Investigation of the limits of the secular and Markov approximations in the dissipative dynamics of laser-aligned molecules

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Abstract. We point out the breakdown of two approximations widely used to describe decoherence in open quantum systems, the secular and Markov approximations. We probe their limits by studying the influence of pressure on the alignment revivals (echoes) created in properly chosen gas mixtures (HCl and CO2, pure and diluted in He) by one (two) intense and short laser pulse(s). Experiments, as well as predictions using molecular dynamics simulations, consistently demonstrate in some of the aforementioned systems the break-down of these approximations at very short times (< 15 ps) after the laser kick(s).

1 Introduction

Studying molecular alignment at very short times enables to investigate the influence of some mechanisms that affect the dissipation of an open system [1]. Here we experimentally and theoretically study the limits of the two widely used secular and Markov approximations. The first one neglects all the exchanges between the quantum coherences that oscillate at different frequencies [2]. The second one considers that all collisions are complete in the time interval of observation, meaning that the behavior of the system can be modeled as a Markov chain of instantaneous and independent events, thus disregarding any memory effect. To test the limits of both approximations, we study the influence of pressure on the decay of the molecular alignment soon after the excitation by a femtosecond laser pulse. Four systems listed in Table 1 have been chosen, involving all the situations at the investigated time scale: Practically secular and Markovian (HCl diluted in Helium) or non-Markovian (pure HCl), nonsecular and Markovian (CO2 diluted in Helium) or non-Markovian (pure CO2) [3]. We show that, depending the studied system, those approximations lead to important errors on the predicted relaxation at short times, before becoming valid after tens of picoseconds.

2 Experimental setup

The experimental study of the aforementioned systems is performed through two different configurations of the pump-probe setup depicted in Fig. 1. To probe the short-time collisional relaxation of CO2 (pure and diluted in Helium) gas samples, it is necessary, due to the long rotational period (43 ps) of CO2, to use a two-pulses excitation leading to the formation of rotational echoes [4], whereas for HCl, the rotational period (1.5 ps) is short enough to allow the use of a single-pulse excitation scheme. The laser beam is produced by a chirped-pulse amplified Ti:Sapphire laser delivering nonresonant pulses centered at 800 nm, of 100 fs duration (FWHM), and operating at 1 kHz repetition rate. A beam splitter is placed at the output of the laser to produce a probe beam, vertically polarized, and a pump beam, polarized at 45° with respect to the probe beam. The latter is frequency doubled in a BBO crystal enabling a filtering out of the 800 nm light scattered by the cell on the detectors. The 800 and 400 nm pulses are temporally delayed using a motorized stage equipped with a corner cube reflector. In the case of the two excitation pulses setup, in order to create rotational echoes, a second beam splitter is added to the path of the pump P1 to create a second pump beam P2 with the same polarization and same direction of propagation as P1, and with an adjustable time delay \( \tau_{12} \) monitored by a second motorized stage placed on the P1 path. The two pump beams are then focused, using a plano-convex lens, on a high-pressure static cell filled with the gas sample. The optical anisotropy following the alignment of the molecules...
along the electric field of the pump(s) was measured by a probe pulse with a balanced detection providing a signal proportional to the alignment factor \( \langle \cos^2 \theta - 1/3 \rangle(t) \) where \( \theta \) is the angle between the molecular axis and the direction of the (linear) polarization of the pump pulse(s).

### 3 Results

The results of the measured density-normalized decay time constants of the alignment features (echoes or revivals), together with the predictions of requantized classical molecular dynamics (rCMDS) simulations, are reported in Fig. 2 for the studied systems. We observe that the secular assumption leads to inaccurate results at short times for both pure CO\(_2\) and CO\(_2\)-He, before they reach a secular behavior after tens of picoseconds. On the other hand, pure CO\(_2\) presents a non-Markovian behavior at short times. If nonsecular effects slow down the collisional relaxation of the systems, non-Markovian effects have the opposite impact, and we clearly see a compensation between these two effects in pure CO\(_2\). In the case of HCl, we always observe a quasi secular behavior, but pure HCl presents a non-Markovian behavior. Both secular and Markovian approximations become then valid for all the studied systems after tens of picoseconds. Recently, we published a Markovian quantum model to calculate nonsecular effects, leading to good agreements with the experimental data presented here for the Markovian systems CO\(_2\)-He and HCl-He[5].

### 4 Conclusion

We demonstrated, by probing the collisional relaxation of aligned molecules at short times (<15 ps), the breakdown of the secular and Markov approximations. The present method allows a direct observation of nonsecular and non-Markovian behaviors, which is not the case with previous frequency domain studies. Although the present work is limited to linear molecules, we believe that the approach reported in this work can be extended to reveal nonsecular and non-Markovian dynamics in more complex molecules.

### References