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Electronic spectral properties of surfaces and adsorbates and atom-adsorbate van der Waals interactions

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The relevance of van der Waals interactions in the scattering of neutral atoms from adsorbates has been recently confirmed by highly sensitive molecular-beam techniques. The theoretical descriptions of the collision dynamics which followed the experimental studies have necessitated very careful qualitative and quantitative examinations and evaluations of the properties of atom-adsorbate van der Waals interactions for specific systems. In this work we present a microscopic calculation of the strengths and reference-plane positions for van der Waals potentials relevant for scattering of He atoms from CO adsorbed on various metallic substrates. In order to take into account the specificities of the polarization properties of real metals (noble and transition metals) and of chemisorbed CO, we first calculate the spectra of the electronic excitations characteristic of the respective electronic subsystems by using various data sources available and combine them with the existing theoretical models. The reliability of the calculated spectra is then verified in each particular case by universal sum rules which may be established for the electronic excitations of surfaces and adsorbates. The substrate and adsorbate polarization properties which derive from these calculations serve as input data for the evaluation of the strengths and reference-plane positions of van der Waals potentials whose computed values are tabulated for a number of real chemisorption systems. The implications of the obtained results are discussed in regard to the atom-adsorbate scattering cross sections pertinent to molecular-beam scattering experiments.

I. INTRODUCTION

Dynamic electronic properties of surfaces and adsorbates have for a long time been in the focus of discussions concerning the interactions of atomic particles or electromagnetic radiation with matter. Inelastic scattering of ionized or neutral atoms and molecules with either clean or adsorbate-covered surfaces, as well as the reflection and absorption of radiation at surfaces, are, to a large extent, determined by the energies and dynamics of the electronic excitations characteristic of the substrates and adsorbates involved. The spectra of these excitations determine also the dynamic polarization properties of the respective systems and hence the strength of the long-range van der Waals (vdW) or dispersive interactions acting between surfaces and adsorbates, between the adsorbates themselves and between the adsorbates and the particles in the gas phase. The interest in the latter interactions, and thereby in the electronic excitation spectra of surfaces and adsorbates, has recently been revived with the development and the application of thermal energy atom scattering (TEAS) in the investigations of the structural and electronic properties of surfaces and adsorbates.[1]

Thermal energy helium scattering from surfaces has proven to be a particularly sensitive tool in studies of the clean surfaces on one hand, and of the properties of adsorbates, on the other hand. Experiments in which He atoms have been scattered from CO and Xe adsorbed at low coverage on noble and transition metals have demonstrated that the low-energy He atom collisions with adsorbates are dominated by the long-range vdW interactions,[2] a feature which had also been noted earlier in analogous collisions in the gas phase.[3] Hence the interpretation of the experimental data on atom-surface collisions which are dominated by the long-range vdW interactions and the calculations of the corresponding cross sections require, as outlined in Sec. II, rather detailed knowledge of the surface and adsorbate electronic spectral properties. These properties are investigated in Secs. III and IV, with a particular emphasis on the atom-adsorbate vdW potentials encountered in real collision systems. A calculation of the strengths of these potentials is presented in Sec. V, together with a discussion of their effects on the atom-adsorbate scattering cross sections.

II. VAN DER WAALS INTERACTIONS AND SURFACE SCATTERING

Massey and Mohr[4] and Landau and Lifshitz[5] have shown that the low-energy scattering cross section σ for two neutral gas-phase atoms a and b is, to a good approximation, given by the formula

$$\sigma=\gamma\left[\frac{C_6}{v}\right]^{2/5}, \tag{1}$$

where γ is a constant which depends on the approximation employed (7.547 and 8.083, as given in Refs. 4 and 5, respectively), v is the relative velocity, and C_6 is the strength of the vdW interaction between the atoms a and

b at relative distance $R = |\mathbf{R}|$, viz.,

$$E_{\mathrm{vdW}}(R) = -\frac{C_6}{R^6} \ . \tag{2}$$

For anisotropic molecules the two-body interaction (2) becomes anisotropic as well, and one has to average over the impact angles in order to get the effective C_6 which, through Eq. (1), would yield the vdW scattering cross section observed experimentally.

In the scattering of atoms from adsorbates the pertinent vdW interactions are much more complicated due to the changes of the electronic configuration of the composite system. This change arises from two major effects.

(i) The presence of a third polarizable body, i.e., the substrate surface, whose polarization affects the direct vdW interaction between the particles a and b.

(ii) The modification of the electronic structure of the adsorbate a caused by the formation of a chemisorptive bond between the adsorbate and the substrate.

The first effect gives rise to the occurrence of two surface-mediated contributions to the direct vdW interaction between a and b, viz., the image and the interference term[6,7] which are anisotropic even if the electronic subsystems a and b are isotropic.[7] However, all three vdW interactions exhibit the same asymptotic dependence R^{-6} for large R.

Of particular interest in regard to TEAS experiments are the vdW interactions between gas-phase He atoms and adsorbed CO molecules.[1,2] In CO adsorption at low coverage on Cu and transition metals, the CO molecule axis is perpendicular to the metal surface[8] and the geometry of the collision is illustrated in Fig. 1. The three atom-adsorbate vdW interactions can be expressed in terms of the coordinates of the particles a and b and the substrate surface located at $z=0$ as[7]

$$E^{\mathrm{dir}}_{\mathrm{vdW}}(\mathbf{R}) = -2(1+2\mu)\frac{C_{ab}}{R^6}\left[1+\frac{1-\mu}{1+2\mu}P_2(\cos\theta)\right] , \tag{3a}$$

$$E^{\mathrm{im}}_{\mathrm{vdW}}(\mathbf{R}) = \frac{C_{aMbM}}{C_{ab}}E^{\mathrm{dir}}_{\mathrm{vdW}}(\mathbf{R}^*) , \tag{3b}$$

$$\begin{aligned} E^{\mathrm{int}}_{\mathrm{vdW}}(\mathbf{R}) = 2\frac{C_{abM}}{(RR^*)^3}\{ & (4-3\cos^2\theta-3\cos^2\theta^*)-(1-\mu)[5+9\cos^2\theta\cos^2\theta^*-6(\cos^2\theta+\cos^2\theta^*) \\ & +9\sin\theta\sin\theta^*\cos\theta\cos\theta^*]\} \ . \end{aligned} \tag{3c}$$

The meaning of $\mathbf{R}$, $\mathbf{R}^*$, θ, and θ^* is defined in Fig. 1; P_2 denotes the second-order Legendre polynomial and $\mu=\alpha_\perp/\alpha_\parallel$ is the ratio of the transverse and longitudinal molecular polarizabilities of CO. The strengths of the interactions (3a)–(3c) are determined by the constants

$$C_{ab} = \int_0^\infty \frac{du}{2\pi}\tilde{\alpha}_a(iu)\alpha_b(iu) , \tag{4a}$$

$$C_{aMbM} = \int_0^\infty \frac{du}{2\pi}\tilde{\alpha}_a(iu)\alpha_b(iu)R_0^2(iu) , \tag{4b}$$

$$C_{abM} = \int_0^\infty \frac{du}{2\pi}\tilde{\alpha}_a(iu)\alpha_b(iu)R_0(iu) , \tag{4c}$$

where $\tilde{\alpha}_a(\omega)$ and $\alpha_b(\omega)$ denote the dynamic polarizabilities of the molecule a in adsorbed phase (chemisorbed CO) and of the gas phase atom b (He), respectively, and $R_0(\omega)$ denotes the long-wavelength limit of the frequency and wave-vector-dependent surface response function $R_0(\omega)$.[9,10] The integrals in (4a)–(4c) are conveniently carried out over the imaginary frequencies iu to avoid the integration across the poles of $R_0(\omega)$.

The interactions (3a)–(3c) are the leading terms in the expansion of the total atom-adsorbate vdW interactions in inverse powers of $|\mathbf{R}|$. The next-order terms, proportional to R^{-7} and higher, will emerge from the higher-order terms in the expansion of the surface response function $R_Q(\omega)$ in powers of the wave vector Q of the surface excitations. The R^{-7} corrections, when combined with the R^{-6} terms (3a)–(3c) enable the definition of the reference planes proper for the atom-adsorbate vdW interactions, either with respect to the outmost crystallographic plane of the metal (the geometric surface) or, with respect to the edge of the equivalent positive background denoted by $Z_B=0$ in Fig. 1. As has been shown in Ref. 11, the positions of the reference planes for the substrate-

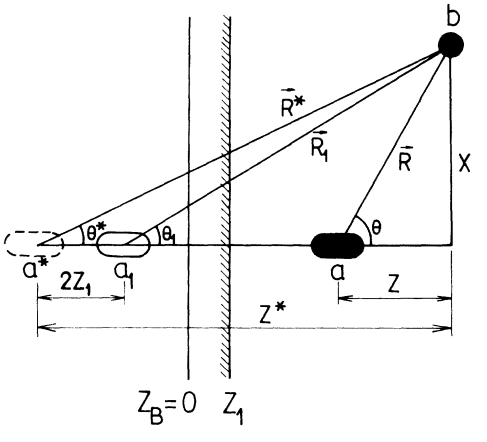

FIG. 1. Geometry of the He-CO collision. The substrate occupies the $z<0$ half-space. a and b represent the adsorbed CO molecule and He atom, respectively. a^* is the image of the CO molecule with respect to the edge of the positive jellium background denoted by $Z_B=0$. a_1 represents the image of the CO molecule with respect to the pertinent vdW reference plane Z_1 [either Z_{aMbM} or Z_{abM}, as defined by (5a) and (5b), for interactions (3b) and 3(c), respectively].

mediated interactions (3b) and (3c), measured relative to Z_B, are given by the expressions

$$Z_{aMbM}=\frac{1}{C_{aMbM}}\int_0^\infty \frac{du}{2\pi}\tilde{\alpha}_a(iu)\alpha_b(iu)R_0^2(iu)d_{IP}(iu)\ , \tag{5a}$$

$$Z_{abM}=\frac{1}{C_{abM}}\int_0^\infty \frac{du}{2\pi}\tilde{\alpha}_a(iu)\alpha_b(iu)R_0(iu)d_{IP}(iu)\ , \tag{5b}$$

where $d_{IP}(\omega)$ is the frequency-dependent centroid of the image charge (see Refs. 12–14 and Sec. III below).

The surface-mediated interactions (3b) and (3c), together with the change of the molecular polarizability upon adsorption from $\alpha_a(\omega)$ in the gas phase to $\tilde{\alpha}_a(\omega)$ in the adsorbed phase, will give rise to the total cross section Σ describing the scattering of atoms b on the adsorbed molecule a which may differ from the corresponding cross section σ in the gas phase. Indeed, an enhancement of Σ over σ amounting to about 20–40% has been observed experimentally,[2] and this feature calls for an interpretation of Σ in terms of the effects (i) and (ii) discussed above. Although the anisotropy of the total vdW potential makes a direct application of Eq. (1) for the determination of C's [Eqs. (4a)–(4c)] from Σ impossible, this expression may still be used as a rule of thumb estimate of the strength of the total vdW atom-adsorbate potential. Due to the $\frac{2}{5}$ exponent in Eq. (1), the enhancement of Σ observed experimentally is recovered if the strength of the vdW potential is approximately doubled.[15] This is in accord with both the physical intuition[2] and the rigorous calculations of Σ based upon the complete (repulsive and attractive) atom-adsorbate potentials which incorporate the constants (4a)–(4c) as parameters. The derivation of Σ in terms of these potentials has been given and discussed in detail in our earlier works.[7,16,17] In the present work we shall concentrate our attention on the derivation of the strength of the vdW potentials for real systems.

The vdW constants (4a)–(4c) are given by the integrals over the entire spectrum of virtual electronic excitations characteristic of the adsorbate, the substrate surface, and the impinging atom. Since both effects (i) and (ii) pointed out above are incorporated into Σ through the expressions (4) and (5), any quantitative study and interpretation of surface scattering experiments requires a detailed knowledge of the spectral properties of the adsorbate, the surface, and the beam atoms.

In our calculations of the vdW interactions at surfaces, we shall first compute the electronic spectral properties of real metal surfaces and the chemically induced changes of the electronic spectra of adsorbates by using various sources available. Then we shall use these as the input data for the calculation of the vdW constants defined by Eqs. (4) and the reference planes defined by Eqs. (5). Due to the diversity of the data sources used, the calculated spectra will be examined by universal sum rules which can be established for both the surface and the adsorbate electronic excitations. The vdW potentials obtained this way may then be employed for the evaluation of the total He-adsorbate scattering cross sections Σ and this procedure has been demonstrated in Refs. 16–18.

III. ELECTRONIC SPECTRAL PROPERTIES OF SURFACES

The sum rules for bulk electronic excitations have been established[19] and investigated in quite some detail only for some metals.[20,21] The development of the surface-sensitive spectroscopies has brought to the fore the problem of the definition and the properties of the surface response function, for a number of transition and noble metals.

A. Surface response function and sum rules

Several derivations of the surface response function have been given in the literature and the most convenient one for the present purpose starts from the quantum analog of the classical image theorem.[22] Here we shall outline the definition and the general properties of the surface response function only briefly, and restrict the discussion to those features which are directly connected with the calculations of the properties of the vdW potentials [Eqs. (4) and (5)].

If an external potential $\phi(\mathbf{r},t)$ is applied outside a metal surface, the latter will respond so as to screen out the applied perturbation. Within the linear response, the total self-consistent potential $V^{\text{tot}}(\mathbf{r},t)$ will be given as a sum of the source potential $\phi(\mathbf{r},t)$ and the induced potential $\phi^{\text{ind}}(\mathbf{r},t)$. For a system occupying the half-space $z<0$, and translationally invariant in the direction parallel to the surface, the two-dimensional Fourier components of these potentials will satisfy the image theorem[22]

$$V_{\mathbf{Q}}^{\text{tot}}(z,\omega)=\phi_{\mathbf{Q}}(z,\omega)+\frac{1-\epsilon_{\mathbf{Q}}(\omega)}{1+\epsilon_{\mathbf{Q}}(\omega)}\phi_{\mathbf{Q}}(-z,\omega)\ , \tag{6}$$

in which the last term on the right-hand side (RHS) represents the Fourier component $\phi_{\mathbf{Q}}^{\text{ind}}(z,\omega)$. Here z is the direction perpendicular to the surface (located at $z=0$), $\mathbf{Q}$ is a two-dimensional wave vector parallel to the surface, $\epsilon_{\mathbf{Q}}(\omega)$ is a complicated two-dimensional analog of the bulk dielectric function $\epsilon(\mathbf{q},\omega)$ with $\mathbf{q}$ denoting the three-dimensional wave vector, and ω is the frequency of the Fourier transform of the time-dependent external potential. Making use of the causal properties of $\epsilon(\mathbf{q},\omega)$, and thereby of $\epsilon_{\mathbf{Q}}(\omega)$, one can show[9,10] that the quantity

$$R_{\mathbf{Q}}(\omega)=\frac{1-\epsilon_{\mathbf{Q}}(\omega)}{1+\epsilon_{\mathbf{Q}}(\omega)}=\int_0^\infty d\omega' S_{\mathbf{Q}}(\omega')\left[\frac{1}{\omega-\omega'+i\delta}-\frac{1}{\omega+\omega'+i\delta}\right] \tag{7}$$

can be identified with the surface response function of the electron system whose standard response function $\chi_{\mathbf{Q}}(z',z'',\omega)$, expressed in terms of the Fourier transform of the electronic density fluctuations translationally invariant in the (x,y) directions, is connected with (7) through the relation[9]

$$R_{\mathbf{Q}}(\omega)=\frac{2\pi}{Q}\int dz' e^{Qz'}\int dz'' e^{Qz''}\chi_{\mathbf{Q}}(z',z'',\omega)\ . \tag{8}$$

The function $S_{\mathbf{Q}}(\omega)$ appearing in the spectral representation on the RHS of Eq. (7) defines the spectrum of surface excitations of wave vector $\mathbf{Q}$ and frequency ω characteristic of the electronic system considered. It can be obtained from the identity

$$S_{\mathbf{Q}}(\omega)=\frac{1}{\pi}\,|\,\mathrm{Im}R_{\mathbf{Q}}(\omega)\,|\ , \tag{9}$$

in which either of the representations of $R_{\mathbf{Q}}(\omega)$ [viz. (7) or (8)] may be used.

The qualitative features of the surface excitation spectrum can be calculated for simple models of metallic surfaces like jellium by using: (i) the power expansion of $S_{\mathbf{Q}}(\omega)$ in the region of small $(\mathbf{Q},\omega)$ values, and (ii) the surface sum rules in the high-energy region of the spectrum. The low-energy part of $S_{\mathbf{Q}}(\omega)$ comprises in this case only electron-hole (e-h) pairs, i.e., intraband transitions, and is linear in ω for $\omega\to 0$ and small Q, as it indeed should be due to the general properties of the Fermi liquid.[10] At higher energies $S_{\mathbf{Q}}(\omega)$ is dominated by a collective (zero sound) mode, i.e., surface plasmon, and in real metals also by interband transitions. There exist two general sum rules for the moments of $S_{\mathbf{Q}}(\omega)$ which originate from the universal conservation laws and which have analogous counterparts in the dielectric theory of bulk electronic systems.[9,10]

1. *Perfect screening sum rule*

This sum rule originates from the requirement of the total charge neutrality of the system. The perfect screening of an external static charge located near the metal surface requires the induced charge of opposite sign and equal magnitude.[23] In terms of the response function, this implies that the long-wavelength limit of the first inverse moment of $S_{\mathbf{Q}}(\omega)$ satisfies[9,10]

$$\lim_{Q\to 0}\int_0^\infty d\omega\frac{S_{\mathbf{Q}}(\omega)}{\omega}=\tfrac{1}{2}(1+2QZ_c)+O(Q^2)\ , \tag{10}$$

where Z_c is the centroid of the static induced charge.[23] If Z_c is taken as the z-coordinate origin, the first term in the power expansion of the first inverse moment of $S_{\mathbf{Q}}(\omega)$ will be quadratic in Q. Hence, we may write

$$\mu_{-1}=\int_0^\infty d\omega\frac{S_0(\omega)}{\omega}=\tfrac{1}{2}\ , \tag{11}$$

with $S_0(\omega)$ being the long-wavelength limit of $S_{\mathbf{Q}}(\omega)$.

2. *Surface f-sum rule*

This sum rule, which derives from the requirement of the conservation of the current parallel to the surface and the number of electrons in the system, reads[9,10]

$$\int_0^\infty d\omega\,\omega S_{\mathbf{Q}}(\omega)=\frac{2\pi e^2Q}{m}\int dz\,e^{2Qz}\rho(z)\ , \tag{12}$$

where m and $\rho(z)$ are the electron mass and the density profile of the electron system in the z direction, respectively. This sum rule holds for arbitrary $\mathbf{Q}$, and in the long-wavelength limit yields

$$\mu_1=\int_0^\infty d\omega\,\omega S_0(\omega)=\frac{\Omega_s^2}{2}\ , \tag{13}$$

where $\Omega_s=(2\pi e^2N/m)^{1/2}$ is the surface plasmon frequency of the electron system whose total density (including the core electrons) is N electrons per unit volume.

For the jellium model of a surface, Eqs. (11) and (13) may be combined to find, for instance, the frequency and the dispersion of the collective mode.[24] Together with the power expansion of $S_{\mathbf{Q}}(\omega)$, they may also be used to determine a qualitative behavior of the surface excitation spectrum of a semi-infinitive electron gas.

As has already been noted in Sec. II, the determination of the reference planes proper for the substrate-mediated vdW interactions (3b) and (3c) requires the knowledge of the linear Q term in the expansion of $R_{\mathbf{Q}}(\omega)$ in powers of Q.[13,14,25–28] In the long-wavelength limit one can conveniently write[12]

$$R_{\mathbf{Q}}(\omega)=R_0(\omega)[1+2Qd_{IP}(\omega)]+O(Q^2)\ , \tag{14a}$$

where $R_0(\omega)$ is the limit of $R_{\mathbf{Q}}(\omega)$ for zero wave vector, and

$$d_{IP}(\omega)=d_{IP}^R(\omega)-id_{IP}^I(\omega) \tag{14b}$$

is the frequency-dependent complex centroid of the image charge, introduced in Sec. II [cf. Eqs. (5)]. The analytic properties of $d_{IP}(\omega)$ are connected with the analytic properties of $S_Q(\omega)$ through Eq. (9), which applied to (14a) yield

$$\lim_{\mathbf{Q}\to 0}S_Q(\omega)=\frac{2}{\pi}Qd_{IP}^I(\omega)\mathrm{Re}[R_0(\omega)]+S_0(\omega)[1+2Qd_{IP}^R(\omega)]\ . \tag{15}$$

Due to its analytic properties, $d_{IP}(\omega)$ can also be written in the spectral representation analogous to Eq. (7), and its imaginary part obeys a form of an f-sum rule as well.[14,25] The calculation of $d_{IP}(\omega)$ is a very formidable task even for simple model systems[28] and its static and large-ω limits have been calculated exactly for a self-consistent jellium model of the surface.[13] Recently, the complete frequency dependence of $d_{IP}(\omega)$ for simple metals has been established.[26(a),26(b)] Hence the sum rules for $d_{IP}^I(\omega)$ provide a useful check in the estimates of the quantitative behavior of $d_{IP}(\omega)$ and thereby of the vdW reference planes for various systems.

B. Surface excitation spectrum of real metals

The sum rules (11) and (13) are quite general and do not depend on the specifities of the models used in the study of real systems. However, the actual shape of the surface excitation spectra of real metals may be very complicated functions of $\mathbf{Q}$ and ω, and could differ considerably from one system to the other due to their specific electronic structures. This situation simplifies only in the long-wavelength limit in which the metal electrons respond to a perturbation homogeneous in the direction parallel to the surface. This particular component of the surface response of real systems, which also determines the properties of the vdW interactions (3a)–(3c), can readily be obtained or computed from the data coming from various independent measurements of the long-wavelength limit of the complex bulk dielectric function $\epsilon(0,\omega)$,[21,29] optical properties such as the complex index of refraction $N(\omega)=n(\omega)+ik(\omega)=[\epsilon(0,\omega)]^{1/2}$,[20,29] the absorption coefficient μ which is related to $k(\omega)$ by $\mu(\omega)=(2\omega/c)k(\omega)$,[21,30] or by fitting the data in the very-low-energy regime ($\omega \lesssim 0.1$ eV) to the classical Drude formula. In the cases in which only the real or imaginary parts of the quantities desired are available, the Kramers-Kronig analysis may be performed to obtain the other part, as, e.g., in the calculation of $n(\omega)$. In our calculations we have used all these sources of data to recover the surface response function (7) pertinent to real metals.

The major simplification in the actual calculations arises from the fact that the bulk and the surface dielectric functions have a common long-wavelength limit[22] and therefore

$$\lim_{Q\to 0} S_Q(\omega)=\frac{2}{\pi}\frac{\epsilon_2(\omega)}{[1+\epsilon_1(\omega)]^2+\epsilon_2^2(\omega)}\ , \tag{16}$$

where $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are the long-wavelength limits of the real and imaginary part of the complex bulk dielectric function $\epsilon(\mathbf{q},\omega)$, respectively. Hence the calculation of $R_0(\omega)$ and $S_0(\omega)$ can be performed directly whenever the values of $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are available. In other cases one has to resort to the analyses of the data as outlined above. However, since the various input quantities for our calculations of $S_0(\omega)$ differ in precision and quality due to the limitations of the methods employed for their derivation (resolution, etc.), we have also tested our computed spectra by subjecting them to the surface sum rules (11) and (13), which in the long-wavelength limit depend only on the macroscopic parameters of the system.

As the most representative metals of various groups, we have chosen Al (free-electron metal), Cu and Pt (noble metals), and Ni, Pd, and W (transition metals) because there are the substrates most frequently encountered in various adsorption systems and in surface scattering. The spectra $S_0(\omega)$ of the long-wavelength surface excitations of these metals are shown in Figs. 2(a) and 2(b), and their properties are summarized in Table I. For Al and Cu we were able to compare the surface sum rule tests of Table I with the corresponding bulk f-sum rules known from the literature [20(b) and 21]. For other metals we have investigated, such bulk (or surface) texts covering the entire frequency interval are not available.

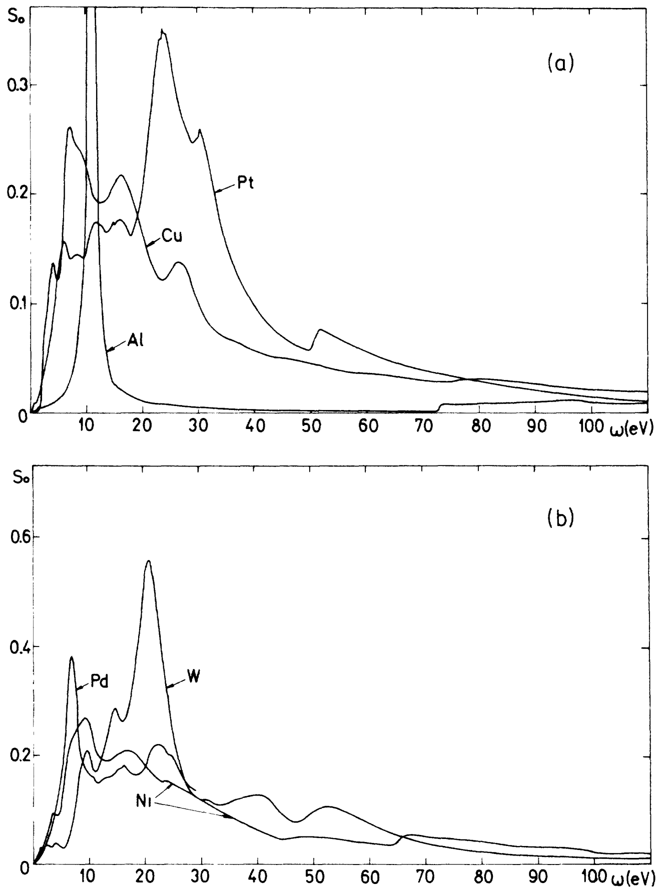

FIG. 2. (a) Spectra of the long-wavelength surface excitations of free-electron (Al) and noble metals (Cu,Pt). (b) Same for typical transition metals (Ni, Pd, and W).

The long-wavelength surface excitation spectrum of Al [Fig. 2(a)] in the energy interval below the 72.7-eV threshold displays a behavior typical of a free-electron gas characterized by the electron density parameter $r_s=2.12$. Above this threshold the excitations from the inner core levels start to contribute to $S_0(\omega)$. However,

TABLE I. Computed properties of the excitation spectra of various real metal surfaces as tested by surface sum rules. The theoretical values are given by Eqs. (11) and (13) for the perfect screening and surface f-sum rule, respectively. Δ is the difference between the computed and the theoretical value, expressed in the percentage of the theoretical value.

	Perfect screening sum rule			Surface f-sum rule		
Surface	Theoretical value	Computed value	Δ (%)	Theoretical value $\frac{\Omega_s^2(N)}{2}$ (eV^2)	Computed value (eV^2)	Δ (%)
Al	$\frac{1}{2}$	0.508	+1.60	270.15	269.79	−0.13
Cu	$\frac{1}{2}$	0.494	−1.20	845.90	806.96	−4.60
Pt	$\frac{1}{2}$	0.520	+4.00	1788.10	1663.60	−6.96
Ni	$\frac{1}{2}$	0.518	+3.60	883.42	864.30	−2.16
W	$\frac{1}{2}$	0.535	+7.00	1609.30	1613.80	+0.28

the majority of the spectral weight is concentrated in the surface plasmon peak at 10.8 eV, whose full width at half maximum is 0.36 eV. Although the data from different energy regions are characterized by different experimental errors and resolution, the Al surface spectrum of Fig. 2(a), including the core excitations, satisfies the sum rules (11) and (13) very accurately, the deviations being of the order of a few percent only (cf. Table I). This should not come as a surprise because the Al bulk excitation spectra have been found to satisfy the bulk f-sum rule with nearly the same accuracy.[20(b)]

All other metals which we have considered are characterized by the d bands close to or overlapping with the Fermi level. Therefore, their surface excitation spectra should be representative also of the interband transitions involving the d bands, in addition to the intraband transitions characteristic of the Al spectrum. A mere inspection of Fig. 2(a) shows that $S_0(\omega)$ for Cu and Pt is characterized by several maxima which can be attributed to various interband excitations and hence an unambigous identification of a collective mode in these systems becomes a formidable task, if possible at all. In spite of the fact that in the spectrum of Cu there arises a peak at about 7.6 eV, which may coincide with the surface plasmon frequency corresponding to $r_s=2.67$, its large width makes its clear identification with a plasmon mode hardly possible. However, although the Cu spectrum is very complicated, we have found that it also satisfies the surface sum rules (11) and (13) to a few percent (cf. Table I), in accordance with the corresponding bulk f-sum rule test.[21] The same applies to the surface excitation spectrum of Pt which, although characterized by electronic transitions in the high-energy region, satisfies both sum rules very nicely. This fact may be regarded as a criterion of the validity of the computed spectral values and of the reliability of any calculated quantity which involves integrals over $S_0(\omega)$.

The surface excitation spectra of the transition metals Ni, Pd, and W are shown in Fig. 2(b). They also exhibit a multiple peak structure characteristic of interband transitions involving the d bands. The dominant peak in the surface excitation spectrum of Ni is located at 9.5 eV, and its flanks extend from 6 to 12 eV. The estimates of the surface plasmon frequency based on the electron density parameters $r_s=2.6$ and 2.09, which correspond to one or two valence electrons per atom, yield the values of the surface plasmon energy of 7.9 and 11 eV, respectively. Although the dominant peak in the Ni surface spectrum indeed lies in the interval bounded by these values, it is hard to attribute it to a distinct collective excitation mode due to its large width and the overlap with the surrounding structure. Again, both sum rules (11) and (13) are satisfied with an accuracy equivalent to the one found for Cu (cf. Table I).

The dominant structure in the long-wavelength surface excitation spectrum of Pd is a relatively distinct peak centered at 7 eV which is much narrower than all other maxima in the part of the spectrum displayed in Fig. 2(b). The number of valence electrons in Pd is uncertain, but if it were around one electron per atom ($r_s=2.6$), the corresponding surface plasmon excitation energy would be 7.9 eV. This correlates relatively well with the position of the dominant peak in the Pd spectrum. Hence, certain manifestations of the surface plasmon mode in the surface response of Pd may not be excluded. Unfortunately, the optical data for Pd were restricted to a low-energy interval (up to the uv region), which prevented us from verifying the completeness of the spectrum through the sum rules. However, since the same methods have been used for the calculation of the Pd spectrum as for the previous ones, we are confident that the values obtained are as reliable as those for which the sum rules have been tested.

The surface excitation spectrum of W [Fig. 2(b)] exhibits a series of peaks of ascending intensity up to about 20 eV. Using $r_s=2.34$, 1.86, and 1.62 corresponding to 2, 4, and 6 valence electrons per atom, one obtains the values of 9.31, 13.14, and 16.16 eV for the surface plasmon energy, respectively. On the other hand, the prominent peak in the W surface spectrum appears around 21 eV, and therefore, any discussion of the observability of the surface plasmon seems immaterial before one knows the detailed structure of the intraband and interband transitions in W. Despite such a complicated structure of the spectrum, the sum rules are obeyed surprisingly well, supporting once again our confidence in using these spectral values for the calculation of the quantities which depend on the long-wavelength limit of the surface response function.

C. vdW reference planes for real metal surfaces

The positions proper of the vdW reference planes Z_{aMbM} and Z_{abM} defined by Eqs. (5a) and (5b), respectively, and Z_3's defined in Sec. IV are given by the integrals involving the frequency-dependent centroid of the image charge d_{IP} continued analytically to the imaginary frequencies iu. In our calculations we have used the expression for d_{IP} as proposed by Persson and Zaremba:[14]

$$d_{IP}(iu)=\frac{\epsilon_f(iu)}{\epsilon_f(iu)+\epsilon_b(iu)}d_1^f(iu)\ , \tag{17}$$

in which $d_1^f(iu)$ is the free-electron contribution to the centroid of the image charge and ϵ_f and ϵ_b are the intraband ("free" electron) and interband ("bound" electron) contributions to the bulk dielectric function, respectively. Hence the total complex bulk dielectric function (16) can be expressed as

$$\begin{aligned}\epsilon(iu)&=1+\frac{2}{\pi}\int_0^\infty d\omega\frac{\omega\epsilon_2(\omega)}{\omega^2+u^2}\\&=1+\epsilon_f(iu)+\epsilon_b(iu)\ ,\end{aligned} \tag{18}$$

where $\epsilon_2(\omega)$ is the imaginary part of $\epsilon(\omega)$, viz.,

$$\begin{aligned}\epsilon(\omega)&=\epsilon_1(\omega)+i\epsilon_2(\omega)\\&=\epsilon_1(\omega)+i[\epsilon_2^f(\omega)+\epsilon_2^b(\omega)]\ .\end{aligned} \tag{19}$$

For the purpose of the present calculations, we have approximated the intraband contribution by the Drude formula

$$\epsilon_2^f(\omega)=\frac{\omega_{pf}^2\Delta}{\omega(\omega^2+\Delta^2)}\ , \tag{20}$$

where ω_{pf} and Δ are the effective plasma density and the inverse lifetime of a free electron, respectively. Since we have determined the dielectric function of real metals as well as the corresponding Drude parameters (cf. Sec. III B) from various optical data, it was not necessary to employ any approximate expression for the interband contribution ϵ_b. In our case this was calculated as the remainder appearing on the RHS of Eq. (18):

$$\epsilon_b(iu)=\epsilon(iu)-1-\epsilon_f(iu)$$
$$=\epsilon(iu)-1-\frac{\omega_{pf}^2}{u^2+u\Delta} . \tag{21}$$

The free-electron contribution to the centroid of the image charge d_1^f has been modeled by the expression corresponding to jellium and consistent with the sum rule derived by Persson and Zaremba.[14] Since there exists some ambiguity in the determination of the proper electronic density of jellium which would simulate the behavior of "free" electrons in metals, we have carried out the calculations with two possible values for the jellium density given either by $r_s=(3/\omega_{pf}^2)^{1/3}$ or by the valence electron densities (cf. Table III). As may be seen from the table, the corresponding Z's differ rather significantly for some metals, but these differences do not affect much the vdW potentials between the subsystems at mutual distances which are physically relevant (i.e., in the region in which the vdW expansion converges).

IV. DYNAMIC POLARIZABILITY OF ADSORBATES

The dynamic polarizability $\alpha(\omega)$ of a gas-phase atom or a molecule is usually expressed in terms of the dipole oscillator strengths $f_m=f_{i\to j}$, which denote the probabilities of electronic transitions from discrete occupied level $|i\rangle$ of energy ϵ_i into an unoccupied level $|j\rangle$ of energy ϵ_j. If the corresponding transition energies are denoted by $\omega_m=\epsilon_j-\epsilon_i$, the polarizability can be expressed as (in atomic units)

$$\alpha(\omega)=\sum_m \frac{f_m}{\omega^2-\omega_m^2} , \tag{22}$$

where, in principle, the summation ranges also over the transitions into the continuum of electronic states above the vacuum level ϵ_v. The oscillator strengths satisfy the well-known sum rule

$$\sum_m f_m=N_a , \tag{23}$$

where N_a is the total number of electrons in the atom (molecule). For anisotropic molecules $\alpha(\omega)$ becomes a tensor, with different values along the axes of molecular symmetry.

The calculation of real f_m and ω_m for atoms and molecules is a difficult task and one usually resorts to pseudo-oscillator strengths and corresponding excitation energies which are constructed so as to describe the electronic transitions between some fictious discrete levels only, but which also satisfy the sum rule (23). The values of such pseudo-oscillator strengths and energies are available for a number of atoms and molecules[31] and in what follows we shall always refer to and deal with such pseudoquantities unless specified otherwise.

When an atom or a molecule is adsorbed on a surface of a metal, the relative positions and widths of both the occupied and unoccupied levels may change due to the interaction of the adsorbate with the substrate. The physisorptive component of the interaction is not expected to give rise to any significant changes in real $\tilde{f}_m$ and $\tilde{\omega}_m$ of an adsorbate (tildes denote the quantities f_m and ω_m for adsorbates). However, the chemisorptive component of the interaction, which is responsible for the formation of the adsorbate-substrate chemisorption bond, may give rise to chemically induced shifts and broadening of the localized adsorbate valence levels and thereby to a modification of some $\tilde{f}_m$ and $\tilde{\omega}_m$ with respect to f_m and ω_m.[32,36]

In regard to the vdW interactions involving CO adsorbed on transition and noble metals we may expect that the main modification of the adsorbate polarizability will be due to the hybridization of the empty CO $2\pi^*$ orbital with the metal valence states. The hybridization-induced broadening of the $2\pi^*$ level into a resonance which crosses the substrate Fermi level will cause a partial occupation of the resonance by the electron charge transfer from the substrate. This back-donation mechanism is believed to be responsible for the stabilization of the CO-metal chemisorption bond and there exists abundant experimental and theoretical evidence of this effect.[8]

The energetics of such fractionally occupied CO $2\pi^*$ derived resonances has been discussed in detail elsewhere.[33,34] Here we shall discuss only the implications of the fractional resonance occupation on the dynamical polarizability of adsorbates, in general, and of chemisorbed CO, in particular.

The major effect on the adsorbate dynamic polarizability which may arise from the partial electronic occupation of a resonance will be the occurrence of a new channel for electronic excitations localized on the adsorbate.[32] Following the experimental evidence,[34] we assert that in CO adsorption on Cu, Pt, and transition metals the CO $2\pi^*$ derived resonances are centered a few eV above ϵ_F (for details see below) with a resonance tail extending below ϵ_F and occupied by the charge transfer from the metal valence band. The magnitude of the charge transfer may be estimated only roughly, e.g., from cluster calculations of CO adsorption,[35] if the pertinent occupation numbers obtained from the population analysis are identified with the resonance occupation in the resonance model of chemisorption.

In fractionally occupied adsorbate valence resonances an electron may be excited from the occupied part below ϵ_F into an unoccupied resonance state above ϵ_F (see Fig. 3). These intraresonance transitions which are characterized by the excitation energy ν will affect the total adsorbate polarizability through their intraresonance oscillator strengths $f_{\text{res}}(\nu)$ (per unit energy interval). Hence the contribution to the adsorbate polarizability due to the excitation of the bosonized intraresonance e-h pairs will be given by (in atomic units)[7(c),36]

$$\alpha_{\text{res}}(\omega)=\int_0^\infty d\nu \frac{f_{\text{res}}(\nu)}{\omega^2-\nu^2} , \tag{24}$$

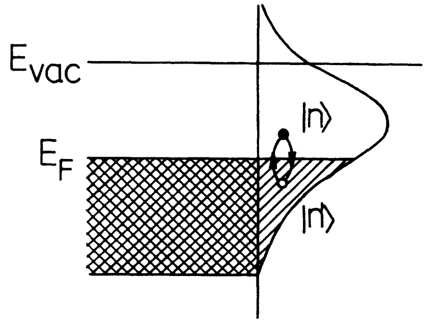

FIG. 3. Electron-hole pair excitation within the adsorbate-derived resonance fractionally occupied by the charge transfer from the substrate. $|n\rangle$ and $|n'\rangle$ denote the unoccupied and occupied localized resonance band states, respectively.

where the integral extends over all intraresonance excitation frequencies ranging from zero to the upper bound given by the resonance bandwidth. To obtain the total adsorbate polarizability $\tilde{\alpha}_a(\omega)$, one should add $\alpha_{\text{res}}(\omega)$ to the polarizability $\alpha_d(\omega)$ originating from the transitions between any two discrete levels of the adsorbate which are not likely to change significantly upon adsorption (cf. discussion above). Hence

$$\tilde{\alpha}_a(\omega)=\alpha_d(\omega)+\alpha_{\text{res}}(\omega) \ , \tag{25}$$

where $\alpha_d(\omega)$ can be calculated with the pseudo-oscillator strengths pertinent to gaseous CO (with due account for the anisotropy of the molecule).

The calculation of the oscillator strengths $f_{\text{res}}(\nu)$ proceeds on noticing that the excitation of an electron-hole (e-h) pair within the resonance is described by the response function $R_{\text{res}}(\nu)$ corresponding to the dynamic polarization process depicted in Fig. 3. This response function can also be written in the Lehmann representation and its spectrum, which yields the intraresonance e-h excitation probability per unit energy interval, represents then the required intraresonance oscillator strength

$$f_{\text{res}}(\nu)=-\frac{1}{\pi}\text{Im}[R_{\text{res}}(\nu)] \ . \tag{26}$$

$R_{\text{res}}(\nu)$ is calculated as a convolution of the intraresonance electron and hole propagators. In the case of g-fold degenerate resonances one has to calculate first f^i_{res} corresponding to the excitations in each of the resonance channels $i=1,\ldots,g$. Each f^i_{res} is, on the other hand, given by the self-convolution of the one-electron density of states $\rho^i_{\text{res}}(\omega)$ in the ith channel.[36,37] Hence the total resonance oscillator strength reads

$$f_{\text{res}}(\nu)=\sum_{i=1}^{g}\int_0^{\nu}d\omega'\rho^i_{\text{res}}(\omega')\rho^i_{\text{res}}(\omega'-\nu) \ . \tag{27}$$

The total resonance occupation which may be identified with the charge transfer then reads

$$N_{2\pi}=\sum_{i=1}^{g}\bar{n}_i \ , \tag{28a}$$

where $\bar{n}_i$ denotes the occupation of the ith channel (component) of the resonance

$$\bar{n}_i=\int_{-\infty}^{\epsilon_F}d\omega\,\rho^i_{\text{res}}(\omega) \ . \tag{28b}$$

To investigate the properties of $f_{\text{res}}(\nu)$ we shall make use of Eq. (27), the causal properties of the density-density response functions in the time representation, and the definition of $R_{\text{res}}(t)$ in terms of the intraresonance electron density fluctuations.[36,37] This enables us to derive the following sum rule for the integrated intraresonance oscillator strength:[32]

$$f_{\text{res}}=\int_0^{\infty}d\nu\,f_{\text{res}}(\nu)=\sum_{i=1}^{g}\bar{n}_i(1-\bar{n}_i) \ . \tag{29}$$

This expression is the desired f-sum rule for chemisorption-induced intraresonance oscillator strengths of an adsorbate and it complements the "atomic" f-sum rule (23) for intra-adsorbate transitions from discrete levels. It should also be noted that in the case of either empty ($\bar{n}_i=0$) or fully occupied resonances ($\bar{n}_i=1$), f_{res} would vanish according to (29). Therefore the contribution $\alpha_{\text{res}}(\omega)$ will be present only in adsorbates with *fractionally* occupied resonances. Thus the expression (29), together with the sum rules (10) and (12), constitutes an indispensable framework for checking the consistency of the calculations of polarization properties of various adsorption systems.

In order to calculate the intraresonance oscillator strengths (27) one needs to know the adsorbate resonance density of states $\rho^i_{\text{res}}(\omega)$. In the present problem of CO adsorption on noble and transition metals we shall reconstruct ρ^i_{res} from the data available from inverse photoemission.[34] Following the experimental evidence we shall first assert that the density of states of the CO $2\pi^*$ derived valence resonances in the systems considered can to a good approximation be represented by a simple Lorentzian

$$\rho^i_{\text{res}}(\omega)=\frac{1}{\pi}\frac{\Delta_{\text{res}}}{(\omega-\epsilon_{\text{res}})^2+\Delta^2_{\text{res}}} \ . \tag{30}$$

Here, $\epsilon_{\text{res}}=\epsilon_{2\pi}>0$ is the $2\pi^*$ resonance energy measured from the substrate Fermi level and $\Delta_{\text{res}}=\Delta_{2\pi}$ is the resonance halfwidth at half maximum, and in some cases it is possible to determine both quantities from the data available from the literature. Another advantage of choosing the Lorentzian form of the resonance density of states (30) is that $f_{\text{res}}(\nu)$ can in this case be calculated analytically, and this guarantees that the f-sum rule (29) would be satisfied automatically.

From the data available, we can fully reconstruct (i.e., determine ϵ_{res} and Δ_{res}) only the CO $2\pi^*$ derived resonances in adsorption systems CO/Cu(110) and CO/Ni(111). Incidently, these systems are characteristic of weak and strong CO chemisorption, respectively. The inverse photoemission experiments give $\epsilon_{2\pi}=2.8$ eV and $\epsilon_{2\pi}=3$ eV for the cases of CO/Cu(110) and CO/Ni(111), respectively, and $\Delta_{2\pi}$ will be estimated by combining Eqs. (28) and (30) and equating $N_{2\pi}$ [Eq. (28a)] with the occupation of the CO $2\pi^*$ derived states obtained from the population analysis of the orbitals of the clusters which model CO adsorption on Cu and Ni.[35] This gives the values of $\Delta_{2\pi}$ shown in Table II.

The intraresonance oscillator strengths for various positions and strengths of the adsorbate resonance are illustrated in Fig. 4(a). $f_{\text{res}}(\nu)$ relevant for the systems CO/Cu(110) and CO/Ni(111) are shown in Fig. 4(b). It should be noted that for low intraresonance excitation energies,[37]

$$\lim_{\nu\to 0} f_{\text{res}}(\nu)=g[\rho^i_{\text{res}}(\epsilon_F)]^2\nu+O(\nu^3)\ , \tag{31}$$

and this limiting behavior becomes important in the case of static polarization. For Lorentzian-like resonances centered close to the substrate Fermi level for which $\bar{n}_i\simeq\frac{1}{2}$, the property (31) enables one to use the ansatz

$$f_{\text{res}}(\nu)\simeq g\,[\rho^i_{\text{res}}(\epsilon_F)]^2\nu\exp[-\sqrt{g}\,\rho^i_{\text{res}}(\epsilon_F)\nu]\ . \tag{32}$$

This ansatz approximates the original expression (27) for $\epsilon_{2\pi}=0$ very accurately [cf. Fig. 4(a) and Eq. 16 of Ref. 7(c)] and satisfies exactly the sum rule (29) for $\bar{n}_i=\frac{1}{2}$. Table II summarizes some of the parameters and the properties of the $2\pi^*$ resonance relevant for the calculation of the polarizability $\alpha_{\text{res}}(\omega)$ of CO chemisorbed on Cu and Ni as obtained in the present Lorentzian model.

V. STRENGTHS OF THE vdW INTERACTIONS IN SURFACE SCATTERING

The functional behavior of $S_0(\omega)$, $d_{IP}(\omega)$, and $f_{2\pi}(\omega)$ calculated in Secs. III A, III B, and IV, respectively, enables us now to compute the strengths of the vdW potentials [Eqs. (4a)–(4c)] and the relevant reference planes [Eqs. (5a) and (5b)] for the case of He scattering from CO adsorbed on various noble- and transition-metal substrates. The required quantities $R_0(\omega)$ and $\alpha_{2\pi}(\omega)$ are obtained as Hilbert transforms of $S_0(\omega)$ and $f_{2\pi}(\omega)$ which, when substituted in Eqs. (4) and (5) yield the results shown in Table III. For the sake of completeness we have also displayed in Table III the constants C_3:

$$C_3=\int_0^\infty \frac{du}{4\pi}\alpha(iu)R_0(iu)\ , \tag{33a}$$

which determine the strengths of the He-substrate and CO-substrate vdW interactions which fall of as $-C_3/(Z-Z_3)^3$, and the corresponding vdW reference-plane position Z_3 measured with respect to the positive jellium background edge:[13,14]

$$Z_3=\frac{1}{C_3}\int_0^\infty \frac{du}{2\pi}\alpha(iu)R_0(iu)d_{IP}(iu)\ . \tag{33b}$$

In both equations $\alpha(iu)$ represents the dynamical polarizability of either the He atom (in the case of He-substrate

TABLE II. $2\pi^*$ resonance parameters and properties for CO adsorption on Cu and Ni substrates. $\epsilon_{2\pi}$, $\Delta_{2\pi}$, $N_{2\pi}$, $\rho^i_{2\pi}$, and $f_{2\pi}$ denote the $2\pi^*$ resonance energy, halfwidth at half maximum, total occupation, density of states, and integrated intraresonance oscillator strength, respectively (cf. Sec. IV).

$2\pi^*$ Resonance	Substrate Cu(110)	Ni(111)
$\epsilon_{2\pi}$ (eV)	2.8	3.0
$\Delta_{2\pi}$ (eV)	0.20	0.57
$N_{2\pi}$	0.09	0.24
$\rho^i_{2\pi}(\epsilon_F)$ (eV^{-1})	0.0080	0.0195
$f_{2\pi}$	0.088	0.226

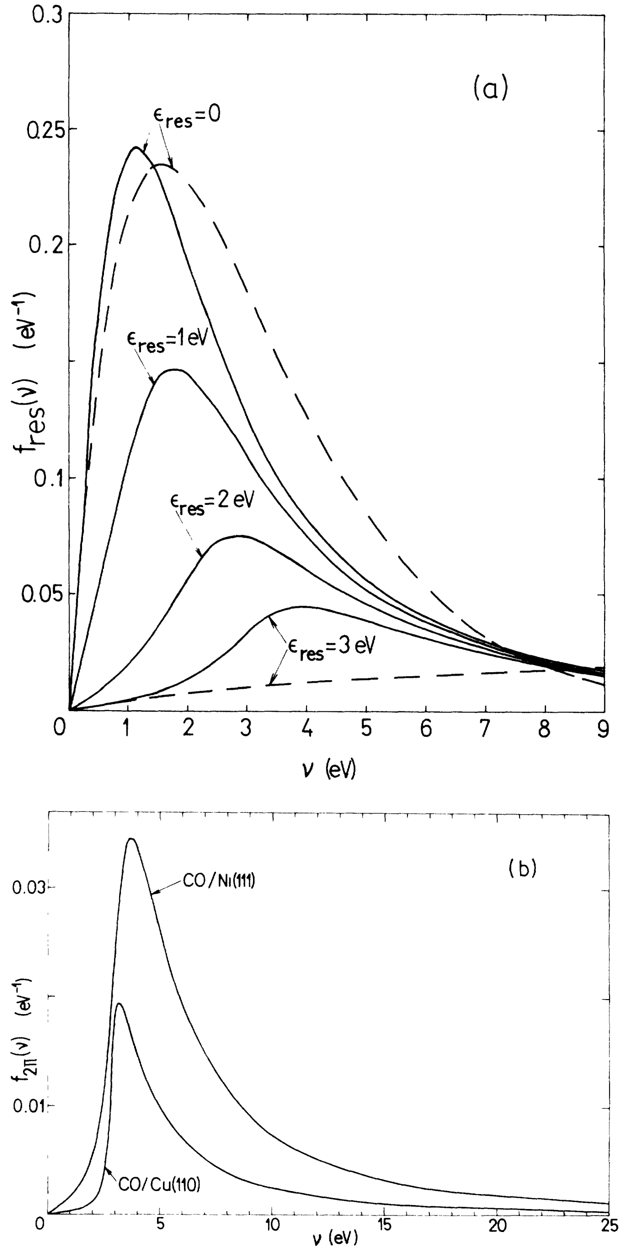

FIG. 4. Oscillator strengths $f_{\text{res}}(\nu)$ of the intraresonance electronic excitations. (a) Solid line, $f_{\text{res}}(\nu)$ calculated from Eq. (27); dashed line, $f_{\text{res}}(\nu)$ as obtained from the ansatz (32). Resonance energies measured relative to the substrate Fermi level. Resonance half-width at half maximum $\Delta_{\text{res}}=1$ eV in all curves displayed. (b) $f_{\text{res}}(\nu)=f_{2\pi}(\nu)$ relevant for CO adsorbed on Ni(111) and Cu(110). The corresponding parameters $\epsilon_{2\pi}$ and $\Delta_{2\pi}$ given in Table II.

TABLE III. van der Waals constants pertinent to He-CO–substrate interactions. The constants C and Z are defined by Eqs. (4) and (5) for He-adsorbate and by (33) for He-substrate and CO-substrate interactions, respectively. The values in columns labeled d and $d+2\pi$ correspond to the case in which the polarizability of the adsorbate is determined by the discrete electronic transitions only [i.e., by $\alpha_d(\omega)$] and by the discrete and intraresonance $(2\pi^*)$ excitations using complete $\alpha(\omega)$ of Eq. (25), respectively. The superscripts 1, 2, 3, 4, and 6 of r_s denote the number of valence electrons per atom which determine the jellium density needed for the evaluation of Z's. The label f in the same column denotes the values of the jellium density as obtained from $r_s+(3/\omega_{pf}^2)^{1/3}$ (cf. Sec. III C).

			He-CO van der Waals interactions										He-substrate van der Waals interaction		CO-substrate van der Waals interaction			
			Direct interaction		Substrate mediated interactions													
		$\omega_s(r_s)$ (eV)	C_{ab} (a.u.)		C_{aMbM} (a.u.)		Z_{aMbM} (a.u.)		C_{abM} (a.u.)		Z_{abM} (a.u.)		C_{bM} (a.u.)	Z_{bM} (a.u.)	C_{aM} (a.u.)		Z_{aM} (a.u.)	
Substrate	r_s		d	$d+2\pi$	d	$d+2\pi$	d	$d+2\pi$	d	$d+2\pi$	d	$d+2\pi$			d	$d+2\pi$	d	$d+2\pi$
Al	$2.12^{(3)}$	10.80	2.394		0.941		0.761		1.291		0.638		0.0504	0.516	0.538		0.575	
	$2.56^{(f)}$	8.13	2.394		0.941		0.666		1.291		0.548		0.0504	0.437	0.538		0.491	
Cu	$2.67^{(1)}$	7.64	2.394	2.521	0.850	0.929	0.756	0.781	1.271	1.367	0.580	0.606	0.0542	0.411	0.558	0.594	0.488	0.514
	$3.06^{(f)}$	6.23	2.394	2.521	0.850	0.929	0.694	0.718	1.271	1.367	0.528	0.552	0.0542	0.372	0.558	0.594	0.443	0.467
Pt	$2.30^{(2)}$	9.55	2.394		0.986		0.296		1.414		0.226		0.0629	0.152	0.635		0.185	
	$2.01^{(3)}$	11.70	2.394		0.986		0.313		1.414		0.240		0.0629	0.162	0.635		0.197	
	$1.82^{(4)}$	13.57	2.394		0.986		0.326		1.414		0.251		0.0629	0.170	0.635		0.206	
	$4.50^{(f)}$	3.50	2.394		0.986		0.202		1.414		0.150		0.0629	0.098	0.635		0.122	
Ni	$2.60^{(1)}$	7.95	2.394	2.705	0.875	1.071	0.366	0.408	1.300	1.537	0.273	0.312	0.0559	0.189	0.573	0.664	0.228	0.265
	$2.09^{(2)}$	11.03	2.394	2.705	0.875	1.071	0.407	0.452	1.300	1.537	0.308	0.349	0.0559	0.215	0.573	0.664	0.257	0.297
	$4.33^{(f)}$	3.70	2.394	2.705	0.875	1.071	0.270	0.306	1.300	1.537	0.196	0.229	0.0559	0.134	0.573	0.664	0.163	0.193
W	$2.34^{(2)}$	9.31	2.394		1.089		0.371		1.495		0.292		0.0670	0.196	0.674		0.239	
	$1.86^{(4)}$	13.14	2.394		1.089		0.412		1.495		0.327		0.0670	0.222	0.674		0.268	
	$1.62^{(6)}$	16.16	2.394		1.089		0.435		1.495		0.348		0.0670	0.237	0.674		0.286	
	$3.72^{(f)}$	4.65	2.394		1.089		0.284		1.495		0.220		0.0670	0.145	0.674		0.178	

interaction) or the CO molecule (in the case of CO-substrate interaction).

Several trends as to the magnitude of the He-adsorbed CO vdW interaction strengths can be deduced from Table III. The strength C_{ab} of the direct interaction is the dominant one and exceeds the strengths of the interference term C_{abM} and of the image term C_{aMbM} by about 120% and 160%, respectively, in all the cases studied. The three constants would be equal only in the hypothetical limit $R_0(\omega)=-1$ characteristic of an extremely high-density electron gas for which $\omega_s \rightarrow \infty$ (i.e., $r_s \rightarrow 0$). Hence an increase of C_{abM} and C_{aMbM} for Pt and W, which exhibit higher valence electron densities than Cu and Ni, is thus hardly surprising. However, this increase is not large, which reflects some common features of the screening properties of the metals investigated, and which has been noted earlier in the study of the surface sum rules (cf. Sec. III B).

An opposite trend, i.e., a decrease of the magnitude of the distance of the vdW reference planes Z_{aMbM} [Eq. (5a)] and Z_{abM} [Eq. (5b)] relative to the positive jellium background edge with the increase of the metal electron density is also evident. This is in accord with the earlier established behavior that the dynamical image reference plane shifts closer to the jellium edge as the frequency of the surface mode(s) of the screening metal is increased.[13] The same conclusion applies also to the properties of the He-surface and CO-surface vdW interactions (cf. Table III).

Lastly, it should be noted that the values of the vdW constants given in Table III differ very little from those calculated in Ref. 7(c) for a free-electron gas characterized by the electron density parameter $r_s=2.6$, which may simulate the free-electron properties of Ni. This can be interpreted as another manifestation of the common screening properties of metal surfaces expressed through the sum rules (11) and (13). Therefore, for the same adsorption geometry the change of the substrate will affect more the chemically induced contribution to the vdW constants (here the 2π-derived quantities) than the physisorption-induced effects which enter C_{ab}, C_{aMbM}, and C_{abM} through the surface response function $R_0(\omega)$. Due to the variety of the metal surfaces studied in the present work, such a conclusion can be safely extrapolated also to other adsorption systems of similar chemisorptive characteristics. Therefore, as the collisions of thermal energy He atoms with CO adsorption complexes are to the greatest extent governed by the long-range vdW interactions, the corresponding total scattering cross sections Σ should not vary appreciably with the change of the substrate unless the chemistry and the geometry of the system are changed. A detailed account of the substrate-induced effects on the magnitude and behavior of Σ for specific (He$\rightarrow$CO)-metal collision systems is given in Ref. 18.

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*Permanent address.

[1] G. Boato, P. Cantini, and R. Tatarek, in *Proceedings of the Seventh International Vacuum Congress and the Third International Conference on Solid Surfaces,* edited by R. Dobrozemsky, F. Rüdenauer, F. P. Viehbäck, and A. Breth (R. Dobrozemsky, Vienna, 1977), p. 1337; D. R. Miller and J. M. Horne, *ibid.*, p. 1385; M. W. Cole and D. R. Frankl, Surf. Sci. **70**, 585 (1978); H. U. Finzel, H. Frank, H. Hoinkes, H. Luschka, H. Nahr, H. Wilsch, and U. Wonka, *ibid.* **49**, 577 (1975); K. H. Rieder, *ibid.* **117**, 13 (1982); K. H. Rieder and T. Engel, Phys. Rev. Lett. **45**, 824 (1980); D. L. Smith and R. P. Merrill, J. Chem. Phys. **52**, 5861 (1970); B. F. Mason, R. Caudano, and B. R. Williams, Phys. Rev. Lett. **47**, 1141 (1981); J. Chem. Phys. **77**, 562 (1982); B. Poelsema, G. Mechtersheimer, and G. Comsa, Surf. Sci. **111**, 519 (1981); B. Poelsema, R. L. Palmer, G. Mechterscheimer, and G. Comsa, *ibid.* **117**, 60 (1982); B. Poelsema, R. L. Palmer, and G. Comsa, *ibid.* **123**, 152 (1982); B. Poelsema, S. T. de Zwart, and G. Comsa, Phys. Rev. Lett. **49**, 578 (1982); **51**, 522 (1983); B. Poelsema, R. L. Palmer, S. T. de Zwart, and G. Comsa, Surf. Sci. **126**, 641 (1983); B. Poelsema, L. K. Verheij, and G. Comsa, Phys. Rev. Lett. **49**, 1731 (1982); **51**, 2410 (1983); A. Luntz. L. Mattera, M. Rocca, S. Terreni, F. Tommasini, and U. Valbusa, Surf. Sci. **126**, 695 (1983); J. Ibáñez, N. Garcia, J. M. Rojo, and N. Cabrera, *ibid.* **117**, 23 (1982); J. Ibáñez, N. Garcia, and J. M. Rojo, Phys. Rev. B **28**, 3164 (1983); T. Engel, J. Chem. Phys. **69**, 373 (1978); D. H. Winicur, J. Hurst, C. A. Becker, and L. Wharton, Surf. Sci. **109**, 263 (1981); H. Wilsch and K. H. Rieder, J. Chem. Phys. **78**, 7491 (1983); J. Lapujoulade, Y. Le Cruër, M. Lefort, Y. Lejay, and E. Maurel, Surf. Sci. **118**, 103 (1982); J. Lee, J. P. Cowin, and L. Wharton, *ibid.* **130**, 1 (1983); J. Lapujoulade, J. Perreau, and A. Kara, *ibid.* **129**, 59 (1983); J. Lapujoulade, Y. Lejay, and G. Armand, *ibid.* **95**, 107 (1980); **63**, 143 (1977); B. F. Mason, K. M. McGreer, and B. R. Williams, *ibid.* **130**, 282 (1983); B. F. Mason and B. R. Williams, *ibid.* **130**, L329 (1983); **130**, 295 (1983); Phys. Rev. Lett. **46**, 1138 (1981); G. Brusdeylins, R. B. Doak, and J. P. Toennies, Phys. Rev. Lett. **44**, 1417 (1980); B. Feuerbacher and R. F. Willis, Phys. Rev. Lett. **47**, 526 (1981); B. Poelsema, L. K. Verheij, and G. Comsa, Surf. Sci. **152/153**, 851 (1985), and references therein; S. M. Francis and N. V. Richardson, *ibid.* **152/153**, 63 (1985).

[2] B. Poelsema, S. T. de Zwart, and G. Comsa, in Ref. 1; B. Poelsema, L. K. Verheij and G. Comsa, in Ref. 1; B. Poelsema, R. L. Palmer, S. T. de Zwart, and G. Comsa, in Ref. 1.

[3] H. P. Butz, R. Fetgen, H. Pauly, and H. Vehmeyer, Z. Phys.

247, 70 (1971).

[4] H. S. W. Massey and C. B. O. Mohr, Proc. R. Soc. London, Ser. A **144**, 188 (1934).

[5] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon, New York, 1959), p. 916.

[6] A. D. McLachlan, Mol. Phys. **7**, 381 (1964).

[7] (a) B. Gumhalter and W.-K. Liu, Surf. Sci. **148**, 371 (1984); (b) B. Gumhalter, D. Lovrić, and W.-K. Liu, *ibid.* **178**, 743 (1986); (c) D. Lovrić and B. Gumhalter, Phys. Status Solidi B **139**, 423 (1987).

[8] For review, see B. Gumhalter, K. Wandelt, and Ph. Avouris, Phys. Rev. B **37**, 8048 (1988).

[9] B. Gumhalter and D. M. Newns, Phys. Lett. **53A**, 137 (1975); B. Gumhalter, J. Phys. (Paris) **38**, 1117 (1975).

[10] B. Gumhalter, Progr. Surf. Sci. **15**, 1 (1984), and references therein.

[11] W.-K. Liu, Phys. Rev. B **32**, 868 (1985).

[12] P. J. Feibelman, Progr. Surf. Sci. **12**, 287 (1982).

[13] E. Zaremba and W. Kohn, Phys. Rev. B **13**, 2270 (1976).

[14] B. N. J. Persson and E. Zaremba, Phys. Rev. B **30**, 5669 (1984).

[15] H. Jónsson, H. J. Weare, and A. C. Levi, Phys. Rev. B **30**, 2241 (1984).

[16] B. Gumhalter, D. Lovrić, and W.-K. Liu, in Ref. 7(b).

[17] W.-K. Liu and B. Gumhalter, Surf. Sci. **180**, 169 (1987).

[18] B. Gumhalter and W.-K. Liu, Surf. Sci. **202**, 300 (1988).

[19] D. Pines and Ph. Nozières, *The Theory of Quantum Liquids* (Benjamin, New York, 1966).

[20] D. Y. Smith, in *Handbook of Optical Constants of Solids*, edited by E. D. Palik (Academic, New York, 1985), and references therein; (b) E. Shiles, T. Sasaki, M. Inokuti, and D. Y. Smith, Phys. Rev. B **22**, 1612 (1980); (c) E. G. Maksimov, I. I. Mazin, S. N. Rashkeev, Yu. A. Uspenski (unpublished).

[21] H. J. Hagemann, W. Gudat, and C. Kunz, DESY Report No. SR-74/7.

[22] D. M. Newns, Phys. Rev. B **1**, 3304 (1970).

[23] N. D. Lang and W. Kohn, Phys. Rev. B **7**, 3541 (1973).

[24] B. Gumhalter, Solid State Commun. **52**, 441 (1984).

[25] B. N. J. Persson and P. Apell, Phys. Rev. B **27**, 6058 (1983).

[26] (a) A. Liebsch, Phys. Rev. B **33**, 7249 (1986); (b) **35**, 9030 (1987).

[27] A. Liebsch, Phys. Rev. Lett. **54**, 67 (1985).

[28] K. Kempa and W. L. Schaich, Phys. Rev. B **34**, 547 (1986); W. L. Schaich and K. Kempa, Phys. Scr. **35**, 204 (1987).

[29] J. H. Weaver, C. Krafka, D. W. Lynch, and E. E. Koch, Phys. Daten (Physics Data) **18**, 1 (1981) (Germany), Fachinformationszentrum Energie, Physik, Mathematik GmbH, Karlsruhe.

[30] B. L. Henke, P. Lee, T. J. Tanaka, R. L. Shimabukuro, and B. K. Fujikawa, At. Data Nucl. Data Tables **27**, 1 (1982).

[31] A. Dalgarno and A. E. Kingston, Proc. Phys. Soc. **72**, 1053 (1958); D. J. Margoliash and W. J. Meath, J. Chem. Phys. **68**, 1426 (1978); B. L. Jhanwar and W. J. Meath, Chem. Phys. **67**, 185 (1982).

[32] B. Gumhalter and K. Wandelt, Phys. Rev. Lett. **57**, 2318 (1986).

[33] See papers quoted in Refs. 7(c) and 8 above.

[34] Th. Fauster and F. J. Himpsel, Phys. Rev. B **27**, 1390 (1983); J. Rogozik, H. Scheidt, V. Dose, K. C. Prince, and A. M. Bradshaw, Surf. Sci. **145**, L481 (1984); J. Rogozik, J. Küppers, and V. Dose, Surf. Sci. **162**, 264 (1985).

[35] P. S. Bagus and M. Seel, Phys. Rev. B **23**, 2065 (1981); K. Hermann and P. S. Bagus, *ibid.* **16**, 4195 (1977); K. Hermann (private communication).

[36] K. Wandelt and B. Gumhalter, Surf. Sci. **169**, 138 (1986).

[37] B. Gumhalter, Phys. Rev. B **19**, 2018 (1979).