

Two-photon evanescent-volume wave monitoring of desorbing Cs atoms

T. Kawalec^{b,*}, V.G. Bordo^{a,1}, L. Józefowski^b, H.-G. Rubahn^a

^a Mads Clausen Institute, University of Southern Denmark, DK-6400 Soenderborg, Denmark

^b Marian Smoluchowski Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Cracow, Poland

Received 6 July 2006; accepted 27 November 2006

Available online 29 November 2006

Abstract

The two-photon fluorescence spectroscopy in the vicinity of the surface has been performed for Cesium atoms. One of the laser beams was directed perpendicularly to the surface, whereas the second one excited an evanescent wave propagating along the surface. To demonstrate its potential, this technique has been applied for a qualitative comparative study of Cs atom desorption from a glass surface versus the same surface coated with a PDMS film. That way the fluorescence line originating primarily from desorbing atoms could be spectrally isolated. The desorption flux from polymer coated surfaces is found to be significantly smaller as compared to the flux from a plain glass surface.

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1. Introduction

Gas-surface scattering plays a crucial role in a variety of applications including heterogeneous catalysis, chemical vapor deposition and aerodynamics. Atoms or molecules desorbing from the surface either represent the products of surface chemical reactions or carry information about the interaction between gas particles, chemically unchanged, and a surface. A traditional approach for the investigation of such processes is atomic or molecular beam scattering at a surface which is applicable obviously only under ultra-high vacuum conditions. The demand of practice is, however, to study processes of that kind also in the presence of a high-pressure gas phase.

Recent progress in resonant optics at a vapor-solid interface exploiting either selective reflection [1] or gas excitation by evanescent waves (EWs) strongly localized near the surface [2] has opened quite new opportunities for resolving this problem. An evanescent wave which exists

at a gas–solid interface under total internal reflection conditions excites only gas atoms in the gas boundary layer and therefore their fluorescence spectrum is sensitive to the gas-surface scattering dynamics. If one combines this excitation with illumination of the gas by a light beam directed perpendicularly to the surface, the contribution of the desorbing atoms can be separated from the approaching atoms using the Doppler effect. The advantages of this technique have been elucidated previously in a system consisting of Na vapor atoms in the vicinity of a glass prism surface [3]. A careful analysis of the corresponding fluorescence spectra has allowed us to extract the parameters of the Na atom – glass surface scattering kernel [4].

An Na atom undergoing a two-step excitation $3S_{1/2}(F=2) \rightarrow 3P_{3/2}(F') \rightarrow 5S_{1/2}(F'')$ represents effectively a three-level system due to a large hyperfine splitting in the ground state and an unresolved hyperfine structure of the excited states $3P_{3/2}$ and $5S_{1/2}$. The desorbing atoms are excited if the frequency of the light beam propagating normally to the surface into the gas interior is larger than the atomic transition frequency. When the hyperfine splittings in the intermediate state are comparable with the Doppler broadening the matter is more complicated. Then

* Corresponding author. Tel.: +48126635735.

E-mail address: kawalec@kawalec.alpha.pl (T. Kawalec).

¹ Present address: Natural Sciences Center, A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, 119991 Moscow, Russia.

the contributions of the desorbing atoms originating from different hyperfine transitions overlap with that from the atoms arriving at the surface. In such a case the extraction of information about the desorbing flux becomes a formidable task.

This more often encountered situation as compared to the case of simple Na atoms is what we are concerned with in the present paper. Our objective is to demonstrate that two-photon evanescent-volume wave spectroscopy is applicable also to the investigation of desorption of atomic systems possessing a complex level structure. This aim can be achieved if instead of a two-step excitation one utilizes a double-quantum transition. For this purpose, we investigate as a model system Cesium (Cs) vapor atoms excited by crossed waves at a prism surface. Being independent on the hyperfine structure of the intermediate state, the registered spectrum of fluorescence following a double-quantum excitation allows one to overcome the spectral complications noted above and to isolate the contribution of desorbing Cs atoms. Hence the evanescent-volume wave spectroscopy technique can be applied for a study of desorption in different systems. In the present paper, we have demonstrated its potential for scattering of Cs atoms emanating either from a reservoir or from a dispenser at a glass prism surface, either uncovered or covered with an organic polymer film. As a polymer we have chosen polydimethylsiloxane (PDMS) since this material is known to be applicable as reservoir for the light-induced atomic desorption (LIAD) technique [5].

2. Theory

The theory of fluorescence from gas atoms excited by crossed volume and evanescent waves has been developed in Ref. [6]. A gas atom was modeled by a three-level system with the ground state $|g\rangle$, the upper excited state $|e\rangle$ and the intermediate state $|i\rangle$. It has been shown that the fluorescence intensity exhibits both one-photon and two-photon resonances between the incident waves and the atomic transitions $|g\rangle \rightarrow |i\rangle$, $|i\rangle \rightarrow |e\rangle$ and $|g\rangle \rightarrow |e\rangle$, respectively. Assume that the volume wave is directed perpendicularly to the surface and has the wave vector \mathbf{k}_1 and the frequency ω_1 , whereas the evanescent wave propagating along the surface has the wave vector \mathbf{k}_2 and the frequency ω_2 . Then in the weak-field limit the positions of the resonances for an atom moving with the velocity \mathbf{v} are determined by the equations

$$\Delta_1 = \mathbf{k}_1 \mathbf{v}, \quad (1)$$

$$\Delta_2 = \mathbf{k}_2 \mathbf{v}, \quad (2)$$

$$\Delta_0 = (\mathbf{k}_1 + \mathbf{k}_2) \mathbf{v}, \quad (3)$$

where $\Delta_1 = \omega_1 - \omega_{ig}$, $\Delta_2 = \omega_2 - \omega_{ei}$, $\Delta_0 = \Delta_1 + \Delta_2 = \omega_1 + \omega_2 - \omega_{eg}$. Eqs. (1) and (2) describe the one-photon resonances in a two-step transition, while Eq. (3) corresponds to a double-quantum resonance [7].

If the frequency ω_1 is resonant to the lower transition and the frequency ω_2 is scanned across the upper transition, the two-step resonance, Eq. (2), and the double-quantum one, Eq. (3), overlap with each other. However in the case where the resonance detuning $|\Delta_1|$ exceeds the Doppler broadening of the lower transition, the latter resonance is well separated from the former one. Then the contribution of the atoms moving under an angle θ with respect to the surface normal to the number of counted fluorescence photons is determined by the integral

$$I(\Delta_0, \theta) \propto \int_0^\infty \frac{\Gamma_{eg}(v, \theta) f(v, \theta) v dv}{[\Delta_0 - (k_1 \cos \theta + k_2 \sin \theta) v]^2 + [\Gamma_{eg}(v, \theta)]^2}, \quad (4)$$

where $f(v, \theta)$ is the atomic flux velocity distribution function and the line width $\Gamma_{eg}(v, \theta)$ includes both the natural broadening and the transit-time broadening in the EW field. The angle θ is counted towards the vector \mathbf{k}_2 . Under the conditions of the present experiment the mean value of the quantity Γ_{eg} is estimated to be about 160 MHz, allowing one to neglect it in comparison with the Doppler broadening. In equilibrium, the velocity distribution function is determined by the cosine law:

$$f(v, \theta) \propto v \cos \theta \exp\left(-\frac{v^2}{v_T^2}\right) \quad (5)$$

with v_T the most probable thermal velocity. Then Eq. (4) is reduced to

$$I(\Delta_0, \theta) \propto \frac{\Delta_0^2 \cos \theta}{(k_1 \cos \theta + k_2 \sin \theta)^2 v_T^2} \times \exp\left[-\frac{\Delta_0^2}{(k_1 \cos \theta + k_2 \sin \theta)^2 v_T^2}\right]. \quad (6)$$

At a fixed θ the function $I(\Delta_0, \theta)$ has a dip when $|\Delta_0|$ tends to zero and has two maxima at $\Delta_0 = \pm(k_1 \cos \theta + k_2 \sin \theta) v_T$. It follows from here that the atoms for which $\delta(\mathbf{v}) \equiv (\mathbf{k}_1 + \mathbf{k}_2) \mathbf{v}$ is positive contribute to the right maximum, whereas those for which $\delta(\mathbf{v})$ is negative contribute to the left maximum.

In the case where the levels participating in the two-photon transition possess hyperfine structure their contributions to the fluorescence intensity must be summed over the hyperfine components. However the double-quantum line, being dependent on the detunings Δ_0 , is not influenced by the hyperfine structure of the intermediate level.

3. Experimental

The experimental setup is shown in Fig. 1. A truncated, right-angle glass prism was placed centrally in the stainless steel vacuum chamber with a base pressure of 1.2×10^{-8} mbar. The prism could be rotated and heated resistively up to 400 K. Its index of refraction was 1.510 and the critical angle for it was 41.47° at 795 nm. The

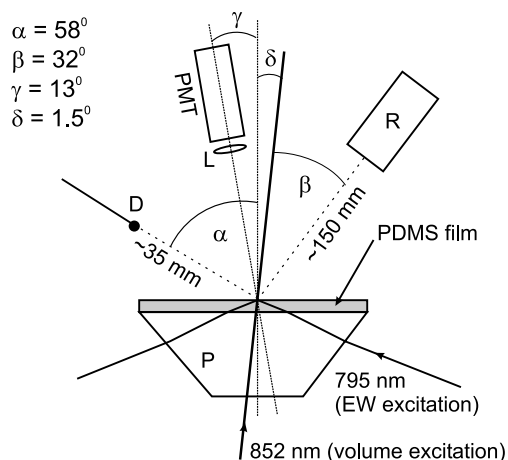


Fig. 1. Sketch of the experimental set up (not to scale): PMT, cooled photomultiplier; L, lenses and interference filter; P, truncated glass prism; D, Cs dispenser; R, glass Cs reservoir. Characteristic angles are shown.

length of the prism hypotenuse was 28 mm and the height (after truncation) was 10 mm. The two-photon excitation of Cs atoms (see Fig. 2) took place in the intersection area of the volume and EW waves generated by two continuous-wave, Littrow configuration diode lasers (TEC 100, Sacher). The spectral width of both lasers was less than 2 MHz and the drift of their frequency during a wavelength scan was negligible. The relative frequency of the lasers were controlled by means of Fabry-Pérot interferometers with FSR = 61.5 MHz and 1 GHz for the 852 nm and 795 nm lasers, respectively. The absolute frequency scale for the 852 nm laser was found with the help of auxiliary absorption spectroscopy performed in a Cs vapor cell at room temperature. An evanescent wave was excited on the prism surface by the 795 nm laser and was resonant with the $6^2P_{3/2} \rightarrow 8^2S_{1/2}$ transition. The angle of incidence is estimated to be 4 mrad above the critical angle for the clean prism and 10 mrad for the PDMS-coated prism. The intensity of the laser beam just before the prism was $(64 \pm 5) \times 10^3 \text{ W/m}^2$. The volume wave (almost perpendicular to the prism surface) came from the 852 nm laser and was resonant with the $6^2S_{1/2} \rightarrow 6^2P_{3/2}$ transition. The intensity of the laser beam just before the prism was

$(45 \pm 4) \times 10^3 \text{ W/m}^2$. The Gaussian diameter (e^{-1}) of both beams was about 1 mm. Cs atoms reaching the prism surface originated either from a SAES-Getters dispenser (run at a current of 6 A) or from a glass reservoir containing 5 g of metallic Cesium. The reservoir was connected to the vacuum chamber via a valve and was heated to 323–343 K. The 460 nm fluorescence photons were collected by a 277 K cooled photomultiplier (Hamamatsu R943-02, photon counting mode) placed behind collection lenses followed by an infrared cut-off filter and an interference filter with 456 nm central frequency and 10 nm FWHM transmission width.

The two-photon fluorescence spectroscopy signal was recorded while scanning the frequency of one of the lasers around a given optical transition and keeping the frequency of the second laser constant. Since the fluorescence signal was very weak, great care had to be taken to suppress any residual light in the vacuum chamber, resulting mainly from both scattered laser beams.

The experiments were performed in two series. The first one concerned an uncoated prism surface heated to 345 K and the second one concerned a surface covered with a rough ($\sim 1 \mu\text{m}$ thick) layer of PDMS, kept at room temperature. The organic layer was prepared by spreading a 5% PDMS in ether solution on the prism hypotenuse and keeping it in an oven for several hours at 373 K. For both experimental series, the measurements were performed for Cs atoms coming directly from the dispenser or from the reservoir. In the latter case the fluorescence signal was recorded for the reservoir opened and heated or the reservoir just closed after a few hours of operation. The detuning of the 852 nm laser (Δ_1) is calculated with respect to the $F = 4 \rightarrow F' = 3$ transition in the D_2 line.

4. Results and discussion

Fig. 3 shows the fluorescence spectra of Cs atoms near an uncoated glass prism surface obtained at a fixed frequency of the laser beam incident normally to the surface while scanning the evanescent wave frequency. Fig. 3a (black line) represents the case where the source of Cs atoms is a reservoir, whereas Fig. 3b displays the spectrum of Cs atoms emanated from the dispenser. In both cases the two-photon fluorescence spectrum consists of two well separated components. The left one has a structure originating from different hyperfine components of the two-step transitions $6S_{1/2}(F=4) \rightarrow 6P_{3/2}(F') \rightarrow 8S_{1/2}(F'')$. Its most intensive line can be identified as that corresponding to the transition $F' = 4 \rightarrow F'' = 4$. Due to the overlapping of different Doppler-broadened absorption lines $6S_{1/2}(F=4) \rightarrow 6P_{3/2}(F'=3,4,5)$, Cs atoms moving in all directions contribute to this component.

The right broad component does not have a hyperfine structure and originates from the right maximum corresponding to the double-quantum transition $6S_{1/2}(F=4) \rightarrow 8S_{1/2}(F''=4)$. This statement is supported by the dependence of the separation between the fluorescence line

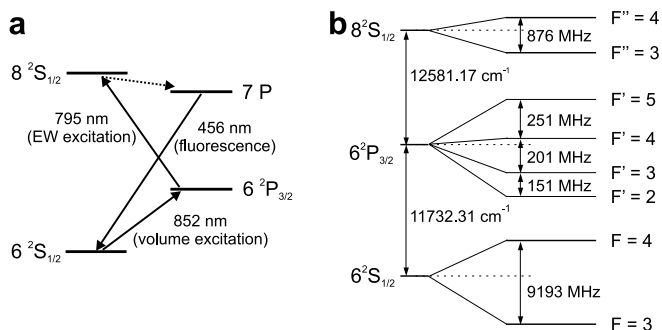


Fig. 2. (a) Scheme of cesium terms used for two-photon excitation. Wavelengths of exciting lasers are noted. (b) Hyperfine splitting of relevant energy levels.

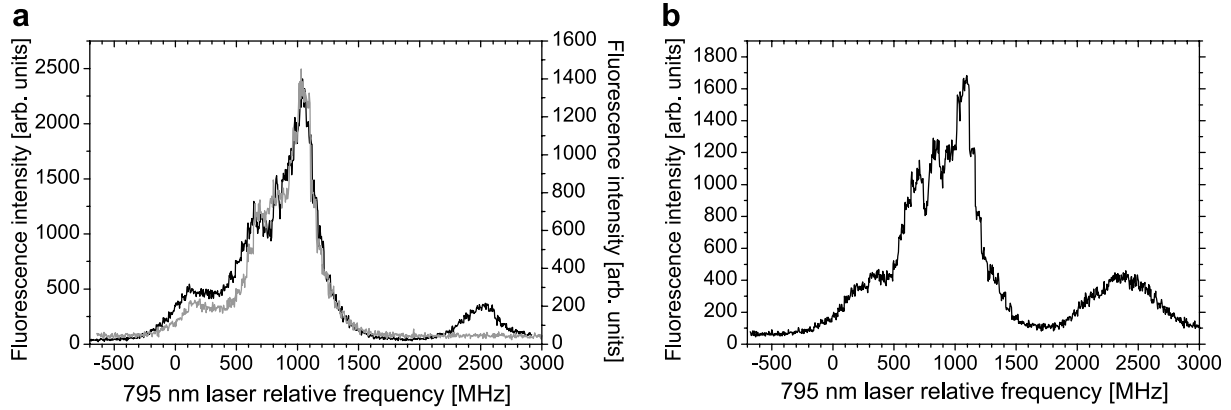


Fig. 3. Two-photon fluorescence spectra obtained for 795 nm laser scanning and an uncoated prism. Relevant parameters are: $\Delta_1 = 230$ MHz, prism surface temperature $T = 345$ K and reservoir temperature 343 K. (a) Spectra taken with Cs reservoir opened (black line) and reservoir just closed after 3 h of operation (gray line), (b) spectra taken for atoms coming from dispenser.

arising from the two-step excitation $6S_{1/2}(F=4) \rightarrow 6P_{3/2}(F'=3) \rightarrow 8S_{1/2}(F''=4)$ and the maximum of the double-quantum fluorescence line on the detuning Δ_1 shown in Fig. 5. The data were taken from the fluorescence spectra obtained for Cs atoms emanating from the dispenser and for different Δ_1 (not shown) where due to a narrow velocity distribution of those atoms the hyperfine components in the spectrum could be clearly identified. The position of the double-quantum line is determined approximately by the condition $\Delta_0^m = \text{const.}$ and hence the corresponding detuning Δ_2^m varies as $-\Delta_1 + \text{const.}$ when Δ_1 is changing.

In the scanning range corresponding to the double-quantum fluorescence line one has $\Delta_2 > 500$ MHz with respect to the transition $6P_{3/2}(F'=3) \rightarrow 8S_{1/2}(F''=4)$. Then, as follows from the discussion in Section 2, the dominant contribution to this line originates from the atoms for which

$$\delta(\mathbf{v}) > \Delta_1 + 500 \text{ MHz.} \quad (7)$$

Taking into account that for the relevant intermediate state $6P_{3/2}(F'=3)$ $\Delta_1 = 230$ MHz, one obtains that in the considered scanning range

$$\delta(\mathbf{v}) > 730 \text{ MHz.} \quad (8)$$

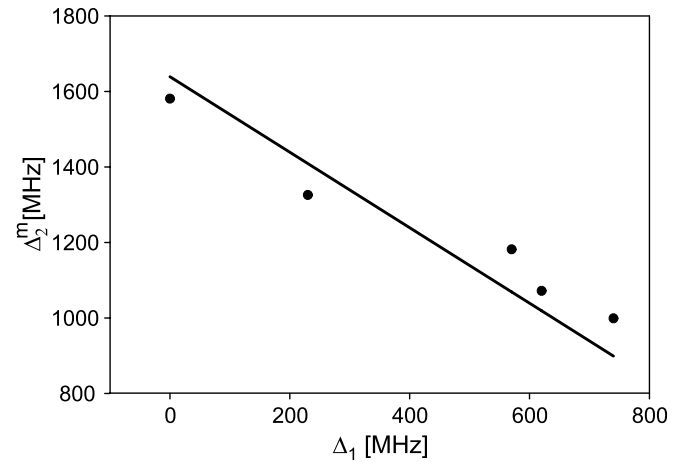


Fig. 5. Dependence of the position of the right maximum corresponding to the double-quantum transition on the detuning Δ_1 . The straight line shows the dependence $\Delta_2 = -\Delta_1 + \text{const.}$ for comparison.

An estimate of this quantity for the parameters of the experimental set up gives $\delta(\mathbf{v}) \approx -70$ MHz for most of the Cs atoms emanated from the reservoir and

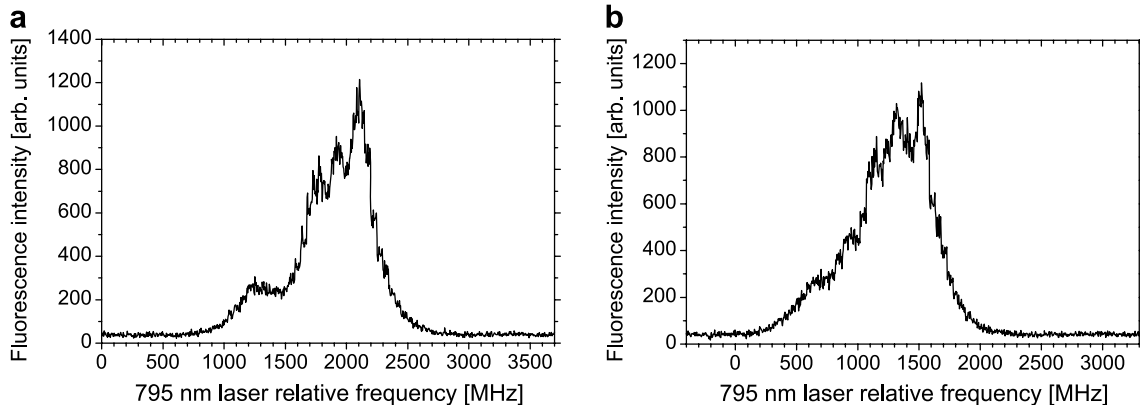


Fig. 4. Two-photon fluorescence spectra obtained for 795 nm laser scanning and a PDMS-coated prism. Relevant parameters are: $\Delta_1 = 230$ MHz, prism surface temperature $T = 293$ K and reservoir temperature 343 K. Cs atoms came from: (a) reservoir, (b) dispenser. Note the disappearance of the double-quantum fluorescence line at high relative frequency, indicating minimum desorption from PDMS.

$\delta(\mathbf{v}) \approx -570$ MHz for those from the dispenser. This can be illustrated graphically as follows. The condition (8) means that the projection of the atomic velocity vector \mathbf{v} onto the vector $\mathbf{k}_1 + \mathbf{k}_2$ is large and positive (see Fig. 6). On the other hand, the velocity vectors of most atoms moving from the reservoir or from the dispenser make an obtuse angle with the vector $\mathbf{k}_1 + \mathbf{k}_2$ and thus their projection is negative. This allows one to conclude that the right component in the spectra shown in Fig. 3 originates primarily from the atoms moving from the surface.

This conclusion is supported by the spectrum shown by the gray line in Fig. 4a. It has been obtained after the reservoir was closed. When the Cs vapor comes to equilibrium, the velocity distribution function of Cs atoms becomes isotropic. As a result, the atomic flux to the illuminated spot on the prism surface is considerably depleted in comparison with the flux emanating from an opened reservoir. In a steady-state regime, this flux is compensated by that from the surface. Thus after closure of the reservoir the flux of desorbing atoms is also greatly reduced, leading to the disappearance of the right component in the spectrum. Nevertheless the left component is still observable as all Cs atoms in the vapor near the surface contribute to it.

The two-photon fluorescence spectra shown in Fig. 4 have been obtained at the prism surface coated with a PDMS film and represent a qualitatively different situation. The components originating from the two-step transition displayed in Fig. 4a and b are very similar to that in Fig. 3a and b, respectively. Thus they reflect mainly the velocity distributions of Cs atoms emanated from the reservoir or from the dispenser. However in this case the line arising from the double-quantum transition is not seen at all indicating that there are no desorbing atoms. This finding can be understood as the manifestation of

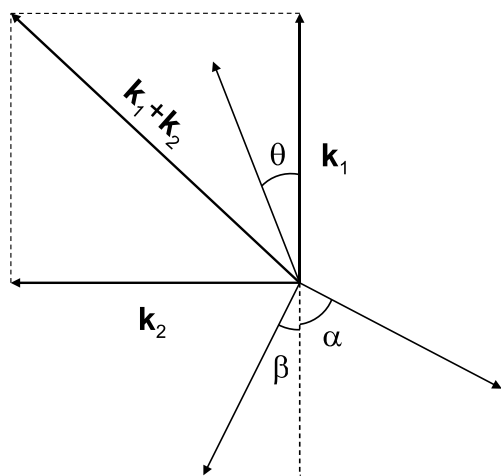


Fig. 6. Scheme illustrating the condition (8). The angles α , β and θ correspond to the directions of the velocity vectors of the atoms moving from the dispenser, those from the reservoir and those desorbing from the surface, respectively.

a fast diffusion of incident Cs atoms into the PDMS film, an effect known from the study of light-induced atomic desorption (LIAD) of PDMS films [5].

5. Conclusion

In the present paper we have demonstrated the potential of two-photon spectroscopy in a laser beam crossed with an evanescent wave propagating along the prism surface. It has been applied for a study of desorption in a model system represented by Cs atoms scattered from different surfaces. We have shown that the corresponding fluorescence spectrum, although being complicated due to the hyperfine structure of the intermediate level, contains a spectrally isolated component originating from desorbing atoms only. As a preliminary, qualitative output of this technique, it has been demonstrated that the monitoring of this component allows one to conclude about the process of desorption into the vapor phase, namely that the desorbing flux from polymer coated surfaces is much smaller than the flux from uncoated surfaces. Further development of these investigations could include the measurement of the integral intensity of the double-quantum fluorescence line as a function of surface temperature. Assuming an Arrhenius-type relation between the rate of desorption and the adsorption potential depth one can then determine the latter quantity. Such measurements can be combined with a variation of surface coverage including nontransparent films of thickness less than the evanescent wave penetration depth into the vapor.

The technique described here has some advantages in the investigation of the LIAD effect compared to that based on measurements of either absorption or fluorescence spectra of alkali atoms desorbed into a cell [5] and also compared to that based on pulsed laser induced desorption experiments in high vacuum environments [8]. The double-quantum fluorescence spectrum excited by crossed waves provides a possibility for real-time observation of the desorbing flux contribution, not shadowed by any effects occurring in the vapor volume. At the same instance the method is especially sensitive to the slow components of desorbed atoms, in contrast to pulsed laser time-of-flight measurements.

Acknowledgements

Financial support from the European Community's Human Potential Programme HPRN-CT-2002-0034, FAST-net and from the Danish Research Foundations SNF (21-03-0469) and FTP (274-05-0015) is gratefully acknowledged.

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