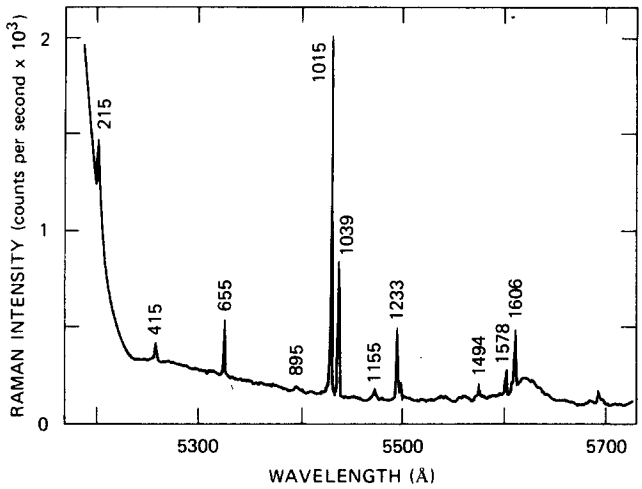

FIG. 1. Surface enhanced Raman spectrum for pyridine adsorbed on Cd electrode at −0.8 V.

dine/Hg[10] systems. The moderately strong peak which appears at 215 cm^{-1} is attributed to a vibration between pyridine and a single Cd metal atom. The calculated force constant k(Cd–pyridine) is 1.27×10^5 dyn/cm, which fits the trend $k_{Hg}<k_{Cd}<k_{Ag}$.[10] The most intense lines for pyridine/Cd are at 1015, 1039, 3074, and 3084 cm^{-1}. These lines and other lines (415, 655, 895, 1233, 1494, 1578, 1606, and 3152 cm^{-1}) show small shifts from their counterparts on Ag and Hg substrates. Two lines that appear in the SER spectra of pyridine on Ag (750 and 1066 cm^{-1}) and Hg (750 and 1073 cm^{-1}) were not seen on Cd.

To elucidate the origin of the enhancement mechanism, the kinds of substrates on which SERS can be obtained must be well understood. Two of the Group IIB elements, namely Cd and Hg are now known to exhibit SERS. The chemistries of Cd and Zn are very similar and there is some resemblance to the *d*-group elements in their ability to form complexes.[12] We believe zinc will also show a SERS effect.

This work was done at the facilities of the Molecular Physics Laboratory. The author thanks Dr. Kenneth M. Sancier for helpful discussions.

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Optical analogs of NMR phase coherent multiple pulse spectroscopy[a)]

W.S. Warren[b)] and A.H. Zewail[c)]

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125 [d)]

(Received 25 August 1981; accepted 15 October 1981)

In recent years, the number of NMR multiple pulse sequences (and their complexity) has grown rapidly because these sequences have proven to be very useful. Sequences have been designed to eliminate inhomogeneous broadening in coupled spin systems,[1,2] eliminate the direct dipole–dipole interaction to measure chemical shift tensors orders of magnitude smaller,[3–5] and pump forbidden transitions.[6–8] For optical transitions in thin samples, single frequency multiple pulse experiments have included two-pulse photon echoes[9–11]; three-pulse photon echoes,[12] where the additional pulse translates the transverse polarization into population inversions, and stimulated photon echoes.[13,14] However, no analogous explosion in the number of optical multiple pulse sequences has yet occurred. Analogs of the more sophisticated NMR sequences would certainly be very important, but these sequences require phase coherent pulse trains (the phase of each pulse must be specified relative to the first), which is technically difficult.

In this communication we present a new technique for producing optical pulse sequences with *independently* variable delays, durations, and phases, using acoustic-optic

 0021-9606/81/245956-03$01.00

modulation. We apply the technique to the optical transition at 590 nm of gaseous I_2. It was previously shown[12] that the three-pulse echo intensity is much smaller than the spontaneous emission background, and that the known echo appears as a hole in the emission. By phase shifting the last pulse by 180° we have turned the hole into a peak, and the difference spectrum (the phase shifted spectrum minus the normal one) completely eliminates the spontaneous emission background (Fig. 1). Some other seuqneces will be discussed later.

The role of the pulse phase can be understood by considering the pulse to be a short segment taken out of a continuous wave. The wave has the functional form $\exp[i(\mathbf{k}\cdot\mathbf{r}-\omega t+\phi)]$, and we define the phase as $\phi+\mathbf{k}\cdot\mathbf{r}$. The phase difference between two collinear pulses (here called the relative phase) is not positionally dependent. The importance of the relative phase can be seen in the polarization vector picture for the effects of pulses on a two-level system[15]; the relative phase specifies the axis about which the vector is rotated (Fig. 2). We can assign positions in the xy plane to different relative phases ($0\equiv x$, $90°\equiv y$, $180°\equiv\bar{x}$, and $270°\equiv\bar{y}$). Two 90° pulses of the same phase would create a complete population inversion, but a 90° pulse of one phase followed by a 90° pulse exactly out of phase (written $90_x-90_{\bar{x}}$) would have no net effect.[16]

At radio frequencies $\lambda\sim 1$ m, so phase shifts are easily and stably accomplished by introducing path length differences (or by using commercially available hybrids) without affecting the delay between pulses. By contrast, many optical experiments are done with pulsed lasers: a single pulse is selected, with beam splitters and optical delay lines generating the pulse sequence. In this case the delay dramatically affects the relative phase. For example, a 1 ns (30 cm) delay line would have to be settable (and stable) to a few parts in 10^7 to establish phase coherence. If the optical pulses are generated instead by electro-optic modulation, then the relative phase and polarization of any two pulses are *not* independent of the delay between them.[2,22]

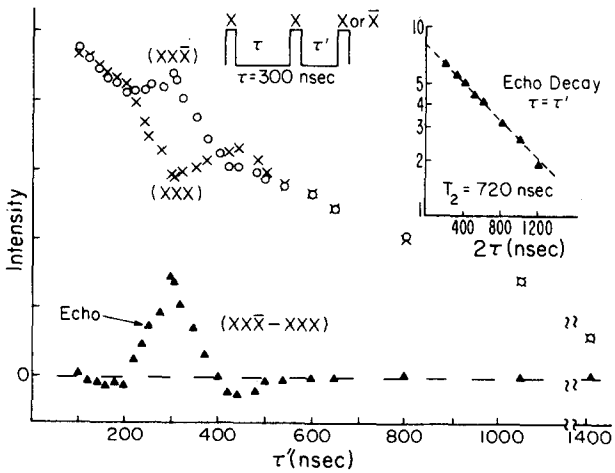

FIG. 1. The difference spectrum (all three pulses in phase, XXX, versus the third pulse out of phase, $XX\bar{X}$) for the three-pulse photon echo of gaseous I_2. The insert displays the decay of the coherent signal when $\tau=\tau$, giving T_2 directly. The sequence XXX by itself gives a sloping baseline which is more intense than the echo. The difference spectrum completely eliminates this baseline (see text). The temperature is −22 °C.

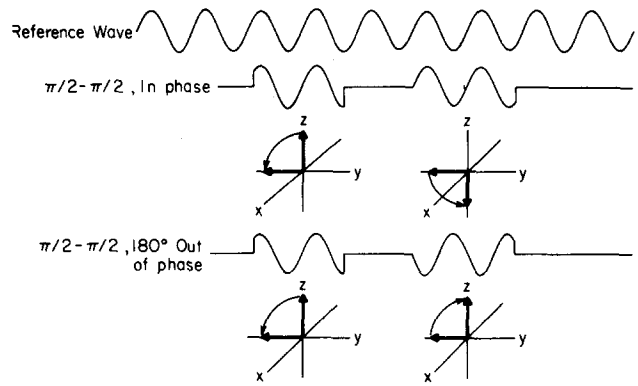

FIG. 2. A schematic illustration of the role of the relative phase of two pulses. The figure also depicts the effect of these pulses on the polarization vector in the FVH[15] picture. Note that two in-phase 90° pulses will create a complete population inversion, while two pulses exactly *out-of-phase* will have no net effect. Thus the relative phase is extremely important and must be specified in multiple pulse sequences.

In our experiments the extracavity acousto-optic modulator creates pulses from a continuous single-mode dye laser. When rf is applied at the acoustic frequency a traveling wave is produced which diffracts a fraction of the incident laser power.[17,18] This diffracted beam is upconverted or downconverted by the rf frequency; thus the modulator acts as a mixer would in the rf region, multiplying the two waveforms together. As long as the laser is monochromatic over the duration of the pulse sequence (perhaps 1 μs) and path lengths are stable over that time, then the relative phases of two-optical pulses will be identical to the relative phases of the rf pulses which generated them. Our modulator was driven to 30% diffraction efficiency by 10 W rf pulses at 460 MHz, provided by a home-built generator equivalent to a conventional NMR transmitter section. The optical pulse rise and fall times were 15 ns, with a peak power of 8 mW. Off-resonance fluorescence was detected by a PMT and gated by a boxcar integrator.

Figure 1 shows the difference spectrum obtained for the two pulse sequences $90_x-\tau-180_x-\tau'-90_x[\equiv(XXX)]$ and $(XX\bar{X})$. For fixed τ we generate a "clean" echo with complete suppression of the spontaneous emission. Fixing $\tau=\tau'$ and varying both delays synchronously results in an excellent exponential decay, shown in the insert, which directly gives $T_2=450\pm20$ ns at the pressure used. We also found that the sequence $(X\bar{X}X)$ was exactly equivalent to (XXX) and the sequence $(\bar{X}XX)$ was exactly equivalent to $(XX\bar{X})$.

These results prove that the already determined phases of the rf pulses have been transferred to the optical sequence. The fluorescence after the third pulse is proportional to the excited state population. This in turn is proportional to a combination of excited state population and transverse polarization immediately *before* that pulse. Phase shifting the last pulse by 180° keeps exactly the same contribution from the excited state population, which gives the background, but inverts

the contribution from transverse polarization, which gives the echo. Time reversal symmetry makes $XX\bar{X}$ equivalent to $\bar{X}XX$. If the Doppler width were much less than the pulse bandwidth, then the sequence $(X\bar{X}X)$ would compensate for flip angle inhomogeneities, and $\tau = \tau' = 0$ would correspond to zero fluorescence. We worked in the opposite limit, however, and theoretical calculations show that shifting the middle pulse then has no effect, as verified experimentally.

In conclusion, we have demonstrated that phase coherent pulse trains can be generated in the optical regime to observe coherent signals. We will list here only a few possible extensions of our technique.[19] Dephasing rates in mixed molecular crystals have been explained[20] by interactions between transition electric dipoles, which can be refocused by well-known NMR line narrowing sequences[3-5] or even simpler dipolar echo sequences.[21] Multiple echo sequences are also useful to reduce the effects of transverse velocity distributions for gaseous samples. Finally, phase coherent pulse trains permit the direct observation of coherences in the rotating frame (i.e., measuring $\langle P_y \rangle$ and not $\langle P_y^2 \rangle$), which can simplify the spectra of multilevel systems.

We thank Russell Chipman for useful discussions and help with the experiments.

[a]Supported in part by grant number DMR81-05034 from the National Science Foundation.
[b]National Science Foundation Postdoctoral Fellow.
[c]Alfred P. Sloan Fellow and Camille & Henry Dreyfus Teacher-Scholar.
[d]Contribution No. 6515.

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Quantum beats and dephasing in isolated large molecules cooled by supersonic jet expansion and excited by picosecond pulses: Anthracene[a)]

Wm. R. Lambert, P. M. Felker, and A. H. Zewail[b)]

Arthur Amos Noyes Laboratory of Chemical Physics,[c)]
California Institute of Technology, Pasadena, California 91125
(Received 28 August 1981; accepted 22 October 1981)

Intramolecular relaxation in isolated large molecules is of considerable current interest. The primary questions are: what is the nature of the states which are excited by the light source, and; how does the deposited energy get transferred within the molecule? In this regard, the possibility of observing coherence effects in the fluorescence decay of large molecules is very important. When large molecules are excited at finite temperatures the existence of many sequence transitions results in spectral broadening and in the masking of

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