Supplementary Information for

Tuning the Vibrational Coupling of H$_3$O$^+$ by Changing Its Solvation Environment

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H. Determination of coupling constants from an experimentally observable (E↔E) Fermi resonance.

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**A. Minimum structures for the singlet H₃O⁺•Rg₃ (Rg=Ne, Ar, Kr, and Xe).**

Table S1. Cartesian coordinates in Angstroms for the minimum structures of singlet H₃O⁺•Rg₃ at MP2/aug-cc-pVDZ for Ne and Ar and MP2/aug-cc-pVDZ-PP for Kr and Xe. The latter basis set was obtained from EMSL basis set library.

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<tr>
<th>H₃O⁺•Ne₃</th>
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<th>Z</th>
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### B. Symmetry Species for the Vibrational Normal Modes of H$_3$O$^+$•Rg$_3$

We briefly describe the group theoretical treatment to determine the symmetry species of the vibrational normal modes for H$_3$O$^+$•Rg$_3$. Interested readers can refer to the excellent work of Douglas and Hollingsworth, *Symmetry in Bonding and Spectra: An Introduction*.

**Point Group: C$_{3v}$**

Character Table:

<table>
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<tr>
<th>C$_{3v}$</th>
<th>E</th>
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<th>3$\sigma_v$</th>
<th>Linear functions</th>
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<td>1</td>
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<td>R$_z$</td>
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<td>0</td>
<td>(x,y) (R$_x$,R$_y$)</td>
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Determination of the reducible representation

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<td></td>
<td></td>
</tr>
<tr>
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<tr>
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<td>$\Gamma_{3N} \otimes \Gamma_n$</td>
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<td></td>
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<td>$\Gamma_{3N}$</td>
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<td>3</td>
<td></td>
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<td>1</td>
<td></td>
</tr>
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<td>$\Gamma_{rot}$</td>
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<td>-1</td>
<td></td>
</tr>
</tbody>
</table>
### Determination of \( \Gamma_{\text{stretch}} \) and \( \Gamma_{\text{bend}} \)

\[
\begin{array}{cccc}
\Gamma_{\text{vib}} & 15 & 0 & 3 \\
\Gamma_{\text{n}} & 7 & 1 & 3 \\
A_1 & 1 & 1 & 1 \\
\Gamma_{\text{stretch}} & 6 & 0 & 2 \\
\Gamma_{\text{bend}} & 9 & 0 & 1 \\
\end{array}
\]

unmoved atoms

\[
\Gamma_{\text{stretch}} = \Gamma_n - A_1 \\
\Gamma_{\text{bend}} = \Gamma_{\text{vib}} - \Gamma_{\text{stretch}}
\]

By either inspection or use of the standard decomposition formula.

\[
\Gamma_{\text{stretch}} = 2A_1 + 2E \quad \text{and} \quad \Gamma_{\text{bend}} = 2A_1 + A_2 + 3E
\]

Table S2. Symmetry species for the 15 normal modes of H\(_3\)O\(^+\)Rg\(_3\).

| Symmetry Classification for the Normal Modes of H\(_3\)O\(^+\)Rg\(_3\). |
|-----------------|----------|----------------|
| Symmetry Species | G09 mode # | Description |
| \( \Gamma_{\text{stretch}} \) | A\(_1\) | 4 | Symmetric Rg\(_3\) stretching |
| | E | 13 | Symmetric H\(_3\)O\(^+\) stretching |
| | | 1 and 2 | Asymmetric Rg\(_3\) stretching |
| | 14 and 15 | Asymmetric H\(_3\)O\(^+\) stretching |
| \( \Gamma_{\text{bend}} \) | A\(_1\) | 3 | H\(_3\)O\(^+\) as one unit bending \( \perp \) to Rg\(_3\) plane |
| | A\(_2\) | 10 | H\(_3\)O\(^+\) umbrella motion |
| | E | 5 and 6 | Degenerate H\(_3\)O\(^+\) swinging above the Rg\(_3\) plane |
| | | 8 and 9 | Degenerate H\(_3\)O\(^+\) deformation |
| | | 11 and 12 | Degenerate H\(_3\)O\(^+\) bending |

### C. Harmonic frequencies in cm\(^{-1}\) and intensities in km/mol for H\(_3\)O\(^+\)Rg\(_3\) (Rg=Ne, Ar, Kr, and Xe) at MP2/aug-cc-pVDZ.

Table S3. Harmonic frequencies (\(\omega_e\)) and absorption intensities in km/mol for the 15 normal modes of H\(_3\)O\(^+\)Rg\(_3\).

<table>
<thead>
<tr>
<th>Normal Mode Numbering</th>
<th>H(_3)O(^+)Ne(_3)</th>
<th>H(_3)O(^+)Ar(_3)</th>
<th>H(_3)O(^+)Kr(_3)</th>
<th>H(_3)O(^+)Xe(_3)</th>
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</thead>
<tbody>
<tr>
<td>Herzberg Order</td>
<td>G09 output</td>
<td>(\omega_e) (cm(^{-1}))</td>
<td>Inten. (km/mol)</td>
<td>(\omega_e) (cm(^{-1}))</td>
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<tr>
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<td>21.3</td>
<td>4.33</td>
<td>19.4</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>21.3</td>
<td>4.33</td>
<td>19.4</td>
</tr>
<tr>
<td>(v_4)</td>
<td>3</td>
<td>35.8</td>
<td>20.45</td>
<td>36.3</td>
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<tr>
<td>(v_3)</td>
<td>4</td>
<td>92.7</td>
<td>7.26</td>
<td>99.2</td>
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<tr>
<td>(v_9)</td>
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<td>131.2</td>
<td>34.57</td>
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<td></td>
<td>6</td>
<td>131.2</td>
<td>34.60</td>
<td>150.6</td>
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</table>
D. Harmonic frequencies in cm$^{-1}$ and intensities in km/mol for D$_3$O$^+$•Rg$_3$ (Rg=Ne, Ar, Kr, and Xe) at MP2/aug-cc-pVDZ.

Table S4. Harmonic frequencies ($\nu$, cm$^{-1}$) and absorption intensities in km/mol for the 15 normal modes of D$_3$O$^+$•Rg$_3$.

<table>
<thead>
<tr>
<th>Normal Mode Numbering</th>
<th>D$_3$O$^+$•Ne$_3$</th>
<th>D$_3$O$^+$•Ar$_3$</th>
<th>D$_3$O$^+$•Kr$_3$</th>
<th>D$_3$O$^+$•Xe$_3$</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>G09 output</td>
<td>$\nu_e$ (cm$^{-1}$)</td>
<td>Inten. (km/mol)</td>
<td>$\nu_e$ (cm$^{-1}$)</td>
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<tr>
<td>$\nu_{10}$</td>
<td>1</td>
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<td>3.91</td>
<td>19.3</td>
</tr>
<tr>
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<td>21.1</td>
<td>3.91</td>
<td>19.3</td>
</tr>
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<td>$\nu_5$</td>
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<td></td>
<td>4</td>
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<td>$\nu_6$</td>
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<td>9</td>
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<td>262.1</td>
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<td>15</td>
<td>2672.3</td>
<td>377.34</td>
<td>2570.5</td>
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E. RDAV-6D frequencies and integrated absorption coefficients for the hydrons (H$_3$O$^+$•Rg$_3$) at MP2/aug-cc-pVDZ (for Ne and Ar) and MP2/aug-cc-pVDZ-PP (for Kr and Xe).

Table S5. RDAV-6D anharmonic frequencies in cm$^{-1}$ and integrated absorption coefficients in km/mol for H$_3$O$^+$•Rg$_3$.

| $|\Psi_R>|$ | H$_3$O$^+$•Ne$_3$ | H$_3$O$^+$•Ar$_3$ | H$_3$O$^+$•Kr$_3$ | H$_3$O$^+$•Xe$_3$ |
|--------|-----------------|-----------------|-----------------|-----------------|
|        | cm$^{-1}$ km/mol | cm$^{-1}$ km/mol | cm$^{-1}$ km/mol | cm$^{-1}$ km/mol |
| 1      | 226.80          | 335.84          | 386.59          | 416.23          |
| 2      | 440.34          | 652.23          | 752.97          | 813.98          |
| 3      | 651.72          | 952.60          | 1102.61         | 1193.95         |
| 4      | 894.15          | 1267.65         | 1455.64         | 1566.76         |
| 5      | 1216.99         | 1607.19         | 1596.02         | 1580.71         |
F. RDAV-6D frequencies and integrated absorption coefficients for the deuterons (D$_3$O•$^*$$\cdot$Rg$_3$) at MP2/aug-cc-pVDZ (for Ne and Ar) and MP2/aug-cc-pVDZ-PP (for Kr and Xe).

Table S6. RDAV-6D anharmonic frequencies in cm$^{-1}$ and integrated absorption coefficients in km/mol for D$_3$O•$^*$$\cdot$Rg$_3$. 

<table>
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<tr>
<th>$\Psi_k$</th>
<th>D$_3$O•Ne$_3$</th>
<th>D$_3$O•Ar$_3$</th>
<th>D$_3$O•Kr$_3$</th>
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<td>km/mol</td>
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G. Determination of coupling constants from an experimentally observable \((A_1 \leftrightarrow A_1)\) Fermi resonance.

In the main article, we discussed that Fermi resonance occurs between the H-O-H bending first overtones and O-H stretching fundamentals. Provided that such special effect is observed in an experimental spectrum, their anharmonic coupling constant can be determined using a simple two-level (two-state) system. We will first briefly review the two-level system and proceed on its utility in extracting coupling constants.

**Part 1: Revisiting the two-level system**

We begin by considering the following \(2 \times 2\) Hamiltonian in the \(\{|1\}, |2\rangle\) representation. The matrix elements are expressed as

\[
\begin{align*}
\langle 1 | H | 1 \rangle &= \varepsilon_1, & \langle 1 | H | 2 \rangle &= J \\
\langle 2 | H | 1 \rangle &= J, & \langle 2 | H | 2 \rangle &= \varepsilon_2
\end{align*}
\]

Furthermore, we impose that \(\varepsilon_1 \leq \varepsilon_2\). The \(2 \times 2\) Hamiltonian is written as

\[
H = \begin{bmatrix} \varepsilon_1 & J \\ J & \varepsilon_2 \end{bmatrix}, \quad \varepsilon_1 \leq \varepsilon_2
\]

Solving the secular determinant, we have

\[
\begin{align*}
\det |H - E\rangle &= \begin{vmatrix} \varepsilon_1 - E & J \\ J & \varepsilon_2 - E \end{vmatrix} = 0 \\
(\varepsilon_1 - E)(\varepsilon_2 - E) - J^2 &= 0 \\
E^2 - (\varepsilon_1 + \varepsilon_2)E + \varepsilon_1 \varepsilon_2 - d^2 &= 0
\end{align*}
\]

The roots, which are the eigenvalues can be obtained using the quadratic formula.
\[
E_i = \frac{(\epsilon_i + \epsilon_2) - \sqrt{(\epsilon_i + \epsilon_2)^2 - 4(\epsilon_i \epsilon_2 - J^2)}}{2} \quad \text{and} \quad E_2 = \frac{(\epsilon_i + \epsilon_2) + \sqrt{(\epsilon_i + \epsilon_2)^2 - 4(\epsilon_i \epsilon_2 - J^2)}}{2}
\]

With a few rearrangements in the radicand, it is straightforward to show that

\[
E_i = \frac{(\epsilon_i + \epsilon_2) - \sqrt{(\epsilon_i - \epsilon_2)^2 + 4J^2}}{2} \quad \text{and} \quad E_2 = \frac{(\epsilon_i + \epsilon_2) + \sqrt{(\epsilon_i - \epsilon_2)^2 + 4J^2}}{2}
\]

The eigenstates will be linear combinations of \(|1\rangle\) and \(|2\rangle\). We will use \(\sin \theta\) and \(\cos \theta\) to ensure that these eigenstates are orthonormal.

\[
|\alpha\rangle = \cos \theta |1\rangle + \sin \theta |2\rangle
\]

\[
|\beta\rangle = -\sin \theta |1\rangle + \cos \theta |2\rangle
\]

To determine the eigenstates, we need to know \(\theta\). Collecting the coefficients of the eigenvectors \(|\alpha\rangle\) and \(|\beta\rangle\) to a matrix \(S\).

\[
S = \begin{bmatrix}
\cos \theta & -\sin \theta \\
\sin \theta & \cos \theta
\end{bmatrix}
\]

This matrix satisfies the matrix equation \(HS = SE\). From here the \(2 \times 2\) Hamiltonian can be diagonalize by a similarity transformation.

\[
E = S^\dagger HS
\]

\[
\begin{bmatrix}
E_1 & 0 \\
0 & E_2
\end{bmatrix} = \begin{bmatrix}
\cos \theta & \sin \theta \\
-\sin \theta & \cos \theta
\end{bmatrix} \begin{bmatrix}
\epsilon_i & J \\
J & \epsilon_2
\end{bmatrix} \begin{bmatrix}
\cos \theta & -\sin \theta \\
\sin \theta & \cos \theta
\end{bmatrix}
\]

Equating the off diagonal elements yields

\[
J(\cos^2 \theta - \sin^2 \theta) + (\epsilon_2 - \epsilon_1)\cos \theta \sin \theta = 0
\]

Multiply equation (9) by 2 on both sides, and using the following trigonometric identities, we have

\[
\cos 2x = \cos^2 x - \sin^2 x
\]

\[
\sin 2x = 2 \cos x \sin x
\]
\[ 2J \cos 2\theta + (\varepsilon_2 - \varepsilon_1) \sin 2\theta = 0 \]
\[ \tan 2\theta = \frac{-2J}{\varepsilon_2 - \varepsilon_1} = \frac{2J}{\varepsilon_1 - \varepsilon_2} \]
\[ \theta = \frac{1}{2} \arctan \left( \frac{2J}{\varepsilon_1 - \varepsilon_2} \right) \]

**Part 2: Using the two-level system to extract coupling constants in a two-state \((a_1 \leftrightarrow a_1)\) Fermi’s resonance**

In a typical two-state Fermi resonance, the zero-order picture is shown in the figure below. The transitions from \(|1\rangle \leftarrow |0\rangle\) is allowed (green arrow) while that of \(|2\rangle \leftarrow |0\rangle\) is forbidden (black arrow). Provided that there is a good matching between \(|1\rangle\) and \(|2\rangle\) with respect to symmetry and energy, plus the existence of a non-zero anharmonic coupling term, the two zero-order states can couple. That is they can mix to produce two new eigenstates \(|\alpha\rangle\) and \(|\beta\rangle\). Their transition from the ground vibrational state will be non-zero.

In order to use the two-level system, to extract the anharmonic coupling constant \(J\). We will make the following assumptions:

1. The ground vibrational state \(|0\rangle\) remains intact of any perturbations or coupling in the system.
2. The experimental absorption intensities, which are the area under the peak can be well described by the integrated absorption coefficient \(A_\beta\).
3. The \(|1\rangle\) and \(|2\rangle\) weakly couples with the rest of the zero-order states, which allows them to be isolated as a first approximation.
4. The effects of electronic anharmonicity is negligible.
From the above figure, it follows that the transition dipole moments for $|1\rangle \leftrightarrow |0\rangle$ and $|2\rangle \leftrightarrow |0\rangle$ are

$$\left\langle 0|\mu|1\right\rangle = 0 \quad \text{and} \quad \left\langle 0|\mu|2\right\rangle = 0$$

(12)

In the coupled states $|\alpha\rangle$ and $|\beta\rangle$, their transition dipole moments are

$$\left\langle 0|\mu|\alpha\right\rangle = \cos \theta \left\langle 0|\mu|1\right\rangle + \sin \theta \left\langle 0|\mu|2\right\rangle = \cos \theta \left\langle 0|\mu|1\right\rangle$$
$$\left\langle 0|\mu|\beta\right\rangle = -\sin \theta \left\langle 0|\mu|1\right\rangle + \cos \theta \left\langle 0|\mu|2\right\rangle = -\sin \theta \left\langle 0|\mu|1\right\rangle$$

(13)

Their corresponding integrated absorption coefficients for the $|\alpha\rangle \leftrightarrow |0\rangle$ and $|\beta\rangle \leftrightarrow |0\rangle$ are

$$A_{\beta\rightarrow 0} = \left(\frac{\pi N}{3\epsilon e_0}\right) v_{\beta\rightarrow 0} |\langle 0|\mu|\beta\rangle|^2$$
$$A_{\alpha\rightarrow 0} = \left(\frac{\pi N}{3\epsilon e_0}\right) v_{\alpha\rightarrow 0} |\langle 0|\mu|\alpha\rangle|^2$$

(14)

Taking their ratio, we have

$$\frac{A_{\beta\rightarrow 0}}{A_{\alpha\rightarrow 0}} = \left(\frac{\pi N}{3\epsilon e_0}\right) \frac{v_{\beta\rightarrow 0} |\langle 0|\mu|\beta\rangle|^2}{v_{\alpha\rightarrow 0} |\langle 0|\mu|\alpha\rangle|^2} = \left(\frac{v_{\beta\rightarrow 0}}{v_{\alpha\rightarrow 0}}\right) \left(\frac{\sin^2 \theta}{\cos^2 \theta}\right) \left|\frac{\langle 0|\mu|1\rangle}{\langle 0|\mu|1\rangle}\right|^2$$

(15)

$$= \left(\frac{v_{\beta\rightarrow 0}}{v_{\alpha\rightarrow 0}}\right) \tan^2 \theta$$

Recall that from our two-level system equation (11) and rearing equation (15) gives

$$\tan 2\theta = \frac{2J}{\epsilon_1 - \epsilon_2}$$
$$\tan^2 \theta = \left(\frac{A_{\beta\rightarrow 0}}{A_{\alpha\rightarrow 0}}\right) \left(\frac{v_{\alpha\rightarrow 0}}{v_{\beta\rightarrow 0}}\right)$$

(16)
Using the trigonometric identity \( \tan 2\theta = \frac{2\tan \theta}{1 - \tan^2 \theta} \) we have

\[
\frac{2J}{\epsilon_1 - \epsilon_2} = \frac{2}{1 - A_{\alpha=0}^2} \begin{pmatrix} A_{\alpha=0} & V_{\alpha=0} \\ A_{\beta=0} & V_{\beta=0} \end{pmatrix}
\] (17)

We can simplify the expression by defining \( z \) and \( Q \).

\[
\frac{2J}{\epsilon_1 - \epsilon_2} = Q
\]

\[
Q = \frac{2z}{1 - z^2} \quad \text{and} \quad z = \frac{A_{\beta=0}}{A_{\alpha=0}} \begin{pmatrix} V_{\alpha=0} \\ V_{\beta=0} \end{pmatrix}
\] (18)

Also from the eigenvalues of our two-level system equation (5), the difference in transition energies is

\[
\Delta E = E_2 - E_1 = V_{\beta=0} - V_{\alpha=0} = \sqrt{(\epsilon_1 - \epsilon_2)^2 + 4J^2}
\] (19)

Squaring both sides of equation (18) and (19) gives

\[
4J^2 = Q^2(\epsilon_1 - \epsilon_2)^2
\]

\[
(\Delta E)^2 = (\epsilon_1 - \epsilon_2)^2 + 4J^2 \Rightarrow (\Delta E)^2 = (\epsilon_1 - \epsilon_2)^2 + Q^2(\epsilon_1 - \epsilon_2)^2
\] (20)

\[
\therefore \epsilon_1 - \epsilon_2 = -\frac{(\Delta E)^2}{1 + Q^2} = -\frac{V_{\beta=0} - V_{\alpha=0}}{1 + Q^2} \quad \text{and} \quad J = \frac{Q(\epsilon_1 - \epsilon_2)}{2}
\]

Where the negative root was taken as we imposed \( \epsilon_1 \leq \epsilon_2 \) in equation (2).

**Part 3: Method Validation**

To illustrate the use of the equations derived from Part 2, consider the following \( 2 \times 2 \) Hamiltonian in the \( \{ |1\rangle, |2\rangle \} \) representation.

\[
H = \begin{bmatrix} 7 & -3\sqrt{3} \\ -3\sqrt{3} & 13 \end{bmatrix}
\] (21)

Using equation 5, its corresponding eigenvalues are
The eigenvectors can be obtained using equations (6) and (11).

\[ \theta = \frac{1}{2} \arctan \left( \frac{-6\sqrt{3}}{7-13} \right) = 30^\circ \]

\[ \cos \theta = \frac{\sqrt{3}}{2} \quad \text{and} \quad \sin \theta = \frac{1}{2} \]

\[ |\alpha\rangle = \frac{\sqrt{3}}{2} |1\rangle + \frac{1}{2} |2\rangle \]

\[ |\beta\rangle = -\frac{1}{2} |1\rangle + \frac{\sqrt{3}}{2} |2\rangle \]

If we set the following transition dipole moments,

\[ \langle 0|\mu|1\rangle = 100 \quad \text{and} \quad \langle 0|\mu|2\rangle = 0 \]

\[ \langle 0|\mu|\alpha\rangle = \cos \theta \langle 0|\mu|1\rangle - 50\sqrt{3} \quad \text{and} \quad \langle 0|\mu|\beta\rangle = -\sin \theta \langle 0|\mu|1\rangle = -50 \]

Then, their corresponding integrated absorption coefficients for \( |\alpha\rangle \leftrightarrow |0\rangle \) and \( |\beta\rangle \leftrightarrow |0\rangle \) are

\[ A_{\mu=0} \quad \frac{\nu_{\mu=0} |\langle 0|\mu|\beta\rangle|^2}{\nu_{\mu=0} |\langle 0|\mu|\alpha\rangle|^2} = \frac{16}{\frac{1}{4}} \left( \frac{-50}{50\sqrt{3}} \right)^2 = \frac{4}{3} \]

Now to check for the consistency of our equations in part 2, let us supposed that our observed peaks for \( |\alpha\rangle \leftrightarrow |0\rangle \) and \( |\beta\rangle \leftrightarrow |0\rangle \) are 4 and 16 units respectively. Their intensity ratio is \( \frac{A_{\mu=0}}{A_{\mu=0}} = \frac{4}{3} \). Our goal is to get to extract \( J \) and \( \varepsilon_1 - \varepsilon_2 \).

From equation (18), we know that

\[ z = \sqrt{\left( \frac{A_{\mu=0}}{A_{\mu=0}} \right) \left( \frac{\nu_{\mu=0}}{\nu_{\mu=0}} \right)} = \sqrt{\left( \frac{4}{16} \right) \left( \frac{4}{16} \right)} = \frac{1}{\sqrt{3}} \]

\[ Q = \frac{2z}{1 - z^2} = \frac{2}{\frac{\sqrt{3}}{1 - \left( \frac{1}{\sqrt{3}} \right)^2}} = \sqrt{3} \]

Then by equation (19)
\[ \begin{align*}
\epsilon_1 - \epsilon_2 &= -\sqrt{\frac{(V_{\beta} - V_{\alpha})^2}{1 + Q^2}} = -\sqrt{\frac{(16 - 4)^2}{1 + 3}} = -6 \\
J &= \frac{Q(\epsilon_1 - \epsilon_2)}{2} = \frac{\sqrt{3}(-6)}{2} = -3\sqrt{3}
\end{align*} \] (27)

Hence, our equations (18) and (19) are mathematically consistent with the Hamiltonian in equation (21).

**H. Determination of coupling constants from an experimentally observable \((E \leftrightarrow E)\) Fermi resonance.**

In section G, we used a simple two-level system to derive expressions for difference in zero-order energy \((\epsilon_1 - \epsilon_2)\) and anharmonic coupling constant \((J)\). In the main manuscript, Fermi resonance between \((E \leftrightarrow E)\) were also observed. In this section, we will attempt to provide the working equations to extract \(\epsilon_1 - \epsilon_2\) and \(J\).

**Part 1: The form of the Hamiltonian matrix**

We will begin with the following \(4 \times 4\) Hamiltonian matrix in the \([1], [2], [3], [4]\) representation.

\[
H = \begin{bmatrix}
\epsilon_1 & 0 & w & x \\
0 & \epsilon_1 & y & z \\
w & y & \epsilon_2 & 0 \\
x & z & 0 & \epsilon_2
\end{bmatrix}
\] (28)

Where the zero elements are a consequence of ensuring that the basis for the degenerate diagonal elements is orthogonal. The secular determinant can be written as

\[
\det[H - E] = \begin{vmatrix}
\epsilon_1 - E & 0 & w & x \\
0 & \epsilon_1 - E & y & z \\
w & y & \epsilon_2 - E & 0 \\
x & z & 0 & \epsilon_2 - E
\end{vmatrix} = \begin{bmatrix} A & C^T \\ C & B \end{bmatrix} = 0
\] (29)

Where \(A, C, C^T,\) and \(B\) block matrices defined as

\[
A = \begin{bmatrix}
\epsilon_1 - E & 0 \\
0 & \epsilon_1 - E
\end{bmatrix}, \quad
B = \begin{bmatrix}
\epsilon_2 - E & 0 \\
0 & \epsilon_2 - E
\end{bmatrix}, \quad
C = \begin{bmatrix}
w & y \\
x & z
\end{bmatrix}, \quad
C^T = \begin{bmatrix}
w & x \\
y & z
\end{bmatrix}
\] (30)

Since \(B\) is an invertible matrix, then
\[
\det |H - E\rangle = \det \begin{bmatrix} A & C^T \\ C & B \end{bmatrix} = \det \left( B \right) \det \left( A - C^T B^T C \right) = 0 
\] (31)

\[
A - C^T B^T C = \begin{bmatrix} \varepsilon_1 - E & 0 \\ 0 & \varepsilon_1 - E \end{bmatrix} - \begin{bmatrix} w & x \\ y & z \end{bmatrix} \begin{bmatrix} \frac{1}{\varepsilon_2 - E} & 0 \\ 0 & \frac{1}{\varepsilon_2 - E} \end{bmatrix} \begin{bmatrix} w & y \\ x & z \end{bmatrix}
\]

\[
= \left( \varepsilon_1 - E \right) - \frac{w^2 + x^2}{\varepsilon_2 - E} \quad \frac{-\left( wy + xz \right)}{\varepsilon_2 - E}
\]

\[
= \left( \varepsilon_1 - E \right) - \frac{-\left( wy + xz \right)}{\varepsilon_2 - E}
\]

So the determinant is

\[
\det |H - E\rangle = \det \left( B \right) \det \left( A - C^T B^T C \right)
\]

\[
= \left( \varepsilon_1 - E \right)^2 \left[ \left( \varepsilon_1 - E \right) - \frac{w^2 + x^2}{\varepsilon_2 - E} \right] \left[ \left( \varepsilon_1 - E \right) - \frac{y^2 + z^2}{\varepsilon_2 - E} \right] - \left( \frac{wy + xz}{\varepsilon_2 - E} \right)^2
\]

\[
= \left[ \left( \varepsilon_1 - E \right) \left( \varepsilon_2 - E \right) - \left( w^2 + x^2 \right) \right] \left[ \left( \varepsilon_1 - E \right) \left( \varepsilon_2 - E \right) - \left( y^2 + z^2 \right) \right] - \left( wy + xz \right)^2 = 0
\] (33)

This produces a characteristic polynomial of degree 4. To obtain two distinct eigenvalues each having a multiplicity of two, the easiest way is to vanish the last term.

\[
w y + x z = 0
\] (34)

There are many possible solutions for this. However, the coupling experienced by the representation \( \phi_1 \) and \( \phi_2 \) with \( \phi_3 \) and \( \phi_4 \) must be the same. Thus

\[
|w| = |z| \quad \text{and} \quad |y| = |x|
\] (35)

By imposing the condition in equations (34) and (35), the secular determinant takes the following form

\[
\det |H - E\rangle = \left[ \left( \varepsilon_1 - E \right) \left( \varepsilon_2 - E \right) - \left( w^2 + x^2 \right) \right] \left[ \left( \varepsilon_1 - E \right) \left( \varepsilon_2 - E \right) - \left( y^2 + z^2 \right) \right] = 0
\] (36)

Now, this looks very familiar. It is just the square of the characteristic polynomial for a two-level system with an off-diagonal element of \( J = \sqrt{w^2 + x^2} \). Its eigenvalues will be given by equation (5). From here, it follows that the Hamiltonian can be recast in the following form
\[
H = \begin{bmatrix}
\varepsilon_1 & J & 0 & 0 \\
J & \varepsilon_2 & 0 & 0 \\
0 & 0 & \varepsilon_1 & J \\
0 & 0 & J & \varepsilon_2
\end{bmatrix}
\] (37)

From here expressions for \( \varepsilon_1 - \varepsilon_2 \) and \( J \) can be determined using the derived relationships in equations (18) and (20).

**Part 2: An illustrative example**

Consider the following \( 4 \times 4 \) Hamiltonian.

\[
H = \begin{bmatrix}
7 & -3\sqrt{3} & 0 & 0 \\
-3\sqrt{3} & 13 & 0 & 0 \\
0 & 0 & 7 & -3\sqrt{3} \\
0 & 0 & -3\sqrt{3} & 13
\end{bmatrix}
\] (38)

Its corresponding secular determinant is

\[
\det[H - E I] = \begin{vmatrix}
7 - E & -3\sqrt{3} & 0 & 0 \\
-3\sqrt{3} & 13 - E & 0 & 0 \\
0 & 0 & 7 - E & -3\sqrt{3} \\
0 & 0 & -3\sqrt{3} & 13 - E
\end{vmatrix} = 0
\] (39)

Using equation (5) the eigenvalues are 4 and 16. Each of these roots have a multiplicity of two. The eigenvectors take the following form.

\[
|\alpha\rangle = \frac{\sqrt{3}}{2} |1\rangle + \frac{1}{2} |2\rangle \\
|\beta\rangle = -\frac{1}{2} |1\rangle + \frac{\sqrt{3}}{2} |2\rangle \\
|\gamma\rangle = \frac{\sqrt{3}}{2} |3\rangle + \frac{1}{2} |4\rangle \\
|\eta\rangle = -\frac{1}{2} |3\rangle + \frac{\sqrt{3}}{2} |4\rangle
\] (40)

These eigenvectors can be grouped into two degenerate pairs: \( (|\alpha\rangle, |\gamma\rangle) \) and \( (|\beta\rangle, |\eta\rangle) \). Furthermore,

\[
v_{\alpha-0} = v_{\gamma-0} = 4 \\
v_{\beta-0} = v_{\eta-0} = 16
\] (41)
If we set the transition dipole moments as follows:

\[
\langle 0 | \mu | 1 \rangle = \langle 0 | \mu | 3 \rangle = 100 \quad \text{and} \quad \langle 0 | \mu | 2 \rangle = \langle 0 | \mu | 4 \rangle = 0 \\
\langle 0 | \mu | \alpha \rangle = \langle 0 | \mu | \gamma \rangle = 50\sqrt{3} \quad \text{and} \quad \langle 0 | \mu | \beta \rangle = \langle 0 | \mu | \eta \rangle = -50
\]  \hspace{1cm} (42)

Then the integrated absorption coefficients for the 4 cm\(^{-1}\) and 16 cm\(^{-1}\) transitions are

\[
\frac{A_{\text{4cm}^{-1}}}{A_{\text{16cm}^{-1}}} = \frac{\nu_{\beta \rightarrow \alpha} |\langle 0 | \mu | \beta \rangle|^2 + \nu_{\eta \rightarrow \alpha} |\langle 0 | \mu | \eta \rangle|^2}{\nu_{\alpha \rightarrow \alpha} |\langle 0 | \mu | \alpha \rangle|^2 + \nu_{\gamma \rightarrow \gamma} |\langle 0 | \mu | \gamma \rangle|^2} = \left( \frac{16}{4} \right) \left( \frac{-50}{50\sqrt{3}} \right)^2 = \frac{4}{3}
\]  \hspace{1cm} (43)

Thus, if we supposed to have a e-e type Fermi resonance, which leads to two peak positions at 4 and 16 units; their intensity ratio is \( \frac{4}{3} \). Then using equation (27), we can get the difference in zero-order energies and coupling constant \( J \).