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Article

A Theoretical Model for the Scattering of I_2 Molecule from a Perfluoropolyeter Liquid Surface

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Neste trabalho desenvolvemos um modelo do potencial de interação para simulação de experimentos de espalhamento de um feixe de moléculas de I_2 sobre a superfície do líquido polimérico poliéterperfluorado e resolvemos a dinâmica do processo de colisão usando o método das trajetórias clássicas. A energia transferida no processo para os modos vibracionais da molécula de I_2 e para o líquido foram investigados como função dos parâmetros do potencial.

In order to simulate experimental results of scattering of an I_2 beam from liquid perfluorpolyeter (PFPE) surface we developed a model potential for the gas-polymer interaction at the liquid surface and solved the dynamics of the collision process by the classical trajectory method. The energy transferred in the process to the vibrational mode of the I_2 molecule and to the liquid surface was investigated as a function of potential parameters.

Keywords: *gas-surface interaction, liquid polymer, perfluorpolyether and chemical dynamics*

Introduction

Although many properties of liquids, such as surface tension, adhesion, lubrication and wetting are related to their microscopic surface chemical structure, the chemical structure of liquid surfaces is less understood than the structure of solid surfaces. Recently, methods that probe directly the liquid surfaces chemical structure have been developed employing rare-gas atomic[1] and ion[2] beam scattering, reactive ion beam scattering[3], nonlinear optical spectroscopy[4], and angle resolved photoelectron spectroscopy[5]. The understanding of the interaction of atoms, molecules and ions with surfaces is of great relevance to establish the dynamics of the fundamental processes occurring in beam/surface collision. When a gas molecule collides with a liquid surface it can scatter away immediately, it can exchange energy with the liquid molecules, or it can bind temporarily to surface molecules and then evaporate, react or dissolve in the liquid bulk. Relevant questions concerning the dynamics of these processes remain unanswered such as: the mechanism of surface reaction, how is the collision energy transferred to the surface and to the vibrational and rotational degrees of freedom of the scattered molecule, the spatial distribution of scattered molecules, and the influence of the surface and the colliding molecule in each process. Recently, scattering experiments have been performed directing a cold beam of iodine molecules to liquid polymer surfaces in vacuum[6]. The experiment can distinguish molecules scattered directly from the surface and molecules desorbed from the surface. The gas molecules are activated by the collision and the energy transferred to the internal modes of the gas is determined and depends on the chemical nature of the surface. Here, we present a calculation of the dynamics of this experiment aiming a characterization of the gas-liquid interaction, and a molecular description of the collision process.

Methods

The experimental results obtained suggest that the direct scattering is characterized by a inelastic collision where a very small amount of the gas translational energy is converted to vibrational and rotational energy or transferred to the liquid surface molecules. When the molecules are adsorbed at the surface the energy conversion and transfer processes are much more effective.

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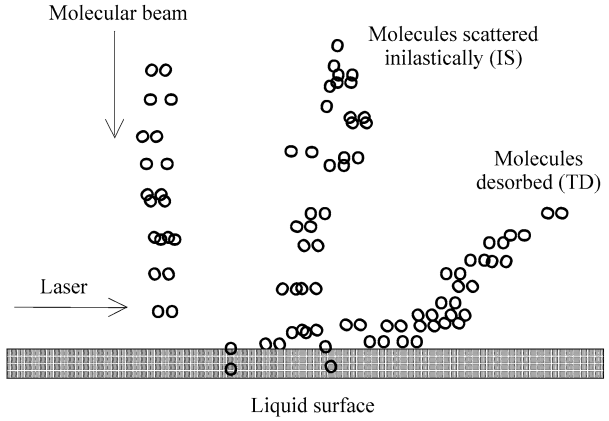

Figure 1. Model of the scattering of a supersonic I_2 beam by a liquid polymer surface indicating the direct inellastic and desorption processes. The laser, placed parallel to the surface, detects the vibrational an rotational state of the scattered molecule.

A theoretical approach to the gas-liquid scattering problem is a diatomic molecule interacting with one liquid surface molecule represented by a *model molecule* with two constrained degrees of freedom. We build a model potential for the interaction of a I_2 molecule with PFPE given by: $V = V_{LEPS} + V_{SUP}$, where V_{LEPS} is a three-body LEPS (London-Eyring-Polanyi-Sato) potential employed in gas phase reaction studies[7] and gas-solid interaction[8], and V_{SUP} describes the motion of the *model* liquid surface molecule. V_{LEPS} is a non-pairwise potential, which for a I_2 molecule and a I- surface S interaction takes the form:

$$V_{LEPS} = Q_{ab} + Q_{ac} + Q_{bc} - [\, J_{ab}^2 + J_{ac}^2 + J_{bc}^2 - J_{ab}\, J_{bc} - J_{ac}\, J_{ab} - J_{bc}\, J_{ac}]^{1/2}$$

in which

$$Q_i\,(R_i) = -\frac{(1-\Delta_i)\, D_i\, (e^{-2\alpha(R_i - R_{0i})} + 2e^{-2\alpha(R_i - R_{0i})})}{4(1+\Delta_i)}$$

$$J_i\,(R_i) = \frac{(1+\Delta_i)\, D_i\, (e^{-2\alpha(R_i - R_{0i})} - 2e^{-2\alpha(R_i - R_{0i})})}{2(1+\Delta_i)}$$

are empirical functions analogous to the Coulomb and exchange integrals of diatoms i = *a-b*, *a-c* and *b-c*, in which *a* and *b* are the two atoms of the I_2 molecule and *c* is the surface group. Here we follow the usual LEPS treatment for evaluation of the two-body Coulomb and exchange integrals assuming that the I-I and I-surface interactions can be adequately described by Morse potentials. Δ_i, D_i, R_{0i}, and α_i are the corresponding Sato parameter, dissociation energy, equilibrium distance and range parameter for the *ith*. two-body interaction. Δ_i adjusts the topology of the potential at close interaction distance(such as the high of the barrier or depth of wells), and α_i the curvature of the potential along the R_i coordinate. The parameters for the I_2 molecule are known from spectroscopical data[9] and the parameters describing the interaction of the I atom and the surface are determined by an optimization procedure from this simulation. This potential function describes correctly all asymptotic atomic configurations, the internal excitation of the I_2 molecule and its dissociation, and can be evaluated numerically.

It is known that PFPE is bound in *trans* configuration with axial -CF_3 groups[10]. A previous study of the liquid PFPE surface using reactive ion beams showed that its surface is primarily composed of fluorine atoms[3] and more recently, X-ray photoelectron spectroscopy revealed that it is mostly composed of -CF_3 chain ends oriented nearly perpendicular to the surface, suggesting that there is a high degree of order in these liquid polymer surfaces[5]. Starting from this experimental evidence we built a *model molecule* describing the surface as a diatom with a reduced mass M corresponding to the mass of the protruding group which vibrates with frequency ν_1 around an equilibrium distance b corresponding to CF_2-CF_3 bond. The constrained movement of M across the surface is assumed as the rocking vibration of the protruding group with frequency ν_2 and equilibrium distance ***a*** .The vibrational frequency ν_1, considered as the group stretching frequency, and the rocking frequency ν_2 are obtained from literature[10,11]. Thus we have a *model molecule* potential representative of the liquid surface, written as a pair of coupled harmonic oscillators which should be applicable to any liquid polymer surface that exhibits some degree of order, regardless the structure of the bulk. Figure 2 shows the liquid *model molecule* and the parameters used to describe V_{SUP}.

The above potential was used in quasi-classical trajectory calculations to determine the dynamics of the scattering process. The equations of motion are the ones derived from a Hamiltonian of 9 relative coordinates and its associated momenta. The initial conditions are the ones established in the experiment: The I_2 molecule has a translational energy of 10 and 40 kJ/mol and always strikes the surface at normal angle. It is initially in the ground vibrational and rotational state. The surface *model molecule* is considered

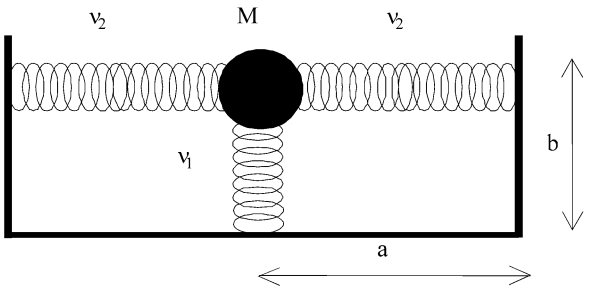

Figure 2. Model molecule representing an ordered polymer surface. M = 56.0 is the reduced mass in a.m.u, *a* = 2.0742 and *b* = 2.8932 are the equilibrium distances in a.u. and ν_1 = 850 and ν_2 = 190 are the vibrational frequencies in cm^{-1}.

also in the ground vibrational state and the remaining undefined initial coordinates for each trajectory were treated as stochastic variables and sampled randomly. The equations of motion are integrated numerically until the relative distance between the molecule and the surface is large enough so the interaction between the gas molecule and the surface vanishes.

Results

The parameters D_i, α_i, and Δ_i for the I-surface interaction potential were systematically changed until we obtained the vibrational temperature close to the one determined from the experiment for the indirect scattering of I_2 from the polymer. The vibrational energy of the scattered I_2 is very sensitive to D_i and Δ_i, that regulate the topology of the surface, (barrier and wells) and the rotational energy of the scattered I_2 is very sensitive to α_i, the potential curvature, as well known from dynamical studies in the gas phase[12]. The initial guess of D_i for the I-surface interaction was approximately the half of the I_2 dissociation energy corresponding to 0.029 a.u. D_i was changed from 0.022 to 0.036 in steps of 0.001. The choice of this interval is arbitrary but it corresponds to a set of values chemically acceptable for the energy of the I-surface bond. The initial guess of α_i was 0.99, the same of the I_2 molecule, and the interval of variation from 0.80 to 0.99 in steps of 0.01 a.u. For each pair of values of D_i and α_i, the equilibrium distance I-surface was taken as the C-I distance and kept constant as R_{0I} = 4.2028 a.u and Δ_i assumed the values 0.2, 0.4 and 0.6 in a total of 900 different set of parameters.

For each set of initial parameters, N = 2500 trajectories were calculated with a Monte Carlo standard error $\lambda = [(P_a(1 - P_a)/N]^{1/2}$ lower than 1%, where P_a, the adsorption probability, was approximated by the fraction of the trajectories in which the I_2 molecule was adsorbed by the surface. The best set of parameters obtained for D_i, α_i and Δ_i were, respectively, 0.026, 0.93 and 0.4, corresponding to a value of λ = 0.6% for P_a = 11,4%. These results are properly converged. With 1500 trajectories, we obtained λ = 0.8% and P_a = 11,0%, values only slightly different from the ones used in this work.

The experimental vibrational temperature T_{vib} of I_2 molecule scattered from PFPE surface with incident translational energy of 40 kJ/mol is 150 K in the direct inelastic scattering and 110 K in the desorption process. We determined in this work T_{vib} = 124 K and 134 K respectively for each collision regime with a maximum error of 17%. T_{vib} is determined experimentally from the integrated area of each vibrational band in the fluorescence spectra of directly scattered I_2 and of desorbed I_2. Here T_{vib} is calculated from the ratio of molecular population in vibrational states 1 and 0 for the direct collision and 2 and 1 for the trajectories that undergo multiple collisions. The two collision regimes are distinguished by a chosen collision time limit. This is an approximate method to estimate T_{vib}. The time of interaction for the direct collision is less than 1ps and for the desorption of the order of 15 ps, as can be seen in Figs. 3a and 3b, respectively.

Experiments of scattering of atoms from liquid surfaces have shown that for sufficiently high collision energies the scattering is dominated by direct collisions. We observe the same result, as illustrated in Fig. 3a where one can see a set of 10 trajectories representative of the average behavior of the process with an incident energy of 40 kJ/mol. At low incident energy (10 kJ/mol) we observe the favorable adsorption at the surface followed by desorption, after multiple collisions, as shown by a set of 10 typical trajectories at this collision energy represented in Fig. 3b. We also observed that for a given value of initial translational energy and the same set of potential parameters, a higher Δ_i implying

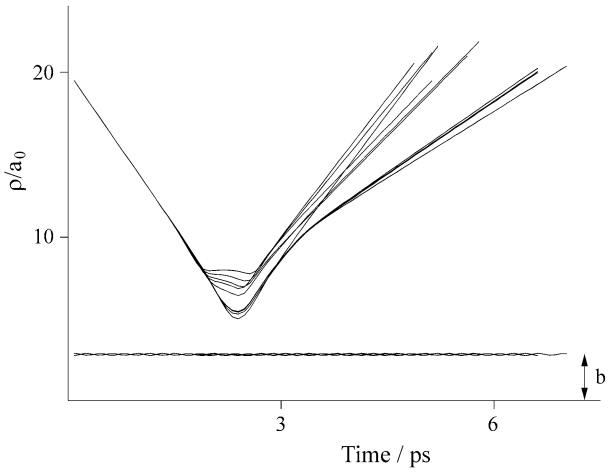

Figure 3a. Temporal evolution of the distance ρ between the surface and the center of mass of the I_2 molecule for 10 typical trajectories in the direct inellastic collision regime PFPE surface. The incident energy is 40 kJ/mol. The horizontal line represents the surface limit.

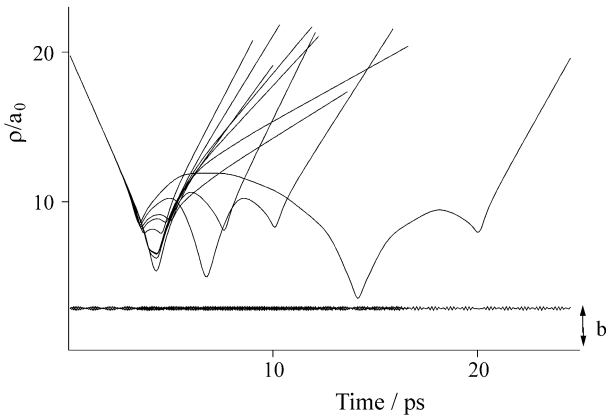

Figure 3b. Temporal evolution of the distance ρ between the surface and the center of mass of the I_2 molecule for 10 typical trajectories in the multiple collision regime for PFPE surface. The incident energy is 10 kJ/mol. The horizontal line represents the surface limit.

a higher desorption barrier, favors the occurrence of multiple collisions of gas molecules with the surface, because the potential traps the I_2 molecule at the surface.

There is a correlation between the amount of energy transferred to the surface with the vibrational frequencies ν_1 and ν_2 of the protruding groups of the liquid polymer surface. The average fraction of energy transferred to the surface in the **b** direction is smaller than in the **a** direction where the vibrational frequency is lower ($\nu_2 < \nu_1$), Fig. 2, although the available energy in the collision is large enough to excite both oscillators. Fig. 4a. illustrates the coupling of the I_2 molecule translational motion with respect to the surface and the vibrational motion of the surface model molecule, as the I_2 molecule approaches the surface for a particular trajectory. In Fig. 4b the PFPE surface vibrational coordinate, associated with the lower frequency mode ν_2, is plotted as a function of time together with the collision coordinate for a typical trajectory. We see in detail the exchange of energy between the I_2 molecule and the surface for the same trajectory showed in Fig. 4a.

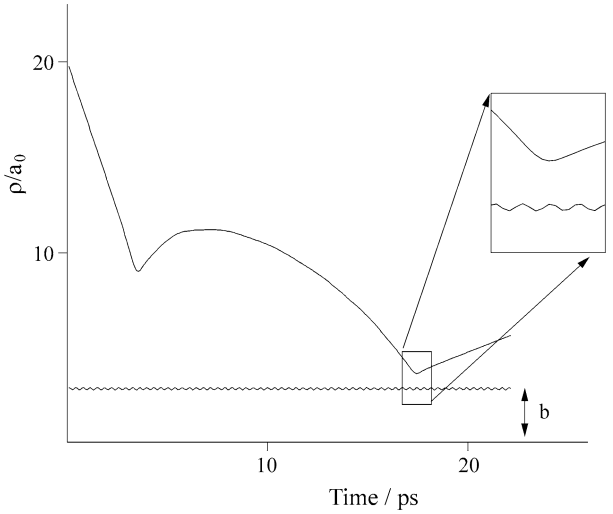

Figure 4a. a) Detailed particular trajectory in the multiple collision regime describing a trapped I_2 at PFPE surface.

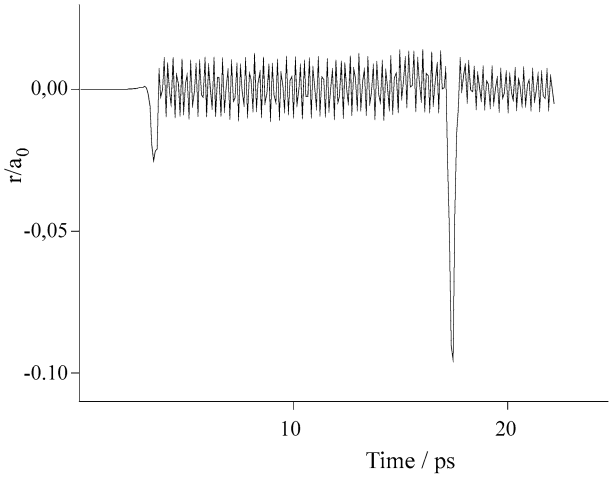

Figure 4b. Time evolution, for the same trajectory showed in Fig. 4a, of the horizontal displacement *r* across the surface of the reduced mass M of the model molecule representative of the surface. The trapped I_2 molecule perturbs the surface vibration mode of lower frequency.

Conclusions

We conclude that this diatom-surface potential function provides a reasonable semi-quantitative model for the interaction of I_2 molecule with the liquid polymer surface. The experimental results can be fitted to the model reproducing the vibrational temperature of the scattered I_2 molecule and some insight into the dynamics of the process is obtained. A comparison with experimental results obtained for scattering experiments performed with other liquids and further refinements of the surface potential employing more realistic vibrational frequencies of the polymer and accounting for the periodicity of the ordered surface are under way.

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