High resolution study of the $\nu_2$ and $\nu_5$ rovibrational fundamental bands of thionyl chloride: Interplay of an evolutionary algorithm and a line-by-line analysis

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Outline

• Context
• Experiments
• Spectral analysis using evolutionary algorithms
• Conclusions
Context

**Industrial compound**
- Cathod in Lithium-SOCl₂ batteries: remarkable energy density and lifetime.
- Global production > 10 000 tons/year
- Chlorinating reagent in the industrial production of organochlorine compounds.
- Reagent preferred due to gaseous by-products: R–OH + SOCl₂ → RCl + HCl + SO₂

**Environmental impact**
- Extremely volatile inorganic compound which reacts rapidly with water.
- Tropospheric lifetime: a few minutes (SOCl₂ + H₂O → 2HCl + SO₂)

**Defense applications**
- Nerve agent, precursor of phosgene, chloropicrine, and sarin gas
**Context**

- $C_s$ point group (pyramid, one plane of symmetry)
- **6 fundamental vibrational modes** (5 modes in the FIR)

\[
\Gamma = 4A' + 2A''
\]

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency (cm$^{-1}$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$ ($A'$)</td>
<td>194</td>
<td>[35,35] [35,37] [37,37]</td>
</tr>
<tr>
<td>$\nu_2$ ($A'$)</td>
<td>492</td>
<td>[3]</td>
</tr>
<tr>
<td>$\nu_3$ ($A'$)</td>
<td>344</td>
<td>[3]</td>
</tr>
<tr>
<td>$\nu_4$ ($A''$)</td>
<td>455</td>
<td>[3]</td>
</tr>
<tr>
<td>$\nu_5$ ($A''$)</td>
<td>284</td>
<td>[1] [2] [2] [2]</td>
</tr>
<tr>
<td>$\nu_6$ ($A''$)</td>
<td>1251</td>
<td>Will be measured in the MIR</td>
</tr>
</tbody>
</table>

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Experiment
FT-FIR spectrometer

- AILES beamline of SOLEIL synchrotron
  - Commercial Bruker IFS125
  - High resolution: $R = 0.001\ \text{cm}^{-1}$
  - White-type absorption cell (293K)

P($\text{SOCl}_2$) = 900$\mu$bar

150 meters of pathlength
Experiment
FT-FIR spectrometer

• **AILES beamline of SOLEIL synchrotron**
  • Commercial Bruker IFS125
  • **High resolution**: $R = 0.001 \text{ cm}^{-1}$
  • Synchrotron source gives a **better S/N** than classical sources (high flux of photons).

In the **100 cm}^{-1}** region

S/N of synchrotron source is **15 times** better than the classical sources

In **acquisition time**, the factor 15 becomes 225 factor!

1 day of acquisition = **225 days**
Experiment
FIR experimental spectrum

$\nu_2$ band of $\text{SO}_2$ arising from the very efficient hydrolysis of $\text{SOCl}_2$ ($\text{H}_2\text{O}$ traces)

$\text{SO}^{35}\text{Cl}_2$ (459.82 cm$^{-1}$)
$\text{SO}^{35}\text{Cl}^{37}\text{Cl}$ (458.07 cm$^{-1}$)

$\text{SO}^{35}\text{Cl}_2$ (500.09 cm$^{-1}$)
$\text{SO}^{35}\text{Cl}^{37}\text{Cl}$ (498.36 cm$^{-1}$)
Outline

- Context
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- **Spectral analysis using evolutionary algorithms**
- Conclusions
Spectral analysis using evolutionary algorithms

Steps of the spectral analysis

**EXPERIMENT**

- FIR measurements (7-1500 cm⁻¹)
- submm measurements (70-900GHz)

**THEORY AND ANALYSIS**

- Quantum chemistry calculations
- Theoretical model (Hamiltonian)

**Description of the rovibrational energy levels (\(\hat{H}\Psi = E\Psi\))**

\[
\hat{H} = V + A\hat{j}_a^2 + B\hat{j}_b^2 + C\hat{j}_c^2 - \Delta_j (\hat{j}_z^2) - \Delta_j\hat{k}\hat{j}_z^2 - \Delta_k (\hat{j}_z^2) - \frac{1}{2}\left[\delta_j\hat{\hat{j}}^2 + \delta_k\hat{j}_z^2, (\hat{j}_z^2 + \hat{j}_z^2)\right]_+
\]

The purpose is to determine the molecular parameters

**Line by line analysis : very long process**

1. We assign observed lines to transitions between rotational energy levels of the molecule \((J', K'_a K'_c \leftrightarrow J'' K''_a K''_c)\)
2. From observed and calculated rotational line frequencies, we fit the molecular parameters up to the experimental accuracy.

**Global & automatic analysis : evolutionary algorithms**

1. The evolutionary algorithms search for the best parameters to optimise directly the correspondance between the experimental and simulated spectra.

**Modelization of the spectrum for detection and monitoring applications**

**Physico-chemical properties**
Spectral analysis using evolutionary algorithms

Context

- The **automatic ga program based on evolutionary algorithms** was developed by the Nijmegen and Düsseldorf groups.

- Funded by the **EOLE excellence fellowship** to develop a collaboration with W. L. Meerts from the Nijmegen University.

- Based on the concept of **natural selection**: over the generations, the best genes are kept.

**Examples of EA analysis of high resolution spectra**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Spectrum</th>
<th>Experiment</th>
<th>Ref.</th>
</tr>
</thead>
</table>
Spectral analysis using evolutionary algorithms

How it works

1. Genes (parameters) are randomly encoded
2. Genes are grouped to form a set of chromosomes (calculated spectra)
3. The fitness function is evaluated for each chromosome
4. Reproduction and mutation of chromosomes leads to a new generation
5. Selection of the best solutions
6. Last generation?
   - Yes: Stop
   - No: Proceed to next generation

The fitness function corresponds to the normalized scalar product between the experimental spectrum (vector $f$) and the calculated spectrum (vector $g$).

$$F(f, g) = \frac{f^T W g}{\sqrt{f^T W f} \sqrt{g^T W g}}$$

Higher is the fitness function, more the calculated and experimental spectra are similar.

Population: 200 chromosomes
Generations: 300 iterations
The evolutionary algorithms have succeeded for the rotational constants and band center of the excited states but it was necessary to complete with a more traditional analysis (Loomis-Wood).

Example of two Loomis-Wood diagrams for each step of analysis

MP2/6-311++G(3df, 3pd)

EAs

Final
Spectral analysis using evolutionary algorithms

Final results

- $\nu_5$ band

<table>
<thead>
<tr>
<th>Transitions</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N$</td>
<td>$N' , J'<em>{\text{max}} , K''</em>{\text{max}}$</td>
</tr>
<tr>
<td>$\nu_5 , ^{32}\text{S}^{16}\text{O}^{35}\text{Cl}_2$</td>
<td>5107</td>
</tr>
<tr>
<td>$\nu_5 , ^{32}\text{S}^{16}\text{O}^{35}\text{Cl}^{37}\text{Cl}$</td>
<td>2885</td>
</tr>
</tbody>
</table>
Spectral analysis using evolutionary algorithms

Final results

- $v_2$ band

<table>
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<tr>
<th>Transitions</th>
<th>Standard deviation</th>
</tr>
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<tbody>
<tr>
<td>$N$</td>
<td>$N'$</td>
</tr>
<tr>
<td>$\nu_2$ $^{32}\text{S}^{16}\text{O}^{35}\text{Cl}_2$</td>
<td>2835</td>
</tr>
<tr>
<td>$\nu_2$ $^{32}\text{S}^{16}\text{O}^{35}_{\text{Cl}}^{\text{37}}\text{Cl}$</td>
<td>1617</td>
</tr>
</tbody>
</table>

![Graph showing spectral analysis results](attachment://spectral_analysis.png)
Spectral analysis using evolutionary algorithms
Complementary analysis in the submm-wave region

- Pure rotational analysis of $v_2=1$, $v_5=1$ and $v_4=1$ states

The frequency multiplier chain of the LPCA (293K)

**Source**
Commercial frequency multiplier chain (VDI)
Electronic source associated with multipliers (70-900GHz)

**Cell**
Simple pass 1.25m absorption cell

**Detection**
Good S/N ratio: 2F frequency modulation
High spectral resolution (10kHz), Doppler limit.
High sensitivity: InSb He cooled bolometer (4K)
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Conclusions

- **Global fit of the data**

  A global fit has been performed including:
  - 84534 transitions for SO$^{35}$Cl$_2$
  - 28386 transitions for SO$^{35}$Cl$^{37}$Cl

- **Advantages of the EAs approach**:
  - Gain in time
  - Efficient to analyse very dense spectra

- **Limitations of the EAs approach**:
  - Subsequent traditional analysis is needed to reach the experimental accuracy.

- Semi empirical *structure of the molecule* from the isotopologue study (CCSD(T)/cc-pV(T+d)Z vibrational correction)
Thank you for your attention

Collaborations:

- University of Nijmegen (The Netherlands)
- University of Köln (Germany)
- Synchrotron SOLEIL et l’Institut des Sciences Moléculaire d’Orsay (France)

Excellence fellowship:

- EOLE, 2 weeks funded in Nijmegen to learn how to use evolutionary algorithms with W. L. Meerts.
Questions

Comparison of the EAs and calculated parameters

\[ \delta = \frac{|\text{experimental} - \text{calculated}|}{\text{experimental}} \]

- **Ab initio calculations**: MP2/6-311++G(3df,3pd) level
- «Estimated»:
  \[ [A, B, C]_{\text{est.}} = [A, B, C]_{\text{exp.}} \times F_{\text{scaling}}^{\text{ab initio}} \] with
  \[ F_{\text{scaling}}^{\text{ab initio}} = \frac{[A, B, C]_{\text{exp.}}([35, 35])}{[A, B, C]_{\text{ab initio}}([35, 35])} \]
- «Refined» for [35,37]:
  \[ [A, B, C]_{\text{refined}}([35, 37]) = [A, B, C]_{\text{exp.}}([35, 37]) \times F_{\text{scaling}}^{\text{exp.}} \] with
  \[ F_{\text{scaling}}^{\text{exp.}} = \frac{[A, B, C]_{\text{exp.}}([35, 35])}{[A, B, C]_{\text{exp.}}([35, 37])} \]
Questions
(sub)millimeter-wave region (70-900GHz)

• The frequency multiplier chain (293K)
  • Source
    • Commercial frequency multiplier chain (VDI)
    • Electronic source associated with multipliers
  • Cell
    • Simple or double pass 1.20m absorption cell
    • P= 8µbar (flow)
  • Detection
    • Good S/N ratio : 2F frequency modulation
    • High spectral resolution (10kHz), Doppler limit.
    • High sensitivity : InSb He cooled bolometer (4K)

Double pass cell modification:
Questions
Result of the EAs

- Evolution of the best solution for each EAs fit:
  - For the main isotopologue [35,35]

\[
C_{f,g} = 100(1 - F_{f,g})
\]

\[
\text{v}_5 \text{ band}
\]

\[
\text{v}_2 \text{ band}
\]

- For the second isotopologue [35,37]

\[
C_{f,g} = 100(1 - F_{f,g})
\]

\[
\text{v}_5 \text{ band}
\]

\[
\text{v}_2 \text{ band}
\]

The best solution \((A,B,C,v)\) at each generation is given for the best cost function:

\[
C_{f,g} = 100(1 - F_{f,g})
\]

Very efficient for the [35,35] and [35,37] isotopologues of the isolated \(v_5\) band.

Efficient for [35,35] of the \(v_2\) band but few improvement for the [35,37] isotopologue, (too weak and congested).