



RAPID COMMUNICATION

Harnessing desktop computers for *ab initio* calculation of vibrational IR/Raman spectra of large molecules

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Abstract. The requirement of huge computational resources makes quantum chemical investigations on large molecules prohibitively difficult. In particular, calculating the vibrational IR/Raman spectra of large molecules employing correlated *ab initio* theory is a herculean task. The present article brings out the utility of our molecular tailoring approach (MTA)-based software for accurate yet economic spectral calculations employing one or more desktop computers. Hartree-Fock and density functional theory-based benchmark calculations on test cases containing over 175 atoms and over 2300 basis functions show excellent agreement with their full calculations (FC) counterparts with large savings in the computer time and memory/hard disk requirements. These savings are even more impressive at MP2 level of theory. Our MTA-based software thus represents an art-of-the-possible for computing vibrational IR/Raman spectra using a handful of desktop machines.

Keywords. Vibrational infrared (IR) and Raman spectra; Hartree-Fock (HF); Density Functional Theory (DFT); Møller-Plesset second-order perturbation theory (MP2); Molecular Tailoring Approach (MTA); large molecules.

1. Introduction

Advents in spectroscopy have made measurements of structures and properties of molecules and materials routinely possible.¹ In particular, Infrared (IR) and Raman spectroscopy are commonly used techniques for exploring structures of large molecular systems.^{2,3} These explorations need to be supplemented or complemented by theoretical studies, *e.g.* quantum chemistry (QC)-, Monte Carlo (MC)-, molecular dynamics (MD)-based computations/simulations, *etc.* Among all of these, QC studies on molecular systems are quite reliable for a meaningful comparison with the corresponding experimental spectra.⁴

Within QC framework, several levels of theory are available, such as Hartree-Fock (HF), Density Functional Theory (DFT), Møller-Plesset second-order perturbation theory (MP2), *etc.*, differing in the construction of wave function/electron density for solving the Schrödinger equation. These theories have to be executed in conjunction with a careful choice of basis set.

The computational cost (in terms of execution time) of a QC method is determined by the level of theory and number of basis functions, N . The hardware capability (such as memory, disk space, *etc.*) is also another limiting parameter for carrying out the calculation of energies and spectra of large molecules. The HF and DFT energy computations typically scale $O(N^3)$ or $O(N^4)$ whereas correlated theories, *e.g.* MP2 and coupled cluster singles and doubles with perturbative triples *viz.* CCSD(T), scale as $O(N^5)$ and $O(N^7)$ respectively.^{5,6} The spectral calculations are even more demanding in terms of CPU time, memory and/or disk space. Pursuing such QC investigations requires huge computational resources and effective parallel algorithms.⁷ The required hardware resources are not readily available at several academic/research institutions for everyday use.

To overcome the computational power requirements and to cut down the scaling complexities of the QC methods, several alternate routes have been proposed by researchers. Density-fitting (DF), Resolution of Identity (RI), Local and fragment-based methods are some of the

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examples.^{8–11} However, the accuracy and efficiency of DF, RI and local methods need to be carefully benchmarked, especially for the calculation of the spectral properties. On account of simplicity in execution, ease in parallelization and high accuracy,^{12,13} fragment-based methods have gained popularity over the last decade. Nevertheless, it should be borne in mind that all such routes are *approximations* to canonical full calculations (FC) which demand huge computational resources.

Many fragmentation-based methods have been developed^{12,14,15} in the quantum chemical literature since the 1970s. The central theme of all fragmentation-based methods is to divide the parent system into subsystems such that the latter can be readily treated computationally. Within the framework of such methods, the most crucial part is the *a priori* generation of quality fragments, assuring adequate accuracy and efficiency. Most of the fragmentation-based methods do not adequately address this inherent problem. Furthermore, most of these methods have been benchmarked only for energy calculation and geometry optimization. On account of extensive computations involved therein (*viz.*, the Hessian matrix, derivatives of dipole moment and polarizability tensor, *etc.*), the accurate theoretical treatment of vibrational IR and Raman spectra for large molecular systems is an arduous task even on large hardware. Moreover, such computations employing contemporary desktop/server computers with multi-core architecture (typically 8 cores, 64/128 GB RAM and 1 to 2 TB hard disk) are either impossible or extremely time-consuming. In the present work, we demonstrate our home-built molecular tailoring approach (MTA)-based software showcasing the calculations of energies and vibrational (within harmonic approximation) IR/Raman spectra of large molecules employing a multi-core desktop machine. Details of MTA have been given in the earlier publications from our group,^{12,13} but a brief summary of MTA is given for the uninitiated reader in the following section.

2. Computational methodology

An indigenous fragmentation-based method, *viz.*, MTA was developed in our group and employed for exploring energetics and spectral features of large molecules/molecular clusters at *ab initio* level such as HF, DFT, MP2, *etc.* MTA is essentially based on the set inclusion-exclusion principle (SIEP). The spatially extended parent molecule under investigation is divided into a series of main and overlapping subsystems, named fragments. These fragments are subjected to the computation instead of the entire parent molecule. A desired electronic property, *P*, of a parent molecule is then estimated by combining the properties of the individual fragments employing SIEP as an approximation, *vide* Eq. (1):

$$P = \sum_i P^{F_i} - \sum_{i < j} P^{F_i \cap F_j} + \dots + (-1)^k \sum_{i < j < \dots < n} P^{F_i \cap F_j \cap \dots \cap F_n} \quad (1)$$

In Eq. (1), P^{F_i} denotes the property associated with i^{th} fragment, $P^{F_i \cap F_j}$ represents the value of property *P* of the binary overlap between the fragments *i* and *j* where as *k* is the order of overlap between the fragments. On account of dividing the parent molecule into small fragments, computational expenses are steeply reduced. However, the estimate of the property *P* produced by the use of MTA carries some errors, essentially due to interatomic interactions that are completely missed out. Sharing the spirit of methods^{16,17} such as ONIOM, G2, *etc.*, a grafting correction¹⁸ was introduced in 2012 with an aim to reduce the error occurring due to the missing interactions within MTA. In this correction, the contribution of the missing interatomic interactions due to fragmentation is estimated from the difference between the energies of MTA and FC calculations at a suitable lower basis set (LB), by keeping the fragmentation scheme unaltered.

$$P^{HB} = P_{MTA}^{HB} + \left(P_{FC}^{LB} - P_{MTA}^{LB} \right) \quad (2)$$

Here, P^{HB} is the electronic property of the parent molecule estimated at higher basis set (HB) after effecting the grafting correction, P_{MTA}^{HB} is the property computed by the MTA (using Eq. 1) procedure at the HB. P_{FC}^{LB} and P_{MTA}^{LB} are the electronic properties computed at the LB set by doing the Full and MTA calculation respectively.

The technical details of the software will be made available in a forthcoming publication. However, we give below brief highlights of the present algorithm. Following is the input needed for running the software, in an interactive mode. A sample input file is given in the Supplementary Information (TS-2).

1. The Cartesian coordinates (in Å) of the parent molecule/cluster (closed shell) in xyz format.
2. The Cartesian coordinates of the fragments.
3. Level of theory such as HF/DFT/MP2.
4. Lower basis set (LB), *viz.*, the basis used for grafting.
5. Higher basis set (HB), *viz.*, the basis at which the property estimation is desired.

All the keywords are to be given as per the format of the Gaussian program. On receiving the above inputs, our MTA-based software initiates the Gaussian program to extract the FC Hessian matrix and/or dipole- and polarizability-derivative tensors at LB followed by MTA calculations [by SIEP of Eq. (1)] at LB and HB. With the use of Eq. (2), the difference between the FC- and MTA-Hessian matrix elements at LB is grafted to those generated by MTA at HB. The flowchart illustrating this algorithm is depicted in Figure 1. The Hessian matrix thus obtained is converted into mass weighted Hessian matrix for generating vibrational frequencies and the corresponding normal modes. In a similar manner, the dipole- and

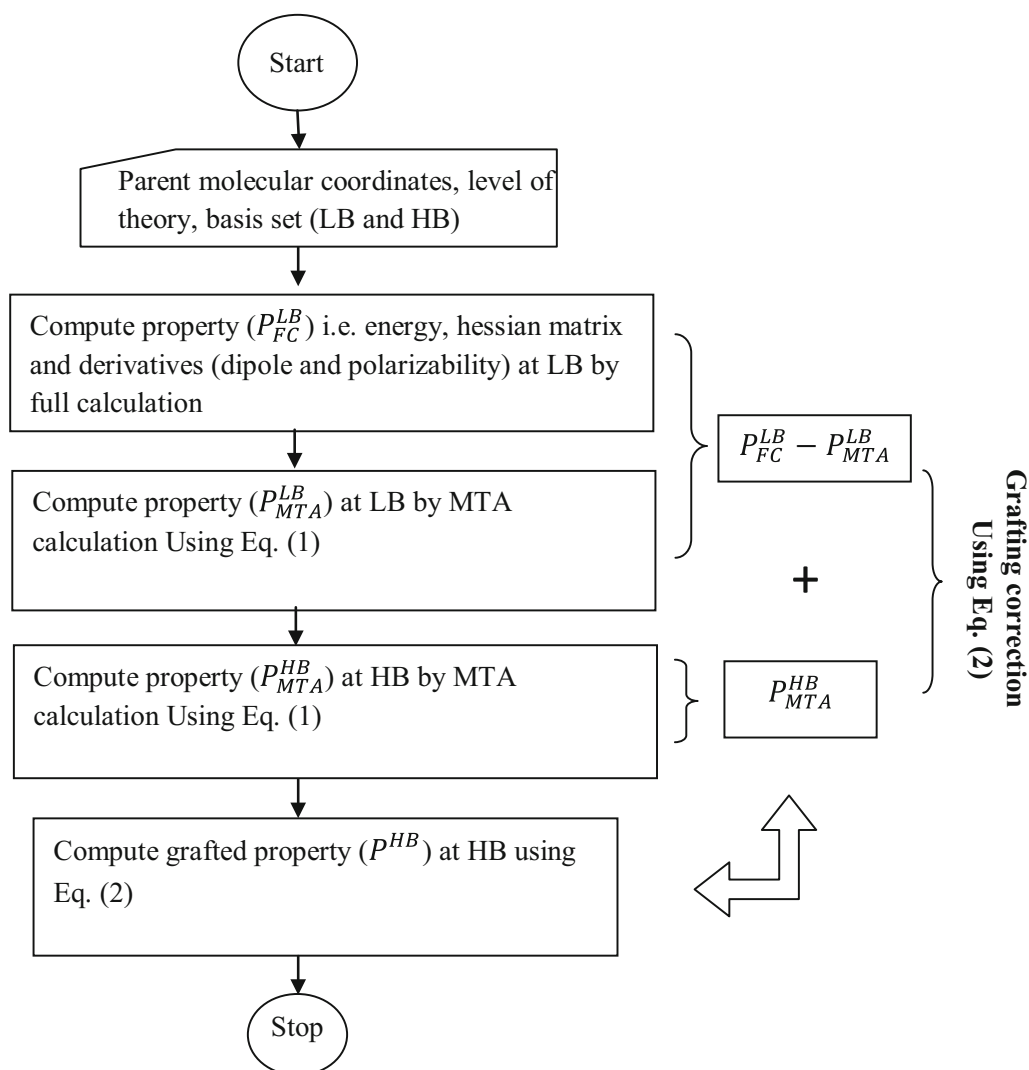


Figure 1. Flowchart of the automated MTA algorithm for calculating vibrational IR/Raman spectra of large molecular systems. See text for details.

polarizability-derivative tensors are generated and used for calculating IR/Raman intensities respectively.^{12,13}

For all the test cases, fragmentation is done manually by the use of visualization software MeTASStudio.¹⁹ However, for the uninitiated user, the utility for automatic generation of fragmentation scheme is also available.²⁰ The computations on fragments are carried out by employing Gaussian 16 software package.²¹ As stated in the previous section, several MTA-based calculations here are done on desktop computers with 4/8 cores and 8/64/128 GB RAM and 1 to 2 TB hard disk. For some larger systems, a 16 core computer with 128/256 GB RAM and upto 4 TB hard disk is used if required.

3. Results and Discussion

Table 1 displays the test cases along with a number of atoms, level of theory and basis sets employed

Table 1. Test systems (molecules/clusters), the corresponding level of theory (LT) and basis set, Number of atoms (NA) and Number of basis functions (NBF). See text for details.

System	LT/Basis Set	NA	NBF
(CO ₂) ₂₅	HF/aug-cc-pVDZ	75	1725
α-Cyclodextrin	B3LYP/6-31++G**	126	1614
subst-acetamide	B3LYP/6-31++G**	66	1025
Vancomycin	B3LYP/6-31++G**	176	2377
Fc@CB[7] ^a	ωB97X/6-31+G*	147	1939
Bz-(H ₂ O) ₈ ^b	MP2/aug-cc-pVDZ	36	520
β-carotene	MP2/aug-cc-pVDZ	96	1424

^aGeometry is adapted from Ref. 28.

^bGeometry is taken from Ref. 27.

for the calculations. Vibrational IR/Raman spectra are benchmarked at HF/DFT (with B3LYP and ωB97X functional) as well as at MP2 level of theory. Table 1

Table 2. Test systems (molecules/clusters), level of theory (LT) and basis set, FC and MTA-based energies, *viz.* E_{FC} and E_{MTA} in a.u. whereas ΔE is the absolute difference between E_{FC} and E_{MTA} energies in mH. See text for details.

System	LT/Basis Set	E_{FC}	E_{MTA}	ΔE
(CO ₂) ₂₅	HF/aug-cc-pVDZ	-4691.68084	-4691.68024	0.60
α -Cyclodextrin	B3LYP/6-31++G**	-3664.79414	-3664.79548	1.34
Subst-acetamide	B3LYP/6-311++G**	-2023.47451	-2023.47489	0.38
Vancomycin	B3LYP/6-31++G**	-5779.06178	-5779.06149	0.29
Fc@CB[7]	ω B97X/6-31+G*	-5862.22884	-5862.22590	2.94
Bz-(H ₂ O) ₈	MP2/aug-cc-pVDZ	-841.76510	-841.76469	0.41
β -Carotene	MP2/aug-cc-pVDZ	-	-1553.10494	-

reveals that the test systems in the present work include closed-shell molecules/molecular clusters containing up to 180 (mostly) first-row atoms and/or 2400 basis functions at DFT levels. The test cases for MP2 level contain typically up to 96 first-row atoms and/or 1400 basis functions. In order to assess the quality of energies and the associated vibrational IR/Raman spectra generated by our MTA-based software, the results for few test cases are compared with their FC counterparts. For the molecular test cases, *viz.*, α -cyclodextrin, substituted acetamide, vancomycin and β -carotene, the initial geometries were taken from Refs. ^{22–25} respectively. These geometries were further optimized respectively at B3LYP/6-31++G**, B3LYP/6-311++G**, B3LYP/6-31+G* and MP2/cc-pVDZ levels of theory. In the case of molecular clusters, the most stable (CO₂)₂₅ structure generated through Monte Carlo procedure by Takeuchi²⁶ and benzene-water cluster (BZ-(H₂O)₈) optimized at MP2/aug-cc-pVDZ as reported by Milioridos *et al.*,²⁷ are also selected as test cases. These geometries are taken up further for IR computations at HF and MP2 respectively levels of theory employing aug-cc-pVDZ (aVDZ) as HB. Furthermore, the test systems also include a host-guest complex of a ferrocenyl derivative with cucurbit[7]uril macrocycle (Fc@CB[7]). For this purpose, the initial geometry is taken from Ref. ²⁸ which is further optimized at ω B97X/6-31++G** level of theory.

Single point energy and spectral calculations are done at the level of theory and basis set specified in Table 1. Before embarking on the MTA computations of vibrational IR/Raman spectra, it is felt worthwhile to assess the accuracy of the MTA energies *vis-à-vis* the respective FC values (whenever feasible). This comparison is shown in Table 2. It may be noticed from Table 2 that the grafted MTA energies obtained with the choice of appropriate LB, match their FC counterparts generally very well, with a typical error of 1 millihartree or less. This observation is in line with our recent study²⁰ bringing out a sub-millihartree error in energies

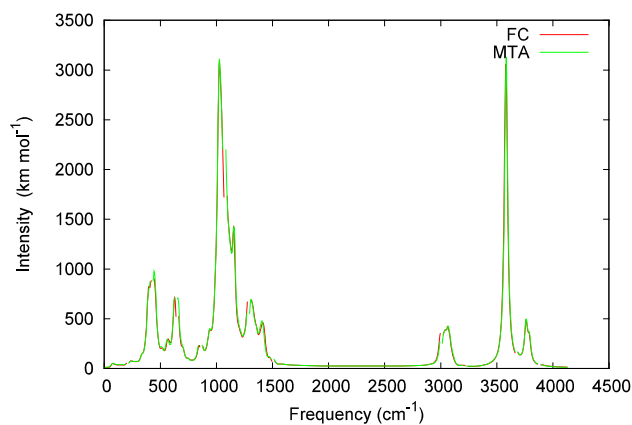


Figure 2. Superimposed MTA and FC vibrational IR spectra for α -cyclodextrin calculated at B3LYP/6-31++G** level of theory. See text for details.

of large molecules or clusters. It may, however, be noted that MTA calculations represent a delicate balance of accuracy and efficacy.²⁰ Thus, due to efficiency-based choosing of fragmentation scheme and use of LB (to ensure the possibility of doing FC at LB), a somewhat larger error is observed in the case of α -cyclodextrin and Fc@CB[7].

With the desired accuracy of MTA energy data achieved, the calculations are taken further for computing the vibrational IR and Raman spectra of these molecules. It may be noted that without the fragmentation approach, such computations are extremely cumbersome especially using low-end hardware. For benchmarking purpose, vibrational IR spectra for some of the test cases, *viz.*, α -cyclodextrin, (CO₂)₂₅, Bz-(H₂O)₈ and subst-acetamide at B3LYP, HF, MP2 and B3LYP level of theories respectively, are compared with the corresponding FC ones. Further, vibrational Raman spectrum for one of the test cases, *viz.*, subst-acetamide has been compared with the corresponding FC Raman spectrum. For effecting the grafting procedure, cc-pVDZ (VDZ) is employed as LB when aVDZ is used as HB. For rest of the cases, 6-31G is used as LB.

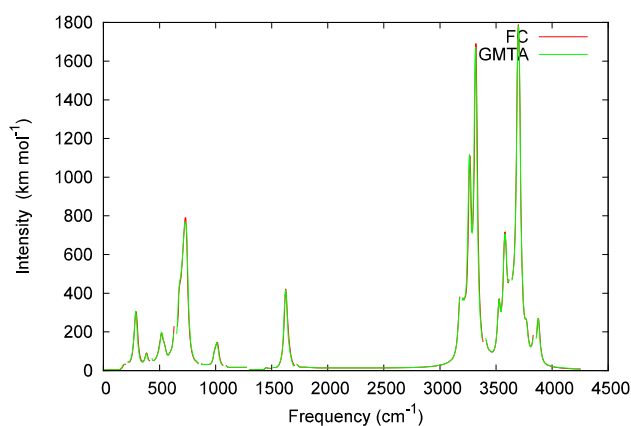


Figure 3. Superimposed MTA and FC vibrational IR spectra for Bz-(H₂O)₈ calculated at MP2/aVDZ level of theory. See text for details.

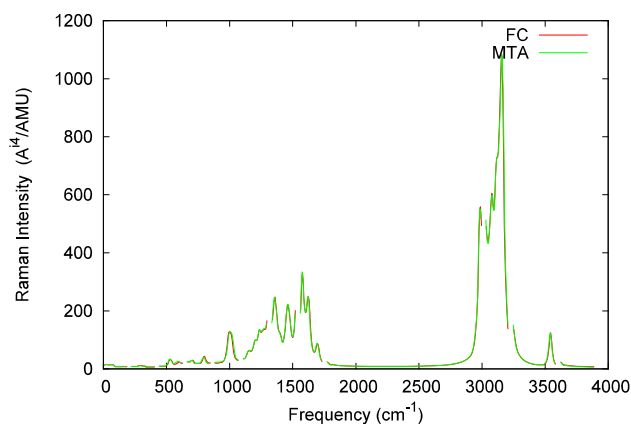


Figure 4. Comparison of MTA and FC vibrational IR spectra for subst-acetamide at B3LYP/6-311++G** level theory. See text for details.

Figure 2 shows the MTA and FC vibrational IR spectra broadened by the Gaussian with FWHM value of 20 cm⁻¹ for α -cyclodextrin calculated at B3LYP/6-311++G** level theory. Figure 3 depicts MTA- along

with FC-vibrational IR spectrum (appropriately broadened) for Bz-(H₂O)₈ complex at MP2/aVDZ theory. Similarly, Figure 4 shows a comparison of MTA and FC vibrational Raman spectrum for subst-acetamide. Within MTA, all the intense peaks are seen to be well preserved in comparison to the corresponding FC ones, with typical error in vibrational frequencies being less than 3 cm⁻¹. In fact, a visual comparison reveals that the MTA- and FC spectra for the test cases (*cf.* Figures 2, 3, 4) are almost indistinguishable from each other.

With this success in benchmarking, we generated the MTA spectra for rest of the test cases and are made available in the Supplementary Information. Table 3 reports the comparison of wall-clock times (total elapsed time calculated by taking the difference between job end and job start time) along with hardware employed, for MTA vis-à-vis FC spectral computations, in order to assess the efficacy of the MTA-based calculations. The FC spectral calculations of some test cases are not feasible on the indicated hardware, and the respective entries are marked with a '-'. Time gain is seen to be very substantial for all the test cases. Moreover, in the case of the test case of β -carotene, the vibrational IR spectrum at MP2/aVDZ is feasible only with the use of MTA. It is significant to note that in the case of Bz-(H₂O)₈, not only the MTA wall-clock time is smaller, but also the computational hardware used (8 core) is substantially lower (16 core for FC).

4. Conclusions

With the increasing sophistication in instrumental facilities, studies on vibrational IR and Raman spectra of molecules have become routinely possible. However,

Table 3. Test systems (molecules/clusters), the corresponding level of theory (LT) and basis set. Wall clock times (in minutes) for FC (T_{FC}) and MTA (T_{MTA}) vibrational IR and Raman spectral computations. See text for details.

	System	LT/Basis	T _{FC}	T _{MTA}
Vibrational IR	(CO ₂) ₂₅	HF/aug-cc-pVDZ	2851 ^a	5700 ^c
	α -Cyclodextrin	B3LYP/6-31++G**	6565 ^a	3191 ^c
	Subst-acetamide	B3LYP/6-311++G**	2082 ^b	413 ^b ,1024 ^c
	Vancomycin	B3LYP/6-31++G**	-	19506 ^b
	Fc@CB[7]	ω B97X/6-31+G*	-	17954 ^b
	Bz-(H ₂ O) ₈	MP2/aug-cc-pVDZ	1738 ^a	947 ^b
	β -Carotene	MP2/aug-cc-pVDZ	-	34960 ^a
Vibrational Raman	α -Cyclodextrin	B3LYP/6-31++G**	-	2480 ^c
	Subst-acetamide	B3LYP/6-311++G**	1903 ^b	1392 ^c

Wall clock time on: 16 core machine,^a 8 core machine^b and 4 core machine^c respectively.

quantum chemical investigations of even medium-sized molecular systems (typically containing ~ 100 atoms) at high-level theories such as DFT/MP2 and/or those employing large basis set, are prohibitively difficult employing any multi-core/high performing nodes. Hence for embarking upon such theoretical investigations, the inexpensive fragmentation-based alternative of using off-the-shelf multi-core machines offers a great advantage.

MTA offers a solution to this formidable challenge of *ab initio* level IR/Raman spectra calculation of large molecules. In the present study, we have described a home-built, fragmentation-based MTA software meant for this purpose. For some of the test cases, we have compared the energetics and vibrational spectra generated by MTA with the respective FC counterparts. The energies for all the test cases (for which FC is feasible) are seen generally to match well their FC counterparts. Since the errors in MTA energies are indeed very small (sub millihartree), it is assured that the relative energies of isomers/conformers are well reproduced within MTA, obviating the need of Full calculations.¹³ Time advantage for the estimation of vibrational IR/Raman at HF/DFT level is comparatively smaller due to the inherent $O(N^3 \text{ to } N^4)$ scaling. However, in the case of a correlated method, *e.g.* MP2, significant time advantage is noticed. Otherwise, such FC is not feasible even on large contemporary hardware.

It is noteworthy that within the MTA procedure, computations on fragments are independent of each other, leading to an excellent parallel performance on a large number of nodes. This feature of MTA has been gainfully employed previously for MP2 level calculations on large water clusters.¹³ With a larger number of computational nodes, the performance of MTA to enable vibrational IR/Raman spectra of large systems is also expected to grow substantially. It is envisaged that with MTA running on a dozen multi-core computers, the calculations of vibrational IR/Raman spectra for spatially extended molecular systems containing ~ 500 atoms would be readily possible in the years to come. The present MTA software would be of interest to the molecular science community. It is planned to make the software available to them on request. Moreover, technical assistance would also be provided for the uninitiated users.

Supplementary Information (SI)

Sample input file, optimized Cartesian coordinates of all the test cases reported in the article at respective levels of theory, Graphical view of all the test molecules/cluster along with the superimposed MTA and FC spectra of the test

systems. Supplementary Information is available at www.ias.ac.in/chemsci.

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