

A theoretical analysis of the nonadiabatic photodissociation of HF and DF molecules: fine-structure distributions of the $F(^2P_J)$ product

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Received 25 January 2010; Accepted (in revised version) 8 February 2010;

Available online 15 February 2010

Abstract. A theoretical analysis is presented for the nonadiabatic photodissociation process of hydrogen fluoride and its deuterated species. Four electronic states $X^1\Sigma^+$, $a^3\Pi$, $A^1\Pi$, and $^3\Sigma^+$ are involved in the studies. Based on the accurate *ab initio* calculations of the potential energy curves, transition dipole moment and spin-orbit couplings among the accessible states, the time dependent quantum wave packet approach with the split-operator scheme is employed to investigate the dissociative dynamics. The dissociative process is analyzed via the evolution of the wave packets. The total cross sections, partial cross sections and branching fractions for both HF and DF initially excited from the vibrational levels $v=0-3$ of the ground state are evaluated. The calculations are compared with the previous investigations and the present prediction for a broad range of the incident photon energies.

PACS: 33.80.Gj

Key words: photodissociation, nonadiabatic interactions, quantum dynamics, time dependent wave packet, split-operator, cross section, branching fraction

1 Introduction

Photodissociation involving multiple dissociative pathways via the nonadiabatic interactions is one of the most interesting phenomena in the interactions between photons and molecules (or radicals) [1–8]. The closed-shell hydrogen halide (HX, X=F, Cl, Br, I) and its deuterated counterpart, provides the typical and simple model to investigate the dynamics of nonadiabatic dissociation

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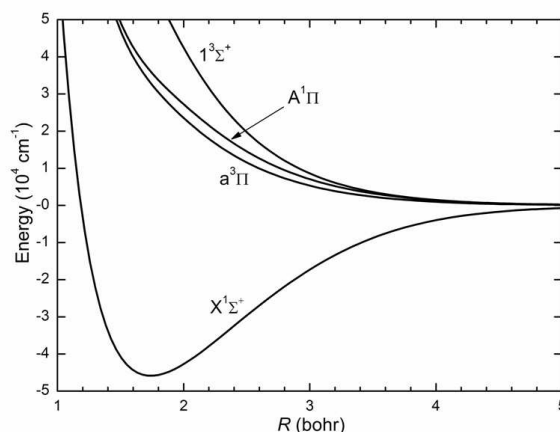
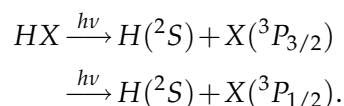


Figure 1: Diabatic potential energy curves for the $X^1\Sigma^+$, $a^3\Pi$, $A^1\Pi$, and $^3\Sigma^+$ states as a function of the internuclear separation obtained from the ab initio calculation. The lower panel displays in more detail the long range feature of the curves.



Four electronic states ($X^1\Sigma^+$, $a^3\Pi$, $A^1\Pi$, and $^3\Sigma^+$) are involved in the hydrogen halide photodissociation process (see, Fig. 1 for HF case), where ground state $X^1\Sigma^+$ is the only bound one and the repulsive states $a^3\Pi$, $A^1\Pi$, and $^3\Sigma^+$ induce the fragmentation. Neglecting the spin-orbit coupling, all of the four states correlate with the lowest energy asymptote $H(^2S)+X(^2P)$. However, considering the nonadiabatic couplings among the dissociative channels either of the spin-orbit states, $X(^2P_{3/2})$ and $X(^2P_{1/2})$, can be yielded, where $X(^2P_{3/2})$ and $X(^2P_{1/2})$ are ground and excited atomic spin-orbit states of the halogen fragment, respectively. Two sub-processes are included in the photodissociation process [9]: (i) initial excitation from the particular vibrational level of the ground electronic state to one (or more) of the repulsive states, and (ii) redistribution of the photodissociation flux via the nonadiabatic transitions between the accessible states. Most ground state of the closed-shell molecules are described by $\Omega' = 0$ (Ω , the projection of the electronic angular momentum along the molecular axis, can be used to classify the electronic states of diatomic molecules.); single-photon excitation can promote the molecule to excited states with $\Omega = 0$ and $\Omega = 1$ through parallel ($\Delta\Omega = 0$) and perpendicular ($\Delta\Omega = \pm 1$) excitations, respectively [10]. For the lighter halogen atom, i.e., F or Cl, the spin-orbit constant is small, the single electronic surface, i.e., $A^1\Pi$, is often reached through the initial excitation [9, 11–15]. However, for the other heavier halogen atoms, Br, and I, since the spin-orbit constant is large, the excitation process is more complicated, where the spin-forbidden excitation can occur [9, 11]. The redistribution of dissociation flux among