



Probing bound-state molecular dynamics via resonance-enhanced photodissociation phenomena

Thesis for the Degree of Doctor of Philosophy (PhD)

Dilfuza Umarova

Supervisor: Dr. András Csehi

UNIVERSITY OF DEBRECEN

Doctoral Council for Natural Sciences and Engineering

Doctoral School of Physics

Debrecen, 2026.

Hereby I declare that I prepared this thesis within the Doctoral Council for Natural Sciences and Engineering, Doctoral School of Physics, University of Debrecen, in order to obtain a PhD Degree in Natural Sciences at Debrecen University.

The results published in the thesis are not reported in any other PhD theses.

Debrecen, 2026.....

Dilfuza Umarova
Candidate

Hereby, I confirm that Dilfuza Umarova candidate conducted her studies with my supervision within the Atomic and Molecular Physics Doctoral Program of the Doctoral School of Physics between 2023 and 2026. The independent studies and research work of the candidate significantly contributed to the results published in the thesis.

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I support the acceptance of the thesis.

Debrecen, 2026.....

Dr. András Csehi
Supervisor

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Dissertation supervisor: Dr. András Csehi

The official opponents of the dissertation:

Dr.
Dr.

The evaluation board:

Chairperson: Dr.
Members: Dr.
Dr.
Dr.
Dr.
Dr.

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The glossary list

AT Autler–Townes

BO Born-Oppenheimer

CAP complex absorbing potential

CI conical intersection

DI dynamic interference

DOF degree of freedom

DSS dynamic Stark shift

DVR discrete variable representation

EM electromagnetic

FC Franck-Condon

FFT fast fourier transformation

LICI light-induced conical intersection

MCTDH multi-configuration time-dependent Hartree

PDM permanent dipole moment

PES potential energy surface

REMPI resonance-enhanced multiphoton ionization

RO Rabi Oscillation

SPF single-particle function

TDH time-dependent Hartree

TDM transition dipole moment

TDSCF time-dependent self-consistent field

TDSE time-dependent Schrödinger equation

TI time-independent

TISE time-independent Schrödinger equation

WF wave function

Introduction

This dissertation compiles the outcomes acquired during my PhD studies at the Doctoral School of Physics of the University of Debrecen from 2023 to 2026.

In my research, I investigated the dynamical processes and their quantum probing and control in diatomic molecules using numerical and analytical calculations. In quantum mechanics, electronic and nuclear motions can be defined by the Schrödinger equation for electrons and nuclei. While solving the time-dependent Schrödinger equation (TDSE) for molecular systems, the Born-Oppenheimer (BO) approximation [1, 2, 3] is commonly used. In this approximation, the electronic and nuclear motions in a molecule can be treated separately: the heavy nuclei move slowly and are almost fixed, while the light electrons move quickly within the potential field created by the stationary nuclei. In this picture, nuclear motion is assumed to move on a single potential energy surface generated by the fast-moving electrons. Although the BO approximation usually works well and provides reasonable results in molecular dynamical processes, it breaks down in certain situations [4, 5, 6]. It fails at what time the electronic states energetically become close or when there are strong non-adiabatic couplings [7, 8, 9], where the nuclear and electronic motions are firmly coupled between various electronic states. The cases in which the BO approximation becomes invalid are called non-adiabatic processes. In the presence of non-adiabatic processes, the potential energy surfaces of molecular systems could intersect with each other, giving rise to a conical intersection (CI) [10, 11]. CIs formed between electronic potential energy surfaces (PESs) play a crucial role in molecular dynamics, as the energy exchange between electrons and nuclei can become significant. Because the diatomic molecules provide only the vibrational degree of freedom (DOF), only avoided crossings (approaching states to each other) can be formed according to the non-crossing rule [3] (CIs never build up in the case of one DOF). When an external laser field is applied to a molecule, it can rotate the system with an angle between the direction of the transition dipole moment of the molecule and the polarization direction of the external field, providing a second DOF, which causes the formation of a light-induced conical intersections (LICIs) [12, 13, 14], even in diatomic molecules.

The study of molecules using various lasers has become a cornerstone of modern scientific research, providing insight into their complex properties and behaviors at the most fundamental level. The light-matter interaction between a target molecule and an applied field has been investigated using infrared [15, 16], VUV/XUV [17, 18], and X-ray lasers [19, 20, 21] in order to explore molecular dynamics. The development of laser technology has revolutionized numerous fields, including chemistry, physics, biology, and materials science. Lasers allow researchers to conduct precise, targeted investigations of molecules.

The intensity, wavelength, and polarization of the laser pulse can be finely tuned, allowing selective excitation of vibronic transitions (between electronic and vibrational states) within molecules, opening the way to study their structure and dynamics in great detail. The main goal of these approaches is to design laser pulses that can bring the investigated system into the desired electronic, vibrational, and rotational state. In this way, quantum control emerges to govern various processes in molecular systems.

When a molecule interacts with a strong, coherent light field, it can exchange energy with the field periodically. In a simple two-level quantum system, this process leads to oscillations in population between the coupled states, known as Rabi oscillations or Rabi floppings [22, 23]. These oscillations are a fundamental feature of intense light-matter interactions and play an essential role in several areas of physics, such as electron microscopy [24], resonance fluorescence [25, 26, 27], and quantum computing [28, 29]. When a resonant laser pulse is applied to such a system, the two energy levels combine to form dressed states whose energies vary with time. The Rabi frequency and the AC Stark shift of the involved levels determine the energy separation of these dressed states. If another photon interacts with the system, the Rabi oscillations become damped, and this damping appears in the spectrum as the Autler-Townes (AT) doublet [23, 30]. The AT doublet is often asymmetric [31, 32], and many factors can contribute to this imbalance. Possible causes include the energy dependence of the bound-to-continuum transition dipoles [31], interference between different quantum pathways [32, 33], AC Stark shifts of the coupled levels [34, 35, 36], and the specific shape of the laser pulse envelope [35]. The Autler-Townes effect, also known as the resonant Stark effect, occurs when an oscillating electric field, such as a laser pulse, is tuned to a transition frequency. This interaction modifies the spectral line associated with that transition, leading to its characteristic splitting or distortion.

Dynamic interference is a time-domain interference phenomenon that occurs when particles (electrons or molecular fragments) are emitted with the same final energy at different times (with a certain time delay) during the rising and falling edges of a short laser pulse [37]. The corresponding quantum amplitudes interfere, producing multi-peak structures in energy spectra. Dynamic interference has been widely investigated in the context of atomic ionization [38, 39, 40, 41], both for direct one-photon ionization at high

photon energies and for resonance-enhanced multiphoton ionization (REMPI) [42]. In these systems, it was shown that dynamic interference (DI) becomes prominent when two conditions are fulfilled: (1) the field-induced Stark shift or Rabi splitting of the relevant levels is larger than the bandwidth of the pulse, so that different emission times correspond to distinguishable phases; and (2) the initial state’s depletion remains small, so that emission occurs on both the rising and falling edges. Under these conditions, the temporal double slit produces pronounced oscillations in the photoelectron spectrum.

These two fundamental manifestations of quantum coherence in intense laser fields—Rabi Oscillations (ROs) and DI—have been widely studied in atomic systems [37, 39, 40, 41, 22, 23]. We investigate these phenomena in the MgH^+ molecule. DI emerges in the resonance-enhanced photodissociation of MgH^+ . Depending on the laser wavelength and detuning, the multi-peak fragment spectra reflect either interference between amplitudes emitted at different Rabi cycles (resonant regime) or dynamic interference between rising- and falling-edge emissions (off-resonant regime), providing a sensitive probe of ultrafast vibronic dynamics.

In my research, I investigated probing bound-state molecular dynamics using resonance-enhanced photodissociation. I studied the dissociation of the molecular ion MgH^+ [43, 44, 45, 46], which is quite appropriate for inspecting (1+1) photon resonance-enhanced multiphoton breakup phenomena due to the fact that the energy difference between the ground and intermediate states is nearly equal to the energy discrepancy between the intermediate and dissociative states of the MgH^+ molecule. The present Thesis is built on two very closely related works.

In my first study, we demonstrate that when the laser is resonant with a specific vibronic transition, narrowband pulses generate clear vibronic ROs between these two levels. We develop a model that explains general characteristics, such as peak splittings, shifting, asymmetry, and the multi-peak fragment spectrum arising from the coherent superposition of fragment amplitudes emitted at successive Rabi cycles. In this model, each Rabi cycle acts as a temporal source, and their interference produces the multipeak structure, splitting, shifting, and asymmetry. And the results obtained by the developed model are confirmed by comparison with accurate multi-configuration time-dependent Hartree (MCTDH) [47, 48, 49] simulations of the full nuclear dynamics. This provides spectral evidence for vibronic Rabi oscillations and shows that the number of Rabi cycles and the details of the bound-state dynamics can be read directly from the fragment energy spectra in a molecular system.

In my second study, we extend this investigation to the broader wavelength dependence by tuning the photon energy $\lambda \sim 200\text{--}310\text{ nm}$ across the intermediate state region. One can selectively address specific vibrational levels of the intermediate electronic state. This re-

veals that detuning from exact resonance fundamentally changes the physical origin of the multi-peak patterns. When the laser is off-resonant (photon energy below or between vibrational levels), pronounced Rabi oscillations are washed out, yet the fragment spectrum still exhibits strong multi-peak modulations. Using asymmetric pulse envelopes—which suppress the contribution from the falling edge while keeping the pulse area constant—we demonstrate that, in this off-resonant regime, the spectral modulations are mainly due to dynamic interference between fragment amplitudes emitted on the rising and falling edges of the pulse. Moreover, we show that the strong energy dependence of the bound-to-continuum dipole couplings from the intermediate state to the dissociative state provides an additional, sensitive control mechanism for the dissociation yield and spectrum shape, making wavelength tuning a powerful tool for both probing and controlling the dissociation dynamics. We also studied the influence of the permanent dipole moments of the MgH^+ molecule on the dissociation dynamics occurred in the resonant and off-resonant transitions.

This dissertation is structured as follows: Chapter 1 provides the theoretical description of molecules, including the TDSE, the BO approximation and its limitations, the description of diatomic molecules, light–matter coupling (including Rabi oscillation, Stark shift, and dynamical interference), and nuclear dynamics. In Chapter 2, the spectral evidence of Rabi oscillations between two vibrational levels corresponding to two various electronic states is detailed. This Chapter includes results obtained by analytically calculating and numerically solving the TDSE for the nuclei of the MgH^+ molecule. In Chapter 3, the frequency dependence of photodissociation is discussed in the presence of a classical laser field. In this Chapter, rich nuclear dynamics, containing Rabi cycles and dynamic interference, are discussed. The signatures of these dynamical effects are revealed in the emitted fragments’ energy spectrum of the molecule. In Chapter 4, a brief summary of the results will be given. The acknowledgments and publication list will be presented at the end.

Chapter 1

Theoretical background

This Chapter summarizes the most critical elements of the theory that are relevant to my research field and results obtained. The theoretical treatment of the molecular system is explained from both the electronic structure and nuclear dynamics perspectives. The molecular dynamics will be treated within the framework of the Born-Oppenheimer approximation, which is a fundamental concept in quantum chemistry that simplifies molecular calculations by separating the fast-moving electrons from the slow-moving, much heavier atomic nuclei. This adiabatic approximation is used to solve the Schrödinger equation in two distinct steps: first, the nuclei are treated as stationary, allowing for the calculation of molecular electronic structures by determining potential energy surfaces and permanent dipole moments (PDMs) of individual electronic states, and transition dipole moments (TDMs) between different electronic states induced by the laser field. Usually, these data can be obtained from one of the efficient quantum packages, Molpro [50, 51]. In my research, these data were taken from the paper published [44]. Then, the resulting potential energy surfaces are used to investigate the motion of the nuclei, which will be discussed in detail in section 1.1. Section 1.2 describes the diatomic molecules and, while section 1.3 provides a brief description of the light-matter coupling, including subsections on Rabi oscillation, the Stark effect, and dynamical interference. Finally, section 1.4 explains the nuclear dynamics of the molecule using the MCTDH method and our developed multi-level method.

1.1 The Born-Oppenheimer approximation

Consider a molecular system consisting of n_{el} electrons and n_{nuc} nuclei. Let us denote the mass of the electrons and the mass of the nuclei m_{el} and M_{α} , respectively. The charge of the electrons is denoted by $-e$, while the charge of the nucleus with label α is denoted

by $Z_\alpha e$, where Z_α is the atomic number. Let the position of the i th electron be denoted by $\vec{r}_i = \{\vec{r}_i, \quad i = 1, 2, \dots, n_{el}\}$, and the position of the α th nucleus by $\vec{R} = \{\vec{R}_\alpha, \quad i = 1, 2, \dots, n_{nuc}\}$, respectively, in the molecular system. The total Hamiltonian of the system comprises the kinetic energy operator of electrons ($\hat{T}_{el}$), the kinetic energy operator of nuclei ($\hat{T}_{nuc}$), the electron-electron potential energy ($V_{el,el}$), the nuclear-nuclear potential energy ($V_{nuc,nuc}$), and the electron-nuclear potential energy ($V_{el,nuc}$).

The kinetic energy operator of the nuclei can be written as [52]

$$\hat{T}_{nuc} = - \sum_{\alpha=1}^{n_{nuc}} \frac{\hbar^2}{2M_\alpha} \nabla_{R_\alpha}^2 \quad (1.1.1)$$

The kinetic energy operator of the electrons can be described as

$$\hat{T}_{el} = - \sum_{i=1}^{n_{el}} \frac{\hbar^2}{2m_{el}} \nabla_{r_i}^2 \quad (1.1.2)$$

Electron-electron potential energy can be written in the form

$$V_{el,el} = \sum_{i=1}^{n_{el}} \sum_{\substack{j=1 \\ j>i}}^{n_{el}} \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \quad (1.1.3)$$

Nuclear-nuclear potential energy can be written as

$$V_{nuc,nuc} = \sum_{\alpha=1}^{n_{nuc}} \sum_{\substack{\beta=1 \\ \beta>\alpha}}^{n_{nuc}} \frac{1}{4\pi\epsilon_0} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|} \quad (1.1.4)$$

Electron-nuclear potential energy can be described as

$$V_{el,nuc} = - \sum_{\alpha=1}^{n_{nuc}} \sum_{i=1}^{n_{el}} \frac{1}{4\pi\epsilon_0} \frac{Z_\alpha e^2}{|\vec{R}_\alpha - \vec{r}_i|} \quad (1.1.5)$$

The total Hamiltonian of the system takes the form

$$\begin{aligned}
\hat{H} &= \hat{T}_{nuc}(\vec{R}) + \hat{H}_{el} \\
&= \hat{T}_{nuc}(\vec{R}) + \hat{T}_{el}(\vec{r}) + V_{el,el}(\vec{r}) + V_{nuc,nuc}(\vec{R}) + V_{el,nuc}(\vec{r}, \vec{R}) \\
&= -\sum_{\alpha=1}^{n_{nuc}} \frac{\hbar^2}{2M_{\alpha}} \nabla_{\vec{R}_{\alpha}}^2 - \sum_{i=1}^{n_{el}} \frac{\hbar^2}{2m_{el}} \nabla_{\vec{r}_i}^2 + \sum_{i=1}^{n_{el}} \sum_{\substack{j=1 \\ j>i}}^{n_{el}} \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \\
&\quad + \sum_{\alpha=1}^{n_{nuc}} \sum_{\substack{\beta=1 \\ \beta>\alpha}}^{n_{nuc}} \frac{1}{4\pi\epsilon_0} \frac{Z_{\alpha}Z_{\beta}e^2}{|\vec{R}_{\alpha} - \vec{R}_{\beta}|} - \sum_{\alpha=1}^{n_{nuc}} \sum_{i=1}^{n_{el}} \frac{1}{4\pi\epsilon_0} \frac{Z_{\alpha}e^2}{|\vec{R}_{\alpha} - \vec{r}_i|}.
\end{aligned} \tag{1.1.6}$$

Here, $\hat{H}_{el}(\vec{r}, \vec{R})$ is the electronic Hamiltonian describing electron structure calculations. $\nabla_{\vec{r}_i}^2$ and $\nabla_{\vec{R}_{\alpha}}^2$ are the second-order derivatives with respect to these coordinates $\vec{r}_i$ and $\vec{R}_{\alpha}$, respectively. $\hbar$ and ϵ_0 are the constants of the reduced Planck and the vacuum permittivity. $Z_{\alpha}e$ is a charge of the α th nuclei. Because the masses of the nuclei (M_{α}) are 3-4 orders of magnitude larger than the masses (m_{el}) of the electron, the light electrons move much more rapidly than the heavy nuclei. According to this fact, the BO approximations [2, 3] allows researchers to simplify the time-independent (TI) Schrödinger equation to solve the nuclear and electronic motions separately. The total wave function of the system within the Born-Oppenheimer framework can be formulated as a product of the electronic and nuclear wave functions:

$$\Psi(\vec{r}, \vec{R}) = \psi_{el}(\vec{r}, \vec{R}) \cdot \phi_n(\vec{R}). \tag{1.1.7}$$

The electronic wave function $\psi_{el}(\vec{r}, \vec{R})$ depends both on the electronic coordinates ($\vec{r}$) and nuclear ($\vec{R}$) coordinates, whereas the nuclear wave function $\phi_n(\vec{R})$ depends only on the nuclear ($\vec{R}$) coordinates. For convenience, I will use atomic units; that is, $\hbar = m_{el} = e = \frac{1}{4\pi\epsilon_0} = 1$ atomic units (or au for short).

The time-independent Schrödinger equation (TISE) takes the following form considering the Born-Oppenheimer Hamiltonian (Eq. 1.1.6) and its total wave function (Eq. 1.1.7),

$$\begin{aligned}
\hat{H}\psi_{el}(\vec{r}, \vec{R}) &= \left[\hat{T}_{nuc} + \hat{T}_{el} + V_{el,el} + V_{nuc,nuc} + V_{el,nuc} \right] \psi_{el}(\vec{r}, \vec{R}) \cdot \phi_n(\vec{R}) \\
&= \left[\hat{T}_{nuc} \right] \psi_{el}(\vec{r}, \vec{R}) \cdot \phi_n(\vec{R}) + \left[\hat{H}_{el} \right] \psi_{el}(\vec{r}, \vec{R}) \phi_n(\vec{R}) \\
&= E\psi_{el}(\vec{r}, \vec{R}) \cdot \phi_n(\vec{R}).
\end{aligned} \tag{1.1.8}$$

Let us calculate the term of the nuclear kinetic operator in Eq. 1.1.8 with the total wave function,

$$\begin{aligned}
\hat{T}_{nuc} \psi_{el}(\vec{r}, \vec{R}) \phi_n(\vec{R}) &= - \sum_{\alpha=1}^{nuc} \frac{1}{2M_{\alpha}} \nabla_{R_{\alpha}}^2 \left[\psi_{el}(\vec{r}, \vec{R}) \phi_n(\vec{R}) \right] \\
&= - \sum_{\alpha=1}^{nuc} \frac{1}{2M_{\alpha}} \left\{ \frac{\partial^2}{\partial X_{\alpha}^2} + \frac{\partial^2}{\partial Y_{\alpha}^2} + \frac{\partial^2}{\partial Z_{\alpha}^2} \right\} \left[\psi_{el}(\vec{r}, \vec{R}) \phi_n(\vec{R}) \right] \\
&= - \sum_{\alpha=1}^{nuc} \frac{1}{2M_{\alpha}} \left[(\nabla_{R_{\alpha}}^2 \psi_{el}(\vec{r}, \vec{R})) \phi_n(\vec{R}) + 2 (\nabla_{R_{\alpha}} \psi_{el}(\vec{r}, \vec{R})) \cdot (\nabla_{R_{\alpha}} \phi_n(\vec{R})) \right. \\
&\quad \left. + \psi_{el}(\vec{r}, \vec{R}) \nabla_{R_{\alpha}}^2 \phi_n(\vec{R}) \right] \\
&= \psi_{el}(\vec{r}, \vec{R}) \hat{T}_{nuc} \phi_n(\vec{R}) - \sum_{\alpha=1}^{nuc} \frac{1}{2M_{\alpha}} \Lambda(\psi_{el}, \phi_n).
\end{aligned} \tag{1.1.9}$$

Here, $\Lambda(\psi_{el}, \phi_n)$ includes the non-adiabatic coupling term, which expresses non-adiabatic effects between the electronic states in a molecule: $\Lambda(\psi_{el}, \phi_n) = (\nabla_{R_{\alpha}}^2 \psi_{el}(\vec{r}, \vec{R})) \phi_n(\vec{R}) + 2 \cdot (\nabla_{R_{\alpha}} \psi_{el}(\vec{r}, \vec{R})) \cdot (\nabla_{R_{\alpha}} \phi_n(\vec{R}))$. The term $\Lambda(\psi_{el}, \phi_n)$ couples the electronic and nuclear motions of the system. In the Born-Oppenheimer approximation, this term $\Lambda(\psi_{el}, \phi_n)$ is neglected because of their very small value compared to $\psi_{el}(\vec{r}, \vec{R}) \hat{T}_{nuc} \phi_n(\vec{R})$. In this representation, nuclear and electronic motions can be decoupled, allowing the nuclei to move on a single potential energy surface defined by the electronic state. In the Born-Oppenheimer approximation, the equation 1.1.8 can be written in the following 1.1.11 form, considering the condition.

$$\hat{T}_{nuc} \psi_{el}(\vec{r}, \vec{R}) \cdot \phi_n(\vec{R}) \approx \psi_{el}(\vec{r}, \vec{R}) \hat{T}_{nuc} \phi_n(\vec{R}), \tag{1.1.10}$$

$$\begin{aligned}
\hat{H} \psi_{el}(\vec{r}, \vec{R}) \phi_n(\vec{R}) &= \psi_{el}(\vec{r}, \vec{R}) \hat{T}_{nuc} \phi_n(\vec{R}) + \hat{H}_{el} \psi_{el}(\vec{r}, \vec{R}) \phi_n(\vec{R}) \\
&= \psi_{el}(\vec{r}, \vec{R}) \left[\hat{T}_{nuc} \phi_n(\vec{R}) \right] + \left[\hat{H}_{el} \psi_{el}(\vec{r}, \vec{R}) \right] \phi_n(\vec{R}) \\
&= E \psi_{el}(\vec{r}, \vec{R}) \phi_n(\vec{R}).
\end{aligned} \tag{1.1.11}$$

Equation 1.1.11 can be solved individually for electronic and nuclear motions. In the framework of the BO approximation, the nuclei can be considered clamped in space, $T_{nuc} = 0$:

$$\hat{H}_{el} \psi_{el}(\vec{r}, \vec{R}) = E \psi_{el}(\vec{r}, \vec{R}) = E_{el_i}(R) \psi_{el_i}(\vec{r}, \vec{R}). \tag{1.1.12}$$

There is a variety of sets of these equations differing from each other for each nuclear configuration; hence, the stationary electronic eigenstates $\psi_{el}(\vec{r}, \vec{R})$ and their corresponding energies ($E_{el_i}(R)$) are parametrically dependent on $\vec{R}$. After obtaining each electronic energy ($E_{el_i}(R)$) for specific points of $\vec{R}$, we can proceed to solve the nuclear motion of the system using the values of $E_{el_i}(R)$ in Eq. 1.1.12.

$$\begin{aligned}\hat{H}\psi_{el_i}(\vec{r}, \vec{R})\phi_n(\vec{R}) &= \psi_{el_i}(\vec{r}, \vec{R}) \left[\hat{T}_{nuc}\phi_n(\vec{R}) \right] + E_{el_i}(R)\psi_{el_i}(\vec{r}, \vec{R})\phi_n(\vec{R}) \\ &= E\psi_{el_i}(\vec{r}, \vec{R})\phi_n(\vec{R})\end{aligned}\tag{1.1.13}$$

$$\hat{T}_{nuc}\phi_n(\vec{R}) + E_{el_i}(R)\phi_n(\vec{R}) = E\phi_n(\vec{R}) = E_{nuc_i}\phi_n(\vec{R}).\tag{1.1.14}$$

By solving equation 1.1.14, we can get the eigenenergies E_{nuc_i} for the motion of the nuclei using electronic eigenenergies ($E_{el_i}(R)$). In the BO approximation, the non-adiabatic coupling term is neglected ($\Lambda(\psi_{el}, \phi_n) \approx 0$).

1.2 Description of diatomic molecules

Diatomic molecules consist of two atoms. If a diatomic molecule is composed of the same two atoms, such as oxygen (O_2) or hydrogen (H_2), it is termed homonuclear. Otherwise, if a diatomic molecule consists of two different atoms, such as magnesium hydride (MgH) or carbon monoxide (CO), it is called heteronuclear.

For a diatomic molecule consisting of two nuclei (A and B) and n_{el} electrons, the stationary Schrödinger equation takes the form [53, 54]

$$\hat{H}\Psi(\vec{r}_i; \vec{R}) = E\Psi(\vec{r}_i; \vec{R}),\tag{1.2.1}$$

where $\vec{r}_i$ ($i = 1, 2, \dots, n_{el}$) are the electron coordinates, $\vec{R} = \vec{R}_A - \vec{R}_B$ represents the relative position vector of the nuclei, while E represents the total energy of the molecule. The total Hamiltonian of a diatomic molecule is

$$\hat{H} = \hat{T}_{el} + \hat{T}_{nuc} + V\tag{1.2.2}$$

where

$$\hat{T}_{el} = -\frac{1}{2} \sum_{i=1}^{n_{el}} \nabla_{\vec{r}_i}^2\tag{1.2.3}$$

$\hat{T}_{el}$ denotes the kinetic energy operator (in atomic units) for the electrons in the system,

$$\hat{T}_{nuc} = -\frac{1}{2\mu}\nabla_R^2 \quad (1.2.4)$$

$\hat{T}_{nuc}$ denotes the nuclear kinetic energy operator. Where

$$\mu = \frac{M_A M_B}{M_A + M_B} \quad (1.2.5)$$

μ denotes the reduced mass associated with nuclei A and B.

$$V = -\sum_{i=1}^{n_{el}} \left(\frac{Z_A}{r_{iA}} + \frac{Z_B}{r_{iB}} \right) + \sum_{i<j} \frac{1}{r_{ij}} + \frac{Z_A Z_B}{R} \quad (1.2.6)$$

is the potential energy, which consists of the sum of the Coulomb interactions between all pairs of particles.

$$V_{el,nuc} = -\sum_i \left(\frac{Z_A}{r_{iA}} + \frac{Z_B}{r_{iB}} \right) \quad (1.2.7)$$

is the electron-nuclei attraction, while

$$V_{el,el} = \sum_{i<j} \frac{1}{r_{ij}} \quad (1.2.8)$$

is the electron-electron repulsion, and

$$V_{nuc,nuc} = \frac{Z_A Z_B}{R} \quad (1.2.9)$$

is the nucleus-nucleus repulsion.

In the Born-Oppenheimer approximation, the nuclei are assumed to be fixed, and the nuclear kinetic-energy terms are assumed to be negligible. The Hamiltonian governing the electronic motion then becomes the following for a diatomic system:

$$\hat{H}_{el} = \hat{T}_{el} + V = -\frac{1}{2} \sum_{i=1}^{n_{el}} \nabla_i^2 - \sum_{i=1}^{n_{el}} \left(\frac{Z_A}{r_{iA}} + \frac{Z_B}{r_{iB}} \right) + \sum_{i<j} \frac{1}{r_{ij}} + \frac{Z_A Z_B}{R}, \quad (1.2.10)$$

and the TISE for the electrons moving in the field of nuclei fixed at the positions R_A and R_B can be written as

$$\hat{H}_{el} \Psi_{el}(\vec{r}_i; \vec{R}) = (\hat{T}_{el} + V) \Psi_{el}(\vec{r}_i; \vec{R}) = E_{el}(\vec{R}) \Psi_{el}(\vec{r}_i; \vec{R}). \quad (1.2.11)$$

where $(\vec{R})$ is a relative vector of nuclei. In the framework of the BO approximation, the slow nuclei can be regarded as moving in the potential field created by the fast electrons. Once the electronic Schrödinger equation is solved, the nuclear Schrödinger equation can be obtained as

$$\left(\hat{T}_{nuc} + E_{el}(\vec{R})\right) \phi_n(\vec{R}) = E \phi_n(\vec{R}). \quad (1.2.12)$$

Having established the field-free BO description of the diatomic molecule, in the following section, we will discuss its interaction with a classical electromagnetic field.

1.3 Light–matter coupling

To understand the impact of light on molecular dynamics, it is useful to begin with the classical description of the electromagnetic (EM) field and its interaction with matter. When the molecule interacts with the external field, the total Hamiltonian of the system takes the form [55]

$$\hat{H}_{tot} = \hat{H}_{mol} + \hat{V}_{int}. \quad (1.3.1)$$

Here, $\hat{H}_{mol}$ is the field-free molecular Hamiltonian consisting of the kinetic energy operators and the potential energy surfaces (PESs) of a target molecular system. The interaction term $\hat{V}_{int}$ represents a time-dependent perturbation that drives transitions between molecular states under the influence of the external field. The EM field itself has a distributed energy between its electric and magnetic components. In this framework, the EM field is treated as a continuous oscillation of electric and magnetic components, and the molecule responds through its induced or permanent dipole moment. The coupling between the molecular dipole moment and the oscillating electric field primarily determines the interaction between a molecule and an external EM field. The interaction term in a classical approach can be expressed as [53]:

$$\hat{V}_{int} = -\vec{\mu} \cdot \hat{H}_{field}, \quad (1.3.2)$$

where $\vec{\mu}$ denotes the dipole moment of the molecule between states $|j\rangle$ and $|k\rangle$, calculated $\mu_{jk} = \langle j | \hat{d}(R) | k \rangle$, with $\hat{d}(R)$ the electric permanent or transition dipole moments. And $\hat{H}_{field}$ is the electromagnetic field. The negative sign shows that alignment of the dipole with the external field lowers the energy of the system.

The total electromagnetic energy in a volume V is expressed by

$$\hat{H}_{field} = \frac{1}{2} \int_V dV \left[\epsilon_0 \vec{E}^2(\mathbf{r}, t) + \frac{1}{\mu_0} \vec{B}^2(\mathbf{r}, t) \right]. \quad (1.3.3)$$

Here, ε_0 is the vacuum permittivity and μ_0 its permeability. For an EM wave on a plane propagating in free space, the electric and magnetic field amplitudes satisfy $E_0 = cB_0$, demonstrating that the electric component dominates in magnitude. However, the total energy is equally shared between both fields. The electric and magnetic fields are derived from the vector potential $\vec{A}$ according to Maxwell's relations [56]:

$$\vec{E} = -\frac{1}{c} \frac{\partial \vec{A}}{\partial t} = \frac{i}{c} \sum_{\mathbf{k}\lambda} \omega_{\mathbf{k}} \hat{\mathbf{e}}_{\mathbf{k}\lambda} [A_{\mathbf{k}\lambda} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)} - A_{\mathbf{k}\lambda}^* e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)}], \quad (1.3.4)$$

and

$$\vec{B} = \nabla \times \vec{A} = \frac{i}{c} \sum_{\mathbf{k}\lambda} \omega_{\mathbf{k}} (\hat{\mathbf{k}} \times \hat{\mathbf{e}}_{\mathbf{k}\lambda}) [A_{\mathbf{k}\lambda} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)} - A_{\mathbf{k}\lambda}^* e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)}]. \quad (1.3.5)$$

The two components are mutually perpendicular and also orthogonal to the propagation direction $\hat{\mathbf{k}}$. The vector potential $\vec{A}$ that describes the EM field is written as a superposition of plane waves:

$$\vec{A} = \sum_{\mathbf{k}\lambda} \hat{\mathbf{e}}_{\mathbf{k}\lambda} [A_{\mathbf{k}\lambda} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)} + A_{\mathbf{k}\lambda}^* e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega_{\mathbf{k}}t)}], \quad (1.3.6)$$

where $\hat{\mathbf{e}}_{\mathbf{k}\lambda}$ represents the unit polarization vector. $A_{\mathbf{k}\lambda}$ is the complex mode amplitude of the field, and $\omega_{\mathbf{k}}$ is the angular frequency associated with this mode. We define the wave vector as $\mathbf{k} = 2\pi/\lambda$, with λ the radiation wavelength. The relations between $\vec{E}$, $\vec{B}$, and $\vec{A}$ originate directly from Maxwell's equations in free space:

$$\vec{E} = -\frac{1}{c} \frac{\partial \vec{A}}{\partial t}, \quad \vec{B} = \nabla \times \vec{A}.$$

This means that both fields satisfy the classical wave equation and propagate at the speed of light. Hence, starting from the light-matter interaction Hamiltonian, the classical approach provides a complete and self-consistent description of how external electromagnetic radiation perturbs molecular systems. If we write the interaction term between a molecule and an external EM field in the framework of the dipole approximation, it looks like

$$\hat{V}_{\text{int}} = -\vec{\mu} \cdot \vec{E}(t), \quad (1.3.7)$$

where $\vec{\mu}$ is the molecular dipole moment, including both TDMs and PDMs contributions, while $\vec{E}(t)$ denotes the time-dependent electric field acting on the system.

1.3.1 Rabi oscillation

When a quantum system is exposed to an intense radiation field, the populations of two (near)resonantly coupled states exhibit periodic oscillations in time. These oscillations, known as ROs [22, 23], are the fundamental manifestation of coherent, nonlinear quantum dynamics. A two-level model can effectively describe the system [57, 58]. Under resonant or near-resonant coupling to a laser field, the interaction gives rise to two dressed states whose energies evolve in time with the envelope of the driving pulse, but in opposite directions. As the field intensity increases, the energy splitting of these dressed states reaches a maximum at the pulse center, a phenomenon known as Rabi splitting. Then it returns to zero as the pulse intensity decays. When additional photons are absorbed, the coherent system can feature partial dissociation or ionization, resulting in an Autler–Townes (AT) doublet structure in the emission spectrum. The higher-energy peak of the AT doublet is dominated by particles emitted from the upper dressed state, while the lower-energy peak is mainly supplied by particles from the lower dressed state. During the last few decades, Rabi oscillations of atomic electrons have attracted considerable attention [22, 23, 34, 35, 32, 33, 59, 60]. In the last few years, the development of intense, ultrashort XUV laser pulses [17, 18] has renewed this field of study. When subjected to such excitation, the resonantly driven atom undergoes damped Rabi oscillations, where ionization can occur in every cycle. The resulting interference between photoelectrons emitted at different times of these oscillations leads to a distinct multippeak structure in the Autler–Townes doublet.

The key spectral features of this doublet, such as its splitting, shifting, asymmetry and multippeak pattern, provide essential information about the underlying electronic dynamics. The asymmetry observed in the Autler–Townes doublet can arise from multiple sources, such as dynamic Stark effects associated with the participating levels [34, 35], the photon energy detuning [32], and the energy dependence of the bound-to-continuum dipole matrix elements [31]. Additional influences include the depletion of the intermediate state [61], the pulse envelope shape [60] and the optical phase of the driving field [62].

We developed a three-level model that reproduces all features of the spectra, such as splitting, shifting, multi-peak patterns, and spectral asymmetry. I will detail the model derivation in Section 1.4.2. Below, I present the Rabi frequencies we used in that model. For a pair of states $|l\rangle$ and $|u\rangle$ coupled by the classical laser field, the bound-to-bound Rabi frequency is defined as

$$\Omega_{lu}(t) = -\frac{1}{2} \mu_{lu} E_0 g(t), \quad \Omega_{lu}(t) = \Omega_0 g(t), \quad (1.3.8)$$

where $\mu_{lu} = \langle l | d(R) | u \rangle$ is the nuclear transition dipole moment between vibrational levels $|l\rangle$ and $|u\rangle$ of bound electronic states calculated using the electric transition or permanent dipole moments $d(R)$, whereas E_0 is the peak electric field amplitude, and $g(t)$ represents the pulse envelope function, which takes $g(t) = \exp(-t^2/T^2)$ for the Gaussian function. The negative sign in Eq. 1.3.8 originates from the semi-classical dipole interaction Hamiltonian (in Eq. 1.3.7) [53, 63], where the Rabi frequency $\Omega_{lu}(t)$ is defined as the off-diagonal matrix element of $\hat{V}_{int}$ between states $|l\rangle$ and $|u\rangle$.

The corresponding bound-to-continuum Rabi frequency can be written as

$$\chi_{\varepsilon u}(t) = -\frac{1}{2} \mu_{\varepsilon u} E_0 g(t), \quad \text{or} \quad \chi_{\varepsilon u}(t) = \chi_0 g(t), \quad (1.3.9)$$

where $\mu_{\varepsilon u}$ represents the dipole coupling between vibrational levels $|\varepsilon\rangle$ and $|u\rangle$ of the continuum and bound electronic states, respectively. This quantity determines the transition probability from a bound level $|u\rangle$ to a continuum level $|\varepsilon\rangle$ during the laser-molecule interaction.

It should be noted that nuclear dipole coupling can significantly influence the Rabi frequency and the Stark shift, and in the following subsection 1.3.2, we will discuss the Stark shift.

1.3.2 Stark shift

When an external electric field is applied, shifts and splittings of atomic or molecular energy levels are known as the Stark effect. A dynamic Stark shift (DSS) is a time-dependent distortion of the energy levels of an atom or molecule interacting with strong, short laser pulses. In spectroscopy, the AC Stark effect is a dynamic form of the Stark shift that occurs when an oscillating electric field is resonant or near resonant, manifesting as Autler–Townes splitting of the energy levels. This interaction can modify the absorption and emission spectra. The AC Stark effect is the time-dependent version of the static Stark effect, which splits the energy levels of atoms and molecules in a constant electric field.

To further analyze the effects of dynamic Stark shifts, I will provide formulas for calculating Stark shifts within our developed three-level model, which we will derive by analytically solving the TDSE (in further subsection 1.4.2, where a three-level model will be detailed). The dynamic Stark shift, expressing interaction of the resonant k -th states ($k = l, u, \varepsilon$) with the nonresonant $|m\rangle$ states, take the following form [64]:

$$\omega_k^{(S)}(t) = - \sum_m \frac{|\mu_{km}|^2 E_0^2 g^2(t)}{4} \frac{\omega_{mk}}{\omega_{mk}^2 - \omega^2}. \quad (1.3.10)$$

Here, the summation runs over all nonresonant states $|m\rangle$, and $\omega_{mk} = \omega_m - \omega_k$ is the energy difference between the nonresonant and resonant states. Since the field amplitude varies with the envelope $g(t)$, the Stark shift follows a quadratic dependence on the pulse intensity:

$$\omega_k^{(S)}(t) = \omega_{k0}^{(S)} g^2(t), \quad (1.3.11)$$

where $\omega_{k0}^{(S)}$ denotes the maximum shift at the pulse peak. The direction of the shift depends on the sign of the detunings ($\omega_{mk} - \omega$). In this model, energy-level shifts due to nuclear permanent dipoles ($V_{kk}(t) = -\mu_{kk}E(t)$) are excluded. However, they are automatically included in the full numerical simulations through the electric permanent dipole terms. These shifts depend on the instantaneous quantity of the electric field $E(t)$. Since the carrier frequency used here, ω , corresponds to a few electronvolts, their impact on the dynamics and on the spectral shape is minor. Such energy shifts are significant mainly in infrared laser fields [65, 66]. The relative and average Stark shifts are written as follows

$$\delta_\omega^{(S)}(t) = \frac{1}{2} \left[\omega_u^{(S)}(t) - \omega_l^{(S)}(t) \right], \quad \Sigma^{(S)}(t) = \frac{1}{2} \left[\omega_u^{(S)}(t) + \omega_l^{(S)}(t) \right], \quad (1.3.12)$$

while the generalized Rabi frequency is defined by the Rabi frequency and the relative Stark shift:

$$\Omega_R(t) = \sqrt{\Omega(t)^2 + \delta_\omega^{(S)}(t)^2}. \quad (1.3.13)$$

It should be noted that the energy splittings become significant as the pulse is on, and when the pulse is off, there are no splittings. This splitting of energy levels is asymmetric due to the contribution of the sum of Stark shifts $\Sigma^{(S)}(t)$. In general, including the dynamical level shifts in the formulas is essential for accurately describing the spectral shape.

1.3.3 Dynamical interference

Dynamic interference (DI) is a time-domain interference effect that appears when particles with the same final energy are emitted with a particular time delay during a short, intense laser pulse, typically at the ascending and descending edges of the pulse [37, 39]. The corresponding amplitudes then interfere, producing an oscillatory multi-peak structure in the energy spectrum. In recent years, DI has attracted considerable attention [38, 40, 42], and has been investigated through a variety of theoretical and experimental approaches, including studies employing attosecond pulses in combination with paired infrared (IR) laser fields [67].

The concept of DI was first developed for direct one-photon ionization [69], where a high-frequency (XUV) photon with energy above the ionization potential, $\omega > E_I$,

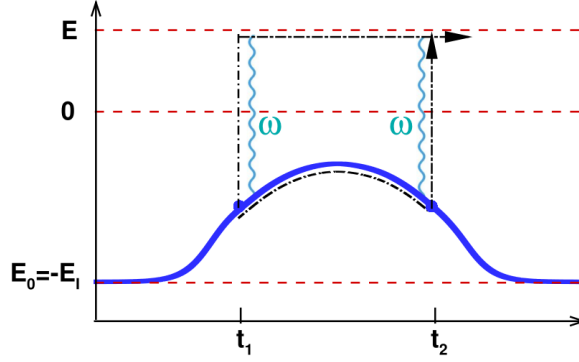


Figure 1.1: Schematic picture (taken from [68]) of an interference between two distinct ionization pathways starting from the atomic ground state in a one-photon process. In the nonlinear regime, the external laser field shifts the ground-state energy (Stark shift) by a large part of the binding energy E_I . Because of this time-dependent shift, the atom can emit electrons at two different times (t_1 and t_2 on the X axis) during the pulse, but to the same final energy.

promotes an electron directly from a bound state to the continuum. In this regime, the pulse contains several optical cycles, and the ac Stark shifts of the bound and continuum levels in an atom adiabatically follow the envelope function (see Figure 1.1). Due to this time-dependent Stark shift, theory predicts that the spectrum's single photoelectron peak, whose width is about $1/T$ (with T the pulse duration), is shifted or even transformed into a multi-peak structure (in the spectrum) [37, 70, 38, 69]. This is referred to as dynamic interference and can be understood as a simple two-path temporal interference process (two wavy vertical lines in Figure 1.1) in the time domain. Electron wave packets that are emitted on the rising edge of the pulse interfere with those emitted on the falling edge if they end up with the same final energy (Fig. 1.1). This happens when the initial state shifted by the ac Stark energy, $E_0(t)$, takes the same value at two different times (t_1 and t_2 in Figure 1.1) during the pulse.

DI typically requires two conditions: (i) the relative Stark shift between the initial bound state and the continuum is larger than the pulse bandwidth, so emissions at different times accumulate different phases for the same energy; (ii) the initial state is not depleted too early, so that significant emission occurs on both the ascending and descending edges of the pulse. For ground-state atoms, these conditions are typically met in a strongly non-perturbative regime and are closely linked to the onset of atomic stabilization in intense [68] XUV fields.

Similar spectral interference patterns have also been observed and predicted in the below-threshold regime [39], where the photon energy is smaller than the ionization potential, $\omega < E_I$, and ionization proceeds via near-resonant bound-bound transitions. In

such REMPI-type scenarios, the laser field resonantly couples two bound states of the atom and induces Rabi cycles. These cycles are introduced most conveniently by considering a two-level atomic system, with transition dipole moment μ , and transition energy ω_0 , driven by a monochromatic external electromagnetic field of angular frequency ω and amplitude E_0 [33]. When the atom that is initially in its ground state is periodically promoted to the excited state with probability according to [39, 42]

$$P(t) = \frac{\Omega^2}{W^2} \sin^2\left(\frac{Wt}{2}\right),$$

where $W = \sqrt{\Omega^2 + \Delta^2}$ is the generalized Rabi frequency, $\Delta = \omega - \omega_0$ is the detuning, and $\Omega = E_0\mu$ is the Rabi frequency. The near-resonant ($\Delta \approx 0$) interaction with the field gives rise to two atomic dressed states, whose energy separation (the Rabi splitting) is equal to W . For short laser pulses, the Rabi dynamics is modified by the temporal envelope: for instance, a Gaussian pulse with a given area can generate roughly 1.5 times more oscillations than a flat-top pulse of the same area, and the splitting between the dressed-state energies becomes explicitly time dependent through the envelope function. Upon absorption of additional photon(s) from the same pulse, ionization damps the Rabi oscillations, and the AT doublet appears in the spectrum. The detailed structure of this AT doublet is highly sensitive to several factors, including the number of Rabi oscillations generated by the system, the dynamical Stark shifts of the included levels, the energy-dependent bound–continuum transition dipole, the pulse envelope’s shape and the phase of the applied field.

In the *REMPI*, DI and Rabi dynamics are therefore closely connected: Rabi oscillations are determined when the intermediate state becomes populated, while DI arises when the same continuum energy is reached at multiple emission times during the pulse. The analysis of DI in atoms outlined above provides general criteria that can be transferred to molecular REMPI: a sufficiently large field-induced splitting (Stark or Rabi) compared to the pulse bandwidth, and only a small depletion of the initial state.

In this Thesis, we analyze DI within the molecule. When the laser is off-resonant (with the photon energy lying below), pronounced Rabi oscillations are largely suppressed, yet the fragment spectrum still shows strong multipeak modulations. By employing asymmetric pulse envelopes that strongly reduce the contribution from the falling edge while keeping the pulse area fixed, we demonstrate that, in this off-resonant regime, the spectral modulations arise predominantly from dynamic interference between fragment amplitudes emitted on the increasing and decreasing edges of the pulse.

1.4 Nuclear dynamics

We work within the BO picture because it allows for an accurate treatment of the nuclear dynamics. In the BO approximation, the nuclear motion is treated separately from the electronic motion, allowing the nuclear wave packet $\Phi(\vec{R}, t)$ to evolve on a potential energy surface defined by the electronic structure. In quantum mechanics, the time evolution of molecular nuclei is governed by the TDSE [48]. The general form of the TDSE for the nuclei is written as

$$i\hbar \frac{\partial}{\partial t} \Phi(\vec{R}, t) = \hat{H} \Phi(\vec{R}, t). \quad (1.4.1)$$

Here, $\Phi(\vec{R}, t)$ represents the nuclear wave function, and $\vec{R} = (\vec{R}_1, \vec{R}_2, \dots, \vec{R}_f)$ denotes the set of nuclear coordinates where f is the number of nuclear DOFs. The Hamiltonian $\hat{H}$ represents the total nuclear energy operator and potential energies between particles (as discussed in Section 1.1 for the TI problem).

Unlike time-independent quantum chemistry calculations, molecular quantum dynamics is inherently more complex and demanding. Time-dependent solutions often provide a more intuitive picture of the evolution of the system. The nuclear wave function $\Phi(\vec{R}, t)$ is highly structured due to the nuclear motion, which can be interpreted as a wave packet propagating on the electronic potential energy surfaces. This nuclear wave-packet is represented as a superposition of eigenstates of the system. One of the simplest methods for solving the TDSE is the *standard method*. In this method, the nuclear wave function $\Phi^{(q)}(\vec{R}, t)$ associated with an electronic state q is expanded in a time-independent basis set as [71]:

$$\Phi^{(q)}(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_f, t) = \sum_{j_1=1}^{n_1} \cdots \sum_{j_f=1}^{n_f} A(q)_{j_1 \dots j_f}(t) \prod_{k=1}^f \chi_{j_k}^{(k)}(\vec{R}_k), \quad (1.4.2)$$

where $\chi_{j_k}^{(k)}(\vec{R}_k)$ are time-independent basis functions for the k th coordinate, and $A_{j_1 \dots j_f}^{(q)}(t)$ are time-dependent expansion coefficients for this method.

The Dirac–Frenkel variational principle can be utilized to derive equations of motion for the expansion coefficients $A_{j_1 \dots j_f}(t)$:

$$\begin{aligned} \langle \delta\Phi(\vec{R}, t) | \hat{H} - i \frac{\partial}{\partial t} | \Phi(\vec{R}, t) \rangle &= 0 \\ \langle \delta\Phi(\vec{R}, t) | \hat{H} \Phi(\vec{R}, t) - i \dot{\Phi}(\vec{R}, t) \rangle &= 0, \end{aligned} \quad (1.4.3)$$

where $\delta\Phi$ and $\dot{\Phi}$ are expressed by the following [72]:

$$\delta\Phi(\vec{R}, t) = \sum_{l_1 \dots l_f} \frac{\partial\Phi(\vec{R}, t)}{\partial A_{l_1 \dots l_f}(t)} \delta A_{l_1 \dots l_f}(t) = \sum_{l_1 \dots l_f} \chi_{l_1}^{(1)}(\vec{R}_1) \dots \chi_{l_f}^{(f)}(\vec{R}_f) \delta A_{l_1 \dots l_f}(t), \quad (1.4.4)$$

and

$$\dot{\Phi}(\vec{R}, t) = \sum_{j_1 \dots j_f} \dot{A}_{j_1 \dots j_f}(t) \chi_{j_1}^{(1)}(\vec{R}_1) \dots \chi_{j_f}^{(f)}(\vec{R}_f). \quad (1.4.5)$$

By substituting Eqs. (1.4.4) and (1.4.5) into Eq. (1.4.3), a set of first order differential equation with constant coefficients can be obtained:

$$i\dot{A}_J(t) = \sum_J \langle \chi_L(\vec{R}) | \hat{H} | \chi_J(\vec{R}) \rangle A_J(t) = \sum_J H_{LJ} A_J(t). \quad (1.4.6)$$

Here, $J = (j_1, \dots, j_f)$ and $\chi_J(\vec{R}) = \prod_{k=1}^f \chi_{J_k}(\vec{R}_k)$. The Hamiltonian matrix elements in Eq. 1.4.6 are given as

$$H_{LJ} = \langle \chi_{l_1}^{(1)} \dots \chi_{l_f}^{(f)} | \hat{H} | \chi_{j_1}^{(1)} \dots \chi_{j_f}^{(f)} \rangle. \quad (1.4.7)$$

This approach quickly becomes computationally expensive, since the number of coupled equations grows exponentially with f DOF. Therefore, this approach is generally restricted to systems with only a few degrees of freedom, for example, molecules with 3 or 4 atoms. To overcome these limitations, we need another method that is the time-dependent Hartree (TDH) method, also known as the time-dependent self-consistent field (TDSCF) approach, provides a more efficient alternative. In this method, the nuclear wave function [72] is approximated as a product of time-dependent single-particle functions (SPFs):

$$\Phi(\vec{R}_1, \vec{R}_2, \dots, \vec{R}_f, t) = a(t) \prod_{k=1}^f \varphi_k(\vec{R}_k, t) = a(t) \phi(t). \quad (1.4.8)$$

Here, $a(t)$ is a time-dependent coefficient for the TDH method, and $\varphi_k(\vec{R}_k, t)$ represents the SPFs associated with the k th coordinate. The product $\phi(t) = \prod_k \varphi_k(\vec{R}_k, t)$ is called a Hartree product.

Since the SPFs are not uniquely defined (their phases and normalizations can shift among themselves), additional constraints are introduced to ensure uniqueness:

$$i\langle \varphi_k(t) | \dot{\varphi}_k(t) \rangle = g_k(t), \quad (1.4.9)$$

where $g_k(t)$ is an arbitrary, typically real, function chosen to fix the gauge.

Applying the variational principle yields the following equations of motion [71, 72]:

$$i\dot{\varphi}_k(t) = [\mathcal{H}^{(k)} - E + g_k(t)] \varphi_k(t), \quad (1.4.10)$$

$$i\dot{a}(t) = \left[E - \sum_{k=1}^f g_k(t) \right] a(t), \quad (1.4.11)$$

where the energy expectation value and the effective Hamiltonian are defined as

$$E = \langle \Phi | \hat{H} | \Phi \rangle, \quad (1.4.12)$$

$$\mathcal{H}^{(k)} = \langle \Phi^{(k)} | \hat{H} | \Phi^{(k)} \rangle. \quad (1.4.13)$$

Although the TDH method allows for the inclusion of more degrees of freedom compared to the standard approach, it often lacks sufficient accuracy because of the constraints imposed on the wave function. In the next subsection 1.4.1, we extend this framework by including multiple configurations, leading to the multi-configuration time-dependent Hartree (MCTDH) method.

1.4.1 Multi-configuration time-dependent Hartree method

In this subsection, we present the multi-configuration time-dependent Hartree method [71, 48, 72, 47], which provides an efficient and numerically accurate framework for solving the TDSE of molecular systems. The MCTDH approach combines the flexibility of the time-dependent Hartree approximation with the accuracy of numerically exact wave function propagation. This method is particularly valuable in studying quantum molecular dynamics and has broad applications in the analysis of scattering processes [73, 74], absorption spectroscopy [75, 76]. In addition, it has been effectively applied in conjunction with complex absorbing potentials (CAPs) [77] to model quantum systems. The MCTDH package [49] also provides a suite of tools for the evaluation of observables and visualization of wave packet dynamics.

In the MCTDH formalism, the nuclear wave function (WF) is expressed as a linear combination of time-dependent Hartree products [71]:

$$\begin{aligned} \Phi(\vec{R}, t) &= \Phi(\vec{R}_1, \dots, \vec{R}_f, t) \\ &= \sum_{j_1=1}^{n_1} \cdots \sum_{j_f=1}^{n_f} C_{j_1 \dots j_f}(t) \prod_{k=1}^f \varphi_{j_k}^{(k)}(\vec{R}_k, t), \end{aligned} \quad (1.4.14)$$

where $C_{j_1 \dots j_f}(t)$ denote the time-dependent expansion coefficients, and $\varphi_{j_k}^{(k)}(\vec{R}_k, t)$ represent

the single-particle functions corresponding to the k th degree of freedom. Each SPF is further expanded in a time-independent primitive basis set:

$$\varphi_{j_k}^{(k)}(\vec{R}_k, t) = \sum_{i_1=1}^{N_k} c_{i_k}^{(k, j_k)}(t) \chi_{i_k}^{(k)}(\vec{R}_k), \quad (1.4.15)$$

where $\chi_{i_k}^{(k)}(\vec{R}_k)$ are the primitive basis functions, typically represented by a discrete variable representation (discrete variable representation (DVR)) or a fast Fourier transform (fast fourier transformation (FFT)) basis, depending on the nuclear vector $\vec{R}_k$.

Moreover, the SPFs are required to fulfil the following constraints:

Because the MCTDH wave function representation in Eq. 1.4.14 is not unique, an unambiguous time evolution is ensured by imposing orthonormality and gauge-like constraints on the SPFs:

$$\langle \varphi_i(t=0) | \varphi_j(t=0) \rangle = \delta_{ij}, \quad (1.4.16)$$

$$\langle \varphi_i^{(k)}(t) | \dot{\varphi}_j^{(k)}(t) \rangle = -i \langle \varphi_i^{(k)}(t) | \hat{g}^{(k)} | \varphi_j^{(k)}(t) \rangle, \quad (1.4.17)$$

where $\hat{g}^{(k)}$ denotes a constraint operator acting on the k th DOF, which may be Hermitian or arbitrary.

By applying the Dirac–Frenkel variational principle (Eq. 1.4.3), one can derive the equations of motion governing both the expansion coefficients and the single-particle functions. The MCTDH ansatz and its first-order variation are given by

$$\begin{aligned} \Phi' &= \sum_{j_1=1} \cdots \sum_{j_f=1} (C_{j_1 \dots j_f} + \delta C_{j_1 \dots j_f}) (\varphi_{j_1}^{(1)} + \delta \varphi_{j_1}^{(1)}) \cdots (\varphi_{j_f}^{(f)} + \delta \varphi_{j_f}^{(f)}) \\ &= \sum_{j_1=1} \cdots \sum_{j_f=1} C_{j_1 \dots j_f} (\varphi_{j_1}^{(1)} + \delta \varphi_{j_1}^{(1)}) \cdots (\varphi_{j_f}^{(f)} + \delta \varphi_{j_f}^{(f)}) \\ &\quad + \sum_{j_1=1} \cdots \sum_{j_f=1} \delta C_{j_1 \dots j_f} (\varphi_{j_1}^{(1)} + \delta \varphi_{j_1}^{(1)}) \cdots (\varphi_{j_f}^{(f)} + \delta \varphi_{j_f}^{(f)}) \end{aligned} \quad (1.4.18)$$

including only those terms in Eq. (1.4.17) that are up to first order in the variations, yields

$$\begin{aligned} \Phi' &= \sum_{j_1=1} \cdots \sum_{j_f=1} C_{j_1 \dots j_f} \prod_{\kappa=1} \varphi_{j_\kappa}^{(\kappa)} \\ &\quad + \sum_{j_1=1} \cdots \sum_{j_f=1} C_{j_1 \dots j_f} \sum_{\kappa=1} \delta \varphi_{j_\kappa}^{(\kappa)} \prod_{\kappa' \neq \kappa} \varphi_{j_{\kappa'}}^{(\kappa')} + \sum_{j_1=1} \cdots \sum_{j_f=1} \delta C_{j_1 \dots j_f} \prod_{\kappa=1} \varphi_{j_\kappa}^{(\kappa)} \end{aligned} \quad (1.4.19)$$

Then, we obtain

$$\Phi' = \Phi + \sum_{j_1=1} \cdots \sum_{j_f=1} C_{j_1 \dots j_f} \sum_{\kappa=1} \delta \varphi_{j_\kappa}^{(\kappa)} \prod_{\kappa' \neq \kappa} \varphi_{j_{\kappa'}}^{(\kappa')} + \sum_{j_1=1} \cdots \sum_{j_f=1} \delta C_{j_1 \dots j_f} \prod_{\kappa=1} \varphi_{j_\kappa}^{(\kappa)}. \quad (1.4.20)$$

The variation $\delta\Phi$ is written as

$$\begin{aligned} \delta\Phi &= \Phi' - \Phi \\ &= \sum_{j_1=1} \cdots \sum_{j_f=1} C_{j_1 \dots j_f} \sum_k \delta \varphi_{j_k}^{(k)} \prod_{k' \neq k} \varphi_{j_{k'}}^{(k')} + \sum_{j_1=1} \cdots \sum_{j_f=1} \delta C_{j_1 \dots j_f} \prod_k \varphi_{j_k}^{(k)}. \end{aligned} \quad (1.4.21)$$

From Eq. (1.4.21), the functional derivatives of Φ with respect to the configuration coefficients and the single-particle functions are obtained as

$$\frac{\delta\Phi}{\delta C_{j_1 \dots j_f}} = \prod_{\kappa=1} \varphi_{j_\kappa}^{(\kappa)}, \quad (1.4.22)$$

and

$$\frac{\delta\Phi}{\delta \varphi_{j_k}^{(\kappa)}} = \sum_{j_1=1} \cdots \sum_{j_{\kappa-1}=1} \sum_{j_{\kappa+1}=1} \cdots \sum_{j_f=1} C_{j_1 \dots j_{\kappa-1} j_k j_{\kappa+1} \dots j_f} \prod_{\kappa' \neq \kappa} \varphi_{j_{\kappa'}}^{(\kappa')}, \quad (1.4.23)$$

The expression on the right side of Eq. (1.4.23) is called the single-hole function $\Phi_{j_k}^{(\kappa)}$, which is a linear combination of all single-particle functions except those belonging to the κ th degree of freedom.

$$\dot{\Phi} = \sum_{j_1} \cdots \sum_{j_f} \dot{C}_{j_1 \dots j_f} \prod_k \varphi_{j_k}^{(k)} + \sum_k \sum_{j_1} \cdots \sum_{j_f} C_{j_1 \dots j_f} \dot{\varphi}_{j_k}^{(k)} \prod_{k' \neq k} \varphi_{j_{k'}}^{(k')}. \quad (1.4.24)$$

Using the variational principle and algebra leads to a set of coupled equations of motion:

$$i\dot{C}_J = \sum_L \langle \phi_J | \hat{H} | \phi_L \rangle C_L - \sum_{k=1}^f \sum_{l=1}^{n_k} \hat{g}_{j_k l}^{(k)} C_{J_l^k}, \quad (1.4.25)$$

Here, J denotes an arbitrary but fixed configuration from the set of all possible index combinations $\{j_1, \dots, j_f\}$, and ϕ_J is the corresponding Hartree product of SPFs, i.e., the product of single-particle functions with indices $j_1, \dots, j_f$ that define the configuration J .

$$i\dot{\varphi}^{(k)} = \hat{g}^{(k)} \mathbf{1}_{n_k} \varphi^{(k)} + (1 - P^{(k)}) \left[(\rho^{(k)})^{-1} \langle \hat{\mathbf{H}} \rangle^{(k)} - \hat{g}^{(k)} \mathbf{1}_{n_k} \right] \varphi^{(k)}, \quad (1.4.26)$$

where $\mathbf{1}_{n_k}$ is the $n_k \times n_k$ identity matrix, $\varphi^{(k)} = (\varphi_1^{(1)}, \dots, \varphi_{n_k}^{(k)})^T$ is the SPF vector, and $\langle \hat{\mathbf{H}} \rangle^{(k)}$ denotes the mean-field operator corresponding to the k th coordinate. The single-

particle density matrix is expressed as

$$\rho_{jl}^{(k)} = \langle \Phi_j^{(k)} | \Phi_l^{(k)} \rangle = \sum_J^K C_{J_j^k}^* C_{J_l^k}. \quad (1.4.27)$$

The projector on the SPF space of the k th coordinate is given by

$$P^{(k)} = \sum_{j=1}^{n_k} |\varphi_j^{(k)}\rangle \langle \varphi_j^{(k)}|, \quad (1.4.28)$$

and the matrix elements of the constraint operator are

$$g_{jkl}^{(k)} = \langle \varphi_{j_k}^{(k)} | g^{(k)} | \varphi_l^{(k)} \rangle. \quad (1.4.29)$$

Although the choice of $\hat{g}^{(k)}$ does not affect the physical accuracy of the MCTDH wave function, an optimal selection can significantly improve the numerical stability and efficiency [71].

The MCTDH scheme, developed by the Heidelberg group [48, 49], provides a highly efficient and accurate wave packet propagation method for multidimensional quantum systems. By employing a DVR basis, both potential and kinetic energy operators (the latter via FFT) can be efficiently represented as diagonal matrices. Owing to its adaptive basis representation, the MCTDH method is especially well suited for simulating light-matter interactions and quantum control of molecular dynamics with classical electromagnetic fields.

1.4.2 Multi-level method

To clarify how each vibrational level contributes to the spectrum, I introduce an alternative but useful multi-level description of the molecular nuclear dynamics. Within this framework, the wavefunction is expanded in the system's eigenstate basis, whereas in MCTDH it is represented in terms of time-dependent SPFs. As a consequence, the underlying multi-level formulation is formally accurate and systematically improvable. However, here we simplify it to obtain the three-level model and subsequently derive an analytic model from it. Molecule's full time-dependent wave function is expressed as an expansion over the eigenstates $|k\rangle$ of the field-free Hamiltonian:

$$\Psi(t) = \sum_k c_k(t) |k\rangle e^{-i\omega_k t}. \quad (1.4.30)$$

Here, ω_k are the eigenenergies. Substitution of this expansion into the TDSE, $i\dot{\Psi} = [H_0 + V(t)]\Psi$, leads to a coupled system of differential equations describing the evolution of amplitudes of the population of both the bound and continuum states:

$$i\dot{c}_j(t) = \sum_k c_k(t)e^{-i\omega_{kj}t}V_{jk}(t), \quad (1.4.31)$$

where $\omega_{kj} = \omega_k - \omega_j$ are the energy differences, and the elements of the dipole interaction matrix are expressed as $V_{jk}(t) = -E(t)\mu_{jk}$. Here, $\mu_{jk} = \langle j|d(R)|k\rangle$ are the nuclear dipole moments, which are evaluated using the electric transition $d(R) = d_{jk}(R)$ or the permanent dipole moments $d(R) = d_g(R)$ ($g = j, k$).

We will move to a specific case from the general form of Eq. 1.4.31; that is, $|l\rangle$ and $|u\rangle$ are the resonant initial vibrational states of the ground and intermediate electronic states, respectively, whereas $|\varepsilon\rangle$ is the resonant final continuum vibrational states. The remaining non-resonant states are denoted as $|m\rangle$. Upon inclusion of the complete set of bound and continuum states of MgH^+ in Eq (1.4.31) would allow an exact solution for the vibrational dynamics. The numerical solution of Eq. in Eq (1.4.31) was obtained using a fourth-order Runge-Kutta method. Direct breakup process starting from the initial (lower) state to dissociative states ($l \rightarrow \varepsilon$) is insignificant for the photon energies considered here, and continuum–continuum ($\varepsilon \leftrightarrow \varepsilon'$) transitions are excluded because we focus on the first photopeak. Direct dissociation from the initial lower state into continuum states ($l \rightarrow \varepsilon$) is negligible for the photon energies considered here, and transitions between continuum states ($\varepsilon \leftrightarrow \varepsilon'$) are ignored because we restrict our analysis to the first photopeak. Considering all of the above, Eq.(1.4.31) can be simplified to the following equations for the above-mentioned specific states [78, 64]:

$$i\dot{c}_l = c_u e^{i\omega_{lu}t}V_{lu}(t) + \sum_m c_m e^{i\omega_{lm}t}V_{lm}(t), \quad (1.4.32.a)$$

$$i\dot{c}_u = c_l e^{i\omega_{ul}t}V_{ul}(t) + \sum_m c_m e^{i\omega_{um}t}V_{um}(t) + \int c_\varepsilon e^{i\omega_{u\varepsilon}t}V_{u\varepsilon}(t) d\omega_\varepsilon, \quad (1.4.32.b)$$

$$i\dot{c}_m = c_l e^{i\omega_{ml}t}V_{ml}(t) + c_u e^{i\omega_{mu}t}V_{mu}(t) + \sum_{m'} c_{m'} e^{i\omega_{mm'}t}V_{mm'}(t) + \int c_\varepsilon e^{i\omega_{m\varepsilon}t}V_{m\varepsilon}(t) d\omega_\varepsilon, \quad (1.4.32.c)$$

$$i\dot{c}_\varepsilon = c_u e^{i\omega_{\varepsilon u}t}V_{\varepsilon u}(t) + \sum_m c_m e^{i\omega_{\varepsilon m}t}V_{\varepsilon m}(t). \quad (1.4.32.d)$$

In these equations, the permanent dipole couplings $V_{kk}(t)$ are neglected because they have a negligible impact on populations and spectra. The analysis is carried out using the rotating-wave approximation (RWA) in combination with the local approximation [79], the last term in Eq. (1.4.32.b) can be evaluated explicitly as

$$\int c_\varepsilon e^{i\omega_{u\varepsilon}t} V_{u\varepsilon}(t) d\omega_\varepsilon = -\frac{i}{2}\Gamma(t)c_u, \quad (1.4.33)$$

where $\Gamma(t) = \Gamma_0 g(t)^2$ and $\Gamma_0 = 2\pi|\mu_{u\varepsilon_0}E_0/2|^2$ is the total rate of dissociation associated with the resonantly excited state $|u\rangle$. The right side of Eq.(1.4.32.d) can be simplified under the RWA as

$$c_u e^{i\omega_{\varepsilon u}t} V_{\varepsilon u}(t) = c_u \chi(t) e^{i\delta t}, \quad (1.4.34)$$

Here, $\chi(t) = -\frac{1}{2}\mu_{\varepsilon u}E_0g(t) = \chi_0g(t)$ is the Rabi frequency for transitions from bound to continuum states and $\delta = \omega_{\varepsilon u} - \omega$ are the corresponding detuning.

Since the nonresonant states $|m\rangle$ are well detuned from resonance, their amplitudes oscillate quickly while the interaction takes place. Integrating Eq.(1.4.32.c) by parts and discarding small terms gives an explicit expression for $c_m(t)$ [64], which is valid as the detuning of the $|m\rangle$ states is much larger than the pulse bandwidth and associated Stark shifts. Substituting this expression back into Eqs. (1.4.32.a) -(1.4.32.d), and applying the RWA while neglecting transitions ($m \leftrightarrow m'$), and assuming exact resonance for the $l \leftrightarrow u$ transition, leads to the minimal three-level model:

$$i\dot{c}_l = \omega_l^{(S)}(t)c_l + \Omega^\dagger(t)c_u, \quad (1.4.35.a)$$

$$i\dot{c}_u = \Omega(t)c_l + \left[\omega_u^{(S)}(t) - \frac{i}{2}\Gamma(t) \right] c_u, \quad (1.4.35.b)$$

$$i\dot{c}_\varepsilon = \chi(t)c_u + [\omega_\varepsilon^{(S)}(t) + \delta] c_\varepsilon. \quad (1.4.35.c)$$

Here, $\Omega(t) = -\frac{1}{2}\mu_{lu}E_0g(t) = \Omega_0g(t)$ is the Rabi frequency for transitions from bound to bound states, whereas $\chi(t) = -\frac{1}{2}\mu_{\varepsilon u}E_0g(t) = \chi_0g(t)$ the bound-continuum Rabi frequency, and $\Gamma(t) = \Gamma_0g^2(t)$ the dissociation rate with $\Gamma_0 = 2\pi|\mu_{u\varepsilon_0}E_0/2|^2$. The essential physics of the (1+1) photon resonance-enhanced dissociation formalism is captured by Eqs. (1.4.35.a) - (1.4.35.c). $\omega_k^{(S)}$ in Eqs. (1.4.35.a) - (1.4.35.c) is the dynamic Stark shift for level k ($k = l, u, \varepsilon$) as discussed in subsection 1.3.2 (Eq. 1.3.10), and it can be re-written as:

$$\omega_k^{(S)}(t) = -\sum_m \frac{|\mu_{km}|^2 E_0^2 g^2(t)}{2} \frac{\omega_{mk}}{\omega_{mk}^2 - \omega^2} = \omega_k^{(S0)} g^2(t), \quad (1.4.36)$$

where the term $\omega_k^{(S0)}$ can be considered as amplitude of the Stark shift. The values of the

$\omega_k^{(S0)}$ for the specific levels can be utilized in the calculations of spectra of the dissociative electronic state of the MgH^+ molecule, which will be discussed in the next chapter.

Chapter 2

Spectral evidence of vibronic Rabi oscillations

In this chapter, we investigate the MgH^+ molecule's resonance-enhanced photodissociation driven by the (1+1) laser pulse and, as a result, identify clear spectral signatures of vibronic Rabi oscillations between two bound (electronic) states of a molecule [64]. While most previous studies of Rabi oscillations have focused on electronic transitions in atoms [22, 42, 39] and analyzed the corresponding Autler–Townes structure [23, 30] in photoelectron spectra, here the oscillations occur between vibrational levels of different electronic states in a molecule and are probed via nuclear photofragments. Magnesium hydride is a light diatomic ion whose simple electronic structure and well-defined potential-energy curves make it an excellent candidate for investigating vibronic interactions. The MgH^+ molecule can be selectively excited via a two-photon resonance mechanism, where the first photon drives the electronic transition, and a second photon induces dissociation. This mechanism allows for the observation of vibrational coherence effects in the time domain, along with their corresponding spectral signatures.

By developing an analytical model based on a minimal three-level model that we developed, we obtain the energy spectrum of the photofragment and clarify the main physical spectral properties—namely, the observed splitting, shifts, multipeak, and asymmetry structure—identified by accurate standard numerical calculations. The strong variations in the spectral intensity pattern arise from the fragment amplitudes' interference released during successive Rabi oscillations due to the upper and lower laser-dressed states produced by the resonant pulse. These variations are strongly affected by both resonant and nonresonant Stark shifts and can be tuned by the driving-pulse parameters. The energy spectra of the emitted fragments are used as sensitive probes of the underlying dynamics, which helps us better understand and control ultrafast coherent phenomena.

In this chapter, I have performed the MCTDH simulations of MgH^+ photodissociation and calculated fragment energy spectra and excitation and dissociation probabilities. By using the developed three-state minimal effective model, I derived analytical expressions and compared them with the MCTDH results. This minimal effective model is based on earlier atomic REMPI work [34] by my supervisor, who gave me the main ideas. However, I adapted this model to a molecular system as an example of MgH^+ , performed the calculations, and interpreted the results. The bound–continuum transition dipole moments were not calculated by me.

The organization of this chapter is as follows. Section 2.1 introduces the $(1+1)$ photon dissociation of MgH^+ , outlining the relevant electronic states and transition mechanisms. Section 2.2 describes the wave-packet dynamics and computational framework, including numerical propagation method and quantities derived from the simulations. Section 2.3 discusses the results, analyzing the emergence of vibronic Rabi oscillations and their dependence on excitation frequency and molecular rotation. Also, Section 2.3 represents the model applied by us to a vibrating molecule, detailing the approximations and parameters and comparing its results with those obtained by the exact method. Furthermore, a vibrating-rotating MgH^+ molecule under the same laser pulses will be discussed. Finally, Section 2.4 summarizes the key conclusions of these findings.

2.1 $(1+1)$ photon description of the MgH^+ molecule

In the present section, we outline the process based on a resonant two-photon $(1+1)$ dissociation of MgH^+ , induced by short laser pulses with narrow spectral bandwidth (Figure 2.1). For the resonance-enhanced $(1+1)$ photon dissociation mechanism analyzed in this Thesis, the dominant and relevant dissociation pathway is $\text{Mg} + \text{H}^+$ (blue curve in Fig. 2.1) rather than $\text{Mg}^+ + \text{H}$. Physically, this means that although the initial excitation step ($X \rightarrow A$) keeps the system on a curve correlating with $\text{Mg}^+ + \text{H}$, the actual bond-breaking event studied throughout the Thesis occurs after the second photon promotes the molecule to the dissociative C state, and the resulting dissociation therefore proceeds to $\text{Mg} + \text{H}^+$. In the framework of the BO approximation, we start from the time-dependent Schrödinger equation describing nuclear motion, which includes all relevant electronic states and coupling terms between them in the system. The photodissociation of the MgH^+ molecular ion under resonant laser excitation can be effectively interpreted within a $(1+1)$ photon framework. In this process, the molecule first absorbs a single photon that promotes it from the ground electronic state $X^1\Sigma^+$ to the first excited electronic state $A^1\Sigma^+$. A second photon from the same laser pulse then induces a transition from this excited state to

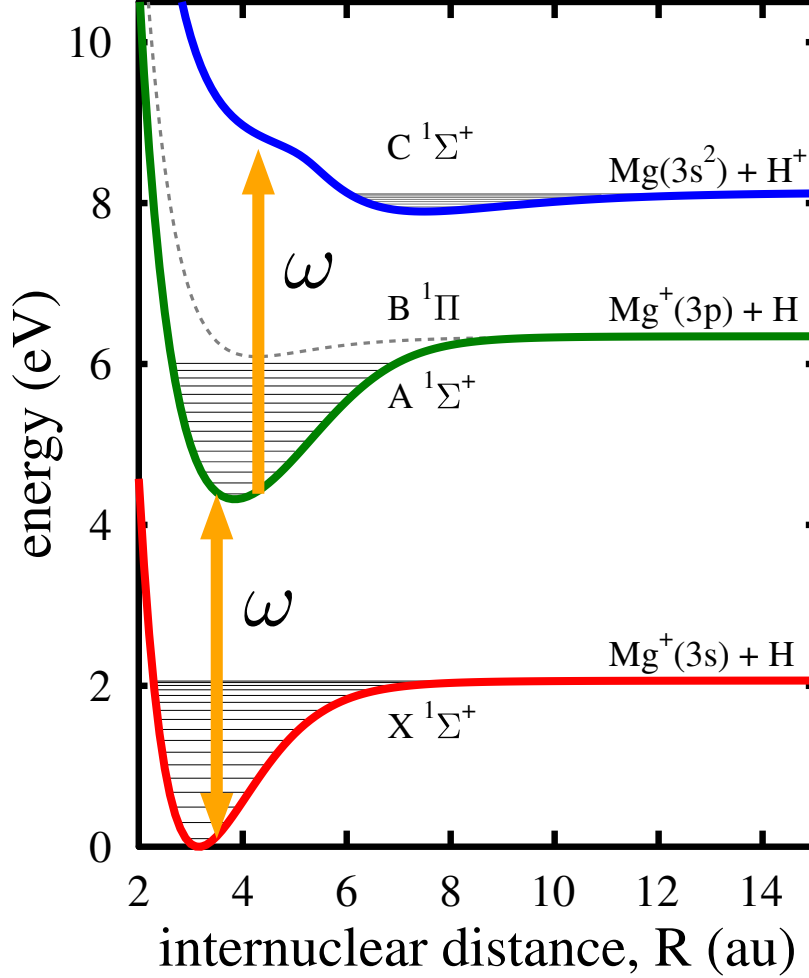


Figure 2.1: Selected field-free potential energy curves of the MgH^+ molecular ion under the 1+1 photon regime are illustrated. The electronic-structure data employed in this study were obtained from [44]. Single-photon-induced Rabi oscillations between the lowest vibrational levels of electronic states X and A, indicated by double arrows, are driven by a single Gaussian-shaped laser pulse tuned to resonance with a narrow spectral bandwidth. Photo-dissociation in the C electronic state is studied via these vibronic Rabi floppings, which are probed from the same laser pulse. The horizontal solid lines indicate the vibrational levels of the electronic states of MgH^+ .

a repulsive continuum C electronic state, resulting in dissociation. Such a stepwise excitation sequence provides a controlled route for probing vibronic coherence and identifying signatures of Rabi oscillations that arise from strong coupling between vibrational levels of different electronic states. The molecular interaction with the laser field is described within the dipole approximation as $V(t) = -\mu E(t)$, where μ is the nuclear dipole moment and $E(t)$ is the applied electric field (calculations are performed using atomic units). All results discussed below were obtained using linearly polarized laser pulses described by the general expression:

$$E(t) = E_0 g(t) \cos(\omega t), \quad (2.1.1)$$

where, E_0 denotes the amplitude electric field (the peak intensity $I_0 = E_0^2/(8\pi\alpha_{\text{FS}})$) with the carrier frequency ω , and the Gaussian envelope,

$$g(t) = e^{-t^2/T^2}. \quad (2.1.2)$$

The full width at half maximum (FWHM) of the pulse is expressed by $T\sqrt{2\ln 2}$, where, T characterizes the pulse duration.

2.2 Wave packet dynamics and numerical quantities

The (total) time-dependent nuclear wave function of our developed model can be expanded in the eigenbasis $\{|k\rangle\}$ of the field-free Hamiltonian H_0 expressed in Eq. 1.4.30. Substituting Eq. (1.4.30) into the TDSE, one obtains the complete system of coupled differential equations expressed in Eq. 1.4.31 (see subsection 1.4.2 for more detail). As discussed in subsection 1.4.2, equation 1.4.31 simultaneously accounts for the bound and continuum vibrational states and governs the complete quantum dynamical evolution of the system under the laser field. Using justified approximations, we construct a simple minimal three-level model (which was detailed in 1.4.2) that captures the essential quantum (including spectral and population) properties of molecular dissociation. This minimal model will serve as a foundation for the analytical assessment of the spectral results.

To obtain a rigorous theoretical explanation of how the photodissociation process proceeds in time, the nuclear wave packet was propagated by solving the TDSE for the MgH^+ molecule in the MCTDH method [71, 48]. In the general formulation, the total Hamiltonian for the rotating-vibrating MgH^+ molecule that consists of four electronic states can

be written as

$$H(t) = \left[-\frac{1}{2M_r} \frac{\partial^2}{\partial R^2} + \frac{J^2}{2M_r R^2} \right] \mathbf{1} + \begin{pmatrix} V_X & 0 & 0 & 0 \\ 0 & V_A & 0 & 0 \\ 0 & 0 & V_B & 0 \\ 0 & 0 & 0 & V_C \end{pmatrix} - E(t) \mathbf{D}(\theta), \quad (2.2.1)$$

where the matrix $\mathbf{D}(\theta)$ describes the interaction couplings between electronic states:

$$\mathbf{D}(\theta) = \begin{pmatrix} d_X \cos \theta & d_{XA} \cos \theta & d_{XB} \sin \theta & d_{XC} \cos \theta \\ d_{AX} \cos \theta & d_A \cos \theta & d_{AB} \sin \theta & d_{AC} \cos \theta \\ d_{BX} \sin \theta & d_{BA} \sin \theta & d_B \cos \theta & d_{BC} \sin \theta \\ d_{CX} \cos \theta & d_{CA} \cos \theta & d_{CB} \sin \theta & d_C \cos \theta \end{pmatrix}. \quad (2.2.2)$$

Here, M_r denotes the reduced mass, R represents the internuclear distance, J is the angular momentum operator, and V_X, V_A, V_B , and V_C represent the potential energy curves corresponding to the four electronic states (as illustrated in Figure 2.1 as $X^1\Sigma^+$, $A^1\Sigma^+$, $B^1\Pi$, and $C^1\Sigma^+$, respectively), or they can be denoted by X, A, B, and C, respectively, for the shorthand notation throughout the Thesis. The parameter θ represents the angle between the molecular axis and the polarization direction of the laser field, and $\mathbf{1}$ represents the identity matrix 4×4 . $d_n(R)$ denotes the permanent electric dipole moments and $d_{mn}(R)$ denotes the transition dipole moments between electronic states m and n ($m, n = X, A, B, C$). The electronic-structure data employed in this study were obtained from [44]. Since the B state is oriented perpendicular to the other relevant states (due to the Π state) and is energetically off-resonant, it is not expected to contribute significantly to the dynamics. However, for completeness, it is included in the general formulation. When the vibrating molecule is aligned with the polarization direction of the laser field, the rotational DOF and the B state can be neglected, leading to a simplified 3×3 Hamiltonian that describes the dynamics:

$$H(t) = \left[-\frac{1}{2M_r} \frac{\partial^2}{\partial R^2} \right] \mathbf{1} + \begin{pmatrix} V_X & 0 & 0 \\ 0 & V_A & 0 \\ 0 & 0 & V_C \end{pmatrix} - E(t) \begin{pmatrix} d_X & d_{XA} & d_{XC} \\ d_{AX} & d_A & d_{AC} \\ d_{CX} & d_{CA} & d_C \end{pmatrix}. \quad (2.2.3)$$

The TDSE written in Eq. 2.2.1 or 2.2.3 can be solved using the MCTDH method as expressed by Eqs. 1.4.14 and 1.4.15 (see for more details subsection 1.4.1). Within the MCTDH method, the primitive basis functions $\chi_{i_k}^{(k)}(R_k)$ are used to build the single-particle functions $\varphi_{j_k}^{(k)}(R_k, t)$ (Eq. 1.4.15), where the total wave function $\Phi(R, t)$ (Eq.

1.4.14) can be built by the time-dependent linear combinations of SPFs. The FFT-DVR (discrete variable representation) grid was used to describe the internuclear degree of freedom R , with N_R basis functions distributed over the range $R = 1.5\text{--}40$ a.u. The rotational degree of freedom θ is expanded in N_θ Legendre polynomials $P_J(\cos\theta)$ with $m = 0$ and $J = 0, 1, \dots, N_\theta - 1$. The θ DOF is not included in cases where only vibrational motion is considered. To achieve satisfactory convergence of the calculations, $N_R = 4096$ functions for the radial grid and $N_\theta = 91$ basis elements were used for the rotational degree of freedom. Moreover, for each electronic state, the SPFs were varied from $n_R = n_\theta = 1$ to 10 for both coordinates. The nuclear dynamics were propagated using the variable mean-field scheme of the MCTDH method, with time integration carried out by an Adams–Bashforth–Moulton predictor–corrector algorithm. An error tolerance of 10^{-7} and a time step of 10^{-4} fs were employed. To prevent spurious reflections and transmission artifacts, a CAP was introduced in the final 10 a.u. of the coordinate R :

$$-iW(R) = -i\eta |R - R_c|^b \Theta(R - R_c), \quad (2.2.4)$$

where the set of optimized parameters are $\eta = 6.67 \times 10^{-5}$, $b = 3$ and $R_c = R_{\max} - 10$ a.u., while $\Theta(x)$ represents the Heaviside step function. The limit of the radial grid was set at $R_{\max} = 40$ a.u, except for the simulations illustrated in Figure 2.3, where the grid was chosen as $R_{\max} = 1000$ a.u. Electronic state populations were determined from the propagated nuclear wave packets

$$p_n(t) = \langle \Phi_n(R, \theta, t) | \Phi_n(R, \theta, t) \rangle, \quad n \in \{X, A, B, C\}. \quad (2.2.5)$$

The probability of dissociation associated with the C state was identified with the absorbed portion of $p_C(t)$ defined by the CAP. According to the exact solution, the corresponding spectrum of the photofragments was then computed by using the CAP:

$$\sigma(\omega_\varepsilon) = \int_0^\infty dt \int_0^\infty dt' \langle \Phi(t) | W | \Phi(t') \rangle e^{-i\omega_\varepsilon(t-t')}. \quad (2.2.6)$$

2.3 Results and discussion

The time-dependent simulations described above provide a detailed view of the vibronic dynamics in the MgH^+ molecular ion. The results reveal characteristic signatures of coherent population transfer and Rabi-type oscillations, which can be traced to the strong coupling between the vibrational states of the $X^1\Sigma^+$ and $A^1\Sigma^+$ electronic states. In this

section, the results are presented in four parts: (1) the vibrating molecule; (2) the applied model; (3) the frequency dependence of the excitation; and finally, (4) the inclusion of rotational motion.

2.3.1 Vibrating molecule

First, the MgH^+ molecule is considered in its lowest vibrational state $\nu = 0$ of the X ground state. The applied laser pulse couples this vibrational state (of X) with the one $\nu = 0$ of the first excited electronic state A . To induce efficient one-photon Rabi oscillations between these two selected vibronic levels, the Gaussian laser parameters (Eq. 2.1.2) must be selected carefully. By choosing a pulse duration of $T = 500$ fs and a carrier frequency $\omega = \omega_A(\nu = 0) - \omega_X(\nu = 0) \approx 4.2868$ eV, a resonant coupling is achieved between the lowest vibrational levels of the electronic state X and A . In contrast, the transfer of the population to other bound levels remains negligible owing to the long pulse duration $T = 500$ fs. The resulting pulse bandwidth, $4\sqrt{\ln 2}/T \approx 4.4 \times 10^{-3}$ eV, is sufficiently narrow to excite the system's selective vibronic levels strongly. This narrow-band excitation further enables a minimal-level description and analytical study (details will be presented below). The time evolution of the dissociation process can be obtained by numerically solving the TDSE (with the Hamiltonian in Eq. (2.2.3) for the vibrating molecule). Figure 2.2(a) shows multiple Rabi oscillations between the X and A states for peak intensities in the range $I_0 \approx 2 \times 10^9 - 1 \times 10^{11}$ W/cm², where the vertical red arrows identify the peak intensities associated with the complete one to five Rabi oscillations, arranged from left to right. The corresponding energy spectra of the photofragments, calculated exactly at these peak intensities, are illustrated in Figure 2.2(b). For better visibility, the spectra were vertically offset. In Figure 2.2(b), several notable spectral features can be identified. The spectrum contains only one peak, corresponding to a single completed Rabi cycle, located symmetrically about the nominal position, as demonstrated by the lowermost trace in Figure 2.2(b). When the laser-molecule coupling becomes stronger, additional Rabi oscillations are completed, leading to increasingly structured spectra. When the system completes two Rabi oscillations ($I_0 = 1.6 \times 10^{10}$ W/cm², see the second curve from the bottom in Figure 2.2(b)), an Autler-Townes doublet becomes visible. This feature is asymmetric and slightly shifted to lower energies. Increasing the coupling (or intensity) leads to larger shifts, greater splittings, and greater asymmetry of the AT doublet. In addition, pronounced modulation patterns emerge with changes in spectral intensity. One of the primary objectives of this project is to supply an easy and explicit description of the spectral features obtained in Figure 2.2(b) and to link these spectral fingerprints with the corresponding molecular dynamics. To further analyze the TDSE solution, we examine

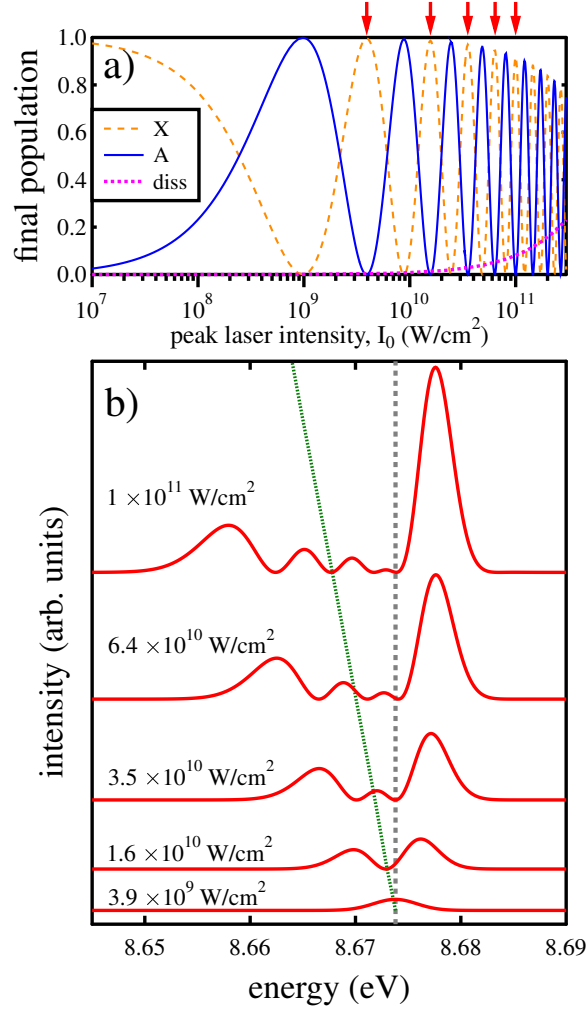


Figure 2.2: Enhanced photo-dissociation dynamics of MgH^+ is investigated. Panel (a) shows the final population probabilities of the X and A electronic states after the pulse is off, together with the system's total dissociation probability. Once a second photon is absorbed from the same laser pulse, the Rabi dynamics generated between the X and A states can start fading away, resulting in enhanced photo-dissociation on C . The peak laser intensities are illustrated by the vertical red arrows at the top of the panel, corresponding to one to five complete Rabi cycles. In panel (b), spectra of the C electronic states are demonstrated for a variety of laser pulses corresponding to the completed Rabi cycles between the X and A electronic states' lowest vibrational levels, where resonant Gaussian laser pulses ($\omega = 4.2868$ eV, $T = 500$ fs) are used in the calculations. The nominal spectral positions are marked by a vertical dashed line: $\omega_{\varepsilon_0} = \omega_{X(\nu=0)} + 2\omega$, while the centers of the spectra are shown by the tilted green line.

the dissociating molecular wavepackets. To avoid the wave packets reaching the end of the grid that can be absorbed by the CAP, the simulations of Figure 2.2(b) are repeated on an extended internuclear grid ($R_{\text{max}} = 1000$ a.u.), as displayed in Figure 2.3.

By extending the spatial grid, we avoid losing any part of the wave packet during propagation, which allows its complete visualization after the laser interaction. As shown in Figure 2.3, the wave-packet densities dissociating that have been obtained after the pulse expires ($|\Phi_C(R, t = 3T)|^2$) reveal increasingly rich structures when the intensity of the laser pulse increases. When the intensity is low ($I_0 = 3.9 \times 10^9$ W/cm²), a single Rabi oscillation occurs, and the resulting wave packet shows only one dominant hump. At the next intensity ($I_0 = 1.6 \times 10^{10}$ W/cm²), two Rabi floppings are completed and, accordingly, the corresponding final wave packet exhibits two prominent humps in Figure 2.3. It can be seen that the number of humps in the density profiles in Figure 2.3 matches the number of Rabi cycles in Figure 2.2. It means that the process in which the system breaks apart into fragments can be regarded as stepwise. Each time the molecule undergoes Rabi cycling and reaches the A state, the molecules in the A state can be dissociated by absorbing an additional photon, thereby transferring them to the C state. As a result, fragment amplitudes populating the C state are created at different emission times, giving rise to the characteristic bumpy density profiles illustrated in Figure 2.3.

To explore this mechanism in more detail, we continue our analysis at an intensity that generates five Rabi cycles ($I_0 = 1 \times 10^{11}$ W/cm²). The time-dependent populations of the states and the corresponding time evolution of the spectrum, calculated for $I_0 = 1 \times 10^{11}$ W/cm², $T = 500$ fs, and $\omega = 4.2868$ eV, are demonstrated in Figure 2.4. As shown in Figure 2.4(a), the Rabi oscillations involve only the X ($\nu = 0$) and A ($\nu = 0$) vibronic levels, as noted earlier. The populations of the remaining vibrational states associated with both electronic states X and A are practically negligible. As indicated by the blue curve, the population of the C state grows in a stepwise fashion at moments t_s ($s = 1, 2, 3, 4, 5$), because the population of the A state ($\nu = 0$) reaches its utmost, as illustrated by the vertical dashed lines in Figure 2.4(a). Since some of the population in the C state is moved back to the A state in each Rabi oscillation, the stepwise growth is not monotonic. These backtransfers are less effective than forward transfers, due to the rapidly rising character of the potential $V_C(R)$ near the Franck-Condon (FC) region, which quickly initiates dissociation. Thus, the overall population of the C state gradually builds up. The dissociation probability, defined as the fraction of $p_C(t)$ absorbed by the CAP, therefore, grows almost monotonically, as demonstrated by the light-blue curve in Figure 2.4(a). It exhibits five ramp-ups corresponding to the five dissociation bursts and converges to a final value of approximately 9%. The dissociation's five ramp-ups are time-delayed relative to the t_s moments of the Rabi floppings since the fragment amplitudes

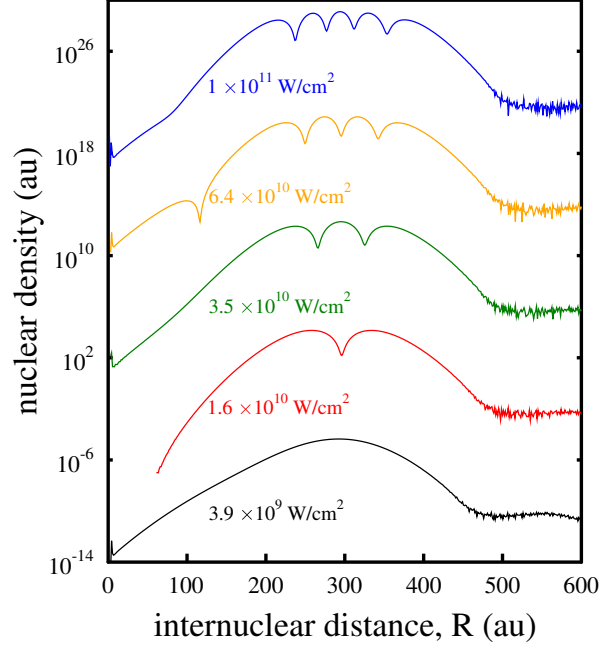


Figure 2.3: Final internuclear wave-packet density distributions of the MgH^+ molecule in the dissociative C state, calculated with the help of the same laser parameters applied in Figure 2.2(b). To prevent the CAP from absorbing the dissociating wave packets, a large internuclear grid with $R_{\text{max}} = 1000$ a.u. is used in these simulations. As the peak laser intensity goes up, one to five notable humps emerge in the nuclear density profiles (ordered from bottom to top). Each hump corresponds to a fragment amplitude produced during a specific Rabi flopping; hence, the number of humps directly depends on the number of complete Rabi oscillations. For clarity, the densities of the individual wave packets are vertically separated by successive multiplications by 10^8 .

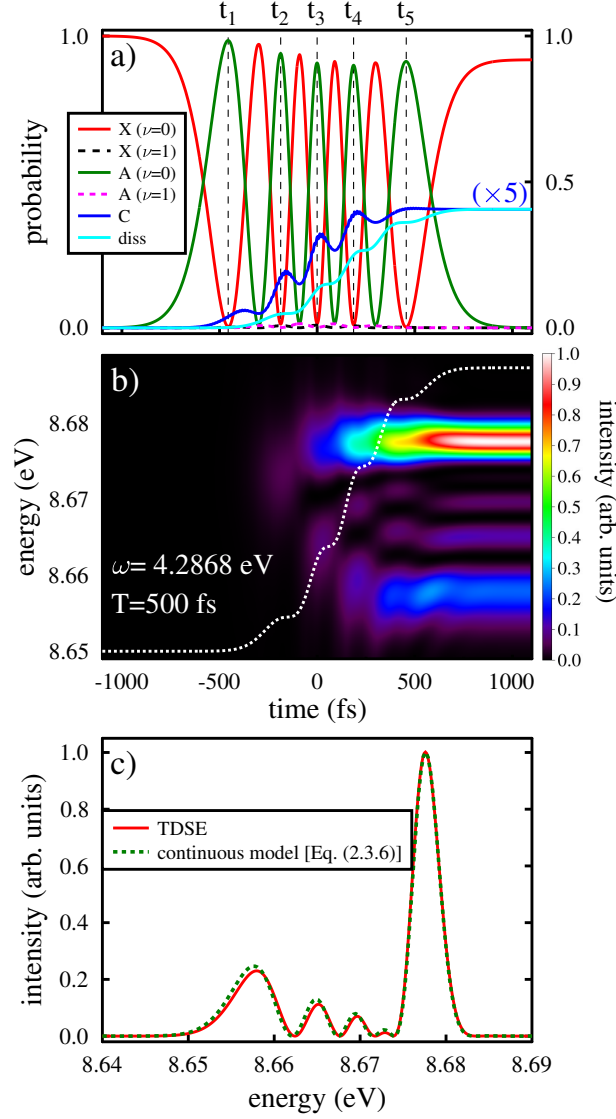


Figure 2.4: (a) Time evolution of vibrational level populations of the MgH^+ molecule, demonstrating five Rabi cycles occurring between the $X (\nu = 0)$ and $A (\nu = 0)$ vibronic levels. The same laser parameters as in Figs. 2.2(b) and 2.3 are used. The light-blue curve shows the dissociation probability of the C -state population absorbed at the end of the CAP region ($R \gtrsim 30$ a.u.). The blue and light-blue curves are scaled by a factor of 5. (b) Time-dependent spectra showing a multipeak structure arising from fragment amplitudes released at distinct times t_s ($s = 1, 2, \dots, 5$). Panel (c) shows the final spectra obtained from interference between different emission times, comparing TDSE results with the analytical model (Eq. 2.3.6).

dissociating require about 200 fs to go to the CAP located at $R_c = 30$ a.u. after being produced around the FC point. The time dependence of the spectrum in Figure 2.4(b) illustrates that the final multipeak structure develops gradually. Each fragment amplitude is created at a different time t_s and reaches the CAP only after an unavoidable time delay (because of the Rabi oscillations). In the first stage, when only the first fragment amplitude has arrived (around $t \approx -300$ fs), the spectrum possesses a single peak and is centered near the nominal spectral position 8.6738 eV. When the second amplitude of the fragment has arrived (around $t \approx -100$ fs), the spectrum splits into two peaks, evolves asymmetrically and shifts toward lower energies. When the subsequent fragment amplitudes reach the CAP, the spectrum becomes increasingly complex due to those fragment amplitudes. Once all of them have arrived, the final multipeak structure — demonstrated by the solid red curve in Figure 2.4(c) — is fully formed. The weakest peak, located near the main peak at approximately 8.672 eV, is barely visible on the color map because of its lower intensity. However, it is clearly identified in the final curve in Figure 2.4(c).

2.3.2 Model applied to a vibrating molecule

To obtain a deeper understanding of the spectral features calculated in the TDSE simulations, we derive the spectrum analytically using the decoupled resonance framework [80]. Our analysis starts with the minimal effective model, equations 1.4.35.a, 1.4.35.b and 1.4.35.c, presented in subsection 1.4.2. Within this model, the dynamics of the coupled levels via resonance $|l\rangle$ and $|u\rangle$, including the influence of the AC Stark shifts, are given by the Hamiltonian:

$$H_{\text{res}}(t) = \begin{pmatrix} \omega_l^{(S)}(t) & \Omega^\dagger(t) \\ \Omega(t) & \omega_u^{(S)}(t) - \frac{i}{2}\Gamma(t) \end{pmatrix}. \quad (2.3.1)$$

Due to the lossy term $-\frac{i}{2}\Gamma(t)$, which is associated with the dissociation from the intermediate state $|u\rangle$, Eq. 2.3.1 leads to two decoupled resonances, $|+\rangle$ and $|-\rangle$, each being a superposition of the field-free eigenstates of the molecule. Assuming that the dissociation process remains well below the saturation threshold, i.e. $|\Omega(t)| \gg |\frac{1}{2}\Gamma(t)|$, the corresponding time-varying energies and wave functions associated with these resonances

are determined by diagonalizing $H_{\text{res}}(t)$:

$$E_{\pm} \simeq \Sigma(t) \pm \Omega_R(t) - \frac{i}{4}\Gamma(t), \quad (2.3.2a)$$

$$|-\rangle \simeq \frac{1}{\sqrt{1 + \lambda_-(t)^2}} [|l\rangle + \lambda_-(t) |u\rangle], \quad (2.3.2b)$$

$$|+\rangle \simeq \frac{1}{\sqrt{1 + \lambda_+(t)^2}} [|l\rangle + \lambda_+(t) |u\rangle], \quad (2.3.2c)$$

$$\lambda_{\pm}(t) = \frac{\delta_{\omega}^{(S)}(t) \pm \Omega_R(t)}{\Omega(t)}, \quad (2.3.2d)$$

where the relative Stark shift $\delta_{\omega}^{(S)}(t) = \frac{1}{2}[\omega_u^{(S)}(t) - \omega_l^{(S)}(t)]$ has been introduced, the sum of the Stark shifts $\Sigma(t) = \frac{1}{2}[\omega_l^{(S)}(t) + \omega_u^{(S)}(t)]$, and the generalized Rabi frequency related to the the Stark shifts, $\Omega_R(t) = \sqrt{\Omega(t)^2 + \delta_{\omega}^{(S)}(t)^2}$. It can be seen that the resonance energies split significantly when the pulse is on, and then split slightly as the pulse starts decaying. The resulting energy splitting is asymmetric owing to the $\Sigma(t)$ term. In the ideal restrict [$\Sigma(t) = \delta_{\omega}^{(S)}(t) = 0$, $|\lambda_{\pm}(t)| = 1$] (where the Stark shifts vanish) is applied, the resulting resonance states can be an equally weighted superposition of $|l\rangle$ and $|u\rangle$ with a symmetric splitting of the energy levels. However, in general, retaining the dynamical level shifts in the expressions is essential for accurately describing the spectral shape. To continue our analysis, we construct the time-dependent amplitudes of the resonance states, employing the initial condition $c_{\pm}(t \rightarrow -\infty) = 1/\sqrt{2}$ and the energy relation presented in Eq. 2.3.2a:

$$c_{\pm}(t) = \frac{1}{\sqrt{2}} e^{-iF_{\pm}(t)}, \quad (2.3.3)$$

with

$$F_{\pm}(t) = \int_{-\infty}^t E_{\pm}(t') dt'.$$

Using Eqs. 2.3.2b - 2.3.2c, $|u\rangle$ can be expressed and substituted into Eq. 2.3.3, one finds the time-dependent intermediate state amplitude:

$$c_u(t) = \frac{1}{\sqrt{8}} \frac{\Omega(t)}{\Omega_R(t)} \left[\sqrt{1 + \lambda_+(t)^2} e^{-iF_+(t)} - \sqrt{1 + \lambda_-(t)^2} e^{-iF_-(t)} \right]. \quad (2.3.4)$$

Using Eq. 2.3.4, the quantity $c_{\varepsilon}(t)$ in Eq. 1.4.35.c (see [79]) and the spectrum defined by $\sigma(\omega_{\varepsilon}) = |c_{\varepsilon}(t \rightarrow \infty)|^2$ can be calculated by using the minimal effective model:

$$\sigma(\omega_\varepsilon) = \frac{1}{8} \left| \int_{-\infty}^{\infty} \frac{\Omega(t) \chi(t)}{\Omega_R(t)} e^{I(t)} \left[\sqrt{1 + \lambda_+(t)^2} e^{i[\delta t + Q(t) - R(t)]} - \sqrt{1 + \lambda_-(t)^2} e^{i[\delta t + Q(t) + R(t)]} \right] dt \right|^2. \quad (2.3.5)$$

In Eq. 2.3.5, the (temporal) integrals $Q(t) = \int_{-\infty}^t [\omega_\varepsilon^{(S)}(t') - \sum(t')] dt'$, $R(t) = \int_{-\infty}^t \Omega_R(t') dt'$, and $I(t) = -\frac{1}{4} \int_{-\infty}^t \Gamma(t') dt'$ are presented. The δ detuning of one photon introduced in Eq. 1.4.30 measures how far ω_ε lies from the spectral center $\omega_{\varepsilon_0} = \omega_l + 2\omega$, where $\delta = \omega_\varepsilon - \omega_{\varepsilon_0}$. On the right side of Eq. 2.3.5, not only the detuning δ but also the Rabi frequency, $\chi(t)$ between bound and continuum states depends on ε . In the regime here $\Gamma(t)$ is negligibly small, the spectrum computed from Eq. 2.3.5 becomes identical to that obtained from Eqs. 1.4.35.a - 1.4.35.c. For this reason, we proceed our investigation with the three-level model that can give us the analytical estimation of the spectrum. When the Stark shifts are not too significant [as in the present case, where $|\Omega(t)| \gg |\delta_\omega^{(S)}(t)|$], their contribution to the prefactors of Eq. 2.3.5 might be neglected ($\lambda_\pm(t)^2 \rightarrow 1$). However, it is essential to keep the Stark shifts within the complex exponential terms to accurately capture the spectral shape. With this simplification, together with the identity $\sin(x) = (e^{ix} - e^{-ix})/(2i)$, we obtain

$$\sigma(\omega_\varepsilon) = \left| \int_{-\infty}^{\infty} \frac{\Omega(t) \chi(t)}{\Omega_R(t)} e^{I(t)} e^{i[\delta t + Q(t)]} \sin[R(t)] dt \right|^2. \quad (2.3.6)$$

In the physical situation considered here, Eqs. 2.3.6 and 2.3.5 produce spectra that agree to graphical precision. However, when the Stark shifts become significant, Eq. 2.3.5 provides a more accurate description. As demonstrated in Fig. 2.4(c), the spectrum computed from Eq. 2.3.6 (referred to here as the continuous model from now on) shows agreement with the TDSE results nicely. This simple expression captures the main characteristics, including multippeak structure, peak splitting, shifts, and asymmetry.

A further simplification of Eq. 2.3.6 is possible. This is based on the observation that the Rabi frequencies $\Omega(t)$, $\chi(t)$, and $\Omega_R(t)$, together with the dissociation rate $\Gamma(t)$ appearing within $e^{I(t)}$, vary only slowly in time, since they evolve following the pulse envelope. Moreover, because the Stark shifts (and therefore $Q(t)$) remain moderate, and $|\delta|$ is small near the spectrum's center, the integrand in Eq. 2.3.6 consists of slowly varying terms multiplied by $\sin[R(t)]$. Under the laser parameters considered here, $R(t)$ accumulates a total phase of $5.058 \times \pi$ radians by the end of the pulse. Consequently, $\sin[R(t)]$ develops five extrema at the time instants t_s satisfying $\sin[R(t_s)] = \pm 1$.

The integral is mainly governed by contributions associated with the stationary points t_s . A Gaussian laser pulse allows the stationary moments to be determined analytically by neglecting the Stark shift $\delta\omega^{(S)}(t)$ in $R(t)$. This leads to $t_s \approx T \operatorname{erf}^{-1} \left[\frac{2(2s-1)\sqrt{\pi}}{\mu_{tu}E_0T} - 1 \right]$, ($s = 1, 2, 3, 4, 5$), where erf^{-1} represents the inverse error function. According to the definition of the model, these time moments t_s correspond exactly to the times when the intermediate state population given by Eq. 2.3.4 reaches its maxima: $|c_u(t)|^2 \sim \sin^2[R(t)]$. In addition, these values have a nice agreement with those obtained from the TDSE calculations for the peak population of the intermediate state (see the top panel of Figure 2.4). As the five stationary contributions at t_s ($s = 1, 2, \dots, 5$) are gathered within the integral in Eq. 2.3.6, the following approximate form of the spectrum is determined as

$$\sigma(\omega_\varepsilon) \simeq \sum_{s=1}^N (-1)^{s-1} \frac{\Omega(t_s)}{\Omega_R(t_s)} \chi(t_s) e^{I(t_s)} e^{i[\delta t_s + Q(t_s)]}. \quad (2.3.7)$$

Here, N denotes the total number of extrema of $\sin[R(t)]$, which is equivalent to the number of Rabi floppings completed in the system (namely, $N = 5$ considered here). As illustrated in Figure 2.5(a), the straightforward analytical expression in Eq. 2.3.7 (referred to as the discrete model from now on) is still able to reproduce the main characteristics of the spectrum, which are the multi-peak pattern as well as the observed shifts, splittings, and asymmetry - obtained by TDSE calculations. Even though the smallest peak near 8.672 eV is not exactly reproduced, a weak remnant of it is visible on the left side of the dominant peak, close to the expected nominal position illustrated by the vertical solid line. When the Stark shifts vanish ($Q(t) = 0$ and $|\Omega(t)/\Omega_R(t)| = 1$), and the bound-to-continuum dipoles $\chi(t)$ becomes independent of the energy ($\chi(t) = -\frac{1}{2}\mu_{\varepsilon_0u}E_0g(t)$), the spectrum becomes symmetric around ω_{ε_0} and Eq. 2.3.7 captures the spectral features even more closely (see Figure 2.5(b)). Equation 2.3.7 helps clarify the physical mechanism behind the multi-peak spectrum pattern. The strong variations in the spectrum originate from the coherent superposition of dissociating wave-packet amplitudes produced during the individual Rabi cycles. When the intermediate state reaches its maximum population, dissociation can occur. The number of spectral peaks directly illustrates how many Rabi oscillations the system completes. The molecular energy levels' Stark shifts lead to an overall shifting of the spectrum (through $\Sigma(t)$ and $\omega_\varepsilon^{(S)}(t)$) and also influence the splitting through $\Omega(t)$ inside $R(t)$. Because $\omega_{l0}^S = -4.8$ meV and $\omega_{u0}^S = -5$ meV are negative, while $\omega_{\varepsilon_0}^S = 3.1$ meV is positive, the resulting spectrum is shifted to slightly lower energies in relation to ω_{ε_0} . Because $\delta\omega_\omega^S(t)$ is small, the splitting determined by $\Omega_R(t)$ is only weakly affected. The overall asymmetry of the spectrum arises from the combined effects of the Stark shifts and the bound-to-continuum dipole moments that depend on energy.

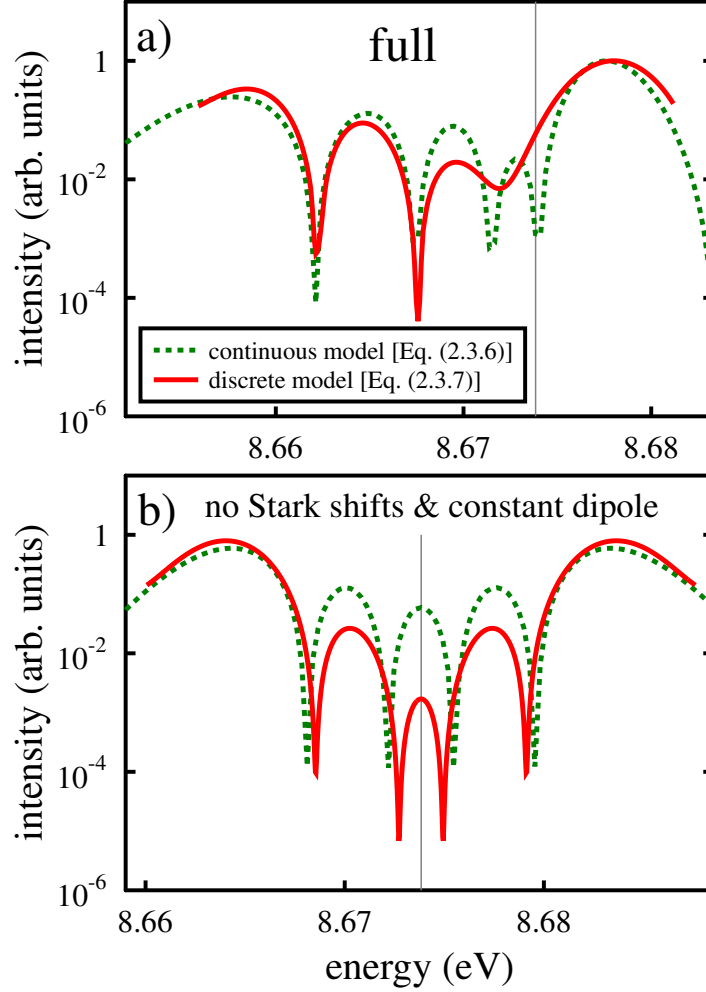


Figure 2.5: Energy spectra of the MgH^+ molecule calculated using the continuous analytical model (Eq. 2.3.6) and the discrete analytical model (Eq. 2.3.7), under identical laser conditions to those used in Figure 2.4 ($I_0 = 1 \times 10^{11} \text{ W/cm}^2$, $T = 500 \text{ fs}$, $\omega = 4.2868 \text{ eV}$). Although the discrete model is pictorial, it accurately reproduces the multipeak structure of the spectrum, demonstrating that the five peaks arise from the time-dependent interference of wave-packet amplitudes formed during the five Rabi oscillations. Panel (a) includes the Stark shifts and the energy dependence of the A–C nuclear dipoles. In panel (b), both of these effects are excluded in the present treatment. The nominal spectral position is represented by the vertical lines: ($\omega_{\varepsilon_0} = \omega_{X(\nu=0)} + 2\omega$). The dashed green spectrum in panel (a) is equal to the dashed green spectrum in Figure 2.4(c); the axis scales differ.

2.3.3 Vibrational-state-dependent dissociation

According to the previous subsection, we note that applying slightly modified photon energies leads to significantly different Rabi dynamics in the vibrating MgH^+ molecule. Figures 2.6(a) and 2.6(b) illustrate that dipole couplings between the vibronic state $A(\nu)$ and the electronic manifold C do not follow a monotonic behavior. The vibrational transition dipole moments reflect the structure of the $A(\nu)$ wavefunctions, featuring $\nu + 1$ peaks and ν nodes. Such behavior is expected to lead to substantial variations within the dissociation probability. For the resonant photon energy $\omega = 4.286$ eV, as discussed up to this point, the strength of the bound-to-continuum dipole is relatively small, as illustrated in Figure 2.6(a), near the crossing between the dipole curve and the vertical line. This weak coupling accounts for the low dissociation probabilities shown in Figure 2.2(a). Even after several Rabi floppings, the dissociation probability remains low. However, When the photon energy is adjusted to be resonant with the $X(\nu = 0) \rightarrow A(\nu = 1)$ pathway, $\omega = \omega_{A(\nu=1)} - \omega_{X(\nu=0)} = 4.422$ eV, the strength of the bound-to-continuum dipole increases by a factor of approximately 13, as shown in Figure 2.6(b) near the vertical line. This demonstrates that the dissociation yield becomes considerably higher at $\omega = 4.422$ eV. To show how strongly the dissociation yield depends on the photon energy, we have used weak Gaussian-shaped pulses ($T = 500$ fs, $I_0 = 1 \times 10^8$ W/cm²) to simulate the (1+1) photon-dissociation dynamics for various values of ω . As demonstrated in Figure 2.6(c), the vibronic excitation probabilities of $X(\nu = 0) \rightarrow A(\nu)$ follow the FC distribution, while the associated probabilities of dissociation show abrupt jumps, as shown in Figure 2.6(d). Sudden changes in the dissociation probability come from the non-monotonic behavior of the dipole couplings between the bound and continuum states. In particular, the resonant pathway via the $A(\nu = 1)$ state is more than two orders of magnitude stronger than the pathway via $A(\nu = 0)$. That is why the probability of dissociation near $\nu = 0$ in Figure 2.6(d) is extremely small, as marked by the vertical arrow. To reveal this difference, we keep the same laser as presented in Figure 2.4, but use a different photon energy that is resonant with the $X(\nu = 0) \rightarrow A(\nu = 1)$ transition, where $\omega = 4.422$ eV. Since the bound-to-continuum coupling is very strong in the $X(\nu = 0) \rightarrow A(\nu = 1)$ transition, the Rabi cycles between vibrational levels of the electronic states $X(\nu = 0)$ and $A(\nu = 1)$ are already fully damped on the rising edge of the pulse. As a result, dissociation becomes highly efficient, as demonstrated in Figure 2.7(a). Because roughly two Rabi oscillations are generated in Figure 2.7(a), the related spectrum in Figure 2.7(b) reveals two pronounced peaks.

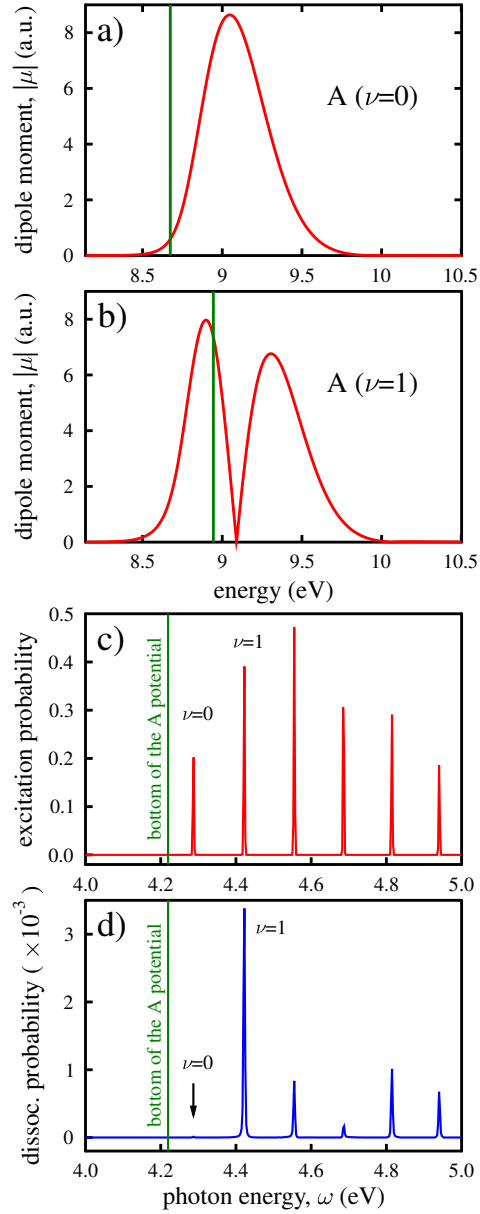


Figure 2.6: (a) illustrates dipole coupling between the vibronic state $A(\nu = 0)$ and the C-state manifold, whereas (b) demonstrates dipole coupling between the vibronic state $A(\nu = 1)$ and the C-state. The vertical (green) lines represent the nominal spectral positions corresponding to photon energies tuned to the resonance with transitions $X(\nu = 0) \rightarrow A(\nu)$. In panel (c), how the excitation probability of the A electronic state changes with photon energy is shown, while panel (d) shows the associated dissociation probability in the C electronic state, calculated for $T = 500$ fs and $I_0 = 1 \times 10^8$ W/cm². The vertical arrow in panel (d) shows that the quantities of the dissociation from A ($\nu = 0$) are roughly 300 times less compared to A ($\nu = 1$).

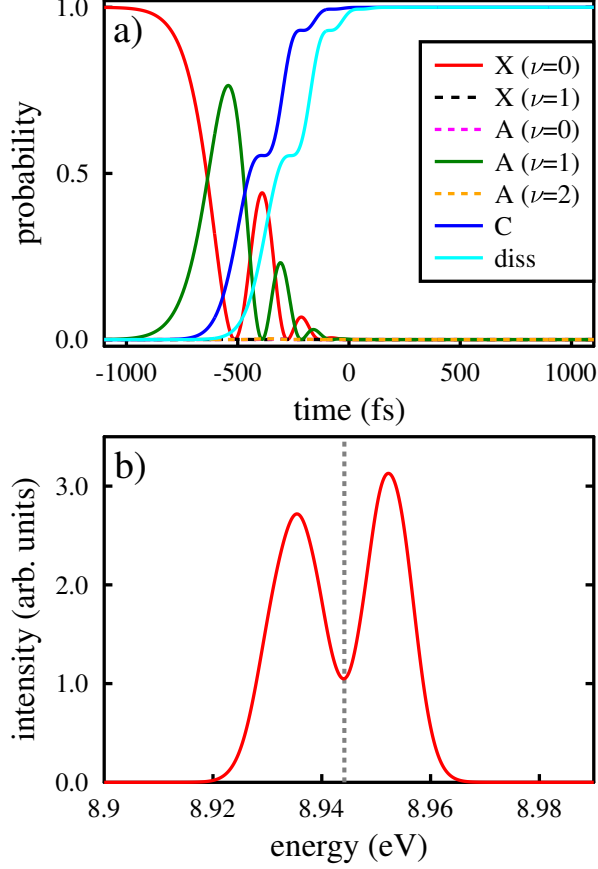


Figure 2.7: Panel (a) shows the time evolution of the state populations of the MgH^+ molecule, calculated with the same pulse duration and intensity presented in Figure 2.4 ($I_0 = 1 \times 10^{11} \text{ W/cm}^2$, $T = 500 \text{ fs}$), but the photon energy tunes to resonantly couple the vibrational levels of electronic states $X(\nu = 0)$ and $A(\nu = 1)$, $\omega = 4.422 \text{ eV}$. Since the dipole interaction between the vibronic state $A(\nu = 1)$ and the manifold of C is strong (in Fig. 2.6(b)), dissociation occurs with high efficiency during the pulse's rising edge ($t < 0$). As a result, the Rabi floppings are thoroughly damped at the pulse maximum ($t = 0$), and the falling edge of the pulse produces no additional fragment amplitude ($t > 0$). Panel (b) shows that the spectrum possesses two distinct peaks corresponding to nearly two Rabi oscillations, as observed in panel (a), where the nominal spectral position $\omega_{\varepsilon_0} = \omega_{X(\nu=0)} + 2\omega$ is shown by the vertical dashed line.

2.3.4 Rotating-vibrating molecule

The spectral characteristics analyzed so far are also observed in the spectrum of a dynamically rotating-vibrating molecule, which includes both rotational and vibrational degrees of freedom. To show this, we simulate the nuclear dynamics by solving the two-dimensional (2D) TDSE using Eq. 2.2.1. To demonstrate this, we explore the nuclear dynamics by solving the 2D TDSE with Eq. 2.2.1, applying the same laser parameters as in the previous analysis: $I_0 = 1 \times 10^{11} \text{ W/cm}^2$, $T = 500 \text{ fs}$, and $\omega = 4.2868 \text{ eV}$. In order to remain consistent with the theoretical framework used so far, it is initially assumed that the molecule occupies the $\nu = 0$ vibrational state and the $J = 1$ rotational level of the X ground electronic state. This selection of $J = 1$ allows us to assume a partial alignment of the molecule with respect to the laser polarization because the probability of the density of the corresponding Legendre polynomial takes large values near $\theta = 0$ and π , while vanishing at $\theta = \pi/2$. However, the state B is also included in Eq. 2.2.1, which is perpendicular to the other states, since a noticeable portion of the population may be transferred to it during dynamical rotation of the system. The results taken from the 2D TDSE calculation are illustrated in Figure 2.8. Under these conditions, approximately four Rabi oscillations are generated between the electronic states X and A , rather than five (due to the fact that the effective intensity felt by the molecule is reduced compared to the 1D perfectly aligned situation). The population of the B state is negligible. Compared with the purely vibrating molecule presented in Figure 2.4(a), the contrast of the oscillations is significantly reduced. These differences in the dynamics of one-dimensional and two-dimensional populations arise from the presence of an additional angular coordinate, θ , which introduces rotational motion and, consequently, rotational states. Because the bandwidth of the applied pulse is considerably wider than the energy spacing between adjacent J levels, the population can be distributed among these states. We note that the amount of rotational excitation in all electronic states remains moderate during the dynamics ($J_{\text{max}} < 8$). Despite these distinctions, the energy spectrum distribution of the (dissociating) fragments presented in Figure 2.8 (b) retains the same qualitative features observed and explained for the vibrating molecule in Figure 2.4(c). Since the molecule completes four Rabi oscillations, four fragment amplitudes are generated, and the resulting spectrum accordingly includes four distinct peaks. The contrast of these peaks is reduced compared with that of a purely vibrating molecule. An interesting question is how the dissociation dynamics and the corresponding spectra discussed in this work respond to changes in other laser parameters, such as the pulse duration T , when these parameters are varied. With longer pulses, the very narrow spectral width enables selective population transfer between distinct rovibrational levels, making it possible to characterize the

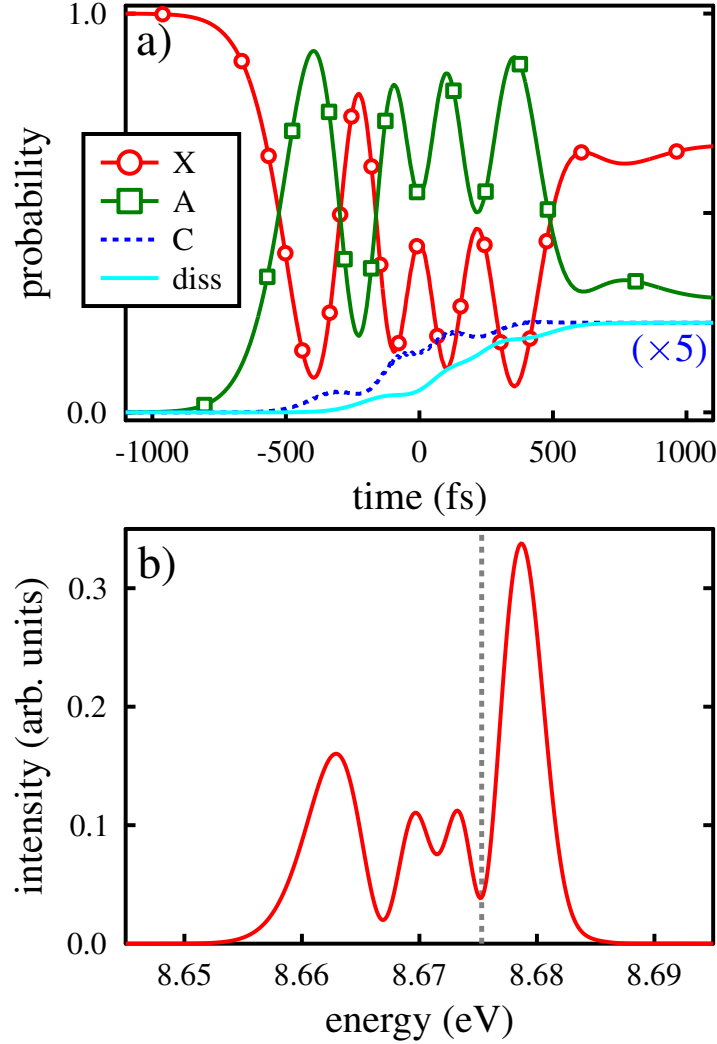


Figure 2.8: (a) Electronic state populations as a function of the propagation time of the rotating-vibrating MgH^+ system are shown, where the same laser parameters are used (as shown in Figure 2.4) utilizing the exact method (MCTDH). Starting from the $X(\nu = 0, J = 1)$ level, the molecule executes roughly four Rabi floppings between electronic states X and A . These floppings generate four fragment amplitudes at distinct times, which are captured by the population of the C state and by the dissociation curves, where their quantities are multiplied by a factor of five to improve visibility. (b) The spectrum computed from the exact model in 2D demonstrates four peaks, consistent with the Rabi floppings in panel (a). The nominal spectral position is shown by the vertical dashed arrow. $\omega\varepsilon_0 = \omega_{X(\nu=0, J=1)} + 2\omega$.

resulting spectrum and its underlying dynamics. In contrast, for shorter pulses, more vibrational states are expected to participate, resulting in a considerably more complex spectral structure. We anticipate that the analysis presented here will provide an essential foundation for studying both of these regimes.

2.3.5 Nuclear dipole matrix elements of MgH^+

Within the X, A, B, and C electronic manifolds of MgH^+ , the nuclear (vibrational) dipole operator can be expressed in a block-matrix form. This structure distinguishes vibrational couplings within a single electronic state from those connecting vibrational levels belonging to different electronic states. Accordingly, the diagonal blocks describe couplings internal to each electronic state, while the off-diagonal blocks contain transition dipole couplings linking states of different electronic manifolds. The dipole matrix can be written as:

$$\boldsymbol{\mu} = \begin{bmatrix} \mu^{(X)} & \mu^{(XA)} & \mu^{(XB)} & \mu^{(XC)} \\ \mu^{(AX)} & \mu^{(A)} & \mu^{(AB)} & \mu^{(AC)} \\ \mu^{(BX)} & \mu^{(BA)} & \mu^{(B)} & \mu^{(BC)} \\ \mu^{(CX)} & \mu^{(CA)} & \mu^{(CB)} & \mu^{(C)} \end{bmatrix}. \quad (2.3.8)$$

Here, each block contains dipole matrix elements between the vibrational states of the corresponding electronic potentials. The diagonal block elements $\mu_{ij}^{(K)}$ are determined from the permanent electric dipole moment function $d_K(R)$ via $\mu_{ij}^{(K)} = \langle i | d_K | j \rangle$, where $K = X, A, B, C$. Transition dipole couplings between different electronic states are obtained using the functions $d_{KL}(R)$, $\mu_{ij}^{(KL)} = \langle i | d_{KL} | j \rangle$, where $K, L = X, A, B, C$. Since the photon energy used in the present work is resonant with the $X \rightarrow A$ and $A \rightarrow C$ transitions, and because of the perpendicular direction of the B state with these dipole-allowed pathways, the terms $\mu^{(XA)}$ and $\mu^{(AC)}$ in Eq. 2.3.8 play the dominant role. Representative absolute values of the relevant $\mu_{ij}^{(XA)}$ dipole matrix elements (in atomic units) are given in Table 2.1 below:

Here, the rows i represent indexing over the vibrational states of the X ground electronic state ($i = 0, 1, 2, \dots, 16$), whereas the column indices j run over the vibrational states of the A excited electronic state ($j = 0, 1, 2, \dots, 14$). The dipole couplings between $A^1\Sigma^+$ and $C^1\Sigma^+$ are also of great interest, as they show how the excited-state dissociation is influenced by the resonance enhancement.

As demonstrated by the figure 2.9, the coupling strength strongly depends on which initial vibrational state of A is coupled to the C manifold during the (1+1) photon dissociation process. (It should be noted that the first photon starts from the initial $\nu = 0$ level of X to the individual vibrational level in all cases in Fig. 2.9). For example, reso-

Table 2.1: Transition dipole matrix elements $\mu_{ij}^{(XA)}$ between the vibrational levels of the X and A electronic states (in atomic units).

0.514	0.729	0.778	0.717	0.603	0.477	0.362	0.265	0.190	0.134	0.094	0.066	0.046	0.032	0.022
0.944	0.775	0.322	0.102	0.380	0.507	0.523	0.476	0.401	0.322	0.250	0.190	0.142	0.105	0.078
1.120	0.142	0.514	0.610	0.373	0.054	0.207	0.364	0.428	0.426	0.386	0.330	0.272	0.218	0.173
0.961	0.686	0.631	0.003	0.437	0.507	0.337	0.090	0.128	0.275	0.350	0.369	0.352	0.315	0.272
0.603	1.091	0.162	0.665	0.351	0.135	0.413	0.431	0.286	0.089	0.088	0.214	0.285	0.312	0.308
0.260	0.899	0.993	0.211	0.499	0.502	0.125	0.228	0.389	0.365	0.237	0.079	0.061	0.163	0.224
0.061	0.431	1.074	0.847	0.411	0.293	0.511	0.290	0.045	0.278	0.354	0.307	0.196	0.072	0.035
0.003	0.086	0.545	1.183	0.745	0.481	0.121	0.453	0.367	0.097	0.153	0.290	0.311	0.255	0.165
0.005	0.021	0.067	0.588	1.264	0.733	0.459	0.001	0.378	0.383	0.186	0.044	0.206	0.273	0.265
0.001	0.008	0.052	0.010	0.539	1.321	0.826	0.361	0.079	0.318	0.364	0.231	0.035	0.125	0.214
0.000	0.004	0.003	0.082	0.143	0.363	1.318	1.016	0.179	0.148	0.294	0.325	0.244	0.083	0.059
0.000	0.000	0.009	0.021	0.074	0.292	0.034	1.159	1.241	0.102	0.251	0.329	0.263	0.242	0.102
0.000	0.001	0.004	0.006	0.058	0.018	0.352	0.406	0.720	1.346	0.455	0.433	0.463	0.147	0.248
0.000	0.000	0.001	0.008	0.019	0.061	0.182	0.165	0.736	0.033	1.069	0.702	0.662	0.724	0.089
0.000	0.000	0.000	0.005	0.001	0.052	0.044	0.244	0.281	0.544	0.729	0.286	0.490	0.667	0.986
0.000	0.000	0.000	0.003	0.004	0.031	0.007	0.172	0.036	0.488	0.212	0.584	0.379	0.181	0.055
0.000	0.000	0.000	0.001	0.003	0.016	0.014	0.096	0.024	0.293	0.016	0.417	0.142	0.042	0.203

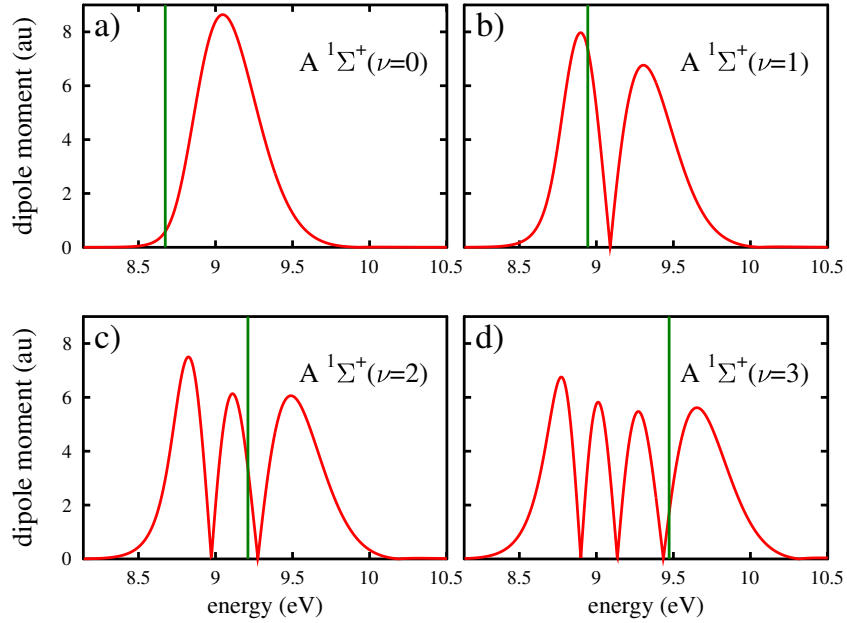


Figure 2.9: Nuclear transitional dipole moments between the vibrational levels $\nu = 0, 1, 2, 3$ of electronic state A and the C -state manifold are shown in panels (a)-(d), respectively, where the initial state is set to $X^1\Sigma^+(\nu=0)$ in all cases of panels. Vertical green arrows indicate the nominal spectral positions when the transition is exactly resonant: $\omega_{X(\nu=0)} + 2 \times \omega_{\text{res}}$, where $\omega_{\text{res}} = \omega_{A(\nu)} - \omega_{X(\nu=0)}$ is the photon energy corresponding to the resonant transition.

nance enhancement via the $A^1\Sigma^+(\nu = 0)$ state is expected to result in small dissociation yields owing to the small nuclear coupling between the $A^1\Sigma^+(\nu = 0)$ and C manifold (Fig. 2.9(a)), whereas as resonance transition occurs between $X^1\Sigma^+(\nu = 0)$ and $A^1\Sigma^+(\nu = 1)$, we should expect large dissociation yields due to the significant nuclear coupling between the $A^1\Sigma^+(\nu = 1)$ and C manifold (Fig. 2.9(b)). This prediction is entirely consistent with Figure 2.7 as discussed. Put differently, as the transition occurs from the $A^1\Sigma^+(\nu = 1)$ level to the dissociative C state (Fig. 2.7), the wave packet has been absorbed by the CAP until $t < 0$ fs (generating only two Rabi oscillations) owing to the strong coupling (shown in Fig. 2.9(b)).

2.4 Conclusions

The MgH^+ molecule’s resonance-enhanced 1 + 1 photon-dissociation was examined by accurately solving the nuclear TDSE, and by a minimal-level model description. By explicitly computing the spectral photofragments analytically [Eq. 2.3.7], we were able to capture the underlying physical origin of all spectral characteristics identified by the accurate solution of the TDSE (Figure 2.5). The strong multi-peak structure in the spectrum results from temporal interference between amplitudes of the dissociating wave packets that are emitted in different Rabi cycles. Therefore, the number of spectral peaks in the spectrum of the dissociative electronic state directly corresponds to how many Rabi floppings the molecule undergoes in the bound electronic states. The Stark shifts of molecular states cause the spectrum to shift and also influence both the splitting and the asymmetry of the spectral profile. The analytical approach developed here for calculating the spectrum of emitted particles that probe the dynamics of the MgH^+ system is quite general. It may be applied to situations such as atomic or molecular ionization in strong laser fields, where electrons are emitted. By linking the spectral properties to the system’s dynamics via Eq. 2.3.7, one can probe the evolution of the system through measurements of the nuclear fragment energy spectrum, the photoelectron spectrum, or both. Given the availability of intense, ultrashort XUV radiation, inducing Rabi dynamics between widely separated electronic states in molecules should become feasible, making the present analysis relevant to such scenarios.

Chapter 3

Frequency dependence of photodissociation

In this chapter, the investigation of resonantly and off-resonantly enhanced two-photon dissociation of MgH^+ [81] will be continued using the same short, narrow-bandwidth Gaussian laser pulses as mentioned in section 2.1. When the photon wavelength is adjusted to the energy range of the intermediate electronic state possessing many vibrational levels ($\lambda = 200\text{--}300\text{ nm}$), the rich nuclear dynamics—including DI and Rabi cycles—become apparent. Solving the TDSE for the nuclei allows us to find signatures of these dynamical effects in the fragments’ energy spectrum. The nuclear dynamics is described within a three-state electronic manifold in the dipole approximation, and the TDSE is solved using the MCTDH method (detailed in subsection 1.4.1). The same potential energy curves and dipole (permanent and transition) moments, and the CAP (Eq. 2.2.4) (see the details in sections 2.1 and 2.2) are used for the calculations presented in this Chapter. Consequently, the Hamiltonian construction as described in Eq. 2.2.3 and wave-packet propagation will follow exactly the formulation given in section 2.2. I performed one- and two-dimensional MCTDH simulations of MgH^+ photodissociation for wavelengths in the region of the intermediate A state in order to calculate fragment spectra, state populations, and dissociation probabilities. In contrast, we use the multi-level model (section 1.4.2) (in which the wavefunction is expanded in the system’s eigenstate basis) to reproduce and compare results with those obtained by me from the exact solutions.

We observe that under exact resonance conditions, dissociation is governed by nuclear Rabi cycles, which dominate the resulting spectrum. In contrast, under off-resonant excitation, the dynamic interference among the amplitudes of the molecular fragments defines the shape of the spectrum. We reveal that the efficiency of off-resonance excitation depends on both intensity and pulse duration. In our second work [81], we aimed to distinguish

Rabi oscillations from dynamic interference by applying different wavelengths. To do that, we fixed the duration and intensity and chose them appropriately; additionally, further enhancing dissociation could help achieve this goal by adjusting the duration and/or intensity. In addition, we demonstrate that the dissociation yield can be controlled with remarkable efficiency because of the strong energy-dependent dipole couplings between the intermediate resonant states and the continuum. The Chapter consists of the following. First, I will discuss the developed N-level model. After that, we proceed to the results section, which covers resonant and off-resonant dissociation in 1D and 2D calculations, as well as asymmetric pulses. In addition, the effect of the PDM on the resonant and off-resonant dissociation will be discussed. At the end of the chapter, a conclusion will be given.

3.1 N-level model developed

To study how each vibrational level contributes to the overall spectral profile, we employ the multi-level vibrational model introduced and discussed in section 1.4.2. In the present Chapter, we simplify the multi-level model for all relevant vibrational states (in equation 1.4.31) of the bound and continuum electronic states to describe the two-photon dissociation process of the MgH^+ system using the short laser pulse with the Gaussian envelope function (Eq. 2.1.2). However, to keep the calculations practical, the state space was limited to the most relevant energy levels, namely the 17 lowest vibrational levels in the electronic state X and the 15 lowest levels in the electronic state A . Moreover, the 400 continuum states of the C manifold were included to ensure accurate spectral results [81].

From the $c_k(t)$ propagated population amplitudes, the time-dependent populations of vibrational levels can be calculated using $p_k(t) = |c_k(t)|^2$. The dissociation spectrum is then obtained as $\sigma(\omega_\varepsilon) = |c_\varepsilon(t \rightarrow \infty)|^2$ (see Eq. 2.3.5 in subsection 2.3.2). The fourth-order Runge–Kutta method was used to obtain the solution of equation 1.4.31. The populations and spectral features predicted by the multi-level model are in good agreement with those obtained from full-wave-packet propagation calculations using the MCTDH, as will be demonstrated in the following sections.

3.2 Results and discussion

To demonstrate the influence of the electronic state A in the photodissociation dynamics of the MgH^+ system, we use photon energies with respect to the range $\omega \approx 4 - 6$ eV (or equivalently $\lambda \approx 200\text{-}310$ nm). The molecule with vibrational motion that is driven

by the (quantized) laser pulse (Eq. 2.1.1 with the Gaussian function 2.1.2) is prepared in the absolute vibrational-rotational ground state $X(\nu = 0)$ at $t = -\infty$. A long laser pulse duration ($T = 500$ fs) is set, which corresponds to a narrow spectral bandwidth of $\delta_\omega = \frac{4\sqrt{\ln 2}}{T} \approx 4.4 \times 10^{-3}$ eV. This bandwidth is significantly smaller than the typical energy separation between adjacent vibrational levels of electronic states X and A , which is on the order of several tenths of an electronvolt (eV). Therefore, the excitation process is almost vibronically selective, allowing a clear interpretation of the vibrational molecular dynamics. However, even minimal population transfer at other levels can have a pronounced effect on the dissociation process under specific conditions. In the following, we present accurate simulations of the dissociation dynamics based on the numerical solution of the one-dimensional TDSE in Eq. 2.2.3. We utilized weak laser pulses with a peak intensity $I_0 = 10^8$ W cm $^{-2}$ for the vibrating MgH^+ molecule. Under resonant conditions, this intensity is low enough that the molecule undergoes less than half a Rabi oscillation. As a result, the population transfer between the relevant states $X(\nu = 0)$ and $A(\nu_A)$ remains smooth. As illustrated in Figure 3.1(a), the probability of the dissociation of the C electronic state, calculated once the laser pulse has ended, reveals a very sharp dependence on the photon energy.

Although the values of the dipole coupling between the vibrational levels of $X(\nu = 0)$ and $A(\nu_A = 0, 1, 2, \dots, 14)$ (Figure 3.1(c)) demonstrate regular behavior similar to the Franck–Condon factors, this behavior is not reflected in the probability of transition from X to A in Figure 3.1(b) or the corresponding probability of dissociation shown in Figure 3.1(a). The underlying reason for this behavior is the substantial variation in the strength of the dipole coupling between the vibrational levels of the $A(\nu_A)$ state and the manifold C . These dipole couplings are demonstrated for $\nu_A = 0, 1, 2, 3$ in Figure 3.2. The corresponding dipole curves (solid red lines) display oscillatory structures that directly reflect molecular vibrational eigenfunctions (meaning that the number of oscillations of the dipole moment matches that of the vibrational eigenfunctions). The number of maxima reflects as $(\nu_A + 1)$, whereas the number of nodes is given by ν_A . In addition to the dipole couplings, Figure 3.2 also includes probabilities of dissociation produced by weak laser pulses when the molecule is initially prepared in the respective $A(\nu_A)$ eigenstate. These probabilities, shown as dashed lines, clearly reflect the energy-dependent dipole couplings indicated by the solid curves. Figure 3.2 helps to demonstrate the irregular behavior observed in Figures 3.1(a) and 3.1(b) for the probabilities of dissociation and population, respectively. For instance, in the case of resonant photon energy from the $X(\nu = 0)$ state to the $A(\nu_A = 0)$ state ($\omega \approx 4.2868$ eV), the amount of population of the A state is not a negligible ($p_A \approx 0.09$, Fig. 3.1(b)). Still, the probability of dissociation in the C state stays extremely low, as seen in Figure 3.1(a) at $\nu_A = 0$. This is because of the very small value of

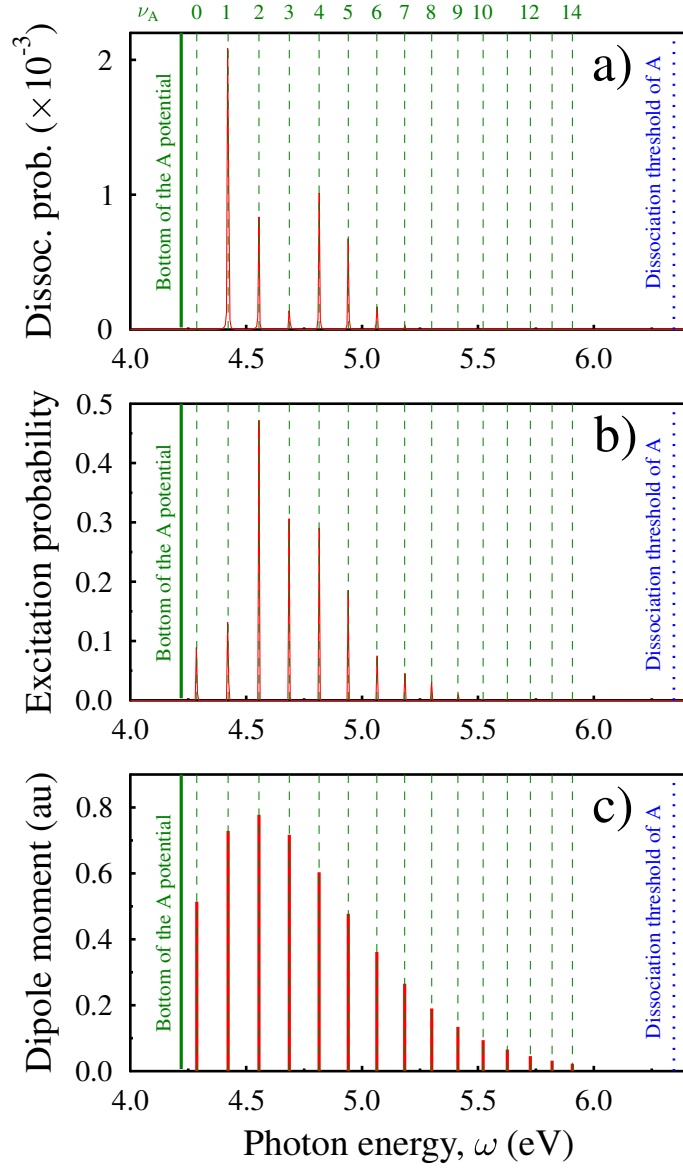


Figure 3.1: Molecular processes (dissociation and excitation), and nuclear dipole moments of MgH^+ as a function of photon energy are shown via vibrational intermediates in the A state. Panel (a) shows final C-state dissociation probabilities for weak laser excitation ($I_0 = 10^8 \text{ W/cm}^2$, $T = 500 \text{ fs}$). In this case, less than half of a Rabi oscillation is completed between the $X(\nu = 0)$ and $A(\nu_A)$ states. In panel (b), the final population of the A electronic state under the same conditions is shown. The observed transition probabilities (panel (b)) do not directly reflect the dipole coupling strengths between the $X(\nu = 0)$ and $A(\nu_A)$ states (panel (c)), but the dipole couplings can be connected to the couplings from $A(\nu_A)$ to the C state (Figure 3.2).

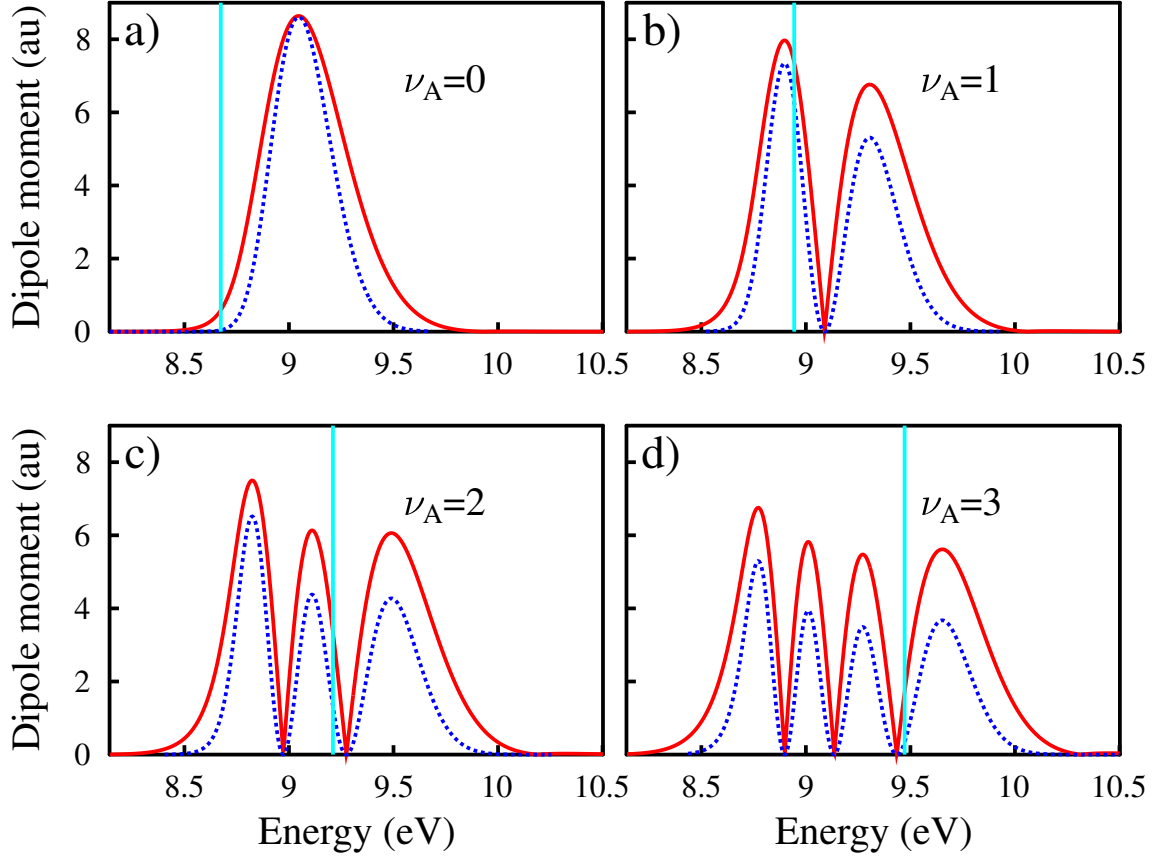


Figure 3.2: The solid red curves represent the absolute strengths of the dipole couplings connecting the initial vibrational levels $\nu_A = 0, 1, 2, 3$ of A with the C manifold. The dashed curves demonstrate the probabilities of dissociation, scaled by a factor of 250, obtained using weak laser pulses with peak intensity $I_0 = 10^8 \text{ W/cm}^2$ and duration $T = 500 \text{ fs}$. The dissociation probabilities display the same oscillatory pattern as the dipole curves and reflect the shape of the wave function of the relevant vibrational level. The solid vertical lines correspond to the nominal spectral positions predicted in the weak-field limit for exact resonance conditions, defined by $\omega_{\varepsilon 0} = \omega_{X(\nu=0)} + 2\omega_{\text{res}}$, where ω_{res} is the resonant photon energy connecting the $X(\nu=0)$ and $A(\nu_A = 0, 1, 2, 3)$ states.

the dipole coupling from the vibronic state $A(\nu_A = 0)$ to the C manifold, as demonstrated by the solid vertical line in Figure 3.2(a). In contrast, as the laser resonantly couples the state $X(\nu = 0)$ with the state $A(\nu_A = 1)$ ($\omega \approx 4.422\text{eV}$), the dissociation proceeds with high efficiency, since the dipole coupling between $A(\nu_A = 1)$ and the C state is strong (the solid vertical line in Figure 3.2(b)). An intermediate dipole coupling strength is observed for $A(\nu_A = 2)$ (Figure 3.2(c)). However, for $A(\nu_A = 3)$, it becomes moderate again [see Figure 3.2(d)], as which is reflected in the associated probabilities of the dissociation (Figure 3.1(a)). Figures 3.1 and 3.2 illustrate that the molecular processes, including dissociation and excitation probabilities, and the bound-state dipole moments, strongly depend on the individual (intermediate) vibrational levels in the presence of the resonantly laser field. Furthermore, the pronounced energy-dependent bound-to-continuum dipole couplings (Figure 3.2) is expected to play an essential role under conditions of off-resonant excitation as well. In this (off-resonant) case, selective population transfer is no longer possible, and the vibrational populations become more evenly balanced. In the following sections, dissociation processes in the resonant and off-resonant pathways of the MgH^+ molecule are discussed separately.

3.2.1 Resonant dissociation

In the present subsection, we focus on the dissociation of MgH^+ for transitions at exact resonance, that is, when $\omega = \omega_{A(\nu_A)} - \omega_{X(\nu=0)}$, where $\nu_A = 0, 1, 2, 3, 4, 5$. Nontrivial vibronic dynamics are induced by keeping the pulse duration ($T = 500$ fs) unchanged, but the peak of the laser intensity will be changed to $I_0 = 10^{11}\text{W/cm}^2$. Figure 3.3 demonstrates the molecular processes (fragment energy spectra, time-dependent electronic state populations and C state dissociation probabilities) of the MgH^+ molecular ion for the vibronic transitions ($X(\nu = 0) \rightarrow A(\nu_A)$). The results from the middle columns show the time-dependent X and A electronic states, while the results from the right columns show the time-dependent populations (dashed orange curves) and dissociation probabilities (solid green curves) of the C state. The results presented are obtained by accurately solving the TDSE for the vibrating molecule. For these laser-parameter values, several Rabi floppings are generated between the electronic states X and A, as shown in the middle columns of Figure 3.3 for $\nu_A = 0, 1, 2, 3, 4$, and 5. Here, the number of full Rabi oscillations completed can be approximately determined from the pulse area $\eta = \int_{-\infty}^{\infty} \varepsilon_0 \mu g(t) dt = \varepsilon_0 \mu \sqrt{\pi} T$, where μ denotes the related dipole moment between the states $X(\nu = 0)$ and $A(\nu_A)$. The values of these pulse areas are presented on the right side of Figure 3.3. It is clear that when the dipole coupling between states ν_A and C and, therefore, the probability of dissociation is small, complete Rabi floppings are produced with a high

amplitude between states X and A (see Figure 3.3(b)).

On the other hand, when the dipole coupling between states ν_A and C is strong, and therefore dissociation occurs with high probability, strongly damped Rabi oscillations prevent a correlation between the number of Rabi cycles and η . For instance, under extreme conditions in which the laser couples the states $X(\nu = 0)$ and $A(\nu_A = 1)$ resonantly, complete dissociation occurs during the laser pulse’s rising edge. As shown in Figure 3.3(e), approximately two Rabi oscillations are produced (the third one has a very small amplitude) rather than the five that were determined by the pulse area. The value of η indicates a clear correlation with the number of Rabi oscillations completed. From the vibrational levels above $\nu_A > 1$, the MgH^+ molecule undergoes highly efficient dissociation. This is illustrated by the pronounced loss of populations of the bound states (seen in the middle panels of Figure 3.3), which is consistent with the large dissociation probabilities revealed in the right panels.

It is clear that how many Rabi oscillations occur is determined by the corresponding bound–bound dipole coupling (Figure 3.1(c)), and is additionally altered by the bound–continuum coupling (Figure 3.2), which causes depletion.

The increases of the step-like behavior (the rump-ups) observed in both the population and dissociation curves reveals that dissociation happens in a stepwise manner. Dissociation efficiently occurs whenever a given $A(\nu_A)$ vibrational level reaches its maximum population at a point where a second photon absorption transfers the molecule to the repulsive C electronic state. This causes the ramp-ups in the C-state populations (dashed curves on the right in Figure 3.3). On the other hand, the flat regions correspond to the times during which the population is transferred back to the ground state $X(\nu = 0)$, and hence dissociation is closed. Moreover, the dissociation curves in Figure 3.3 are time delayed, corresponding to the C-state-population curves. These delays provide a direct measure of the time required for the nuclear wave packet to propagate to the absorbing boundary at $R_c = 30$ a.u., where the complex absorbing potential completely absorbs it.

The resonance-enhanced energy spectra of the molecular fragments released are demonstrated in the left panels of Figure 3.3. These spectra exhibit a variety of characteristics, including energy shifts, peak splitting, multipeak structure, and asymmetry, phenomena well known from studies of atomic ionization processes. As previously demonstrated for electrons, the spectral multipeak pattern directly depends on the Rabi oscillations that occur during the breakup process [42]. We have recently demonstrated this correspondence in the case of molecular dissociation as well, using a simple analytic model [64]. It was demonstrated that the multi-peak spectral pattern arises from temporal interference among photo-fragment amplitudes generated in successive Rabi cycles. Consequently, as shown in Figure 3.3, when N Rabi oscillations are generated, N ramp-ups are observed in

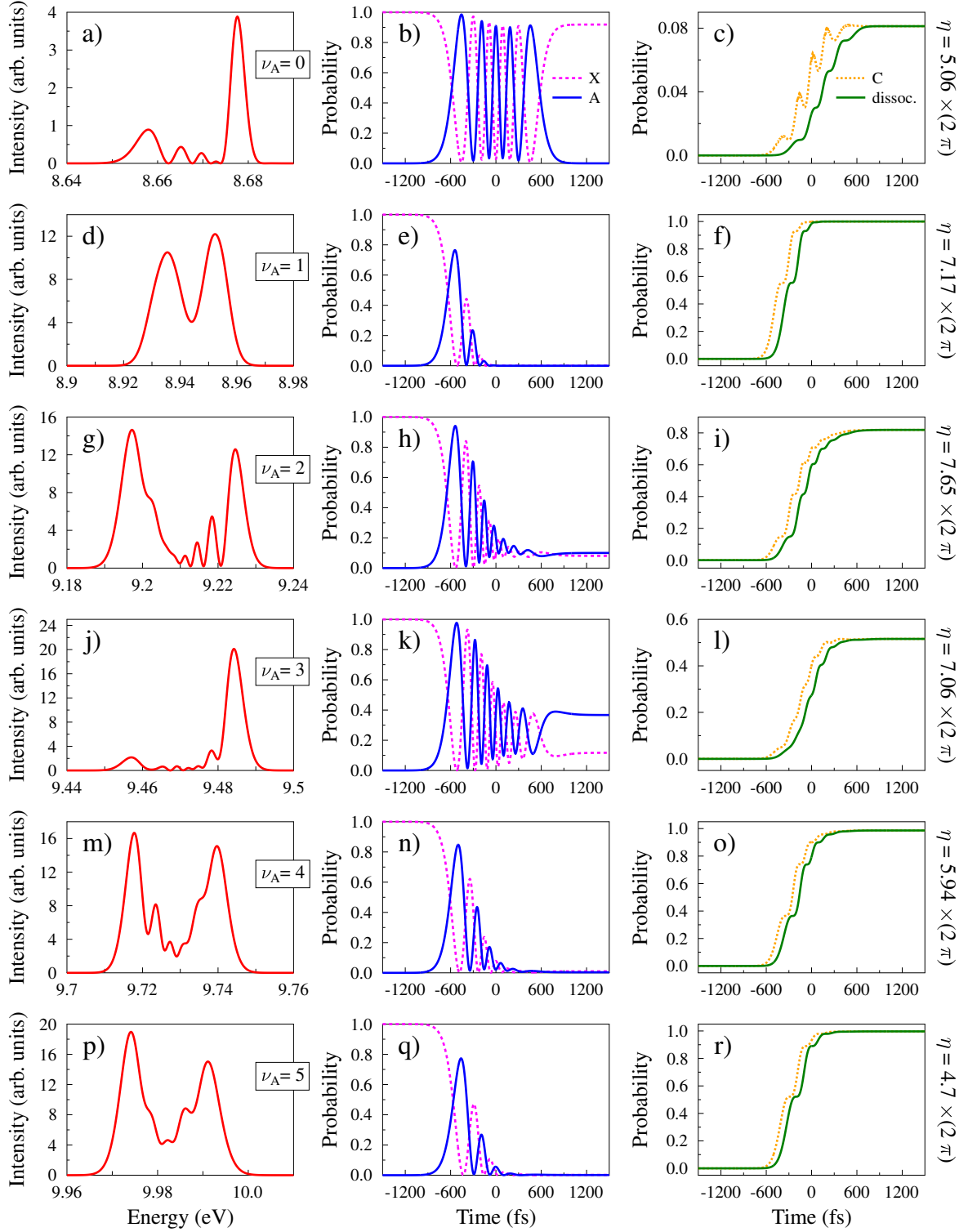


Figure 3.3: The MgH^+ molecule's photodissociation driven by the resonant $(1+1)$ laser fields tuned to the $X(\nu=0) \rightarrow A(\nu_A)$ vibronic transitions $\nu_A = 0, 1, 2, \dots, 5$, with the laser parameters of $I_0 = 10^{11} \text{ W cm}^{-2}$ and $T = 500 \text{ fs}$.

the dissociation curves, and the corresponding spectral features exhibit N peaks. A few of these peaks exhibit low yield, whereas the others are not completely formed. We note that using a narrower pulse bandwidth could improve the resolution of the individual subpeaks of the AT doublets. Moreover, for such pulses, the influence of neighboring states can also be undervalued. In the case of $\nu_A = 2$, corresponding to the third-row panels of Figure 3.3, the resonant coupling between the vibrational states of $X(\nu = 0)$ and $A(\nu_A = 2)$, leads the molecule to complete about 7.5 Rabi oscillations, in agreement with a pulse area of $\eta = 2\pi \times 7.65$. Due to the strong dipole interaction with the C state, as indicated in Figure 3.2(c), these oscillations' amplitudes decay rapidly as time passes, as clearly visible in Figure 3.3(h). At the end of the process, the dissociation probability exceeds 80%.

To elucidate the possible contribution of adjacent states to spectral formation, we computed the energy spectrum of fragments using a multilevel model by extending the description to include additional levels of A-state. Figure 3.4 demonstrates two photon dissociation dynamics for the transition $X(\nu = 0) \rightarrow A(\nu_A = 2) \rightarrow C$ using multilevel model [Eqs. 1.4.31]. In Figure 3.4(b), the population of the vibronic state $A(\nu_A = 2)$ is more than two orders of magnitude larger than that of the other A-state levels. This suggests that the final shape of the spectrum is exclusively defined by state $A(\nu_A = 2)$ (see the green curve in Figure 3.4(c)). In Figure 3.4(c), including only $A(\nu_A = 2)$ allows most spectral features to be recovered, but fails to capture the correct symmetry. However, when neighboring levels of the $A(\nu_A = 1)$ and $A(\nu_A = 3)$ states are included (dark blue line), all features of the spectrum are recovered, containing the correct asymmetry. The addition of the other two states ($\nu_A = 0$ and $\nu_A = 4$) does not significantly alter the shape of the spectrum (light-blue dashed line). Figure 3.4(c) shows that the adjacent states $A(\nu_A = 1)$ and $A(\nu_A = 3)$ alter the overall spectral symmetry. Moreover, these two vibrational levels cause the spectral peaks near 9.2 eV in Figure 3.4(c) to merge. The coalescence of the peaks in the spectrum at approximately 9.2 eV is caused by these two vibronic states, as shown in Figure 3.4(c). In spite of their small populations, these states are relevant to dissociation dynamics because of their intense dipole moments relative to the C continuum, as illustrated in Figure 3.4(a). Even though states $A(\nu_A = 0)$ and $A(\nu_A = 4)$ also have significant dipole moments, their suppressed populations do not allow them to contribute to the spectrum. Taking into account $\nu_A = 1, 2, 3$ levels is thus adequate to obtain a well-converged spectrum computed by the multi-level approach [thick red curve in Figure 3.4(c)], which is strongly supported by the precise spectrum derived through wave packet propagation (solved by the MCTDH) [Figure 3.3(g)].

We now analyze the spectrum asymmetry produced by dissociation through the level $A(\nu_A = 2)$. Previous studies [31, 32] on resonant ionization show that spectral asymmetry can result from several mechanisms, including relevant levels' Stark shifts, the

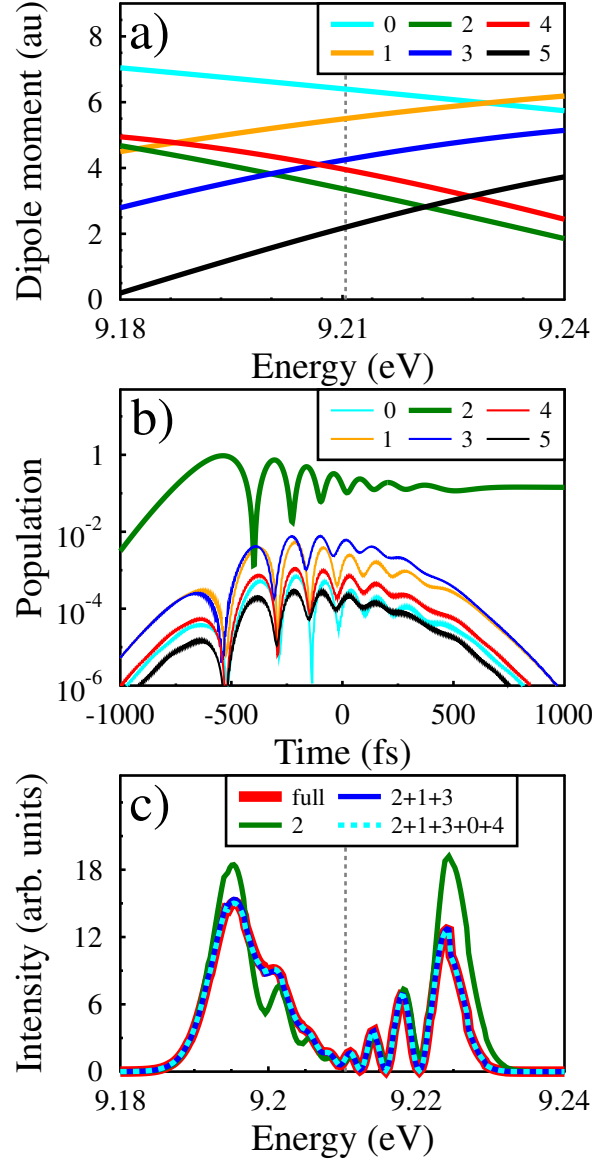


Figure 3.4: The (1 + 1) photon dissociation of MgH^+ obtained by resonant excitation of the $A(\nu_A = 2)$ level from $X(\nu = 0)$ at $\omega = 4.5551 \text{ eV}$ with laser parameters: $I_0 = 1 \times 10^{11} \text{ W/cm}^2$ and $T = 500 \text{ fs}$. Panel (a) shows the dipole couplings from these $\nu_A = 0, 1, 2, 3, 4, 5$ vibrational levels of the A state to the C manifold within the relevant spectral range. Panel (b) indicates the time evolution of the populations associated with the $A(\nu_A = 0, 1, 2, 3, 4, 5)$ vibrational levels. Panel (c) shows the final energy spectra obtained from the multi-level model as successively higher vibrational states of the A state are included. The nominal spectral positions are shown by vertical dashed lines, $\omega_{\varepsilon_0} = \omega_{X(\nu=0)} + 2\omega$.

energy-dependent bound–continuum dipole moments, the contribution of other states, or interference among different breakup pathways. Therefore, perfectly symmetric spectra are rarely observed and occur only under specific conditions. We thus introduce an asymmetry parameter to quantify spectral asymmetry and determine when the spectrum is symmetric

$$Q = \frac{|Q_L - Q_H|}{Q_L + Q_H}, \quad (3.2.1)$$

where Q represents the heights of the prominent peaks of the Autler–Townes doublet at lower (Q_L) and higher (Q_H) energies. The asymmetry parameter Q thus quantifies the imbalance between the two peaks (Q_L and Q_H). Values of $Q \approx 1$ close to unity indicate a strongly asymmetric spectrum, whereas a value of $Q = 0$ corresponds to a fully symmetric spectrum with equal peak heights. Figure 3.5 shows that, for a fixed pulse area, using longer pulses suppresses the factors that lead to spectral asymmetry. When the pulse duration is increased from $T = 500$ to $T = 1000$ fs, all peaks in the spectrum’s lower-energy part, near 9.2 eV of the AT doublet, become completely resolved. Consequently, the

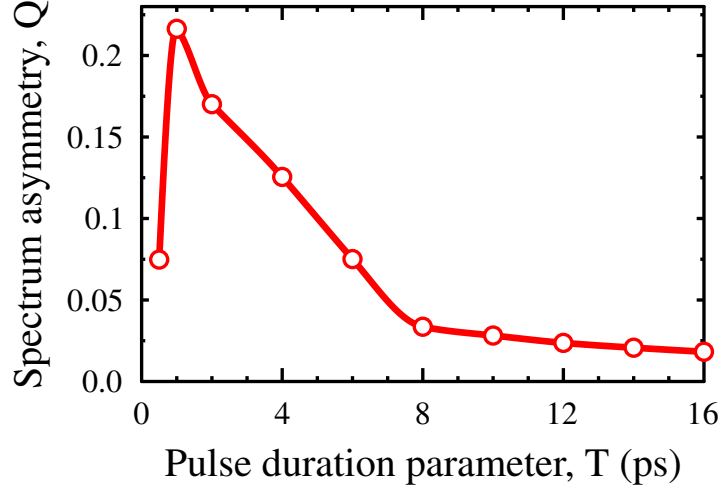


Figure 3.5: At the resonant photon energy $\omega = 4.5551$ eV, corresponding to excitation of the $A(\nu_A = 2)$ level from $X(\nu = 0)$, the asymmetry parameter Q [Eq. 3.2.1] is shown as a function of varying pulse durations. All calculations are performed at a fixed pulse area of $\eta = 2\pi \times 7.65$.

lower-energy AT doublet’s prominent peak is significantly enhanced, which gives rise to an increase in the spectral asymmetry. However, for pulse durations exceeding $T = 1000$ fs, the shape of the spectrum gradually and monotonically becomes a more symmetric form. As demonstrated in Figure 3.5, because of the narrow spectral bandwidth (of the long pulses) and reduced peak intensity, the effects of Stark shifts and contributions from other intermediate states are progressively suppressed. For pulse durations $T = 8$ ps,

the decrease in the asymmetry parameter Q becomes noticeably slower. This behavior can be explained by the very steep energy-dependent bound-continuum dipole function $A(\nu_A = 2) \rightarrow C$ near the spectrum's nominal position, as illustrated in Figure 3.2(c). For dissociation pathways involving other states, a fully symmetric spectrum ($Q = 0$) can be achieved using comparatively shorter pulses.

3.2.2 Off-resonant dissociation

We now take into account a more general situation in which the laser's photon energy is nonresonant with the A state's all intermediate (vibrational) levels. Figure 3.6 shows the off-resonant two-photon dissociation, where the photon energy lies below the minimum of the potential energy curve A , $\omega = 4.18 \text{ eV}$. In order to compensate for the lower population, the laser intensity is supposed to be intensified to $I_0 = 5.3 \times 10^{11} \text{ W cm}^{-2}$ (from $I_0 = 1 \times 10^{11} \text{ W cm}^{-2}$ used for the resonant case in the previous subsection). Figure 3.6(b) demonstrates that the transferred population diminishes as the ν_A vibrational quantum number increases. Unlike the resonant case shown in Figure 3.4, where the population is shared among several vibronic levels $A(\nu_A)$, no single state emerges as dominant, as illustrated in Figure 3.6(b). Consequently, for the off-resonant excitation, more $A(\nu_A = 0, 1, 2, \dots, 10)$ states are involved in the dynamics to obtain the convergent spectral profile. For the A state's additional vibrational levels, the spectrum is calculated using a multi-level model as presented in Figure 3.6. Remarkably, all features of the spectrum are already reproduced with just the $\nu_A = 0$ level, except for the proper dissociation outcome. To achieve the proper spectral intensity, vibrational levels up to approximately $\nu_A \approx 10$ must be incorporated in the multi-level model. Although their populations are small, the significant dipole couplings of these states with state C (seen in Figure 3.6(a)) make their inclusion essential for obtaining converged results. In the multi-level model, including levels with $\nu_A \leq 4$, the height of the spectrum gradually grows (presented by the blue curve of Figure 3.6(c)), primarily due to the growing dipole coupling strength of these relevant states. In contrast, the higher vibronic levels with $\nu_A > 4$ contribute to a reduction in the intensity of the spectrum until the accurate spectral profile is eventually achieved, as indicated by the thick red line in Figure 3.6(c). Differences in how higher and lower vibronic states affect the spectral shape arise from constructive and destructive interference between fragment amplitudes emitted from the various $A(\nu_A)$ levels. With regard to the spectral asymmetry, it should be noted that for off-resonant case, the Autler-Townes doublet cannot be rendered symmetric using long pulses, unlike the resonant case illustrated in Figure 3.5. Because the laser is strongly detuned from explicit resonance, the well-converged spectrum in Figure 3.6(c) shows a pronounced asymmetry similar to

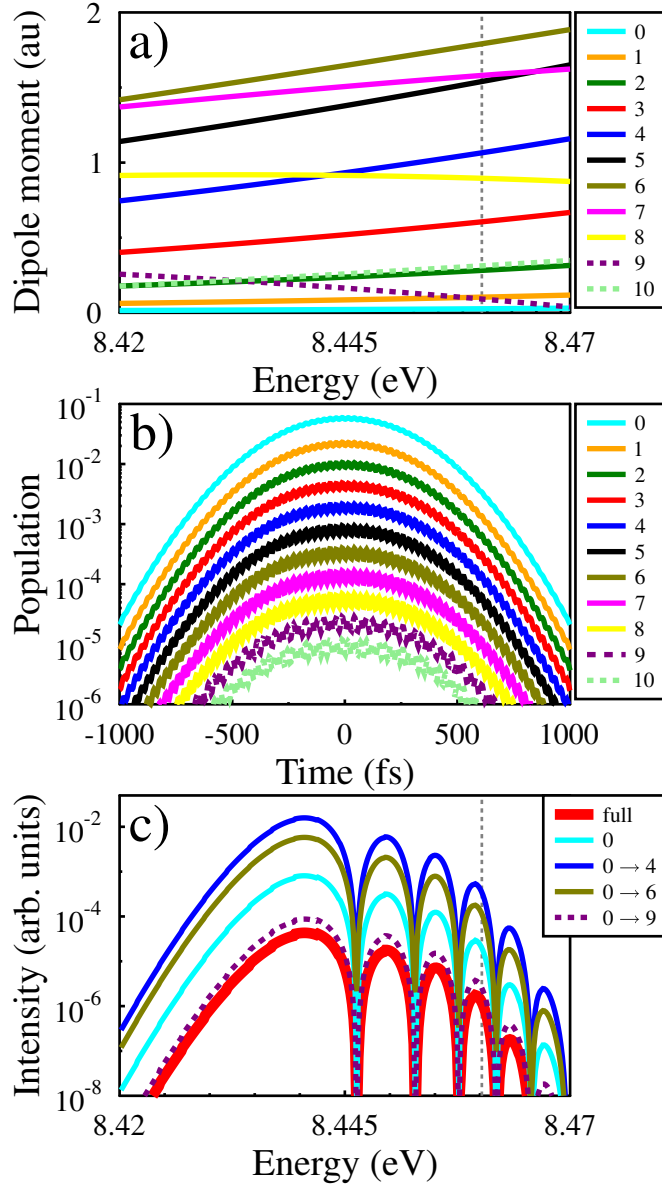


Figure 3.6: Off-resonant two-photon dissociation of MgH^+ through multiple vibronic levels $A(\nu_A = 0, 1, 2, \dots, 10)$, where the (off-resonant) photon energy is selected below the minimum of the A state potential (by the same laser of $\omega = 4.18 \text{ eV}$, $T = 500 \text{ fs}$, $I_0 = 5.3 \times 10^{11} \text{ W/cm}^2$). Panel (a) shows absolute dipole coupling strengths between the $A(\nu_A = 0, 1, 2, \dots, 10)$ vibrational levels and the C manifold with respect to the relevant energy range. (b) Time evolution of the populations of these ($A(\nu_A = 0, 1, 2, \dots, 10)$) vibrational levels. (c) Energy spectra obtained from the multi-level model as successive vibrational levels of A are included. The nominal spectral positions are marked by vertical dashed lines, $\omega_{\varepsilon_0} = \omega_{X(\nu=0)} + 2\omega$.

atomic ionization spectra [32, 39, 42]. When the photon energy approaches exact resonance, the large asymmetry parameter $Q \approx 1$ obtained in Figure 3.6(c) is substantially reduced to smaller values similar to those obtained in Figure 3.5 near the resonant AT doublets. Moreover, as the photon energy is tuned between two various vibronic levels in the resonant case, the Rabi floppings are still strongly damped (for example, second and third rows of Figure 3.3), and the dissociation dynamics closely resemble those obtained in Figure 3.6. Suitable setting of the photon energy between two vibronic levels leads to maximal population of these (two) states and more substantial molecular depletion. This is because of larger dipole moments of $\nu_A - C$ for energies above $\omega_{\varepsilon_0} \approx 8.5$ eV rather than below 8.5 eV (Figure 3.2). Since Rabi cycles entirely disappear under the off-resonant excitation, the underlying physical mechanism must be different, which is an interesting question of what causes the multiple-peak modulations observed in the spectral intensity of Figure 3.6(c). The multippeak spectral structure in Figure 3.6(c) is similar to that shown recently ([42, 39]) in REMPI driven by off-resonant laser pulses. In those studies, the oscillatory behavior of the AT doublet was ascribed to DI of photoelectrons, which are emitted with the same energy at both the laser pulse’s rising and falling edges. Two key conditions allow DI to occur under off-resonant driving. First, dressed states’ the Rabi splitting $W = \sqrt{\Omega^2 + \Delta^2}$, where $\Omega = \varepsilon_0 \mu$ and $\Delta = \omega - \omega_{\text{res}}$ representing the Rabi frequency and the detuning, respectively, can exceed the pulse bandwidth. Secondly, the depletion of the atom can remain low due to the lowered efficiency of population transfer to the intermediate level. Here, similar physical behavior is observed in a molecular system, with nuclei rather than electrons as participants. To examine the DI’s possible role in producing the multi-peak spectral pattern, we follow [42] and use asymmetrically shaped laser pulses in the following subsection.

3.2.3 The impact of asymmetric pulses on dissociation

In this subsection, we analyze asymmetric Gaussian pulse envelopes, which can be written as

$$g(t) = \begin{cases} e^{-t^2/T_1^2}, & t \leq 0, \\ e^{-t^2/T_2^2}, & t > 0, \end{cases} \quad (3.2.2)$$

where T_1 and T_2 represent the pulse duration parameters on the pulse’s increasing and decreasing edges, respectively. To keep the pulse area constant, the condition $T_1 + T_2 = 2T$ is introduced, where T is the pulse duration of the symmetric pulse in Eq. 2.1.2 ($T = 500$ fs). Keeping the pulse area constant enables the investigation of pulse-shape effects, such as the potential influence of the DI on dissociation. When transitioning from

a completely symmetric envelope ($T_1 = T_2 = T$) to a fully asymmetric one ($T_1 = 2T$, $T_2 = 0$), the pulse abruptly drops to zero after its peak, which diminishes the possible DI role in the dissociation dynamics owing to the fact that it reduces fragment emission on the falling edge of the pulse and thus the second arm of the interferometer becomes inefficient.

Fragment energy spectra of MgH^+ are shown in Figure 3.7 calculated by both exact solution and multi-level model for the resonant and off-resonant cases. As illustrated in Figure 3.7(a), for the resonant dissociation, the number of peaks in the spectrum is not affected by the pulse envelope symmetry. Since the pulse area is kept constant, the number of completed Rabi oscillations is equal for both asymmetric and symmetric pulses. The persistence of the multipeak spectral pattern in the presence of a fully asymmetric envelope suggests that Rabi dynamics primarily control the AT doublet. In contrast, the DI has only a minor influence in the resonant regime. Off-resonant dissociation demonstrates a strong sensitivity of the multipeak spectrum to the asymmetric envelope, seen in Figure 3.7(b), indicating a non-negligible role of the DI in the spectral features calculated with a symmetric pulse. When we have the two cases (resonant and off-resonant), the DI can be more effective by modifying the off-resonant spectrum under the symmetric laser pulse. When an asymmetric pulse envelope is applied, as shown in Figure 3.7(b), fragment emission during the falling part is diminished. The low-contrast peaks of the symmetric spectrum remain observable for $\omega_\epsilon < \omega_{\epsilon_0} \approx 8.5 \text{ eV}$, arising from the interference amplitudes emitted shortly before the pulse reaches its maximum in the asymmetric pulse envelope.

For the resonant case, the fragment spectra calculated using the multilevel model, as shown in Figure 3.7(a), are in good agreement with the TDSE solution (not presented here). For the off-resonant case, nevertheless, the spectra obtained using the model in Figure 3.7(b) are not in agreement with the spectra obtained from the exact solution for $\omega_\epsilon > \omega_{\epsilon_0}$, as shown in Figure 3.7(c). It should be noted that the permanent dipole moment of the C state is included in the exact solution but is eliminated in the model, which complicates the identification of DI. Therefore, we anticipate that observation of the DI will be easier for apolar molecules not possessing permanent electric dipole moments.

We now turn to illustrate another significant benefit of the asymmetric envelope functions. In the off-resonant case, the molecule completes one Rabi oscillation for all vibrational levels of the A state as presented in Figure 3.6(b). The populations of the various $A(\nu_A)$ vibronic levels increase along the rising edge of the pulse (until $t < 0 \text{ fs}$ in Figure 3.6) and subsequently decrease along its falling edge. A similar behavior is observed on the C-state population dynamics (not presented here). This behavior arises from amplitudes of the fragment that is promoted to the C electronic state during the rising edge of the pulse, while the amplitudes of the fragment become de-excited to the bound states during

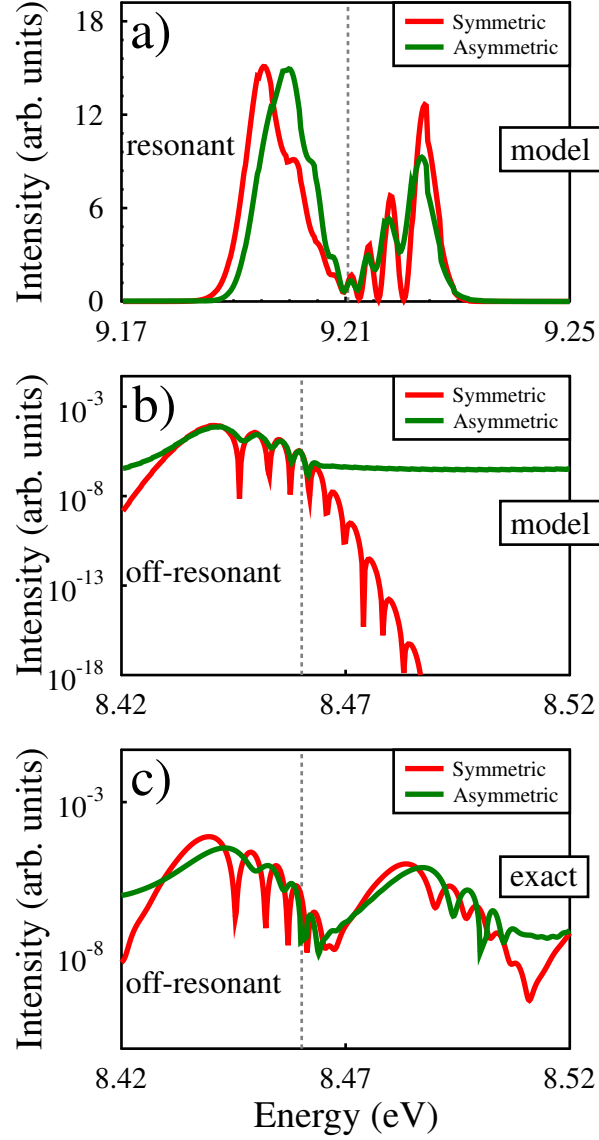


Figure 3.7: Energy spectra of the MgH^+ molecule calculated using symmetric ($T = 500$ fs) and asymmetric ($T_1 = 1000$ fs, $T_2 = 0$) laser pulses, corresponding to (a) resonant and (b), (c) off-resonant excitation. The laser parameters (I_0 , T , ω) of panel (a) and panels (b) and (c) are the same as those in Figures 3.4 and 3.6, respectively. Under resonant excitation (panel (a)), the pulse symmetry does not affect the number of spectral peaks. In contrast, under off-resonant conditions, the asymmetric pulse strongly affects the multippeak spectral structure and the molecular depletion predicted by the model in (b). The permanent dipole moment of the C state washes out this effect, as shown by the accurate solution in (c). The nominal spectral positions are shown by vertical dashed lines, $\omega_{\varepsilon_0} = \omega_{X(\nu=0)} + 2\omega$.

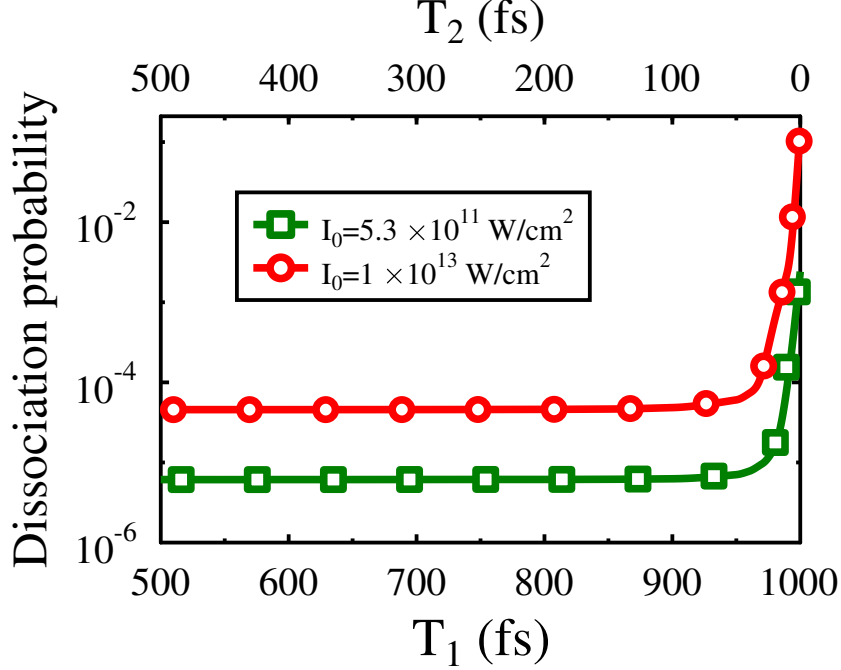


Figure 3.8: Dissociation probabilities of MgH^+ under off-resonant laser excitation are demonstrated as a function of varying pulse durations (T_1 and T_2) with the asymmetric Gaussian envelope functions [Eq. 3.2.2]. The pulse durations are completely symmetric on the left side ($T_1 = T_2 = 500 \text{ fs}$), whereas they are completely asymmetric on the right side ($T_1 = 1000 \text{ fs}$, $T_2 = 0 \text{ fs}$). The pulse area is fixed according to the condition $T_1 + T_2 = 2T$, with $T = 500 \text{ fs}$. The same photon energy is applied as in Figure 3.6, $\omega = 4.18 \text{ eV}$. All results were obtained from the exact solution via wave-packet propagation.

the falling edge of the pulse. Consequently, only a small fraction of the C-state populations remain at the end of the pulse interaction and can undergo dissociation. We note that the large temporary population of the C state is manifested as a prominent peak in the time-dependent spectrum around 9.1 eV (not presented here), which disappears at the end of the symmetric pulse (Figure 3.7(b)). Applying asymmetric laser pulses with $T_1 > T_2$ reduces recapture populations from the continuum state on the falling edge, thereby resulting in increasing dissociation probabilities. This process is illustrated for two distinct peak intensities ($I_0 = 5.3 \times 10^{11}$ and 10^{13} W/cm^2) in Figure 3.8. Put differently, for $T_1 > 900 \text{ fs}$ and correspondingly $T_2 < 100 \text{ fs}$, the dissociation yield is enhanced by nearly three orders of magnitude. In the case of a fully asymmetric laser pulse ($T_1 = 1000 \text{ fs}$, $T_2 = 0$), dissociation probability p_{diss} increases substantially because the recapture of the wave packet fragment is reduced on the falling edge of the pulse.

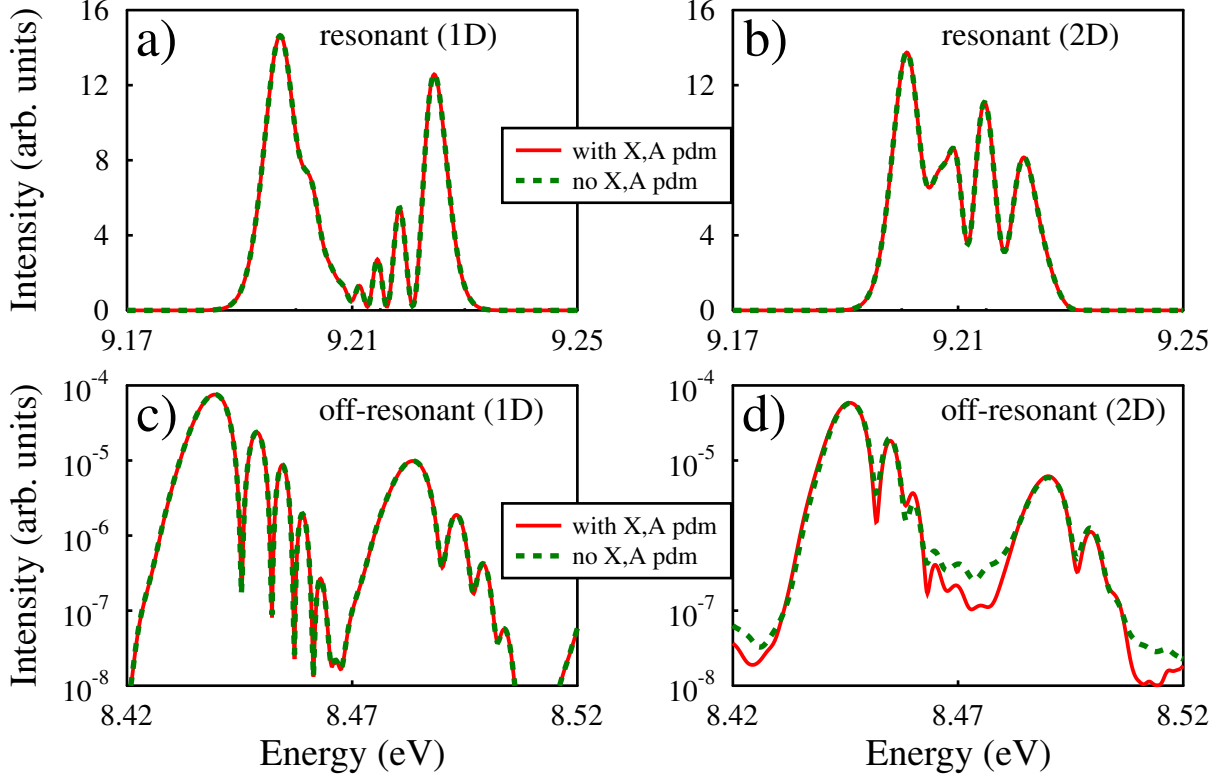


Figure 3.9: The effect of the PDMs of MgH^+ on the energy spectra is investigated using the exact (wave-packet propagation) solution for the resonant and off-resonant cases in 1D and 2D. The PDMs of electronic states X and A are either included (solid red curves) or neglected (dashed green curves). The parameters of the applied laser are selected as in Figure 3.4 for the resonant case panels (a) and (b), while they are selected as the same as in Fig. 3.6 for the off-resonant case panels (c) and (d). One-dimensional spectral calculations were calculated using Eq. 2.2.3, whereas the two-dimensional calculations were obtained from Eq. 2.2.1, where the initial state was set to $X(\nu = 0, J = 1)$.

3.2.4 The impact of the permanent dipole moment on dissociation

In this subsection, we will discuss the influences of the PDMs on the resonant and off-resonant solutions in the 1D and 2D models. To obtain a more accurate characterization of the effects discussed in the previous subsection and to highlight specific differences between molecular resonance and off-resonance dissociation, we present numerical solutions of the two-dimensional TDSE for MgH^+ under different dynamical conditions. Figure 3.9 shows the effect of the PDMs of MgH^+ for the resonance and off-resonance processes in the 1D and 2D calculations. As shown in Figure 3.9(b), the inclusion of rotational dynamics (2D) in the resonant driving results in a reduction in the number of spectral peaks from five

to four, which is caused by a decrease in the number of completed Rabi oscillations from five to four (not presented here). This effect is a direct result of the reduced effective laser coupling experienced by a vibrating rotating molecule that is not aligned with the laser polarization, as in the 1D description. In addition, the inclusion of θ DOF provides multiple spaced rotational levels in 2D. Because these rotational levels lie within the pulse’s spectral bandwidth, the population is distributed among these levels. As a result, Rabi oscillations can be reduced, resulting in diminishing the number of peaks of the spectrum in the 2D calculations (Figure 3.9(b)). A further outcome of the 2D results is the reduction in the spectral splitting. Similarly, in the off-resonant case, the number of peaks decreases in the 2D case as well (see Figures 3.9 (c) and (d)). By analyzing Figure 3.9, one can explore the influence of the PDMs of the MgH^+ molecule on the dissociation dynamics of resonance and non-resonance. As shown in Figure 3.9, the permanent electric dipole moments of the bound X and A states have only a minor influence on the resulting spectral shape (all panels of Figure 3.9). By contrast, the permanent dipole moment of the C state causes pronounced modifications of the spectrum in the off-resonant case, consistent with the behavior previously observed in Figures 3.7 (b) and (c). (It should be noted that the electric permanent dipole moment of C has been included in Figure 3.7(c), whereas it is excluded in Figure 3.7(b)). In particular, the absence of this dipole (in the model, Figure 3.7(b)) leads to large differences in the spectra between symmetric and asymmetric pulses, whereas this difference is not observed in the exact solution where this dipole is included (Figure 3.7(c)). Consequently, investigations of dynamic interference effects are expected to be more favorable in molecular systems having no permanent dipole moments.

3.3 Conclusion

We investigated the resonance-enhanced (1+1) photon dissociation of the MgH^+ system, in which multiple vibrational levels of a bound intermediate electronic state mediate the process. Based on propagating wave packets constructed by a multi-level model, we showed that tuning the frequency of the laser to explicit resonance with a given vibrational level efficiently generates Rabi oscillations. The fragment amplitudes’ interference released at successive Rabi cycles produces a pronounced multipeak structure in the dissociation spectrum.

When the laser is detuned from resonance, the ROs are intensively damped, and the multipeak pattern arises mainly from DI between fragment amplitudes of the same energy that are emitted with a certain time delay, namely at the increasing and decreasing edges of the pulse. In this way, the photon frequency plays a central role in governing the

competition between Rabi cycles and DI, consistent with similar behavior reported in atomic ionization [39, 42].

By finely adjusting the photon wavelength, we can also strongly control both the dissociation outcome and dynamics of the bound state. This connection arises from the pronounced energy-dependent dipole moment between the bound states and the continuum (Figure 3.2), which is expected to be a common characteristic of molecules. In addition, we showed that the use of laser pulse envelopes possessing various asymmetric profiles plays an essential role in the dissociation dynamics and their control.

Chapter 4

Summary

In my Dissertation, I investigate molecular processes and dynamics, and their quantum control and probing, using short UV laser pulses. As a concrete example, the MgH^+ molecule was considered.

Solutions of the electronic TISE have been used to solve the time-dependent problems for nuclear motion. To investigate time-dependent molecular processes, I have used two independent approximations: (i) one of the modern numerical packages, namely MCTDH, developed by the Heidelberg group, and (ii) my own multi-level script developed for the same purpose during my PhD study. This multi-level model is an alternative description compared to the MCTDH. The main difference is that here the total WF in the multi-level model is expanded in the basis of the system's eigenstates, whereas in MCTDH the total WF is expanded as a time-dependent linear combination of time-dependent Hartree products.

In collaboration with my supervisor, we have used our multi-level models in our published papers to investigate molecular-dynamical processes and compare our results with exact wave-packet propagation solutions obtained with MCTDH. Here, we are glad to report that, in general, the results obtained by both methods are in good agreement (see Figures 2.4, 2.5, or 3.4). The current work is based on two published papers, and I will briefly present their main conclusions below.

■ Rabi oscillations and fragment energy spectrum. When the laser pulses have a narrow spectral width (owing to the long pulse duration, $T = 500$ fs), this pulse tends to populate only a few vibrational selective levels, allowing us to have only a few-level system. This is illustrated in Figure 2.4(a), which shows that only two dominant vibrational levels associated with $X(\nu = 0)$ and $A(\nu = 0)$ are present, demonstrating Rabi oscillations between these two levels. The strong multi-peak structure of the spectrum is

illustrated to arise from temporal interference between wave-packet components released during separate Rabi cycles. The analysis and results have shown that the Rabi oscillations generated between the $X(\nu = 0)$ and $A(\nu = 0)$ states were reflected in the spectrum of the C electronic state, where the number of Rabi oscillations equals the number of peaks in the spectrum (which was demonstrated with the analytic model).

■ **Implication of the analytic model.** When the results obtained by the exact solution are compared with the results from the continuous model [Eq. 2.3.6] developed/used by us (now Stark shifts included), the compared outcome was almost identical to each other (Figure 2.4(c)). This continuous model successfully captures all main characteristics, such as multipeak structure, peak splittings, shifting and asymmetry. In addition, the Stark shifts of the participating molecular levels lead to displacements of the spectral peaks and modify both their splitting and their asymmetry. On the other hand, we simplified this continuous model to the so-called discrete model [Eq. 2.3.7]. Analytically calculating the fragment spectrum from the discrete model accurately reproduces the multipeak structure of the spectrum, demonstrating that the five peaks arise from the time-dependent interference of wave-packet amplitudes formed during the five Rabi oscillations (Figure 2.5). Based on wave-packet propagation, which a multi-level model supports, we observed that when the laser frequency is exactly resonant with a given vibrational state, the Rabi oscillations are efficiently produced.

■ **Wavelength-dependent dissociation and the nuclear dipole couplings.** I studied resonance-enhanced dissociation in the MgH^+ molecule using theoretical and numerical methods, controlled by the Gaussian pulses with varying parameters. The results indicate that tuning the photon wavelength to the intermediate electronic state’s energy region is important for photodissociation dynamics. Accurate tuning of the photon wavelength was also illustrated to enable effective control over both the dissociation outcome and dynamics of the bound state. The high degree of control achieved here is based on the strong energy dependence of the dipole coupling between the bound states and the continuum (in Figure 3.2) that is therefore expected to occur broadly in molecular systems. The selected laser pulse couples resonantly different vibrational levels of the electronic states, and nuclear dipole moments between these levels have been calculated for transitions between the electronic states X and A and between the $A(\nu = 0, 1, 2, 3)$ and the C manifold. The results have shown that the values of the photon energy and the corresponding nuclear dipole couplings play an important role in dissociation dynamics (see Figures 2.6, 2.7, 3.2, or 3.6).

■ **Resonant and off-resonant transitions.** The resonance-enhanced (1+1) breakup of the MgH^+ molecule has been studied using various vibrational states of the intermediate-bound electronic states. To obtain a more accurate characterization of the specific differ-

ences between molecular resonance and off-resonance dissociation, we conducted numerical solutions of the two-dimensional TDSE for MgH^+ under different dynamical conditions. For example, only 3 vibrational levels were enough to acquire the convergent spectrum with all features (peaks, splitting, oscillations) via the multi-level method for resonant transition (Figure 3.4), whereas the convergent spectrum was not obtained until approximately 10 vibrational levels were included in the calculations for the off-resonant transition (Figure 3.6). For the resonant case, the fragment spectra calculated using the multilevel model (Figure 3.7(a)) are in good agreement with the TDSE solution. For the off-resonant case, however, the spectra obtained using the model (Figure 3.7(b)) are not in agreement with the spectra obtained from the exact solution for $\omega_\varepsilon > \omega_{\varepsilon_0}$ (Figure 3.7(c)) due to the fact that the PDM of the dissociative state C significantly alters the shape of the spectrum. Moreover, the permanent dipole of state C makes it difficult to observe the impact of DI, displayed by asymmetric pulses in Figure 3.7(b). In the off-resonant transition, when the frequency of the laser is shifted away from the resonant transition, the Rabi oscillations disappear. In this regime, the observed multipeak structure in the spectrum predominantly arises from dynamical interference among fragment amplitudes with identical energies but released at different times, specifically during the rising and falling wings of the laser pulse. Therefore, the photon frequency emerges as a central control parameter that governs the interplay between Rabi oscillations and dynamic interference (consistent with analogous observations previously reported in atomic ionization [39, 42]). Interference between the fragment amplitudes released during each Rabi oscillation produces clear multi-peak structures in the spectrum of the breaking molecule. Another interesting differences between resonance and off-resonance population dynamics are explained in detail. In addition, we demonstrated that converting a temporally asymmetric laser pulse into a symmetric one provides an additional and efficient means of controlling the dissociation yield. Notably, the off-resonant pulse’s rapidly decaying falling edge can significantly increase the dissociation probability by suppressing population recapture from the continuum. Eventually, I could also explore the influence of the PDMs of the MgH^+ molecule on the dissociation dynamics of resonant and off-resonant transitions. The permanent electric dipole moments of the bound X and A states have only a minor influence on spectral shape, whereas the permanent dipole moment of C causes pronounced modifications of the spectrum in the off-resonant case.

■ **Further importance.** From an experimental perspective, the laser pulse parameters required to observe the general effects are well within the range of standard laboratory capabilities. Nevertheless, achieving high-precision detection of molecular fragments with low kinetic energies (on the order of ~ 1 meV), which exceeds the typical spacing of vibrational levels, remains technically demanding with current instrumentation. This

limitation contrasts with REMPI measurements in atomic systems, where photoelectron energy distributions are typically measured with considerably lower spectral resolution [33].

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Publication list

The Thesis is based on the following publications.

P1. Dilfuza Umarova, Otabek Umarov, Attila Tóth and András Csehi. Spectral evidence of vibronic Rabi oscillations in the resonance-enhanced photodissociation of MgH^+ . *Physical Review A* 110, 033112, 2024.

P2. Dilfuza Umarova, Otabek Umarov and András Csehi. Wavelength-dependent photodissociation of MgH^+ via intermediate resonances. *J. Phys. B: At. Mol. Opt. Phys.* 58 245001, 2025.

List of other publications.

P3. Otabek Umarov and Dilfuza Umarova. Light-induced pulse-dependent photodissociation in the triplet states of NH. *Optics Communications*, 617, 133415, 2026.

Talks and Posters

1. A.Jumabayev, A.Absanov, D.Umarova, O.Umarov: “Electric dipole moments between vibrational levels”, Republic Conference titled ”The role of gifted youth in the development of physics”, National University of Uzbekistan named after Mirzo Ulugbek, Uzb, 4-5 April 2025 (speaker).
2. A.Jumabayev, H.Hushvaktov, D.Umarova O. Umarov: “The role of the multi-configuration time-dependent Hartree method in nuclear dynamics”, International Conference “Fundamental and applied research in physics”, National University of Uzbekistan named after Mirzo Ulugbek, Uzb, 16-17 May 2025 (co-author).
3. A.Jumabayev, H.Hushvaktov, D.Umarova, O.Umarov: “Population dynamics in molecular systems”, International Conference titled ”Optical and computing technologies”, Bukhara State Technical University, Uzb, 23-24 May 2025 (co-author).
4. A.Jumabayev, A.Absanov, D.Umarova, O.Umarov: ”Kinetic energy release spectra and angular distribution of photofragment“, International Conference titled ”Optical and computing technologies”, Buhara State Technical University, Uzb, 23-24 May 2025 (co-author).
5. D.Umarova: ”Applying the MCTDH method in teaching molecular Physics”, International Scientific-Practical Conference titled “Prospects and Challenges of Digitalization in the Educational Process”, Samarkand Branch of Kimyo International University in Tashkent, Uzb, 21-22 November 2025 (speaker).

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