Rank The Following Molecules In Terms Of Their Carbonyl Stretching Frequency, V(C=O), In The Infrared

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Understanding the vibrational frequencies of molecules is fundamental in organic chemistry, especially when interpreting infrared (IR) spectra. One of the most prominent features in IR spectroscopy is the carbonyl (C=O) stretching vibration, which typically appears in the region of 1600–1800 cm-1. The precise position of this absorption band can vary significantly depending on the molecular environment surrounding the carbonyl group. Therefore, ranking molecules based on their carbonyl stretching frequency, V(C=O), requires a thorough understanding of the factors influencing IR absorption, including conjugation, hydrogen bonding, ring strain, and substituents.

This article provides a comprehensive guide to ranking various molecules based on their IR carbonyl stretching frequencies, explaining the underlying principles, the effects of different structural features, and practical examples. Whether you are a student preparing for exams or a researcher analyzing spectral data, this detailed discussion will deepen your understanding of IR spectral shifts associated with carbonyl groups.

Fundamentals of Carbonyl Stretching in IR Spectroscopy

Vibrational Modes of Carbonyl Groups

The carbonyl group (C=O) exhibits a strong, characteristic IR absorption due to its stretching vibration. In IR spectra, this appears as a sharp peak typically between 1650 and 1850 cm-1. The exact frequency depends on multiple factors, including electronic effects and the molecular environment.

The key to understanding the varying positions of C=O stretches lies in the nature of the bond and its interactions:

- Fundamental Vibrations: The C=O stretching vibration involves the oscillation of the carbon and oxygen atoms along the bond axis.
- Influencing Factors: Electron distribution, conjugation, hydrogen bonding, and ring strain can alter the strength and character of this vibration.

Typical Range of C=O Stretching Frequencies

Type of Carbonyl	Typical IR Absorption (cm-1)	Notes
Ketones	1705–1725	Usually sharp and strong
Aldehydes	1720–1740	Slightly higher than ketones
Carboxylic acids	1700–1725	Broader due to hydrogen bonding
Esters	1735–1750	Slightly higher than ketones
Amides	1640–1690	Lower due to resonance and hydrogen bonding

Understanding these ranges provides a starting point for ranking molecules based on their IR absorption frequencies.

Factors Affecting the Carbonyl Stretching Frequency

Multiple structural and electronic factors influence the position of the C=O stretch. Recognizing these effects enables accurate ranking and interpretation.

1. Conjugation with Pi Systems

Conjugation involves the overlap of the carbonyl □ orbital with adjacent □ systems, such as aromatic rings or double bonds. It significantly affects the IR absorption:

- Effect: Conjugation delocalizes electron density, reducing the double-bond character of the C=O bond.
- Result: The C=O bond becomes less stiff, leading to a lower stretching frequency.
- Typical Shift: Conjugation can decrease V(C=O) by approximately 30–50 cm-1.

Example: Acetone (non-conjugated ketone) shows a higher frequency (~1715 cm-1) than an □,□-unsaturated ketone (~1680 cm-1).

2. Hydrogen Bonding

Hydrogen bonding, especially in molecules like carboxylic acids or amides, can cause significant shifts:

- Effect: Hydrogen bonds weaken the C=O bond, decreasing its vibrational frequency.
- Result: Broader and shifted IR peaks toward lower frequencies.
- Note: In solution or solid-state, extensive hydrogen bonding can lower V(C=O) by up to 100 cm-1.

Example: Carboxylic acids display broad IR peaks around 1700 cm-1, often lower than in the absence of hydrogen bonding.

3. Ring Strain and Cyclic Structures

Cyclic compounds influence the C=O stretching frequency through ring strain and geometric constraints:

- Effect: Increased ring strain can alter bond angles and lengths, affecting vibrational frequencies.
- Result: Generally, strained rings (like cyclopropanones) exhibit higher C=O stretching frequencies due to increased bond stiffness.

4. Electron-Donating and Electron-Withdrawing Substituents

Substituents attached to the carbonyl carbon or adjacent atoms influence electron density:

- Electron-Donating Groups (EDGs): Such as alkyl groups, push electron density toward the C=O group, weakening the bond and lowering V(C=O).
- Electron-Withdrawing Groups (EWGs): Such as halogens or nitro groups, pull electron density away, increasing bond strength and raising V(C=O).

Practical Examples and Ranking of Molecules

To illustrate the ranking process, consider the following molecules:

- A. Acetone (Propanone)
- B. Acetic acid
- C. Benzaldehyde
- D. Cyclopentanone
- E. □-Unsaturated ketone (like methyl vinyl ketone)
- F. Amide (like acetamide)

Let's analyze each.

1. Acetone (Propanone)

- Type: Ketone
- V(C=O): Approximately 1715 cm-1
- Notes: No significant conjugation or hydrogen bonding; typical ketone.

2. Acetic Acid

- Type: Carboxylic acid
- V(C=O): Around 1700–1725 cm-1
- Notes: Hydrogen bonding broadens and shifts the peak downward.

3. Benzaldehyde

- Type: Aromatic aldehyde
- V(C=O): Approximately 1700–1720 cm-1
- Notes: Slight conjugation with aromatic ring; slightly lower than unconjugated aldehyde.

4. Cyclopentanone

- Type: Cyclic ketone
- V(C=O): About 1715–1725 cm-1
- Notes: Minimal ring strain; similar to acetone.

5. □-Unsaturated Ketone (Methyl Vinyl Ketone)

- Type: Conjugated ketone
- V(C=O): Around 1680–1695 cm-1
- Notes: Conjugation with the alkene lowers the frequency significantly.

6. Acetamide

- Type: Amide
- V(C=O): Approximately 1640–1690 cm-1
- Notes: Hydrogen bonding and resonance delocalization lower the frequency.

Ranking Based on V(C=O) Frequencies

Considering the factors discussed:

1. □-Unsaturated Ketone (~1680–1695 cm-1) – Lowest due to conjugation.
2. Amide (~1640–1690 cm-1) – Lower because of resonance and hydrogen bonding.
3. Acetic acid (~1700–1725 cm-1) – Slightly lower than ketones due to hydrogen bonding.
4. Benzaldehyde (~1700–1720 cm-1) – Slightly lower than non-conjugated aldehyde due to aromatic conjugation.
5. Acetone (~1715 cm-1) – Standard ketone, no conjugation or hydrogen bonding.
6. Cyclopentanone (~1715–1725 cm-1) – Similar to acetone, minimal ring strain effects.

Final Order (from lowest to highest V(C=O)):

1. □-Unsaturated ketone (most conjugated)

2. Amide

3. Acetic acid

4. Benzaldehyde

5. Acetone

6. Cyclopentanone

Additional Factors and Tips for Accurate Ranking

- Solvent Effects: Polar solvents can enhance hydrogen bonding, shifting peaks downward.
- Sample State: Solid, liquid, or gas phase can influence hydrogen bonding and peak width.
- Spectral Resolution: Overlapping peaks may complicate precise determination.

Practical Tips:

- Always consider the molecular environment.
- Use known reference values for common functional groups.
- Interpret IR spectra in conjunction with other spectroscopic data (like NMR).

Conclusion

Ranking molecules based on their carbonyl stretching frequency in IR spectroscopy involves understanding how conjugation, hydrogen bonding, ring strain, and substituents influence the

Frequently Asked Questions

What factors influence the carbonyl stretching frequency (V(C=O)) in infrared spectroscopy?

Factors such as conjugation, hydrogen bonding, ring strain, and the nature of substituents attached to the carbonyl group influence the V(C=O) frequency. Conjugation and hydrogen bonding tend to lower the frequency, while electron-withdrawing groups can increase it.

How does conjugation affect the carbonyl stretching frequency in IR spectra?

Conjugation of the carbonyl group with a double bond or aromatic system delocalizes the electrons, reducing the double bond character of C=O and thus lowering the V(C=O) frequency.

What is the typical range of the carbonyl stretching frequency for ketones in IR spectra?

Ketones generally exhibit V(C=O) absorption between 1715 and 1725 cm^{-1}, with variations depending on conjugation and other effects.

How does hydrogen bonding influence the carbonyl stretching frequency?

Hydrogen bonding weakens the C=O bond, resulting in a lower V(C=O) frequency, often shifting the absorption to below 1700 cm^{-1}.

Rank the following molecules in order of decreasing V(C=O): acetone,

acetic acid, benzaldehyde, and cyclohexanone.

Acetone > benzaldehyde > cyclohexanone > acetic acid.

Why does acetic acid have a lower V(C=O) compared to ketones like acetone?

Because in acetic acid, the carbonyl is involved in hydrogen bonding (as in dimer formation), which weakens the C=O bond and lowers its IR stretching frequency.

How does ring strain in cyclic compounds affect the V(C=O) frequency?

Ring strain can alter the electron density around the carbonyl group, potentially lowering or raising the V(C=O) depending on the specific strain and conjugation effects.

Compare the V(C=O) of aldehydes and ketones. Which generally absorbs at a higher frequency?

Aldehydes generally have a slightly higher V(C=O) than ketones, typically around 1725–1740 cm^{-1}, due to less steric hindrance and different electronic effects.

What is the effect of electron-withdrawing groups attached to the carbonyl carbon on the IR stretching frequency?

Electron-withdrawing groups increase the polarity and double-bond character of C=O, raising the V(C=O) frequency.

How can the IR spectrum be used to distinguish between different

carbonyl-containing functional groups?

Different functional groups have characteristic V(C=O) ranges: esters (~1735–1750 cm^{-1}), aldehydes (~1725–1740 cm^{-1}), ketones (~1715–1725 cm^{-1}), carboxylic acids (~1700–1725 cm^{-1} with broad O-H stretch), allowing identification based on the exact frequency and other spectral features.

Additional Resources

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Introduction

Infrared (IR) spectroscopy remains an indispensable tool in organic chemistry for the structural elucidation of molecules. Among its various vibrational modes, the carbonyl (C=O) stretch is one of the most prominent and diagnostically valuable features. The characteristic absorption around 1700 cm-1 allows chemists to identify and analyze a wide array of carbonyl-containing compounds, including ketones, aldehydes, esters, carboxylic acids, amides, and more.

However, the exact position of the carbonyl stretch varies significantly depending on the molecular environment, conjugation, hydrogen bonding, and other substituents. This variation can be used to infer structural features and electronic effects within molecules. Given a set of molecules, a common investigative approach involves ranking them based on their V(C=O) – the frequency of the carbonyl stretching vibration.

This article offers a comprehensive review of the factors influencing V(C=O), discusses the typical ranges for different classes of compounds, and demonstrates how to rank molecules based on their IR carbonyl frequencies. The goal is to equip researchers with a detailed understanding of how molecular structure modulates the IR carbonyl stretch, ultimately enabling accurate interpretation of IR spectra

and informed structural analysis.

Fundamental Principles of Carbonyl Vibrational Frequencies

The Nature of the C=O Stretch

The carbonyl group features a strong, intense IR absorption primarily due to the stretching vibration of the C=O bond. The vibrational frequency (V) depends on the bond strength and the reduced mass of the oscillating system, described by the diatomic oscillator model:

$$
V = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}
$$

where:

- k is the force constant of the C=O bond,
- μ is the reduced mass of the C and O atoms,
- c is the speed of light.

Since the reduced mass and bond strength are influenced by electronic effects and molecular interactions, the observed IR frequency provides indirect information about the electronic environment surrounding the carbonyl.

Typical Ranges of V(C=O)

- Aldehydes and Ketones: 1705–1725 cm-1
- Esters: 1735–1750 cm-1
- Carboxylic Acids: 1700–1725 cm-1

- Amides: 1640–1690 cm-1 (lower due to resonance delocalization)

These ranges are approximate and can shift based on specific substituents, conjugation, and hydrogen bonding.

Factors Affecting the Carbonyl Stretch Frequency

Understanding how various structural factors influence V(C=O) is critical for accurate spectral interpretation and ranking. The main factors include:

1. Conjugation

Mechanism: Conjugation between the carbonyl group and an adjacent □-system (e.g., double bonds, aromatic rings) delocalizes the □-electron density, effectively weakening the C=O bond and lowering its vibrational frequency.

Effect: Conjugated carbonyls typically display a shift of approximately 20–50 cm-1 to lower frequencies compared to isolated carbonyls.

Examples:

- Conjugated enones: ~1680–1650 cm-1
- Aromatic ketones: ~1680–1650 cm-1

2. Hydrogen Bonding

Mechanism: Hydrogen bonding involving the carbonyl oxygen stabilizes the transition state of the vibrational mode, reducing the force constant.

Effect: Strong hydrogen bonding causes a significant decrease in V(C=O), often shifting absorption to as low as 1650 cm-1 or lower.

Examples:

- Carboxylic acids in DMSO: 1700–1725 cm-1
- Carboxylic acids in water: 1650–1700 cm-1

3. Steric and Electronic Effects of Substituents

Electron-Donating Groups (EDGs): Increase electron density on the carbonyl carbon, weakening the C=O bond, thus lowering V(C=O).

Electron-Withdrawing Groups (EWGs): Decrease electron density, strengthening the C=O bond, and raising V(C=O).

Effect: The nature and position of substituents impact the vibrational frequency accordingly.

4. Resonance and Delocalization

Resonance stabilization of the carbonyl group, as seen in amides or conjugated systems, typically results in a lower V(C=O).

5. Ring Strain and Conformational Effects

In cyclic systems, bond angles and strain influence the bond strength and thus the vibrational frequency.

Comparative Analysis of Different Carbonyl-Containing Molecules

To rank molecules based on their V(C=O), it is essential to understand their structural features and how these influence the IR absorption.

Typical Ranges for Common Functional Groups

Functional Group	Approximate V(C=O) Range (cm-1)	Notes
Aldehydes	1725–1705	Usually slightly higher than ketones
Ketones	1715–1705	Slightly lower than aldehydes
Esters	1735–1750	Higher due to less conjugation
Carboxylic Acids	1700–1725	Variable, influenced by hydrogen bonding
Amides	1640–1690	Lower due to resonance delocalization
Conjugated carbonyls	1650–1680	Significantly lower than isolated carbonyls

Case Studies: Structural Impact on V(C=O)

1. Acetone versus Benzophenone

- Acetone (a simple ketone): ~1715 cm-1
- Benzophenone (aromatic ketone): ~1675 cm-1

Explanation: Benzophenone's conjugation with aromatic rings delocalizes the □-electrons, reducing the force constant and lowering V(C=O).

2. Ethyl Acetate versus Acetic Acid

- Ethyl Acetate (ester): ~1740 cm-1
- Acetic Acid (carboxylic acid): ~1700–1720 cm-1 (affected by hydrogen bonding)

Explanation: Ester's higher V(C=O) reflects less conjugation and hydrogen bonding compared to acids, which can significantly shift the frequency downward.

Practical Approach to Ranking Molecules

Given these principles, ranking molecules based on their V(C=O) involves:

1. Identifying the functional group (ketone, aldehyde, ester, acid, amide, etc.).
2. Assessing conjugation: Is the carbonyl conjugated with double bonds or aromatic systems?
3. Considering hydrogen bonding: Are molecules in a solvent or environment capable of hydrogen bonding with the carbonyl?
4. Examining substituents: Are there electron-donating or withdrawing groups nearby?
5. Accounting for ring strain or conformational effects.

Example Ranking

Suppose we have the following molecules:

- Molecule A: Simple ketone (acetone)
- Molecule B: Aromatic ketone (benzophenone)
- Molecule C: Ester (ethyl acetate)
- Molecule D: Carboxylic acid (acetic acid)
- Molecule E: Amide (acetamide)

Expected order from highest to lowest V(C=O):

1. Molecule C (ethyl acetate): ~1740 cm-1
2. Molecule A (acetone): ~1715 cm-1
3. Molecule E (acetamide): ~1650–1690 cm-1
4. Molecule D (acetic acid): ~1700–1725 cm-1 (but shifted downward if hydrogen-bonded)
5. Molecule B (benzophenone): ~1675 cm-1

This order reflects the influence of conjugation, hydrogen bonding, and the nature of the functional group.

Advanced Considerations and Exceptions

Influence of Solvent and Temperature

- Solvent Effects: Polar solvents capable of hydrogen bonding can lower V(C=O).
- Temperature: Elevated temperatures may cause broadening or slight shifts but generally do not drastically alter V(C=O).

Overlapping Vibrations

In complex molecules, overlapping peaks can complicate precise ranking. Deconvolution techniques and computational methods can assist.

Computational Predictions

Quantum chemical calculations, such as density functional theory (DFT), can predict V(C=O) with high accuracy, aiding in spectral interpretation and ranking when experimental data are ambiguous.

Summary and Conclusions

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