Van der Waals induced polarization of molecules adsorbed on small metallic spheres : anisotropy and nonlocality effects

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The calculation of Van der Waals induced polarization of molecules interacting with small metallic spheres is based on the spherical-tensor theory by using the response field susceptibility of the sphere. The first Euler angle appearing in the expression giving this polarization exhibits the anisotropy of the molecule. In order to illustrate the non locality and anisotropy effects as well as the importance of the metallic sphere curvature on the induced polarization magnitudes, we present numerical results for typical systems (HF, HCl) on (Ag, Al and Cu).

I. INTRODUCTION

The dispersion interaction (dispersion energy, induced polarization by dispersive effect…) between gases and solid surfaces has been subjected to many theoretical investigations [1-9], allowing the interpretation of various experiments, such as the measurement of heats of desorption, work-function changes and alteration of spectroscopic properties. Indeed, the dispersion interaction is known to be due to the presence of fluctuating multipolar moments in the physisorbed system (atoms, molecules…) and to fluctuating charge density in the substrate. In the case of metallic surfaces, several approaches [3,10] based on the theory developed by Zaremba and al, or on the theory of Lifshitz, have been proposed in the literature, either using a local description of the metal or by introducing the spacial dispersion effect in the electric response of the substrate.

The most often, these approaches are devoted to adatoms. In this paper, we present the induced polarization in molecules exhibiting an experimental interest when they are adsorbed on noble metals. The estimation of this polarization requires the knowledge of the dynamic hyperpolarizabilities of admolecules and the dynamic response functions of the substrate (in general, the dielectric function). However, the 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 for example atoms or molecules at the tip of a near-field microscope, spectroscopic properties are dramatically changed.

The paper is organized as follows. In sec.II, we present a formulation of the dipole moment induced by physisorption in a diatomic molecule adsorbed on a small metallic sphere. We assume the sphere to be so small that retardation effects can be neglected. The theoretical approach is based on a formalism which uses *generalized susceptibilities, or electric-field propagators* ${}^{l_1}\mathbf{S}^{l_2}(\mathbf{r},\mathbf{r}',\omega)$, connecting two points $\mathbf{r}$, $\mathbf{r}'$ outside the sphere. The adsorption of an atom on the sphere can be processed as particular case of the adsorption of the diatomic molecule and will be thus subjected to sec.III. We conclude in sec.IV by studying numerically variations of the first contribution to dipole moment as functions of the orientation of the molecule, the molecular-sphere distance of approach and the radius of the sphere for molecules HF and HCl adsorbed on metals (Ag, Al and Cu). The metal response is assumed to be non local and the infinite barrier model is used for the free electrons. Moreover, to describe the dynamical properties of admolecules ; we use a Drude oscillator model.

Short title: Molecule at the vicinity of a metallic sphere

II. DIPOLE MOMENT INDUCED BY PHYSISORPTION IN A DIATOMIC MOLECULE PLACED AT THE VICINITY OF A METALLIC SPHERE

The dipole moment, $\boldsymbol{\mu}(\mathbf{R})$, induced by physisorption in a molecule, which the center of mass G is referred to the center O of a sphere by the point $\mathbf{R}$ (see Fig.1), can be written :

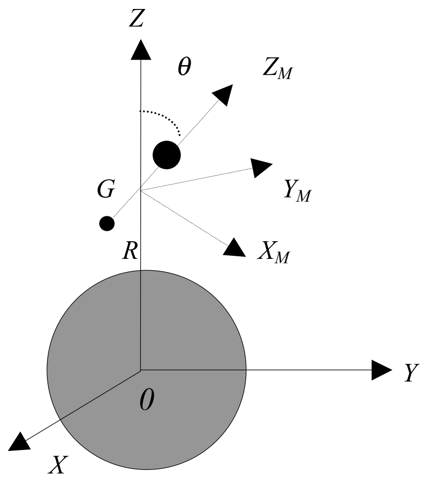


FIG. 1 : Interaction between a molecule and a metallic sphere of radius *a*, centered at point *O*. (O,X,Y,Z) : absolute frame ; (G,X_M,Y_M,Z_M) : molecular frame.

$$\mu(\mathbf{R}) = \frac{\hbar}{2\pi}\sum_{l_1,l_2}\frac{1}{(2l_1-1)!!}\int_0^{+\infty} {}^1\chi_s^{l_1+l_2}(i\xi,-i\xi)\,[l_1+l_2]\,{}^{l_1}\mathbf{S}^{l_2}(\mathbf{R},\mathbf{R},i\xi)\,d\xi \tag{1}$$

${}^1\chi_s^{l_1+l_2}(i\xi,-i\xi)$ is the molecular hyperpolarizability tensor with respect to the absolute frame *(O, X, Y, Z)* tied to the sphere and ${}^{l_1}\mathbf{S}^{l_2}(\mathbf{R},\mathbf{R},i\xi)$ is the electric-field propagator at the vicinity of the surface of the sphere. This latter quantity, also called ″electric-field susceptibility″, takes into account only the properties of the isolated surface. The symbol $[l_1 + l_2]$ means a contracted tensor product of order $l_1 + l_2$ and $i\xi$ is an imaginary frequency.

A. MULTIPOLAR PROPAGATORS

The multipolar propagators ${}^{l_1}\mathbf{S}^{l_2}(\mathbf{r},\mathbf{r}',\omega)$, connecting two points $\mathbf{r}$, $\mathbf{r}'$ outside the sphere, have been defined as a tensor establishing the relationship between the gradients of the response field $\mathbf{E}^{(l_1)}(\mathbf{r},\omega)$ and the multipolar moments $\mathbf{m}^{(l_2)}(\omega)$. In the framework of the theory of the linear electric response of the surface to fluctuating external sources, this definition can be expressed under the following form [11]:

$$\mathbf{E}^{(l_1)}(\mathbf{r},\omega) = {}^{l_1}\mathbf{S}^{l_2}(\mathbf{r},\mathbf{r}',\omega)[l_2]\mathbf{m}^{(l_2)}(\omega) \tag{2}$$

After a development of the response field, $\mathbf{E}(\mathbf{r},\omega)$, on the basis of the spherical harmonics $Y_n^m(\Omega)$, the multipolar propagators ${}^{l_1}\mathbf{S}^{l_2}(\mathbf{r},\mathbf{r}',\omega)$, at the vicinity of a metallic sphere of radius *a,* can be expressed in the Cartesian basis by [12, 13]:

$${}^{l_1}\mathbf{S}^{l_2}(\mathbf{r},\mathbf{r}'_{l_2},\omega) = -\sum_{n,m} a^{2n+1}\Delta_n(a,\omega)\,\tilde{\nabla}_{\mathbf{r}}^{(l_1)}\left\{\frac{Y_n^m(\Omega)}{r^{n+1}}\right\}\mathbf{T}_{n,m}^{(l_2)}(\mathbf{r}'_{l_2}) \tag{3}$$

where $\tilde{\nabla}_{\mathbf{r}}^{(l_1)}$ is the gradient operator of order l_1 in the Cartesian basis, $\mathbf{T}_{n,m}^{(l_2)}(\mathbf{r}'_{l_2})$ is a tensor whose analytical expressions are given in the Appendix and $\Delta_n(a,\omega)$ is the reflection factor containing dynamical properties of the metallic sphere,

$$\Delta_n(a,\omega) = \frac{\frac{n}{a}F_n(a,\omega) - 1}{\frac{n+1}{a}F_n(a,\omega) + 1} \tag{4}$$

with :

$$F_n(a,\omega) = a^2\sum_{k,k'} B_{k,n}B_{k',n}j_n(ka)j_n(k'a)E_n^{-1}(k,k',\omega) \tag{5}$$

$E_n(k,k',\omega)$ is the dielectric matrix, $j_n(ka)$ is a regular spherical Bessel function and $B_{k,n}$ is a normalization constant [12],

$$B_{k,n} = \left(\frac{2}{\left(j_n^2(ka) - j_{n-1}(ka)j_{n+1}(ka)\right)a^3}\right)^{1/2} \tag{6}$$

B. DIPOLE MOMENT

From Eq.(1), the Cartesian components of the dipole moment induced in the diatomic molecule can be separated into various contributions,

$$\mu_\alpha(\mathbf{R}) = \mu_\alpha^{(1)}(\mathbf{R}) + \mu_\alpha^{(2)}(\mathbf{R}) + \ldots \tag{7}$$

with

$$\mu_\alpha^{(1)}(\mathbf{R}) = \frac{\hbar}{2\pi}\int_0^{+\infty} d\xi \sum_{\beta,\gamma}\sum_{\alpha',\beta',\gamma'} M_{\alpha\alpha'}M_{\beta\beta'}M_{\gamma\gamma'}\,{}^1\chi_{\alpha'\beta'\gamma'}^{1+1}(i\xi,-i\xi)\,{}^1S_{\beta\gamma}^1(\mathbf{R},\mathbf{R},i\xi) \tag{8}$$

$$\mu_\alpha^{(2)}(\mathbf{R}) = \frac{\hbar}{2\pi}\int_0^{+\infty} d\xi \sum_{\beta,\gamma,\delta}\sum_{\alpha',\beta',\gamma',\delta'} M_{\alpha\alpha'}M_{\beta\beta'}M_{\gamma\gamma'}M_{\delta\delta'}\left\{{}^1\chi_{\alpha'\beta'\gamma'\delta'}^{1+2}(i\xi,-i\xi)\,{}^1S_{\beta\gamma\delta}^2(\mathbf{R},\mathbf{R},i\xi) + \frac{1}{3}\,{}^1\chi_{\alpha'\beta'\gamma'\delta'}^{2+1}(i\xi,-i\xi)\,{}^2S_{\beta\gamma\delta}^1(\mathbf{R},\mathbf{R},i\xi)\right\} \tag{9}$$

where ${}^1\chi_{\alpha'\beta'\gamma'}^{1+1}$ and ${}^1\chi_{\alpha'\beta'\gamma'\delta'}^{1+2}$ (or ${}^1\chi_{\alpha'\beta'\gamma'\delta'}^{2+1}$), respectively, are the components of third and fourth rank hyperpolarizability tensors defined in the molecular frame (G, X_M, Y_M, Z_M). $M_{ii'}$ ($i=\alpha, \beta, \gamma$ and δ) are the elements of the transformation matrix from molecular frame to absolute frame. This matrix is given, in the case of a linear molecule (see Fig.1), by

$$\mathbf{M}(\theta,\varphi)=\begin{pmatrix} \cos\varphi\cos\theta & -\sin\varphi & \cos\varphi\sin\theta \\ \sin\varphi\cos\theta & \cos\varphi & \sin\varphi\sin\theta \\ -\sin\theta & 0 & \cos\theta \end{pmatrix} \quad (10)$$

θ and φ are first Euler angles of the molecular frame.

By applying results obtained from the symmetry of third and fourth rank tensors in $C_{\infty v}$ group ; the nonvanishing components of hyperpolarizabilities, defined in the molecular frame, can be written as [14,15]

$$^{1}\chi^{1+1}_{xxz} = {}^{1}\chi^{1+1}_{yyz} = {}^{1}\chi^{1+1}_{xzx} = {}^{1}\chi^{1+1}_{yzy} = {}^{1}\chi^{1+1}_{zxx} = {}^{1}\chi^{1+1}_{zyy} = {}^{1}\chi^{1+1}_{\perp}$$

$$\begin{aligned}
&^{1}\chi^{1+1}_{zzz} = {}^{1}\chi^{1+1}_{//} \\
&^{1}\chi^{1+2}_{zzzz} = \chi_1 \\
&^{1}\chi^{1+2}_{zzxx} = \chi^{1+2}_{zzyy} = -\chi_1/2 \\
&^{1}\chi^{1+2}_{zxxz} = \chi^{1+2}_{zyyz} = \chi^{1+2}_{zxzx} = \chi^{1+2}_{zyzy} = \chi_2 \\
&^{1}\chi^{1+2}_{xzzx} = \chi^{1+2}_{yzzy} = \chi^{1+2}_{xzxz} = \chi^{1+2}_{yzyz} = \chi_3 \qquad (11) \\
&^{1}\chi^{1+2}_{xxyy} = \chi^{1+2}_{yyxx} = \chi_4 \\
&^{1}\chi^{1+2}_{xyxy} = \chi^{1+2}_{yxyx} = \chi^{1+2}_{xyyx} = \chi^{1+2}_{yxxy} = \chi_5 \\
&^{1}\chi^{1+2}_{xxzz} = \chi^{1+2}_{yyzz} = -2(\chi_4+\chi_5) \\
&^{1}\chi^{1+2}_{xxxx} = \chi^{1+2}_{yyyy} = \chi_4 + 2\chi_5
\end{aligned}$$

Using Eqs.(7) to (11) together with Eqs.(3), (A.1) and (A.2) (see Appendix), the Cartesian components of $\boldsymbol{\mu}(\mathbf{R})$ take, in the case where $\mathbf{R} = (0, 0, R)$ (see Fig.1), the following form :

$$\begin{cases} \mu_x(\mathbf{R}) = \cos\varphi\, \mu_\perp(\mathbf{R}) \\ \mu_y(\mathbf{R}) = \sin\varphi\, \mu_\perp(\mathbf{R}) \\ \mu_z(\mathbf{R}) = \mu_{//}(\mathbf{R}) \end{cases} \qquad (12)$$

where

$$\begin{aligned}
\mu_\perp(\mathbf{R}) = -\frac{\hbar}{4\pi R^3}\sum_n \left(\frac{a}{R}\right)^{2n+1}(n+1)\sin\theta \int_0^{+\infty} d\xi\ \Delta_n(a,i\xi) \\
\Big\{ \big(3(n+2)\sin^2\theta - 4\big)\, {}^{1}\chi^{1+1}_{\perp}(i\xi,-i\xi) + \big((n+2)\cos^2\theta + n\big)\, {}^{1}\chi^{1+1}_{//}(i\xi,-i\xi) \\
-\frac{(n+2)\cos\theta}{R}\Big\{ \chi_1(i\xi,-i\xi)\big((n+3)\cos^2\theta + n - 1\big) - \frac{4}{3}\chi_2(i\xi,-i\xi)\big((n+3)\cos^2\theta - 3(n+1)\big) \\
-\frac{4}{3}\chi_3(i\xi,-i\xi)\big((n+3)\cos^2\theta + n\big) + 2\chi_4(i\xi,-i\xi)\big((n+3)\cos^2\theta - n - 1\big) \\
+\frac{4}{3}\chi_5(i\xi,-i\xi)\big(2(n+3)\cos^2\theta - 4n - 3\big)\Big\}\Big\}
\end{aligned} \qquad (13)$$

.

and

$$\begin{aligned}
\mu_{//}(\mathbf{R}) = -\frac{\hbar}{4\pi R^3}\sum_n \left(\frac{a}{R}\right)^{2n+1}(n+1) \int_0^{+\infty} d\xi\ \Delta_n(a,i\xi) \\
\Big\{ \cos\theta\Big[\big(3(n+2)\sin^2\theta + 2n\big)\, {}^{1}\chi^{1+1}_{\perp}(i\xi,-i\xi) + \big((n+2)\cos^2\theta + n\big)\, {}^{1}\chi^{1+1}_{//}(i\xi,-i\xi)\Big] \\
-\frac{(n+2)}{R}\Big\{ \cos^2\theta\Big[\chi_1(i\xi,-i\xi)\big((n+3)\cos^2\theta + n - 1\big) - \frac{4}{3}\chi_2(i\xi,-i\xi)\big((n+3)\cos^2\theta - 3(n+1)\big)\Big] \\
-\sin^2\theta\Big[-\frac{4}{3}\chi_3(i\xi,-i\xi)\big((n+3)\cos^2\theta + n\big) + 2\chi_4(i\xi,-i\xi)\big((n+3)\cos^2\theta - n - 1\big) \\
+\frac{4}{3}\chi_5(i\xi,-i\xi)\big(2(n+3)\cos^2\theta - 4n - 3\big)\Big]\Big\}\Big\}
\end{aligned} \qquad (14)$$

In this instance, the molecule-sphere interaction presents a cylindrical symmetry since the dipole momental norm is only θ dependent.

III. CONNECTION WITH THE INTERACTION BETWEEN AN ATOM AND A METALLIC SPHERE

If instead of a diatomic molecule one places, at the vicinity of the sphere, an atom at point $\mathbf{R} = (0, 0, R)$; the tensors ${}^{1}\boldsymbol{\chi}^{1+1}$ will vanish identically since the atom has a spherical symmetry. While the tensors ${}^{1}\boldsymbol{\chi}^{1+2}$ and ${}^{1}\boldsymbol{\chi}^{2+1}$ will be independent of Euler angles (θ and φ) and their Cartesian components will have the following structure [16],

$$ {}^{1}\chi^{1+2}_{\alpha\beta\gamma\delta}(\omega_a,\omega_b) = {}^{1}\chi^{1+2}_{zzzz}(\omega_a,\omega_b)\left[\frac{3}{4}\left(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}\right) - \frac{1}{2}\delta_{\alpha\beta}\delta_{\gamma\delta}\right] \tag{15} $$

$$ {}^{1}\chi^{2+1}_{\alpha\beta\gamma\delta}(\omega_a,\omega_b) = {}^{1}\chi^{2+1}_{zzzz}(\omega_a,\omega_b)\left[\frac{3}{4}\left(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\beta}\delta_{\gamma\delta}\right) - \frac{1}{2}\delta_{\alpha\delta}\delta_{\beta\gamma}\right] \tag{16} $$

with

$$ {}^{1}\chi^{1+2}_{zzzz}(\omega_a,\omega_b) = {}^{1}\chi^{2+1}_{zzzz}(\omega_a,\omega_b) \tag{17} $$

Thus, in the case of an atom, the hyperpolarizabilities χ_m ($m = 1, ..., 5$) reduce to a single scalar parameter,

$$ \chi_1(\omega_a,\omega_b) = {}^{1}\chi^{1+2}_{zzzz}(\omega_a,\omega_b) $$

$$ \chi_2(\omega_a,\omega_b) = {}^{1}\chi^{1+2}_{zxxz}(\omega_a,\omega_b) = \frac{3}{4}\,{}^{1}\chi^{1+2}_{zzzz}(\omega_a,\omega_b) $$

$$ \chi_3(\omega_a,\omega_b) = {}^{1}\chi^{1+2}_{xzzx}(\omega_a,\omega_b) = \frac{3}{4}\,{}^{1}\chi^{1+2}_{zzzz}(\omega_a,\omega_b) \tag{18} $$

$$ \chi_4(\omega_a,\omega_b) = {}^{1}\chi^{1+2}_{xxyy}(\omega_a,\omega_b) = -\frac{1}{2}\,{}^{1}\chi^{1+2}_{zzzz}(\omega_a,\omega_b) $$

$$ \chi_5(\omega_a,\omega_b) = {}^{1}\chi^{1+2}_{xyxy}(\omega_a,\omega_b) = \frac{3}{4}\,{}^{1}\chi^{1+2}_{zzzz}(\omega_a,\omega_b) $$

The dipole moment, $\boldsymbol{\mu}(\mathbf{R})$, induced in an atom by the presence of the surface of the sphere is obtained then easily from that induced in a molecule. It suffices for that to put $\theta = \varphi = 0$ and replace the hyperpolarizabilities χ_m ($m = 1, ..., 5$) by the above expressions. In the line of the preceding considerations, the Cartesian components of the dipole moment induced in an atom adsorbed on a spherical metallic surface would be written, from equations (12), (13) and (14), under the following form :

$$ \boldsymbol{\mu}(\mathbf{R}) \equiv \mu_z(\mathbf{R}) = \frac{\hbar}{2\pi R^4}\sum_n (n+1)(n+2)(2n+1)\left(\frac{a}{R}\right)^{2n+1}\int_0^{+\infty} {}^{1}\chi^{1+2}_{zzzz}(i\xi,0)\Delta_n(a,i\xi)d\xi \tag{19} $$

IV. APPLICATIONS

In this section, we will study numerically the norm of the first-order dipole moment, $\mu^{(1)}(\mathbf{R})$, which can be written under the following form :

$$ \mu^{(1)}(\mathbf{R}) = \left[\left(\mu^{(1)}_{\perp}(\mathbf{R})\right)^2 + \left(\mu^{(1)}_{//}(\mathbf{R})\right)^2\right]^{1/2} \tag{20} $$

where

$$ \mu^{(1)}_{\perp}(\mathbf{R}) = \frac{1}{2R^3}\sum_n\left(\frac{a}{R}\right)^{2n+1}\sin\theta\left\{(3(n+1)\sin^2\theta - 4)\,C^{\perp}_n + ((n+2)\cos^2\theta + n)\,C^{//}_n\right\} \tag{21} $$

$$ \mu^{(1)}_{//}(\mathbf{R}) = \frac{1}{2R^3}\sum_n\left(\frac{a}{R}\right)^{2n+1}\cos\theta\left\{(3(n+1)\sin^2\theta + 2n)\,C^{\perp}_n + ((n+2)\cos^2\theta + n)\,C^{//}_n\right\} \tag{22} $$

with

$$C_n^{///\perp} = \frac{(n+1)\hbar}{2\pi}\int_0^{+\infty}\Delta_n(a,i\xi)\ {}^1\chi_{///\perp}^{1+1}(i\xi,-i\xi)\ d\xi \quad (23)$$

where $C_n^{//}$ and $C_n^{\perp}$ are the dispersion coefficients, which include the nonlocal behavior of the metal and the anisotropy of the molecule along and perpendicular to its internuclear axis.

A. MODEL OF THE MOLECULE AND THE METALLIC SPHERE

The parallel and perpendicular hyperpolarizabilities of the molecule ${}^1\chi_{//}^{1+1}$ and ${}^1\chi_{\perp}^{1+1}$ can be evaluated, from the model of tridimensional anisotropic oscillator, by [17]

$$ {}^1\chi_{///\perp}^{1+1}(i\xi,-i\xi) = \frac{{}^1\chi_{///\perp}^{1+1}(0)\omega_{///\perp}^2}{\omega_{///\perp}^2+\xi^2} \quad (24)$$

Numerical values of the static hyperpolarizabilities ${}^1\chi_{//}^{1+1}(0)$ and ${}^1\chi_{\perp}^{1+1}(0)$ and the corresponding frequencies $\omega_{//}$ and $\omega_{\perp}$ are given in Table.I (see refs.[14,17]).

Molecule	$\omega_{//}$	$\omega_{\perp}$	${}^1\chi_{//}^{1+1}(0)$	${}^1\chi_{\perp}^{1+1}(0)$
HF	1.561	0.375	2.193	0.319
HCl	0.737	0.898	12.408	2.015

Table I : Numerical data for the molecule (see text), from Ref.[14,17].

However, to describe dynamical and electrical properties of the metal, we use the hydrodynamical model to express the reflection factor as [18,19,20]:

$$\Delta_n(a,i\xi) = \frac{\left\{\left(\xi^2 + (2n+1)\ \omega_p^2\ I_{n+1/2}(u)K_{n+1/2}(u)\right) \big/ \left(\xi^2 + \omega_p^2\right)\right\} - 1}{\left\{(n+1)\left(\xi^2 + (2n+1)\ \omega_p^2\ I_{n+1/2}(u)K_{n+1/2}(u)\right) \big/ n\left(\xi^2 + \omega_p^2\right)\right\} + 1} \quad (25)$$

with

$$u(a,i\xi) = \frac{a}{\delta}\left(\omega_p^2 + \xi^2\right)^{1/2} \quad (26)$$

$I_{n+1/2}$ and $K_{n+1/2}$ are modified Bessel functions.

This model requires numerical parameter values ω_p and δ (see Table.II).

Metal	ω_p	δ
Al	0.562	0.697
Ag	0.845	1.031
Cu	0.735	0.911

Table II : Numerical data for the metal (see text), from Ref.[10].

ω_p characterizes the free-electron plasma frequency and δ a parameter related to the Fermi velocity v_F ($\delta \approx \sqrt{3/5}\ v_F$). Note that the local limit could be trivially obtained when δ vanishes.

B. RESULTS

The dispersion coefficients $C_n^{//}$ and $C_n^{\perp}$ and the dipole moment $\mu^{(1)}$ are calculated, from Eqs. (20), (21), (22), (23), (24) and (25) together with the numerical data of Tables I and II, for molecules HF and HCl adsorbed on (Al, Ag and Cu) spheres. Some comments about these results, presented in Figs.2 to 5, worthwhile to be made.

(i) Figs.2-a,b show the dependence of dispersion coefficients $C_n^{//}$ and $C_n^{\perp}$ on the radius *a* of the sphere for the molecule HF adsorbed on an Al particle. This behavior is due to the non local response of the metal electrons by opposition to the local response where the coefficients C_n become independent on *a*. These figures show also that the dependence of non local results on *a* becomes more important when *n* increases.

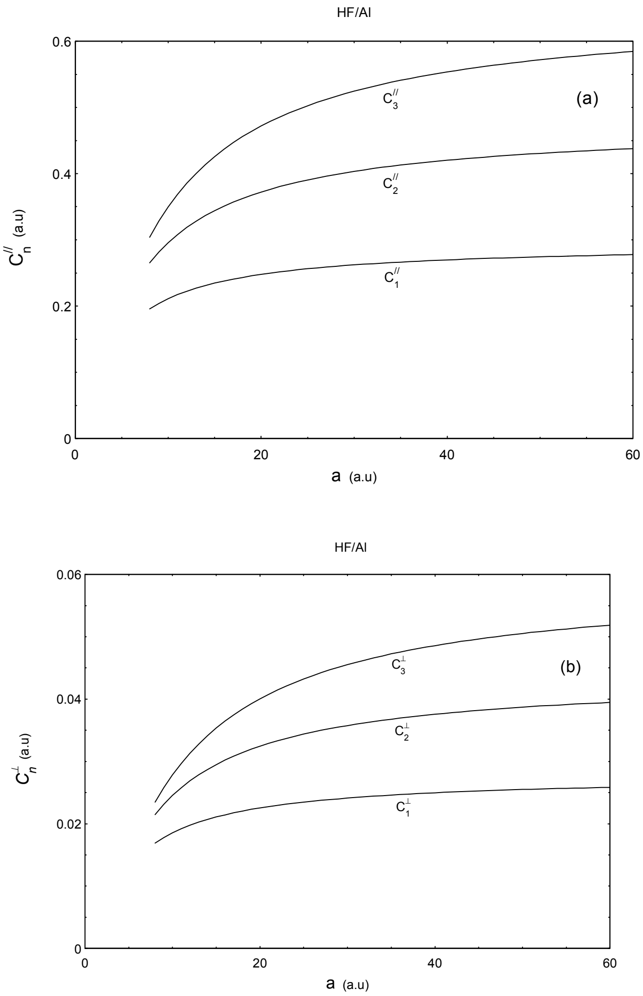


FIG. 2 : Dispersion coefficients $C_n^{//}$ and $C_n^{\perp}$ as functions of radius a in the case of HF molecule adsorbed on Al sphere. **(a)** : $C_n^{//}$; **(b)** : $C_n^{\perp}$

(ii) Fig.3 illustrates the influence of the orientation of the molecule on $\mu^{(1)}$ as well as the difference between local and non local response of the metal electrons. However, a variation of the orientation of the molecule pass $\mu^{(1)}$ from a maximum when the molecule is parallel to the *Z* axis to a minimum when it becomes there perpendicular. On the other hand, the comparison between local and non local response of the metal electrons shows that the spacial dispersion effects decrease the polarization magnitude of the molecule.

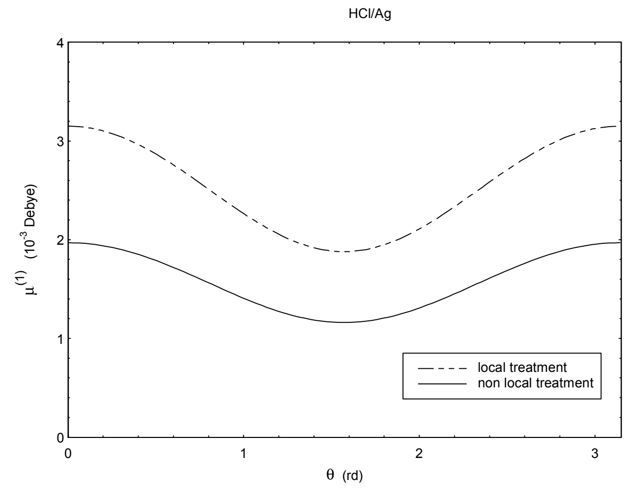


FIG. 3 : Dipole moment $\mu^{(1)}$ as functions of θ in the case of HCl molecule at a distance $d = 6$ a.u from an Ag sphere of radius $a = 40$ a.u .
Full line : non local treatment ; *Broken line* : localtreatment.

(iii) We represent on Fig.4, by a non local calculation, the dipole moment variations as function of the radius *a* for the perpendicular ($\theta = \pi/2$) and parallel ($\theta = 0$) configurations of the molecule HCl adsorbed on a Cu particle. We notice thus, that the gap between these two configurations increases with the radius of the sphere, mainly for small values of *a* ($a \leq 40$ a.u).

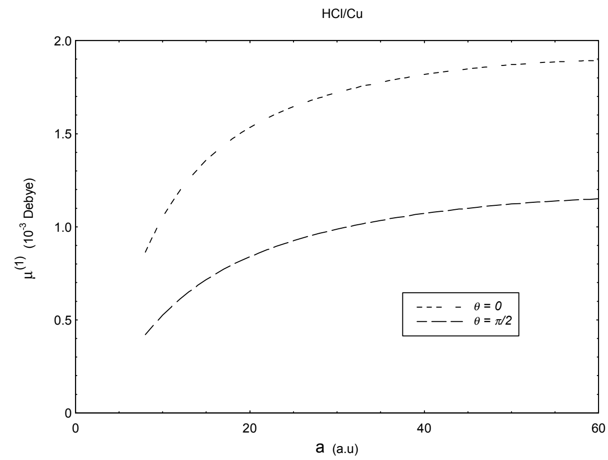
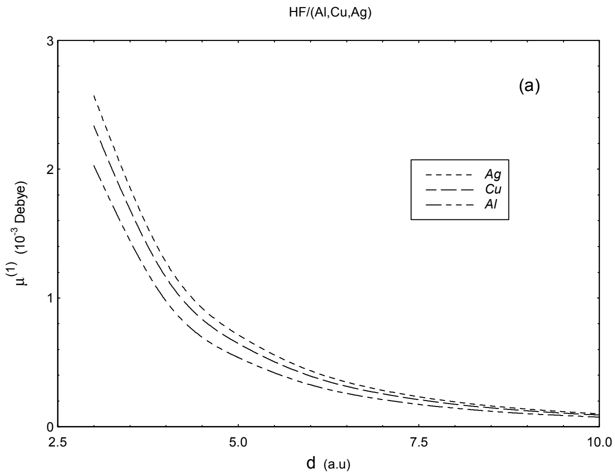


FIG. 4 : Dipole moment $\mu^{(1)}$ calculated by a non local treatment for $\theta = 0$ and $\theta = \pi/2$ at a distance $d = 6$ a.u, as functions of radius a . The molecule is HCl and the metal is Cu.

(iv) The dipole moment variations for the parallel configuration of the molecule, as function of the distance of approach $d = R - a$ (Fig.5-a) and as function of the radius a of the sphere (Fig.5-b) for the molecule HF adsorbed on (Ag, Al and Cu), show that the induced polarization magnitudes are increasing functions of ω_p. On another hand the behaviors of these moments, as functions of a and d, are rather similar for all metals.



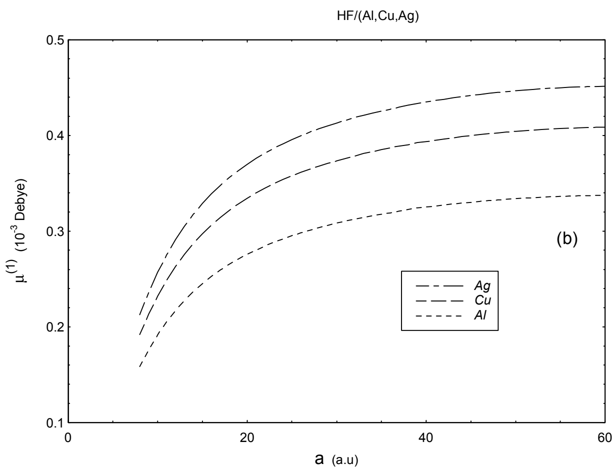


Fig.5 : Dipole moment $\mu^{(1)}$ calculated by a non local treatment for $\theta = 0$ in the case of HF molecule adsorbed on (Al, Cu and Ag) particles.
(a) : as functions of a distance of approach $d = R - a$ for $a = 40$ a.u.
(b) : as functions of radius a at a distance $d = 6$ a.u.

V. CONCLUSION

In this investigation ; we have presented the dipole moment induced by physisorption in diatomic molecules adsorbed on metallic spheres. The elaboration of this contribution to the induced polarization has necessitated the determination of the electric field susceptibility of the sphere, based on the spherical-tensor theory, as well as the determination of third and fourth rank hyperpolarizability tensors of the molecule. The tensors hyperpolarizability have illustrated, by the means of the first Euler angle θ, the influence of the orientation of the molecule on the induced polarization. This investigation has been then, completed by a numerical study of first-order dipole moment as functions of the orientation of the molecule, the radius of the metallic particle curvature and the distance of approach of the two partners for typical systems (HF, HCl) on (Ag, Al and Cu) by taking into account the non local character of the response of the metal electrons.

APPENDIX : The tensors $\mathbf{T}^{(1)}_{nm}(\mathbf{R})$ and $\mathbf{T}^{(2)}_{nm}(\mathbf{R})$

For $\mathbf{R} = (0,\, 0,\, R)$; the tensors $\mathbf{T}^{(1)}_{nm}(\mathbf{R})$ and $\mathbf{T}^{(2)}_{nm}(\mathbf{R})$ would have, in the Cartesian basis, the following expressions :

$$\begin{cases} \left(T^{(1)}_{n,m}(\mathbf{R})\right)_x = \left(\dfrac{n(n+1)}{2n+1}\pi\right)^{1/2} \dfrac{(\delta_{m,-1} - \delta_{m,1})}{R^{n+2}} \\ \left(T^{(1)}_{n,m}(\mathbf{R})\right)_y = i\left(\dfrac{n(n+1)}{2n+1}\pi\right)^{1/2} \dfrac{(\delta_{m,-1} + \delta_{m,1})}{R^{n+2}} \\ \left(T^{(1)}_{n,m}(\mathbf{R})\right)_z = -2(n+1)\left(\dfrac{\pi}{2n+1}\right)^{1/2} \dfrac{\delta_{m,0}}{R^{n+2}} \end{cases} \qquad \text{(A.1)}$$

$$\left(\mathbf{T}^{(2)}_{n,m}(\mathbf{R})\right) = \frac{1}{R^{n+3}}\left(\frac{n(n+1)(n+2)}{2n+1}\pi\right)^{1/2}$$

$$\begin{pmatrix} \frac{(n-1)^{1/2}}{6}\left(\delta_{m,2}+\delta_{m,-2}\right) & -i\frac{(n-1)^{1/2}}{6}\left(\delta_{m,2}-\delta_{m,-2}\right) & \frac{(n+2)^{1/2}}{3}\left(\delta_{m,1}-\delta_{m,-1}\right) \\ -i\frac{(n-1)^{1/2}}{6}\left(\delta_{m,2}-\delta_{m,-2}\right) & -\frac{(n-1)^{1/2}}{6}\left(\delta_{m,2}+\delta_{m,-2}\right) & -i\frac{(n+2)^{1/2}}{3}\left(\delta_{m,1}+\delta_{m,-1}\right) \\ \frac{(n+2)^{1/2}}{3}\left(\delta_{m,1}-\delta_{m,-1}\right) & -i\frac{(n+2)^{1/2}}{3}\left(\delta_{m,1}+\delta_{m,-1}\right) & \left(\frac{(n+1)(n+2)}{n}\right)^{1/2}\delta_{m,0} \end{pmatrix} \quad \text{(A.2)}$$

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