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Published in:
Journal of Chemical Physics

DOI:
[10.1063/1.4755372](https://doi.org/10.1063/1.4755372)

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):

Meng, Q., Faraji, S., Vendrell, O., & Meyer, H-D. (2012). Full dimensional quantum-mechanical simulations for the vibronic dynamics of difluorobenzene radical cation isomers using the multilayer multiconfiguration time-dependent Hartree method. *Journal of Chemical Physics*, 137(13), [134302].
<https://doi.org/10.1063/1.4755372>

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

View online: <https://doi.org/10.1063/1.4755372>

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

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(Received 16 July 2012; accepted 13 September 2012; published online 1 October 2012)

Full dimensional multilayer multiconfiguration time-dependent Hartree (ML-MCTDH) calculations of the dynamics of the three difluorobenzene cationic isomers in five lowest-lying doublet electronic states using the *ab initio* multistate multimode vibronic coupling Hamiltonian (MMVCH) model are carried out using the Heidelberg MCTDH package. The same dynamical problems, but treated with the MCTDH scheme and using a reduced dimensional *ab initio* MMVCH model, have been previously reported [S. Faraji, H.-D. Meyer, and H. Köppel, “Multistate vibronic interactions in difluorobenzene radical cations. II Quantum dynamical simulations,” *J. Chem. Phys.* **129**, 074311 (2008)]. For easy comparison with the reduced dimensional results, 11D or 10D ML-MCTDH calculations are also performed. Extensive ML-MCTDH test calculations are performed to find appropriate ML-MCTDH wavefunction structures (ML-trees), and the convergence of the ML-MCTDH calculations are carefully checked to ensure accurate results. Based on the appropriate ML-trees, the photoelectron (PE) spectrum and the mass analyzed threshold ionization (MATI) spectrum are simulated, analyzed, and compared with corresponding experimental spectra. Because of its efficient simulation capability for large systems, ML-MCTDH calculations save a considerable amount of central processing unit (CPU)-time, even when a reduced dimensional MMVCH is used, i.e., the same reduced model as in the corresponding MCTDH calculations. Simulations of the experimental PE spectra by full dimensional ML-MCTDH calculations reproduced main peaks, which originate from different electronic states. The agreement is improved as compared to the reduced dimensionality calculations. Unfortunately, the experimental PE spectra are not very well resolved. Therefore, we compare our calculations additionally with highly resolved MATI spectra, which, however, are only available for the $\tilde{X}$ state. Based on a series of ML-MCTDH simulations with longer propagation time for $\tilde{X}$, a number of vibrational modes, including fundamentals, their combinations, and overtones are simulated and assigned by comparing with the experimental assignments and the *ab initio* frequencies. Excellent correlation between the experimental and full dimensional ML-MCTDH results show that ML-MCTDH is accurate and very efficient and that the *ab initio* MMVCH model is very suitable for ML-MCTDH calculations. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4755372>]

I. INTRODUCTION

The three difluorobenzene cationic isomers, i.e., *o*-, *m*-, and *p*-difluorobenzene radical cations, represent a prototype family of molecules for studying the ultrafast internal conversion processes, in which the molecular systems undergo non-Born-Oppenheimer transitions between different adiabatic potential energy surfaces on the same time scale as the molecular vibrations.¹ As is well known, the vibronic interactions among electronic states and vibrational modes are the key factors governing such ultrafast excited-state dynamics, and have been shown to also lead to complex structures in the photoelectronic spectra.¹ A particularly successful approach

for describing an ultrafast internal conversion process relies on a low-order Taylor series expansion of the Hamiltonian matrix elements in a diabatic electronic representation, where the nuclear kinetic energy is taken to be diagonal and the pertinent coupling elements arise from the potential energy.^{1,2}

Recently, Faraji *et al.*^{2–5} reported a set of theoretical investigations on these three radical cations in the five lowest-lying doublet electronic states, among which multiple conical intersections are found. All of these investigations are based on the well-established linear vibronic coupling (LVC) approach, augmented by diagonal quadratic vibronic coupling (QVC) terms for the totally symmetric modes.^{1,2,6} The coupling constants of the model were obtained by fitting its parameters to *ab initio* adiabatic energies obtained at the

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coupled cluster level. Considering the numerical effort of the dynamical calculations as well as the determination of linear and quadratic couplings of the 30 vibrational modes for each isomer, Faraji *et al.*^{2,3} chose the most important vibrational modes to set up the reduced dimensional LVC + QVC Hamiltonian, namely, 10D Hamiltonian in cases of *m*- and *p*-isomers and 11D in the case of *o*-isomer. On the basis of such reduced dimensional VC Hamiltonian, wavepacket propagation calculations for the nuclear motion were performed using the multiconfiguration time-dependent Hartree (MCTDH) algorithm.^{7–13} Recently, Sardar *et al.*¹⁴ simulated photoelectron (PE) and mass analyzed threshold ionization (MATI) spectra based on the same reduced dimensional VC Hamiltonian model as in the MCTDH calculations, employing their parallelized time-dependent discrete variable representation (TDDVR) methodology. They¹⁴ found that the TD-DVR results show agreement with the MCTDH results reported in Ref. 2. It should also be noted that Mondal and Mahapatra^{15,16} have recently investigated the vibronic dynamics of mono-, di- (*o*- and *m*-), and and penta-fluorinated neutral benzene molecules using MCTDH.

By comparing computational results with recorded experimental spectra, namely, the PE¹⁷ and MATI spectra,¹⁸ Faraji *et al.*² found that the simulated spectra were in satisfactory qualitative agreement with the corresponding experimental PE and MATI spectra. However, the calculated envelopes of the PE spectra exhibit more structure than their experimental counterparts, which imply that these MCTDH calculations contain artifacts due to reduced dimensionality.² In order to remove these artifacts and then to quantitatively simulate the PE and MATI spectra, in the present work we set out to systematically investigate full dimensional multistate multimode nonadiabatic dynamics of these three difluorobenzene cationic isomers making use of the *ab initio* LVC + QVC Hamiltonian model.³

From a technical point of view, the quantum dynamics of medium-sized systems using the standard wavepacket propagation method is a very difficult job when more than six degrees of freedom (DOFs) are involved.¹² For solving the time-dependent Schrödinger equation of large systems, the MCTDH method,^{7–13} which has become an important tool of choice to accurately describe the quantum dynamics of complex multidimensional systems, was developed over the past two decades. However, with increasing dimensionality of the system, the multidimensional single-particle functions (SPFs), the A-vector, or both, become harder and harder to propagate using current computational resources. Generally speaking, the number of DOFs that can be treated for a correlated vibrational problem nowadays is about 20,^{16,19–25} although problems with 61²⁶ and even 80²⁷ DOFs have been successfully tackled with MCTDH. We would remind the reader that the dimensionality alone is not a good measure of complexity. The rigid and/or weaker coupled systems are much easier to treat than flexible, strongly coupled systems. Moreover, the amount of excitation energy plays a decisive role.

As discussed above, in order to efficiently treat the present problems on the full dimensional ultrafast nonadiabatic dynamics of the three difluorobenzene cationic

isomers, we use the multilayer MCTDH (ML-MCTDH) algorithm,^{28–30} which was recently implemented into the Heidelberg MCTDH package.³¹ The basic idea of ML-MCTDH is that the nuclear wavefunction can be written as a layered structure and the SPFs of combined DOFs can be expanded in MCTDH form instead of retaining their original direct-product form.^{28–30} In other words, the SPFs are propagated in the MCTDH scheme instead of the standard scheme. This multilayer strategy can be applied recursively until SPFs of a size are obtained that can be efficiently propagated. With the ML-MCTDH scheme several hundreds (or even thousands) of DOFs can be accounted for quantum dynamically.^{30,32–36} As a general remark, the lower the correlation the larger is the number of DOFs which can be treated. This makes ML-MCTDH very suitable for treating system-bath problems, where a single bath mode couples weakly with the system, but the coupling of the whole bath with the system is decisive. However, ML-MCTDH can also tackle rather strongly correlated medium-sized system, as the recent investigations of Hammer and Manthe on the tunnelling-splitting of malonaldehyde has shown.^{37,38}

This paper is organized as follows: in Sec. II, we will describe the theoretical framework for the present problem, namely, the multistate multimode VC Hamiltonian model, the ML-MCTDH wavepacket propagation, and the computational methods for the dynamical observables. Section III presents the results for the PE spectra and MATI spectra. Finally, Sec. IV concludes with a summary.

II. THEORETICAL FRAMEWORK

A. The multistate multimode vibronic coupling Hamiltonian (MMVCH) model

Obviously, accurate multidimensional potential energy surfaces are necessary prerequisites for quantum dynamics simulation of the nuclear motion. Since the ultrafast dynamics of the three difluorobenzene radical cations are dominated by the vibronic coupling between electronic states and vibrational modes near the conical intersections, we shall adopt the MMVCH model which was recognized as the proper Hamiltonian model for simulating such ultrafast dynamics.^{1,16,19,20,39–42} As this model is discussed in detail in Refs. 1 and 6 only a brief description will be provided here. A diabatic electronic representation is employed, where the off-diagonal coupling matrix elements are derived from the potential energy part rather than from the nuclear kinetic energy, i.e., $\mathbf{H} = (T_N + V_0)\mathbf{1} + \mathbf{W}_x$, where x denotes *o*-, *m*-, or *p*-difluorobenzene cationic isomer. The diabatic electronic potential energies are generally smooth functions of the nuclear coordinates, even at the degeneracies of potential energy surfaces. Therefore, the electronic matrix elements in the diabatic basis may be expanded as a Taylor series in the nuclear coordinates and only low-order terms are retained. The truncation after the first-order coupling terms constitutes the LVC approach. In more complex cases, second-order coupling terms of the Taylor expansion play an important role and must be included to achieve good agreement with

experimental spectra.^{16,19} This constitutes the QVC model. Often one accounts only for diagonal quadratic couplings. Such LVC + QVC Hamiltonian have been reported and discussed in detail in Ref. 3. In this scheme, the operator $T_N + V_0$

takes the simple form of

$$T_N + V_0 = \sum_i \frac{\omega_i}{2} \left(-\frac{\partial^2}{\partial q_i^2} + q_i^2 \right) \quad (1)$$

with ω_i being the ground-state vibrational frequency of the i th normal mode, and the $\mathbf{W}_{o,m}$ and $\mathbf{W}_p$ matrices³ can be written as

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

and

$$\begin{pmatrix} E_X + \kappa_X \mathbf{q} + \mathbf{g}_X \mathbf{q}^2 & \sum_{j \in B_{1g}} \lambda_j^{(X,A)} q_j & 0 & 0 & 0 \\ \sum_{j \in B_{1g}} \lambda_j^{(X,A)} q_j & E_A + \kappa_A \mathbf{q} + \mathbf{g}_A \mathbf{q}^2 & \sum_{j \in B_{3g}} \lambda_j^{(A,B)} q_j & 0 & 0 \\ 0 & \sum_{j \in B_{3g}} \lambda_j^{(A,B)} q_j & E_B + \kappa_B \mathbf{q} + \mathbf{g}_B \mathbf{q}^2 & \sum_{j \in A_u} \lambda_j^{(B,C)} q_j & \sum_{j \in B_{2u}} \lambda_j^{(B,D)} q_j \\ 0 & 0 & \sum_{j \in A_u} \lambda_j^{(B,C)} q_j & E_C + \kappa_C \mathbf{q} + \mathbf{g}_C \mathbf{q}^2 & \sum_{j \in B_{2g}} \lambda_j^{(C,D)} q_j \\ 0 & 0 & \sum_{j \in B_{2u}} \lambda_j^{(B,D)} q_j & \sum_{j \in B_{2g}} \lambda_j^{(C,D)} q_j & E_D + \kappa_D \mathbf{q} + \mathbf{g}_D \mathbf{q}^2 \end{pmatrix}, \quad (3)$$

respectively, where $\kappa_I \mathbf{q} \equiv \sum_{i \in A_1 \text{ or } A_g} \kappa_i^{(I)} q_i$ and $\mathbf{g}_I \mathbf{q}^2 \equiv \sum_{i \in A_1 \text{ or } A_g} g_i^{(I)} q_i^2$. Here, the vertical ionization potential (IP) E_I refers to the electronic state I (namely, $\tilde{X}$, $\tilde{A}$, $\tilde{B}$, $\tilde{C}$, and $\tilde{D}$) and all the q_i represent dimensionless normal coordinates of the electronic ground state of the neutral difluorobenzenes. For the totally symmetric modes, the intra-state linear couplings $\kappa_i^{(I)}$ and quadratic couplings $g_i^{(I)}$ are, respectively, given by

$$\kappa_i^{(I)} = \left(\frac{\partial V_I(\mathbf{q})}{\partial q_i} \right)_{\mathbf{q}=\mathbf{0}}, \quad (4)$$

$$g_i^{(I)} = \frac{1}{2} \left(\frac{\partial^2 V_I(\mathbf{q})}{\partial q_i^2} \right)_{\mathbf{q}=\mathbf{0}}, \quad (5)$$

where the derivative is to be taken at the Frank-Condon zone center $\mathbf{q} = \mathbf{0}$.^{1,6} Whereas the inter-state linear couplings $\lambda_i^{(I,J)}$

are given by

$$\lambda_i^{(I,J)} = \sqrt{\frac{1}{8} \left(\frac{\partial^2 \Delta V_{IJ}}{\partial q_i^2} \right)_{\mathbf{q}=\mathbf{0}}}, \quad (6)$$

where ΔV_{IJ} is the difference of the adiabatic surfaces V_I and V_J .

The various parameters entering the Hamiltonian have been calculated by Faraji and Köppel,³ in which coupled-cluster single and double (CCSD) and equation of motion ionization potential (EOMIP)-CCSD for the ground-state geometries and ionization energies, respectively, have been carried out with the TZ2P one-particle basis set using the ACES II program.⁴³ The various coupling constants were computed using analytic gradient techniques or finite displacements along the various normal coordinates. While for the totally symmetric modes first derivatives are needed; the computation of the off-diagonal or interstate coupling constants requires the second derivatives, or a least-squares fitting

procedure adapting the eigenvalues of the model potential matrix to the computed adiabatic energies.³ The full list of parameters is given in the supplementary material.⁵²

B. The multilayer multiconfiguration time-dependent Hartree method

The MCTDH algorithm was first formulated by Meyer, Manthe, and Cederbaum⁷ in 1990, and is continuously further developed since. The ML-MCTDH method, which is an extension of MCTDH, was first implemented by Wang and Thoss²⁸ in 2003. Later, Manthe re-analyzed the ML-MCTDH working equations and showed that they can be formulated in a recursive manner.²⁹ By this the program can work with an arbitrary number of layers.²⁹ Following the way paved by Manthe, Vendrell and Meyer³⁰ have implemented ML-MCTDH into the Heidelberg MCTDH package,³¹ and applied it to 24D VC Hamiltonian of pyrazine and to Henon-Heiles Hamiltonian with up to 1458 DOFs.³⁰ Through their work, Vendrell and Meyer³⁰ showed that (i) the Heidelberg ML-MCTDH implementation works correctly and (ii) ML-MCTDH is indeed much superior to MCTDH for treating large systems (more than 15D, say). In particular, if there are many weakly coupled modes, ML-MCTDH performs excellently, allowing the treatment of hundreds of DOFs as shown already by Thoss, Wang, and their co-workers^{28,32–35,44} as well as by Manthe and his co-workers.³⁶

Now let us outline the route from the standard wavepacket propagation method over the MCTDH algorithm to ML-MCTDH. The nuclear wavefunction, $\Psi(q_1, \dots, q_f, t)$, which depends on f distinguishable DOFs (normal modes in the present case) and the time t , can be conveniently represented as an expansion in terms of direct products of orthonormal time-independent (TI) basis functions, one for each DOF,^{28–30} namely, SPFs,

$$\Psi(q_1, \dots, q_f, t) = \sum_{j_1}^{N_1} \cdots \sum_{j_f}^{N_f} A_{j_1, \dots, j_f}^1(t) \cdot \chi_{j_1}^1(q_1) \cdots \chi_{j_f}^f(q_f), \quad (7)$$

where the coefficients $A_{j_1, \dots, j_f}^1(t)$ denote the TD coefficients of the first layer of TD expansion terms. Such so-called standard wavepacket propagation method can be thus classified as a one-layer scheme. In the MCTDH approach,^{7,10} the nuclear wavefunction is expanded in terms of direct products of orthonormal TD SPFs, which are themselves expanded in terms of the underlying primitive basis. Using a mode-combination scheme the MCTDH wavefunction $\Psi(Q_1^1, \dots, Q_p^1, t)$ reads

$$\Psi(Q_1^1, \dots, Q_p^1, t) = \sum_{j_1}^{n_1} \cdots \sum_{j_p}^{n_p} A_{j_1, \dots, j_p}^1(t) \cdot \varphi_{j_1}^{1:1}(Q_1^1, t) \cdots \varphi_{j_p}^{1:p}(Q_p^1, t), \quad (8)$$

where $Q_1^1, \dots, Q_p^1$ denote logical coordinates (also referred to as combined modes), which are obtained by combining the physical coordinates $q_1, \dots, q_f$. Each logical coordinate comprises one or several of the physical coordinates, such as $Q_\kappa^1 = \{q_{1_\kappa}, \dots, q_{d_\kappa}\}$. Here, a more general notation to

designate a combined coordinate has been introduced that will be useful when discussing multilayer schemes. Note that the TD SPFs $\varphi_{j_\kappa}^{1:\kappa}(Q_\kappa^1, t)$ are multidimensional and are given by

$$\varphi_m^{1:\kappa}(Q_\kappa^1, t) = \sum_{j_{1_\kappa}}^{N_{1_\kappa}} \cdots \sum_{j_{d_\kappa}}^{N_{d_\kappa}} A_{m; j_{1_\kappa}, \dots, j_{d_\kappa}}^{2:\kappa}(t) \cdot \chi_{j_{1_\kappa}}^{\kappa,1}(q_{1_\kappa}) \cdots \chi_{j_{d_\kappa}}^{\kappa,d_\kappa}(q_{d_\kappa}), \quad (9)$$

where the multidimensional SPFs $\varphi_m^{1:\kappa}(Q_\kappa^1, t)$ are represented as an expansion in terms of underlying TI primitive basis functions, i.e., using the standard method, see Eq. (7). In the same way shown above when a TD basis was introduced in going from the standard ansatz to MCTDH, effectively adding a second layer of TD expansion coefficients, a MCTDH expansion can be used to represent the $\varphi_m^{1:\kappa}(Q_\kappa^1, t)$ SPFs, effectively adding a third layer of expansion coefficients. This results in a three-layer ML-MCTDH wavefunction. Using the same approach deeper layer schemes can be constructed. That is, the SPFs in the $(l-1)$ th layer are expanded using the SPFs in the l th layer,^{29,30}

$$\begin{aligned} \varphi_m^{z-1;\kappa_{l-1}}(Q_{\kappa_{l-1}}^{z-1}, t) &= \sum_{j_1}^{n_1} \cdots \sum_{j_{p_{\kappa_l}}}^{n_{p_{\kappa_l}}} A_{m; j_1, \dots, j_{p_{\kappa_l}}}^{z;\kappa_l}(t) \prod_{\kappa_l=1}^{p_{\kappa_l}} \varphi_{j_{\kappa_l}}^{z;\kappa_l}(Q_{\kappa_l}^z) \\ &= \sum_J A_{m; J}^z \cdot \Phi_J^z(Q_{\kappa_l}^z), \end{aligned} \quad (10)$$

where the symbols z and $z-1$ mean $z = \{l; \kappa_1, \dots, \kappa_{l-1}\}$, $z-1 = \{l-1; \kappa_1, \dots, \kappa_{l-2}\}$ while l denotes the layer depth, and $Q_{\kappa_{l-1}}^{z-1}$ is a combination of logical coordinates with $Q_{\kappa_{l-1}}^{z-1} = \{Q_1^z, \dots, Q_{p_{\kappa_l}}^z\}$. The SPFs of the last layer are expanded by TI primitive basis functions similar to Eq. (9).

Therefore, MCTDH can be seen as a two-layer scheme with TD coefficients $A_{j_1, \dots, j_f}^1(t)$ at the top layer, and sets of second layer TD coefficients $A_{m; j}^{2:\kappa}(t)$ for each DOF. We usually call a one-layer scheme the standard method, a two-layer scheme simply MCTDH, and deeper layering schemes ML-MCTDH. It is important to emphasize that all SPFs of a certain mode are expanded in terms of the same underlying basis set of next layer SPFs or finally primitive functions.

Simply speaking, in a high dimensional system, since the combined SPFs are too large to be efficiently propagated, one breaks the combined modes into even smaller groups of logical coordinates introducing a new layer of coefficients, whose size is then manageable. This procedure can be repeated over and over until the (possibly combined) primitive DOFs are reached. Thus, the ML-MCTDH layering scheme can be very flexible. Owing to this flexibility of the layering scheme, and the fact that ML-MCTDH wavefunctions can be many layers deep, it is convenient to introduce a diagrammatic notation to represent these objects.^{29,30} In this notation, wavefunctions are represented by trees (namely, ML-trees) using connected graphs without loops. Each node in the tree represents a set of vectors of coefficients $A_{m; j_1, \dots, j_{p_{\kappa_l}}}^{l;\kappa_1, \dots, \kappa_{l-1}}$, where l denotes the layer depth. The lines connecting one node with

FIG. 1. The ML-MCTDH wavefunction structures (ML-tree structures) for the 30D ML-MCTDH simulations of the *o*-difluorobenzene, in which (a) is the ML-tree for excitation to the $\tilde{X}^2B_1$ and $\tilde{A}^2A_2$ states; (b) is for excitation to $\tilde{B}^2B_1$; (c) is for excitation to $\tilde{C}^2A_1$; and (d) is for excitation to $\tilde{D}^2B_2$. The maxima depths of the trees are six layers, and the first layer separates the 30 vibrational coordinates from the discrete electronic DOF. The number of SPFs denoted by N_i ($i \neq 0$) need not be necessarily the same, and in fact in some of the ML-MCTDH simulations they are chosen to be different (see Table I). The numbers of primitive basis sets to represent SPFs of the deepest layer are given next to the lines connecting with the squares. The vibrational modes with a star are the ones which are included in the reduced dimensional Hamiltonian. Note that in the reduced model the DOFs 17a and 5 are replaced by one effective mode.

its descendant nodes in such diagrams represent the tensor indices $j_1, \dots, j_{p_{\kappa_1, \dots, \kappa_l}}$, one line per index, and the numbers at the side of each line refer to the maximum possible value of the corresponding index. Each node is uniquely described by the values of its label $z = \{l; \kappa_1, \dots, \kappa_{l-1}\}$. Finally, the primitive basis sets, at which the tree ends, are denoted by squares. In the present work, a number of ML-trees are designed and shown in Figure 1, as well as in the supplementary material.⁵²

Next, using the wavefunction in the multilayer scheme and the Dirac-Frenkel variational principle, the ML-MCTDH EOM for arbitrary layering schemes have been provided together with an algorithm for the recursive evaluation of all intermediate quantities entering the ML-MCTDH EOM.^{28–30} According to Wang and Thoss,²⁸ Manthe,²⁹ and Vendrell and Meyer,³⁰ the ML-MCTDH EOM have a very similar structure to the usual MCTDH equations, and for the top layer coefficients they are identical to the MCTDH ones, i.e.,

$$i \frac{\partial A_J^1}{\partial t} = \sum_J \langle \Phi_J^1 | \hat{H} | \Phi_J^1 \rangle A_J^1, \quad (11)$$

where the top layer configurations $\Phi_J^1 = \varphi_{j_1}^{1;1}(Q_1^1, t) \dots \varphi_{j_p}^{1;p}(Q_p^1, t)$, are defined as direct products of SPFs and the multi-index $J = j_1, \dots, j_p$ has been implicitly introduced. The EOM for the propagation of the SPFs are formally the same for all layers

$$i \frac{\partial \varphi_n^{z, \kappa_l}}{\partial t} = (1 - \hat{P}_{\kappa_l}^z) \sum_{j, m} (\rho^{z, \kappa_l})_{nj}^{-1} \cdot \langle \hat{H} \rangle_{jm}^{z, \kappa_l} \varphi_m^{z, \kappa_l}, \quad (12)$$

where $\hat{P}_{\kappa_l}^z = \sum_j |\varphi_j^{z, \kappa_l}\rangle \langle \varphi_j^{z, \kappa_l}|$ is the projector onto the space spanned by the φ_j^{z, κ_l} SPFs, ρ^{z, κ_l} is a density matrix, and $\langle \hat{H} \rangle^{z, \kappa_l}$ is a matrix of mean-field operators acting on the φ_j^{z, κ_l} functions. In its form above, the EOM for the SPFs look identical to the usual EOM for the SPFs in the usual MCTDH.¹⁰ Only the computation of the density matrices and mean-fields entering the EOM is now more involved than in a single-layer MCTDH scheme.^{28–30}

C. Dynamical observables

Now let us briefly expose how to obtain PE and MATI spectra employing the initial and propagated wavepackets.

The PE spectral intensity distribution, $P(E)$, is generated within the framework of Fermi's golden rule^{3,45}

$$P(E) = \sum_n |\langle \Psi_n^f | \hat{T} | \Psi_0^i \rangle|^2 \delta(E - E_n^f + E_0^i). \quad (13)$$

Here, $|\Psi_n^f\rangle$ represent the eigenstates of the vibronic coupling Hamiltonian with energies E_n^f . $\hat{T}$ is the appropriate transition operator. The initial state $|\Psi_0^i\rangle$ with energy E_0^i is the electronic and vibrational ground state of the neutral molecular system. We assume that it has the form $|\Psi_0^i\rangle = |\Phi_0\rangle|\mathbf{0}\rangle$, with an electronic component $|\Phi_0\rangle$ and a vibrational component $|\mathbf{0}\rangle$, which is assumed to be harmonic and taken to be the ground state of the zero-order Hamiltonian $T_N + V_0$. Assuming the Condon approximation, the initial wavepacket $|\Psi(0)\rangle$ is a direct product of $|\mathbf{0}\rangle$ and one of the electronic vector states for $\tilde{X}$, $\tilde{A}$, $\tilde{B}$, $\tilde{C}$, and $\tilde{D}$. The autocorrelation function $C(t) = \langle \Psi(0) | \Psi(t) \rangle$ measures the overlap between the time evolving wavepacket $|\Psi(t)\rangle = \exp(-i\mathbf{H}t) |\Psi(0)\rangle$ and the initial one $|\Psi(0)\rangle$. Fourier transform of the autocorrelation function gives the corresponding spectrum, $P(E)$,^{1,3,45} namely,

$$\begin{aligned} P(E) &\sim \int \exp[i(E + E_0^i)t] C(t) dt \\ &= 2\text{Re} \int_0^{+\infty} \exp[i(E + E_0^i)t] C(t) dt. \end{aligned} \quad (14)$$

Wavepacket dynamical methods which deliver the action of the time evolution operator on the initial wavepacket $|\Psi(0)\rangle$, and hence the autocorrelation function are an essential part of the present work. Using the ML-MCTDH wavepacket propagation techniques, the wavepacket $|\Psi(t)\rangle$ and thus the autocorrelation function are numerically evaluated as time evolves.

In the practical calculation, one never will be able to perform the propagation up to $t = \infty$ but will stop at some finite time T . Rather than replacing the upper integral limit by T , we introduce a window function $g(t)$ of compact support and then have the spectrum in the form of¹⁰

$$P_g(E) \sim \int d\epsilon P(E - \epsilon) \tilde{g}(\epsilon) \quad (15)$$

with $\tilde{g}$ being the Fourier transform of g . In the present work, we shall always use a window function of the form

$$g_2(t) = \cos^2\left(\frac{\pi t}{2T}\right) \theta\left(1 - \frac{|t|}{T}\right) \quad (16)$$

with θ being the Heaviside step function. The Fourier transform $\tilde{g}$ is discussed, e.g., in Refs. 10 and 12. We also use the so-called $t/2$ -trick, $C(t) = \langle \Psi^*(t/2) | \Psi(t/2) \rangle$, which doubles the length of the autocorrelation function. It is valid for symmetric Hamiltonians and real initial states.¹⁰

D. Numerical details

In the present work, we are dealing with the five lowest-lying doublet electronic states of the three difluorobenzene radical cations. A complete set of vertical IPs and coupling constants $\kappa_i^{(I)}$, $\lambda_i^{(I,J)}$, and $g_i^{(I)}$ appearing in Eqs. (2) and (3)

are determined by *ab initio* calculations. Using these data, we set up the present full dimensional MMVCH model. Because of their importance, on-diagonal quadratic coupling terms are always included in the present dynamical calculations.

All the quantum dynamical calculations reported here are performed using the Heidelberg MCTDH package.³¹ In all the following calculations unless otherwise specified, the initial wavefunction is taken to be the ground state harmonic oscillator wavepacket, located on one of the diabatic potential energy surfaces at the center of the Frank-Condon zone $\mathbf{q} = \mathbf{0}$, i.e., the vibrational ground state of the neutral molecule is placed directly at one of the cation's diabatic potential energy surfaces. The resulting spectra are finally summed to yield the PE spectrum.

In order to compare the ML-MCTDH results with those obtained from reduced dimensional MCTDH calculations, the 10D or 11D MCTDH calculations are also carried out using the same DVR grid points and Hamiltonians as in the previous work.² As shown previously² these MCTDH calculations were based on a mode-combination scheme in which the 11 or 10 primitive coordinates are grouped into four combined modes. For a detailed description of these vibrational modes, we refer the reader to Ref. 2 and we will discuss them again in Sec. III C. All of the MCTDH simulations reported here are based on this set of combined modes. The reduced dimensional ML-MCTDH simulations are also performed based on the same reduced dimensional MMVCH model. This makes the ML-MCTDH calculations numerically easier to compare to previous MCTDH calculations.

All of the simulations, including full dimensional ML-MCTDH, reduced dimensional ML-MCTDH and MCTDH calculations, are carried out on the same machine and CPU type (AMD OpteronTM 246, 2000 MHz) for comparing the computational efficiency. All of the vibrational modes are given in Wilson notation and we shall always use this notation in the following text, unless otherwise specified where using the Mulliken notation. In these specific cases, the corresponding Wilson notation will be given in the square bracket.

For optimal convergence, a series of different ML-tree schemes have to be used in ML-MCTDH calculations which differ in the initially populated electronic state of the system. Before analyzing the results of ML-MCTDH calculations, we have to determine the appropriate ML-tree for optimal convergence of the ML-MCTDH calculations. We shall discuss how to determine the appropriate ML-tree after some general remarks on the previous *ab initio* calculations.³ All reported simulations, including ML-MCTDH and MCTDH, are run with an integrator precision of 10^{-6} in the variable mean-field scheme.

III. RESULTS AND DISCUSSION

A. Remarks on the previous electronic structure calculations

The symmetry assignments and vertical IPs of the three isomers at the equilibrium geometry of the neutral species are

as follows:^{2,3}

<i>o</i> -difluorobenzene	<i>m</i> -difluorobenzene	<i>p</i> -difluorobenzene
C_{2v}	C_{2v}	D_{2h}
$\tilde{X}^2B_1$ (9.4 eV)	$\tilde{X}^2A_2$ (9.6 eV)	$\tilde{X}^2B_{3g}$ (9.4 eV)
$\tilde{A}^2A_2$ (9.8 eV)	$\tilde{A}^2B_1$ (9.9 eV)	$\tilde{A}^2B_{2g}$ (10.0 eV)
$\tilde{B}^2B_1$ (12.3 eV)	$\tilde{B}^2B_1$ (12.5 eV)	$\tilde{B}^2B_{1u}$ (12.4 eV)
$\tilde{C}^2A_1$ (12.6 eV)	$\tilde{C}^2A_1$ (13.1 eV)	$\tilde{C}^2B_{1g}$ (12.8 eV)
$\tilde{D}^2B_2$ (13.1 eV)	$\tilde{X}^2B_2$ (13.3 eV)	$\tilde{D}^2B_{3u}$ (13.6 eV)

(17)

All parameters appearing in Eqs. (2) and (3), including the vertical IPs E_I , coupling constants $\kappa_i^{(I)}$, $\lambda_i^{(I,J)}$, and $g_i^{(I)}$ have been tabulated in Ref. 3 and are again reproduced in the supplementary material.⁵²

From group theory, within the vibronic coupling scheme, a vibrational mode q has to satisfy the selection rule $\Gamma_n \otimes \Gamma_q \otimes \Gamma_m \supset A_x$ ($x = 1$ or g for C_{2v} or D_{2h} , respectively) in order to couple the electronic states n and m . Here, Γ denote the irreducible representations of the electronic states n and m and vibrational mode q . For *o*- and *m*-isomers, according to this selection rule, all 30 modes are involved in the vibronic coupling between pairs of the above five electronic states. For the *p*-isomer, however, only 22 modes are involved. The reason is that according to the present *ab initio* calculations, the neglected B_{1u} and B_{3u} vibrational modes exhibit only negligible vibronic coupling between $\tilde{A}/\tilde{D}$ and $\tilde{A}/\tilde{B}$, respectively. Therefore, in what follows a full dimensional problem means 30D in cases of *o*- and *m*-isomers and 22D in the case of *p*-isomer.

B. The ML-tree structures

For nonadiabatic systems with more than one electronic state MCTDH is often used in its multi-set formulation,^{10,12} in which different sets of SPFs are used for each electronic state. In the multi-set formalism, the SPFs of each state are optimal for that state, so that a smaller number of SPFs per state are needed than in a single-set calculation. For ML-MCTDH calculation, a multi-set formulation would be extremely cumbersome because one would end up with several ML-tree structures to be specified, one for each electronic state. On the other hand, the favorable scaling of ML-MCTDH with the number of DOFs makes it unnecessary to use a multi-set ML formulation. In simulations of nonadiabatic systems with ML-MCTDH, the electronic DOF is hence just another coordinate that indexes the electronic states, as in usual single set MCTDH calculations, and ML-MCTDH remains unchanged. Consequently, in constructing the ML-tree, one is free to group the electronic DOF in any convenient way with other coordinates and set it in any level of the tree where it may seem appropriate. In our simulations, the top layer contains coordinates Q_{vib} and q_{el} , where Q_{vib} groups the 30 vibrational modes of the system and q_{el} is a discrete variable for the electronic DOF indicating the five states. Q_{vib} is further divided into two groups of coordinates, one containing modes of the “system” and the other one containing the rest of modes, that is, the modes of the “bath.” Therefore, the first branching of the tree after separating electronic and vibra-

tional coordinates can be understood as a system-bath separation. The resulting “system” and “bath” coordinates are further divided until modes of a manageable size are reached. Generally speaking, the “system” modes play a more important role in the ultrafast internal conversion processes than the “bath” modes. Therefore, a set of larger SPF sizes should be used for the “system” modes while the SPF sizes for the “bath” modes are smaller.

In particular, before starting a ML-MCTDH calculation with an initial wavepacket placed on one particular electronic state, one has to design an initial ML-tree based on intuition or experience, and then optimize it iteratively to obtain a set of smaller mode natural populations as small populations indicate convergence. The final ML-tree can then be considered as an appropriate ML-tree. This iterative process is steered by the coupling intensities among the ML-tree nodes which are expressed by the node populations.³⁰ The larger the node populations, the larger are the couplings among the nodes in the lower layers.

Keeping such ideas in mind, we first put two or three strongly coupled vibrational coordinates together as one combination coordinate, namely, the logical coordinates. The vibrational modes which are strongly coupled with each other usually have similar frequencies or similar normal vibrational styles. Second, on the basis of intuition or experience, modes are further combined and a whole initial ML-tree (first ML-tree) is set up. A simple initial guess for the ML-tree should be one that takes the modes involved in the reduced dimensional Hamiltonian as the system and takes the other modes in a manageable ML-tree structure as the bath. Using this initial ML-tree the first ML-MCTDH calculation is launched to obtain the node populations. From the node populations of the upper layer, one can find the nodes of the lower layer which are strongly coupled which then allows us to put the strongly coupled nodes together to set up a new ML-tree (the second ML-tree). At the same time, modifying the logical coordinates may also be necessary. On the basis of the second ML-tree, the second ML-MCTDH calculation is launched to obtain the new set of node populations. Based on such set of node populations, one can set up the third ML-tree and launch the third ML-MCTDH calculation. As in the second step, it may be necessary to modify the ML-tree structure and/or the logical coordinates. Using this iterative process the n th ML-MCTDH calculation is launched using the n th ML-tree to obtain the n th set of node populations for building the $(n + 1)$ th ML-tree. Finally, a converged ML-MCTDH calculation can be found and this iterative optimization process is ended. For saving the calculation time, one can use a set of relatively small SPF size in these test ML-MCTDH calculations. Also a rather short propagation time suffices for these tests. Using the above iterative process, we obtained 16 and 11 appropriate ML-trees for full and reduced dimensional ML-MCTDH calculations, respectively. The full and reduced dimensional ML-trees are given in Figure 1 and in the supplementary material.⁵²

As explained above, based on the size of their coupling parameters, a certain number of vibrational modes were chosen for the reduced dimensional Hamiltonian. These modes are marked in the full dimensional ML-trees by stars as shown

in Figure 1 and named as star-modes. From these ML-trees, one can find that there exists a high probability for these star-modes surviving in the final system-region of the ML-tree. For the *o*-isomer, the ratios of star-modes:modes in the system-region are 50%, 100%, 75%, and 75% for the $\tilde{X}$ - $\tilde{A}$, $\tilde{B}$, $\tilde{C}$, and $\tilde{D}$ states, respectively. The latter ratios in the bath-region are 36%, 18%, 17%, and 17% for the $\tilde{X}$ - $\tilde{A}$, $\tilde{B}$, $\tilde{C}$, and $\tilde{D}$ states, respectively. For the other two isomers, we can also find the same rule about the ratios of star-modes:modes. That is, there are more star-modes in the system region than in the bath region, which implies that most of the star-modes should play an important role for the dynamical simulations and that the above iterative process for finding ML-trees works reliably.

C. Numerical results

Based on the above final ML-trees, the ML-MCTDH calculations are performed in both full and reduced dimensionality. Additionally, we reproduce the reduced dimensional MCTDH calculations reported in Ref. 2 using the same mode-combination scheme as previously, and slightly reduced sets of SPFs, as we found these smaller sets to be sufficient for convergence. The parameters and numerical results, including CPU time, total number of coefficients, and SPF size, of the various full and reduced dimensional calculations for the three isomers in the five states are given in Tables I–III. As shown above, since all simulations are run on the same machine and CPU type, the CPU times can be compared with each other. For ML-MCTDH simulations, the number of the

SPFs are given according to the representation of N_i values shown in ML-tree figures. For the MCTDH calculations, the number of SPFs are given according to the combined modes as follows: (16a, 6a, 19b), (14, 8a, 8b), (17b, 6b), and (17a + 5, 12, 7a) for *o*-isomer; (10a, 6a), (13, 8a, 8b), (16b, 6b), and (1, 17a, 5) for *m*-isomer; and (4, 6a), (7a, 8a, 8b), (18a, 17a), and (19a, 10a, 12) for *p*-isomer. The notation 17a + 5 indicates that an effective mode was introduced to represent the DOFs 17a and 5. Hence, the reduced dimensionality *o*-isomer calculation is technically a 11D one, but, due to the effective mode, accounts (approximately) for 12 DOFs. (See Ref. 2.)

As shown in Table I which reports the results on the *o*-isomer, the CPU times of the 11D ML-MCTDH calculations for the $\tilde{X}$, $\tilde{A}$, $\tilde{B}$, $\tilde{C}$, and $\tilde{D}$ states (in the range of 8–47 h) are much lower than the corresponding CPU times of the 11D MCTDH calculations (in the range of 124–195 h). However, both 11D ML-MCTDH and 11D MCTDH simulations provide identical PE spectra, as shown in Subsection III D. This implies that the corresponding ML-MCTDH can produce the same spectral result as MCTDH while saving a considerable amount of CPU time. In other words, the ML-MCTDH calculations converge more easily than the corresponding MCTDH calculations since the number of total coefficients used by the former (the order of magnitude is 10^4) is much less than those used by the latter (the order of magnitude is 10^6). One observes a similar performance in cases of *m*- and *p*-isomers, see Tables II and III. For example, the 10D ML-MCTDH calculations for the *m*-isomer took less than 40 h using 10^4 – 10^5 coefficients to converge, whereas the corresponding 10D MCTDH

TABLE I. Simulation parameters of the various 30D ML-MCTDH, 11D ML-MCTDH, and 11D MCTDH (top-down list for each electronic state) calculations for *o*-difluorobenzene radical cation using the vibronic coupling Hamiltonian. The second column contains the single-CPU time of each of ML-MCTDH or MCTDH simulation using a total propagation time of 300 fs. All simulations were run on the same machine and CPU type (AMD Opteron™ Processor 246, 2000 MHz). The third column shows the total number of time-dependent coefficients propagated in each case. The fourth column contains, for ML-MCTDH simulations, the number of SPFs for each node of the tree according to the representation in ML-tree figures (see Figure 1 for the denotations of the 30D ML-tree, as well as Figure S3 in the supplementary material⁵² for 11D ML-trees). The parentheses in the square brackets indicate that different N values are taken for each of the branches. For the MCTDH calculations, we use different sets of SPFs for each electronic state, namely, the multi-set formalism. Thus, for MCTDH the fourth column for each electronic state contains in square brackets the numbers of SPFs for combined modes: (16a, 6a, 19b), (14, 8a, 8b), (17b, 6b), and (17a + 5, 12, 7a), respectively. We use the same numbers of SPFs for all initial states (see also the text).

State	Method	CPU time (h:m)	Total coeffs.	SPF size
$\tilde{X}^2B_1$	30D ML-MCTDH	57:44	39 106	[(22,20),20,(15,7),(14,7),4,13,12,5,5,3,3,3]
	11D ML-MCTDH	8:01	24 216	[(18,12,6),15,8,4]
	11D MCTDH	195:57	2 205 085	[34,34,23,25]
$\tilde{A}^2A_2$	30D ML-MCTDH	72:35	46 227	[22,20,(18,7),(12,10),4,15,15,6,5,3,3,3]
	11D ML-MCTDH	22:30	38 818	[(24,17,6),19,10,(3,5)]
	11D MCTDH	197:04	2 205 085	[34,34,23,25]
$\tilde{B}^2B_1$	30D ML-MCTDH	87:27	68 222	[15,18,15,10,8,18,18,10,9,8,6,6]
	11D ML-MCTDH	4:39	26 288	[(15,10,8),15,10,(10,8)]
	11D MCTDH	124:05	2 205 085	[30,25,20,24]
$\tilde{C}^2A_1$	30D ML-MCTDH	77:33	55 748	[(15,10),(13,12,12),7,7,5,13,10,10,6,6,5,5]
	11D ML-MCTDH	18:53	57 142	[(18,18,15),15,(18,15),(18,8)]
	11D MCTDH	146:50	2 205 085	[30,25,20,26]
$\tilde{D}^2B_2$	30D ML-MCTDH	72:28	54 077	[15,12,8,7,5,12,12,10,7,6,5,5]
	11D ML-MCTDH	47:18	88 833	[(25,20,18),22,15,15]
	11D MCTDH	130:13	2 205 085	[21,21,15,19]

TABLE II. Same as Table I, except for *m*-difluorobenzene. Note that the reduced dimensionality for *m*-difluorobenzene is 10D. The ML-trees for this case and the denotations of SPFs size can be found in Figures S1 and S4 in the supplementary material.⁵² The fourth column contains in square brackets the numbers of SPFs for combined modes: (10*a*, 6*a*), (13, 8*a*, 8*b*), (16*b*, 6*b*), and (1, 17*a*, 5), respectively (see also the text).

State	Method	CPU time (h:m)	Total coeffs.	SPF size
$\tilde{X}^2A_2$	30D ML-MCTDH	56:31	41 340	[(20,18),20,(10,4),(5,5,8),3,(18,12),15,4,4,5,3,3]
	10D ML-MCTDH	7:09	22 419	[(12,8),(10,12,8),(8,5)]
	10D MCTDH	287:39	2 552 851	[35,35,23,25]
$\tilde{A}^2B_1$	30D ML-MCTDH	85:19	49 542	[(22,16),22,(10,8),7,3,(22,15),13,5,5,5,3,3]
	10D ML-MCTDH	13:58	34 422	[12,12,(10,6)]
	10D MCTDH	228:13	2 552 851	[35,35,23,28]
$\tilde{B}^2B_1$	30D ML-MCTDH	66:07	58 603	[15,15,12,12,6,10,13,12,8,4,3]
	10D ML-MCTDH	38:52	73 175	[15,15,15]
	10D MCTDH	231:12	2 552 851	[31,25,21,28]
$\tilde{C}^2A_1$	30D ML-MCTDH	88:00	70 689	[(12,10),12,6,6,6,12,10,12,6,6,5,5]
	10D ML-MCTDH	15:01	184 238	[15,15,22]
	10D MCTDH	225:25	2 552 851	[31,25,21,28]
$\tilde{D}^2B_2$	30D ML-MCTDH	109:14	82 255	[(12,8),12,6,12,10,10,6,6,5]
	10D ML-MCTDH	4:23	119 980	[10,8,15]
	10D MCTDH	227:34	2 552 851	[21,21,16,21]

calculations took more than 200 h using about 2.5×10^6 coefficients to obtain the same spectral results.

D. Photoelectron spectra

The PE spectra are calculated through a Fourier transformation of the autocorrelation function. In Figures 2–4, we show the simulated PE spectra of the three isomers and compare the results with the corresponding experimental spectra.¹⁷ The relevant energy range is always 9–14 eV which covers the five electronic states in questions, spectral features appearing in the experimental recording of difluorobenzene radical cations above 14 eV are irrelevant for our purpose.

Regarding peak positions and intensities, the general features of the spectra are reproduced. The comparison between

theory and experiment shows satisfactory agreement. In some cases, the calculated envelopes exhibit more structure than their experimental counterparts. This may be due to the finite experimental resolution, i.e., the effective linewidth of the simulation may be still too small. For *o*- and *m*-isomers, the PE spectra are seen to consist of two distinct groups of bands, representing the $\tilde{X}$ and $\tilde{A}$ states and the $\tilde{B}$, $\tilde{C}$, and $\tilde{D}$ states, while for the *p*-isomer there are four distinct bands, representing $\tilde{X}$, $\tilde{A}$, $\tilde{B}$ - $\tilde{C}$, and $\tilde{D}$. The difference between the *p*-isomer and the other two isomers arises due to the larger vertical IP difference between *p*-C₆H₄F₂⁺ ($\tilde{C}^2B_{1u}$) and *p*-C₆H₄F₂⁺ ($\tilde{D}^2B_{3u}$). As shown in Eq. (17), the vertical IP differences between $\tilde{C}$ and $\tilde{D}$ are only 0.5 and 0.2 eV for *o*- and *m*-isomers, respectively, whereas this difference is 1.2 eV for *p*-isomer. Therefore, the *p*-C₆H₄F₂⁺ ($\tilde{D}^2B_{3u}$) band is separated from the

TABLE III. Same as Table I, except for *p*-difluorobenzene. Note that the full and reduced dimensionalities for *p*-difluorobenzene are 22D and 10D, respectively. The ML-trees and the denotations of SPFs size can be found in Figures S2 and S5 in the supplementary material.⁵² The fourth column contains in square brackets the numbers of SPFs for combined modes: (4, 6*a*), (7*a*, 8*a*, 8*b*), (18*a*, 17*a*), and (19*a*, 10*a*, 12), respectively, (see also the text).

State	Method	CPU time (h:m)	Total coeffs.	SPF size
$\tilde{X}^2B_{3g}$	22D ML-MCTDH	2:29	13 127	[7,7,3,5,7,7,3,3]
	10D ML-MCTDH	0:11	6604	[4,3,(8,7)]
	10D MCTDH	123:56	2 552 851	[35,35,23,25]
$\tilde{A}^2B_{2g}$	22D ML-MCTDH	30:01	41 319	[8,(10,15,15),4,8,13,15,3,3]
	10D ML-MCTDH	1:39	14 876	[(7,10),4,15]
	10D MCTDH	158:33	2 552 851	[35,35,23,28]
$\tilde{B}^2B_{1g}$	22D ML-MCTDH	13:54	25 910	[10,10,5,10,8,4,4,4]
	10D ML-MCTDH	7:40	26 082	[8,12,7]
	10D MCTDH	142:48	2 552 851	[31,25,21,28]
$\tilde{C}^2B_{1u}$	22D ML-MCTDH	21:32	35 184	[15,15,7,13,15,6,6,6]
	10D ML-MCTDH	10:54	35 336	[10,13,10]
	10D MCTDH	162:07	2 552 851	[31,25,21,28]
$\tilde{D}^2B_{3u}$	22D ML-MCTDH	31:08	43 334	[15,15,8,16,(18,15),7,6,6]
	10D ML-MCTDH	10:44	34 878	[12,12,10]
	10D MCTDH	155:41	2 552 851	[21,21,16,21]

FIG. 2. Comparison of the 30D ML-MCTDH and 11D MCTDH theoretical vs experimental¹⁷ (upper panel) photoelectron (PE) spectrum of *o*-difluorobenzene radical cation. The 30D ML-MCTDH and 11D MCTDH theoretical spectra are obtained by a Fourier-transform of the autocorrelation function. The spectra are broadened by convoluting them with a Gaussian. The resulting resolution is 72 meV FWHM for the summed spectra. The solid line (—) represents the full dimensional ML-MCTDH PE spectra while the dashed line (---) represents the reduced dimensional MCTDH PE spectra. For clarity the reduced dimensional ML-MCTDH PE spectrum is not shown here, because based on the same reduced dimensional MMVCH model, MCTDH and ML-MCTDH simulations provide identical PE spectra (see text). The spectra of each of the five electronic bands computed with 30D ML-MCTDH are shown separately in the lower part of the figure. Here, the resolution is 36 meV FWHM. Top panel: Reprinted with permission from Bieri, Åsbrink, and Von Niessen, *J. Electron. Spectrosc. Relat. Phenom.* **23**, 281 (1981). Copyright 1981 Elsevier.

$\tilde{B}$ - $\tilde{C}$ band. The vibronic structure is revealed more clearly by the lower drawings which correspond to a higher resolution. The low-energy range in both groups of bands is characterized by a rather well-resolved and regular structure, whereas the high-energy range exhibits irregular structure and a diffuse spectral envelope. This is the consequence of the conical intersections of $\tilde{X}$ - $\tilde{A}$ and $\tilde{B}$ - $\tilde{C}$ - $\tilde{D}$.²

Because full dimensional vibronic coupling Hamiltonians are used here, all of the vibrational modes and the couplings among them and the electronic states are involved in the present full dimensional simulations. Therefore, the full dimensional ML-MCTDH simulations reproduce the main peaks with a better agreement to experiment (as shown in Figures 2–4) than the reduced dimensional (ML-MCTDH or

MCTDH) calculations, which result in a somewhat too large intensity for the high-energy absorption band since a number of coupling constants are missing in the reduced Hamiltonian. On the other hand, as they are based on the same reduced dimensional Hamiltonians, the reduced dimensional MCTDH and ML-MCTDH simulated PE spectra fully agree with each other. For the sake of simplicity, the reduced dimensional ML-MCTDH simulated PE spectra are not shown in Figures 2–4.

E. Mass analyzed threshold ionization spectra

For a more detailed investigation of the spectral features, we now consider the lower group of electronic states. The

FIG. 3. Same as Figure 2, except for *m*-difluorobenzene radical cation. Note that the reduced dimensionality is 10D. Top panel: Reprinted with permission from Bieri, Åsbrink, and Von Niessen, *J. Electron. Spectrosc. Relat. Phenom.* **23**, 281 (1981). Copyright 1981 Elsevier.

$\tilde{X}$ bands of these radical cations, in particular, have been analyzed experimentally by Kwon *et al.*¹⁸ through MATI spectroscopy. The theoretical $\tilde{X}$ spectral envelope and the experimental MATI spectra are drawn separately to reveal their differences and similarities. The MATI experimental results¹⁸ are largely confined to an energetic range corresponding to the cationic electronic ground state. There is a propensity to preferentially excite transitions to the electronic ground state of the cation in the MATI spectra. This may have to do with the resonant excitation process, similar to zero-kinetic-energy (ZEKE) spectroscopy, and was found also for monofluorobenzene.⁴⁶

In the present work, we simulate the MATI spectra of the three cationic isomers by populating initially only the $\tilde{X}$ state and performing both full and reduced dimensional ML-MCTDH propagations. The computed ML-MCTDH

spectra for *o*-, *m*-, and *p*-difluorobenzene radical cations are depicted in Figures 5–7, respectively, and correspondingly compared with the experimental MATI spectra.¹⁸ We note that Fermi's golden rule, and hence the simple computation of the spectra by Fourier transformation of the autocorrelation function, is no longer correct when calculating threshold ionization spectra. The excitation energies come out correctly, but the intensities may differ. Keeping this in mind, the agreement of the full dimensional ML-MCTDH computed spectrum with the experimental MATI spectrum is good. In Tables IV–VI, we compared the experimental assignments with the full and reduced dimensional ML-MCTDH simulated results. For reference, the B3LYP/6-311++G(2df,2dp) vibrational frequencies¹⁸ of these three radical cations are also given in these tables.

FIG. 4. Same as Figure 2, except for *p*-difluorobenzene radical cation. Note that the full and reduced dimensionalities in the present simulations for *p*-difluorobenzene are 22D and 10D, respectively. Top panel: Reprinted with permission from Bieri, Åsbrink, and Von Niessen, *J. Electron. Spectrosc. Relat. Phenom.* **23**, 281 (1981). Copyright 1981 Elsevier.

In the Born-Oppenheimer scheme, starting from the vibrational ground state of S_0 (vibrationally totally symmetric) transitions to non-totally symmetric excited vibrational states of D_0 are not allowed. Namely, among fundamentals, only those of the totally symmetric modes will appear in the one-photon MATI spectrum. Overtones and combinations of the totally symmetric modes and even numbered overtones of the non-totally symmetric modes are also allowed. Thus, in our simulated ML-MCTDH MATI spectra, we can find almost all of the fundamental peaks belonging to the total symmetric irreducible representation except for the C–H stretching modes which have frequencies larger than 3000 cm^{-1} . The funda-

mentals of non-totally symmetric modes appear very weakly in the MATI spectrum via vibronic coupling. The larger the coupling, the more intense the peak. In fact, except for several very tiny peaks we do not find any non-totally symmetric peaks in the simulated spectra with the S_0 vibrational ground state as the initial state. For including non-totally symmetric modes in the simulated spectra, we set the initial wavepacket as a vibrational excited state of this mode. Subsequently, a series of ML-MCTDH calculations are performed to calculate the absorption peaks of the non-totally symmetric modes. The assignments of the non-totally symmetric modes are also given in Tables IV–VI.

FIG. 5. Comparison of the 30D ML-MCTDH (middle panel) and 11D ML-MCTDH (lower panel) calculated $o\text{-C}_6\text{H}_4\text{F}_2^+$ ($\tilde{X}^2B_1$) band vs the experimental MATI spectrum¹⁸ (upper panel). To improve the resolution a propagation time of 800 fs, and hence an autocorrelation length of 1.6 ps, is used. The resulting resolution, using a cosine-squared filter, is 20 cm^{-1} FWHM. Upper panel: Reprinted with permission from Kwon, Kim, and Kim, J. Chem. Phys. **118**, 6327 (2003). Copyright 2003 American Institute of Physics.

FIG. 6. Same as Figure 5, except for *m*-difluorobenzene radical cation. Note that the reduced dimensionality is 10D. Given in the upper panel is the experimental MATI spectrum.¹⁸ Upper panel: Reprinted with permission from Kwon, Kim, and Kim, J. Chem. Phys. **118**, 6327 (2003). Copyright 2003 American Institute of Physics.

FIG. 7. Same as Figure 5, except for *p*-difluorobenzene radical cation. Note that the full and reduced dimensionalities in the case of *p*-isomer are 22D and 10D, respectively. Given in the upper panel is the experimental MATI spectrum¹⁸ reported in 2003. Upper panel: Reprinted with permission from Kwon, Kim, and Kim, J. Chem. Phys. **118**, 6327 (2003). Copyright 2003 American Institute of Physics.

TABLE IV. The theoretical and experimental vibrational frequencies (in cm^{-1}) and their assignments for the *o*-difluorobenzene radical cation in the ground electronic state. The second column gives the experimental assignments from MATI spectra. The third and fourth columns contain the assignments from 30D and 11D ML-MCTDH simulations, respectively. Given in the parentheses are the qualitative relative intensity of the peak in the experimental MATI and simulated ML-MCTDH spectra (see also Figure 5). The right most column give the B3LYP frequencies of the cation in ground state.

Mode ^a	MATI ¹⁸	30D ML-MCTDH ^b	11D ML-MCTDH ^b	B3LYP ¹⁸
0	0.0 (strong)	0.0 (strong)	0.0 (strong)	...
16[10 <i>b</i>]	148 (tiny)	194 ^c	...	150
20[10 <i>a</i>]	254 ^d (very tiny)	289 ^c	...	262
11[15]	294 (weak)	320 (weak)	...	297
30[9 <i>b</i>]	382 ^d (very tiny)	393 ^c	...	394
19[16 <i>b</i>]	442 (very tiny)	462 ^c	...	456
15[16 <i>a</i>]	413 (very tiny)	478 ^c	473 ^c	423
29[6 <i>b</i>]	505 ^d (very tiny)	506 ^c	500 ^c	533
10[6 <i>a</i>]	553 (strong)	556 (strong)	553 ^e (strong)	572
11 ²	588 (tiny)	597 (tiny)	...	...
14[4]	704 (very tiny)	674 ^c	...	746
9[1]	749 ^d (weak)	786 (tiny)	...	762
18[11]	799 (very tiny)	775 ^c	...	782
10 ¹ 11 ¹	848 (weak)	893 (weak)	...	...
28[12]	...	843 ^c	838 ^c	856
13[17 <i>a</i>]	887 (very tiny)	855 ^c	...	883
8[18 <i>b</i>]	966 (weak)	960 (very tiny)	...	979
17[17 <i>b</i>]	994 (very tiny)	961 ^c	946 ^c	992
12[5]	...	975 ^c	...	1012
27[18 <i>a</i>]	1065 (tiny)	1062 (tiny)	...	1124
10 ²	1104 (weak)	1129 (weak)	1091 ^f (weak)	...
7[9 <i>a</i>]	1171 (tiny)	1208 (tiny)	...	1196
25[3]	1202 (very tiny)	1277 (tiny)	...	1206
6[7 <i>a</i>]	1342 ^g (tiny)	1309 (weak)	1432 ^c	1364
24[19 <i>a</i>]	1342 ^g (tiny)	1309 (weak)	...	1346
5[14]	1397 ^h (tiny)	1367 (tiny)	...	1399
10 ² 11 ¹	1397 ^h (tiny)	1367 (tiny)	...	...
26[13]	1435 (very tiny)	1452 ⁱ (tiny)	...	1473
4[19 <i>b</i>]	1487 (tiny)	1452 ⁱ (tiny)	...	1516
23[8 <i>b</i>]	1523 (very tiny)	1542 ^j (weak)	1542 ^j (weak)	1534
3[8 <i>a</i>]	1548 (tiny)	1542 ^j (weak)	1542 ^j (weak)	1575
10 ³	1658 (very tiny)	1630 (weak)	1685 (weak)	...
7 ¹ 10 ¹	1723 (very tiny)	1711 (tiny)	...	...
4 ¹ 11 ¹	1778 (very tiny)	1760 (very tiny)	...	...
17 ¹ 28 ¹	1842 (very tiny)	1833 (weak)	1865 (weak)	...
6 ¹ 10 ¹	1896 (very tiny)	1877 (very tiny)	...	...
4 ¹ 10 ¹	2039 (very tiny)	2022 (tiny)	2037 (very tiny)	...
3 ¹ 10 ¹	2099 (very tiny)	2098 (tiny)	2089 (tiny)	...
2[20 <i>b</i>]	3032 (very tiny)	3040 (tiny)	3040 (tiny)	3210

^aAssignments for fundamentals are given in Mulliken notation. The corresponding Wilson notation is also given in the square bracket. Overtones and combinations of normal modes are indicated like 10²11¹ which denotes the combination line consisting of the second excited state of mode 10 and the first excited state of mode 11.

^bThe present work.

^cTo calculate these frequencies, the center of the initial wavefunction is set to be 0.3 in the corresponding coordinate.

^dFrom the dissociation spectra of the *o*-difluorobenzene radical cation which was prepared by [1+1'] REMPI,⁴⁹ the vibrational frequencies of 20¹, 30¹, 29¹, and 9¹ are 277, 396, 540, and 831 cm^{-1} , respectively.

^eFor 10¹, 11D MCTDH² calculation gives the peak at 550 cm^{-1} .

^fFor 10², 11D MCTDH² calculation gives the peak at 1100 cm^{-1} .

^gThe peak at 1342 cm^{-1} of the MATI experiment may be assigned to 6¹ or 24¹.

^hThe peak at 1397 cm^{-1} of the MATI experiment may be assigned to 5¹ or 10²11¹.

ⁱThe 1452 cm^{-1} peak in the 30D ML-MCTDH simulated spectra may be assigned alternatively to 26¹ or 4¹.

^jThe 1542 cm^{-1} peak in both 30D and 11D ML-MCTDH simulated spectra may be assigned alternatively to 23¹ or 3¹.

1. *o*- and *m*-difluorobenzene

For the *o*-difluorobenzene radical cation, there are 11 totally symmetric (a_1) normal modes, which were given previously.^{3,18} As shown in Figure 5, the 30D ML-MCTDH calculation simulates 10 peaks assigned to the totally sym-

metric modes as well as the 0-0 peak, which is set to the zero-point (0.0 cm^{-1}). The green dotted lines have been used to highlight the correspondence between the experimental and simulated peaks in Figure 5. The totally symmetric mode 2 with the high frequency of 3089 cm^{-1} is almost beyond the scope of the experimental observation and has a very tiny

TABLE V. The theoretical and experimental vibrational frequencies (in cm^{-1}) below 3000 cm^{-1} and their assignments for the *m*-difluorobenzene radical cation in the ground electronic state. The second column gives the experimental assignments from MATI spectra. The third and fourth columns contain the assignments from 30D and 10D ML-MCTDH simulations, respectively. Given in the parentheses are the qualitative relative intensity of the peak in the experimental MATI and simulated ML-MCTDH spectra (see also Figure 6). The right most column give the B3LYP frequencies of the cation in ground state.

Mode ^a	MATI ¹⁸	30D ML-MCTDH ^b	10D ML-MCTDH ^b	B3LYP ¹⁸
0	0.0 (strong)	0.0 (strong)	0.0 (strong)	...
20[10 <i>b</i>]	190 ^c (very tiny)	225 ^d	...	190
14[10 <i>a</i>]	199 (very tiny)	240 ^d	245 ^d	204
11[9 <i>a</i>]	343 ^c (tiny)	347 (tiny)	...	346
19[16 <i>b</i>]	379 (very tiny)	450 ^d	...	399
30[15]	418 (very tiny)	420 ^d	...	421
29[6 <i>b</i>]	467 ^c (very tiny)	410 ^d	424 ^d	489
10[6 <i>a</i>]	505 (strong)	510 (strong)	510 ^e (strong)	519
18[4]	587 (very tiny)	580 ^d	...	599
13[16 <i>a</i>]	614 (very tiny)	610 ^d	...	622
9[1]	728 (tiny)	745 (tiny)	738 ^e (tiny)	740
17[11]	784 (very tiny)	812 ^f (tiny)	...	802
10 ¹ 11 ¹	846 (tiny)	812 ^f (tiny)	860 (very tiny)	...
16[17 <i>b</i>]	885 (tiny)	886 ^g (tiny)	...	904
12[17 <i>a</i>]	909 (tiny)	886 ^g (tiny)	887 ^d	933
28[7 <i>b</i>]	923 (very tiny)	950 ^d	...	928
8[12]	987 (weak)	1000 ^h (weak)	1000 ^h (weak)	997
10 ²	1008 (weak)	1000 ^h (weak)	1000 ^h (weak)	...
15[5]	...	1000 ^h (weak)	1000 ^h (weak)	1006
7[18 <i>a</i>]	1092 (tiny)	1104 (very tiny)	...	1111
26[9 <i>b</i>]	...	1160 ^d	...	1119
9 ¹ 10 ¹	1231 (very tiny)	1250 ⁱ (very tiny)	1245 ⁱ (very tiny)	...
27[18 <i>b</i>]	1258 (very tiny)	1250 ⁱ (very tiny)	1245 ⁱ (very tiny)	1228
24[3]	...	1305 ^j	...	1279
6[13]	1355 (weak)	1305 (weak)	1300 ^e (weak)	1374
25[14]	1377 (very tiny)	1365 (very tiny)	...	1399
22[8 <i>b</i>]	1429 (very tiny)	1415 ^d , 1400 ^j	...	1432
23[19 <i>b</i>]	1496 (tiny)	1500 ^k (tiny)	1500 ^k (tiny)	1523
10 ³	1513 (tiny)	1500 ^k (tiny)	1500 ^k (tiny)	...
5[19 <i>a</i>]	1559 (tiny)	1500 ^k (tiny)	1500 ^k (tiny)	1538
4[8 <i>a</i>]	1605 (very tiny)	1611 (very tiny)	...	1572
6 ¹ 11 ¹	1694 (very tiny)	1650 (tiny)	1650 (tiny)	...
6 ¹ 10 ¹	1859 (weak)	1850 (weak)	1850 (weak)	...
10 ⁴	2020 (very tiny)	2030 ^l (tiny)	2030 ^l (tiny)	...
5 ¹ 10 ¹	2060 (very tiny)	2030 ^l (tiny)	2030 ^l (tiny)	...
6 ¹ 9 ¹	2085 (very tiny)	2030 ^l (tiny)	2030 ^l (tiny)	...
6 ¹ 10 ²	2363 (very tiny)	2320 (tiny)	2320 (tiny)	...
4 ¹ 8 ¹	2585 (very tiny)	2540 (very tiny)	2550 (very tiny)	...
6 ²	2706 (very tiny)	2700 (very tiny)	2700 (very tiny)	...
6 ¹ 23 ¹	2848 (very tiny)	2830 ^m (tiny)	2830 ^m (tiny)	...
6 ¹ 10 ³	2864 (very tiny)	2830 ^m (tiny)	2830 ^m (tiny)	...
5 ¹ 6 ¹	2910 (very tiny)	2903 (very tiny)	2903 (very tiny)	...

^aAssignments for fundamentals are given in Mulliken notation. The corresponding Wilson notation is also given in the square bracket. Overtones and combinations of normal modes are indicated like 6¹ 10³ which denotes the combination line consisting of the first excited state of mode 6 and the third excited state of mode 10.

^bThe present work.

^cFrom the dissociation spectra of the *m*-difluorobenzene radical cation which was prepared by [1+1'] REMPI spectra,⁴⁹ the vibrational frequencies of 20¹, 11¹, and 29¹ modes are 184, 335, and 411 cm^{-1} , respectively.

^dTo calculate these frequencies, the centre of the initial wavefunction is set to be 0.3 in the corresponding coordinate.

^eThe 10D MCTDH² calculation gives the peak positions at 500, 750, and 1300 cm^{-1} for 10¹, 9¹, and 6¹ modes, respectively.

^fThe 812 cm^{-1} peak in the 30D ML-MCTDH simulated spectra may be assigned alternatively to 17¹ or 10¹ 11¹.

^gThe 886 cm^{-1} peak in the 30D ML-MCTDH simulated spectra may be assigned alternatively to 16¹ or 12¹.

^hThe 1000 cm^{-1} peak in 30D and 10D ML-MCTDH simulated spectra may be assigned alternatively to 8¹, 10², or 15¹. This peak was predicted also by 10D MCTDH² calculation.

ⁱThe 1250 cm^{-1} peak in 30D and 1245 cm^{-1} peak in 10D ML-MCTDH simulated spectra may be assigned alternatively to 9¹ 10¹ or 27¹.

^jTo calculate 24¹ and 22¹, the second single-particle function of these two vibrational modes are populated initially.

^kThe 1500 cm^{-1} peak in both 30D and 10D ML-MCTDH simulated spectra may be assigned alternatively to 23¹, 10³, or 5¹.

^lThe 2030 cm^{-1} peak in both 30D and 10D ML-MCTDH simulated spectra may be assigned alternatively to 10⁴, 5¹ 10¹, or 6¹ 9¹.

^mThe 2830 cm^{-1} peak in both 30D and 10D ML-MCTDH simulated spectra may be assigned alternatively to 6¹ 23¹ or 6¹ 10³.

TABLE VI. The theoretical and experimental vibrational frequencies (in cm^{-1}) below 3000 cm^{-1} and their assignments for the *p*-difluorobenzene radical cation in the ground electronic state. The second and third columns give the experimental assignments from MATI spectra reported in 2003 and 1998, respectively. The fourth and fifth columns contain the assignments from the PE spectra (PES) and ZEKE experiments, respectively. The sixth and seventh columns give the assignments from 22D and 10D ML-MCTDH simulations, respectively. Given in the parentheses are the qualitative relative intensity of the peak in the experimental MATI and simulated ML-MCTDH spectra (see also Figure 7). The right most columns give the B3LYP frequencies of the cation in ground state.

Mode ^a	MATI03 ¹⁸	MATI98 ⁴⁷	PES ⁵⁰	ZEKE ⁴⁸	22D ML-MCTDH ^b	10D ML-MCTDH ^b	B3LYP ¹⁸
0	0.0 (strong)	0.0	0.0	0.0	0.0 (strong)	0.0 (strong)	...
30[11]	124 (very tiny)	127	129	126	... ^c	...	129
17[10b]	303 (very tiny)	303	...	302	360 ^d	...	306
22[15]	368 ^e (very tiny)	...	...	...	... ^c	...	368
8[16a]	368 ^{e,f} (very tiny)	...	...	...	420 ^g	...	374
27[9b]	...	430	...	...	460 ^g	...	436
6[6a]	441 ^f (strong)	439	427	440	440 (strong)	440 ^h (strong)	449
29[16b]	515 (very tiny)	...	508	...	... ^c	...	524
26[6b]	583 (very tiny)	...	...	...	610 ^d	...	591
16[4]	743/731 ⁱ (very tiny)	...	...	...	680 ^d	658 ^d	743
14[12]	743/731 ⁱ (very tiny)	...	...	...	755 ^d	...	749
9[10a]	768 (very tiny)	...	...	...	750 (very tiny)	820 ^d	780
5[1]	839 ^f (very tiny)	836	831	836	880 ^j (strong)	880 ^j (strong)	849
6 ²	881 (weak)	...	...	880	880 ^j (strong)	880 ^j (strong)	...
28[17b]	...	859	...	...	... ^c	...	891
13[18a]	983 (very tiny)	...	...	...	980 ^d	1028 ^d	985
15[5]	1015 ^k (very tiny)	...	...	...	940 ^d	916 ^d	1005
7[17a]	1015 ^k (very tiny)	...	...	...	1030 ^d	964 ^d	1001
21[18b]	1113 (very tiny)	...	...	...	... ^c	...	1131
4[9a]	1152 (tiny)	1150	1113	1149	1187 (tiny)	...	1174
25[3]	1278 ^l (very tiny)	...	...	...	1260 (weak)	1260 (weak)	1277
6 ¹ 5 ¹	1278 ^l (very tiny)	...	...	1276	1260 (weak)	1260 (weak)	...
12[13]	...	...	...	...	1315 ^m (weak)	1315 ^m (weak)	1317
6 ³	1319 (tiny)	...	...	1319	1315 ^m (weak)	1315 ^m (weak)	...
20[14]	1351 (very tiny)	...	...	...	... ^c	...	1352
3[7a]	1379 (very tiny)	...	1339	1375	1360 (very tiny)	...	1396
11[19a]	...	...	...	...	1572 ^d	1568 ^d	1507
24[8b]	1459 (very tiny)	...	...	...	1490 ^d	1488 ^d	1432
19[19b]	1526 (very tiny)	...	...	...	... ^c	...	1518
6 ¹ 4 ¹	1590 (tiny)	...	...	1589	1630 ⁿ (weak)	1630 ⁿ (weak)	...
2[8a]	1640 (tiny)	...	1597	1640	1630 ⁿ (weak)	1630 ⁿ (weak)	1680
6 ² 5 ¹	1716 (very tiny)	...	...	1714	1716 (weak)	1716 (weak)	...
6 ⁴	1761 (very tiny)	...	...	1759	1770 (weak)	...	...
6 ² 4 ¹	2031 (tiny)	...	...	2028	2030 (tiny)	...	...
6 ¹ 2 ¹	2077 (weak)	...	...	2077	2100 (weak)	2080 (weak)	...
6 ³ 5 ¹	2152 (very tiny)	...	...	2154	2170 (very tiny)	2150 (very tiny)	...
6 ³ 4 ¹	2470 (tiny)	...	...	2471	2480 (tiny)	...	...
6 ² 2 ¹	2518 (tiny)	...	...	2517	2520 (weak)	2520 (weak)	...
6 ⁴ 4 ¹	2908 (tiny)	...	...	...	2900 (tiny)	2900 (tiny)	...
6 ⁴ 4 ¹ 3 ¹	2968 (tiny)	...	...	...	2980 (tiny)	2980 (tiny)	...

^aAssignments for fundamentals are given in Mulliken notation. The corresponding Wilson notation is also given in the square bracket. Overtones and combinations of normal modes are indicated like 6²25¹ which denotes the combination line consisting of the second excited state of mode 6 and the first excited state of mode 25.

^bThe present work.

^cThese modes are not involved in the present full dimensional MMVCH model because they belong to B_{1u} and B_{3u} irreducible representations which can not arise vibronic coupling between any pair of the $\tilde{X}^2B_{3g}$, $\tilde{A}^2B_{2g}$, $\tilde{B}^2B_{1g}$, $\tilde{C}^2B_{1u}$, and $\tilde{D}^2B_{3u}$ states of *p*-difluorobenzene.

^dTo calculate the frequencies, the centre of the initial wavefunction is set to be 0.3 in the corresponding coordinate.

^eThe peak at 368 cm^{-1} from the MATI experiment may be assigned to 22¹ or 8¹.

^fFrom the dissociation spectra of the *p*-difluorobenzene radical cation which was prepared by [1+1'] REMPI spectra,⁵¹ the vibrational frequencies of 8¹, 6¹, and 5¹ modes are 355, 436, and 837 cm^{-1} , respectively.

^gTo calculate these frequencies, the second single-particle function of these vibrational modes are populated initially.

^hFor 6¹, the 10D MCTDH² calculation gives the peak positions at 445 cm^{-1} .

ⁱThe 743 and 731 cm^{-1} peaks from the 2003 MATI experiment may be assigned to 14¹ or 16¹.

^jThe 880 cm^{-1} peak in both 30D and 10D ML-MCTDH simulated spectra may be assigned alternatively to 5¹, 6², or 28¹. And for 5¹, the 10D MCTDH² calculation gives the peak at 830 cm^{-1} .

^kThe 1015 cm^{-1} peak from the 2003 MATI experiment may be assigned to 15¹ or 7¹.

^lThe 1278 cm^{-1} peak from the 2003 MATI experiment may be assigned to 25¹ or 6¹5¹.

^mThe 1315 cm^{-1} peak in both 30D and 10D ML-MCTDH simulated spectra may be assigned alternatively to 12¹ or 6³.

ⁿThe 1630 cm^{-1} peak in both 30D and 10D ML-MCTDH simulated spectra may be assigned alternatively to 6¹4¹ or 2¹.

peak. We therefore do not assign that mode to one of the peaks in the simulated spectrum. By comparing with previous experimental assignments,¹⁸ one can find the totally symmetric fundamentals from the prominent peaks of 30D ML-MCTDH spectra, namely, peaks at 3040, 1542, 1452, 1367, 1309, 1208, 960, 786, 556, 320 cm^{-1} being assigned to the normal modes 2-11 using Mulliken notation, respectively. However, because of its reduced dimensional feature, the 11D ML-MCTDH calculation only simulates 3 peaks of totally symmetric modes and 5 peaks of combinations and/or overtones, for example, 3040, 1542, and 553 cm^{-1} for modes 2, 3, and 10, respectively. By performing a series of 30D ML-MCTDH calculations for non-totally symmetric modes, one can simulate almost all peaks of the experimental MATI spectra below 2100 cm^{-1} . These experimental and theoretical assignments are given in Table IV. As given in Table IV, the absolute values of the deviations between experimental and simulational results are less than 45 cm^{-1} except for 16a and 3 for which those deviations are 65 and 75 cm^{-1} , respectively.

For the *m*-difluorobenzene radical cation, like the case of *o*-isomer, there are also 11 totally symmetric (a_1) normal modes.^{3,18} As shown in Figure 6, the 30D ML-MCTDH calculation simulates 8 peaks assigned to the totally symmetric modes as well as the 0-0 peak, the zero-point (0.0 cm^{-1}). The green dotted lines have been used to highlight the correspondence between the experimental and simulated peaks in Figure 6. The other 3 totally symmetric modes 7a, 2, and 20a with high frequencies larger than 3200 cm^{-1} are beyond the scope of the experimental observation. We therefore do not assign these 3 modes in the simulated spectrum. By comparing with previous experimental assignments,¹⁸ one can find the totally symmetric fundamentals from the prominent peaks of 30D ML-MCTDH spectra, namely peaks at 1611, 1500, 1305, 1104, 1000, 745, 510, and 347 cm^{-1} being assigned to the normal modes 4-11 using Mulliken notation, respectively. However, because of its reduced dimensional feature, the 10D ML-MCTDH calculation only simulates 5 peaks of totally symmetric modes, namely, 1500, 1300, 1000, 738, and 510 cm^{-1} for modes 19a, 13, 12, 1, and 6a, respectively. By performing a series of 30D ML-MCTDH calculations for non-totally symmetric modes, one can simulate almost all peaks of the experimental MATI spectra below 2910 cm^{-1} . These experimental and theoretical assignments are given in Table V. As given in Table V, the absolute values of the deviations between experimental and simulated results are less than 50 cm^{-1} except for 16a, 6b, and 19a for which those deviations are 71, 57, and 59 cm^{-1} , respectively.

2. *p*-difluorobenzene

Unlike the cases of *o*- and *m*-isomers, more experimental spectra have been available on the *p*-difluorobenzene photoionization, including the MATI spectrum measured by Lembach and Brutschy⁴⁷ (denoted as MATI98) as well as the one by Kwon *et al.*¹⁸ (denoted as MATI03) and the ZEKE spectra.⁴⁸ Shown in Figure 7 is comparison of the 22D ML-MCTDH spectrum and experimental MATI03 spectrum. The comparisons of the 22D ML-MCTDH spectrum and MATI98

and ZEKE experimental spectra are shown in the supplementary material.⁵²

Since the *p*-isomer belongs to D_{2h} symmetry, there are only 6 totally symmetric (a_g) normal modes.³ As shown in Figure 7, the full dimensional 22D ML-MCTDH calculation simulates 5 peaks assigned to the totally symmetric modes as well as the 0-0 peak, as usual, the zero-point (0.0 cm^{-1}). The green dotted lines have been used to highlight the correspondence between the experimental and simulated peaks in Figure 7. By comparing with previous MATI03 assignments,¹⁸ one can find the totally symmetric fundamentals from the prominent peaks of 22D ML-MCTDH spectra, namely, peaks at 440, 880, 1187, 1360, and 1630 cm^{-1} being assigned to the normal modes 2-6 using Mulliken notation, respectively. However, because of the reduced dimensionality, the 10D ML-MCTDH calculation only reproduces 3 peaks of totally symmetric modes, namely, 440, 880, and 1630 cm^{-1} for modes 6a, 1, and 8a respectively. By performing a series of ML-MCTDH calculations for non-totally symmetric modes, one can simulate many non-totally symmetric peaks in the experimental MATI03 spectra below 3000 cm^{-1} . These experimental and theoretical assignments are given in Table VI. As given in Table VI, the absolute values of the deviations between experimental and simulational results are less than 50 cm^{-1} except for 10b and 5 for which those values are 57 and 70 cm^{-1} , respectively. Thus, these simulated results are in good agreement to the corresponding experimental results.

Kwon *et al.*¹⁸ assigned peaks in the experimental MATI spectra by straightforwardly comparing with the B3LYP/6-311++G(2df,2pd) calculation frequencies, which are also given in the right most columns of Tables IV-VI. The absolute values of the differences between the present ML-MCTDH simulated frequencies and the B3LYP results are less than 50 cm^{-1} except for mode 4 of *p*-isomer.

IV. CONCLUSIONS

In the present work, the full and reduced dimensional nuclear dynamics of difluorobenzene cationic isomers in the five lowest-lying doublet electronic states were reported using the ML-MCTDH wavepacket propagation method based on the *ab initio* multistate multimode vibronic coupling Hamiltonian model.³ The full dimensional simulations were compared with reduced dimensional results, including the ML-MCTDH simulations performed in the present work and the MCTDH results² of the literature. For easily comparing with the ML-MCTDH simulations, reduced dimensional MCTDH calculations were re-done.

Because of its efficiency for simulating the quantum dynamics of large systems, the reduced dimensional ML-MCTDH calculations consume much less CPU time than corresponding MCTDH calculations. Before starting the ML-MCTDH calculations, extensive ML-MCTDH test calculations were performed to find the appropriate ML-trees, and the convergence of the ML-MCTDH calculations were carefully checked to ensure accurate results. On the basis of the appropriate ML-trees, the PE spectra and the MATI spectra

were simulated, analyzed, and compared with corresponding experimental spectra.

Comparing with the less resolved and somewhat old experimental PE spectra of the three isomers, we concluded the following two points: (i) the full dimensional ML-MCTDH simulations gave the main peaks with better intensity profiles when compared to the experimental spectra than the reduced dimensional (ML-MCTDH or MCTDH) results; and (ii) the reduced dimensional ML-MCTDH simulated PE spectra agree with the MCTDH simulated one.

To simulate the experimental MATI spectra, ML-MCTDH calculations with longer propagation time were performed for an initially populated $\tilde{X}$ state of the three radical cations. By a series of full dimensional ML-MCTDH calculations, several vibrational peaks, including fundamentals, their combinations, and overtones were simulated and could be assigned successfully by comparing with the MATI spectrum and the *ab initio* frequencies. For all of these peaks, the absolute values of deviations between ML-MCTDH and experimental frequencies are less than 50 cm^{-1} , except for about ten modes, where such values are less than 70 cm^{-1} . Note that these differences are likely to be due to the limited accuracy of the MMVCH model. Excellent correlation between the experimental and full dimensional ML-MCTDH results show that the ML-MCTDH calculations are accurate. Furthermore, the *ab initio* vibronic coupling Hamiltonian model is shown to be very suitable for ML-MCTDH calculations, because it makes ML-MCTDH propagations very efficient.

ACKNOWLEDGMENTS

The financial support by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged. The authors are grateful to Dr. F. Otto for help regarding the ML-MCTDH code, to Professor Alex Brown for carefully reading the paper, and acknowledge helpful scientific discussions with Professor H. Köppel.

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