Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information for

Tuning the Vibrational Coupling of H_3O^+ by Changing Its Solvation Environment

Jake A. Tan [abc], *Jheng-Wei Li* [ad], *Cheng-chau Chiu* [a], *Hsin-Yi Liao* [e], *Hai Thi Huynh* [a], and *Jer-Lai Kuo* [acd*†]

[a] Institute of Atomic and Molecular Sciences, Academia Sinica, No.1 Roosevelt Road, Section 4, Taipei 10617, Taiwan (ROC)

[b] Department of Chemistry, National Tsing Hua University, 101 Kuang-Fu Road, Section 2, Hsinchu 30013, Taiwan (ROC)

[c] Molecular Science and Technology Program, Taiwan International Graduate Program, Academia Sinica, 128 Academia Road, Section 2, Nangang, Taipei 115, Taiwan (ROC)

[d] Department of Physics, National Taiwan University, No.1 Roosevelt Road, Section 4, Taipei 10617, Taiwan (ROC)

[e] Department of Science Education, National Taipei University of Education, No.134, Section 2, Heping E. Rd., Da-an District, Taipei City 106, Taiwan (ROC)

AUTHOR INFORMATION

Corresponding Author

* E-mail: jlkuo@pub.iams.sinica.edu.tw

Present Addresses

† Institute of Atomic and Molecular Sciences, Academia Sinica, No. 1 Roosevelt Road, Section 4, Taipei 10617, Taiwan (ROC)

Table of Contents

A. Minimum structures for the singlet H_3O^+•Rg_3 (Rg=Ne, Ar, Kr, and Xe).

Table S1. Cartesian coordinates in Angstroms for the minimum structures of singlet H_3O^+•Rg_3 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.

H_3O^+•Ne_3			
	X	Y	Z
O	0.000401	-0.000165	0.553918
H	-0.337567	0.874636	0.255860
H	-0.588314	-0.730178	0.255869
H	0.926883	-0.144921	0.255564
Ne	-1.016100	2.629071	-0.173242
Ne	-1.769668	-2.194016	-0.173272
Ne	2.785347	-0.434876	-0.173350
H_3O^+•Ar_3			
	X	Y	Z
O	0.000734	0.000007	0.744866
H	0.939151	-0.059257	0.437176
H	-0.417269	0.842395	0.437512
H	-0.519913	-0.783145	0.437615
Ar	3.022460	-0.190398	-0.134943
Ar	-1.346476	2.711533	-0.134855
Ar	-1.676420	-2.521138	-0.134159
H_3O^+•Kr_3			
	X	Y	Z
O	-0.000128	-0.000385	0.838224
H	0.802715	-0.491688	0.52211

H	0.023879	0.940561	0.522119
H	-0.827109	-0.450100	0.522412
Kr	2.651749	-1.622940	-0.0766
Kr	0.080074	3.107370	-0.076574
Kr	-2.731781	-1.484310	-0.076615
H_3O^+•Xe_3			
	X	Y	Z
O	-0.000041	-0.000052	0.944159
H	-0.930699	-0.140529	0.616803
H	0.586962	-0.735766	0.616785
H	0.343623	0.876193	0.616898
Xe	-3.232500	-0.488039	-0.05805
Xe	2.038921	-2.555341	-0.058048
Xe	1.193588	3.043389	-0.058046

B. Symmetry species for the vibrational normal modes of H_3O^+•Rg_3

We briefly describe the group theoretical treatment to determine the symmetry species of the vibrational normal modes for H_3O^+•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:

C_{3v}	E	$2C_3$	$3\sigma_v$	Linear functions
A_1	1	1	1	z
A_2	1	1	-1	R_z
E	2	-1	0	(x,y) (R_x,R_y)

Determination of the reducible representation

C_{3v}	E	$2C_3$	$3\sigma_v$	Comment
Determination of $\Gamma_{total} = \Gamma_{3N}$				
Γ_{trans}	3	0	1	A_1+E
Γ_n	7	1	3	unmoved atoms
Γ_{3N}	21	0	3	$\Gamma_{3N} \otimes \Gamma_n$
Determination of Γ_{vib}				
Γ_{3N}	21	0	3	
Γ_{trans}	3	0	1	
Γ_{rot}	3	0	-1	

$\boldsymbol{\Gamma_{vib}}$	15	0	3	$\Gamma_{3N} - \Gamma_{trans} - \Gamma_{rot}$
Determination of $\boldsymbol{\Gamma_{stretch}}$ and $\boldsymbol{\Gamma_{bend}}$				
$\boldsymbol{\Gamma_{vib}}$	15	0	3	
$\boldsymbol{\Gamma_{n}}$	7	1	3	unmoved atoms
A_1	1	1	1	A_1
$\boldsymbol{\Gamma_{stretch}}$	6	0	2	$\Gamma_n - A_1$
$\boldsymbol{\Gamma_{bend}}$	9	0	1	$\Gamma_{vib} - \Gamma_{stretch}$

By either inspection or use of the standard decomposition formula.

$$\Gamma_{stretch} = 2A_1 + 2E \qquad and \qquad \Gamma_{bend} = 2A_1 + A_2 + 3E$$

Table S2. Symmetry species for the 15 normal modes of H_3O^+•Rg_3

Symmetry Classification for the Normal Modes of H_3O^+•Rg_3			
	Symmetry Species	G09 mode #	Description
$\boldsymbol{\Gamma_{stretch}}$	A_1	4	Symmetric Rg_3 stretching
		13	Symmetric H_3O^+ stretching
	E	1 and 2	Asymmetric Rg_3 stretching
		14 and 15	Asymmetric H_3O^+ stretching
$\boldsymbol{\Gamma_{bend}}$	A_1	3	H_3O^+ as one unit bending ⊥ to Rg_3 plane
		10	H_3O^+ umbrella motion
	A_2	7	H_3O^+ hindered rotation
	E	5 and 6	Degenerate H_3O^+ swinging above the Rg_3 plane
		8 and 9	Degenerate H_3O^+ deformation
		11 and 12	Degenerate H_3O^+ bending

C. Harmonic frequencies in $\mathbf{cm^{-1}}$ and intensities in km/mol for $\mathbf{H_3O^+}$•$\mathbf{Rg_3}$ (Rg=Ne, Ar, Kr, and Xe) at MP2/aug-cc-pVDZ.

Table S3. Harmonic frequencies (ω_e) and absorption intensities in km/mol for the 15 normal modes of H_3O^+•Rg_3.

Normal Mode Numbering		H_3O^+•Ne_3		H_3O^+•Ar_3		H_3O^+•Kr_3		H_3O^+•Xe_3	
Herzberg Order	G09 output	ω_e (cm^{-1})	Inten. (km/mol)	ω_e (cm^{-1})	Inten. (km/mol)	ω_e (cm^{-1})	Inten. (km/mol)	ω_e (cm^{-1})	Inten. (km/mol)
ν_{10}	1	21.3	4.33	19.4	1.65	14.5	0.75	11.2	0.38
	2	21.3	4.33	19.4	1.65	14.5	0.75	11.2	0.38
ν_4	3	35.8	20.45	36.3	8.64	31.1	4.30	24.8	2.12
ν_3	4	92.7	7.26	99.2	11.11	95.2	12.40	92.8	10.85
ν_9	5	131.2	34.57	150.5	55.74	162.3	61.92	164.1	62.52
	6	131.2	34.60	150.6	55.82	162.4	61.96	164.1	62.53

ν_5	7	255.1	0.00	338.4	0.00	398.5	0.00	419.7	0.00
ν_8	8	263.6	87.12	368.2	69.72	427.9	65.65	453.7	60.85
	9	263.6	87.15	368.2	69.63	428.0	65.58	453.7	60.89
ν_2	10	917.4	354.05	962.1	226.50	991.8	166.59	1016.2	113.11
ν_7	11	1679.7	65.98	1668.9	25.18	1661.6	10.80	1649.5	2.69
	12	1679.7	66.01	1669.0	25.14	1661.6	10.86	1649.5	2.70
ν_1	13	3528.0	54.26	3418.9	103.19	3354.6	128.97	3291.8	158.27
ν_6	14	3634.2	748.54	3491.9	1410.93	3406.3	1879.68	3322.5	2456.17
	15	3634.2	1.09	3491.9	1.09	3406.4	1.09	3322.6	1.09

D. Harmonic frequencies in cm^{-1} and intensities in km/mol for D_3O^+•Rg_3 (Rg=Ne, Ar, Kr, and Xe) at MP2/aug-cc-pVDZ.

Table S4. Harmonic frequencies (ω_e) and absorption intensities in km/mol for the 15 normal modes of D_3O^+•Rg_3.

Normal Mode Numbering		D_3O^+•Ne_3		D_3O^+•Ar_3		D_3O^+•Kr_3		D_3O^+•Xe_3	
Herzberg Order	G09 output	ω_e (cm^{-1})	Inten. (km/mol)	ω_e (cm^{-1})	Inten. (km/mol)	ω_e (cm^{-1})	Inten. (km/mol)	ω_e (cm^{-1})	Inten. (km/mol)
ν_{10}	1	21.1	3.91	19.3	1.53	14.5	0.72	11.1	0.36
	2	21.1	3.91	19.3	1.53	14.5	0.72	11.1	0.36
ν_4	3	34.3	17.42	35.1	7.72	30.4	4.04	24.4	2.02
ν_3	4	91.7	5.68	96.9	9.07	91.6	10.4	88.5	9.23
ν_9	5	126.3	30.64	143.2	50.02	153.2	55.72	154.4	56.26
	6	126.4	30.68	143.2	50.09	153.3	55.75	154.4	56.27
ν_5	7	180.9	0.00	239.7	0.00	282.0	0.00	297.0	0.00
ν_8	8	187.6	38.29	262.1	28.22	304.5	26.04	322.9	23.97
	9	187.7	38.3	262.1	28.2	304.6	26.01	322.9	23.98
ν_2	10	691.9	162.6	723.5	103.2	744.9	75.37	763.3	50.4
ν_7	11	1217.1	22.12	1207.7	4.98	1201.6	0.77	1192.3	0.17
	12	1217.1	22.13	1207.7	4.98	1201.6	0.78	1192.3	0.16
ν_1	13	2511.3	28.92	2434.8	53.81	2389.8	66.79	2346.1	81.45
ν_6	14	2672.3	377.46	2570.4	709.69	2508.2	947.5	2446.6	1243.08
	15	2672.3	377.34	2570.5	709.4	2508.2	947.37	2446.6	1242.95

E. RDAV-6D frequencies and integrated absorption coefficients for the hydrons (H_3O^+•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_3O^+•Rg_3.

$\lvert\Psi_k\rangle$	**H_3O^+•Ne_3**		**H_3O^+•Ar_3**		**H_3O^+•Kr_3**		**H_3O^+•Xe_3**	
	cm^{-1}	km/mol	cm^{-1}	km/mol	cm^{-1}	km/mol	cm^{-1}	km/mol
1	226.80	0.0	335.84	0.0	386.59	0.0	416.23	0.0
2	440.34	1.6	652.23	2.2	752.97	2.4	813.98	2.4
3	651.72	0.0	952.60	0.0	1102.61	0.0	1193.95	0.0
4	894.15	0.0	1267.65	0.0	1455.64	0.0	1566.76	0.0
5	1216.99	0.0	1607.19	38.7	1596.02	20.0	1580.71	7.8

6	1618.60	86.7	1607.26	38.8	1596.13	20.1	1580.78	7.8
7	1618.63	86.7	1610.12	0.0	1822.04	0.0	1934.64	0.0
8	1713.67	0.0	1929.85	34.3	1969.14	51.4	1983.38	73.2
9	1833.70	12.8	1929.88	34.3	1969.22	51.3	1983.42	73.3
10	1833.74	12.8	2173.97	0.0	2162.96	0.0	2271.78	0.0
11	2039.07	0.1	2234.76	0.0	2323.64	0.0	2368.97	0.0
12	2039.12	0.1	2234.78	0.0	2323.69	0.0	2368.98	0.0
13	2247.42	0.1	2527.06	0.5	2334.13	0.0	2479.21	0.0
14	2247.52	0.2	2527.08	0.5	2663.99	1.0	2738.71	2.4
15	2482.37	0.0	2552.00	0.0	2664.01	1.0	2738.71	2.4
16	2482.45	0.0	2602.51	0.0	2777.86	0.0	2955.69	0.0
17	2761.19	0.0	2834.28	0.0	3009.95	0.0	3019.51	2467.5
18	2761.24	0.0	2834.30	0.0	3009.96	0.0	3020.27	2467.2
19	3208.79	5.7	3165.29	58.5	3108.21	125.0	3031.97	168.3
20	3224.84	33.9	3178.84	9.7	3118.18	1595.7	3103.10	0.0
21	3226.76	34.6	3178.86	7.0	3118.64	1601.9	3103.11	0.0
22	3283.91	0.0	3184.21	482.3	3187.46	23.1	3148.15	8.1
23	3283.97	0.0	3185.52	496.4	3207.80	434.5	3165.09	142.8
24	3352.68	60.8	3231.86	61.4	3209.46	416.6	3166.83	141.0
25	3412.71	0.0	3268.73	1045.0	3375.88	0.0	3457.23	0.1
26	3429.14	115.1	3269.62	1032.9	3375.90	0.0	3457.82	0.1
27	3429.70	197.6	3488.14	0.0	3500.05	0.0	3463.02	0.0
28	3432.03	624.9	3504.56	0.4	3511.84	0.3	3468.14	0.0
29	3432.16	619.5	3505.63	0.4	3512.61	0.3	3468.14	0.0

F. RDAV-6D frequencies and integrated absorption coefficients for the deuterons (D_3O^+•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_3O^+•Rg_3.

$\vert\Psi_k\rangle$	**D_3O^+•Ne_3**		**D_3O^+•Ar_3**		**D_3O^+•Kr_3**		**D_3O^+•Xe_3**	
	cm^{-1}	km/mol	cm^{-1}	km/mol	cm^{-1}	km/mol	cm^{-1}	km/mol
1	165.97	0.0	239.94	0.0	275.40	0.0	295.45	0.0
2	321.04	0.6	471.60	0.8	541.31	0.9	582.39	0.9
3	471.55	0.0	696.53	0.0	797.37	0.0	859.85	0.0
4	640.72	0.0	924.83	0.0	1045.37	0.0	1126.97	0.0
5	827.96	0.0	1161.65	0.0	1166.69	2.9	1155.40	0.2
6	1170.21	0.0	1175.06	9.2	1166.75	2.9	1155.42	0.2
7	1183.98	30.4	1175.11	9.2	1278.92	0.0	1376.87	0.0
8	1184.00	30.4	1403.87	0.0	1436.07	16.1	1444.85	22.4
9	1344.11	4.2	1409.09	11.0	1436.11	16.1	1444.86	22.4
10	1344.13	4.2	1409.12	11.0	1490.21	0.0	1607.51	0.0
11	1494.64	0.0	1501.83	0.0	1668.21	0.0	1726.11	0.0
12	1494.67	0.0	1635.30	0.0	1696.36	0.0	1726.11	0.0
13	1647.76	0.0	1635.33	0.0	1696.39	0.0	1812.95	0.0
14	1649.91	0.0	1728.12	0.0	1947.50	0.1	1998.39	0.2
15	1808.47	0.0	1855.81	0.1	1947.51	0.1	1998.40	0.2
16	1808.52	0.0	1855.83	0.1	2044.80	0.0	2213.22	85.4
17	1983.01	0.0	2080.74	0.0	2191.34	0.0	2215.73	0.0

18	1993.08	0.0	2080.76	0.0	2191.34	0.0	2260.89	0.0
19	1998.25	0.0	2308.44	44.5	2264.76	68.3	2260.90	0.0
20	1998.29	0.0	2318.05	0.0	2316.51	243.7	2272.22	882.2
21	2329.82	0.0	2318.06	0.0	2317.13	249.2	2272.36	879.0
22	2329.86	0.0	2340.16	64.3	2330.96	6.5	2303.91	3.0
23	2348.69	4.7	2340.80	65.0	2380.19	760.7	2325.97	412.4
24	2361.25	9.4	2355.49	17.4	2380.36	757.3	2325.99	415.2
25	2361.83	9.5	2444.22	701.1	2422.63	0.1	2507.65	0.0
26	2423.39	30.9	2444.36	700.4	2422.65	0.1	2507.67	0.0
27	2505.18	0.0	2548.23	0.0	2545.79	0.0	2516.26	0.0
28	2515.94	0.1	2557.08	0.0	2584.36	0.0	2569.72	0.0
29	2517.07	0.1	2557.12	0.0	2584.96	0.0	2569.76	0.0

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 2×2 Hamiltonian in the $\{|1\rangle,|2\rangle\}$ representation. The matrix elements are expressed as

$$\begin{aligned}\langle 1|\mathbf{H}|1\rangle &= \varepsilon_1 \qquad & \langle 1|\mathbf{H}|2\rangle &= J \\ \langle 2|\mathbf{H}|1\rangle &= J \qquad & \langle 2|\mathbf{H}|2\rangle &= \varepsilon_2\end{aligned} \tag{1}$$

Furthermore, we impose that $\varepsilon_1 \leq \varepsilon_2$. The 2×2 Hamiltonian is written as

$$\mathbf{H} = \begin{bmatrix} \varepsilon_1 & J \\ J & \varepsilon_2 \end{bmatrix} \qquad \varepsilon_1 \leq \varepsilon_2 \tag{2}$$

Solving the secular determinant, we have

$$\begin{aligned}&\det|\mathbf{H}-\mathbf{E1}| = \begin{vmatrix} \varepsilon_1 - E & J \\ J & \varepsilon_2 - E \end{vmatrix} = 0 \\ &(\varepsilon_1 - E)(\varepsilon_2 - E) - J^2 = 0 \\ &E^2 - (\varepsilon_1 + \varepsilon_2)E + \varepsilon_1\varepsilon_2 - d^2 = 0\end{aligned} \tag{3}$$

The roots, which are the eigenvalues can be obtained using the quadratic formula.

$$E_1 = \frac{(\varepsilon_1 + \varepsilon_2) - \sqrt{(\varepsilon_1 + \varepsilon_2)^2 - 4\left(\varepsilon_1\varepsilon_2 - J^2\right)}}{2} \quad \text{and} \quad E_2 = \frac{(\varepsilon_1 + \varepsilon_2) + \sqrt{(\varepsilon_1 + \varepsilon_2)^2 - 4\left(\varepsilon_1\varepsilon_2 - J^2\right)}}{2} \tag{4}$$

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

$$E_1 = \frac{(\varepsilon_1 + \varepsilon_2) - \sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4J^2}}{2} \quad \text{and} \quad E_2 = \frac{(\varepsilon_1 + \varepsilon_2) + \sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4J^2}}{2} \tag{5}$$

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.

$$\begin{aligned} |\alpha\rangle &= \cos\theta|1\rangle + \sin\theta|2\rangle \\ |\beta\rangle &= -\sin\theta|1\rangle + \cos\theta|2\rangle \end{aligned} \tag{6}$$

To determine the eigenstates, we need to know θ . Collecting the coefficients of the eigenvectors $|\alpha\rangle$ and $|\beta\rangle$to a matrix $\mathbf{S}$.

$$\mathbf{S} = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix} \tag{7}$$

This matrix satisfies the matrix equation $\mathbf{HS} = \mathbf{SE}$. From here the 2×2 Hamiltonian can be diagonalize by a similarity transformation.

$$\begin{aligned} &\mathbf{E} = \mathbf{S}^{-1}\mathbf{HS} \\ &\begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} \varepsilon_1 & J \\ J & \varepsilon_2 \end{bmatrix} \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix} \\ &\begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} = \begin{bmatrix} \varepsilon_1 \cos^2\theta + \varepsilon_2 \sin^2\theta + 2J\cos\theta\sin\theta & J\left(\cos^2\theta - \sin^2\theta\right) + \left(\varepsilon_2 - \varepsilon_1\right)\cos\theta\sin\theta \\ J\left(\cos^2\theta - \sin^2\theta\right) + \left(\varepsilon_2 - \varepsilon_1\right)\cos\theta\sin\theta & \varepsilon_2 \cos^2\theta + \varepsilon_1 \sin^2\theta + 2J\cos\theta\sin\theta \end{bmatrix} \end{aligned} \tag{8}$$

Equating the off diagonal elements yields

$$J\left(\cos^2\theta - \sin^2\theta\right) + \left(\varepsilon_2 - \varepsilon_1\right)\cos\theta\sin\theta = 0 \tag{9}$$

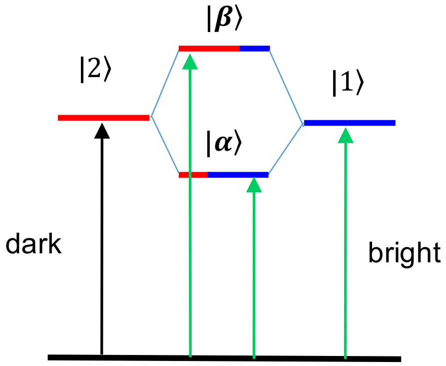
Multiply equation (9) by 2 on both sides, and using the following trigonometric identities, we have

$$\begin{aligned} \cos 2x &= \cos^2 x - \sin^2 x \\ \sin 2x &= 2\cos x \sin x \end{aligned} \tag{10}$$

$$
\begin{aligned}
&2J\cos 2\theta + \left(\varepsilon_2 - \varepsilon_1\right)\sin 2\theta = 0 \\
&\tan 2\theta = \frac{-2J}{\varepsilon_2 - \varepsilon_1} = \frac{2J}{\varepsilon_1 - \varepsilon_2} \\
&\theta = \frac{1}{2}\arctan\left(\frac{2J}{\varepsilon_1 - \varepsilon_2}\right)
\end{aligned} \tag{11}
$$

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_{fi}.
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 $|1\rangle \leftarrow |0\rangle$ and $|2\rangle \leftarrow |0\rangle$ are

$$\left\langle 0 \middle| \boldsymbol{\mu} \middle| 1 \right\rangle \neq 0 \qquad \text{and} \qquad \left\langle 0 \middle| \boldsymbol{\mu} \middle| 2 \right\rangle = 0 \tag{12}$$

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

$$\begin{aligned} \left\langle 0 \middle| \boldsymbol{\mu} \middle| \alpha \right\rangle &= \cos\theta \left\langle 0 \middle| \boldsymbol{\mu} \middle| 1 \right\rangle + \sin\theta \left\langle 0 \middle| \boldsymbol{\mu} \middle| 2 \right\rangle = \cos\theta \left\langle 0 \middle| \boldsymbol{\mu} \middle| 1 \right\rangle \\ \left\langle 0 \middle| \boldsymbol{\mu} \middle| \beta \right\rangle &= -\sin\theta \left\langle 0 \middle| \boldsymbol{\mu} \middle| 1 \right\rangle + \cos\theta \left\langle 0 \middle| \boldsymbol{\mu} \middle| 2 \right\rangle = -\sin\theta \left\langle 0 \middle| \boldsymbol{\mu} \middle| 1 \right\rangle \end{aligned} \tag{13}$$

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

$$\begin{aligned} A_{\beta\leftarrow 0} &= \left(\frac{\pi N_A}{3c\varepsilon_0} \right) \nu_{\beta\leftarrow 0} \left| \langle 0 | \hat{\boldsymbol{\mu}} | \beta \rangle \right|^2 \\ A_{\alpha\leftarrow 0} &= \left(\frac{\pi N_A}{3c\varepsilon_0} \right) \nu_{\alpha\leftarrow 0} \left| \langle 0 | \hat{\boldsymbol{\mu}} | \alpha \rangle \right|^2 \end{aligned} \tag{14}$$

Taking their ratio, we have

$$\begin{aligned} \frac{A_{\beta\leftarrow 0}}{A_{\alpha\leftarrow 0}} &= \frac{\left(\frac{\pi N_A}{3c\varepsilon_0} \right) \nu_{\beta\leftarrow 0} \left| \langle 0 | \hat{\boldsymbol{\mu}} | \beta \rangle \right|^2}{\left(\frac{\pi N_A}{3c\varepsilon_0} \right) \nu_{\alpha\leftarrow 0} \left| \langle 0 | \hat{\boldsymbol{\mu}} | \alpha \rangle \right|^2} = \frac{\nu_{\beta\leftarrow 0} \left| \langle 0 | \hat{\boldsymbol{\mu}} | \beta \rangle \right|^2}{\nu_{\alpha\leftarrow 0} \left| \langle 0 | \hat{\boldsymbol{\mu}} | \alpha \rangle \right|^2} = \left(\frac{\nu_{\beta\leftarrow 0}}{\nu_{\alpha\leftarrow 0}} \right) \left(\frac{\sin^2\theta}{\cos^2\theta} \right) \left| \frac{\left\langle 0 \middle| \boldsymbol{\mu} \middle| 1 \right\rangle}{\left\langle 0 \middle| \boldsymbol{\mu} \middle| 1 \right\rangle} \right|^2 \\ &= \left(\frac{\nu_{\beta\leftarrow 0}}{\nu_{\alpha\leftarrow 0}} \right) \tan^2\theta \end{aligned} \tag{15}$$

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

$$\begin{aligned} \tan 2\theta &= \frac{2J}{\varepsilon_1 - \varepsilon_2} \\ \tan^2\theta &= \left(\frac{A_{\beta\leftarrow 0}}{A_{\alpha\leftarrow 0}} \right) \left(\frac{\nu_{\alpha\leftarrow 0}}{\nu_{\beta\leftarrow 0}} \right) \end{aligned} \tag{16}$$

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

$$\frac{2J}{\varepsilon_1 - \varepsilon_2} = \frac{2\sqrt{\left(\frac{A_{\beta\leftarrow 0}}{A_{\alpha\leftarrow 0}}\right)\left(\frac{\nu_{\alpha\leftarrow 0}}{\nu_{\beta\leftarrow 0}}\right)}}{1-\left(\frac{A_{\beta\leftarrow 0}}{A_{\alpha\leftarrow 0}}\right)\left(\frac{\nu_{\alpha\leftarrow 0}}{\nu_{\beta\leftarrow 0}}\right)} \tag{17}$$

We can simplify the expression by defining z and Q.

$$\begin{aligned} &\frac{2J}{\varepsilon_1 - \varepsilon_2} = Q \\ &Q \equiv \frac{2z}{1-z^2} \qquad \text{and} \quad z \equiv \sqrt{\left(\frac{A_{\beta\leftarrow 0}}{A_{\alpha\leftarrow 0}}\right)\left(\frac{\nu_{\alpha\leftarrow 0}}{\nu_{\beta\leftarrow 0}}\right)} \end{aligned} \tag{18}$$

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

$$\Delta E = E_2 - E_1 = \nu_{\beta\leftarrow 0} - \nu_{\alpha\leftarrow 0} = \sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4J^2} \tag{19}$$

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

$$\begin{aligned} &4J^2 = Q^2(\varepsilon_1 - \varepsilon_2)^2 \\ &(\Delta E)^2 = (\varepsilon_1 - \varepsilon_2)^2 + 4J^2 \Rightarrow (\Delta E)^2 = (\varepsilon_1 - \varepsilon_2)^2 + Q^2(\varepsilon_1 - \varepsilon_2)^2 \\ &\therefore \varepsilon_1 - \varepsilon_2 = -\sqrt{\frac{(\Delta E)^2}{1+Q^2}} = -\sqrt{\frac{(\nu_{\beta\leftarrow 0} - \nu_{\alpha\leftarrow 0})^2}{1+Q^2}} \qquad \text{and} \qquad J = \frac{Q(\varepsilon_1 - \varepsilon_2)}{2} \end{aligned} \tag{20}$$

Where the negative root was taken as we imposed $\varepsilon_1 \le \varepsilon_2$ in equation (2).

Part 3: Method Validation

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

$$\mathbf{H} = \begin{bmatrix} 7 & -3\sqrt{3} \\ -3\sqrt{3} & 13 \end{bmatrix} \tag{21}$$

Using equation 5, its corresponding eigenvalues are

$$E_1 = \frac{(7+13)-\sqrt{(7-13)^2+4\left(-3\sqrt{3}\right)^2}}{2} = 4 \qquad \text{and} \qquad E_2 = \frac{(7+13)+\sqrt{(7-13)^2+4\left(-3\sqrt{3}\right)^2}}{2} = 16 \quad (22)$$

The eigenvectors can be obtained using equations (6) and (11).

$$\begin{aligned}
&\theta = \frac{1}{2}\arctan\left(\frac{-6\sqrt{3}}{7-13}\right) = 30^o \\
&\cos\theta = \frac{\sqrt{3}}{2} \qquad \text{and} \qquad \sin\theta = \frac{1}{2} \\
&|\alpha\rangle = \frac{\sqrt{3}}{2}|1\rangle + \frac{1}{2}|2\rangle \\
&|\beta\rangle = -\frac{1}{2}|1\rangle + \frac{\sqrt{3}}{2}|2\rangle
\end{aligned} \qquad (23)$$

If we set the following transition dipole moments,

$$\begin{aligned}
&\left\langle 0\middle|\boldsymbol{\mu}\middle|1\right\rangle = 100 \qquad \text{and} \qquad \left\langle 0\middle|\boldsymbol{\mu}\middle|2\right\rangle = 0 \\
&\left\langle 0\middle|\boldsymbol{\mu}\middle|\alpha\right\rangle = \cos\theta\left\langle 0\middle|\boldsymbol{\mu}\middle|1\right\rangle = 50\sqrt{3} \qquad \text{and} \qquad \left\langle 0\middle|\boldsymbol{\mu}\middle|\beta\right\rangle = -\sin\theta\left\langle 0\middle|\boldsymbol{\mu}\middle|1\right\rangle = -50
\end{aligned} \qquad (24)$$

Then, their corresponding integrated absorption coefficients for $|\alpha\rangle \leftarrow |0\rangle$ and $|\beta\rangle \leftarrow |0\rangle$ are

$$\frac{A_{\beta\leftarrow 0}}{A_{\alpha\leftarrow 0}} = \frac{\nu_{\beta\leftarrow 0}\,|\langle 0|\hat{\boldsymbol{\mu}}|\beta\rangle|^2}{\nu_{\alpha\leftarrow 0}\,|\langle 0|\hat{\boldsymbol{\mu}}|\alpha\rangle|^2} = \left(\frac{16}{4}\right)\left(\frac{-50}{50\sqrt{3}}\right)^2 = \frac{4}{3} \qquad (25)$$

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

From equation (18), we know that

$$\begin{aligned}
&z = \sqrt{\left(\frac{A_{\beta\leftarrow 0}}{A_{\alpha\leftarrow 0}}\right)\left(\frac{\nu_{\alpha\leftarrow 0}}{\nu_{\beta\leftarrow 0}}\right)} = \sqrt{\left(\frac{4}{3}\right)\left(\frac{4}{16}\right)} = \frac{1}{\sqrt{3}} \\
&Q = \frac{2z}{1-z^2} = \frac{\frac{2}{\sqrt{3}}}{1-\left(\frac{1}{\sqrt{3}}\right)^2} = \sqrt{3}
\end{aligned} \qquad (26)$$

Then by equation (19)

$$\varepsilon_1 - \varepsilon_2 = -\sqrt{\frac{\left(\nu_{\beta\leftarrow 0} - \nu_{\alpha\leftarrow 0}\right)^2}{1+Q^2}} = -\sqrt{\frac{(16-4)^2}{1+3}} = -6$$
$$J = \frac{Q(\varepsilon_1 - \varepsilon_2)}{2} = \frac{\sqrt{3}(-6)}{2} = -3\sqrt{3} \tag{27}$$

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↔E)* Fermi resonance.

In section G, we used a simple two-level system to derive expressions for difference in zero-order energy $(\varepsilon_1 - \varepsilon_2)$ and anharmonic coupling constant (J). In the main manuscript, Fermi resonance between *(E↔E)* were also observed. In this section, we will attempt to provide the working equations to extract $\varepsilon_1 - \varepsilon_2$ and J.

Part 1: The form of the Hamiltonian matrix

We will begin with the following 4×4 Hamiltonian matrix in the $\{|1\rangle,|2\rangle,|3\rangle,|4\rangle\}$ representation.

$$\mathbf{H} = \begin{bmatrix} \varepsilon_1 & 0 & w & x \\ 0 & \varepsilon_1 & y & z \\ w & y & \varepsilon_2 & 0 \\ x & z & 0 & \varepsilon_2 \end{bmatrix} \tag{28}$$

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

$$\det|\mathbf{H}-\mathbf{E1}| = \begin{vmatrix} \varepsilon_1 - E & 0 & w & x \\ 0 & \varepsilon_1 - E & y & z \\ w & y & \varepsilon_2 - E & 0 \\ x & z & 0 & \varepsilon_2 - E \end{vmatrix} = \begin{vmatrix} \mathbf{A} & \mathbf{C^T} \\ \mathbf{C} & \mathbf{B} \end{vmatrix} = 0 \tag{29}$$

Where **A, C, C^T^,** and **B** block matrices defined as

$$A = \begin{bmatrix} \varepsilon_1 - E & 0 \\ 0 & \varepsilon_1 - E \end{bmatrix} \qquad B = \begin{bmatrix} \varepsilon_2 - E & 0 \\ 0 & \varepsilon_2 - E \end{bmatrix} \qquad C = \begin{bmatrix} w & y \\ x & z \end{bmatrix} \qquad C^T = \begin{bmatrix} w & x \\ y & z \end{bmatrix} \tag{30}$$

Since **B** is an invertible matrix, then

$$\det|\mathbf{H}-\mathbf{E1}| = \begin{vmatrix} \mathbf{A} & \mathbf{C}^{\mathrm{T}} \\ \mathbf{C} & \mathbf{B} \end{vmatrix} = \det(\mathbf{B})\det\left(\mathbf{A}-\mathbf{C}^{\mathrm{T}}\mathbf{B}^{-1}\mathbf{C}\right) = 0 \tag{31}$$

$$\begin{aligned} \mathbf{A}-\mathbf{C}^{\mathrm{T}}\mathbf{B}^{-1}\mathbf{C} &= \begin{bmatrix} \varepsilon_1 - E & 0 \\ 0 & \varepsilon_1 - E \end{bmatrix} - \begin{bmatrix} w & x \\ y & z \end{bmatrix} \begin{bmatrix} \dfrac{1}{\varepsilon_2 - E} & 0 \\ 0 & \dfrac{1}{\varepsilon_2 - E} \end{bmatrix} \begin{bmatrix} w & y \\ x & z \end{bmatrix} \\ &= \begin{bmatrix} (\varepsilon_1 - E) - \dfrac{w^2 + x^2}{\varepsilon_2 - E} & \dfrac{-(wy+xz)}{\varepsilon_2 - E} \\ \dfrac{-(wy+xz)}{\varepsilon_2 - E} & (\varepsilon_1 - E) - \dfrac{y^2 + z^2}{\varepsilon_2 - E} \end{bmatrix} \end{aligned} \tag{32}$$

So the determinant is

$$\begin{aligned} &\det|\mathbf{H}-\mathbf{E1}| = \det(\mathbf{B})\det\left(\mathbf{A}-\mathbf{C}^{\mathrm{T}}\mathbf{B}^{-1}\mathbf{C}\right) \\ &= (\varepsilon_2 - E)^2 \left\{ \left[(\varepsilon_1 - E) - \frac{w^2 + x^2}{\varepsilon_2 - E}\right]\left[(\varepsilon_1 - E) - \frac{y^2 + z^2}{\varepsilon_2 - E}\right] - \left[\frac{wy + xz}{\varepsilon_2 - E}\right]^2 \right\} \\ &= \left[(\varepsilon_1 - E)(\varepsilon_2 - E) - (w^2 + x^2)\right]\left[(\varepsilon_1 - E)(\varepsilon_2 - E) - (y^2 + z^2)\right] - (wy + xz)^2 = 0 \end{aligned} \tag{33}$$

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.

$$wy + xz = 0 \tag{34}$$

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

$$|w| = |z| \qquad \text{and} \qquad |y| = |x| \tag{35}$$

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

$$\det|\mathbf{H}-\mathbf{E1}| = \left[(\varepsilon_1 - E)(\varepsilon_2 - E) - (w^2 + x^2)\right]\left[(\varepsilon_1 - E)(\varepsilon_2 - E) - (w^2 + x^2)\right] = 0 \tag{36}$$

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

$$\mathbf{H} = \begin{bmatrix} \varepsilon_1 & J & 0 & 0 \\ J & \varepsilon_2 & 0 & 0 \\ 0 & 0 & \varepsilon_1 & J \\ 0 & 0 & J & \varepsilon_2 \end{bmatrix} \tag{37}$$

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 4×4 Hamiltonian.

$$\mathbf{H} = \begin{bmatrix} 7 & -3\sqrt{3} & 0 & 0 \\ -3\sqrt{3} & 13 & 0 & 0 \\ 0 & 0 & 7 & -3\sqrt{3} \\ 0 & 0 & -3\sqrt{3} & 13 \end{bmatrix} \tag{38}$$

Its corresponding secular determinant is

$$\det\left|\mathbf{H} - \mathbf{E1}\right| = \begin{vmatrix} 7-E & -3\sqrt{3} & 0 & 0 \\ -3\sqrt{3} & 13-E & 0 & 0 \\ 0 & 0 & 7-E & -3\sqrt{3} \\ 0 & 0 & -3\sqrt{3} & 13-E \end{vmatrix} = 0 \tag{39}$$

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

$$\begin{aligned} |\alpha\rangle &= \frac{\sqrt{3}}{2}|1\rangle + \frac{1}{2}|2\rangle \\ |\beta\rangle &= -\frac{1}{2}|1\rangle + \frac{\sqrt{3}}{2}|2\rangle \\ |\gamma\rangle &= \frac{\sqrt{3}}{2}|3\rangle + \frac{1}{2}|4\rangle \\ |\eta\rangle &= -\frac{1}{2}|3\rangle + \frac{\sqrt{3}}{2}|4\rangle \end{aligned} \tag{40}$$

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

$$\begin{aligned} \nu_{\alpha\leftarrow 0} &= \nu_{\gamma\leftarrow 0} = 4 \\ \nu_{\beta\leftarrow 0} &= \nu_{\eta\leftarrow 0} = 16 \end{aligned} \tag{41}$$

If we set the transition dipole moments as follows:

$$\begin{aligned} \langle 0|\boldsymbol{\mu}|1\rangle &= \langle 0|\boldsymbol{\mu}|3\rangle = 100 \qquad \text{and} \qquad \langle 0|\boldsymbol{\mu}|2\rangle = \langle 0|\boldsymbol{\mu}|4\rangle = 0 \\ \langle 0|\boldsymbol{\mu}|\alpha\rangle &= \langle 0|\boldsymbol{\mu}|\gamma\rangle = 50\sqrt{3} \qquad \text{and} \qquad \langle 0|\boldsymbol{\mu}|\beta\rangle = \langle 0|\boldsymbol{\mu}|\eta\rangle = -50 \end{aligned} \tag{42}$$

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

$$\frac{A_{16\leftarrow 0}}{A_{4\leftarrow 0}} = \frac{\nu_{\beta\leftarrow 0}\left|\langle 0|\hat{\boldsymbol{\mu}}|\beta\rangle\right|^2 + \nu_{\eta\leftarrow 0}\left|\langle 0|\hat{\boldsymbol{\mu}}|\eta\rangle\right|^2}{\nu_{\alpha\leftarrow 0}\left|\langle 0|\hat{\boldsymbol{\mu}}|\alpha\rangle\right|^2 + \nu_{\gamma\leftarrow 0}\left|\langle 0|\hat{\boldsymbol{\mu}}|\gamma\rangle\right|^2} = \left(\frac{16}{4}\right)\left(\frac{-50}{50\sqrt{3}}\right)^2 = \frac{4}{3} \tag{43}$$

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 .