Studies of collisional dephasing of two-photon excited atomic sodium

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Abstract

Coherence relaxation in Na vapor was studied utilizing a "pump-probe" method with femtosecond pulses. The coherence was created by the pump pulse, which excited the Na atoms to the 4S state. The atoms were further excited to the 7P state by the probe pulse. As a result a coherent UV radiation was emitted by the atoms. This emission was used to study the relaxation of both the 4S-3S and 7P-3S coherent superpositions. The relaxation is mainly due to collisions with the Ar atoms serving as a buffer gas. Coherence relaxation times and collisional cross-sections for the Na-Ar collision pairs were extracted experimentally.

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The development of femtosecond pulses has led to a breakthrough in experimental methods and technologies. These new techniques make it possible to obtain detailed information on the dynamics of various processes, which occur on a pico- and sub-picosecond timescale. Ultrashort pulse duration allows for real-time monitoring of such processes. The most widely used experimental method here is the "pump-probe" technique [1, 2, 3, 4, 5, 6]. The pump pulse, which is used to excite the system under study, is followed by the probe pulse, which is applied after the time delay $\tau$ and detects the changes occurring in the system during this time interval. The time delay $\tau$ is varied by varying the optical path length of the probe pulse. The system's response, which depends on this time delay, is recorded via various methods including fluorescence, absorption, rotation of polarization plane of the probe pulse, as well as nonlinear methods using four-wave mixing, etc.

The study presented in this paper investigates coherence relaxation in atomic vapors. The atomic coherence, which is excited by the pump pulse, relaxes exponentially with the characteristic decay time $T_2$ [7, 8, 9]. This dynamics occur on a picosecond timescale, therefore requiring ultrashort (femtosecond) pulses to study it. In this study femtosecond pulses are used to excite Na atoms to a coherent superposition of the atomic field-free eigenstates. The decay of this superposition is studied then utilizing the resonance-mediated generation of coherent UV radiation.

Consider a three-level atom, with levels $|1\rangle$, $|2\rangle$ and $|3\rangle$ as depicted in Fig. 1. States $|1\rangle$ and $|2\rangle$ are of the same symmetry, while state $|3\rangle$ is of a different symmetry. Suppose the atom is irradiated by a pump-probe sequence of two collinear femtosecond pulses. The pulses are separate in time with a time delay $\tau$. In what follows both pulses are assumed to be much shorter than all the relaxation times of the atom, and therefore will be treated as $\delta$-function. The pump pulse, which is taken to be centered at $t = 0$, excites a coherent superposition of the states $|1\rangle$ and $|2\rangle$, via a two-photon transition. The probe pulse excites the state $|3\rangle$, via a one-photon transition, thus creating a coherent superposition of the states $|1\rangle$ and $|3\rangle$. As a result an atomic dipole moment is formed between the $|1\rangle$ and $|3\rangle$ states. This dipole moment oscillates at the $|3\rangle$-$|1\rangle$ transition frequency [10].

Now consider a collection of atoms described above. The atomic dipoles will combine to form a matter polarization wave, which will cause an emission of light at the $|3\rangle$-$|1\rangle$ transition frequency, $\omega_{3,1}$. This polarization is given by the expectation value of the dipole
moment operator, which can be calculated is follows:

\[ P(t, \tau) = \langle \mu \rangle = tr(\rho \mu) \] (1)

where \( \rho \) is the density matrix of the system and \( \mu \) is the matrix representing the dipole moment operator. When considering the selection rules of the atom (see above), it turns out that only one density matrix element, \( \rho_{3,1} \), needed to calculate the polarization above, thus:

\[ P(t, \tau) = \rho_{3,1}(t, \tau) \mu_{3,1} + c.c. \] (2)

This matrix element is easily calculated, provided the pulses are approximated by \( \delta \)-functions. It is given by:

\[ \rho_{3,1}(t, \tau) \propto \begin{cases} \exp[(i\omega_{2,1} - \gamma_{2,1})\tau] \cdot \exp[(i\omega_{3,1} - \gamma_{3,1})(t - \tau)] & t \leq \tau \\ 0 & t > \tau \end{cases} \] (3)

where \( \omega_{2(3),1} \) is the \( |2(3)\rangle\rangle |1\rangle \) transition frequency and \( \gamma_{2(3),1} = 1/T_{2(3),1}^2 \), with \( T_{2(3),1}^2 \) being the relaxation time of the \( |2(3)\rangle\rangle |1\rangle \) coherence. The first exponential term in Eq. 3 describes the evolution of the \( |2\rangle\rangle |1\rangle \) coherent superposition created by the pump pulse at \( t = 0 \), while the second exponential term describes the evolution of the \( |3\rangle\rangle |1\rangle \) coherent superposition created by the probe pulse at \( t = \tau \) (\( \tau > 0 \)). In atomic vapors the relaxations times \( T_{2(3),1}^2 \) are determined by collisional dephasing processes governed by the collisional cross section given by:

\[ \sigma = \frac{1}{\tilde{N}v_r T_2} \] (4)

where \( v_r = (8kT/\pi\mu)^{1/2} \) is the mean relative velocity of the collision pair, \( \tilde{N} = P/kT \) is the number density of the colliding atoms, with \( \mu \) being the reduced mass of the collision pair, \( T \) being the absolute temperature, \( P \) being the pressure and \( k \) being the Boltzmann constant.

When dealing with atomic vapors, one must also consider the "Doppler effect" when calculating the field generated by the polarization in Eq. 2 [11]. Since according to the "Doppler effect" each atom has resonance frequencies, which depend on its velocity, \( v \), i.e, \( \omega_{n,m}(v) = \omega_{n,m}^0 + \frac{v}{c}\omega_{n,m}^0 \), the vapor can be said to consist of various collections of atoms, while each such collection is composed of atoms having the same velocity. As a result each such collection of atoms creates its own polarization given by modification of Eqs. 2-3.

\[ P(t, \tau, v) \propto \exp[(i\omega_{2,1}(v) - \gamma_{2,1})\tau] \cdot \exp[(i\omega_{3,1}(v) - \gamma_{3,1})(t - \tau)] \] (5)
The total electric field of the emitted light will be given by a coherent sum over various polarizations, each of which is created by atoms of different velocity:

\[ E(t, \tau) \propto \int_{-\infty}^{\infty} W(v) P(t, \tau, v) dv \]  

(6)

where \( W(v) = \frac{1}{\sqrt{4\pi v}} e^{-\frac{(v-u)^2}{4\sigma^2}} \) is the Boltzmann velocity distribution, with \( u = \sqrt{\frac{2kT}{m}} \), where \( m \) is the mass of the atom.

As will be shown below the collisional cross sections (see Eq. 4) can be extracted experimentally by measuring the total energy of the field in Eq. 6 as a function of the pump-probe delay \( \tau \), i.e., \( S(\tau) = \int_{-\infty}^{\infty} |E(t, \tau)|^2 dt \).

The above theoretical scheme was implemented with Na atoms, with argon serving as a buffer gas. The relevant energy levels of the Na atom are shown in Fig. 1 with the 3S state serving as the \( |1\rangle \) state, the 4S state serving as the \( |2\rangle \) state and the 7P state serving as the \( |3\rangle \) state. The two-photon coupling between the 3S and the 4S states is provided by the various P-states that are far from resonance and are not shown. The corresponding transition frequencies are \( \omega_{4S,3S} = 25740 \text{ cm}^{-1} \) (two 777 nm photons) and \( \omega_{7P,4S} = 12801 \text{ cm}^{-1} \) (one 781.2 nm photon). Experimentally atomic Na vapor is held in a heated cell at a temperature of 400 °C filled with Ar buffer gas.

The spectrum of the NIR femtosecond pulses used in the experiment is shown in Fig. 1. It is centered around 777.4 nm with a spectral bandwidth of 7.6 nm (FWHM) (corresponding to 117 fs pulse duration). The initial pulse was divided into two replicas of itself constituting the pump and the probe pulses. The pump pulse was passed trough a 4f pulse shaping setup, where it had its spectrum blocked at the low-frequency side (see Fig. 1) to eliminate resonant access to the 7P state[10], thus the pump populates the 4S state only, in correspondence with theoretical scheme above. The probe pulse is sent trough a delay arm, where the pump-probe delay \( \tau \) is set. Then both pulses are recombined and are focused in the Na cell. The UV emission, induced by the pulses, is separated from the NIR excitation by a proper optical filter and the total energy of this emission is then measured as a function of \( \tau \), thus corresponding to \( S(\tau) \) described above (see Fig. 1 for the experimental setup).

As can be seen from Eqs. 5-6, the rate of decay of \( S(\tau) \) with \( \tau \) is governed by the coherence relaxation times \( T_{4S}^{2} \) and \( T_{7P}^{2} \). The knowledge of these relaxation times at different pressures should provide the collisional cross-sections \( \sigma_{4S} \) and \( \sigma_{7P} \), between Ar and Na atoms in 3S-4S and 3S-7P superpositions, respectively, according to Eq. 4.
Experimentally $S(\tau)$ was measured at different pressure of Ar. First, $S(\tau)$ was measured at low Ar pressure (1.2 torr) to verify the effect of Doppler broadening (see Eqs. 5-6). The experimental results are presented in Fig. 2(a) (circles) along with the numerical results (solid line) calculated based on Eqs. 5-6, where the coherence decay constants $\gamma_{4S(7P),3S}$ were set to zero and the temperature set to 400 °C. The excellent agreement between the measured and calculated results confirms the fact that the main dephasing mechanism at low pressures is the inhomogenous Doppler broadening. At the temperature of the experiment ($T = 400^0C$) it was calculated to be $0.1 cm^{-1}$ and $0.15 cm^{-1}$ for the 4S-3S and for the 7P-3S transitions respectively.

The coherence relaxation times $T_{4S}^2$ and $T_{7P}^2$ were determined experimentally by measuring $S(\tau)$ for different Ar pressures. The experimental results are presented in Fig. 2(b)-(h) (circles). By performing a least-squares fit between numerical calculation, and the entire experimental data, the relaxation times and the collisional cross-section were obtained. The numerical results are shown in Fig. 2 (b)-(h) (solid lines). The collisional cross-sections were extracted from the slopes of the plots of $T_{4S(7P)}^2$ vs $1/P$ (acc. to Eq. 4). These plots are shown in Fig. 2(i)-(j), and the collisional cross-sections were found to be $\sigma_{4S} = 488 \pm 23.6 \AA^2$ and $\sigma_{7P} = 1004 \pm 13.3 \AA^2$. These values agree qualitatively with previously measured results [7, 12] for collisional cross-section between Ar and Na atoms, excited to different levels.

In summary, we have used the nonlinear generation of UV emission to probe the coherences in a Na atom. The calculation, based on the theoretical model developed here, agree well with the experimental results and numerical values for the coherence relaxation times were obtained. Based on those, the collisional cross-section for for the collisions of Ar and Na atoms in a 4S-3S and 7P-3S coherent superpositions, were established.

[1] E. Carpene, E. Mancini, C. Dallera, G. Ghiringhelli, C. Manzoni, G. Cerullo, S. De Silvestri, Rev. Scient. Inst. 80, 055101 (2009)
[2] T. Hertel, E. Knoesel, M. Wolf, and G. Ertl, Phys. Rev. Let. 76, 535, (1996).
[3] S. Park, M. Odelius, K. J. Gaffney, J. Phys. Chem. B, 113, 7825, (2009)
[4] S. M. Hurley, T. E. Dermota, D. P. Hydutsky, A. W. Castleman Jr, Science 298, 202, (2002)
[5] T. V. Truong, L. Xu, Y. R. Shen, Phys. Rev. Let. 90, 193902, (2003)
[6] C. H. Kim, T, Joo, Opt. Exp. 16, 20742 (2008)
[7] J. E. Golub, T. W. Mossberg, J. Opt. Soc. Am. B., 3, 554 (1986)
[8] M. D. Rotondaro, G. P. Perram, J. Quant. Spect. Rad. Trans. 57, 497 (1997).
[9] N. Allard, J. Kielkopf, Rev. Mod. Phys. 54, 1103 (1982)
[10] L. Rybak, L. Chuntonov, A. Gandman, N. Shakour, Z. Amitay, Opt. Exp. 16, 21738 (2008).
[11] Z. Zuo, J. Sun, X. Liu, L.A. Wu, P. Fu., Phys. Rev. Let. A 75, 023805 (2007)
[12] T. J. Chen, D. DeBeer, S. R. Hartmann, J. Opt. Soc. Am. B. 3, 493 (1986)
FIG. 1: (a) The model system. The 4S state is excited by the pump pulse via a two-photon transition, followed by a one photon excitation of the 7P state. (b) The spectra of the pump (black) and the probe (gray) pulses. The pump pulse spectrum was blocked at the low frequency side (see text). (c) Experimental scheme.
FIG. 2: (a)-(h) Experimental (circles) and numerical (solid) results for $S(\tau)$ at different Ar pressures. (i)-(j) Plots of $T_2^{S(7P)}$ vs $1/P$ for determination of $\sigma_{4S(7P)}$. The collisional cross-section $\sigma$ is determined from the slope of the plots (see text).