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2006 Europhys. Lett. 74 43

(http://iopscience.iop.org/0295-5075/74/1/043)

EUROPHYSICS LETTERS 1 April 2006

Europhys. Lett., **74** (1), pp. 43–48 (2006)
DOI: 10.1209/epl/i2005-10510-7

Molecular vibrational ladder climbing using a sub-nanosecond chirped laser pulse

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received 7 December 2005; accepted in final form 13 February 2006
published online 1 March 2006

PACS. 42.50.Hz – Strong-field excitation of optical transitions in quantum systems; multiphoton processes; dynamic Stark shift.
PACS. 33.80.-b – Photon interactions with molecules.
PACS. 33.80.Wz – Other multiphoton processes.

Abstract. – A comparison between the quantum ladder climbing and the classical autoresonance for robust molecular vibrational excitation from the ground state shows the disadvantage of shortening the exciting infrared laser pulse to the sub-picosecond range. Therefore, we demonstrated ladder climbing in HF molecule by a sub-nanosecond chirped laser pulse.

Introduction. – Molecular dissociation without ionization or excitation of higher molecular vibrational levels is of great importance for the initiation of certain chemical reactions. For example, vibrational excitation along the reaction coordinate might yield increased reaction efficiency [1]. Therefore, since the emergence of lasers, a long-standing goal of molecular physics has been excitation and control of molecular vibrations and dissociation by laser radiation. Direct excitation of high vibrational levels in a molecule by a monochromatic radiation is inefficient, due to the small value of the transition dipole moment between the initial and final states [2]. Another disadvantage of the direct excitation is the need of energetic photons which can excite the electronic states instead of the vibronic states. An alternative is to create a cascading transition from the initial to the final state through a series of intermediate levels by using a chirped light pulse having a continuously varying frequency. This method is usually referred to as vibrational *ladder climbing* (LC) [3]. Several authors address this approach, both classically and in quantum-mechanical terms [2–6]. In this paper we give some guide-lines for choosing the right parameters for the most efficient molecular excitation by a chirped laser pulse. Finally, we demonstrate ladder climbing in an HF molecule to its $\nu = 3$ vibrational level by a sub-nanosecond pulse.

Autoresonance vs. ladder climbing. – The autoresonance (AR) is a method to excite a *classical* oscillatory nonlinear system to high energies and control the excited state by changing the frequency of the driving perturbation. The approach uses slow passage through the linear resonance in the system leading to a persistent nonlinear self-phase-locking with the drive. The capture into the nonlinear resonance in this excitation approach is guaranteed if the driving frequency chirp rate is small enough, and yields adiabatic control of the energy of the

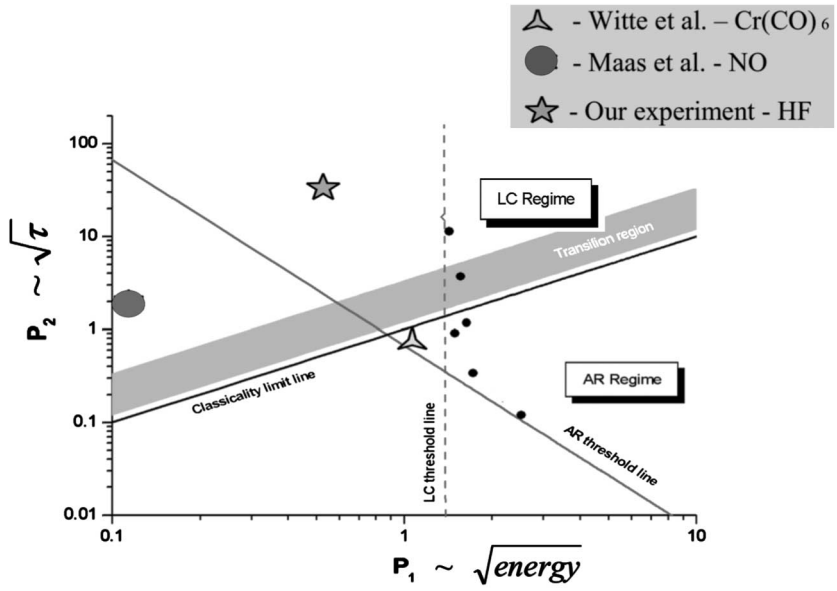

Fig. 1 – Different regimes of excitation in the P_1-P_2 parameter space. Note that if we fix the bandwidth of the radiation source, P_1 is proportional to the square root of the total pulse energy, and P_2 is proportional to the square root of the pulse duration. The black dots correspond to thresholds found in numerical simulations [13]. Also, we put two important LC experiments (see refs. [2,6]) along with our experiment on the P_1-P_2 parameter space for comparison.

driven system, as the latter self-adjusts its state for staying in resonance with the chirped frequency drive. The AR method is general and has been applied in many fields of physics, including fluid dynamics [7], plasmas [8], nonlinear waves [9], and planetary dynamics [10, 11]. It has been found that in both the AR and the LC, the amplitude of the external forcing (the laser radiation in the present application) should exceed a threshold in order to excite the system efficiently [3, 12]. Generally, the threshold is a function of the chirp rate and physical parameters of the system, such as the coupling parameter (the dipole moment) and the nonlinearity coefficient. Unlike the ladder climbing, the autoresonance is a classical phenomenon. The important question in this context is whether autoresonance is related to LC excitation of molecules. Recently, this question was addressed by comparing the theories of the two excitation schemes [13]. Three relevant time scales in the problem were discussed, *i.e.* the Rabi time $T_R = \sqrt{2m\hbar\omega_0}/\varepsilon$, the frequency sweep time $T_S = 1/\sqrt{\alpha}$, and the nonlinear time $T_{NL} = 2\omega_0\beta/\alpha$, where α is the driving frequency chirp rate and β is the nonlinearity coefficient defined by the unharmonicity of the vibrational energy, $E_n = \hbar\omega_0[(n + 0.5) - \beta(n + 0.5)^2]$.

If the Rabi frequency, $\Omega_R = 1/T_R$, is much larger than the nonlinear frequency shift, $2\omega_0\beta = T_{NL}/T_S^2$, one expects a classical behavior of the driven system. This condition in combination with the predictions of the LC and AR theories yields a set of inequalities, defining regions of efficient excitation in the quantum-mechanical (LC) and classical (AR) regimes [13]. These regions are fully characterized by two dimensionless parameters, $P_1 = T_S/T_R$ and $P_2 = T_{NL}/T_S$, as illustrated in fig. 1.

Fixing the bandwidth of the radiation source and expressing $P_{1,2}$ in terms of the total pulse energy E_t and duration τ, one finds that $P_1 \propto \sqrt{E_t}$, while $P_2 \propto \sqrt{\tau}$. One can see in fig. 1 that

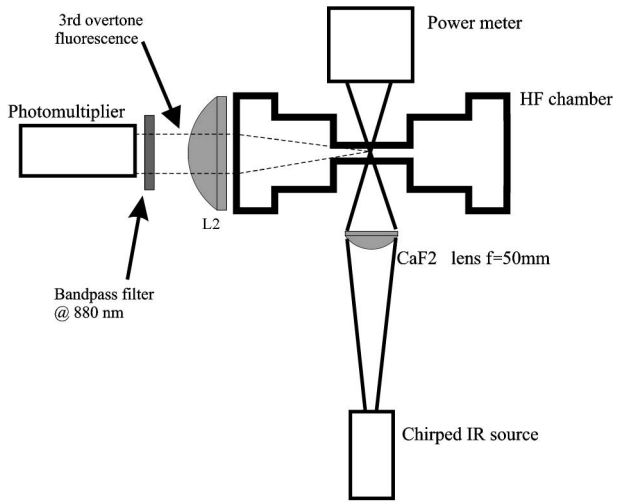

Fig. 2 – The schematic experiment setup. The width of the HF chamber at the interaction region with the IR beam is 3 mm. The distance from the center of the chamber to the collimating lens (L2) is 35 mm. A 10 nm bandpass filter at 880 nm was placed in front of the cooled photomultiplier to allow only the 2nd overtone to enter into the photomultiplier.

in the quantum-mechanical LC regime, the threshold driving amplitude is determined by the threshold energy, E_t^{th}, and is independent of pulse duration. By shortening the pulse one enters the classical AR regime, where along the threshold line, one needs larger energies as the pulse duration is getting shorter. Seeking quantum-mechanical LC excitation regime, we require $P_2 > 1$ (see fig. 1), *i.e.*, $\sqrt{\alpha} < 2\omega_0\beta$. If we set $\alpha = \Delta\omega/\tau = N(2\omega_0\beta)/\tau$ (N being the desired final level number in the LC process), we obtain $\tau > N/(2\omega_0\beta)$. For example, excitation of NaCl molecule to its tenth level ($\omega_0\beta = 1.88 \times 10^{11}$ Hz [14]), would require $\tau > 26$ ps.

Ladder climbing in HF *molecule.* – Next, we describe our experiment which demonstrates ladder climbing by a sub-nanosecond radiation source in the case of HF molecule. HF is a natural candidate to serve as a test case, because this molecule serves as a model in many applications, including the LC (see, for example, [3, 15–18]). The schematic of our experiment is shown in fig. 2. Our chirped infrared (IR) radiation source is described in detail elsewhere [19]. Here we shall present only a brief description of this source. The radiation source is an optical parametric generation/amplification (OPG-OPA) configuration pumped by an amplified stretched Ti-Sapphire laser. Our Ti-Sapphire laser parameters are: energy up to 15 mJ, repetition rate of 10 Hz, duration of 430 ps and bandwidth of 247 cm^{-1} around $\bar{\nu_0} = 12423\,\mathrm{cm}^{-1}$. A (1 mm × 2 mm × 30 mm) periodically poled KTP crystal served as the OPG while a (1 mm × 10 mm × 18 mm) periodically poled LiTaO3 crystal served as the OPA. A cylindrical telescope is focusing the Ti-Sapphire laser into the OPA in order to use the whole width of the crystal. The resulting IR parameters are: energy up to 200 μJ, bandwidth 3333 cm^{-1} to 4545 cm^{-1}, pulse duration of 186 ps and chirp rate of about $-1.23 \cdot 10^{24}\,\mathrm{s}^{-2}$. The spectral bandwidth of the IR allowed climbing the ladder of the HF molecule up to the 3rd and even to the 4th vibrational level (see fig. 4 below). The IR radiation was focused by a CaF_2 lens ($f = 50$ mm) into a chamber filled with HF (see fig. 2). The spot size of the focused beam was measured to be 60 μm × 700 μm corresponding to a maximum flounce of

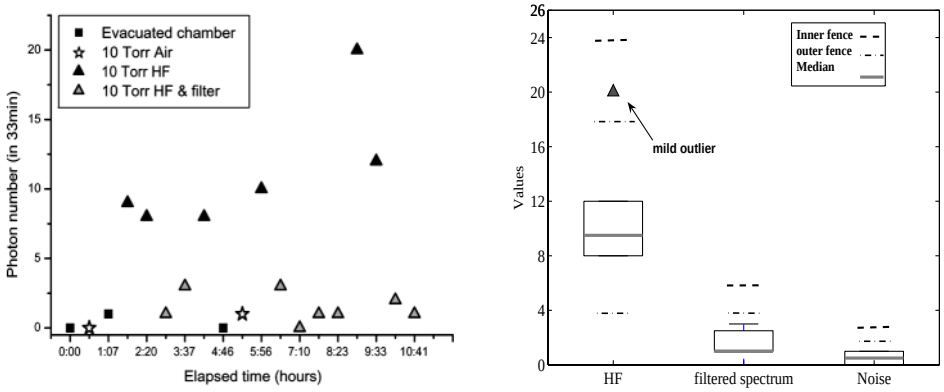

Fig. 3 – Left-hand frame: accumulated photons for four different sets of conditions. Right-hand frame: box-plot which summarizing the results from the left-hand frame. Each box is drawn between the upper quartile to the lower quartile. Median, inner fences and outer fences for each set are also drawn. From the evacuated-chamber and from the air-filled chamber we expect to get only noise signals, therefore we combined those two sets into one set to represent the noise level of our experiment. Note also that the HF-filled set has one point (20 counts) which is above the upper inner fence but below the upper outer fence. Therefore, this point is considered as a mild outlier.

$\Phi \approx 475\,\mathrm{mJ/cm^2}$. The asymmetrical spot size is due to the cylindrical optics used to pump the OPA and the asymmetry of the OPA crystal itself. The experimental procedure was as follows. Initially we evacuated the HF chamber, using a diffusion pump. Then we filled it with HF to the desired pressure. HF fluorescence at the 2nd overtone was monitored using Hamamatsu R943-02 photomultiplier, cooled to $-30\,^{\circ}\mathrm{C}$ and connected to a gated photon counter

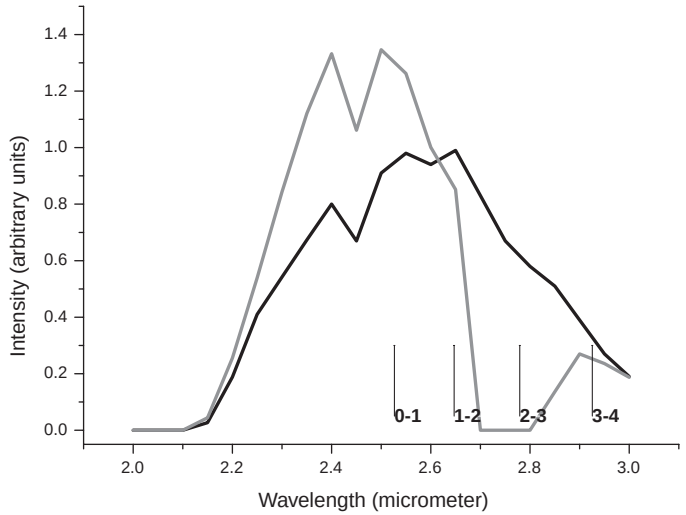

Fig. 4 – IR spectrum (black) and filtered spectrum with Suprasill window (gray). The vertical lines mark the wavelengths of different vibrational transitions.

(Stanford Research SR400). Accumulation time of about 33 min ($2 \cdot 10^4$ pulses) for a single point was required due to a very small signal. Our experimental results are summarized in fig. 3. The photon counting from HF was done at 10 Torr of HF, while three additional sets of conditions served as control sets. These control sets were: 1) a chamber filled with 10 Torr of air, 2) a continuously evacuated chamber, and 3) a chamber filled with 10 Torr of HF, but IR radiation filtered with a Suprasil window in order to cut a portion of the spectrum (see fig. 4). The total pulse energy was kept constant in all four experimental setups. From the first two control experiments (air-filled and evacuated chamber) we expect to get only noise and their goal is to set the noise level of our experiment. We also tried other pressures of HF in the ranges of 1–2 Torr and 20–30 Torr, but the best signal-to-noise ratio was achieved at about 10 Torr. In the 10 Torr of HF experiment we obtained an average count of about 11.16 photons. The evacuated and air-filled chamber control sets yielded noise level results with average count of about 0.4 photons and the experiment with the filtered spectrum yielded an average count of 1.87 photons. We used a Mann-Whitney test to test the significance of the results. We have found that the results from the HF experiment are significantly different from the results of the filtered-spectrum experiment with two-tailed P value equal to 0.0007 and the results from the filtered-spectrum experiment are significantly different from the noise level with two-tailed P value equal to 0.045; hence, the filtered-spectrum control set yielded small but above noise level results. We conjecture that the exothermic process $\mathrm{HF}(\nu = 2)+\mathrm{HF}(\nu = 1)\rightarrow \mathrm{HF}(\nu = 3)+\mathrm{HF}(\nu = 0)$ accounts for the presence of $\mathrm{HF}(\nu = 3)$, even though the spectral bandwidth of the IR radiation is not wide enough to excite the third level. The lack of a reliable energy transfer rate constant in this process, prevented us from quantifying this possibility.

Summary. – In summary, we have discussed similarities and differences between the quantum-mechanical ladder-climbing (LC) and the classical autoresonance (AR) [13]. We have shown that by shortening the laser pulse, one enters the classical AR regime. As a result, one must follow the AR threshold line in order to efficiently excite molecules in this case. Consequently, a larger pulse energy is required as the pulse duration gets shorter. Therefore, seeking quantum-mechanical LC conditions, one has to balance between the need of shortening the pulse for overcoming relaxation processes and the need of having laser pulse long enough for staying in the LC regime.

We also have demonstrated, experimentally, ladder climbing in a simple HF molecule, using stretched sub-nanosecond mid-infrared optical pulses. We have shown that the LC process yields excitation of vibrational states as high as $\nu = 3$ in our experiments. These levels were significantly populated using chirped laser pulse of proper intensity. Further development of sources having broad infrared spectra combined with this approach might lead to capability for exciting large molecules to the transition state, with the molecule remaining in its electronic ground state during the entire excitation process.

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