

Resonance Effects in the Raman Optical Activity Spectrum of $[\text{Rh}(\text{en})_3]^{3+}$

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Supporting Information

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S1 Cartesian Coordinates of $[\text{Rh}(\text{en})_3]^{3+}$

Below we give the Cartesian coordinates of $[\text{Rh}(\text{en})_3]^{3+}$ as obtained from the structure optimization. All values are given in Å.

C	-2.56007083	-1.35708902	-0.54082819
H	-3.10328879	-2.24869940	-0.86238831
H	-3.08660763	-0.49282315	-0.95265826
C	-2.47421399	-1.28021359	0.95943603
H	-3.46617474	-1.19818162	1.40985356
H	-2.00345265	-2.17345255	1.37692725
N	-1.16889899	-1.35936049	-1.09006688
H	-1.21286788	-1.16089489	-2.08908158
H	-0.80398432	-2.31021408	-1.04209812
N	-1.63162263	-0.09834763	1.31900179
H	-1.37112102	-0.16978020	2.30207886
H	-2.21364735	0.73774283	1.27663904
Rh	-0.00002018	0.00010660	0.00233207
C	-0.02679481	2.88428537	-0.60574077
C	2.35191497	-1.42093764	-1.06582865
H	-0.58752840	3.79240567	-0.83894857
H	3.35099977	-1.38928934	-1.50663534
H	0.88253316	2.90273817	-1.21114681
H	1.80857443	-2.23169584	-1.55717426
C	0.29510901	2.80224385	0.86182796
C	2.41748095	-1.63037140	0.42278229
H	0.93417380	3.63108091	1.17516908
H	2.87727091	-2.59042055	0.66869121
H	-0.61140381	2.84628607	1.47013288
H	3.01413515	-0.85371141	0.90728810
N	-0.81152322	1.66769055	-0.98163326
N	1.61872404	-0.14367645	-1.32703344
H	1.35244579	-0.11627064	-2.31077538
H	-0.82072619	1.58682826	-1.99789514
H	2.27364722	0.63115483	-1.22583125
H	-1.78870042	1.82488763	-0.73660797
N	0.96576365	1.49089727	1.12047395
N	1.02648486	-1.55627954	0.96667280
H	0.97308157	1.32058012	2.12565099
H	1.07697248	-1.45807464	1.98016955

H	1.95183719	1.57898160	0.87656334
H	0.57692005	-2.46074498	0.82712764

S2 Damping Factor

In order to investigate the influence of the damping value, we calculated the ROA spectrum of $[\text{Rh}(\text{en})_3]^{3+}$ for two different damping values. In the first case, we adopted a rather small damping value of 0.0037 a.u.; in the second case, a larger value of 0.008 a.u. was used. For both damping values, we calculated the spectrum with an excitation wavelength of 307.66 nm, *i.e.*, under full-resonance conditions, and with an excitation wavelength of 370 nm. The four resulting spectra are shown in Fig. S1. As one can see, when an excitation wavelength of 370 nm is adopted, the two different damping values lead to virtually identical spectra, and therefore have no influence (*cf.*, the top two spectra in Fig. S1). Under full-resonance conditions, however, the damping value has a rather large influence on the overall spectral intensity. With larger damping value, the overall intensity is greatly reduced (up to a factor of about five). However, the relative intensities as well as the overall band shape is much less affected by changes in the damping value. We therefore conclude that the exact numerical value adopted for the damping value is not of primary importance as long as one and the same value is used throughout our study. This will suffice to make the individual spectra comparable to each other.

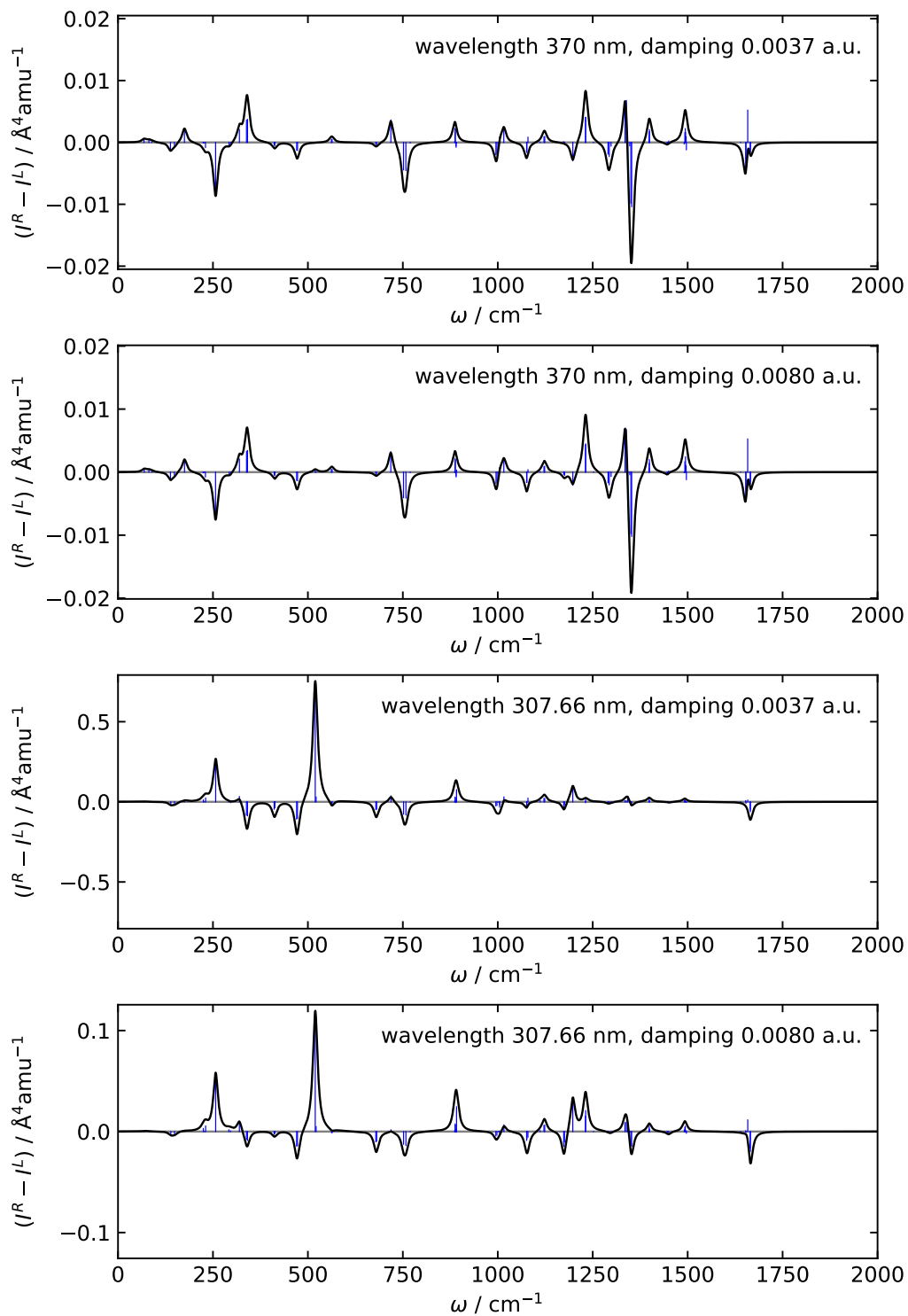


Figure S1: ROA spectra of $[\text{Rh}(\text{en})_3]^{3+}$ for two different excitation wavelengths and two different damping values. A wavelength of 307.66 nm yields full-resonance spectra. Note that the individual spectra span different intensity ranges.

S3 Origin Dependence

In order to check whether the methodology followed in this work yields ROA spectra which are origin independent, we shifted the molecule by 10 Å in each of the three spatial directions and recalculated the spectrum under full-resonance conditions. As can be seen by comparing the first and third spectrum in Fig. S2, the spectrum does literally not change. We therefore conclude that our spectra are not dependent on the choice of origin.

As a further test, we also calculated the ROA spectrum under full-resonance conditions without gauge-including atomic orbitals (GIAOs), both with the molecule at its original location and with the molecule shifted by 10 Å in all three spatial directions. As can be seen from Fig. S2, in our case the use of GIAOs apparently has no observable effects on the ROA spectrum.

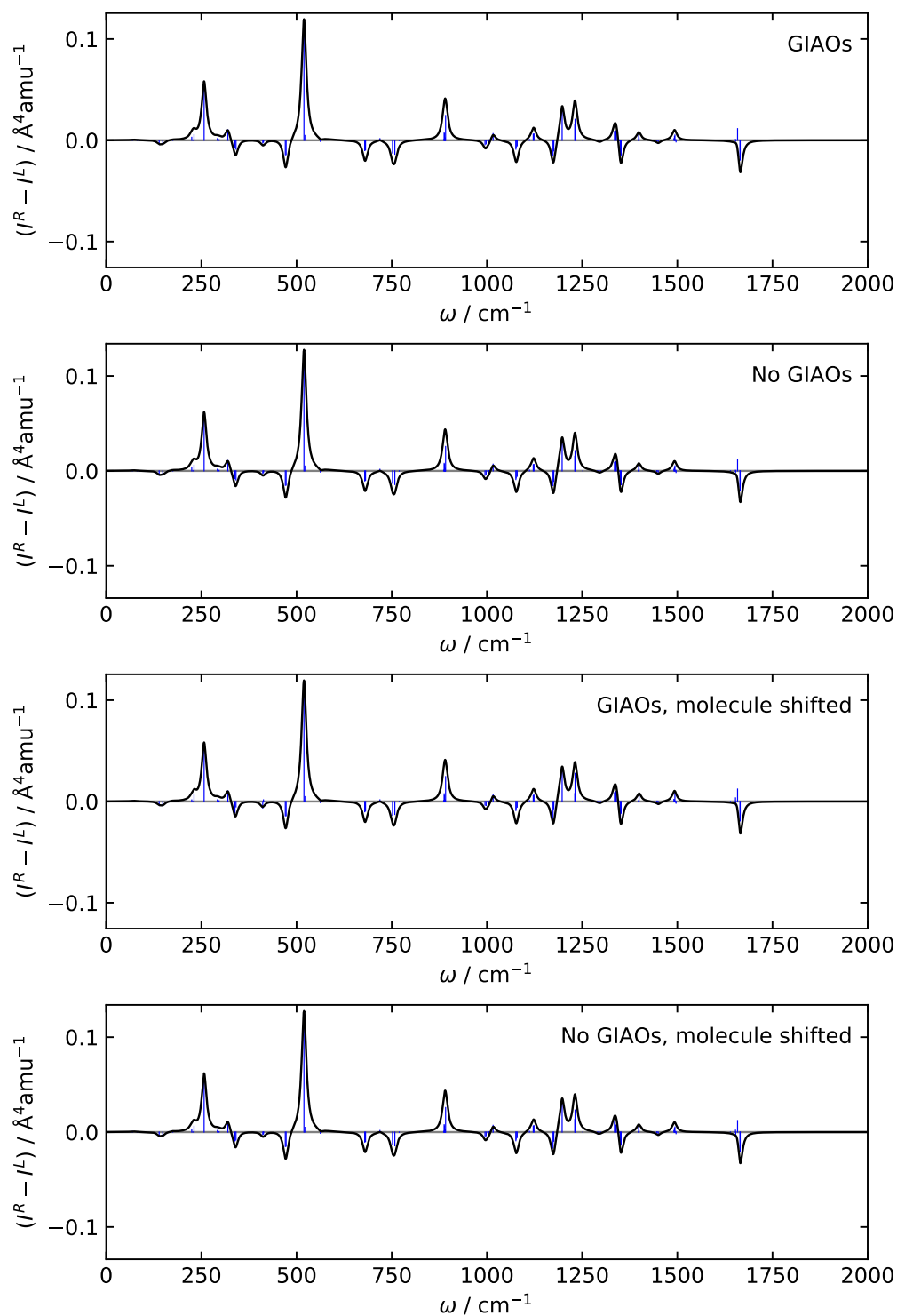


Figure S2: ROA spectra of $[\text{Rh}(\text{en})_3]^{3+}$ calculated either with or without gauge-including atomic orbitals. In the upper two spectra, the molecule is placed very close to the origin, while in the lower two spectra, the molecule is shifted by 10 $\text{\AA}$ in all three spatial directions.

S4 Example Input File

Below we give an example NWChem input file as used in this work to calculate the ROA spectra. The nuclear coordinates have been omitted in this example; in the actual calculations, the distorted structures as generated by MOVIPAC have been inserted.

```
echo

title "RROA calculation of [Rh(en3)]3+ in vacuum"

memory 2048 mb

start rh_en

geometry units au nocenter noautosym nucleus point
symmetry c1
...
end

basis "ao basis" spherical
  * library def2-TZVP
end

ecp
  Rh library def2-ECP
end

scf
  singlet
  rhf
  direct
end

charge 3

dft
  grid xfine nodisk
  tolerances tight
  convergence energy 1d-8
```

```
convergence density 1d-7
maxiter 50
xc pbe0
disp vdw 3
direct
noio
end
```

```
set prop:newaoresp 1
set aor:roadata T
set cphf:maxsub 30
set cphf:maxiter 50
```

```
property
  response 1 0.14809645
  bdtensor
  convergence 1e-4
  damping 0.0080
  giao
end
```

```
task dft property
task dft gradient
```


S5 Intensities of Normal Modes

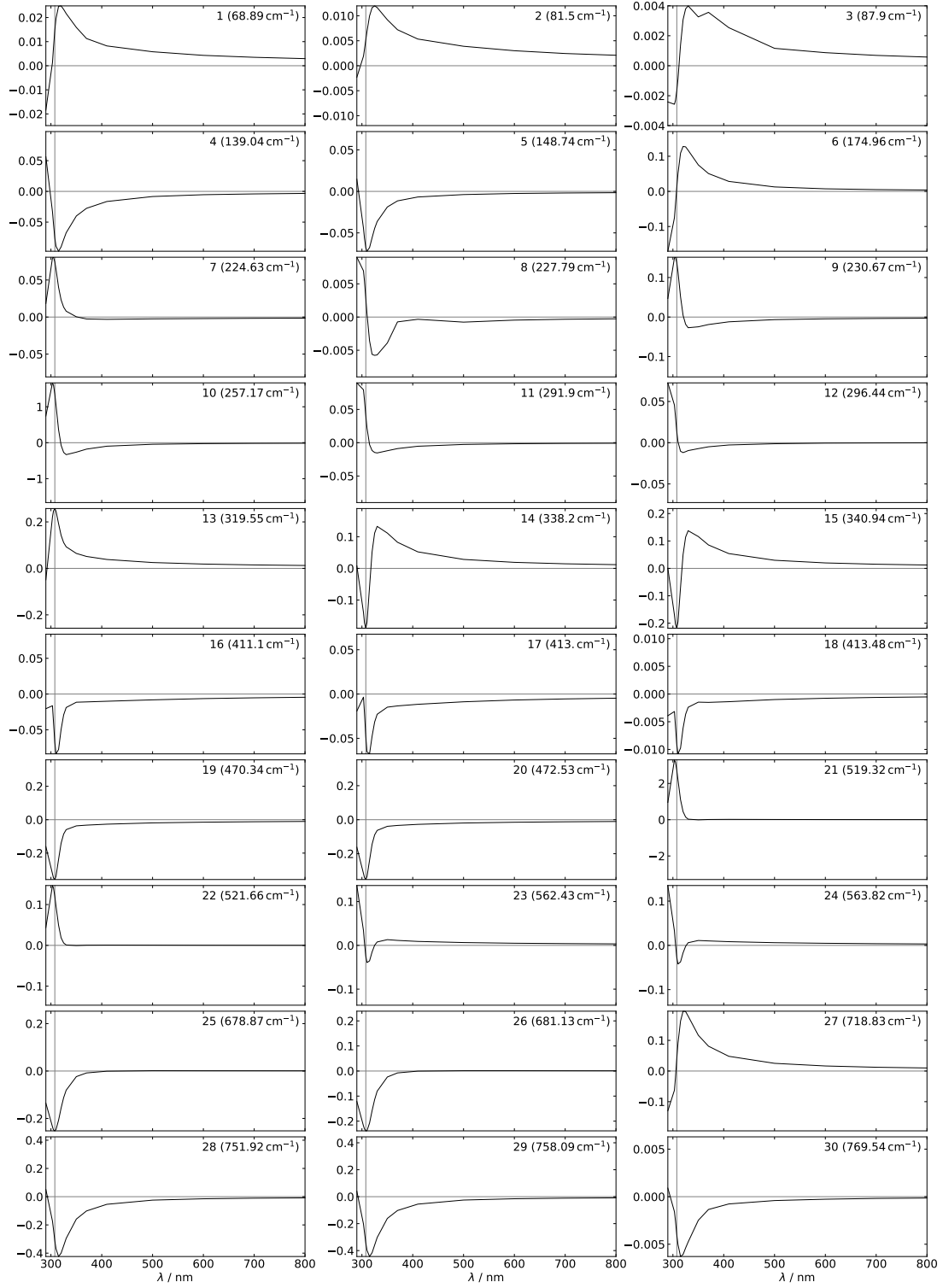


Figure S3: Intensities of normal modes 1 to 30 as a function of excitation wavelength. All intensities are given in $\text{\AA}^4/\text{amu}^{-1}$. The vertical line highlights the full-resonance wavelength.

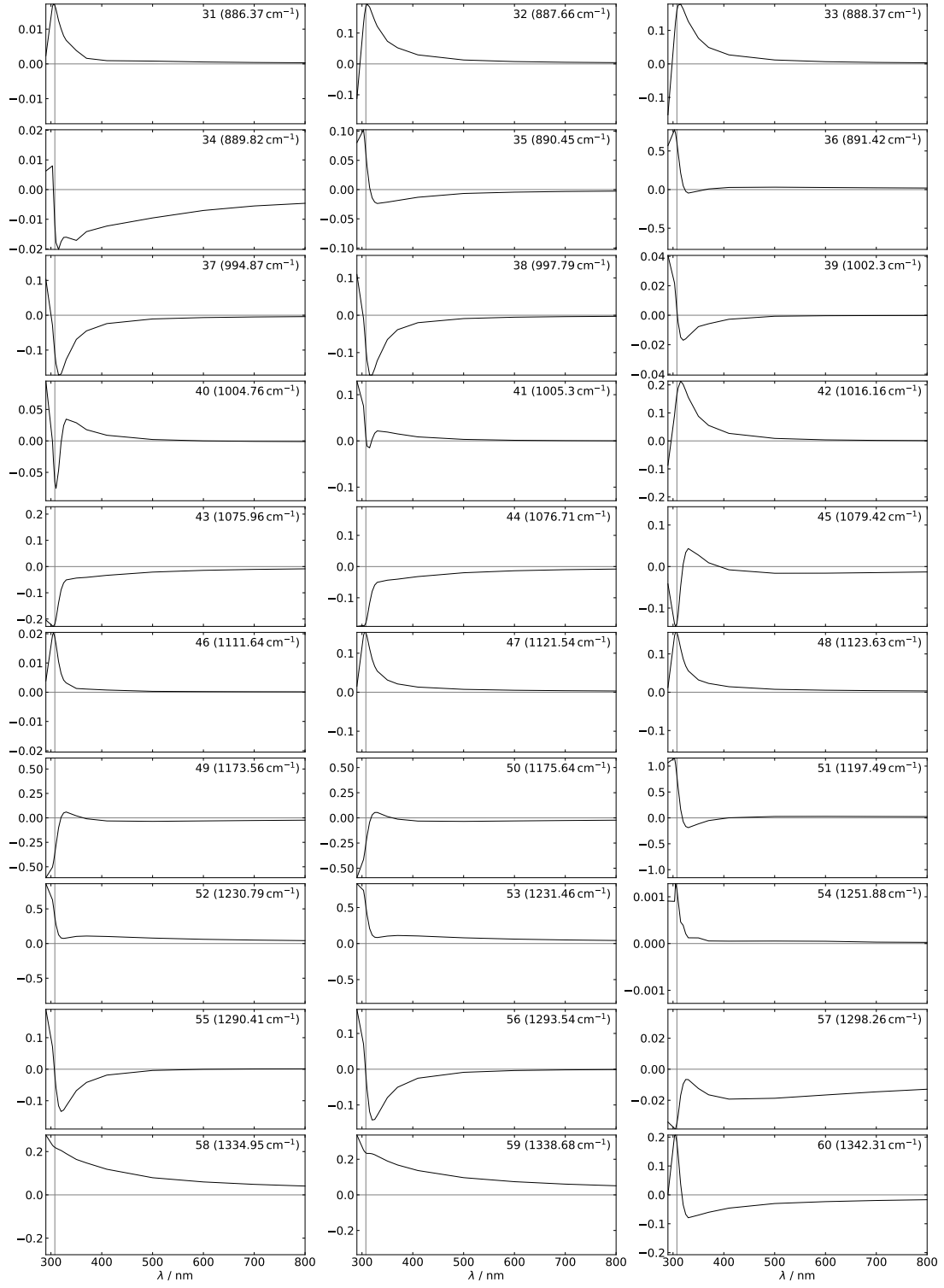


Figure S4: Intensities of normal modes 31 to 60 as a function of excitation wavelength. All intensities are given in $\text{\AA}^4/\text{amu}^{-1}$. The vertical line highlights the full-resonance wavelength.

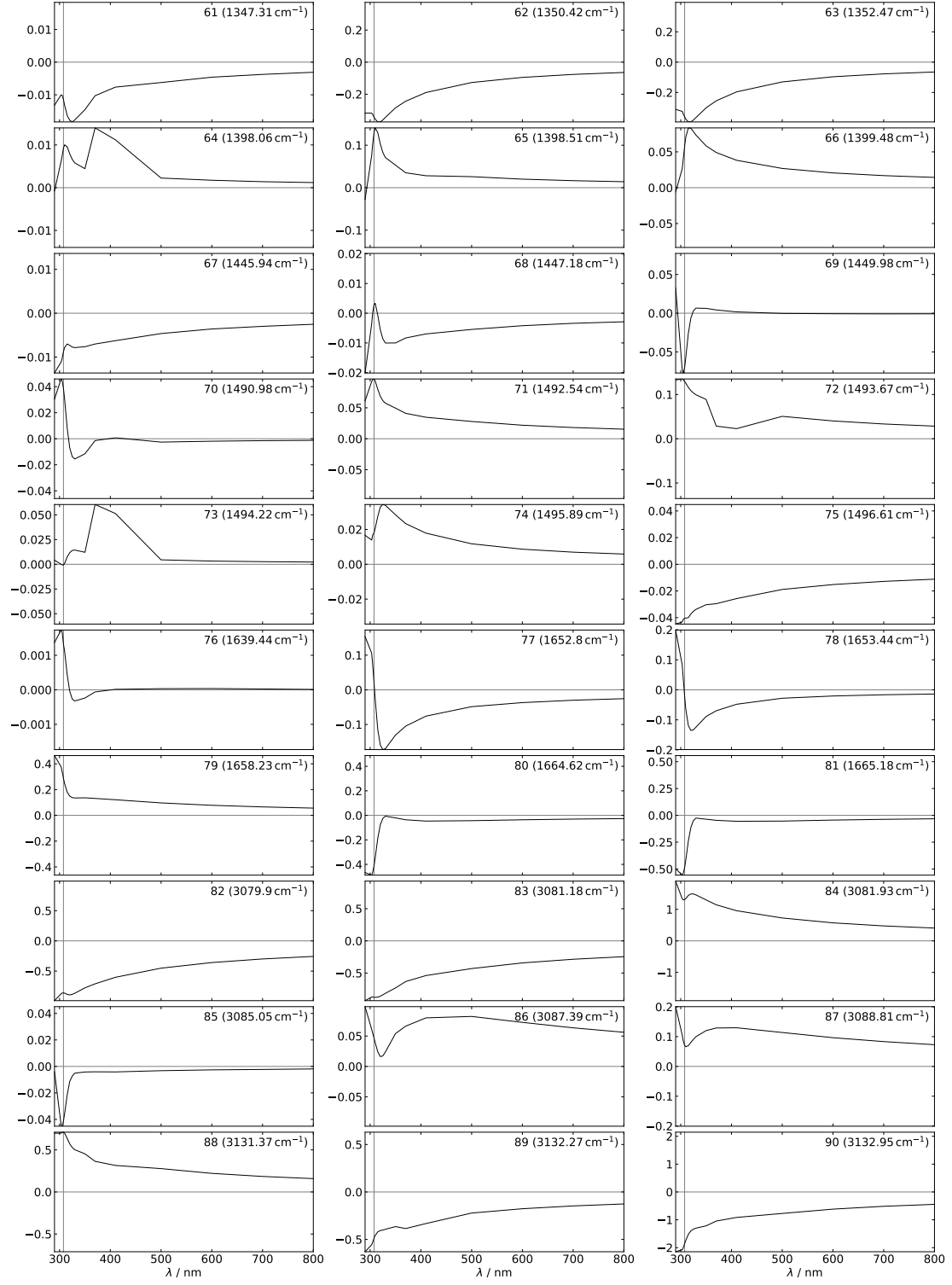


Figure S5: Intensities of normal modes 61 to 90 as a function of excitation wavelength. All intensities are given in $\text{\AA}^4/\text{amu}^{-1}$. The vertical line highlights the full-resonance wavelength.

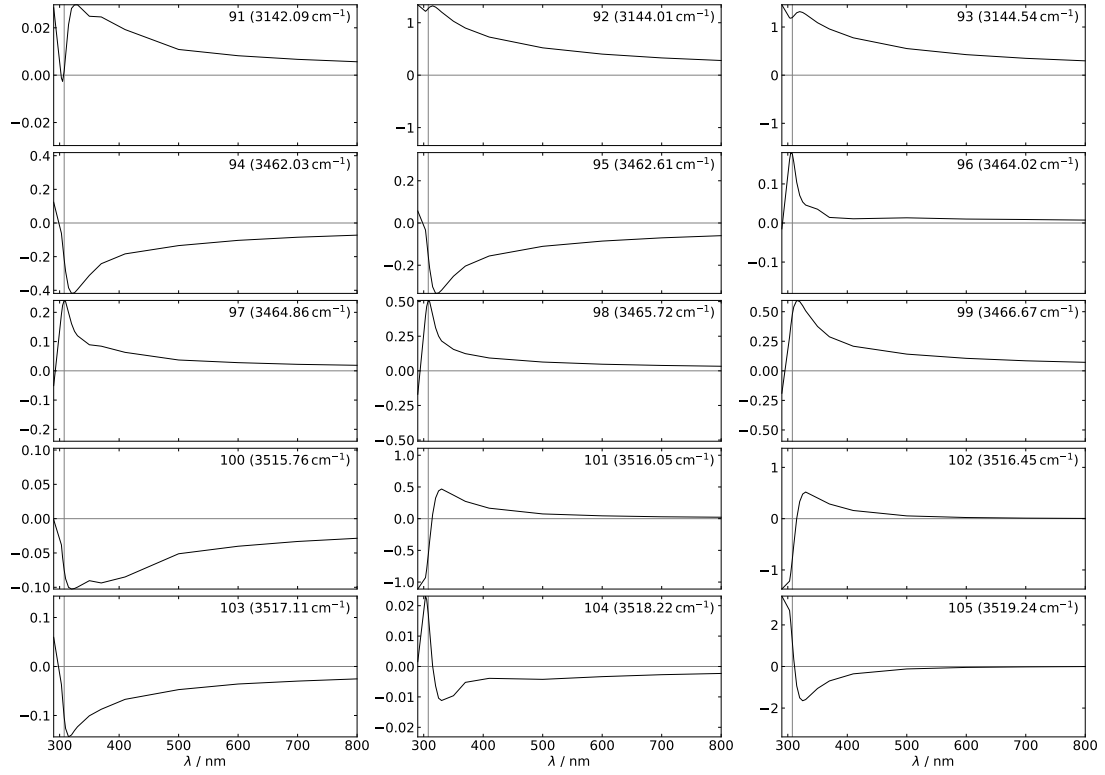


Figure S6: Intensities of normal modes 91 to 105 as a function of excitation wavelength. All intensities are given in $\text{\AA}^4/\text{amu}^{-1}$. The vertical line highlights the full-resonance wavelength.