

Intensity Tracking for Vibrational Spectra of Large Molecules

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Abstract: We briefly review our work on theoretical vibrational spectroscopy and elaborate on a recent approach for the selective calculation of high-intensity features in vibrational spectra developed in our laboratory. Conventional methods for the determination of frequencies and intensities describe all vibrations on the same footing, irrespectively of their intensity. This becomes increasingly demanding for larger molecules. In our intensity-driven approach the total intensity is iteratively distributed to individual distinct bands as well as to fingerprint regions so that only the subset of vibrations that dominates the appearance of the spectrum is determined. In turn, normal mode approximations are obtained.

Keywords: Intensity tracking · Mode tracking · Quantum chemistry · Vibrational spectroscopy

1. Introduction

Vibrational spectroscopic techniques play an important role in the investigation of structure and function of molecules. This is of particular interest for the identification or structure elucidation of synthetic or biological species in catalytic cycles – especially in the condensed phase. Functional groups give rise to distinct marker bands in vibrational spectra which can serve to identify these building blocks in larger units. An example is the stretching vibration of carbonyl groups. Molecules may also be identified by their unique fingerprint in vibrational spectra. This fingerprint reflects the fact that the bonding situation and also the environment of a group of atoms have a strong influence on the exact peak positions and intensities.

Large molecules exhibit crowded spectra with many close-lying vibrations because of the increasing number of vibrations with molecular size. Still, characteristic features of the spectrum are often easily identified in experiment. However, if the relationship between structure and spectral features is not obvious as it is, for instance, the case for reactive intermediates, it may be rather difficult to uniquely assign a structure to a vibrational spectrum. Then, quantum chemical predictions are indispensable. In such theoretical investigations, the relation between spectrum and molecular structure is immediate. Many groups have worked on the establishment of theoretical vibrational spectroscopy for large molecules – too many to be reviewed here, and we may therefore simply refer to textbooks on computational chemistry for references.^[1]

Still, theoretical approaches feature distinct difficulties.

- i) Unavoidable approximations need to be thoroughly investigated. In particular the harmonic approximation for the calculation of vibrational frequencies of large molecules and the effect of a chosen electronic-structure method on vibrational intensities must be mentioned.
- ii) The computational effort of any quantum chemical method scales with the size of the system, which can be conveniently measured in terms of the number of atoms in the molecule. A prediction of a vibrational spectrum needs to be done fast in order to be useful for the experimental progress. This implies that the quantum chemical optimization of molecular structures and the subsequent calculation of a vibrational

spectrum should be carried out on a time scale of a couple of days only.

- iii) For special vibrational techniques even the theory may require further elaboration and resonance Raman spectroscopy may be taken as an example.

In the past years, we have worked on all three obstacles^[2] in order to complement existing work (because of the limited space available we may refer to the references cited below for an overview of the relevant literature on quantum chemical developments for the diverse vibrational approaches that exist).

Regarding the reliability of *harmonic* vibrational frequencies, which are often applied in direct comparisons with the experimental *fundamental* ones after scaling by some proper factor, we could contribute results of practical relevance. Density functional theory (DFT)^[3] is the most important workhorse for the calculation of vibrational spectra of large molecules. Especially the BP86 exchange–correlation density functional^[4] turned out to produce harmonic frequencies in remarkable agreement with experiment (see *e.g.* refs. [5]), and a thorough statistical investigation on a test set of molecules confirmed that the BP86 functional does not require scaling of harmonic frequencies because of a cancellation of errors from the neglect of anharmonic effects and the approximations inherent in the BP86 functional.^[6]

Especially spectroscopic techniques that require the evaluation of high-order molecular properties could only be assessed quite recently after the development of the appropriate quantum chemical tools. This is, for instance, the case for any variant of (non-resonant) Raman spectroscopy,^[7] which requires the calculation of

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derivatives of polarizability tensors with respect to nuclear displacements. Raman optical activity (ROA) (see refs. [8] for reviews) may be taken as a special example. For the prediction of infrared (IR) and Raman spectra of large molecules we implemented a flexible semi-numerical, massively parallel computer program^[9,10] and provided the first comparison of multi-reference, coupled-cluster, and DFT Raman intensities of *polyatomic* molecules.^[11] In addition, we could contribute to the assessment of DFT ROA spectra^[12] and the quest for rules of thumb in ROA spectroscopy is ongoing in our laboratory.^[13] Other work^[14] concerns the calculation of vibrational circular dichroism spectra,^[15] in particular in cases in which intermolecular interactions play a role.

If vibrational excitation is combined with an electronic transition, resonance variants emerge, which often feature a specific selection of active vibrations and finally yield a spectrum with only few lines ideally suited for structure elucidation and reaction control. Resonance Raman spectroscopy is of this type and we may refer to ref. [16] for an overview and comparison of state-of-the-art theoretical approaches. Especially Heller's short-time approximation^[17] offers a fast and – depending on the nature of the vibronically excited states – often quite accurate way to predict resonance Raman spectra.^[18] The calculation of vibronic couplings is also of increasing importance in calculations on the vibrational structure of electronic spectra (see ref. [19] for an example).

Regarding the computational effort for the prediction of vibrational spectra, often only a few modes of sufficient intensity are relevant for the identification or structure elucidation of a large molecule in condensed phase. Special procedures to determine only a subset of modes are therefore desirable. A convenient one that does not introduce additional approximations is the mode-tracking approach^[20] which requires only a guess for the vibration to be targeted. This guess is always very easy to obtain. For instance, a guess for a dinitrogen stretching vibration is defined by elongating the bond distance. Examples for the successful application of mode-tracking can be found in refs. [21]. Recently, mode-tracking also became available in the CP2K computer program.^[22]

If the mode-tracking approach is applied to a characteristic local vibration, its frequency and intensity are easily obtained. If this band stands also isolated in the experimental spectrum, the identification is often easy. However, the typical look of a vibrational spectrum is not reproduced in a mode-tracking calculation although it is very characteristic for the molecular structure. Hence, an ideal, smart algorithm

would mimic the experimental selectivity so that all intense modes would be calculated, resulting also in a higher efficiency if a molecule features comparatively few intense modes.

In order to obtain the intense modes, a hypothetical vibration which represents a superposition of the most intense modes weighted by their intensities is needed as a starting distortion. This idea should in principle work for any kind of vibrational spectroscopy for which an intensity expression in terms of the normal modes can be derived in closed form. In the case of the short-time approximation of resonance Raman spectroscopy, such a starting approximation is naturally provided by the excited-state gradient for the state under resonance, which determines the intensity in the final spectrum. It is important to note that the intensity-tracking algorithm is distinctly different from mode-tracking regarding its start and end points as it neither requires a guess distortion close to a converged vibrational motion for the start nor does it aim at producing only a few vibrations but instead the complete structure-characteristic finger print. Algorithmic details on how this can be realized are given in the original papers.^[23] The implementation of such an intensity-tracking approach for the selective calculation of intense modes in infrared and resonance Raman spectra is investigated further below.

2. Intensity-Tracking Theory

The core of the intensity-tracking algorithm is based on the iterative solution

$$(\mathbf{H}^{mw} - \lambda_i^{(k)})\mathbf{L}_i^{(k)} = \mathbf{r}_i^{(k)} \quad (1)$$

of the exact Hessian eigenvalue problem,

$$(\mathbf{H}^{mw} - \lambda_i)\mathbf{L}_i = \mathbf{0}, \quad (2)$$

for selected modes – as in the mode-tracking algorithm.^[20] Here, \mathbf{H}^{mw} is the mass-weighted Hessian, $\lambda_i^{(k)}$ and $\mathbf{L}_i^{(k)}$ are the approximate eigenvalues and eigenvectors in iteration (k), respectively, and $\mathbf{r}_i^{(k)}$ is the corresponding residuum vector, which is a measure for the deviation of $\mathbf{L}_i^{(k)}$ from an exact eigenvector. The approximate eigenvectors $\mathbf{L}_i^{(k)}$ are expanded in an increasing basis of collective-distortion vectors. After every iteration, the intensity is calculated for all approximate normal modes using an appropriate intensity expression, and the most intense ones are chosen for optimization. To specifically improve the description of these normal modes, a new basis vector is added for each of the select-

ed modes based on their residuum vector of the previous iteration. If the residuum vectors of the selected modes are small enough, the algorithm terminates. From the final solutions for λ_i and \mathbf{L}_i , wavenumbers and normal modes are calculated.

The basic steps of an intensity-tracking calculation may be summarized as follows:

- i) Construct a nuclear distortion that carries high intensity (depends strongly on the spectroscopic technique under consideration).
- ii) Refine intense vibrations by increasing the basis into which the normal modes are expanded. This also increases the total number of approximate modes in the algorithm.
- iii) Pick those (approximate) vibrations with largest intensity.
- iv) Check whether these modes correspond to Hessian eigenvectors. If so, continue. If not, go back to step ii).
- v) Calculate the final approximation to the vibrational spectrum.

This intensity-tracking algorithm can be applied very generally to the calculation of vibrational spectra, provided that a suitable starting distortion and an expression to identify the intense modes during the intensity-tracking calculation are available. The intensity-tracking algorithm then gives access to an approximate spectrum, with the possibility to control accuracy and computational cost by the selection of the convergence criteria for the normal modes and criteria for the selection of the intense modes.^[23] Additionally, the subset of the most intense modes can be subjected to a further treatment. For example for resonance Raman spectra, the interaction of two or more excited states in resonance and inclusion of non-Franck-Condon contributions may be taken into account.

What remains to be done to successfully apply the intensity-tracking algorithm is to construct some distortion of the nuclear positions corresponding to a hypothetical vibration of high intensity. For resonance Raman intensities in the framework of Heller's short-time approximation, such a starting distortion is obvious as is explained in detail in ref. [23a]. As mentioned above, the direction defined by the gradient of the excited state under resonance is taken as a starting distortion for the most intense vibration. For other vibrational spectroscopic techniques, however, the construction of such a starting distortion is not always straightforward. In some cases, it can be derived from the intensity expression by maximizing the intensity with respect to the elements of the collective Cartesian distortion of the (hypothetical) starting vibration. By following this procedure, optimum starting vectors can in principle be found for all types of vibration-

al spectra for which the intensity is known explicitly in terms of the normal modes. We will work through the example of infrared intensities in the following.

The IR intensity of a vibration can be written in terms of the derivative of the electric dipole moment components ($\mu_{x,y,z}$) along the corresponding normal coordinate Q_k ,^[9,24]

$$I_k \sim \left[\left(\frac{\partial \mu_x}{\partial Q_k} \right)_0^2 + \left(\frac{\partial \mu_y}{\partial Q_k} \right)_0^2 + \left(\frac{\partial \mu_z}{\partial Q_k} \right)_0^2 \right] \quad (3)$$

where the subscript zero indicates that the derivatives are taken at the equilibrium structure of the molecule. If we now define the electric dipole moment derivatives in terms of the mass-weighted ('mw') nuclear Cartesian coordinates \mathbf{R}^{mw} as

$$\mathbf{U}_\alpha^{mw} \equiv \frac{\partial \mu_\alpha}{\partial \mathbf{R}^{mw}},$$

the Hessian eigenvector \mathbf{L}_k can be employed to obtain the derivative with respect to the normal coordinate according to the chain rule of differentiation,

$$I_k \sim \left[(\mathbf{U}_x^{mw} \cdot \mathbf{L}_k)^2 + (\mathbf{U}_y^{mw} \cdot \mathbf{L}_k)^2 + (\mathbf{U}_z^{mw} \cdot \mathbf{L}_k)^2 \right] \quad (4)$$

(the dimension of the vectors is the total number of coordinates $3M$ where M is the number of atoms).

For the intensity-tracking calculation, we need a starting distortion $\mathbf{L}_k^{(0)}$ which may be considered a hypothetical mode with maximum intensity. The conditions for maximizing the intensity with respect to the components of the starting vector of distortions, $\mathbf{L}_{kj}^{(0)}$, are defined in terms of the variation of a Lagrangian functional,

$$\frac{\partial}{\partial L_{kj}^{(0)}} \left[(\mathbf{U}_x^{mw} \cdot \mathbf{L}_k^{(0)})^2 + (\mathbf{U}_y^{mw} \cdot \mathbf{L}_k^{(0)})^2 + (\mathbf{U}_z^{mw} \cdot \mathbf{L}_k^{(0)})^2 - a_k \left(\sum_{i=1}^{3M} (L_{ki}^{(0)})^2 - 1 \right) \right] = 0, \quad (5)$$

in which the Lagrangian multiplier a_k ensures normalization. The result of the variation,

$$\sum_{i=1}^{3M} \sum_{\alpha=1}^3 U_{\alpha,i}^{mw} U_{\alpha,j}^{mw} L_{ki}^{(0)} = a_k L_{kj}^{(0)}, \quad (6)$$

can be written as a matrix eigenvalue equation,

$$\mathbf{M} \tilde{\mathbf{L}}_k = a_k \tilde{\mathbf{L}}_k, \quad (7)$$

where $\tilde{\mathbf{L}}_k$ are the normalized solution vectors fulfilling Eqn. (5). \mathbf{M} is a matrix with elements

$$M_{ji} = \sum_{\alpha=1}^3 U_{\alpha,j}^{mw} U_{\alpha,i}^{mw}$$

and the eigenvalue a_k is proportional to the infrared intensity of the hypothetical normal mode \mathbf{L}_R .

In general, there are three intense modes due to the x -, y - and z -components of the electric dipole moment. These are the so-called 'intensity-carrying' modes, which were found by Torii *et al.*^[25] via an alternative derivation of Eqn. (7). For the intensity-tracking calculations presented in the following for tryptophan, we chose the solution vector with the largest eigenvalue, *i.e.* the largest intensity, as the initial starting distortion.

3. Intensity Tracking in Practice

To illustrate how purpose-driven algorithms such as infrared or resonance Raman intensity tracking selectively lead to a different evolution of the vibrational spectra, we consider tryptophan as a show case since it contains functional groups giving rise to certain high-intensity features in both types of spectra shown in Fig. 1. The DFT calculations presented in the following were performed using the hybrid functional B3LYP^[26] in combination with Ahlrichs' TZVP basis set as implemented in Turbomole.^[27] For the intensity-tracking calculations, a modified version of the program Akira^[20] was applied. It has to be noted that the resonance Raman calculation for tryptophan assumes resonances with the 2^1A state, which is a simplification to the situation in experiment, where the 2^1A and 3^1A bands are overlapping.^[28]

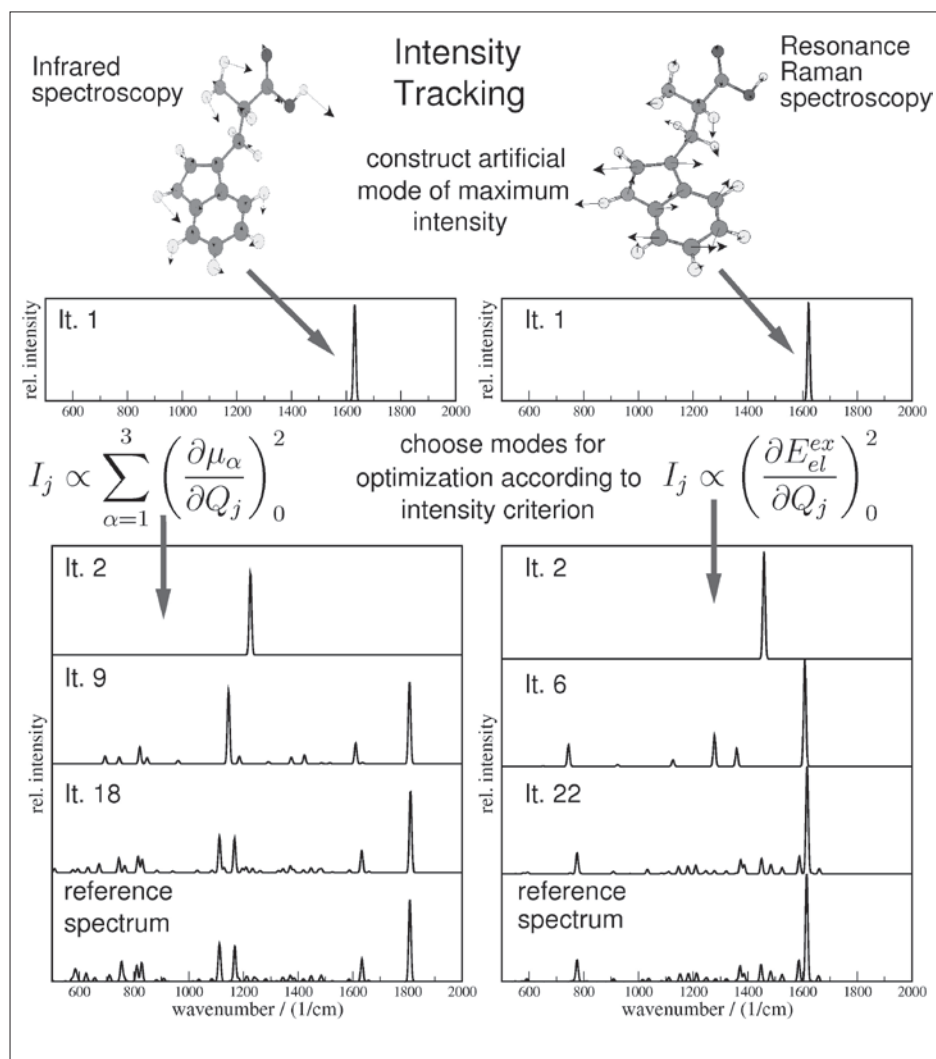


Fig. 1. Intensity tracking for B3LYP/TZVP infrared (left) and Resonance Raman (right) spectra of tryptophan. In the first panel the approximate spectra derived from the starting vectors depicted above are shown. Below the first panel, the intensity expressions according to which the intensities are calculated and intense modes are selected for optimization can be found. The following panels show intermediate spectra of the intensity-tracking calculation and a comparison of the final converged spectrum to the conventionally calculated reference spectrum.

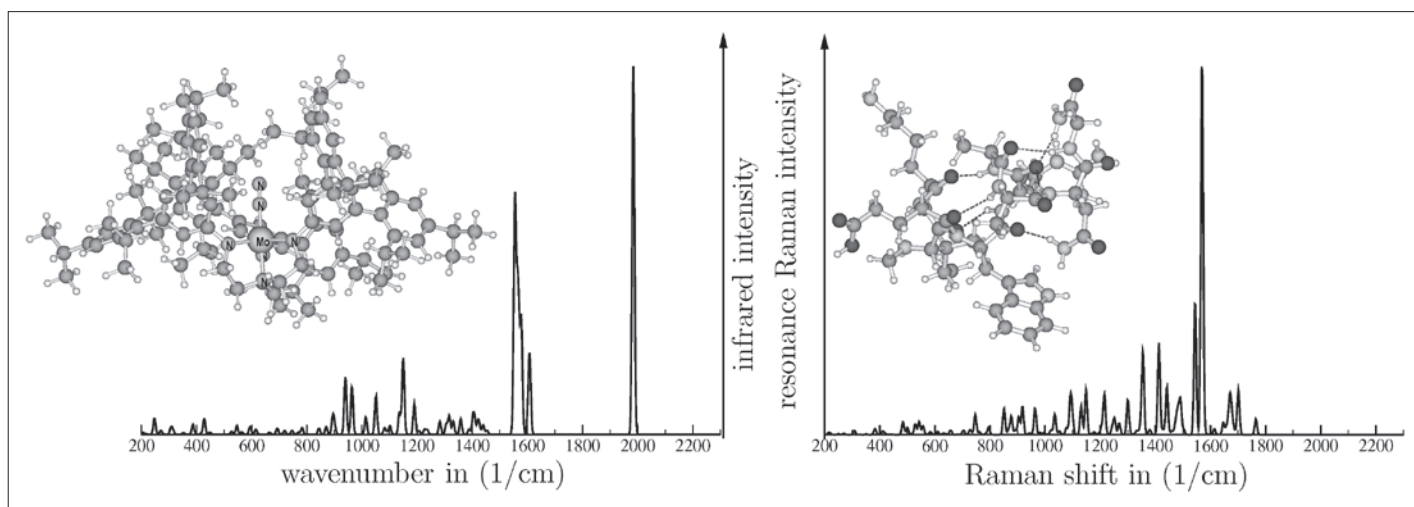


Fig. 2. Examples for the application of intensity tracking to the infrared spectrum of Schrock's dinitrogen molybdenum complex^[23b] and the resonance Raman spectrum of a model of the Im7 protein^[23a].

Fig. 1 shows the starting distortions, several intermediate spectra and the intensity expressions applied for the selection of the modes to be optimized. The first approximation for the infrared and resonance Raman spectra obtained with the starting vector lead to very similar wavenumbers for the intense peaks. A closer inspection of the starting modes reveals, however, that they are entirely different. The infrared starting mode corresponds to a motion delocalized over the whole molecule, whereas strong contributions of the indole moiety can be found in the resonance Raman starting mode.

These different starting vectors and the different infrared and resonance Raman intensity criteria lead to different subsets of modes chosen for optimization, so that different sets of new basis vectors are generated to correct for the errors in the description of the selected modes. Already in the second iteration the peaks observed in the spectra deviate considerably. After a few iterations, the intensity distribution over the wavenumber ranges shown in Fig. 1 is already quite good in comparison to the reference spectra, and the most intense peaks are already at their correct position. By adding further basis vectors, additionally the details which form the fingerprint of the molecule can be reproduced, which can be seen by comparing the converged spectra to the reference spectra. To this end, rather strict criteria for convergence and intensity-selection have to be employed, which lead to convergence after 18 and 22 iterations for infrared and resonance Raman spectra, respectively.

Note that the spectra in intensity-tracking calculations are guaranteed to converge to the conventional spectra if a full set of basis modes is employed, *i.e.* a set of (3M-6) orthogonal vibrational basis vectors in case of non-linear molecules. The efficien-

cy of the algorithm can be measured by the percentage of basis vectors actually needed to converge the spectrum. In general, the efficiency can be expected to be the higher the smaller the number of atoms involved in the intense vibrations compared to the total number of atoms is. Therefore, the small tryptophan molecule presented here is certainly not a perfect example to demonstrate the efficiency, and 60 basis vectors are needed for both types of spectra, which corresponds to 80% of the full basis given by the number of vibrational degrees of freedom.

Intensity tracking should work best for large molecules with a few localized vibrations that determine the spectrum. For example, the resonance Raman spectrum for a rather large model of the E-colicin binding immunity protein Im7^[29] (see Fig. 2), where the excited state considered in resonance is located mainly on the tryptophan residue of Im7, converges using only 44% of the total vibrational basis (see the original work in ref. [23a]). The overall appearance of the Im7-model spectrum and the tryptophan spectrum is very similar, especially in the region between 1350 and 1650 cm^{-1} nearly identical features are displayed, which shows the strongly local character of this spectrum. The frequency shifts of the intense modes are partly due to the fact that for the Im7 model a different density functional, namely BP86,^[4] was employed.

In contrast to this resonance Raman spectrum, which is dominated by one intense peak, IR intensity is usually distributed over a larger number of intense modes which often leads to the necessity to employ more basis vectors in the IR intensity-tracking calculation. In order to reduce the computational effort, a combination of intensity- and mode-based selection criteria has been proven to be useful.^[23b] This

means that the optimization is restricted to those approximate normal modes which are intense *and* involve only (pre-)selected atoms or occur in a chosen wave number range.

An example for an application of a mode-based criterion in addition to the intensity-based one is the intensity-tracking calculation of Schrock's dinitrogen molybdenum complex,^[30] which we investigated in a series of papers on Schrock-type dinitrogen fixation.^[31] In this case, the vibrations belonging to the metal center at which the reactions take place are of interest. As a consequence, an intensity-tracking calculation was performed where only those approximate normal modes were selected which fulfilled the intensity criterion and in which the metal atom and the nitrogen atoms directly bound to it contribute significantly to the approximate normal mode as analyzed in ref. [23b].

The resulting spectrum is shown in Fig. 2, where the intense metal-center involving vibrations can be seen at about 940 cm^{-1} and at 1984 cm^{-1} . The latter vibration is easily recognizable as the dinitrogen-stretching vibration. The calculation terminated with only 126 basis vectors, which corresponds to the evaluation of only 15% of the total number of normal modes.

4. Conclusion

The examples discussed in this article demonstrate that intensity tracking is a smart and versatile method to obtain approximate vibrational spectra. With appropriate starting vectors and intensity criteria, the algorithm may easily be extended to additional vibrational spectroscopic techniques. Still, the results obtained may not be accurate enough, since anharmonic effects or non-Franck-Condon contributions

(in the case of resonance Raman spectra) may play a significant role, which are, however, also neglected in conventional approaches. But a subset of vibrations may offer the possibility to go beyond the standard approximations for a restricted number of degrees of freedom, which would not be feasible for the entire molecule. To study such a more sophisticated treatment for the subset of intense modes obtained *via* intensity tracking will be explored in future work.

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