FTIR spectroscopy of N_2O

1 Preparation

1.1 Molecular Physics

- **normal modes**
  "A normal mode of an oscillating system is a pattern of motion in which all parts of the system move with the same frequency and with a fixed phase relation." (Wikipedia)
  i.e. collective movement of the atoms of a molecule so that the center of mass is conserved.
  There are several possibilities for such collective movements. For molecules with N atoms, linear molecules have $3N - 5$ vibrational degrees of freedom, whereas nonlinear molecules have $3N - 6$ vibrational modes. I.e. simple diatomic molecules have only one bond and only one vibrational band. More complex molecules have many bonds, and their vibrational spectra are correspondingly more complex.

- **IR activity**
  In order for a vibrational mode in a molecule to be *IR active*, it must be associated with changes in the dipole moment. A permanent dipole moment (as for pure rotation) is not necessary, since the rule requires only a *change* in the dipole moment. Hence, although CO_2 does not have a permanent dipole moment, it does have IR active bands, since the asymmetric stretching and the bending vibration cause a change in the dipole moment. If a diatomic molecule is symmetrical, e.g. N_2 or O_2, the vibrational bands are not observed in the IR spectrum.

- **fundamental frequencies, overtone and combination bands**
  The simplest and most important IR bands arise from the normal modes, the simplest distortions of the molecule. These are the fundamental bands. Overtone bands arise from the absorption of a photon leading to a doubly excited vibrational state. Such bands appear at approximately twice the energy of the fundamental mode. The so-called combination modes involve more than one vibrational mode.

- **vibration-rotation energies and resulting spectra**
  In general, molecules vibrate and rotate at the same time, giving rise to vibration-rotation spectra. The selection rules are obtained simply by combining the pure rotational selection rules $\Delta J = 0, \pm 1$ with the vibrational selection rules $\Delta v = \pm 1 (\pm 2, ...)$. The transitions are organized into branches on the basis of the change in J value.
  The energy of a given v, J level of a diatomic molecule (only one vibrational mode) is

$$
\begin{aligned}
E_{vJ} &= G(v) + F(J) \\
&= \omega_e(v + \tfrac{1}{2}) - \omega_e x_e(v + \tfrac{1}{2})^2 + \omega_e y_e(v + \tfrac{1}{2})^3 + ... \\
&\quad + B_v J(J+1) - D_v[J(J+1)]^2 + ... \quad (1)
\end{aligned}
$$

$$(2)$$

Reminder: The anharmonicity of the potential (no pure harmonic oscillator) gives rise to the anharmonicity parameters $\omega_e x_e$, $\omega_e y_e$, etc. The vibration of the molecule causes a change in the rotational constants (due to change of the bond length). Therefore, every vibrational state v has its own set of rotational constants B_v, D_v, etc.

Line positions (without centrifugal distortion) for transitions in the R- and P-branch:

$$\nu_R(v', J+1 \leftarrow v'', J) = \nu_0 + 2B' + (3B' - B'')J + (B' - B'')J^2 \tag{3}$$

$$\nu_P(v', J-1 \leftarrow v'', J) = \nu_0 - (B' + B'')J + (B' - B'')J^2 \tag{4}$$

with $\nu_0 = G(v') - G(v'')$.

For polyatomic molecules the total vibrational energy is the sum of the energies of the $3N - 6$ ($3N - 5$) oscillators:

$$G(v_1, ...v_{3N-6}) = \sum_{i=1}^{3N-6} \omega_i(v_i + \tfrac{1}{2}) + \text{anharmonicity...} \tag{5}$$

- **bending vibration of linear molecules (l quantum number)**
  The bending mode of a linear molecule is doubly degenerate because of the possibility of bending in plane or out of plane (two degrees of freedom, but same energy/frequency). The vibrational energy of this mode is then given by a d-dimensional harmonic oscillator

$$G(v_{deg}) = \omega_{deg}(v + \tfrac{d}{2})$$

  with $d = 2$ for the bending of a linear molecule.

  The 2-dim harmonic oscillator Hamiltonian can be converted to plane polar coordinates $\rho = (x^2 + y^2)^{1/2}$ and $\phi = \tan^{-1}(y/x)$ and results in a wavefunction
$$\Psi_{vl} = R_{vl}(\rho)e^{il\phi}$$

  where the new quantum number l is associated with a vibrational angular momentum of $\pm|l|\ \hbar$ with $|l| = v, v - 2, ...0$ or 1.

  Classically, the two oscillators in the x and y directions can be phased such that the nuclei execute circular motion of small amplitude about the z-axis. In quantum mechanics this motion is quantized and only $\pm l\hbar$ units of angular momentum are possible. The double degeneracy for each value of l is associated with clockwise or counterclockwise motion of the nuclei in a linear molecule. The energy states are often labeled with Σ, Π, Δ to designate the vibrational angular momentum; often l is used as a superscript v_2^l.
  Vibrational energy-level pattern for the bending mode of a linear molecule: See Bernath, Fig. 6.23., p. 179 (1st ed.), p. 180 (2nd ed.).
  Rotational structure of the first few bending vibrational and rotational energy levels of a linear triatomic molecule: See Bernath, Fig. 6.25., p. 180 (1st ed.), p. 181 (2nd ed.).
  $\Sigma - \Sigma$ transitions exhibit only R- and P-branch (rotational angular momentum perpendicular to molecular axis, $\Delta J = \pm 1$).
  $\Sigma - \Pi$ transitions (i.e. for $l = 1$) exhibit R-, P-, *and* Q-branch (rotational angular momentum $\vec{R}$ and vibrational angular momentum $\vec{l}$ couple to give the total angular momentum $\vec{J}$, which is no longer perpendicular to the molecular axis, $\Delta J = 0, \pm 1$).

- **vibration-rotation interaction constants**
  Each vibrational level has a different rotational constant B_v (see Eq. (1)), which is expressed as

$$B_v = B_e - \sum \alpha_i \left(v_i + \frac{d}{2}\right) \tag{6}$$

  B_e is the equilibrium rotational constant, and the α_i are the vibration-rotation interaction constants. d_i is the degeneracy of the ith mode.

- **anharmonicity constants**
  The vibrational energy for a linear triatomic molecule (3 fundamental modes; ν_2 bending vibration) is given by (see Herzberg, p. 211 or Bernath, p. 254 (1st ed.), p. 257 (2nd ed.)):

$$
\begin{aligned}
G(v_1, v_2, v_3, l_2) = {} & \omega_1(v_1 + \tfrac{1}{2}) + \omega_2(v_2 + 1) + \omega_3(v_3 + \tfrac{1}{2}) + x_{11}(v_1 + \tfrac{1}{2})^2 + x_{22}(v_2 + 1)^2 + x_{33}(v_3 + \tfrac{1}{2})^2 \\
& + x_{12}(v_1 + \tfrac{1}{2})(v_2 + 1) + x_{13}(v_1 + \tfrac{1}{2})(v_3 + \tfrac{1}{2}) + x_{23}(v_2 + 1)(v_3 + \tfrac{1}{2}) + g_{22}l_2^2
\end{aligned}
$$

$$(7)$$

1.2 Techniques

- **FTIR spectroscopy**
  Rather than shining a monochromatic beam of light at the sample, the technique of fourier transform infrared (FTIR) spectroscopy uses a broadband light source and measures, how much of that light is absorbed by the sample. Next, the beam is modified to contain a different combination of frequencies, giving a second data point. This process is repeated many times. The beam modification is realized by a Michelson interferometer (see Fig. 1). The beam of light is split into two paths, reflected at two mirrors and recombined. One of the mirrors is moving, which results in different pathlengths for the two beams in the interferometer. If the pathlengths differ by an integer of the wavelength, the two beams will interfere constructively creating a strong signal at the detector. If the pathlengths differ by an integer of half the wavelength, the interference will be destructive resulting in a weak signal. Hence, the different wavelengths of the broadband source are modulated at different rates, so that at each moment the beam leaving the interferometer has a different spectral composition. Afterwards, computer processing (i.e. Fourier transformation) is required to turn the raw data (light absorption for each mirror position = interferogram) into a spectrum (light absorption for each wavelength).
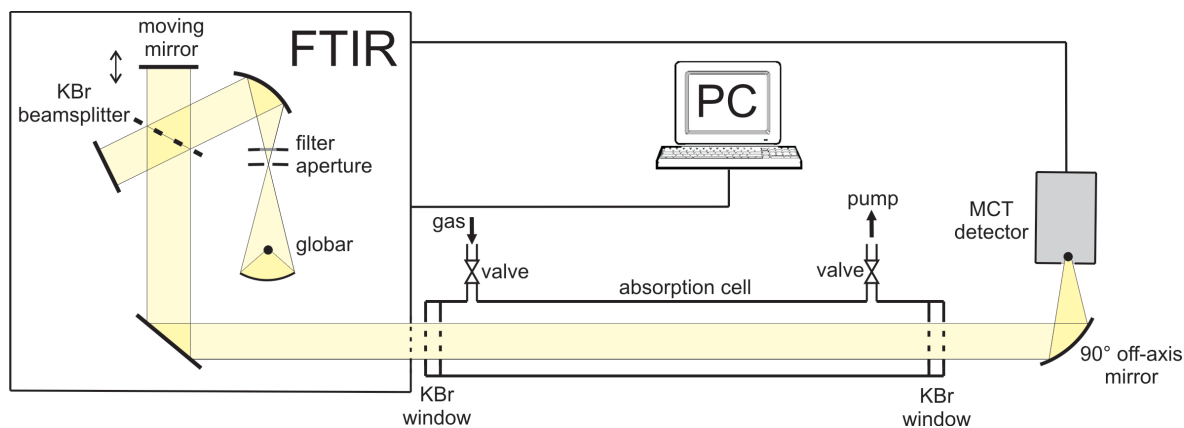

Figure 1: Experimental setup

- **Fourier transformation: Apodisation, Zerofilling, Phase correction**
  Apodisation: A transmittance spectrum is obtained when Fourier transformation is applied to the measured interferogram. However, actual measurements differ from the ideal state. In particular, the integration range for a theoretical Fourier transformation is from 0 to infinity. This would require an infinite range of movement of the moving mirror. Hence, in practice the integration has to be cut off in a finite range. This results in the creation of ripples around a large peak in the resulting spectrum. To suppress these ripples, different apodization functions can be chosen rather than suddenly discontinuing the calculation in the integration range (corresponding to a box-car waveform). The standard choice for an apodization function is the Blackman-Harris-3-Term function.

Zerofilling: *Zero-filling* means extending the length of an interferogram with a straight line. This corresponds to an interpolation between the data points of the spectrum so that the spectral lines have a smoother shape. However, a zerofilling with a factor of n results in about n-times longer computing time and n-times larger memory requirement.

Phase correction: Phase correction is the symmetrization of the measured interferogram. This is always neccessary, since in reality the interferogram is not symmetric due to optical and electrical effects causing a wavelength-dependent phase shift. The standard method for phase correction is "Mertz". It uses a small symmetric region around the center burst of the interferogram to determine the phase and extrapolates this to correct the whole spectrum.

- **MCT detector**
  MCT (Mercury Cadmium Telluride) detectors are photoconductive devices with a tunable bandgap spanning the shortwave infrared to the very long wave infrared regions. The amount of cadmium (Cd) in the alloy can be chosen to tune the optical absorption of the material to the desired infrared wavelength. Detection occurs when an infrared photon of sufficient energy kicks an electron from the valence band to the conduction band. Such an electron is collected by a suitable external readout integrated circuit and transformed into an electric signal.

2   Molecule N_2O

- linear molecule, not symmetric (N-N-O)

- $3N - 5 = 4$ normal modes: sym. stretching, antisym. stretching, bending vibration (2-fold degenerate), all infrared active

- common gas for calibration

- spectrum shows all fundamentals, as well as a large number of overtone and combination bands

- all bands are rotationally resolved

- bending vibration with Q-branch (l quantum number!)

- fitting yields rotational constants and band centers for up to 15 vibrational modes

- determination of vibration-rotation interaction constants and anharmonicity constants possible

3   Experiment

- familiarize with the experiment

- take spectrum of N_2O at about 10 mbar pressure – check visibility of rotational structure for each band (take additional spectrum with higher pressure, if neccessary)

- check background spectrum – discuss features: basic shape; molecular absorption bands

- analyze N_2O spectrum

4 Analysis

- identify fundamental bands in the spectrum (strongest bands); assign vibrational modes v_1, v_2, and v_3

- identify remaining vibrational bands to overtones or combination bands (table with frequencies and assignment for all bands)

- determine harmonic constants ω_1, ω_2, ω_2 and anharmonicity constants x_{11}, x_{22}, x_{33}, x_{12}, x_{13}, and x_{23} (see eq. (10) by fitting the observed band frequencies in a least squares analysis (e.g. with Maple)
  Note: With all 15 band center frequencies it is possible to also fit g_{22}. Without v_{040} (which is very difficult/unsecure to obtain!), $g_{22} = 3.6$ cm^{-1} has to be taken as a constant[1].

- pick a few vibrational bands (at least three *including* v_{021}) for rotational analysis[2]

- use PGopher to fit band center v_i and rotational constants for the ground state B_0 and the excited state B_i for the selected bands

- determine the vibration-rotation interaction constants α_i and the equilibrium rotational constant B_e by a least squares analysis (e.g. with Maple) using the ground state B_{000} and at least three values for the rotational constant B_i in the excited state *including* B_{021}.

4.1 Equations

4.1.1 Determination of the Anharmonicity of the Potential

Vibrational energy (see Herzberg, p. 211 or Bernath, p. 254 (1st ed.), p. 257 (2nd ed.)):

$$G(v_1, v_2, v_3, l_2) = \omega_1(v_1 + \tfrac{1}{2}) + \omega_2(v_2 + 1) + \omega_3(v_3 + \tfrac{1}{2}) + x_{11}(v_1 + \tfrac{1}{2})^2 + x_{22}(v_2 + 1)^2 + x_{33}(v_3 + \tfrac{1}{2})^2 \tag{8}$$
$$+ x_{12}(v_1 + \tfrac{1}{2})(v_2 + 1) + x_{13}(v_1 + \tfrac{1}{2})(v_3 + \tfrac{1}{2}) + x_{23}(v_2 + 1)(v_3 + \tfrac{1}{2}) + g_{22}l_2^2$$

For the ground state:

$$G(0,0,0,0) = \tfrac{1}{2}\omega_1 + \omega_2 + \tfrac{1}{2}\omega_3 + \tfrac{1}{4}x_{11} + x_{22} + \tfrac{1}{4}x_{33} + \tfrac{1}{2}x_{12} + \tfrac{1}{4}x_{13} + \tfrac{1}{2}x_{23} \tag{9}$$

Transition from ground vibrational state to excited state:

$$v_i(v_1, v_2, v_3, l_2) = G_i - G_0$$
$$= \omega_1 v_1 + \omega_2 v_2 + \omega_3 v_3 + x_{11}(v_1^2 + v_1) + x_{22}(v_2^2 + 2v_2) + x_{33}(v_3^2 + v_3) \tag{10}$$
$$+ x_{12}(v_1 v_2 + v_1 + \tfrac{v_2}{2}) + x_{13}(v_1 v_3 + \tfrac{v_1}{2} + \tfrac{v_3}{2}) + x_{23}(v_2 v_3 + \tfrac{v_2}{2} + v_3) + g_{22}l_2^2$$

4.1.2 Vibration-Rotation Interaction

Rotational constant in an excited vibrational state:

$$B_{v_1, v_2, v_3} = B_e - \alpha_1(v_1 + \tfrac{1}{2}) - \alpha_2(v_2 + 1) - \alpha_3(v_3 + \tfrac{1}{2}) \tag{11}$$

---

[1] value taken from Bryant, Reeve, Burns, *J. Chem. Educ.* **85** (2008); Herzberg: $g_{22} = 3.03$ cm^{-1}

[2] When adding a simulation for a vibrational band in PGopher, which is located *before* the previously fitted band in the spectrum, the whole analysis is screwed up. Hence, the bands which were selected for fitting have to be analyzed in the right frequency order