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Resonance scattering of electrons from N_2 adsorbed on a metallic surface

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The energy and width of the $^2\Pi$ shape resonance in e-N_2 collisions are calculated for N_2 molecules physisorbed on a metallic surface. The breaking of the molecular symmetry by the surface is found to increase the resonance width as compared to that for collisions in the gas phase. The metallic image potential is found to broaden the resonance and lower its energy. The calculated broadening and energy shift agree in order of magnitude with the observed values.

I. INTRODUCTION

Many molecules are known to sustain electron scattering resonances in the low-energy (<10 eV) range.[1,2] For example, in the scattering of electrons off gaseous N_2 there is a shape resonance centered around $E=2.3$ eV with a width of about a volt. Recently, several experiments have demonstrated resonances in the scattering of electrons off molecules adsorbed on a metallic surface.[3-6] The cross sections for the adsorbate resonances generally resemble their gas-phase counterparts, but differ in a number of ways (see Fig. 1). In this paper, we will investigate some of the factors which give rise to these differences.

The term "resonance" refers to a scattering state in which an electron becomes temporarily trapped in a localized orbital of the target. For the resonances we consider in this paper the trapping mechanism consists of a short-ranged attractive potential surrounded by a repulsive centrifugal potential which forms a tunneling barrier for the trapped electron. This quasistable negative ion decays with a lifetime inversely proportional to the resonance width. The characteristic feature of a scattering resonance is a probability amplitude that is much larger inside the target than outside. In this way, resonance scattering is fundamentally different from direct scattering, where the projectile does not penetrate into the core of the target to any large extent. This difference is manifest in the experiments: The angular distribution from a resonance reflects the symmetry of the quasibound orbital, unlike that from direct scattering, which is usually peaked in the forward direction. Also, and more importantly, the resonant trapping of an electron is an exceedingly efficient way of exciting vibrations in a molecule. The added (antibonding) electron modifies the internuclear potential of the molecule, pushing the nuclei apart. When the electron escapes, the molecule finds itself with a modified nuclear wave function, thus having some probability of being left in an excited vibrational state. For a molecule such as N_2 with no permanent dipole, the vibrational excitation cross sections for scattering through a resonance are 2 orders of magnitude greater than those given by the Born approximation.[7]

The above remarks apply equally to a molecule in the gas phase or near a surface; however, when the molecule is adsorbed onto a surface, a number of additional factors come into play.

(i) The centrifugal barrier crucial to the trapping of an electron at a shape resonance will be modified due to the breaking of the molecule's symmetry by the surface; this should affect the width of the resonance.

(ii) An electron trapped near a metallic surface induces an image charge in the metal; the attraction between these two charges can be expected to shift the energy of the resonance.

(iii) The surface fixes the orientation of the molecule, leading to an angular distribution different from that of randomly oriented molecules in the gas phase.[8]

(iv) Charge transfer between the metal and a (chemisorbed) molecule would be expected to modify the vibrational parameters of the molecule; this would be detectable in the cross sections for inelastic electron scattering.[4]

From these considerations, it is not hard to see why the study of electron scattering resonances for molecules adsorbed on a surface may be interesting. One might hope

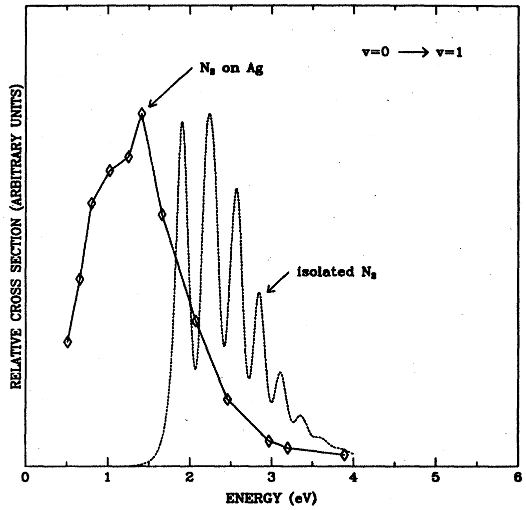

FIG. 1. Relative vibrational excitation cross sections $\sigma_{0\rightarrow 1}$ for e-N_2 collisions. (◇) represents the experimental cross section for N_2 physisorbed on Ag (from Ref. 3); ($\cdots$) represents the cross section for gas-phase N_2 (from Ref. 10). The heights of the two cross sections have arbitrarily been set equal.

to extract information regarding the orientation, equilibrium distance from the surface, binding site geometry, and vibrational parameters of the adsorbed species.

The object of this paper is to identify the mechanisms which cause the resonance broadening and energy shift seen in the experiments of Demuth *et al.*[3,4] for submonolayer N_2 physisorbed on silver. Our calculations establish orders of magnitude for the broadening and energy shift resulting from two mechanisms: multiple scattering between the molecule and the surface, and interaction of the projectile electron with the metallic image potential.

II. EXTRACTION OF THE RESONANCE ENERGY AND WIDTH FROM THE EXPERIMENTS

The energy of the absorbate resonance can be estimated by simple inspection of the experimental results shown in Fig. 1. The center of the cross section for the $v=0 \rightarrow v=1$ excitation lies at about 1.2 eV; this gives a shift of -1.1 eV from the gas-phase energy of 2.3 eV.

The width of the adsorbate resonance can be estimated from the rate at which the integrated cross sections $I_v \equiv \int \sigma_{0\rightarrow v}(E)dE$ decrease with increasing vibrational quantum number v. The magnitude of I_v for a given value of v depends on how strongly the distorted nuclear wave function of the negative ion projects onto the vth vibrational state of the molecule when the resonance decays. For a very broad resonance, I_v falls off rapidly with v, since the electron escapes before the nuclear wave function has been appreciably perturbed. However, if the resonance is narrow, the nuclei may be substantially displaced from the molecular equilibrium when the electron escapes. Then the probability of exciting higher vibrations is large, and I_v falls off more gradually with increasing v. In the case of gaseous N_2, the nuclei execute about an entire vibrational cycle in the negative ion potential; this explains why high vibrations (up to $v=10$) have been observed.[1,2]

Our method for estimating the width of the adsorbate resonance is to vary Γ in a calculation of I_v versus v until our calculated dependence agrees with experiment.[9] The cross sections $\sigma_{0\rightarrow v}(E)$ were determined by the method of Refs. 10 and 11 for vibrational excitation of molecules in the gas phase. This method contains two adjustable functions: $E(R)$, the real internuclear potential of the neutral molecule, and $W(R)=E^{-}(R)-\frac{1}{2}i\Gamma(R)$, the complex internuclear potential of the negative ion. Γ depends on the nuclear separation R because, as the nuclei move apart, the energy of the trapped electron is lowered, and so the barrier through which the electron must tunnel out becomes stronger. Thus, when we assign a single value to the "width" of a resonance, what we really mean is the function $\Gamma(R)$ evaluated at the molecular equilibrium R_0; we will denote this quantity Γ_0. However, in order to obtain reliable cross sections, it is necessary to specify $\Gamma(R)$ accurately throughout the entire region of nuclear motion. In this way, our calculation differs from that of Ref. 12, where Γ was assumed to be a constant.

E and E^{-} were fitted to Morse potentials, and Γ was approximated by[13]

$$\Gamma(R)=\Gamma_0 \frac{k(R)v_l(k(R)\rho)}{k(R_0)v_l(k(R_0)\rho)} , \qquad (1)$$

where $k(R)=\{2[E^{-}(R)-E(R)]\}^{1/2}$, ρ is the radius of the molecule, and v_l is the penetrability of a centrifugal barrier for angular momentum l (a.u., with $\hbar=e=m_e=1$, are used throughout).[14] For the gas-phase resonance, Γ_0 was found to be 0.54 eV.[11]

To calculate the cross sections for the surface-broadened resonance, we assumed $E(R)$ and $E^{-}(R)$ to be essentially the same as in the gas phase, since the physisorbed molecule interacts only weakly with the surface.[4] The main effect of the surface is to change $\Gamma(R)$, either by changing Γ_0 or v_l, or both. The gas-phase resonance has ${}^2\Pi_g$ symmetry, so its primary component is d wave ($l=2$). If we fit I_v versus v to the experimental data using $l=2$, we obtain a best fit with $\Gamma_0=1.75$ eV. However, using v_2 in Eq. (1) is not strictly appropriate when the molecule is near the surface: as we will show in the next section, the surface breaks the inversion symmetry of the scattering potential, thus mixing a strong p-wave component into the adsorbate resonance. If we assume, therefore, that the tunneling barrier becomes essentially p wave (a more reasonable assumption when the molecule is close to the surface), then with $l=1$ the best fit is obtained for $\Gamma_0=1.25$ eV. The calculated values of I_v versus v using $l=1$ and $\Gamma_0=1.25$ eV are shown, along with the experimental data in Fig. 2. Finally, if Γ is assumed to be a constant, as was done in Ref. 12, then the best fit is obtained for $\Gamma_0=1.00$ eV. The experimental data of I_v versus v are not sufficiently detailed to allow a precise determination of $\Gamma(R)$ for all values of R, and thus of Γ_0. However, our calculations indicate a figure in the range of 1.00 eV $<\Gamma_0<$ 1.75 eV for the adsorbate resonance, as opposed to 0.54 eV in the gas phase.

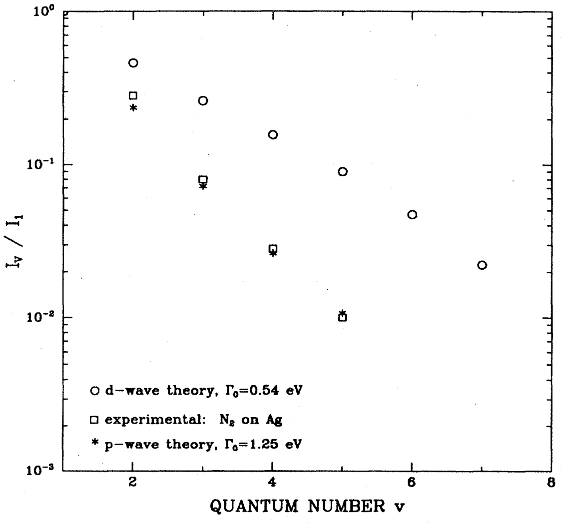

FIG. 2. I_v/I_1 vs vibrational quantum number v [$I_v \equiv \int \sigma_{0\rightarrow v}(E)dE$]. The d-wave theory is for isolated molecules in the gas phase. The experimental data for N_2 physisorbed on Ag are from Ref. 4. (*) represents the best fit of the p-wave theory to experiment, with $\Gamma_0=1.25$ eV. Comparable fits were obtained in a d-wave theory with $\Gamma_0=1.75$ eV and a constant Γ theory with $\Gamma=1.00$ eV.

III. BREAKING OF MOLECULAR SYMMETRY BY THE SURFACE: MULTIPLE SCATTERING

We will now investigate the first mechanism responsible for the broadening of the resonance: multiple scattering between the molecule and the surface. A resonance occurs when an incident electron becomes temporarily trapped in the lowest unfilled orbital of the molecule, which is $^2\Pi_g$ in the case of N_2. Since N_2 has a center of inversion symmetry, the electronic orbitals have definite inversion parity; that is, they receive contributions from either even or odd angular momenta, but not both. The $^2\Pi_g$ state is made up of spherical waves with $|\mu|=1$ and $l=2, 4, \ldots,$ where μ is the projection of angular momentum onto the molecular axis (not necessarily the z axis). The width of the resonance is governed by the leakiest centrifugal barrier through which the trapped electron can escape;[2] thus, the $^2\Pi_g$ resonance decays through a d-wave ($l=2$) barrier. When the molecule is moved up to a surface, the total scattering potential no longer has an inversion center, so the resonant wave functions can contain both even and odd angular momenta. As we will show, multiple scattering between the molecule and the surface introduces a p-wave component into the resonance, whose magnitude increases as the molecule approaches the surface. The $l=1$ centrifugal barrier is lower than that for $l=2$, so the tunneling current is higher and the resonance is broadened.

It should be noted that situations in which the breaking of an inversion symmetry broadens a resonance are not unfamiliar in molecular physics. The width of the lowest shape resonance in e-CO scattering is greater than that for N_2, even though the two molecules are isoelectronic. The asymmetric nuclear potential of CO breaks the inversion symmetry of the electronic wave functions, so that even and odd angular momenta can be mixed together in the resonance. The lowest unfilled molecular orbital in CO ($^2\Pi$, as opposed to $^2\Pi_g$ in N_2) contains a p-wave component; thus the CO resonance decays through a p-wave centrifugal barrier, which is leakier than the d-wave barrier of the N_2 resonance.[2]

We wish to calculate the complex resonance energy $W\equiv E-\frac{1}{2}i\Gamma$ for the combined surface—molecule system. Our model consists of a single N_2 molecule located at a distance z_0 from a step potential surface of height $V_s=-9.8$ eV; this height is the sum of the Fermi energy and the work function in silver. The origin of coordinates is at the center of the molecule, and the positive z axis points in toward the surface (see Fig. 3). We consider two different possible orientations of the molecule: perpendicular to the surface (along z) and parallel to the surface (along x). To describe the molecular scattering we have used N_2 eigenphase sums calculated by Buckley and Burke[15] for the channels $^2\Pi_g$, $^2\Pi_u$, and $^2\Sigma_u$. These eigenphase sums are calculated with the nuclei fixed in their equilibrium position, so the width obtained is equivalent to Γ_0. We have made the approximation of equating the eigenphase sum for a given molecular scattering channel to the phase shift for the lowest angular-momentum component contributing to that channel. Thus, for instance, we used the $^2\Pi_g$ eigenphase sum to represent scattering in a channel with $|\mu|=1$ and $l=2$. This is allowable, since it is the lowest angular momenta which determine the width of the resonance.

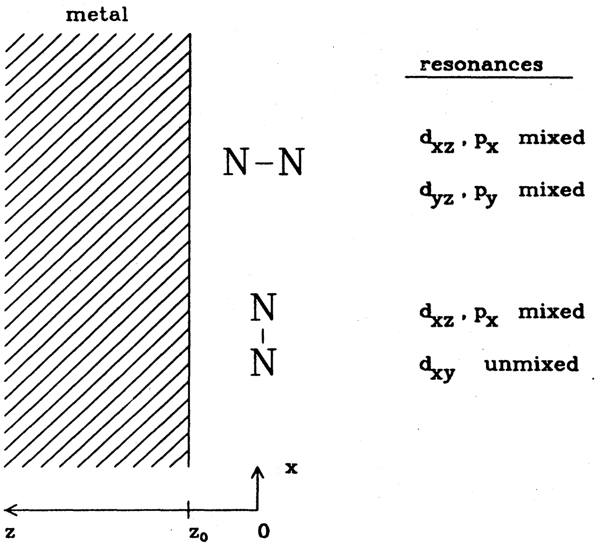

FIG. 3. Resonances occurring in e-N_2 scattering for the parallel and perpendicular orientations of N_2 relative to a surface. The symbols d_{xz}, p_x, etc., are defined in Table I.

Consider first the case of scattering off the isolated molecule. The total wave function is a solution to the wave equation:

$$(K+V_{\rm mol}-E)\Psi=0\ , \tag{2}$$

where $K=-\frac{1}{2}\nabla^2$ and $V_{\rm mol}$ is the interaction between the electron and the molecule. For scattering off a molecule, Ψ can be broken up into an incident wave and an outgoing scattered wave; the two are related through an operator which we will denote M:

$$\Psi=\Psi_{\rm inc}+\Psi_{\rm mol}^{\rm scat}\ , \tag{3}$$

$$\begin{aligned}\Psi_{\rm mol}^{\rm scat}&=M\Psi_{\rm inc}\\ &=M\sum_{l,\mu}a_{l,\mu}j_l(kr)Y_{l,\mu}(\hat{\mathbf{r}})\\ &=\sum_{l,\mu}a'_{l,\mu}h_l^+(kr)Y_{l,\mu}(\hat{\mathbf{r}})\quad (r\rightarrow\infty)\ .\end{aligned} \tag{4}$$

The last equality is valid for radii sufficiently large to make the molecular potential vanish.

If $\Psi_{\rm inc}=e^{i\mathbf{k}\cdot\mathbf{r}}$ then $a_{l,\mu}=4\pi i^l Y^*_{l,\mu}(\mathbf{k})$. The coefficients $a'_{l,\mu}$ are determined uniquely from the $a_{l,\mu}$ by the relation

$$a'_{l,\mu}=\sum_{l,\mu}M_{l,\mu\leftarrow l',\mu'}a_{l',\mu'}\ . \tag{5}$$

Because N_2 has an axis of rotational symmetry, M is diagonal in μ. As mentioned earlier, we have made the assumption that only the lowest angular momentum contributes to each scattering channel; this is equivalent to saying that M is also diagonal in l. We may therefore write

$$M_{l,\mu\leftarrow l',\mu'}=\delta_{l,l'}\delta_{\mu,\mu'}M_l^\mu\ ,$$

where M_l^μ takes the form $M_l^\mu=\frac{1}{2}(e^{2i\delta_{l,\mu}}-1)$. Our approximation says that $\delta_{2,\pm 1}$ is given by the ${}^2\Pi_g$ eigenphase sum, $\delta_{1,\pm 1}$ by the ${}^2\Pi_u$ sum, and $\delta_{1,0}$ by the ${}^2\Sigma_u$ sum. (Note that M_l^μ depends only on the absolute value of μ.) Near a resonance in the l,μth partial wave, the matrix element M_l^μ has a pole in the complex energy plane at an energy $W=E-\frac{1}{2}i\Gamma$.

Equations similar to (4) and (5) can be written down for scattering off an isolated surface. When a wave Ψ_{inc} impinges on a surface, there is a reflected wave which we may write $S\Psi_{\text{inc}}$, where S is an operator. If Ψ_{inc} is a plane wave then the form of the reflected wave is reasonably simple. However, for the purpose of multiple scattering we also need to know the way in which a vector of waves outgoing from the center of the molecule reflects off the surface; such a vector might be, for instance, a wave just scattered off the molecule. We call such a vector Ψ^+. It is scattered by the surface as follows:

$$\begin{aligned}\Psi_{\text{surf}}^{\text{scat}}&=S\Psi^+\\&=S\sum_{l,m}a'_{l,m}h_l^+(kr)Y_{l,m}(\hat{\mathbf{r}})\\&=\sum_{l,m}a''_{l,m}j_l(kr)Y_{l,m}(\hat{\mathbf{r}})\quad(r<2z_0)\ ,\end{aligned}\tag{6}$$

so that we may write

$$a''_{l,m}=\sum_{l,m}S_{l,m\leftarrow l',m'}a'_{l',m'}\ .\tag{7}$$

In a limited region near the molecule $(r<2z_0)$, S reflects a vector of waves propagating outward from the molecule into a vector of waves regular at the center of the molecule, as indicated in Eq. (6). The matrix elements of S (derived in the Appendix for a step-potential surface) have the general form $S_{l,m\leftarrow l',m'}=\delta_{m,m'}S_{l,l'}^{|m|}$. The surface potential is rotationally symmetry about the z axis, so scattering off the surface conserves m; however, states with different l values are mixed. In particular, the presence of surface destroys the inversion symmetry of the molecular scattering potential, so that a resonance that was d wave in the gas phase can now be mixed with a p-wave component. (Note that the matrix elements of S depend only on the absolute value of m.)

Now, we consider the scattering of an electron off the combined molecule—surface potential. We define $\Psi_{\text{mol}}^{\text{scat}}$ as the sum of all waves scattered by the molecule and $\Psi_{\text{surf}}^{\text{scat}}$ as the sum of all waves scattered by the surface. It can be seen that $\Psi_{\text{mol}}^{\text{scat}}$ and $\Psi_{\text{surf}}^{\text{scat}}$ satisfy the relations

$$\Psi_{\text{mol}}^{\text{scat}}=M(\Psi_{\text{inc}}+\Psi_{\text{surf}}^{\text{scat}})\ ,\tag{8a}$$

$$\Psi_{\text{surf}}^{\text{scat}}=S(\Psi_{\text{inc}}+\Psi_{\text{mol}}^{\text{scat}})\ .\tag{8b}$$

The molecule scatters the incident wave plus all waves coming off the surface. Likewise, the surface scatters the incident wave plus all waves coming off the molecule. Equations (8) can be solved for $\Psi_{\text{mol}}^{\text{scat}}$ and $\Psi_{\text{surf}}^{\text{scat}}$ in terms of Ψ_{inc}. The total wave is then given by

$$\begin{aligned}\Psi&=\Psi_{\text{inc}}+\Psi_{\text{mol}}^{\text{scat}}+\Psi_{\text{surf}}^{\text{scat}}\\&=(1+M)(1-SM)^{-1}(1+S)\Psi_{\text{inc}}\ .\end{aligned}\tag{9}$$

If the inverse operator in (9) is expanded out in a geometric series, one sees that Ψ represents the sum of all possible multiple-scattering events between the molecule and the surface.

It can be shown that any pole in M is cancelled between the numerator and denominator of (9). Therefore, the molecular resonances disappear when the molecule is coupled to the surface. In their place arise new resonances at the complex energies which make an eigenvalue of $1-SM$ equal to zero. These poles can be found by solving the equation

$$\det(\underline{\mathbb{1}}-\underline{S}\,\underline{M})=0\ .\tag{10}$$

We expect that, as the distance of the molecule from the surface becomes large, the shifted poles will converge to the molecular poles, since then multiple scattering between the surface and the molecule becomes negligible.

In solving (10), we retain only terms which couple to the poles in M, since we are interested in how these poles shift as the molecule approaches the surface. Two degenerate poles occur in M for the terms $l=2$ and $\mu=\pm 1$. We make the distinction between μ and m to allow for the case where the molecule lies along x; obviously, when the molecule lies along z the two are the same. It is convenient to switch from spherical harmonics to an angular basis with definite x, y, and z parity. Table I shows how

TABLE I. Composition of x-, y-, z-parity states from Y_{l,m_z}'s and Y_{l,m_x}'s.

State	In terms of Y_{l,m_z}'s	In terms of Y_{l,m_x}'s	l	$\vert m_z \vert$	$\vert m_x \vert$
$p_x\equiv r^{-1}\left[\frac{3}{4\pi}\right]^{1/2}x$	$\frac{1}{\sqrt{2}}(Y_{1,-1}+Y_{1,1})$	$Y_{1,0}$	1	1	0
$p_y\equiv r^{-1}\left[\frac{3}{4\pi}\right]^{1/2}y$	$\frac{i}{\sqrt{2}}(Y_{1,-1}-Y_{1,1})$	$\frac{1}{\sqrt{2}}(Y_{1,-1}+Y_{1,1})$	1	1	1
$d_{xz}\equiv r^{-1}\left[\frac{15}{4\pi}\right]^{1/2}xz$	$\frac{1}{\sqrt{2}}(Y_{2,-1}-Y_{2,1})$	$\frac{i}{\sqrt{2}}(Y_{2,-1}+Y_{2,1})$	2	1	1
$d_{yz}\equiv r^{-1}\left[\frac{15}{4\pi}\right]^{1/2}yz$	$\frac{i}{\sqrt{2}}(Y_{2,-1}+Y_{2,1})$	$\frac{i}{\sqrt{2}}(Y_{2,-2}-Y_{2,2})$	2	1	2
$d_{xy}\equiv r^{-2}\left[\frac{15}{4\pi}\right]^{1/2}xy$	$\frac{i}{\sqrt{2}}(Y_{2,-2}-Y_{2,2})$	$\frac{1}{\sqrt{2}}(Y_{2,-1}-Y_{2,1})$	2	2	1

the states p_x, p_y, d_{xz}, d_{yz}, and d_{xy} are formed, both from the usual set of spherical harmonics with z as the polar axis ($Y_{l,m}$), and also from the set where x is the polar axis ($Y_{l,\mu}$); the latter is obtained from the former by a cyclic permutation of the indices ($x \to y$, $y \to z$, $z \to x$). In terms of these states, the poles in M occur in the (d_{xz},d_{xz}) and (d_{yz},d_{yz}) matrix elements when the molecular axis is along z, and in the (d_{xz},d_{xz}) and (d_{xy},d_{xy}) matrix elements when the molecule lies along x. Therefore, we retain these terms, plus any terms with $l<2$ which are coupled to them by scattering off the surface.

We can now solve (10) in terms of the matrix elements $M_l^{|\mu|}$ and $S_{l,l'}^{|m|}$ for the two different orientations of the molecule. For the molecule perpendicular to the surface we obtain two degenerate poles given by the equation

$$(1-M_1^1 S_{11}^1)(1-M_2^1 S_{22}^1)-M_1^1 M_2^1 (S_{21}^1)^2=0\ . \qquad (11a)$$

For the molecule parallel to the surface the degeneracy is lifted, and we obtain two new equations

$$(1-M_1^0 S_{11}^1)(1-M_2^1 S_{22}^1)-M_1^0 M_2^1 (S_{21}^1)^2=0\ , \qquad (11b)$$

$$1-M_2^1 S_{22}^2=0\ . \qquad (11c)$$

The effect of the surface on the resonance is to mix together waves with the same $|m|$ value and the same reflection parity across the $x=0$ and $y=0$ planes. The surface reduces the symmetry of the problem in the z direction only, so the reflection parity of states across the $x=0$ and $y=0$ planes cannot be affected. Thus, for the molecule along the z axis, the d_{xz} resonance is mixed with a p_x wave (both odd in x, even in y) and the d_{yz} resonance is mixed with a p_y wave (both odd in y, even in x). These mixed resonances are given by (11a). For the molecule lying along the x axis, the d_{xz} resonance is again mixed with a p_x wave (11b). However, in this configuration, the second resonance, d_{xy} has no wave of the same x,y parity and $|m|$ value ($|m|=2$) with which to mix, so it can only be modified by scattering back off the surface into itself (11c). These results are summarized in Fig. 3.

Equations (11) were solved by fitting the functions $S_{l,l'}^{|m|}$ and $(M_l^{|\mu|})^{-1}$ to polynomials along the real energy axis, and then continuing them analytically into the complex energy plane. The $S_{l,l'}^{|m|}$'s are analytic everywhere except at the point $W=0$; the $M_l^{|\mu|}$'s are singular at the molecular resonances, but their inverses are analytic everywhere.

The complex energy roots of Eqs. (11) for the mixed and unmixed resonances are shown in Fig. 4 as a function of z_0. The roots of (11a) and (11b) are nearly identical, so only that of (11a) is shown (this suggests that the resonance pole is not very sensitive to the exact form of the p-wave phase shift). The important feature to notice is that the width of the mixed p/d resonance becomes large as the molecule approaches the surface, whereas that of the unmixed d resonance does not. This is because the mixing in of a p-wave component allows the resonance to decay through an $l=1$ centrifugal barrier, which is substantially lower than the $l=2$ barrier of the pure d-wave resonance. Unlike the widths, the resonance energies are not strongly affected by multiple scattering off the surface. This suggests that another mechanism is responsible for the real energy shifts observed in the experiments, as will be discussed in the next section. As expected, the width and energy of both mixed and unmixed resonances converge to the molecular values as $z_0 \to \infty$.

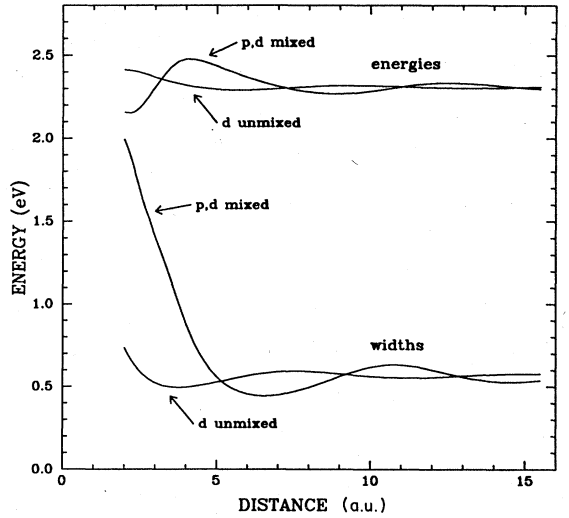

FIG. 4. Complex energy roots ($W=E-\frac{1}{2}i\Gamma_0$) of Eq. (11) for the mixed and unmixed resonances as a function of distance between the molecule and the surface. E is the resonance energy and Γ_0 is the resonance width. The mixed resonance is substantially broadened near the surface, whereas the unmixed resonance is not. The roots to (11a) and (11b) are nearly identical, so only that of (11a) is shown.

To make an estimate of the magnitude of the broadening of the p/d mixed resonance, it is necessary to know the equilibrium distance that physisorbed N_2 lies from a silver surface. For Ar on a $r_s=3$ jellium metal, Lang has calculated this distance to be 4.25 a.u.[16] We might expect the distance for N_2 in the parallel orientation to be somewhat smaller than this, since N_2 is isoelectronic to Ar, but the electron cloud is stretched out between two nuclei. Assuming z_0 to be in the range 3—4 a.u., we obtain a width for the adsorbate resonance in the range $0.9<\Gamma_0<1.4$ eV, as opposed to 0.54 eV in the gas phase; this is about the degree of broadening seen experimentally.

IV. IMAGE POTENTIAL

A second mechanism for the broadening of the physisorbed N_2 resonance involves the lowering of the centrifugal barrier by the metallic image potential. The image potential is also responsible for the lowering of the real part of the resonance energy. The image potential is the self-energy of the scattering electron due to its interaction with the conduction electrons in the metal. Asymptotically, it takes the classical form $-1/[4(z_0-z)]$ (where z_0 is the effective location of the surface[17]), but near the surface it reaches a finite value rather than diverging. The response of the metallic electrons to the projectile is essentially adiabatic in our case, since the resonance energy is well below the surface plasmon energy of Ag [≈ 3.6 eV (Ref. 18)]; therefore it is not unreasonable to treat the image potential as being independent of velocity.

The form of a static image potential near a metallic surface has been investigated by a number of authors.[19] Ideally, one would like to place the molecule in the vicinity of such a potential and calculate its effect on the resonance pole. However, the lack of symmetry makes the calculation difficult. In order to eliminate this obstacle, we have adopted a simple, spherically-symmetric model (see Fig. 5) which demonstrates, at least qualitatively, the effects of an imagelike potential on a resonance. The spherical problem is simple because a simple outgoing-wave boundary condition can be imposed to define the resonance.[20] However, the magnitude of the broadening and energy shift obtained will be larger than those seen in the experiments; this is because the image potential from a two-dimensional surface affects the centrifugal barrier strongly only on the side of the molecule nearest the surface, whereas in a spherically-symmetric model the image potential is equally strong on all sides. Nonetheless, the model should provide an order-of-magnitude estimate for the effect of the image potential on the resonance energy and width.

The model is depicted in Fig. 5. For the purpose of this calculation, we replace the N_2 molecule by a spherical square well of depth V_w and radius a. The complex resonance energy W for the isolated well is then obtained by solving for the root of the equation $j_2(Ka)=h_2^+(ka)$, where $K=[2(W+V_w)]^{1/2}$ and $k=(2W)^{1/2}$. The values $V_w=33.4$ eV and $a=2.7$ a.u. reproduce the "molecular" resonance at an energy of 2.3 eV with a width of 0.54 eV. Our spherical well model yields a d-wave phase shift nearly identical to that of the molecule for energies about the resonance; this explains why such a seemingly naive representation of the molecule is adequate for the present purpose.

On top of the spherical well we superimpose a spherically-symmetric model "image potential" given by

$$V_{im}(r)=\frac{V_s}{2}\left[\frac{2}{\pi}\arctan\left[\frac{d-r}{s}\right]-1\right], \tag{12}$$

where d is the radius of a spherical "surface," s is the surface thickness, and $V_s=9.8$ eV is the total potential difference between the vacuum and the interior of the metal. As can be seen in Fig. 5, V_{im} resembles a smoothed out, spherically-symmetric version of the step potential used in Sec. III. We used $s=\pi/4V_s$ to reproduce the form of the classical image potential in the asymptotic limit $d\rightarrow\infty$. Unlike the classical potential (also shown in Fig. 5), V_{im} has a finite value of $-V_s/2$ at the surface.

The resonance pole is identified as a complex eigenvalue W of the equation

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{l(l+1)}{2r^2}-V_w\Theta(a-r)+V_{im}-W\right]\Psi(r)=0 \tag{13}$$

with an outgoing-wave boundary condition on Ψ at some radius b.[20] A WKB approximation was used to determine the form of the outgoing wave at $r=b$. The radius b was chosen to be outside the centrifugal barrier $\{b>[l(l+1)/2E]^{1/2}\}$, but smaller than an electron wavelength (to maximize the spacing between eigenvalues). In practice we used $b=8$ a.u.

The width and energy of the resonance corresponding to $W=E-\frac{1}{2}i\Gamma$ are shown in Fig. 6 as a function of d. As the distance between the surface and the molecule becomes small, the resonance becomes dramatically broadened and down shifted in energy. The energy shift is a manifestation of the negative potential added throughout the region where the electron is trapped. The broadening occurs because the image potential acts to tear down the centrifugal barrier outside the molecular core,

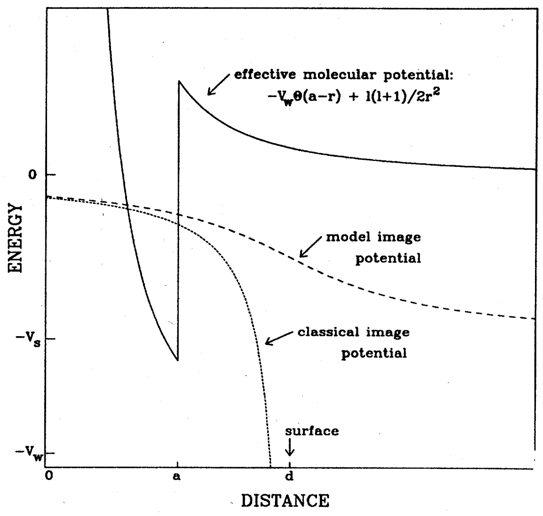

FIG. 5. Spherically-symmetric image potential model. The effective molecular potential is the sum of the spherical square well and centrifugal potentials. The model image potential is given by Eq. (12); also shown is a spherically-symmetric version of the classical image potential, given by $-1/[4(d-r)]$. The center of the molecule is at $r=0$ and the surface is at $r=d$.

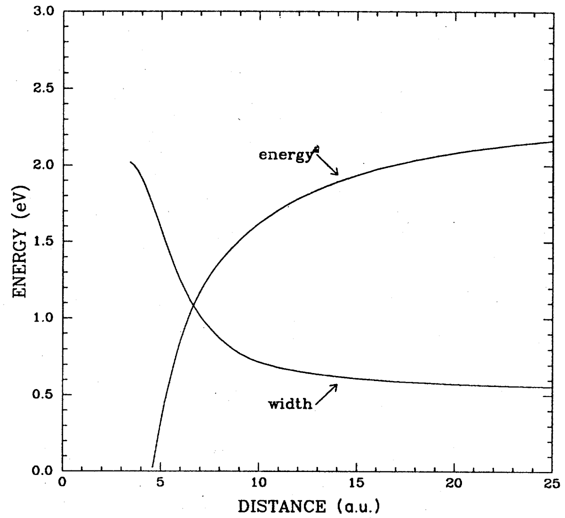

FIG. 6. Resonance pole of the spherically-symmetric image potential model, as a function of distance d between the molecule and the surface. The pole corresponds to the lowest eigenvalue of Eq. (13), $W\equiv E-\frac{1}{2}i\Gamma$, where E is the resonance energy and Γ is the width.

thus increasing the outward tunneling current of the trapped electron. The image potential also lowers the energy of the electron inside the core, an effect which alone would strengthen the effective tunneling barrier; however, the net effect is to broaden the resonance because the image potential is substantially stronger outside the core than inside.

Our calculation yields an energy shift of about -2.3 eV and a broadening of about 1.5 eV for $d=4$ a.u. As expected, these values are somewhat larger than those seen in the experiments, since we have wrapped our "image potential" around the molecule. However, the fact that the signs and orders of magnitude agree with experiment indicates that the image potential probably plays an important role in determining the energy and width of an electron scattering resonance for a molecule adsorbed on a metallic surface.

V. CONCLUSION

We have investigated two basic effects of a metallic surface on the energy and width of an electron-molecule scattering resonance. Our results can be summarized as follows.

(i) Multiple scattering between the molecule and the surface broadens the resonance by about the observed amount, but does not appreciably shift its energy. The broadening is attributed to the breaking of the molecule's inversion symmetry by the surface; this mixes waves of lower angular momentum into the resonance, thus lowering the effective centrifugal barrier through which a trapped electron must tunnel to escape.

(ii) The metallic image potential also broadens the resonance for the adsorbed molecule by directly pulling down the centrifugal barrier. In addition, the image potential lowers the real part of the resonance energy by adding a negative potential throughout the region where the electron is trapped.

APPENDIX: SURFACE SCATTERING

The wave equation for the scattering of a single electron off a surface potential $V_{\text{surf}}(\mathbf{r})$ is

$$(K+V_{\text{surf}}-E)\Psi=0 \tag{A1}$$

where $K=-\frac{1}{2}\nabla^2$. For a scattering problem, Ψ can be broken up into incident and scattered waves

$$\Psi=\Psi_{\text{inc}}+\Psi_{\text{surf}}^{\text{scat}}\ , \tag{A2}$$

where Ψ_{inc} obeys the free-particle wave equation. We are interested in the case where Ψ_{inc} is a vector of outgoing waves from the center of the molecule; this vector is denoted Ψ^+ in Sec. III. $\Psi_{\text{surf}}^{\text{scat}}$ is related to Ψ^+ by the operator S, as shown in (6). In a limited region about the molecule ($r<2z_0$), $\Psi_{\text{surf}}^{\text{scat}}$ is a vector of regular waves; therefore, we write

$$h_l^+(kr')Y_{l,m}(\hat{\mathbf{r}}') \xrightarrow{\text{reflection}} \sum_{l',m'} S_{l',m'\leftarrow l,m}\, j_{l'}(kr) \times Y_{l',m'}(\hat{\mathbf{r}}) \quad (r<2z_0)\ . \tag{A3}$$

We wish to derive the matrix elements of S in a spherical wave basis, with the surface represented by the potential

$$V_{\text{surf}}(\mathbf{r})=\begin{cases}-\,|V_s|\,, & z>z_0\\ 0, & z<z_0\ .\end{cases} \tag{A4}$$

Recall that the origin of coordinates is at the center of the molecule, and the positive z axis points orthogonally in towards the surface, which is located along the plane $z=z_0$. The method is as follows. In the region $z<z_0$ the scattering electron propagates freely, and is thus described by a free-electron Green's function, which can be expanded either in spherical or plane waves as

$$G(\mathbf{r},\mathbf{r}',k_0)=-2ik_0\sum_{l,m} Y_{l,m}^*(\hat{\mathbf{r}})Y_{l,m}(\hat{\mathbf{r}}') \times j_l(k_0 r_<)h_l^+(k_0 r_>) \tag{A5a}$$

$$=-2\int \frac{d^3k}{(2\pi)^3}\,\frac{e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}}{(k^2-k_0^2-i0)}\ , \tag{A5b}$$

where $r_>$ is the greater and $r_<$ the lesser of the two radii $|\mathbf{r}|$ and $|\mathbf{r}'|$. The electron coordinate is $\mathbf{r}$, whereas the length $|\mathbf{r}'|$ will be made very small, so that $|\mathbf{r}|>|\mathbf{r}'|$. While we ultimately want S in terms of spherical waves, it is the plane-wave version of the Green's function which is convenient for reflecting off a surface. Breaking the wave vector into components parallel and perpendicular to the surface, $\mathbf{k}=\mathbf{k}_{\parallel}+k_{\perp}\hat{\mathbf{z}}$, Eq. (A5) becomes

$$G(\mathbf{r},\mathbf{r}',k_0)=-\frac{2}{(2\pi)^2}\int d^2k_{\parallel}\, e^{i\mathbf{k}_{\parallel}\cdot(\mathbf{r}_{\parallel}-\mathbf{r}'_{\parallel})} \times \int_{-\infty}^{\infty} dk_{\perp}\,\frac{e^{ik_{\perp}(z-z')}}{k_{\perp}^2-(k_0^2-k_{\parallel}^2)-i0}\ . \tag{A6}$$

The integral over $k_{\perp}$ can be closed in the upper half plane for $z>z'$, and in the lower half plane for $z<z'$. The result is

$$G(\mathbf{r},\mathbf{r}',k_0)=-\frac{1}{4\pi^2}\int d^2k_{\parallel}\, e^{i\mathbf{k}_{\parallel}\cdot(\mathbf{r}_{\parallel}-\mathbf{r}'_{\parallel})}\left[i\Theta(k_0^2-k_{\parallel}^2)\frac{e^{i(k_0^2-k_{\parallel}^2)^{1/2}|z-z'|}}{(k_0^2-k_{\parallel}^2)^{1/2}} + \Theta(k_{\parallel}^2-k_0^2)\frac{e^{-(k_{\parallel}^2-k_0^2)^{1/2}|z-z'|}}{(k_{\parallel}^2-k_0^2)^{1/2}}\right], \tag{A7}$$

where the unit step function $\Theta(x)$ has the value 1 if $x>0$ and the value 0 if $x<0$. The first term in (A7) represents a traveling wave along the z axis, outgoing from the source at z'. The second term is an evanescent wave along the z axis, decaying from the point z'.

The Green's function for the reflected electron is found by reflecting the plane waves in (A7) off the surface. This reverses the z component of their wave vectors, and changes their amplitude by a factor $R(k_{\parallel})$. The reflected Green's function thus has the form

$$G^{\mathrm{ref}}(\mathbf{r},\mathbf{r}',k_0)=-\frac{1}{4\pi^2}\int d^2k_{\parallel}e^{i\mathbf{k}_{\parallel}\cdot(\mathbf{r}_{\parallel}-\mathbf{r}'_{\parallel})}R(k_{\parallel}) \times\left[i\Theta(k_0^2-k_{\parallel}^2)\frac{e^{i(k_0^2-k_{\parallel}^2)^{1/2}(-z-z')}}{(k_0^2-k_{\parallel}^2)^{1/2}}+\Theta(k_{\parallel}^2-k_0^2)\frac{e^{-(k_{\parallel}^2-k_0^2)^{1/2}(-z-z')}}{(k_{\parallel}^2-k_0^2)^{1/2}}\right]. \tag{A8}$$

The function $R(k_{\parallel})$ is found by matching logarithmic derivatives of plane waves on either side of the step at $z=z_0$. $R(k_{\parallel})$ is given by

$$R(k_{\parallel})=\begin{cases}\left[\dfrac{(k_0^2-k_{\parallel}^2)^{1/2}-(k_0^2+2V_s-k_{\parallel}^2)^{1/2}}{(k_0^2-k_{\parallel}^2)^{1/2}+(k_0^2+2V_s-k_{\parallel}^2)^{1/2}}\right]e^{2iz_0(k_0^2-k_{\parallel}^2)^{1/2}}, & k_0^2>k_{\parallel}^2\ \ (k_{\perp}^2>0)\\[2ex] \left[\dfrac{(k_{\parallel}^2-k_0^2)^{1/2}+i(k_0^2+2V_s-k_{\parallel}^2)^{1/2}}{(k_{\parallel}^2-k_0^2)^{1/2}-i(k_0^2+2V_s-k_{\parallel}^2)^{1/2}}\right]e^{-2z_0(k_{\parallel}^2-k_0^2)^{1/2}}, & 2V_s+k_0^2\geq k_{\parallel}^2\geq k_0^2\ \ (2V_s+k_{\perp}^2\geq 0\geq k_{\perp}^2)\\[2ex] \left[\dfrac{(k_{\parallel}^2-k_0^2)^{1/2}-[k_{\parallel}^2-(k_0^2+2V_s)]^{1/2}}{(k_{\parallel}^2-k_0^2)^{1/2}+[k_{\parallel}^2-(k_0^2+2V_s)]^{1/2}}\right]e^{-2z_0(k_{\parallel}^2-k_0^2)^{1/2}}, & k_{\parallel}^2>2V_s+k_0^2\ \ (0>2V_s+k_{\perp}^2)\,.\end{cases} \tag{A9}$$

In the first case, the z component of the wave function is a traveling wave both outside and inside the metal. In the second case, the wave is evanescent outside the metal but travels inside. In the third case, the wave is evanescent on both sides of the surface.

Once the Green's function is reflected, it is reexpanded in terms of spherical waves so that we can compare it with the unreflected Green's function (A5a) and pick off the matrix elements of S. The reflected Green's function (A8) can be rewritten as

$$\begin{aligned}G^{\mathrm{ref}}(\mathbf{r},\mathbf{r}',k_0)=&-\frac{i}{4\pi^2}\int d^2k_{\parallel}\frac{\Theta(k_0^2-k_{\parallel}^2)}{(k_0^2-k_{\parallel}^2)^{1/2}}R(k_{\parallel})e^{i[\mathbf{k}_{\parallel}-(k_0^2-k_{\parallel}^2)^{1/2}\hat{\mathbf{z}}]\cdot\mathbf{r}}(e^{i[\mathbf{k}_{\parallel}+(k_0^2-k_{\parallel}^2)^{1/2}\hat{\mathbf{z}}]\cdot\mathbf{r}'})^*\\&+\frac{1}{4\pi^2}\int d^2k_{\parallel}\frac{\Theta(k_{\parallel}^2-k_0^2)}{(k_{\parallel}^2-k_0^2)^{1/2}}R(k_{\parallel})e^{i[\mathbf{k}_{\parallel}-i(k_{\parallel}^2-k_0^2)^{1/2}\hat{\mathbf{z}}]\cdot\mathbf{r}}(e^{i[\mathbf{k}_{\parallel}+i(k_{\parallel}^2-k_0^2)^{1/2}\hat{\mathbf{z}}]\cdot\mathbf{r}'})^*\,.\end{aligned} \tag{A10}$$

If we now expand the plane waves in (A10) in terms of spherical waves, we obtain

$$\begin{aligned}G^{\mathrm{ref}}(\mathbf{r},\mathbf{r}',k_0)=&-2\sum_{l,m}j_l(k_0r')Y^*_{l,m}(\hat{\mathbf{r}}')\sum_{l',m'}2(-1)^{l+l'+m'}(i)^{l+l'}j_{l'}(k_0r)Y_{l',m'}(\hat{\mathbf{r}})\\&\times\left[i\int d^2k_{\parallel}\frac{\Theta(k_0^2-k_{\parallel}^2)}{(k_0^2-k_{\parallel}^2)^{1/2}}R(k_{\parallel})Y^*_{l',m'}(\mathbf{k}_{\parallel}+(k_0^2-k_{\parallel}^2)^{1/2}\hat{\mathbf{z}})Y_{l,m}(\mathbf{k}_{\parallel}+(k_0^2-k_{\parallel}^2)^{1/2}\hat{\mathbf{z}})\right.\\&\left.+\int d^2k_{\parallel}\frac{\Theta(k_{\parallel}^2-k_0^2)}{(k_{\parallel}^2-k_0^2)^{1/2}}R(k_{\parallel})Y^*_{l',m'}(\mathbf{k}_{\parallel}+i(k_{\parallel}^2-k_0^2)^{1/2}\hat{\mathbf{z}})\,Y_{l,m}(\mathbf{k}_{\parallel}+i(k_{\parallel}^2-k_0^2)^{1/2}\hat{\mathbf{z}})\right],\end{aligned} \tag{A11}$$

where use has been made of the fact that $Y_{l,m}(\pi-\theta,\varphi)=(-1)^{l+m}Y_{l,m}(\theta,\varphi)$. After the φ integration in $\mathbf{k}_{\parallel}$, Eq. (A11) becomes

$$\begin{aligned}G^{\mathrm{ref}}(\mathbf{r},\mathbf{r}',k_0)=&-2ik_0\sum_{l,m}j_l(k_0r')Y^*_{l,m}(\hat{\mathbf{r}}')\\&\times\sum_{l'}(-1)^{l+l'+m}(i)^{l+l'}\left[(2l+1)(2l'+1)\frac{(l-|m|)!(l'-|m|)!}{(l+|m|)!(l'+|m|)!}\right]^{1/2}j_{l'}(k_0r)Y_{l',m}(\hat{\mathbf{r}})\\&\times\left[\int_0^{k_0}dk_{\parallel}\frac{k_{\parallel}}{k_0}\frac{R(k_{\parallel})}{(k_0^2-k_{\parallel}^2)^{1/2}}P_{l',m}([1-(k_{\parallel}/k_0)^2]^{1/2})P_{l,m}([1-(k_{\parallel}/k_0)^2]^{1/2})\right.\\&\left.-i\int_{k_0}^{\infty}dk_{\parallel}\frac{k_{\parallel}}{k_0}\frac{R(k_{\parallel})}{(k_{\parallel}^2-k_0^2)^{1/2}}P_{l',m}(i[(k_{\parallel}/k_0)^2-1]^{1/2})P_{l,m}(i[(k_{\parallel}/k_0)^2-1]^{1/2})\right].\end{aligned} \tag{A12}$$

The matrix elements of S may now be obtained by comparison of (A12) with the unreflected Green's function (A5a), with the aid of (A3):

$$S_{l,l'}^{|m|}=\left\{(-1)^{l+l'+m}(i)^{l+l'}\left[(2l+1)(2l'+1)\frac{(l-|m|)!(l'-|m|)!}{(l+|m|)!(l'+|m|)!}\right]^{1/2}\right\}$$
$$\times\left[\int_0^{k_0}dk_{\parallel}\frac{k_{\parallel}}{k_0}\frac{R(k_{\parallel})}{(k_0^2-k_{\parallel}^2)^{1/2}}P_{l'm}([1-(k_{\parallel}/k_0)^2]^{1/2})P_{l,m}([1-(k_{\parallel}/k_0)^2]^{1/2})\right.$$
$$\left.-i\int_{k_0}^{\infty}dk_{\parallel}\frac{k_{\parallel}}{k_0}\frac{R(k_{\parallel})}{(k_{\parallel}^2-k_0^2)^{1/2}}P_{l',m}(i[(k_{\parallel}/k_0)^2-1]^{1/2})P_{l,m}(i[(k_{\parallel}/k_0)^2-1]^{1/2})\right]. \tag{A13}$$

If we denote the factor in the curly brackets $C_{l,l'}^{|m|}$, use (A9) for $R(k_{\parallel})$, and define a variable $x\equiv|1-(k_{\parallel}/k_0)^2|^{1/2}$ and a constant $\alpha\equiv(2V_s/k_0)^{1/2}$, Eq. (A13) becomes

$$S_{l,l'}^{|m|}=C_{l,l'}^{|m|}\left[\int_0^1 dx\,e^{2ik_0z_0x}\left[\frac{x-(x^2+\alpha^2)^{1/2}}{x+(x^2+\alpha^2)^{1/2}}\right]P_{l,m}(x)P_{l',m}(x)\right.$$
$$-i\int_0^{\alpha}dx\,e^{-2k_0z_0x}\left[\frac{x+i(\alpha^2-x^2)^{1/2}}{x-i(\alpha^2-x^2)^{1/2}}\right]P_{lm,}(ix)P_{l',m}(ix)$$
$$\left.-i\int_{\alpha}^{\infty}dx\,e^{-2k_0z_0x}\left[\frac{x-(x^2-\alpha^2)^{1/2}}{x+(x^2-\alpha^2)^{1/2}}\right]P_{l,m}(ix)P_{l',m}(ix)\right]. \tag{A14}$$

These coefficients can be obtained numerically for arbitrary values of potential step height, V_s and wave number k_0. In the special case of a perfectly reflecting surface ($V_s\rightarrow\infty$), the integrals have been performed analytically.

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