MolExplorer:

A New Tool for Computation and Display of Spectra from the HITRAN Database

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I. **Motivation**

II. **Data Handling and Prerequisites**

III. **MolExplorer Platform**

IV. **Conclusion**

Introduction

In this talk a platform for the calculation and display of spectra is presented using the main features of the Hitran database.

This platform is called **MolExplorer**.

The talk starts with two spectroscopic examples which gave the motivation to develop such platform, then the data handling and necessary prerequisites are described, before demonstrating how the MolExplorer works and can be used.

Terahertz Spectroscopy

Since 1990 the Hamburg group has a close cooperation with Prof. D. Grischkowsky (Oklahoma State University) to study coherence and response phenomena in gases in the far infrared with fs THz pulses.

Such input pulses are completely reshaped, attenuated and delayed when transmitting a gas cell, in this case filled with 2 atm of methyl chloride. From the Fourier transform of these pulses the absorption and dispersion of the gas is calculated over a spectral range of several THz.

input pulse
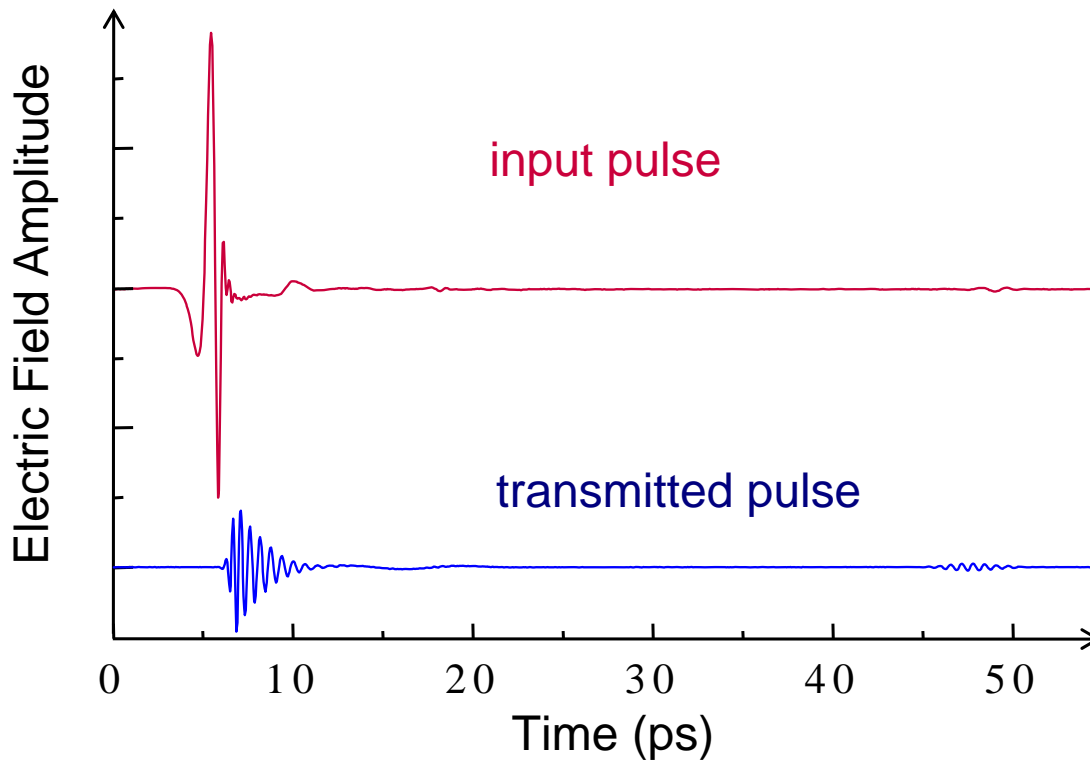
transmitted pulse

through 2 atm CH_3Cl
cell length: 22.5 cm

Electric Field Amplitude

Time (ps)

Spectra of methyl chloride

The next slide shows the FT-spectrum of the transmitted pulse as the red graph in direct comparison to the spectrum of the input pulse (green line).

At this pressure the rotational lines are strongly overlapping and the gas is completely opaque in the central region. However, in the wings to lower and higher frequencies it gets transparent.

The absorption, shown as blue graph, can be measured with high sensitivity and dynamic range up to 200 line widths and up to 5 times the transition frequencies away from the lines.

While the central rotational band structure shows good agreement with theory (calculated for a symmetric top molecule or based on the Hitran database), the high frequency wing absorption, as displayed on a magnified scale by the lower figure, indicates significant deviations to both the Lorentz and the van Vleck-Weisskopf theory.

These discrepancies – obviously caused by the line profile of the transitions - were the reason to develop a new, extended line shape theory which is a unification of the classical theories and which considers the temporal response of molecules to the exciting electric field.
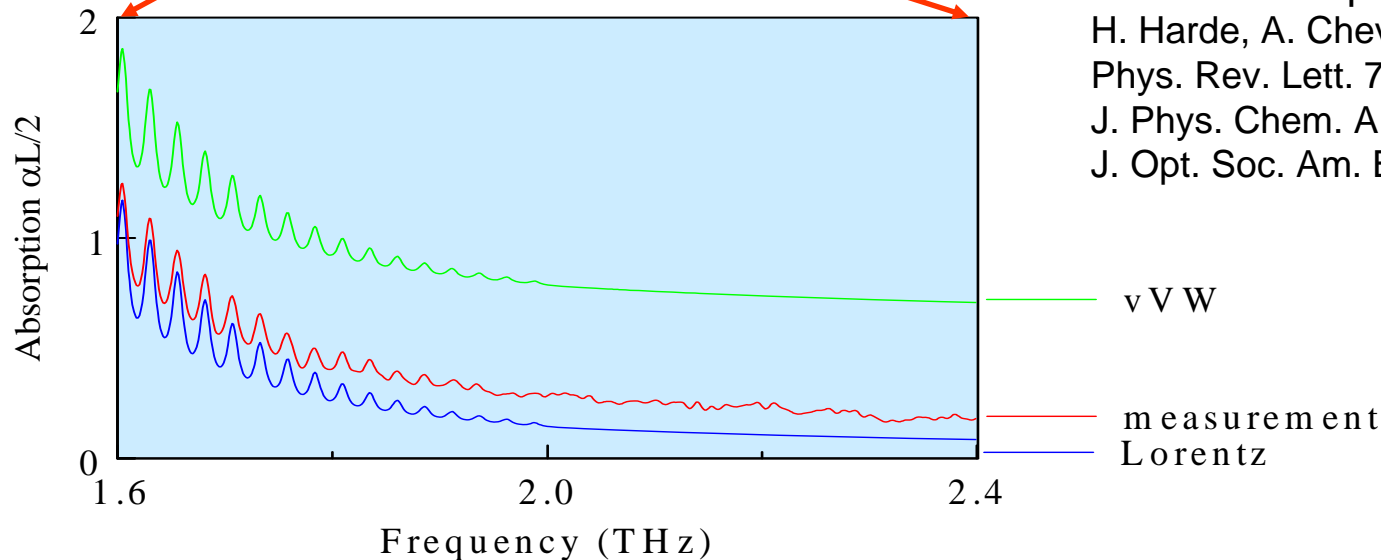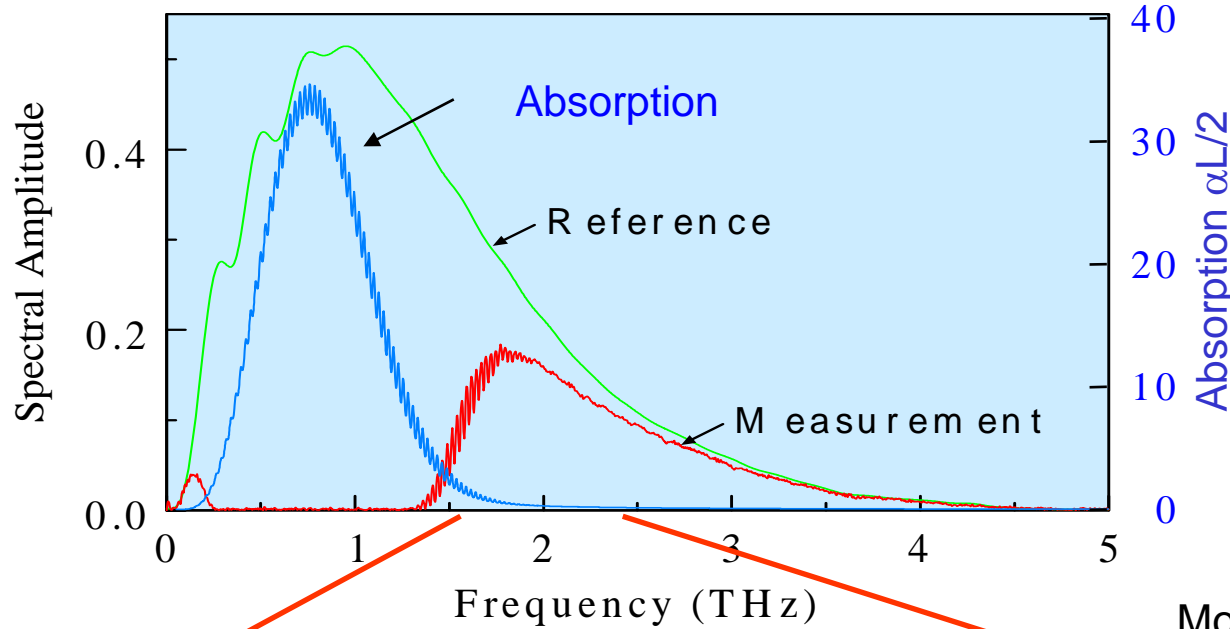
Molecular response theory
H. Harde, A. Cheville, D. Grischkowsky
Phys. Rev. Lett. 74, 1307 (1995)
J. Phys. Chem. A 101, 3646 (1997)
J. Opt. Soc. Am. B 14, 3282 (1997)

Photoacoustic spectroscopy in the NIR

A second branch of spectroscopic investigations attends to the development of gas sensors for environmental or medical applications, based on photoacoustic spectroscopy with semiconductor lasers in the near infrared.

The next slide gives an example for measuring the concentration of $^{13}CO_2$ in the respiration of a patient. This concentration is increasing, when this person suffers from stomach ulcer and has drunk an isotope marked cocktail of urea. In the presence of the bacteria helicobacter pylori the urea is metabolized and an increasing concentration of $^{13}CO_2$ is found in the breath, which is detected by means of the photoacoustic set-up.

CO_2 measurement

An example of a photo-acoustically measured spectrum - in this case 100% CO_2 - is shown in slide 8. The semiconductor laser was modulated via the injection current and the wavelength was tuned by the temperature over a wavelength range of 3.8 nm.
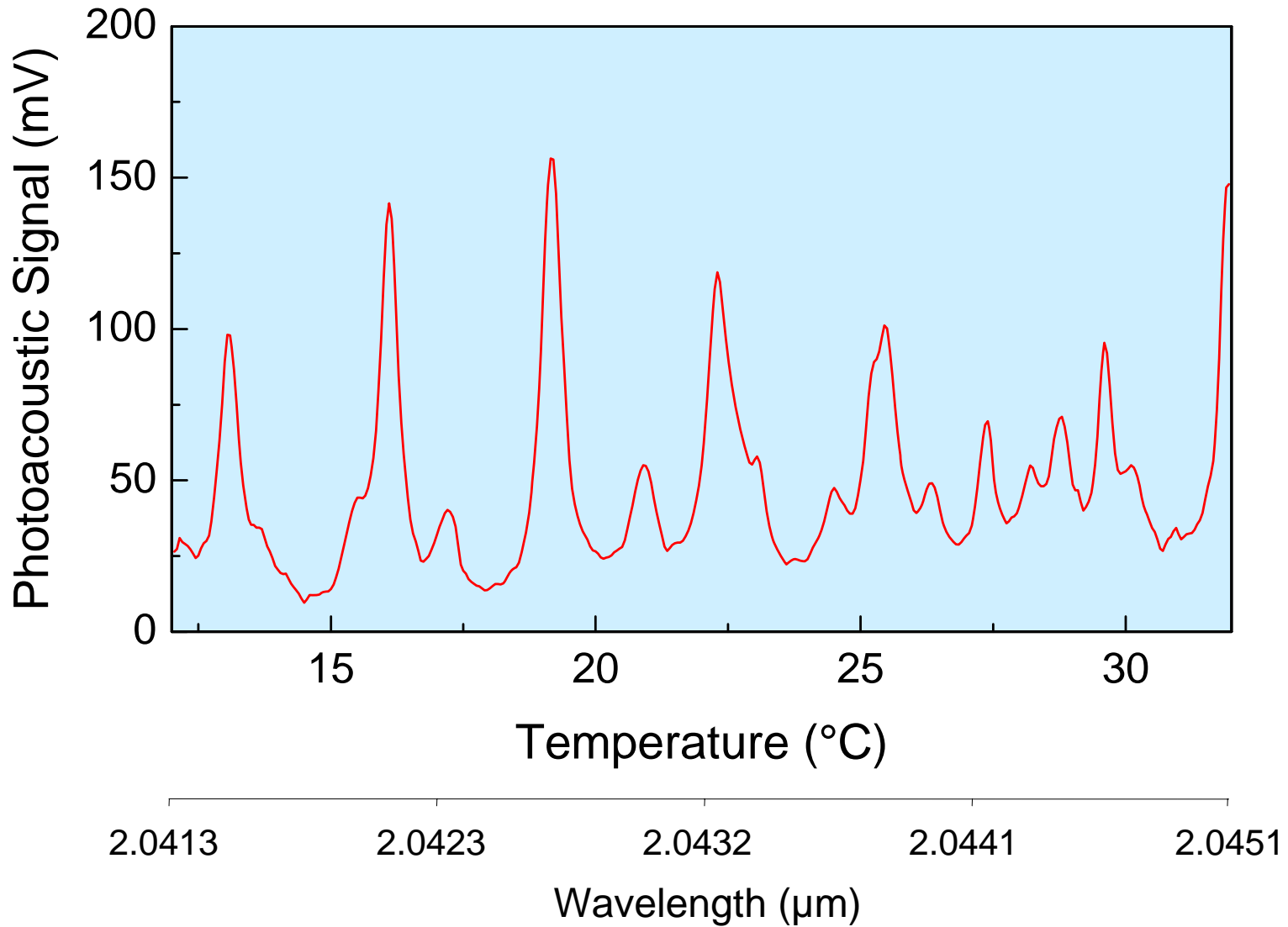
Decision

For both applications the Hitran database is extremely helpful for the analysis of these data and the identification of individual spectral components. However, as everyone knows, it is a stony way to prepare the data in a manner, that one gets spectra which can directly be compared with measured data or used for simulations of the measurements.

Because of the lack of adequate programs which might help to generate and plot such spectra, an own program platform was developed, which we call the **MolExplorer** and which runs under Windows on a standard PC. This program calculates and displays the spectra based on the Hitran database, and in the latest version also allows to directly compare these spectra with measurements.

Block diagram

The MolExplorer uses the Hitran04.par file, which for faster program access is stored on the hard drive of the computer. From this file an index file was generated which contains the addresses of all lines and molecules stored in the Hitran04.par file.

Specifying a molecule, its isotopologue and spectral range of interest, the program contacts the index file, reads the addresses for this isotope and with this information retrieves the data from the Hitran04.par file (see next slide).

To perform a calculation with these data the concentration or partial pressure of the gas, a buffer gas pressure and temperature have to be entered.

The calculated spectrum is displayed on the screen, can be sent to a printer or can be stored on a separate file for treatment with an external plot program.
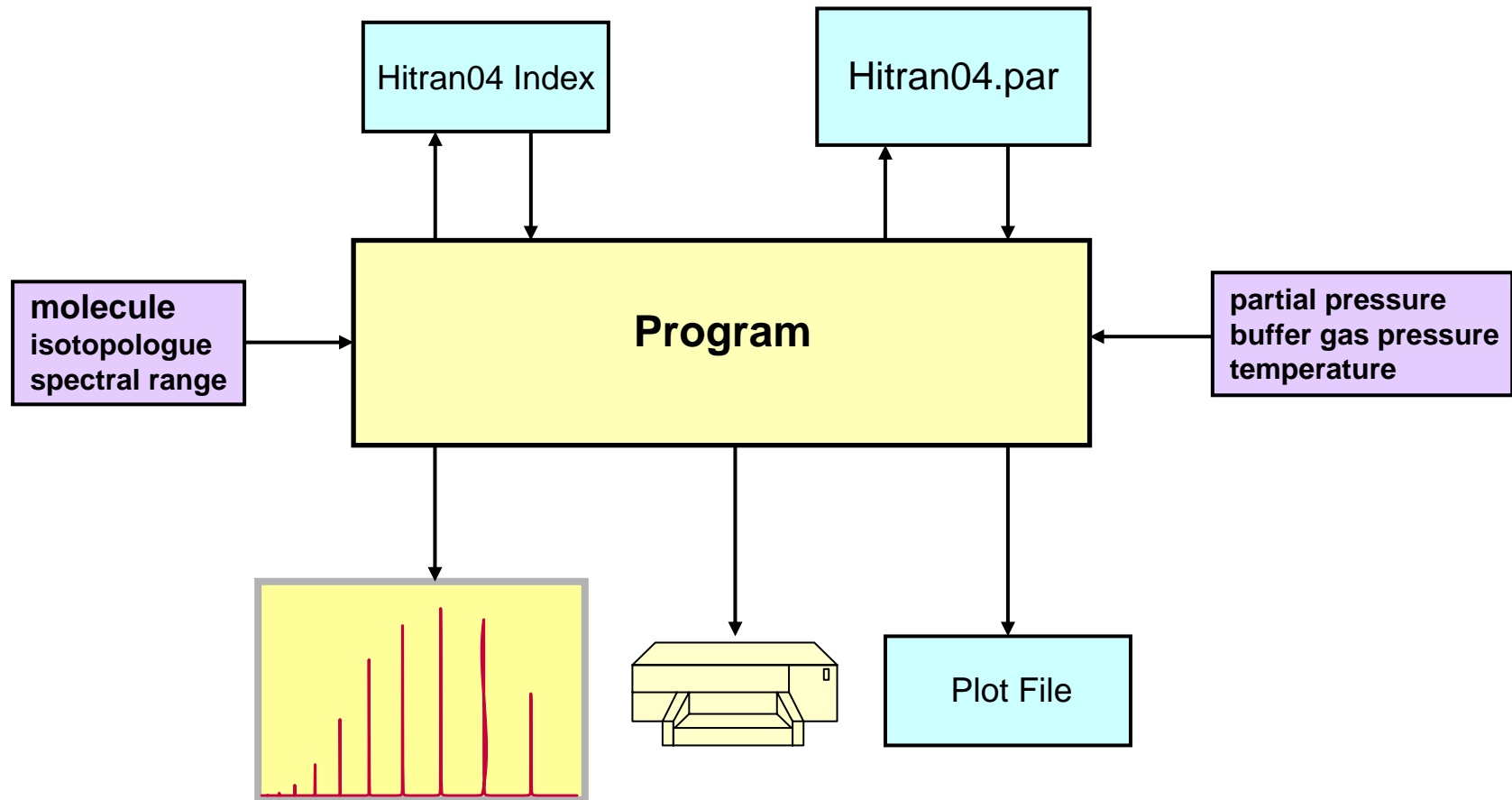
MolExplorer Platform

The program platform consists of a graphical user interface and the display area.

From this window all operations of the MolExplorer are controlled. The lower right part contains the input fields for the gases, the zoom control and logarithmic display function for the spectrum. At the left hand side are found all other control elements necessary for a compilation.

The handling and the main features of the program are demonstrated for a quite simple example, the hydrofluoric acid.
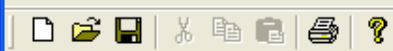
Selection of the gas

The control panel contains 10 fields provided to select molecules by clicking to a drop-down menu. The molecules then appear in alphabetic order and can be selected from this list. Up to 10 different gases can be activated in this way for a computation.

With the choice of the molecule also the adjacent fields for the isotope and partial pressure are set to *natural mixture* and *1 hPa* as the default parameters. In this case only one isotopologue exists, so this appears in the field.

Notice: For best reproduction of the screen shots (following slides) use
Full Screen for monitors with 1024x768 pixels resolution and
106 % magnification for 1280x768 pixels resolution.

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File   Edit   View   ?

Welcome to the HSU MolExplorer

X-Axis
Maximal Range
0.5
1.0
Scale
○ 1/cm
● µm
○ THz

Parfile   Mesurement
Read   Read
Write   Fit
Export Data

X: 0.5 µm
Y: 0 cm-1
Max: 0 cm-1
Lines: 0 out of 0

Display-Modus
Absorp-Coeff.

Min. Intens:
0.0   N

Channels
4096   □ On

□ Measurement
□ Double Plot
● Partial Pressure
○ Concentration
□ Marker

Buffer Gas [hPa]
0   1013.00   N

Temperature [K]
296.0   N

Path Length [cm]
100

Response Time [ps]
10   □ On

Check   Display   STOP

Parfile: CA

Active Gas   Isotope Partial Pressure [hPa]   Active Gas   Isotope Partial Pressure [hPa]

Log Range
□ Log10   3.0   -   +
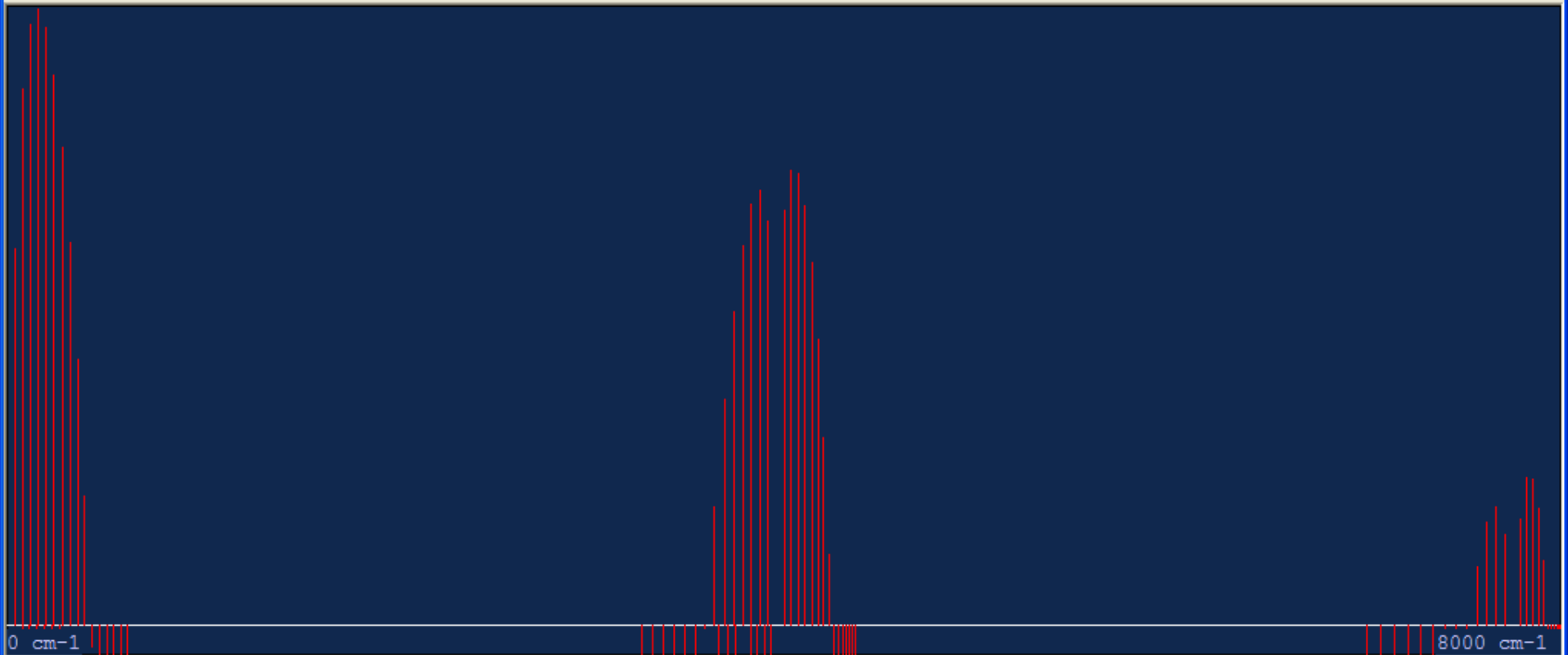
Zoom
<   +   0   -   >

JP

Ready

Spectral range

For any calculation of a spectrum the start and stop values have to be determined. The abscissa can be chosen in wavenumbers, in frequencies or wavelengths. A click on the respective radio button opens a sub-window to key in these values.

To get a survey over the spectrum the start is set to 0 and the stop to 8.000 cm^{-1}. A click on the *Check* button starts the retrieval of HF lines, and in this spectral region

84 from 107 lines in the data base are found.

Spectral line intensity

With the display modus set to *Spectral Intensity* the MolExplorer displays the spectral line intensities, similar to the Hawks program.

To identify also weak lines the ordinate can be changed to a logarithmic scale (see next slide) by clicking on the respective check-box. The lower red lines represent those transitions, for which the line intensities are more than 3 orders of magnitude smaller than the strongest transitions.

File   Edit   View   ?

0 cm-1   8000 cm-1

X-Axis
Maximal Range
0
8000
Scale
⊙ 1/cm
○ µm
○ THz

Parfile   Mesurement
Read   Read
Write   Fit
Export Data

X: 3217.391 cm-1
Y: 0.0 cm-1/(mol/cm2)
Max: 1.44e-017 cm-1/(mol/cm2)
Lines: 84 out of 84

Display-Modus
Line Intensity

Min. Intens:
0   N

Channels
4096

☐ Measurement
☐ Double Plot
⊙ Partial Pressure
○ Concentration
☐ Marker

Buffer Gas [hPa]
0   0.00   N

Temperature [K]
296.0   N

Path Length [cm]
100   ☐ On

Response Time [ps]
10   ☐ On

Parfile: HF-gesamt

	Active	Gas	Isotope	Partial Pressure [hPa]	CA		Active	Gas	Isotope	Partial Pressure [hPa]	
🟥	☑	HF	19	1	NA C	🟪	☐			0.0	NA C
🟩	☐			0.0	NA C	⬜	☐			0.0	NA C
🟦	☐			0.0	NA C	⬜	☐			0.0	NA C
🟦	☐			0.0	NA C	🟥	☐			0.0	NA C
🟨	☐			0.0	NA C	🟩	☐			0.0	NA C

Check   Display   STOP

Log Range
☑ Log10   3.0   -   +

Zoom
<   +   0   -   >

JP

Ready

Cursor Operation

To observe some part of the spectrum in more detail and at an increased resolution new start and stop values can be typed into the sub-window or the spectral interval can be pre-elected with the cursor, which is moved to the desired start position (within the graphic screen) and the left mouse button is pressed. A vertical line (magenta colour) shows up and indicates this position. The exact start wavenumber is also displayed by the cursor's x-coordinate in the left part of the control panel. Moving the mouse to the right and marking the stop position in the same way, the spectral interval is defined.

A further click to this interval activates the plot over the desired range on the magnified scale.

Linear scale: In the linear modus for the y-axis the cursor display function can also be used to determine the line strength by moving the cursor to the top of a line (see next slide).

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File   Edit   View   ?

3588.933 cm-1   4245.059 cm-1

Parfile: HF-gesamt

X-Axis
Maximal Range
0
8000
Scale
○ 1/cm
○ µm
○ THz

Parfile   Mesuement
Read   Read
Write   Fit
Export Data

X: 3876.799 cm-1
Y: 1.89e-018 cm-1/(mol/cm2)
Max: 2.37e-018 cm-1/(mol/cm2)
Lines: 23 out of 84

□ Measurement
□ Double Plot
○ Partial Pressure
○ Concentration
□ Marker

Display-Modus
Line Intensity ▾

Min. Intens:
0   N

Channels
4096 ▾   □ On

Buffer Gas [hPa]
0   0.00   N

Temperature [K]
296.0   N

Path Length [cm]
100

Response Time [ps]
10   □ On

Active	Gas	Isotope	Partial Pressure [hPa]	CA		Active	Gas	Isotope	Partial Pressure [hPa]	
☑	HF ▾	19 ▾	1	NA C		□	▾	▾	0.0	NA C
□	▾	▾	0.0	NA C		□	▾	▾	0.0	NA C
□	▾	▾	0.0	NA C		□	▾	▾	0.0	NA C
□	▾	▾	0.0	NA C		□	▾	▾	0.0	NA C
□	▾	▾	0.0	NA C		□	▾	▾	0.0	NA C

Check   Display   STOP

Log Range
□ Log10   3.0   -   +

Zoom
<   +   0   -   >

JP

S-plot: 23 Lines

Absorption Coefficient

For the calculation of the absorption spectrum the pressure and temperature of the gas have to be specified, which are set to the default values (1 hPa, 296 K). And the display modus has to be changed to *Absorption Coefficient.*

The displayed spectrum (next slide), showing the P- and R-branch of the fundamental ro-vibronic band structure, looks similar to the previous case, but is no longer a pure line spectrum, as this can be foreseen from the slightly broadened lines, which still appear quantized due to the limited pixel number of the screen.

Absorption

The program also displays the absorption of the gas, which is found by multiplying the absorption coefficient with the propagation length of the radiation. The path length is set in the lower window in units of cm.

Transmission

And the respective transmission is displayed when selecting the transmission modus.

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File Edit View ?
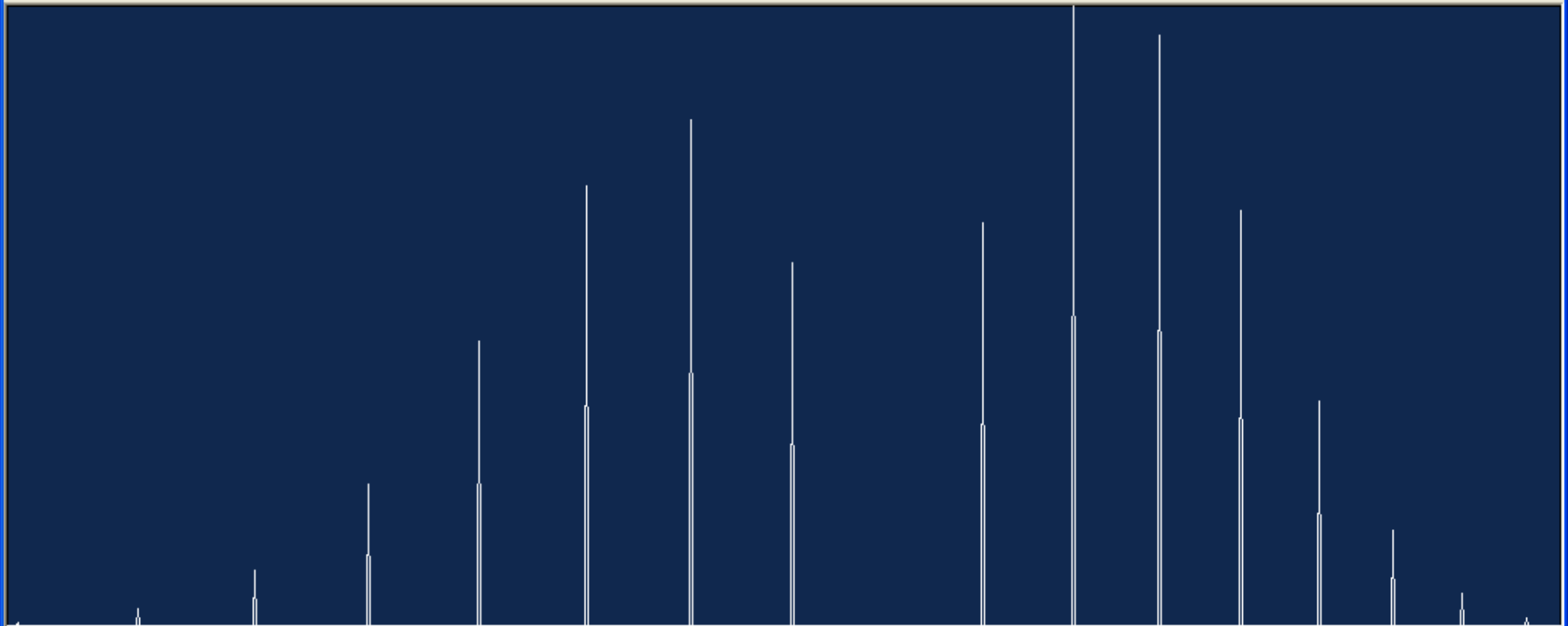
3588.933 cm-1   4245.059 cm-1

X-Axis
Maximal Range
0
8000
Scale
⦿ 1/cm
○ µm
○ THz

Parfile   Mesurement
Read   Read
Write   Fit
Export Data

X: 3896.897 cm-1
Y: 2.37e-018 cm-1
Max: 4.46 cm-1
Lines: 23 out of 84

Display-Modus
Absorp-Coeff.

Min. Intens:
0   N

Channels
4096

☐ Measurement
☐ Double Plot
⦿ Partial Pressure
○ Concentration
☐ Marker

Buffer Gas [hPa]
0   0.00   N

Temperature [K]
296.0   N

Path Length [cm]
100

Response Time [ps]
10   ☐ On

Calculation: Gauss-Profile

	Active	Gas	Isotope	Partial Pressure [hPa]	
🟥	☑	HF	19	1	NA C
🟩	☐			0.0	NA C
🟦	☐			0.0	NA C
🟦	☐			0.0	NA C
🟨	☐			0.0	NA C

CA

Parfile: HF-gesamt

	Active	Gas	Isotope	Partial Pressure [hPa]	
🟪	☐			0.0	NA C
⬜	☐			0.0	NA C
⬛	☐			0.0	NA C
🟥	☐			0.0	NA C
🟩	☐			0.0	NA C

Check   Display   STOP

Log Range
☐ Log10 3.0   - +

Zoom
<   +   0   -   >

JP

Ready

Line Shapes

On a further magnified scale the true line shape and width of an individual transition can be identified, which under these conditions is determined by a Gaussian due to Doppler broadening. This width is about 0.01 cm^{-1} and is at least 5x larger than any self-pressure broadening. At 200 hPa the opposite situation is found, now collisional broadening is at least 5x larger than Doppler broadening, and the program automatically switches to a pure Lorentzian shape.

For pressures somewhere between, the program uses a Voigt profile as a convolution of a Gaussian and Lorentzian (see next slide).
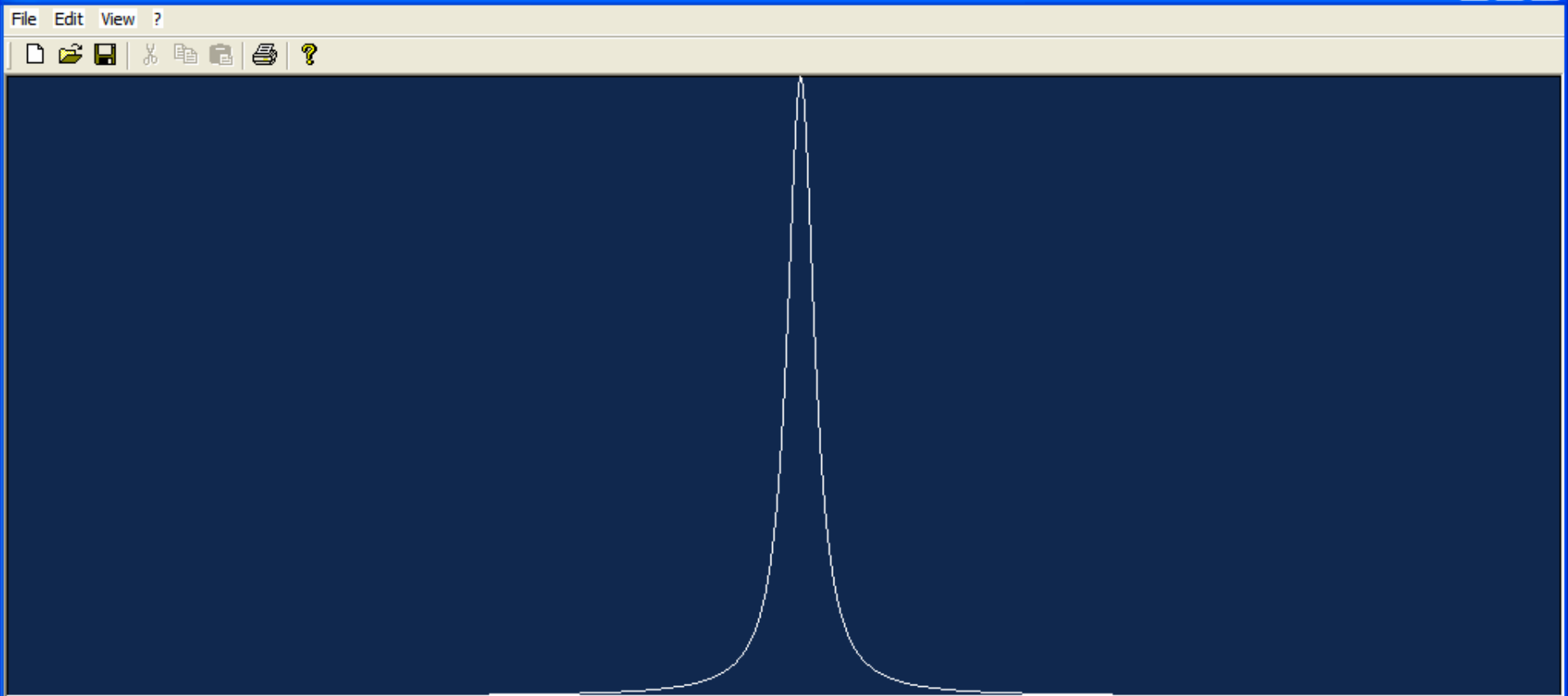
Air broadening

If HF is considered in air, in addition to the partial pressure a buffer gas pressure has to be specified. It accounts for the surrounding air pressure with a default value of *1013 hPa.*

Now, besides Doppler and self-pressure broadening also foreign gas broadening exists and is automatically included in the calculation.

Concentration

Sometimes it may be advantageous not to specify the partial pressure, but the concentration of the gas. The display is converted to ppm by clicking on the respective radio button. This option is favourably used when small pollutions in the atmosphere or in another buffer gas are considered.

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File Edit View ?

3876.584 cm-1   3878.785 cm-1

Calculation: Voigt-Profile   Parfile: HF-gesamt

X-Axis
Maximal Range
0
8000
Scale
○ 1/cm
○ µm
○ THz

Parfile   Mesurement
Read   Read
Write   Fit
Export Data

X: 3878.117 cm-1
Y: 0.0 cm-1
Max: 19.6 cm-1
Lines: 1 out of 84

Display-Modus
Absorp-Coeff.

Min. Intens:
0   N

Channels
4096

☐ Measurement
☐ Double Plot
○ Partial Pressure
○ Concentration
☐ Marker

Buffer Gas [hPa]
0 0.00   N

Temperature [K]
296.0   N

Path Length [cm]
100

Response Time [ps]
10   ☐ On

	Active	Gas	Isotope	Partial Pressure [hPa]		
🟥	☑	HF	19	30	NA	C
🟩	☐			0.0	NA	C
🟦	☐			0.0	NA	C
🟦	☐			0.0	NA	C
🟨	☐			0.0	NA	C

CA

	Active	Gas	Isotope	Partial Pressure [hPa]		
🟪	☐			0.0	NA	C
⬜	☐			0.0	NA	C
⬜	☐			0.0	NA	C
🟥	☐			0.0	NA	C
🟩	☐			0.0	NA	C

Check   Display   STOP

Log Range
☐ Log10 3.0   - +

Zoom
<   +   0   -   >

Ready

Marker function

Under regular atmospheric conditions the HF molecule interferes with spectra of other pollutants in the atmosphere. At least water vapor with a typical partial pressure in air of about 5 hPa (or 5000 ppm) has to be examined on its superposition with HF lines. To restrict the retrieval to the most prominent isotopologue 161, only this isotope is selected from the drop down menu. For the spectral range 0 – 8000 cm^{-1} more than 20.000 water lines of this isotope are identified.

Already at this concentration and more than ever at lower HF concentrations it is hard to identify the different species. Therefore, a marker function can be activated, which is extremely helpful to distinguish between different gases or isotopes.

Each line position is indicated by a marker which carries the colour of the respective gas, and the marker length (or height) is identical with the maximum absorption of an individual line – slightly dependent on the line shape function.
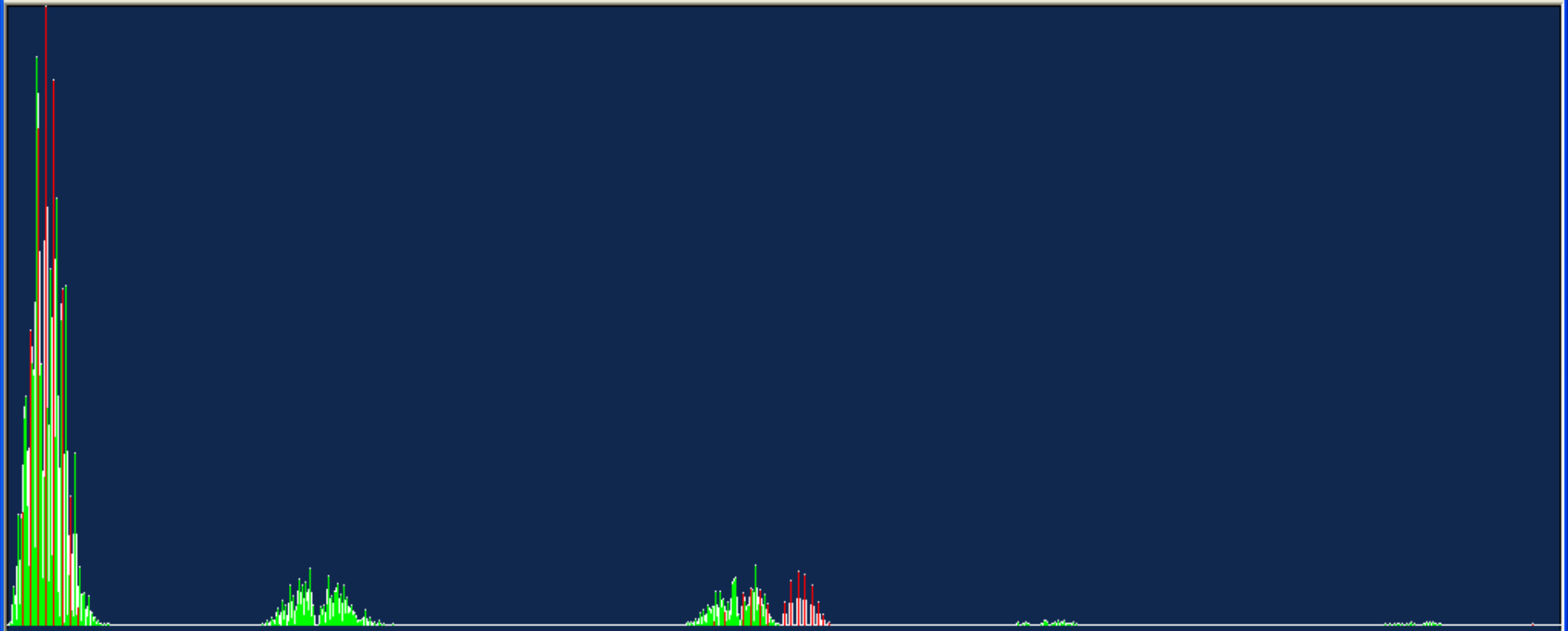
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File Edit View ?

0 cm-1   8000 cm-1

X-Axis
Maximal Range
0
8100
Scale
○ 1/cm
○ µm
○ THz

Parfile   Mesuerement
Read   Read
Write   Fit
Export Data

X: 4845.85 cm-1
Y: 0.635 cm-1
Max: 2.75 cm-1
Lines: 20246 out of 20285

Display-Modus
Absorp-Coeff.

Min. Intens:
0   N

Channels
1024

Buffer Gas [hPa]
0   1013.00   N

Path Length [cm]
100

Temperature [K]
296.0   N

Response Time [ps]
10   □ On

□ Measurement
□ Double Plot
○ Partial Pressure
○ Concentration
☑ Marker

Calculation: Lorentz-Profile   Parfile: HF-gesamt

	Active	Gas	Isotope	Partial Pressure [hPa]				Active	Gas	Isotope	Partial Pressure [hPa]		
🟥	☑	HF	19	1	NA	C		🟪	□			0.0	NA	C
🟩	☑	H2O	161	5	NA	C		⬜	□			0.0	NA	C
🟦	□			0.0	NA	C		⬛	□			0.0	NA	C
🟦	□			0.0	NA	C		🟥	□			0.0	NA	C
🟨	□			0.0	NA	C		🟩	□			0.0	NA	C

CA

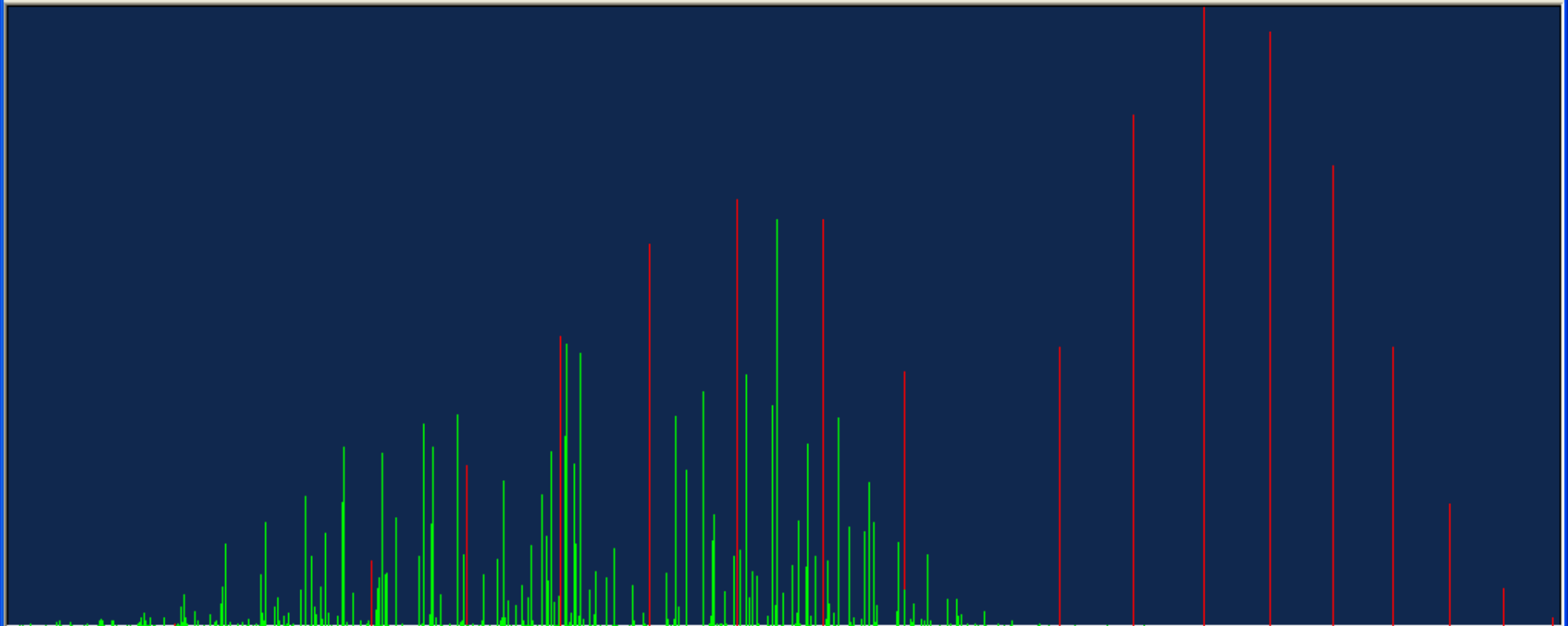Check   Display   STOP

Log Range
□ Log10 3.0   - +

Zoom
< + 0 - >

Ready

Line positions

A further display modus, called *Line Positions*, shows a pure line spectrum, identical with the marker function. This is quite helpful to get a rapid survey over the spectrum. Similar to the spectral line intensities each line position reflects the transition frequency, but the line height directly represents the maximum absorption coefficient at the center of the transition in [cm^{-1}].

The next figure displays the P- and R-branch of the fundamental ro-vibronic HF structure together with the interfering water lines in this modus.

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File   Edit   View   ?

3454.545 cm-1   4260.87 cm-1

X-Axis
Maximal Range
0
8100
Scale
● 1/cm
○ µm
○ THz

Parfile   Mesurement
Read   Read
Write   Fit
Export Data

X: 3624.256 cm-1
Y: 0.0 cm-1
Max: 0.241 cm-1
Lines: 3248 out of 20285

Display-Modus
Line Positions

Min. Intens:
0   N

Channels
1024

☐ Measurement
☐ Double Plot
● Partial Pressure
○ Concentration
☑ Marker

Buffer Gas [hPa]
0   1013.00   N

Temperature [K]
296.0   N

Path Length [cm]
100   ☐ On

Response Time [ps]
10   ☐ On

Parfile: HF-gesamt

Active	Gas	Isotope	Partial Pressure [hPa]
☑	HF	19	1
☑	H2O	161	5
☐			0.0
☐			0.0
☐			0.0

Active	Gas	Isotope	Partial Pressure [hPa]
☐			0.0
☐			0.0
☐			0.0
☐			0.0
☐			0.0

CA

Check   Display   STOP

Log Range
☐ Log10   3.0   - +

Zoom
<   +   0   -   >

Ready

Line Parameter

While the two gases can well be distinguished by the coloured markers, it may be of interest to get more specific information on an individual line.

This is easily accomplished by moving the cursor to the desired line and marking it by a double click with the left mouse button. Then a vertical line appears for 1 s and indicates, which line was marked and identified, before the graphic screen changes to a white field, in which all data stored in the HITRAN04 database of this line are listed.

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File   Edit   View   ?

Original HITRAN04(R) Database values for the selected spetral line
----

Database line: 1483944
Molecule number: 14   (HF)
Isotopologue number: 1   (19)
Natural abundance: 0.99884400%   Molecular weight: 20.00622900 g/mol
Transition frequency: 3788.227700   [cm-1]
Line intensity (S):   1.011e-018   [cm-1/(Molecules / cm2)] @296K
Einstein A-coefficient: 1.190e+002   [s-1]
Air broadened width: 0.0502   [cm-1 atm-1] Half width @ 296K
Self broadened width: 0.5424   [cm-1 atm-1] Half width @ 296K
Lower state energy: 410.3479   [cm-1]
T dependence of air width: 0.50
Pressure shift: -0.009200   [cm-1 atm-1] @296K
Upper vibrational quanta :   1
Lower vibrational quanta: 0
Upper local quanta:
Lower local quanta: P 4
Error codes: 467000
Reference codes: 2 1 2 0 0 0
Flag for line mixing:
Upper statistical weight: 28.0
Lower statistical weight: 36.0

X-Axis
Maximal Range
0
8100
Scale
( ) 1/cm
( ) μm
( ) THz

Parfile   Mesurement
Read   Read
Write   Fit
Export Data

X: 4017.857 cm-1
Y: 0.0 cm-1
Max: 0.241 cm-1
Lines: 3248 out of 20285

Display-Modus
Line Positions

Min. Intens:
0   N

Channels
1024

[ ] Measurement
[ ] Double Plot
( ) Partial Pressure
( ) Concentration
[✓] Marker

Buffer Gas [hPa]
0   1013.00   N

Path Length [cm]
100

Temperature [K]
296.0   N

Response Time [ps]
10   [ ] On

Parfile: HF-gesamt

Active	Gas	Isotope	Partial Pressure [hPa]		
■ [✓]	HF	19	1	NA	C
■ [✓]	H2O	161	5	NA	C
■ [ ]			0.0	NA	C
■ [ ]			0.0	NA	C
■ [ ]			0.0	NA	C

Active	Gas	Isotope	Partial Pressure [hPa]		
■ [ ]			0.0	NA	C
■ [ ]			0.0	NA	C
■ [ ]			0.0	NA	C
■ [ ]			0.0	NA	C
■ [ ]			0.0	NA	C

Check   Display   STOP

Log Range
[ ] Log10   3.0   -   +

Zoom
<   +   0   -   >

JP

Parameter Files

The parameters used to calculate a spectrum can be stored on a parameter file, which contains all necessary information like the molecules, isotope choice, the partial and buffer gas pressure, or the spectral range and the display modus. A click on the button *Write Parfile* opens a sub-window, and allows to save this file.

This or any other parameter set can be called for further checks or recurring use, when clicking on the button *Read Parfile*.

Printer

For fast inspection or preliminary documentation the spectrum as viewed on the monitor can be printed on a standard printer. Before starting the print it can be checked by the *Page View* function. In addition to the spectrum the most important data used for the calculation are listed.

Data Export

For high quality data representation the spectrum may be stored on a file, which then is further processed by an external plot program. This file may consist of up to 32768 data points and can be automatically processed, e.g., by a table calculation program like Xact or Excel (see next slide) for the graphic representation of the data.
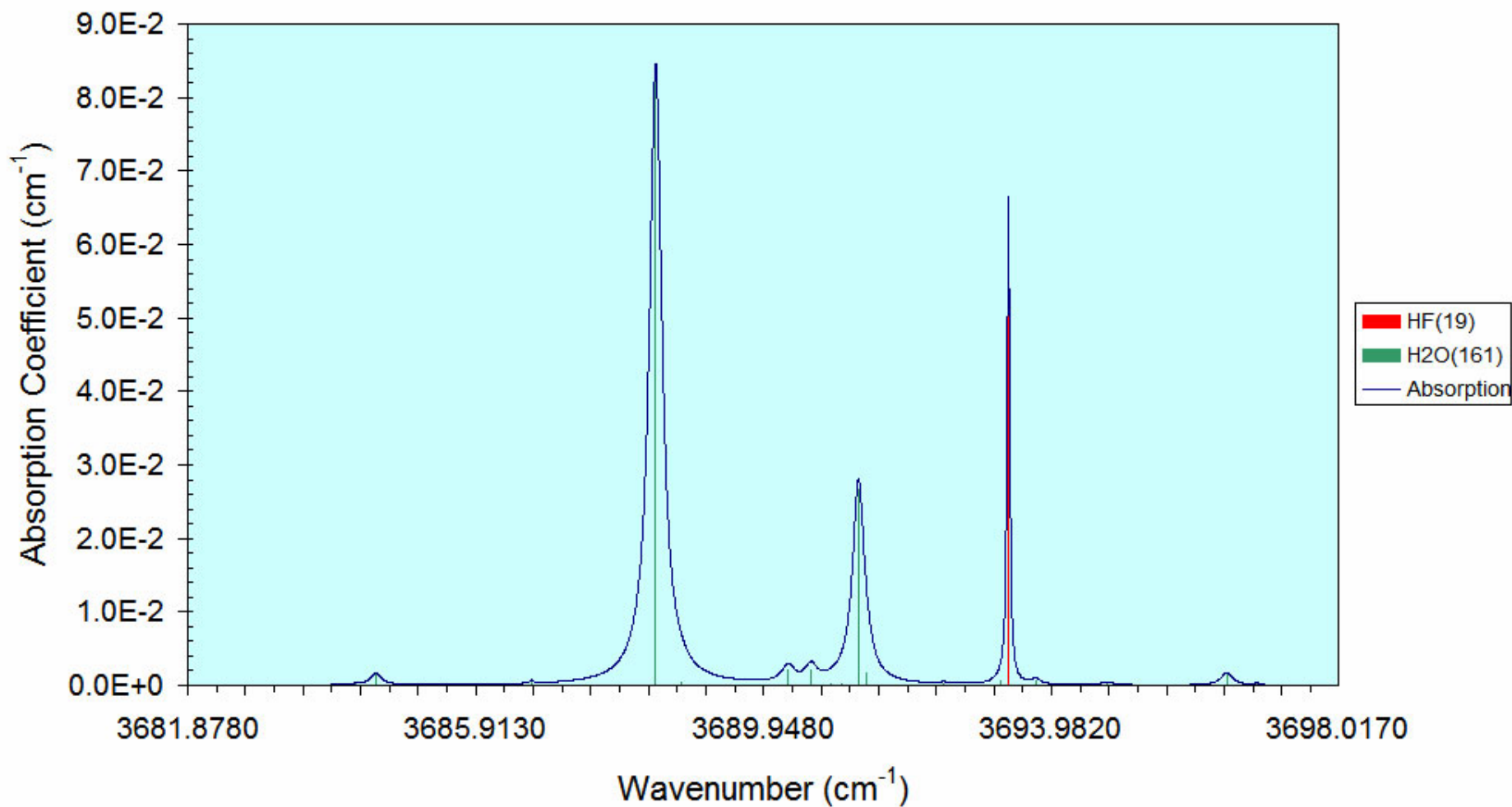
CO$_2$ breath test

Having demonstrated the most important features of the MolExplorer, this program is applied to analyse the earlier shown CO$_2$-measurement.

For the ^{13}CO$_2$ breath test it is necessary to measure small changes in the concentration of this isotopologue of the order of a few thousandths and this in relation to the overall concentration of CO$_2$, which in the respiration is about 4.5%.
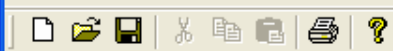
An interesting spectral range for such type of measurement is the NIR at 2 µm, where semiconductor lasers with sufficient output power and good beam quality are available.

To identify the ^{13}CO$_2$ lines in the spectrum, it is advantageous to select and calculate the spectrum for the most frequent isotopes individually, together with water vapor.

As long as the natural mixture of a gas is used, the specified pressure represents the sum over all isotopologues of the molecule, weighted with their natural abundances. In the case of individual isotopes it represents the partial pressure. To compute this pressure in relation to the abundance, the button NA (next to the pressure entrance field) has to be pressed and the pressure is multiplied by the abundance of this isotope.

The next slide shows the CO$_2$-band structure together with water from 1.9 – 2.1 µm. The weaker 636-lines (red) are laying in a spectral range, where the 626-lines are almost vanishing or have comparable strength, while water is almost negligible.

MolExplorer Rev: 2.9.0E (C) 12.07.06 Helmut-Schmidt-Universität Hamburg   CO2

File   Edit   View   ?

1.9 µm

2.1 µm

Parfile: CO2

Measurement
Double Plot
Partial Pressure
Concentration
Marker
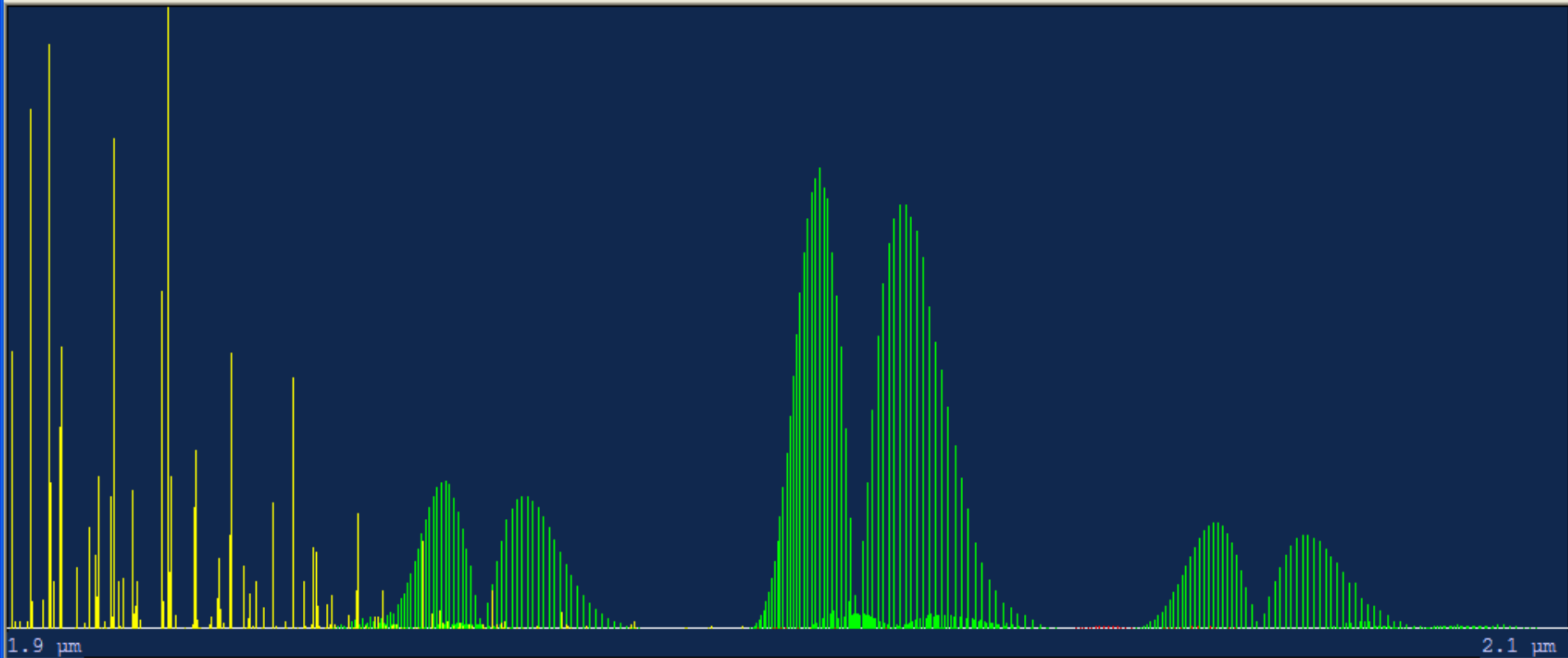
X-Axis
Maximal Range
1.9
2.1
Scale
○ 1/cm
● µm
○ THz

Parfile   Mesuement
Read   Read
Write   Fit
Export Data

X: 1.974901 µm
Y: 0.0 cm-1
Max: 0.00834 cm-1
Lines: 6001 out of 6001

Display-Modus
Line Positions

Min. Intens:
0   N

Channels
2048   □ On

Buffer Gas [hPa]
0   970.00   N

Temperature [K]
296.0   N

Path Length [cm]
100

Response Time [ps]
10   □ On

Active	Gas	Isotope	Partial Pressure [hPa]			Active	Gas	Isotope	Partial Pressure [hPa]		
☑	CO2	636	0.4975830	R	C	□			0.0	NA	C
☑	CO2	626	44.2891800	R	C	□			0.0	NA	C
☑	CO2	628	0.1776181	R	C	□			0.0	NA	C
☑	CO2	627	0.0330295	R	C	□			0.0	NA	C
☑	H2O	161	5	NA	C	□			0.0	NA	C

CA

Check   Display   STOP

Log Range
□ Log10 3.0   -   +

Zoom
<   +   0   -   >

JP

Comparison with measurement

Further magnification of this spectral range indeed indicates that this is an interesting range to measure the 636-concentration and to use the 626-isotope as a reference.

The latest version of the MolExplorer allows a direct comparison of a measurement with a calculated spectrum.

The next slide shows the photoacoustic CO_2 measurement as red graph together with the simulated spectrum (white line).

In this way any discrepancies in the line position, the shape, width, intensity or missing features are easily identified.

The photoacoustic measurement deviates in the observed peak intensities, while the line positions are in excellent agreement with the calculated absorption spectrum. The intensity variations may be explained by a transition dependent energy transfer to generate an acoustic wave, when part of the excitation energy is converted into internal degrees of freedom.

This example demonstrates how beneficial the database can be used for the interpretation of a measured spectrum and the identification of individual isotopic lines.
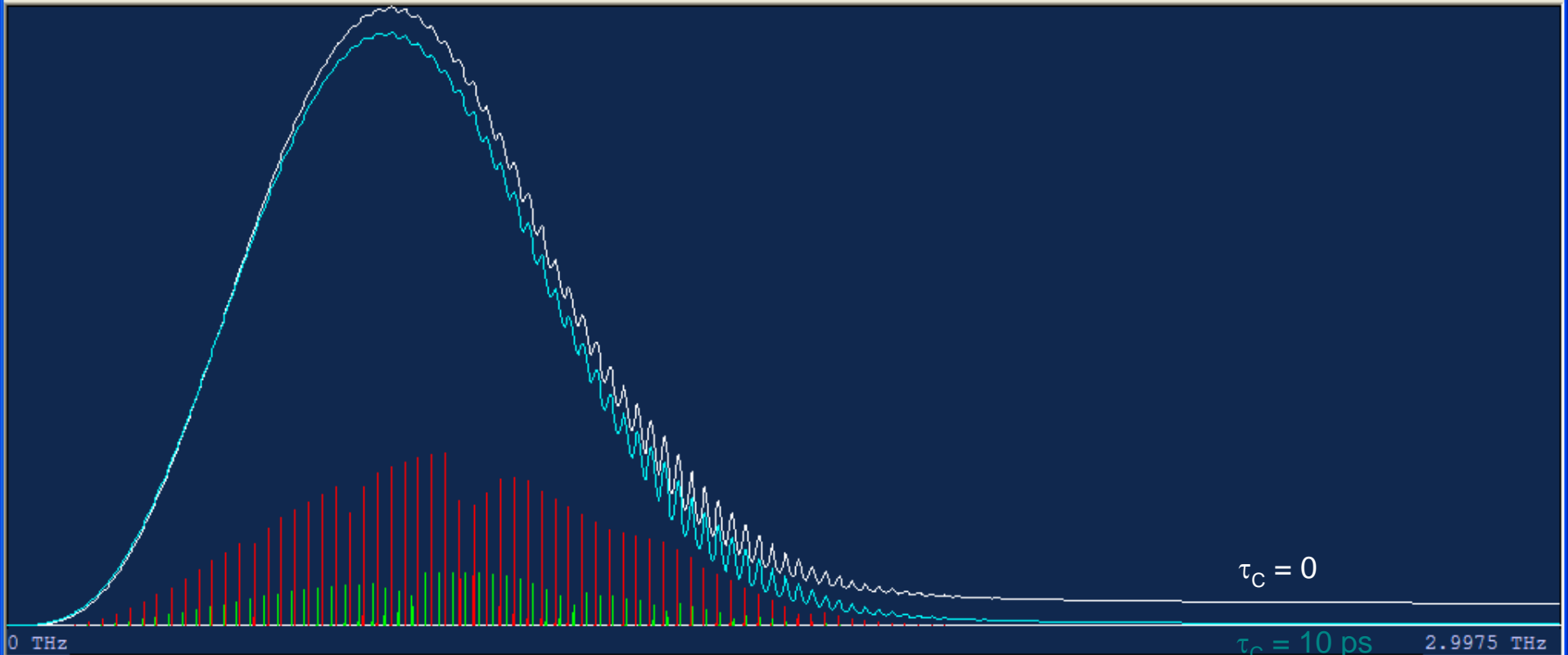
Line shape investigations in the THz range

In the mm- and THz-range the line width of a transition caused by collisions can be comparable to the transition frequency of a line. Then the line shape can no longer be described by a standard Lorentzian, but is much better approximated by a shape derived from molecular response theory (see slide 5). This theory introduces a finite time, the response time, which molecules require to come into thermal equilibrium with an external field in the presence of molecular collisions. It is a unification of the classical collision theories of Lorentz and van Vleck-Weisskopf, where the response time τ_C acts as a control parameter, which for large values (typically > 10 ps) already well reproduces a Lorentzian and for $\tau_C = 0$ gives a van Vleck-Weisskopf line shape.

A click on the check box *Response Time* activates the generalized line shape calculation.

The next slide shows two calculated spectra of methyl chloride which simulate the measurement of slide 5 applying a response time of 10 ps (blue curve) and $\tau_C = 0$ (white graph). The markers indicate the line positions and strengths of the two isotopologues.

At 10 ps or more the response of the molecules is already too slow to follow any faster oscillations on this scale, and a pure Lorentzian is approximated with the response theory. An infinitely fast response is given for $\tau_C = 0$, which represents the v.Vleck-Weisskopf case. Comparison with the Lorentzian shows significantly higher absorption in the high frequency wings of the rotational lines.

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File Edit View ?

$\tau_C = 0$

$\tau_C = 10\ ps$

0 THz

2.9975 THz

X-Axis
Maximal Range
0
2.9975
Scale
○ 1/cm
○ μm
● THz

Parfile   Mesuement
Read   Read
Write   Fit
Export Data

X: 0.8115761 THz
Y: 1
Max: 28.7
Lines: 12775 out of 12775

Display-Modus
Absorption

Min. Intens:
0   N

Channels
1148   ☑ On

☐ Measurement
☑ Double Plot
○ Partial Pressure
○ Concentration
☑ Marker

Buffer Gas [hPa]
0   0.00   N

Temperature [K]
293.0   N

Path Length [cm]
11.25

Response Time [ps]
0   ☑ On

Calculation: Harde-Profile

	Active	Gas	Isotope	Partial Pressure [hPa]		
🟥	☑	CH3Cl	215	1422.98030	R	C
🟩	☑	CH3Cl	217	455.032900	R	C
🟦	☐			0.0	NA	C
🟦	☐			.0	NA	C
🟨	☐			0.0	NA	C

Parfile: CH3Cl2000-Messung.txt

	Active	Gas	Isotope	Partial Pressure [hPa]		
🟪	☐			0.0	NA	C
⬜	☐			0.0	NA	C
	☐			0.0	NA	C
🟥	☐			0.0	NA	C
🟩	☐			0.0	NA	C

CA

Check   Display   STOP

Log Range
☐ Log10 3.0 - +

Zoom
< + 0 - >

JP

Ready

Lasertechnik &
Werkstoffkunde

Line Shape Investigations

III. MolExplorer

HELMUT SCHMIDT
UNIVERSITÄT

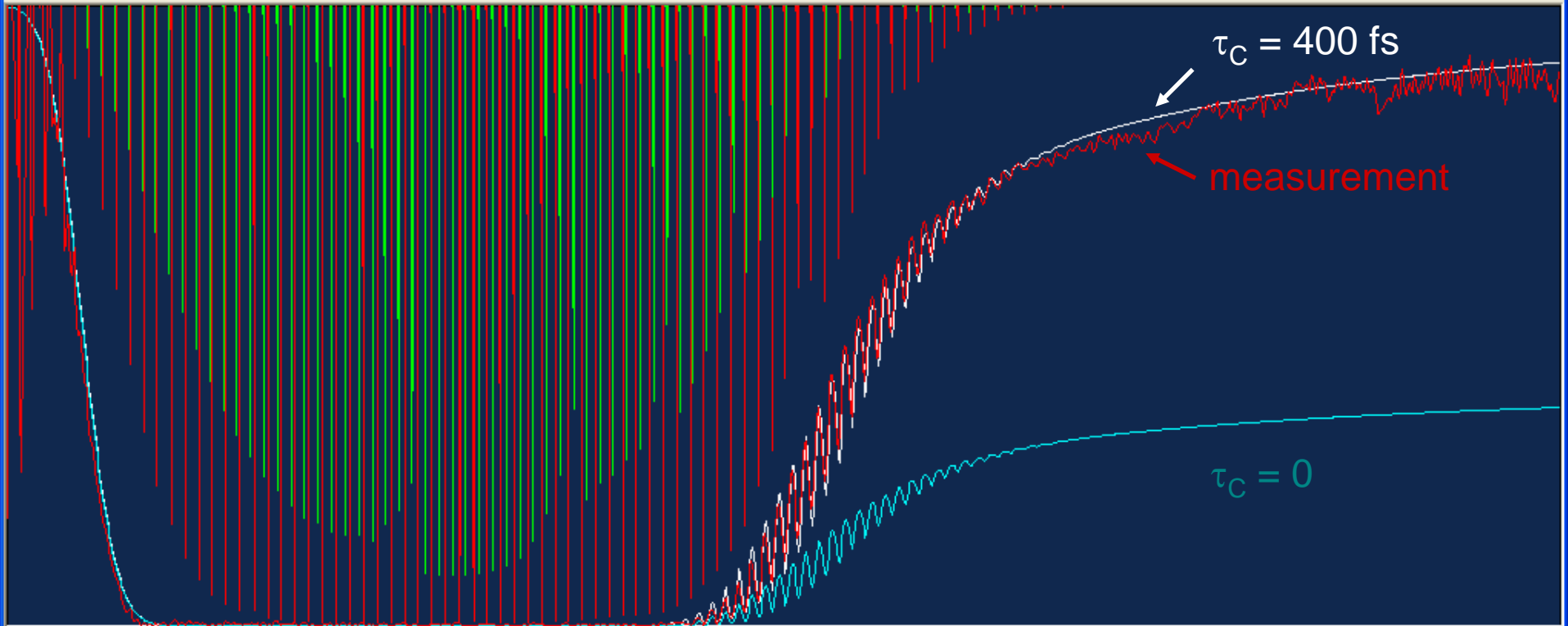**Fit to methyl chloride measurement**

A fit of the simulated spectrum to the measurement then allows to determine the response time. More distinctly is this wing absorption observed in transmission.

The following slide shows the measured transmittance as the red graph and the calculation (white curve) for τ_C = 400 fs. Additionally depicted is the van Vleck-Weisskopf case (τ_C = 0) as the blue graph. The red and green lines again represent the line positions and strengths of the two isotopologues.

Spikes at very low frequencies in the measured data are caused by the very weak and noisy THz signal at these frequencies.

Since in THz spectroscopy electric field amplitudes and not intensities are measured, the calculated transmission has to be corrected by a factor of one half. Therefore the real path length was divided by two.

This example again demonstrates, how the Hitran database together with the new tool, the **MolExplorer,** can favourably be applied for the interpretation and understanding of complex spectral data.

- **New tool for calculation and display of spectra from the HITRAN database**

- **Allows plots over a wide spectral range as well as with highest resolution for all relevant gases in the atmosphere**

- **Different gases or isotopologues can be distinguished by colored markers**

- **Five display modes: spectral line intensity, line position with the peak absorption coefficient, absorption, absorption coefficient and transmission**

- **Automatic choice of the line profile, dependent on the broadening mechanism**

- **Direct comparison and fit to measurements**

- **Line shape investigations based on the molecular response theory**

Persons interested in the MolExplorer may contact

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