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Probing Vibrationally Mediated Ultrafast Excited-State Reaction Dynamics with Multireference (CASPT2) Trajectories

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§Supporting Information

ABSTRACT: Excited-state trajectories computed at the complete active space second-order perturbation theory (CASPT2) reveal how vibrational excitation controls the molecular approach to the intersection space that drives the photodissociation of a prototypical halogenated methyl radical, namely CF2I. Translating the Franck–Condon structure along the ground-state CASPT2 vibrational modes in this system followed by propagating the displaced structures in the first excited doublet state simulates specific vibrational excitations and vibrationally mediated dynamics, respectively. Three distinct situations are encountered: the trajectories (i) converge to an energetically flat segment of the intersection space, (ii) locate a segment of the intersection space, and (iii) access a region where the intersection space degeneracy is lifted to form a ridge of avoided crossings. The computational protocol documented herein can be used as a tool to design control strategies based on selective excitation of vibrational modes, including adaptive feedback schemes using coherent light sources.

INTRODUCTION

Nuclear motion is a prerequisite for chemical transformations, the control of which has rattled several generations of scientists. The key to controlling the outcome of a chemical reaction is the ability to selectively localize energy in a favorable reaction coordinate. A viable approach is to employ vibrational excitation, which may steer a molecular system toward a desired reaction pathway, either in the ground or in the excited electronic states, as demonstrated in early studies. To date, this concept and techniques which stemmed from such studies have been applied in various systems, including (i) vibrationally mediated photodissociation and bimolecular reactions in the gas phase, mediated photodissociation and bimolecular reactions in the gas phase, (ii) vibrationally mediated dynamics, respectively. Three distinct situations are encountered: the trajectories (i) converge to an energetically flat segment of the intersection space, (ii) locate a segment of the intersection space, and (iii) access a region where the intersection space degeneracy is lifted to form a ridge of avoided crossings. The computational protocol documented herein can be used as a tool to design control strategies based on selective excitation of vibrational modes, including adaptive feedback schemes using coherent light sources.

Efficient control over chemical reaction dynamics presupposes a molecular level understanding of complex multidimensional energy landscapes. In photochemical transformations, the picture is further complicated by molecular evolution on at least two electronic surfaces. Recognizing that the degeneracy of electronic states is a common occurrence in polyatomics, one also needs to identify the molecular and electronic structures of conical intersections (CIs), which mediate ultrafast radiationless decay pathways in photoinduced processes. To account for multiple electronic configurations encountered at the degeneracy points, designing predictive schemes for vibrationally mediated photochemical processes defaults a practitioner to the use of tools of multiconfigurational quantum chemistry, i.e., wave functions flexible enough to account for multiple electronic configurations. A general description of vibrationally mediated nonadiabatic photochemical transformations also ought to account for all decay paths dynamically and energetically feasible to an evolving molecular system in multidimensional conformational subspace. The major challenge in achieving optimal control is that it requires an extensive knowledge of all such decay paths.

In this work, we model the excited-state branch of a vibrationally-state-specific photochemical/photophysical transformation in a prototypical halogenated alkane radical, CF2I, by computing on-the-fly excited-state adiabatic trajectories using the complete active space second-order perturbation (CASPT2) level of theory. This is a development of our previous study of CF2I, where we mapped the minimum energy photochemical reaction pathways from the lowest-lying electronically excited state using the CASPT2//CASSCF protocol. A CI was located between the ground D0 and first excited D1 doublet states at the CASSCF level and found to drive the excited-state species to the reactant (CF2I) and photoproduct (CF2 + I) wells on the ground state. Trajectories based on gradients from multireference approaches have been recently computed by several groups. However, in the present study we systematically sample the effect of the degree

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of initial vibrational excitation on how the excited-state species access different surface crossing regions using the ab initio multireference method, which reproduces the spectroscopy of the system under investigation.28 We isolate the effect of individual modes by populating (one at a time) different vibrational levels and computing the subsequent evolution of the molecule on the excited-state surface. This is done at a chemically accurate level of theory,32,33 not limited to a CF2I radical but extendable to molecules of small-to-moderate sizes, which are of interest to computational and experimental physical chemistry communities. Although isolating the effect of an individual mode can only be done computationally, such computations may be considered as a precursor to experimental studies and provide the practitioners with an insight what to expect from a molecule approaching a surface crossing when vibrational energy is initially localized on a specific normal mode, and as such can be helpful for experimentalists working on control strategies.

**METHODS**

The calculations were performed using a developer’s version of Molcas 7.6.27 In the present work, energies, forces (equilibrium structures and trajectories), and vibrational frequencies are all obtained using two-root CASPT2(9,8)/ANO-RCC-VDZP. The choice of active space (9 electrons in 8 orbitals) for the underlying CASSCF wave function has been rationalized in a previous study.28 The two lowest roots (equally weighted) were included in the reported calculations. To simulate various vibrational excitation in CF2I, we optimize its ground-state equilibrium structure and compute its frequencies and normal modes at the CASPT2(9,8)/ANO-RCC-VDZP level of theory (using numerical gradients and Hessians), and then translate the global minimum on the ground state by different increments along the calculated CASPT2 normal modes. These increments are designated $v_{rj}$, where $r = 1$ are the lowest four vibrations in ascending order of energy and $j$ corresponds to displacements in positive ($+$) or negative ($-$) directions along the $r$th mode in 0.05 au increments. The $v_{1-4}$ modes were selected according to two criteria: (a) they are the most likely to be thermally populated under ambient laboratory conditions, and (b) they would have the greatest degree of overlap with the bandwidth ($\Delta \nu \approx 700 \text{ cm}^{-1}$) of a $\sim 50 \text{ fs}$ laser pulse. Nowadays, such a bandwidth can be supplied even by commercially available femtosecond laser sources. The displaced structures are subsequently promoted to the first excited state, and their excited-state evolution is traced by molecular dynamics simulations. Our approach (displacing the geometries rather than using velocities) is more prudent from an experimentalist’s perspective. It naturally simulates vibrational mediation experiments in a pump–probe scheme, and it can be extended to model coherent processes, such as vibrational sum-frequency generation spectroscopy, and coherent anti-Stokes Raman scattering.

The trajectories were calculated using the velocity Verlet algorithm, where the equations of motion were numerically integrated with a time step of 1 fs.34 The choice of a 1 fs time step is based on (i) the choice of numerical integrator (the velocity formulation of the Verlet algorithm used is well-documented to yield conserved total energies with step sizes on the order of 2–3 fs),35 and (ii) the physics of our specific target system (the fastest molecular vibration in CF2I is the asymmetric CF2 stretching vibration with a time period of $\sim 30 \text{ fs}$). In the Supporting Information section (Figure S1), we illustrate that these two criteria are reasonable, as gauged by the conservation of total energy within $\sim 1 \text{ kcal/mol}$ (root mean square deviation) for a few randomly selected trajectories.

**Figure 1.** $D_0$ (blue) and $D_1$ (wine) CASPT2 relative energies along the trajectories obtained by displacing the CF2I global minimum along the four low-energy normal modes in $D_0$ and promoting the displaced structures to the excited $D_1$ state. Panels correspond to the motion along (a) $\nu_1$ (CF2 stretch, 266 cm$^{-1}$), (b) $\nu_2$ (umbrella coupled with weak C–I stretch, 290 cm$^{-1}$), (c) $\nu_3$ (umbrella coupled with CF2 scissor, 560 cm$^{-1}$), and (d) $\nu_4$ (CF2 scissor coupled with C–I stretch, 642 cm$^{-1}$).28 Trajectories in each panel are launched from structures distorted by different increments designated as $r_{05}$ for a 0.05 au increment, $r_1$ for a 0.1 au increment, etc. Red dots schematically depict the positions of the CIs reached by the trajectories. The excited-state CASPT2 trajectory $v_{00}$ computed from the $D_0$ global minimum is shown as black lines for reference. A vector representation of the respective displacements is illustrated in the insets.
which is within the desired accuracy. Finally, the trajectories were initiated with zero kinetic energy. Indeed, by displacing the molecule along a vibrational mode $\nu_n$, we populate $\nu_n$ only. At the turning point where excitation occurs, the molecule has zero kinetic energy along that mode. Moreover, we assume that all other modes have zero energy to isolate the effect of only $\nu_n$ and to not bias the trajectories by our choice of nuclear velocities, but rather to allow the excited-state gradient to drive the starting structures. If one randomly populates other modes by geometric distortion or by adding velocities along these modes, it would no longer be possible to isolate the effect of the $\nu_n$ alone on the trajectory calculations. We stress that the objective of our work is to explore vibrational eigenstate-specific effects, which is why we do not adopt the standard practice of random sampling to simulate wavepacket preparation/propagation. Our objective cannot be achieved by randomly populating all the vibrational levels at the same time, where the effect of each vibrational mode will be lost.

**RESULTS AND DISCUSSION**

A reference excited-state CASPT2 trajectory $v_{00}$ is computed by releasing the system $D_0$ equilibrium structure (the FC point) along the $D_1$ energy surface with no initial kinetic energy, and terminated at the first intercepted CI point, which is then taken as the reference CI, $v_{00}$-CI. The fact that the reference trajectory hits a CI point in only 15 fs (Figure 1) indicates that the reaction coordinate must have a large component along one of the branching plane vectors at $v_{00}$-CI. We begin by inspecting the $D_1$ trajectories resulting from translating the FC point along the lowest energy normal mode, $\nu_1$, Figure 1a. The resulting trajectories bear a resemblance to the reference $v_{00}$ trajectory in terms of (i) the resulting time-dependent energy profiles, (ii) energies of the $D_1$ FC points, and (iii) the relative energy of the different $D_1-D_0$ CI points reached by these trajectories. Because the molecules following $v_{00}$ and $\nu_1$ trajectories have different initial geometries and the CI point structures have slightly different geometries along the FCI angle, the above similarities can be rationalized only by the fact that $\nu_1$ is a low-energy mode mostly displacing the trajectories along a flat region of the intersection subspace. In other words, it appears that for displacement along $\nu_1$, excited-state species are channeled through nearly parallel paths along the $N = 2$-dimensional intersection subspace accessed by $v_{00}$ where $N = 6$ is the number of vibrational degrees of freedom in the system.

On the other hand, the trajectories resulting from the displacement along $\nu_2$ do not have the properties (i−iii) of

![Figure 2](https://example.com/fig2.png)

Figure 2. Left column: 2D energy plots of the $D_0$ and $D_1$ states of CF$_2$I as a function of the displacement along the $\Delta \nu_{11}$ and $\Delta \nu_{21}$, $\Delta \nu_{11}$ and $\Delta \nu_{41}$, and $\Delta \nu_{11}$ and $\Delta \nu_{41m}$ vectors. Right column: the corresponding $D_0-D_1$ energy gaps. The full line on the coordinate base represents loci of the intersection space. Dashed lines indicate the region where the degeneracy has been lifted.
those displaced along \( \nu_1 \). When the FC point is displaced along \( \nu_2 \), a locus of conical intersections, i.e., a segment of the intersection space with different geometries and energies, is traced by the CASPT2 excited-state trajectories. This implies that \( \nu_2 \) like \( \nu_3 \) has a projection on the intersection space, but samples a steeper excited state in the FC region. To support the conclusions drawn above, we scanned the \( D_3 \) and \( D_1 \) potential energy surfaces in the vicinity of the \( v_{00}\)-CI structure. We displaced the \( v_{00}\)-CI structure along \( \Delta \nu_{13} \) and \( \Delta \nu_{23} \) vectors, where \( \Delta \nu_{13} \) is defined as the difference in internal coordinates between \( \nu_0 \) and \( \nu_3 \), and where the subscript \( k \) is the vibrational mode number and the unit designates the displacement of 0.1 au, Figure 2a,b. We found that the displacement of the \( v_{00}\)-CI along \( \Delta \nu_{13} \) causes little degeneracy splitting, whereas the splitting is even less pronounced along \( \Delta \nu_{23} \), and a combination of \( \Delta \nu_{13} \) and \( \Delta \nu_{23} \) leads to a plane of intersection points. Therefore, populating a normal mode that has a large projection on the space orthogonal to the branching plane defined by the gradient difference and derivative coupling vectors allows sampling of different conical intersection points along the seam, Figure 1a,b.

We then translate the FC point along \( \nu_2 \), a displacement that resembles the excited-state reaction vector pointing toward the minimum energy conical intersection characterized in the CASSCF study.\(^{28}\) Not surprisingly, the Franck–Condon region is steep for translation along \( \nu_2 \) as is evident from inspecting Figure 1c. As a result, a small displacement along this mode causes (i) a large drop in the energy of the starting structure, and (ii) a systematic decrease in the relative energies of the intercepted CIs for larger displacements. Nonetheless, the computed trajectories reach their respective degeneracy points at the same time. This is interpreted in terms of cancellation effects. Namely, a decrease in acceleration due to smaller local curvature of PES is annulled by a smaller “time of travel” from the \( \nu_2 \)-displaced starting structure to the seam. Therefore, \( \nu_2 \) is interpreted as orthogonal to the intersection space and parallel to one of the branching plane vectors such as to the gradient different vector, i.e., the difference in the gradients of the \( D_3 \) and \( D_1 \) energy surfaces.

A conceptually different and practically interesting scenario is encountered when the system is displaced along \( \nu_3 \), Figure 1d. The positive \( \nu_3 \) displacement propels CF2I toward the CI seam. In contrast, the negative \( \nu_3 \) displacement leads to a region where \( D_3-D_1 \) degeneracy is gradually lifted. In fact, these computed trajectories trace an avoided crossing and the prepared excited-state species do not reach the seam within the computed time scale. The additional time spent by the excited-state species at the avoided crossing would be expected to slave the \( \nu_3 \) populated species to intra- and intermolecular vibrational energy dissipation pathways in practical applications. On the basis of the large energy drop of the starting structure along \( \nu_3 \), this mode must have a projection on the reaction coordinate vector, similar to \( \nu_2 \). We note that the reaction vector has a large component of C–I stretching.\(^{27}\) In fact, \( \nu_3 \), \( \nu_4 \), and to a smaller extent \( \nu_2 \), have a significant C–I stretch character (Figure 1b–d), which explains their dynamic similarities. Consistent with our prior analysis in Figure 2a,b, the topological features resulting from the \( v_{00}\)-CI structure displaced along \( \Delta \nu_{13} \) and \( \Delta \nu_{23} \) vectors in combination with \( \Delta \nu_{13} \) reveal that both \( \Delta \nu_{13} \) and \( \Delta \nu_{23} \) exhibit a surface with a conical shape and hence have components along the branching plane, supporting our reasoning above, Figure 2c–f. Conversely, \( \nu_3 \) and \( \nu_4 \) appear to have a larger projection on the intersection space.

### CONCLUSIONS

Overall, uncovering the relationship between the normal modes, the topologies of the ground and excited states, and the branching plane vectors, aided either (i) by vibrational mediation where the laser frequency is simply tuned to selectively populate specific vibrational modes or (ii) by creating superpositions of vibrational states in optimal control schemes and nonlinear spectroscopy, is prerequisite for understanding how effective control over the excited-state dynamics and, therefore, the outcome of a nonadiabatic photochemical reaction can be achieved. Clearly, controlling the excited-state path is a challenge but the only sensible approach is to learn about it as much as possible and computational theory helps us to do that. We rigorously illustrate how excited-state species access different regions of the conical intersection seam or avoid it by using on-the-fly CASPT2 excited-state dynamics of a small polyatomic radical, which trace the locus of the CI in the basis of the vibrational normal modes, thus enabling us to visualize different segments of the intersection space. The concepts illustrated herein, combined with ultrafast time-resolved techniques and the advances in multidimensional quantum simulations with an explicit inclusion of the laser field,\(^{37}\) should aid in designing and rationalizing the outcome of experiments aiming at exploiting vibrational-state specificity to optimize photochemical reactivity.

### ASSOCIATED CONTENT

#### Supporting Information

Computational details, energy conservation plot, active space orbitals, energy profiles, Cartesian coordinates, and movies illustrating the molecular motion for four trajectories in which the FC structure is displaced along \( \nu_1 - \nu_2 \). This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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