8. Molecular Spectroscopy of I$_2$

U. Diemer, H.J. Jodl

8.1 Introduction

The experiment described in this chapter is used to teach the students some specific problems of molecular spectroscopy. This is important, because students do not touch this topic within standard lectures, and the special lectures on this subject are attended only by a few of them.

To start learning molecular physics, it would be a good idea to choose a system which is not too complicated in theory and practice. The hydrogen-like diatomic molecules are such systems. Looking for a suitable molecule which is easily handled, not too reactive (as alkali metals are), possessing transitions in the visible region of the spectrum, and a reasonable vapour pressure at not too high temperatures, iodine is a very good candidate.

The transition $X^1\Sigma_g^+ \rightarrow B^3\Pi_u^+$ of the I$_2$ molecule can be treated as a prototype example with which the students learn that molecular spectra, even in the case of the bandspectra of a diatomic molecule, are much more complicated than atomic spectra (line spectra), because of the enormous amount of lines appearing due to different excitations within the molecule.

On the experimental side, the students will become familiar with the classical method of absorption spectroscopy and recognize that this technique can be used to get information about the groundstate and the excited states of the molecule. At the same time it will be clear that this advantage will be balanced by the disadvantage of the large amount of information included in such a spectrum, which makes the analysis pretty complicated.

In addition, the students will learn the modern technique of laser-induced fluorescence (LIF), and its advantages and disadvantages. The analysis of such a spectrum is much easier than in the case of an absorption spectrum, because only one upper level is excited (in most cases well known), and there exist selection rules for allowed transitions. So there are only a few lines in the spectrum, and the advantage of easy interpretation of the spectrum is purchased for the price of less information (only about the groundstate).

In connection with those types of measurements where the computer is used as a tool to record data, the students will use the computer as a powerful aid in analysing data, although they use classical methods such as Deslandres tables and Birge–Sponer plots\(^1\) to deduce molecular constants.

\(^1\) See the next section for a short explanation of these methods.
from their spectroscopic data. The students will also model a Morse potential containing the studied molecular states by using their calculated molecular constants.

If there is some time left for pleasure at the end of all that work, the students may do some optional exercises applying the computer. Here they can use a lot of useful tools available in a software pool at our physics department to do their investigations. For example, they can use a nonlinear fit routine (NLFIT) to fit a theoretical curve to the measured line shape of a fluorescence line, or to fit the shape of an absorption band system.

If they wish, the students can also use a special program to calculate a potential curve based on their measured data using the RKR (Rydberg, Klein, Rees) method and compare this RKR potential with the Morse potential they calculated before; a typical procedure, well established in spectroscopic research laboratories.

8.2 Some Basic Physics of the Diatomic Molecule

Because the recorded spectra are doppler limited, no rotational structure is resolved. Therefore it is sufficient to describe the diatomic molecule $I_2$ by the model of an anharmonic oscillator, explaining the obtained spectra. The energy levels of the anharmonic oscillator are given by

$$G(v) = \omega_e (v + 1/2) + \omega_e x_e (v + 1/2)^2 + \cdots$$

(8.1)

(see [8.1]). $\omega_e$ and $\omega_e x_e$ are called vibrational constants of the molecule. Notice that the sign of $\omega_e x_e$ is negative, therefore this value decreases the energy gap between two vibrational levels, referred to by the vibrational quantum numbers $v$ and $v + 1$. To distinguish the constants and quantum numbers of the groundstate and the excited state, it is usual to refer the groundstate by a double prime (\textsuperscript{''}) and the excited state by a single prime (\textsuperscript{'}).

The energy of an observed line in the spectrum is due to the difference of the energy of the ground and the excited state:

$$\tilde{v}(v'', v') = G(v') - G(v'') =$$

$$[T_0 + \omega_e (v' + 1/2) + \omega_e x_e (v' + 1/2)^2 + \cdots] - [\omega_e (v'' + 1/2) + \omega_e x_e (v'' + 1/2)^2 + \cdots].$$

(8.2)

$T_0$ is the energy difference between the minima of the two potentials, representing the pure electronic transition. Usually these energies are expressed in cm\textsuperscript{-1}, i.e. the reciprocal of the wavelength in centimeters. As one can see from dimensional considerations, this value is proportional to the energy by the factor of $hc$ ($c$ expressed in cm/s).