University of Groningen

Multi-state vibronic interactions in the 1,2,3-trifluorobenzene radical cation

Faraji, Shirin; Koeppel, Horst

Published in:
Journal of Chemical Physics

DOI:
[10.1063/1.4746159](https://doi.org/10.1063/1.4746159)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2012

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Faraji, S., & Koeppel, H. (2012). Multi-state vibronic interactions in the 1,2,3-trifluorobenzene radical cation. *Journal of Chemical Physics*, 137(22), [ARTN 22A531]. <https://doi.org/10.1063/1.4746159>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Multi-state vibronic interactions in the 1,2,3-trifluorobenzene radical cation

Shirin Faraji, and Horst Köppel

Citation: [The Journal of Chemical Physics](#) **137**, 22A531 (2012); doi: 10.1063/1.4746159

View online: <https://doi.org/10.1063/1.4746159>

View Table of Contents: <http://aip.scitation.org/toc/jcp/137/22>

Published by the [American Institute of Physics](#)

Articles you may be interested in

[Full dimensional quantum-mechanical simulations for the vibronic dynamics of difluorobenzene radical cation isomers using the multilayer multiconfiguration time-dependent Hartree method](#)

[The Journal of Chemical Physics](#) **137**, 134302 (2012); 10.1063/1.4755372

[Multistate vibronic interactions in difluorobenzene radical cations. II. Quantum dynamical simulations](#)

[The Journal of Chemical Physics](#) **129**, 074311 (2008); 10.1063/1.2958918

[Multistate vibronic interactions in difluorobenzene radical cations. I. Electronic structure calculations](#)

[The Journal of Chemical Physics](#) **129**, 074310 (2008); 10.1063/1.2958915

[Ab initio quantum dynamical study of the multi-state nonadiabatic photodissociation of pyrrole](#)

[The Journal of Chemical Physics](#) **135**, 154310 (2011); 10.1063/1.3651536

[Toward large scale vibrational configuration interaction calculations](#)

[The Journal of Chemical Physics](#) **131**, 124129 (2009); 10.1063/1.3243862

[Towards converging non-adiabatic direct dynamics calculations using frozen-width variational Gaussian product basis functions](#)

[The Journal of Chemical Physics](#) **137**, 22A548 (2012); 10.1063/1.4765087

PHYSICS TODAY

WHITEPAPERS

ADVANCED LIGHT CURE ADHESIVES

Take a closer look at what these environmentally friendly adhesive systems can do

READ NOW

PRESENTED BY

Multi-state vibronic interactions in the 1,2,3-trifluorobenzene radical cation

Shirin Faraji^{a)} and Horst Köppel^{b)}*Theoretische Chemie, Physikalisch-Chemisches Institut, INF 229, Universität Heidelberg, D-69120 Heidelberg, Germany*

(Received 31 May 2012; accepted 2 August 2012; published online 27 August 2012)

The multi-state and multi-mode vibronic interactions between the five lowest electronic states of the title compound are investigated theoretically by an *ab initio* quantum dynamical approach. The well-established linear vibronic coupling scheme is adopted, augmented by quadratic coupling terms for the totally symmetric modes. The pertinent system parameters are obtained from outer valence Greens function and equation-of-motion coupled-cluster *ab initio* calculations. Large-scale quantum dynamical simulations are performed employing a powerful wavepacket propagation scheme. The band shapes and line structures (as far as available) of the experimental photoelectron spectra are well reproduced. Time-dependent electronic populations reveal ultrafast internal conversion processes and allow for important insight into the fluorescence properties of the radical cation. The relation to other fluoro derivatives of the benzene radical cation is discussed. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4746159>]

I. INTRODUCTION

Conical intersections, that is crossings between potential energy surfaces (PES) of the same multiplicity, and vibronic interactions^{1–5} are among the key factors governing molecular structure, excited-state dynamics, and spectroscopy. They lead to strongly coupled electronic and nuclear motions such that the familiar adiabatic (or Born-Oppenheimer) approximation fails severely, giving rise to what is now called nonadiabatic chemistry. In other words, the nonadiabatic interaction cannot be treated as a weak perturbation. Rather, it has to be treated on the same footing as the vibrational motion itself. Molecular motion in systems which exhibit such topologies can easily hop between electronic states through the “funnel”⁶ of the conical intersection. As a result, the correct description of molecular spectroscopy and dynamics in the presence of a conical intersection requires all nonadiabatic couplings between the conically intersecting PES to be taken into account. The vibronic coupling of molecular electronic states opens up numerous pathways for the nuclei to move. Speaking pictorially, the nuclei move on several PES simultaneously, with frequent jumps occurring on the timescale of the vibrational motion. The first historic example in the literature relates to the Jahn-Teller (JT) effect where the degeneracy between the PES is caused by symmetry. The JT effect is often viewed as a mechanism for symmetry-lowering through asymmetric modes, which lift the degeneracy in first order in the nuclear displacements. However, at the symmetry-point in nuclear coordinate space, the first-order coupling leads to the formation of a conical intersection of the PES with all the consequences for nonadiabatic nuclear motion indicated above.^{2,7} Moreover, the JT-induced symmetry lowering is considered “spontaneous” because no critical coupling strength is to be exceeded for the reduction in symmetry to occur. For a fi-

nite energy gap between the interacting states, the symmetry lowering is still possible provided the coupling is sufficiently strong. This is considered another important, more generic aspect of the coupling between the different PES.^{3,8,9}

The signature of conical intersections in excited-state processes is usually related to the occurrence of short excited-state lifetimes of tens of femtoseconds or less, since the intersection provides a funnel of fast access to the ground state. This is the case when the conical intersection is accessible from the Franck-Condon region without significant energy barriers. Broad and diffuse vibronic spectra and a low quantum yield of fluorescence can be related to this observation. Species that are prime candidates to be subject to vibronic interactions and undergo the related JT distortion are highly symmetrical organic molecules with open shell electronic states, i.e., free radicals and ions. An important class of systems in this respect are the benzene and benzenoid cations, for which the electronic structure, spectroscopy, and dynamics have received great attention in the literature.^{10–14} The fluorobenzene derivatives are of systematic interest for at least two different reasons. (1) The reduction of symmetry by incomplete substitution/fluorination leads to a disappearance of the JT effect present in the parent cation. (2) A specific, more *chemical* effect of fluorination consists in the energetic increase of the lowest σ -type electronic states of the radical cations. As a consequence, there is a strong dependence of their emission properties on the degree of fluorination. Fluorobenzene cations having more than three fluorine atoms are highly fluorescent, while the monofluorobenzene cation, like the parent cation itself, is nonemissive, and their emission quantum yield is reported to be $<10^{-5}$.¹² The difluorobenzene cations appear to be an intermediate case.^{11–13} As has been demonstrated, the interactions between five different states play a role^{15–17} and have been identified as being responsible for the absence of detectable emission in the benzene cation Bz⁺ (Refs. 18 and 19) and several derivatives.¹² This is caused by ultrafast internal conversion processes due

^{a)}Electronic mail: Shirin.Faraji@pci.uni-heidelberg.de.^{b)}Electronic mail: Horst.Koepfel@pci.uni-heidelberg.de.

to nonadiabatic interactions that are so strong that fluorescence cannot compete.^{15,16,18–22} It is therefore one purpose of the present work to extend our earlier studies^{23–26} on multi-mode and multi-state vibronic interactions in the benzene radical cation and its mono- and difluoro derivatives to cover also the 1, 2, 3-trifluorobenzene radical cation, and thus shed further light on the trends in this family of compounds. To this end, the multi-mode and multi-state vibronic interactions between the five lowest electronic states of the 1, 2, 3-trifluorobenzene radical cation will be investigated theoretically, based on *ab initio* electronic structure data, and employing the well-established linear vibronic coupling model (LVC), augmented by quadratic coupling terms for the totally symmetric vibrational modes. Wave-packet dynamical calculations for these coupled potential energy surfaces, utilizing the powerful multi-configuration time-dependent Hartree (MCTDH) method are performed. Ultrafast internal conversion processes and the analysis of the photoelectron (PE) spectra provide a detailed understanding of the spectroscopy and fluorescence dynamics of this species. We mention that a related study has been published recently on the 1, 3, 5-trifluorobenzene radical cation.²⁷

This paper is organized as follows. In Sec. II, we detail the theoretical approach and the electronic structure and quantum dynamical methods used. Section III presents the analysis of resulting coupling constants, PES, and associated conical intersections. Section IV is devoted to the dynamical quantities, namely, spectral intensity distribution and time-dependent electronic populations, and to the discussion of the fluorescence dynamics. Finally, Sec. V concludes.

II. THEORETICAL FRAMEWORK

A. Vibronic coupling Hamiltonian

In the present paper, we are focusing on the five lowest electronic states of the 1, 2, 3-trifluorobenzene radical cation. These states lie in the ionization energy range from 9 to 14 eV and give rise to the low energy band systems of the experimental PE spectra.¹⁰ At the equilibrium geometry of the neutral, the symmetry assignments of these cationic doublet states, ordered by ascending vertical ionization potentials, are listed as follows:

$$\begin{aligned} \tilde{X}^2 B_1(\pi) & (9.63 \text{ eV}), \\ \tilde{A}^2 A_2(\pi) & (9.66 \text{ eV}), \\ \tilde{B}^2 B_1(\pi) & (12.71 \text{ eV}), \\ \tilde{C}^2 B_2(\sigma) & (13.58 \text{ eV}), \\ \tilde{D}^2 A_1(\sigma) & (13.59 \text{ eV}). \end{aligned} \quad (1)$$

Note, 1, 2, 3-trifluorobenzene is a planar molecule and belongs to the point group C_{2v} . The choice of coordinate axes underlying the symmetry assignment is such that the molecule lies in the y,z-plane, with the z-axis being the C_2 rotation axis. The symbols in the first parentheses refer to the character of the underlying orbitals out of which ionization takes place, the numbers in the following ones represent the *ab initio* ver-

tical ionization potentials obtained at the outer valence Greens function (OVGF) level of theory.

In order to study the vibronic dynamics and spectra resulting from the coupled electronic and vibrational motion, we use the same approach as in earlier related work, the vibronic coupling (VC) model.^{3,7,28} This model relies on the use of a (quasi) diabatic representation of the electronic states. Contrary to the usual adiabatic electronic basis, the off-diagonal matrix elements, which generate the couplings within the electronic manifold, arise from the potential energy part of the Hamiltonian, rather than from the nuclear kinetic energy. This has the advantage to get rid of the singularities of the derivative couplings at degeneracies of electronic states. Indeed, diabatic functions are usually smooth functions of the nuclear coordinates $\mathbf{Q}$.^{29–34} As a consequence, the potential energy matrix elements in the diabatic basis can be expanded in a Taylor series in $\mathbf{Q}$ and only low-order terms be retained. Truncating the series after the first-order terms defines the *linear vibronic coupling* (LVC) model, while including second-order terms leads to the *quadratic vibronic coupling* (QVC) model, and so forth.

In recent papers,^{15,16,24–26} we have analyzed the multi-state vibronic interactions in the five lowest (doublet) states of Bz^+ , $F-Bz^+$, and the difluorobenzene isomers theoretically, based on an *ab initio* quantum dynamical approach. The pertinent coupling constants have been extracted from high-level equation-of-motion coupled-cluster (EOM-CCSD) calculations^{35–38} for the underlying ionization potentials and coupling constants. The LVC has been successfully used, for instance, to describe the parent ion,^{15,16} Bz^+ , but it could not explain the absence of detectable emission in $F-Bz^+$. The studies²⁴ revealed that inclusion of the quadratic couplings leads to an essential energetic lowering of several seams of conical intersection, rendering all five states strongly coupled. Contrary to the LVC results, this is able to provide a mechanism for explaining the absence of fluorescence in this species and will be used in the present work.

The 30 vibrational modes of 1, 2, 3-trifluorobenzene are of the following symmetry species:

$$\Gamma_{vib} = 11A_1 \oplus 3A_2 \oplus 6B_1 \oplus 10B_2. \quad (2)$$

Twenty one of these 30 vibrational degrees of freedom are planar, nine represent out-of-plane motions. In applying the LVC Hamiltonian to the subset of electronic states, one has to take into account symmetry selection rules,³ which impose important restrictions on the modes appearing in the various summations of Eq. (4). These are relevant, in particular, for the linear coupling terms, for which they read

$$\Gamma_\alpha \otimes \Gamma_i \otimes \Gamma_\beta \supset \Gamma_A. \quad (3)$$

Explicitly, a given vibrational mode with symmetry Γ_i can couple electronic states with symmetries Γ_α and Γ_β in first order only if the direct product on the left-hand side of Eq. (3) comprises the totally symmetric irreducible representation Γ_A of the point group in question. The generalization to the second-order terms should be apparent, though it is less restrictive. Obviously, all totally symmetric modes can couple to the electronic motion in first order, emphasizing the important role of these modes in the vibronic coupling problem.

The totally symmetric modes are referred to as *tuning* modes due to the fact that they tend to modulate the separation of the interacting electronic states. In molecules with high symmetry, the first order interstate coupling constants $\lambda_i^{(\alpha\beta)}$ are usually nonzero for nontotally symmetric modes, which are correspondingly called *coupling* modes. In the Abelian C_{2v} and D_{2h} molecular point groups, only nondegenerate irreducible representations, and thus no symmetry-induced

degeneracies, occur; therefore, the JT effect as in Bz^+ (Ref. 15) is absent here. This makes it straightforward to apply the above symmetry selection rule to deduce the vibronic Hamiltonian matrices for the description of the five lowest $\tilde{X} - \tilde{D}$ doublet states of the 1, 2, 3-trifluorobenzene cation,

$$\mathbf{H} = (T_N + V_0) \mathbf{1} + \mathbf{W}, \quad (4)$$

$$\mathbf{W} = \begin{pmatrix} E_X + \kappa_X \mathbf{Q} + \mathbf{g}_X \mathbf{Q}^2 & \sum_{j \in B_2} \lambda_j^{(X,A)} Q_j & 0 & 0 & 0 \\ \sum_{j \in B_2} \lambda_j^{(X,A)} Q_j & E_A + \kappa_A \mathbf{Q} + \mathbf{g}_A \mathbf{Q}^2 & 0 & \sum_{j \in B_1} \lambda_j^{(A,C)} Q_j & 0 \\ 0 & 0 & E_B + \kappa_B \mathbf{Q} + \mathbf{g}_B \mathbf{Q}^2 & \sum_{j \in A_2} \lambda_j^{(B,C)} Q_j & \sum_{j \in B_1} \lambda_j^{(B,D)} Q_j \\ 0 & \sum_{j \in B_1} \lambda_j^{(A,C)} Q_j & \sum_{j \in A_2} \lambda_j^{(B,C)} Q_j & E_C + \kappa_C \mathbf{Q} + \mathbf{g}_C \mathbf{Q}^2 & \sum_{j \in B_2} \lambda_j^{(C,D)} Q_j \\ 0 & 0 & \sum_{j \in B_1} \lambda_j^{(B,D)} Q_j & \sum_{j \in B_2} \lambda_j^{(C,D)} Q_j & E_D + \kappa_D \mathbf{Q} + \mathbf{g}_D \mathbf{Q}^2 \end{pmatrix},$$

where

$$\kappa \mathbf{Q} = \sum_{i \in A_1} \kappa_i^{(\alpha)} Q_i \quad \text{and} \quad \mathbf{g} \mathbf{Q}^2 = \sum_{i \in A_1} g_i^{(\alpha)} Q_i^2, \quad (5)$$

with Γ_i being the irreducible representation to which the mode i belongs. In Eq. (4), E_α corresponds to the vertical IP for the state α ordered as in Eq. (1). (This is due to our particular choice of the diabatic states, chosen to coincide with the adiabatic ones at the center of the Franck-Condon zone, $\mathbf{Q} = \mathbf{0}$.) The quantities $\kappa_i^{(\alpha)}$ and $\lambda_j^{(\alpha\beta)}$ are the intrastate and interstate (linear) coupling constants, respectively, and similarly for the $g_{ii}^{(\alpha)}$, etc. The zero-order Hamiltonian $T_N + V_0$ in Eq. (4) represents the set of ground state harmonic oscillators of neutral 1, 2, 3-trifluorobenzene and all the Q_i entering Eq. (4) denote dimensionless normal coordinates for this state.

The vibrational modes entering the various coupling terms, i.e., diagonal and off-diagonal matrix elements, are determined by the previous Eqs. (2) and (3), and their symmetry is indicated under the corresponding summation symbol. Some of the off-diagonal entries in Eq. (4) are put to zero for clarity, because the subsequent electronic structure calculations reveal only negligible interactions between these electronic states, in particular conical intersections, which are so high in energy (≥ 0.3 eV higher than the vertical IP of the highest energy electronic state) that they are inaccessible to the nuclear motion. Therefore, we confine ourselves in the following to those terms which will be found below to be significant for the 1, 2, 3-trifluorobenzene cation. As well known,³ the nonadiabatic dynamics described by the above vibronic coupling Hamiltonian is essentially controlled by the energies of the minima of the various diabatic surfaces as well as of the various conical intersection seams.^{3,28} Sim-

ple analytic expressions for these quantities, deduced within the LVC scheme, have been derived in Sec. III of Ref. 3. One should note that the determination of the seam minima in the presence of quadratic couplings represents a nontrivial extension of the LVC model, because this equation becomes nonlinear. Pertinent aspects are discussed in the appendix of Ref. 24.

In order to determine the various coupling parameters entering the vibronic coupling Hamiltonian, Eq. (4), *ab initio* electronic structure calculations have been performed using two different methods. In the first method, called outer valence Greens function (OVGF) method, the ionization potentials are determined directly, i.e., without forming the energy difference of electronic states of ionic and neutral species.³⁹⁻⁴¹ The OVGF method accounts for reorganization and correlation effects in a balanced way without giving up the quasi-particle picture for ionization. It leads to an improved description of vibrational structures in photoelectron spectra^{39,42} as long as satellite lines are not important in the spectrum. The calculations were performed using the Gaussian program package.⁴³ In addition to the OVGF calculations, calculations have also been performed at the coupled cluster level using the so called equation-of-motion coupled-cluster (EOMIP-CCSD) method (also known as coupled-cluster Greens function method)^{35,36} implemented in the local version of the ACES program system.⁴⁴ Here again, the ionization potentials are determined directly. The relation of this method to the OVGF method was discussed in detail by Nooijen and Snijders.⁴⁵ EOMIP-CCSD is considered to be less approximate than OVGF. However, EOMIP-CCSD is more expensive since no perturbational truncation is involved. Therefore, we have also applied the second-order

approximation to EOMIP-CCSD known under different names (EOMIP-CCSD(2), EOMIP-MBPT(2), and MBPT(2)-GF).^{46,47} This approximate version has been extensively tested and has been shown not to introduce substantial errors in the energies of ionized states, but somewhat less expensive than OVGf.^{15,46} A standard triple-zeta (TZ2P) (Ref. 48) basis set has been employed for both sets of calculations. This basis consists of the triple zeta set of Dunning⁴⁹ augmented by polarization functions as given in Refs. 50 and 51. EOMIP-CCSD gives degenerate energies for the $\tilde{C}$ and $\tilde{D}$ states along the B_2 vibrational modes, which makes the calculation of the coupling constants for the corresponding states incomplete. Therefore, we rely on the OVGf results for these cases.

B. Dynamical calculations

Quantum dynamics simulations represent an essential tool for understanding key experiments, in particular those in the field of femto-chemistry,^{52,53} which require accompanying calculations for interpretation. The dynamical calculations performed in this work and reported below rely on fully quantal, time-dependent methods, namely wavepacket propagation techniques. The MCTDH method^{54–59} uses a time development of the wavefunction expanded in a basis of sets of variationally optimized time-dependent functions $\varphi^{(\kappa)}$ called single-particle functions (SPFs). The MCTDH equations of motion are obtained from the Dirac-Frenkel variational principle. By virtue of this optimization, the length of this expansion can be much smaller than in standard integration schemes (so-called MCTDH contraction effect). The efficiency is even enhanced by two important additional features: each of the coordinates used in the integration scheme can comprise several physical coordinates Q_i . Furthermore, for vibronically coupled systems, the wave function is written as a sum of several wavefunctions, which is called *multi-set* formulation,

$$\Psi(t) = \sum_{\alpha}^{n_s} \Psi_{\alpha}(t) |\alpha\rangle. \quad (6)$$

The SPFs may then be optimized separately for each electronic state, and therefore fewer coefficients are needed in the wavefunction expansion. Both choices are employed in this work and, in combination, lead to an MCTDH contraction⁵⁷ effect of about six orders of magnitude in typical applications. This reduces the basis-set size from $\sim 10^{13}$ primitive basis functions to roughly $\sim 10^6$ time-dependent basis functions, thus making the quantum dynamical calculations feasible at all.

The solution of the equations of motion requires the frequent computation of the mean-fields. The efficiency of the MCTDH method thus demands their fast evaluation, and necessitates to avoid the explicit calculation of high-dimensional integrals. We emphasize that the form, Eq. (4), of the VC Hamiltonian represents a sum of low-order products of the Q_i , which is exactly the form that makes the application of the MCTDH algorithm efficient.

Given the time-dependent wavepacket (6), various time-dependent and time-independent quantities can be computed directly or indirectly. PE spectra can be obtained directly from

a time-dependent treatment as the Fourier transform of the autocorrelation function $C(t)$, assuming a direct transition from the initial to the final states within the framework of Fermi's golden rule:^{3,60}

$$P(E) \propto \int e^{iEt} C(t) dt, \quad (7)$$

with

$$C(t) = \langle \Psi(0) | \Psi(t) \rangle = \langle 0 | \tau^{\dagger} e^{-i\mathbf{H}t} \tau | 0 \rangle, \quad (8)$$

$$= \langle \Psi(t/2)^* | \Psi(t/2) \rangle. \quad (9)$$

In Eq. (8), $|0\rangle$ is the vibrational ground state of the initial electronic state—the ground state of the neutral species in our case, and $\tau^{\dagger}$ is the vector of individual transition matrix elements τ_{α} between the initial state and the final electronic states labelled by α . The autocorrelation function $C(t)$ measures the overlap between this time-evolving wave-packet and the initial one, and its Fourier transform gives the corresponding spectrum according to Eq. (7). The scalar product involving the vector τ of transition matrix elements implies a summation over various partial spectra, each being proportional to $|\tau_{\alpha}|^2$ (different final electronic states). The total spectrum can thus be obtained in two equivalent ways: (i) by exciting initially all electronic states, or (ii) by summing partial “single-state” spectra obtained after the excitation of only one electronic state at a time. Equation (9) is valid here because our Hamiltonian is hermitean and the initial wavepacket is real,^{61,62} and allows to reduce the propagation time by a factor of two.

Due to the finite propagation time T of the wavepacket, the Fourier transformation causes artifacts known as the Gibbs phenomenon.⁶³ In order to reduce this effect, the autocorrelation function is first multiplied by a damping function $\cos^2(\pi t/2T)$.^{57,64} Furthermore, to simulate the experimental line broadening, the autocorrelation functions are damped by an additional multiplication with a Gaussian function $\exp[-(t/\tau_d)^2]$, where τ_d is the damping parameter. This multiplication is equivalent to a convolution of the spectrum with a Gaussian with a full width at half maximum (FWHM) of $4(\ln 2)^{1/2}/\tau_d$. The convolution thus simulates the resolution of the spectrometer used in experiments, plus intrinsic line broadening effects.

The two other quantities of interest are the time-evolving (diabatic) electronic populations, $P_{\alpha}(t)$, and two-dimensional reduced densities $\rho_{\alpha}(Q_i, Q_j, t)$ for the electronic state α . These quantities are defined as follows, using the wavefunction given by Eq. (6):

$$P_{\alpha}(t) = \langle \Psi_{\alpha}(t) | \Psi_{\alpha}(t) \rangle, \quad (10)$$

$$\rho_{\alpha}(Q_i, Q_j, t) = \int \Psi_{\alpha}^*(t) \Psi_{\alpha}(t) \prod_{l \neq i, j} dQ_l. \quad (11)$$

All these quantities will be exploited in the following to decipher the dynamical properties of the 1, 2, 3-trifluorobenzene cation.

TABLE I. Comparison of the *ab initio* CCSD, OVGF, and adjusted data for the vertical IPs of the 1, 2, 3-difluorobenzene cation. All quantities are in eV.

	CCSD	OVGF	Adjusted
$\tilde{X}^2B_1$	9.73	9.63	9.83
$\tilde{A}^2A_2$	9.78	9.66	9.86
$\tilde{B}^2B_1$	12.96	12.71	12.76
$\tilde{C}^2B_2$	13.48	13.58	13.50
$\tilde{D}^2A_1$	13.59	13.59	13.50

III. ELECTRONIC STRUCTURE RESULTS

A. Vertical ionization potentials and vibronic coupling constants

As a basis for the subsequent dynamical calculations, we start here with the key quantities, the vertical ionization potentials (IPs) and present them in tabular form in Table I. In Table I are listed various sets of vertical IPs, first *ab initio* results obtained through EOM-CCSD and OVGF calculations. These are considered accurate calculations, which nevertheless require minor adjustment for a better comparison with experiment.¹⁰ The latter has been achieved by a careful analysis of PE spectroscopic data.^{16,24–26} The adjusted numbers

are seen to deviate by typically 0.1–0.2 eV from the pure *ab initio* data (IPa), which is considered quite satisfactory. Comparison of the adjusted values with both sets of *ab initio* data (EOM-CCSD and OVGF) shows that EOM-CCSD gives better results for the $\tilde{X}$ and $\tilde{A}$ states; however, OVGF produces slightly better agreement for the $\tilde{B}$ – $\tilde{D}$ states. For the 1, 2, 3-trifluoro isomer, all the coupling parameters entering the vibronic coupling Hamiltonian (Eq. (4)) as well as the subsequent dynamical treatments are based on the OVGF results.

Formally, the various coupling constants can be computed by using analytic gradient techniques or finite displacements along the various normal coordinates entering Eq. (4). While for the totally symmetric modes first derivatives are needed, the computation of the off-diagonal or inter-state coupling constants requires the second derivatives, or a least-squares fitting procedure using the eigenvalues of an appropriate coupling matrix. The more important modes, together with the values for the frequencies and coupling constants, are collected in Table II. These are defined in relation to the vibronic Hamiltonian of Eq. (4) and have been obtained *ab initio* as described above without further readjustment. The *ab initio* calculations reveal that not all vibrational modes of the trifluorobenzene radical cation play a significant role in the vibronic coupling mechanism within

TABLE II. Frequencies and coupling constants entering the Hamiltonian (4) for the 1, 2, 3-trifluorobenzene cation. Wilson numbering is included in parentheses wherever available. All quantities are in eV.

		Freq.	$\tilde{X}^2B_1$	$\tilde{A}^2A_2$	$\tilde{B}^2B_1$	$\tilde{C}^2B_2$	$\tilde{D}^2A_1$
A_1	ν_5	0.0382	−0.0268	0.0190	−0.0013	−0.0200	0.0057
	$\nu_6^*(6a)$	0.0603	−0.0638	0.0750	0.0008	0.0236	−0.0527
	ν_{12}	0.0872	−0.0330	0.0097	0.0484	0.0570	−0.0937
	ν_{14}^*	0.1039	−0.0363	0.0165	−0.0280	0.1240	−0.1153
	ν_{18}	0.1347	0.0635	0.0125	0.1156	−0.0699	0.0584
	ν_{20}	0.1570	−0.0223	0.0466	0.0196	−0.0514	0.0060
	ν_{23}^*	0.1669	0.1238	0.1838	0.2202	0.1695	0.0253
	ν_{25}^*	0.1952	0.1637	0.1089	0.1099	0.1159	0.1617
	$\nu_{27}^*(8a)$	0.2082	0.1719	−0.1491	0.0171	0.1151	−0.2533
B_2	ν_3	0.0349		0.0181			0.0076
	$\nu_7^*(6b)$	0.0631		0.0658			0.0343
	ν_{10}^*	0.0726		0.0505			0.0511
	ν_{17}	0.1298		0.0070			0.0052
	ν_{19}	0.1463		0.0621			...
	ν_{21}^*	0.1575		...			0.1173
	ν_{22}	0.1602		0.0073			0.0268
	ν_{24}	0.1904		...			0.0612
	$\nu_{26}^*(8b)$	0.2077		0.1483			0.2452
B_1	ν_1	0.0191			0.0173	0.0449	
	ν_4^*	0.0379			0.0912	0.0397	
	ν_8^*	0.0676			0.0937	0.1059	
	ν_{11}	0.0831			...	0.0373	
	ν_{13}	0.0967			...	...	
	ν_{16}^*	0.1192			...	0.1483	
A_2	ν_2	0.0316				0.0682	
	ν_9^*	0.0723				0.0779	
	ν_{15}^*	0.1104				0.1604	

the QVC scheme because of small coupling constants. This holds, e.g., for all C–H stretching modes. These are therefore suppressed for clarity in Table II, which collects the linear coupling constants as well as the harmonic frequencies of the relevant vibrational modes. Also suppressed in the tables are small interstate coupling constants, for example $\tilde{X}-\tilde{D}$ couplings. The vibrational modes with most significant coupling constants, which are considered in the subsequent dynamical calculations, are marked with an asterisk. As revealed there, we are dealing with 14 nonseparable degrees of freedom, which still represent a formidable numerical problem.

The coupling constants of Table II implies a rich variety of conical intersections between the potential energy surfaces of the $\tilde{X}-\tilde{D}$ states of the 1, 2, 3-trifluorobenzene radical cation; several of them are low in energy and thus accessible to the nuclear motion following photoionization. They will be analyzed in Sec. III B. In the earlier study^{23–26} on mono- and di-fluorobenzene isomers, where quadratic couplings have been included, it was pointed out that quadratic couplings may play a crucial role in the energetic lowering of several seams of conical intersection. Thus, in the present study, we have also computed the quadratic coupling terms for totally symmetric modes using standard procedures described earlier. The quadratic coupling terms for the totally symmetric modes are given in Table III.

TABLE III. Quadratic coupling constants g_i^q entering the Hamiltonian (4) for totally symmetric modes and the five electronic states of the 1, 2, 3-trifluorobenzene cation. All quantities are in eV.

Mode	$\tilde{X}^2 B_1$	$\tilde{A}^2 A_2$	$\tilde{B}^2 B_1$	$\tilde{C}^2 B_2$	$\tilde{D}^2 A_1$
ν_5	0.0022	0.0034	0.0023	0.0017	0.0029
ν_6^*	−0.0022	−0.0015	−0.0011	−0.0075	0.0013
ν_{12}	−0.0011	−0.0005	−0.0002	−0.0004	−0.0043
ν_{14}^*	−0.0029	−0.0006	−0.0007	−0.0187	−0.0105
ν_{18}	0.0010	−0.0013	0.0046	−0.0138	−0.0069
ν_{20}	−0.0040	−0.0011	−0.0016	−0.0141	−0.0145
ν_{23}^*	−0.0012	−0.0004	−0.00003	−0.0194	−0.0093
ν_{25}^*	−0.0070	−0.0037	0.0043	−0.0312	−0.0120
ν_{27}^*	−0.0030	0.0029	0.0009	−0.0272	−0.0113

Figure 1 represents the ionization potentials along the coordinates of some selected totally (upper panels) as well as nontotally (lower panels) symmetric modes. The individual data points of the former panels refer to the *ab initio* data and the full lines to the fitted quadratic vibronic coupling potential energy curves. The intra-state coupling constants of the upper panels are evaluated numerically using finite difference techniques or a least-squares fitting procedure, and values of the normal coordinate displacements up to $Q_i = \pm 7$. This gives an illustration of how well the quadratic coupling approach

FIG. 1. Comparison of the QVC ionization potential curves (full lines) with *ab initio* calculated ionization potentials (symbols) for the 1, 2, 3-trifluorobenzene cation. Further details are given in the text.

FIG. 2. Representative cuts through the potential energy surfaces of the 1, 2, 3-trifluorobenzene cation. The panels on the left side show the results for the linear vibronic coupling model, while on the right side the quadratic coupling terms are additionally included.

reproduces the *ab initio* data. The inter-state coupling constants of the lower panels are evaluated using a least-squares fitting procedure for the eigenvalues of an appropriate coupling matrix, and values of the normal coordinate displacements up to $Q_i = \pm 2$. The states treated in the fitting procedure are indicated in red. The plots give an illustration how well the vibronic coupling approach reproduces the *ab initio* data (for small displacements). The situation is a representative also for the other modes of the 1, 2, 3-trifluorobenzene radical cation (not presented here). This points to the minor importance of higher-order cubic or quartic coupling terms and indicates that the quadratic coupling scheme provides an adequate description of the relevant vibronic interactions in the 1, 2, 3-trifluorobenzene radical cation.

B. Potential energy surfaces and conical intersections

The sets of coupling constants together with the Hamiltonians, Eq. (4), define the high-dimensional potential energy surfaces of the lowest five electronic states of the 1, 2, 3-trifluorobenzene cation. Five totally symmetric modes and nine non-totally symmetric modes are found to have substantial coupling constants. The underlying multidimensional PES imply a rich variety of different conical intersections. Effective-mode cuts through these PES are presented in Fig. 2. The curves represent the potential energies along a straight line from the origin $\mathbf{Q} = \mathbf{0}$ to the minimum energy of intersection between the $\tilde{A}$ and $\tilde{C}$ electronic states, utilizing expressions given in Ref. 3. The value of the effective coordinate Q_{eff} denotes the distance from the origin $\mathbf{Q} = \mathbf{0}$ (center of the Franck-Condon zone) along this line. Figure 2 shows a whole set of interstate curve crossings, which interconnect all states of the electronic manifold. Low-energy curve crossings are visible in the figures, each representing a point on a seam of conical intersections, especially between the $\tilde{X}-\tilde{A}$, $\tilde{B}-\tilde{C}$, $\tilde{C}-\tilde{D}$, and $\tilde{B}-\tilde{D}$ states. These are expected to give rise to a rich vibronic dynamics, which will be explored in Secs. IV A–IV C. It should be emphasized that the curve crossings other than the $\tilde{A}-\tilde{C}$ crossing do not occur at their minimal energy in the figure since the same “cut” (effective coordinate) is used in the drawing for all electronic states. However, the differences turn out to be minor, and a full list of the various seam minima, as well as minima of diabatic PES is compiled in Table IV (to be further discussed below).

Similar to the mono- and difluorobenzene cations, the five cationic states of the 1, 2, 3-trifluoro derivative are seen to split into two different sets of states, $\tilde{X}-\tilde{A}$ on one hand, and $\tilde{B}-\tilde{C}-\tilde{D}$ on the other hand, which are interconnected through the $\tilde{A}-\tilde{C}$ curve crossing. Note that the $\tilde{A}-\tilde{C}$ curve crossing comes into the relevant energy range only by the inclusion of quadratic coupling terms (for the totally symmetric modes). Without those, it is way too high in energy to play any role for the dynamics, cf. Figs. 2(a) with 2(b), which is consistent with our earlier studies^{24–26} on the mono- and difluoro derivatives. Nevertheless, even with these quadratic coupling terms included, the $\tilde{A}-\tilde{C}$ curve crossing is rather high in energy and the interaction between the $\tilde{X}-\tilde{A}$ and $\tilde{B}-\tilde{C}-\tilde{D}$ sets of states is possibly not as significant as in the mono- and difluorobenzene cations. The importance of the $\tilde{A}-\tilde{C}$ curve crossing for the 1, 2, 3-trifluoro derivative will be explored below.

We emphasize the analogy between the states exhibiting the $\tilde{X}-\tilde{B}$ crossing in Bz^+ and the $\tilde{A}-\tilde{C}$ crossing in its fluoro derivatives. This is apparent by inspecting Fig. 3 which shows that the electronic states indeed correlate with each other, e.g., by analogous bonding properties of the molecular orbitals. As a by-product, there is indeed only one low-energy crossing between the PES from the two different sets ($\tilde{X}-\tilde{A}$ and $\tilde{B}-\tilde{C}-\tilde{D}$) of electronic states of the fluorobenzene cations, just as there is only one such pair of crossings between the $\tilde{B}-\tilde{C}$ states and those of the $\tilde{X}$ state surfaces of Bz^+ .¹⁵ For Bz^+ , the two component states are degenerate by symmetry, and the slopes of the potential energy surfaces are necessarily oppositely equal at the origin $\mathbf{Q} = \mathbf{0}$ (see Ref. 15). By the asymmetric substitution, the degeneracy is lifted and the slopes in question are no longer equal in modulus and opposite in sign at $\mathbf{Q} = \mathbf{0}$. Thus, the JT effect in the parent cation “disappears” in the fluoro derivatives such as the 1, 2, 3-trifluoro isomer; nevertheless, the deviation from the high-symmetry case Bz^+ is seen to be minor from Fig. 2. Therefore, this has also been termed a replica of the JT intersection in Bz^+ (Ref. 65), which is also symmetry-induced in the 1, 3, 5-trifluoro benzene radical cation.²⁷ This topological, or more “physical” effect is complemented by the second, more “chemical” effect, caused by the energetic increase of the second π -type IP by fluorination. This trend is specially related to the substituent (F) atoms and manifests itself in a growing separation of the $\tilde{X}-\tilde{A}$ and the $\tilde{B}-\tilde{C}-\tilde{D}$ sets of states. The effect increases upon increasing fluorination

TABLE IV. Summary of important electronic energies, for the interacting states of the 1, 2, 3-trifluorobenzene cation, using (a) adjusted and (b) *ab initio* (OVGF) vertical IPs. The diagonal values represent the minima of the diabatic potential energies, off-diagonal entries are minima of the corresponding intersection seams. The panels on the left side display the results for the linear vibronic coupling (LVC) scheme, i.e., when quadratic terms are neglected, while the right side displays the results obtained upon including the quadratic coupling terms (QVC). The lower right part of the table also contains (in italics) the results of CCSD full geometry optimizations for the minima of the various potential energy surfaces and the $\tilde{A} - \tilde{C}$ intersection seam. Full geometry optimization data for the other intersection seams are not available.

		(a)				
		LVC				
		$\tilde{X}$	$\tilde{A}$	$\tilde{B}$	$\tilde{C}$	$\tilde{D}$
$\tilde{X}$		9.57	9.72	22.49	21.79	17.42
$\tilde{A}$			9.61	22.71	21.21	19.11
$\tilde{B}$				12.52	13.36	13.13
$\tilde{C}$					13.22	13.41
$\tilde{D}$						13.13
		LVQ + QVC				
		$\tilde{X}$	$\tilde{A}$	$\tilde{B}$	$\tilde{C}$	$\tilde{D}$
$\tilde{X}$		9.56	9.72	26.04	15.12	15.64
$\tilde{A}$			9.61	23.46	14.90	16.20
$\tilde{B}$				12.52	13.12	13.08
$\tilde{C}$					13.12	13.38
$\tilde{D}$						13.08
		(b)				
		LVC				
		$\tilde{X}$	$\tilde{A}$	$\tilde{B}$	$\tilde{C}$	$\tilde{D}$
$\tilde{X}$		9.37	9.52	23.55	23.35	18.36
$\tilde{A}$			9.42	23.78	22.68	20.34
$\tilde{B}$				12.46	13.54	13.25
$\tilde{C}$					13.29	13.49
$\tilde{D}$						13.21
		LVC + QVC				
		$\tilde{X}$	$\tilde{A}$	$\tilde{B}$	$\tilde{C}$	$\tilde{D}$
$\tilde{X}$		9.36	9.52	27.77	15.49	16.21
		<i>9.44</i>				
$\tilde{A}$			9.41	24.58	15.24	16.81
			<i>9.51</i>		<i>15.58</i>	
$\tilde{B}$				12.47	13.21	13.17
				...		
$\tilde{C}$					13.19	13.46
					<i>13.14</i>	
$\tilde{D}$						13.16
						<i>13.10</i>

and thus leads to a higher energy of the corresponding intersection. The same situation has been observed for the 1, 3, 5-trifluoro isomer,²⁷ where the doubly degenerate $\tilde{X}$ state is energetically well separated from the rest and does not reveal any significant coupling with the other states considered.

Although the multidimensional PES for the totally symmetric modes are harmonic oscillators, we emphasize that (pronounced) anharmonicity of the adiabatic PES comes into play as soon as non-totally symmetric modes are included.³ The minima of the diabatic PES can be determined by retaining only the totally symmetric modes, and the corresponding energies are listed as the diagonal entries in Table IV(a) using adjusted vertical IPs. The numbers may be compared to the analogous data from Table IV(b) where the *ab initio* vertical IPs have been employed. Comparing with the vertical IPs of Table I, one can infer the stabilization energies of typically 0.2–0.4 eV for the various electronic states. These minimum energies deriving from the quadratic coupling scheme can be compared with numbers obtained from a full geometry optimization for all five states (written in italics in Table IV(b)). Agreement is found to within typically 0.05–0.08 eV (with very few exceptions) and taken to indicate the applicability of the quadratic coupling scheme to reproduce the energy lowering due to geometric distortion very well.^{24–26} It provides further evidence that higher order coupling terms, and also bilin-

ear terms describing Duschinsky rotation,⁶⁶ play only a minor role for our purposes. As stated above, for every pair of states, the minimum energy of intersection has also been computed and the result is included as the corresponding off-diagonal

FIG. 3. Correlation between the lowest ionization potentials of benzene and its mono-, di-, and trifluoro derivatives according to the adjusted IPs. The Hartree-Fock canonical orbitals are included for the E_{1g} and the E_{1g} -derived states (for details see the text).

TABLE V. Summary of important electronic energies, for the interacting states of the 1, 2, 3-trifluorobenzene radical cation including the quadratic coupling terms (QVC) and considering only the modes, which are included in the dynamical calculations (marked by *) in Tables II–III). The diagonal values represent the minima of the diabatic potential energies, off-diagonal entries are minima of the corresponding intersection seams.

	$\tilde{X}$	$\tilde{A}$	$\tilde{B}$	$\tilde{C}$	$\tilde{D}$
$\tilde{X}$	9.63	9.76	33.46	16.31	16.52
$\tilde{A}$		9.63	28.80	15.11	18.20
$\tilde{B}$			12.81	13.19	13.30
$\tilde{C}$				13.19	13.41
$\tilde{D}$					13.30

entry. To further test the possible importance of higher order coupling terms and thus be more precise in the location of the minimum of the intersection seams, unrestricted searches for these minima are useful as recently proposed in Refs. 67 and 68. Preliminary calculations for the minimum of the $\tilde{A}$ – $\tilde{C}$ intersection seam yielded 15.58 eV for the 1, 2, 3-trifluoro isomer. Comparing the latter number with the corresponding one (15.24 eV) from the QVC scheme (see Table IV(b)) is satisfactory. The coupling scheme can be taken to faithfully represent the actual situation in these systems.

For comparison with Table IV (considering all totally symmetric modes), in Table V, only those modes are included which have been retained in the dynamical calculations reported below. The small deviations nicely demonstrate the validity of the mode selection for the subsequent dynamical calculations. As can be seen from Table V, the curve crossing which interconnects the two upper and lower sets of electronic states ($\tilde{X}$ – $\tilde{A}$ and $\tilde{B}$ – $\tilde{D}$) is higher by ~ 1.5 eV than in the other fluoro derivatives studied previously.^{24–26} In Sec. IV B, the ultrafast electronic population dynamics within the $\tilde{X}$ – $\tilde{D}$ electronic manifolds will show the importance of this difference in detail. The two trends, caused by the substitution in general and fluorination in particular, will provide useful guidelines in the discussion of the dynamical results in Secs. IV A and IV B.

As is well known, vibronic interactions not only manifest themselves in nonadiabatic coupling effects, but also in symmetry breaking. The latter phenomenon means that the minimum of the lower surface occurs at a nuclear geometry that is of lower symmetry than the equilibrium geometry of the molecule in its electronic ground state. The symmetry breaking is simply a consequence of the repulsion of the diabatic surfaces via the vibronic coupling.³ In the present study, the criteria for the existence of a stabilized minimum of a reduced symmetry³ have been checked and no symmetry breaking has been found.

IV. TIME-INDEPENDENT AND TIME-DEPENDENT DYNAMICAL OBSERVABLES

A. The photoelectron spectrum

The quantum dynamical calculations of the time-independent quantities focus on the vibronic structure of elec-

FIG. 4. Comparison of theoretical (lower panel) and experimental (upper panel) (Ref. 10) photoelectron spectra of the 1, 2, 3-trifluorobenzene. The linewidths of the theoretical spectra are FWHM = 66.6 meV (upper curve) and 13.3 meV (lower curve). In the higher resolution theoretical spectrum, the $\tilde{X}$ – $\tilde{A}$ electronic bands are drawn separately.

tronic transitions into the interacting sets of states. We start with the photoelectron spectroscopic studies. Figure 4 shows the simulated PE spectra and compares the results with the experimental recording of Ref. 10. It should be mentioned here that the adjusted vertical IPs have been used for all the dynamical calculations. The theoretical spectra are presented for two different resolutions: the upper traces correspond to a Lorentzian line width FWHM = 66.6 meV for a better comparison with experiment, while for the lower ones, we have used a higher resolution (FWHM = 13.3 meV) to reveal more vibronic structure in the spectral envelopes. Also, the latter spectra have been decomposed into $\tilde{X}$ and $\tilde{A}$ bands for clarity. The relevant energy range is 9–14 eV to cover the five electronic states in question. The PE spectrum is seen to consist of two distinct groups of bands, representing the $\tilde{X}$ – $\tilde{A}$ and $\tilde{B}$ – $\tilde{C}$ – $\tilde{D}$ electronic states. The nonadiabatic coupling effects manifest themselves as irregularities in the spectral structures of Fig. 4, as is revealed more clearly by the lower drawing, which corresponds to higher resolution. It gives an impression of the highly complex, irregular, and dense underlying line structure, which is not fully resolved even here, because the resolution is still too limited except for the low-energy spectral regimes. The comparison of both panels of Fig. 4 shows that the calculated envelope nicely

reproduces the essential features of the experiment. The two main peak systems and the nearly zero-intensity regime between them come out well in the theoretical spectrum. The $\tilde{X} - \tilde{A}$ group of bands is indeed rather regular for low vibronic energies ($\tilde{X}$ -state), but becomes increasingly irregular in the energy region of the $\tilde{A}$ -state, that is, for energies above the $\tilde{X} - \tilde{A}$ seam of conical intersections. According to Table V, its energetic minimum is at 9.76 eV compared to the $\tilde{X}$ state energetic minimum, which is at 9.63 eV. Therefore, there is a particularly small “adiabatic” $\tilde{X}$ state energy range. This follows from the near-degeneracy of the $\tilde{X}$ and $\tilde{A}$ states and renders this system in the 1, 2, 3-trifluorobenzene cation, a particularly close replica of the JT effect in the parent system Bz^+ . For the other isomers, a somewhat intermediate situation prevails.^{24–26} The lowest-energy range in the higher group of $\tilde{B} - \tilde{C} - \tilde{D}$ -bands is also characterized by a rather well-resolved and regular structure. Here, the energies are again slightly below that of the conical intersection (13.19 eV according to Table V). The complexity rapidly increases for higher energy, especially when exceeding that of the conical intersection. Under low-to-moderate resolution, a diffuse spectral profile results, because the highly irregular and very dense individual spectral lines cannot be resolved any more. This is another typical consequence of conical intersections between the various PESs (Ref. 3) and generalized here to multi-state coupling situations.

The only fluorobenzene cation considered in our studies whose mass-analyzed threshold ionization (MATI) spectrum has apparently not been recorded so far is the 1, 2, 3-trifluorobenzene isomer. This is not commercially available but can be obtained via a potassium fluoride dimethyl sulfone halogen-exchange reaction on 2, 3-difluorochlorobenzene.⁶⁹ The Raman spectrum of 1, 2, 3-trifluorobenzene using a time-resolved laser fluorescence apparatus has been recorded by Bondybey *et al.*⁷⁰ Unfortunately, most of the low frequency bands are nearly depolarized, and the A_1 modes could not be identified with certainty. Obviously, a detailed study of the 1, 2, 3-trifluorobenzene vibrational spectrum would be needed.

B. Electronic population dynamics

In order to get further insight into the multi-state dynamics, the time-dependent (diabatic) electronic populations have been systematically computed for all possible initial electronic states. The results are presented in Fig. 5. As for the parent cation Bz^+ (Ref. 16) as well as other fluoro derivatives, we see a rich population dynamics proceeding on the *fs* time scale. Broadband excitation to the $\tilde{A}$ state (initial location of the wavepacket on the $\tilde{A}$ state at $\mathbf{Q} = \mathbf{0}$) displays essentially a two-state population dynamics for the joint ultrafast motion in the two lowest ($\tilde{X}$ and $\tilde{A}$) electronic states. The higher states are not involved since the $\tilde{B} - \tilde{C} - \tilde{D}$ electronic states are always high in energy (by about 2 eV) and thus inaccessible to the nuclear motion. The situation becomes more complicated for the excitation to the higher-energy states $\tilde{B} - \tilde{C} - \tilde{D}$. The panels again amount to broadband excitations, in the sense of vertically exciting the system to each of the $\tilde{B} - \tilde{C} - \tilde{D}$ electronic states at a time. The electronic populations reveal a

femtosecond internal conversion dynamics within the higher-energy ($\tilde{B} - \tilde{C} - \tilde{D}$) manifold as is typical for intersecting potential energy surfaces. As one can clearly see, independent of whether the initial wavepacket is located on the $\tilde{D}$ or $\tilde{C}$ state, $\sim 80\%$ of the electronic population is transferred to the $\tilde{B}$ state, which is relevant for the fluorescence dynamics (see Sec. IV C). The diabatic minima for the $\tilde{B}$, $\tilde{C}$, and $\tilde{D}$ states (12.81, 13.19, and 13.30 eV, respectively) help to understand their different populations: it is always the lower-energy state at the diabatic minimum, which is more likely populated for long propagation times. Accordingly, the $\tilde{B}$ state remains even more populated for long propagation time when the wavepacket is located initially on the $\tilde{B}$ state.

In general, no population transfer is observed from the $\tilde{B} - \tilde{C} - \tilde{D}$ to the $\tilde{X} - \tilde{A}$ group of states. We attribute this to the relatively high-energy curve crossing interconnecting these two sets of states. This occurs only for a single pair of potential energy surfaces ($\tilde{A} - \tilde{C}$), and its energetic minimum is found to be quite high (15.11 eV) with respect to the minimum of the $\tilde{B}$ state (12.81 eV), which is dominantly populated for longer propagation times in the higher electronic manifold. Similar to the 1, 3, 5-trifluoro isomer,²⁷ this renders the excited states long lived to make emission eventually possible. Although we cannot make quantitative predictions, the electronic populations allow to draw important conclusions on the different emission properties of these systems. These will be discussed in Subsection IV C.

C. Relation to the fluorescence yield

The behavior of the time-dependent electronic populations has important consequences for the fluorescence of the 1, 2, 3-trifluorobenzene radical cation. The parent cation Bz^+ , as well as the monofluoro-derivative, are non-emitting species, with an upper limit for the fluorescence quantum yield of 10^{-4} – 10^{-5} .^{12,18,19} Given the typical radiative lifetimes of 10^{-8} s, these low quantum yields imply a subpicosecond timescale for the radiationless deactivation of the electronically excited radical cations. Increasing fluorination, however, changes the situation, and for at least threefold fluorination of the parent cation, there is clear emission.^{12,13,71–78} The difluorobenzene cations represent a transitional regime, and only one of them, the 1, 3-isomer, has been found to emit weakly.¹² Also, it has been conjectured²⁰ that the stabilization of the e_{2g} (σ) orbital by fluorination leads to an increase of the corresponding ionization potential and a corresponding increase of the (minimum energy of) conical intersection, thus weakening the vibronic interactions and rendering the excited states long lived to make emission eventually (i.e., for a sufficient degree of fluorination) observable (see Fig. 3). This earlier conjecture is fully confirmed, regarding the general trends upon fluorination, in our earlier studies^{24–26} as well as through the present mechanism and results. The radiationless deactivation in the Bz^+ is not a direct one (from the state where dipole-allowed transitions are possible, the $\tilde{C}$ state, to the ground state) but involves the $\tilde{B}$ state as an intermediate.^{15,16} Already for the monofluoro derivative, the two IPs deriving from the σ orbital of benzene (the $\tilde{C}$ and $\tilde{D}$

FIG. 5. Electronic population dynamics of the 1, 2, 3-trifluorobenzene cation for initial preparation of the system in all relevant electronic states ($\tilde{A}$, $\tilde{B}$, $\tilde{C}$, $\tilde{D}$ states).

states of the monofluoro benzene cation) are sufficiently high in energy so that their energetic ordering with the π -type IP is interchanged.^{10,23,24,79} For the three difluoro isomers and the 1, 2, 3-trifluorobenzene cation, the shifts in energy are more pronounced (see Fig. 3) and the π - π - π - σ - σ ordering holds for all of them. This leads to a clear decoupling of the $\tilde{X} - \tilde{A}$ and $\tilde{B} - \tilde{C} - \tilde{D}$ sets of states, which is even stronger in the 1, 2, 3-trifluoro derivative than in the 1, 3-difluoro isomer.

Additional evidence comes from the consideration of the dipole transition matrix elements (see Table VI). It is well known that the transition from the σ -type state of the benzene cation to the ground state is dipole forbidden.^{15,19} For the fluoro derivatives, the molecular symmetry is reduced and the selection rules are relaxed.²⁵ One finds that there is always one component of the σ -type ($\tilde{C} + \tilde{D}$) states that has a finite dipole matrix element for transitions to one component of the lower π -type ($\tilde{X} + \tilde{A}$) states (at least for the C_{2v} molecular point group). Nevertheless, EOM-CCSD/TZ2P calculations clearly show that the corresponding transition dipole matrix elements are smaller by 2–3 orders of magnitude than those for the $\tilde{B} - (\tilde{X} + \tilde{A})$ transition, corresponding to the dipole-allowed transition in the case of Bz^+ .²⁶ This earlier finding for the mono and difluoro Bz^+ cations is extended here to the 1, 2, 3-trifluoro derivative, see Table VI. Thus, the π -

type electronic state is the “emitting” state in all fluorobenzene cations treated in our previous and present works. Its combined $\tilde{X} + \tilde{A}$ oscillator strength is almost the same for all five systems. Comparing again the various populations of Fig. 5, we find that the $\tilde{B}$ state stays populated (probability 0.9–0.95) for longer propagation time. Similar results are obtained for broadband excitation of the $\tilde{B} - \tilde{C} - \tilde{D}$ electronic states (unpublished results). This confirms that the 1, 2, 3-

TABLE VI. Oscillator strengths of electronic dipole transitions between the five lowest electronic states of the fluorinated benzene cations. An empty entry (...) means that the quantity vanishes by symmetry.

		$\tilde{B}$	$\tilde{C}$	$\tilde{D}$
Mono	$\tilde{X}$	0.0935	...	$<10^{-4}$
	$\tilde{A}$	0.0552	$<10^{-4}$	...
1, 2	$\tilde{X}$	0.0999	0.0001	...
	$\tilde{A}$	0.0644	...	0.0001
1, 3	$\tilde{X}$	0.1002	...	0.0002
	$\tilde{A}$	0.0641	0.0001	...
1, 4	$\tilde{X}$	0.1282	...	...
	$\tilde{A}$	0.0474	...	0.0003
1, 2, 3	$\tilde{X}$	0.0889	...	$<10^{-4}$
	$\tilde{A}$	0.0907	0.0002	...

trifluorobenzene cation is an emissive species, and also underlines the similarity of the 1, 3-isomer with the systems with three or more fluorine atoms (in agreement with the observations¹²). It demonstrates that the internal conversion mechanism considered here, namely multiple conical intersections involving one of the σ -type electronic states of benzene and its fluoro derivatives, indeed governs the fluorescence dynamics in this family of compounds.

V. CONCLUDING REMARKS

We have performed a comprehensive theoretical analysis of the multi-state nonadiabatic dynamics in the 1, 2, 3-trifluorobenzene cation, based on an *ab initio* quantal approach and the well established LVC + QVC coupling scheme. The system parameters have been obtained through large-scale electronic structure computations using the OVGf and EOM-CCSD methods. Fourteen important vibrational modes have been identified, which lead to a variety of low-energy conical intersections between the PES of the five lowest electronic states. These cause strong nonadiabatic coupling effects within the $\tilde{X} - \tilde{A}$ and $\tilde{B} - \tilde{D}$ electronic manifolds, which manifest themselves in irregular spectral structures (diffuse under low resolution) and a fs population transfer to the lower states in each set. The two sets of PES are interconnected by an $\tilde{A} - \tilde{C}$ curve crossing, which is, however, rather high in energy, also when taking quadratic coupling terms into account. Thus, the two sets of states are approximately decoupled in the trifluoro derivative of Bz⁺. This differs from the mono- and difluoro derivatives where substantial inter-set couplings were found to prevail.

Together with the 1, 3, 5-trifluorobenzene cation studied²⁷ recently, the 1, 2, 3-trifluoro isomer “bridges the gap” between the lesser and the more fluorinated Bz⁺ derivatives. The increase of the highest σ -type IP with increasing fluorination has been confirmed in our earlier work and been demonstrated to lead to an energetic increase of the conical intersection interconnecting the $\tilde{X} - \tilde{A}$ and $\tilde{B} - \tilde{D}$ sets of electronic states. For the mono- and two of the three difluoro derivatives, this intersection is still rather low energetically so that a sub-ps population transfer is possible, and indeed no fluorescence is observed in these species. The other difluoro derivative represents a transitional regime with very weak fluorescence and indeed a slower population transfer. Bz⁺ derivatives with at least threefold fluorination exhibit strong emission. The present study has shown that in the 1, 2, 3-trifluorobenzene cation, similar to the 1, 3, 5-trifluoro isomer,²⁷ the relevant conical intersection is indeed shifted so high in energy that the corresponding population transfer is slow and negligible on a fs time scale. Thus, the excited state ($\tilde{B}$) with a dipole-allowed transition is indeed sufficiently long-lived so that emission is possible with a substantial quantum yield. For other isomers, and for more than threefold fluorination, either no differences or even a higher energy of the relevant intersection with a correspondingly slower nonradiative $\tilde{B} - \tilde{X}$ transition is to be expected. Thus, the present study completes our theoretical analysis of the emission properties of fluorinated benzene radical cations and their dependence on the number of substituent (F) atoms.

ACKNOWLEDGMENTS

This work has been supported financially by the Deutsche Forschungsgemeinschaft through the Graduiertenkolleg 850 “Modeling of Molecular Properties” and the Heidelberger Graduiertenschule der mathematischen und computergestützten Methoden für die Wissenschaften.

- ¹G. Fischer, *Vibronic Coupling* (Academic, London, 1984).
- ²I. B. Bersuker, *Vibronic Interactions in Molecules and Crystals* (Springer-Verlag, Berlin, 1989).
- ³H. Köppel, W. Domcke, and L. S. Cederbaum, *Adv. Chem. Phys.* **57**, 59 (1984).
- ⁴M. Klessinger and J. Michl, *Excited States and Photochemistry of Organic Molecules* (VCH, New York, 1995).
- ⁵T. A. Barckholtz and T. Miller, *Int. Rev. Phys. Chem.* **17**, 435 (1998).
- ⁶J. Michl, in *Conical Intersections: Electronic Structure, Dynamics and Spectroscopy*, edited by W. Domcke, D. R. Yarkony, and H. Köppel (World Scientific, Singapore, 2004).
- ⁷*Conical Intersections: Electronic Structure, Dynamics and Spectroscopy*, edited by W. Domcke, D. R. Yarkony, and H. Köppel (World Scientific, Singapore, 2004).
- ⁸H. A. Jahn and E. Teller, *Proc. R. Soc. London, Ser. A* **161**, 220 (1937).
- ⁹E. R. Davidson and W. T. Borden, *J. Phys. Chem.* **87**, 4783 (1983).
- ¹⁰G. Bieri, L. Asbrink, and W. von Niessen, *J. Electron Spectrosc. Relat. Phenom.* **23**, 281 (1981).
- ¹¹M. Allan and J. P. Maier, *Chem. Phys. Lett.* **34**, 442 (1975).
- ¹²M. Allan, J. P. Maier, and O. Marthaler, *Chem. Phys.* **26**, 131 (1977).
- ¹³C. Cossart-Magos, D. Cossart, and S. Leach, *Mol. Phys.* **37**, 793 (1979).
- ¹⁴S. Faraji, E. Gindensperger, and H. Köppel, *Springer Ser. Chem. Phys.* **97**, 239 (2009).
- ¹⁵M. Döschner, H. Köppel, and P. G. Szalay, *J. Chem. Phys.* **117**, 2645 (2002).
- ¹⁶H. Köppel, M. Döschner, I. Báldea, H.-D. Meyer, and P. G. Szalay, *J. Chem. Phys.* **117**, 2657 (2002).
- ¹⁷H. Köppel, L. S. Cederbaum, and W. Domcke, *J. Chem. Phys.* **89**, 2023 (1988).
- ¹⁸J. P. Maier, *Kinetics of Ion-Molecule Reactions* (Plenum, New York, 1979).
- ¹⁹O. Braitbart, E. Castellucci, G. Dujardin, and S. Leach, *J. Phys. Chem.* **87**, 4799 (1983).
- ²⁰H. Köppel, *Chem. Phys. Lett.* **205**, 361 (1993).
- ²¹H. Köppel, I. Báldea, and P. Szalay, *Adv. Quantum Chem.* **44**, 199 (2003).
- ²²H. Köppel and I. Báldea, *J. Chem. Phys.* **124**, 064101 (2006).
- ²³I. Báldea, J. Franz, P. Szalay, and H. Köppel, *Chem. Phys.* **329**, 65 (2006).
- ²⁴E. Gindensperger, I. Báldea, J. Franz, and H. Köppel, *Chem. Phys.* **338**, 207 (2007).
- ²⁵S. Faraji and H. Köppel, *J. Chem. Phys.* **129**, 074310 (2008).
- ²⁶S. Faraji, H.-D. Meyer, and H. Köppel, *J. Chem. Phys.* **129**, 074311 (2008).
- ²⁷T. Mondal and S. Mahapatra, *Phys. Chem. Chem. Phys.* **11**, 10867 (2009).
- ²⁸H. Köppel and W. Domcke, in *Encyclopedia of Computational Chemistry*, edited by P. von Ragué Schleyer (Wiley, New York, 1998), p. 3166.
- ²⁹H. C. Longuet-Higgins, *Proc. R. Soc. London, Ser. A* **344**, 147 (1975).
- ³⁰W. Lichten, *Phys. Rev.* **131**, 229 (1963).
- ³¹F. T. Smith, *Phys. Rev.* **179**, 111 (1969).
- ³²T. F. O'Malley, *Adv. At. Mol. Phys.* **7**, 223 (1971).
- ³³A. Thiel and H. Köppel, *J. Chem. Phys.* **110**, 9371 (1999).
- ³⁴T. Pacher, L. S. Cederbaum, and H. Köppel, *Adv. Chem. Phys.* **84**, 293 (1993).
- ³⁵M. Nooijen and J. G. Snijders, *Int. J. Quantum Chem., Symp.* **26**, 55 (1992).
- ³⁶J. F. Stanton and J. Gauss, *J. Chem. Phys.* **101**, 8938 (1994).
- ³⁷J. Paldus and X. Li, *Adv. Chem. Phys.* **110**, 1 (1999).
- ³⁸J. F. Stanton and R. J. Bartlett, *J. Chem. Phys.* **98**, 7029 (1993).
- ³⁹L. S. Cederbaum and W. Domcke, *Adv. Chem. Phys.* **36**, 205 (1977).
- ⁴⁰W. von Niessen, J. Schirmer, and L. S. Cederbaum, *Comput. Phys. Rep.* **1**, 57 (1984).
- ⁴¹L. S. Cederbaum, *J. Phys. B* **8**, 290 (1975).
- ⁴²J. Eiding, R. Schneider, W. Domcke, H. Köppel, and W. von Niessen, *Chem. Phys. Lett.* **177**, 345 (1991).
- ⁴³M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98, Revision A.1, Gaussian, Inc., Pittsburgh, PA, 1998.
- ⁴⁴J. F. Stanton, J. Gauss, J. D. Watts *et al.*, ACES II Mainz-Austin-Budapest version; integral packages: MOLECULE (J. Almlöf and P. R. Taylor); PROPS (P. R. Taylor); ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, and J. Olsen); current version, see <http://www.aces2.de>.

- ⁴⁵M. Nooijen and J. G. Snijders, *Int. J. Quantum Chem., Symp.* **48**, 15 (1993).
- ⁴⁶M. Nooijen and J. G. Snijders, *J. Chem. Phys.* **102**, 1681 (1995).
- ⁴⁷J. F. Stanton and J. Gauss, *J. Chem. Phys.* **103**, 1064 (1995).
- ⁴⁸T. H. Dunning, Jr. and P. J. Hay, in *Methods of Electronic Structure Theory*, 3rd ed., edited by H. F. Schaefer (Plenum, 1977), Vol. 2.
- ⁴⁹T. H. Dunning, *J. Chem. Phys.* **55**, 716 (1971).
- ⁵⁰O. Christiansen, J. Stanton, and J. Gauss, *J. Chem. Phys.* **108**, 3987 (1998).
- ⁵¹P. Szalay, J. F. Stanton, and R. J. Bartlett, *Chem. Phys. Lett.* **193**, 573 (1992).
- ⁵²C. B. Harris, E. P. Ippen, G. A. Mourou, and A. H. Zewail, *Ultrafast Phenomena VII* (Springer-Verlag, Berlin-Heidelberg, 1990).
- ⁵³A. H. Zewail, *Femtochemistry: Ultrafast Dynamics of the Chemical Bond* (World Scientific, Singapore, 1994).
- ⁵⁴H.-D. Meyer, U. Manthe, and L. S. Cederbaum, *Chem. Phys. Lett.* **165**, 73 (1990).
- ⁵⁵U. Manthe, H.-D. Meyer, and L. S. Cederbaum, *J. Chem. Phys.* **97**, 3199 (1992).
- ⁵⁶G. A. Worth, H.-D. Meyer, and L. S. Cederbaum, *J. Chem. Phys.* **105**, 4412 (1996).
- ⁵⁷M. Beck, A. Jäckle, G. A. Worth, and H.-D. Meyer, *Phys. Rep.* **324**, 1 (2000).
- ⁵⁸H.-D. Meyer and G. A. Worth, *Theor. Chem. Acc.* **109**, 251 (2003).
- ⁵⁹H.-D. Meyer, F. Gatti, and G. A. Worth, *Multidimensional Quantum Dynamics: MCTDH Theory and Applications* (Wiley VCH, Weinheim, 2009).
- ⁶⁰R. Schinke, *Photodissociation Dynamics* (Cambridge University Press, Cambridge, 1991).
- ⁶¹U. Manthe, H.-D. Meyer, and L. S. Cederbaum, *J. Chem. Phys.* **97**, 9062 (1992).
- ⁶²V. Engel, *Chem. Phys. Lett.* **189**, 76 (1992).
- ⁶³A. J. Jerri, *The Gibbs Phenomenon in Fourier Analysis, Splines and Wavelet Approximations* (Kluwer, New York, 1998).
- ⁶⁴A. Raab, G. A. Worth, H.-D. Meyer, and L. S. Cederbaum, *J. Chem. Phys.* **110**, 936 (1999).
- ⁶⁵T. S. Venkatesan, S. Mahapatra, H. Köppel, and L. S. Cederbaum, *J. Mol. Struct.* **838**, 100 (2007).
- ⁶⁶F. Duschinsky, *Acta Physicochim. USSR* **7**, 551 (1937).
- ⁶⁷M. Dallos, H. Lischka, R. Shepard, D. R. Yarkony, and P. G. Szalay, *J. Chem. Phys.* **120**, 7330 (2004).
- ⁶⁸R. A. Young and D. R. Yarkony, *J. Chem. Phys.* **125**, 234301 (2006).
- ⁶⁹R. H. Shiley, D. R. Dickerson, and G. C. Finger, *J. Fluorine Chem.* **2**, 19 (1972).
- ⁷⁰V. E. Bondybey, J. H. English, and T. A. Miller, *J. Mol. Spectrosc.* **83**, 124 (1980).
- ⁷¹T. Miller and V. E. Bondybey, in *Molecular Ions: Spectroscopy, Structure and Chemistry* (North-Holland, Amsterdam, 1983), p. 201.
- ⁷²C. Cossart-Magos, D. Cossart, and S. Leach, *Chem. Phys.* **41**, 345 (1979).
- ⁷³V. E. Bondybey, T. J. Sears, J. H. English, and T. A. Miller, *J. Chem. Phys.* **73**, 2063 (1980).
- ⁷⁴T. J. Sears, T. A. Miller, and V. E. Bondybey, *J. Am. Chem. Soc.* **103**, 326 (1981).
- ⁷⁵C. Cossart-Magos, D. Cossart, S. Leach, J. P. Maier, and L. Misev, *J. Chem. Phys.* **78**, 3673 (1983).
- ⁷⁶G. Dujardin and S. Leach, *J. Chem. Phys.* **79**, 658 (1983).
- ⁷⁷D. Klapstein, S. Leutwyler, and J. P. Maier, *Mol. Phys.* **51**, 413 (1984).
- ⁷⁸D. Winkoun, D. Champoulaud, G. Dujardin, and S. Leach, *Can. J. Phys.* **62**, 1361 (1984).
- ⁷⁹R. Anand, J. E. LeClaire, and P. M. Johnson, *J. Phys. Chem. A* **1999**, 2618 (1999).