Answers to Student Assignment

Winspec: Microwave Spectroscopy Tutor

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The answers given below are examples of correct responses to the Student Exercises. In some cases answers will vary with the student's choice of molecule, transition, or other variable.

Exercise 1

Qualitative Effect of Centrifugal Distortion

Qualitative difference between the two spectra.

The spacing between the lines at high values of J is less than the spacing at low values of J. The intensity dies away more rapidly in the spectrum including centrifugal distortion.

Rotational and Centrifugal Distortion Constants

Molecule ***XYZ***

J	ν / GHz	$(J + 1)^2$	$\nu/2(J + 1)$ / GHz
0	***40.448000***	***1***	***20.224000***
1	***80.884000***	***4***	***20.221000***
2	***121.296000***	***9***	***20.2160000***
3	***161.672000***	***16***	***20.2090000***
4	***202.000000***	***25***	***20.2000000***
5	***242.268000***	***36***	***20.1890000***

Intercept at $J = -1$ / GHz	***20.22500***
Slope / GHz	***–0.0010000***
B / GHz	***20.22500***
D / kHz	***500.0***

Exercise 2

Effect of Temperature

Describe the effect of the temperature change.

As the temperature increases the maximum intensity moves to higher J values.

Molecule	***HCN***
Temperature / K	***300***

J	height	ν / GHz
9	***70.6 mm***	***885.970554***
10	***81.5 mm***	***974.487000***

Temperature / K ***299***

Exercise 3

Rotation-Vibration Interaction

Molecule	***OCS***
Transition	$J = \mathbf{2} \leftarrow J = \mathbf{1}$

$v_1 v_2^{\lvert\ell\rvert} v_3$	ν / GHz	*B* / GHz
00^00	***24.325927***	***6.0814818***
10^00	***24.24397***	***6.060992***
01^10	***24.36843***	***6.092108***
00^01	***24.1768***	***6.04420***

α_1 / MHz	***20.490***
α_2 / MHz	***–10.626***
α_3 / MHz	***37.28***
B_e / GHz	***6.09974***

Why should the 1 ← 0 transition not be chosen?

If J = 0 then $\lvert\ell\rvert = 0$***, so there is no*** 01^10***.***

List the missing values of v_2 and explain why they are absent.

For the 1 ← 0 transition odd values of v_2 ***are missing. For the 2 ← 1 transition no values of*** v_2 ***are missing. If J = 0 then*** $\lvert\ell\rvert = 0$***.*** ℓ ***varies through the sequence*** $v_2, v_2 - 2, \ldots, -v_2$ ***and so for*** $\lvert\ell\rvert = 0$***,*** v_2 ***must be even, no odd values can occur. If J = 1 then*** $\lvert\ell\rvert = 0$ ***and 1, and*** v_2 ***can take even or odd values.***

Exercise 4

ℓ -type Doubling

Molecule ***ClCN***

Transition: J = ***3*** ← J = ***2***	ν / GHz
$01^{1}{}_{2}0$	***35.94549***
$01^{1}{}_{1}0$	***35.90077***
Splitting	***0.04472***
q_{ℓ}	***0.007453***

$01^{1}{}_{2}0$	***23.96373 GHz***
$01^{1}{}_{1}0$	***23.93392 GHz***
$11^{1}{}_{2}0$	***23.86628 GHz***
$11^{1}{}_{1}0$	***23.83623 GHz***
$03^{1}{}_{2}0$	***24.1095 GHz***
$03^{1}{}_{1}0$	***24.0498 GHz***
Splitting of $01^{1}0$	***29.81 MHz***
Splitting of $11^{1}0$	***30.05 MHz***
Splitting of $03^{1}0$	***59.7 MHz***

Explain the relative sizes of the splittings in $11^{1}0$, $01^{1}0$ and $03^{1}0$.

$11^{1}0$ and $01^{1}0$ have the same value of v_2 and therefore the same splitting for a given J. $03^{1}0$ has $v_2 + 1$ twice as large as $01^{1}0$ and so the splitting is twice as large.

Exercise 5

Nuclear Quadrupole Interaction

Molecule	***ClCN***
Nuclear Spin I	***3/2***
Transition	J = ***2*** ← J = ***1***
Quantum Numbers $F_h \rightarrow F'_h$	***3/2*** → ***1/2***
Quantum Numbers $F_{\ell} \rightarrow F'_{\ell}$	***1/2*** → ***3/2***
Frequency $F_h \rightarrow F'_h$ / GHz	***23.92069***
Frequency $F_{\ell} \rightarrow F'_{\ell}$ / GHz	***23.86243***
Frequency Difference / GHz	***0.05826***
$Y(J + 1, I, F'_h)$	***1/4***
$Y(J, I, F_h)$	***–1/5***
$Y(J + 1, I, F'_{\ell})$	***0***
$Y(J, I, F_{\ell})$	***1/4***
eQq / MHz	***–83.23***
v_0 / GHz	***23.88324***

Exercise 6

Stark Effect

Molecule	***ICN***
Transition	$J =$ ***3*** $\leftarrow$ $J =$ ***2***
Unperturbed Frequency / GHz	***19.353228***

$\mathcal{E}$ / V cm^{-1}	M_J	ν / GHz	$\mathcal{E}$ / V cm^{-1}	M_J	ν / GHz
300	***0***	***19.35199***	***700***	***1***	***19.35132***
300	***1***	***19.35288***	***700***	***2***	***19.36583***
300	***2***	***19.35553***	***900***	***0***	***19.34209***
500	***0***	***19.34979***	***900***	***1***	***19.35008***
500	***1***	***19.35226***	***900***	***2***	***19.37405***
500	***2***	***19.35966***			
700	***0***	***19.34649***			

M_J	Δ ν / MHz	$\mathcal{E}^2$ / V^{2}m^{-2}	M_J	Δ ν / MHz	$\mathcal{E}^2$ / V^{2}m^{-2}
0	***–1.24***	9×10^8	***2***	***6.43***	25×10^8
0	***–3.44***	25×10^8	***2***	***12.60***	49×10^8
0	***–6.74***	49×10^8	***2***	***20.82***	81×10^8
0	***–11.14***	81×10^8			
1	***–0.35***	9×10^8			
1	***–0.97***	25×10^8			
1	***–1.91***	49×10^8			
1	***–3.15***	81×10^8			
2	***2.30***	9×10^8			

M_J	$f(J, M_J)$	Slope / Hz m^2/V^2	μ / C m	μ / D
0	***–288/7560***	-1.375×10^{-3}	1.238×10^{-29}	***3.71***
1	***–81/7560***	-3.891×10^{-4}	1.242×10^{-29}	***3.72***
2	***540/7560***	-2.572×10^{-3}	1.237×10^{-29}	***3.71***

Exercise 7

Structure Determination

Molecule HCN

J	ν / GHz	$(J + 1)^2$	ν/2(J + 1) / GHz
0	***88.631602***	***1***	***44.315801***
1	***177.261111***	***4***	***44.3152778***
2	***265.886432***	***9***	***44.3144052***
3	***354.505472***	***16***	***44.3131840***
4	***443.116137***	***25***	***44.3116137***
5	***531.716333***	***36***	***44.3096944***

Intercept at $J = -1$ / GHz	***44.3159755***
Slope / GHz	***-1.74476×10^{-4}***
B / GHz	***44.3159755***
D / kHz	***87.24***
I / kg m^2	***$1.8936789 \times 10^{-46}$***

Molecule DCN

J	ν / GHz	$(J + 1)^2$	ν/2$(J + 1)$ / GHz
0	***72.414694***	***1***	***36.207347***
1	***144.828002***	***4***	***36.2070005***
2	***217.238539***	***9***	***36.2064232***
3	***289.644920***	***16***	***36.2056150***
4	***362.045758***	***25***	***36.2045758***
5	***434.439669***	***36***	***36.2033058***

Intercept at $J = -1$ / GHz	***36.2074624***
Slope / GHz	***-1.15461×10^{-4}***
B / GHz	***36.2074624***
D / kHz	***57.73***
I / kg m^2	***2.317761×10^{-46}***

m_H / amu	1.00782
m_H / kg atom^{-1}	***1.67353×10^{-27}***
m_D / amu	2.01410
m_D / kg atom^{-1}	***3.34449×10^{-27}***
m_C / amu	12.00000
m_C / kg atom^{-1}	***1.99265×10^{-26}***
m_N / amu	14.00307
m_N / kg atom^{-1}	***2.32527×10^{-26}***
m_{HCN} / amu	***27.01089***
m_{HCN} / kg molecule^{-1}	***4.48527×10^{-26}***
m_{DCN} / amu	***28.01717***
m_{DCN} / kg molecule^{-1}	***4.65236×10^{-26}***
a / m	***1.62250×10^{-10}***
d / m	***5.8274×10^{-12}***
$c = (m_H a + m_C b) / m_N$	***$1.16774 \times 10^{-11} + 0.856955\, b$***
b / m	***5.6009×10^{-11}***
c / m	***5.9675×10^{-11}***
r(H–C) / m	***1.0624×10^{-10}***
r(H–C) / Å	***1.0624***
r(C≡N) / m	***1.1568×10^{-10}***
r(C≡N) / Å	***1.1568***

Exercise 8

Diatomic Molecules

Molecule ***$^{79}Br^{35}Cl$***

v	*J*	ν / GHz
0	***0***	***9.118908***
0	***1***	***18.237764***
0	***2***	***27.356517***
0	***3***	***36.475115***
1	***0***	***9.07261***
1	***1***	***18.14516***
1	***2***	***27.21762***
1	***3***	***36.28991***

v	*J*	$(J + 1)^2$	ν/2(*J* + 1) / GHz
0	***0***	***1***	***4.559454***
0	***1***	***4***	***4.5594410***
0	***2***	***9***	***4.5594195***
0	***3***	***16***	***4.5593894***
1	***0***	***1***	***4.53631***
1	***1***	***4***	***4.536290***
1	***2***	***9***	***4.536270***
1	***3***	***16***	***4.536239***

v	0	1
Intercept / GHz	***4.559458***	***4.536309***
Slope / GHz	***-4.326×10^{-6}***	***-3.94×10^{-6}***
B_v / GHz	***4.559458***	***4.53631***
D_v / kHz	***2.163***	***1.97***

B_e / GHz	***4.57103***
α_e / MHz	***23.149***

ω_e / Hz	***1.33×10^{13}***	ω_e / cm^{-1}	***443***
$\omega_e x_e$ / Hz	***5.45×10^{10}***	$\omega_e x_e$ / cm^{-1}	***1.82***
$\mathcal{D}$ / cm^{-1} molecule^{-1}	***2.70×10^4***	$\mathcal{D}$ / kJ mol^{-1}	***323***

Molecule	***BrCl***
Temperature / K	***300***

v	height
0	***202.8 mm***
1	***24.6 mm***

ν_0 / cm^{-1} ***440***

Bond Length

I / kg m^2	***5.420058 x 10^{-46}***
m_1 /amu	34.96885
m_2 /amu	18.99840
μ / amu	***12.31028***
μ / kg molecule^{-1}	***2.04417 x 10^{-26}***
r / m	***1.6283 x 10^{-10}***
r / Å	***1.6283***