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Femtochemistry in the electronic ground state: Dynamic Stark control of vibrational dynamics

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Abstract

We study the interplay of vibrational and rotational excitation in a diatomic molecule due to the non-resonant dynamic Stark effect. With a fixed peak intensity, optimal Gaussian pulse durations for maximizing vibrational or rotational transitions are obtained analytically and confirmed numerically for the H_2 and Cl_2 molecules. In general, pulse trains or more advanced pulse shaping techniques are required in order to obtain significant vibrational excitation. To that end, we demonstrate that a high degree of selectivity between vibrational and rotational excitation is possible with a suitably phase-modulated Gaussian pulse.

Keywords: Vibrational excitation, Dynamic Stark Effect, Pulse shaping

1. Introduction

The majority of the pioneering femtochemistry studies by Ahmed Zewail and coworkers have been conducted for electronically excited states of molecules [1, 2, 3]. In general, excited electronic states set the stage for photochemistry, whereas the electronic ground state is associated with the large class of thermally activated chemical reactions. Far fewer studies of femtosecond dynamics have addressed molecules in the electronic ground state (see, e.g. [4, 5, 6] and references therein) where, in general, it is more difficult to induce significant structural change via laser excitation.

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