Spectrum of molecular nitrogen

Introduction

A single atom has an energy which is associated with its electrons. A molecule, with two or more atoms, and hence two or more nuclei, also has energy associated with the motion of the nuclei. There are two components to this nuclear motion
  - Periodic changes in the distance between the nuclei (vibration)
  - Motion of the nuclei around each other (rotation)

We shall be restricting the discussion to diatomic molecules, which have only one vibrational mode. Nitrogen will be the example. Polyatomic molecules have a similar spectroscopic properties, although the presence of multiple vibrational modes makes interpreting the spectra much harder, and in many cases impossible.

Vibrational Motion

Vibrational motion is normally the more energetic of the nuclear motions. In the first approximation the two nuclei form an harmonic quantum mechanical oscillator, for which the energies are given by

$$E(v) = \hbar\omega_e (v + \tfrac{1}{2})$$

in which v is the vibrational quantum number ($v \geq 0$), and ω_e is a constant for a given electronic state, equal to the classical angular frequency of oscillation. A better approximation is the anharmonic oscillator, for which

$$E(v) = \hbar\omega_e (v + \tfrac{1}{2}) + \hbar\omega_e x_e (v + \tfrac{1}{2})^2 + \ldots \ldots$$

Rotational Motion

The first approximation to the rotational motion of the nuclei is the rigid rotator, two nuclei orbiting each other with a constant separation. The energies of a rigid rotator are given by

$$E(J) = B \, J \, (J+1)$$

where J is the rotational quantum number ($J \geq 0$), and B is known as the rotational constant. A better approximation allows for variation in the distance between nuclei as the molecule rotates, and

$$E(J) = B \, J \, (J+1) - D \, [J(J+1)]^2 + \ldots \ldots$$

Electronic energy levels

In the approximation that the electronic motion and the nuclear motions can be separated (the WKB approximation) the total energy of the molecule is the sum of its electronic, vibrational, and rotational energies

$$E = T_e + \hbar\omega_e (v + \tfrac{1}{2}) + \hbar\omega_e x_e (v + \tfrac{1}{2})^2 + B \, J \, (J+1) - D \, [J(J+1)]^2 + \ldots \ldots$$

in this expression the term T_e is the energy that a non-vibrating, non-rotating molecules would have. Note that no molecule can have this energy, even when $v = J = 0$.

Spectra

For this project you will record the spectrum of nitrogen in the range 300 nm to 450nm (3000 Å to 4500 Å). You should be able to

- identify the vibrational bands and assign their upper and lower quantum numbers
- show what is meant by the term "violet degraded", and explain what that implies.

Resources

- http://www.astro.uwo.ca/~jlandstr/p467/lec5-mol_spect/index.html
- http://mackenzie.chem.ox.ac.uk/teaching/Molecular%20Electronic%20Spectroscopy.pdf