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Two-photon excitation spectroscopy of 1,5–Diphenyl-1,3,5-hexatriene using phase modulation

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Abstract

We have used two-photon Fourier transform spectroscopy to investigate the first singlet excited state (S_1) of a prototypical polyene molecule 1,5—Diphenyl-1,3,5-hexatriene. As the S_1 state in the polyenes is a one-photon forbidden transition, the structure of its vibrational levels cannot be studied using resonant linear excitation. Although this level is accessible with two-photon excitation, previous studies done by using wavelength tunable pulsed lasers did not have enough resolution to investigate the details of the vibrational levels. In Fourier transform spectroscopy, one uses a pair of laser beams to excite the sample. The measurements are done by varying the time delay between the pulses. The spectral resolution is given by the inverse of the maximum time delay rather than the spectral width of the pulses. We have used the method to investigate the vibrational levels of the S_1 state. In our implementation, we have used phase modulation to carry out the measurements in the rotating frame, which requires less data points along the time delay thereby significantly reducing the measurement time.

1. Introduction

Two-photon absorption (TPA) was theoretically predicted by Maria Göppert-Mayer in 1931 [1] and observed experimentally in the early 1960's [2]. Since the development of pulsed lasers, TPA has been used in a variety of photonic and biological applications such as two-photon laser scanning microscopy, [3] upconversion lasing, [4, 5] optical power limiting, [6] 3-D microfabrication, [7, 8] ultrafast pulse characterization, [9] optical data storage, [10, 11] sensors [12] and photodynamic therapy [13]. TPA has also been important in spectroscopy of atoms, molecules and larger systems. Some unique features of TPA include Doppler-free spectroscopy [14] and spectroscopy of electronic states that are not directly accessible by one photon transition [15].

Different methods have been used to measure the TP-excitation spectra. In the early days, tunable narrow band high power lasers were used [16]. This technique has been deprecated as many different types of nonlinear interactions, apart from TPA, can contribute because of the long pulse duration. It is now accepted that impulsive excitation by ultrashort pulses that are substantially shorter than a picosecond yield accurate results. However, when the ultrashort pulses are used for spectroscopy by scanning the wavelength, spectral resolution is limited by the laser bandwidth. Two-photon Fourier transform (FT) spectroscopy has been implemented to circumvent this limitation [17]. Similar methods have also been combined with IR spectroscopy to obtain detailed information about the vibrational levels in molecular systems [18, 19].

In the FT spectroscopy, one uses two broadband beams (usually ultrashort pulses), and records the response of the system as a function of time delay between the beams. The Fourier transforms of the transients give the spectra in the frequency domain. The spectral resolution is given by the inverse of the maximum time delay, which can easily be longer than the dephasing time of the system. Nevertheless, the technique is difficult to implement in the visible and ultraviolet wavelength regions mainly because it is an interferometric method that demands an extremely stable setup. The data have to be acquired at very short intervals of the time delay to