TDSPEC User Manual

Version 1.0

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1 Introduction

TDSPEC is a program designed to simulate spectra based on vibrational-electronic coupling ("vibronic" coupling) using a set of parameters based on molecular electronic transitions and normal modes. Simulations of spectra based on the time-dependent theory pioneered by Heller *et al.*[1–4] are numerous in the literature, both applying theory at various levels[5–9] and experimentally determined simulation parameters.[10–18] Such simulations are important for correctly describing observations of vibrationally resolved transitions (vibronic shoulders) on absorption spectra, such as those found for rhodamine 6G and tris(2-2' bipyridine)ruthenium(II). Vibronic shoulders may be fit using approximations where multiple Gaussian peaks are used to approximate the bandshape of an electronic transition.[19] A more refined method to simulate absorption bandshapes involves inclusion of the vibrational structure of the absorption band, which may yield a more rigorous analysis of the observed structure.

The benefit of the time-dependent formalism is that spectra for several optical processes are simulated using very similar equations, and thus use the same quantum chemistry calculations to determine all parameters required. As indicated above, the parameters can be derived either from experimental data or from theory. This leads to a very general framework that can be applied in numerous circumstances, and may possibly be extended to various models including solvent effects (either continuum or explicit solvent) and surfaces (like the DIM model).[20] Analysis of observed spectral features is simplified in this model because those features are closely related to parameters used in the simulation.

This package can simulate a variety of spectra. The initial goal of the program was understanding interactions of light with molecules. This naturally led to the implementation of simulations

of one-photon absorbance and resonance Raman scattering.[9,21] Based on the expressions given in Ref. 7, the fluorescence bandshape can now be simulated as well. Growing interest of our research group in nonlinear optical processes has led to the development of a time-dependent vibronic approach for processes such as two-photon absorbance and resonance hyper-Raman scattering.[22–25] Recent developments in the code have enabled the simulation of double-resonance IR-visible sum-frequency generation[26] and also the anti-Stokes versions of resonance Raman and resonance hyper-Raman scattering. A particularly unique feature of TDSPEC is the simulation of spectra including Herzberg-Teller terms (non-Condon effects), allowing studies beyond the Franck-Condon approximation. In particular this has lead to interesting results for the nonlinear optical processes. The model relies on the harmonic oscillator and Born-Oppenheimer approximations in the expressions derived for each technique. These approximations work well for most medium and large molecules, but can be problematic for smaller molecules.

It may seem that the program may be better served as a module in a quantum chemistry program, but the main drawback of that is that it makes the program available only to a small set of users. In that regard, TDSPEC is a standalone program designed to be completely general. Parameters used in the simulations may be taken from any of the quantum chemistry programs that have the capability to do: ground state geometry optimizations, normal mode analysis, and linear response (excitation energies and transition dipole moments). To simulate the two-photon processes, the quantum chemistry program must also be able to calculate single-residues of the quadratic response function (i.e. obtain the two-photon transition moments). TDSPEC reads parameters calculated from a quantum chemistry program, but it is completely determined by the user how those parameters are calculated.

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2   Program Functionality

TDSPEC is currently written in Fortran 90, including several modules and subroutines that will be described in this section. The general features of the program are:

1. One-photon absorbance

2. Resonance Raman scattering (both Stokes and anti-Stokes)

3. Fluorescence

4. Two-photon absorbance

5. Resonance hyper-Raman scattering (both Stokes and anti-Stokes)

6. Double-resonance IR-visible sum-frequency generation

7. Capability to calculate Franck-Condon and Herzberg-Teller terms for each spectrum

8. Overtones/combination bands for both types of Raman scattering

TDSPEC has been tested using ADF,[27–29] Dalton 2.0,[30] and NWChem[31] quantum chemistry programs. As stated in the introduction, the quantum chemistry program used is irrelevant as long as the appropriate level of treating the molecular response to incident radiation is available. Different methodologies of treating the molecular electronic structure may also be employed, as long as it is possible to determine response properties (excitation energies and transition moments).

TDSPEC contains the following programs and subroutines:

1. The main program, *tdspec.f90*, contains the equations required to simulate the different spectra. It is separated into blocks that read the input data, generate the numerical integration

grid, and perform the simulation of the spectrum requested by the user. This manual will describe how to use TDSPEC in a later section to keep the discussion in this section brief.

2. The subroutine, *gauleg.f90*, determines the numerical integration grid based on Gauss-Legendre quadrature.

3. The subroutine, *fcfactor.f90*, evaluates Franck-Condon factors based on a report by Ruhoff and Ratner.[32] Briefly, using the parameters that determine the intensity of each peak on the Raman spectrum, the program calculates Franck-Condon factors with a Poisson distribution. This program calls the routines *nexstate.f90*, *position.f90*, and *fact.f90* to generate all possible fundamentals, overtones, and combination bands up to a given excitation number for the normal modes. Based on a user defined frequency and Franck-Condon factor threshold, this program decides which combination bands are important.

4. Other subroutines handle specifics of simulating different spectra. The files containing related to simulating different spectra are named based on what they simulate.

Future releases of the code will clean up the main program and rewrite the code with more emphasis on easier program maintenance. It is also planned to incorporate Python to make the input file generation more efficient and also make reading the input files much simpler.

3 Running TDSPEC

The TDSPEC program interfaces with two user generated files: an input file and a data file. The input file contains information relevant to what type of spectrum is being simulated. The data file contains all of the parameters for simulating the spectrum. We will describe these files in the sections below. Keywords in each of the types of files will be bold and italicized.

3.1 Input Files

A typical TDSPEC input file might appear as shown in Fig. 1.

Runtype Raman
Freq 601.0
Gamma2 1600.0
Shift 0.0031
Datafile carbazole_tcne.data
Width 20.0
End

Figure 1: A typical TDSPEC input file.

This example illustrates a minimal input file. The options for each keyword in the file are described below:

1. ***Runtype*** - the type of spectrum being plotted. There are eight options for this keyword: Abs (one-photon absorbance), Raman (Stokes resonance Raman scattering), ASRaman (anti-Stokes resonance Raman scattering), Fluor (fluorescence), TwoAbs (two-photon absorbance), HyperRaman (Stokes resonance hyper-Raman scattering), ASHyperRaman (anti-Stokes resonance hyper-Raman scattering), and SFG (double-resonance IR-visible sum-frequency generation, DR-SFG). At minimum, nonlinear optical processes require both a linear response

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(excitation energies and transition dipole moments) and quadratic response (two-photon transition moments) calculation at the ground state optimized geometry. The DR-SFG code only requires linear response calculations, and for many electronic structure theories the transition dipole moment derivatives required for Herzberg-Teller terms can be evaluated at no extra cost after obtaining electron-vibration coupling constants.

2. ***Freq*** - the incident wavelength, in nanometers, shone on the molecule. For the absorbance and fluorescence spectra, this defines the starting point for plotting the spectrum, while for Raman, hyper-Raman, and DR-SFG spectra it defines the incident frequency used in the sum over states expression.

3. ***Gamma2*** - the inhomogeneous broadening parameter in cm^{-1}. This assigns a Gaussian peakshape to the spectrum, which is meant to account for broadening of an absorbance spectrum due to solvent.

4. ***Shift*** - the solvent shift in Hartrees. When an experimental absorbance spectrum is available, this can be used to shift the simulated absorbance spectrum to the appropriate spectral range.

5. ***Datafile*** - the name of the data file. TDSPEC looks in the same directory as the input file for a datafile containing simulation parameters that are molecule specific.

6. ***Width*** - the width of the Lorentzian used for convolution with a Raman stick spectrum, in wavenumbers.

7. ***End*** - defines the end of the input file. This must be the last option in the file.

The keywords described above are those that are required to be present in the input file. Several additional options are present depending on the user's needs. These are detailed below:

8. ***Int*** - for the Raman-type spectra, this determines whether the convolution with a Lorentzian is performed. The options for this keyword are Yes or No. By default, this option is set to No. If the user requests this option, a stick spectrum is printed into the output file.

9. ***HerzTell*** - for any spectrum, this option defines if Herzberg-Teller terms are used in plotting the spectrum requested. The options for this keyword are Yes or No. By default, this option is set to No. This option may be used with with any of the spectral types. It requires that derivatives of the transition dipole moment along each normal mode be calculated.

10. ***IRCoupling*** - for resonance hyper-Raman scattering, this applies an approximation allowing the coupling of ground state dipole moment derivatives to hyper-Raman scattering.[33] The options for this keyword are Yes or No. By default, this option is set to No. At the moment, this is implemented incorrectly by assuming a one-mode approximation, which neglects the sum over normal modes that contributes to the lineshape function.

11. ***Normalize*** - for Raman-type spectra this normalizes the spectrum to the tallest peak. The options for this keyword are Yes or No. By default, this option is set to No.

12. ***FullHerzTell*** - for hyper-Raman spectra, this calculates the full first Herzberg-Teller term as a sum of two B terms. The options for this keyword are Yes or No. By default, this option is set to No. Users requesting this option need to have the derivatives of the two-photon transition moment.

13. ***ATermOff*** - for Raman-type spectra, this causes the program to neglect the Franck-Condon (A term) contribution to the spectrum. The options for this keyword are Yes or No. By default, this option is set to No.

14. ***ExcNum*** - for Raman-type spectra, this allows the calculation of both overtones and combination bands. In principle, this can be set up to an excitation number of 8. Note that setting this larger than 3 for a medium to large molecule may cause a memory bottleneck for the program. By default, the excitation number is set to 1 (fundamentals only). This option can be used with both Franck-Condon and Herzberg-Teller terms.

15. ***FCScreen*** - determines the minimum value of Franck-Condon factors that defines whether a combination band is to be plotted. This is set to 0.0001 by default. Testing of this value has determined that the default yields the most important combination bands. Setting this screening to 1.0 will result in no combination bands being plotted.

16. ***FrqScreen*** - determines the maximum wavenumber shift that defines whether a combination band is to be plotted. This is set to 8000 cm^{-1} by default. For most molecules this value is adequate, unless one is concerned about higher wavenumber modes. Setting this screening to 0 cm^{-1} will result in no combination bands being plotted.

17. ***TStop*** - this is the stopping point for the numerical integration. The default value is 0.300 a.u. which may be set higher if a large spectral (wavelength) range is desired for the absorbance spectrum.

18. ***TStep*** - this is the number of steps in the numerical integration range (basically, the fineness of the integration grid). The default value is 500. It may be necessary to set this to a larger value to remove baseline oscillations in an absorbance spectrum.

19. ***NABSpts*** - number of frequencies used to plot the one- or two-photon absorbance spectrum. By default this is set to 10000. Integration is started at the incident frequency (defined by

Freq) and ending at a frequency 20000 cm^{-1} higher. Setting this to a larger value is required if a large wavelength range is needed on an absorbance spectrum.

20. **HTInts** - integrals involved in Herzberg-Teller terms are printed out if this option is activated (more for code testing and understanding). This will generate a lot of output because Herzberg-Teller term integrals are normal mode dependent.

21. **Fluorstate** - set the excited state fluorescence originates from.

22. **HTPref** - calculate the prefactors involved in Herzberg-Teller terms.

23. **RamanPts** - set the number of points used in the convolution of Raman-type spectra with Lorentzian lineshape. The default is 2000.

24. **FrqCut** - cutoff value for the largest frequency used to determine the vibrational contribution to the Stokes shift in fluorescence. This is set at $k_b T = 417$ cm^{-1} (for $T = 300$ K) by default.

25. **StokesSolv** - solvent contribution to the Stokes shift in fluorescence. This is set at 400 cm^{-1} by default.

26. **VOverlap** - calculate the vibrational contribution to the lineshape function, assuming that the detuning effect is set to unity (more for code testing and understanding). This also ignores the prefactors.

27. **RHRSB2** - for resonance hyper-Raman scattering, calculate the B$_2$ term without the B$_1$ term when Herzberg-Teller terms are included. The options for this keyword are Yes or No.

28. **Polarization** - for double-resonance IR-visible sum-frequency generation, the orientational averaging is based on the polarization of the incident radiation (both IR and visible lasers)

and the emitted radiation. Values for the polarization range from 1-7, where the sum-frequency, visible, and IR field polarizations are:

- 1 - ppp (measure of $\chi^{(2)}_{zzz}$)

- 2 - pss (measure of $\chi^{(2)}_{zxx}$)

- 3 - sps (measure of $\chi^{(2)}_{xzx}$)

- 4 - ssp (measure of $\chi^{(2)}_{xxz}$)

- 5 - ssp (measure of $\chi^{(2)}_{xyz}$)

- 6 - sps (measure of $\chi^{(2)}_{xzy}$)

- 7 - pss (measure of $\chi^{(2)}_{zxy}$)

29. **Angles** - for double-resonance IR-visible sum-frequency generation, read in ϕ and θ, which are the Euler angles for orientational averaging. These are important for determining the molecular orientation on a surface.

30. **Temp** - temperature used for the simulation. If not defined by the user, the program defaults to 300 K. This option is mainly useful when used in conjunction with solvent models II and III (described below).

31. **SolvMod** - defines the "solvent" model used. The following options may be used:

   I. *Simple* - The homogeneous broadening is Lorentzian and the inhomogeneous broadening is Gaussian, giving a Voigt profile. This is the default.

   II. *HighTemp* - High temperature limit of the overdamped Brownian oscillator model.

III. *GenTemp* - General temperature limit of the overdamped Brownian oscillator model. This is an expert option.

Unless the user requires a specific functionality, most of the keywords are unnecessary to specify. For example, if the user requires only Franck-Condon terms, the keywords specified in the sample input (Fig. 1) would be all that is required. Specification of keywords must be done in a fashion where the **End** keyword comes at the end of the input file.

One other point that is worth mentioning is that it is possible to plot only overtones and completely neglect combination bands. This may be accomplished by setting **FCScreen** to a very large screening value of 1.0 or by defining **FrqScreen** as a very small frequency of $0.0 \, \text{cm}^{-1}$. Not choosing these parameters with some caution may result in segmentation faults due to the large amount of data from the numerous combination bands that may satisfy a given criterion.

3.2   Data Files

This section details the contents of the data file. An abbreviated TDSPEC data file is shown in Fig. 2. The data file contains all of the remaining simulation parameters that were not defined in the input file. Keywords that are present in the data file are as follows:

1. **NEXCI** - number of excited states used in the simulation, defined by the value given for this keyword. A data file must contain at least one excited state, but the example in Fig. 2 illustrates how to incorporate multiple excited states.

2. **Excitation** - the number of the excited state.

3. **Energy** - the excitation energy in Hartrees for the excited state.

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4. **Gamma** - the homogeneous broadening parameter (also referred to as a lifetime or damping parameter) in cm^{-1}.

5. **Tdip** - the transition dipole moment in a.u. $(e \cdot a_0)$. This should be ordered as a list of the three components of the transition dipole moment: (x, y, z).

6. **Frequencies** - number of frequencies used in the simulation.

```
NEXCI 2
Excitation 1
Energy 0.065473283
Gamma 300
Tdip 0.30160 -0.60296 -0.30556
Frequencies 70
   154.08    1.05
   159.78   -2.77
   215.25    0.78
   252.10    0.12
      ⋮        ⋮
  2287.67    0.33
  2290.71    0.29
  2293.91    0.06
  2313.33    0.00
End
Excitation 2
Energy 0.072345525
Gamma 250
Tdip -0.31443 0.62123 0.36182
Frequencies 70
   154.08    1.01
   159.78   -3.00
   215.25   -0.85
   252.10    0.00
      ⋮        ⋮
  2287.67    0.33
  2290.71    0.30
  2293.91    0.07
  2313.33    0.01
End
```

Figure 2: A typical TDSPEC data file including everything required to simulate a one-photon absorbance or resonance Raman spectrum in the Franck-Condon approximation.

7. ***End*** - defines the end of the list of data for the excited state. The program either stops reading data at this point or if ***NEXCI*** is greater than 1, the program reads data from each excited state up to the given value of ***NEXCI***.

The data after the ***Frequencies*** keyword are the normal mode frequencies and dimensionless displacements. Additional data may be presented in the input file that is relevant to simulating Herzberg-Teller terms and two-photon properties. Inclusion of the keyword ***Stpm*** with the 6 components of the two-photon transition moment tensor (S_{xx}, S_{yy}, S_{zz}, S_{xy}, S_{xz}, S_{yz}) allows the simulation of the two-photon absorbance and resonance hyper-Raman scattering. If requested (setting the ***HerzTell*** or ***FullHerzTell*** keywords to Yes in the input file), TDSPEC will read in derivatives of the transition dipole moment and two-photon transition moment when appropriate. Shown in Fig. 3 is a portion of an input file containing those derivatives.

As shown in Fig. 3, additional columns of data must be present for each normal mode to calculate Herzberg-Teller terms. The third through fifth columns contain derivatives of the transition dipole moment, while the sixth through eleventh columns contain the derivatives of the two-photon moment. Specifically, the order of the derivatives of the transition dipole moment are listed as: $\left(\frac{\partial \mu_x}{\partial Q_a}, \frac{\partial \mu_y}{\partial Q_a}, \frac{\partial \mu_z}{\partial Q_a} \right)$. If the Herzberg-Teller term for two-photon absorbance or full Herzberg-Teller term for resonance hyper-Raman is requested, the order of the derivatives of the two-photon transition moment is: $\left(\frac{\partial S_{xx}}{\partial Q_a}, \frac{\partial S_{yy}}{\partial Q_a}, \frac{\partial S_{zz}}{\partial Q_a}, \frac{\partial S_{xy}}{\partial Q_a}, \frac{\partial S_{xz}}{\partial Q_a}, \frac{\partial S_{yz}}{\partial Q_a} \right)$. In either case, the derivative is taken with respect to the particular normal mode Q_a.

3.3   Input/Data Files for other solvent models

For a detailed description of the overdamped Brownian oscillator model, the user is directed to

```
NEXCI 1
Excitation 1
Energy 0.16124207
Gamma 400.0
Tdip 0.00000 0.00000 1.92336
 Stpm -0.9618 -4.6094 98.1899 0.0000 0.0000 0.0000
Frequencies 29
   415.60   0.00  0.00   0.00   0.00   0.00   0.00   0.00  -0.15   0.00   0.00
   425.97   0.00  0.00   0.00   0.00   0.00   0.00   0.00  -0.19   0.00   0.00
   496.92   0.00  0.04   0.00   0.00   0.00   0.00   0.00   0.00  -1.05   0.00
   530.14   0.00  0.00   0.11   0.00   0.00   0.00   0.00   0.00   0.00   0.97
   630.28  -0.04  0.00   0.00  -0.03   0.04   0.04  -3.05   0.00   0.00   0.00

     ⋮       ⋮     ⋮      ⋮      ⋮      ⋮      ⋮      ⋮      ⋮      ⋮      ⋮
  1504.95   0.25  0.00   0.00   0.16  -1.05   0.31   1.45   0.00   0.00   0.00
  1567.33   0.00  0.00  -0.31   0.00   0.00   0.00   0.00   0.00   0.00  -0.12
  1593.08  -0.18  0.00   0.00   0.13   0.22  -0.37   3.16   0.00   0.00   0.00
  1620.48   0.00  0.00   0.55   0.00   0.00   0.00   0.00   0.00   0.00   3.33
  1632.29   0.48  0.00   0.00   0.35   0.11  -0.03 -12.36   0.00   0.00   0.00
End
```

Figure 3: A typical TDSPEC data file, including data required to simulate any type of spectrum at the Franck-Condon and Herzberg-Teller level of theory. Parts of the data file specific to two-photon absorbance and resonance hyper-Raman scattering (Stokes and anti-Stokes) are hilighted in gray.

Ref. 34.

3.3.1   High Temperature Limit of the Overdamped Brownian Oscillator

In Figs. 4 and 5, the modifications to input and data files required to use the overdamped Brownian oscillator model in the high temperature limit are highlighted. When this model is used, TDSPEC will also output the solvent contribution to the reorganization energy. This is not possible with the simple model.

```
Runtype HyperRaman
Freq 644.0
Gamma2 0.0
Shift 0.0250
Datafile PNAlcpbedeltas.data
Width 20.0
SolvMod HighTemp
End
```

Figure 4: A typical TDSPEC input file using the *HighTemp* solvent model.

```
NEXCI 1
Excitation 1
Energy 0.16124207
Gamma 1400.0
Kappa 0.10
Tdip 0.00000 0.00000 1.92336
Frequencies 29
  415.60   0.00   0.00   0.00   0.00
  425.97   0.00   0.00   0.00   0.00
  496.92   0.00   0.04   0.00   0.00
  530.14   0.00   0.00   0.11   0.00
  630.28  -0.04   0.00   0.00  -0.03
     ⋮      ⋮      ⋮      ⋮      ⋮
 1504.95   0.25   0.00   0.00   0.16
 1567.33   0.00   0.00  -0.31   0.00
 1593.08  -0.18   0.00   0.00   0.13
 1620.48   0.00   0.00   0.55   0.00
 1632.29   0.48   0.00   0.00   0.35
End
```

Figure 5: A typical TDSPEC data file, including data required to simulate linear optical processes at the Franck-Condon and Herzberg-Teller level of theory with the *HighTemp* solvent model.

3.3.2 General Temperature Limit of the Overdamped Brownian Oscillator

In Figs. 6 and 7, the modifications to input and data files required to use the overdamped Brownian oscillator model in the general temperature limit are highlighted. When this model is used, TDSPEC will also output the solvent contribution to the reorganization energy. This is not possible with the simple model.

```
Runtype HyperRaman
Freq 644.0
Gamma2 0.0
Shift 0.0250
Datafile PNAlcpbedeltas.data
Width 20.0
SolvMod GenTemp
End
```

Figure 6: A typical TDSPEC input file using the *GenTemp* solvent model.

```
NEXCI 1
Excitation 1
Energy 0.16124207
Gamma 1400.0
Kappa 0.10
OmegaBath 200.0
DeltaBath 1.0
Tdip 0.00000 0.00000 1.92336
Frequencies 29
   415.60    0.00   0.00    0.00    0.00
   425.97    0.00   0.00    0.00    0.00
   496.92    0.00   0.04    0.00    0.00
   530.14    0.00   0.00    0.11    0.00
   630.28   -0.04   0.00    0.00   -0.03
       ⋮        ⋮      ⋮       ⋮       ⋮
  1504.95    0.25   0.00    0.00    0.16
  1567.33    0.00   0.00   -0.31    0.00
  1593.08   -0.18   0.00    0.00    0.13
  1620.48    0.00   0.00    0.55    0.00
  1632.29    0.48   0.00    0.00    0.35
End
```

Figure 7: A typical TDSPEC data file, including data required to simulate linear optical processes at the Franck-Condon and Herzberg-Teller level of theory with the *GenTemp* solvent model.

4 Time-Dependent Theory

4.1 Calculating Dimensionless Displacements

Dimensionless displacements are related to the gradient of the excited state along normal mode Q_a. In this section, the normal mode in mass-weighted units is written as Q_a while it is written as q_a if it is written in terms of normal (dimensionless) coordinates. Based on approximations where the ground and excited state potential energy surfaces are harmonic and that there is no change in the normal mode frequencies when the ground and excited state are compared (i.e. no Duschinsky rotations), the dimensionless displacement is calculated as

$$V_{q_a} = \left(\frac{\partial E^n}{\partial q_a} \right)_{q_a=0} = -\omega_{a0}\Delta_a^n \tag{1}$$

where ω_{a0} is the normal mode frequency and Δ_a^n is the dimensionless displacement of mode q_a for the nth excited state. In general it is simpler to evaluate the gradient with respect to Q_a more directly. This circumstance requires an additional step,[35]

$$\frac{\partial E^n}{\partial q_a} = \left(\frac{dQ_a}{dq_a} \right) \frac{\partial E^n}{\partial Q_a} = \sqrt{\frac{\hbar}{2\pi c \nu_{a0}}} \frac{\partial E^n}{\partial Q_a} = \sqrt{\frac{\hbar}{2\pi c \nu_{a0}}} V_{Q_a} \tag{2}$$

The only variability in this expression is how the excited state gradient in terms of mass-weighted coordinates V_{Q_a} is evaluated. Some authors evaluate this gradient numerically[9] while others have demonstrated the use of analytical geometry optimizations of the excited state.[8] Both methods will be outlined below

4.1.1 Numerical Excited State Energy Gradients

The numerical evaluation of excited state energy gradients revolves around calculating the linear response of a molecule up to a particular excitation. For any molecule, there are $3N - 5$ or $3N - 6$ (N is the number of atoms) normal modes. Performing a numerical evaluation of the excited state energy gradient requires either $6N - 10$ or $6N - 12$ calculations, because a step in the plus and minus direction along every normal mode is required. This can be reduced significantly by focusing on a portion of the normal modes in a wavenumber region.

For numerical evaluation of the excited state gradients, formulas analogous to those discussed by Reiher *et al.*[36] for the derivatives of the polarizability along normal mode Q_a are used, substituting the excitation energy in place of the polarizability. These derivatives are expressed using a three-point central differences formula as:

$$\left(\frac{\partial E^n}{\partial Q_a}\right)_{Q_a=0} = \frac{E^n(\mathbf{R}_{eq} + s_R\mathbf{R}_a) - E^n(\mathbf{R}_{eq} - s_R\mathbf{R}_a)}{2s_{Q_a}|\mathbf{Q}_a^{norm}|} \tag{3}$$

In Eq. 3, $\mathbf{R}_{eq}$ is a vector of the optimized coordinates of the molecule's ground state, $\mathbf{R}_a$ is the Cartesian normal mode vector, s_R is the Cartesian step size (typically 0.01 is used), and $|\mathbf{Q}_a^{norm}|$ is the norm of the normalized mass-weighted normal mode vector. The latter quantity is used to give the equation appropriate dimensions, but is clearly equal to one. In this expression, s_{Q_a} is

$$s_{Q_a} = \frac{s_R}{|\mathbf{R}_a|} = s_R \left[\sum_{i=1}^{3N} \frac{(Q_{a,i}^{norm})^2}{m_j}\right]^{-1/2} \qquad j = ceil(i/3) \tag{4}$$

Either the middle expression or the right side expression may be used to find s_{Q_a}. If the right side is used, the norm of the mass-weighted normal mode vector is found to obtain the normalized

components of that vector ($Q_{a,i}^{norm}$), and then the mass of the jth atom is divided into that component. The notation "$ceil(i/3)$" indicates that non-integer values are rounded up.

4.1.2 Analytical Excited State Energy Gradients

If analytical geometry optimizations are available in a quantum chemistry program, a significant advantage can be used in calculating the dimensionless displacements. In the numerical method described above, the majority of the time spent involves the $6N - 10$ or $6N - 12$ calculations to obtain all of the simulation parameters. In general, for all but the smallest molecules, collection of that data requires weeks worth of CPU and wall time. Analytical gradients of the excited state energy, which come from performing an analytical excited state geometry optimization, are used to determine the dimensionless displacements and require 1 calculation. A side by side comparison of the numerical and analytical method shows that if you account for the redundant calculations (the ground state geometry optimization and normal mode analysis), with the analytical method a significant reduction in both CPU and wall time is observed. This does not mean that the numerical method is obsolete, because it is currently employed to evaluate property derivatives for Herzberg-Teller terms.

This section employs the review of spectroscopic simulation methods by Neese *et al.*,[8] and specifically focusing on pp. $318 - 320$ in that article. The analytical method involves two different techniques: analytical excited state geometry optimization (method I) and analytical excited state gradients at the ground state equilibrium position (method II). We will briefly examine both methods.

In method I, the dimensionless displacement is calculated by projecting the mass-weighted difference in Cartesian coordinates between the excited state and ground state equilibrium geome-

tries onto the normal modes. This is expressed mathematically in terms of the mass-weighted displacement Δ_{Q_a}

$$\Delta_{Q_a} = \sum_i L_{ia} D_i^{(m)} \tag{5}$$

where L_{ia} are components of the normal mode vector for q_a and $D_i^{(m)}$ is a vector containing the mass-weighted difference in Cartesian coordinates between the ground state and excited state optimized coordinates. Applying dimensional analysis, the units of Δ_{Q_a} are $\sqrt{mass \cdot length}$, so the dimensionless displacement is obtained as

$$\Delta_a = \sqrt{\frac{\omega_a}{\hbar}} \Delta_{Q_a} \tag{6}$$

where $\omega_a = 2\pi c \tilde{v}_{a0}$.

For method II, the dimensionless displacement is calculated by projecting the gradient of the excited state energy at the ground state equilibrium position onto the normal modes. This method is written as

$$V_{Q_a} = \sum_i \frac{1}{\sqrt{m_i}} V_{X,i} L_{ia} \tag{7}$$

where m_i is the mass of the atom corresponding to component i and $V_{X,i}$ is the Cartesian excited state energy gradient at the ground state equilibrium position. This is obtained from the first cycle of the excited state geometry optimization, assuming that the ground state equilibrium geometry is the starting point of that optimization. From the gradient V_{Q_a}, the dimensionless displacement is calculated from Eq. 1.

4.2 Spectral Simulations

Simulations of different spectra require a variety of different molecule-dependent properties. Each spectral type is related by employing the Born-Oppenheimer approximation and harmonic oscillator model via the time-dependent wavepacket approach. Some understanding of the underlying processes is assumed in the descriptions. Each of the following sections describes the required properties, units in the output file, and expressions for the simulated properties in the Franck-Condon approximation. For more thorough discussion of these expressions, see Ref. 24.

4.2.1 One-Photon Absorbance

Required Properties

1. The molecular normal modes and vibrational frequencies.

2. Electron-vibrational coupling constants (dimensionless displacements, or deltas).

3. Excitation energies.

4. Transition dipole moment at the ground state equilibrium geometry.

5. (For Herzberg-Teller Terms) Derivatives of the transition dipole moment along each normal mode at the ground state equilibrium geometry.

The absorbance spectrum of a molecule is output with the x-axis as energy in wavenumbers (cm^{-1}) and the y-axis in absorbance cross section, σ_{OPA}, in $Å^2$/molecule. By applying the Beer-Lambert law, the absorbance cross section may be converted to molar absorptivity:

$$\varepsilon = \frac{1}{ln(10)}\left(1 \times 10^{-19}\frac{L}{cm \cdot Å^2}\right)N_A\sigma_{OPA} = \left(26153.21\frac{L}{cm \cdot mol \cdot Å^2}\right)\sigma_{OPA} \tag{8}$$

where N_A is Avogadro's number.

The expression for σ_{OPA} in the Franck-Condon approximation is:

$$\sigma_{OPA}^{FC}(\omega) = \frac{4\pi\omega}{3c} \sum_j (M_{0j})^2 Re \int_0^\infty \langle I_0 | I_j(t) \rangle e^{i(\varepsilon_{I_0} + \omega)t - \Gamma_j t} dt \tag{9}$$

In this expression, ω is the incident frequency, $(M_{0j})^2$ is the transition strength, ε_{I_0} is the sum of the zero-point energies of every harmonic oscillator in the system, Γ_j is the homogeneous broadening parameter, and $\langle I_0 | I_j(t) \rangle$ is the nuclear overlap integral of the initial vibrational state $|I_0\rangle$ and the Gaussian wavepacket $|I_j(t)\rangle = e^{\frac{-i\hat{H}_j t}{\hbar}} |I_0\rangle$. The summation in the expression goes over all electronic excited states. The transition strength is defined: $(M_{0j})^2 = |(\mu_x^{0j})^{eq}|^2 + |(\mu_y^{0j})^{eq}|^2 + |(\mu_z^{0j})^{eq}|^2$, where the $(\mu_i^{0j})^{eq}$ are transition dipole moment components.

4.2.2 Fluorescence

Required Properties

1. The molecular normal modes and vibrational frequencies.

2. Electron-vibrational coupling constants (dimensionless displacements, or deltas).

3. Excitation energies.

4. Transition dipole moment at the ground state equilibrium geometry.

5. (For Herzberg-Teller Terms) Derivatives of the transition dipole moment along each normal mode at the ground state equilibrium geometry (not yet implemented).

The fluorescence spectrum of a molecule is output with the x-axis as energy in wavenumbers (cm^{-1}) and the y-axis in differential fluorescence rate, $\frac{dk}{dE}$, in s^{-1} eV^{-1}. It is highly unusual for an

experimental spectrum to have units on the y-axis (usually the shape of the band is studied), and thus it is difficult to estimate the correct order of magnitude of this quantity. We will hopefully be able to integrate this quantity and yield meaningful fluorescence emission rates.

The expression for $\frac{dk}{dE}$ in the Franck-Condon approximation is:

$$\left(\frac{dk}{dE}\right)^{FC} = \frac{4\omega_R^3}{3\pi\hbar^2 c^3 e^2}(M_{0j})^2 Re \int_0^\infty \langle I_0|I_j(t)\rangle e^{i(\varepsilon_{I_0}-\omega_R)t - \Gamma_j t} dt \tag{10}$$

In this expression, ω_R is the emitted frequency, $(M_{0j})^2$ is the transition strength, ε_{I_0} is the sum of the zero-point energies of every harmonic oscillator in the system, Γ_j is the homogeneous broadening parameter, and $\langle I_0|I_j(t)\rangle$ is the nuclear overlap integral of the initial vibrational state $|I_0\rangle$ and the Gaussian wavepacket $|I_j(t)\rangle = e^{\frac{-i\hat{H}_j t}{\hbar}}|I_0\rangle$. Here only a particular excited state is studied and therefore there is no summation. The transition strength is defined: $(M_{0j})^2 = |(\mu_x^{0j})^{eq}|^2 + |(\mu_y^{0j})^{eq}|^2 + |(\mu_z^{0j})^{eq}|^2$, where the $(\mu_i^{0j})^{eq}$ are transition dipole moment components.

4.2.3 Resonance Raman Scattering

Required Properties

1. The molecular normal modes and vibrational frequencies.

2. Electron-vibrational coupling constants (dimensionless displacements, or deltas).

3. Excitation energies.

4. Transition dipole moment at the ground state equilibrium geometry.

5. (For Herzberg-Teller Terms) Derivatives of the transition dipole moment along each normal mode at the ground state equilibrium geometry.

Resonance Raman spectra are plotted where the x-axis is in wavenumber (or wavenumber shift) in cm^{-1} and the y-axis is the differential Raman scattering cross section, $\frac{d\sigma}{d\Omega}$, in units of cm^2/sr. Most A term scatterers have $\frac{d\sigma}{d\Omega}$ on the order of 10^{-28} cm^2/sr or larger for resonance Raman scattering. These units are identical regardless of whether Stokes or anti-Stokes scattering is simulated.

In resonance Raman scattering, the differential Raman scattering cross section is related to the molecular transition polarizability as: $\frac{d\sigma}{d\Omega} \propto |\alpha|^2$. The expression for a particular component of the molecular transition polarizability, $\alpha_{\alpha\beta}^A$, in the Franck-Condon approximation is (Stokes scattering):

$$\alpha_{\alpha\beta}^A = \sum_j (\mu_\alpha^{0j})^{eq}(\mu_\beta^{j0})^{eq} i \int_0^\infty dt \langle F_0|I_j(t)\rangle e^{i(\varepsilon_{I_0}+\omega)t - \Gamma_j t} \tag{11}$$

In this expression, ω is the incident frequency, $(\mu_\alpha^{0j})^{eq}$ is the transition dipole moment at the ground state equilibrium geometry for excitation to electronic excited state $|j\rangle$, ε_{I_0} is the sum of the zero-point energies of every harmonic oscillator in the system, Γ_j is the homogeneous broadening parameter, and $\langle F_0|I_j(t)\rangle$ is the nuclear overlap integral of the final vibrational state $|F_0\rangle$ and the Gaussian wavepacket $|I_j(t)\rangle = e^{\frac{-i\hat{H}_j t}{\hbar}}|I_0\rangle$. For anti-Stokes resonance Raman scattering, Eq. 11 in modified by accounting for starting in an excited vibrational state by changing the vibrational overlap integral and changing ε_{I_0} to ε_{I_n}, where the n refers to the mode in its vibrational excited state.

4.2.4 Two-Photon Absorbance

> **Required Properties**
>
> 1. The molecular normal modes and vibrational frequencies.
>
> 2. Electron-vibrational coupling constants (dimensionless displacements, or deltas).
>
> 3. Excitation energies.
>
> 4. Two-photon transition moment at the ground state equilibrium geometry.
>
> 5. (For Herzberg-Teller Terms) Derivatives of the two-photon transition moment along each normal mode at the ground state equilibrium geometry.

The two-photon absorbance spectrum is output with the x-axis as energy in wavenumbers (cm^{-1}) and the y-axis in two-photon absorbance cross section, σ_{TPA}, in cm^4 s/photon. It is sometimes convenient due to the small magnitude of the two-photon absorbance cross section to write the y-axis in terms of Goeppert-Mayer (GM) units, where 1 GM = 1×10^{-50} cm^4 s/photon.

The expression for σ_{TPA} in the Franck-Condon approximation is:

$$\sigma_{TPA}^{FC}(\omega) = \frac{4\pi^3\alpha^2\omega^2\hbar^3}{e^4}\sum_k \delta_{TPA}^{0k} Re \int_0^\infty \langle I_0|I_k(t)\rangle e^{i(\varepsilon_{I_0}+2\omega)t-\Gamma_k t}dt \tag{12}$$

In this expression, 2ω accounts for having two the incident photons, δ_{TPA}^{0k} is the two-photon transition strength, ε_{I_0} is the sum of the zero-point energies of every harmonic oscillator in the system, Γ_k is the homogeneous broadening parameter, and $\langle I_0|I_k(t)\rangle$ is the nuclear overlap integral of the initial vibrational state $|I_0\rangle$ and the Gaussian wavepacket $|I_k(t)\rangle = e^{\frac{-i\hat{H}_k t}{\hbar}}|I_0\rangle$. The summation in the expression goes over all electronic excited states. The two-photon transition strength is defined:

$$\delta_{TPA}^{0k} = 2\sum_{\alpha,\beta} \frac{1}{30} \left[(S_{\alpha\alpha}^{0k})^{eq}(S_{\beta\beta}^{k0})^{eq} + (S_{\alpha\beta}^{0k})^{eq}(S_{\beta\alpha}^{k0})^{eq} + (S_{\alpha\beta}^{0k})^{eq}(S_{\alpha\beta}^{k0})^{eq} \right] \tag{13}$$

$$= 2\delta_F^{0k} + 2\delta_G^{0k} + 2\delta_H^{0k}$$

where the two-photon transition moments, $S_{\alpha\beta}^{0k}$, are given by the expression

$$S_{\beta\gamma}^{k0} = \sum_l \left\{ \frac{\mu_\beta^{kl}\mu_\gamma^{l0} + \mu_\gamma^{kl}\mu_\beta^{l0}}{(E_l - E_0 - \omega)} \right\} \tag{14}$$

The excitation goes through an intermediate electronic state $|l\rangle$, which is not an electronic excited state of the molecule.

4.2.5 Resonance Hyper-Raman Scattering

Required Properties

1. The molecular normal modes and vibrational frequencies.

2. Electron-vibrational coupling constants (dimensionless displacements, or deltas).

3. Excitation energies.

4. Transition dipole moment at the ground state equilibrium geometry.

5. Two-photon transition moment at the ground state equilibrium geometry.

6. (For Herzberg-Teller Terms) Derivatives of the transition dipole moment along each normal mode at the ground state equilibrium geometry.

7. (For Herzberg-Teller Terms) Derivatives of the two-photon transition moment at the ground state equilibrium geometry.

Resonance hyper-Raman spectra are plotted where the x-axis is in wavenumber (or wavenumber shift) in cm^{-1} and the y-axis is the differential hyper-Raman scattering cross section, $\frac{d\sigma}{d\Omega}$, in units of cm^4 s $photon^{-1}$ sr^{-1}. Most A term scatterers have $\frac{d\sigma}{d\Omega}$ on the order of 10^{-60} cm^4 s $photon^{-1}$ sr^{-1} or larger for resonance hyper-Raman scattering. These units are identical regardless of whether Stokes or anti-Stokes scattering is simulated.

In resonance hyper-Raman scattering, the differential hyper-Raman scattering cross section is related to the molecular transition hyperpolarizability as: $\frac{d\sigma}{d\Omega} \propto |\beta|^2$. The expression for a particular component of the molecular transition polarizability, $\beta^A_{\alpha\beta\gamma}$, in the Franck-Condon approximation is (Stokes scattering):

$$\beta^A_{\alpha\beta\gamma} = \sum_k (\mu^{0k}_\alpha)^{eq} (S^{k0}_{\beta\gamma})^{eq} i \int_0^\infty dt \langle F_0 | I_k(t) \rangle e^{i(\varepsilon_{I_0} + 2\omega)t - \Gamma_k t} \tag{15}$$

In this expression, ω is the incident frequency, $(\mu^{0k}_\alpha)^{eq}$ and $(S^{0k}_{\alpha\beta})^{eq}$ are the transition dipole moment and two-photon transition moment, respectively, at the ground state equilibrium geometry for excitation to electronic excited state $|k\rangle$, ε_{I_0} is the sum of the zero-point energies of every harmonic oscillator in the system, Γ_k is the homogeneous broadening parameter, and $\langle F_0 | I_k(t) \rangle$ is the nuclear overlap integral of the final vibrational state $|F_0\rangle$ and the Gaussian wavepacket $|I_j(t)\rangle = e^{\frac{-i\hat{H}_k t}{\hbar}} |I_0\rangle$. For anti-Stokes resonance Raman scattering, Eq. 15 in modified by accounting for starting in an excited vibrational state by changing the vibrational overlap integral and changing ε_{I_0} to ε_{I_n}, where the n refers to the mode in its vibrational excited state.

4.2.6 Double-Resonance Sum-Frequency Generation

Required Properties

1. The molecular normal modes and vibrational frequencies.

2. Electron-vibrational coupling constants (dimensionless displacements, or deltas).

3. Excitation energies.

4. Transition dipole moment at the ground state equilibrium geometry.

5. Derivatives of the ground state dipole moment along each normal mode at the ground state equilibrium geometry.

6. (For Herzberg-Teller Terms) Derivatives of the transition dipole moment along each normal mode at the ground state equilibrium geometry.

Double-resonance IR-visible sum-frequency generation spectra are plotted where the x-axis is in wavenumber (or wavenumber shift) in cm^{-1} and the y-axis is the squared molecular first hyperpolarizability, $|\beta_{ijk}|^2$, in units of $\text{m}^8 \text{ V}^{-2}$ (so-called alternative SI units).[37] If the number density N of emitters present on the surface is known, one can directly convert the y-axis to the squared first nonlinear susceptibility, $|\chi_{ijk}^{(2)}|^2 = N^2 |\beta_{ijk}|^2$. An order of magnitude for the number density is $\sim 10^{17}$ molecules m^{-2}.[26] For the fluorescent dye rhodamine 6G, the calculated value of $|\chi^{(2)}|^2$ is $\sim 10^{-41} \text{ m}^4 \text{ V}^{-2}$.

This process is a surface sensitive technique, capable of resolving the orientation of the molecule on the surface. From the theoretical standpoint, this method is easier to investigate than resonance hyper-Raman scattering, even though both are nonlinear optical processes. The reason for this observation is that double-resonance sum-frequency generation only requires linear response equations to be solved, because one of the transitions is an IR transition in the manifold of the ground state. Double-resonance sum-frequency generation is related to the square of the molecular transition hyperpolarizability, $|\beta_{\alpha\beta\gamma}^A|^2$, where the hyperpolarizability is calculated as

$$\beta_{\alpha\beta\gamma}^A = \sum_j \sqrt{\frac{\hbar}{2\omega_a}} \frac{(\mu_\alpha^{00})^{a'}}{-i\Gamma_a} (\mu_\beta^{0j})^{eq} (\mu_\gamma^{j0})^{eq} i \int_0^\infty dt \langle F_0 | I_j(t) \rangle e^{i(\varepsilon_{I_0} + \omega_a + \omega)t - \Gamma_j t} \tag{16}$$

In this expression, ω is the incident frequency for the visible laser, ω_a is the incident frequency for the IR laser $(\mu_\alpha^{00})^{a'}$ is the derivative of the ground state dipole moment along normal mode Q_a, $(\mu_\beta^{0j})^{eq}$ and $(\mu_\gamma^{j0})^{eq}$ are the transition dipole moments at the ground state equilibrium geometry for excitation to electronic excited state $|j\rangle$, ε_{I_0} is the sum of the zero-point energies of every

harmonic oscillator in the system, Γ_j is the homogeneous broadening parameter for the excited electronic state, Γ_a is the homogeneous broadening parameter for the excited vibrational state, and $\langle F_0 | I_j(t) \rangle$ is the nuclear overlap integral of the final vibrational state $|F_0\rangle$ and the Gaussian wavepacket $|I_j(t)\rangle = e^{\frac{-i\hat{H}_j t}{\hbar}} |I_0\rangle$.

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