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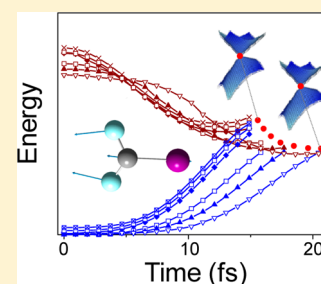
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S Supporting Information

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,¹ either in the ground or in the excited electronic states, as demonstrated in early studies.^{2–4} 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,^{4–10} (ii) state-selective dissociative chemisorption on metal surfaces^{11,12} and (iii) more recently, condensed-phase photochemical reactions such as cis–trans isomerization and energy transfer in natural and artificial light-harvesting complexes, where selective excitation of vibrational modes is achieved using optimal control schemes^{13,14} utilizing femto-second laser pulse shaping.^{15–20}

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,^{21–26} 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 vibrational-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 theory (CASPT2)²⁷ 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.²⁸ 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.^{25,29–31} However, in the present study we systematically sample the effect of the degree

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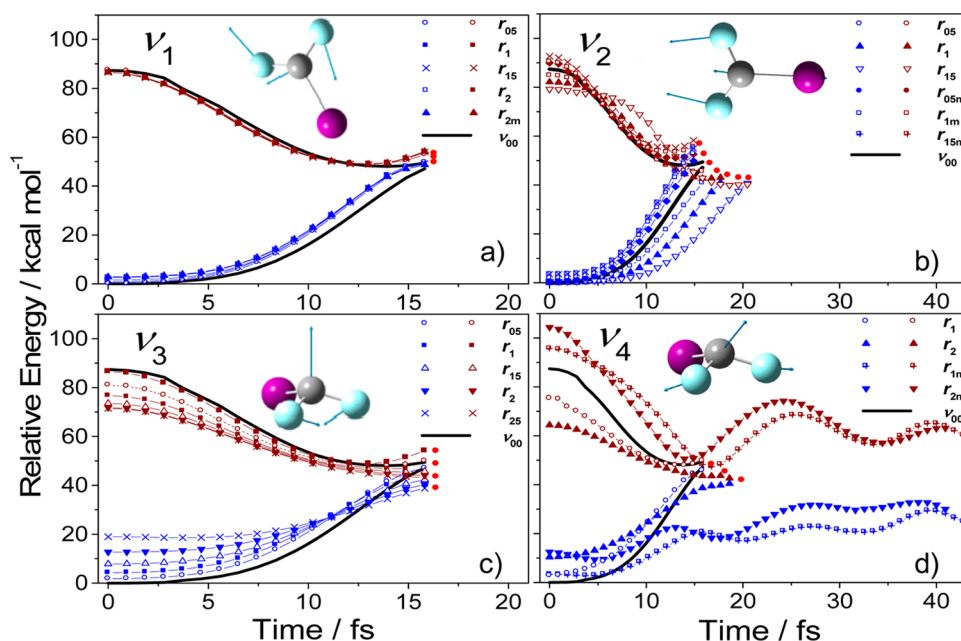


Figure 1. D_0 (blue) and D_1 (wine) CASPT2 relative energies along the trajectories obtained by displacing the CF_2I global minimum along the four low-energy normal modes in D_0 and promoting the displaced structures to the excited D_1 state. Panels correspond to the motion along (a) ν_1 (CF_2 rock, 266 cm^{-1}), (b) ν_2 (umbrella coupled with weak C–I stretch, 290 cm^{-1}), (c) ν_3 (umbrella coupled with CF_2 scissor, 560 cm^{-1}), and (d) ν_4 (CF_2 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 ν_{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.

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 CF_2I 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 CF_2I , 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 $\nu_j r_{j(m)}$, where ν_1 – ν_4 are the lowest four vibrations in ascending order of energy and r corresponds to displacements in positive (j) or negative (jm) directions along the ν th mode in 0.05 au increments. The ν_{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 ~ 50 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 CF_2I is the asymmetric CF_2 stretching vibration with a time period of ~ 30 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 ~ 1 kcal/mol (root mean square deviation) for a few randomly selected trajectories,

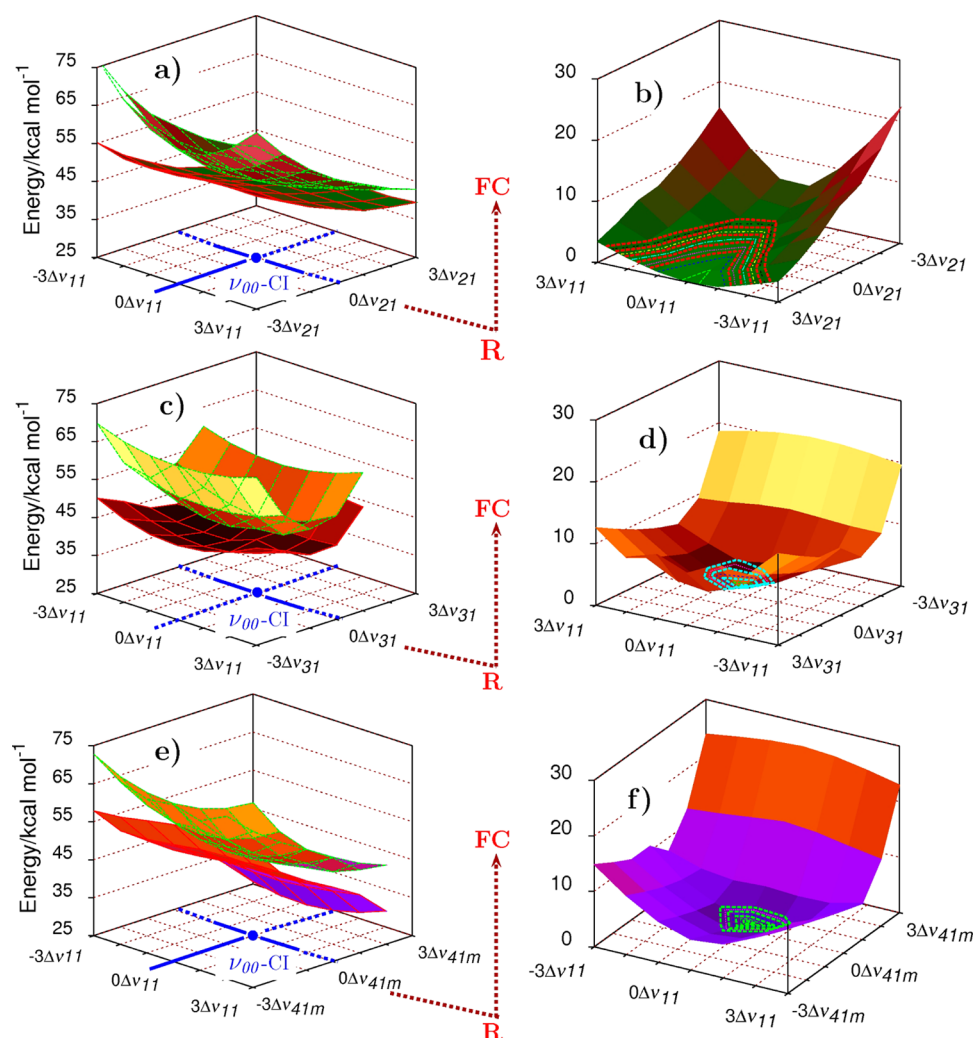


Figure 2. Left column: 2D energy plots of the D_0 and D_1 states of CF_2I as a function of the displacement along the $\Delta\nu_{11}$ and $\Delta\nu_{21}$, $\Delta\nu_{11}$ and $\Delta\nu_{31}$, and $\Delta\nu_{11}$ and $\Delta\nu_{41m}$ vectors. Right column: the corresponding $D_0 - D_1$ energy gaps. The full line on the coordinate base represents loci of the intersection space. Dashed lines indicate the region where the degeneracy has been lifted.

which is within the desired accuracy. Finally, the trajectories were initiated with zero kinetic energy. Indeed, by displacing the molecule along a vibrational mode ν_m we populate ν_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 ν_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 ν_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 sampling³⁶ 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 ν_{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, $\nu_{00}\text{-CI}$. 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 vectors²¹ at $\nu_{00}\text{-CI}$. We begin by inspecting the D_1 trajectories resulting from translating the FC point along the lowest energy normal mode, ν_1 , Figure 1a. The resulting trajectories bear a resemblance to the reference ν_{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 $D_1\text{-}D_0$ CI points reached by these trajectories. Because the molecules following ν_{00} and ν_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 ν_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 ν_1 , excited-state species are channeled through nearly parallel paths along the $N - 2$ -dimensional intersection subspace accessed by ν_{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 ν_2 do not have the properties (i–iii) of

those displaced along ν_1 . When the FC point is displaced along ν_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 ν_2 like ν_1 , 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_0 and D_1 potential energy surfaces in the vicinity of the ν_{00} -CI structure. We displaced the ν_{00} -CI structure along $\Delta\nu_{11}$ and $\Delta\nu_{21}$ vectors, where $\Delta\nu_{k1}$ is defined as the difference in internal coordinates between ν_{00} and ν_{k1} , and where the subscript k is the vibrational mode number and the unity designates the displacement of 0.1 au, Figure 2a,b. We found that the displacement of the ν_{00} -CI along $\Delta\nu_{11}$ causes little degeneracy splitting, whereas the splitting is even less pronounced along $\Delta\nu_{21}$, and a combination of $\Delta\nu_{11}$ and $\Delta\nu_{21}$ 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 ν_3 , 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 ν_3 , 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 ν_3 -displaced starting structure to the seam. Therefore, ν_3 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_1 and D_0 energy surfaces.

A conceptually different and practically interesting scenario is encountered when the system is displaced along ν_4 , Figure 1d. The positive ν_4 displacement propels CF_2I toward the CI seam. In contrast, the negative ν_4 displacement leads to a region where D_0 – 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 ν_4 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 ν_4 , this mode must have a projection on the reaction coordinate vector, similar to ν_3 . We note that the reaction vector has a large component of C–I stretching.²⁸ In fact, ν_3 , ν_4 , and to a smaller extent ν_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 ν_{00} -CI structure displaced along $\Delta\nu_{31}$ and $\Delta\nu_{41}$ vectors in combination with $\Delta\nu_{11}$ reveal that both $\Delta\nu_{31}$ and $\Delta\nu_{41}$ exhibit a surface with a conical shape and hence have components along the branching plane, supporting our reasoning above, Figure 2c–f. Con-

versely, ν_1 and ν_2 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 ν_1 – ν_4 . 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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