

Reflection Spectroscopy of an Atomic Vapour

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Our ability to probe spatially selected atoms at small distances from a surface enabled us to obtain information about atom-surface interaction. We review two experiments in which we monitor the reflected signal from a solid/resonant-vapour interface. One experiment demonstrates the quantum electrodynamical effect induced by the presence cavity on a resonant atomic level. In the other experiment we use inhomogenous fields to probe the adsorption of atoms on a dielectric surface. We studied the effects of the surface Van der Waals potential on the low excited levels of Cs spectrum by the Selective Reflection Technique, and obtain the residence time of the Cs atoms on a dielectric window using evanescent waves.

I. Introduction

The interest on surface process is quite general in many areas of physics and, in particular, an important development of optical techniques has been accomplished to probe the mechanisms occurring at or near a surface. In fact the singularity represented by an interface, breaking the symmetry of space in one direction was first explored to generate nonlinear optical response originated by the discontinuity as demonstrated by the early work of Bloembergen et al¹ on the second harmonic generation at a surface. More recently Shen² has used this effect and developed a technique to probe molecular species at a surface with a sub-monolayer sensitivity.

At small distances between atom and surface, i.e., for distances of the order of the atomic dimensions, the adsorption mechanism is important and the techniques using laser light become very useful for diagnostics of these mechanisms in spite of the difference of a few orders of magnitude between the wavelength and the atomic scale.

The presence of a surface is also responsible for the particular spectroscopic behavior of the atoms (molecules) at its vicinity. After the extensive work by Drexhage³ on dye molecules deposited at controlled distances from a surface, an important number of results about the behavior of confined quantum systems has been published⁴⁻⁶. These results concern with the problem of coupling a quantum system with the available modes of vacuum⁷⁻⁹. The presence of a surface alters that distribution resulting in the modification of physical quantities as the lifetime and the energy levels of the atoms^{4,5}, molecules^{3,6} and solids¹⁰. This process becomes relevant for distances between atoms and sur-

faces of the order of the optical wavelength associated to the atomic transitions.

In consideration of this general interest for the optical study of processes near surface, we will present in the following the basic aspects of resonant reflection spectroscopy at an interface, which combines the possibilities of high resolution spectroscopy of a vapour with the observation of typical signature of atom/surface interaction. We will show that various techniques enable us to get information on short range as well as long range surface interaction.

II. Reflection techniques to probe an atomic vapour

In most of the high-resolution spectroscopy techniques, including Doppler-free vapour spectroscopy, the information is averaged over the macroscopic dimensions of the sample. Interactions with the container walls are neglected, so that volume spectroscopy is generally performed. Reflection spectroscopy exploits the resonant behavior of the intensity of the reflected radiation from a solid vapour interface for a light frequency close to the frequency associated to the atomic transition. The signal which appears as a (resonant) change of reflectivity is sensitive to the atoms close to the surface (with in a distance corresponding to the wavelength of light).

Such a selective reflection was first observed by Wood in 1901¹¹, at an interface with Hg vapour. The classical explanation for the resonant structure of the spectrum is given by a local theory. The intensity variation of the reflected radiation has a dispersive lineshape¹², with Doppler broadening as expected from Fresnel formulae (i.e., local index theory).

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With the advent of high resolution laser spectroscopy, Woerdman and Schuurmans¹³ observed a sub-Doppler structure on the selective reflection spectrum of Na vapour under normal incidence. This structure was later interpreted by Schuurmans¹⁴ as due to the transient effects of the atomic polarization response to the incident field. Indeed, there is a non-instantaneous adaptation of the dipole phase oscillation to the electromagnetic field. Typical response time is γ^{-1} . Due to the atomic motion in the vapour, the optical excitation is transported through a "memory" length given by

$$l_m = \frac{v_{th}}{\gamma} \quad (1)$$

where v_{th} is the thermal velocity of the atoms. The key point is that when departing from the surface atoms (adatoms) are excited and have to undergo this transient regime of dipolar excitation while arriving atoms are already in a permanent regime. This results in a response singularity centered around $v_n = 0$, where v_n is the velocity along the normal to the surface.

Apart from the usual application of reflection spectroscopy to optically dense media (pressure effects), a major interest on selective reflection spectroscopy is concerned with its ability to be turned into a purely Doppler-free technique. Indeed, if one applies a frequency modulation (FM) to the incident beam, the modulated reflectivity-change signal is the frequency-derivative of the selective reflection lineshape. Therefore the large Doppler dispersion vanishes while the sub-Doppler singularity becomes a purely Doppler-free dispersive lineshape. Under these conditions the SR spectroscopy becomes a Doppler-free technique for linear spectroscopy in a vapour cell.

In section III we will report on the observation of long-range Van der Waals surface attraction for Cs atoms in a cell with dielectric windows probed by modulated selective reflection^{5,15}.

An alternate method of reflection spectroscopy for the study of interfaces by optical techniques uses inhomogeneous fields which are spatially confined, like evanescent waves and surface plasmons. As in the previous case of normal incidence, the reflection signal sensitivity from a low density media, like atomic vapours, is limited by the smallness of the probed volume. The detection sensitivity could be enhanced using known techniques of nonlinear spectroscopy. In this sense, a saturated absorption technique with evanescent waves was developed¹⁶, demonstrating additional elimination of Doppler broadening. We present in section IV results obtained using this experimental method which could be applied to measure the typical dwell time of Cs atoms on an ordinary cell glass window^{15,17}.

III. Spectral observation of the surface-induced Van der Waals attraction on atomic vapour

The Van der Waals attraction between an atom and its induced electric image on a reflecting surface performs an important role in many chemical-physics processes. However this interaction depends on the cube of the distance to the wall and until now this effect was observed only through the mechanical deflection of a beam of atoms at the ground state¹⁸ or in Rydberg atoms which are strongly polarized and have long lifetime⁴.

The observation of this effect was obtained by comparison of a Doppler-free transmission spectrum (volume spectroscopy through saturated absorption) and the spectrum of atoms near a surface, obtained by linear selective reflection with frequency modulation. Frequency modulated selective reflection is quite convenient to observe the effects of a long-range surface potential because the atomic response essentially originates in atoms remaining in the vicinity of the surface²⁰. We have made a systematic comparison between saturated absorption spectrum in volume and the frequency modulated selective reflection for the two first resonance transitions of Cs vapour ($\lambda_1 = 852$ nm and $\lambda_2 \approx 455$ nm). Both transitions exhibit a displacement of the line center towards the low frequency side (red shift) as well as an asymmetry on the lineshape with a smooth variation on the red side (figure 1b), due to an attractive potential. As expected for a more excited (and more polarizable) level, the effects are larger on the $6S_{1/2} \rightarrow 7P_{3/2}(\lambda_2)$ transition than on the resonant transition $6S_{1/2} \rightarrow 6P_{3/2}(\lambda_1)$ ¹⁹. Indeed, the strength of the Van der Waals attraction is related with the atomic polarizability.

A theoretical model of selective reflection including the z^{-3} term for the attractive potential²⁰ gives an excellent agreement with the experiment and fits the shift and the asymmetry experimentally observed (figure 1) with a single parameter.

It is important to remark that for $z \leq \lambda/10$ the Van der Waals term (z^{-3}) is the dominant contribution. For large distances, $z \gg \lambda/10$, the resonant interference between spontaneous emission and the reflecting wall, which change the quantum atomic structure, is predominant²¹. However, this contribution appears negligible in selective reflection experiments because of a spatial averaging typical of a reflected field generated by the atomic dipoles.

Thus, the selective reflection the study enables of atom-surface interaction, that becomes non-negligible at distances $z \leq \lambda/10$ to the wall, and makes possible to study the Van der Waals interaction for an excited short lifetime atomic level.

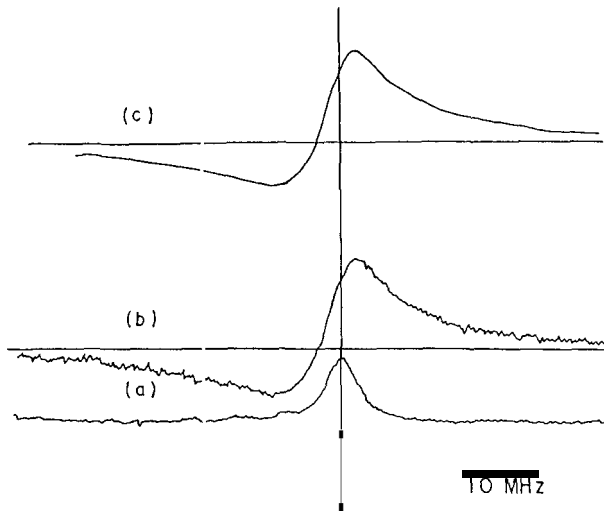


Figure 1.: Simultaneous recordings of (a) amplitude modulated saturated absorption and (b) FM - selective reflection (SR) spectra across the $F = 4 \rightarrow F' = 5$ component in experimental conditions of normal incidence, low pressure and low-power irradiation; (c) theoretical (FM) SR lineshape.

IV. Saturated absorption with evanescent waves and adsorption time measurement

Let us recall that when total reflection occurs at an interface (i.e., for an incidence angle larger than the critical angle, α_{cr}), continuity relationships for the electromagnetic field impose the presence of the evanescent field in the lower index medium (resonant vapour, in our configuration). The penetration length is typically:

$$\Lambda = \frac{\lambda}{2\pi}(\alpha - \alpha_{cr})^{-1/2} \quad (2)$$

Although there is no energy propagation by the evanescent waves in the vapour, an energy exchange is possible between the resonant electromagnetic field and the absorbing vapour. The Fresnel formulae show that for a radiation with frequency near to the vapour resonance, the variation of the reflection coefficient is related essentially to the imaginary part of the refractive index $n_v(\omega)$, so that for a low density vapour with $|\Delta n_v(\omega)| \ll 1$ and $(\alpha - \alpha_{cr}) \gg \Delta n_v(\omega)$, the reflection signal has an absorption-like profile. The spectroscopy using evanescent waves is currently used to probe condensed media²², but the first work on a vapour was made by Boissel and Kerchervé in 1981²³, with a configuration for linear absorption. Their spectrum is not essentially different from a Doppler-broadened absorption obtained by ordinary transmission (volume) spectroscopy but the sensitivity is low and limited by the laser fluctuations and by smallness of the explored volume. An important improvement is obtained if we use two beams on the experiment:

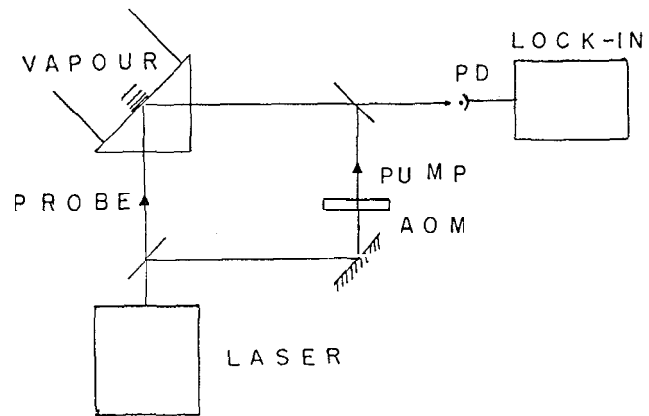


Figure 2.: Experimental set up for a saturated absorption with evanescent waves.

a pump and a probe, propagating in opposite directions, as shown in figure 2. Then the known advantages of the saturation absorption technique are recovered, since the signal is recorded on a black background via the detection of the induced modulation on the probe by the modulation induced in the medium by the modulated pump. Moreover velocity selection is achieved resulting the elimination of the Doppler broadening. Notice that the velocity selection is done parallel to the wall and, in this sense, this technique is complementary to the selective reflection. Moreover when the penetration of the electromagnetic field on the vapour is of the order of the light wavelength of (i.e., if $a - a_c \ll 1$), the transit time associated with the atomic motion on the normal direction, becomes responsible for line broadening. Hence the best resolution is obtained when $\alpha \rightarrow \alpha_{cr}$, and typically requires the mean transit time (along the normal) to be larger than the inverse homogeneous width.

As an example of the applicability of this saturation absorption technique, we show a Doppler-free spectrum obtained at a Cs vapour/glass interface (figure 3a). This technique could be used also for diagnostics of collisional processes with the surface, which are typically associated with short-range surface interaction. Indeed, with such a Doppler-free velocity selective technique, we expect a signature of velocity changing collisions, which should appear as an extra Doppler-broadened contribution as shown in figure 3b. An easy manner to discriminate between the broad pedestal and the narrow Doppler-free peaks is to take into account the two different typical times associated with these contributions which are respectively the mean dwell time on the surface, and the excited atomic state lifetime. In saturated absorption, a fast pump modulation induces a phase delay on the probe response, so that the atoms pumped before collision and the atoms probed after

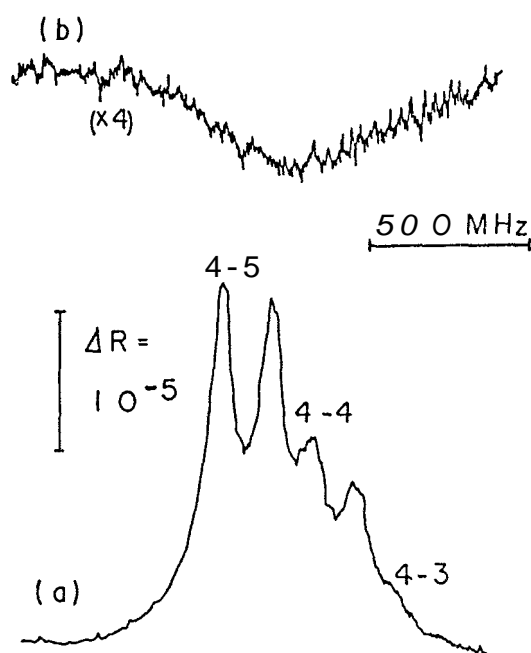


Figure 3.: Saturated absorption spectra of the resonant Cs transition ($6S - 6P$, $\lambda = 852\text{nm}$) using evanescent waves, where the pump beam was amplitude modulated at $\omega = 10\text{ kHz}$. (a) Probe signal obtained by an "in phase" lock-in detection. (b) "in quadrature" detection.

their departure from the surface have a response which is phase-shifted and spectrally broader (figure 3b) than the spectrum insensitive to surface collision (figure 3a).

The analysis of the lineshape of this broad line indicated a complete thermalization of the velocities. In a simple model of desorption the induced modulation on the probe varies as $(\delta + i\tau^{-1})$, where δ is the pump modulation frequency and τ is the mean desorption time. τ is assumed to be much larger than γ^{-1} . Thus, by measuring the relative amplitude of the broad spectrum, as a function of the modulation frequency δ , we have obtained the mean desorption time (dwell time) of $\tau = 4\mu\text{s}$ ($\pm 2\mu\text{s}$) for the Cs atoms on a saturated glass window²⁴, at a temperature of $\sim 350\text{ K}$. This value of τ , much larger than the excited state lifetime ($\sim 30\mu\text{s}$), justifies the initial hypothesis that the atoms left the wall in the ground state. As there is no way for the atoms on the surface to keep an optical memory of the pump modulation, this demonstrates as a complementary information, that (modulated) hyperfine optical pumping is not totally destroyed at the surface.

This outline of evanescent wave technique and the preliminary results guide the perspectives for a spectroscopy with inhomogeneous waves, including the study of the atomic thermalization internal and external degrees of freedom.

V. Conclusions

We have used the reflection techniques to probe atoms near a dielectric surface. The potential of these techniques was illustrated by two measurements related to the Cs atom interaction with a dielectric window. Possibilities of further experimental investigation can be considered such as thermalization and exchange between the external and internal degrees of freedom of neutral species, or ions, near or at the surface.

The reflection methods open the possibility to study the long-range interaction involving low excited levels. Complementary information should be obtained through the study of atoms near a metallic surface, in particular by the use of the electromagnetic surface modes.

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