Two-Photon Evanescent-Volume Wave Spectroscopy: A New Account of Gas-Solid Dynamics in the Boundary Layer

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A novel type of laser spectroscopy for the investigation of the collisional dynamics of atoms in the close vicinity of a surface has been developed. The technique utilizes excitation of the vapor atoms in two crossed laser fields, one of which is directed normally to the surface, whereas the other one excites an evanescent wave propagating along the surface. The results, obtained for sodium atoms near a dielectric prism surface, are quantitatively reproduced by a rigorous theoretical approach. This new, nonintrusive method allows one to distinguish by pure optical means between different groups of atoms and to extract their *two-dimensional* velocity distributions.

Processes running in the boundary layer at a gas-solid interface play a crucial role for a thorough understanding of surface dynamics, e.g., in the context of surface chemical reactions or momentum and heat transfer between a gas flow and a streamlined surface. Also, laser-induced interface phenomena to a great extent depend on the relaxation of excited gas molecules in the boundary layer. In all such cases one has to discriminate between the gas flux arriving at the surface and the one departing from it. This condition is easily fulfilled under molecular beam conditions. However, as the gas pressure increases, the methods developed in surface science for this purpose become inappropriate. This is the essence of the so-called "pressure gap" problem in heterogeneous catalysis. Conventional optical techniques also cannot be applied because the signal from the boundary layer is negligible as compared to the one from the gas volume.

An attractive new tool for such studies is evanescent waves (EW's) which propagate along the gas-solid interface [1,2]. They can be excited in total internal reflection at a transparent dielectric surface. On a metal or a semiconductor surface such waves can exist as surface polaritons [3]. Another case where the signal arises from the gas atoms in the vicinity of the surface is selective reflection at near normal incidence [4–6]. In both cases the optical response of the gas is essentially transient since the atoms which have undergone collisions with the surface contribute strongly to the spectrum [7–9]. An extension of this technique to cascade three-level atomic systems allows one to observe a new type of reflection resonance associated with atoms desorbing from the surface. Hence the one-dimensional velocity distribution of the atoms along the normal to the surface can be monitored [10,11]. The transient contribution of the atoms desorbed from the surface can be even dominant when one observes fluorescence in the EW field [12]. A two-photon fluorescence spectrum excited by two counterpropagating EW's then is very sensitive to the velocity distribution function of the atoms

leaving the surface. This made it recently possible to confirm Knudsen's cosine law for surface desorption by spectroscopic means [13].

An advantageous feature of the EW is that its penetration depth into the gas is of the order of the wavelength of the exciting wave and thus can be easily made smaller than the mean free path of the atoms in the gas even for relatively high gas pressures. On the other hand, if one excites the gas by a wave traveling normally to the interface (i.e., a volume wave), a spectral distinction between gas atoms moving to the surface and those which move away from the surface becomes possible. Combining now an evanescent and a volume wave in a two-photon excitation scheme one can spectrally distinguish between the contributions of atoms just before they collide with the surface and just after they leave it. The Doppler-broadened two-photon line shape then will contain comprehensive information about the dynamics of the atoms interacting with the surface. Namely, it will directly provide the *two-dimensional* velocity distribution functions of different groups of atoms. In the present work we experimentally realize this idea and theoretically analyze the results for the first time for a model system, sodium (Na) vapor near a glass surface.

The experimental setup consists of a truncated glass prism, mounted on a heatable and coolable manipulator in an ultrahigh vacuum chamber, as well as two frequency tunable, single mode ring dye lasers with a linewidth of 3 MHz. The evanescent wave is excited at the glass prism surface at an angle in the vicinity of the critical angle for total internal reflection, whereas the volume wave propagates perpendicularly to the prism surface via the truncated apex of the prism towards the vacuum side [14]. One of the waves (from laser 1) is resonant to the $3S_{1/2} \leftarrow 3P_{3/2}$ Na atomic transition and the other one (from laser 2) is resonant to the $3P_{3/2} \leftarrow 5S_{1/2}$ transition. We have investigated two configurations: (i) laser 1 excites a volume wave and laser 2 excites an EW (the so-called "normal configuration") [Fig. 1(a)] and (ii) the character of the waves is
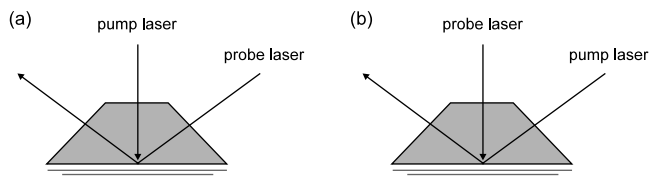
FIG. 1. Geometry of the experimental setup: the "normal" (a) and the "inverse" (b) configurations.

exchanged (the "inverse configuration") [Fig. 1(b)]. In both cases the frequency of laser 1 is fixed whereas the frequency of laser 2 is scanned across the resonance with the upper transition. The flux of sodium atoms reaches the prism surface at an angle $\theta_0 = 55 \pm 5°$ with respect to the surface normal. The flux is directed in the plane of incidence of the laser beam exciting the EW along its propagation direction. It determines the velocity distribution function of the atoms arriving at the surface. Representative two-photon fluorescence spectra obtained in the normal configuration are shown in Fig. 2. For negative detunings of laser 1 from the resonance with the lower transition $[3S_{1/2}(F = 2) \leftarrow 3P_{3/2}]$ besides the Doppler-broadened line a narrow peak is observed, which is situated at the right wing of the broad line. The position of this latter peak changes when the detuning of laser 1 varies. For positive detunings the intensity of the narrow peak significantly decreases. In the inverse configuration (Fig. 3) a similar narrow peak can be seen for positive detunings of laser 1, but this time it is located at the left wing of the Doppler-broadened line. For negative detunings the peak disappears. In this configuration the broad line is split into two components. The separation between the two maxima does not depend on either the detuning or the laser intensities.

Let us choose the x axis to be along the EW wave vector and the z axis to be along the normal to the surface towards the vacuum side. Then the two-photon resonance conditions allow one to identify contributions of different groups of atoms specified by the signs of the velocity components v_x and v_z or, in other words, by a quadrant in the plane (v_x, v_z). Based on these conditions we can identify the narrow line in the fluorescence spectra as a contribution of the atoms emanating from the source. A plot of the position of this peak as a function of the detuning Δ_1 of laser 1 with respect to the lower transition frequency results in a linear dependence with a slope corresponding to an angle of 53°. This value agrees within error bars with the measured value for the angle between the axis of the atomic flux and the surface normal. The slight difference means that the spot on the prism surface illuminated by the lasers does not exactly coincide with the maximum flux intensity. In the inverse configuration, for negative detunings of laser 1, the narrow peak disappears because the resonance condition for the lower transition is fulfilled only for atoms with $v_x < 0$, whereas the atoms from the source obey $v_x > 0$. However, on the left wing of the fluorescence line a broad contribution is observed which arises
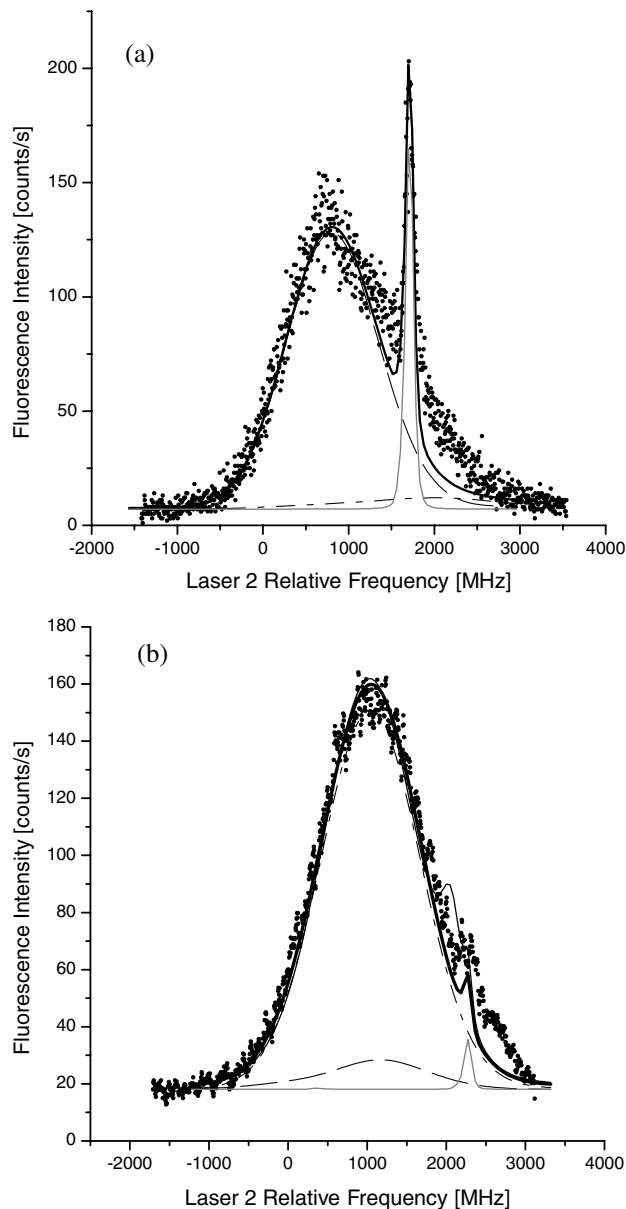

FIG. 2. Two-photon fluorescence spectra observed in the "normal configuration" (dots). Laser 1 power $P_1 = 15$ mW, laser 2 power $P_2 = 15$ mW, and $\Delta_1 = -800$ MHz, surface temperature $T = 396$ K (a); $\Delta_1 = 800$ MHz, $T = 399$ K (b). The fits are obtained for a Rabi frequency for the lower transition $\Omega_1/(2\pi) = 90.5$ MHz and for an EW penetration depth $\delta = 196 \mu$m. The contributions of different groups of atoms are shown separately: atoms flying directly from the dispenser (gray line), atoms scattered before the surface (dashed line), and atoms desorbed from the surface (dash-dotted line). In (b) two calculated spectra are presented: for the sticking probability $s = 1$ (thick solid line) and for $s = 0.5$ (thin solid line).

also from atoms moving to the surface. This observation reveals that the atoms emitted by the source have undergone collisions with each other before they reach the surface. We have confirmed this conclusion by a measurement of the one-photon fluorescence spectrum of the atomic flux from the source in a cell in the direction perpendicular to the flux. Note also that the mean free path of sodium atoms from the source is about 4 cm, i.e., comparable to
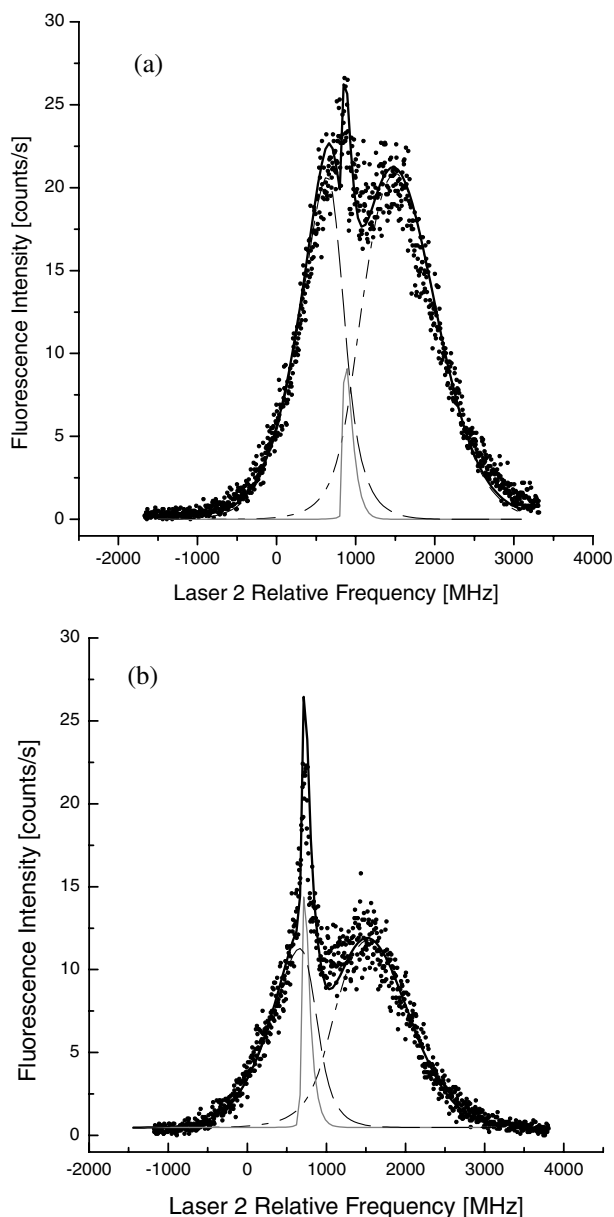
FIG. 3.   Two-photon fluorescence spectra observed in the "inverse configuration" (dots) at $P_1 = 53$ mW, $P_2 = 15$ mW, and $T = 407$ K: $\Delta_1 = 0$ MHz (a); 200 MHz (b). The fits (solid lines) are obtained for $\Omega_1/(2\pi) = 275$ MHz, $\delta = 196\ \mu$m, $\pi_{ii} = 1$, and $\pi_{ei} = 0.01$. The other notations are as in Fig. 1.

the distance between the source and the surface, which is 3 cm. Thus we can specify four different groups of atoms, which contribute to the two-photon spectra: those, which emanate from the source, those, which undergo collisions before the surface, those, which are diffusely and those which are specularly scattered by the surface.

Let us now perform a quantitative analysis of the data by applying a rigorous theory of two-photon fluorescence in crossed evanescent and volume waves [15]. We shall consider the functions π_{ii} and π_{ei} (see [13]), which determine the effective power broadening and Stark splitting in an EW field, and the penetration depth of the EW, δ, as fitting parameters.

An important output of the following quantitative comparison between theory and experiment is two-dimensional velocity distribution functions of the atoms close to the surface. Extensive measurements and calculations have led to the following choice of distribution functions: For the contribution of atoms from the source without collisional interactions and for specularly scattered atoms we use a velocity distribution function which has been confirmed by one-photon fluorescence spectra measured in a cell in the directions along the flux and perpendicular to it [15]. It can be represented as

$$f_d(v) = \frac{1}{C} \frac{v^2 \cos(\theta - \theta_0)}{v^2 \sin^2(\theta - \theta_0) + w^2}$$
$$\times \exp\left[-\frac{v^2 \cos^2(\theta - \theta_0)}{v_d^2}\right],$$

where C is a normalization constant, $\theta = 53°$, $w = 1.1 \times 10^4$ cm/s is a width along the normal to the flux axis, and $v_d = 8.0 \times 10^4$ cm/s is the most probable velocity determined by the temperature of the dispenser, $T_d = 900$ K. For the contribution of the atoms emanating from the source but scattered in front of the surface we use a Maxwellian distribution function with an effective temperature T_{ds} as a fitting parameter. Finally, the velocity distribution function of the atoms diffusively scattered from the surface is supposed to obey Knudsen's cosine law and can be written as follows:

$$f(v_x, v_z) = \frac{2}{\sqrt{\pi}\, v_T^3}\, v_z \exp\left(-\frac{v_x^2 + v_z^2}{v_T^2}\right)$$

with v_T the most probable velocity determined by the surface temperature T. We have considered only the reduced distribution functions which do not depend on the v_y component because the integration over v_y gives a factor of unity due to the planar geometry of the vapor excitation.

The results of numerical calculations and the relevant values of the parameters are shown in Figs. 2 and 3. First, a fit was obtained for a single spectrum in the inverse configuration [Fig. 3(a)]. The other plots were obtained using the detuning of laser 1 given by the measurement and keeping all other parameters constant. For the calculation of the spectrum in the normal configuration (Fig. 2) we have used the same values of the parameters, except a change of the intensity of laser 1 which differs between evanescent and volume wave. The extraordinarily good agreement between theory and measurement confirms that all contributions have been properly identified. The fit for the inverse configuration gives the effective temperature of the ensemble of atoms emanating from the source which have been scattered after collisions with each other, $T_{ds} = 260$ K. In this configuration one scans the velocity distribution along the normal to the surface. Therefore the calculated value of T_{ds} should be associated with the cross section of the velocity distribution in two dimensions by the plane $v_x = $ const. Another cross section by the plane $v_z = $ const is obtained in the normal configuration. For

negative detunings of laser 1 [Fig. 2(a)] the fluorescence spectrum arises from the atoms arriving at the surface. The broad fluorescence line is asymmetric: the right wing originates from the contribution of the atoms with $v_x > 0$ and is broader than the left wing, which originates from the atoms with $v_x < 0$. There is a slight discrepancy between theoretical and experimental data at the right wing of the fluorescence line, which can be attributed to a broader velocity distribution for $v_x > 0$ compared to that for $v_x < 0$. This conclusion is quite reasonable. Since the distance between the source and the surface is comparable with the mean free path the velocity distribution of the atoms scattered by collisions with each other is essentially nonequilibrium. Hence it cannot be described by a Maxwellian distribution function. The velocities rather have some preferable direction along the initial atomic flux. The same reason causes the slight discrepancy between theory and experiment for the case of large positive detunings [Fig. 2(b)]. Here the frequency of laser 1 is somewhere in between the energetic positions of the two hyperfine sublevels of the ground state $3S_{1/2}$. This means that for the upper sublevel the detuning is positive, whereas for the lower one it is negative. Hence both arriving and departing atoms contribute to the spectrum.

A remarkable feature of the fluorescence spectra is that they are qualitatively different in the normal as compared to the inverse configurations: the broad line in the former case has a single maximum, whereas in the latter case it is double peaked. The reason for this variation is the factor v_z in the velocity distribution function of the atoms desorbing from the surface which expresses Knudsen's cosine law. In the normal configuration the velocity distribution is scanned along the surface and this factor does not influence the spectrum. In the inverse configuration one follows the velocity distribution in the direction perpendicular to the surface and this leads to a dip in the spectrum arising from small v_z.

We have assumed throughout that the atoms arriving at the surface stick on it with probability unity. If this probability is smaller than unity, then one could observe a narrow line whose spectral position can be undoubtedly identified in the normal configuration with positive detuning [Fig. 2(b)]. From the present data we conclude that the sticking probability for Na atoms at a glass surface is practically 1 even at slightly elevated surface temperatures (407 K).

In conclusion, we have investigated the two-photon fluorescence spectra of Na vapor in the close vicinity of a dielectric surface. The atomic vapor was in thermodynamical nonequilibrium: the atoms desorbed from the surface could be characterized by Knudsen's cosine law, i.e., were in equilibrium with the surface temperature; the velocity distribution of the atoms arriving at the surface were dictated by the sodium source. Using our spectroscopic technique we were able to distinguish between the contributions from different groups of atoms and to derive de-

tails of their velocity distributions both normally to and along the surface. Hence such a technique opens up the unique opportunity to reconstruct the velocity distributions of atomic fluxes approaching to and departing from the surface in the boundary layer of a gas. Once these distributions are known, important quantities characterizing a gas-solid interface can be calculated: the scattering kernel and various accommodation coefficients [16]. Another application of this technique is found in surface chemistry. Since the contributions of gas species moving to the surface and apart from it have different spectral signatures one can extract the probability for a gas molecule to enter a reactive channel at the surface just by measuring the intensity ratio of the relevant fluorescence lines [17]. By the same token, the technique also provides a spectroscopic tool for studying elastic and inelastic gas scattering from surfaces under high gas pressure conditions.

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