Time-dependent CARS spectroscopy of atoms: spectral exchange in the system of hyperfine components and slowing of Doppler dephasing by collisions

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A slowing of Doppler dephasing by collisions has been detected in experiments on time-dependent CARS spectroscopy of thulium (Tm) atoms. This slowing corresponds to the Dicke contraction in steady-state spectroscopy. A spectral exchange has also been detected. These effects have not been observed previously in atomic spectroscopy in the optical range. The $4F_{7/2}$–$4F_{5/2}$ transition of Tm atoms was excited and probed. Spectral exchange was observed in the system of hyperfine components of this transition.

1. A spectral exchange leading to the coalescence of closely spaced spectral components of transitions in the optical range, as a result of the nonadiabatic nature of collisions, has been discussed theoretically by Burshteĭn and Naberukhin[1] and Alekseev and Sobel'man.[2] Experimentally, this effect has been observed by (for example) the method of steady-state CARS spectroscopy in the Q lines of certain molecules.[3]

The limitation imposed on the free motion of the atoms (or molecules) by collisions gives rise to a minimum on the plot of the width of the Doppler-broadened line versus the pressure (Dicke narrowing) if the collisional broadening is sufficiently

small. As Rautian and Sobel'man[4] have shown, this minimum can be observed under the condition $\Gamma\tau_V \leqslant 0.5$, where Γ is the collisional linewidth, and τ_V is the velocity correlation time.

Dicke narrowing has been observed on only a few transitions by methods of steady-state optical-range spectroscopy. These lines are vibrational-rotational and rotational transitions of hydrogen and deuterium[5,6] and transitions between high-lying rotational levels of the water molecule.[7] In time-dependent spectroscopy, the limitation on the free motion is manifested as a slowing of the Doppler dephasing. This effect was observed in Ref. 8 on a vibrational-rotational transition of hydrogen by a method of picosecond CARS spectroscopy. When the hydrogen pressure was raised to ≈ 3 atm, it was found that there was a slowing of the decay of the temporal response, i.e., of the dependence of the energy of the pulse at the anti-Stokes frequency, $W_a(\tau)$, on the delay of the probing pulse with respect to the exciting pulses. For transitions in the hydrogen molecule, we have $\Gamma\tau_V \approx 0.02$, and Dicke narrowing is extremely obvious. In contrast, for the overwhelming majority of transitions we would have $\Gamma\tau_V > 0.5$, and this narrowing could not be observed.

If we turn to time-dependent spectroscopy and define the dephasing time τ_{de}^* as the time it takes the temporal response to decay from the level $W_a(0)$ to the level $W_a(0)e^{-2m}$, then for sufficiently large values of m the maximum on the plot of τ_{de}^* versus the pressure, i.e., the slowing of the Doppler dephasing, could in principle also be observed for transitions with $\Gamma\tau_V > 0.5$, as was shown by D'yakov.[9] The values of $\Gamma\tau_V$ for which this hope is realistic depend on the dynamic range of the measurements of the temporal response.

2. In this letter we are reporting some experiments on time-dependent CARS spectroscopy of thulium (Tm) atoms. In these experiments, a slowing of Doppler dephasing and a spectral-exchange effect have been detected for the first time in optical-range atomic spectroscopy. The experiments were carried out on a picosecond CARS spectrometer. The laser oscillator was a neodymium-doped garnet laser with passive mode locking, negative feedback, and an instability of $\pm 2\%$ in the pulse parameters. The energy of the exciting pulse at the wavelength 1.06 μm was 5 mJ. The energy of the exciting pulse at the wavelength of the dye laser, 0.55 μm, was 0.5 mJ. The energy of the second-harmonic probing pulse was 3 mJ. The lengths of these pulses were ≈ 30 ps. The pulses were focused by a lens with a focal length of 50 cm into the central region of a heated cell filled with Tm vapor and a buffer gas. The cell temperature was measured by a thermocouple or an optical pyrometer and maintained at 1500 ± 30 K.

3. Figure 1 shows a diagram of the excitation and probing of the $4F_{7/2}$–$4F_{5/2}$ transition of the Tm atom, the hyperfine splitting of these levels, and the relative amplitudes of the hyperfine components (1:20:27:0) in the steady-state CARS spectrum. These results were calculated from the expressions of Ref. 10 for the antisymmetric scattering, which is an order of magnitude more intense than the anisotropic scattering (isotropic scattering is forbidden by selection rules). The $4F$ shell in Tm is an inner shell, so Γ is small enough that the slowing of dephasing could be detected in the dynamic measurement range of 10^5–10^6 achieved in these experiments.

4. The temporal responses were measured at various helium or neon pressures

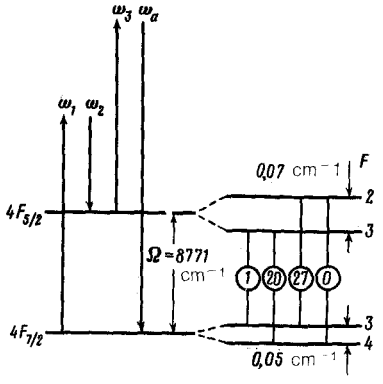

FIG. 1. Quantum diagram of the excitation and probing of the $4F_{7/2}$–$4F_{5/2}$ transition of the thulium atoms. ω_1 and ω_2—Frequencies of the exciting pulses; ω_3 and ω_a—frequencies of the probing and anti-Stokes pulses; F—total quantum number. The hyperfine splitting of the levels is indicated. The calculated amplitudes of the components in the spectrum of steady-state CARS for antisymmetric scattering are also shown.

from 40 torr to 20 atm. Figure 2a shows some of the most characteristic responses. The solid line shows a response calculated in the Doppler limit for the amplitudes of the components shown in Fig. 1. The slowing of the dephasing reaches a maximum at a neon pressure $\approx$7 atm and a helium pressure $\approx$12 atm. Figure 2b shows curves of $\tau^*_{de}(p)$, found at the level of 10^{-5} of $W_a(0)$. The maxima on these curves occur in the

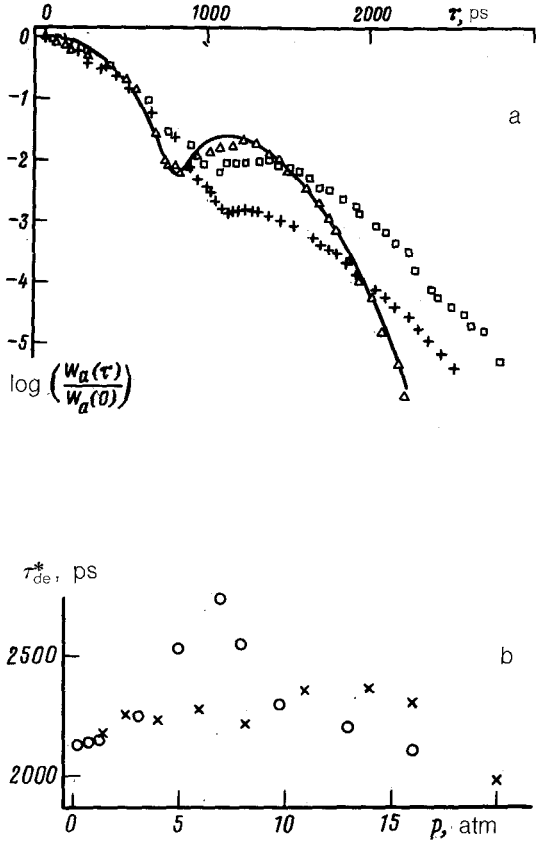

FIG. 2. a: Temporal responses (curves of the energy of the pulse at the anti-Stokes frequency versus the delay of the probing pulse with respect to the exciting pulses) at various pressures of the buffer gases. Δ—Neon, 40 torr; □—neon, 7 atm; + —helium, 11 atm. The solid line shows the calculated response in the Doppler limit for a temperature of 1500 K and for the component amplitudes shown in Fig. 1. b: The dephasing time τ^*_{de} versus the pressure of the buffer gas. ○—Neon; x—helium. The dependence was determined at the level of 10^{-5} of $W_a(0)$.

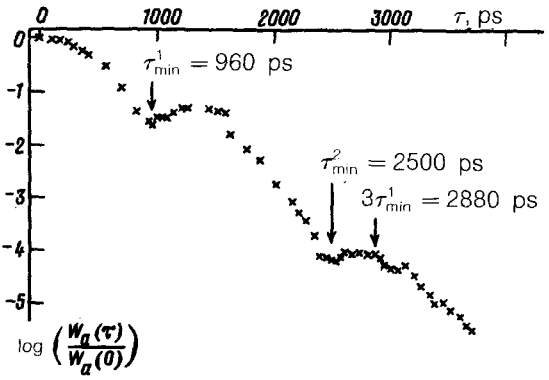

FIG. 3. Temporal response at a xenon pressure of 825 torr. Shown here are the delay times $\tau^{1,2}_{min}$, which determine the positions of the first and second minima of beats of the hyperfine-structure components, and the delay time $3\tau^1_{min}$, which determines the position of the second minimum of the beats in the absence of spectral exchange.

region of the smallest slope of the temporal responses at $\tau > 2$ ns. The slope in helium for $\tau = 2.3$ ns and $p = 11$ atm is half that in the Doppler case.

5. Along with the slowing of the dephasing, we observe a simultaneous shift of the first minimum of the temporal response (the quantum beats stem from hyperfine splitting). This shift might be an ordinary collisional shift, or it might be due to spectral exchange. If we assume that there is no spectral exchange, then the decrease in the frequency interval between the hyperfine components in the helium is 2×10^{-3} cm^{-1}/amagat. The absolute shift should be larger by a factor of several units.[11] This transition was studied previously by Fourier spectroscopy by Agladze *et al.*,[12] who found a shift $<5\times10^{-4}$ cm^{-1}/amagat of the center of the hyperfine components in helium. Comparison of these values shows that the shift of the first minimum is apparently not an ordinary collisional shift.

The spectral exchange is manifested, in particular, by a phase shift between components.[13] In time-dependent spectroscopy, this shift causes a temporal shift of the delay of the pattern of quantum beats. As a result, while we have $\tau^2_{min}/\tau^1_{min} = 3$ in the absence of exchange, where $\tau^{1,2}_{min}$ are the delay times which determine the positions of the first and second minima, in the case with spectral exchange we would have $\tau^2_{min}/\tau^1_{min} \neq 3$. We were able to detect the second minimum when we used xenon, in which the slowing of the dephasing is more pronounced (Fig. 3). We found $\tau^2_{min}/\tau^1_{min} = 2.6 \pm 0.1$. We are thus dealing with a manifestation of spectral exchange.

Working from the experimental responses, we calculated steady-state CARS spectra. These calculations showed that the Dicke narrowing in neon is 5%, that in xenon is 30%, and there is no such narrowing in helium. These results agree with the calculated values of $\Gamma\tau$: 0.22 for neon, 0.12 for xenon, and 0.67 for helium. Consequently, although Dicke narrowing does not occur in helium, time-dependent spectroscopy still makes it possible to observe a slowing of Doppler dephasing.

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