Analysis and simulation of spectra of linear molecule

0 Abstract

High resolution molecular spectra contain abundant information on structure and dynamics of molecules. However, extraction of such useful information necessitates a procedure of spectral assignment in which each spectral line is assigned to a set of quantum numbers. This procedure has been traditionally performed by making use of regular patterns that are obviously seen in the observed spectrum. The goal of this project is to learn one of the methods of spectral analysis, which directly uses such patterns of lines in the spectrum by drawing so-called Loomis-Wood diagrams. The method was originally proposed by Loomis and Wood [1].

We will investigate the properties of spectra of linear molecules. Considering its Hamiltonian we will construct Loomis-Wood diagrams in order to assign the spectrum of the OSC molecule, which is a benchmark of spectra of linear molecules. Fitting of the main parameters of the Hamiltonian will provide us information about spectral and structural properties of the OCS molecule. Integrated intensities of the rovibrational transitions will be calculated, which finally will allow to construct a simulated spectrum of the molecule.

1 Assignment of spectrum.

Assignment of the spectrum is the first stage of a spectral analysis. To assign the spectrum means to provide every line with quantum numbers of the initial and final energy level. Usually the assignment is simplified making use of the Ground State Combination Differences (GSCD) method. Using of information from rotational energy level structure of the ground state one can find transitions with the same value of $J'$, but different $J''$, in the branches (in the notation when transitions occur from level $J''$ to $J'$).

In accordance with the general theory, selection rules for ro-vibrational transitions in spectra of linear molecule are given by $\Delta J = \pm 1$ (those with $\Delta J = 0$ are forbidden).

Transitions with decreasing rotational quantum number $J$ form the so-called $P-$branch, and transitions with increasing $J$ form the $R-$branch. In a first approximation several lines in the spectrum are separated by the distance, which equal to twice the value of rotational constant $B$ of the molecule. Transitions in the $Q-$branch are forbidden, which leads to the fact that lines corresponding to transitions with $J' = J''$ are missing in the spectrum and the distance between lines $P(1)$ and $R(0)$ is approximately equal to $4B$ (How would you recognize, where the band center is located?). Thereby the problem of assignment of transitions in the spectrum of linear molecule becomes easy. With that in mind assign the transitions in the spectrum, providing each line with corresponding quantum numbers.

An experimental spectrum of OCS molecule to be analyzed is presented on Figure 1. It was measured with a Bruker IFS 125 HR spectrometer with an optical path length of 20 cm at room temperature and a pressure of 0.4 mbar with resolution of 0.001 cm$^{-1}$. 
2 Hamiltonian of linear molecule.

The rotational contribution to the energy levels of an unperturbed linear rotor in any vibrational state can be shown to be (Eq. (3.34), lecture notes):

\[ F_v(J) = B_v J(J + 1) - D_v J^2(J + 1)^2 + ... \]  

(1)

Thus, from selection rules \( \Delta J = \pm 1 \), rovibrational transitions in P-branch for linear molecule can be described by:

\[
\tilde{\nu}[P(J)] = \tilde{\nu}_0 + F_v'(J - 1) - F_v''(J) \\
= \tilde{\nu}_0 + B_v' J(J - 1) - D_v'(J - 1)^2 J^2 + ... \\
- [B_{v'} J(J + 1) - D_{v'} J^2(J + 1)^2] + ...
\]

(2)

Using relations, which connect rotational and centrifugal distortion constants of upper and lower vibrational states, one can rewrite this expression as:

\[ B_{v'} = B_{v''} + \Delta B \]  

(3)

\[ D_{v'} = D_{v''} + \Delta D \]  

(4)

\[
\tilde{\nu}[P(J)] - \tilde{\nu}_0 = (2B_{v''} + \Delta B)(-J) + (\Delta B - \Delta D)(-J)^2 \\
-2(2D_{v''} + \Delta D)(-J)^3 - \Delta D(-J)^4 + ...
\]

(5)

or in common, for transitions in \( P- \) and \( R- \) branches one can write polynomial function on powers of \( m \) (\( m = -J \) for \( P- \) branch and \( m = J + 1 \) for \( R- \) branch):

\[
\tilde{\nu}(m) = (2B_{v''} + \Delta B)m + (\Delta B - \Delta D)m^2 \\
-2(2D_{v''} + \Delta D)m^3 - \Delta Dm^4 + ...
\]

(6)
For simplicity at the first stage let us consider the rigid rotor approximation, taking into account the only first linear term of Eq.(6). By varying of $\Delta B$ find such value of $(2B_{\nu'} + \Delta B)$ that describes the spectrum correct. Check each step of the iteration procedure by plotting of a Loomis-Wood diagram.

3 Loomis-Wood diagrams.

The method of recognizing of regular patterns in molecular spectra has been originally proposed by Loomis and Wood in 1928 [1]. In accordance with this method in a first approximation the rovibrational spectrum is cutted on slices of width of $(2B_{\nu'} + \Delta B)$. Then each of the slices is standing on the previous one such that lines belonging to the same series of transitions are placed on one line in the case if we have correct values of parameters. Otherwise the parameters should be fitted in order to observe a regular pattern of lines on the diagram.

On the frame of the present part of the project we will consider only one main parameter, which is the rotational constant of the OCS molecule. Initial value of $B$ to be varied you can extract directly from the spectrum. The goal is to find out correct value of the parameter by the fitting procedure. Loomis-Wood diagrams will be a good visualisation of your results. An example of diagram is presented on Figure 2.

![Figure 2: An example of Loomis-Wood diagram [2].](image)

In an ideal fit you would obtain a straight vertical line dots on your diagram, which correspond to series of the transitions in the spectrum. Will you observe it on your sketches? Explain your answer. What should you do to make the pattern on the diagram more straight, i.e. to describe the spectrum more correct?

Take into account higher terms in the polynomial expression of Hamiltonian. How much differs the value of rotational constant from that, which you obtained in the rigid rotor approximation?
4 Intensity calculations.

The line strength of individual rovibrational transition can be calculated in accordance with following formula (e.g. [2]):

\[ S_{fi} = \int_{0}^{\infty} \sigma_{fi}(\nu) d\nu = \frac{1}{C_i L} \int_{0}^{\infty} \ln(I_0/I) d\nu, \]  

where \( \sigma_{fi}(\nu) \) is the molecular absorption cross section at frequency \( \nu \), associated with transition from state \( i \) to state \( f \); \( C_i \) is the concentration of absorbing particles, \( L \) is absorption path length, \( I_0 \) is the intensity before absorption and \( I \) is the intensity after absorption by the line. This expression is valid for any particular transition and is not influenced on the line width.

We will make use of well known [3] formula for intensity calculations:

\[ S_{fi} = \frac{8\pi^2}{(4\pi\epsilon_0)^2} g_{fi} [1 - \exp(-\nu_{fi})] \frac{N}{Q_{vib}Q_{rot}} \exp(-\frac{E_i}{kT}) A_{KJ} |R_{n'n''}^v|^2, \]

where \( \nu_{fi} \) is transition wavenumber in units of cm\(^{-1}\); \( T \) is the temperature in kelvin; \( N \) represents isotopic abundance of elements; \( Q_{vib} \) and \( Q_{rot} \) are the vibrational and rotational partition function correspondingly; \( E_i \) and \( g_i \) are energy and degeneracy factor of the initial state; \( A_{KJ} \) is the H"{o}nl-London factor and \( |R_{n'n''}^v| \) is vibrational transition moment in debye units.

The degeneracy factor for the rotational levels of a linear molecule are given by \( g_v=2J+1 \) [3]. The Value of isotopic abundance \( N \) of \(^{16}\)O\(^{12}\)C\(^{32}\)S is known to be [4] \( N=0.937395 \). Partition functions can be calculated in accordance with following formulæ [3]:

\[ Q_{vib} = (1 - e^{-\omega_1 h\nu/(kT)})^{-d_1} (1 - e^{-\omega_2 h\nu/(kT)})^{-d_2} (1 - e^{-\omega_3 h\nu/(kT)})^{-d_3}, \]
\[ Q_{rot} = \sum_J (2J+1) e^{-BJ(J+1) h\nu/(kT)} \approx 0.6951 \frac{T}{B}, \]

where \( d_i \) is the degree of degeneracy of the vibration \( \omega_i \); \( B \) is the rotational constant. H"{o}nl-London factors for linear molecule [3] can be expressed as:

\[ A_{KJ} = \frac{(J+1)^2}{(J+1)(2J+1)} \]  

\[ A_{KJ} = \frac{J^2}{J(2J+1)}, \]

for \( \Delta J=\pm 1 \) correspondingly. The value of the vibrational transition moment is derived [5] as \( R_{n'n''}^v=0.0632 \) Debye (1 Debye = 3.336 \( \times 10^{30} \) C m).

5 Line shape.

Due to termal motion of the molecules the resulting line profile is known to be a Doppler profile. The broadening of the line depends only on the frequency of the spectral line,
the mass of the emitting particles, and their temperature. In Exercise 1 you found out line shape caused by Doppler broadening. Use the results of Problem 3 in Exercise 1 for the calculation of line shape and the construction of the simulated spectrum.

References


