Spectroscopic probe of the van der Waals interaction between polar molecules and a curved surface

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We study the shift of rotational levels of a diatomic polar molecule due to its van der Waals interaction with a gently curved dielectric surface at temperature T, and submicron separations. The molecule is assumed to be in its electronic and vibrational ground state, and the rotational degrees are described by a rigid rotor model. We show that under these conditions retardation effects and surface dispersion can be neglected. The level shifts are found to be independent of T, and given by the quantum state averaged classical electrostatic interaction of the dipole with its image on the surface. We use a derivative expansion for the static Green's function to express the shifts in terms of surface curvature. We argue that the curvature induced line splitting is experimentally observable, and not obscured by natural linewidths and thermal broadening.

I. INTRODUCTION

The van der Waals (vdW) interaction of neutral particles like atoms and molecules with macroscopic surfaces underlies many surface induced processes in physics, chemistry, and biology [1]. Also appearing in the guises of London and Casimir-Polder forces [2,3] these interactions originate from quantum dipole fluctuations of the particle that induce correlated fluctuations on the surface. While generally attractive, resonant coupling to surface excitations can lead to repulsive forces [4]. These fluctuation induced forces have typically been measured for macroscopic bodies, while the vdW interaction of a free atom or molecule is less studied.

Vacuum fluctuations of the electromagnetic field not only give rise to Casimir forces between bodies, but also have observable effects on *isolated* particles; notably they modify energy levels of an atom, an effect known as the Lamb shift. When a quantum particle is brought near a surface, the vdW interaction perturbs its energy levels. It has been shown that surface curvature leads to small corrections to the interaction of the particle with the surface [5,6]. Hence, one can expect also small corrections to the level shifts due to curvature. Here we shall demonstrate and explicitly quantify these shifts for the rotational levels of polar molecules.

For a flat metallic surface, the attractive vdW interaction potential was measured with high precision for a sodium atom in 1992 by looking at the shifts of spectral lines using laser spectroscopy in the micrometer distance range [7]. More recently, for a sapphire surface supporting polariton excitations, a repulsive vdW potential acting on excited cesium atoms was observed in the 100-nm distance range, by using selective reflection spectroscopy that allows for the observation of short-lived states [4]. Thermal fluctuations within a hot surface can excite surface-polariton modes which can cause a strong temperature dependence of the vdW interaction. Indeed, an up to 50% increase was measured spectroscopically for a cesium atom at short distances of 100 nm away from a sapphire surface in the 500–1000-K temperature range [8].

Unlike atoms, polar molecules have rotational and vibrational states that can be excited by radiation, or via the interaction with fluctuations in macroscopic bodies. The corresponding transition energies are often small compared to thermal energies. The resulting rotational and vibrational heating of cold diatomic molecules placed near a hot surface can impose severe lifetime limits to the trapping of these particles which is relevant to the development of "molecular chips" using structured surfaces [9]. These and other specially designed nano- or microstructured surfaces provide another tool to control vdW interactions. Hence, it is important to understand the influence of nontrivial surface geometries on the internal dynamics of polar molecules which is governed by their spectral transitions. Recently, the nonequilibrium vdW force on a polar molecule near a metallic surface was computed and shown to saturate for high temperatures, making it distinct from the interaction for atoms [10].

The paper is organized as follows: In the next section we review the general theory for the finite temperature Casimir-Polder interaction between a quantum particle in an excited state and a dielectric surface. In Sec. III we compute shifts of the rotational levels of a diatomic molecule in terms of the static Green's function, and summarize characteristic parameters for experimentally relevant molecules and surface materials. A derivative expansion for the Green's function of curved surfaces is presented in Sec. IV, and this result is then used in Sec. V to estimate the curvature corrections to the energy levels of a simple rigid rotor model for a diatomic polar molecule. Finally, in the last section the magnitude and curvature dependence of the transition lines
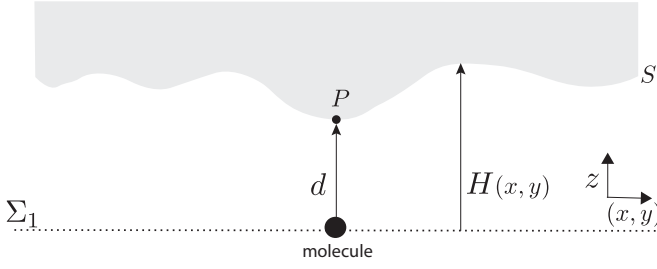
FIG. 1. Parametrization of the profile of a gently curved dielectric surface near an atom or molecule.

of the modified rotational spectrum is estimated, and their experimental observability is discussed.

II. CASIMIR-POLDER INTERACTION: GENERAL FORMULAS

We consider a quantum particle in a nondegenerate state $|a\rangle$, placed at a point $\mathbf{r}$ having (minimum) distance d from a dielectric surface S at temperature T (see Fig. 1). We assume the separation d to be much larger than the particle's size, such that the particle can be modeled as a dipole. The material constituting the surface is assumed to be homogeneous and isotropic, described by (complex) dynamic permittivity $\epsilon(\omega)$. The Casimir-Polder (CP) interaction of the particle with the surface engenders a shift ΔF_a in the free energy of state $|a\rangle$. As shown in Refs. [11,12], ΔF_a can be conveniently expressed as a sum of two terms,

$$\Delta F_a = \Delta F_a^{\mathrm{nr}} + \Delta F_a^{\mathrm{r}}. \tag{1}$$

The first term, ΔF_a^{nr}, is a nonresonant contribution having a form similar to the familiar expression of the CP energy shift for a particle *in equilibrium* with a surface at temperature T [13]:

$$\Delta F_a^{\mathrm{nr}} = -k_B T \sum_{n=0}^{\infty}{}' \alpha_{ij}^{(a)}(i\,\xi_n)\, G_{ij}^{(S)}(\mathbf{r},\mathbf{r};i\,\xi_n), \tag{2}$$

while the second term represents a *resonant out-of-equilibrium* contribution:

$$\Delta F_a^{\mathrm{r}} = \sum_{b\neq a} n(\omega_{ab},T)\mu_i^{ab}\,\mu_j^{ba}\mathrm{Re}\big[G_{ij}^{(S)}(\mathbf{r},\mathbf{r};|\omega_{ba}|)\big]. \tag{3}$$

In these equations $\omega_{ab} = (E_b - E_a)/\hbar$ are the particle's transition frequencies, $\xi_n = 2\pi n k_B T/\hbar$ are the (imaginary) Matsubara frequencies, $\mu_i^{ba} = \langle b|\hat{\mu}_i|a\rangle$ are the matrix elements of the Cartesian components (labeled by the latin index i) of the dipole moment operator $\hat{\mu}$, $n(\omega,T) = [\exp(\hbar\omega/k_B T) - 1]^{-1}$ is the Bose-Einstein distribution function, the prime symbol in the sum over n in Eq. (2) indicates that the $n = 0$ term is taken with weight 1/2, and $\alpha_{ij}^{(a)}(i\,\xi)$ is the polarizability (relative to the state $|a\rangle$) of the particle:

$$\alpha_{ij}^{(a)}(i\,\xi_n) = \frac{2}{\hbar}\sum_{b\neq a}\mu_i^{ab}\,\mu_j^{ba}\frac{\omega_{ab}}{\xi_n^2 + \omega_{ab}^2}. \tag{4}$$

Finally, $G_{ij}^{(S)}(\mathbf{r},\mathbf{r}',\omega)$ denotes the (Fourier transform of the) surface contribution to the electromagnetic Green's function, which is constructed as follows. Recall that the Green's

function $G_{ij}(\mathbf{r},\mathbf{r}',\omega)$ provides the electric field $\mathbf{E}(\mathbf{r})$ at point $\mathbf{r}$ sourced by an oscillating dipole $\mathbf{p}(\omega) = \mathbf{p}_0 e^{-i\omega t}$ placed at the point $\mathbf{r}'$, as

$$E_i(\mathbf{r}) = G_{ij}(\mathbf{r},\mathbf{r}',\omega)\, p_j(\omega). \tag{5}$$

The surface Green's function $G_{ij}^{(S)}(\mathbf{r},\mathbf{r}',\omega)$ is defined by the following decomposition of $G_{ij}(\mathbf{r},\mathbf{r}',\omega)$:

$$G_{ij}(\mathbf{r},\mathbf{r}',\omega) = G_{ij}^{(0)}(\mathbf{r},\mathbf{r}',\omega) + G_{ij}^{(S)}(\mathbf{r},\mathbf{r}',\omega), \tag{6}$$

where $G_{ij}^{(0)}(\mathbf{r},\mathbf{r}',\omega)$ is the free-space Green's function. Thus $G_{ij}^{(S)}(\mathbf{r},\mathbf{r}',\omega)$ can be physically interpreted as describing the field generated by the induced dipoles on the surface S. We note that in the coincidence limit $\mathbf{r} = \mathbf{r}'$, the surface Green's function $G_{ij}^{(S)}(\mathbf{r},\mathbf{r}',\omega)$ attains a finite limit [unlike from the free space contribution $G_{ij}^{(0)}(\mathbf{r},\mathbf{r}',\omega)$ which diverges in this limit], which ensures that the CP energy shift in Eq. (1) is well defined. It is also important to bear in mind that the frequency dependence of the surface Green's function $G_{ij}^{(S)}(\mathbf{r},\mathbf{r}',\omega)$ is twofold: besides an explicit frequency dependence, due to *retardation effects*, there is the implicit frequency dependence due to *dispersion* in the response function $\epsilon(\omega)$ of the surface.

III. SHIFTS OF ROTATIONAL LEVELS OF DIATOMIC MOLECULES

We shall use Eqs. (1)–(3) to estimate the shifts ΔF_a of the rotational levels of a polar diatomic molecule with a closed electronic shell (i.e., in a $^1\Sigma^+$ state), in its ground electronic and vibrational state (for a review of rotational spectroscopy of diatomic molecules see Ref. [14]).

Some characteristic parameters (the angular frequency ω_r and the wavelength λ_r corresponding to transitions from the ground state to the first excited rotational state, and the dipole moment μ) of typical polar molecules are listed in Table I. The computation of the shifts of rotational levels of diatomic molecules is indeed very simple, thanks to the simplifying circumstance that in the evaluating Eqs. (1)–(3) both sources of frequency dependence in the dynamic Green's function $G_{ij}^{(S)}(\mathbf{r},\mathbf{r}',\omega)$, i.e., retardation effects and surface dispersion, can be neglected.

Let us consider retardation effects first. We will see later on that measurable shifts of the rotational levels occur only for submicron separations between the molecule and the surface. For such small separations, we can safely neglect retardation effects. This is so because for a polar diatomic molecule the largest matrix elements μ_i^{ba} of the dipole moment operator are relative to transitions between adjacent rotational

TABLE I. Characteristic parameters of some polar diatomic molecules with closed electron shells.

	$\omega_r(10^9\ \mathrm{rad/s})$	$\lambda_r\ (\mathrm{mm})$	$\mu\ (10^{-30}\ \mathrm{C\,m})$
LiH	2790	0.7	19.6
LiRb	83	22.7	13.5
LiCs	73	25.8	21.0
NaRb	25.5	73.8	11.7
NaCs	22.2	84.8	19.5

levels [14], which have characteristic frequencies of order ω_r. This implies at once that both the resonant and the nonresonant contributions to the shift ΔF_a are dominated by frequencies of order ω_r or smaller. This is obvious for the resonant contribution ΔF_a^{r}, because from Eq. (3) we see that the frequency argument of $G^{(S)}(\mathbf{r},\mathbf{r}; |\omega_{ba}|)$ is indeed of order ω_r. As to the nonresonant contribution, we see from Eq. (2) that ΔF_a^{nr} receives its dominant contribution from the Matsubara modes ξ_n such that the molecule's polarizability $\alpha_{ij}^{(a)}(i\,\xi_n)$ is significant. In view of Eq. (4) it is clear that this is the case only if ξ_n is of order ω_r or smaller. It follows from these considerations that retardation effects become important only for separations of the order of $\lambda_r = 2\pi c/\omega_r$ or larger. As seen from Table I, the wavelength of transitions between rotational states of diatomic molecules is of the order of millimeters, showing that for experimentally relevant distances retardation effect are indeed negligible.

Dispersion effects within the surface can also be ignored as the angular motion of diatomic molecules is much slower than relaxation processes characterizing typical dielectric materials. Common dielectrics used in experiments are sapphire, CaF_2, BaF_2, and SiC. Among these, sapphire is frequently employed in atom-surface interaction experiments, while SiC is normally used in experiments on near-field heat transfer. The common feature of these materials is that their optical properties is well described by a single-resonance model over a wide range frequencies extending to visible range. In this model, the complex permittivity $\epsilon(\omega)$ is described by

$$\epsilon(\omega) = \epsilon_{\mathrm{inf}} + \frac{(\epsilon_{\mathrm{st}} - \epsilon_{\mathrm{inf}})\,\omega_T^2}{\omega_T^2 - \omega^2 - i\,\Gamma\omega}, \qquad (7)$$

where ϵ_{st} and ϵ_{inf} represent the static and optical dielectric constants respectively, Γ is a phenomenological relaxation frequency, and ω_T is the transverse optical (TO) phonon frequency. Values of these parameters for the materials considered are listed in Table II [12].

According to Eq. (7) the frequency-dependent permittivity $\epsilon(\omega)$ is well approximated by the static dielectric constant ϵ_{st} for frequencies $\omega \ll \omega_T$. The shifts ΔF_a of the rotational levels of a molecule arise mostly from transitions between adjacent rotational states, with characteristic frequencies of the order of ω_r. By comparing Table I with Table II, we see that for all considered molecules and dielectrics $\omega_r \ll \omega_T$, and thus the static permittivity ϵ_{st} of the surface can be safely used to estimate the shifts ΔF_a.

Summarizing the above considerations, for experimentally relevant molecule-surface separations and for realistic dielectric materials, the CP energy shifts of rotational levels of diatomic molecules can be estimated by substituting into

TABLE II. Parameters for complex permittivity of sapphire, CaF_2, BaF_2, and SiC.

	ϵ_{st}	ϵ_{inf}	$\omega_T(10^{12}\,\mathrm{rad/s})$	$\Gamma(10^{12}\,\mathrm{rad/s})$
BaF_2	7.16	2.12	33.9	0.4
CaF_2	6.82	2.02	48.7	0.8
Sapphire	9.32	3.03	97.6	0.5
SiC	10	6.7	149.4	0.14

Eqs. (1)–(3) the static Green' function $\bar{G}_{ij}^{(S)}(\mathbf{r},\mathbf{r}; \epsilon_{\mathrm{st}})$ for the full dynamical Green's function $G_{ij}^{(S)}(\mathbf{r},\mathbf{r}; i\,\xi_n)$ or $G_{ij}^{(S)}(\mathbf{r},\mathbf{r}; i\,|\omega_{ba}|)$. In what follows, we shall denote by $\bar{G}_{ij}^{(S)}(d,\epsilon_{\mathrm{st}}) \equiv \bar{G}_{ij}^{(S)}(\mathbf{r},\mathbf{r},\epsilon_{\mathrm{st}})$ the static Green's function of the surface S evaluated at the position $\mathbf{r}$ occupied by the molecule. After substituting $G_{ij}^{(S)}(\mathbf{r},\mathbf{r}; i\,\xi_n)$ by $\bar{G}_{ij}^{(S)}(d,\epsilon_{\mathrm{st}})$, the expression for ΔF_a^{nr} simplifies considerably. Summing over the Matsubara frequencies, ΔF_a^{nr} is obtained as

$$\Delta F_a^{\mathrm{nr}} = -\frac{1}{2}\bar{G}_{ij}^{(S)}(d,\epsilon_{\mathrm{st}}) \sum_{b\neq a} \mu_i^{ab}\,\mu_j^{ba}\,\coth\left(\frac{\hbar\omega_{ab}}{2k_B T}\right). \quad (8)$$

Similarly for ΔF_a^{r}, using the identity

$$n(\omega,T) = \frac{1}{2}\left[\coth\left(\frac{\hbar\omega_{ab}}{2k_B T}\right) - 1\right], \qquad (9)$$

and noting that $\mathrm{Re}[\bar{G}_{ij}^{(S)}(d,\epsilon_{\mathrm{st}})] = \bar{G}_{ij}^{(S)}(d,\epsilon_{\mathrm{st}})$ since ϵ_{st} is real, we find

$$\Delta F_a^{\mathrm{r}} = \frac{1}{2}\bar{G}_{ij}^{(S)}(d,\epsilon_{\mathrm{st}}) \sum_{b\neq a} \mu_i^{ab}\,\mu_j^{ba}\left[\coth\left(\frac{\hbar\omega_{ab}}{2k_B T}\right) - 1\right]. \quad (10)$$

Adding Eqs. (8) and (10) now leads to the compact form [see also Eq. (10) of Ref. [10]]

$$\Delta F_a = -\frac{1}{2}\,\bar{G}_{ij}^{(S)}(d,\epsilon_{\mathrm{st}})\,\sum_{b\neq a} \mu_i^{ab}\,\mu_j^{ba}$$

$$= -\frac{1}{2}\,\bar{G}_{ij}^{(S)}(d,\epsilon_{\mathrm{st}})\,\langle a|\mu_i\,\mu_j|a\rangle. \qquad (11)$$

The final result is very simple: it shows that the energy shift of the rotational state $|a\rangle$ of a diatomic molecule is independent of the surface temperature, and coincides with the classical electrostatic interaction energy of the dipole with its image on the surface [15], averaged over the quantum state $|a\rangle$ of the molecule. The temperature independence of the nonretarded Casimir-Polder potential for a molecule placed near a dielectric surface has been noted before in the literature, as a result of cancellations between nonresonant potential components and those due to evanescent waves [10,16].

IV. DERIVATIVE EXPANSION OF THE STATIC GREEN's FUNCTION

The static Green's function $\bar{G}_{ij}^{(S)}(d,\epsilon_{\mathrm{st}})$ for a dielectric surface S, even if simpler than the dynamic Green's function $G_{ij}^{(S)}(\mathbf{r},\mathbf{r}',\omega)$, still cannot be determined for surfaces of arbitrary shapes. Analytical expressions for $\bar{G}_{ij}^{(S)}(\mathbf{r},\mathbf{r}',\epsilon)$ are known only for simple geometries of the surface such as planes and spheres [17], while for general shapes the problem has to be attacked numerically. Here we show that a *derivative expansion* can be used to obtain the asymptotic small-distance form of $\bar{G}_{ij}^{(S)}(d,\epsilon_{\mathrm{st}})$ for any gently curved dielectric surface. The derivative expansion has been recently applied successfully to estimate curvature corrections to the Casimir interaction between two gently curved surfaces [18–20], and to the CP interaction of a nanoparticle with a curved surface [5,6]. Here, we apply it to the CP interaction of a quantum particle with a surface.

Let us denote by Σ_1 (see Fig. 1) a plane through the molecule which is orthogonal to the distance vector (which we take to be the $\hat{\mathbf{z}}$ axis) connecting the molecule to the point P of the surface S closest to the molecule. We assume that the surface S is described by a *smooth* profile $z = H(\mathbf{x})$, where $\mathbf{x} = (x,y)$ is the vector spanning Σ_1, with the origin at the molecule's position. In what follows latin indices $i,j,k\ldots$ shall label all coordinates (x,y,z), while greek indices $\alpha,\beta,\ldots$ shall refer to coordinates (x,y) on the plane Σ_1.

In the present context, the key idea behind the gradient expansion is simple to explain: As dipole-dipole interaction falls off rapidly with distance, it is reasonable to expect that for small separations d the Green's function $\bar{G}_{ij}^{(S)}(d)$ is mainly determined by the shape of the surface S in a small neighborhood of the point P closest to the molecule. This physically plausible idea suggests that for small separations the Green's function can be expanded as a series in an increasing number of derivatives of the height profile, evaluated at the molecule's position. Up to second order, and assuming that the surface is homogeneous and isotropic, the most general expression that is invariant under rotations of the (x,y) coordinates, and that involves at most two derivatives of H [but no first derivatives, since $\nabla H(\mathbf{0}) = 0$], has the form

$$\bar{G}_{\alpha\beta}^{(S)}(d) = \bar{G}_{\alpha\beta}^{(\text{plane})}(d) + \frac{1}{32\pi\epsilon_0 d^2}\left\{\beta_2^{(2)}\nabla^2 H \delta_{\alpha\beta}\right.$$
$$\left. + \beta_3^{(2)}\left(\partial_\alpha\partial_\beta H - \frac{1}{2}\delta_{\alpha\beta}\nabla^2 H\right)\right\}, \quad (12)$$

$$\bar{G}_{zz}^{(S)}(d) = \bar{G}_{zz}^{(\text{plane})}(d) + \frac{\beta_1^{(2)}}{32\pi\epsilon_0 d^2}\nabla^2 H, \quad (13)$$

$$\bar{G}_{\alpha z}^{(S)}(d) = \bar{G}_{z\alpha}^{(S)}(d) = 0. \quad (14)$$

Here, ∇ is the gradient in the plane Σ_1, ϵ_0 is the vacuum permittivity, $\bar{G}_{ij}^{(\text{plane})}(d)$ is the well-known Green's function for a planar dielectric surface, while the coefficients $\beta_q^{(2)}$ are

dimensionless functions of the permittivity ϵ. The geometric significance of the expansion in Eqs. (12) and (13) becomes more transparent when x and y are chosen to be coincident with the principal directions of S at P, in which case the local expansion of H takes the simple form $H(x,y) = d + x^2/(2R_1) + y^2/(2R_2) + \ldots$, where R_1 and R_2 are the radii of curvature at P. To be definite, we assume that $d/R_1 \geqslant d/R_2$. In this coordinate system, the derivative expansion of $\bar{G}_{ij}^{(S)}(d,\epsilon)$ reads

$$\bar{G}_{zz}^{(S)}(d) = \bar{G}_{zz}^{(\text{plane})}(d) + \frac{\beta_1^{(2)}}{32\pi\epsilon_0 d^3}\left(\frac{d}{R_1} + \frac{d}{R_2}\right), \quad (15)$$

$$\bar{G}_{xx/yy}^{(S)}(d) = \bar{G}_{xx/yy}^{(\text{plane})}(d) + \frac{1}{32\pi\epsilon_0 d^3}\left[\beta_2^{(2)}\left(\frac{d}{R_1} + \frac{d}{R_2}\right)\right.$$
$$\left. \pm \frac{\beta_3^{(2)}}{2}\left(\frac{d}{R_1} - \frac{d}{R_2}\right)\right]. \quad (16)$$

The procedure to determine the coefficients $\beta_q^{(2)}$ is explained in detail in Refs. [5,6], and based on the following: The derivative expansion in Eqs. (12) and (13) is valid for surfaces of small slope, i.e., for $d/R \ll 1$ where R is a characteristic radius of curvature. However, for height profiles of small amplitude $H(x,y) = d + h(x,y)$ such that $h(x,y)/d \ll 1$, the Green's function $\bar{G}_{ij}^{(S)}(d)$ can also be Taylor expanded in powers of $h(x,y)$. It is sufficient to consider the latter expansion to first order in $h(x,y)$,

$$\bar{G}_{ij}^{(S)}(d) = \bar{G}_{ij}^{(\text{plane})}(d) + \int \frac{d^2\mathbf{k}}{(2\pi^2)}\bar{G}_{ij}^{(2)*}(\mathbf{k},d)\tilde{h}(\mathbf{k}), \quad (17)$$

where $\mathbf{k}$ is the in-plane wave vector and $\tilde{h}(\mathbf{k})$ is the Fourier transform of the $h(x,y)$. After the kernel $\bar{G}_{ij}^{(2)}(\mathbf{k},d)$ is computed, the coefficients $\beta_q^{(2)}$ are determined by matching, in the common domain of validity, the derivative expansion of $\bar{G}_{ij}^{(S)}(d)$ in Eqs. (13) and (12) with the Taylor expansion in Eq. (17). By following these steps one arrives at the following small-distance expansion:

$$\bar{G}_{xx/yy}^{(S)}(d) = \frac{1}{32\pi\epsilon_0 d^3}\frac{\epsilon-1}{\epsilon+1}\left\{1 - \frac{5+3\epsilon}{4(\epsilon+1)}\left(\frac{d}{R_1} + \frac{d}{R_2}\right) \mp \frac{1+3\epsilon}{8(\epsilon+1)}\left(\frac{d}{R_1} - \frac{d}{R_2}\right) + O\left[\left(\frac{d}{R}\right)^2\right]\right\}, \quad (18)$$

$$\bar{G}_{zz}^{(S)}(d) = \frac{1}{16\pi\epsilon_0 d^3}\frac{\epsilon-1}{\epsilon+1}\left\{1 - \frac{3+\epsilon}{4(\epsilon+1)}\left(\frac{d}{R_1} + \frac{d}{R_2}\right) + O\left[\left(\frac{d}{R}\right)^2\right]\right\}. \quad (19)$$

V. A SIMPLE MODEL: THE RIGID ROTOR

In this section we use Eq. (11), together with Eqs. (18) and (19), to estimate the shifts ΔF_a of the rotational levels of a diatomic polar molecule, near a gently curved surface. To estimate the matrix elements of the dipole-moment operator in the rotational states of the molecule in its ground electronic state, we shall model the diatomic polar molecule as a simple rigid rotor [14]. In what follows, we shall neglect the hyperfine structure of the rotational spectrum. For molecules in a $^1\Sigma^+$ state the hyperfine structure is mainly due to the electric quadrupole interaction between the nuclear quadrupole moment and the electric-field gradient at the nucleus [14]. The nuclear quadrupole hyperfine splitting in $^1\Sigma^+$ states typically

ranges from tens of kHz to one or two hundred kHz. We shall see later on that the level splitting determined by the CP interaction can be as large as several MHz, which justifies neglecting the hyperfine structure.

According to the rigid rotor model, far from the surface, the Hamiltonian operator $\hat{H}$ describing the molecule is

$$\hat{H} = \frac{\hat{\mathbf{L}}^2}{2I}, \quad (20)$$

where $\hat{\mathbf{L}}$ is the rotational angular momentum, and I is the moment of inertia. The energy eigenstates $|l,m\rangle$ are labeled by the quantum numbers $l = 0,1,2,\ldots$ and m, with $-l \leqslant m \leqslant l$ corresponding, respectively, to the rotational angular

momentum and to its z component $\hat{L}_z$ (we choose as the z axis the line connecting the molecule to the point P of the surface S closest to the molecule; see Fig. 1), such that

$$\hat{\mathbf{L}}^2 |l,m\rangle = \hbar^2 \, l\,(l+1)|l,m\rangle, \tag{21}$$

$$\hat{L}_z |l,m\rangle = \hbar \, m |l,m\rangle. \tag{22}$$

Then,

$$\hat{H}|l,m\rangle = E_l |l,m\rangle, \tag{23}$$

where

$$E_l = \frac{\hbar \omega_r}{2} \, l\,(l+1), \tag{24}$$

and we set $\omega_r = \hbar/I$. The level of energy E_l consists of $2l+1$ degenerate states, distinguished by the azimuthal quantum number m.

When the molecule is brought near the surface, the CP interaction perturbs its energy levels. To analyze the effect of the interaction with the surface, we consider that for a gently curved surface such that $d/R \ll 1$, curvature effects are expected to cause a small correction to the perturbation determined by a planar surface. This suggests to split the computation of the energy shifts ΔF_a in two steps: in the first step, we study the planar problem, and then we consider how the energy levels for a planar surface are further modified by curvature effects. As we shall see below, this procedure has the advantage that it allows us to use the theory of CP energy shifts for nondegenerate quantum states, presented in Sec. II.

A. A planar surface

For a planar surface (and more generally for any axisymmetric surface) the Green's function $\bar{G}_{ij}^{(S)}(d)$ is invariant under rotations around the $\hat{z}$ axis, and therefore the azimuthal label m remains a good quantum number in the presence of the surface. The CP interaction does not mix states with different values of m, and therefore we can straightforwardly use the results in Sec. II to compute the shifts $\Delta F_{l,m}$. Using the relations

$$\langle l,m|\hat{\mu}_x^2|l,m\rangle = \langle l,m|\hat{\mu}_y^2|l,m\rangle$$
$$= \mu^2 \, \frac{l(l+1)+m^2-1}{4l(l+1)-3}, \tag{25}$$

and

$$\langle l,m|\hat{\mu}_z^2|l,m\rangle = \mu^2 \, \frac{2l(l+1)-2m^2-1}{4l(l+1)-3}, \tag{26}$$

we find

$$\Delta F_{l,m}^{(\mathrm{plane})} = -\mathcal{E} \, \frac{3l(l+1)-m^2-2}{4l(l+1)-3}, \tag{27}$$

where

$$\mathcal{E} = \frac{\mu^2}{32\pi\epsilon_0 d^3} \, \frac{\epsilon_{\mathrm{st}}-1}{\epsilon_{\mathrm{st}}+1}. \tag{28}$$

According to Eq. (27), the CP interaction of the molecule with a plane splits the $(2l+1)$-fold degenerate level E_l into l distinct levels of energies $E_{l,|m|}^{(\mathrm{plane})} = E_l + \Delta F_{l,m}^{(\mathrm{plane})}$, labeled by the absolute value of the azymuthal quantum number $|m|$.
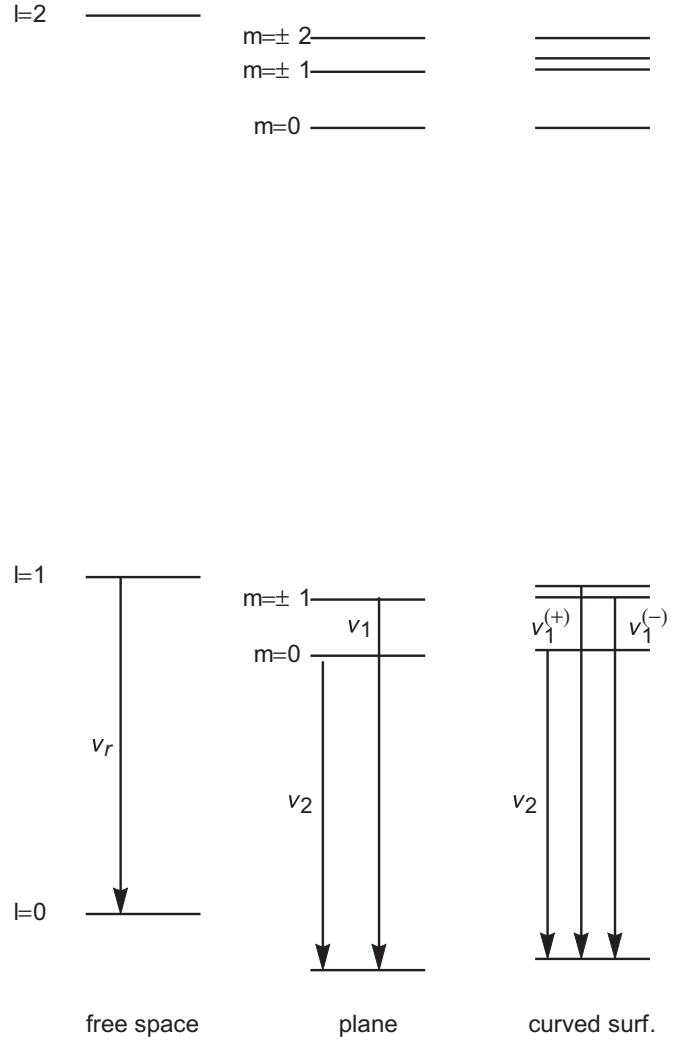

FIG. 2. Qualitative structure of the energy levels of a diatomic polar molecule in free space (left), near a planar surface (middle), and near a curved surface with different radii of curvature (right).

Of these levels, only $m=0$ is nondegenerate, while those with $m \neq 0$ form degenerate doublets (see Fig. 2).

B. Curvature corrections

Having determined the structure of the energy levels $E_{l,|m|}^{(\mathrm{plane})}$ of a diatomic molecule near a planar surface, we now study how the levels $E_{l,|m|}^{(\mathrm{plane})}$ are affected by the surface curvature. As we pointed out above, we consider that for $d/R \ll 1$ curvature corrections are small, compared to the CP energy shift for a planar surface. This suggests that we take the (possibly) doubly degenerate levels $E_{l,|m|}^{(\mathrm{plane})}$ determined in the previous step as our unperturbed states, and compute curvature corrections to their energies using again Eq. (11). The following remark is crucial: to the order d/R that we consider, the Green's function $\bar{G}_{ij}^{(S)}(d)$ in Eqs. (18) and (19) is no longer invariant under rotations around the z axis. However $\bar{G}_{ij}^{(S)}(d)$ is still invariant under reflections of the x and y coordinates. In order to take advantage of this reflection symmetry, within each doublet $E_{l,|m|}^{(\mathrm{plane})}$, $m \neq 0$ we replace the two states $|l, \pm m\rangle$ by the new

states $|l,|m|,s\rangle$, with $s = \pm 1$, given by

$$|l,|m|,\pm\rangle = \frac{1}{\sqrt{2}}(|l,m\rangle \pm (-1)^{|m|}|l,-m\rangle),$$
$$m = 1,\ldots,l, \qquad (29)$$

which possess definite parity under independent reflections of the coordinates x and y. For the $m = 0$ singlets, we just set

$$|l,0,+\rangle \equiv |l,0\rangle. \qquad (30)$$

Since

$$\hat{R}_x|l,m\rangle = |l,-m\rangle, \qquad (31)$$
$$\hat{R}_y|l,m\rangle = (-1)^m|l,-m\rangle, \qquad (32)$$

it is easy to verify that the states $|l,|m|,\pm\rangle$ indeed have definite parity under reflections of x and y:

$$\hat{R}_x|l,|m|,\pm\rangle = \pm(-1)^{|m|}|l,|m|,\pm\rangle, \quad m = 0,\ldots,l, \quad (33)$$
$$\hat{R}_y|l,|m|,\pm\rangle = \pm|l,|m|,\pm\rangle, \quad m = 0,\ldots,l. \quad (34)$$

Since to order d/R the Green's function is reflection invariant, the CP interaction does not mix rotational states of different parity, and therefore in the basis $|l,|m|,s\rangle$ we are allowed to use the nondegenerate theory underlying Eq. (11) to compute

the *leading* curvature correction to the energy levels $E_{l,|m|}^{(\text{plane})}$. The matrix elements of $\hat{\mu}_i^2$ in the new basis are

$$\langle l,|m|,s|\hat{\mu}_x^2|l,|m|,s\rangle = \langle l,|m|,s|\hat{\mu}_y^2|l,|m|,s\rangle$$
$$= \mu^2 \frac{l(l+1) + m^2 - 1}{4l(l+1) - 3}, \quad |m| \neq 1, \quad (35)$$

$$\langle l,1,+|\hat{\mu}_x^2|l,1,+\rangle = \langle l,1,-|\hat{\mu}_y^2|l,1,-\rangle$$
$$= 3\mu^2 \frac{l(l+1)}{8l(l+1) - 6}, \qquad (36)$$

$$\langle l,1,-|\hat{\mu}_x^2|l,1,-\rangle = \langle l,1,+|\hat{\mu}_y^2|l,1,+\rangle$$
$$= \mu^2 \frac{l(l+1)}{8l(l+1) - 6}, \qquad (37)$$

and

$$\langle l,|m|,s|\hat{\mu}_z^2|l,|m|,s\rangle = \mu^2 \frac{2l(l+1) - 2m^2 - 1}{4l(l+1) - 3}. \qquad (38)$$

Using the above relations, the leading curvature correction $\Delta F_{l,|m|,s}^{(\text{curv})}$ to the rotational energy levels is found to be

$$\Delta F_{l,|m|,s}^{(\text{curv})} = \mathcal{E}\left(\frac{d}{R_1} + \frac{d}{R_2}\right) \frac{l(l+1)(11 + 5\epsilon_{\text{st}}) + m^2(\epsilon_{\text{st}} - 1) - 4(2 + \epsilon_{\text{st}})}{4(\epsilon_{\text{st}} + 1)[4l(l+1) - 3]}, \quad |m| \neq 1, \qquad (39)$$

$$\Delta F_{l,1,\pm}^{(\text{curv})} = \mathcal{E}\left\{\left(\frac{d}{R_1} + \frac{d}{R_2}\right) \frac{l(l+1)(11 + 5\epsilon_{\text{st}}) - 3(3 + \epsilon_{\text{st}})}{4(\epsilon_{\text{st}} + 1)[4l(l+1) - 3]} \pm \left(\frac{d}{R_1} - \frac{d}{R_2}\right) \frac{l(l+1)(1 + 3\epsilon_{\text{st}})}{16(\epsilon_{\text{st}} + 1)[4l(l+1) - 3]}\right\}. \qquad (40)$$

We see that for $|m| > 1$ surface curvature just determines an extra overall shift in the energy of the doublets $E_{l,|m|}^{(\text{plane})}$, without lifting their twofold degeneracy. By contrast, the $|m| = 1$ doublets split into two distinct levels, whose spacing is proportional to $(d/R_1 - d/R_2)$ (see Fig. 2). The splitting of the $|m| = 1$ rotational levels constitutes the characteristic signature of curvature effects on the CP interaction of the molecule with the surface.

VI. STRUCTURE OF THE ROTATIONAL SPECTRUM

In a polar molecule, rotational transitions between adjacent rotational levels ($\Delta l = \pm 1$) are electric-dipole allowed [14]. Let us consider as an example the emission lines corresponding to transitions from $l = 1$ states to the rotational ground state $l = 0$, i.e., $l = 1 \to 0$. When the molecule is far from the surface, these transitions correspond to a single spectral line of frequency $\nu_r = \omega_r/(2\pi)$ (see Table I). As the molecule approaches the surface, this line splits into several components. The precise number of lines depends on whether the surface is planar or curved. Let us consider first the case of a planar surface. According to Eq. (27), the free-space line $1 \to 0$ splits in two components corresponding to the transitions

$$\nu_1: \quad |1,\pm 1\rangle \to |0,0\rangle, \quad \text{and} \quad \nu_2: \quad |1,0\rangle \to |0,0\rangle.$$

Suppose that we observe the molecule from a point along the z axis, i.e., in a direction perpendicular to the planar surface. Since the x and y components of the dipole-moment operator $\hat{\mu}_x$ and $\hat{\mu}_y$ do not couple two $m = 0$ states, it follows that in the dipole approximation the line ν_2 cannot be seen from this observation direction, and only the line ν_1 is detected. When the observation line is instead in the plane of the surface, both lines are visible, and is it easy to verify that the line ν_1 is polarized in the plane of the surface, while the line ν_2 is polarized along the normal direction to the surface. According to Eq. (27), the difference $\Delta\nu_{12} = \nu_1 - \nu_2$ between the two lines is

$$\Delta\nu_{12} = \nu_1 - \nu_2 = \frac{\mathcal{E}}{5h}, \qquad (41)$$

with $\mathcal{E}$ as defined in Eq. (28).

For a *curved surface*, Eqs. (39) and (40) indicate that the line ν_1 of the planar surface splits into two components $\nu_1^{(\pm)}$ corresponding to the transitions (see Fig. 2)

$$\nu_1^{(+)}: \quad |1,1,+\rangle \to |0,0,+\rangle,$$
$$\nu_1^{(-)}: \quad |1,1,-\rangle \to |0,0,+\rangle. \qquad (42)$$

According to Eq. (40) the difference $\Delta\nu_{\pm}$ between the frequencies $\nu_1^{(+)}$ and $\nu_1^{(-)}$ of these two lines is proportional

to the difference in radii of curvature, as

$$\Delta\nu_\pm = \nu_1^{(+)} - \nu_1^{(-)} = \frac{\mathcal{E}}{h}\left(\frac{d}{R_1} - \frac{d}{R_2}\right)\frac{1}{20}\frac{3\,\epsilon_{st}+1}{\epsilon_{st}+1}. \quad (43)$$

In addition to the two lines $\nu_1^{(\pm)}$, we of course have a third line, corresponding to the line ν_2 of the planar surface:

$$\nu_2: \quad |1,0,+\rangle \rightarrow |0,0,+\rangle,$$

Thus, the single $l = 1 \rightarrow 0$ line of free-space splits (in general) into three lines, when the molecule is brought near a curved surface.

Suppose again that we observe the molecule from a point along the z axis. Reasoning as before, we see that in the dipole approximation the line ν_2 cannot be detected from this observation direction, and only the lines $\nu_1^{(+)}$ and $\nu_1^{(-)}$ are visible. Using Eqs. (31) and (32) it is easy to verify that $\nu_1^{(+)}$ and $\nu_1^{(-)}$ are linearly polarized along the x and the y axes, respectively.

Similarly, it is possible to verify that when the observation direction is along the x axis (y axis), the visible lines are $\nu_1^{(-)}$ ($\nu_1^{(+)}$) and ν_2; the former linearly polarized in the y direction (x direction), and the latter along the z axis. Up to small curvature corrections, the frequency differences $\Delta\nu_{12}^{(\pm)} = \nu_1^{(\pm)} - \nu_2$ coincide with the frequency difference $\Delta\nu_{12}$ for the planar surface in Eq. (41). By comparing Eq. (43) with Eq. (41) we thus see that the curvature-induced splitting $\Delta\nu_\pm$, is suppressed by factor of order d/R, compared to the splittings $\Delta\nu_{12}^{(\pm)}$. From our perspective, though, the most interesting quantity to observe is $\Delta\nu_\pm$ since it represents a pure curvature effect. Using Eq. (28), we estimate the magnitude of $\Delta\nu_\pm$ for a polar molecule with an electric dipole moment $\mu = 2 \times 10^{-29}$ C m (see Table I), as

$$\Delta\nu_\pm \simeq \frac{3\,\mu^2}{640\,\pi\,\epsilon_0\,h\,d^3}\left(\frac{d}{R_1} - \frac{d}{R_2}\right)$$
$$= 100\text{ kHz}\left(\frac{100\text{ nm}}{d}\right)^3\left(\frac{d}{R_1} - \frac{d}{R_2}\right). \quad (44)$$

Note that our derivation only assumes that $d/|R_1| \ll 1$ and $d/|R_2| \ll 1$. However it does not assume that $|R_1 - R_2|/|R_1| \ll 1$. In particular, in the case of a cylindrical surface $R_1 \rightarrow \infty$ and $|R_1 - R_2|/|R_1| = 1$. To determine if the frequency difference $\Delta\nu_\pm$ is potentially measurable, it is important to compare $\Delta\nu_\pm$ with the typical width of rotational spectral lines. Their natural width $\Delta\nu$ can be estimated by the simple formula [14]

$$\Delta\nu = \frac{\nu^3|\mu|^2}{3\,\epsilon_0\,\hbar\,c^3}. \quad (45)$$

For the molecules listed in Table I, the natural linewidth ranges from a maximum of 4×10^{-4} Hz for LiH to a minimum of 1.2×10^{-10} Hz for NaRb, and is thus many orders of magnitude smaller than $\Delta\nu_\pm$, for reasonable values of the separation d, and of d/R. Next we consider the thermal Doppler broadening, which for a gas of molecules in equilibrium at temperature T is given by [14]

$$\Delta\nu = \frac{2\nu}{c}\sqrt{\frac{2N_A k_B T \ln 2}{M}} = 7.15 \times 10^{-7}\,(T/M_r)^{1/2}\,\nu, \quad (46)$$

where N_A is Avogadro's number, M and M_r are the mass and the relative molecular mass of the molecule, respectively. Using the above formula, we estimate that at room temperature $T = 300$ K, the Doppler broadening ranges from a maximum of 2 MHz for LiH, to a minimum of 5 kHz for NaRb and NaCs. So, while for the light molecule LiH the large thermal Doppler broadening prevents observation of the frequency shift $\Delta\nu_\pm$ even at cryogenic temperatures, in the case of the heavier molecules listed in Table I the thermal Doppler broadening is favorably smaller than $\Delta\nu_\pm$ even at room temperature.

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