

The Letters to the Editor section is subdivided into four categories entitled Communications, Notes, Comments, and Errata. The textual material of each Letter is limited to 1200 words minus the following: (a) 200 words for a square figure one-column wide. Larger figures are scaled in proportion to their area; (b) 50 words for each displayed equation; (c) 7 words for each line of table including headings and horizontal rulings. Proof will be sent to authors. See the issue of 1 July 1983 for a fuller description of Letters to the Editor.

COMMUNICATIONS

Broadband population inversion by phase modulated pulses

J. Baum, R. Tycko, and A. Pines

Department of Chemistry and Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

(Received 19 May 1983; accepted 16 August 1983)

For many experiments in NMR and coherent optics, it is necessary to invert populations over a broad band of frequencies.¹⁻³ Recently, phase shifted pulse sequences for this purpose have been derived by several methods.^{4,5} In this Communication, we present an alternative analytical approach to broadband population inversion.

An exact broadband "2 π " pulse, employing amplitude modulation, exists in the context of self-induced transparency.⁶ No analogous exact solution to broadband inversion is known. Allen and Eberly have presented a class of amplitude and phase modulated pulses that invert exactly on resonance.⁷ We investigate the off resonance inversion behavior of similar phase modulated pulses. To derive such pulses, consider the Hamiltonian for nuclear spins under radio frequency (rf) radiation in a rotating frame related to the laboratory frame by the transformation $T = \exp\{-i\int \omega_1(t) dt + \phi(t)\}$. We call this the frequency modulated (FM) frame. The Hamiltonian is

$$\mathcal{H} = [\Delta\omega + \dot{\phi}(t)]I_x + \omega_1(t)I_z, \quad (1)$$

where $\omega_1(t)$, $\phi(t)$, and ω are the laboratory frame rf amplitude, phase, and frequency, respectively. In the FM frame, $\Delta\omega$ is the resonance offset and the phase derivative $\dot{\phi}(t)$ can be viewed as a frequency modulation. The Hamiltonian for a two-level optical system has the same form. The problem is to find $\dot{\phi}(t)$ and $\omega_1(t)$ that produce good inversion over a large range of values of $\Delta\omega$.

The inversion of on resonance ($\Delta\omega = 0$) spins can be described by a trajectory from $+z$ to $-z$ on a unit sphere in the FM frame.⁸ For any given trajectory, the Bloch equations without relaxation^{9,10} determine the pairs of rf phase and amplitude functions that produce that trajectory. A particularly simple class of inverting trajectories are those which follow a great circle from the $+z$ to the $-z$ axis with an azimuthal angle $-\gamma$. Assuming a constant rf amplitude equal to ω_1^0 , these trajectories dictate a $\dot{\phi}(t)$ characterized by the single parameter γ . The derived $\dot{\phi}$ functions are

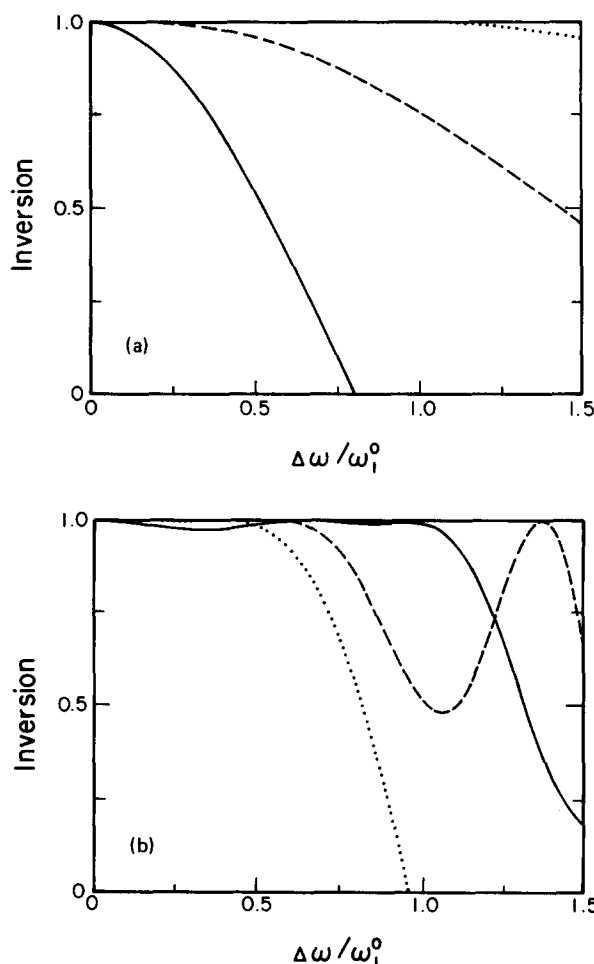


FIG. 1. Simulations of population inversion vs relative resonance offset. (a) Continuously phase modulated pulse of Eq. (2) for $\gamma = \pi/2$ (solid line), $\gamma = 0.245$ (dashed line), $\gamma = 0.111$ (dotted line). $\gamma = \pi/2$ corresponds to a π pulse. (b) Discrete pulse sequences derived from continuously phase modulated pulse: $(84)_{94} (251)_0 (84)_{94}$ (dotted line); $(64)_{322} (122)_{96} (310)_0 (122)_{96} (64)_{322}$ (dashed line); $39_{419} (54)_{209} (66)_{139} (84)_{70} (267)_0 (84)_{70} (66)_{139} (54)_{209} (39)_{419}$ (solid line). The notation here is $(\theta)_\phi$ where θ and ϕ are the flip angles and phases of individual pulses in degrees.

$$\dot{\phi}(t) = -\omega_1^0 \cos \gamma \tan(\omega_1^0 \sin \gamma) t$$

$$-\frac{\pi}{2\omega_1^0 \sin \gamma} \leq t \leq \frac{\pi}{2\omega_1^0 \sin \gamma} \quad (2)$$

The overall pulse area is $\pi/\sin \gamma$. The pulses suggested by Allen and Eberly produce the same on-resonance inverting trajectory but have variable ω_1 and extend from $-\infty$ to $+\infty$ in time.

In Fig. 1(a), we show calculated plots of the inversion accomplished by the pulse of Eq. (2) as a function of the offset $\Delta\omega$ for various values of γ . For all values of γ , the on-resonance inversion is perfect. When $\gamma = \pi/2$, the pulse of Eq. (2) reduces to the usual π pulse. As γ approaches zero, the range of frequencies over which good inversion is achieved increases.

The inversion of the off resonance spins can be understood by considering $\dot{\phi}(t)$ in the FM frame as an adiabatic frequency sweep.⁹ Typically, in NMR and optics, an adiabatic sweep is linear, i. e., $\dot{\phi}(t) = kt$, where k is the constant sweep rate.^{11,12} A nonlinear sweep can produce adiabatic inversion more efficiently, i. e., in a significantly shorter time. For small values of γ , $\dot{\phi}(t)$ is an example of an efficient adiabatic sweep. In addition, because $\dot{\phi}(t)$ derives from the on-resonance inverting trajectory, the inversion for $\Delta\omega = 0$ is exact for all values of γ .

Experimentally, it is usually more convenient to use a sequence of phase shifted rf pulses rather than a single pulse with a continuously varying phase. To generate such a pulse sequence, we examine the inverting trajectory in a rotating frame related to the laboratory frame by the transformation $T = \exp(-iI_z \omega t)$. We call this the phase modulated (PM) frame. After choosing a series of points along the PM frame trajectory, we calculate the phases and lengths of the pulses that cause on-resonance spins to move between successive points. In this way, we arrive at pulse sequences that approximate the pulse of Eq. (2). Inversions resulting from

some representative pulse sequences are shown in Fig. 1(b). The three pulse sequence is similar to one previously derived by a different method.⁴

The continuously phase modulated pulses presented here invert populations over any desired bandwidth and always invert on resonance. Deriving pulse sequences from the continuously modulated pulses has the advantage, over previous methods, that the discrete sequences can also be constructed for inversion over any bandwidth with minimal computer optimization.

We are grateful to Yitzhak Weissman, James Murdoch, and Robert Harris for helpful discussions and to Herman Cho for assistance with computer simulations. R. Tycko acknowledges a National Science Foundation graduate fellowship. This work was supported by the Director, Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy under Contract Number DE-AC03-76SF00098.

¹R. L. Vold, J. S. Waugh, M. P. Klein, and D. E. Phelps, *J. Chem. Phys.* **48**, 3831 (1968).

²M. H. Levitt and R. Freeman, *J. Magn. Reson.* **43**, 502 (1981).

³D. Abella, N. A. Kurnit, and S. R. Hartmann, *Phys. Rev.* **141**, 391 (1966).

⁴M. H. Levitt, *J. Magn. Reson.* **50**, 95 (1982); W. S. Warren and A. H. Zewail, *J. Chem. Phys.* **78**, 2279 (1983).

⁵R. Tycko and A. Pines (submitted for publication).

⁶S. L. McCall and E. L. Hahn, *Phys. Rev.* **183**, 457 (1969).

⁷L. Allen and J. H. Eberly, *Optical Resonance and Two Level Atoms* (Wiley, New York, 1975), p. 101.

⁸R. P. Feynman, F. L. Vernon, and R. W. Hellwarth, *J. Appl. Phys.* **28**, 49 (1957).

⁹A. Abragam, *The Principle of Nuclear Magnetism* (Oxford University, Oxford, 1961), p. 44.

¹⁰Reference 9, p. 34.

¹¹M. M. T. Loy, *Phys. Rev. Lett.* **32**, 814 (1974).

¹²M. M. T. Loy, *Phys. Rev. Lett.* **41**, 473 (1978); A. Pines, D. J. Ruben, S. Vega, and M. Mehring, *ibid.* **36**, 110 (1976).

Unimolecular decomposition and vibrationally induced electron autodetachment of acetone enolate ion

Robert F. Foster, William Tumas, and John I. Brauman

Department of Chemistry, Stanford University, Stanford, California 94305
(Received 6 June 1983; accepted 16 August 1983)

Highly vibrationally excited molecules often have unique reactivities.¹ We report here the results of the infrared multiphoton activation of acetone enolate negative ion under collisionless conditions, in which branching is observed between bond dissociation and vibrationally induced electron autodetachment. From these results, the lifetime of the vibrationally excited anion prior to electron autodetachment is estimated to be $\sim 10^{-7}$ s at an energy of ~ 1 eV above threshold. The electron loss pathway represents a type of vibrational-

to-electronic energy coupling which probably takes place between two close but nonintersecting potential surfaces.^{2,3} The observed branching therefore involves a competition between an adiabatic (bond dissociation) and a nonadiabatic (electron loss) channel.

Little detailed information is available on the mechanism of vibrationally induced autodetachment, and there are few estimates of the lifetime of the excited negative ion relative to electron loss.^{4,5} A direct measure of