## Q1: Explain what is meant by ‘vibrational mode’ of a molecule.

A vibrational mode is a characteristic way in which the atoms in a molecule oscillate about their equilibrium positions. In each mode, all atoms move in a well-defined pattern and with a specific frequency. These modes are called normal modes, and in the harmonic approximation they are independent of each other. ✓

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## Q2: In the first column, the number of the vibrational mode is shown. Why does the list start counting from mode number 6 for non-linear molecules?

For a molecule with N atoms there are 3N nuclear degrees of freedom. For a non-linear molecule, 3 of these correspond to pure translation of the whole molecule and 3 to overall rotation, leaving 3N−6 degrees of freedom for vibrations.
In the frequency analysis, the first 6 modes therefore correspond to 3 translations and 3 rotations and have (ideally) zero frequency. The vibrational modes start only after these, so the program labels the first genuine vibrational mode as mode 6, and the list of vibrational modes begins from there. ✓

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## Q3: How many vibrational modes does a molecule consisting of N atoms have?

A molecule with N atoms has 3N nuclear degrees of freedom. After subtracting overall translation and rotation, the number of vibrational modes is:

3N−6 for a non-linear molecule, 3N−5 for a linear molecule. ✓

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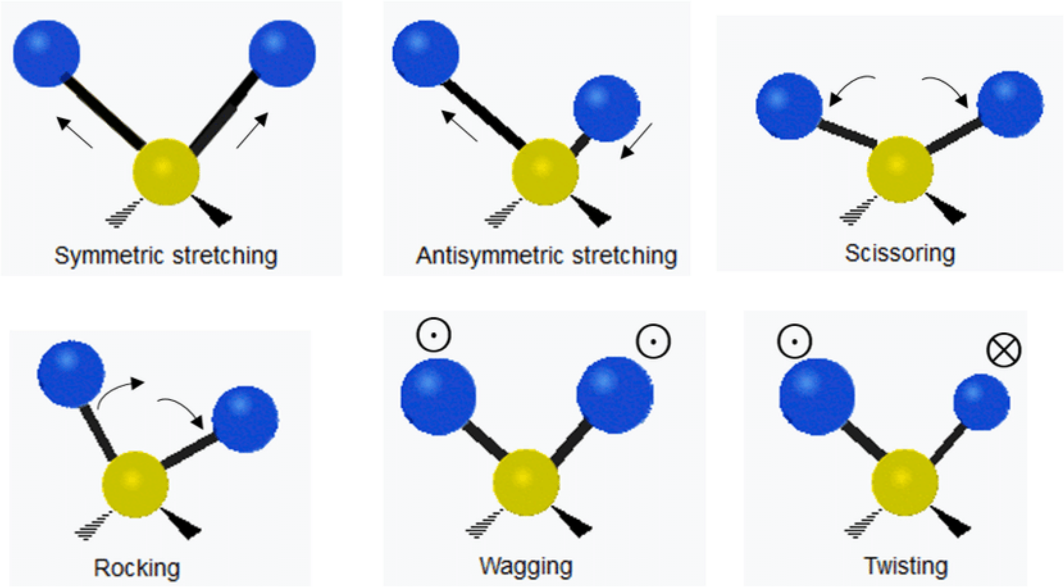
**Q4: Present a table for each molecule with the vibrational frequencies obtained using the various methods and compare the calculated results to experimental values. Also, describe each vibrational mode in the table as 'symmetric stretch', 'asymmetric stretch', 'bend', ...**



## $H_2O$ – Vibrational frequencies ($cm^{-1}$)

| Mode | Description | HF ($cm^{-1}$) | MP2 ($cm^{-1}$) | B3LYP ($cm^{-1}$) | Exp. ($cm^{-1}$) [1] |
|---|---|---|---|---|---|
| $\nu_2$ | H–O–H bending | 1750.79 | 1666.85 | 1637.39 | 1595 |
| $\nu_1$ | Symmetric O–H stretch | 4141.75 | 3904.63 | 3805.89 | 3657 |
| $\nu_3$ | Asymmetric O–H stretch | 4237.01 | 4012.12 | 3902.52 | 3756 |

✓

## $CO_2$ – Vibrational frequencies ($cm^{-1}$)

| Mode | Description | HF ($cm^{-1}$) | MP2 ($cm^{-1}$) | B3LYP ($cm^{-1}$) | Exp. ($cm^{-1}$) [1] |
|---|---|---|---|---|---|
| $\nu_2$a | O–C–O bending | 766.87 | 538.71 | 663.21 | 667 |
| $\nu_2$b | O–C–O bending | 766.91 | 538.91 | 666.33 | 667 |
| $\nu_1$ | Symmetric C–O stretch (IR inactive) | 1521.96 | 1504.74 | 1374.45 | 1333 |
| $\nu_3$ | Asymmetric C–O stretch (strongly IR active) | 2591.22 | 2748.30 | 2433.31 | 2349 |

## CH4 – Vibrational frequencies (cm$^{-1}$)

| Mode | Description | HF (cm$^{-1}$) | MP2 (cm$^{-1}$) | B3LYP (cm$^{-1}$) | Exp. (cm$^{-1}$) [1] |
|---|---|---|---|---|---|
| $\nu_4$a | C–H bending | 1453.01 | 1363.31 | 1340.88 | 1306 |
| $\nu_4$b | C–H bending | 1453.01 | 1363.34 | 1340.88 | 1306 |
| $\nu_4$c | C–H bending | 1453.01 | 1363.34 | 1340.88 | 1306 |
| $\nu_2$a | C–H bending (umbrella) | 1667.59 | 1579.73 | 1559.58 | 1534 |
| $\nu_2$b | C–H bending (umbrella) | 1667.59 | 1579.73 | 1559.58 | 1534 |
| $\nu_1$ | Symmetric C–H stretch ($A_1$) | 3150.48 | 3075.75 | 3023.44 | 2917 |
| $\nu_3$a | Asymmetric C–H stretch | 3253.58 | 3213.08 | 3128.64 | 3019 |
| $\nu_3$b | Asymmetric C–H stretch | 3253.58 | 3213.15 | 3128.64 | 3019 |
| $\nu_3$c | Asymmetric C–H stretch | 3253.58 | 3213.15 | 3128.64 | 3019 |

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## CH2O – Vibrational frequencies (cm$^{-1}$)

| Mode | Description | HF (cm$^{-1}$) | MP2 (cm$^{-1}$) | B3LYP (cm$^{-1}$) | Exp. (cm$^{-1}$) [1] |
|---|---|---|---|---|---|
| $\nu_6$ | H–C–H wagging (out-of-plane bend) | 1337.08 | 1211.06 | 1200.42 | 1167 |
| $\nu_5$ | H–C–H rocking (in-plane bend) | 1372.20 | 1289.45 | 1268.99 | 1251 |
| $\nu_4$ | H–C–H scissoring (in-plane bend) | 1656.60 | 1567.14 | 1538.04 | 1501 |
| $\nu_3$ | C=O stretch | 2005.96 | 1776.69 | 1825.16 | 1746 |
| $\nu_2$ | Symmetric C–H stretch | 3091.73 | 2964.96 | 2864.94 | 2843 |
| $\nu_1$ | Asymmetric C–H stretch | 3160.10 | 3030.54 | 2913.65 | 2776 |

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## Q5: Which mode(s) of CO2 give(s) the largest 'greenhouse effect'? Which mode(s) cannot be excited by an electromagnetic wave?

The IR-active modes are responsible: $\nu_2$ (bending) and $\nu_3$ (asymmetric stretch). In atmospheric terms, the bending mode $\nu_2$ (667 cm$^{-1}$ around 15 µm) is especially important because it lies near the maximum of the Earth's thermal emission spectrum, so it contributes strongly to the greenhouse effect. The asymmetric stretch $\nu_3$ also absorbs IR, but at shorter wavelength (~4.3 µm), where the Earth emits less strongly.

The symmetric stretch $\nu_1$ of $CO_2$ is IR inactive (it does not change the dipole moment), so it cannot be excited by interaction with an IR electromagnetic wave**.**

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### Q6: Which method gives the best agreement with experiment? How good is the agreement? Do some of the methods systematically under or overestimate the vibrational frequencies?

For all four molecules, B3LYP gives the best agreement with experiment. From the tables it is clear that B3LYP frequencies are usually within a few percent of the experimental fundamentals. MP2 also improves significantly over HF and often gives a similar level of accuracy to B3LYP, but for some modes (e.g. $CO_2$ bending and certain C=O stretches) its deviations are slightly larger. ✓

In contrast, HF systematically overestimates the vibrational frequencies for all molecules, particularly the stretching modes, reflecting the lack of electron correlation. MP2 and B3LYP still tend to overestimate the experimental fundamentals on average, but to a much smaller extent. This systematic overestimation is expected because the calculations use the harmonic approximation, which neglects anharmonicity; including anharmonic corrections or applying empirical scaling factors would further improve the agreement. ✓

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### Q7: What is meant by anharmonicity? Would you expect anharmonicity to decrease or increase a vibrational frequency calculated using the harmonic approximation? Why?

Anharmonicity refers to the fact that the real vibrational potential of a molecule is not perfectly quadratic in the nuclear displacements but deviates from the ideal parabolic (harmonic) form, especially at larger amplitudes and near bond dissociation. In real molecules the potential typically flattens as the bond is stretched, which reduces the effective restoring force and leads to vibrational energy levels that are closer together than in the harmonic model. Therefore, the true fundamental vibrational frequencies are usually lower than those obtained within the harmonic approximation, so the harmonic calculation tends to overestimate the experimental vibrational frequencies. ✓

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### Q8: Compare the anharmonic vibrational frequencies to the harmonic approximation and to experimental values.

| Mode | Description | HF harm | HF VPT2 fund | B3LYP harm | B3LYP VPT2 fund | Exp. |
|---|---|---|---|---|---|---|
| $\nu_2$ | H–O–H bending | 1750.9 | 1703.2 | 1637.6 | 1594.8 | 1595 |
| $\nu_1$ | Symmetric O–H stretch | 4142.1 | 3979.7 | 3806.2 | 3630.2 | 3657 |
| $\nu_3$ | Asymmetric O–H stretch | 4237.4 | 4063.5 | 3902.9 | 3715.0 | 3756 |

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### Q9: Of the fundamental vibrational modes of CO2, which one is least affected by the inclusion of anhar- monicity? Why is that?

For $CO_2$, the bending mode $\nu_2$ is the least affected by anharmonicity because $\nu_2$ is an angular (bending) vibration, so the nuclei move mainly by changing the O–C–O angle while the C–O bond lengths remain close to equilibrium. Around the linear geometry the angular potential is relatively close to quadratic, so the harmonic approximation is quite good, and the anharmonic correction is small. ✓

### Q10: The anharmonic correction can also introduce new peaks in the IR spectrum. Explain.

In the harmonic approximation, the vibrational Hamiltonian and the dipole moment are expanded only up to second and first order, respectively. When anharmonicity is included (e.g. in a VPT2), higher-order terms in both the potential and the dipole moment expansion are taken into account. These anharmonic terms relax the simple harmonic selection rule and allow weak intensity for overtones (0 → 2, 0 → 3, …) and combination bands. Furthermore, anharmonic coupling between states (e.g. Fermi resonances) can redistribute intensity from strong fundamentals to nearby overtone or combination levels. As a result, new, usually weaker, peaks appear in the anharmonic IR spectrum that are not present in the purely harmonic description. ✓

### Q11: The harmonic approximation of the energy surface places a limitation on the dynamics of the atoms in the molecule and the flow of energy between the various degrees of freedom. Describe these limitations.

In the harmonic approximation the potential energy surface is represented as a purely quadratic function of the normal coordinates. This implies that the normal modes are completely independent harmonic oscillators with fixed frequencies and no coupling between them. As a consequence, the motion of each mode is strictly periodic and the energy in a given normal mode is conserved; there is no possibility flow of energy between different vibrational degrees of freedom. the harmonic potential is symmetric and unbounded (parabolic) and therefore cannot describe bond dissociation, anharmonic softening at large amplitudes, or changes in frequency with vibrational excitation. In reality, anharmonicity allow energy transfer between modes, frequency shifts with increasing excitation, overtones and combination bands, and ultimately chemical bond breaking, none of which are captured within the harmonic approximation. ✓

### Reference:

[1]: Shimanouchi, T., & Shimanouchi, T. (1980). *Tables of molecular vibrational frequencies*. US Government Printing Office.