Determination of the gas-surface scattering kernel from two-photon evanescent-volume-wave fluorescence spectra

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The gas-surface scattering kernel for Na atoms interacting with a dielectric surface is obtained by measuring and theoretically reproducing two-photon evanescent-volume-wave spectra. From a detailed analysis of the spectral line shapes the contribution of inelastically scattered atoms is identified and a mean energy transfer of 36 meV is deduced for atoms having initial mean thermal energies of 79 meV. The mean probability of direct scattering mediated by surface phonons increases from 0.03 to 0.05 by increasing the surface temperature from 386 K to 398 K.

I. INTRODUCTION

The scattering kernel represents a fundamental quantity in gas-surface interactions. It summarizes the basic information on gas-surface scattering. Further reduction to a small set of accommodation coefficients leads to "lack of clarity, misinterpretation of experiments, bad definitions of terms, and misunderstanding of concepts" [1]. The computation of the scattering kernel from a physical model of the surface requires a rather detailed knowledge of the interaction between gas particle and surface. Thus in trying to do so one faces usually numerous problems. An alternative and rather artificial way is to construct a mathematical model in the form of a kernel that satisfies the basic physical properties and is not otherwise restricted except by the condition of not being too complicated. The only source of experimental data on this quantity are beam scattering experiments. Such experiments are restricted in application by the boundary condition that they can be carried out only under-ultra-high vacuum conditions.

Recently, a novel approach to this problem has been provided by laser spectroscopy of the gas boundary layer [2,3]. Excitation of gas fluorescence by crossed electromagnetic waves, one of which is evanescent and propagates along the surface and the other one is volume and is directed normally to the surface, enables one to separate spectrally the contribution of atoms arriving at the surface from that of the atoms scattered by it. Being determined by the Doppler broadening, the spectral line shapes provide the velocity distribution functions of both groups of atoms. It is the scattering kernel that relates the velocity distribution function of the scattered atoms to that of the arriving atoms.

In the present paper we have investigated a model system consisting of sodium vapor atoms in the close vicinity of a glass prism surface. The atomic transition $3S_{1/2} \leftarrow 3P_{3/2}$ was excited by a laser beam traveling along the normal to the surface whereas the adjacent transition $3P_{3/2} \leftarrow 5S_{1/2}$ was scanned by the evanescent wave at the prism surface. Basing on a detailed analysis of the resulting fluorescence line shapes we have determined the parameters of the scattering kernel for such a system.

II. GAS-SURFACE SCATTERING KERNEL

Taken as a steady-state problem the gas-surface scattering kernel $R(\mathbf{v} \rightarrow \mathbf{v}')$ is the probability density that an atom striking the surface with velocity between $\mathbf{v}$ and $\mathbf{v}+d\mathbf{v}$ will reemerge at practically the same point with velocity between $\mathbf{v}'$ and $\mathbf{v}'+d\mathbf{v}'$ [4,1]. The function $R(\mathbf{v} \rightarrow \mathbf{v}')$ is normalized by the condition

$$\int_{v_z'>0} R(\mathbf{v} \rightarrow \mathbf{v}') d\mathbf{v}' = 1, \tag{1}$$

where we have chosen the z axis along the normal to the surface towards the gas. The scattering kernel determines the boundary condition for the velocity distribution function $f(\mathbf{v})$ of the gas atoms as follows:

$$f^+(\mathbf{v}') v_z' = \int R(\mathbf{v} \rightarrow \mathbf{v}') f^-(\mathbf{v}) |v_z| d\mathbf{v}, \tag{2}$$

where the superscripts "$-$" and "$+$" denote the atoms arriving at the surface for which $v_z < 0$ and the atoms scattered by the surface for which $v_z > 0$, respectively. In thermodynamic equilibrium between the gas and the surface both groups of atoms have a Maxwellian distribution function f_M and hence the function $R(\mathbf{v} \rightarrow \mathbf{v}')$ must satisfy the equality

$$f_M(\mathbf{v}') v_z' = \int_{v_z<0} R(\mathbf{v} \rightarrow \mathbf{v}') f_M(\mathbf{v}) |v_z| d\mathbf{v} \tag{3}$$

with $v_z' > 0$.

A simple model for gas-surface scattering proposed by Maxwell corresponds to the kernel

$$R(\mathbf{v} \rightarrow \mathbf{v}') = S v_z' f_M(\mathbf{v}') + (1-S)\delta(\mathbf{v}_\parallel' - \mathbf{v}_\parallel)\delta(v_z' + v_z), \tag{4}$$

where $\mathbf{v}_\parallel$ is the projection of the vector $\mathbf{v}$ onto the surface plane and $\delta(x)$ is Dirac's delta function. The model implies that a fraction S of atoms striking the surface gets adsorbed on it and then desorbs having a Maxwellian velocity distribution dictated by the surface temperature. The remaining fraction $(1-S)$ undergoes a reflection in the specular direc-

tion (directly scattered fraction). To satisfy the condition (1) the Maxwellian f_M should be normalized to a unit probability flux from the surface,

$$\int_{v'_z > 0} v'_z f_M(\mathbf{v}') d\mathbf{v}' = 1, \tag{5}$$

and have the form

$$f_M(\mathbf{v}) = \frac{2}{\pi v_T^4} \exp\left(-\frac{v^2}{v_T^2}\right), \tag{6}$$

with v_T the most probable velocity determined by the surface temperature.

Based on more general grounds, the reflection from the surface can also be mediated by substrate phonons. This results in a broadening of the angular distribution of the reflected atoms [5]. According to the different scattering mechanisms we shall divide the scattering kernel in two parts,

$$R(\mathbf{v} \to \mathbf{v}') = R_{des}(\mathbf{v} \to \mathbf{v}') + R_{dir}(\mathbf{v} \to \mathbf{v}'), \tag{7}$$

where the kernel

$$R_{des}(\mathbf{v} \to \mathbf{v}') = S v'_z f_M(\mathbf{v}') \tag{8}$$

corresponds to desorption following trapping at the surface and the kernel $R_{dir}(\mathbf{v} \to \mathbf{v}')$ describes direct scattering. The latter quantity can be expressed in terms of the probability $N(\epsilon, \mathbf{Q})$ that the state of the substrate phonon system after scattering differs from its initial state by energy ϵ and momentum $\mathbf{Q}$ related to the velocities $\mathbf{v}$ and $\mathbf{v}'$ by the conservation laws

$$m\mathbf{v}'_\parallel = m\mathbf{v}_\parallel + \mathbf{Q}, \tag{9}$$

$$\frac{m}{2} v'^2 = \frac{m}{2} v^2 + \epsilon. \tag{10}$$

Here, m is the mass of an atom and it is assumed that energy and momentum transfer during scattering occurs via the surface (Rayleigh) phonons.

In the trajectory approximation assuming a classical motion of the scattering atom the probability $N(\epsilon, \mathbf{Q})$ is represented as a product of two Gaussians in energy and momentum separately [6],

$$N(\epsilon, \mathbf{Q}) = N(\epsilon) N(\mathbf{Q}), \tag{11}$$

where

$$N(\epsilon) = \frac{1}{\sqrt{\pi} \Delta \epsilon} \exp\left[-\frac{(\epsilon - \delta)^2}{\Delta \epsilon^2}\right], \tag{12}$$

$$N(\mathbf{Q}) = \frac{1}{\pi \Delta K^2} \exp\left[-\frac{Q^2}{\Delta K^2}\right], \tag{13}$$

with $\Delta \epsilon = 2\sqrt{k_B T \delta}$, $\Delta K = \Delta \epsilon / (\sqrt{2} v_R)$. Here, k_B is Boltzmann's constant, T is the surface temperature, v_R is the Rayleigh mode velocity, and δ is the mean energy transfer independent of surface temperature that can be considered as an empirical parameter. The probability $N(\epsilon, \mathbf{Q})$ describes both the direct and the trapping-desorption channels and is normalized to unity,

$$\int_{-\infty}^{\infty} \int N(\epsilon, \mathbf{Q}) d\epsilon d\mathbf{Q} = 1. \tag{14}$$

The results (11)–(13) correspond to the multiphonon scattering of atomic particles at surfaces and can also be obtained from a rigorous quantum-mechanical treatment in the semiclassical limit [7]. The knowledge of the function $N(\epsilon, \mathbf{Q})$ in principle allows one to calculate the sticking probability S. However, this would involve solving the master equation for the transitions between the adatom states [6]. Instead of that we shall consider this quantity as an empirical parameter. In such a case the direct scattering kernel has the form

$$R_{dir}(\mathbf{v} \to \mathbf{v}') = C(1 - S) N(\epsilon, \mathbf{Q}), \tag{15}$$

where ϵ and $\mathbf{Q}$ are related to $\mathbf{v}$ and $\mathbf{v}'$ by means of Eqs. (9) and (10) and ϵ is restricted by the condition that v'_z is real. As it follows from Eqs. (1), (5), and (8) the integral on the right-hand side of Eq. (15) over the range corresponding to the direct scattering should equal $1 - S$. This provides the value of the normalization constant C. Finally, one gets

$$R_{dir}(\mathbf{v} \to \mathbf{v}') = 2(1 - S)\left[\pi^{3/2} \text{erfc}\left(\frac{\delta}{\Delta \epsilon}\right) \Delta \epsilon \Delta K^2\right]^{-1}$$

$$\times m^3 v'_z \exp\left[-\frac{m^2 |\mathbf{v}'_\parallel - \mathbf{v}_\parallel|^2}{\Delta K^2}\right]$$

$$\times \exp\left\{-\frac{1}{\Delta \epsilon^2}\left[\frac{m}{2}(v'^2 - v^2) - \delta\right]^2\right\}, \tag{16}$$

where $\text{erfc}(x)$ is the complementary error integral [8] and we have taken into account the Jacobian of the transformation from the variables $\{\epsilon, \mathbf{Q}\}$ to $\{\mathbf{v}'\}$. Also, we have assumed that the mean kinetic energy of the atoms striking the surface is much less than the atom-surface-potential well depth. Given that the potential-well depth between Na atoms and a glass surface is about 0.8 eV, this condition is well fulfilled for the present experiments.

III. LASER SPECTROSCOPY OF THE GAS BOUNDARY LAYER

The velocity distribution functions f^- and f^+ introduced in the preceding section are directly related to the fluorescence line shapes obtained via excitation of the gas near the surface by crossed evanescent and volume waves resonant to adjacent atomic transitions [2,3]. The theory of fluorescence spectra in such a system has been considered in detail [3] and here we shall review it only briefly. Let us assume that the volume wave (wave 1) is resonant with the transition be-
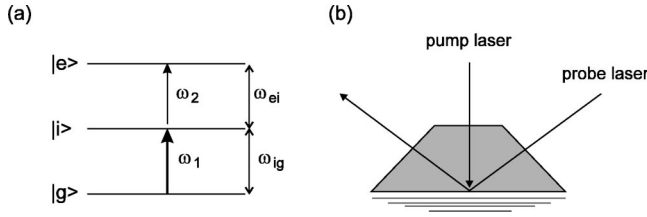
FIG. 1. (a) The excitation scheme of the atomic levels. (b) Truncated prism and configuration of laser beams.

tween the ground atomic state $|g\rangle$ and the intermediate excited state $|i\rangle$, whereas the evanescent wave (wave 2) scans the transition between the state $|i\rangle$ and the upper excited state $|e\rangle$ [Fig. 1(a)]. Assume also that the penetration depth of the evanescent wave into the gas is much less than the mean-free path of gas atoms so that within the excitation region the interatomic collisions can be neglected. The intensity of fluorescence from the upper state $|e\rangle$ is determined by the sum of the contributions from the atoms arriving at and departing from the surface,

$$I = I^- + I^+, \qquad (17)$$

where

$$I^\pm \propto \int f^\pm(\mathbf{v}) \hat{\sigma}_{ee}^\pm(0,\mathbf{v}) d\mathbf{v} \qquad (18)$$

with $\hat{\sigma}(p,\mathbf{v})$ the Laplace transformation of the atomic density matrix [9]. The latter quantity can be found by solving the optical Bloch equations with the boundary conditions set separately for the arriving and departing atoms. The result takes the most simple and transparent form when saturation at both transitions is negligible. In such a case,

$$\hat{\sigma}_{ee}^\pm(0,\mathbf{v}) = \frac{\pi^2}{16} \delta_p \frac{\Omega_1^2 \Omega_2^2}{\gamma_i \gamma_e} \delta(\omega_1 - k_1 v_z - \omega_{ig})$$
$$\times \delta(\omega_2 - k_2 v_x - \omega_{ei}), \qquad (19)$$

where δ_p is the penetration depth of the evanescent wave into the gas, $\delta(x)$ is the Dirac delta function, Ω_1 and Ω_2 are the Rabi frequencies associated with the corresponding waves, ω_1 and ω_2 are the frequencies of wave 1 and wave 2, ω_{ig} and ω_{ei} are the frequencies of the corresponding transitions, γ_i and γ_e are the relaxation rates of the states $|i\rangle$ and $|e\rangle$, $\mathbf{k}_1$ is the wave vector of the volume wave directed along the z axis, and $\mathbf{k}_2$ is the wave vector of the evanescent wave directed along the x axis. The two δ functions in Eq. (19) express the fact that only those atoms which are in resonance simultaneously with two transitions get excited and fluoresce. Substituting Eq. (19) in Eq. (18) we get

$$I^- \propto \tilde{f}^- \left(\frac{\Delta_2}{k_2}, \frac{\Delta_1}{k_1} \right) [1 - \Theta(\Delta_1)], \qquad (20)$$

$$I^+ \propto \tilde{f}^+ \left(\frac{\Delta_2}{k_2}, \frac{\Delta_1}{k_1} \right) \Theta(\Delta_1), \qquad (21)$$

where $\Delta_1 = \omega_1 - \omega_{ig}$ and $\Delta_2 = \omega_2 - \omega_{ei}$ are the detunings of the transitions, $\Theta(x)$ is the unit step function, and we have introduced the velocity distribution functions reduced to the plane (v_x, v_z),

$$\tilde{f}^\pm(v_x, v_z) = \int_{-\infty}^{\infty} f^\pm(v_x, v_y, v_z) dv_y. \qquad (22)$$

The Θ functions in Eqs. (20) and (21) arise from the fact that for negative detunings Δ_1 only the atoms moving to the surface are in resonance with the volume wave, whereas for positive Δ_1 only the atoms moving from the surface are resonantly excited.

Let us assume that the velocity distribution function of the atoms approaching the surface can be factorized into two independent distributions with respect to (v_x, v_z) and v_y [10], namely,

$$f^-(\mathbf{v}) = \tilde{f}^-(v_x, v_z) f_y^-(v_y). \qquad (23)$$

In such a case, as it follows from Eq. (2),

$$\tilde{f}^+ \left(\frac{\Delta_2'}{k_2}, \frac{\Delta_1'}{k_1} \right) = \int \int \tilde{R} \left(v_x, v_z \to \frac{\Delta_2'}{k_2}, \frac{\Delta_1'}{k_1} \right)$$
$$\times \tilde{f}^-(v_x, v_z) |v_z| dv_x dv_z, \qquad (24)$$

or, changing the integration over velocities to the integration over frequencies,

$$\tilde{f}^+ \left(\frac{\Delta_2'}{k_2}, \frac{\Delta_1'}{k_1} \right) = \frac{1}{k_1^2 k_2} \int \int \tilde{R} \left(\frac{\Delta_2}{k_2}, \frac{\Delta_1}{k_1} \to \frac{\Delta_2'}{k_2}, \frac{\Delta_1'}{k_1} \right)$$
$$\times \tilde{f}^- \left(\frac{\Delta_2}{k_2}, \frac{\Delta_1}{k_1} \right) |\Delta_1| d\Delta_1 d\Delta_2, \qquad (25)$$

where

$$\tilde{R}(v_x, v_z \to v_x', v_z') = \int \int R(\mathbf{v} \to \mathbf{v}') f_y^-(v_y) dv_y dv_y' \qquad (26)$$

is the scattering kernel reduced to the plane (v_x, v_z). Now from Eqs. (20) and (21) one can conclude that the fluorescence line shape obtained for $\Delta_1 > 0$ and that obtained for different $\Delta_1 < 0$ are related by means of the reduced scattering kernel $\tilde{R}$.

In the following, basing on the experimental results on two-photon fluorescence in a model gas-surface system we shall determine the parameters of the scattering kernel in the framework of the physical model described above.

IV. EXPERIMENTAL SETUP

The experimental setup is shown in Fig. 1(b). A truncated glass prism is mounted on a manipulator in a high-vacuum ($p_0 \leq 10^{-8}$ mbar) chamber. It is heated resistively to fixed values of 371 K, 386 K, and 398 K, respectively. The light of two-frequency tunable, single mode ring dye lasers is transferred into the apparatus via glass windows and optical fi-
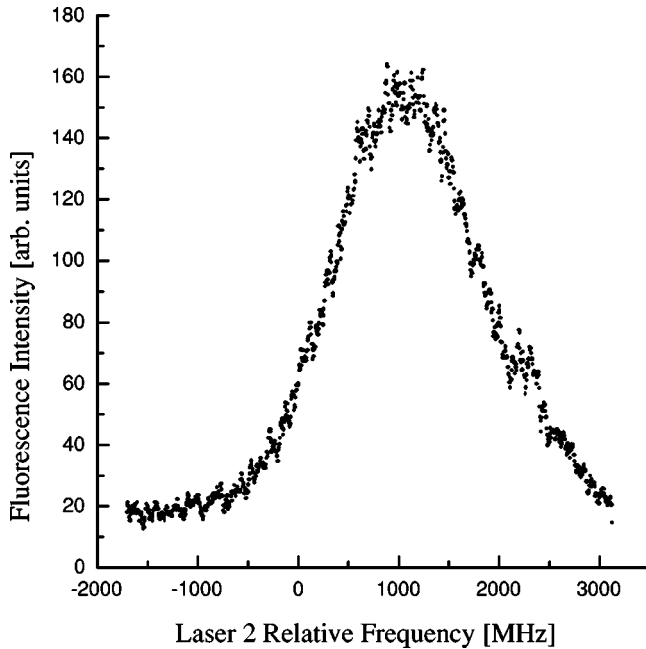
FIG. 2. Two-photon fluorescence spectrum observed at Δ_1 $=800$ MHz, $T=398$ K.
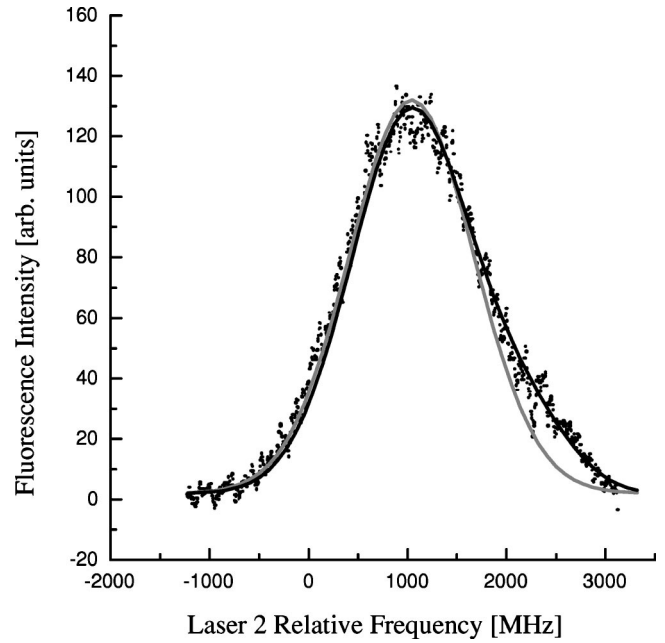

FIG. 3. The net contribution from the atoms scattered by the surface (dots). It has been obtained by means of subtracting the calculated contribution from the atoms approaching the surface from the spectrum in Fig. 2. (See Ref. [3] for details.) The calculated spectrum of the desorbed atoms and the best fit obtained for $\eta=0.05$ are shown by the gray and black lines, respectively.

bers. The total linewidth of both lasers is about 3 MHz with a measured drift of far less than 90 MHz during a typical wavelength scan. The diameters of the laser beams are 0.5 mm (laser 1) and 2 mm (laser 2), respectively, and laser powers of 15 mW each are used.

An evanescent wave is excited by laser 2 at the glass prism surface at an angle in the vicinity of the critical angle for total internal reflection. Laser 1 generates a volume wave, which propagates perpendicularly to the prism surface via the truncated apex of the prism towards the vacuum side. While laser 1 is resonant to the $3S_{1/2}\leftarrow 3P_{3/2}$ Na atomic transition ($16\,973.33$ cm^{-1}), laser 2 is scanned around the $3P_{3/2}\leftarrow 5S_{1/2}$ resonance transition. The starting frequency ("0" on the frequency axis in Figs. 2–9) corresponds to $16\,227.2741$ cm^{-1}, as determined by an iodine absorption cell. The blue shifted fluorescence light from the $4P_{1/2,3/2}$ $\rightarrow 3S_{1/2}$ transitions ($30\,267.28$ cm^{-1} and $30\,272.88$ cm^{-1}) is observed as a measure of the excitation probability by a photomultiplier and photon counting electronics.

A flux of about 5×10^{15} sodium atoms per second from a Na dispenser (SAES getters) 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 evanescent wave along its propagation direction. It determines the velocity distribution function of the atoms arriving at the surface.

V. RESULTS AND DISCUSSION

The fluorescence spectra obtained for two positive values of the detuning Δ_1 upon scanning the detuning Δ_2 at different surface temperatures are shown in Figs. 2–7. As noted above, such spectra should arise from the atoms departing from the surface. In order to analyze them we have calcu-

lated the contribution from the desorbed atoms corresponding to the relevant surface temperature. The calculations were carried out using the rigorous theory developed in Ref. [3] and taking into account the optical pumping to the other hyperfine sublevel of the ground state, $3S_{1/2}(F=1)$ [11].
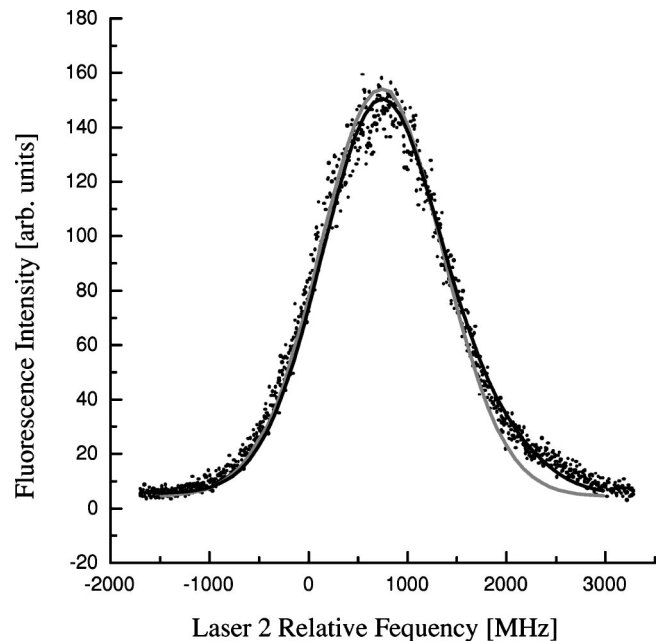

FIG. 4. Two-photon fluorescence spectrum observed at Δ_1 $=800$ MHz, $T=386$ K (dots). The other notations are as in Fig. 3. The best fit corresponds to $\eta=0.03$.
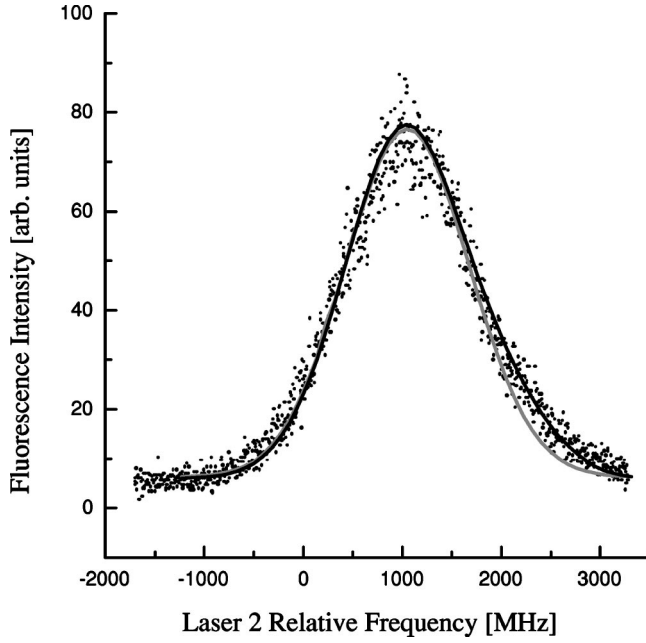
FIG. 5. Same as Fig. 4, but for $\Delta_1 = 600$ MHz, $T = 398$ K. The best fit corresponds to $\eta = 0.05$.

One observes a clear discrepancy between the measured and the calculated spectra (gray curves) at the right wings in Figs. 3–5. This difference has to be attributed to the atoms which were scattered without being trapped at the surface, i.e., via a direct scattering channel. In Figs. 6 and 7 no remarkable difference is seen: in that cases the contribution of the directly scattered atoms is negligible. For further analysis we have subtracted the calculated contributions of the desorbed atoms from the measured signals in Figs. 3–5. The
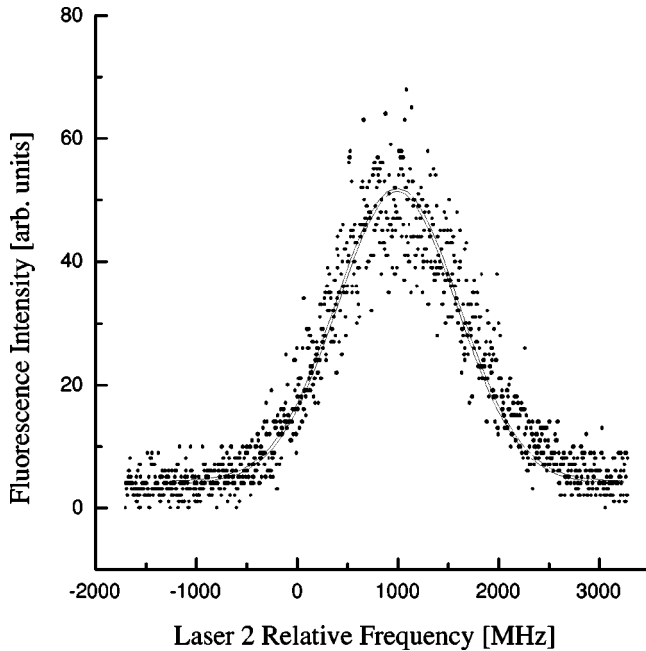

FIG. 6. Two-photon fluorescence spectrum observed at $\Delta_1 = 600$ MHz, $T = 386$ K, (dots), and the calculated spectrum of the desorbed atoms (gray line).
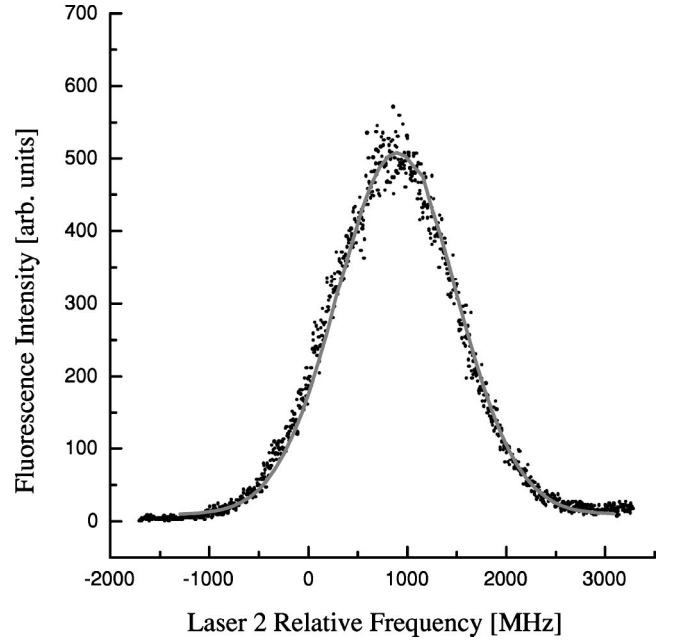

FIG. 7. Same as Fig. 6, but for $T = 371$ K.

results are shown in Figs. 8–10 which are plotted as a function of the velocity component v'_x deduced from the resonance condition $\Delta_2 - k_2 v'_x = 0$, the detuning Δ_2 taken with reference to the center of the fluorescence line.

The obtained signal should be described in terms of the scattering kernel R_{dir} introduced by Eq. (7) and determined by Eq. (16). As an input for the velocity distribution function of the atoms approaching the surface we use the result obtained in Ref. [3]. Namely, the atomic flux to the surface is represented as a sum of two contributions: (i) a contribution from the atoms moving directly from the dispenser with the velocity distribution

$$f_d^-(v_x, v_z) = \frac{1}{C_d} \frac{(v_x^2 + v_z^2)^{1/2} \cos(\Delta\theta)}{(v_x^2 + v_z^2)\sin^2(\Delta\theta) + w^2}$$

$$\times \exp\left[-\frac{(v_x^2 + v_z^2)\cos^2(\Delta\theta)}{v_d^2} \right], \quad (27)$$

and (ii) a contribution from the atoms that have undergone mutual collisions in front of the surface with a Maxwellian distribution

$$f_{ds}^-(v_x, v_y, v_z) = \frac{1}{\pi^{3/2} u^3} \exp\left(-\frac{v_x^2 + v_y^2 + v_z^2}{u^2} \right). \quad (28)$$

Here, C_d is a normalization constant, $\Delta\theta = 7°$ is the angle between the direction of the dispenser axis and the direction from the dispenser to the spot on the surface illuminated by the lasers; the parameters $v_d = 8.0 \times 10^4$ cm/s, $w = 1.1 \times 10^4$ cm/s, and $u = 4.4 \times 10^4$ cm/s determine the widths of the corresponding distributions. The energy distribution function
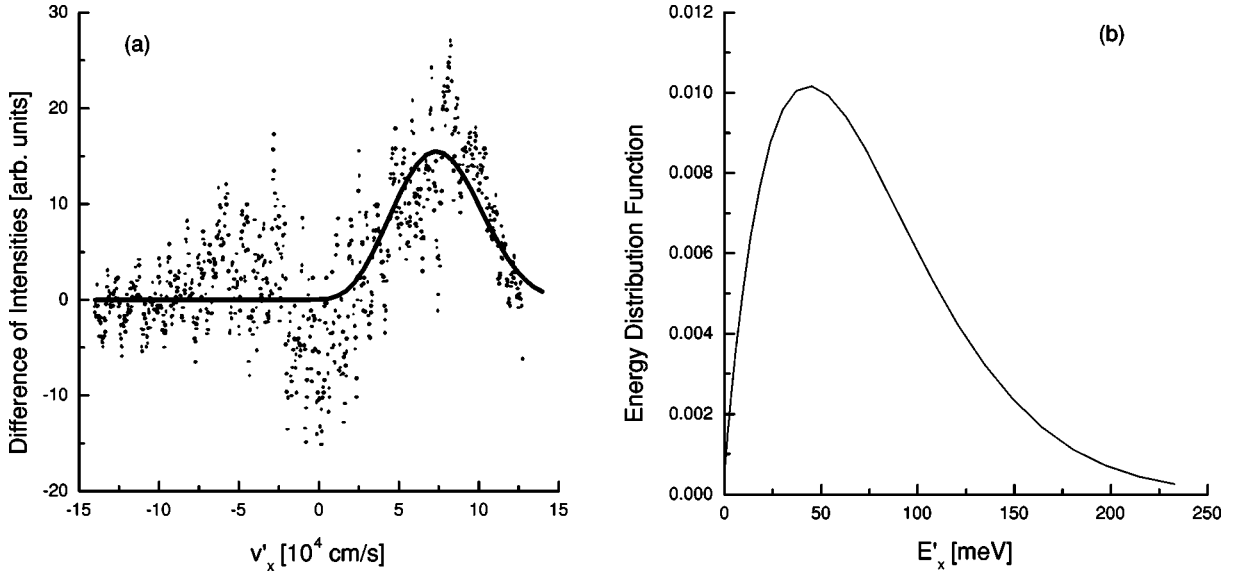
FIG. 8. (a) The contribution of the directly scattered atoms for $\Delta_1 = 800$ MHz, $T = 398$ K (dots). The best fit (black line) corresponds to $\delta = 420$ K. (b) The energy distribution function $\tilde{f}^+(E'_x)$ of the directly scattered atoms determined by Eq. (31) and corresponding to the data of (a).

$$f_d^-(E) = \frac{1}{m} f_d^-(v_x, v_z) \qquad (29)$$

with $E = m(v_x^2 + v_z^2)/2$ is shown in Fig. 11. Its maximum determines the most probable energy of 24 meV in the flux from the dispenser whereas the mean kinetic energy calculated with $f_d^-(E)$ is equal to 79 meV. The corresponding quantities for the atoms which have collided with each other in front of the surface are 12 meV and 34 meV, respectively.

Obviously, the atoms approaching the surface with a Maxwellian distribution function would be scattered in the direct channel having a velocity distribution axially symmetric about the surface normal. This would lead to a symmetric signal line shape with respect to the resonance frequency. However, we see no such contribution above the noise background in Figs. 8–10. This finding allows us to conclude that all the atoms which have undergone collisions in front of the surface are scattered after being trapped at the surface. Hence, they contribute to the desorption channel only. Therefore, the direct-scattering channel originates from the atoms flying directly from the dispenser and having a higher mean thermal velocity.

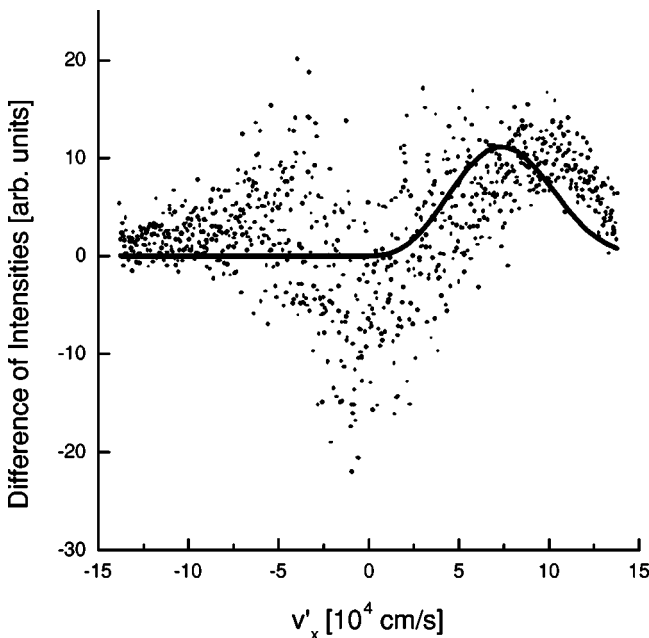As it follows from Eq. (16) the width of the velocity distribution of the directly scattered atoms is determined by

FIG. 9. Same as Fig. 8, but for $\Delta_1 = 800$ MHz, $T = 386$ K.
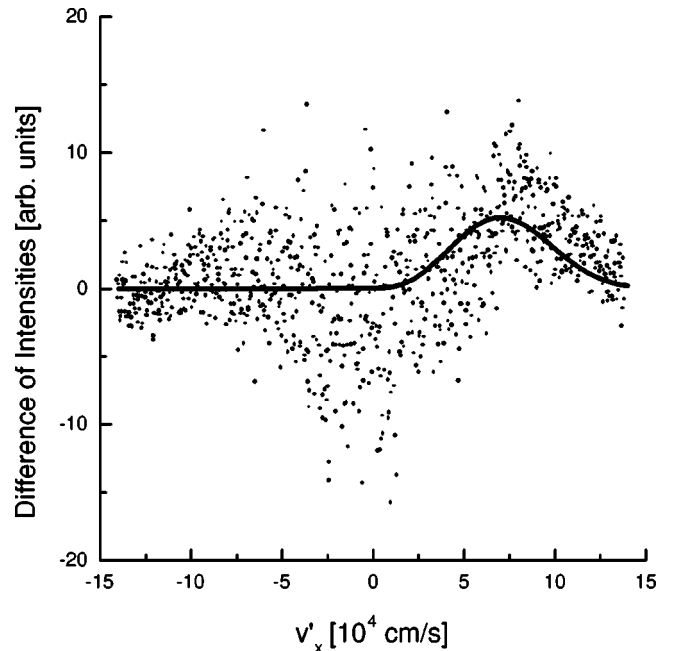
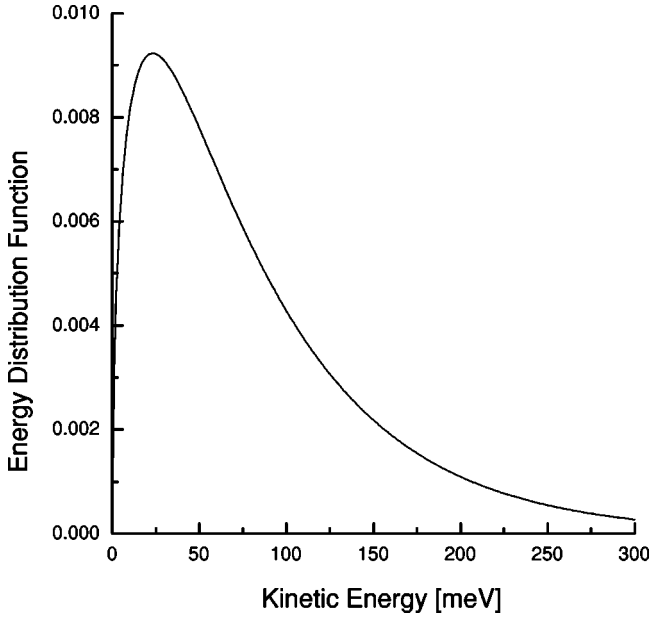FIG. 10. Same as Fig. 8, but for $\Delta_1 = 600$ MHz, $T = 398$ K.

FIG. 11. The energy distribution function of the atoms moving directly from the dispenser.

the quantity $(2\Delta\epsilon/m)^{1/2}$. For the values of $\Delta\epsilon$ of the order of a few hundred degrees this quantity is of the order of the mean thermal velocity. The width of the resonance maxima of the function $\hat{\sigma}_{ee}^{+}$ is given mainly by the power broadening which in our case is much less than the Doppler broadening or in terms of a velocity dependence is much less than the mean thermal velocity. Therefore the resonance behavior of $\hat{\sigma}_{ee}^{+}$ in the integrand of Eq. (18) can be approximated by δ functions as in the case of the weak laser fields limit presented by Eq. (19). Thus in accordance with Eq. (21) we can conclude that the signal line shapes presented in Figs. 8–10 give the velocity distribution function $\tilde{f}^{+}(v_x',v_z')$ of the directly scattered atoms subject to the condition $v_z'=\Delta_1/k_1$ [12].

We have fitted the shape of the signal in Fig. 8 using Eq. (24) with the substitution $\tilde{f}^{-}\rightarrow f_d^{-}$ and with the kernel $\tilde{R}$ replaced by

$$\tilde{R}_{dir}(v_x,v_z\rightarrow v_x',v_z')=\int\int R_{dir}(\mathbf{v}\rightarrow\mathbf{v}')dv_y dv_y',$$
(30)

where the kernel R_{dir} is determined by Eq. (16). The only adjustable parameter besides the signal amplitude was the mean energy transfer, δ. The parameter ΔK was expressed in terms of δ using the calculated value of the Rayleigh mode velocity. The latter quantity can be obtained from its relation with the transverse sound velocity and the ratio between the transverse and longitudinal sound velocities [13]. For a regular crown glass such an estimate gives $v_R=3\times10^5$ cm/s. The best fit obtained for $\delta=420$ K (or 36 meV) is shown in Fig. 8(a). Figure 8(b) presents the corresponding energy distribution function calculated as

$$\tilde{f}^{+}(E_x')=\frac{1}{mv_x'}\tilde{f}^{+}(v_x',v_{z0}'),$$
(31)

with $E_x'=mv_x'^2/2$ and $v_{z0}'=\Delta_1/k_1$, and normalized to unity. The so defined distribution function has the sense of a conditional probability that the kinetic energy of the motion along the x axis for the scattered atoms lies in the interval between E_x' and $E_x'+dE_x'$ provided that $E_z'=mv_{z0}'^2/2$. Thus from Fig. 8(b) we obtain that for the directly scattered atoms having $E_z'=26$ meV the most probable E_x' is equal to 45 meV and the mean value of E_x' is equal to 50 meV.

Using the found value of the parameter δ we have calculated the contribution of the directly scattered atoms for the other cases represented in Figs. 9 and 10. The agreement between the experimental and the calculated curves is rather satisfactory in Fig. 10. Two remarks are in order.

(i) Whereas the peak on the right-hand side of Figs. 8–10 is well above the noise background, this is hardly the case for the slight deviations seen on the left-hand sides. A possible reason for difference signal intensity at low frequencies is that some small fraction of the atoms scattered in front of the surface has been directly scattered by the surface, thus giving signal intensity at lower kinetic energies. The negative dip could be explained by the following: The atoms which contribute to the spectrum near the resonance with the upper transition move perpendicularly to the surface and have higher mean thermal velocities along this direction as compared with the atoms moving at large angles with respect to the surface normal. The interaction time with the surface for them is therefore shorter than for the atoms contributing to the spectrum wings and hence the process of excitation relaxation is less effective. This means that such atoms are reflected from the surface while still being in the upper excited state. If we take now into account that the laser light that is stimulating two-photon emission is permanently on, it will result to stimulated emission to the $3P_{3/2}$ state at some distance from the surface, while the reflected ground-state atoms are again excited. Hence the contribution of the atoms being reflected in the excited state to the total fluorescence signal decreases as compared with the contribution of the atoms which are desorbed from the surface in the ground state. As a consequence, one observes a negative dip corresponding to the resonance with the upper transition.

(ii) Although the theoretical curve in Fig. 9 reproduces the measured signal shape, its maximum is shifted to lower frequencies. Since the position of the maximum of the directly scattered atoms is determined by both the direction of the incoming atomic flux and by the detuning Δ_1 we suppose that uncertainty in the determination of the laser frequencies absolute values as well as instability of the flux from the sodium dispenser from one measurement to another, leading to a slight deviation of the flux axis, are the main reasons for the disagreement.

Further we have fitted the measured two-photon fluorescence line shapes using the scattering kernel in the form (7) with the kernels R_{des} and R_{dir} determined by Eqs. (8) and (16) and considering the quantity S as an adjustable parameter. The result is shown in Figs. 3–5. From the fitting pro-

cedure we have found that for $T = 398$ K the mean probability [14] of direct scattering $\eta = 1 - S = 0.05$, both for $\Delta_1 = 800$ MHz and $\Delta_1 = 600$ MHz, whereas for $T = 386$ K, $\eta = 0.03$. This result is consistent with the fact that atoms stick better on a colder surface.

VI. CONCLUSIONS

In the present paper we have investigated two-photon fluorescence spectra of Na vapor atoms excited in the close vicinity of a glass surface. A detailed analysis of their line shapes has allowed us to deduce that the departing flux of atoms also contains a small fraction of atoms that have been inelastically scattered by the surface. From theoretically modeling the experimental line shapes we obtain a value of the mean energy transfer for such a process as well as the mean probability of direct scattering mediated by surface phonons. This probability increases with increasing surface temperature. A comparison between the contribution of the atoms which have been scattered in front of the surface (mean kinetic energy 34 meV) and those coming directly from the Na source (mean kinetic energy 79 meV) allows us to conclude that atoms approaching the surface with different kinetic energies have different probabilities for being trapped at it. All this information has allowed us to reconstruct in fact the scattering kernel for the investigated model system.

In the present experiment the vapor-surface system has been kept under thermodynamically nonequilibrium conditions. One could ask whether it would be possible to distinguish between desorbed and inelastically scattered atoms under equilibrium conditions. From Eqs. (3), (7), and (8) we see that in such a case both components would have identical velocity distributions. So, in the absence of external fields one would expect that "no" is the correct answer [15]. However, according to Eq. (18), the two-photon fluorescence spectrum of the scattered atoms is determined not only by the velocity distribution function, but also by the population of their excited states. Hence, if the boundary conditions for the atomic density matrix at the surface are different for the desorbed atoms and for those directly scattered, we should answer "yes." The latter condition can be realized if the relaxation processes near the surface are not fast enough to fully quench the directly scattered excited atoms.

[1] C. Cercignani, *Rarefied Gas Dynamics. From Basic Concepts to Actual Calculations* (Cambridge University Press, Cambridge, London, 2000), Chap. 1.11.

[2] V.G. Bordo, J. Loerke, and H.-G. Rubahn, Phys. Rev. Lett. **86**, 1490 (2001).

[3] V.G. Bordo, J. Loerke, L. Jozefowski, and H.-G. Rubahn, Phys. Rev. A **64**, 012903 (2001).

[4] E.M. Lifshitz and L.P. Pitaevskii, *Physical Kinetics* (Pergamon Press, Oxford, 1986), Chap. 15.

[5] A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, London, 1988), Chap. 14.

[6] R. Brako and D.M. Newns, Phys. Rev. Lett. **48**, 1859 (1982); Surf. Sci. **117**, 42 (1982).

[7] J.R. Manson, Phys. Rev. B **43**, 6924 (1991).

[8] *Handbook of Mathematical Functions*, edited by M. Abramowitz and I.A. Stegun (Dover, New York, 1972).

[9] Here the function $f^+(\mathbf{v})$ has a sense of the velocity distribution function of the atoms leaving the surface. This means that the "flux factor" v_z' appearing in the left side of Eq. (2) has already been included in the $f^+(\mathbf{v}')$. See F.O. Goodman and H.Y. Wachman, *Dynamics of Gas-Surface Scattering* (Academic Press, New York, 1976), Chap. 2.

[10] This is obviously valid for a Maxwellian velocity distribution. Another case is realized in the present experiment where the atomic flux towards the illuminated spot at the surface has only two components along the x and z axes.

[11] V.G. Bordo and H.-G. Rubahn, Phys. Rev. A **60**, 1538 (1999).

[12] Here we take into account that we observe the fluorescence signal integrated over the frequencies of the emitted photons arising from the decay of the $4P_{1/2,3/2}$ states. Hence such a signal does not depend on the velocities of the emitting atoms.

[13] L.D. Landau and E.M. Lifshitz, *Theory of Elasticity* (Pergamon Press, Oxford, 1986), Chap. 24.

[14] The term "mean probability" in this context means a probability averaged over the kinetic energies of the atoms in the total flux towards the surface.

[15] G. Comsa and R. David, Surf. Sci. Rep. **5**, 145 (1985).