TABLE I. The transition parameters.

Isotope	Transition volume cm^3/mol	Transition pressure (Kbar) Experiment[a]	SG	YR
H_2	3.00	Above 900	1500	1170
D_2	4.37	278	500	390

[a] Reference 5.

$$\psi(\omega_1,\ldots,\omega_N) = \prod_{i=1}^{N}\phi(\omega_i)\prod_{j<k}^{N}F(\omega_j,\omega_k), \tag{3}$$

where

$$\phi(\omega) = Y_{00}(\omega) + \gamma Y_{20}(\omega), \tag{4}$$

$$f(\omega_j,\omega_k) = \exp[\lambda w_{jk} b(\omega_j) b(\omega_k)], \tag{5}$$

where λ, γ are variational parameters, and $w_{jk} = 1$ if j,k are nearest neighbors, and zero otherwise. The function b is defined by $b(\omega_j) = \cos^2 \xi_j$ where ξ_j is the polar angle of the direction ω_j, with respect to the symmetry axis of molecule j. The multiple integrals appearing in the expectation of the potential energy [Eq. (2)], as well as in the rotational kinetic energy, were evaluated by a Monte Carlo simulation procedure. The search for the transition density was carried out by mapping the total energy as a function of the variational parameters λ, γ, and of the density (or specific volume), and by looking for a jump in the location of the minimum. The transition pressure was determined in Ref. 1 with the help of the equation of state proposed by Silvera and Goldman.[3] The values are given in Table I, column SG. In the high density region where the transitions occur for both para-H_2, and ortho-D_2, their (PV) curves are almost indistinguishable.

The equation of state recently discussed by Ross, Ree, and Young (YR in Ref. 4), gives significantly lower values for the transition pressure (see Table I, column YR), bringing them closer to the experimental values.[5] While in the case of the SG equation of state the agreement for D_2 with experiment was relatively better than for H_2, suggesting the fact that this equation was not well suited for the high density region, the YR equation of state seems to agree with the experiment to a comparable extent for both isotopes.

Although YR do not give an equation of state for D_2, we have assumed in analogy with the SG equation of state, that the (PV) curves of both isotopes are almost indistinguishable in the high density region of the transition.

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Femtosecond study of the recovery dynamics of malachite green in solution

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Interest has developed in the absorption dynamics of the triphenyl methane dyes in solution, especially in their nonradiative ground state recovery process. The characteristic time for this internal conversion process exhibits a sublinear dependence on viscosity which has been attributed to a conformational change in the excited state to a new structure characterized by enhanced rates of nonradiative decay.[1] Since this conformational change is thought to involve the rotation of a phenyl ring about the central carbon atom, it should be hindered by the viscous drag introduced by the solvent molecules, resulting in a ground state recovery time which increases with solvent viscosity. For low viscosity ($\eta \cong 0.01$ P) solvents, such as water, this relaxation process is very fast, ~1 ps. Previous measurements of the relaxation time in this low viscosity regime have either been in the frequency domain,[2–4] or in the time domain with a temporal resolution comparable to the decay times being measured.[5] We present here the first time-domain study of the triphenyl methane dye malachite green (MG) in both water and ethylene glycol (EG) using the recently developed equal-pulse correlation technique[6] and using a time resolution significantly better than previous time-domain studies.

Our measurement is based upon the saturation effect in the transmission characteristics of a thin jet of MG in solution. The sample is excited by two ~90 fs, 612 nm laser pulses of equal powers and orthogonal polarizations, which are collinearly propagating and have a delay τ between the pulses. The time-averaged combined transmitted flux of both pulses is measured as a function of τ. Because of rapid population relaxations, both out of the excited and into the ground state, reducing the degree of saturable absorption, the time-averaged transmitted power reaches a peak when $\tau = 0$ and decreases to a background value for large τ. The shape of this peak is related to the convolution between the laser pulse autocorrelation and the relaxation processes that govern the population difference between ground and excited states.

To interpret our data, we model the vibrational-rotational manifolds of the ground (S_0) and electronically excited (S_1) states of MG in solution as a four-level system (see inset

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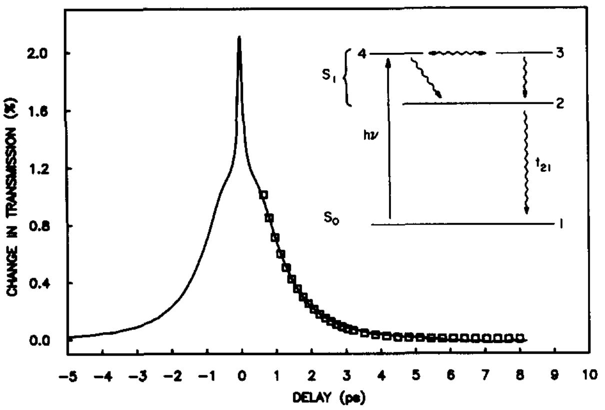

FIG. 1. The solid line is a typical experimental scan of the ground state recovery of MG in water. The squares correspond to an exponential fit of the form $\exp(-t/t_{21})$, with $t_{21} = 0.93 +/- 0.05$. Inset: schematic diagram of the energy levels for MG.

Fig. 1). Optical absorption excites an electron from level 1 to 4, which is approximately 800 cm^{-1} above the bottom of S_1. Level 3 is isoenergetic with level 4, but not optically connected to the ground state. Extremely rapid intramolecular redistribution of vibrational energy redistributes the populations between levels 4 and 3. Relaxation from levels 3 and 4 to 2, lower in the vibrational manifold of S_1, then follows through collisions with solvent molecules. Finally, nonradiative repopulation of the ground state proceeds with a time constant t_{21}.

Our experimental setup and procedure are described in Ref. 7. The sample is a 30 μm jet of malachite green dissolved in ethylene glycol or distilled water at a concentration of 10^{-3} M. Figure 1 exhibits a typical experimental scan for MG in water. The narrow central peak is not relevant to this ps experiment. It consists of a contribution due to a fast incoherent saturation process and a coherent artifact.[8] The long time component is due to repopulation of the ground state and fits well to a single exponential decay law $\exp(-t/t_{21})$ with $t_{21} = 0.93 +/- 0.05$ ps. Similarly, in ethylene glycol ($\eta = 0.13$ P), we measure $t_{21} = 4.46 +/- 0.05$ ps. Note that the details of the shape of the transition region between the central peak and the long decay component will depend on the specifics of the dynamics within the excited state manifold and are not considered here.

We can compare these results with those already obtained in both the time and the frequency domains. The time domain experiment of Ippen *et al.*,[5] using a 0.5 ps laser, revealed a 2.1 ps, single exponential recovery for MG in methanol ($\eta = 0.006$ P) and a 6 ps recovery for MG in EG. Although they do not measure the recovery time of MG in water, their results indicate that it should be longer than 2.1 ps, since the viscosity of water is greater than that of methanol. The rather large discrepancy between our results and theirs can only be partially explained by the difference in laser pulse widths. However, our results compare more favorably with several frequency domain measurements. Song *et al.*[2] report $t_{21} = 1.2 +/- 0.1$ ps for MG in water. Saikan *et al.*[3] give $t_{21} = 0.7$ ps for MG in water and $t_{21} = 5$ ps for MG in a mixture of water and glycerol ($\eta = 0.13$ P). The slight difference between their result and ours may be due to the difference in the wavelengths used in the two experiments (580 nm vs 612 nm). Finally, Trebino *et al.*[4] report that their data, when fitted to a single exponential decay law, yields $t_{21} = 1.4 +/- 0.1$ ps. However, they obtain a better fit to either a sum of exponentials, or a uniform range of exponential decays. Our data fits the latter forms less well than it does a single exponential.

In conclusion, we have studied the ground state recovery of malachite green in water and in ethylene glycol in the time domain with 50 fs resolution and have observed recovery laws consistent with single exponential decays. Moreover, we have demonstrated the usefulness of the equal-pulse correlation technique for studying molecular dynamics in the picosecond regime.

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