**Femtosecond Fourier-Transform Spectroscopy Of Low-Frequency
Intermolecular Motions In Weakly Interacting Liquids**

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MAY 22 1993
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Running Title: Fs F-T Spectroscopy of CCl₄

Keywords: femtosecond, collision-induced, OHD-RIKES, intermolecular-vibrations

Abstract: We present new results on the temperature-dependent collision-induced low-frequency Raman spectrum of the spherical top molecule CCl₄, obtained using optical-heterodyne-detected, femtosecond Fourier-transform Raman-induced Kerr-effect spectroscopy. A spectral shift to lower frequencies with increasing temperatures has been observed.

Recent work on the subject of solvation dynamics has concentrated on understanding the ultrafast dynamics of intermolecular interactions in strongly interacting, polar, and hydrogen-bonding solvents. In general, investigations into the effects of solvation dynamics on chemical reactions have concentrated on the highly polar liquids because it is in these solvents that the largest spectroscopic changes with solvent relaxation are observed. In these very polar liquids, however, the intermolecular dynamics are very complex, consisting of contributions from reorientational diffusion, inertially limited rotations, intermolecular vibrations involving

both reorientational (librational) and translational degrees of freedom, and interaction-induced collisional effects.

The role of collisional interaction-induced effects in shaping the intermolecular dynamics of molecular liquids has been a subject of considerable discussion. Molecular dynamics simulations have suggested that collisional effects can have a significant role in shaping the femtosecond dynamics and nonlinear-optical properties of molecular liquids. However, for anisotropic molecules, it is difficult to separate experimentally the collisional effects from other phenomena. In this paper we examine the intermolecular dynamics of the weakly interacting liquid carbon tetrachloride (CCl_4). Because carbon tetrachloride is a spherical top molecule (belonging to the T_d point group), its intermolecular light-scattering spectrum is purely interaction-induced. By studying this purely collision-induced feature in CCl_4 , we hope to gain insight on the lowest-frequency intermolecular vibrational behavior of more complex systems.

We have studied carbon tetrachloride using optical-heterodyne-detected, femtosecond Fourier-transform, Raman-induced Kerr-effect spectroscopy (OHD-RIKES). This nonlinear-optical polarization spectroscopy measures the liquid phase molecular dynamics directly in the time domain. We measure the transient birefringence induced by an intense femtosecond laser pulse, which is a direct measure of the contribution of nuclear-coordinate motions to the total molecular anisotropy tensor. Our laser pulses are nearly Fourier-transform limited, with a time-bandwidth product $\Delta\nu \cdot \Delta t = 0.36$. The pulse width is 50 fs, and the spectral FWHM is 240 cm^{-1} . Thus our data contains spectral information in the frequency range from 0-400 cm^{-1} . This spectral information is accessible directly by a Fourier-transform.

The OHD-RIKES technique has evolved over the past decade, and has been used extensively to study both inertial and diffusive types of relaxation dynamics in liquids. Greene et al. have used the optical-Kerr-effect technique to study collision-induced phenomena in the simple liquids argon, xenon, and O₂ [1]. McMorro and Lotshaw have studied many liquids, especially CS₂ [2], acetonitrile [3], and substituted benzene and aromatic analogs [4]. Recently we have begun to apply the technique to hydrogen-bonding liquids such as the formamides, water, acetic acid, and ethylene glycol. Fleming and co-workers have studied the linear-chain alkanols [5], and Wynne, et al., [6] have studied pyrrole H-bonded dimers. A preliminary report of the CCl₄ collisional dynamics obtained from OHD-RIKES data was given by McMorro, et al. [2]. The ultrafast Kerr profile of CCl₄ also was measured by Hattori, et al. [7], using an analogous phase-derivative technique, though these authors did not analyze the collision-induced part of the spectrum.

In carbon tetrachloride, the low-frequency Raman spectrum shows the collision-induced band peaked at 20 cm⁻¹, and extending to almost 110 cm⁻¹. At slightly higher frequencies, two intramolecular Cl-C-Cl bending modes occur, the ν_2 and ν_4 modes at 217 and 314 cm⁻¹, respectively. These two modes give rise to a beating pattern quite similar to that observed for an analogous halomethane, CH₂Br₂, which was detected using a complementary technique in the time domain, impulsive stimulated Raman scattering [8]. The damping constants of two modes may be obtained from our data, and provide the dephasing rates (or inverse vibrational linewidths) of the intramolecular bending vibrations. The dephasing rates increase with increasing temperature.

Our raw data are shown in Figure 1. The rapid rise and decay of the signal near zero-time-delay arises from the electronic hyperpolarizability response of CCl₄. This dominant pulse feature overrides the smaller nuclear-coordinate motion

component of the signal arising from the intramolecular modes and the collision-induced interactions. The beating pattern between the 217 and 314 cm^{-1} modes persists for several picoseconds before vibrational dephasing is complete. In this case, vibrational population relaxation is assumed to be occurring more rapidly than pure vibrational dephasing.

Following the treatment of McMorro [9], complications arising from the dominant electronic hyperpolarizability can be removed by deconvolution using spectral analysis techniques. The electronic hyperpolarizability response is instantaneous on our time scale, and thus is a map of the temporal profile of the laser pulse autocorrelation function. Making use of the symmetry of the second-order autocorrelation function and invoking the Born-Oppenheimer approximation, the pure nuclear coordinate response in the frequency domain is obtained. This spectral density may now be compared directly with the low-frequency Raman spectrum. The collision-induced spectrum of interest to us is completely separated from the two intramolecular modes, as shown in Figure 2. Our ultimate experimental results on the collision-induced spectra of CCl_4 as a function of temperature are shown in the inset of Figure 2. The band center moves towards lower frequencies as the temperature increases in the range from 20 to 75 $^{\circ}\text{C}$. The inset of Figure 1 shows the intermolecular collision-induced nuclear response function generated by an inverse Fourier-transform of the $T = 75^{\circ}\text{C}$ spectrum of Figure 2.

A rotational diffusion signal is absent from our data because of the spherical top symmetry of carbon tetrachloride. However, we can obtain a measure of the rotational diffusion time by examining the line-broadening of the vibrational bands, such as the ν_2 and ν_4 modes, as was done in the frequency domain by Bartoli and Litovitz [10, 11]. These authors arrived at a value of 1.8 ps for the rotational reorientation time at 22 $^{\circ}\text{C}$, which is consistent with the present results. In our

experiment, this analysis can be done directly on the time domain data by fitting the dephasing rate of each of the modes, or the analysis can be done in the frequency domain from the spectrum we construct via the Fourier-transform deconvolution procedure.

This collision-induced spectrum is observed for CCl_4 by both low-frequency Raman and far-infrared (FIR) absorption techniques, where the relevant selection rules pertain to the molecular polarizability and dipole moments, respectively. For the case of the FIR absorption, Joslin and Gray [12] have made a convincing argument that the transition dipoles necessary to allow for any absorption are induced via the permanent octupole and hexadecapole moments of the tetrahedral CCl_4 molecule, because there are no lower order electric multipoles (charge, dipole, or quadrupole moments) present. We assume that a similar treatment will apply for our experiment where the transitions are arising from the molecular polarizability-tensor.

Alternative models for explaining this low-frequency collision-induced spectrum include a Brownian oscillator model [13], or the instantaneous-(intermolecular)-normal-mode theory of Buchner, Ladanyi, and Stratt [14]. At present we are investigating which lineshape theory can provide the best overall model to our experimental data on the temperature dependence of the collision-induced spectrum in CCl_4 .

Acknowledgments

This research was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences, and at the Naval Research Laboratory, Office of Naval Research.

Figure Captions

Figure 1. A plot of the OHD-RIKES intensity versus time is shown for CCl_4 at $T = 75^\circ\text{C}$. The inset shows the collision-induced, intermolecular nuclear-coordinate response obtained from analysis of the main figure, with the ν_2 and ν_4 modes filtered out in the frequency-domain during the deconvolution procedure.

Figure 2. The frequency domain representation of the collision-induced intermolecular spectrum is shown for CCl_4 at $T = 22^\circ\text{C}$ and $T = 75^\circ\text{C}$.

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Figure 1

Figure 2

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