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Surface light-induced drift affected by chemical reactions

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Surface light-induced drift caused by backscattering from rough surfaces can be strongly affected by surface-enhanced state-specific chemical reactions. Expressions for the drift fluxes of the incident resonant-gas component and of the reaction product are presented. A resulting asymmetry in the spatial distributions of the components in a T-shaped enclosure is discussed, as a possible sensitive tool for studying the state specificity of the scattering and reaction processes.

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The study of the molecule-surface interaction and, in particular, its change with the internal state of the molecules, is of great importance both in fundamental science and in applications. A new sensitive tool for determining such changes can be provided by surface light-induced drift (SLID) [1–3], recently studied by Hermans and coworkers in a number of experiments [4–6]. A laser beam is travelling through a cell with a rarefied molecular gas, with its frequency ω slightly tuned off a molecular resonance frequency ω_0. Due to the Doppler effect, the laser excites only molecules with an x projection of their velocity near $v_0=(\omega-\omega_0)/k$ (where x is the direction of the laser beam, and k is the wave vector). Whenever the accommodation coefficient α_0 (describing the transfer of parallel momentum to the cell wall) is larger (smaller) for excited (e) molecules than for the nonexcited (g) ones, the molecules in the excited velocity group near v_0 will be attenuated by the cell walls more (less) efficiently than molecules in the opposing velocity group (around $-v_0$), thus giving rise to a net flux of gas-phase molecules.

It was recently shown [7] that the scope of physical situations in which SLID might arise can be broadened. It may persist in a rough surface, in which backscattering from the roughness facets can occur even when the scattering is *locally* completely diffusive. The magnitude of the backscattered fraction should depend on the molecular adsorptivity and the mobility of the adsorbed species [7].

Rough surfaces are known to be the site of enhanced chemical activity [8]. Moreover, the rate of surface chemical reaction can be increased several orders of magnitude by laser irradiation of the gas-phase molecules [9]. Such dramatic differences in the behavior of excited versus nonexcited molecules scattered by the surface can cause a drift of significant magnitude, when the excitation is velocity selective.

In order to provide a quantitative description, we adopt here a simple model of molecular scattering at rough surfaces proposed by Berman and Maegly [10]. It is assumed in this model that a fraction a of the incident molecules undergoes completely diffuse scattering with respect to the average plane of the surface, while the remaining fraction b undergoes direct backscattering (that is, the incident molecules constituting this direct fraction have their velocity vectors reversed at scattering). Note that in the absence of chemical reactions $a+b=1$. It is interesting that, despite its extreme simplicity, this model provides even slightly better agreement with the experimental data concerning rarefied gas flow through long capillaries than a model assuming locally diffuse scattering [11]. As an extension of the Berman-Maegley model to reactive scattering, we expect that a fraction a_g (a_e) of the incident nonexcited (excited) particles undergoes diffuse scattering without chemical reactions. Similarly, a fraction b_g (b_e) undergoes backscattering without chemical reactions. Furthermore, a fraction $a_{cg}(b_{cg})$ $[a_{ce}(b_{ce})]$ undergoes diffuse scattering [backscattering] following a chemical reaction. Finally, let A and B be the fractions of *products* of a chemical reaction which undergo diffuse scattering and backscattering, respectively, in their collisions with the surface. We assume here that (i) the reaction is not reversible, and that (ii) the products are not state selective in their behavior. Thus,

$$a_g+b_g+a_{cg}+b_{cg}=a_e+b_e+a_{ce}+b_{ce}=A+B=1\ .$$

Using this model, we get the following set of kinetic equations to describe the stationary, spatially homogeneous state of the incident molecules and of the reaction products:

$$va_e(1-\zeta)N_eW+vb_ef_e(-\mathbf{v})-vf_e(\mathbf{v})+s(\mathbf{v})-\gamma f_e(\mathbf{v})=0\ , \tag{1a}$$

$$va_gN_gW+va_e\zeta N_eW+vb_gf_g(-\mathbf{v})-vf_g(\mathbf{v})-s(\mathbf{v})+\gamma f_e(\mathbf{v})=0\ , \tag{1b}$$

$$n[va_{ce}N_eW+vb_{ce}f_e(-\mathbf{v})+va_{cg}N_gW+vb_{cg}f_g(-\mathbf{v})]+v_cAN_cW+v_cBf_c(-\mathbf{v})-v_c\mathrm{f}_c(\mathbf{v})=0\ , \tag{1c}$$

$$va_e(1-\zeta)N_eW+vb_ef_e(\mathbf{v})-vf_e(-\mathbf{v})+s(-\mathbf{v})-\gamma f_e(-\mathbf{v})=0\ , \tag{1d}$$

$$va_gN_gW+va_e\zeta N_eW+vb_gf_g(\mathbf{v})-vf_g(-\mathbf{v})-s(-\mathbf{v})+\gamma f_e(-\mathbf{v})=0\ , \tag{1e}$$

$$n[\nu a_{ce}N_e W+\nu b_{ce}f_e(\mathbf{v})+\nu a_{cg}N_g W+\nu b_{cg}f_g(\mathbf{v})] +\nu_c AN_c W+\nu_c Bf_c(\mathbf{v})-\nu_c f_c(-\mathbf{v})=0 \ . \tag{1f}$$

Equations (1a)–(1c) describe the evolution of the velocity distribution functions of the nonexcited (f_g) and excited (f_e) particles, and of the reaction products (f_c). Since each velocity group ($\mathbf{v}$) is coupled to the opposite velocity group ($-\mathbf{v}$) by backscattering, the set of equations must be complemented by Eqs. (1d)–(1f) for the opposing velocity group. In these equations, $\nu=v_t/d$ and $\nu_c=v_{ct}/d$ are the mean rates of surface scattering for resonant molecules and reaction products (c), respectively, where v_t nd v_{ct} are the mean thermal velocities of the corresponding molecules, and d is the distance between the cell walls. We consider here a rarefied (Knudsen) gas, in which molecules collide with the surface rather than with each other. It is also assumed that some fraction ξ of the diffuse collisions of excited molecules is accompanied by quenching. Also,

$$W(v)=(\alpha/\pi)^{3/2}\exp(-\alpha v^2)$$

is the equilibrium velocity distribution formed by diffusive scattering (Maxwellian) and n is a stoichiometric coefficient of the chemical reaction. Furthermore, γ is the rate of spontaneous decay of the excited state, and

$$s(\mathbf{v})=Q(\mathbf{v})[f_g(\mathbf{v})-f_e(\mathbf{v})]$$

is the velocity-selective laser excitation rate, where

$$Q(\mathbf{v})=\int d\omega\, B_0 M(\omega)\{\Gamma^2/[\Gamma^2+(\Omega-\mathbf{k}\cdot\mathbf{v})^2]\}$$

is the excitation probability per unit molecule moving with velocity $\mathbf{v}$, B_0 is the Einstein coefficient, $M(\omega)$ is the spectral intensity of the laser radiation, $\Omega=\omega-\omega_0$, and Γ is the homogeneous width of the absorption line. Finally, N_e, N_g, and N_c are the corresponding molecular concentrations.

The set of equations (1a)–(1f) was solved for the non-Maxwellian (NM) parts of the total velocity distribution $f(\mathbf{v})=f_e+f_g$ of the resonant molecules and of the distribution $f_c(\mathbf{v})$ of the reaction products, respectively, obtained by removing the symmetrical Maxwellian distribution:

$$f^{\mathrm{NM}}(\mathbf{v})=\frac{b_e-b_g}{(1-b_g^2)[\gamma+\nu(1-\varphi b_e^2)]}\left[(b_e+b_g)s+(1+b_e b_g)\hat{s}-\frac{\gamma}{\nu+\gamma}(b_e s+b_e b_g\hat{s})\right] , \tag{2a}$$

$$\begin{aligned} f_c^{\mathrm{NM}}(\mathbf{v})=&\frac{\xi}{(1-B^2)(1-b_g^2)[\gamma+\nu(1-\varphi b_e^2)]}((b_{ce}-b_{cg})(1-b_g^2)[(B+\varphi b_e)s+(1+\varphi Bb_e)\hat{s}] \\ &+(b_e-b_g)b_{cg}\{[1+\varphi b_e b_g+B(b_g+\varphi b_e)]s+[\varphi b_e+b_g+B(1+\varphi b_e b_g)]\hat{s}\}) \ . \end{aligned} \tag{2b}$$

In (2a) and 2(b) $s\equiv s(\mathbf{v})$, $\hat{s}\equiv s(-\mathbf{v})$, $\varphi\equiv\nu/(\nu+\gamma)$, and $\xi\equiv n v_t/v_{ct}$. In the derivation of Eqs. (2), we have used the obvious relationships

$$\hat{f}_{e,g,c}(s,\hat{s})=f_{e,g,c}(\hat{s},s) \quad [\hat{f}\equiv f(-\mathbf{v})]$$

between the distributions of opposite velocity groups treated as dependent on the corresponding velocity-selective excitation rates (s and $\hat{s}$). Let us note that, in accordance with the results of Refs. [10] and [11], the fraction of molecules which undergo backscattering does not usually exceed $b\sim10^{-1}$. Therefore, as one can easily see from (2a) and 2(b), the deformation of the total velocity distribution f (and in the distribution f_c of the reaction products) is determined by the absorption of radiation at the opposite velocity group ($-\mathbf{v}$), and vice versa. In order to obtain information on backscattering in the cell, one should observe the distortion formed in the opposite velocity group by means of a weak high-resolution probing beam.

The asymmetry of the velocity distributions indicates the presence of drifts of resonant and of reaction-product molecules in the mixture:

$$J\equiv\int d^3v\, v_x f^{\mathrm{NM}}(\mathbf{v})=(b_g-b_e)\frac{1-b_e-b_g+b_e b_g+\dfrac{\gamma}{\nu+\gamma}b_e(1-b_g)}{(1-b_g^2)[\gamma+\nu(1-\varphi b_e^2)]\hbar\omega}\frac{dS}{dx}v_0 \tag{3a}$$

and

$$\begin{aligned} J_c\equiv&\int d^3v v_x f_c^{\mathrm{NM}}(\mathbf{v}) \\ =&\frac{\xi}{(1-B^2)(1-b_g^2)[\gamma+\nu(1-\varphi b_e^2)]}((b_{cg}-b_{ce})(1-b_g^2)(1-B-\varphi b_e+\varphi Bb_e) \\ &+(b_e-b_g)b_{cg}\{1-B-\varphi b_e-b_g+B[b_g+\varphi b_e(1-b_g)]+\varphi b_e b_g\})(\hbar\omega)^{-1}\frac{dS}{dx}v_0 \ , \end{aligned} \tag{3b}$$

respectively. Here

$$v_0 \equiv \frac{\int d^3v\, v_x s(v)}{\int d^3v\, s(v)}$$

is the center of the excited velocity group, and $S \equiv S(x)$ is the laser-radiation power density. In order to obtain Eq. (3), the relationship

$$\int d^3v\, v_x \hat{s} = -\int d^3v\, v_x s$$

has been used. One should note that J and J_c can be nonvanishing even when $(b_g + b_{cg}) = (b_e + b_{ce})$, that is, when the total fraction of incident resonant molecules scattered in a nondiffuse way does not change upon excitation, contrary to situations studied previously (see Refs. [1] and [7]).

The magnitudes of J and J_c should yield interesting information concerning surface reactions. For example, if $J_c \neq 0$ it means that the reaction products were scattered without diffusing first over surface distances much exceeding the size of surface-roughness facets. There remains, however, the question of how to measure J and J_c experimentally. In a cell with closed ends, the flux of molecules leads to a pressure gradient in the resonant gas along the cell. In previous experiments [4–6], the magnitude of the stationary pressure drop resulting from continuous irradiation has been detected in order to calculate the value of the flux. However, in the case studied here such a simple way would be ineffective, since due to the chemical reaction one may not achieve a stationary molecular distribution. One could use a constant flux of resonant molecules injected into the cell from the lateral side, but then it would be necessary to register changes in the density gradients caused by switching on the laser light. These changes may be too small to detect on the ground of fluctuations. Perhaps, the most advantageous scheme in this case would be a T-shaped enclosure (Fig. 1) like the one previously used in experiments on bulk light-induced drift of sodium vapor immersed in helium [12]. Quite evidently, the resonant gas penetrating the tube irradiated by the laser will preferably move in the drift flux (**J**) direction. Therefore, the characteristic lengths l_1 and l_2 of the "wings" describing the resonant gas spatial distributions in the two opposing directions will differ from each other [Fig. 1(b)]. By measuring the value $l_2 - l_1$, one should be able to determine the value of J, and therefore calculate the magnitude of $(b_g - b_e)$. A similar analysis should be applicable to the determination of $(b_{cg} - b_{ce})$, by observing the spread of the reaction products.

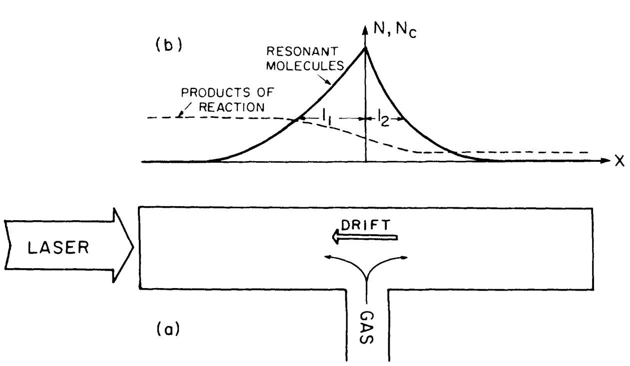

FIG. 1. (a) The form of the cell suggested for studying surface light-induced drift in the presence of surface-enhanced chemical reactions. (b) A schematic spatial distribution of the resonant molecules (solid line) and of reaction products (dashed line) along the cell.

The spatial distribution of the resonant molecules can be derived by using an equation similar to the one used in the case of velocity-selective photodissociation and photoionization [13],

$$D\frac{d^2N}{dx^2} - \frac{dJ}{dx} - cN = 0 \,, \tag{4}$$

which describes the conservation of molecule number in each layer along the x axis. In Eq. (4), $N = N_e + N_g$ is the (now inhomogeneous) concentration of resonant molecules, c is a constant describing the rate of chemical reaction, and $D \simeq v_t d$ is the diffusion coefficient for the rarefied gas. Let us suppose that the concentration near the central (entrance) point is constant, i.e., $N(x=0) = N_0$. Obviously, far from the exit N should vanish. Equation (4) will then lead to the following solution:

$$N(x) = \begin{cases} N_0 \exp(x/l_1), & x < 0 \\ N_0 \exp(-x/l_2), & x > 0 \,, \end{cases} \tag{5}$$

where $l_1^{-1} \equiv R + F$, $l_2^{-1} \equiv R - F, F \equiv V/(2D)$, and $R \equiv (c/D + F^2)^{1/2}$, while $V \equiv J/N$ is the velocity of the light-induced flux. In the derivation of this result we have made the obvious assumption that dS/dx is proportional to N, and consequently [see Eq. (3a)] V is determined by the radiative absorption rate $dq/dx \equiv N^{-1} dS/dx$ of a single molecule. From Eq. (5) it follows immediately (see also Ref. [12]) that

$$V \cong v_t \frac{d}{l_1} \frac{l_2 - l_1}{l_2} \,. \tag{6}$$

One can see from Eq. (6) that the method suggested here may lead to the experimental observation of very small drift velocities V, and therefore to the determination of small values of $(b_g - b_e)$ through the use of Eq. (3a). If, for example, $d/l_1 = 10^{-2}$, then V values as small as $10^{-3} v_t$ should lead to a comparatively large difference between the lengths of the right- and left-spreading wings in the spatial density distribution, i.e., $(l_2 - l_1)/l_2 \sim 10^{-1}$.

In order to derive an expression for a similar asymmetry in the spatial distribution of the reaction products, one can use the condition of a balance between the light-induced and the diffusion fluxes,

$$D_c dN_c/dx - J_c = 0 \,. \tag{7}$$

This would yield

$$\Delta N_c=\frac{\xi}{(1-B^2)(1-b_g^2)[\gamma+\nu(1-\varphi b_e^2)]}$$
$$\times((b_{cg}-b_{ce})(1-b_g^2)(1-B-\varphi b_e+\varphi B b_e)$$
$$+(b_e-b_g)b_{cg}\{1-B-\varphi b_e-b_g+B[b_g+\varphi b_e(1-b_g)]+\varphi b_e b_g\})(\hbar\omega)^{-1}\frac{\Delta S}{v_{ct}d}v_0\ , \tag{8}$$

where ΔN_c is the drop in the concentration of the reaction products along the cell, and ΔS is the change of the absorbed radiation power density between the edges.

One should note that the directions of the fluxes of resonant and product gas components can either coincide or oppose, depending on the respective signs of [14] $(b_{cg}-b_{ce})$ and (b_g-b_e). Both fluxes should, however, change their sign under the small change (~ 100 MHz) of laser frequency that would lead v_0 to change its sign. This fact can be used to detect the phenomenon discussed here on the background of parasitic ones.

In conclusion, we have shown here how surface light-induced drift can be affected by surface-enhanced chemical reactions. Quantitative results were obtained by using a simple model [10] of gas-surface scattering. Expressions for the drift fluxes of the resonant gas component and of the reaction products have been presented. The resulting spatial distributions of the components in a T-shaped enclosure have been discussed as a sensitive tool for studying the state specificity of the scattering and reaction processes. The state specificity here refers to resonant excitation by a single photon. Multiphoton excitations, which happen to be a common source of laser-enhanced reactivity [9], can be treated by a straightforward modification of this model in a manner suggested elsewhere [13].

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[14] As was mentioned above, typically the value of coefficients of backscattering is $b \le 0.1$. So, according to the result of Eq. (8), the value of ΔN_c is determined mainly by $(b_{cg}-b_{ce})$, not by (b_e-b_g).