$\Omega - \Omega'$, and shows an absorptive tuning behavior. Consequently, at short times the first and third-order FID interfere in a variety of interesting ways which depend on the particular conditions imposed. At long times, the third order signal prevails.

These properties follow from a density matrix solution of the Schrödinger wave equation and is exact within the rotation wave approximation and the slowly varying envelope approximation for an optically thin sample. An expression for the Doppler-averaged polarization has been reported[5] and can be expressed in terms of the error function $W(x + iy)$ of complex argument.[6] Analytic results are derived here for both the short and the long time behavior, and numerical solutions, which are compared with the experimental data obtained on line, are facilitated by an error function subroutine.

Initial experiments were performed mainly on the sodium D line at 16 956.16 cm^{-1} and also on I_2 vapor where the observations fully confirm the theoretical predictions. The experiment utilizes a cw dye laser, and the arrangement is similar but not identical to that reported previously.[1] Since the laser frequency can be shifted over the range $\Omega - \Omega' = 0$ to ± 10 GHz with a rise time of 100 ps or less, it is possible for the first time to switch completely outside the Doppler linewidth, which for Na is 0.77 GHz. We find that when $\omega_{21} - \Omega \sim 0$ the third-order Na FID is evident for times longer than ~400 ps; its beat frequency is given by $\Omega - \Omega'$; and the signal shows an absorptive tuning behavior.

However, when the laser is tuned far off the Na Doppler peak so that $\omega_{21} - \Omega > 2$ GHz, the first order FID dominates. Its decay is complete in 400 ps; the beat frequency is properly given by $\omega_{21} - \Omega'$; and the signal shows a dispersive tuning behavior as the laser frequency Ω is tuned.

An additional modulation which we believe is due to the Na ground state hyperfine splitting of 1.8 GHz has been observed as well. This interference becomes large when the laser is tuned midway between the two hyperfine lines and is being investigated more carefully by examining the Fourier transform spectrum of these signals. It appears likely that this effect is a manifestation of a quantum beat where the laser field excites two coupled transitions and places three quantum levels (not two) in coherent superposition.[7] In this case, the two close-lying levels can be either in the lower or the upper electronic state. We also note that this is the highest frequency quantum beat observed in this manner, the only rival being that seen spatially in beam foil spectroscopy.

These preliminary results suggest many interesting coherence problems which can now be attempted in the subnanosecond region.

* Work supported in part by the Office of Naval Research.

[1] R. G. Brewer and A. Z. Genack, Phys. Rev. Lett. 36, 959 (1976).

[2] R. M. Macfarlane, A. Z. Genack, and R. G. Brewer, Phys. Rev. (to be published).

[3] A. Z. Genack, R. M. Macfarlane and R. G. Brewer, Phys. Rev. Lett. 37, 1078 (1976); see reference 2 also; A. H. Zewail, T. E. Orlowski, and D. R. Dawson, Chem. Phys. Lett. 44, 379 (1976); H. deVries, P. deBree, and D. A. Wiersma, Chem. Phys. Lett. (to be published).

[4] R. G. Brewer and R. L. Shoemaker, Phys. Rev. A 6, 2001 (1972).

[5] K. L. Foster, S. Stenholm, and R. G. Brewer, Phys. Rev. A 10, 2318 (1974).

[6] P. F. Liao, J. E. Bjorkholm, and J. G. Gordon, Phys. Rev. Lett. 39, 15 (1977).

[7] A. Schenzle and R. G. Brewer, *Proceedings of the Second International Laser Spectroscopy Conference* (Springer-Verlag, New York, 1975), p. 420.

R.3. Multilevel Echo Relaxation Studies in Gaseous Media,*

A. FLUSBERG, T. MOSSBERG, R. KACHRU, AND S. R. HARTMANN, *Columbia Radiation Laboratory, Department of Physics, Columbia University, New York, N. Y. 10027.* (15 min.)

Optical echoes can be used to study relaxation rates and linewidths of coherently excited atomic (or molecular) states. When the coherence of interest is on a forbidden transition, the atomic state may be excited by multiphoton or stepwise excitation. A major advantage of the echo spectroscopic technique is that the spectral width of the exciting laser pulses may be much wider than the largest relevant linewidth of the medium (e.g., the inhomogeneous linewidth of the transition).

Consider a Boltzmann gas of atomic systems, each consisting of three states, $|0\rangle$, $|1\rangle$, and $|2\rangle$, of energies $\hbar\Omega_{0,1,2}$, respectively. $|0\rangle$ (the ground state) and $|2\rangle$ have the same parity, opposite to that of $|1\rangle$. We refer to the level array as "straight" or "folded" according to whether $\Omega_2 > \Omega_1$ or $\Omega_2 < \Omega_1$. Two types of echo phenomena which may be used to study the relaxation of the $|0\rangle - |2\rangle$ superposition state are the two-photon echo (called the Raman echo[1] when the array is folded) and the tri-level echo.[2] In each case the echo is produced by a sequence of optical pulses of frequencies ω_1, ω_2, where $\omega_1 + \omega_2 = \Omega_{20} \equiv |\Omega_2 - \Omega_0|$ ($\omega_1 - \omega_2 = \Omega_{20}$ for the folded array). The two-photon echo consists of a macroscopic coherence on the $|0\rangle - |2\rangle$ superposition state at the time 2τ, after the medium is excited by a sequence of two pulses (at times 0 and τ, respectively), each containing both frequencies ω_1 and ω_2. The two-photon echo should occur whether state $|1\rangle$ is excited adiabatically ($\omega_1, \omega_2 \neq \Omega_{10}$) or resonantly ($\omega_1 = \Omega_{10}$). In either case, the τ-dependence of the echo amplitude should not depend on the relaxation properties of $|1\rangle$. The two-photon echo technique may thus be used to directly measure the $|0\rangle - |2\rangle$ state decay. We have made the first observation of the two-photon echo in a resonantly excited ($\omega_1 = \Omega_{10}$) gas (Na vapor, with $|0\rangle = |3^2S_{1/2}\rangle$, $|1\rangle = |3^2P_{1/2}\rangle$, and $|2\rangle = |4^2D_{3/2}\rangle$).

The tri-level echo is an even more promising and versatile spectroscopic technique for the measurement of relaxation of superposition states of the type $|0\rangle - |2\rangle$. It is primarily, although not necessarily, a resonance phenomenon ($\omega_1 = \Omega_{10}, \omega_2 = \Omega_{21}$). The excitation usually consists of three pulses, two of them at one of the frequencies (ω_1 or ω_2) and the third at the other. The echo occurs on one of the electric-dipole-allowed transitions, but it depends for part of the interval between the excitation and echo on the nonradiating $|0\rangle - |2\rangle$ superposition. Thus the echo intensity monitors the decay properties of the $|0\rangle - |2\rangle$ superposition when the decay of the $|0\rangle - |1\rangle$ and $|1\rangle - |2\rangle$ superpositions are properly taken into account. Since the pulses are all resonant, only low laser intensities (several W/cm^2) are required to produce relatively large echoes. In the small-angle limit, in fact, the polarization which radiates the tri-level echo is of third order in the electric field of the incident pulses. Thus the tri-level echo may be viewed as a third-order effect, just like the ordinary two-pulse photo echo. This distinguishes the tri-level echo from the two-photon echo, which in this sense is a sixth- or seventh-order effect.

We have used tri-level echoes to study the $3^2S_{1/2}$-$3^2P_{1/2}$-$n^2D_{3/2}$ ($|0\rangle - |1\rangle - |2\rangle$) system of atomic Na, where $n = 4$ to 9. Data on the decay of the $3^2S_{1/2}$-$n^2D_{3/2}$ state as a function of foreign-gas pressure will be presented. We will discuss the dependence of the corresponding collisional cross sections on principal quantum number n. These results will be extended to higher n, i.e., Rydberg states. In addition, we will discuss the application of tri-level echoes to relaxation studies of other level arrays: e.g., the $n^2P_{1/2}$-$n^2P_{3/2}$ superposition state in Na, and the $6^2P_{1/2}$-$6^2P_{3/2}$ state in Tl.

* Work is supported by the Joint Services Electronics Program (U.S. Army, U.S. Navy, and U.S. Air Force) under Contract No. DAAB 07-74-C-0341.

[1] S. R. Hartmann, IEEE J. Quat. Electron. 4, 802 (1968).

[2] T. Mossberg, A. Flusberg, R. Kachru, and S. R. Hartmann, Phys. Rev. Lett. 39, 1525 (1977).

R.4. Coherent Transients by Laser-Acoustical Diffraction Spectroscopy,

A. H. ZEWAIL, *Arthur Amos Noyes Laboratory of Chemical Physics,* California Institute of Technology, Pasadena, Calif. 91125.* (15 min.)

Recently we have reported[1] on the measurements of electronic dephasing (T_2) and radiationless decay (T_1) in molecules using emission spectroscopy as a probe for the detection of the photon echo. This right-angle photon echo utilizes a single mode of a narrow-band (~MHz) cw dye laser and an intracavity electro-optical (EO) element that modulates the frequency of the laser.[2] Applying voltage pulses into the EO crystal switches the laser frequency from ω_0 (the peak frequency of the transition resonance) into another frequency ω. This switching procedure introduced by Brewer *et al.* for the observation of transients in the forward direction of the laser allows one to observe coherent transients in gases,[1,2] solids[3-5] and molecular beams.[6] Typically, the dispersion of the nonlinear EO crystal (e.g., AD*P) gives a 60 MHz frequency shift within the inhomogeneous resonance of the optical transition (width ~GHz or larger). Therefore, to switch the laser frequency further, one must use high-voltage signals that are usually hard to obtain especially for multiple-pulse experiments. Secondly, there is a limit on the frequency shift which is conditioned by the mode spacing of the cavity. Thirdly, because the laser is switched into a new group of molecules some complications may arise in

696

interpreting the transient spectra especially in *large* molecules. This is because in large molecules the density of excited states is high and thus the buildup of transients of ω molecules (which could be complex) will be superimposed on the decay of ω_0 molecules. Finally, off-resonance effects (e.g., beats) between the molecules at frequency ω and ω_0 cannot be avoided.

In this paper we present a laser-acoustical diffraction spectroscopic (LADS) technique that resolves the above mentioned problems and provide optical T_2 and T_1 directly. Using LADS we show new results concerning the dephasing and the decay in small (iodine) and large (pentacene) molecules in the gas and condensed phases.

To measure the rate of electronic dephasing the single-mode of the cw dye laser was diffracted by an *extracavity* acousto-optical element. The sample sees optical pulses of finite duration only when an rf pulse train (e.g., $\pi/2$, π, $\pi/2$) is fed into the transducer which provides acoustic waves that diffract the light. By feeding the rf pulse train at a certain repetition rate the system (gas or solid) is excited coherently at this repetition rate and at ω_0 without pumping other molecules in the inhomogeneous frequency distribution of the optical transition. This simple method for the measurement of optical T_2 and T_1 relies on the well-known acousto-optical effect[7] that has been used before for the measurement of fluorescence kinetics and is different from the techniques of gating cw lasers by Pockels cells.[8]

The transient spectrum of iodine gas, and pentacene in p-terphenyl at 1.8 K are quite different. In iodine when the rf pulse is turned on (i.e., the laser beam is diffracted to the sample) the population builds up in the state at 5897.5 Å. When the rf is terminated the beam is deflected away from the sample and the molecules decay freely. We have studied the pressure and laser power dependence of the build up and the decay. At lower pressure the build up in emission intensity is biexponential and is sensitive to the laser power. On the other hand the decay on the falling edge of the pulse gives T_1 which depends on the pressure according to the Stern-Volmer relationship: $1/T_1\ \mu s^{-1} = (0.783 \pm 0.032) + (0.0143 \pm 0.0005)P$, where P is the pressure in mTorr. One notices that: (i) the results of LADS are in very good agreement with that obtained using the frequency switching technique;[6] (ii) the cross section for quenching (pressure dependent T_1 processes) is the same when the laser is switched into a new group of molecules in the Doppler resonance or completely turned off (LADS method), and finally (iii) the extrapolated zero pressure value of T_1 (1.28 ± 0.05 μs) is in excellent agreement agreement with our earlier results for an iodine molecular beam.[6] In the pentacene case the situation is different,[4] and the results indicate the presence of cross relaxation in the pumped molecular "packet".

In addition to the T_1 measurements reported above we have observed the photon echo of I_2 gas using LADS. The emission at right angles to the exciting beam was detected while the separation between the second and the third rf pulse of the 3-pulse train was changed. At 7 mTorr and using 3 pulses ($\pi/2$, π, $\pi/2$) an echo was seen on the emission. Two pulses ($\pi/2$ and π), on the other hand gave no echo on the emission and only a sloping base line was observed. The photo echo observed by LADS does not show the beat pattern observed using the EO switching method.[1] Furthermore, as expected, when we lowered the laser power by a factor of 2, the echo decreased in intensity and the time width became larger indicating the presence of some power broadening contribution to the echo width which depends on the intrinsic linewidth of the laser, the Fourier transform width of the $\pi/2$ pulse and the power broadening term. The decay of the echo gives directly the dephasing time. Scanning the separation between pulses synchronously while monitoring the emission showed that the echo amplitude decreases at long times. The decay gives $T_2 = 0.5 \pm 0.15$ μs at 7 mTorr. The dephasing time is close to that obtained previously by the frequency switching method, and gives a homogeneous line broadening (~636 kHz) similar to that reported before for iodine.[6] Details of experiments on solids will be reported at the conference.

Finally, I would like to acknowledge a fruitful discussion with M. Levenson of USC regarding the possible connections between the observation of the beats in the echo (EO) experiment and Ramsey's fringes.

* Contribution No. 5721.

[1] A. H. Zewail, T. E. Orlowski, K. E. Jones, and D. E. Godar, Chem. Phys. Lett. **48**, 256 (1977); *ibid.* **44**, 379 (1976).
[2] R. G. Brewer and A. Genack, Phys. Rev. Lett. **37**, 959 (1976).
[3] A. H. Zewail and T. E. Orlowski, Chem. Phys. Lett. **45**, 399 (1977).
[4] A. H. Zewail, D. E. Godar, K. E. Jones, T. E. Orlowski, R. R. Shah, and A. Nichols, in *Advances in Laser Spectroscopy I, Vol. 113*, edited by A. H. Zewail (SPIE Publishing Company, 1977), p. 42.
[5] A. Genack, R. M. Mcfarlane, and R. G. Brewer, Phys. Rev. Lett. **37**, 1078 (1976).
[6] A. H. Zewail, T. E. Orlowski, R. R. Shah, and K. E. Jones, Chem. Phys. Lett. **49**, 520 (1977).
[7] R. Alder, IEEE Spectrum, **4**, 42 (1967).
[8] P. F. Liao, R. Leigh, P. Hu, and S. R. Hartmann, Phys. Lett. A **41**, 285 (1972).

R.5. Two-Photon Optical Frequency Standards, J. L. HALL,* O. POULSEN, S. A. LEE, AND J. C. BERGQUIST, *Joint Institute for Laboratory Astrophysics, National Bureau of Standards and University of Colorado, Boulder, Colo. 80309.* (15 min.)

We report here the preliminary observation of the two-photon transitions within the lowest $(6p)^3$ configuration of Bi as a first step in the systematic investigation of the feasibility of optical frequency standards based on two-photon transitions.[1] The main advantage of two-photon systems is their freedom from problems which limit saturated absorption or other one-photon frequency control systems, namely two-photon transitions are not influenced in first order by wavefront errors,[2] do not have strong velocity selection effects which inhibit reliable estimation of the second order Doppler correction,[3] and are singlets with respect to the recoil effect.[4] The disadvantages of two-photon transitions include intensity shifts due to virtual transitions, relative weakness of the transitions, and a shortage of really attractive transitions, in spite of some previous efforts in this direction.[5]

Our present experimental effort centers around the two-photon transition from the $(6p)^3\ 4S_{3/2}$ ground state of ^{209}Bi to the $(6p)^3\ ^2P_{3/2}$ metastable level. The main advantage of this system is its transition wavelength [$2h\nu = 2hc/(6030.5083$ Å)], its suitability for atomic beam studies and its long metastable state lifetime (4 ms).[6] The overwhelming disadvantage of this transition is its low transition strength: the most-nearly-resonance intermediate state for the two-photon process is the $(6p^2)7s\ ^2P_{3/2}$ which is off-resonance by about 33 kcm^{-1} and has an oscillator strength $\sim 10^{-5}$ for the second half of the two-photon process. For a given laser intensity this represents a transition probability some 5 1/2 powers of 10 reduced from the well-studied Na $3S$-$4D$ transition. Thus we have been obliged to use a high finesse resonator inside the vacuum system to build up the laser intensity, by a factor $\simeq 150$ in the present case, and to servo-control it to the laser frequency as it is scanned. Future use of the Ramsey fringe technique[7] will help to suppress the intensity shifts as well as to narrow the line. By use of a Cs-coated target it is possible to selectively detect metastable Bi atoms with tolerable quantum efficiency (~4%) via Auger electron emission. The channeltron output pulses are stored in a signal average swept synchronously with the laser. The dye laser (CR 599) is now spectrally narrowed to 200 kc RMS by locking it to an auxiliary cavity whose length is servo controlled to an infrared 3.39 μm local oscillator laser which is in turn frequency-offset-locked from a CH_4-stabilized HeNe laser. This system provides excellent long term stability, digital scanning via the frequency synthesizer in the FOL loop, and importantly improved short-term performance of the commerical dye laser by use of a fast PZT transducer behind a small dye laser cavity end mirror.

Present status of the work is the following: three hyperfine components of the two-photon transition have been observed, using an earlier frequency servo that removed dye laser drift but did not narrow the line appreciably. Count rates of ≈100 c/s were observed with a 2.6 MHz full width. Improvements in the atomic beam solid angle and detector sensitivity are being prepared. It will be interesting to use this apparatus to excite Rydberg states in the alkalis (especially rubidium) and in the ^3P series of the alkaline earths (especially calcium). Principal quantum numbers in the range 30–50 may lead to narrow enough lines (<10 kHz) without excessive dc polarizability shifts. It seems likely that the presence of many transitions, highly efficient detection, and relatively strong transition strengths will lend these Rydberg systems a special significance in future work.[8]

* Staff member, Quantum Physics Div. Natl. Bur. of Stand., Boulder, Colo. 80302.

[1] The Soviet proposals for two-photon frequency standards have had a fundamental and stimulating effect in this field. See, e.g., E. V. Baklanov and V. P. Chebotayev, Opt. Commun. **12**, 312 (1974).

697