

# Week 9: Electronic Spectroscopy

Simon Elias Schrader

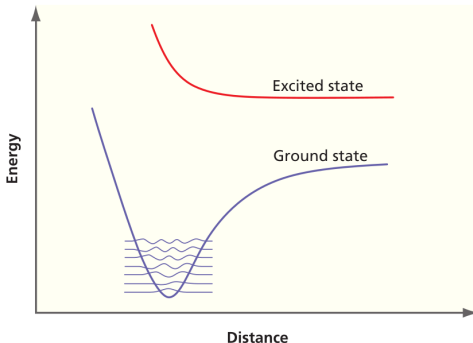
November 1<sup>st</sup> 2024

- Q14.7 The rate of fluorescence is higher than that for phosphorescence. Can you explain this fact?
- Q14.16 The ground state of  $O_2^+$  is  $X^2\Pi_g$ , and the next few excited states, in order of increasing energy, are  $a^4\Pi_u$ ,  $A^2\Pi_u$ ,  $b^4\Sigma_g^-$ ,  $^2\Delta_g$ ,  $^2\Sigma_g^-$ , and  $c^4\Sigma_u^-$ . On the basis of selection rules, which of the excited states can be accessed from the ground state by absorption of UV light?
- How many distinguishable states belong to the following terms:
  - 1  $^1\Sigma_g^+$
  - 2  $^3\Sigma_g^-$
  - 3  $^2\Pi$
  - 4  $^2\Delta$

# Flere diskusjonsoppgaver

- Q14.21 In a simple model used to analyze UV photoelectron spectra, the orbital energies of the neutral molecule and the cation formed by ejection of an electron are assumed to be the same. In fact, some relaxation occurs to compensate for the reduction in the number of electrons by one. Would you expect the orbital energies to increase or decrease in the relaxation? Explain your answer.

**Q14.13** What do you expect the electronic spectrum to look like for the ground and excited states shown here?



- **P14.2** The ground electronic state of  $\text{O}_2$  is  $^3\Sigma_g^-$ , and the next two highest energy states are  $^1\Delta_g$  ( $7918 \text{ cm}^{-1}$ ), and  $^1\Sigma_g^+$  ( $13195 \text{ cm}^{-1}$ ), where the value in parentheses is the energy of the state relative to the ground state.
  - a. Determine the excitation wavelength required for a transition between the ground state and the first two excited states.
  - b. Are these transitions allowed? Why or why not?

## En oppgave til

**P14.6** Consider a diatomic molecule for which the bond force constant in the ground and excited electronic states is the same, but the equilibrium bond length is shifted by an amount  $\delta$  in the excited state relative to the ground state. For this case, the vibrational wave functions for the  $n = 0$  state are:

$$\psi_{g,0} = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha r^2}, \quad \psi_{e,0} = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{1}{2}\alpha(r-\delta)^2}, \quad \alpha = \sqrt{\frac{k\mu}{\hbar^2}}$$

Calculate the Franck–Condon factor for the 0–0 transition for this molecule by evaluating the following expression:

$$\left| \int_{-\infty}^{\infty} \psi_{g,0}^* \psi_{e,0} dr \right|^2$$

In evaluating this expression, the following integral will be useful:

$$\int_{-\infty}^{\infty} e^{-ax^2-bx} dx = \left(\frac{\pi}{a}\right)^{1/2} e^{\frac{b^2}{4a}} \quad (a > 0).$$

- **P14.7** One method for determining Franck–Condon factors between the  $n = 0$  vibrational state of the ground electronic state and the  $n$ th vibrational level of an electronic excited state is (note change to lower-case delta for consistency with previous problem):

$$FC_{0 \rightarrow n} = \frac{1}{n!} \left( \frac{\delta^2}{2} \right)^n \exp \left( -\frac{\delta^2}{2} \right)$$

where  $\delta$  is the dimensionless displacement of the excited state relative to the ground state and can be related to atomic displacements through:

$$\delta = \left( \frac{\mu\omega}{\hbar} \right)^{1/2} (r_e - r_g)$$

- a. Determine the Franck–Condon factors for  $n = 0$  to  $n = 5$  when  $\delta = 0.20$  corresponding to the excited-state potential surface being slightly displaced from that of the ground state.
- b. How would you expect the Franck–Condon factors to change if the excited-state displacement increases to  $\delta = 2.0$ ? Verify your expectation by calculating the Franck–Condon factors from  $n = 0$  to  $n = 5$  for this displacement.

**P14.1** Determine if the following transitions are allowed or forbidden:

a.  ${}^3\Pi_u \rightarrow {}^3\Sigma_g^-$

b.  ${}^1\Sigma_g^+ \rightarrow {}^1\Pi_g$

c.  ${}^3\Sigma_g^- \rightarrow {}^3\Pi_g$

d.  ${}^1\Pi_g \rightarrow {}^1\Delta_u$