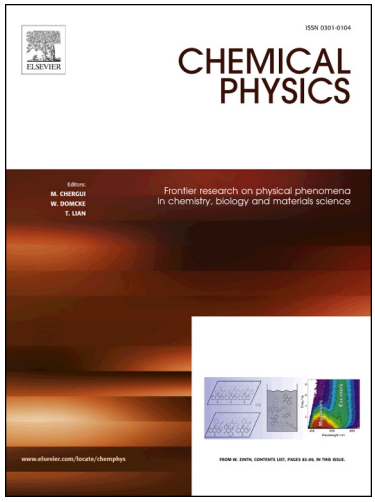

Two-dimensional photon-echo spectroscopy at a conical intersection: a two-mode pyrazine model with dissipation

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Two-dimensional photon-echo spectroscopy at a conical intersection : a two-mode pyrazine model with dissipation

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The multi-dimensional electronic spectroscopy of ultrafast nuclear dynamics at conical intersections (CI) is an emerging field of investigation, which profits also from the recent extension of the techniques to the UV domain. We present a detailed computational study of oscillatory signatures in two-dimensional (2D) photon-echo spectroscopy (also known as 2D electronic spectroscopy, 2DES) for the two-mode pyrazine model with dissipation. Conventional 2D signals as well as the resulting beating maps are considered. Although of a reduced character, the model captures quite well all the main signatures of the excited-state dynamics of the molecule. Due to the ultrafast relaxation via the CI and no excited-state absorption from the low-lying dark state, the oscillatory components of the signal are found to be predominantly determined by the ground state bleach contribution. They reflect, therefore, the ground-state vibrational coherence induced in the Raman active mode. Beating maps provide a way to experimentally differentiate between ground state bleach and stimulated emission oscillatory components. The ultrafast decay of the latter constitutes a clear indirect signature of the CI. In the considered model, because of the sign properties of the involved transition dipole moments, the dominance of the ground-state coherence leads to anti-correlated oscillations of cross peaks located at symmetric positions with respect to the main diagonal.

I. INTRODUCTION

Understanding the dynamics of molecular systems triggered by the absorption of light is a major goal of modern physical chemistry. Tremendous progress has been made in this field since the advent of time-resolved spectroscopy, allowing one to monitor the dynamics of photoexcited molecular systems in real time [1]. It is well established that conical intersections (CIs) play a central role in a large number of systems [2, 3]. CIs, when energetically accessible after photoexcitation, are at the origin of radiationless transition between different electronic states occurring on a femtosecond time scale. Time-resolved fluorescence and pump-probe techniques (such as time-resolved photoelectron or transient absorption spectroscopy) can probe the decay of electronic state populations caused by the presence of CIs [4, 5]. More recently, experiments devoted to the detection of coherent motion in systems exhibiting CIs have been reported, providing information about the structural distortion accompanying the electronic radiationless transition and showing that the induced coherence can survive long after the system has crossed the CI [6–11].

In this context, the so-called two-dimensional electronic spectroscopy (2DES) techniques [12, 13] have gained an increasing popularity. This technique has been widely used to probe the coherent energy and charge transfer dynamics in light-harvesting biological complexes [14–18] as well as organic and nanostructured materials [19–24]. In addition, with the recent development of 2DES in the UV domain [25–27], applications to simpler organic molecules, the dynamics of which is known to be often strongly affected by the presence of CIs, have begun to appear [28–30], opening new possibilities in the investigation of the signatures of CIs in 2DES.

These experimental developments have motivated a number of theoretical investigations of the 2DES of model systems exhibiting CIs. Engel *et al.* studied the 2DES of a one-dimensional model including several vibronically coupled electronic states [31] and pointed out the impossibility of distinguishing between vibrational and electronic coherences in the case of strong vibronic coupling. Jonas *et al.* studied the 2DES of a Jahn-Teller system [32] and found evidence of a loss of electronic coherence on a femtosecond time scale, associated with the passage of the system through the CI. Krčmář *et al.* studied the 2DES of well established two- and three-mode CI models of pyrazine [33, 34] and found that the structure of the spectra at fixed population time reflects the high density of irregularly spaced vibronic states which is a characteristic of CIs. Their study also revealed that the evolution of the spectra with the waiting time predominantly reflects the dynamics of the wavepacket in the ground electronic state. Duan and Thorwart investigated the 2DES of a generic two-state two-mode CI model in the presence of strong vibrational damping and found negative cross peaks arising from secondary excitation of the wavepacket after passing through the CI [35].

In this work, we reconsider the two-mode model of pyrazine [36, 37] and extend the computational study of its 2DES of ref. [33]. Over the years, pyrazine has become a benchmark system for the study of various aspects of the dynamics of molecular systems at CIs. Models of increasing dimensionality have been constructed and used as test cases in computational investigations of the femtosecond time-resolved spectroscopy [38–41] or the strong field control [42–47] of the excited state dynamics at CIs. Our study extends the previous work of Krčmář *et al.* [33] in several ways. First, we incorporate the effects of a weak dissipative environment in our calculations through the use of the multi-level Redfield theory. The dissipative dynamics of the few-mode pyrazine models has been studied in Refs. [48, 49]. Here we adopt the two-mode model, but do not invoke the secular approximation to the Redfield theory as is the case in ref. [48], and we study the effect