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Excitation transfer in the vicinity of a dielectric surface

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Abstract

Using the quantum electrodynamics method, we present the resonance excitation transfer matrix element in the vicinity of a dielectric surface. Depending on the geometry and orientations of two dipoles, our results show that the excitation transfer can be suppressed or enhanced by the presence of the dielectric surface in comparison to that of the free space. Both near-zone and wave-zone limits are discussed.

Resonance excitation transfer between two molecules, one in the excited state and the other in the ground state, is proportional to the square of the resonance excitation transfer matrix element [1–8],

$$M=\bar{\boldsymbol{\mu}}_A\cdot\tilde{V}^0(k,r)\cdot\bar{\boldsymbol{\mu}}_B, \qquad (1)$$

where $\bar{\boldsymbol{\mu}}_m$ is the electric transition dipole matrix element of mth molecule and $\tilde{V}^0(k,r)$ is the retarded interaction potential tensor depending on the intermolecular distance, r,

$$\tilde{V}^0(k,r)=\frac{\tilde{1}-3\hat{\boldsymbol{r}}\hat{\boldsymbol{r}}}{r^3}[\cos(kr)+kr\sin(kr)]-\frac{\tilde{1}-\hat{\boldsymbol{r}}\hat{\boldsymbol{r}}}{r^3}k^2r^2\cos(kr). \qquad (2)$$

$\hat{\boldsymbol{r}}$ is the unit vector of $\boldsymbol{r}$ that is the vector displacement of the molecule B from molecule A. Here $k=\omega/c$ and ω is the transition frequency. In the near-zone limit where the intermolecular distance is smaller than the wavelength of the transition frequency, $kr\ll 1$, the interaction potential tensor is simply equal to the usual electrostatic dipole–dipole interaction tensor

$$\tilde{V}^0(k,r)=(\tilde{1}-3\hat{\boldsymbol{r}}\hat{\boldsymbol{r}})/r^3 \quad \text{for } kr\ll 1. \qquad (3)$$

On the other hand in the wave-zone limit, $kr\gg 1$, the potential reduces to

$$\tilde{V}^0(k,r)=-(\tilde{1}-\hat{\boldsymbol{r}}\hat{\boldsymbol{r}})k^2\cos(kr)/r \quad \text{for } kr\gg 1. \qquad (4)$$

In this case the potential tensor differs from the near-zone limit by both the modulation factor $\cos(kr)$ and $1/r$ instead of $1/r^3$. In this limit, the resonance transfer is describable as photon emission from the excited molecule followed by photon absorption by the ground state molecule.

In this Letter we consider the same resonance excitation transfer process when it occurs in the vicinity of a dielectric surface. We find that the total interaction potential tensor $\tilde{V}$ is given by a sum of the free space

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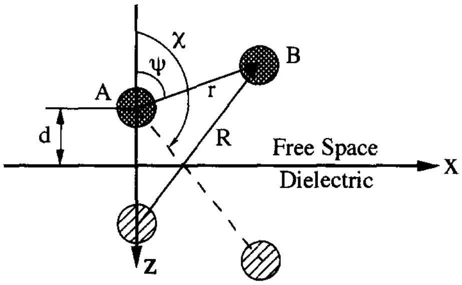

Fig. 1. Geometry of the two molecules (upper two circles) in the vicinity of a dielectric surface. Lower two shaded circles represent the images. The coordinate system is chosen to make the two molecules lie within the x, z-plane.

contribution ($\tilde{V}^0$) and the boundary-dependent contribution denoted by $\tilde{V}'$. The latter is strongly dependent on the distances of the molecules from the surface as well as the angles describing the geometry of the two molecules against the interface (see Fig. 1). The interaction potential tensor can be most easily obtained by considering the dielectric surface as a macroscopic continuum described by the frequency-dependent dielectric permittivity, $\epsilon(\omega)$, and expressing the interaction potential tensor in terms of the mode functions of the quantized electric field.

We now use the conventional second-order perturbation theory with respect to the multipolar form of the interaction Hamiltonian, $H_I = -\hat{\mu}_A\hat{D}(\boldsymbol{R}_A) - \hat{\mu}_B\hat{D}(\boldsymbol{R}_B)$ where $\hat{\mu}_m$ is the electric dipole operator of the mth molecule. The electric displacement field operator, in the quantized form, is given by, in the upper-half free space

$$\hat{D}(\boldsymbol{r}) = \mathrm{i}\sum_{\boldsymbol{k}\lambda}\left(\frac{2\pi\hbar\omega_k}{V}\right)^{1/2}\left\{\left[f^{\mathrm{I}}_{\boldsymbol{k}\lambda}(\boldsymbol{r})\hat{a}^{\mathrm{I}}_{\boldsymbol{k}\lambda} + f^{\mathrm{II}}_{\boldsymbol{k}\lambda}(\boldsymbol{r})\hat{a}^{\mathrm{II}}_{\boldsymbol{k}\lambda}\right] - \left[f^{\mathrm{I}^*}_{\boldsymbol{k}\lambda}(\boldsymbol{r})\hat{a}^{\mathrm{I}^+}_{\boldsymbol{k}\lambda} + f^{\mathrm{II}^*}_{\boldsymbol{k}\lambda}(\boldsymbol{r})\hat{a}^{\mathrm{II}^+}_{\boldsymbol{k}\lambda}\right]\right\}, \tag{5}$$

where $\hat{a}^{\mathrm{I}^+}_{\boldsymbol{k}\lambda}$ and $\hat{a}^{\mathrm{I}}_{\boldsymbol{k}\lambda}$ are creation and annihilation operators for triplet modes incident from the free space toward the interface (type I), whereas $\hat{a}^{\mathrm{II}^+}_{\boldsymbol{k}\lambda}$ and $\hat{a}^{\mathrm{II}}_{\boldsymbol{k}\lambda}$ are those for triplet modes incident from the dielectric (type II). $f^{\mathrm{I}}_{\boldsymbol{k}\lambda}(\boldsymbol{r})$ and $f^{\mathrm{II}}_{\boldsymbol{k}\lambda}(\boldsymbol{r})$ are mode functions associated with the type I and II modes, respectively. The forms of these modes were first presented by Carniglia and Mandel [9] and recently used by Khosravi and Loudon [10] to evaluate the spontaneous emission rate of an excited atom in the vicinity of a dielectric surface. V is the quantization volume.

To second-order with respect to H_I the excitation transfer matrix element is written as [8]

$$M = \sum_{I}\frac{\langle \mathrm{f}|H_I|I\rangle\langle I|H_I|\mathrm{i}\rangle}{E_I - E_i}, \tag{6}$$

where the initial and final states are product states given by $|\mathrm{i}\rangle = |\mathrm{A}^*, \mathrm{B}; \{0\}\rangle$ and $|\mathrm{f}\rangle = |\mathrm{A}, \mathrm{B}^*; \{0\}\rangle$, respectively. A* and B* denote the excited states of molecules A and B, respectively. {0} denotes the vacuum state of the field. For the initial and final states given above, there are two possible intermediate states, $|\mathrm{A}^*, \mathrm{B}^*; 1_k\rangle$ and $|\mathrm{A}, \mathrm{B}; 1_k\rangle$. The former intermediate state involves two excited states of both A and B molecules and one excitation of the kth electric field. The second one involves two ground states of A and B molecules and one excitation of the kth field. Although we considered vacuum states for the both initial and final field states, we found that the excitation transfer matrix element defined in Eq. (6) does not depend on the initial photon numbers as long as the final *field* state is identical to that of the initial *field* state.

Inserting the electric displacement field operator given in Eq. (5) into (6), we find the excitation transfer matrix element is,

$$M = \overline{\mu}_A \cdot \tilde{V}(k, \boldsymbol{R}_A, \boldsymbol{R}_B) \cdot \overline{\mu}_B, \tag{7}$$

where the interaction potential tensor is

$$\tilde{V}(k, \boldsymbol{R}_{\mathrm{A}}, \boldsymbol{R}_{\mathrm{B}}) = \frac{1}{2\pi^2}\mathrm{Re}\int_0^{\infty} \mathrm{d}k' \, \frac{k'^4}{k^2 - k'^2}\Bigg(\int \mathrm{d}\Omega \sum_{\lambda} \boldsymbol{f}^{\mathrm{I}}_{k'\lambda}(\boldsymbol{R}_{\mathrm{A}}) \boldsymbol{f}^{\mathrm{I}^*}_{k'\lambda}(\boldsymbol{R}_{\mathrm{B}}) + \int_{\theta' < \theta_{\mathrm{c}}} \mathrm{d}\Omega \, \sum_{\lambda} \boldsymbol{f}^{\mathrm{II}}_{k'\lambda}(\boldsymbol{R}_{\mathrm{A}}) \boldsymbol{f}^{\mathrm{II}^*}_{k'\lambda}(\boldsymbol{R}_{\mathrm{B}}) + \epsilon^{3/2}\int_{\theta' > \theta_{\mathrm{c}}} \mathrm{d}\Omega' \, \sum_{\lambda} \boldsymbol{f}^{\mathrm{II}}_{k\lambda}(\boldsymbol{R}_{\mathrm{A}}) \boldsymbol{f}^{\mathrm{II}^*}_{k\lambda}(\boldsymbol{R}_{\mathrm{B}})\Bigg). \tag{8}$$

Here $\mathrm{d}\Omega = \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi$ and $\mathrm{d}\Omega' = \sin\theta' \, \mathrm{d}\theta' \, \mathrm{d}\phi'$ where (θ, ϕ) and (θ', ϕ') are defined in the free space and the dielectric, respectively. The first integral in (8) represents the contribution from the incident and reflected modes, that belong to type I modes. For this case, one can find four combinations of products of modes, such as incident–incident, incident–reflected, reflected–incident, and reflected–reflected. The second term in Eq. (8) is due to the transmitted modes when the incident angle, θ', in the dielectric is smaller than the critical angle θ_{c}. The last term in Eq. (8) is from the evanescent modes so that the range of the incident angle, θ', should be larger than the critical angle and smaller than $\pi/2$. We find that the last integral can be obtained more conveniently by taking the integral in the dielectric space with a variable θ'. The additional factor $\epsilon^{3/2}$ in the last integral is necessary since k' in the dielectric is related to k in the free space by $k' = \sqrt{\epsilon} \, k$. From Eq. (8) we find six combinations of products of modes overall.

Carrying out the integrations over angles (ϕ and ϕ') and after some laborious algebra we find the interaction potential tensor can be recast in the form

$$\tilde{V}(k, \boldsymbol{R}_{\mathrm{A}}, \boldsymbol{R}_{\mathrm{B}}) = \tilde{V}^{0}(k, r) + \tilde{V}'(k, R), \tag{9}$$

where $\tilde{V}^{0}(k, r)$ is identical to the free space result given in Eq. (2) and the additional surface-dependent term, $\tilde{V}'(k, R)$, is given by

$$\tilde{V}'(k, R) \equiv \frac{2}{\pi}\mathrm{Re}\int_0^{\infty} \mathrm{d}k' \, \frac{k'^4}{k^2 - k'^2}\left[\left(\int_1^0 \mathrm{d}p + \int_0^{\mathrm{i}\sqrt{\epsilon - 1}} \mathrm{d}p\right)\tilde{H}(p, k')\right]. \tag{10}$$

The integrand in Eq. (10), $\tilde{H}(p, k)$, is

$$\tilde{H}(p, k) \equiv \left\{\frac{\epsilon p - s}{\epsilon p + s}\left[\tilde{1}'\left(f(X) + \frac{1}{X}\frac{\mathrm{d}f(X)}{\mathrm{d}X}\right) - \hat{R}\hat{R}'\left(\frac{1}{X}\frac{\mathrm{d}f(X)}{\mathrm{d}X} - \frac{\mathrm{d}^2 f(X)}{\mathrm{d}X^2}\right)\right] - \frac{1}{2}\left(\frac{p - s}{p + s} + \frac{\epsilon p - s}{\epsilon p + s}\right)\tilde{M} \, \mathrm{e}^{-\mathrm{i}Xp\cos\chi}\right\}, \tag{11}$$

where

$$X \equiv kR,$$

$$f(X) \equiv \exp(-\mathrm{i}Xp\cos\chi) J_0\left(X\sqrt{1 - p^2}\sin\chi\right),$$

$$\hat{R}' \equiv \left(\hat{R}_x, \hat{R}_y, -\hat{R}_z\right),$$

$$\tilde{1}' \equiv \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix},$$

$$\tilde{M} \equiv \begin{pmatrix} J_0\left(X\sqrt{1 - p^2}\sin\chi\right) + J_2\left(X\sqrt{1 - p^2}\sin\chi\right) & 0 & 0 \\ 0 & J_0\left(X\sqrt{1 - p^2}\sin\chi\right) - J_2\left(X\sqrt{1 - p^2}\sin\chi\right) & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{12}$$

$J_n(X)$ are Bessel functions. Variables p and s are defined as $p = \cos\theta$ and $s = \sqrt{\epsilon - 1 + p^2}$, respectively. R is the distance between one of the two molecules and the image of the other in the dielectric (see Fig. 1). The angle χ is defined in Fig. 1. The second term in (9) represents the contributions from the reflected as well as evanescent modes. Among the six combinations of products of modes, the incident–incident, reflected–reflected, and transmitted–transmitted combinations are combined to give the first term in Eq. (9) if one notes the energy conservation condition. The remaining three combinations, e.g. incident–reflected, reflected–incident, and evanescent–evanescent pairs, are the ingredients in the second term in Eq. (9). Since the evanescent (total reflected) modes are not propagating modes in the free space, the integration in the last term in (10) should be evaluated over the imaginary p-axis from 0 to $i\sqrt{\epsilon - 1}$ and thus those evanescent mode contributions appear to be exponentially decaying functions. Although we have assumed that $\epsilon(\omega) > 1$ for any arbitrary frequency, it is straightforward to show the same formal expressions can be obained in the region of $\epsilon(\omega) < 1$ [11].

Near-zone limit. In the near-zone limit, $r < R \ll \lambda_0$, where $\lambda_0 = 2\pi c/\omega$, the total interaction potential tensor including surface-dependent term becomes

$$\tilde{V}(k, \boldsymbol{R}_\mathrm{A}, \boldsymbol{R}_\mathrm{B}) = \frac{1}{2r^3}\begin{pmatrix} 3\cos 2\psi - 1 & 0 & 3\sin 2\psi \\ 0 & 2 & 0 \\ 3\sin 2\psi & 0 & -3\cos 2\psi - 1 \end{pmatrix} - \frac{1}{2R^3}\left(\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 1}\right)\begin{pmatrix} 3\cos 2\chi - 1 & 0 & 3\sin 2\chi \\ 0 & 2 & 0 \\ -3\sin 2\chi & 0 & 3\cos 2\chi + 1 \end{pmatrix}, \tag{13}$$

where $R = \sqrt{r^2 + 4d^2 + 4dr\cos\psi}$ and $\chi = \pi - \tan^{-1}[r\sin\psi/(2d + r\cos\psi)]$. The first term in Eq. (13) is again the free space result, where the tensorial part is identical to $\tilde{I} - 3\hat{r}\hat{r}$. The second term represents the surface-dependent contribution depending on the distances between the two molecules and the interface via R and χ. Each tensor component is strongly affected by the surface-dependent contributions. The interaction potential tensor of two permanent dipoles can be obtained by replacing ω with zero, since in this limit the excited state and ground state become identical.

If the two molecules are on the surface of the dielectric and are far apart but closer than λ_0, i.e. still in the near-zone limit, then $r \approx R$ and $\psi = \chi = \pi/2$. Eq. (13) becomes

$$\tilde{V}(k, \boldsymbol{R}_\mathrm{A}, \boldsymbol{R}_\mathrm{B}) = \frac{1}{r^3}\left[\begin{pmatrix} -2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} - \left(\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 1}\right)\begin{pmatrix} -2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\right]. \tag{14}$$

In this geometry, the $[x, x]$- and $[y, y]$-components of the interaction potential tensor decrease because of the existence of the surface, whereas the $[z, z]$-component increases in magnitude. These effects can easily be understood by using image methods. The dipole aligned along the z axis can create an image dipole in the dielectric with the same orientation, and the overall combined magnitude of the two dipoles becomes larger than just one in the free space. On the other hand, the dipole whose direction is parallel to the surface creates an oppositely oriented image dipole, leading to some cancellation in the magnitude of the combined dipole experienced by the second molecule.

Now suppose that one of the two molecules is on top of the other. In this case we have $\psi = 0$ and $\chi = \pi$. The interaction potential tensor is then

$$\tilde{V}(k, \boldsymbol{R}_\mathrm{A}, \boldsymbol{R}_\mathrm{B}) = \frac{1}{r^3}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} - \frac{1}{(r + 2d)^3}\left(\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 1}\right)\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}. \tag{15}$$

The overall enhancement of $[z, z]$-component and cancellations of $[x, x]$- and $[y, y]$-components are again manifested.

Wave-zone limit. We next consider the wave-zone limit, i.e. $\lambda_0 \ll r < R$. In this limit, one can replace the frequency-dependent dielectric permittivity $\epsilon(\omega)$ with static (zero-frequency) dielectric constant, ϵ_0. Even with this approximation it is not possible to integrate over k' and p in Eq. (10). However if we consider a perfect conducting material, that is, we assume the static dielectric permittivity approaches infinity, we find the interaction potential to be

$$\tilde{V}(k, \boldsymbol{R}_{\mathrm{A}}, \boldsymbol{R}_{\mathrm{B}}) = -k^2 \left[\frac{\cos kr}{r} \begin{pmatrix} \cos^2\psi & 0 & \sin 2\psi/2 \\ 0 & 1 & 0 \\ \sin 2\psi/2 & 0 & \sin^2\psi \end{pmatrix} - \frac{\cos kR}{R} \begin{pmatrix} \cos^2\chi & 0 & \sin 2\chi/2 \\ 0 & 1 & 0 \\ -\sin 2\chi/2 & 0 & -\sin^2\chi \end{pmatrix} \right]. \tag{16}$$

Similar enhancement and cancellation effects can be seen in Eq. (16) also in the wave-zone limit. For example, consider the case when two molecules are on the surface. Then $\tilde{V}(k, \boldsymbol{R}_{\mathrm{A}}, \boldsymbol{R}_{\mathrm{B}})$ reduces to

$$\tilde{V}(k, \boldsymbol{R}_{\mathrm{A}}, \boldsymbol{R}_{\mathrm{B}}) = -\frac{k^2 \cos kr}{r} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 2 \end{pmatrix}. \tag{17}$$

In this case, there is total cancellation of the $[x, x]$- and $[y, y]$-components and the $[z, z]$-component is enhanced 100% by the presence of the metal surface.

In summary, we have calculated the resonance excitation transfer matrix element by using second-order perturbation theory in the context of the multipolar Hamiltonian. In two limiting cases, near-zone and wave-zone limits, we obtained analytic expressions for the interaction potential tensors which show strong geometry-dependent aspects of the excitation transfer matrix element. In both cases, we found that the $[z, z]$-component of the interaction potential tensor increases by the presence of the dielectric surface, whereas the other two components, $[x, x]$- and $[y, y]$-components, are suppressed by the surface-dependent contribution. Experimental measurements (such as fluorescence depolarization measurement) on these predictions will be very useful in clarifying the role of the dielectric surface in the energy transfer between adsorbed molecules on any surfaces, e.g., metal, membrane, two immiscible liquids, etc. We finally note that the competing process of excitation transfer from an excited molecule to the dielectric medium has been extensively studied by classical methods [12]. Also a similar but more general problem, dipole–dipole interactions near interfaces, was considered by Urbakh and Klafter recently [13], where the two dipoles are embedded in a liquid characterized by a nonlocal dielectric function. We find that a limiting case of our result, Eq. (14), shows a close agreement with their results in the limiting case when the liquid is replaced with vacuum.

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