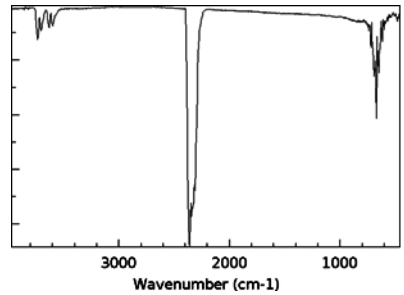
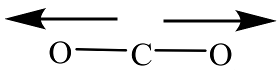
Assigning the IR Spectra of Polyatomic Molecules

Model 1: CO_2

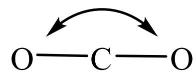
The IR spectrum of CO_2 from 600 – 4000 cm^{-1} is shown opposite and contains three bands.

The bands at 667 cm^{-1} and 2349 cm^{-1} are due to the bend, ν_2, and asymmetric, ν_3, vibrations respectively.

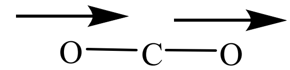




ν_1 = 1388 cm^{-1}
(symmetric stretch)



ν_2 = 667 cm^{-1}
(doubly degenerate bend)



ν_3 = 2349 cm^{-1}
(asymmetric stretch)

Critical thinking questions

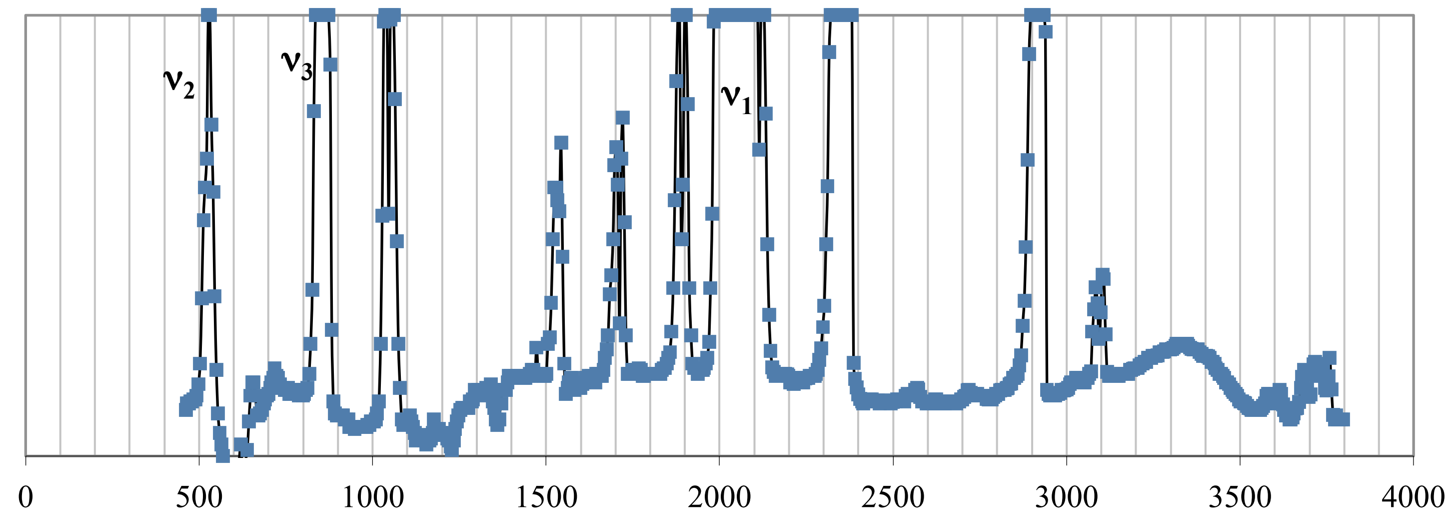
1. Why does the symmetric stretch not appear in the IR spectrum?

2. Given that the vibrational frequency (in wavenumbers) is given by $\omega = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$, what would be the effect on the frequencies if the spectrum of $^{13}CO_2$ were measured? Only a qualitative answer is required. (*Hint*: consider the motion of the carbon atom in each vibrational mode).

3. There is a third, weak band in the spectrum of CO_2 at around 3700 cm^{-1}. It is a *combination* band due to excitation of two of the modes. Which two?

Model 2: OCS

OCS is isoelectronic with CO_2 and both involve carbon doubly bonded to two group 16 elements. The full IR spectrum of OCS is shown overleaf. The fundamentals corresponding ν_1, ν_2 and ν_3 have been labelled and are at 2062, 520 cm^{-1} and 859 cm^{-1} respectively. **<u>Impurities</u>**: CS_2 (1530 cm^{-1}) CO_2 (2350 cm^{-1}) **Mark these on the spectrum!**



The remaining bands are:

- **Overtones** where $\Delta v = 2, 3, 4$ in each mode. These have rapidly decreasing intensity as Δv increases. The *approximate* frequency of these bands in a simple multiple of the fundamental. For example, the first overtone for ν_2 has $\Delta v = 2$ and frequency $\approx 2 \times 520$ cm^{-1} = 1040 cm^{-1}
- **Combinations** where the modes are simultaneously excited. The *approximate* frequency of these bands is a simple sum of the frequencies of the fundamentals being excited.

  For example, the combination of exciting 1 quanta in ν_1 and 2 quanta in ν_2 leads to the approximate frequency $\approx (1 \times 2062 + 2 \times 520)$ cm^{-1} = 3102 cm^{-1}

Critical thinking questions

1. By considering whether the modes will be local or coupled, *sketch* the form of ν_1, ν_2 and ν_3 in OCS.

2. Complete the table below to assign the spectrum as completely as you can.

ν_1	ν_2	ν_3	ω	Obs?
0	1	0	520	Yes
0	2	0	1040	Yes
0	3	0		
0	4	0		
0	5	0		
0	6	0		
0	7	0		
0	0	1	859	Yes
0	0	2		
0	0	3		
0	0	4		

ν_1	ν_2	ν_3	ω	Obs?
1	0	0		
0	1	1		
0	2	1		
0	3	1		
0	4	1		
0	5	1		
0	6	1		
0	1	2		
0	2	2		
0	3	2		
0	4	2		

ν_1	ν_2	ν_3	ω	Obs?
0	1	3		
0	2	3		
0	1	4		
1	1	0		
1	2	0	3102	Yes
1	3	0		
1	0	1		
1	0	2		
1	1	1		
1	2	1		