

Solution Exercise 4

Problem 1: Molecular Structure of O₂

a) For the construction of the molecular orbital (MO) scheme it is sufficient to consider only the atomic valence orbitals of the second shell, since the overlap of the inner shell atomic orbitals (AOs) is usually too small to significantly contribute to the molecular orbitals of the valence shell. The MOs arising from the 1s AOs are almost completely localized on the atoms and lie very low in energy.

The MO scheme for O₂ is shown in Figure 1-1. Note that the relative ordering of the molecular orbital energies as depicted in Figure 1-1 is only valid for F₂ and O₂. The ordering is different for the other homonuclear diatomic molecules of the second row elements. Those molecules exhibit another ordering where the binding σ_g MO lies between the binding π_u and the antibinding π_g^* MOs.

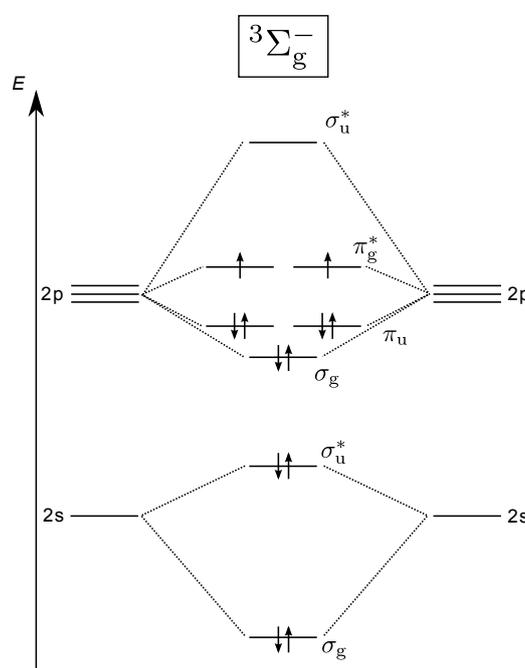


Figure 1-1: Molecular orbital scheme for O₂. The electron occupation is shown for the ground state.

b) The two energetically lowest lying configurations (molecular orbital occupations) are:

$$\text{lowest energy configuration: } (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^4 (1\pi_g^*)^2$$

$$\text{first excited configuration: } (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^3 (1\pi_g^*)^3$$

Since the first excited configuration has one electron more in an antibonding orbital, the bond order is decreased, *i.e.* the strength of the bond is weakened, which results in an increased equilibrium bond length (R_e). Hence the potential energy curves of the electronic states resulting from the first excited configuration are shifted to a larger equilibrium internuclear separation. The potential energy curves for the three states of the most stable configuration and of some excited states are shown in Figure 1-2.

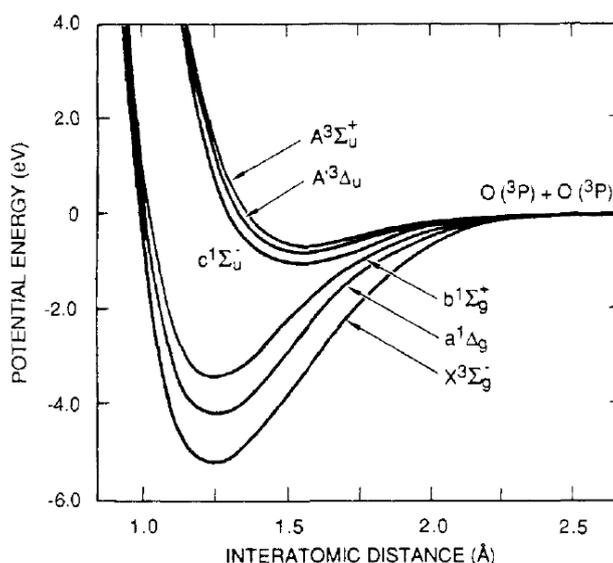


Figure 1-2: O₂ potential energy curves for bound states correlating asymptotically to two ground-state atoms (from T. G. Slanger, P. C. Cosby *J. Phys. Chem.* 92 (1988) 267–282).

- c) An intuitive picture of how to place two electrons into two degenerate π_g orbitals is given to the right. The two microstates yielding $\Lambda=2$ require paired electrons, resulting in a $^1\Delta_g$ term. The four microstates with $\Lambda=0$ result in a $^1\Sigma_g$ and a $^3\Sigma_g$ state. The Pauli principle requires that the orbital wave function of the singlet (triplet) term is symmetric (antisymmetric), thus the full term labels are $^1\Sigma_g^+$ and $^3\Sigma_g^-$.

$\lambda = -1$	$\lambda = 1$	Λ
$\uparrow\downarrow$		2
	$\uparrow\downarrow$	2
\uparrow	\uparrow	0
\uparrow	\downarrow	0
\downarrow	\uparrow	0
\downarrow	\downarrow	0

Considering the irreducible representations given in the exercise and applying the Pauli principle as indicated above one also obtains the following term symbols:

$$(\dots) (1\pi_u)^4 (1\pi_g^*)^2 \rightarrow ^3\Sigma_g^-(\text{paramagnetic}), ^1\Delta_g(\text{paramagnetic}), ^1\Sigma_g^+(\text{diamagnetic}).$$

In the first excited configuration the two electrons are in different molecular orbital shells and thus the Pauli principle does not impose any restriction on the symmetry of the wave function (*i.e.* all combinations of symmetric and antisymmetric spatial and spin wave functions are allowed):

$$(\dots) (1\pi_u)^3 (1\pi_g^*)^3 \rightarrow ^1\Sigma_u^-(\text{diamagnetic}), ^3\Delta_u(\text{paramagnetic}), ^3\Sigma_u^+(\text{paramagnetic}), \\ ^3\Sigma_u^-(\text{paramagnetic}), ^1\Delta_u(\text{paramagnetic}), ^1\Sigma_u^+(\text{diamagnetic}).$$

The ordering is with respect to the energy of the states. Hund's rule can be applied for the electronic states resulting from the most stable configuration. For states with the same spin multiplicity the term with the higher angular momentum quantum number $|\Lambda|$ is lower in energy. In case of the excited configuration Hund's rule is no longer valid and therefore a singlet state can be the lowest.

The magnetic properties of a term are most easily obtained by looking at the term symbol: according to Herzberg [3], for light diatomic molecules the magnetic moment associated with the total angular momentum of the electron around the internuclear axis is

$$\mu_\Omega = (\Lambda + 2\Sigma)\mu_0, \quad (1.1)$$

where μ_0 is the Bohr magneton. For a $^1\Sigma$ state, μ_Ω always vanishes and thus the term is diamagnetic. The $^3\Sigma$ and $^1\Delta$ terms can have finite values of μ_Ω and are thus paramagnetic.

- d) The ground state for O_2 is the ${}^3\Sigma_g^-$ state because it has the highest multiplicity.
- e) As depicted in the potential energy curve diagram, the three states of the ground configuration lie fairly close to each other, which results in energy gaps in the red part of the visible spectrum and in the near infrared. Although the transition from the ground state to the two other states is spin forbidden, the molecule is no longer an isolated system in the condensed phase and spin flips are no longer strictly forbidden. Hence the pale blue color arises because of the absorption of red light. This behavior cannot be observed in the gas phase, since there the molecules behave almost like isolated systems.

Problem 2: Electronic Spectrum of N_2

- a) The molecular orbital (MO) scheme for N_2 for the ground and excited configuration is shown in Figure 2-1.

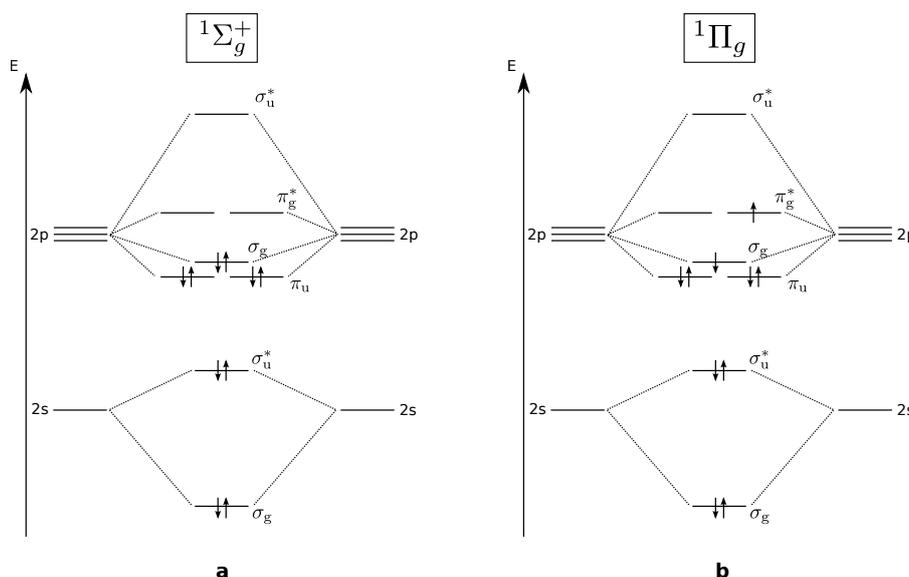


Figure 2-1: MO schemes for N_2 . **a** shows the ground state and **b** the excited state.

- b) For the vibrational constants of the excited state, take the progression from the absorption data $v'' = 0$. For the ground state the progression with $v' = 0$ can be taken for example. The energy for one transition is given by the difference between two vibrational levels of the electronic ground and excited state. With $E_{\text{vib}}(v)/hc = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2$ the transition energy reads

$$E(v', v'')/hc = \omega_e'(v' + \frac{1}{2}) - \omega_e' x_e'(v' + \frac{1}{2})^2 - \omega_e''(v'' + \frac{1}{2}) + \omega_e'' x_e''(v'' + \frac{1}{2})^2 . \quad (2.1)$$

For the emission progression with $v' = 0$ the difference of consecutive levels v'' is

$$\Delta E(v) = E(v' = 0, v'' = v) - E(v' = 0, v'' = v + 1) = \omega_e'' - 2\omega_e'' x_e'' - 2\omega_e'' x_e'' v. \quad (2.2)$$

A fit of this expression to the experimental data can be used to determine the vibrational constants ω_e'' and x_e'' of the electronic ground state. For the absorption progression with $v'' = 0$ one arrives at

$$\Delta E(v) = E(v' = v + 1, v'' = 0) - E(v' = v, v'' = 0) = \omega_e' - 2\omega_e' x_e' - 2\omega_e' x_e' v . \quad (2.3)$$

Fitting the parameters of these expression to the given data, one obtains the vibrational constants for both electronic states. Note that the transition positions are given in Å. Here the results are presented in cm^{-1} . The literature value from Ref. [2] is given in brackets.

$${}^1\Sigma_g^+ : \quad \omega_e'' = 2358.49 (2358.57) \text{ cm}^{-1} \quad x_e'' = 0.0061 \quad \omega_e'' x_e'' = 14.387 (14.324) \text{ cm}^{-1}$$

$${}^1\Pi_g : \quad \omega_e' = 1691.63 (1694.20) \text{ cm}^{-1} \quad x_e' = 0.0081 \quad \omega_e' x_e' = 13.702 (13.949) \text{ cm}^{-1}$$

- c) Plotting of the absorption intensities (Figure 2-2) reveals the typical pattern for an excited state which has a different equilibrium bond length than the ground state. This means that the potential energy curve of the excited state is shifted to longer or shorter bond lengths with respect to the ground state potential energy curve.

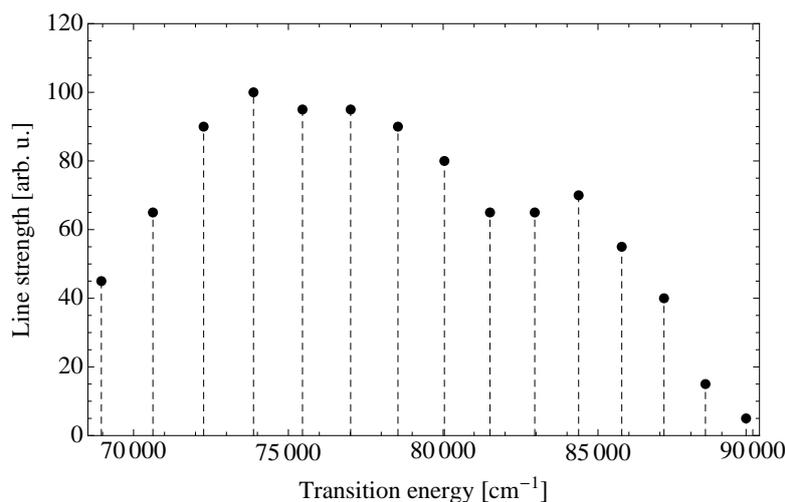


Figure 2-2: Line spectrum of the absorption intensities.

Typical vibrational progression intensity distributions for the two cases of almost equal and significantly different equilibrium distances r_e are shown in Figure 2-3.

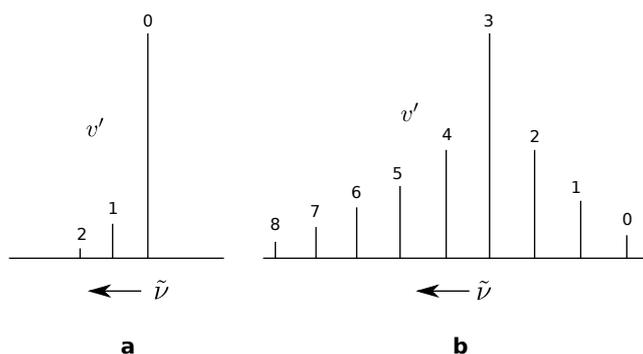


Figure 2-3: Qualitative intensity distributions for the case where $r'_e = r''_e$ (a) and the case $r'_e > r''_e$ (b)

- d) The intensities are influenced by the population of the vibrational levels and by the overlap of the vibrational wavefunctions (Franck-Condon factors).
- e) As discussed above, the intensity of a transition in the absorption spectrum is determined by the transition probability and by the population of the initial level. In a sample of light molecules in thermal equilibrium at room temperature (or below), most molecules will be in the $v'' = 0$ level (Boltzman factor). Thus one can expect a prominent progression in the absorption from this level.

Problem 3: Rovibrational spectroscopy of HCl

a) The electronic ground state of HCl is a $^1\Sigma^+$ term. For diatomics the rotational selection rule for transitions between states with $\Lambda=0$ (Σ states) is $\Delta J = J' - J'' = \pm 1$. We obtain therefore a so-called P branch with $\Delta J = -1$ and an R branch with $\Delta J = +1$. The transition wavenumbers $\tilde{\nu} = T(v', J') - T(v'', J'')$ are given by

$$\begin{aligned}\tilde{\nu}_{\Delta J}(J) &= T(v', J + \Delta J) - T(v'', J) \\ &= G(v') - G(v'') + B'(J + \Delta J)(J + \Delta J + 1) - B''J(J + 1) \\ &\quad - D'(J + \Delta J)^2(J + \Delta J + 1)^2 + D''J^2(J + 1)^2 + \dots, \\ \tilde{\nu}_{\text{P}}(J) &= G(v') - G(v'') + B'(J - 1)J - B''J(J + 1) \\ &\quad - D'(J - 1)^2J^2 + D''J^2(J + 1)^2 + \dots, \\ &= G(v') - G(v'') + B'(-J)(-J + 1) - B''(-J)(-J - 1) \\ &\quad - D'(-J)^2(-J + 1)^2 + D''(-J)^2(-J - 1)^2 + \dots, \tag{3.1}\end{aligned}$$

$$\begin{aligned}\tilde{\nu}_{\text{R}}(J) &= G(v') - G(v'') + B'(J + 1)(J + 2) - B''(J + 1)J \\ &\quad - D'(J + 1)^2(J + 2)^2 + D''(J + 1)^2(J)^2 + \dots \tag{3.2}\end{aligned}$$

Eqs. (3.1) and (3.2) may be replaced by a single formula

$$\begin{aligned}\tilde{\nu}(m) &= G(v') - G(v'') + B'm(m + 1) - B''m(m - 1) \\ &\quad - D'm^2(m + 1)^2 + D''m^2(m - 1)^2 + H'm^3(m + 1)^3 - H''m^3(m - 1)^3 + \dots \\ &= \tilde{\nu}_0 + (B' + B'')m + (B' - B'' + D'' - D')m^2 + [-2(D' + D'') + (H' + H'')]m^3 \\ &\quad + [(D'' - D') + 3(H'' - H') + \dots]m^4 + \dots \\ &\approx \tilde{\nu}_0 + (B' + B'')m + (B' - B'')m^2 - 4Dm^3 \tag{3.3}\end{aligned}$$

where $\tilde{\nu}_{\text{P}}(J) = \tilde{\nu}(m=-J)$ and $\tilde{\nu}_{\text{R}}(J) = \tilde{\nu}(m=J+1)$. Note that there is no line for $m = 0$. For vibrational transitions starting from $v'' = 0$ we obtain

$$\begin{aligned}\tilde{\nu}_0 &= G(v') - G(0) = v'\omega_e - v'(v' + 1)\omega_e x_e, \\ B' + B'' &= 2B_e - (v' + 1)\alpha_e, \\ B' - B'' &= -v'\alpha_e.\end{aligned}$$

For the fundamental vibration we get

$$\begin{aligned}\tilde{\nu}_{\text{P}}(J) &= \omega_e - 2\omega_e x_e - 2B_e J - \alpha_e J(J - 2) + 4DJ^3, \\ \tilde{\nu}_{\text{R}}(J) &= \omega_e - 2\omega_e x_e + 2B_e(J + 1) - \alpha_e(J + 1)(J + 3) - 4D(J + 1)^3 \\ \tilde{\nu}(m) &= \omega_e - 2\omega_e x_e + 2B_e m - \alpha_e m(m + 2) - 4Dm^3.\end{aligned}$$

The definitions for the first harmonic can be written down in full analogy. As the form of Eq. (3.3) suggests, the spectroscopic constants can be obtained by fitting a polynomial function to the observed transition wavenumbers.

- b) The assignment of the transitions in the fundamental band are shown in table 3.1. The transitions of the first harmonic can be assigned in full analogy, which is not shown explicitly. The additional resonances appearing in the spectrum of the $v' = 2 \leftarrow v'' = 0$ vibrational band of HCl are due to the isotopolog H^{37}Cl .
- c) In the solution we will employ the method of combination differences. For the fundamental one finds the following expressions for the combination differences:

$$\begin{aligned}\Delta\tilde{\nu}_{\text{P}}(J) &= \tilde{\nu}_{\text{P}}(J + 1) - \tilde{\nu}_{\text{P}}(J) = -2B_e - \alpha_e(2J - 1) + 4D(3J^2 + 3J + 1), \\ \Delta\tilde{\nu}_{\text{R}}(J) &= \tilde{\nu}_{\text{R}}(J + 1) - \tilde{\nu}_{\text{R}}(J) = 2B_e - \alpha_e(2J + 5) - 4D(3J^2 + 9J + 7), \\ \Delta^2\tilde{\nu}_{\text{P}}(J) &= \Delta\tilde{\nu}_{\text{P}}(J + 1) - \Delta\tilde{\nu}_{\text{P}}(J) = -2\alpha_e + 24D(J + 1), \\ \Delta^2\tilde{\nu}_{\text{R}}(J) &= \Delta\tilde{\nu}_{\text{R}}(J + 1) - \Delta\tilde{\nu}_{\text{R}}(J) = -2\alpha_e - 24D(J + 2),\end{aligned}$$

Table 3.1: Assignment and experimental differences, second and third differences of the vibrational band $v' = 1 \leftarrow v'' = 0$.

	J	m	$\tilde{\nu}(m)/\text{cm}^{-1}$	$\Delta\tilde{\nu}(m)/\text{cm}^{-1}$	$\Delta^2\tilde{\nu}(m)/\text{cm}^{-1}$	$\Delta^3\tilde{\nu}(m)/\text{cm}^{-1}$
P(12)	12	-12	2599.03962	26.70536	-0.46434	-0.01054
P(11)	11	-11	2625.74498	26.24102	-0.47488	-0.01605
P(10)	10	-10	2651.98600	25.76614	-0.49093	-0.01156
P(9)	9	-9	2677.75214	25.27521	-0.50249	-0.01432
P(8)	8	-8	2703.02735	24.77272	-0.51681	-0.01346
P(7)	7	-7	2727.80007	24.25591	-0.53027	-0.01289
P(6)	6	-6	2752.05598	23.72564	-0.54316	-0.01289
P(5)	5	-5	2775.78162	23.18248	-0.55605	-0.01398
P(4)	4	-4	2798.96410	22.62643	-0.57003	-0.01351
P(3)	3	-3	2821.59053	22.05640	-0.58354	
P(2)	2	-2	2843.64693	21.47286		
P(1)	1	-1	2865.11979			
R(0)	0	1	2906.27016	19.64891	-0.63174	-0.01431
R(1)	1	2	2925.91907	19.01717	-0.64605	-0.01086
R(2)	2	3	2944.93624	18.37112	-0.65691	-0.01115
R(3)	3	4	2963.30736	17.71421	-0.66806	-0.01239
R(4)	4	5	2981.02157	17.04615	-0.68045	-0.01060
R(5)	5	6	2998.06772	16.36570	-0.69105	-0.01217
R(6)	6	7	3014.43342	15.67465	-0.70322	-0.00972
R(7)	7	8	3030.10807	14.97143	-0.71294	-0.01223
R(8)	8	9	3045.07950	14.25849	-0.72517	-0.00881
R(9)	9	10	3059.33799	13.53332	-0.73398	
R(10)	10	11	3072.87131	12.79934		
R(11)	11	12	3085.67065			

or, when using Eq. (3.3),

$$\begin{aligned}\Delta\tilde{\nu}(m) &= \tilde{\nu}(m+1) - \tilde{\nu}(m) = (B' + B'') + 2(B' - B'')(2m+1) - 4D(3m^2 + 3m + 1) \\ &= (2B_e - 3\alpha_e - 4D) - (2\alpha_e + 12D)m - 12Dm^2, \\ \Delta^2\tilde{\nu}(m) &= \Delta\tilde{\nu}(m+1) - \Delta\tilde{\nu}(m) = 2(B' - B'') - 24D(m+1) \\ &= -(2\alpha_e + 24D) - 24Dm, \\ \Delta^3\tilde{\nu}(m) &= \Delta^2\tilde{\nu}(m+1) - \Delta^2\tilde{\nu}(m) = -24D,\end{aligned}$$

where $\Delta^n\tilde{\nu}_P(J) = (-1)^n\Delta\tilde{\nu}(m=-J-n)$ and $\Delta^n\tilde{\nu}_R(J) = \Delta^n\tilde{\nu}(m=J+1)$.

The average of the third differences $\Delta^3\tilde{\nu}$ in Table 3.1 yields $D = 5.13 \cdot 10^{-4} \text{ cm}^{-1}$, (the first harmonic can be assigned in full analogy, which is not shown explicitly) from which the other parameters can be deduced. A polynomial fit of third order (including also the first harmonic $v' = 2 \leftarrow v'' = 0$) yields

$$\begin{aligned}D &= 5.200(33) \cdot 10^{-4} \text{ cm}^{-1}, \\ \alpha_e &= 0.30259(18) \text{ cm}^{-1}, \\ B_e &= 10.59108(57) \text{ cm}^{-1}, \\ \tilde{\nu}_{01} &= \omega_e - 2\omega_e x_e = 2885.9838 \text{ cm}^{-1}.\end{aligned}$$

With the value $\tilde{\nu}_{02} = G(2) - G(0) = 2\omega_e - 6\omega_e x_e = 5668.006(2) \text{ cm}^{-1}$ we obtain
 $\omega_e = 3(G(1) - G(0)) - (G(2) - G(0)) = 2989.878(44) \text{ cm}^{-1}$ and
 $\omega_e x_e = (G(1) - G(0)) - (G(2) - G(0))/2 = 51.956(12) \text{ cm}^{-1}$.

Huber & Herzberg [2] give the following values: $\omega_e = 2990.946 \text{ cm}^{-1}$, $\omega_e x_e = 52.8186 \text{ cm}^{-1}$,
 $B_e = 10.59341 \text{ cm}^{-1}$, $\alpha_e = 0.30718 \text{ cm}^{-1}$, $D = 5.3194 \cdot 10^{-4} \text{ cm}^{-1}$.

- d) The bond length of the H^{35}Cl molecule at equilibrium R_e can be derived from the rotational constant B_e :

$$B_e = \frac{\hbar}{4\pi c I} \quad \text{with: } I = \mu R^2$$

$$= \frac{\hbar}{4\pi c \mu R_e^2} \quad (3.4)$$

$$\mu = [(1.008 \text{ u})^{-1} + (34.9689 \text{ u})^{-1}]^{-1} = 1.62693 \cdot 10^{-27} \text{ kg} \quad (3.5)$$

$$R_e = \sqrt{\frac{h}{8\pi^2 c \mu B_e}} = 1.274584(3) \cdot 10^{-10} \text{ m} = 1.274584(3) \text{ \AA} \quad (3.6)$$

References

- [1] A. Lofthus, The Spectrum of Molecular Nitrogen, *J. Phys. Chem. Ref. Data*, **6**(1) (1977) 113–307.
- [2] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. IV: Constants of diatomic molecules*, Van Nostrand Reinhold Company Inc. New York, 1979.
- [3] G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. I: Spectra of diatomic molecules*, Krieger Publishing Company Inc. Malabar (Florida), 1989.