Faraday Effect as a Probe of Hindered Electronic Precession in Atoms

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We compare the Faraday spectrum with the dispersion spectrum near the D_2 line of Rb atoms immersed in a high density Xe buffer gas. We observe deviations from the standard Becquerel relation, which relates the Faraday effect of an atomic gas to its dispersion. The deviations are due to coupling of the Rb valence electron to the Xe environment. The Rb D_2 transition dipole moment becomes rotationally locked to the instantaneous collision axes at Xe densities of $\sim 10^{20}$ cm^{-3}.

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When linearly polarized light passes through matter the plane of polarization will rotate when a longitudinal magnetic field is applied. This so-called Faraday effect has been studied intensively for more than a century. The microscopic origin of the effect is that the magnetic dipole moments of the atoms in the medium precess in the magnetic field, thus leading to magnetic optical activity. In a dilute atomic gas the magnetic precession is undisturbed and the Faraday rotation angle, θ_{Far}, is proportional to the dispersion, $dn/d\omega$, as expected from classical electrodynamics. This result is called the Becquerel relation [1–3],

$$\theta_{\mathrm{Far}} = \theta_{\mathrm{Becq}} = \alpha \frac{e}{2mc} BL\omega \frac{dn}{d\omega}, \tag{1}$$

where B is the longitudinal magnetic field, L is the length of the sample, and $\alpha = 1$ for a spinless transition. Quantum mechanically, Eq. (1) remains valid for an optical transition in the presence of nuclear and/or electron spin if we deal with an *isolated* transition. In this case the lower and upper levels have well-defined g factors ($\neq 1$), generally leading to $\alpha \neq 1$ in Eq. (1) [2,3].

For molecular systems the Faraday effect is substantially more complicated than for atoms due to their internal structure [3–5] and violations of the Becquerel relation are observed. In some cases it is possible to use information from Faraday spectra to assist in the determination of molecular structure [5]. For condensed matter the complications are even more severe and it is difficult to find relations between internal structure and the Faraday effect.

Even for an atomic gas nontrivial behavior of the Faraday effect leading to violation of the Becquerel relation can be expected if the density is high enough. Such violations have been predicted for the case that the broadening of the optical transition cannot be described within the impact approximation even close to line center [2]. It corresponds to the onset of quasimolecular behavior of the gas or, more specifically, Born-Oppenheimer (BO) coupling. In this Letter we report experimental observation of this violation of the Becquerel relation for a high density atomic gas; it corresponds to the first step on the route towards molecular complexity of the Faraday effect.

We start by illustrating the microscopic mechanism responsible for this kind of non-Becquerel behavior. Consider an isolated, binary collision between a ^1S state perturber atom and a probe atom with a ^1S ground state and a ^1P excited state connected by an optical transition, as illustrated in Fig. 1. If the electrostatic interaction between the two atoms has only a weak angular dependence, the excited p state maintains its orientation due to electronic inertia [Fig. 1(a)]. If the electrostatic interaction has a strong angular dependence, the corresponding torque orients the p state along the internuclear axis [Fig. 1(b)]. Thus rotational BO coupling takes place when the electrostatic splitting $(V_\Sigma - V_\Pi)/\hbar$ of the p state exceeds the angular velocity v/R [6],

$$V_\Sigma - V_\Pi \geq \hbar v/R, \tag{2}$$

where $V_\Sigma(R)$ and $V_\Pi(R)$ are adiabatic potentials, v is the relative velocity of the atoms and R is their distance. Solving the inequality (2) for R leads to $R \leq R_{\mathrm{lock}}$, where R_{lock} is the locking radius. For distances smaller than R_{lock} the p state and thereby the electric dipole moment responsible for the S-P transition becomes locked to the internuclear axis. The same takes place for the magnetic dipole moment of the p state leading to modification of the magnetic precession. For alkali noble-gas systems $R_{\mathrm{lock}} \sim 10$ Å.

The spectroscopic interpretation of the inequality (2) is that V_Σ and V_Π correspond to line shifts and splittings

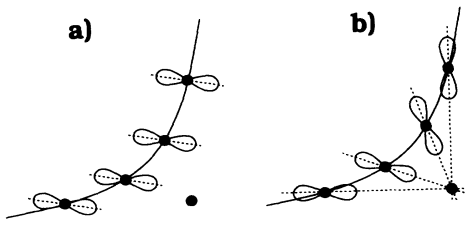

FIG. 1. The evolution of an electronic p state during a collision with an s-state perturber. When electronic inertia dominates (a) the wave function is fixed in the laboratory frame; when Born-Oppenheimer coupling dominates (b) the p state is locked to the collisional axis.

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(assuming $V=0$ for the ground state) and $\hbar v/R$ is the bandwidth of the radiation absorbed or emitted during a collision. If inequality (2) is satisfied, a gas-phase atom always feels a (time dependent) axis; it corresponds to invalidity of the impact approximation at line center and the onset of quasistatic behavior (normally occurring exclusively in the far wing) in the line core.

The detailed connection between the adiabatic potentials and gas-phase spectra is made by spectral line broadening theories. The most advanced of these, the so-called unified line broadening (ULB) theory [7], describes the full shape of the line, reducing to the quasistatic theory in the far wings and the impact theory at the line core [8]. However, the ULB theory is a perturbation theory which makes the binary collision approximation, i.e., $\Gamma\tau \ll 1$, where Γ is the rate of impact broadening collisions (homogeneous linewidth) and τ the duration of such a collision, thus excluding predominance of quasistatic conditions in the line core. Therefore the theory can at most be expected to describe the *onset* of Becquerel violation due to quasistatic conditions [9]. Attempts to include the effect of multiple (overlapping) collisions in spectral line broadening theory have met only limited success [7]. A formal treatment based on the ULB theory leads to the following expression:

$$\theta_{\text{Becq}} - \theta_{\text{Far}} = \omega \left(\delta' \frac{dn}{d\omega} + \gamma' \frac{d\kappa}{d\omega} \right) \frac{e}{2mc} BL , \qquad (3)$$

where κ is the imaginary part of the refractive index (absorption) and δ', γ' are small parameters of order $\Gamma\tau$ [9,10].

We choose the D_2 resonance line of Rb atoms highly diluted in Xe buffer gas as an experimental system to observe this effect. As compared to other alkali noble-gas systems Rb:Xe has a small v and large $V_\Sigma - V_\Pi$ and thus inequality (2) can be satisfied at relatively low buffer gas density. Note that the contribution of unresolved bands due to RbXe molecules [11] does not have to be addressed since this is implicitly taken into account by using the adiabatic Rb:Xe potentials and assuming thermal equilibrium in the ULB theory.

The effects of the Rb electron spin and nuclear spin are easily accounted for if we choose the Xe density such that the homogeneous linewidth, Γ, satisfies $\Delta_{\text{hf}} \ll \Gamma \ll \Delta_{\text{fs}}$, where Δ_{hf} and Δ_{fs} are the hyperfine and fine structure splittings. For Rb we have $\Delta_{\text{hf}} \leq 2\pi \times 6.8$ GHz and $\Delta_{\text{fs}} \approx 2\pi \times 7100$ GHz. In this case we deal with effectively isolated lines and we can still use Eq. (1), with $\alpha = \frac{4}{3}$ for the D_1 line and $\alpha = \frac{7}{6}$ for the D_2 line [2,3]. To fulfill the above condition we choose the Xe density, [Xe], in the range 3×10^{19} cm^{-3} < [Xe] < 1.3×10^{21} cm^{-3}. Use of Racah algebra then shows that remaining spin-induced tensorial Becquerel violations are smaller than 1%. Outside this density range the treatment is more complicated since we deal with partially resolved transitions. Equation (1) must then be generalized into a tensorial relation. We will treat the combination of a tensorial Becquerel relation (due to nuclear spin) and the onset of BO coupling, as described by Eq. (3), in a later publication [12]. We choose to investigate violations of Eq. (1) near the D_2 line since the upper $^2\Pi_{1/2}$ level for the D_1 line is effectively spherical [13] and lacks the quasistatic anisotropy (Σ-Π splitting) necessary for violations of Eq. (1) in the ULB picture.

We use the experimental setup shown in Fig. 2 to investigate deviations from the Becquerel relation. The frequency of a semiconductor laser is current tuned over part of the pressure broadened Rb line. Using different laser temperatures it is possible to cover more than 600 GHz, without mode hopping, with two selected Hitachi HL7838G lasers. Light output in side modes below threshold is filtered out with the monochromator. Scans are linearized along the frequency axis using interferometer fringes for calibration. Absolute frequency calibration is made with vacuum cells filled with Rb and I_2. As a sample cell we use a 4 cm long glass vessel filled with Rb metal and Xe. For $T \approx 350$ K we have [Rb] $\approx 10^{12}$ cm^{-3}, which gives approximately one absorption length (L_{abs}) at the center of the D_2 line for [Xe] $\approx 6.0\times10^{19}$ cm^{-3}. This corresponds to $\Gamma \approx 2\pi \times 45$ GHz [14], i.e., much larger than the Doppler width, $2\pi \times 0.5$ GHz.

The absorption and Faraday spectra are recorded simultaneously in a balanced bridge configuration. A longitudinal magnetic field ($B \approx 0.03$ T) is supplied by two coils. A polarizing beam splitter is oriented at about 45° relative to the incoming polarization to obtain equal intensities I_1 and I_2 at the two photodiodes 1 and 2 for the case $B=0$. By suitably switching the magnetic field between B and $-B$ we obtain the absorption spectrum from $I = I_1 + I_2$ and the Faraday rotation spectrum, θ_{Far}, from $\theta_{\text{Far}} = [\theta(B) - \theta(-B)]/2$ where $2\theta(B) = \sin^{-1}[(I_2 - I_1)/I]$. If we choose $L = L_{\text{abs}}$ and tune the laser to the center of the absorption line we expect $\theta_{\text{Far}} \sim \Omega_L/\Gamma$ [2],

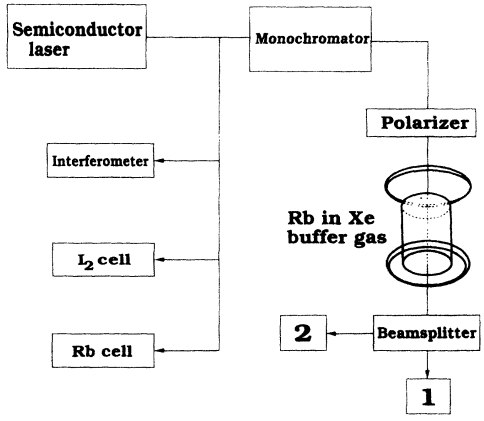

FIG. 2. Experimental setup to measure the Faraday spectrum and absorption spectrum of Rb atoms immersed in a noble gas.

where $\Omega_L \approx 2\pi \times 0.5$ GHz is the Rb Larmor frequency at $B = 0.03$ T. Therefore we have to measure rotations of the order of 10^{-2} rad.

The dispersion spectrum is calculated from the absorption spectrum using Kramers-Kronig inversion. This procedure assumes linear absorption and is therefore only correct if there is no optical pumping [15]. Because of the high buffer gas densities diffusion in the cell is very slow and we estimate that it takes ~ 1 s before a Rb atom is replaced by a spin-relaxed one from the cell wall. Therefore it may be expected that optical pumping effects only become negligible when every atom absorbs less than 1 photon/s. This occurs at a power level around 1 nW as we observed for Rb in He buffer gas. For Xe buffer gas the situation is more favorable since the larger polarizability of Xe allows spin relaxation in the gas phase [16]. Experimentally we find no effect of optical pumping at 70 nW where we perform our Rb:Xe experiments. We obtain virtually shot-noise limited detection at this power level.

It is important to notice that the results do not depend on the integrated density of Rb, $\int_0^L [\mathrm{Rb}]dz$, since both the dispersion and Faraday rotation are proportional to this. We calibrate the effective magnetic field B to $\sim 1\%$ by measurements of the Faraday effect for low Xe densities ($[\mathrm{Xe}] \sim 5 \times 10^{18}$ cm^{-3}) where the Faraday effect can be directly calculated, i.e., without BO complications, using Racah algebra [12]. For all measurements, including this calibration, we can ignore Doppler broadening since it is at least 1 order of magnitude smaller than the pressure broadening for $[\mathrm{Xe}] \geq 5 \times 10^{18}$ cm^{-3}.

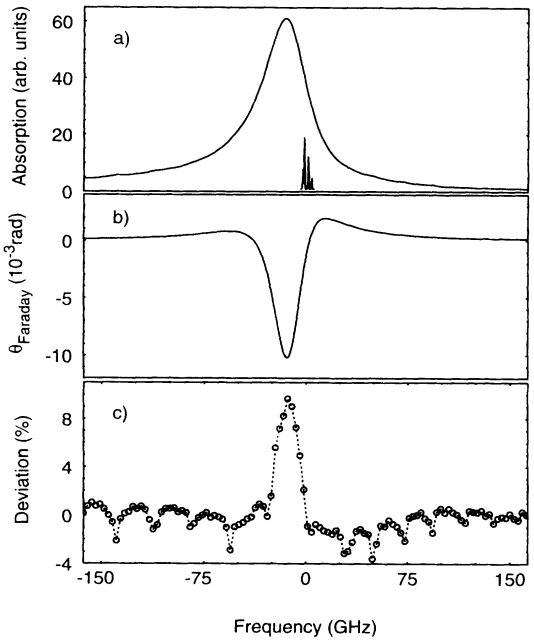

FIG. 3. Absorption spectrum (a) and Faraday spectrum (b) for the Rb D_2 line at $[\mathrm{Xe}] = 6.0 \times 10^{19}$ cm^{-3}. The refractive index is calculated using Kramers-Kronig inversion of the absorption spectrum. Finally, the Becquerel deviation (c), $\theta_{Becq} - \theta_{Far}$, is calculated using Eq. (1). It is expressed in percentage of the Faraday rotation at line center.

Figure 3 illustrates some typical results obtained with the setup. Figure 3(a) shows the absorption spectrum of the Rb D_2 line obtained at $[\mathrm{Xe}] = 6.0 \times 10^{19}$ cm^{-3} ($T = 365$ K, $P_{Xe} = 2.95$ atm). A clear shift and asymmetry is observed for the pressure broadened spectrum compared to the Rb spectrum in vacuum which is shown as a small insertion. The Rb vacuum spectrum consists of four lines; two hyperfine lines from each of the two isotopes, ^{85}Rb and ^{87}Rb. Hyperfine structure of the upper state is not resolved. Figure 3(b) shows the Faraday spectrum. This spectrum is also shifted and asymmetric. At the bottom the deviation from the Becquerel relation is extracted. The maximum observed deviation is approximately 10% of the Faraday rotation at line center. The spectra have been recorded over a frequency range of at least 20 times FWHM to assure the validity of the Kramers-Kronig inversion. In Fig. 3 we only show the central part of this range which contains the interesting structure. The main experimental uncertainty comes from alignment-dependent etalon effects in cell windows, polarizers, and other optical elements. These give rise to oscillations with a periodicity of ~ 25 GHz.

In order to improve the signal to noise ratio we add the spectra from three different measurements performed with Xe densities near 6.0×10^{19} cm^{-3}. Before the addition the spectra are properly shifted in frequency and scaled in width to account for the slight difference in pressure broadening and shift. The result is shown in Fig. 4 together with a fit to the data using Eq. (3). We find it most reasonable to give δ' and γ' as a complex number $\phi' = (\gamma' + i\delta')/[\mathrm{Xe}]$ where ϕ' has the modulus $|\phi'| = (3.6 \pm 0.5) \times 10^{-21}$ cm^3 and phase angle $(70.6 \pm 1.0)°$. This value of ϕ' also gives a good fit to a series of spectra ob-

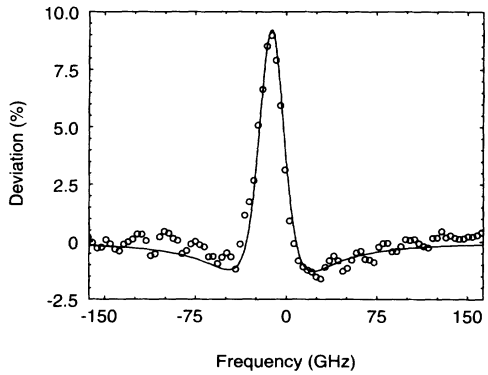

FIG. 4. The circles show the experimental deviation from the Becquerel relation Eq. (1) for a Xe density around 6.0×10^{19} cm^{-3}. The experimental data points represent an average over measurements at 4.4×10^{19}, 6.0×10^{19}, and 7.7×10^{19} cm^{-3}. The curve is a fit to the data using Eq. (3).

tained at lower densities when α is treated correctly as a tensor [12]. From the good quality of the fit we conclude that the Becquerel violation can be parametrized as in Eq. (3). This is noteworthy since the ULB theory used to derive Eq. (3) is based on the binary collision approximation $\Gamma\tau \ll 1$. In fact, for the experimental conditions in Figs. 3 and 4 we have $\Gamma\tau \sim 1$ since $\tau = \rho_W/\bar{v} \sim 5\times 10^{-12}$ s where ρ_W is the Weisskopf radius and $\bar{v}$ is the mean relative velocity of Rb and Xe [2,14]. This invalidity of the impact approximation is confirmed by the fact that we observe appreciable asymmetry in the line core. Nevertheless, the parametrization Eq. (3) apparently still works. Theoretical values for δ' and γ' are not yet available. It should be possible to calculate these [17] using the ULB theory and available RbXe potentials [18]. It would be interesting to see whether the binary ULB approach also gives the correct quantitative result for δ' and γ'.

What will happen at higher densities when the ULB theory is expected to break down and the line shape will become even more asymmetric? One would expect that beyond a certain Xe density the Faraday effect will become greatly reduced by locking of the total electronic angular momentum, **J**, to the collision axes by very strong BO coupling. The Xe environment around a Rb atom will then behave as one large molecule in which magnetic precession is hindered. A somewhat similar situation occurs in condensed matter magnetic resonance in the quenching of orbital angular momentum. In that case the orbital contribution to the g factor of a valence electron of an ion in a crystalline lattice is reduced by a sufficiently low symmetry of the crystal field [19].

Finally, it is interesting to note that while suppressing the magnetic Faraday effect, electronic rigidity will allow the mechanical Faraday effect [2,3,20,21]; the latter may occur as a consequence of mechanical rotation of the sample and is complementary to the former via Larmor's theorem.

In conclusion, we have observed violations of the Becquerel relation for the Faraday effect of Rb atoms in Xe buffer gas. These violations are associated with quasimolecular RbXe behavior (long-range collision pairs). Presently, we are extending the investigations to higher gas densities where we expect to see development of condensed matter aspects of the Faraday effect.

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