C5855

Vibrační spektroskopie

Jan Novotný

2019

Intro

Compare wavenumbers for following vibration modes:

1. Stretch C=N vs Stretch C-N
2. Stretch C-H vs Stretch C-C
3. Bend N-H vs Stretch N-H

Calculate number of normal modes of CO_2 and select IR active ones.

Campbell textbook

In CO_2 IR spectra, two (degenerate) bending vibrations are observed at 667 cm^{-1} and one asymmetric stretch is observed at 2349 cm^{-1} . A further (symmetric stretch) band is predicted at 1537 cm^{-1} but is not observed. Comment on these results.

Campbell textbook

When CO_2 binds to carbonic anhydrase, a zinc-containing enzyme that catalyzes CO_2 hydration, no change in the 2349 cm^{-1} asymmetric stretch band was observed. Comment on this result.

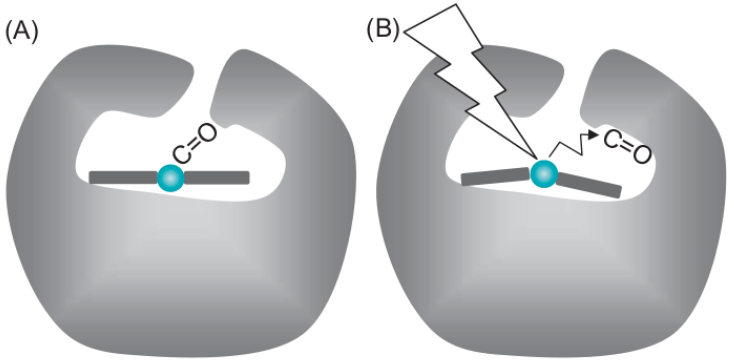
Unaffected bond force constant indicated that CO_2 is bound noncovalently into catalytic site. Contrarily, Zn coordinates and polarizes H_2O molecule which is activated for hydration.

Campbell textbook

Alanine has a band at 1308 cm^{-1} , assigned to –CH deformation. In deuteroalanine this band is absent, but a new band appears at 960 cm^{-1} . Why?

Campbell textbook

5.2.5 CO binds covalently to the heme group in myoglobin (Mb). When it is bound, the heme is planar and its Fe atom lies in the heme plane (state a) (see also Problem 5.1.3). The bond between Fe and CO can be broken by light. The figure illustrates myoglobin, irradiated with a light pulse to displace the bound CO atom. The rate of rebinding can be monitored by FTIR.



After photodissociation, the heme group buckles and the Fe moves out of the heme plane (state B). At low temperatures, CO ultimately rebinds and the system returns to state A. The stretching frequency of free CO is 2140 cm^{-1} for the isotope combination $^{12}C^{16}O$. When bound to Mb, this changes to 1945 cm^{-1}.

(i) What would the stretching frequencies be for $^{13}C^{16}O$, when free and bound?

Campbell textbook

Applications of resonance Raman techniques are limited by chromophore fluorescence". Give an explanation for this statement.

-

	Rayleigh	Stokes (Raman)	Anti-Stokes
Scattering is	elastic	inelastic	inelastic
Energy transfer	none	Photon → Molecule	Molecule → Photon
Effect on molecule	None	Excitation of vibrations or rotations	De-excitation of preexcited vibrations or rotations
Effect on photon	change in direction, same wavelength	change in direction, higher wavelength	change in direction, lower wavelength
Probability of occurrence	common	very rare	extremely rare