

Field optimized initial state based control of photodissociation

K VANDANA, DEEPA B BAIRAGI, PETER GROSS*[†] and MANOJ K MISHRA

Department of Chemistry, Indian Institute of Technology, Powai, Mumbai 400 076, India

*Tata Institute of Fundamental Research, Homi Bhabha Road, Mumbai 400 005, India

[†] Present address: Chemistry Department, Michigan State University, USA

Abstract. A new scheme for controlling photodissociation through preparation of a variationally optimized linear superposition of field free vibrational eigenstates is applied for selective control of IBr and HI dissociation. The dependence of photodissociation on various field parameters and initial conditions is examined to investigate the mechanistic basis of selective control. The parametric equations of motion approach for determining vibrational dynamics as a function of field parameters without having to solve the time dependent Schrödinger equation explicitly for each field parameter separately is outlined and its use to identify field characteristics which will provide the requisite population mix represented by the optimal linear superposition of vibrational states is advocated.

Keywords. Photodynamics; selective control; optimal initial state; time dependent Schrödinger equation.

PACS No. 31.10

1. Introduction

The easy availability of ultrafast high intensity lasers has fueled the dream of their use as molecular scissors to cleave selected bonds [1, 2]. Theoretical approaches to laser assisted selective control of chemical reactions have kept pace and demonstrated remarkable success [3, 4] and some experimental results [5, 6] buttress these theoretical claims. The different established theoretical approaches to control have been reviewed recently [7]. Some of these approaches, based on field induced control have been perturbative [8] and hence of somewhat limited utility or have provided fields with undesirable attributes like very high intensity and require computationally demanding procedures for their specification [4]. While the focus of these theoretical approaches has been on field design, the photodissociation yield has also been found to be extremely dependent on the choice of initial vibrational state from which photolysis is induced and results for HI [9, 10], HCl [5] and HOD [6] reveal a crucial role for the initial condition of the system in product selectivity and enhancement.

This critical dependence on initial vibrational state indicates that a suitably optimized linear superposition of the initial vibrational levels may be another route to selective control of photodissociation. In any case, since in the field design based control, high intensity is undesirable, phase dependence has been found to be weak [11] and considerable success has been demonstrated using a single carrier frequency, it seems desirable