

## Exercise 6

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Learning objectives:

The first task is a repetition of some important concepts discussed in the course. After the second and third tasks, you can

- analyze a rotational spectrum and, in particular,
- obtain the parameters that describe the rotational spectrum analytically,
- distinguish spherical top, symmetric top, and asymmetric top molecules and know their relations,
- decompose rotational Hamiltonian using ladder operators.

### Exercise 1: Concept Questions

- a) An important parameter in spectroscopic measurements is the linewidth of a transition. Is there a fundamental limit of the linewidth?

*Hint:* An excited state has a finite lifetime due to spontaneous emission.

- b) What are typical energy differences between the ground and first excited state of

- rotational levels
- vibrational levels
- electronic states (at nuclear equilibrium configuration)

in a molecule? Give the values in eV along with the corresponding value in wavenumber ( $\text{cm}^{-1}$ ) and wavelength (nm).

- c) How can the state distribution of a sample in thermal equilibrium at  $T = 300 \text{ K}$  be described? How could you measure the temperature of the sample using spectroscopic methods? Describe a suitable experimental setup.
- d) Write the product form of the wavefunction of a homonuclear diatomic molecule in the Born-Oppenheimer approximation. Consider the  $\text{H}_2$  molecule in the electronic ground state. What is the ground state term symbol?
- e) What is the symmetry of the different contributions to the wavefunction upon exchange of an H atom. What is the requirement for the full wavefunction? Derive the allowed rotational states for *ortho* and *para*  $\text{H}_2$ .

What is the symmetry of the different contributions to the wavefunction upon exchange of the hydrogen nuclei ( $I=1/2$ ). What is the requirement for the full wavefunction? Derive the allowed rotational states for *ortho* and *para*  $\text{H}_2$ . What is the ratio of *para* to *ortho* states? How would the situation change for the metastable molecule  $\text{He}_2$  ( $^3\Sigma_u^+$ , nuclear spin  $I=0$ ).

- f) Each state of a diatomic molecule corresponds to a single energy value, hence you could visualize its states as an energy level diagram.

Sketch the energy level diagram of the hydrogen atom. Next, draw the potential energy curve of a diatomic molecule in its electronic ground state as a function of the internuclear distance. Explain why the Born-Oppenheimer approximation allows you to draw this potential curve as a function of the internuclear separation.

- g) The irreducible representations of all finite point groups are labelled using the Mulliken symbols (A, B, E and T with super-/subscripts). What information about the eigenstates belonging to a given irreducible representation is contained in these symbols? How do the Mulliken symbols change in the case of infinite point groups?

- h) The intensity of a vibronic transition is proportional to the absolute square of the transition moment,

$$I \propto |\langle \phi'_{\text{el}} \phi'_{\text{vib}} | \vec{\mu} | \phi''_{\text{el}} \phi''_{\text{vib}} \rangle|^2, \quad (1.1)$$

where  $\phi_{\text{el}}$  and  $\phi_{\text{vib}}$  are electronic and vibrational wavefunctions, respectively. Explain under which conditions the integral in Eq. 1.1 can be separated into an electronic part and vibrational part, the latter known as the Franck-Condon factor.

- i) In some cases, electronically forbidden transitions may become allowed if the vibrational states of the initial and final states are also considered. Discuss the vanishing integral theorem for such a case.

## Exercise 2: Ro-vibrational spectroscopy of silane

Silane ( $\text{SiH}_4$ ) is a tetrahedral molecule and a spherical top. The moment of inertia about any axis passing through the central Si atom is the same.

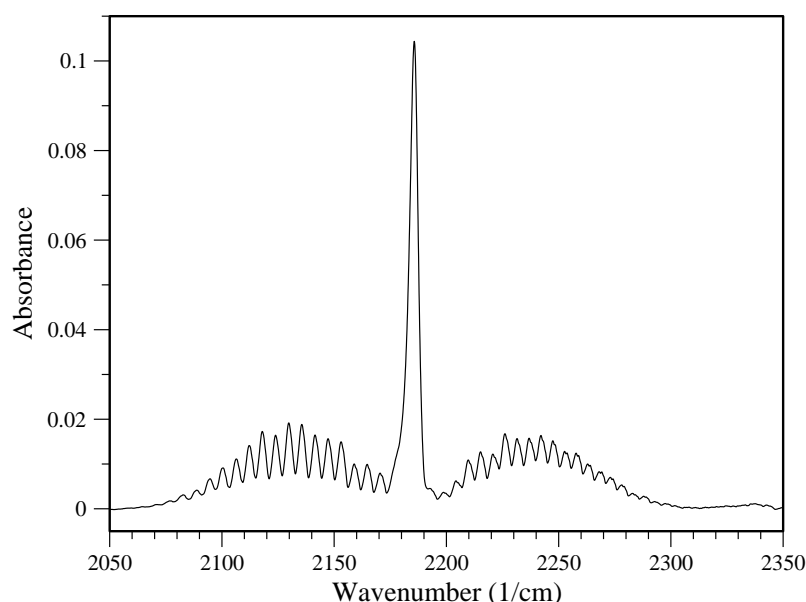


Figure 2-1: FTIR spectrum of the  $\nu_3$  vibrational mode of  $\text{SiH}_4$

- a) How many vibrational degrees of freedom does  $\text{SiH}_4$  have?

In 1942, Tindal, Straley and Nielsen [1] measured the infrared bands of  $\text{SiH}_4$  at high resolution. In particular, they determined the rotational constant  $B_e = 3.00 \text{ cm}^{-1}$  in the vibronic ground state.

- b) Given that the equilibrium nuclear structure in the electronic ground state is tetrahedral, calculate the moment of inertia of silane (in  $\text{kg m}^2$ ) and the Si-H equilibrium bond length (in  $\text{\AA}$ ). *Hint:* Use  $m_{\text{H}} = 1.6726 \cdot 10^{-27} \text{ kg}$ .

Fig. 1 (see above) shows the infrared absorption spectrum of the antisymmetric stretching mode  $\nu_3$  of silane measured at a resolution of about  $1 \text{ cm}^{-1}$  in a 1 m long cell.

- c) *Bonus* - Plot the spectrum<sup>1</sup> with an appropriate program (e.g. MATLAB or R). Determine the positions of the P and R branch lines. *Hint:* The resolution of the spectrum does not allow separation of P(1) and P(2) from the Q branch, so the P branch effectively starts at P(3).

As a result, you should obtain the peak positions provided in table 2.1.

Table 2.1: Line positions and assignments of the  $\nu_3$  vibrational mode of  $\text{SiH}_4$ .

Assignment	$J''$	$\tilde{\nu} / \text{cm}^{-1}$
P(14)	14	2106.49
P(13)	13	2112.28
P(12)	12	2118.07
P(11)	11	2124.02
P(10)	10	2129.87
P(9)	9	2135.64
P(8)	8	2141.59
P(7)	7	2147.39
P(6)	6	2153.14
P(5)	5	2159.04
P(4)	4	2164.79
P(3)	3	2170.63
R(1)	1	2199.17
R(2)	2	2204.83
R(3)	3	2210.11
R(4)	4	2215.43
R(5)	5	2221.43
R(6)	6	2226.33
R(7)	7	2231.72
R(8)	8	2237.25
R(9)	9	2242.34

In exercise 4 we investigated the rovibrational spectra of a linear molecule. In our analytical treatment of the problem, we treated the molecule as a rigid rotor, neglecting centrifugal

<sup>1</sup>The data file is provided in the attachment on the website <https://atto.ethz.ch/education/lectures/spectroscopyFS23.html>

distortion. In silane, this treatment is no longer sufficient as the hydrogen nuclei that surround the central silicon are so light. The distortion can be taken into account with the addition of the centrifugal term  $(-D_v J^2 (J+1)^2)$  to the expression for the ro-vibrational energy,

$$T_{v,J} = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2 + B_v J(J+1) - D_v J^2 (J+1)^2 .$$

- d) Show that the expression for the difference between two term values for transitions that start in the same rotational state is

$$\begin{aligned} \frac{\Delta' E(J)}{hc} &= \tilde{\nu} [R(J)] - \tilde{\nu} [P(J)] \\ &= 2(2J+1) [(B_1 - 2D_1) - 2D_1 J(J+1)] . \end{aligned} \quad (2.1)$$

- e) Show that the expression for the difference between two term values that end in the same rotational state is:

$$\begin{aligned} \frac{\Delta'' E(J)}{hc} &= \tilde{\nu} [R(J-1)] - \tilde{\nu} [P(J+1)] \\ &= 2(2J+1) [(B_0 - 2D_0) - 2D_0 J(J+1)] . \end{aligned} \quad (2.2)$$

- f) Using equations (2.1) and (2.2), generate a table containing the following information;  $J$ ,  $\frac{\Delta' E(J)}{2(2J+1)hc}$ ,  $\frac{\Delta'' E(J)}{2(2J+1)hc}$ . Plot the last two columns as a function of  $J(J+1)$ .
- g) Using a linear fit, extract the values of  $B_0$ ,  $B_1$ ,  $D_0$ , and  $D_1$  from the provided data.

The technique you have used to extract these values is called the combination of differences and is often used for determining  $B_v$ ,  $D_v$

### Exercise 3: Rotational energy structure of asymmetric top molecules

In this exercise we use the rigid rotor approximation (centrifugal distortion is neglected). This approximation is particularly good for low rotational levels with  $J = 0$  to  $J = 2$ .

The inertia matrix of a molecule can be written as

$$\mathbf{I} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix} \quad (3.1)$$

- a) What is the difference between symmetric top and asymmetric top molecules? Please provide one example for each type.
- b) If the molecule has a symmetry operation represented by matrix  $\mathbf{A}$ , then  $\mathbf{AI} = \mathbf{IA}$ . If  $\mathbf{A}$  is representing a  $C_3$  rotation about the  $z$ -axis, what is  $\mathbf{A}$  and what can you say about the inertia matrix  $\mathbf{I}$ ? Can the same conclusion be drawn for a  $C_2$  symmetry operation?

The Hamiltonian operator of an asymmetric rigid rotor is

$$\hat{H}_{\text{rot}} = \frac{1}{2I_a} \hat{J}_a^2 + \frac{1}{2I_b} \hat{J}_b^2 + \frac{1}{2I_c} \hat{J}_c^2 ,$$

where  $\hat{J}_{g(g=a,b,c)}$  are the components of the rotational angular momentum  $\hat{J}$  expressed in the molecule-fixed principal axes  $a$ ,  $b$ , and  $c$ , and  $I_{g(g=a,b,c)}$  are the principal moments of inertia ( $I_a < I_b < I_c$ ). The energy eigenvalues of  $\hat{H}_{\text{rot}}$  are calculated using linear combinations of the symmetric rotor basis functions  $|J, K, M\rangle$ . It is important to take note of the fact that individual symmetric rotor basis functions are not eigenfunctions of  $\hat{H}_{\text{rot}}$  but they do form a useful basis for this problem.

The quantum numbers  $K$  and  $M$  represent the projections of  $J$  onto the molecule-fixed axis  $z$  and the space-fixed axis  $Z$ , respectively:  $\hat{J}_z |J, K, M\rangle = \hbar K |J, K, M\rangle$  and  $\hat{J}_Z |J, K, M\rangle = \hbar M |J, K, M\rangle$ . The molecule-fixed components of the angular momenta follow the reverse commutation relation  $[\hat{J}_x, \hat{J}_y] = -i\hbar \hat{J}_z$  (and cyclic permutations)<sup>2</sup>, whereas for the space-fixed components the relation  $[\hat{J}_X, \hat{J}_Y] = i\hbar \hat{J}_Z$  (and cyclic permutations) holds.<sup>3</sup> Whenever two operators do not commute, as is the case here, ladder operators ( $\hat{J}_{\pm}$ ) can be constructed whose action is to raise or lower the eigenstates of an eigenvector. This shall be shown in this exercise.

c) Show that  $[\hat{J}_z, \hat{J}_{\pm}] = \mp \hbar \hat{J}_{\pm}$ , where  $\hat{J}_{\pm} = \hat{J}_x \pm i\hat{J}_y$ .

d) Show that

$$\hat{J}_z \hat{J}_{\pm} |J, K, M\rangle = \hbar (K \mp 1) \hat{J}_{\pm} |J, K, M\rangle . \quad (3.2)$$

From Eq. (3.2) we can conclude that  $\hat{J}_{\pm} |J, K, M\rangle$  is an eigenfunction of  $\hat{J}_z$  with eigenvalue  $\hbar (K \mp 1)$ . We can therefore write

$$\hat{J}_{\pm} |J, K, M\rangle = c_{JK}^{\pm} |J, K \mp 1, M\rangle \quad (3.3)$$

where  $c_{JK}^{\pm}$  is a constant. Because  $|K| \leq J$ ,

$$\hat{J}_+ |J, -J, M\rangle = \hat{J}_- |J, J, M\rangle = 0 . \quad (3.4)$$

e) Show that

$$\hat{J}_{\mp} \hat{J}_{\pm} = \hat{J}_x^2 + \hat{J}_y^2 \pm \hbar \hat{J}_z = \hat{J}^2 - \hat{J}_z^2 \pm \hbar \hat{J}_z \quad (3.5)$$

and therefore that

$$\langle J, K, M | \hat{J}_{\mp} \hat{J}_{\pm} | J, K, M \rangle = \hbar^2 [J(J+1) - K(K \mp 1)] . \quad (3.6)$$

f) Derive the coefficient  $c_{JK}^{\pm}$  in Eq. (3.3).

<sup>2</sup>An observer in the space-fixed frame sees the molecule-fixed frame rotate in a sense opposite to that of an observer in the molecule-fixed frame looking at the space-fixed frame. This is exactly the same as time reversal in classical mechanics, where the sign of the time variable  $t$  is changed to  $-t$ . In quantum mechanics, time reversal corresponds not only to substituting  $-t$  for  $t$  but also taking the complex conjugate, so that the time-dependent Schrödinger equation  $\hat{H}\psi = (-\hbar/i) \partial\psi/\partial t$  is invariant under time reversal for a time-independent Hamiltonian. Note that  $\theta \hat{J} \theta^{-1} = \hat{J}^* = -\hat{J}$ ,  $\theta \hat{J}_z \theta^{-1} = -\hat{J}_z$ ,  $\theta \hat{J}_{\pm} \theta^{-1} = -\hat{J}_{\mp}$ , where  $\theta$  denotes the time reversal operator.

<sup>3</sup>Note that  $[\hat{J}^2, \hat{J}_i] = [\hat{J}^2, \hat{J}_{\alpha}] = [\hat{J}_i, \hat{J}_{\alpha}] = 0$  for all  $i = x, y, z$  and  $\alpha = X, Y, Z$ .

g) Show that

$$\begin{aligned}\hat{J}_x |J, K, M\rangle &= \frac{\hbar}{2} \sqrt{J(J+1) - K(K-1)} |J, K-1, M\rangle \\ &+ \frac{\hbar}{2} \sqrt{J(J+1) - K(K+1)} |J, K+1, M\rangle, \text{ and}\end{aligned}\quad (3.7)$$

$$\begin{aligned}\hat{J}_y |J, K, M\rangle &= -i \frac{\hbar}{2} \sqrt{J(J+1) - K(K-1)} |J, K-1, M\rangle \\ &+ i \frac{\hbar}{2} \sqrt{J(J+1) - K(K+1)} |J, K+1, M\rangle.\end{aligned}\quad (3.8)$$

- h) Give explicit matrix representations of  $\hat{J}_x$ ,  $\hat{J}_y$ ,  $\hat{J}_z$  and  $\hat{J}_{\pm}$  for  $J = 2$ . Use the sequence of basis functions  $|J, J, M\rangle, \dots, |J, -J, M\rangle$  to construct the matrices.
- i) Having found appropriate representations for  $\hat{J}_x$ ,  $\hat{J}_y$  and  $\hat{J}_z$ , find representations for  $\hat{J}_x^2$ ,  $\hat{J}_y^2$  and  $\hat{J}_z^2$ . Show and explain why in the limit of the spherical top (i.e.  $I_a = I_b = I_c$ ), the total energy of the system loses its dependence on  $K$ .
- j) By examining the matrix representation of  $\hat{J}_x^2$  and  $\hat{J}_y^2$ , assign the elements that prevent the symmetric rotor basis functions from being eigenfunctions. Show, by referring to the matrix representations, that taking the limit of the symmetric top (i.e.  $I_b = I_c$ ) results in a Hamiltonian whose eigenfunctions are the symmetric rotor basis functions.

## References

- [1] C. H. Tindal, J. W. Straley and H. H. Nielsen, *Phys. Rev.* **62**, 151 (1942).