# LASER SPECTROSCOPY AND QUANTUM CHAOS: AN EXAMPLE THROUGH THE FOURIER TRANSFORM OF A STIMULATED EMISSION PUMPING SPECTRA OF C2H2 AT VERY HIGH VIBRATIONAL ENERGY

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# LASER SPECTROSCOPY AND QUANTUM CHAOS : AN EXAMPLE THROUGH THE FOURIER TRANSFORM OF A STIMULATED EMISSION PUMPING SPECTRA OF $C_2H_2$ AT VERY HIGH VIBRATIONAL ENERGY

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The spectra of polyatomic molecules at high levels of vibrational excitation are extremely complex and are technically difficult to obtain because of very small Franck Condon factors. Stimulated Emission Pumping (SEP) technique is capable to enormously simplify such spectra by restricting the number of rotational transitions and by forcing the population of an intermediate state to the ground state using high peak power lasers. SEP spectroscopy is basically a variant of Optical-Optical-Double-Resonance (OODR) spectroscopy (figure 1).

In our experiment two lasers (Pump and Dump) transfered $C_2H_2$ molecules from an initial thermally populated level via a single rovibrational level of an excited electronic state to target rovibrational levels of the ground electronic state. Large geometry modification between fundamental and excited states allows the access to very high vibrational energy (26500 $cm^{-1}$ from the ground state is about 25 quanta of vibration in the trans-bend mode of $C_2H_2$ !). In this experiment we monitored the fluorescence decrease versus the tuning of dump transitions.

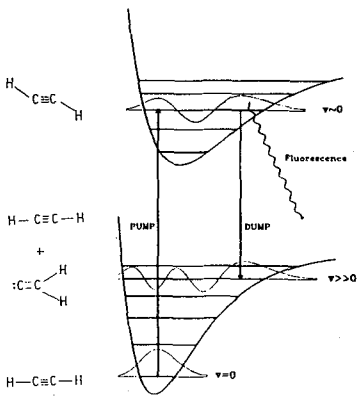


Figure 1.

The enormous interest of getting such spectra is to study "quantum chaos" in polyatomic molecules. According to one definition of quantum chaos, such spectra are intrinsically unassignable because of partial or complete loss of vibrational quantum numbers. Our goal is to show how structural and dynamical informations can be extracted directly from the Fourier Transform (FT) of such spectra. Unlike the spectrum, the FT is simple and gives very nice informations. An enormous interest of FT is to provide easily very short time resolution (few femtosecond !).

We show in this paper just an example through the FT of a low resolution (0.3 $cm^{-1}$) and very long (1400 $cm^{-1}$) SEP spectrum at 26500 $cm^{-1}$ above the ground state (figure 2). The intermediate single rovibronic state was excited with J'=1, K'=1 and two quanta of vibration in the trans-bend mode $\nu_3$. The SEP spectrum is nearly purely vibrational.

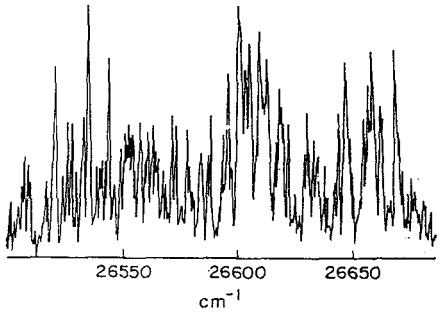


Figure 2.

The FT (figure 3) gives a time evolution with a resolution of 20 femtoseconds of an initial wave packet :

$$|\psi> = \sum_n \alpha_n(\mu) \; |n>$$

where $|n>$ are eigenstates and the expansion coefficients $\alpha_n$ are a dipole moment ($\mu$) function.

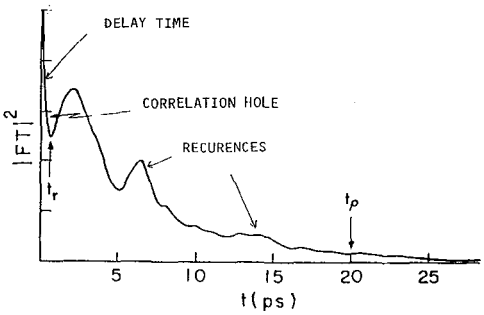


Figure 3.

A rapid discussion of this FT (for more detail see ref. 1,2,3) give mainly three important informations :

i) the initial "delay time", a pure quantum effect, is a direct measure of the non integrable part of the hamiltonian. This initial decay is exponential. A random matrix simulation shows (figure 4) that the corresponding time constant $\tau$ obey the relation :

$$\frac{1}{\tau} = 2 \, \Pi \, \rho \, <V^2>$$

where $\rho$ is the energy density and $<V^2>$ the second moment of the non integrable part of the hamiltonian. $\tau$ is the time that the initial system has to wait to see the chaos.

FT OF A RANDOM MATRIX EIGENSPECTRUM

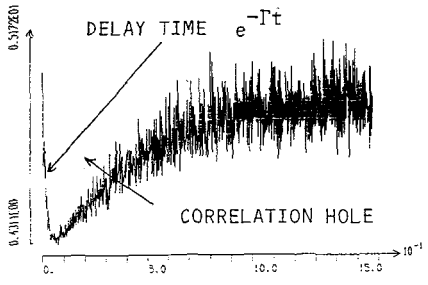


Figure 4.

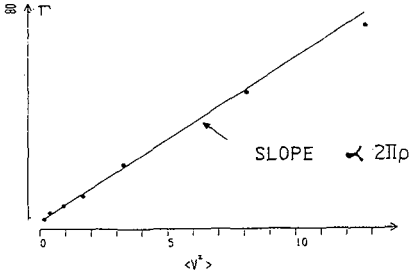


Figure 5.

ii) the correlation hole is a direct signature for quantum chaos. The rise of this hole on the long time side is related to fraction of phase space which is available.

iii) the recurrences after the correlation hole show that there is new periodic orbital which correspond to regular motion.

As we are well above the vinylidene isomer and to take into account of the large amplitude motion needed to react from acetylene to vinylidene, we propose a model with a sort of H-Rydberg molecule (figure 5) to explain these recurrences.

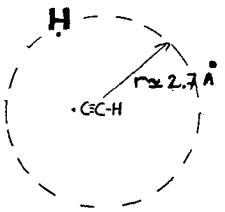


Figure 6.

To conclude, the FT is the revealer of complex spectra. Could you see these three informations directly on the spectrum ?

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