van der Waals interaction between a molecule and a spherical cavity in a metal: Nonlocality and anisotropy effects

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The electric response field of a small spherical metallic cavity to a molecule characterized by fluctuating dipolar and quadrupolar moments is built from spherical tensor theory. The electric susceptibility of the field gradient between the two points inside the metallic cavity is formulated by a general expression of the van der Waals energy between the two partners. The induction contribution is introduced by using the field gradient susceptibilities of the cavity at zero frequency. In order to illustrate the nonlocal effects as well as the importance of the curvature of the metallic cavity on the magnitude of the physisorption energy, we present numerical results for typical systems (HF, HCl on Ag, Al, and Cu). [S0163-1829(97)03407-3]

I. INTRODUCTION

Intrinsic dynamical properties of microscopic systems are significantly altered by the proximity of a surface.[1–9] The theory of atom- or molecule-surface interactions and physisorption mechanisms has already received a great deal of attention, allowing the interpretation of various experiments, such as the measurement of desorption heats, work-function changes, and alteration of spectroscopic properties.[10–12] All these alterations of atomic or molecular properties at the vicinity of a surface are of special importance when the surface presents a positive or negative radius of curvature at a μm or nm scale. For such confined systems as atoms in microcavities,[13–15] molecule in porous materials,[16] or carbon nanotubes,[17] or at the tip of a near-field microscope, spectroscopic properties are dramatically changed (spontaneous emission and level shift of atoms,[18] enhancement of molecular Raman scattering,[19] and molecular fluorescence[20]).

In spite of the great complexity of the problem, most of the dispersion and induction effects which occur when a microscopic system interacts with a solid limited by a surface can be calculated by means of a very concise formalism using the generalized susceptibilities of both partners.[9,21,22] The main advantage of such a treatment comes from the fact that the calculation of van der Waals energy reduces to that of the susceptibility tensor $^{(n)}\mathbf{S}^{(m)}(\mathbf{r}_1,\mathbf{r}_2,\omega)$ of the field gradient associated with the surface. This latter quantity, also called the "propagator," connects two different points $\mathbf{r}_1$ and $\mathbf{r}_2$ outside of the surface. In recent publications[22,23] the response field of a small metallic sphere to fluctuating dipolar and quadrupolar moments has been constructed using spherical-tensor theory.

The main goal of the present study is to apply this theory to determine the van der Waals interaction between a hollow spherical cavity in a metal and an anisotropic molecule placed inside the cavity. In order to give a treatment beyond the local approximation,[24] spatial dispersion effects are deduced from the diagonal dielectric function $\varepsilon(k,\omega)$, assuming a homogeneous response of the metal electrons.[25] This latter approximation is sufficient to obtain a good estimation

of the van der Waals energy. Indeed, in this case, this energy is calculated by integrating the dielectric function with an imaginary argument $i\xi$, over the range $\xi=0$ to infinity. This makes an average of the electronic response, and does not imply any detailed knowledge of the response, especially knowledge of possible resonance effects which have been taken into account in previous works.[26] In Sec. II, expressions for the dispersion and induction energies of the system (molecule-spherical cavity) are given. In Secs. III and IV the dispersion coefficients $C_n^{\parallel}$, $C_n^{\perp}$ (respectively parallel and perpendicular to the principal symmetry axis of the molecule) are calculated. In this section the dependences of the long-range interaction on the molecular orientation and on the radius of the metallic cavity (Al, Cu, Ag) are also given, for molecules with a permanent dipolar moment (HF, HCl).

II. van der WAALS ENERGY

At large distances, the van der Waals energy is a sum of the dispersive and inductive contributions[21]

$$V(\mathbf{R}) = V_i(\mathbf{R}) + V_d(\mathbf{R}) \tag{1}$$

where

$$V_i(\mathbf{R}) = -\tfrac{1}{2}\boldsymbol{\mu}\cdot{}^{(1)}\mathbf{S}^{(1)}(\mathbf{R},\mathbf{R},0)\cdot\boldsymbol{\mu} + \tfrac{1}{3}\boldsymbol{\mu}^{(1)}\mathbf{S}^{(2)}(\mathbf{R},\mathbf{R},0)\!:\!\boldsymbol{\Theta}$$
$$+ \tfrac{1}{3}\,\boldsymbol{\Theta}\!:\!{}^{(2)}\mathbf{S}^{(1)}(\mathbf{R},\mathbf{R},0)\cdot\boldsymbol{\mu} + \cdots \tag{2}$$

and

$$V_d(R) = \frac{\hbar}{2\pi}\sum_{m,m'}\frac{1}{(2m-1)!!(2m'-1)!!}\int_0^{+\infty}d\xi^{(m)}\boldsymbol{\alpha}^{(m')}$$
$$\times (i\xi)[m+m']^{(m)}\mathbf{S}^{(m')}R,R,(i\xi) \tag{3}$$

$^{(m)}\boldsymbol{\alpha}^{(m')}(i\xi)$ and $^{(n)}\mathbf{S}^{(m)}(\mathbf{R},\mathbf{R},\omega)$, respectively, are the multipolar polarizability of the molecule at frequency $\omega=i\xi$, and the susceptibility tensor of the field gradient of the spherical cavity. The symbol $[m+m']$ stands for the contraction of these two tensors, the order of which is ($m+m'$). In the inductive contribution, $\boldsymbol{\mu}$ and $\boldsymbol{\Theta}$, respectively,
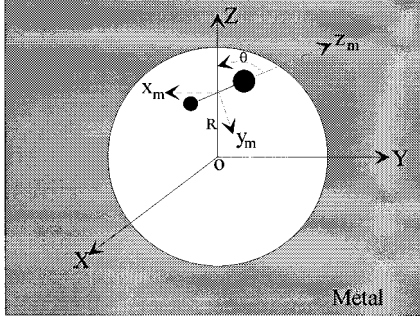
FIG. 1. A linear molecular interacts with a hollow cavity in a metal. (X,Y,Z) is the fixed frame, (X_m,Y_m,Z_m) is the body-fixed frame.

are the permanent dipolar and quadrupolar moments of the molecule, the center of which is located at the position vector $\mathbf{R}(0,0,R)$ (Fig. 1).

III. DIPOLAR CONTRIBUTION

Using previous results dealing with the dynamical response of a metallic spherical cavity[27] (cf. the Appendix), the dipolar contribution to the van der Waals energy takes the following form:

$$V^{(1)}(\mathbf{R})=V_i^{(1)}(\mathbf{R})+V_d^{(1)}(\mathbf{R}), \qquad (4)$$

where

$$V_i^{(1)}(\mathbf{R})=\tfrac{1}{2}\mu^2\,\frac{1}{a^3}\sum_{n=1}^{\infty}\,\Delta_n(a,0)\left(\frac{R}{a}\right)^{2n-2}$$

$$\times\left\{\frac{n(n+1)}{2}\sin^2\theta+n^2\cos^2\theta\right\} \qquad (5)$$

and

$$V_d^{(1)}(\mathbf{R})=\frac{1}{a^3}\sum_{n=1}^{\infty}\left(\frac{R}{a}\right)^{2n-2}\left\{C_n^{\parallel}\left(\frac{n(n+1)}{2}\sin^2\theta+n^2\cos^2\theta\right)\right.$$

$$\left.+C_n^{\perp}\left(\frac{n(n+1)}{2}(1+\cos^2\theta)+n^2\sin^2\theta\right)\right\}. \qquad (6)$$

a is the radius of the cavity; θ, φ, χ are Euler angles of the molecular frame (X_m, Y_m, and Z_m) in the fixed frame (XYZ) (Fig. 1) (θ and φ are the polar angles of the Z_m axis, and χ is a rotation angle around this axis). While expressions (5) and (6) can be generalized to polyatomic molecules, only molecules with axial symmetry will be considered further. In this instance, the molecule-cavity interaction presents a cylindrical symmetry and is only θ dependent. The dispersion coefficients $C_n^{\parallel}$ and $C_n^{\perp}$, which include the nonlocal behavior of the metal and the anisotropy of molecule, parallel and perpendicular to the internuclear axis, can be written as:

$$C_n^{\parallel/\perp}=\frac{\hbar}{2\pi}\int_0^{+\infty}d\xi\,\Delta_n(a,i\xi)\alpha^{\parallel/\perp}(i\xi), \qquad (7)$$

where $\alpha^{\parallel/\perp}(i\xi)$ are the parallel and perpendicular polarisabilities of the molecule,

$$\alpha^{\parallel}(i\xi)={}^{(1)}\alpha^{(1)}{}_{zz}(i\xi), \quad \alpha^{\perp}(i\xi)={}^{(1)}\alpha^{(1)}{}_{xx}(i\xi). \qquad (8)$$

The quantities $\Delta_n(a,i\xi)$ are the reflection coefficients of the cavity walls. Their expressions are given in the Appendix. It is worthwhile noting that if the discrete aspect of the metallic surface is taken into account, then the axis symmetry is broken and the propagator ${}^{(n)}\mathbf{S}^{(m)}(\mathbf{R},\mathbf{R},i\xi)$ no longer has $C_{\infty v}$ symmetry.

III. METHOD OF CALCULATION

In order to show the influence of the surface curvature on the physisorption energy of linear molecules, numerical calculations have been performed for the systems HF, HCl/Al, Ag, and Cu. To carry out these calculations, several functions involved in the molecular-cavity interaction need to be known.

A. Characterization of the physisorbed molecule

The model of the tridimensional harmonic oscillator allows us to obtain the parallel and perpendicular dynamic polarizabilities of the physisorbed molecule:[28]

$$\alpha^{\parallel/\perp}(i\xi)=\frac{\alpha^{\parallel/\perp}(0)\omega_{\parallel/\perp}{}^2}{\xi^2+\omega_{\parallel/\perp}{}^2}, \qquad (9)$$

where $\omega_{\parallel/\perp}$ are the effective frequencies of the harmonic oscillator for the parallel and perpendicular directions.

B. Hollow cavity in a metal

If the off-diagonal elements of the dielectric matrix $E_n(k,k',\omega)$ are neglected in the analytical expression of terms $\Delta_n(a,\omega)$ [cf. the Appendix, Eq. (A7)], then a relationship between the diagonal terms of this matrix and the Lindhard dielectric function $\varepsilon(k,\omega)$ can be derived:[28]

$$E_n(k,k',\omega)=k^2\varepsilon(k,\omega)\delta_{k,k'} \qquad (10)$$

By replacing the discrete sum in Eq. (A7) by an integral over the wave number k, one obtains

$$\Delta_n(a,i\xi)=\frac{\dfrac{n}{a}F_n(a,i\xi)-1}{\dfrac{n+1}{a}F_n(a,i\xi)+1}, \qquad (11)$$

where

$$F_n(a,i\xi)=\frac{2(2n+1)}{n\pi}\int_0^{+\infty}dk\,\frac{j_n{}^2(ka)}{\varepsilon(k,i\xi)}. \qquad (12)$$

j_n is a spherical Bessel function.

The dispersive spatial effect can be described by expressing the Lindhard function in the hydrodynamical model,[29,30] using the following expressions for the functions $F_n(a,i\xi)$:

$$F_n(a,i\xi)=\frac{a}{n}\left[\frac{1}{\varepsilon(i\xi)}+\left((2n+1)\left(\frac{a\omega_p}{\delta u(i\xi)}\right)^2\right.\right.$$

$$\left.\left.\times I_{n+(1/2)}(u(i\xi))K_{n+(1/2)}(u(i\xi))\right)\right] \qquad (13)$$

where

$$\varepsilon(i\xi) = 1 + \frac{\omega_p^2}{\xi^2} \tag{14}$$

and

$$u(i\xi) = a(\omega_p^2 + \xi^2)^{1/2}/\delta. \tag{15}$$

ω_p is the metal plasmon frequency in a free-electron model, and δ is a parameter the value of which is very close to $(\frac{3}{5})^{1/2}v_F$, where v_F is the Fermi velocity; $I_{n+1/2}$ and $K_{n+1/2}$ are the modified Bessel functions.

The zero-frequency contribution to the inductive part $V_i^{(1)}$ of the energy [Eq. (5)] must coincide with the electrostatic energy of a permanent dipole inside the cavity. This point is easily verified in the special case where the distance of approach $d = a - R$ is finite, whereas a tends to infinity.

Indeed under such conditions $|\varepsilon|^{-1} \to 0$ and $I_{n+1/2}(u(0))K_{n+1/2}(u(0))$ behaves like a^{-1}. Therefore $F_n(a,0)$ [Eq. (13)] takes a finite value, and then $\Delta_n(a,0) \to -1$ as $a \to \infty$. For sake of simplicity let us assume that $\theta = \pi/2$. The electrostatic limit of the inductive energy is then

$$[V_i^{(1)}]_{\text{stat}} = \lim_{a \to \infty}\left[\frac{\mu^2}{4a^3}\sum_1^\infty n(n+1)\left(\frac{R}{a}\right)^{2n-2}\right] = \frac{1}{2}\frac{\mu^2}{(2d)^3},$$

which is the electrostatic energy of the dipole in front of its image.

IV. DISPERSION COEFFICIENTS: NUMERICAL CALCULATIONS

By substituting Eqs. (11) and (13) into Eq. (7), one obtains the following expression for the dispersion coefficients:

$$C_n^{\parallel/\perp} = \frac{n\hbar}{2\pi}\,\alpha^{\parallel/\perp}(0)\,\omega_{\parallel/\perp}^2\int_0^{+\infty}d\xi\,\frac{\dfrac{1}{\varepsilon(i\xi)} + f_n(a,i\xi) - 1}{(\xi^2 + \omega_{\parallel/\perp}^2)\left[(n+1)\left\{\dfrac{1}{\varepsilon(i\xi)} + f_n(a,i\xi)\right\} + n\right]}, \tag{16}$$

where the functions

$$f_n(a,i\xi) = (2n+1)\left(\frac{a\omega_p}{\delta u(i\xi)}\right)^2 I_{n+(1/2)}(u(i\xi))K_{n+(1/2)}(u(i\xi)) \tag{17}$$

are related to the nonlocal behavior of the metal.

Using these expressions and the numerical data shown in Tables I and II, it is now possible to evaluate the dispersion coefficients and the corresponding physisorption energy. The results are presented in Figs. 2(a)–2(c) and 3–5. Several remarks are worth noting about these results.

(a) For all the systems investigated here, the dispersion coefficients depend on the radius a of the cavity, which is a signature of the nonlocality of the electronic response [Eq. (16)]. This dependence on the radius becomes more and more visible with increasing values of n [Figs. 2(a)–2(c)]. In a local description the functions $f_n(a,i\xi)$ are equal to zero, and the dispersion coefficients take the simpler form

$$C_n^{\parallel/\perp}(\text{local}) = \frac{-\hbar}{4}\left(\frac{n}{2n+1}\right)^{1/2}\alpha^{\parallel/\perp}(0)\,\omega_{\parallel/\perp}\,\omega_p$$

$$\Bigg/\left\{\omega_{\parallel/\perp} + \left(\frac{n}{2n+1}\right)^{1/2}\omega_p\right\}, \tag{18}$$

where any dependence on the radius has disappeared. In Figs. 3(a) and 3(b) the van der Waals energies are shown as functions of the radius a, at a fixed value of d ($=6$ a.u.), the molecule being oriented parallel to the surface ($\theta = \pi/2$).

(b) The anisotropy of the molecule makes the van der Waals energy θ-dependent. It is seen in Figs. 4(a) and 4(b) that $|V^{(1)}|$ is maximum at $\theta = 0$, π, i.e., when the molecule is perpendicular to the surface. The general behavior of the anisotropy effect is similar to that obtained in the electrostatic approximation. It is, however, quantitatively different. At higher multipolar orders the symmetry with respect to $\theta = \pi/2$ disappears.

(c) The behavior of $V^{(1)}$ as a function of the distance of approach $d = a - R$ is similar for the three metals (Ag, Al, and Cu) and the two molecules (HF and HCl). Only the magnitude of $|V^{(1)}|$ depends on the system. In order to emphasize the comparison with a pure van der Waals interaction with a planar surface, in Figs. 5(a) and 5(b) we plotted $V^{(1)}(d)d^3$ as a function of d, for a fixed value of a ($=60$ a.u.). By an extrapolation of these results at $d=0$, one can estimate the van der Waals constants for the systems HF/Ag,

TABLE I. Molecular patterns used in the calculation of dispersive and inductive energies.

	μ (D)	$\alpha_\parallel(0)$ (a.u.)	$\alpha_\perp(0)$ (a.u.)	$\omega_\parallel(0)$ (a.u.)	$\omega_\perp(0)$ (a.u.)
HF[a]	1.736	5.20	3.84	1.561	0.375
HCl[a]	1.08	14.08	4.27	0.737	0.898

[a]Reference 23.

TABLE II. Parameters ω_p, δ of the metals (see text).

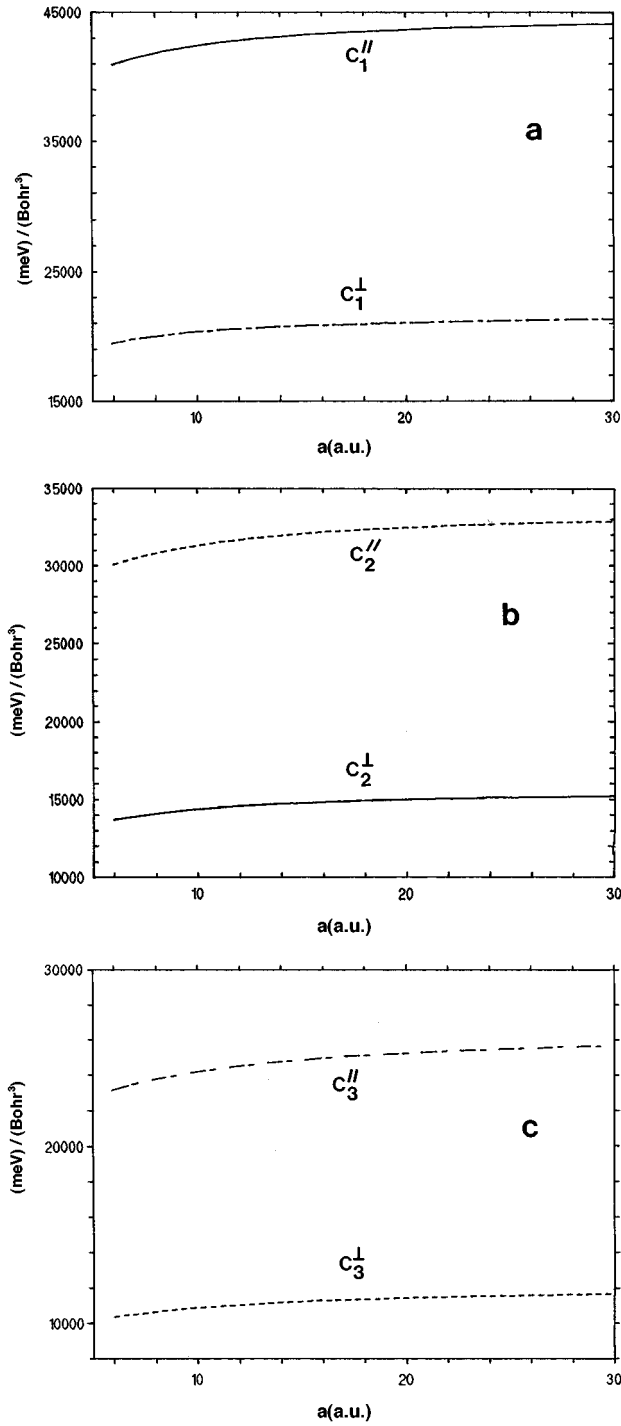|	Al[a]	Cu[a]	Ag[a]
ω_p (a.u.)	0.562	0.735	0.845
δ (a.u.)	0.697	0.911	1.031

[a]Reference 28.

FIG. 2. Dispersion coefficients $C_n^{\parallel/\perp}$ as functions of the radius a of the cavity. The calculation is made for the system HF/Al. (a) $n=1$. (b) $n=2$. (c) $n=3$.

Al, and Cu to be 0.126, 0.105, and 0.120 a.u., respectively and, for the systems HCl/Ag, Al, and Cu, 0.208, 0.166, and 0.193 a.u., respectively. It may be also observed that the deviation from a simple d^{-3} dependence becomes very important when d is comparable to radius of the sphere.

V. CONCLUSION

A general method to calculate long-range van der Waals energies for a diatomic molecule inside a hollow cavity in a
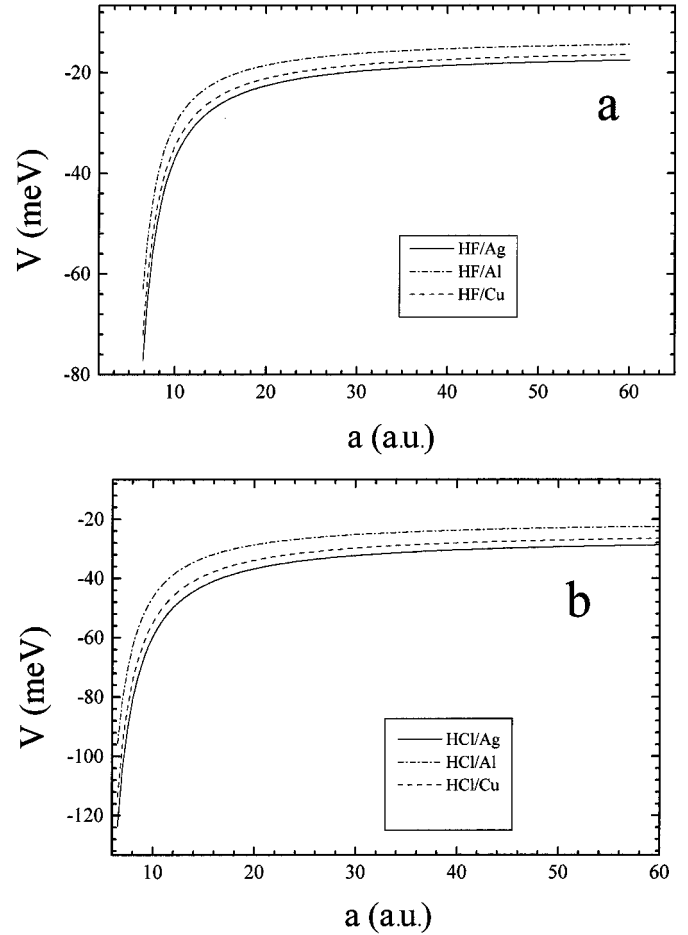
FIG. 3. van der Waals energy as a function of the radius a, for $d=6$ a.u. and $\theta=\pi/2$. (a) HF/Ag (full line), Al (dotted line), and Cu (dashed line). (b) HCl/Ag (full line), Al (dotted line), and Cu (dashed line).

metal has been presented. The spatial dispersive effect has been introduced by means of the hydrodynamical model for the metal electrons, and treated within a nonlocal approximation. Evidence of the influence of the surface curvature and of the molecular anisotropy has been shown. The present method can be extended to the case of low-symmetry polyatomic molecules physisorbed on substrates of various geometries, by introducing higher-order multipolar effects.

APPENDIX: SUSCEPTIBILITY TENSOR $^{(1)}S^{(1)}(\mathbf{r},\mathbf{r}_1,\omega)$

The susceptibility tensor $^{(1)}S^{(1)}(\mathbf{r},\mathbf{r}_1,\omega)$ of the dipolar field can be derived from the linear response of a small spherical cavity to a fluctuating dipole $\boldsymbol{\mu}(\omega)$,

$$\mathbf{E}(\underline{r},\omega) = {}^1S^1(\mathbf{r},\mathbf{r}_1,\omega)\boldsymbol{\mu}(\omega), \qquad (A1)$$

where $\mathbf{E}(\mathbf{r},\omega)$ is the response field of the cavity.

Using the boundary conditions at the surface and the spherical tensor formalism, one obtains the susceptibility tensor in the form

$$^1\mathbf{S}^1(\mathbf{r},\mathbf{r}_1,\omega)=\mathbf{M}(\theta,\varphi)\sum_{n,m}[\Delta_n(a,\omega)r^{n+1}]/a^{2n+1}\mathbf{O}^{(1)}Y_n^m(\theta,\varphi)\mathbf{T}_{n,m}^d(\mathbf{r}_1),\tag{A2}$$

where $Y_n^m(\theta,\varphi)$ is a spherical harmonic, and $\mathbf{M}(\theta,\varphi)$ is the matrix of the transformation of spherical coordinates into Cartesian coordinates:

$$\mathbf{M}(\theta,\varphi)=\begin{pmatrix}\sin\theta\cos\varphi & \cos\theta\cos\varphi & -\sin\varphi\\ \sin\theta\sin\varphi & \cos\theta\sin\varphi & \cos\varphi\\ \cos\theta & \sin\varphi & 0\end{pmatrix}.\tag{A3}$$

The tensors $\mathbf{O}^{(1)}$ and $\mathbf{T}_{nm}^d(r_1)$ in Eq. (A2) are given by

$$\mathbf{O}^{(1)}=\left(n+1,\frac{\partial}{\partial\theta},-\frac{im}{\sin\theta}\right),\tag{A4}$$

$$(\mathbf{T}_{n,m}^d)_x=\frac{\beta_n}{2^{1/2}}\{C(1,n,n+1,1,1-m)Y_n^{m-1}(\theta_1,\varphi_1)$$
$$-C(1,n,n+1,-1,-1-m)Y_n^{m+1}(\theta_1,\varphi_1)\},$$

$$(\mathbf{T}_{n,m}^d)_y=\frac{i\beta_n}{2^{1/2}}\{C(1,n,n+1,1,1-m)Y_n^{m-1}(\theta_1,\varphi_1)$$
$$+C(1,n,n+1,-1,-1-m)Y_n^{m+1}(\theta_1,\varphi_1)\},\tag{A5}$$

$$(\mathbf{T}_{n,m}^d)_z=\beta_n\{C(1,n,n+1,0,-m)Y_n^m(\theta_1,\varphi_1)\},$$

where

$$\beta_n=4\pi\left(\frac{n+1}{2n+3}\right)^{1/2}r_1^{-(n+2)}.\tag{A6}$$

Symbols C are Clebsh-Gordan coefficients.

The reflection factors $\Delta_n(a,\omega)$, which contain the dynamical properties of the metallic cavity are given by
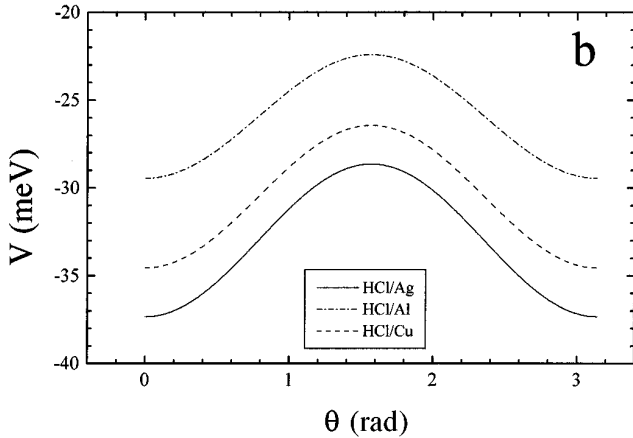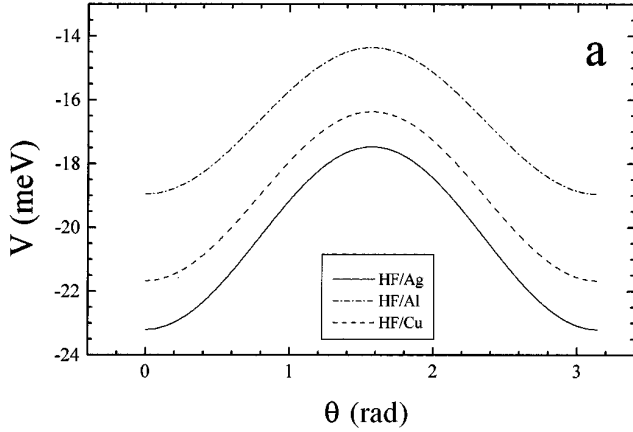

FIG. 4. van der Waals energy as a function of the polar angle Θ, for $d=6$ a.u. and $a=60$ a.u. (a) HF/Ag (full line), Al (dotted line), and Cu (dashed line). (b) HCl/Ag (full line), Al (dotted line), and Cu (dashed line).
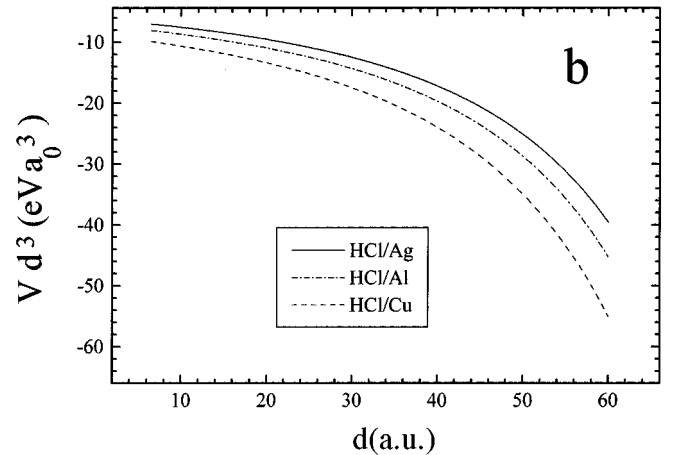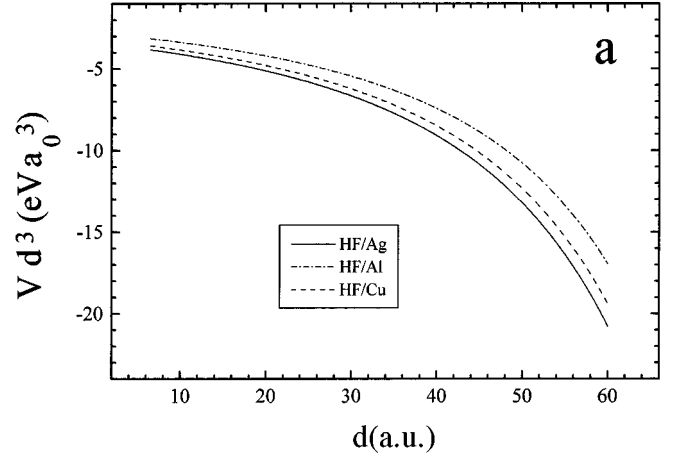
FIG. 5. Product of the van der Waals energy by d^3, as a function of the distance of approach $d=a-R$, for $\theta=\pi/2$ and $a=60$ a.u. (a) HF/Ag (full line), Al (dotted line), and Cu (dashed line). (b) HCl/Ag (full line), Al (dotted line), and Cu (dashed line).

$$\Delta_n(a,\omega) = \frac{na\sum_{k,k'} B_{k,n}B_{k',n}J_n(ka)J_n(k'a)E_n^{-1}(k,k',\omega) - 1}{(n+1)a\sum_{k,k'} B_{k,n}B_{k',n}J_n(ka)J_n(k'a)E_n^{-1}(k,k',\omega) + 1}, \tag{A7}$$

where

$$B_{k,n} = \sqrt{2}\{[j_n(ka) - j_{n-1}(ka)j_{n+1}(ka)]a^3\}^{-1/2}. \tag{A8}$$

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