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Self-alignment of a polar molecule colliding with a solid surface

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It is shown that polar molecules colliding with a solid are subject to efficient self-alignment caused by an interaction with their own electrostatic image dipole when the permanent dipole moment of the molecule exceeds 3 D.

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The physical processes occurring during the collision of a molecule with the surface of a solid have been the subject of numerous investigations of both experimental and theoretical nature (see, for instance, [1–12] and references cited therein). It was reported that only involved molecular dynamics calculations taking account of a number of fine details of the molecule-surface interaction (e.g., the phonon spectrum of the solid, inclusion of an attractive well in the interaction potential, surface roughness, etc.) can properly explain the main characteristics of the process [9–12]. This means that details of the process are crucially dependent on the peculiarities of both the colliding molecule and the solid and thus, generally speaking, the conclusions made are strongly dependent on the theoretical model used. This makes quantitative predictions difficult for the processes at hand.

In this paper we show that for a polar molecule possessing a dipole moment $d > 3$ D the electrostatic interaction of the molecule with its image dipole [13] works as an efficient source of molecule self-alignment: the molecule colliding with the surface is oriented in such a manner that its dipole tends to be perpendicular to the surface. This process is a quite universal and model-independent one, and such a self-alignment is obviously important for the numerous processes where polar molecules are used—e.g., catalysis, chemical and surface physics, and so on. Of course, it is also important for the understanding and correct interpretation of molecule-surface scattering experiment results which are the main source of information about molecule-surface interactions. For a detailed discussion see [1–12] and references therein.

For simplicity, below we will consider only a linear polar molecule with dipole moment d and rotational constant B, which approaches the surface with normal velocity component v (see Fig. 1). From the known expression for the dipole electric field $E = 3(dr)r/r^5 - d/r^3$ [13], it follows that the molecule's interaction with the electrostatically reflected dipole $d' = [(\epsilon - 1)/(\epsilon + 1)]d$ [13] is described by the potential

$$U = -\frac{1}{2} dE = -(dd'/16l^3)(1 + \cos^2\vartheta). \tag{1}$$

Here ϵ is the dielectric constant of the solid (below we will consider the case when ϵ is large and thus $d' \approx d$), l is the polar molecule–surface distance, and ϑ is the angle between the molecule's symmetry axis and the surface normal (Fig. 1). Under the action of this potential the molecule will be accelerated [the angle-independent term in Eq. (1)] and oriented (the angle-dependent term). For simplicity, below we will consider the case of sufficiently large v, when the effect of acceleration can be neglected. For example, for a KCl molecule ($d = 10.27$ D, $B = 0.1286\ \mathrm{cm}^{-1}$) having velocity $v = 600$ m/s (which is quite typical for both rotationally and vibrationally cool molecules seeded in supersonic beams and molecules in thermal beams), the velocity will increase up to 670 m/s when the molecule approaches the surface to the distance of $l = 0.5$ nm, so this increase really can be neglected. Consideration of smaller molecule-surface distances makes no sense, because when this distance is of the order of the interatomic distance the dipole approximation is no longer valid. At the same time, as follows from theory and experiments concerning the van der Waals interaction, the dipole approximation is quite reasonable up to such a distance—see, for instance, Ref. [14].

The Schrödinger equation governed the molecule self-alignment is

$$i\hbar \frac{d\psi}{dt} = \left(BJ^2 - \frac{d^2}{16(l_0 - vt)^3} \cos^2\vartheta \right) \psi. \tag{2}$$

Here $\mathbf{J}$ is the angular momentum operator and l_0 is the initial molecule-surface distance. Searching, as usual, for a solution as a sum $\psi = \Sigma_j c_j |J = j, M\rangle$ of the eigenfunctions $|J,M\rangle$ of the operators $\mathbf{J}, J_z$ and using properties of these functions, one reduces Eq. (2) to the following system:

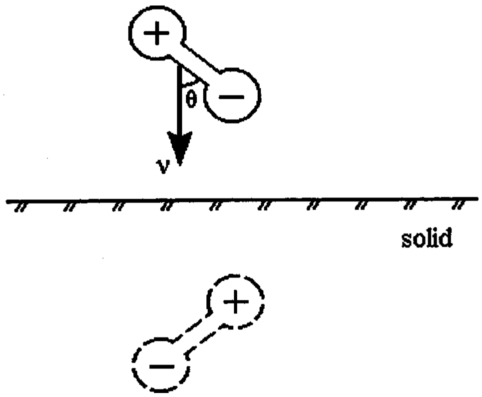

FIG. 1. Illustration of the geometry of the problem.

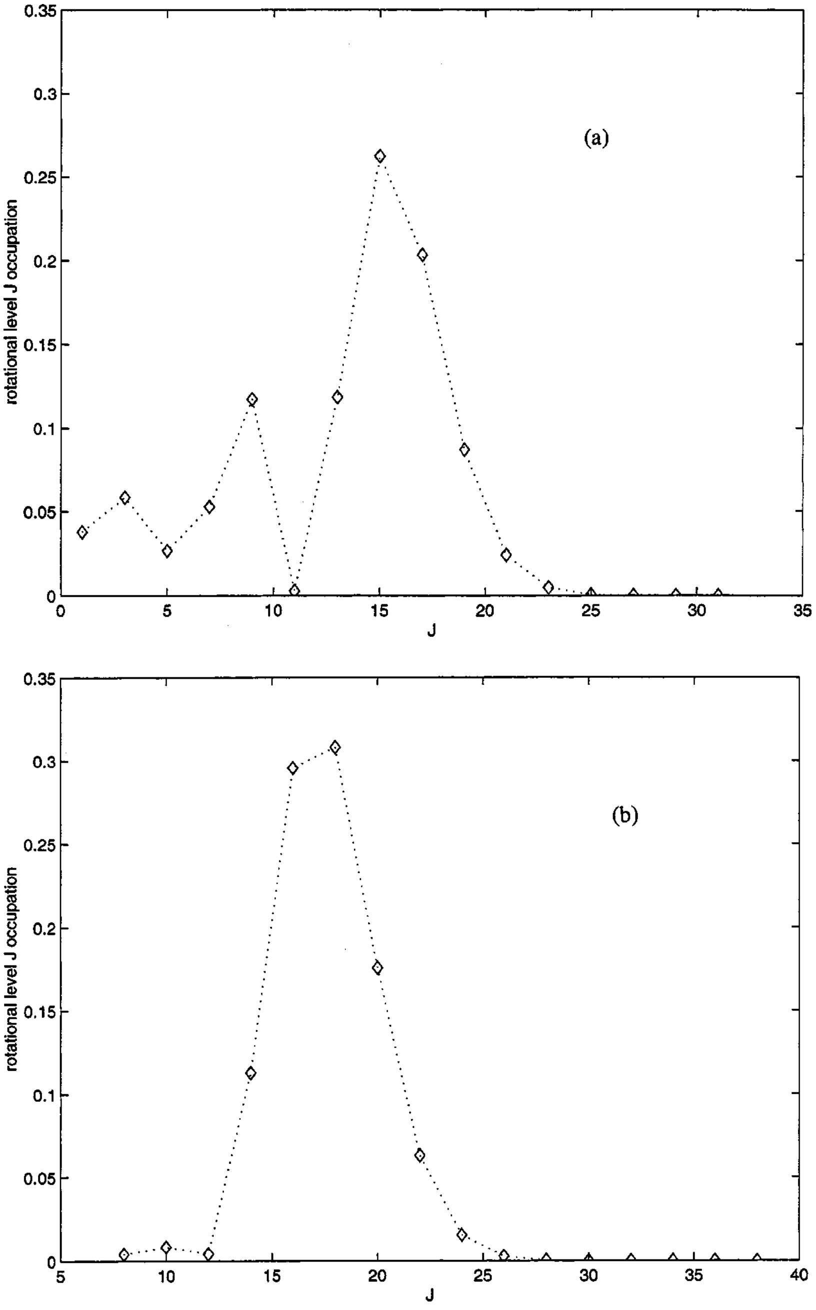

FIG. 2. The populations of the rotational levels $|J,M\rangle$ for a KCl molecule as a result of its electrostatic interaction with a solid upon approach. The molecule initially occupies the level (a) $|1,1\rangle$; (b) $|8,7\rangle$.

$$i\hbar\frac{dc_j}{dt}=Bj(j+1)c_j - \frac{d^2}{16(l_0-vt)^3}[W_{j,j}c_j+W_{j-2,j}c_{j-2}+W_{j+2,j}c_{j+2}]. \tag{3}$$

Here $W_{i,j}=\langle J=i,M|\cos^2\vartheta|J=j,M\rangle$ are nonzero matrix elements of the $\cos^2\vartheta$ operator [15]:

$$W_{J,J}=\frac{2J^2+2J-2M^2-1}{(2J+3)(2J-1)},$$

$$W_{J+2,J}=\left(\frac{[(J+1)^2-M^2][(J+2)^2-M^2]}{(2J+1)(2J+3)^2(2J+5)}\right)^{1/2},$$

$$W_{J-2,J}=\left(\frac{[J^2-M^2][(J-1)^2-M^2]}{(2J+1)(2J-1)^2(2J-3)}\right)^{1/2}.$$

We have also omitted the quantum number M which is one and the same for all the levels involved. Introducing the variable change

$$\tau=\frac{d^2}{32v\hbar(l_0-vt)^2} \tag{4}$$

Eq. (3) can be rewritten as

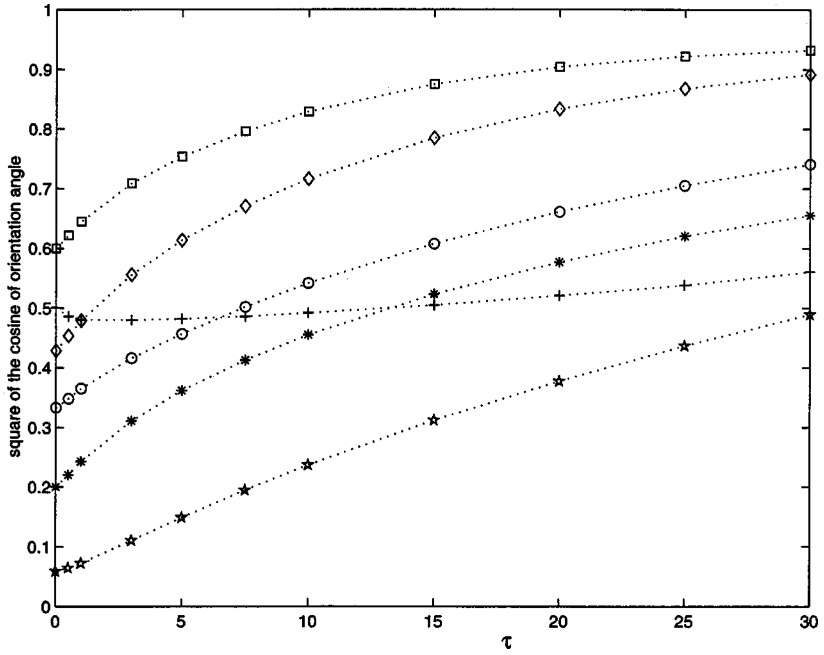

FIG. 3. Dependence of the orientation of a KCl molecule on the dimensionless parameter τ. Initial state of the molecule is as follows: stars, $|13,0\rangle$; asterisks, $|1,1\rangle$; circles, $|0,0\rangle$; diamonds, $|2,1\rangle$; squares, $|1,0\rangle$; pluses, $|7,7\rangle$.

$$i\frac{dc_j}{d\tau}=\frac{Bd}{8\sqrt{2}(v\hbar)^{3/2}}j(j+1)\tau^{-3/2}c_j - W_{j,j}c_j - W_{j-2,j}c_{j-2} - W_{j+2,j}c_{j+2}. \qquad (5)$$

Without the first term on the right side, which often can be neglected, the derivatives $dc_j/d\tau$ do not depend on time, and this is, of course, the reason to introduce the variable change (cf., e.g., [16,17]). For such a case this equation can be solved using the Laplace transform (see, for example, [18]) and, for some relations between the coefficients W_{ij}, an analytical solution is also available [16,17]. However, the solution obtained by the Laplace transform method is not more explicit and easy to use than the result of direct numerical calculation, which is not so difficult to obtain taking account of the first term. Note also that the problem at hand is somewhat similar to the problem of orientation of a polar molecule by an external dc electric field [19–21]. Important differences are that (i) for our case only rotational levels of the same parity can be mixed, and (ii) we have at hand a purely attractive case: the energy change due to the interaction of the molecule with its electrostatic dipole can only be negative while both attraction and repulsion of the molecule from an external electric field can happen. For the stationary case, the Schrödinger equation with a Hamiltonian similar to that used in Eq. (2), i.e., $(BJ^2-a\cos^2\vartheta+b)\psi=E\psi$, where $a,b=\mathrm{const}$, describes the orientation of an anisotropic molecule in a strong linearly polarized laser field, and the corresponding solution can be expressed via spheroidal functions [22].

Before we proceed to a discussion of the results of calculations, we would like to underline the following. In addition to the permanent dipole-moment-caused orientation, which we discuss here, a similar effect can be caused also by the anisotropic polarizability of the molecule. [In the terminology of van der Waals intermolecule interactions these parts of the full potential are called, respectively, the Keesom-Debye and dispersion (London) interactions; see, e.g., [14].] It was shown earlier that for anisotropic molecules, whose polarizations by the fields parallel and perpendicular to the symmetry axis are, respectively, $\alpha_\parallel$ and $\alpha_\perp$, the total van der Waals interaction coefficient C_3 ($U=-C_3/l^3$) can be divided into orientation-independent and orientation-dependent parts C_3^1 and C_3^2, where $C_3^2=(1/4)(\alpha_\parallel-\alpha_\perp)$ [23]. The orientation-dependent part of the van der Waals interaction is given by the term $U=-C_3^2\cos^2\vartheta/l^3$, whose form is quite similar to that used in Eqs. (1)–(3) if we identify $d_{\mathrm{eff}}=4\sqrt{C_3^2}$. However, an analysis of the polarizabilities of real molecules [24] shows that this part of the molecule-solid interaction is not strong enough to cause a noticeable self-alignment (with the exception of the CS_2 molecule [25]), and this effect will be neglected below.

The results of numerical solution of the system (5) using the MATLAB program are presented in Figs. 2 and 3 and Table I. For the given case of the KCl molecule, it is easy to see that the maximal value of the parameter τ, defined in Eq. (4), is equal to ~ 20 for $l=0.5$ nm, $v=600$ m/s; thus we integrated Eq. (5) from $\tau=0$ [in practice, the value $\tau=0.01$ was used; the first term on the right side of Eq. (5) was not neglected] to $\tau=20$ for different initial conditions. Calculations showed that we need to take into account ~ 25 rotational levels of the molecule: an increase of this number does not influence the result.

First, to demonstrate the typical quantum dynamics of the system in the space of $|J,M\rangle$, in Figs. 2(a) and 2(b) we present the populations of rotational levels for a molecule initially occupying such different levels as $|1,1\rangle$ [26] and $|8,7\rangle$. It is easy to see that for both cases the rotational levels up to $J\sim 25$ are populated. The alignment is illustrated in Table I where the mean values of the cosine square $\langle\psi|\cos^2\vartheta|\psi\rangle$ are presented for some initial states of the KCl molecule. This parameter attains as large a value as 0.90 for the initial state $|1,0\rangle$ and is rather large for a number of other

TABLE I. Values of $\langle\psi|\cos^2\vartheta|\psi\rangle$ for different initial states of a KCl molecule approaching a surface up to a distance of 0.5 nm with a velocity of 600 m/s.

Initial state $|J,M\rangle$	$\langle\psi|\cos^2\vartheta|\psi\rangle$
$|00\rangle$	0.661
$|10\rangle$	0.903
$|11\rangle$	0.577
$|20\rangle$	0.683
$|21\rangle$	0.833
$|22\rangle$	0.543
$|30\rangle$	0.736
$|31\rangle$	0.615
$|32\rangle$	0.772
$|33\rangle$	0.510
$|63\rangle$	0.583
$|80\rangle$	0.578
$|84\rangle$	0.518
$|88\rangle$	0.346

initial states, which means that numerous KCl molecules seeded in a supersonic beam will be well aligned upon approach. Averaging of the value of $\langle\psi|\cos^2\vartheta|\psi\rangle$ for the rotational temperature of 5 K (all the 81 states with $J\leqslant 8$, i.e., $>95\%$ of all molecules, were taken into account) gives the cosine square mean value of 0.62. Note that here we really have an alignment rather than an orientation: all the equations are symmetric with respect to the sign of the angle ϑ. This means that one-half of all molecules will be oriented with the K atom closest to the surface, and the other half in the opposite fashion.

The dependence of the $\langle\psi|\cos^2\vartheta|\psi\rangle$ value on the parameter τ for the KCl molecule is presented in Fig. 3. These dependencies can be used in different ways. For example, one can consider the KCl molecule occupying initially (i.e., far from the surface when $\tau=0$) the state $|J,M\rangle$ and approaching the surface with a velocity v. Then Fig. 3 gives the value of the orientation achieved at a distance $l=(d/\sqrt{32v\hbar})\tau^{-1/2}$ from the surface; for our case of KCl molecules with $v=600$ m/s l (nm)$=2.24\tau^{-1/2}$. Or, the other way around, one can consider KCl molecules approaching the surface up to the distance l but with different velocities $v=(d^2/32\hbar l^2)\tau^{-1}$; for our case of KCl molecules and $l=0.5$ nm, v (m/s)$=1.2\times10^4\tau^{-1}$. By the same token an arbitrary combination of v,l can be considered. It is seen that the degree of alignment drops when initial states with larger J are considered, and, for example, the orientation of the state $|7,7\rangle$ remains practically the same upon approach despite the fact that rotational polulations for this and neighboring initial states are essentially redistributed [Fig. 2(b)].

Figure 3 can be used for the estimation of the degree of orientation for molecules other than KCl. To do this, the maximum value of the parameter τ should be calculated from Eq. (4) using the corresponding dipole moment d. The exact degree of orientation depends on the rotational constant B; hence it can be found only by the numerical solution of Eq. (3) or Eq. (5). However, our analysis of such solutions obtained for different real (ICN, NaCl, CS_2) and imaginary model molecules with given d and B values shows that the results presented in Fig. 3 can be used for such an estimation when B ranges from 0.1 to 1 cm^{-1}. Thus rotationally cool polar molecules possessing a permanent dipole moment $d>3$ D are subject to noticeable self-alignment caused by the electrostatic interaction with their own ‘‘reflected’’ dipole.

Throughout the paper we considered the velocity $v=600$ m/s, which corresponds to the normal (or close to normal) collision of the molecule with the surface. For other collision angles the value of the velocity can be considerably smaller and thus the value of the parameter τ will be larger. This leads to more efficient alignment. Of course, for such a case it is not possible to neglect the self-acceleration of the dipole due to its interaction with its own electrostatic image. For example, for the KCl molecule such an interaction causes an acceleration from 0 m/s at infinity to 290 m/s when the distance of 0.5 nm from the surface is reached. Nevertheless, the numerical integration of a generalized equation similar to Eq. (3) or Eq. (5) still poses no problems. We did not do this here only to underline the physical essence of the self-alignment process rather than to discuss technical details. For the same reason we also did not consider different imperfections on the surface, which obviously could in some cases modify the electrostatic interaction and hence the alignment. It should be noted, however, that a quantitatively correct description of electrons levitating under the surface of a cryodielectric (solid hydrogen, etc.) is achieved using an electrostatic image potential up to distances of 1 Å or so [27]. Finally, we would like to mention that the process considered resembles to some extent the action of an intense picosecond laser pulse on an anisotropic molecule (cf. [17]): the total duration of the process is of the order of 10 ps (the molecule-surface distance from 10 to 0.5 nm is important) while the maximal electric field attains the value of 3×10^7 V/cm, which corresponds to a light intensity of $\sim10^{12}$ $\mathrm{W/cm^2}$.

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[25] Using the data given in Ref. [24] for this molecule, $\alpha_{\parallel}=15\times10^{-24}$ cm^3 and $\alpha_{\perp}=5.5\times10^{-24}$ cm^3 together with the experimental data on the typical C_3 van der Waals coefficient, $C_3\approx5\times10^{-36}$ Erg/cm^3 for the polarizability of 4×10^{-24} cm^3 [see, for example, G. Vidali, G. Ihm, H.-Y. Kim, and M. W. Cole, Surf. Sci. Rep. **12**, 133 (1991)], one can easily calculate that for the CS$_2$ molecule $d_{\mathrm{eff}}\approx7$ D.

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