

UNEX Tutorial

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Introduction

In this document you will find basic examples on how to prepare UNEX inputs for some typical jobs, run them and analyse respective outputs. In the various examples below I have tried to utilize real experimental data as much as possible, so you can see realistic use cases. Some theoretical values, mostly from quantum chemical calculations, occasionally can appear. They also correspond to modern state of the art in this field.

Rotational spectroscopy

In context of rotational spectroscopy UNEX can be used for refinement of molecular structure from rotational constants.

A simple example of structure refinement

As a simple example we take sulfur dichloride SCl_2 , for which rotational constants have been experimentally determined in the work of Bizzocchi et al. [1]. Below you will find a step-by-step tutorial on how to refine the structure of this molecule using UNEX.

First steps

In the C_{2v} symmetry SCl_2 molecule has only two independent geometrical parameters and we can refine them from three experimental rotational constants of only single parent isotopologue. Lets create UNEX input file and as the very first lines we add the following minimal set of commands:

```
BASE: READ <BASE>,</BASE>
ZMATRIX: READ mol <ZMAT>,</ZMAT>
LSQFUNC: MINIMIZE ROTCON
STOP:
```

UNEX will interpret these commands line by line:

1. **BASE:READ** — reading of basic information, including definition of the molecule, which is located between tags **<BASE>** and **</BASE>**.
2. **ZMATRIX:READ** — for the molecule **mol** reading of Z-matrix located between tags **<ZMAT>** and **</ZMAT>**.
3. **LSQFUNC:MINIMIZE** — minimization of least squares functional consisting of rotational constants, i.e. refinement of the molecular structure.
4. **STOP** — termination of UNEX execution.

Now we need to provide the field of data expected by the **BASE:READ** command. Add to the input file the block:

```
<BASE>
  Molecules=mol
</BASE>
```

which contains the only single keyword **Molecules**. We use it to define the identifier **mol** for our molecule. When interpreting this keyword UNEX expects a molecule-specific field between tags constructed on the basis of the molecule identifier as **<mol>** and **</mol>**. Lets create and fill in this field with required for our purposes data:

```

<mol>
  Formula=SCl2
  RotConModel=rrpatm
  # Experimental constants from Bizzocchi et. al, J. Mol. Spectr., 204 (2000) 275.
  RotAExpVal=14613.57789
  RotAExpStdev=0.00057
  RotBExpVal=2920.86641
  RotBExpStdev=0.00013
  RotCExpVal=2430.69088
  RotCExpStdev=0.00012
</mol>

```

Here we define:

- the formula of the molecule as `Formula=SCl2`;
- for demonstration purposes, the model for rotational constants as `rrpatm`, although this is not strictly necessary in our case;
- experimental values for rotational constants using the `RotAExpVal`, `RotBExpVal` and `RotCExpVal` keywords. Note, the input units are MHz, which is the default option in UNEX;
- respective standard deviations with the keywords `RotAExpStdev`, `RotBExpStdev` and `RotCExpStdev`.

Now for the `ZMATRIX:READ` command we need to provide the actual Z-matrix of our molecule. Add to the file the following block:

```

<ZMAT>
Cl
S 1 Rsc1
Cl 2 Rsc1 1 Aclcl

Rsc1      2.0  1
Aclcl    103.0  2
</ZMAT>

```

This Z-matrix defines two internal geometrical parameters, the bond length `Rsc1` (one parameter for both bonds) and the angle `Aclcl`, with respective initial values. We want to refine both parameters, so next to their values we also define refinement group numbers as `1` and `2`. Note, here we use two different groups, thus the parameters will be refined independently from each other.

Now your input file is ready, its content must be similar to that of the file `SCl2_1.inp` coming with this tutorial. We can run UNEX with this file and inspect the produced output file. The part of the output from the refinement goes after the line `LSQ functional processing ...`. You can see some information on experimental data, parameters to be refined, the convergence of the iterative procedure and different statistics. In the statistics we may be particularly interested in line `Rotational constants: ESD=3.279e+00 MaxD=2.29e+00 RMSD=1.89e+00 WRMSD=2.09e+00 MHz`, which gives us maximal, root-mean-square and weighted root-mean-square deviations of rotational constants in MHz. In particular the weighted root-mean-square deviation is equal to 2.09 MHz. Also after the

convergence a table with parameters is printed, for example:

Refined parameters:

Errors are 1.00 times LSQ standard deviations.

Group	Type	Old value	Refined value	Error	RelErr	d(X ²)/dP
1	ZmR	2.0000000000e+00	2.0129185079e+00	6.2e-04	3.1e-04	1.2e+04
2	ZmAng	1.0300000000e+02	1.0282286064e+02	3.7e-02	3.6e-04	1.1e+04

The meaning of the table content is essentially self-explaining. The refined values of the parameters are now $r(\text{S—Cl}) = 2.0129(6)$ Å and $\alpha(\text{Cl—S—Cl}) = 102.82(4)$ degrees, with least-squares standard deviations in parentheses. Note, we used rotational constants A_0 , B_0 and C_0 without any vibrational corrections. Thus, the refined structure is in fact of the r_0 type.

After the table with parameters you can find the matrix of correlations printed as

Matrix of correlations:

```
-----  
1.0000  
0.1553 1.0000  
-----
```

Fortunately, in our example this matrix is very compact. It shows that the refined parameters have correlation coefficient equal to 15.5 %.

Adding isotopologues

Bizzocchi et al. [1] determined rotational constants not only for the parent molecule of sulfur dichloride but also for its three isotopologues. We can utilize these data in our structural refinement. First of all, in the input UNEX file we need to define additional molecules corresponding to the three additional isotopologues. For this, we use the keyword **IsotopMols** in the field of the parent molecule:

```
# Parent isotopologue  
<mol>  
Formula=SCl2  
IsotopMols=iso1;iso2;iso3  
# Bizzocchi et al., J. Mol. Spectr., 204 (2000) 275.  
# The values for the parent molecule:  
RotAExpVal=14613.57789  
RotAExpStdev=0.00057  
RotBExpVal=2920.86641  
RotBExpStdev=0.00013  
RotCExpVal=2430.69088  
RotCExpStdev=0.00012
```

```
</mol>
```

Accordingly, we add three molecule-specific fields with data for **iso1**, **iso2** and **iso3**:

```
# [32]S[35]Cl[37]Cl
<iso1>
  Formula=SCl2
  # Bizzocchi et al., J. Mol. Spectr., 204 (2000) 275.
  RotAExpVal=14490.19459
  RotAExpStdev=0.00058
  RotBExpVal=2841.19803
  RotBExpStdev=0.00013
  RotCExpVal=2371.96585
  RotCExpStdev=0.00013
</iso1>

# [32]S[37]Cl2
<iso2>
  Formula=SCl2
  # Bizzocchi et al., J. Mol. Spectr., 204 (2000) 275.
  RotAExpVal=14365.1421
  RotAExpStdev=0.0026
  RotBExpVal=2763.20280
  RotBExpStdev=0.00024
  RotCExpVal=2314.12120
  RotCExpStdev=0.00019
</iso2>

# [34]S[35]Cl2
<iso3>
  Formula=SCl2
  # Bizzocchi et al., J. Mol. Spectr., 204 (2000) 275.
  RotAExpVal=14024.5853
  RotAExpStdev=0.0068
  RotBExpVal=2921.00225
  RotBExpStdev=0.00056
  RotCExpVal=2413.85131
  RotCExpStdev=0.00034
</iso3>
```

Just like for the parent molecule, we must define Z-matrices also for the additional isotopologues using the **ZMATRIX:READ** command:

```
ZMATRIX: READ iso1 <ZMAT1>,</ZMAT1>
ZMATRIX: READ iso2 <ZMAT2>,</ZMAT2>
ZMATRIX: READ iso3 <ZMAT3>,</ZMAT3>
```

and by providing the respective data fields:

```

<ZMAT1>
Cl 36.96590260
S 1 Rsc1
Cl 2 Rsc1 1 Ac1c1

Rsc1      2.0  1
Ac1c1    103.0  2
</ZMAT1>

<ZMAT2>
Cl 36.96590260
S 1 Rsc1
Cl 36.96590260 2 Rsc1 1 Ac1c1

Rsc1      2.0  1
Ac1c1    103.0  2
</ZMAT2>

<ZMAT3>
Cl
S 33.96786700 1 Rsc1
Cl 2 Rsc1 1 Ac1c1

Rsc1      2.0  1
Ac1c1    103.0  2
</ZMAT3>

```

Notice how the atomic masses for the non-standard isotopes are declared right in Z-matrix bodies, next to atomic symbols. In this way we indicate only non-standard isotopes. For the other atoms UNEX automatically assigns built-in atomic masses of the most abundant isotopes, in this case ^{32}S and ^{35}Cl . Also note that the initial values of bond lengths and angles in all isotopologues are the same and constitute two refinement groups, **1** and **2**. Thus, we are going to refine two parameters under assumption that all isotopologues have the same r_0 structure.

Now your input file must be similar to the file [SC12_2.inp](#) of this tutorial and it is ready to be processed by UNEX. The least squares refinement converges very quickly and takes less than a second on modern hardware. Note that we have now in total 12 experimental constants:

```

Statistics:
Number of refined parameters: 2
Number of data: 12
Degrees of freedom: v=10

```

Interestingly, the overall agreement of model with data is now even slightly better, $\text{WRMSD}=2.03\text{e}+00$ MHz, than in the previous case of only one isotopologue with three experimental constants in total. Due to the increased number of statistically independent experimental data the refined parameters are now more precise, $r(\text{S—Cl}) = 2.0129(2)$ Å and $\alpha(\text{Cl—S—Cl}) = 102.82(1)$ degrees, and the correlation coefficient has lowered to 10 %.

We can also print Cartesian coordinates of atoms in all or selected isotopologues. After the `LSQFUC` command add the line

```
PRINT: MOLXYZ mol
```

This will give you the coordinates of atoms in `mol`. In the default format you can also see the atomic masses actually used by UNEX. In context of rotational spectroscopy it makes sense to print Cartesian coordinates in the system of principal axes of inertia tensor. For this, add the keyword `PrintXYZPAS=true` to the field of basic information. On the output you should get

```
Cartesian coordinates (Angstroms) of atoms in mol
Format: UNEX
Orientation: PAS
-----
 N | At | An |      Mass      |      X      |      Y      |      Z
-----
 1 | Cl | 17 | 34.968852690000 | -1.57337179879261e+00 | 3.93893392440875e-01 | 0.00000000000000e+00
 2 | S  | 16 | 31.972071173500 | 0.00000000000000e+00 | -8.61627008214962e-01 | 0.00000000000000e+00
 3 | Cl | 17 | 34.968852690000 | 1.57337179879261e+00 | 3.93893392440875e-01 | 0.00000000000000e+00
-----
Rot. const. (RRPATM, MHz): 1.46117876060391e+04 2.91906050564133e+03 2.43300790959393e+03
```

The coordinates can be visualized producing a structure like in the figure below.

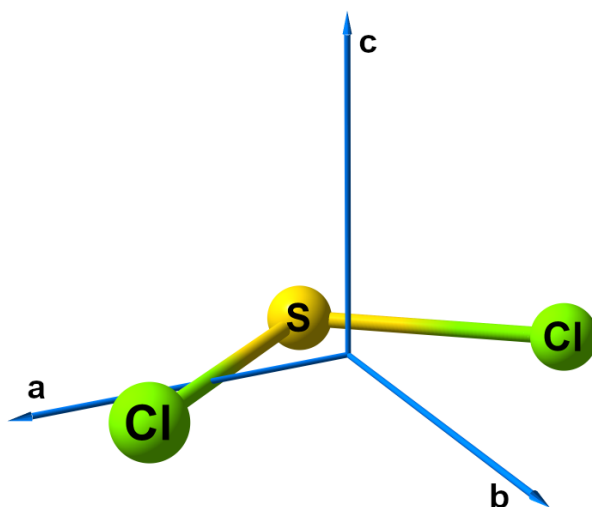


Figure 1. SCl_2 in the principal axes system.

Using vibrational corrections

Until now we refined r_0 structure directly from experimental rotational constants A_0 , B_0 and C_0 . Omitting a discussion of disadvantages related to this type of structure, we can proceed directly to the example on how to refine structures corrected for vibrational effects. For this, next to experimental rotational constants we need to define respective vibrational corrections. Nowadays in many cases they can be routinely calculated theoretically with reasonable confidence. Even better is when you have them refined from experimental ro-vibrational spectra. In any case they must be introduced in UNEX using the keywords `RotAVibCorVal`, `RotBVibCorVal` and `RotCVibCorVal`. Taking your previous input file you can add the following data to the field of the parent molecule:

```
RotAVibCorVal=-19.2076
RotBVibCorVal=9.4715
RotCVibCorVal=9.5976
```

to the first isotopologue **iso1**:

```
RotAVibCorVal=-18.6655
RotBVibCorVal=9.1457
RotCVibCorVal=9.2892
```

to **iso2**:

```
RotAVibCorVal=-18.1413
RotBVibCorVal=8.8313
RotCVibCorVal=8.9889
```

and to **iso3**:

```
RotAVibCorVal=-18.6646
RotBVibCorVal=9.3391
RotCVibCorVal=9.4141
```

All these values are quantum-chemically calculated corrections to equilibrium structure. As a reference this tutorial provides a file `SCl2_3.inp`, which should also contain all the required information. Running UNEX with the prepared input leads to a much better fit with WRMSD equal to 3.50e-02 MHz. This may be compared with the previous value (2.03e+00 MHz) from the example above without any vibrational corrections. Thus we are getting here more consistent model. The refined parameters, $r_e^{se}(\text{S—Cl}) = 2.011023(3) \text{ \AA}$ and $\alpha_e^{se}(\text{Cl—S—Cl}) = 102.6808(2)$ degrees, are now much more precise, at least nominally. Also, in comparison to the previous values, $r_0(\text{S—Cl}) = 2.0129(2) \text{ \AA}$ and $\alpha_0(\text{Cl—S—Cl}) = 102.82(1)$, we see significant deviations due to the different types of structures. Note, we use the r_e^{se} designation to underline that the structure is in fact semi-experimental (also known as semi-empirical) due to using theoretical vibrational corrections. Please keep in mind that obtained in this example very small standard deviations manifest only random noise in experimental data. Of course, the total errors must be larger at least due to uncertainties in vibrational corrections. This is, however, a different topic.

What we can also do in this example is to print details about rotational constants. For this, you can add the following line after the `LSQFUNC` command:

```
PRINT: ROTCON mol
```

On the output you get the following data for the parent molecule **mol**:

Model rotational constants for mol

Units: MHz

Model: rrp atm-vibc-elc1

	RRPATM	El. Cor.	Vib. Cor.	Total Model
A	1.459434063286e+04	0.000000000000e+00	-1.920760000000e+01	1.461354823286e+04
B	2.930307872201e+03	0.000000000000e+00	9.471500000000e+00	2.920836372201e+03
C	2.440329187413e+03	0.000000000000e+00	9.597600000000e+00	2.430731587413e+03

Experimental and model rotational constants for mol

Units: MHz

Model: rrp atm-vibc-elc1

Errors are 1.00 times standard deviations.

	Experimental	Error	Model	Error	Delta
A	1.461357789000e+04	5.70e-04	1.461354823286e+04	7.80e-02	2.97e-02
B	2.920866410000e+03	1.30e-04	2.920836372201e+03	1.35e-02	3.00e-02
C	2.430690880000e+03	1.20e-04	2.430731587413e+03	9.41e-03	-4.07e-02

For the defined values: RMSD=3.39e-02 WRMSD=3.61e-02 MHz

Here in the first table you can see the particular components of the model values, including the vibrational corrections. Note, in sulfur dichloride these corrections constitute about 0.1 — 0.5 % of the total rotational constants. The default model `rrp atm-vibc-elc1` has also electronic correction, which will be discussed in the next example. In the second table are provided experimental and model values and respective deviations for the rotational constants separately.

Applying electronic corrections

In addition to vibrational correction our model for rotational constants contains also an electronic correction (consult UNEX manual for details). Usually they are negligibly small but in investigations of some molecules can play significant role. In UNEX the corrections are internally calculated from diagonal `aa`, `bb` and `cc` components of rotational g-tensors. The latter can be determined experimentally or, most usually, calculated theoretically. In the input file we define them with the keywords `RotGTaaVal`, `RotGTbbVal` and `RotGTccVal` for each molecule. In this example we add the following values for the parent isotopologue `mol`:

```
RotGTaaVal=-0.0361
RotGTbbVal=-0.0147
RotGTccVal=-0.0232
```

for `iso1`:

```
RotGTaaVal=-0.0358
RotGTbbVal=-0.0143
RotGTccVal=-0.0226
```

for `iso2`:

```
RotGTaaVal=-0.0355
RotGTbbVal=-0.0139
RotGTccVal=-0.0221
```

and for `iso3`:

```
RotGTaaVal=-0.0348
RotGTbbVal=-0.0147
RotGTccVal=-0.0231
```

Now the file is ready for running and must be similar to `SC12_4.inp` from this tutorial. After the least-squares refinement with `LSQFUNC:MINIMIZE` you can see that the overall agreement is now even better, `WRMSD=3.13e-02 MHz`, although to a very small extent. Thus, the vibrational corrections do the major job and the electronic corrections lead to only slight improvement. The latter can sometimes even slightly worsen the agreement due to inaccuracy and inconsistency with other data. Looking at the refined parameters, $r_e^{se}(\text{S—Cl}) = 2.011010(3) \text{ \AA}$ and $\alpha_e^{se}(\text{Cl—S—Cl}) = 102.6811(2) \text{ degrees}$, we can see some notable shift in the bond length compared to the previous refinement without electronic corrections, i.e. $r_e^{se}(\text{S—Cl}) = 2.011023(3) \text{ \AA}$ and $\alpha_e^{se}(\text{Cl—S—Cl}) = 102.6808(2) \text{ degrees}$. Formally, if we consider only the provided in parentheses standard deviations, this effect could be accepted as significant. However, we keep in mind that the other sources of uncertainties are not taken into account and thus the seeming effect is rather unreliable in this particular case. After the refinement we can get lots of interesting information by executing `PRINT: ROTCON all`. This variant of the command prints rotational constants for all defined molecules, so that you do not need to call `PRINT` for each molecule individually.

In particular, for `mol` we get

```
Model rotational constants for mol
Units: MHz
Model: rrp atm-vibc-elc1
```

	RRPATM	El. Cor.	Vib. Cor.	Total Model
A	1.459462922084e+04	-2.870183433458e-01	-1.920760000000e+01	1.461354980250e+04
B	2.930334240812e+03	-2.346613381449e-02	9.471500000000e+00	2.920839274678e+03
C	2.440355543757e+03	-3.084242581278e-02	9.597600000000e+00	2.430727101331e+03

```
-----
Experimental and model rotational constants for mol
```

Units: MHz

Model: rrpam-vib-elc1

Errors are 1.00 times standard deviations.

	Experimental	Error	Model	Error	Delta
A	1.461357789000e+04	5.70e-04	1.461354980250e+04	6.98e-02	2.81e-02
B	2.920866410000e+03	1.30e-04	2.920839274678e+03	1.21e-02	2.71e-02
C	2.430690880000e+03	1.20e-04	2.430727101331e+03	8.43e-03	-3.62e-02

For the defined values: RMSD=3.08e-02 WRMSD=3.23e-02 MHz

Now you can see how large are the absolute values of electronic corrections in sulfur dichloride. For the parent molecule, as well as for other isotopologues, they are of the order 3×10^{-1} MHz for A and 3×10^{-2} MHz for B and C, which is 0.5 — 1.5 % of the corresponding vibrational correction or 0.001 — 0.002 % of the total rotational constant.

At this point we can consider our refinement as complete.

Gas electron diffraction

Historically UNEX has been designed as a full-featured software for comprehensive support of experimental gas-phase electron diffraction (GED) studies. Below are presented some use cases with usually appearing scenarios.

Structure refinement

One of the most important stages in a typical GED investigation is the structure refinement. In this chapter you can learn how to solve this problem using UNEX.

A simple example

As an example we take a portion of experimental diffraction data measured for carbon tetrachloride CCl_4 in the work of Vishnevskiy et al. [2]. The molecules of CCl_4 are small and highly symmetric (T_d point group) and thus are very convenient for a GED structural analysis. It is also handy from the experimental point of view, since diffraction patterns can be easily measured for this compound.

In this simple example we assume that the data reduction and electron wavelength calibration have already been done and we take for the analysis only one experimental total intensity curve. Our next steps are briefly as follows:

1. We define the complete initial model of our molecule with all parameters required for the calculation of the model molecular intensity,
2. introduce the experimental total diffraction intensity,
3. extract molecular part from the total intensity,
4. refine the molecular parameters using the least-squares method,
5. print and analyze the results.

So let's start from the very beginning. Below are described commands, which should be added line-by-line to a newly created UNEX input file.

First, we must introduce some basic information

```
BASE: READ <BASE>,</BASE>
STOP:

<BASE>
  Molecules=mol
</BASE>

<mol>
  Formula=CCl4
</mol>
```

Next we define a geometrical model for the molecule. In this example we use geometrically-consistent GED model, so the structure must be defined as a Z-matrix with the command (right after **BASE:**)

```
ZMATRIX: READ mol <ZMAT>,</ZMAT>
```

and providing the required field

```
<ZMAT>
Cl
C 1 R1
Cl 2 R1 1 A1
Cl 2 R1 1 A1 3 A1 -1
Cl 2 R1 1 A1 3 A1 1

R1      1.763                2
A1     109.4712206344907
</ZMAT>
```

Note, to the **R1** parameter we already assigned the group number **2**. This is not required now, but will be used below in the actual refinement procedure. When introducing Z-matrices it is advised to check their correctness by printing calculated Cartesian coordinates. This can be done with the command

```
PRINT: MOLXYZ mol
```

and visualizing the printed coordinates by any suitable software. Note, you can print data in different formats, see manual for details. You may also want to check the symmetry of your input structure by using

```
PRINT: MOLSYM mol
```

For our example this command must produce some information on symmetry elements and also the line

```
Point group: Td [4C3,3C2,3S4,6P,E]
```

which is what we expect for CCl_4 .

Next we introduce information on GED terms (interatomic pairs) for the molecule with the **EDTERMS** command:

```
EDTERMS: READ mol <TERMS>,</TERMS> Format=unex
```

Add the corresponding data field to the input file with precalculated values:

```
<TERMS>
#At1 At2      r_a      l      cor      G
C2  C11    1.7609    0.0521  -0.0066    3
C2  C13    1.7609    0.0521  -0.0066    3
C2  C14    1.7609    0.0521  -0.0066    3
C2  C15    1.7609    0.0521  -0.0066    3
C11 C13    2.8755    0.0676  -0.0090    4
C11 C14    2.8755    0.0676  -0.0090    4
C11 C15    2.8755    0.0676  -0.0090    4
C13 C14    2.8755    0.0676  -0.0090    4
C13 C15    2.8755    0.0676  -0.0090    4
C14 C15    2.8755    0.0676  -0.0090    4
</TERMS>
```

Here we are tying together amplitudes for the bonded distances C—Cl in the refinement group number **3**, and the amplitudes for the non-bonded distances Cl...Cl in the group **4**.

At this point the molecular model is defined completely and we can introduce the diffraction data. With the command **EDDATA** UNEX will read-in the experimental total diffraction intensity:

```
EDDATA: READ <EDINT>,</EDINT>
```

The initial part of the respective data field looks like:

```
<EDINT>
Set=ed1 Data=s;iTotExp ImolSf=1.0 ImolSfRefGrp=1
6.20 11.7659129739
6.40 11.9934137749
6.60 12.3881941876
```

For the complete data see the file **CC14_1.inp** supplemented to this tutorial. For the refinement we assign the group number **1** to the scale factor of the molecular intensity. The initial value for this factor is also explicitly defined as **ImolSf=1.0**. Now the ED data set **ed1** is defined and we can use this identifier later in other commands.

For the calculation of model intensities we must introduce ED scattering factors. In UNEX they can be calculated simply by calling the **EDSCATFAC** command. Add the following line after the **EDDATA:READ** call:

```
EDSCATFAC: CALC mol Lambda=0.048707
```

With the keyword **Lambda** we indicate the calibrated electron wavelength.

For the least-squares refinement we need experimental molecular intensity function. It must be

extracted from the total intensity, which is in the ED data set **ed1**. For this use the command **EDIMOL**:

```
EDIMOL: GETEXP ed1 BgrSplNInflMax=3 ItotModel=mbgr
```

In this procedure the total intensity is decomposed into molecular and background components. As the model we choose **mbgr**, i.e. containing multiplicative background. The background will be approximated with a cubic spline and as a smoothness criterion we allow no more than **3** inflection points. Note, the actual number of inflection points may be smaller. UNEX prints this information on output. In this example you should get

```
Number of inflection points 2, requested 3
```

Finally we have both model and data ready for the refinement. For the least-squares determination of parameters we must use the **LSQFUNC** command. Add the following line for minimization of the LSQ functional built on ED **sM(s)** function from the **ed1** data set:

```
LSQFUNC: MINIMIZE EDSMS ed1
```

From this command UNEX prints lots of important information to the output file, including the initial values of parameters and LSQ functional, convergence during the iterations and at the end, statistics of the refinement, a table with refined parameters and correlation matrix. After the convergence we have the best (minimal) achieved *R*-factor

```
Total sM(s) Rf=6.157 wRd=6.157
```

Initial and refined parameters, as well as corresponding least-squares standard deviations, are printed in the table:

Refined parameters:

Errors are 1.00 times LSQ standard deviations.

Group	Type	Old value	Refined value	Error	RelErr	d(X ²)/dP
1	EDImoLSf	1.0000000000e+00	8.8210443905e-01	7.6e-03	8.6e-03	-2.8e-14
2	ZmR	1.7630000000e+00	1.7604005167e+00	2.6e-04	1.5e-04	3.5e-07
3	EDTrmAmpl+	5.2100000000e-02	4.7047497358e-02	8.9e-04	1.9e-02	-6.5e-08
4	EDTrmAmpl+	6.7600000000e-02	6.9215439794e-02	5.4e-04	7.8e-03	-3.4e-07

Next are printed the correlation coefficients:

Matrix of correlations:

```
-----  
1.0000
```

```
0.0498 1.0000
0.4876 0.0026 1.0000
0.7298 0.0264 0.3702 1.0000
-----
```

As you can see, the refinement procedure has changed the values of parameters substantially. We need to keep in mind that the `EDIMOL:GETEXP` procedure used model-dependent background (see UNEX manual for details). Thus, if the model has significantly changed, it makes sense to repeat again the combination of molecular intensity extraction and parameter refinement. Add these two lines (same as before) to the input file:

```
EDIMOL: GETEXP ed1 BgrSplNInflMax=3 ItotModel=mbgr
LSQFUNC: MINIMIZE EDSMS ed1
```

After the second LSQ functional minimization you should get a better (lower) *R*-factor

```
Total sM(s) Rf=5.054 wRd=5.054
```

and the refined parameters

Errors are 1.00 times LSQ standard deviations.

Group	Type	Old value	Refined value	Error	RelErr	d(X ²)/dP
1	EDImoLSf	8.8210443905e-01	8.6731619200e-01	6.1e-03	7.0e-03	-5.6e-14
2	ZmR	1.7604005167e+00	1.7601265599e+00	2.1e-04	1.2e-04	4.6e-07
3	EDTrmAmpl+	4.7047497358e-02	4.6372855337e-02	7.3e-04	1.6e-02	1.6e-08
4	EDTrmAmpl+	6.9215439794e-02	6.9282520045e-02	4.4e-04	6.4e-03	-3.3e-08

The changes between the old (before this last refinement) and new (after the refinement) values are now much smaller. The correlation matrix remained nearly the same

```
1.0000
0.0498 1.0000
0.4906 0.0026 1.0000
0.7293 0.0265 0.3721 1.0000
```

and shows that the largest correlation (73 %) is between the molecular intensity scale factor `EDImoLSf` (group 1) and the vibrational amplitudes `l(Cl...Cl)` tied together in group 4.

We may want to check the electron diffraction data and plot various functions for better analysis. Add the following command after the last LSQ minimization:

```
PRINT: EDDATA ed1 Data=iTotExp;iBgr;iMolExp;iMolMod;iMolDif
```

With the keyword `Data` is indicated that the following data types from the set `ed1` are printed together:

1. experimental total intensity,
2. background intensity,
3. experimental molecular intensity,
4. model molecular intensity,
5. difference between experimental and model molecular intensities.

These data can be visualized by any suitable software. We can use the `UIntPlot` program bundled together with `UNEX`. Starting it in the command line as

```
uintplot --data tot,bgr --curves ed1 CCl4_1.log
```

will produce a plot of the experimental total intensity with the respective background line. Note, `UIntPlot` requires that the `Gnuplot` program [3] is already installed and can be started simply as `gnuplot` from your working directory. Also make sure that last command line argument to `uintplot` is the actual name of your `UNEX` output file.

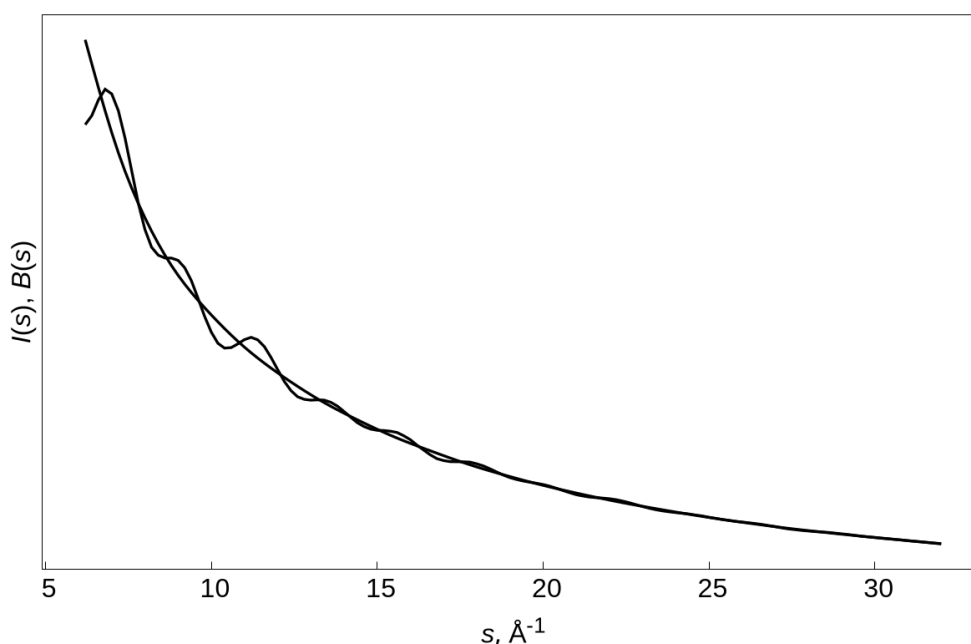


Figure 2. Experimental total ED intensity and background line of CCl_4 .

Visual inspection of molecular intensity functions is also very important. We plot them running `uintplot` as

```
uintplot --data mol,mmol,dmol --curves ed1 CCl4_1.log
```

which produces the following image.

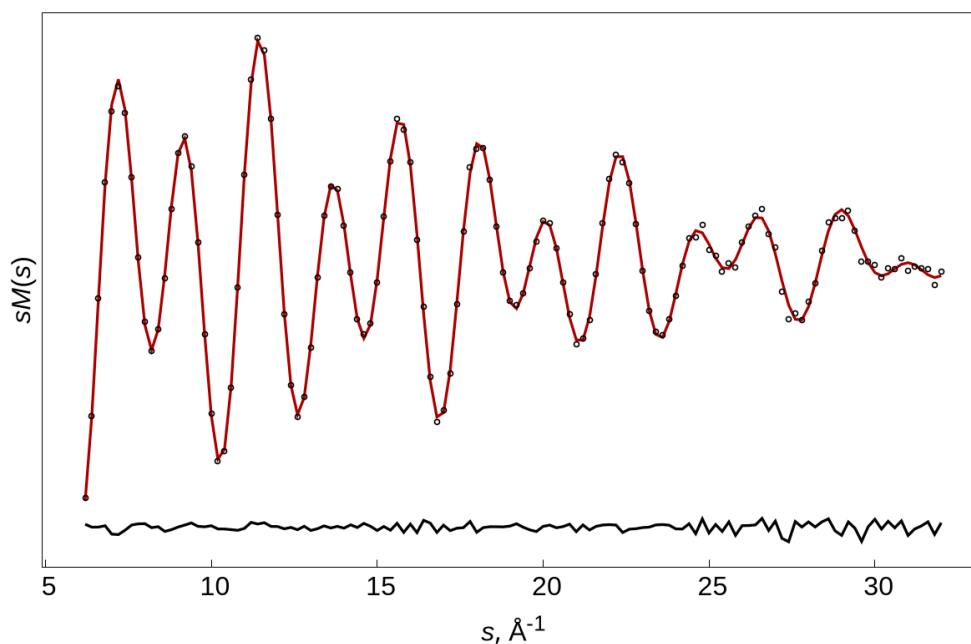


Figure 3. Model (red line) and experimental (dots) ED molecular $sM(s)$ intensity functions of CCl_4 . Below is the difference curve.

As we can see, the difference curve is rather small and shows mostly random deviations between experimental data and model. Thus the fit is acceptable.

Usually electron diffraction data are also represented in the form of radial distribution functions (RDF). UNEX will calculate them, if you add the following command:

```
EDRDF: CALC ed1
```

Also, for the visualization it is convenient to print the ED terms as

```
PRINT: EDTERMS mol Format=urdfplot
```

Now after processing of all commands your UNEX output file must contain all the data required by the URDFPlot program (also bundled together with UNEX), which is useful for plotting RDFs. Start it simply as (provide the actual name of your output file as the argument):

```
urdfplot CCl4_1.log
```

and you will get the following image.

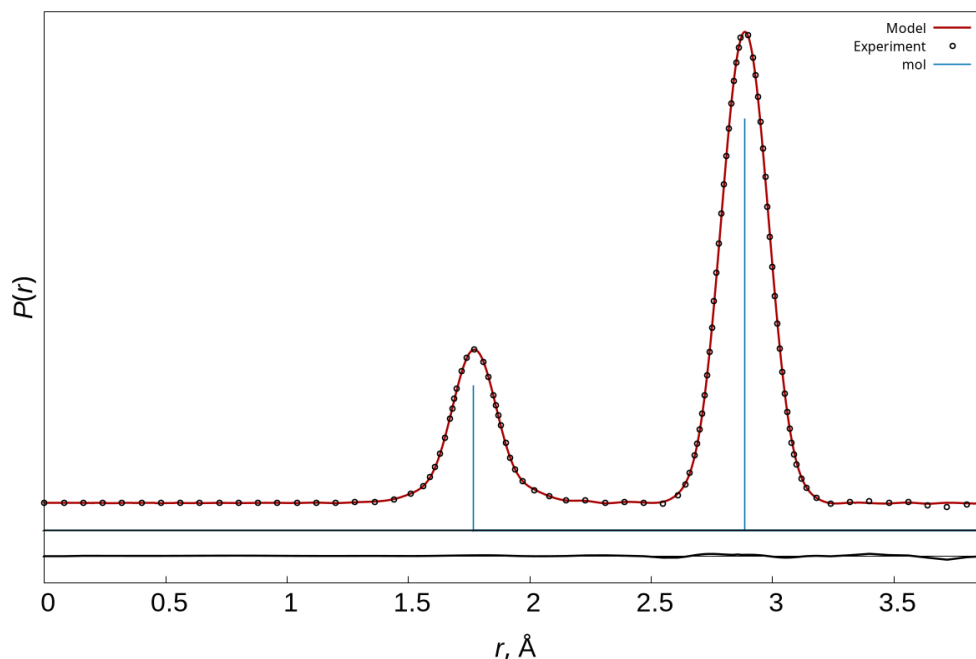


Figure 4. Model (red line) and experimental (dots) radial distribution functions of CCl_4 . Vertical lines show positions and estimated contributions of interatomic pairs into diffraction patterns. Below is the difference curve between the experimental and model data.

As we can see, in the RDF representation the difference between the experimental data and model is also small.

On the basis of the R -factor value of 5.05 % and visual inspection of deviations between experimental data and best refined model, we may now summarize the main results of our investigation of CCl_4 as $r_e^{\text{se}}(\text{C—Cl}) = 1.7601(2) \text{ \AA}$, $l(\text{C—Cl}) = 0.0464(4) \text{ \AA}$ and $l(\text{Cl...Cl}) = 0.0693(4) \text{ \AA}$, where values in parentheses are least-squares standard deviations. Note, because of the used theoretical vibrational corrections (we introduced them with **EDTERMS:READ**) to the equilibrium geometry, the determined structural parameter is semi-experimental r_e^{se} .



The obtained here least-squares standard deviations of the refined parameters may in no case be considered as total uncertainties. In addition to random noise in experimental data, there are other various sources of errors. Their consideration is another, more difficult topic.

References

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- [2] Y. V. Vishnevskiy, S. Blomeyer, & C. G. Reuter, Gas standards in gas electron diffraction: accurate molecular structures of CO₂ and CCl₄. *Struct. Chem.*, **31** (2020) 667–677. <https://doi.org/10.1007/s11224-019-01443-5>.
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