

Spectroscopy of atomic rubidium at 500-bar buffer gas pressure: Approaching the thermal equilibrium of dressed atom-light states

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We have recorded fluorescence spectra of the atomic rubidium D-lines in the presence of several hundreds of bars of buffer gas pressure. The large collisional broadening of this system interpolates between usual atomic physics gas phase and solid-liquid phase conditions. In our buffer gas cell, with additional saturation broadening, a spectral linewidth comparable to the thermal energy of the atoms in the cell is achieved. An observed intensity-dependent blue asymmetry of the spectra is interpreted as evidence for the onset of thermal equilibrium of dressed atom-light states.

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Thermal equilibrium is defined as the state of maximized entropy of a statistical ensemble coupled to a thermal bath. It is a prerequisite for most known phase transitions, such as Bose-Einstein condensation of dilute atomic gases or many solid-state physics concepts [1]. More recently, phase transitions of coupled particle-light degrees of freedom have been investigated in the framework of polariton quasiparticle condensation [2]. Experimentally, exciton polariton systems gave compelling evidence for condensation [3,4]; however, the short polariton lifetimes in the order of 1 ps raised the question of whether the system is fully thermalized [4].

In the area of atomic physics, extremely long coherence times of excitations are readily achieved [5]. On the other hand, light sources along with spontaneous decay here usually drive the system far from thermal equilibrium. The lack of a sufficiently fast thermalization process has so far prevented equilibrium thermodynamics of coupled atom-light states to be a useful concept.

We report here on experiments in which up to 500 bars of buffer gas pressure induce a linewidth of a few nanometers for the rubidium D-lines. At high optical power of the exciting continuous-wave laser source, the fluorescence spectra are broadened by additional power broadening to values exceeding the thermal energy $k_B T$ in the heated gas cell. In this regime, we observe a strong blue asymmetry of the spectra. The spectral asymmetry increases further when extrapolating our data toward infinitely high excitation intensity. We interpret our results as evidence for the coupled atom-light states (“dressed states”) to approach thermal equilibrium, with the thermalization being due to frequent rubidium-buffer gas collisions. Notably, equilibrium is achieved in the presence of an external monochromatic driving optical field.

Our experiment benefits from collisional aided excitation, which allows us to saturate the atomic transition at large detuning with a cw laser of moderate power and spectroscopically detect the onset of thermal equilibrium. Pressure broadening of atomic spectral lines is a long investigated topic [6–11], although the high-pressure regime where multiparticle collisions become significant has remained largely unexplored. For binary collisions at large laser detunings, the impact limit ceases to be fulfilled, and atomic lines often become asymmetric. A prediction of the absorption profile requires knowledge of the molecular potential curves of the

collisional partners, and can be expressed, e.g., in terms of modulated dipole approaches [12]. For an analysis of the extreme wing of fluorescence spectra, models that account for the partition function of atom-perturber quasimolecules were used [13]. In an interesting experiment, deviations from the Einstein coefficients for absorption and stimulated emission were observed for far off-resonant excitation in a collisionally broadened system [14].

We use an optical thin ensemble in a single-pass configuration to minimize the influence of propagation effects. Consider a two-level system with ground state $|g\rangle$ and excited state $|e\rangle$ subject to laser irradiation and coupled to a thermal bath. When tuned into resonance, the optical field of frequency ω connects the states $|g, n+1\rangle$ and $|e, n\rangle$, respectively, where the first quantum number denotes the internal atomic state and the second one the photon number; see Fig. 1(a). The eigenstates of the coupled atom-light Hamiltonian are the dressed states $|1(n)\rangle = \cos \Theta |e, n\rangle + \sin \Theta |g, n+1\rangle$ and $|2(n)\rangle = -\sin \Theta |e, n\rangle + \cos \Theta |g, n+1\rangle$. Here Θ denotes the mixing angle defined by $\tan 2\Theta = -\Omega_0 / \delta$, where $\delta = \omega - \omega_{\text{atom}}$ is the laser detuning from atomic resonance and Ω_0 is the resonant Rabi coupling. The splitting between $|1(n)\rangle$ and $|2(n)\rangle$ is $\Omega = \sqrt{\delta^2 + \Omega_0^2}$. In this dressed state basis, the physics

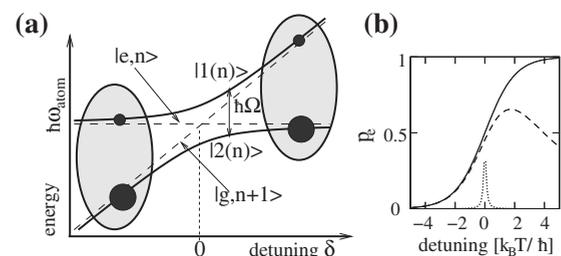


FIG. 1. (a) Dressed state energy levels as a function of laser detuning. A thermalization process and the corresponding equilibrium populations for a red and a blue detuning value are indicated. The size of the splitting between dressed state components near resonance has been exaggerated. (b) Excited-state population versus detuning, where a Lorentzian line shape was taken for the detuning-dependent saturation parameter $s(\delta)$: For $s(k_B T / \hbar) \ll 1$, i.e., small linewidth, which yields a line shape resembling that of $s(\delta)$ (dotted line), $s(k_B T / \hbar) \approx 1$ (dashed line), and $s(\delta) \gg 1$, i.e., thermal equilibrium of dressed states (solid line).

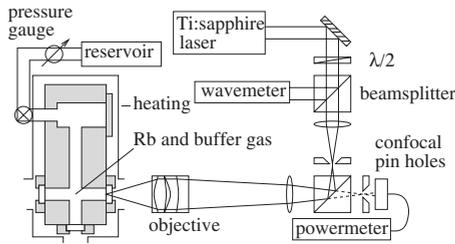


FIG. 2. Scheme of the experimental setup.

can be described by a two-state system coupled to a thermal bath. It is noteworthy that in the case that our bath can be modeled by a series of bosonic oscillations, a mapping to the spin-boson model is obtained [15]. If the thermalization time constant is smaller than the spontaneous decay time of the excited state, we expect in a simple picture that for a given laser detuning, the dressed states are populated according to Boltzmann's distribution function, as indicated in Fig. 1(a). For a splitting between dressed state components comparable to the thermal energy $k_B T$, the lower dressed state will be predominantly populated.

The onset of thermal equilibrium of the coupled atom-light system leads to a drastic modification of the expected fluorescence line shape: For far red laser detuning, the energetically favored lower dressed state coincides with the ground-state component $|g, n+1\rangle$, while it evolves into the (spontaneously decaying) excited component $|e, n\rangle$ for far blue detuning. If thermal equilibrium can be achieved for all used detuning values, we expect the excited-state population to increase with laser frequency. This increase is relatively slow, i.e., with a characteristic detuning scale of $k_B T/\hbar$ arising from the Boltzmann factor. An extreme blue asymmetry of the line profile is obtained, which we expect to resemble a Fermi-Dirac-type profile as the relevant partition function of the two-level dressed state system. This line profile is indicated by the solid line in Fig. 1(b). On the other hand, if the achieved saturation $s(\delta)$ is moderate or small, spontaneous decay drives the system out of thermal equilibrium, which is the usual case for the required large detuning values. The dashed and dotted lines of Fig. 1(b) give corresponding examples of line profiles, as derived from a theoretical model (given below).

A scheme of our experimental setup is shown in Fig. 2. A rubidium filled stainless steel oven with volume of a few cm^3 and sapphire windows is used as a pressure cell. Buffer gas (supplier, Air Liquide; purity, 5.0) is filled into the chamber through an attached valve with pressures near 230 bars (at room temperature). During operation, the cell is heated to 260 °C, which results in a vapor pressure limited rubidium number density of $\approx 1.0 \times 10^{16} \text{ cm}^{-3}$. In the sealed chamber, the buffer gas pressure then increases to approximately 400 bars (40 MPa) for helium and 500 bars (50 MPa) for argon.

Tunable laser radiation for excitation of the atoms is provided by a Ti:sapphire ring laser. The laser radiation is focused into the rubidium chamber to a beam radius of $\sim 3 \mu\text{m}$. The beam focal plane within the cell is placed near the sapphire window. To selectively record the atomic fluorescence from regions of high laser intensity, we furthermore

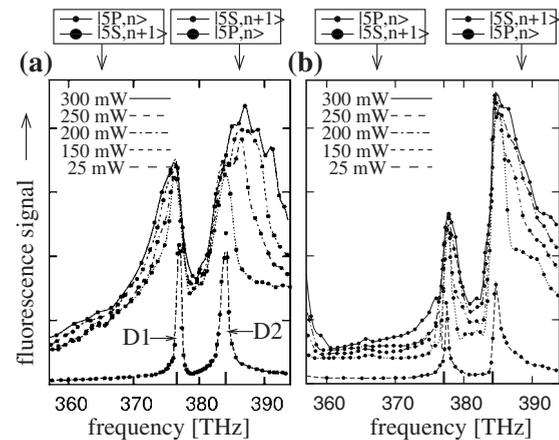


FIG. 3. Rubidium fluorescence signal versus laser detuning at (a) 500-bar argon and (b) 400-bar helium buffer gas pressure for different optical beam powers. The small drawings on the top indicate the population of the atom-light states on the red and blue sides of the electronic transition, respectively. The unperturbed positions of the rubidium D1- (377,1 THz) and D2-line (384,2 THz) are marked on the frequency axis, respectively.

spatially filter both the incident optical beam and the outgoing fluorescence with pinholes. The estimated optical density within the beam focal length, which equals the length of the investigated region in this confocal geometry, is below 5% on resonance.

In initial experiments, we have measured the lifetime of the rubidium 5P state at high buffer gas pressures. At pressure values of 200 bar (20 MPa), which was the maximum achieved pressure value achieved in these early data sets, the measured lifetime was, within our measurement accuracy of 5 ns, in agreement with the ~ 27 ns natural lifetime of the transition. At a collisional rate of 10^{11} s^{-1} , the atoms experience more than 10^3 collisions within a natural lifetime. This confirms the remarkable elasticity of excited atoms with rare-gas collisions [16], and is a prerequisite for the thermalization of dressed states in our experiment. The excited-state lifetime is some four orders of magnitude above the values observed in semiconductor exciton systems [2].

Typical fluorescence spectra recorded under constant high-pressure buffer gas conditions for variable light intensities are shown in Fig. 3. While the observed line shapes differ somewhat for both used buffer gases, indicating the “transiently chemical” nature of optical collisions in a regime beyond the impact limit, let us draw our attention to some general features for both spectra. At moderate optical power ($P \approx 25$ mW), the linewidths are clearly below the thermal energy $k_B T$ (≈ 11 THz at $T = 530$ K). At higher power levels, the linewidths increase to values around $k_B T$. Notably, the far red side of the D1-line tends to saturate to a comparatively low fluorescence level, while at the blue side of the D2-line much higher fluorescence is observed, though in the far wings even at maximum power levels (300 mW) the transition is less saturated. We attribute this asymmetry to the dressed state system approaching thermal equilibrium for high power levels. The resonant Rabi coupling $\Omega_0/2\pi$ at full optical power is of order 0.1 THz, i.e., much smaller than $k_B T/\hbar$, so that on the detuning scale of Fig. 3 except very

close to resonance the mixing of ground and excited states is small. For the sake of simplicity, let us restrict the discussion to the red side of the D1-line and the blue side of the D2-line, as in these limits the influence of the upper state fine-structure splitting is smallest. While on the red side the energetically lower dressed state component coincides with $|g, n+1\rangle$, leading to an enhanced ground-state population in thermal equilibrium, on the blue side of the transition the lower dressed state coincides with $|e, n\rangle$ so that the excited atomic state is expected to be favored in equilibrium, as indicated in the boxes at the top of Fig. 3 and in Fig. 1(a). At low optical power levels, the upper state spontaneous decay drives the system out of equilibrium.

For a theoretical model of the transition to thermal equilibrium of such coupled atom-light states, we consider the relevant rates for excitation and deexcitation. A comprehensive treatment of dressed state approaches to collisional broadening is given in [17]. When a buffer gas atom approaches, the atomic energy levels are shifted, and a transfer between the dressed state energy levels can occur once the laser transiently becomes resonant. Let c_{21} and c_{12} denote the rate constants for collisional transfer between the dressed state energy levels $|2(n)\rangle$ and $|1(n)\rangle$, which for binary collisions in the secular limit at large detunings ($|\delta| \gg \Omega_0 \gg \Gamma$) can be shown to be proportional to both the buffer gas density and the laser intensity [17]. For a nonzero spontaneous decay rate Γ of the excited state, also a coupling between states of different manifolds occurs. If we assume our system to be optically thin, we can trace over the photonic quantum numbers and obtain the following Boltzmann-like rate equations:

$$\dot{p}_1 = c_{21}(\delta)p_2 - c_{12}(\delta)p_1 - \Gamma \cos^4 \Theta p_1 + \Gamma \sin^4 \Theta p_2, \quad (1a)$$

$$\dot{p}_2 = -c_{21}(\delta)p_2 + c_{12}(\delta)p_1 + \Gamma \cos^4 \Theta p_1 - \Gamma \sin^4 \Theta p_2, \quad (1b)$$

where p_1 and p_2 are the populations of states $|1(n)\rangle$ and $|2(n)\rangle$, respectively. To derive a relation between the rates c_{12} and c_{21} , consider the equilibrium solution ($\dot{p}_1 = \dot{p}_2 = 0$) in the absence of spontaneous decay (i.e., $\Gamma \rightarrow 0$). In this limit, usual Boltzmann statistics yields $p_1 = e^{\hbar\Omega/k_B T} / (1 + e^{\hbar\Omega/k_B T}) = 1 / (1 + e^{-\hbar\Omega/k_B T})$, which resembles the Fermi-Dirac distribution function. From Eqs. (1) we obtain $p_1 = 1 - p_2 = 1 / (1 + c_{12}/c_{21})$ so that the following relation of the rate constants must apply:

$$c_{12} = c_{21} \exp(\hbar\Omega/k_B T) \equiv c(\delta), \quad (2)$$

similar to that shown in [14]. Physically, the increased rate toward a population of the lower dressed state can be understood for a binary collisional system in terms of the equilibrium population distribution of quasimolecular states, as follows from [13]. Spontaneous decay drives the dressed state system out of equilibrium, and the full Eq. (1) yields a stationary solution

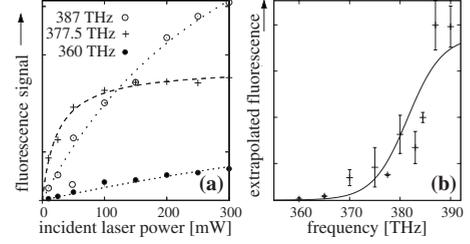


FIG. 4. (a) Fluorescence signal at 400-bar helium buffer gas as a function of optical power for three different values of the laser frequency. (b) Expected atomic fluorescence signal at infinite laser power, obtained from extrapolation curves as in (a), versus laser frequency. The shown error bars were obtained from the extrapolation fits. The data have been fitted with a Fermi-Dirac distribution, assuming thermal equilibrium of the two-level dressed state system.

$$p_1 = \frac{\sin^4 \Theta + s(\delta)e^{-\hbar\Omega/k_B T}/2}{(\cos^4 \Theta + \sin^4 \Theta) + s(\delta)(1 + e^{-\hbar\Omega/k_B T})/2}, \quad (3)$$

where $s(\delta) = 2c(\delta)/\Gamma$ denotes a generalized saturation parameter.

In our experiment, fluorescence spectra are observed so that our measurement is in the bare state basis. In the experimentally relevant limit $|\delta| \gg \Omega_0$, the upper state population simplifies to

$$p_e = \frac{s(\delta)/2}{1 + s(\delta)(1 + e^{-\hbar\delta/k_B T})/2}. \quad (4)$$

An illustration of the modification of the line shape when approaching thermal equilibrium has been shown in Fig. 1(b). From Eq. (4), the usual (saturated) line shape of a two-level system $p_e \approx [s(\delta)/2]/[1 + s(\delta)]$ is recovered in the limit $k_B T \gg \hbar|\delta|$. On the other hand, if at large transition linewidth and laser intensity, saturation is achieved even at detuning values as large as the thermal energy $k_B T$, the detuning dependence of the exponential term in Eq. (4) becomes relevant and one readily finds that the formula [and Eq. (3)] reduces to a Fermi-Dirac distribution. This corresponds to the case of thermal equilibrium of the two-level dressed state system. A prediction of the saturation curve $s(\delta)$ involves a derivation of the transition rate between avoided crossings of dressed state quasimolecular levels. This is a highly non-trivial task in the dense buffer gas regime investigated here, especially since we expect multiple particle collisions to play an important role. On the other hand, if thermal equilibrium can be achieved for all used laser detunings, the predicted line shape reduces to a Fermi-Dirac profile independently of the form of $s(\delta)$.

Figure 4(a) shows the experimentally observed fluorescence versus optical power for three different laser frequencies for the data with helium buffer gas. These saturation curves have been fitted with Eq. (4). This fitting procedure assumes $|\delta| \gg \Omega_0$ and that $s(\delta)$ is linearly dependent on the laser intensity, an assumption in agreement with present theories of optical collisions, whose validity in the yet largely unexplored high-pressure buffer gas regime with large multiparticle collisional rate, however, remains to be tested [18]. Near a line center (crosses), the curve saturates

already at a relatively low power level to an intermediate fluorescence level. For significant detuning, the optical power at which saturation is achieved is higher, as visible both for blue (circles) and red (dots) detunings. Interestingly, the saturation level of fluorescence is clearly different in both cases, with the blue (red) detuning leading to largest (smallest) values. At full saturation, where spontaneous processes are negligible compared to stimulated processes, we expect the dressed state populations to be in thermal equilibrium. This also follows from Eq. (4) in the limit of infinite saturation.

Figure 4(b) shows the value of fluorescence extrapolated to infinite beam power, as taken from such curves, as a function of laser frequency. This is to provide an estimate for the upper state population at thermal equilibrium [without knowledge of an explicit expression for the detuning dependence of $s(\delta)$]. Usually, one would now expect a constant value. However, our data can be well fitted with a Fermi-Dirac distribution $p_e(\delta) = 1/(1 + e^{-\delta/k_B T})$ as expected for the excited-state population of the thermalized atom-light system, where the detuning δ was measured relative to the center of the D-lines. The agreement between theory and experiment is quite reasonable, which supports the assumption of the dressed states to approach thermal equilibrium at high laser power. From the fit to the theoretical curve, we anticipate that, notably, on the far blue side of the spectrum, even inversion is achieved despite the presence of thermal equilibrium. Due to an exponential suppression of the stimulated emission rate for $\delta \gg 0$ [see Eq. (2)], this does not lead to amplification (or even lasing) at frequency ω . An issue remaining to be clarified is that a best fit is obtained with a temperature $T = 162(58)$ K, which is significantly below the cell temperature. For a comparable fit with the argon buffer

gas spectral data, a temperature of 270(91) K was obtained. At present, the origin of this disagreement of temperatures is not resolved, and clearly a more detailed theoretical model is required. One explanation would be that laser cooling (heating) processes of the thermal gas occur on the red (blue) side of the transition due to the energy loss (gain) during collisional aided excitation, as was proposed in [19]. If the spontaneously emitted photons are energy-shifted by an amount comparable to $k_B T$, respectively, to the incident photon wavelength, efficient cooling may be possible in such pressure-broadened systems, comparable to results obtained on the optical cooling of solids [20].

To conclude, we have recorded spectra of rubidium atoms in a collisionally broadened regime interpolating between usual atomic physics gas phase and solid-liquid phase conditions. The saturation dependence of the line profiles is interpreted as evidence for the onset of thermal equilibrium of dressed atom-light states.

In the future, it would be interesting to study novel laser cooling mechanisms of high-pressure atomic gases based on collisionally aided excitation. A different perspective of the demonstrated method includes a BEC-like phase transition to a condensed atom-light polariton phase [21,22]. This requires a continuum of available states, as can be provided by the transverse modes of an optical cavity [2]. In a cavity, the optical thick regime is easily reached, where in the strongly coupled limit polaritons become the relevant excitations [22].

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