid.* **47**, 1169 (1981); G. M. McClelland, G. D. Kubiak, H. G. Rennagel, and R. N. Zare, *ibid.* **46**, 831 (1981); J. W. Hepburn, F. J. Northrup, G. L. Ogram, J. C. Polanyi, and J. M. Williamson, Chem. Phys. Lett. **85**, 127 (1982); R. R. Cavanagh and D. S. King, Phys. Rev. Lett. **47**, 1829 (1981); J. B. Cross and J. B. Lurie, Chem. Phys. Lett. **100**, 174 (1983).

[5] M. Asscher, W. L. Guthrie, T. H. Lin, and G. A. Somorjai, Phys. Rev. Lett. **49**, 76 (1982); J. Chem. Phys. **78**, 6992 (1983); H. Zacharias, M. M. T. Loy, and P. A. Roland, Phys. Rev. Lett. **49**, 1790 (1982); J. S. Hayden and G. J. Diebald, J. Chem. Phys. **77**, 4767 (1982).

[6] D. Ettinger, K. Honma, K. Keil, and J. C. Polanyi, Chem. Phys. Lett. **87**, 413 (1982).

[7] D. A. Mantell, S. B. Ryali, G. L. Haller, and J. B. Fenn, J. Chem. Phys. **78**, 4250 (1982); D. A. Mantell, Y. F. Maa, S. B. Ryali, G. L. Haller, and J. B. Fenn, *ibid.* **78**, 6338 (1983).

[8] J. Misewich, C. N. Plum, G. Blyholder, P. L. Houston, and R. P. Merrill, J. Chem. Phys. **78**, 4245 (1983).

[9] L. A. West and G. A. Somorjai, J. Chem. Phys. **57**, 5143 (1972); S. L. Bernasek and G. A. Somorjai, *ibid.* **60**, 4552 (1974); S. T. Ceyer and G. A. Somorjai, Annu. Rev. Phys. Chem. **28**, 447 (1977), and references therein.

[10] For atom-surface system, see J. P. Toennies, Phys. Scr. **T1**, 89 (1982); G. Lillienkamp and J. P. Toennies, J. Chem. Phys. **78**, 5210 (1983); G. Brusdeylins, R. B. Doak, and J. P. Toennies,

ibid. **75**, 1784 (1981); G. Boato, P. Cantini, and L. Mattera, Surf. Sci. **55**, 141 (1976); G. Boato, P. Cantini, and R. Tatarek, Phys. Rev. Lett. **40**, 887 (1978); P. Cantini and R. Tatarek, Surf. Sci. **114**, 471 (1982).

[11] J. P. Cowin, C. F. Yu, S. J. Sibener, and J. E. Hurst, J. Chem. Phys. **75**, 1033 (1981); C. F. Yu, C. S. Hogg, J. P. Cowin, K. B. Whaley, J. C. Light, and S. J. Sibener, Isr. J. Chem. **22**, 305 (1982); J. P. Cowin, C. F. Yu, S. J. Sibener, and L. Wharton, J. Chem. Phys. **79**, 3537 (1983); C. F. Yu, K. B. Whaley, C. S. Hogg, and S. J. Sibener, Phys. Rev. Lett. **51**, 2218 (1983).

[12] A. Kaufhold and J. P. Toennies, Surf. Sci. **173**, 320 (1986).

[13] P. Cantini and R. Tatarek, Phys. Rev. B **3**, 3030 (1981).

[14] V. Celli, N. Garcia, and J. Hutchinson, Surf. Sci. **87**, 112 (1979).

[15] H. Feshbach, Ann. Phys. (N.Y.) **5**, 357 (1958); **19**, 287 (1962); **43**, 410 (1967).

[16] G. Wolken, Jr., J. Chem. Phys. **58**, 3047 (1973); **59**, 1159 (1973).

[17] H. Chow and E. D. Thompson, Surf. Sci. **59**, 225 (1976).

[18] K. B. Whaley, J. C. Light, J. P. Cowin, and S. J. Sibener, Chem. Phys. Lett. **89**, 89 (1982); R. Schinke, *ibid.* **87**, 2352 (1982).

[19] K. L. Wolfe and J. H. Weare, Phys. Rev. Lett. **41**, 1663 (1978).

[20] J. C. Tully, Annu. Rev. Phys. Chem. **31**, 319 (1980), and references therein; M. Shugard, J. C. Tully, and A. Nitzan, J. Chem. Phys. **66**, 2534 (1977); J. C. Tully, *ibid.* **73**, 1975 (1980).

[21] J. L. Beeby and B. K. Agrawal, Surf. Sci. **122**, 447 (1982).

[22] B. H. Choi, R. T. Poe, and K. T. Tang, J. Chem. Phys. **81**, 4979 (1984).

[23] I. C. Percival, Proc. Phys. Soc. London **76**, 206 (1960); M. J. Seaton, *ibid.* **77**, 174 (1961); G. G. Balint-Kurti and R. D. Levine, Chem. Phys. Lett. **7**, 107 (1970); R. D. Levine, Mol. Phys. **22**, 497 (1971); S. Bosanac and G. G. Balint-Kurti, *ibid.* **29**, 1797 (1975).