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**N**ANOSYSTEMS

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## SPONSORS

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## ORGANISATION

The organisers of UPAMON2020 are

Ágnes Vibók, Department of Theoretical Physics, University of Debrecen

Gábor Halász, Department of Information Technology, University of Debrecen

András Csehi, Department of Theoretical Physics, University of Debrecen

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# SCHEDULE

Please note that the allocated 35 minutes for the speakers shown below includes not only the talk but a 5-minute-long discussion segment as well.

Times are UTC+1:00.

## Session I

Chair: Ágnes Vibók

- |               |                    |
|---------------|--------------------|
| 9.00 – 9.05   | Opening            |
| 9.05 – 9.40   | Bing Gu            |
| 9.40 – 10.15  | Markus Kowalewski  |
| 10.15 – 10.50 | Csaba Fábri        |
| 10.50 – 11.25 | Tamás Szidarovszky |
| 11.25 – 11.45 | tea/coffee break   |
| 11.45 – 12.20 | Tamás Rozgonyi     |
| 12.20 – 12.55 | Mátyás Pápai       |
| 12.55 – 13.30 | Attila Bende       |
| 13.30 – 15.00 | Lunch break        |

## Session II

Chair: András Csehi

- |               |                             |
|---------------|-----------------------------|
| 15.00 – 15.35 | Péter Földi                 |
| 15.35 – 16.10 | Attila Czirják              |
| 16.10 – 16.45 | Sándor Borbély              |
| 16.45 – 17.05 | tea/coffee break            |
| 17.05 – 17.40 | Benjamin Lasorne            |
| 17.40 – 18.15 | Mariusz Pawlak              |
| 18.15 – 18.50 | Sebastián Carrasco          |
| 18.50 – 19.25 | Fabien Gatti ( <b>TBA</b> ) |

# TITLE OF TALKS

(in order of appearance)

- 1 Bing Gu – Manipulating conical intersection dynamics by optical cavities
- 2 Markus Kowalewski – Nonadiabatic Dynamics in Molecules – From Ultra-Fast Detection of Conical Intersections to Control of Avoided Crossings with Quantum Light
- 3 Csaba Fábri – Quantum light-induced nonadiabatic phenomena in the absorption spectrum of formaldehyde
- 4 Tamás Szidarovszky – Light-dressed spectroscopy of confined molecular systems
- 5 Tamás Rozgonyi – Simulating ultrafast pump-probe experiments with quantum wavepacket and trajectory surface hopping methods
- 6 Mátyás Pápai – Molecular Nonadiabatic Dynamics Simulations by Quantum Wavepacket and Semiclassical Trajectory Methods
- 7 Attila Bende – Laser-Induced Molecule Excitations Using Real-Time, Time-Dependent Density Functional Theory
- 8 Péter Földi – High-order harmonics as induced by a quantized field: a phase-space picture
- 9 Attila Czirják – Improved one-dimensional model potentials for strong-field simulation of small atomic systems
- 10 Sándor Borbély – Photoelectron holography in multi-cycle regime
- 11 Benjamin Lasorne – On the preservation of coherence in the electronic wavepacket of a neutral and rigid polyatomic molecule
- 12 Mariusz Pawlak – Rydberg States and Spectral Lines of a Single Ion in a Paul Trap
- 13 Sebastián Carrasco – Anti-alignment Dynamics in Strong Fields: The Whole Picture
- 14 Fabien Gatti – **(TBA)**

# LIST OF ABSTRACTS

# Manipulating conical intersection dynamics by optical cavities

Bing Gu, Shaul Mukamel

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Molecular polaritons, hybrid light-matter states, are formed when the coupling between cavity photon mode and molecular transitions reach the strong coupling regime where the coupling strength is stronger than the decay rates of both matter and the cavity photon. Numerous experiments have clearly demonstrated their potential to modify chemical processes including the electronic and optical properties of materials, chemical reaction rates, and reaction selectivity. Here we demonstrate how molecular photochemical processes can be manipulated by strong light-matter coupling<sup>1-3</sup>. For pyrazine molecule with an inherent conical intersection, by exact real-time quantum dynamics simulations of the hybrid photon-molecular system, we demonstrate that the photodynamics is significantly altered upon strong coupling by either creating novel polaritonic conical intersections or light-induced crossings. We further explore the cooperative polariton dynamics with two pyrazine molecules coupled to a common cavity photon mode. We find that whether cooperative effects emerge in the polariton dynamics depends on how the molecule is coupled to the cavity mode. Cooperative dynamics emerge when the cavity mode is coupled to the transition between the ground and excited states, manifested in the cooperative polaritonic potential energy surfaces as enhanced cooperative coupling strength and collective dark states.

We further discuss two nonlinear optical signals to probe polaritons and to monitor polariton dynamics: the pump-probe transient absorption and the entangled two-photon absorption. We demonstrate the signatures of polaritons in the transient absorption spectroscopy, and discuss the implications of employing entangled photons for nonlinear spectroscopy for polaritonic systems. Particularly, we show that entangled two-photon absorption can probe classically forbidden two-polariton resonance.

1. Gu, B. & Mukamel, S. Manipulating nonadiabatic conical intersection dynamics by optical cavities. *Chem. Sci.* **11**, 1290–1298 (2020).
2. Gu, B. & Mukamel, S. Cooperative Conical Intersection Dynamics of Two Pyrazine Molecules in an Optical Cavity. *J. Phys. Chem. Lett.* **11**, 5555–5562 (2020).
3. Gu, B. & Mukamel, S. Manipulating Two-Photon-Absorption of Cavity Polaritons by Entangled Light. *J. Phys. Chem. Lett.* **11**, 8177–8182 (2020).

# Nonadiabatic Dynamics in Molecules – From Ultra-Fast Detection of Conical Intersections to Control of Avoided Crossings with Quantum Light

Markus Kowalewski<sup>1,\*</sup>, András Csehi<sup>2,3</sup>, Gábor J. Halász<sup>4</sup> and Ágnes Vibók<sup>2,3</sup>

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Non-adiabatic processes are responsible for non-radiative decay in a large number of photochemical and photobiological processes. These fast sub-100-femtosecond decay channels are dominated by conical intersections (CIs). At a CI, the electronic and nuclear degrees of freedom frequencies are comparable and strongly mix due to the breakdown of the Born-Oppenheimer approximation. A major challenge for their direct detection is the rapidly varying gap between the electronic surfaces in their vicinity. Modern XUV/X-ray light sources provide spectral broad and temporal short pulses, which potentially allow for monitoring CIs directly.

We present theoretical studies on ultra fast X-Ray methods, which make use of ultrashort X-Ray laser pulses and compare the results for different probes to detect a conical intersection in pyrrole.

In the second part of the talk we will present the latest result on how optical cavities may be used to create non-adiabatic interactions. Here will focus on the interplay with the influence of dissipation introduced by the mirrors.

## References

- [1] András Csehi, Gábor J. Halász, Ágnes Vibók, and Markus Kowalewski. Quantum Control with Quantum Light of Molecular Nonadiabaticity. *Phys. Rev. A*, 100:053421, 2019.
- [2] Markus Kowalewski, Kochise Bennett, Konstantin E Dorfman, and Shaul Mukamel. Catching conical intersections in the act: Monitoring transient electronic coherences by attosecond stimulated x-ray raman signals. *Phys. Rev. Lett.*, 115(19):193003, 2015.

# Quantum light-induced nonadiabatic phenomena in the absorption spectrum of formaldehyde

C. Fábri,<sup>1,a</sup> B. Lasorne,<sup>2</sup> G. J. Halász,<sup>3</sup> L. S. Cederbaum<sup>4</sup> and Á. Vibók<sup>5,6,b</sup>

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The coupling of a molecule to an optical cavity can induce conical intersections of the arising polaritonic potential energy surfaces. Such quantum light-induced conical intersections give rise to strong nonadiabatic effects in the absorption spectrum of molecules. By choosing formaldehyde as an example which does not possess any natural nonadiabatic effects, we can study the emergence of quantum light-induced nonadiabatic effects in a polyatomic molecule taking into account all vibrational degrees of freedom for the first time [1], complementing earlier results with a classical laser field [2]. The full-dimensional results are compared to those of reduced-dimensional models and the shortcomings and merits of the latter are analyzed. Moreover, we investigate the applicability of the Born-Oppenheimer approximation, neglecting the nonadiabatic coupling between polaritonic surfaces, and show that the Born-Oppenheimer approximation may fail even if one vibrational degree of freedom is treated and generally fails for two- or more-dimensional models due to the appearance of conical intersections induced by the cavity [3].

## References

- [1] C. Fábri, B. Lasorne, G. J. Halász, L. S. Cederbaum, and Á. Vibók, Quantum light-induced nonadiabatic phenomena in the absorption spectrum of formaldehyde: Full- and reduced-dimensionality studies, submitted to *J. Chem. Phys.*
- [2] C. Fábri, B. Lasorne, G. J. Halász, L. S. Cederbaum, and Á. Vibók, *J. Phys. Chem. Lett.* 11, 5324 (2020).
- [3] C. Fábri, G. J. Halász, L. S. Cederbaum, and Á. Vibók, *Chem. Sci.* 2021, accepted manuscript (<https://doi.org/10.1039/D0SC05164K>).



# Light-dressed spectroscopy of confined molecular systems

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Within the context of polaritonic chemistry [1], we investigate theoretically the rovibronic spectrum of a simple molecule, Na<sub>2</sub>, when it interacts with the radiation mode of a microscopic cavity. The dependence of the spectrum on the light-matter coupling strength in the cavity and on the frequency of the cavity mode is studied in detail [2]. When additional atoms are added to the system, the indirect coupling between atoms and the molecule, realized by their interaction with the cavity radiation mode, leads to a coherent mixing of atomic and molecular states, and at strong enough cavity field strengths hybrid atom-molecule-photon polaritons are formed. It is shown that by changing the cavity wavelength and the atomic transition frequency, the potential energy landscape of the polaritonic states and the corresponding spectrum could be changed significantly [3]. This demonstrates that by adding a second type of entity to a quantum system confined in a microscopic cavity, the dynamics of the system and its response to light can be modified, implying possible new directions in polaritonic chemistry.

## References

- [1] T. W. Ebbesen, *Acc. Chem. Res.* **49** (2016) 2403.
- [2] T. Szidarovszky *et al.*, *J. Phys. Chem. Lett.* **9** (2018) 6215.
- [3] T. Szidarovszky, G. J. Halász and Á. Vibók, *New J. Phys.* **22** (2020) 053001

# Simulating ultrafast pump-probe experiments with quantum wavepacket and trajectory surface hopping methods

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Photoinduced ultrafast excited-state molecular dynamics play a central role in many fundamental processes in nature and are also exploited in functional molecules. In order to follow these processes in real time, many different time-resolved experimental techniques have been developed. The most insight is typically gained by comparing the results of such pump-probe measurements with theoretical calculations of the related observables via dynamical simulation of the underlying processes. Here we present examples of simulating pump-probe measurements for two different types of systems and processes that have been extensively studied in ultrafast pump-probe experiments: (i) the photorelaxation of functional iron complexes and (ii) the photodissociation of a halogenated methane molecule. In case (i) we used quantum wavepacket propagation to model the excited state dynamics of  $[\text{Fe}(\text{bmip})_2]^{2+}$  (bmip = 2,6-bis(3-methyl-imidazole-1-ylidene)-pyridine) [1,2], which has long metal-to-ligand charge transfer state lifetime and could thus be utilized as photosensitizers. We studied how the laser pulse parameters could influence the relaxation dynamics and how it would be reflected in a transient x-ray scattering (TR-XRS) signal. We also performed computations for  $[\text{Fe}(\text{terpy})_2]^{2+}$  (terpy = 2,2':6',2''-terpyridine) which has long high-spin state lifetime, thus being a potential photo-switchable element. The wavepacket motion here was simulated in the lowest quintet state after photorelaxation in order to rationalize measured TR-XRS signal. In case (ii) the studied system was the  $\text{CH}_2\text{I}_2$ , one of the most investigated benchmark systems in femtochemistry. The photodissociation dynamics of this molecule was simulated by a trajectory surface hopping method and experimental signals from time-resolved photoelectron spectroscopy (TRPES) and ultrafast electron diffraction (UED) were compared with the results of calculations to get insight into the structural and nonadiabatic dynamics involved. [3]

## References

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- [2] M. Pápai, T. Rozgonyi, T.J. Penfold, M.M. Nielsen, K.B. Møller, *J. Chem. Phys.* **151**, (2019) 104307
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# Molecular Nonadiabatic Dynamics Simulations by Quantum Wavepacket and Semiclassical Trajectory Methods

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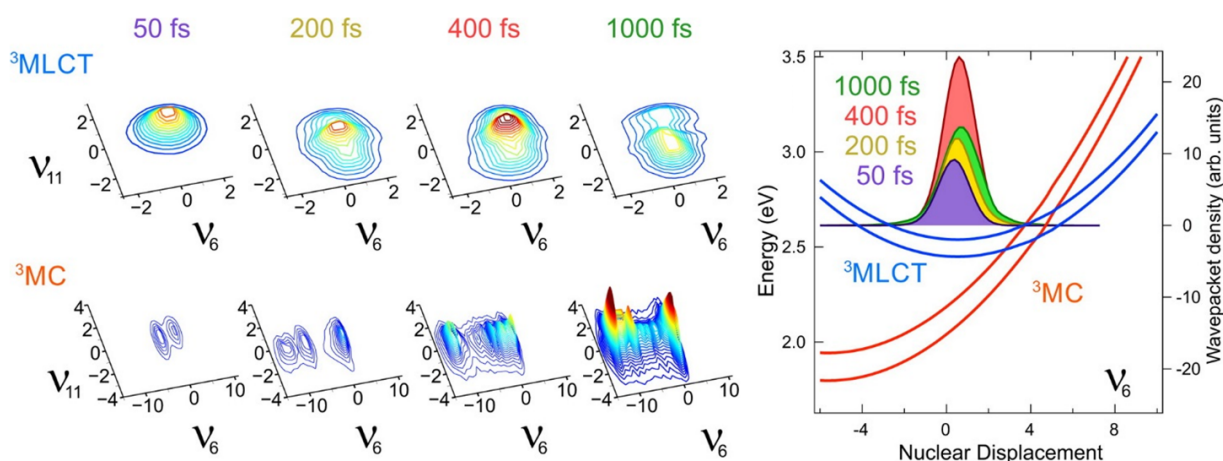
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Understanding, and subsequently being able to manipulate, the excited-state decay pathways of functional molecules is of utmost importance in order to solve grand challenges in new technologies, such as solar energy conversion and molecular data storage. Herein, we exploit the complementary character of quantum wavepacket dynamics (exact solution to the time-dependent Schrödinger equation) and trajectory surface hopping (access to full-dimensional simulations) to address the coupled nuclear-electronic (nonadiabatic) dynamics in functional molecules. The presented theoretical investigations lead to a detailed understanding on the chemical control of photophysics in Fe-carbene photosensitizers [1-4], and excited-state mechanisms of photochemical reactions [5,6]. These results, alongside with the related ultrafast spectroscopic and scattering experiments, will contribute to the improved design of novel high-efficiency functional molecules.



**Figure 1:** Graphical illustration of wavepacket dynamics in excited triplet metal-to-ligand charge transfer (<sup>3</sup>MLCT) and metal-centered (<sup>3</sup>MC) states.  $v_6$  and  $v_{11}$  denote the nuclear (vibrational) degrees of freedom dominant for the excited-state dynamics; nuclear displacements are given in dimensionless mass-frequency weighted normal coordinates.

## References

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- [2] M. Pápai, T. J. Penfold, K. B. Møller, *J. Phys. Chem C*, **2016**, 120, 17234–17241.
- [3] M. Pápai, M. Abedi, G. Levi, E. Biasin, M. M. Nielsen, K. B. Møller, *J. Phys. Chem C*, **2019**, 123, 2056–2065.
- [4] M. Pápai, T. Rozgonyi, T. J. Penfold, M. M. Nielsen, K. B. Møller, *J. Chem. Phys.* **2019**, 151, 104307.
- [5] M. Abedi, M. Pápai, K. V. Mikkelsen, N. E. Henriksen, K. B. Møller, *J. Phys. Chem. Lett.*, **2019**, 10, 3944–3949.
- [6] M. Pápai, X. Li, K. B. Møller *to be submitted*.

# Laser-Induced Molecule Excitations Using Real-Time, Time-Dependent Density Functional Theory

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## Abstract

The fully propagated real time-dependent density functional theory (RT-TDDFT) method for describing the laser-induced electron excitation and charge fluctuation is presented. The briefly presentation of the theoretical background together with different numerical solutions used for the efficient propagation of the electron density in real time is followed by a discussion of several real-case applications, including the computation of the full electronic absorption spectrum, resonant and charge-transfer-type excitations, as well as the dynamics of different orbital populations in real time [1,2]. In the next step, the implementation of the RT-TDDFT method in different quantum chemistry codes is discussed. The roles of the different laser field parameters as: direction, strength, wavelength, or pulse shape needed in order to get efficient and selective excitation behaviors for a specific molecular system are also presented. Finally, some remarks about the advantage and disadvantage of RT-TDDFT as well as about the possible further developments are given.

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# High-order harmonics as induced by a quantized field: a phase-space picture

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The interaction of matter with a quantized electromagnetic mode is considered. Representing a strong exciting field, the mode is assumed to contain a large number of photons. As a result, the material response is highly nonlinear: the completely quantized description results in generation of high harmonics. In order to understand the essence of the physical processes that are involved, we consider a finite dimensional model for the material system. Using an appropriate description in phase space, this approach leads to a transparent picture showing that the interaction splits the initial, exciting coherent state into parts, and the rapid change of the populations of these parts (that are coherent states themselves) results in the generation of high-order harmonics as secondary radiation. The method we use is an application of the discrete lattice of coherent states that was introduced by J. von Neumann.

## Reference

Á. Gombkötő, S. Varró, P. Mati, P. Földi, Phys. Rev. A. **101** (2020) 013418.

# Improved one-dimensional model potentials for strong-field simulation of small atomic systems

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We present accurate one-dimensional (1D) strong-field simulation results based on novel 1D atomic model potentials that we derive using the reduced ground state density of a three-dimensional (3D) single-active-electron atom [Majorosi et.al., Phys. Rev. A, 98 (2018) 023401]. We construct improved 1D models of the H and He atoms and of  $H_2^+$  and  $H_2$  using improved parameters of the soft-core Coulomb potential [Majorosi et.al., Phys. Rev. A, 101 (2020) 023405]. We test these 1D models by comparing the corresponding simulation results with their 3D counterparts in typical strong-field physics scenarios with near- and mid-infrared laser pulses, having peak intensities in the  $10^{14} - 10^{15} \text{ W/cm}^2$  range, and we find an impressively increased accuracy in the dynamics of the most important atomic quantities. It is especially important for attosecond physics that the high-order harmonic spectra obtained from 1D simulations have a very good match in structure and phase with their 3D counterparts.

# Photoelectron holography in multi-cycle regime

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The photoelectron hologram of atomic and molecular targets is formed when a continuum electronic wave-packet created during ionization is scattered by the parent ion [1] during its laser-driven quiver motion. In our previous works, we have investigated how the photoelectron hologram is influenced by the laser field parameters [2], and by the shape of parent ion's binding potential [3]. In those studies, as driving field a time-symmetric two-cycle laser pulse was employed, which ensured that only one dominant continuum wave packet was created. This allowed for a detailed study on the properties of the photoelectron hologram without contamination from multi-cycle interference effects. In the case of a longer driving laser pulse, several continuum wave packets with comparable norm are created and during their laser-driven motion in each of these wave packets a hologram is formed. The final momentum distribution of the photoelectrons is formed as a coherent superposition (interference) of these wave packets. In this work we investigate how this wave packet interference is influencing the final photoelectron hologram.

## References

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# On the preservation of coherence in the electronic wavepacket of a neutral and rigid polyatomic molecule

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We present [1] a rigid model of five nuclear dimensions and three electronic states for the pyrazine molecule to investigate the time evolution of electronic coherences. By an ultrafast optical pumping in the ground state ( $1^1A_g$ ), we prepare a coherent superposition of the  $1^1B_{2u}$  and  $1^1B_{1u}$  excited states and reveal the effect of the nuclear motion on the preservation of the created electronic coherence. More specifically, two aspects are considered: the anharmonicity of the potential energy surfaces and the coordinate-dependence of the transition dipole moments (TDM). To this end, we define an ideal model by making three approximations: (i) only the five totally symmetric modes move, (ii) which correspond to uncoupled harmonic oscillators, and (iii) the TDMs from the ground electronic state to the two bright states are constant (Franck-Condon approximation). We then lift the second and third approximations by considering, first, the effect of anharmonicity, second, the effect of coordinate-dependence of the TDMs (first-order Herzberg-Teller contribution), third, both. Our detailed numerical study confirms long-term revivals of the electronic coherence even for the most realistic level of the presented model.

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# Rydberg States and Spectral Lines of a Single Ion in a Paul Trap

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Long storage time and fast gate operations are among the most desirable features to assess any quantum computing platform. Trapped Rydberg ions have recently drawn considerable attention as promising candidates that may meet the both criteria. We develop an accurate numerical scheme to calculate and analyze Rydberg states and spectral lines of an ion in a Paul trap. The energy spectra of a highly excited singly ionized calcium are calculated for  $S$ ,  $P$ ,  $D$ ,  $F$ , and  $G$  states, using the one-electron model potential with spin-orbit coupling. The coupling of the Rydberg electron and the ion to the electric potential of the trap is incorporated in the Floquet method. Detailed comparison with recent experimental data is made.

## Anti-alignment Dynamics in Strong Fields: The Whole Picture

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Quantum control in molecules is particularly challenging for the interplay of different degrees of freedom in the coherent response of the system: electronic, vibrational, and rotational. From the theoretical point of view, it is almost impossible to study the system fully quantum-mechanically. When this is done, it requires separating the different motions. However, under strong fields, when ionization and dissociation can take place and conical intersections are pervasive, it is important to treat the system as much as possible in a fully consistent way.

In recent work, we tested the assumption that the molecular axis aligns with the field, which is implicitly used in the proposal of many quantum control scenarios using strong non-resonant fields. In this talk we will show that the assumption proves incorrect not only in  $\text{H}_2^+$  but even in isotopes with a permanent dipole, as  $\text{HD}^+$ , using a fully quantum description of the dynamics. Even for aligned molecules, the initial dispersion in the nuclear wave function is enough to lead to molecular dissociation at angles perpendicular to the field polarization in roughly on rotational period. This whole picture of the anti-alignment dynamics allows to evaluate in detail the fate of excited states, clarifying the role of field-induced conical intersections, providing hints of a more general phenomenon that may be observable in larger molecules.