A mode-selective quantum chemical method for tracking molecular vibrations applied to functionalized carbon nanotubes

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The theoretical investigation of mesoscopic objects requires new techniques which are particularly suited for the study of selected aspects of these systems. Vibrational spectroscopy is a main source for structural information on heterogeneous systems. We present an efficient quantum chemical method, which relies on a modified Davidson algorithm for targeting selected vibrations in infrared and Raman spectra. This approach is applied to the characteristic breathing modes of single-walled carbon nanotubes. [DOI: 10.1063/1.1523908]

I. INTRODUCTION

The study and rational design of nanosized molecular structures has evolved to an important branch of chemistry in recent years.[1–4] This steady increase in system sizes affords new experimental techniques, which allow one to resolve the detailed processes on a nanometer length scale. While x-ray crystallography is the most important tool for structure analysis in classical chemistry, it is of little value if the objects get very large and the systems are heterogeneous and not crystal-like structured.

The size of the nanomolecules thus requires new experimental but also theoretical approaches. Infrared and especially Raman spectroscopy have proven to be of particular value in nanoscale chemistry. Here, our focus will be on the application of theoretical vibrational spectroscopy on carbon nanotubes, which play an important role in fast growing nanoscience.[5,6] We shall show that the dependence of the vibrational frequencies on the diameter of the nanotubes and frequency shifts resulting from sidewall functionalization, for which first experimental investigations have been undertaken,[7–13] can be studied within our approach.

The standard procedure for the quantum chemical calculation of vibrational spectra is the diagonalization of the full Hessian matrix within the harmonic approximation, i.e., of the matrix of all second derivatives of the total electronic energy with respect to the Cartesian nuclear coordinates (see Ref. 14 for a recent compilation of the state of the art). This produces all normal modes of the molecule under consideration and the experimentally important modes are identified by inspection of these modes. Here, we turn the procedure upside-down in order to account for the fact that it is *a priori* known, which modes will be important in the experimental spectrum. It is thus desirable to target the important vibrations directly and to omit all other modes. Our methodology thus starts with a definition of those atoms whose vibrational motion is considered to be important and projects then iteratively on all these relevant vibrations. This "projection technique" is an extended version of the one suggested by Filippone and Parrinello.[15] It is decisive for our approach that it can be made much more efficient than the parallelized calculation of all vibrational modes such that large (nanoscaled) objects can be investigated. In this way, quantum chemistry can be the eyes of the experimentalists in those cases where experimental spectroscopic methods do not provide detailed structural information.

This work is organized as follows: Section II describes in detail the methodology, Sec. III gives some test calculations, which demonstrate the accuracy and efficiency of the method, and Sec. IV demonstrates how it can be applied to single-walled carbon nanotubes.

II. METHODOLOGY

In order to calculate the vibrational frequencies, we have to solve the eigenvalue equation

$$\mathbf{H}^{(m)}\mathbf{q}_k = \lambda_k \mathbf{q}_k , \tag{1}$$

where $\mathbf{H}^{(m)}$ is the mass-weighted Cartesian Hessian, which contains the (mass-weighted) second derivatives of the total electronic energy with respect to nuclear Cartesian coordinates, and $\{\lambda_k, \mathbf{q}_k\}$ is the eigensystem to be determined (with $\lambda_k \sim \omega_k^2$ and ω_k being the kth vibrational frequency; see Refs. 16 and 17).

The conventional procedure is to calculate *all* elements of the matrix $\mathbf{H}^{(m)}$ (either analytically or numerically) and to diagonalize this matrix to obtain all $3N$ eigenvalues and eigenvectors for a molecule containing N atoms. If only selected vibrations are of interest, one can apply subspace iteration methods like those by Lanczos[18] or by Davidson.[19] This has the major advantage that the full Hessian need not be calculated, which is the time limiting step in the standard procedure.

Filippone and Parrinello[15,20] have shown that already a Lanczos-type algorithm can yield substantial improvements on the standard procedure in periodic-boundary calculations. However, the number of iterations (and thus the number of eigenvectors) in Ref. 15 appears still too large for standard

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isolated-molecule calculations, which led us to an investigation of the Davidson method with suitably chosen preconditioning approaches.

Our Davidson-type method starts with a collective displacement $\mathbf{b}$ of all atoms (cf. Ref. 15)

$$\mathbf{b}=\sum_{j=1}^{3N} b_j \mathbf{e}_j^{(m)}, \tag{2}$$

where $\mathbf{e}_j^{(m)}$ are the $3N$ (mass-weighted) nuclear Cartesian basis vectors, and b_j are the components of the displacement. The element k of the vector $\boldsymbol{\sigma}=\mathbf{H}^{(m)}\cdot\mathbf{b}$, which is the first approximation to the left-hand side of Eq. (1), is then given as

$$\sigma_k=\{\mathbf{H}^{(m)}\cdot\mathbf{b}\}_k=\sum_l \frac{\partial^2 E}{\partial R_l^{(m)}\partial R_k^{(m)}} b_l=\frac{\partial^2 E}{\partial R_k^{(m)}\partial \mathbf{b}}. \tag{3}$$

$\partial^2 E/[\partial R_l^{(m)}\partial R_k^{(m)}]$ is the second derivative of the total electronic energy with respect to (mass-weighted) nuclear Cartesian coordinates. This relation allows us to calculate the vector $\boldsymbol{\sigma}$ as a numerical derivative of the gradient of the total electronic energy E with respect to the collective displacement $\mathbf{b}$,[15,20]

$$\boldsymbol{\sigma}=\mathbf{H}^{(m)}\cdot\mathbf{b}=\begin{pmatrix}\sum_l H_{1,l}^{(m)} b_l\\ \sum_l H_{2,l}^{(m)} b_l\\ \vdots\\ \sum_l H_{3N,l}^{(m)} b_l\end{pmatrix}=\begin{pmatrix}\sum_l \frac{\partial^2 E}{\partial R_1^{(m)}\partial R_l^{(m)}} b_l\\ \sum_l \frac{\partial^2 E}{\partial R_2^{(m)}\partial R_l^{(m)}} b_l\\ \vdots\\ \sum_l \frac{\partial^2 E}{\partial R_{3N}^{(m)}\partial R_l^{(m)}} b_l\end{pmatrix}=\begin{pmatrix}\frac{\partial^2 E}{\partial R_1^{(m)}\partial \mathbf{b}}\\ \frac{\partial^2 E}{\partial R_2^{(m)}\partial \mathbf{b}}\\ \vdots\\ \frac{\partial^2 E}{\partial R_{3N}^{(m)}\partial \mathbf{b}}\end{pmatrix}. \tag{4}$$

The vector $\boldsymbol{\sigma}$ can thus be calculated as the numerical derivative of the analytic gradients of the total energy. For this numerical differentiation it is necessary to carry out single point calculations for the along-$\mathbf{b}$ distorted structures such that n-point central difference formulas[21] for the numerical finite-difference approximation of the second derivative can be applied. For the generation of these distorted structures, we use displacements which result in a preselected norm of the corresponding (non-mass-weighted) Cartesian displacement vector; in general, a step size of 0.01 bohr proved to yield reliable and numerically stable derivatives.[14]

In the ith subspace iteration we build the Davidson matrix $\tilde{\mathbf{H}}^{(m),i}$ as

$$\tilde{\mathbf{H}}^{(m),i}=\mathbf{B}^{i\,T}\mathbf{H}^{(m)}\mathbf{B}^i=\mathbf{B}^{i\,T}\boldsymbol{\Sigma}^i, \tag{5}$$

where all vectors $\mathbf{b}^l$ and $\boldsymbol{\sigma}^l$ (with $l=1,\ldots,i$ and i being the actual iteration step) are collected in the matrices $\mathbf{B}^i$ and $\boldsymbol{\Sigma}^i$, respectively. We then solve the eigenvalue problem for the small Davidson matrix,

$$\tilde{\mathbf{H}}^{(m),i}\mathbf{u}^i=\rho^i\mathbf{u}^i, \tag{6}$$

where ρ^i is the ith approximate eigenvalue, from which we can calculate approximate wave numbers in every iteration step. The desired eigenvector $\mathbf{u}_s^i$ is selected from the set of vectors obtained from Eq. (6) and the residuum vector reads

$$\mathbf{r}_s^i=\sum_{l=1}^{i} u_{s,l}^i[\boldsymbol{\sigma}^l-\rho_s^i\mathbf{b}^l] \tag{7}$$

(note that i always denotes the actual ith iteration and s marks the selected vector). The sum is over all basis vectors $\mathbf{b}^l$, and the number of basis vectors is increased in each iteration. In the standard Davidson method, the number of basis vectors is equal to the number of iterations, since in each iteration one new basis vector is introduced. For each new basis vector $\mathbf{b}^{i+1}$, we obtain a new vector $\boldsymbol{\sigma}^{i+1}$ as the numerical derivative of the gradient with respect to the collective displacement $\mathbf{b}^{i+1}$.

The ith approximation $\mathbf{v}_s^i$ to the exact eigenvector $\mathbf{q}_s$ in Eq. (1) is obtained as

$$\mathbf{v}_s^i=\sum_{l=1}^{i} u_{s,l}^i\mathbf{b}^l. \tag{8}$$

The new basis vectors are generated from the residuum vectors,

$$\mathbf{b}^{i+1}=\mathbf{X}^i\mathbf{r}_s^i, \tag{9}$$

where $\mathbf{X}^i$ is a preconditioner, which should ideally be as close as possible to $[\mathbf{H}^{(m)}-\rho_s^i\mathbf{1}]^{-1}$. The simplest approximation for the inverse matrix of $[\mathbf{H}^{(m)}-\rho_s^i\mathbf{1}]$ is to use a diagonal preconditioner with diagonal elements $X_{jj}=1/(H_{jj}^{(m)}-\rho_s^i)$. However, this is only a good approximation for diagonally dominant matrices, a condition which is fulfilled for configuration interaction matrices, but not for the Hessian matrices investigated here. This procedure is repeated until the convergence criterion drops below a predefined threshold. Convergence criteria are: (i) the maximum element of the residuum vector, (ii) the norm of the residuum vector, and (iii) the contribution $u_{s,i}^i$ of the latest basis vector i in Eq. (8) to the selected eigenvector.

The convergence characteristics of this algorithm strongly depend on the reliability of (i) the initial guess of the first basis vector $\mathbf{b}^1$, which is the first approximation to the desired exact eigenvector $\mathbf{q}_s$ and of (ii) the preconditioner. The latter problem is delicate since we do not have any information about the matrix $\mathbf{H}^{(m)}$; only matrix–vector products $\boldsymbol{\sigma}^l=\mathbf{H}^{(m)}\mathbf{b}^l$ are known.

The Hessian may be approximated using the inverse transformation of Eq. (5)

$$\mathbf{H}^{(m)}=\mathbf{B}\tilde{\mathbf{H}}^{(m)}\mathbf{B}^T, \tag{10}$$

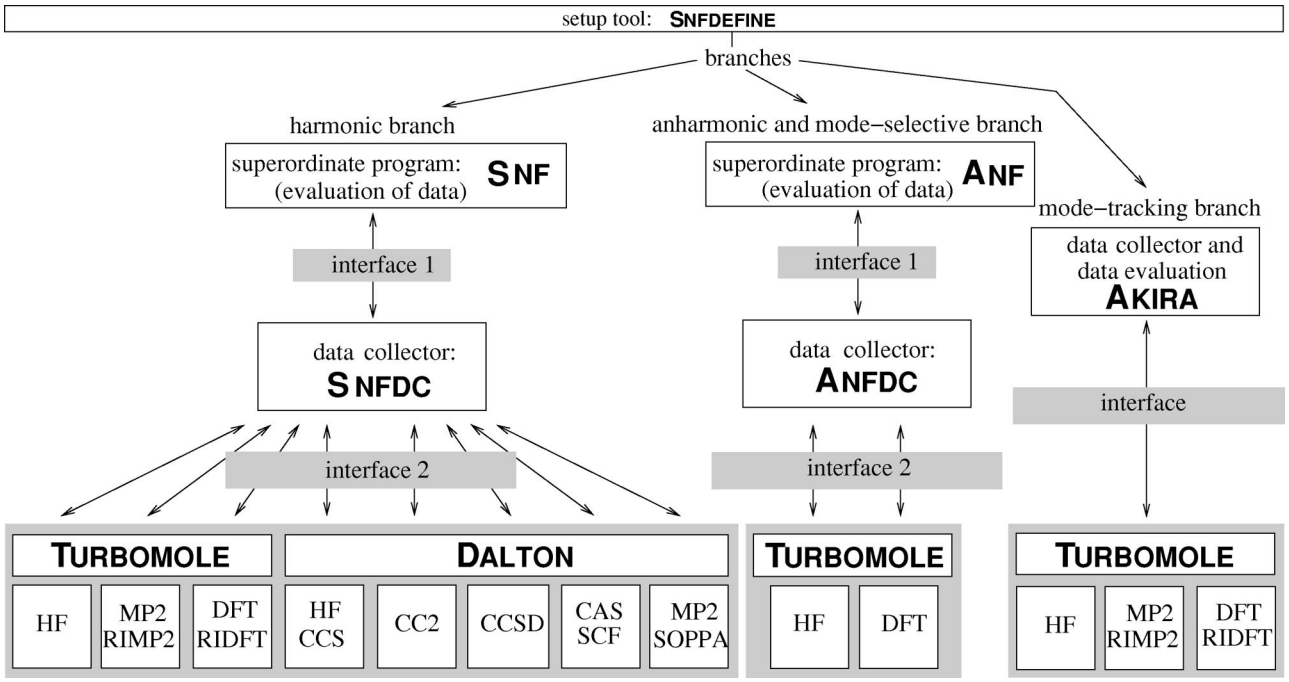

FIG. 1. Hierarchical structure of programs for the calculation of vibrational spectra: SNF is the standard package (Ref. 35), ANF has been developed by J. Neugebauer for anharmonic spectra (Ref. 44), and the module AKIRA represents the implementation according to the algorithm described in this work.

with $\mathbf{B}:=\mathbf{B}^{3N}$. This transformation would thus only be exact if we used a complete set of $3N$ basis vectors. If the basis set is not complete, we may use the approximation

$$H^{(m)}_{jj,\mathrm{appr}}=\sum_{kl}\ \tilde{H}^{(m),i}_{kl}B^{i}_{kj}B^{i}_{lj} \tag{11}$$

for the default preconditioner, where the sum is over all basis vectors $\mathbf{b}^l$ $(l=1,\ldots,i)$ stored in the matrix $\mathbf{B}^i$. But this is usually a poor approximation and yields only as many approximate diagonal elements as basis functions are used in the current iteration (for the other diagonal elements, one could use either unit entries or the last diagonal element determined in this way for all other diagonal entries). However, the more iterations needed the better the preconditioner in this default preconditioning scheme. Furthermore, $1/(H^{(m)}_{jj}-\rho^i_s)$ is a poor approximation to the inverse of a matrix $(\mathbf{H}^{(m)}-\rho^i_s\mathbf{1})$ if $\mathbf{H}^{(m)}$ is not diagonally dominant. Consequently, this approach is in most cases not better than using a unit matrix as a preconditioner at the very beginning of the procedure, when only very few basis vectors are available.

Both problems mentioned previously in connection with the convergence criteria can be overcome by using a semiempirical calculation as an initial approximation: We calculate an estimate for the Hessian and approximate normal modes using the PM3 model (of course, other semiempirical models can also be utilized). An initial guess for the eigenvector can be chosen from the set of semiempirical normal modes, while the semiempirical Hessian can be used for the preconditioning procedure. Since the Hessian matrices under investigation are of dimensions of about a few hundred rows and columns, it is—in contrast with configuration interaction matrices—possible to explicitly calculate the inverse preconditioner matrix

$$\mathbf{X}^i=[\mathbf{H}^{(m)}_{\mathrm{PM3}}-\rho^i_s]^{-1} \tag{12}$$

in each iteration. It should be emphasized that the bottleneck of the calculation is not this matrix inversion, which takes only a couple of seconds, but the single point calculations of electronic energies and gradients for the displaced structures. Using a three-point central differences formula[21] for the numerical differentiation, we need two single-point calculations for structures distorted along each basis vector, which are performed in a coarse-grained parallelized way using standard parallelization techniques as provided by PVM and MPI. Unfortunately, it is not possible to perform *all* single-point calculations at once as the basis vectors of iteration i depend on the results of all $(i-1)$ former iterations. Therefore, the little computational effort for the generation of more accurate preconditioners is easily compensated by the resulting reduction of the number of iterations.

In course of the calculation of $\mathbf{H}^{(m)}_{\mathrm{PM3}}$ we also obtain the PM3 normal modes, which we use as the first approximation $\mathbf{b}^1$. Note that this "guessing of normal modes" is different from the standard projection operator technique, which always requires a certain point group in order to set up the projector from the irreducible representations of this point group. Instead, we project out a selected mode and do not rely on any group theoretical tools. Consequently, our approach is applicable also in C_1-symmetric cases. Nevertheless, these projection operator techniques can be used to determine an initial guess for the desired normal modes.

We have implemented the above-described algorithm with a Davidson as well as a Lanczos solver to become the new AKIRA module in our program package SNF[14] for quantum chemical vibrational analyses (see Fig. 1 for the modular structure of the program). A comparison of both diagonaliza-

TABLE I. Results for the mode-tracking calculation of a C–F stretching mode in fluorobenzene C_6H_5F using different initial guesses and preconditioners. Wave numbers of the selected vectors $\tilde{\nu}_{sel}$ are given in cm^{-1}; i is the number of iterations necessary to achieve convergence (it equals the number of basis vectors), "conv." is the number of normal modes which are converged after i iterations.

		Normal mode guess					
		Pure C–F stretch			PM3		
	Preconditioner	i	conv	$\tilde{\nu}_{sel}$	i	conv	$\tilde{\nu}_{sel}$
Davidson	Default	10	10	508.6	6	1	511.5
	Unit matrix	10	10	508.6	6	1	511.5
	Inverse Hessian, Eq. (12)	8	1	1246.9	3	1	511.5
Lanczos	⋯	10	10	508.8	6	1	511.5

tion schemes shows that they perform equally well if the preconditioning is not well chosen (see the following). But, in case of a good preconditioning through a PM3 or similarly sophisticated guess we obtain a significantly better convergence of the Davidson-type algorithm.

Our implementation allows one to optimize several eigenvectors simultaneously, which is known as the *Davidson–Liu* or *block-Davidson* method.[22,23] Root homing is also guaranteed.[24] For root homing, there exist two promising protocols in the case of normal modes as eigenvectors: (i) selection of the eigenvector with the largest overlap with the initial guess vector; (ii) selection of the eigenvector with the largest overlap with the approximate eigenvector chosen in the last iteration. Both methods are implemented in our program. While the first method can cause convergence problems if only a poor initial guess vector is available, the second method usually shows better convergence characteristics; however, it may converge to a different, nondesired eigenvector due to poor initial vectors in combination with some preconditioners (see Sec. III for an example). In all calculations on fullerenes presented in this work, we used the second method to track the eigenvectors.

For all calculations we employed the density functional programs provided by the TURBOMOLE 5.4 suite.[25] The results are obtained from fully optimized all-electron restricted Kohn–Sham calculations. We employ the Becke–Perdew functional dubbed BP86[26,27] as implemented in TURBOMOLE. In connection with this functional we always apply the resolution-of-the-identity (RI) technique.[28,29] For the efficient calculation of the polarizabilities for the displacement structures we used the ESCF module of the TURBOMOLE package, which is capable of using the resolution-of-the-identity technique. Ahlrichs' SV(P) basis set[30] featuring a valence double-zeta basis set with polarization functions on all atoms except hydrogen atoms was used throughout (we shall demonstrate in Sec. III that this basis set yields results comparable to those from a triple-zeta plus polarization basis set,[31] which has proven to give reliable Raman intensities for buckminsterfullerene[14]).

Raman intensities are given in terms of the system-inherent Raman scattering factors S,

$$S = 45a_k'^2 + 7\gamma_K'^2, \tag{13}$$

where a_k' and γ_k' contain the derivatives of the polarizability tensor components with respect to normal coordinates (cf. Refs. 14 and 32). We calculate the activities S by numerical differentiation of polarizabilities obtained for structures which are distorted along the normal coordinate.[33]

For the calculation of the initial guesses, we used the program MOPAC.[34] We employed for the PM3 preconditioner Hessians for the PM3 *optimized* structures, such that possible negative eigenvalues of a PM3 Hessian for the DFT optimized structure are avoided. This choice requires that the optimized structures from PM3 and DFT do not differ largely, which would affect the convergence behavior in which case a more suitable low-level method for the generation of the preconditioner should be sought.

For a further decrease of the wall time our implementation allows us to use the parallelized version of the density functional programs in the TURBOMOLE package, such that every slave node in the coarse-grained parallel calculation for the two single point calculations in each Davidson step acts as a master node for the fine-grained parallel single point calculation.

III. TEST CASES

We would like to present some test calculations in order to analyze the features of our algorithm. As a first test case we chose fluorobenzene and applied different preconditioning procedures in order to find the most appropriate one, which is essential for the efficient application of the algorithm. The second test case is buckminsterfullerene, whose complete Raman spectrum has already been studied in great detail.[14]

A. Fluorobenzene

We test our implementation for the fluorobenzene molecule and compare the data to those obtained in a *full* harmonic force field calculation with SNF[14,35] (see Fig. 1). Our aim is to determine the frequency of a mode which involves a stretching of the C–F bond (note that there exist several modes of a_1 symmetry which show this behavior).

Table I compares data for different preconditioners and different guesses for the initial basis vector. As initial guesses we used (i) a pure C–F bond stretching and (ii) a C–F stretching mode, which also involves a squeezing of the benzene ring and which was obtained from a PM3 calculation (the PM3 wave number is 531.6 cm^{-1}).

TABLE II. Breathing mode of C_{60} in cm^{-1} as calculated with different basis sets (PM3 value: 622.9 cm^{-1}; exp. (Ref. 45): 496 cm^{-1}). The Raman activities S are given in $Å^4$/u.

Method	$\tilde{\nu}_{sel}$	S	S_{rel}
SNF/BP86(RI)/TZVP	478.8	190.0	0.4733
SNF/BP86(RI)/SVP	487.0	152.9	0.4261
AKIRA/BP86(RI)/SVP	487.2	155.7	⋯

The method for root-homing, which tests on the largest overlap with the approximate eigenvector selected in the last iteration, and is used throughout, can converge to different eigenvectors if different preconditioners are applied (see Table I): All methods converge to the vector for which a complete harmonic force field calculation yields a wave number of 509.0 cm^{-1}, only the pure-C–F-stretch guess in combination with an explicit inversion of $(\mathbf{H}^{(m)}_{\text{guess}} - \rho^i_s \mathbf{1})$ converges to a different normal mode at 1246.9 cm^{-1} involving a C–F stretch vibration (SNF result for this vector: 1247.0 cm^{-1}). In the other cases, the pure-C–F-stretch guess yields 508.6 cm^{-1}, which is in satisfactory agreement with the 509.0 cm^{-1} reference value. The PM3 guess for the normal modes, which exhibits the best convergence behavior, yields 511.5 cm^{-1} due to numerical inaccuracies, which can be diminished through a better choice of the step size for numerical differentiation. However, since these calculations are intended to be test calculations for the convergence behavior we refrain from improving on the current results. The experimental value for this vibration is 519 cm^{-1} (and 1220 cm^{-1} for the additionally found normal mode involving C–F stretching),[36] which is in good agreement with the harmonic wave number.

It can be understood from Table I that three methods converge to ten roots within ten iterations. This poor convergence is due to the inappropriate choices of the preconditioners as diagonal matrices in the first two cases and due to the missing preconditioning possibility of the Lanczos method. These ten a_1-symmetric roots are equal for all three cases. The full calculation shows that there are eleven vibrations of a_1 symmetry, which demonstrates the poor convergence in the case of ineffective preconditioning. Therefore, the important result of this comparison is that a PM3 guess for the normal mode and, in particular, the use of the inverse PM3 Hessian yields by far the best convergence behavior. If the preconditioning for the Davidson procedure is not optimal it shows the same poor convergence like the Lanczos method.

B. Buckminsterfullerene

Owing to the regular structure of fullerenes, we have already shown that the TZVP basis set[31] can reliably be used for the calculation of Raman intensities for C_{60}. In order to test whether it is possible to use an even smaller basis set for the large nanotubes, we investigate the basis set effect on the a_g breathing mode of C_{60} (Table II).

First of all, we note that our Davidson algorithm gives almost the same wave number for the breathing mode like the SNF reference value, which is computed by numerical differentiation in terms of Cartesian coordinates. The difference in numerical differentiation, i.e., in terms of Cartesian coordinates and in terms of distortions along selected normal coordinates, is responsible for the different values for the Raman activity S: 152.9 and 155.7 $Å^4$/u. Although these SVP values for S differ by about 34 $Å^4$/u from the TZVP result, the relative values for S, which are calculated with respect to the most intense peak in the total spectrum, compare very well (cf. Table II). The wave number obtained with the smaller basis set is about 8 cm^{-1} larger than the corresponding one obtained with the TZVP basis set. Because of an error compensation of the *smaller* basis set and the *harmonic* approximation (see also Ref. 37), this wave number is closer to the experimental result than the TZVP value is.

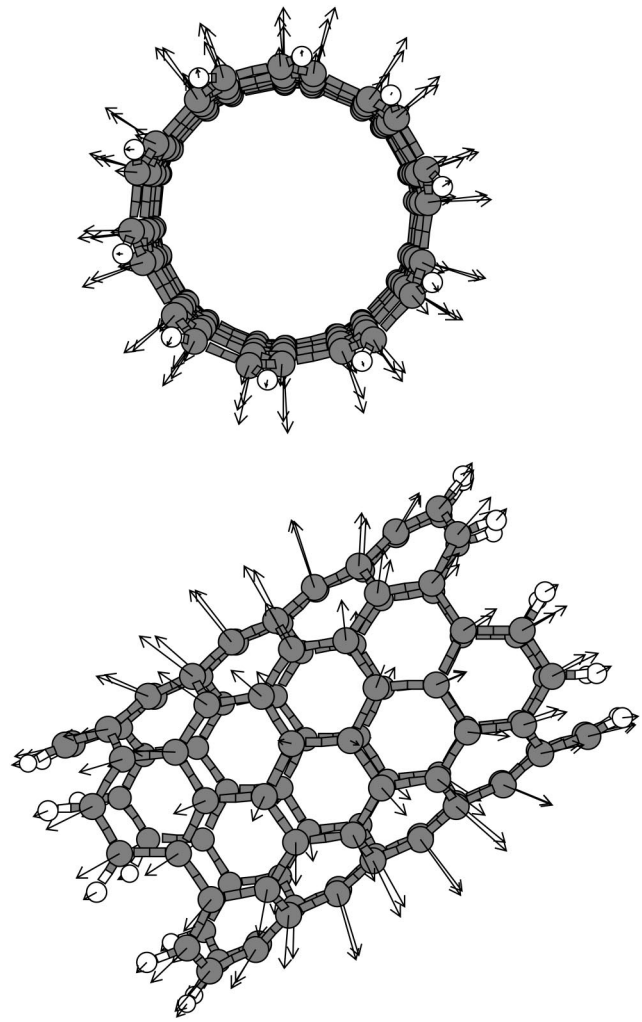

FIG. 2. Breathing mode of the [5,5]-nanotube **1**.

IV. MODE TRACKING FOR SINGLE-WALLED CARBON NANOTUBES

For our study of large molecules, we chose the model **1** for an armchair [5,5] nanotube, in which we have saturated the free valencies of the edge carbon atoms by hydrogen atoms (the structure of **1** and the corresponding breathing mode are depicted in Fig. 2). The electronic structure of such [5,5] nanotubes has been investigated very recently.[38,39] We should note that the carbon nanotube models used for this

study can be analyzed within a few days on a personal computer cluster. The size of the nanotubes which is accessible by our methodology is actually larger than the 120 atoms of our model.

A. Breathing modes of carbon nanotubes

Wave numbers of certain normal modes can be used as diagnostic tools for the determination of the diameter of a nanotube.[7] As an example, we calculated the breathing mode (Fig. 2) of our [5,5]-nanotube model.

The convergence of our algorithm is excellent and the breathing mode is obtained after the first iteration because of the regular shape of the molecule, which allows us to obtain a very accurate initial guess $\mathbf{b}^1$. The actual point group of nanotube **1** is D_{5d}, though we did not take advantage of this and calculated the breathing mode in C_1 symmetry. However, the totally symmetric breathing mode belongs to the irreducible representation a_{1g}, such that the good quality of the PM3 normal mode is mainly due to the high symmetry, which was implicitly adopted in the DFT and PM3 calculations though it was not explicitly specified.

The DFT wave number of 341.5 cm^{-1} differs largely from the PM3 wave number of 426.8 cm^{-1} (like in the case of C_{60}), which demonstrates that the semiempirical PM3 model without application of empirical wave-number-scaling techniques does not provide a reliable description of vibrations of fullerenes.

It is thus possible to calculate the diameter-dependent vibrations of $[n,m]$ nanotubes in order to support the assignment of experimental bands.

B. Functionalized carbon nanotubes

Functionalization of carbon nanotubes[9,40–42] is the first step toward their possible application in molecular machines (cf. the recent review—Ref. 43). Apart from the specific control of functionalization reactions it is very important to verify that the desired functionalization has taken place. Our methodology can be a valuable tool for the distinction of potential reaction products through comparison of theoretical and experimental vibrational frequencies. The fluorination of nanotubes is a prominent example for the first step toward more sophisticated, planned synthetic approaches. For a sample calculation we thus added one F_2 and one HF molecule, respectively, to our model nanotube **1** to obtain the structures **2a**, **2b**, and **3** in Fig. 3.

For comparison with the parent model **1**, we calculated all breathing modes of these fluorinated nanotubes (Table III). The number of iterations needed for convergence is increased in part because the structural distortions are not treated properly by the PM3 guess. A second reason for this somewhat worse convergence behavior for the functionalized carbon nanotubes is based on the fact that the breathing mode is largely distorted upon functionalization when compared to **1**. In this case, several normal modes in the same wave number range show similar collective movements of the atoms like the desired distorted breathing mode.

The Davidson procedure cannot project out a single mode in such a case but increases the number of iteration steps such that all physically relevant modes are obtained. In this sense the increasing number of iterations is *no* drawback of the method but a nice feature, which guarantees a correct physical description of the sought-for vibrations: Through the additional iterations we obtain all other relevant normal

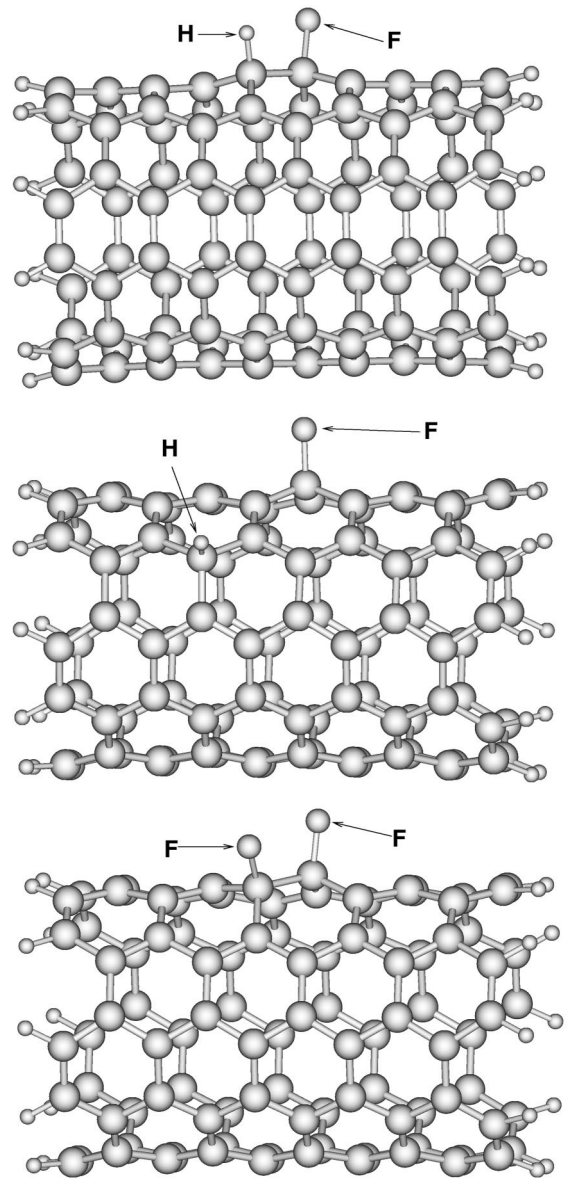

FIG. 3. Three models for functionalized [5,5] nanotubes. (Top) **2a**, HF added in a 1,2-position; (middle) **2b**, HF added in a 1,4-position; (bottom) **3**, F_2 added in a 1,2-position.

TABLE III. Wave numbers of breathing modes of the [5,5]-nanotube **1** and the functionalization models **2** and **3** in cm^{-1} (method: Davidson; guesses: inverse Hessian and normal modes from PM3 calculations). The Raman activity S is given in $Å^4$/u.

Tube	$\tilde{\nu}_{sel}$ ($\tilde{\nu}_{sel,PM3}$)	i	S
1	341.5 (426.8)	1	149.4
2a	345.4 (415.0)	7	26.6
2b	342.7 (418.1)	7	89.2
3	335.0 (415.7)	12	84.8

modes. The accuracy of these additional modes can easily be checked by means of the convergence criteria, which are calculated in every iteration for each of the approximate eigenvectors. If the norm and the maximum component of the residuum vector for these modes are small enough, they are also reliable approximations to the exact normal modes.

It should be noted that the slightly slow convergence for the fluorinated nanotubes is not to be confused with the bad convergence which was found for the C_6H_5F molecule owing to the unsuitable choice of the preconditioner. Here, the total number of vibrational basis vectors is 360 in irrep *a* of C_1. The maximum number of twelve iterations is thus very small: convergence within seven (compounds **2a** and **2b**) or twelve (compound **3**) iterations is still very satisfactory. For instance, we had to carry out 14 single point calculations for the seven iterations necessary for compound **2a**. By contrast, $6\times 122=732$ single point calculations (i.e., $3N$ times two in the case of a three-point central differences formula) would be needed in the traditional seminumerical approach, which calculates the complete Hessian.

The results further on demonstrate that the wave number shifts compared with **1** can become sufficiently large for $(F_2)_x$ nanotubes such that they can be distinguished from each other in the Raman spectrum. However, it is most likely that other characteristic vibrations, which contain C–F stretching, can also be utilized for this purpose. Quantum chemical calculations can thus serve as efficient diagnostic tools for structure analysis of experimental vibrational spectra of carbon nanotubes.

V. CONCLUSION

In this study we have shown how the standard procedure of calculating all vibrational normal modes of a molecule for an analysis of certain bands in a vibrational spectrum can be reversed. This ''reversion'' is important because it allows us to select a desired vibration from the very beginning. Only this particular vibration or a small number of related vibrations are projected out of the large number of all collective modes of large molecules. The steadily increasing amount of normal modes for increasing system sizes does not make the calculation unfeasible if a single point calculation is possible, which is always the case because optimized structures would have to be generated first. The vibrational eigenvalue problem is solved in a small subspace of the complete normal coordinate space and one or a couple of predefined modes are projected out of all $3N$ modes of the molecule. Since the calculation of the full Hessian is not necessary, comparatively little computational effort is needed compared to the standard procedure.

For a good convergence behavior of the method it is most important to generate a sufficiently accurate guess for the desired normal modes and for the preconditioner. This guess should be based on a quantum chemical method, which is computationally less expensive than the method which shall be used finally. Therefore, we chose semiempirical methods to speed up our density functional calculations. But it is, of course, also possible to use density functional calculations in the case of smaller molecules for a high-quality guess for subsequent computer resource demanding *ab initio* correlation methods like the popular coupled cluster model CCSD(T). Our methodology thus applies also in these cases where only a small number of modes exists in total but the calculation of the full Hessian matrix is unfeasible because the calculation of only one of its elements is extremely time consuming.

With the methodology presented, it is possible to study large molecules, which we have demonstrated for single-walled carbon nanotubes. Particular vibrational modes can efficiently be used for structure determination if an assignment to experimental vibrational bands is possible. These modes are chosen in advance by selection of those atoms in the molecule whose motion will set up the desired collective vibration; the above-mentioned advanced guesses for the desired normal mode are just sophisticated means for this simple idea, which has directly been implemented if a guess is not available. In those cases in which the sought-for vibration is not represented by a single mode, our algorithm will produce all physically relevant modes by automatic enlargement of the number of basis vectors through the number of iterations. This procedure makes one aware of additional modes, which can become important but which have not been recognized *a priori*.

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