Resonant Quenching of Gas-Phase Cs Atoms Induced by Surface Polaritons

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Near-field coupling between an excited atom and a surface-polariton mode can dramatically modify atomic branching ratios, because of surface-induced enhancement of a resonant decay channel. We show here that Cs($6D_{3/2}$) transfer towards Cs($7P_{1/2}$) (at $\lambda = 12.15\ \mu$m), negligible in free space, becomes efficient in the vicinity ($\leqslant$100 nm) of a sapphire window, due to a 12 μm resonance in the surface-polariton modes. The experiment relies on a selective reflection probing on the $7P_{1/2}$-$10D_{3/2}$ transition.

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Since the early days of cavity quantum electrodynamics (cavity QED) [1], it has been known that the lifetime, and related branching ratios, of an excited atom can be modified by the properties of the environment. For an atom in the vicinity of a surface, one may distinguish several situations. With an ideal reflector, boundary conditions at the surface—described by an image theory—impose enhancement or inhibition of the spontaneous emission (depending upon the orientation of the atomic dipole); in the far field, the spontaneous emission rate exhibits a damped oscillating behavior with the distance to the surface and observation of such a behavior has been one of the long-standing goals of cavity QED. Close to a transparent *dielectric* cavity, specific *near-field* effects take place, in addition to a decrease in the electric image amplitude: a fluorescent light is emitted in the "forbidden cone" associated with refraction angles larger than the critical one [2]. The atomic excitation couples to the evanescent modes of the vacuum field, yielding a photon freely propagating in the transparent dielectric medium [3]. This increases, up to a *finite* limit, the spontaneous decay of the atomic excitation.

In this Letter, we analyze another type of *near-field* effect originating in a *resonant* atom-surface coupling: in a *nonradiative* decay, the *atomic excitation* can be directly transferred to a *collective excitation mode of the surrounding medium* (surface-polariton mode, i.e., surface plasmon, surface phonon,...), with no emission of a freely propagating photon (see [4] and references therein). Such a resonant coupling, analogous to a coupling between two oscillators, has a dramatic influence on the atomic properties (see [5] for a quantum treatment). In a recent work [6] we have demonstrated that thanks to the *dispersive* part of such a coupling, the van der Waals (vdW) interaction, induced by a *virtual* energy exchange between the atom and the surface, can even be turned into a repulsion when the two oscillators are out of phase. Here, we analyze the *dissipative* part of this oscillator coupling: when the atomic dipole and its surface image oscillate in quadrature, the near-field emission of the atom is efficiently absorbed, in a *real transfer* process, by the surface polariton. This energy coupling is governed by the dissipative part $\mathrm{Im}[S(\omega)]$ (always $\geq$0) of the surface response $S(\omega)$, with $S(\omega) = [\varepsilon(\omega) - 1]/[\varepsilon(\omega) + 1]$ for a plane interface. $S(\omega)$ exhibits resonances (surface modes) linked to the bulk resonances of the dielectric permittivity $\varepsilon(\omega)$. In the nonretarded regime (implying *near-field limit*), this coupling of the atom with its own image—mediated by the surface mode coupling—leads to the same sharp $1/z^3$ dependence (z: atom-surface distance) as the vdW interaction. The decay rate becomes [5]

$$\gamma_{ij}(z) = \gamma_{ij}^{\infty}\left(1 + \frac{1}{4}\frac{\mathrm{Im}[S(\omega_{ij})]}{(k_{ij}z)^3}\right). \tag{1}$$

In Eq. (1), γ_{ij}^{∞} is the spontaneous transfer rate in free space for an atom in $|i\rangle$ decaying to $|j\rangle$, $\gamma_{ij}(z)$ is the actual decay rate at z, $k_{ij} = \omega_{ij}/c$, and ω_{ij} is the frequency of the $|i\rangle \rightarrow |j\rangle$ transition. For simplicity, in Eq. (1) the atomic structure is assumed to be only weakly perturbed; i.e., $\omega_{ij} = \omega_{ij}(z)$. A major consequence of Eq. (1) is that for a multilevel atom, the resonant behavior of $\mathrm{Im}[S(\omega_{ij})]$ dramatically modifies the branching ratios close to the surface.

This Letter reports on the observation, for an excited Cs atom, of such a surface-polariton-induced transfer along the $6D_{3/2} \rightarrow 7P_{1/2}$ decay channel [Fig. 1(a)]. In vacuum, the corresponding spontaneous emission in the far IR range at 12.15 μm is negligible, in relation with the λ^{-3} law: it contributes only ~0.45% to the natural decay rate of Cs($6D_{3/2}$) [the decay to Cs($6P$) at 876 and 921 nm is responsible for the 50 ns lifetime of Cs($6D_{3/2}$)]. The excitation transfer is observed in the vicinity of a *sapphire* surface because the surface response $\mathrm{Im}[S(\omega)]$ exhibits a peak in the 12 μm range [see [7] and Fig. 1(b)]. To our knowledge, such a surface-induced transfer is observed for the first time on free atoms: related near-field modifications of fluorescence lifetime had been observed with solid state emitters embedded in multilayer systems [8] but retardation effects could not be totally neglected, and changes in the quantum yield were not monitored. To monitor the induced $7P_{1/2}$ population, we choose selective reflection spectroscopy (SR) (see [6] and references

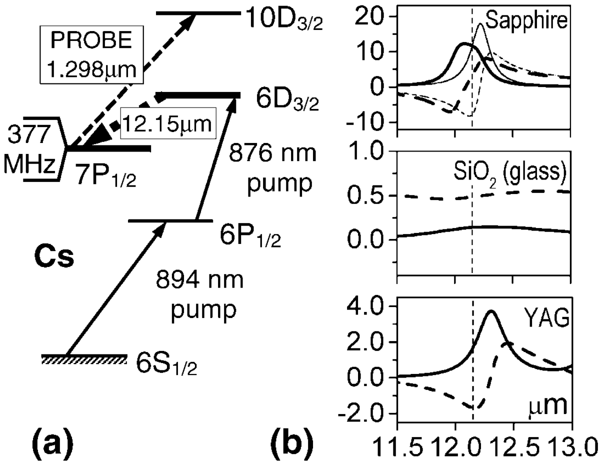

FIG. 1. (a) Energy diagram of the Cs atom; (b) surface spectral response Im[$S(\omega)$] (solid line) and Re[$S(\omega)$] (dashed line) for sapphire (*parallel* c-axis: bold lines; or *perpendicular* c-axis: light lines), silica glass (amorphous SiO_2), and yttrium aluminum garnet (YAG). Note the marker at 12.15 μm, and the changes in the vertical scale.

therein) on a transition coupling Cs($7P_{1/2}$) to an empty high-lying level, rather than a fluorescence detection, because of the SR ability to monitor quantities sharply varying with the distance to the surface, as expected for the Cs($7P_{1/2}$) population. Indeed, SR monitors the change $\Delta R(\omega)$ in the reflectivity R at the vapor interface. At normal incidence, it is proportional to $\mathrm{Re}\int_0^\infty p(z) \times \exp(2ikz)\,dz$, with k the wave number associated to the probing transition, and $p(z)$ the induced dipole polarization. In a homogeneous resonant medium, the SR technique probes the dispersive part of the response; in a gas medium, atomic motion makes the response to the optical field *nonlocal,* while transient effects induce a sub-Doppler singularity originating in the specific response of slow atoms. In the presence of spatial inhomogeneities, as induced by the surface van der Waals potential, there appears line shape distortions—mixing-up absorptive and dispersive contributions.

Here, one expects a strong spatial dispersion in the $7P_{1/2}$ population, due to the z^{-3} position-dependent transfer rate $6D_{3/2} \rightarrow 7P_{1/2}$. Because the transfer is not instantaneous, it is relatively more efficient for slow atoms. In addition, the population of the initial $6D_{3/2}$ level is nonthermal but generated through a nonlinear pumping sensitive to both Doppler and vdW shifts, so that it exhibits an inhomogeneous space and velocity distribution. In spite of these difficulties, a numerical modeling [9] has been worked on. Its predictions strongly vary with the numerous parameters to be chosen (e.g., the sign of the SR signal is occasionally reversed with the experimental conditions). However, it shows consistently that the SR signal should remain narrower than the Doppler-broadened volume spectrum, and in the vicinity of it (in spite of the vdW shift suffered by the probed transition, ~200 kHz $\cdot$ $\mu\mathrm{m}^3$ in our case). It also predicts that the SR signal "amplitude" is a valid indicator of the transfer to the $7P_{1/2}$ level, and of the "average" $7P_{1/2}$ population. Indeed, the $7P_{1/2}$ population is generated so close to the dielectric wall that the SR phase factor "$\exp(2ikz)$" does not affect dramatically the spatial averaging over the population.

In the experiment, an efficient pumping to Cs($6D_{3/2}$) is obtained thanks to a two-step excitation [see Fig. 1(a)] at $\lambda = 894$ nm ($D1$ resonance line) and $\lambda = 876$ nm with slightly focused pump beams (intensity in the 1–10 mW/cm^2 range). For the SR probing of the $7P_{1/2}$ population, we use the relatively weak transition to Cs($10P_{3/2}$) (oscillator strength $\sim 2.5 \times 10^{-2}$) because convenient sources are available at $\lambda = 1.298$ μm. All three lasers are commercial tunable narrow bandwidth diode lasers. To optimize the SR detection, both pump beams are independently amplitude modulated, respectively, in the 0.1–1 kHz range for the $D1$ laser, and in the 10–100 kHz range for the 876 nm pump line. A cascading of lock-in detectors enables a sensitivity approaching the shot noise limit: with a time constant $t = 0.3$ s, a reflectivity change $\Delta R/R \sim 10^{-7}$ is currently detected with a ~10 μW beam falling onto the detector, i.e., an incident power of 200 μW (beam diameter = 1 mm). We compared various Cs sealed cells, with different interfaces, and notably a cell with a sapphire window and a cell with a silica glass window [a material with no surface resonance in the 12 μm range—see Fig. 1(b)]. For each cell, the temperature-dependent Cs density was calibrated through a SR spectroscopy experiment on the $D1$ resonance, yielding an accuracy better than 30%–40% (equivalent to a ~5 °C accuracy). Note that here, the c axis of the birefringent sapphire is oriented parallel ($c_\parallel$) to the interface, a situation predicted [see [10] and Fig. 1(b)] and shown experimentally [6,11] not to lead to a strong resonant vdW interaction (this differs from our previous observation of a vdW repulsive potential, with Cs ($6D_{3/2}$) in the vicinity of a $c_\perp$ sapphire interface).

Typical results for the comparison between sapphire and silica (glass) are presented in Fig. 2, with the incident pumping conditions identical for all the spectra (for an ideal comparison, the pumping conditions *inside* the vapor should be identical; however, the index-dependent window transmission and the vdW interaction may induce some differences in the pumping). A different setting of the pumping conditions induces phenomenological differences only in the spectra, which does not alter the discussion above. At a high Cs density ($T = 150$–$170\,^\circ\mathrm{C}$, i.e., density: $(2$–$7) \times 10^{14}$ atoms/cm^3), nearly similar spectra (amplitude and line shapes) are obtained with glass and sapphire. We attribute this $7P_{1/2}$ population to a collisional pumping (in the volume), rather than to a surface-induced $6D_{3/2} \rightarrow 7P_{1/2}$ transfer (or to the weak IR fluorescence transfer). Indeed, even when pumping only with the 894 nm line, a (weak) SR signal is observed due to energy pooling collisions [12]. Differences between sapphire and silica

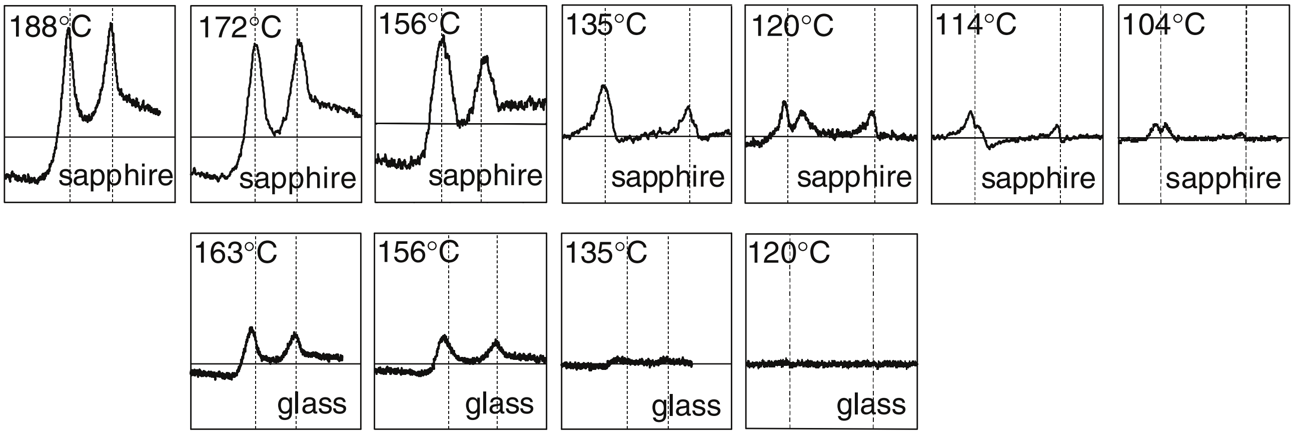

FIG. 2. Comparison as a function of Cs temperature of the $7P_{1/2}-10D_{3/2}$ SR frequency line shapes recorded at a sapphire ($c_{\parallel}$) interface, and at a silica interface. The cell with a sapphire window, owing to a sapphire body, allows a higher temperature than the silica cell. The dashed vertical lines are saturated absorption markers: note the 377 MHz hyperfine structure of Cs($7P_{1/2}$).

windows become visible when decreasing the Cs density. Indeed, the collisional pumping to $7P_{1/2}$ population is expected to vary rapidly with the density of (excited) atoms while the $7P_{1/2}$ population induced in an elementary surface-induced transfer should depend only linearly—at a given z position—on the Cs($6D_{3/2}$) population. For temperatures 135 °C or below, one observes in Fig. 2 that the SR signal at the silica interface has vanished before any observable change has occurred for the line shape. Conversely, for the sapphire interface, the SR signal remains clearly observable (down to ~100 °C, i.e., a Cs density ~10 times smaller than at 135–140 °C), while its line shape undergoes a notable evolution, owing to the onset of a strong spatial dispersion in the surface-induced $7P_{1/2}$ population. In addition, the SR line shape becomes much more sensitive to a change in the experimental conditions: the 876 nm pump detuning selects, through the vdW interaction, the distance at which the pumping rate to $6D_{3/2}$ is maximized, and the (temperature-dependent) pressure-broadening affects both the observed resonance (at 1.298 μm) and the pumping. These features confirm that in the low Cs density regime, the $7P_{1/2}$ population results from a surface-induced transfer, and no more from interatomic collisions.

We also studied the case of a YAG interface. YAG had been proved [see [11] and Fig. 1(b)] to exhibit, in front of Cs($6D_{3/2}$), a resonant repulsive behavior comparable (although weaker) to the one demonstrated with sapphire ($c_{\perp}$). The YAG behavior appears here rather similar to the one of sapphire ($c_{\parallel}$): the amplitude is smaller at low density, but there is an equivalent modification in the line shape. Figure 3 summarizes the comparison between the various interfaces, with the (normalized) SR signal "peak-to-peak" amplitude clearly exhibiting 1 order of magnitude difference between the silica window on the one hand, and the sapphire and YAG windows on the other hand. These differences are a signature of a specific surface effect, efficient for sapphire and for YAG, but not for glass.

The present demonstration is essentially qualitative, because extracting a quantitative measurement with SR spectroscopy between excited states is a quite difficult task, notably because pumping to $6D_{3/2}$ requires a nonlinear two-step process. It is also worth noting that there are little differences in the signal amplitude for sapphire and YAG, when in the regime of surface-induced transfer. This is in spite of the smaller surface-induced transfer rate for YAG [predicted [13] to be smaller by a factor of ~6 than for sapphire; see Fig. 1(b)]. This relates to the sudden transfer imposed by the z^{-3} law. Indeed, one predicts that the $6D_{3/2} \rightarrow 7P_{1/2}$ surface-transfer rate exceeds the natural decay (in vacuum) of Cs($6D_{3/2}$) for distances smaller than $Z_0 \sim 450$ nm for sapphire, and $Z_0 \sim 250$ nm for YAG. Because the atomic motion cannot be neglected during the time required for the transfer, the $7P_{1/2}$ transfer

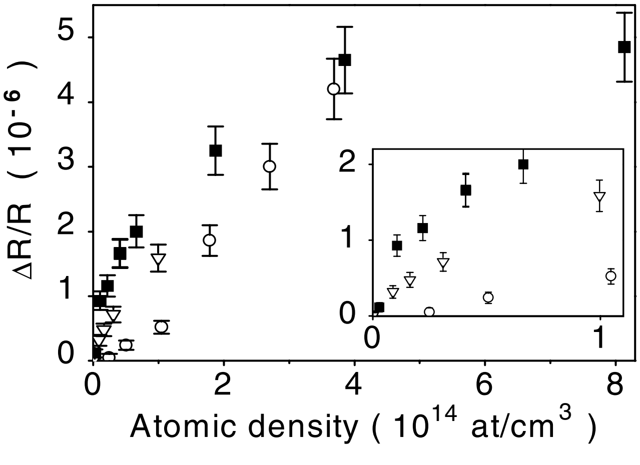

FIG. 3. Comparison of the peak-to-peak amplitudes of the SR signal as a function of the atomic density, for different types of windows (sapphire: ■; silica: ○; YAG: ▽). The inset enlarges the low density region ($<10^{14}$ atoms/cm^3), corresponding to a dominant surface interaction. For YAG and silica data, the vertical axis is normalized by a factor proportional to $(R_{\text{sapph}}/R)^{1/2}$ to compare the $7P_{1/2}$ population.

occurs at a smaller (and velocity-dependent) distance, so that the $7P_{1/2}$ level is currently populated only at distances on the order of $Z_0/2 - Z_0/3$. For sapphire and YAG, this distance range is just comparable with the depth typically probed in SR spectroscopy at 1.298 μm, as determined by the "coherence length," $(2k)^{-1} \sim 100$ nm, and the higher transfer rate for sapphire may be partly washed out by the phase factor $\exp(2ikz)$. For silica, the transfer rate is $\sim$100 times smaller than for sapphire, Z_0 drops to $\sim$100 nm, and the population transfer occurs typically at distances $\leq$30 nm. Hence, the $7P_{1/2}$–$10D_{3/2}$ transition SR signal should be notably reduced in amplitude because of the incomplete filling of the region probed in SR spectroscopy while undergoing a severe vdW shift (along with a strong inhomogeneous broadening), so that the $7P_{1/2}$ population signature should lie only in the remote wings of the $7P_{1/2}$–$10D_{3/2}$ SR spectrum.

In conclusion, the present work provides a direct signature of a dramatic surface-induced quenching of Cs($6D_{3/2}$) that makes dominant at short distances a decay channel negligible in vacuum (branching ratio $<10^{-2}$). In spite of the apparent requirement of a coincidence between the atomic excitation and the surface mode resonances, this transfer process is very general for high-lying atomic states because the width of surface resonances is considerably broader than the one of atomic transitions. Even in the nearly nonresonant case of a silica surface, one understands that the surface-induced transfer Cs($6D_{3/2}$) $\rightarrow$ ($7P_{1/2}$)—connected to the infrared absorption band of silica—has not been seen only because it occurs at small distances, well below the limits of our spatial resolution. Finally, this transfer process, with its dramatically increasing efficiency at small distances, can be of large importance when atomic control close to a surface is required, as in nanotechnologies, especially if a state-selective control is envisioned (e.g., for nanochemistry applications), or in the dynamics of a single molecule close to surfaces [14]. In addition, the angular momentum selectivity of the surface-induced transfer [15], not considered presently, could result in the preparation of a *polarized* gas layer of excited atoms, close to the surface. Among prospects, one may apply this transfer to a molecular species, which would undergo, after preparation through a chemical excitation, a vibrational cooling before reaching a given surface. Also, the reverse process of resonant atom-surface coupling with an *excited* surface could lead to the transfer of a surface quantized excitation into an atomic *absorption*. Hence, the near-field resonances of a thermally excited surface [16] would be susceptible to appear as an important heating source (relative to *internal* degrees of freedom) for neighboring atoms, excited or not.

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