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VIBRATIONAL DYNAMICS IN MOLECULAR CONDENSED PHASES WITH THE CLIO FREE ELECTRON LASER

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Single color pump-probe and photon-echo experiments have been performed on the CO stretching mode of $W(CO)_6$ at about 1983 cm^{-1} in various liquids and solid environments. Combined with absorption data, the measured T_1 and T_2 times suggest the following conclusions: in all liquids studied, the IR absorption band is homogeneously broadened, whereas, inhomogeneous broadening is observed in solid matrices and in a xerogel. At low temperature, the echo decay is much faster in methane than in argon host.

Keywords: Pump-probe spectroscopy; photon-echoes; free-electron laser; matrices; liquids; xerogels; tungsten hexacarbonyl

INTRODUCTION

We have recently developed an experimental set up devoted to single color pump-probe and photon echoes experiments. Our aim is to study the vibrational dynamics of molecules dispersed in various environments. Owing to its exceptionally large transition dipole moment

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($\approx$ 1D), the CO stretching mode of tungsten hexacarbonyl is particularly well suited for experiments with the FEL as already shown by Fayer and coworkers [1].

EXPERIMENTAL

Experiments were performed with the CLIO free-electron laser (FEL) which delivers infrared radiation tunable from 3.5 to 50 μm. The FEL generates 10 μs macropulses at a 25 Hz repetition rate. Each macropulse consists of $\approx$ 1 ps micropulses separated by 32 ns. The maximum average power available for experiments is about 100 mW corresponding to an energy of 20 μJ per micropulse. To avoid sample heating problems, only a small fraction of this energy was used. Pump-probe and photon-echoes were performed with the same experimental set-up. The two pulses were obtained with an uncoated ZnSe beam splitter (20%). According to the experiment, the reflected beam was the probe pulse or the first pulse of the echo sequence. The delay between the pump and the probe or the first and the second pulse of the echo sequence was generated with a PC controlled delay line. The average power of each pulse was controlled independently with iris diaphragms. Two parabolic mirrors were used, one to focus the two beams on the sample, the other one to collect the desired signal. In order to increase the signal to noise ratio in pump-probe experiments, the probe signal was collected through a monochromator and compared to a reference signal. In echo experiments, the echo signal was selected by a pinhole.

RESULTS AND DISCUSSION

Vibrational population relaxation and dephasing times of $W(CO)_6$ have been measured in 2-methylpentane (2MP), *n*-hexane and carbon tetrachloride at room temperature. The results are in qualitative agreement with previous work [1, 2]. The measured echo decay suggests that the IR absorption band is essentially homogeneously broadened. For instance, the very short time (0.5 ps) measured in the photon echo experiment on CCl_4 is correlated to the 10.6 cm^{-1}

absorption bandwidth. The population relaxation time T_1 is nearly the same (about 60–70 ps for the long component) in the very similar solvents 2 MP and *n*-hexane while it is much longer in CCl_4 (about 125 ps). In 2 MP and *n*-hexane, a short component of 2–4 ps is tentatively assigned to $T_{1u} \rightarrow E_g$ phonon induced population transfer.

Preliminary experiments have also been performed on $W(CO)_6$ dispersed in a methyl-triethoxysilane (MTEOS) xerogel at room temperature as well as in an argon or a methane matrix at $T = 6$–30 K. For the three solids, the IR absorption band is inhomogeneously broadened. For instance in the MTEOS xerogel, the homogeneous

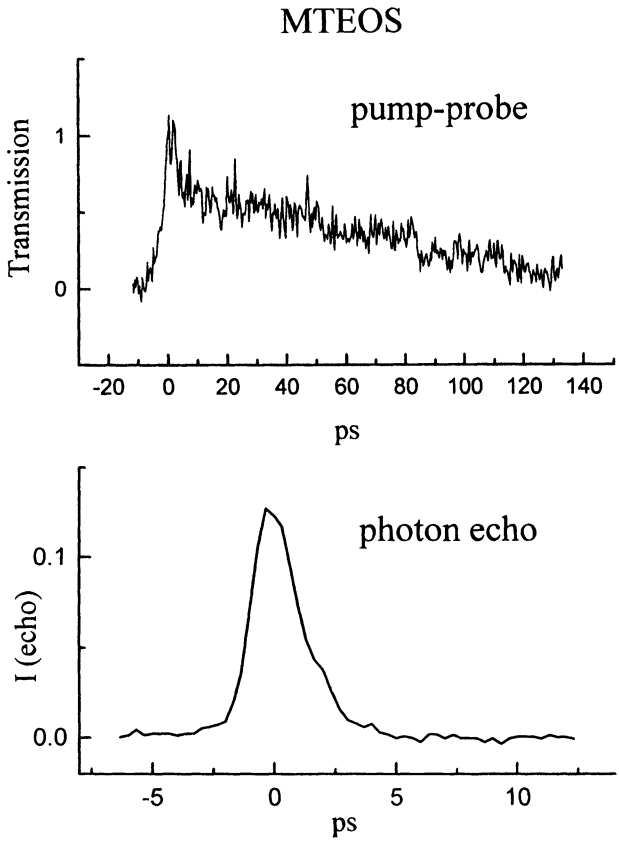

FIGURE 1 Pump-probe (top) and photon-echo (bottom) signals for $W(CO)_6$ inserted in a MTEOS xerogel host at room temperature.

width deduced from the echo signal at 300 K is 2.7 cm^{-1}, to be compared with the 11.5 cm^{-1} absorption bandwidth. Also in MTEOS, T_2 ($\sim$4 ps) is much shorter than T_1 ($\sim$100 ps) as shown in Figure 1. Only photon echo experiments have been performed in low temperature condensed gas matrices. Selected results are shown in Figure 2. The echo decay turns out to be fast in methane even at T = 8 K and becomes shorter at higher temperature (up to 30 K). It is tempting to relate it to the contribution of methane rotation in the solid phase. In contrast, in solid argon, the echo signal exhibits a much

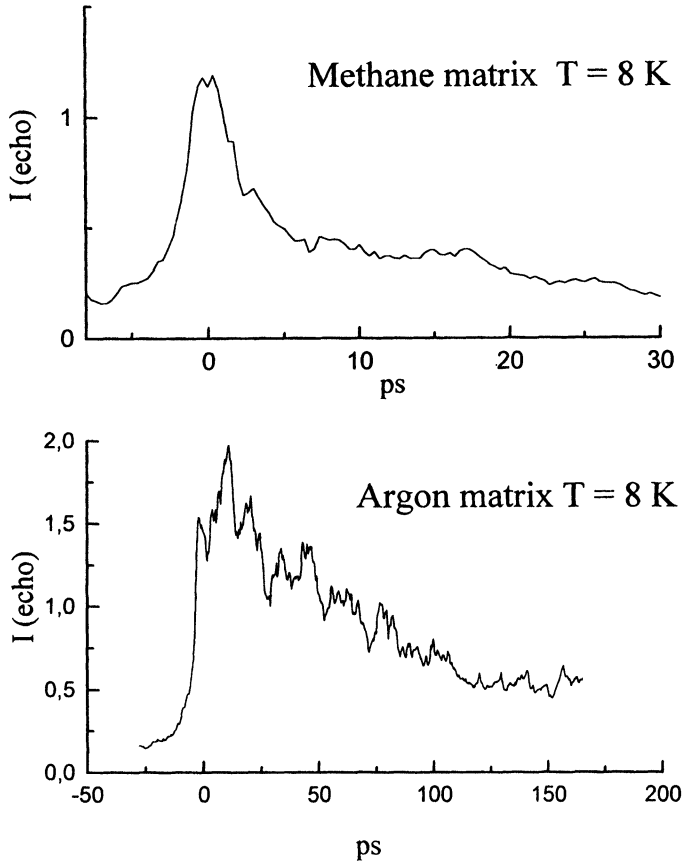

FIGURE 2 Photon-echo data for $W(CO)_6$ trapped at low temperature in a methane (top) or an argon (bottom) matrix.

slower decay ($T_2 = 100$ ps) which, as expected, is faster at higher temperature. In conclusion, $W(CO)_6$ appears to be an attractive probe for different liquid and solid environments. Further experiments with the FEL CLIO are in progress.

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References

[1] Tokmakoff, A. and Fayer, M. D. (1995). *J. Chem. Phys.*, **103**, 2810, *Accounts Chem. Res.*, **28**, 437.

[2] Heilweil, E. J., Cavanagh, R. R. and Stephenson, J. C. (1987). *Chem. Phys. Lett.*, **134**, 181; Arrivo, S. M., Dougherty, T. P., Grubbs, W. T. and Heilweil, E. J. (1995). *Chem. Phys. Lett.*, **235**, 247.