Fluctuation Spectroscopy by Tunable Energy Compensation: Application to Radiator Reorientation Kernels

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A new method for investigating fluctuations in macroscopic coherences is suggested and demonstrated by measurement of radiator reorientation kernels in Stark-tunable infrared transitions of $^{13}CH_3F$. The dominant ($\Delta M = 1$) kernel is obtained by a scale transformation from the *shape* of a curve of two-pulse photon-echo intensity versus Stark voltage, at fixed large echo time delay.

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Laser-induced transients have wide application as probes of relaxation phenomena in vapors and condensed media. However, the fluctuations which are the underlying cause of the relaxation are often difficult to characterize in detail. In this Letter we describe a new method for studying fluctuations in macroscopic coherences. The method singles out those processes which transfer coherence between superposed states whose energy separations have been made identical by means of a tunable external field. Such fluctuations have special significance because they tend to preserve the phase of the macroscopic coherence for long observation times.

We demonstrate this idea by measuring radiator reorientation velocity-changing kernels in Stark-tunable infrared transitions of $^{13}CH_3F$. The dominant kernel is obtained as the *shape* of a curve of two-pulse photon-echo intensity versus Stark voltage, at fixed large echo time delay. The method works by singling out those collisions for which the collision-induced Doppler frequency shift is compensated by the (tunable) Stark frequency change of the oscillator which accompanies infrared radiator reorientation. A simple scale transformation of the applied Stark voltage to velocity units yields the reorientation kernel.

Radiator reorientation is a form of (infrared) coherence transfer, and is described by the quantum transport equation.[1–3] However, the physical picture and conditions for which collision-induced coherence transfer can occur are not well established and presently there is no experimental information on the correlation between radiator reorientation and velocity changes.[4] Processes of this type have been analyzed theoretically in some detail with neglect of the accompanying velocity changes.[5,6] Previous experiments have been confined to Zeeman coherence and microwave coherence rotational transfer (intramolecular),[7] for which velocity changes were not measured.

In our experiments, two-pulse photon echoes are used to study infrared radiator reorientation kernels for molecules with a first-order Stark effect, by application of a small dc electric field parallel to the $\hat{z}$ direction. A pulse of linearly polarized ($\hat{z}$) laser radiation then excites a number of uncoupled ($JM \rightarrow J'M$) infrared transitions, so that a molecule initially in the state M becomes a dipole radiator, d_M, with an orientation labeled by M. The electric field causes the dipolar radiation frequency to be orientation (M) dependent, the Stark shift being $\nu_s M$, where ν_s is the transition-frequency shift for $M = 1$.

Under the assumption that the input pulse bandwidth and dc Stark shifts are small compared to the Doppler width, echoes due to velocity dephasing and rephasing for each M transition will all have a center frequency equal to that of the laser. Consequently, in the absence of collisions, dipoles of different orientation M contribute to the echo signal in phase, and no beating phenomena will occur,[8] in contrast to some sublevel and quantum-beat echo experiments.[9]

In the presence of collisions, the situation is quite different. According to the isotropic collision approximation,[10,11] dipole radiator reorientation requires that both the excited and the ground states of the infrared transition undergo the same reorientation ΔM. Hence, a dipole d_M changes its orientation to become $d_{M+\Delta M}$, which results in a frequency change as a result of the Stark field. Since all of the dipoles are initially excited by the first pulse at the same time, $t = 0$, a dipole d_M reorienting at a later time to $d_{M+\Delta M}$ will have a time-dependent phase relative to dipoles previously in the orientation $M + \Delta M$. This leads to a *collision-induced* oscillatory echo decay curve versus echo time delay at fixed Stark field. A Fourier component at the frequency $\Delta M\, \nu_s$ will be present for each possible reorientation ΔM. The shape of the decay curve also contains information about the velocity changes Δv which accompany ΔM transfer, since these alter the oscillator frequency also, leading to phase randomization of the macroscopic coherence.

In order to understand how the combined velocity- and M-changing processes affect the macroscopic coherence, we consider the evolution of the (slowly varying) dipole amplitude $d_M(v,t)$ corresponding to each orientation. The equation of motion takes the form[12]

$$\dot{d}_M(v,t) = -\Gamma_M(v)\,d_M(v,t) + \sum\nolimits'_{M'} \int dv'\, W^{(v\leftarrow v')}_{M\leftarrow M'} e^{i[q(v-v')+(M-M')\omega_s]t} d_{M'}(v',t). \tag{1}$$

The first term of Eq. (1) is the loss rate of dipoles, due to inelastic collisions (for example, J changes), reorientation, or velocity changes. The second term describes the transfer of dipoles of orientation M' and velocity v' into the orientation M with velocity v at an arrival rate determined by the one-dimensional kernels $W^{(v\leftarrow v')}_{M\leftarrow M'}$. The time-dependent phase of the arriving dipoles is determined by the Doppler and Stark frequency changes accompanying the transfer, where $\omega_s(\text{rad/sec}) = 2\pi\nu_s$ and $q = 2\pi/\lambda$ (λ is the infrared wavelength).

An analytic solution to Eq. (1) can be obtained with the following fairly general simplifying assumptions: (i) An excitation bandwidth that is large compared to $(M-M')\omega_s$ and $q(v-v')$; (ii) velocity-selective excitation with v' much less than the perturber speed so that the kernel is symmetric in $\Delta v = (v-v')$ for the small-angle collisions which the coherence survives[13]; (iii) high-J limit so that both $d_{M'}$ and $W_{M\leftarrow M'}$ are slowly varying functions of M' for the transitions which contribute most to the echo signal. In this case, the kernel can be considered to be a function of $\Delta M = M - M'$ and Δv only, so that $d_{M'}(v') \simeq d_M(v)$ and $\Gamma_M(v) \simeq \text{const}$ for the range of ΔM and Δv for which transfer rates are appreciable. Since Q-branch transitions have a very small first-order Stark tuning (for $JM \to JM$), we consider only R- or P-branch transitions for which d_M is peaked at small $M < J$. In this case, $W(-\Delta M) \simeq W(\Delta M)$, where we measure kernels for small initial M'.

With these assumptions, using the facts that the second (π) input pulse conjugates the slowly varying polarization and that the echo signal is proportional to the square of the macroscopic polarization, one obtains the echo intensity, I_e:

$$\ln\left[\frac{I_e(\omega_s=0)}{I_e(\omega_s)}\right] = 16\,\text{Re}\sum_{\Delta M>0}\int_0^\infty d(\Delta v)\, W(\Delta M,\Delta v)\int_0^T dt\, \cos(q\,\Delta v\, t)[1-\cos(\Delta M\,\omega_s t)]. \tag{2}$$

By taking the ratio of the echo intensities with the Stark field off ($\omega_s = 0$) and on ($\omega_s \neq 0$), only Stark-dependent transfer kernels ($\Delta M > 0$) are studied. Generally, Fourier analysis of the slope of $\ln I_e(\omega_s, T)$ vs T at fixed ω_s can be used to obtain *all* of the *kernels* (including $\Delta M = 0$) as a series of peaks separated by ω_s (where ω_s is chosen to be larger than the average collision-induced Doppler shift).

In this Letter, we consider an alternative experiment, namely, the curves obtained by variation of ω_s at fixed large T, which has novel features. In particular, for fixed large T, where $q\,\Delta v T \gg 1$, the time integral in Eq. (2) is proportional to $\delta(q\,\Delta v) - \delta(q\,\Delta v + \Delta M\,\omega_s)$.[14] (Note that convergence to this limit is ensured by the finite kernel width in Δv.) If the transfer rates are dominated by a particular ΔM, then the corresponding kernel may be written in terms of the data in the remarkably simple form

$$\text{Re}\, W(\Delta M, \Delta v) = \frac{q}{8\pi}\ln\left[\frac{I_e(\omega_s = q\,\Delta v/\Delta M)}{I_e(\omega_s \to \infty)}\right], \tag{3}$$

in the limit $T \gg (q\,\Delta v)^{-1}$, where the fact that the kernel must vanish for large Δv has been used.

Equation (3) shows that the kernel [in (rad s^{-1})/(cm s^{-1})] is obtained by use of the asymptotic value ($\omega_s \to \infty$) as the baseline, with a scale transformation, $\Delta v = \Delta M\,\omega_s/q$, for the Stark tuning axis, and $q/8\pi$ for the logarithmic axis, where $q = 2\pi/\lambda$. This amounts essentially to a turning of the data curve which scans the Stark voltage from 0 to ∞ upside down!

Physically, Eq. (3) arises because at large T all random frequency changes due to $\Delta M\,\omega_s$ or $q\,\Delta v$ tend to destroy the macroscopic coherence. The exception is for collisions where $q\,\Delta v + \Delta M\,\omega_s = 0$, for which there is no frequency change. Such collisions occur with a probability $\sim T(1/qT)\,W(\Delta M, \Delta v = \Delta M\,\omega_s/q)$ where $1/qT = \lambda/2\pi T$ is approximately the velocity resolution corresponding to the delay T.

For our experiments (Fig. 1), we employ the $R(\nu_3, J=4, K=3)$ transition of $^{13}CH_3F$,[15] which is excited using a stable cw CO_2 laser (9P32) and acousto-optic intensity modulation for pulse generation. A digitally enabled oscillator driver eliminates rf leakage so that acousto-optic rejection (on/off) ratios are scattered-light limited at $\sim 10^6{:}1$. Reproducible input pulses with a rise time < 80 ns and a repetition rate > 20 kHz are readily obtained. Echoes are measured with a fast HgCdTe detector, sampled by an SRS boxcar (model 250).

A small variable dc Stark field is applied to the interaction region by means of two aluminum plates, 2 in. wide and 54 in. long, spaced by 1 in. (± 0.002 in.), and housed in a $3\frac{1}{2}$-in.-diam stainless-steel cell. The laser field occupies only a $\sim 1\text{-cm}^2$ portion in the center of the $1\times 2\text{-in.}^2$ region. A Stark tuning rate $\nu_s = 17.5$ kHz/V is calculated from measured values of the permanent dipole moment.[16] The excitation bandwidth, ~ 5 MHz, is measured by means of a

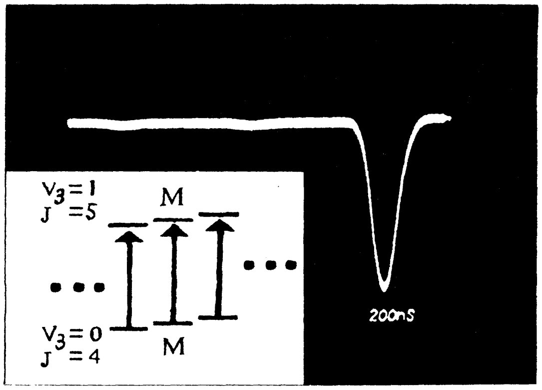

FIG. 1. Oscilloscope trace showing typical photon-echo signal and scattered excitation pulses. The inset shows parallel transitions and energy levels in the presence of the Stark field.

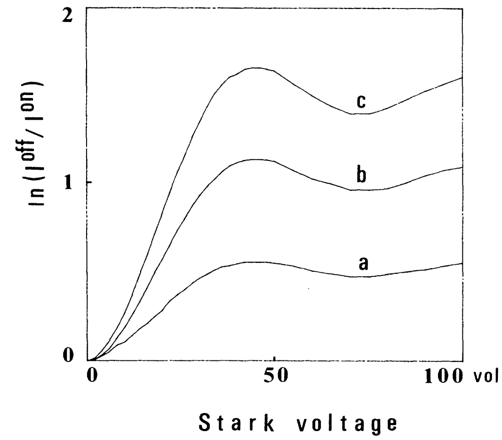

FIG. 2. $\ln(I^{\text{off}}/I^{\text{on}})$ vs Stark voltage at $2T=2$ μs and fixed $^{13}CH_3F$ pressure of 3.93 mTorr. Total pressure of $^{13}CH_3F$ plus $^{12}CH_3F$ is (curve *a*) 3.93, (curve *b*) 7.95, and (curve *c*) 11.6 mTorr.

pump-probe grating experiment in which two $\pi/2$ input pulses separated by 1 μs create Ramsey-fringe frequency markers. The Doppler full width is ~ 66 MHz.

Echo intensity measurements were performed for pure $^{13}CH_3F$ in the pressure range 1–20 mTorr (measured with an MKS model 390 1-Torr-range capacitance manometer) and for $^{13}CH_3F$ perturbed by $^{12}CH_3F$. Results for $^{12}CH_3F$ perturbers at $2T=2$ μs (Fig. 2) show two prominent features: (i) An oscillation with Stark voltage; and (ii) a linear scaling with total perturber pressure. Note that for $^{12}CH_3F$, which is not excited by the laser, the echo intensity decreases with increasing perturber pressure. Identical curves are obtained for pure $^{13}CH_3F$ at the same total pressure. The oscillation period corresponds accurately to the calculated fundamental Stark frequency and therefore indicates that $\Delta M = \pm 1$ collisions are dominant. [Note that $\Delta M = 0$ collisions are Stark-field independent and do not contribute to the signal given in Eq. (2) as discussed above.] This is expected, since for $J=4$ and $K=3$, CH_3F-CH_3F $\Delta J=0$ radiator reorientation is dominated by dipole-dipole collisions. According to the Anderson model,[10,17] one expects about 30% of the $\Delta J = 0, \pm 1$ collision rate to be $\Delta J = 0$ collisions in this case. Further, higher-order (van der Waal's) collisional interactions with $\Delta J = 0$ for $J=4$ and $K=3$ are expected to be negligible, the $\Delta J=0$ contribution being $<1\%$ of the total rank-2 rate, as is readily verified from the corresponding $3j$ symbols.[17] In this case, Eq. (3) is applicable.

A plot of data obtained versus Stark voltage for different values of T (Fig. 3) shows how the shape of the curve changes until it is nearly independent of T at $2T \sim 5$ μs. The data are plotted upside down (relative to Fig. 2) and two scales are provided, one corresponding to the data as taken, and the other to a scale change to units $(\text{kHz Torr}^{-1})/(\text{cm s}^{-1})$ and cm/s, when applicable to the kernel. Apparently, the limit $T \rightarrow \infty$ is already attained at $2T \sim 5$ μs since thereafter the curve shape changes little with T. Note, by contrast, that in the absence of measurable velocity changes $(\Delta v\, T \ll 1)$, Eq. (2) shows that the large-voltage asymptote scales linearly with T. This is found to be the case for small T.

Under the assumption that the 5-μs data are the kernel itself, the outer scales of Fig. 3 are applicable. Numerically integrating the area under this curve, we obtain the combined rate for $\Delta M = \pm 1$ collisions which is ~ 5.0 MHz/Torr. This is consistent with the large-voltage asymptotes obtained at small T which yield for the sum of the $\Delta M = \pm 1$ rates $\sim$5–6 MHz/Torr, which interestingly is comparable with $\Delta J = 0$ population transfer rates from previous work.[18] In addition, 5 MHz/Torr is $\sim 30\%$ of the broadening rate ~ 15

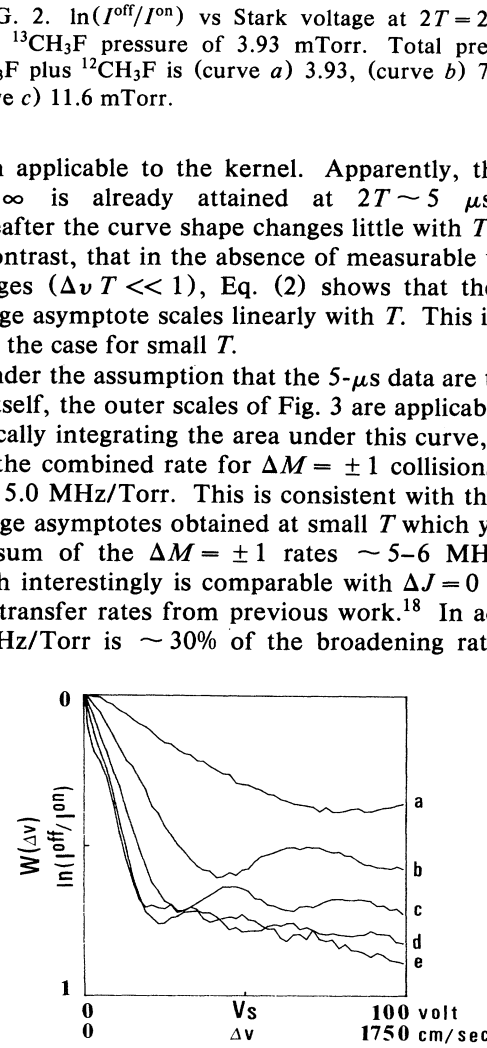

FIG. 3. Radiator reorientation kernel by scale transformation of echo intensity vs Stark voltage. Curve *a*, $2T=1$ μs; curve *b*, $2T=2$ μs; curve *c*, $2T=3$ μs; curve *d*, $2T=4$ μs; curve *e*, $2T=5$ μs. Full vertical scale: $\ln(I^{\text{off}}/I^{\text{on}}) = 242$ Torr^{-1}; $W(\Delta M=1, \Delta v) = 9.6$ (kHz/Torr)/(cm/s).

MHz/Torr.[19] The $1/e$ kernel width estimated from the $2T = 5$-μs data is ~ 230 cm/s. This is consistent with that expected for a collision in which only one unit of angular momentum ($\Delta M = 1$) is transferred at long range. In the case that this angular momentum is taken up by the relative (active-perturber) angular momentum, the laboratory velocity change will be such that $M_a \, \delta v_0 \, b_0 \sim \hbar$, where $M_a = 35$ amu and b_0 is the radius for M-changing collisions. With $\pi b_0^2 \sim 156$ Å^2 (corresponding to the rate 5 MHz/Torr for $\Delta M = \pm 1$ collisions), $b_0 \sim 7$ Å and $\delta v_0 \sim 256$ cm/s, consistent with the data.

Some important possible sources of systematic error in the experiments include the following: (i) pressure-independent voltage effects, (ii) field inhomogeneity, and (iii) imperfect laser polarization. Replotting the data at fixed voltage and time versus pressure indicates that (i) is negligible. Computer modeling shows that large field inhomogeneities ($\sim 30\%$) are needed to fit the data if velocity changes are neglected and predicts linear scaling of the large-voltage asymptote with T, contrary to the data. Slightly rotating the wire-grid input polarizer shows that the small feature near $v = 0$ increases as a result of quantum-beat echoes and therefore probably is spurious.

In conclusion, we have demonstrated the use of tunable energy compensation to study coherence fluctuations. We have exploited the analogy between collisional coherence transfer in velocity space, which produces a Doppler frequency shift corresponding to velocity changes Δv, and collision-induced radiator reorientation or transfer in M space, where a linear Stark or Zeeman effect can be used to associate a frequency with each ΔM. The techniques are readily extended to the visible region. Further, many other echo techniques in the visible and infrared (trilevel, stimulated, etc.) are applicable. For example, by varying both an applied field and a time delay, one can create gratings in velocity and M space to study M-changing kernels of a single state or inelastic transfer to another rovibrational state. Finally, tunable energy compensation may be particularly useful for picosecond studies in condensed media, which are conveniently performed at fixed time delays.

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[12]Note that the kernel is generally a four-index quantity (see Refs. 1–3). We assume here for simplicity that the isotropic model is approximately valid for the kernel.

[13]The one-dimensional kernels can be written as functions of the active-molecule initial velocity $v' = v_z'$ and velocity change $v - v' = v_z - v_z'$. The pure v_z dependence arises from the distribution for the z component of the atom-perturber relative velocity which depends on the perturber thermal distribution (for a given v_z). When v_z is much less than the perturber velocity this v_z dependence disappears. See, for example, P. R. Berman, T. W. Mossberg, and S. R. Hartmann, Phys. Rev. A **25**, 2550 (1982), and J. L. Le Gouet and P. R. Berman, Phys. Rev. A **24**, 1831 (1981), for the general kernel structure.

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