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PROGRESS REPORT

PICOSECOND LASER STUDY OF POLYATOMIC MOLECULES

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The present research program is directed towards the study of intramolecular energy relaxation dynamics in large molecules of interest to combustion. The question of how fast the excess electronic and vibrational energies are redistributed among the various modes and bonds in the molecule is an important one and is directly related to the chemical reactivity of these excited molecules.

In the past year, we have improved our temporal resolution from the picosecond to the femtosecond regime in measuring the energy relaxation times. This improvement of over 3 orders of magnitude is due to the use of a new technique of time-delayed correlation spectroscopy [1]. Traditionally, pump-probe experiments were used to extract information on the T_1 relaxation time. This approach, for example, was used in our earlier measurement of the internal conversion rate ($S_1 \rightarrow S_o$) in CrO_2Cl_2. The probe in that case was provided by picosecond multiphoton ionization of the vibrationally excited S_o^* molecules [2]. The vibrational quantum number dependence of the internal conversion rate was measured for the first time [3].

In the time-delayed correlation technique, both T_1 and T_2 information are intermingled. By carefully designing the experiment, it is possible to obtain the ultrafast T_2 dephasing time. We successfully performed such a measurement on several aromatic Rhodamine dye molecules. T_2 times as fast as 10 fs have been obtained. These results are significantly shorter than previous measurements by other groups using pump-probe techniques [4]. Our results are the first of its kind in applying this correlation technique using picosecond laser pulses.

The experimental arrangement is shown in Fig. 1. A broadband picosecond dye laser is essential in this experiment. We have previous experience with generating 10 ps dye lasers in transient oscillation type cavity [5]. These dye lasers have bandwidths of 150 Å depending on the dye used. Such bandwidths corresponds to correlation time τ_c of 40 fs. It can be shown that we can obtain T_2 information that are much shorter than τ_c by the present technique.

The configuration shown in Fig. 1 is basically a time-delayed-Transient Four-Wave Mixing (TD-TFWM) experiment [1]. The two pump beams propagating in the $\mathbf{k}_1$ and $\mathbf{k}_2$ directions generate a transient grating in the sample which scatters the input beams in the $2\mathbf{k}_1$-$\mathbf{k}_2$ and $2\mathbf{k}_2$-$\mathbf{k}_1$ directions. A time delay of τ between the two pump beams and the T_1,T_2 times of the excited upper level determine the scattering efficiency, or the signal levels S_1 and S_2. It can be shown that the signals are given by the correlation function:

$$S_1(\tau) = \int_0^{\infty} d\Omega \; \exp(-i\Omega t)\, g(\Omega) \int_{-\infty}^{t} dt_3 \int_{-\infty}^{t_3} dt_2 \int_{-\infty}^{t_2} dt_1 \; \exp\;((t_2-t_3)/T_1$$

$$+ \; (t_3+t_2-t_1)/T_2 \; - i(\omega_L-\Omega)\, t_3)\, E^*(t_2-\tau)\, E(t_1) \exp\,(i(\omega_L-\Omega)\,(t_1-t_2)$$

where $g(\Omega)$ is the absorption lineshape function, $E(t)$ is the sum of the two input beams, ω_L is the laser frequency and Ω is the material frequency.

Fig. 2 shows the results for Rhodamine 6G. At 300°K, the two singnals S_1 and S_2 overlap, indicating that T_1 and T_2 are much shorter than τ_C. At 120°K, a shift in the peak scattering of S_1 and S_2 can be seen. From the magnitude of the peak shift, T_1 and T_2 can be deduced. A theoretical calculation using eq.(1) shows that $T_1 = 200$ fs and $T_2 = 20$ fs. In the theoretical fit, a Gaussian inhomogeneous line was assumed for the absorption band $g(\Omega)$.

The ultrafast dephasing time of 20 fs is shorter than previous results in similar dye molecules measured using standard pump-probe methods [4]. The shorter dephasing time is in qualitative agreement with the fact that our pumping wavelength is shorter so that the upper level is highly vibrationally excited. This leads to a higher density of states and hence shorter T_2. It should be noted that within the fs timescale, there is absolutely no collision with the solvent so that the molecules can be treated as isolated. The possible perturbation by the solvent is a cage effect where the wavefunctions are distorted leading to more efficient intramolecular damping. At present, we are studying the effects of different solvents as well as their pH values on T_1 and T_2.

An interesting oscillation of the signals S_1 and S_2 occurs when the pump wavelength is such that the bandedge of S_1 is excited. Near the bandedge, the density of states is not high so that intramolecular damping is less efficient. Fig. 3 shows the results for R560 at 300°K. It can be seen that the peak shift is much larger indicating larger T_1 and T_2. A quantum beat like oscillation is also seen. The oscillation period of 30 fs corresponds to a vibrational mode frequency of 900 cm^{-1}. The inefficient relaxation of the particular mode leads to the quantum beat in the upper state population [4]. Similar quantum beat has also been observed in the picosecond regime in Na[5]. As far as correlation measurements go, it is the first time that quantum beats are observed in large molecules on such fast timescales.

The technique of TD-TFWM is a powerful one capable of generating dephasing and relaxation data in the fs regime. At present, quite a few unknowns have been left unexplored, such as the detail modeling of the system as a multi-level system [6], or as a heat bath for mode-mixing and relaxation. This is in a sense very similar to the traditional intramolecular vibrational relaxation (IVR) problem in multiphoton dissociation studies [7]. The exact nature of the quantum beat observed in Fig. 3 is worth looking into. It is possible to use this method to identify vibrational modes that are decoupled from the heat bath. Such behavior is similar to the isolated Raman mode results of Mazur et al [8], except that those results are in the nanosecond regime. It is believed that TD-TFWM can be a powerful tool for the study of the vibrational quasicontinuum in polyatomic molecules.

In the continuation proposal, we shall discuss specific experiments taking advantage of the TD-TFWM scheme. With the present set of experimental data, we expect to be able to write at least 3 papers, to be published in 1989.

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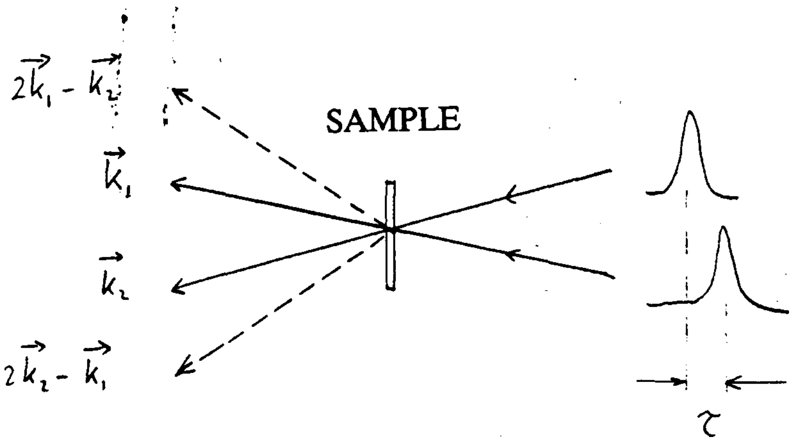

Fig. 1 Experimental Configuration.

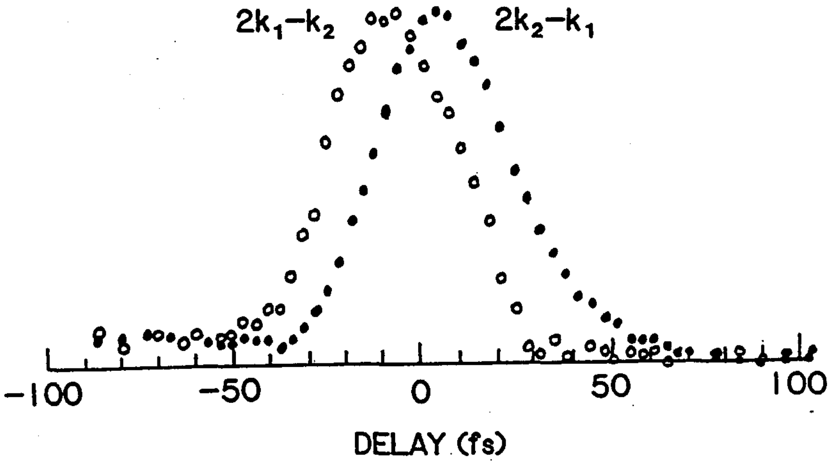

Fig. 2 Results for R6G showing peak shifts.

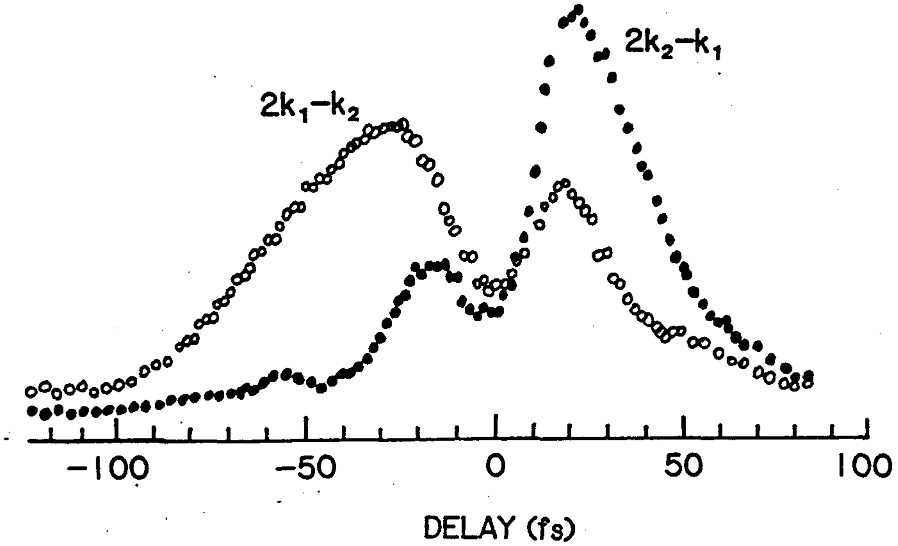

Fig. 3 Results for R560 showing quantum beat-like behavior.