Resonant van der Waals Repulsion between Excited Cs Atoms and Sapphire Surface

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(Received 17 May 1999)

We explore a situation where the van der Waals long-range atom-surface interaction is repulsive. This repulsion originates in a resonant coupling between a virtual emission at 12.15 μm of a $\mathrm{Cs}^*(6D_{3/2})$ atom and a virtual excitation of a surface polariton in sapphire. The experimental evidence is based upon the analysis of the spectroscopic response of Cs* in the near-infrared range with a technique that probes a distance range $\sim$100 nm away from the sapphire surface. We also demonstrate the critical dependence of atom-surface forces on the sapphire crystal orientation.

PACS numbers: 34.50.Dy, 12.20.Fv, 42.50.–p, 71.36.+c

The van der Waals (vW) force between neutral polarizable systems [1,2] represents a universal interaction of paramount importance in numerous fields of physics, chemistry, and biology. Its attractive character is essential for the cohesion of many chemical or biological systems. vW attraction between atomic systems and metallic or dielectric bodies is also a fundamental property in cavity quantum electrodynamics (QED) [3], and its main characteristics have been experimentally studied by means of mechanical approaches (atomic beam deflection produced by surfaces [4,5], energy threshold in atomic mirrors [6]), or, in our group, spectroscopic approaches (spectral monitoring of surface-induced atomic level shifts [7–10]).

In the nonretarded regime, the vW interaction between an atom and a surface originates in the quantum fluctuations of the atomic dipole: The fluctuating dipole polarizes the surface, and induces a dipole image instantaneously correlated with the atomic dipole. This near-field image is responsible for the *attractive* character of the vW interaction, which scales in $1/z^3$ (z is the atom-surface distance) [1].

Is it possible to turn this near-field attraction into a *repulsion*? The answer is yes, if a resonant coupling between the fluctuating atomic dipole and a surface excitation can occur [11–13]. For a dispersive *dielectric* medium with a complex permittivity $\varepsilon(\omega)$, the well-known *electrostatic image* coefficient $\mathbf{S} = (\varepsilon - 1)/(\varepsilon + 1)$ (with $0 \leq \mathbf{S} \leq 1$) has to be generalized to a complex frequency-dependent surface response [13]:

$$\mathbf{S}(\omega) = [\varepsilon(\omega) - 1]/[\varepsilon(\omega) + 1], \tag{1}$$

whose resonances ("surface polaritons" [14]) are determined by the poles of $\mathbf{S}(\omega)$.

Consider an excited atom for which one of the dipole-allowed deexcitation channels (at frequency ω_a) is near resonant with a surface polariton. Because of nonradiative, virtual coupling between the atom and surface (atomic decay followed by surface excitation), the surface response at frequency ω_a is magnified, implying a *dielectric image* coefficient, $2\mathrm{Re}[\mathbf{S}(\omega_a)]$, possibly larger than one—the value obtained for an ideal reflector. Because of the resonant enhancement, $\mathbf{S}$ is complex and the image dipole is dephased as well. When this image is phase reversed, the near-field vW attraction is turned into a near-field vW repulsion, also scaling in $1/z^3$. This is one among the rare situations of a *long-range, state-selective repulsion* exerted by a cavity wall on an atom, at distances spanning from a few nm up to $z_a = c/\omega_a$.

In this Letter, we present experimental evidence for the existence of such a repulsive van der Waals potential exerted by a sapphire surface on cesium atoms excited to the $6D_{3/2}$ level. From infrared solid-state spectroscopic data, one predicts that sapphire surface resonances should occur at about $\lambda_s \sim 12\ \mu$m and $\lambda_s \sim 21\ \mu$m, with respective linewidths 10 and 6 cm^{-1} [13]. On the other hand, the $6D_{3/2}$ Cs level can decay to the $7P_{1/2}$ level via a transition at 12.15 μm (Fig. 1). We thus expect a resonant enhancement of the Cs*-sapphire surface interaction. To study this interaction potential, we have made use of selective reflection (SR) spectroscopy in the frequency modulation (FM) mode (see, e.g., [9], and references therein), a technique that allows one to explore the response of short-lived excited states. Let us recall that it consists of monitoring the frequency dependence of light reflectivity near atomic resonances at a dielectric-vapor interface. At normal incidence, it allows one to monitor the vapor refractive index associated solely with those atoms moving

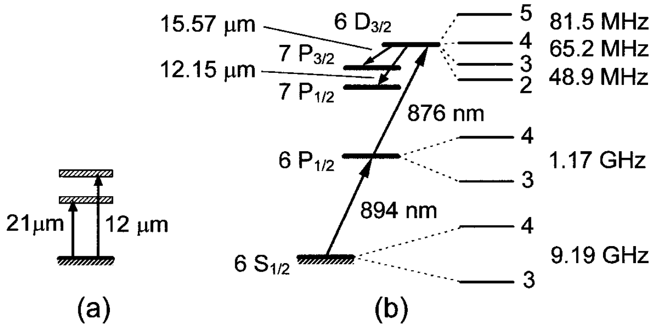

FIG. 1. Schematics of (a) the surface polariton resonances of sapphire and (b) the relevant atomic energy levels of Cs.

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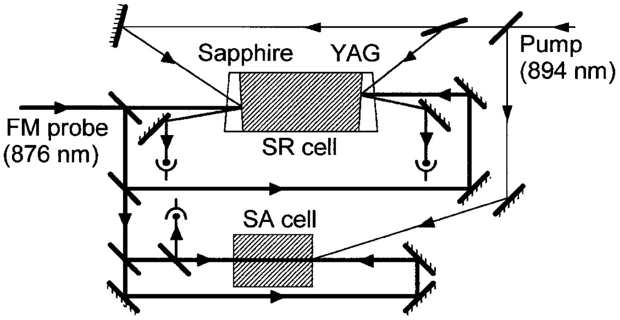

FIG. 2. Scheme of the experimental setup.

parallel to the interface in a region smaller than one optical wavelength. Their spectral response is very sensitive to long-range atom-surface interactions, and has been extensively shown to give access to the vW shift of atomic resonance lines [7–10].

To monitor the $6D_{3/2}$ level, one extends *linear* SR spectroscopy to a transition between excited states, using a two-step process, $6S_{1/2}$-$6P_{1/2}$-$6D_{3/2}$ (Fig. 1). A scheme of the experiment is given in Fig. 2. A semiconductor laser at 894 nm (pump) populates the Cs $6P_{1/2}$ level via the D_1 resonance line. Another semiconductor laser at 876 nm (probe), of weak intensity (kept $\ll 1$ mW/mm^2), monitors the refractive index of the Cs* vapor. The 876 nm laser is both frequency-stabilized onto a Fabry-Pérot cavity via optical feedback [15] and frequency modulated. An important point is to minimize any frequency correlations between the two irradiations, in order to avoid competition with the direct $6S_{1/2}$-$6D_{3/2}$ excitation, through two-photon resonance or velocity-selective stepwise excitation. Hence, the pump beam (10 mW, diameter 2 mm) is *off-axis*, and has a broad emission linewidth. It is also slightly frequency detuned, and eventually tuned to *one* of the two hyperfine states ($F = 3, 4$) of the $6P_{1/2}$ level, while the 876 nm laser is tuned to the *other* hyperfine state. Excitation transfer between the two states is carried out by incoherent processes such as resonance photon trapping in the vapor and Cs*-Cs resonant collisions. This produces a full velocity *redistribution* inside the thermal range, as was checked by transmission spectroscopy at 876 nm. The Cs vapor cell is a 8 cm long cell, contained in an oven, heated in the range $T = 110$ °C–145 °C ($p = 1$-7 mTorr) and terminated by two slightly overheated windows, one in sapphire (with a perpendicular c-axis) and one in YAG ($Y_3Al_5O_{12}$). For purposes of comparison, this setup allows one to monitor simultaneously the reflection spectra on the two end windows; sensitive photodiodes and lock-in amplifiers monitor the intensity modulation of the FM probe reflected from each window. In addition, a frequency reference is obtained due to a saturated absorption (SA) experiment performed at 876 nm on a auxiliary low-pressure Cs cell, similarly excited at 894 nm. In a side study [16], a similar SA setup, at higher temperatures, was used to analyze the pressure broadening and shift of the $6P_{1/2}$-$6D_{3/2}$ transition: We showed that, for Cs pressure up to 10 m Torr (e.g., $T < 150$ °C), the collisional line shift remains smaller than 1 MHz.

The SR spectra simultaneously monitored on YAG and sapphire windows are compared in Fig. 3, for the $6P_{1/2}(F = 4) \rightarrow 6D_{3/2}$ ($F' = 3, 4, 5$) transitions. There are striking differences between the two spectra, typical of the resonant influence of the sapphire surface, which turns the vW atom-surface interaction into the "strong coupling regime" [8]. In particular, (i) the *line shift* can be as large as 12 MHz for the Cs/sapphire spectrum, while the Cs/YAG spectrum is nearly centered on the free-space resonances; (ii) the resonance *line shapes* are notably different, and the *width* much larger for the sapphire window; (iii) the overall *amplitude* of the resonance is smaller than for YAG. Note also that a behavior essentially similar to the one monitored on the Cs/YAG interface, that is amenable to the "weak (perturbative) regime" of vW interaction, has been observed in a complementary experiment at a Cs/silica window interface.

These reflection spectra have been interpreted by a fitting with a theoretical model [17] of a (FM) SR technique, in which a nonretarded vW interaction is assumed:

$$\omega_0(z) = \omega_0 - C_3/z^3, \tag{2}$$

with $\omega_0(z)$ being the frequency of the probed transition, and ω_0 its limit in free space. In the fitting process [10], the free-space line center frequencies and hyperfine splittings are imposed by the SA resonances, so that a single set of adjustable parameters [transition homogeneous linewidth (γ), resonance amplitude, and dimensionless vW strength $A = 2C_3k^3/\gamma$, i.e., vW shift in $\gamma/2$ units at a distance $z_0 = k^{-1} = c/\omega_0 \sim 140$ nm] governs both the *shift* of the resonance "center" and the line-shape *distortion*. Acceptable fittings can be obtained *only* if we assume a *negative* value of A, corresponding to a surface-induced *blueshift* ($C_3 < 0$). Figure 4 illustrates the high quality of these fittings. Note also that different hyperfine manifolds are found to be fitted with similar values for A and γ, as theoretically expected. In the same spirit as in [8], the consistency of the interpretation is also corroborated by the Cs-pressure dependence of the

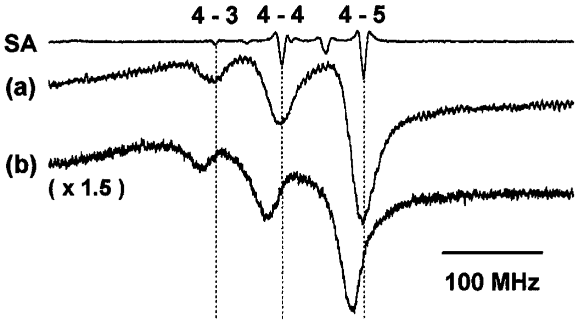

FIG. 3. FM selective reflection spectra observed on the 876 nm line on (a) the YAG window and (b) the sapphire window. Cs cell temperature: 130 °C ($p \sim 4$ mTorr). SA spectrum is recorded through second harmonic demodulation.

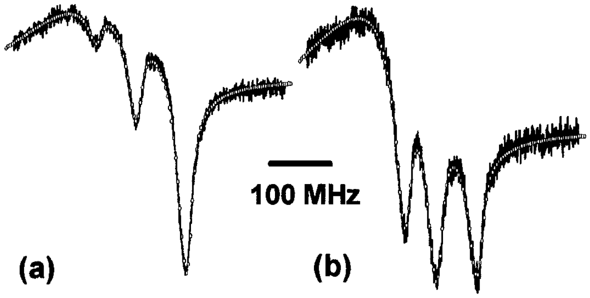

FIG. 4. Theoretical fit of an experimental FM selective reflection spectrum (876 nm line, interface sapphire/Cs vapor at 125 °C). (a) $6P_{1/2}(F = 3)$-$6D_{3/2}$ manifold, fit with $A = -7$ and $\gamma = 15.6$ MHz for all of the hyperfine components. (b) $6P_{1/2}(F = 4)$-$6D_{3/2}$ manifold, fit with $A = -7$ and $\gamma = 15.9$ MHz.

fit parameters (Fig. 5). In spite of large variations of the homogeneous linewidth γ (revealing the same linear pressure broadening ~2 MHz/mTorr, as independently measured by the SA technique [16]), the extrapolated vW strength $C_3 = A\gamma/2k^3$ is density independent, and estimated to $\sim -160 \pm 40$ kHz · μm^3. This large blueshift must be entirely ascribed to the sapphire-Cs ($6D_{3/2}$) repulsive interaction, since the $6P_{1/2}$ shift is negligible (+2 kHz · μm^3) [9].

To interpret this large value (the attraction in front of an ideal mirror is ~+22 kHz · μm^3 [18]), one has to analyze the sapphire surface response in more detail. As discussed above, the surface polariton at $\lambda_s \sim 12$ μm plays a major role. For an accurate interpretation, one needs to account for the anisotropy of the bulk phonon modes, responsible for sapphire optical birefringence. From far infrared (FIR) reflectivity data [13], one calculates that the surface resonance [pole of Re(**S**)], associated with the *ordinary refractive index*, is centered at $\lambda_s = 12.0$ μm (i.e., at 10 cm^{-1} in the blue wing of the atomic resonance), which would imply a magnified vW attraction for Cs($6D_{3/2}$). However, due to a relative shift in the frequency of the mode vibrating along the *extraordinary* axis, the surface polariton resonance, as calculated from an effective permittivity model for the c-axis normal to the surface [13], is predicted to be *redshifted* to $\lambda_s = 12.2$ μm, i.e., at 3 cm^{-1} on the *red* side of the Cs resonance, thus producing a magnified vW *repulsion*. In this case, calculations based on known Cs [18] and sapphire data predict a surface-induced blueshift of 100 kHz · μm^3 for the 876 nm line, in qualitative agreement with the experimental findings. As will be discussed elsewhere, the accuracy of such a prediction is limited because it is extrapolated from poorly accurate FIR reflectivity data [19].

The critical influence of sapphire birefringence has been observed by monitoring the 876 nm SR line-shape dependence on the window c-axis orientation. By testing different windows, we have been able to demonstrate the extreme sensitivity of the Cs($6D_{3/2}$) response to the direction of the birefringence axis. Indeed, changing the crystal *orientation* is a way of continuously *tuning* the surface polariton frequency, as will be theoretically described elsewhere. As an example, Fig. 6 compares reflection spectra for a c-axis (a) normal to the interface and (b) parallel to the interface. In the latter case, the strong repulsion has disappeared due to surface polariton detuning [20].

The spectroscopic evidence for a state-selective long-range surface repulsion opens new ways to prevent atom-surface collisions, by exciting the atom approaching the surface into a chosen quantum state. For the Cs $6D_{3/2}$ level, the experimental value of the C_3 coefficient corresponds to a repulsive potential of 0.66 meV at $z = 10$ nm, i.e., a repulsive barrier reflecting atoms with velocities up to 30 m/s, a non-negligible fraction of room-temperature atoms. An evanescent wave excitation should allow one to overcome the limitation imposed by the finite lifetime of the $6D_{3/2}$ level (~50 ns in free space). However, a tougher limitation could be associated with the dissipative surface coupling, governed by Im[$\mathbf{S}(\omega)$]. This coupling originates in the quadrature component of the (polariton-enhanced) near-field dipole image: It implies a *real* excitation transfer to the surface and therefore a reduction of the atom excited-state lifetime [11,12]. Let us outline that, here, the resonant atom-surface coupling is *irreversible*, as opposed to the *strong coupling regime* [3] in cavity QED, when the excitation energy oscillates back and forth between the atom and the microresonator.

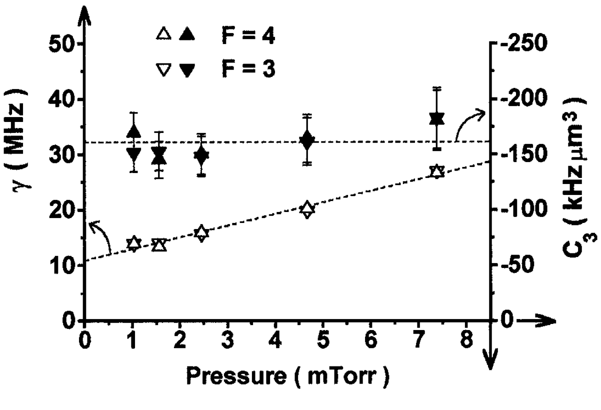

FIG. 5. Cs-pressure dependence of the linewidth γ and of the strength of interaction C_3.

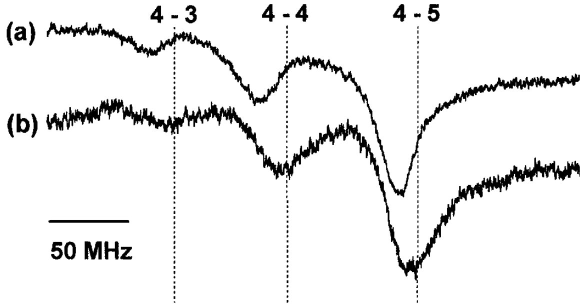

FIG. 6. Reflection spectra at the Cs/sapphire interface with (a) the c axis perpendicular to the window and (b) the c axis parallel to the window. Vertical dashed lines: references provided by the SA spectrum.

SR spectroscopy is not as well adapted to the observation of this *nonradiative* decay. The strong modification of the $6D_{3/2}$ decay branching ratio in favor of the $6D_{3/2} \rightarrow 7P_{1/2}$ deexcitation channel (whose efficiency is only 5×10^{-3} in free space) could be monitored via the observation of the induced population in the $7P_{1/2}$ level close to the surface, after selective excitation of the $6D_{3/2}$ level. This should yield complementary information on the surface polariton line strength and frequency. The properties of sapphire surface resonances could be more precisely explored by studying various well-chosen excited states of Cs, or other alkalis, such as Rb [21]. This would allow for a fine monitoring of surface polariton spectroscopy [9,22], with the accuracy of an atomic resonance frequency, and should be complementary to the refined predictions which should be expected from today's techniques in FIR ellipsometry [23].

Let us finally mention a few of the prospects opened by this experimental evidence of a quantized resonance between an excitation at the atomic level and a macroscopic dielectric body.

(i) Because of the position dependence of the atomic transition—finally shifted off-resonance with the surface modes—the potential explored by an atom traveling towards the surface may become much less monotonic than the usual z^{-3} dependence. This may allow for the appearance of trapping regions induced by a combination of several dispersive surface resonances, and for populating the molecular bound states of the "atom + image" complex, through avoided crossings with other levels (e.g., for the Cs sapphire, $6D_{3/2}$ and $6D_{5/2}$ levels cross at $z \sim 5$ nm).

(ii) It is conceivable to heat the sapphire window and thermally excite the surface modes. Hence, one might expect to induce the *reversal* of the presently demonstrated resonance, i.e., a resonant coupling between a virtual photon *absorption* [e.g., for $\mathrm{Cs}^*(7P_{1/2})$ towards $6D_{3/2}$], and surface mode *deexcitation*. Such a resonance in cavity QED, typical of a nonzero temperature surface, could even be expected for an atom in the ground state. Note that, conversely, the colored bath of thermal photons, responsible for changes in the lifetime [24], is not expected to induce *resonant* effects.

(iii) A precise engineering of the interaction between selected atomic states and a dielectric wall appears feasible, notably through the doping of a window with adequate dispersive material, or by structuring the surface (orientation of the birefringence, dielectric waveguide, sandwiches of controlled thickness, photonic bandgaps, etc.).

We thank G. Rahmat for the diode lasers, and J. R. R. Leite for various contributions. The sapphire cells were prepared at the Armenian Institute of Physics, by the group of D. Sarkisyan. H. F. and S. S. acknowledge support from the French Government.

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[1] J. E. Lennard-Jones, Trans. Faraday. Soc. **28**, 334 (1932).

[2] E. M. Lifchitz, Sov. Phys. JETP **2**, 73 (1956); **2**, 360 (1956).

[3] S. Haroche, in *Fundamental Systems in Quantum Optics*, edited by J. Dalibard, J. M. Raimond, and J. Zinn-Justin (North-Holland, Amsterdam, 1992), pp. 767–940; E. A. Hinds, Adv. At. Mol. Opt. Phys. Suppl. **2**, 1–56 (1994).

[4] A. Anderson, S. Haroche, E. A. Hinds, W. Jhe, and D. Meschede, Phys. Rev. A **37**, 3594 (1988).

[5] C. I. Sukenik, M. G. Boshier, D. Cho, V. Sangoghdar, and E. A. Hinds, Phys. Rev. Lett. **70**, 560 (1993).

[6] A. Landragin, J.-Y. Courtois, G. Labeyrie, N. Vansteenkiste, C. I. Westbrook, and A. Aspect, Phys. Rev. Lett. **77**, 1464 (1996).

[7] M. Oria *et al.,* Europhys. Lett. **14**, 527 (1991).

[8] M. Chevrollier *et al.,* Opt. Lett. **16**, 1879 (1991).

[9] M. Chevrollier *et al.,* J. Phys. II (France) **2**, 631 (1992).

[10] N. Papageorgiou *et al.,* Laser Phys. **4**, 392 (1994).

[11] R. R. Chance, A. Prock, and R. Silbey, Phys. Rev. A **12**, 1448 (1975), and references therein.

[12] J. M. Wylie and J. E. Sipe, Phys. Rev. A **32**, 2030 (1985).

[13] M. Fichet *et al.,* Phys. Rev. A **51**, 1553 (1995).

[14] See, e.g., E. Burstein *et al.,* J. Vac. Sci. Technol. **11**, 1004 (1974).

[15] B. Dahmani, L. Hollberg, and R. Drullinger, Opt. Lett. **12**, 876 (1987).

[16] H. Failache *et al., (*to be published).

[17] M. Ducloy and M. Fichet, J. Phys. II (France) **1**, 1429 (1991). Here, an additional hypothesis is that the $6P_{1/2}$ population is spatially homogeneous. The corresponding tests will be reported elsewhere.

[18] Cs values tabulated in Ref. [13] are corrected in H. Failache, Ph.D thesis, Université Paris-Nord, 1999 (unpublished).

[19] If one assigns the measured repulsive potential to the resonant coupling only, it yields $\mathrm{Re}(\mathbf{S}) = -11.8 \pm 3$ for the surface dispersive response at 12.15 μm. This value stands at the maximum negative value predicted for sapphire [13], thus corresponding to a surface polariton further redshifted by approximately 2 cm^{-1} from the predicted line center at 12.2 μm (i.e., largely inside the FIR data accuracy).

[20] For the parallel c-axis, the line shape was insensitive to polarization changes, in spite of the break in cylindrical symmetry. This should result from the loss of resonant behavior.

[21] In particular, Rb $(6D)$, whose experimental study is presently in progress, is also strongly coupled to the $7P$ levels, through virtual transitions at 12.21 μm $(6D_{5/2}\text{-}7P_{3/2})$ and at 11.74 and 12.24 μm $(6D_{3/2}, 7P_{1/2}, 7P_{3/2})$, suitable for exploring the sapphire surface resonance.

[22] M. R. Philpott, Chem. Phys. Lett. **19**, 435 (1973).

[23] J. Kircher *et al.,* J. Opt. Soc. Am. B **14**, 705 (1997); J. Humlicek and A. Röseler, Thin Solid Films **234**, 332 (1993); A. Brunet-Bruneau *et al.,* Appl. Opt. **35**, 4998 (1996).

[24] K. S. Lai and E. A. Hinds, Phys. Rev. Lett. **81**, 2671 (1998), and references therein.