

Module 3

H₂ molecular emission and collisional-radiative modelling

Lecture viewgraphs

Hugh Summers, Francisco Guzman, Kurt Behringer, Martin O'Mullane and Alessandra Giunta

University of Strathclyde

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1.1 Preliminaries

ADAS has restricted interest to diatomic molecules only.

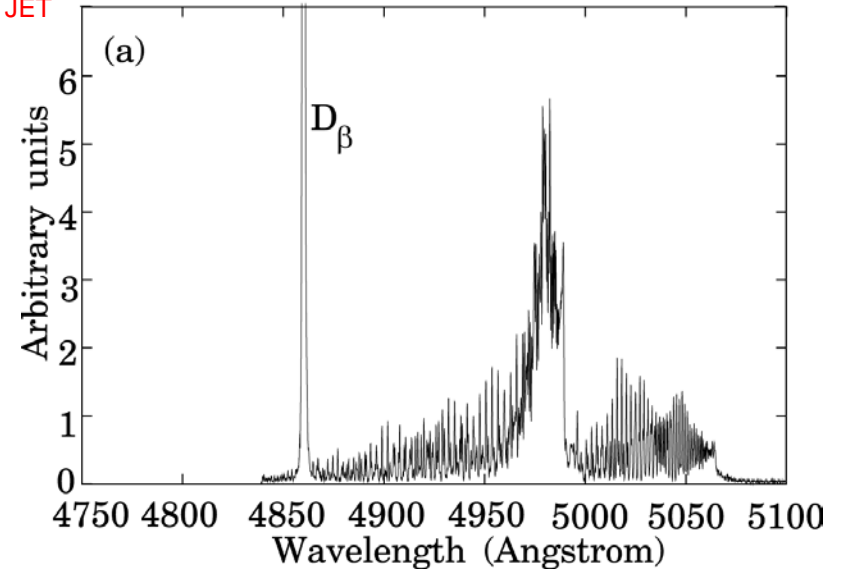
There are two primary motivations:

- (a) analysis of observations of band spectral features at visible wavelengths, which discriminate isotopomers, temperatures (T_r & T_v) and clarify sources.
- (b) Collisional-radiative modelling of H_2 isotopomers for plasma models and quantitative spectroscopy in the visible and UV.

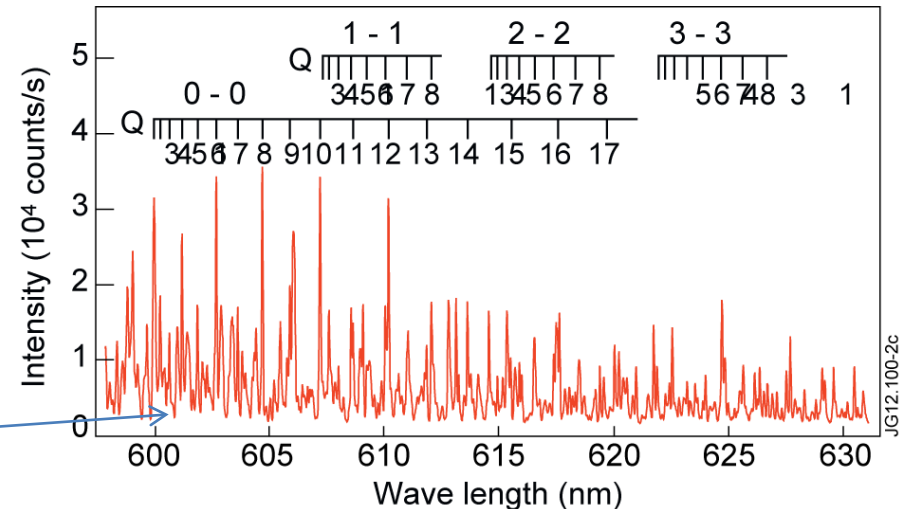
For the former, ADAS models rovibrational band wavelengths between electronic states, with assumptions of upper emitting state populations.

For the latter, ADAS has developed a vibronic collisional radiative model for the H_2 system. This model can provide upper state population information for quantitative/calibrated spectroscopy of hydrogen molecular emission.

Green band of BeD observed at JET



Fulcher spectrum of D2 observed at JET.



Careful comparison with ADAS rovibrational models indicate a weak HD contribution to the primary D_2 spectrum.

1.2 Fundamental molecular constants and data

Following the ADAS practice for atoms and ions, a number of data formats have been introduced for the molecular problem. They are called *molecular data formats* (such as *mdf00*). These fall into the two categories of fundamental data and derived (collisional-radiative) data.

We have tried as far as possible to follow the data format numbering of the atomic case. Thus *mdf00*, *mdf01*, *mdf02* and *mdf04* are fundamental data collections. *mdf04* is a *specific molecular system file* which, as for its atomic counterpart, can support a collisional-radiative (vibronic) model.

In magnetic confinement fusion research, it is necessary to work with various isotopic combinations, such as H₂, D₂, T₂, HD, HT and DT. It is assumed that the electronic states and their electronic transitions are independent of the nuclear masses. The vibrational and rotational sub-states do reflect the specific isotopic masses.

In practical terms, molecular studies must focus on molecular systems. Thus the D₂ system includes D₂, D₂⁺, D, D⁺ (and in principle D₃ and D₃⁺) and these must be treated together in collisional-radiative modelling. For example, the direct formation of D(n=3) by molecular dissociation is an important parameter.

Molecular constants:

- mdf00: enu** sub-directories by isotopomer – separate datasets of vibrational substate energies for each electronic state.
- pot** separate datasets of electronic potential curve for each electronic state.
- dip** separate datasets of electronic dipole curve for each electronic state.
- aval** sub-directories by isotopomer – separate datasets of vibrationally resolved A-values for each electronic state pair.
- fcf** sub-directories by isotopomer – separate datasets of vibrationally resolved Franck-Condon factors for each electronic state pair.

- mdf01: nist** sub-directories by isotopomer - extract of NIST molecular constant table for selected electronic states.
- behr** sub-directories by isotopomer - driver parameter file for ADAS908 rovibrational spectral analysis - relevant electronic and vibrational transitions.
- pickett** sub-directories by isotopomer - driver parameter file for ADAS908 rovibrational spectral analysis - relevant electronic and vibrational transitions.

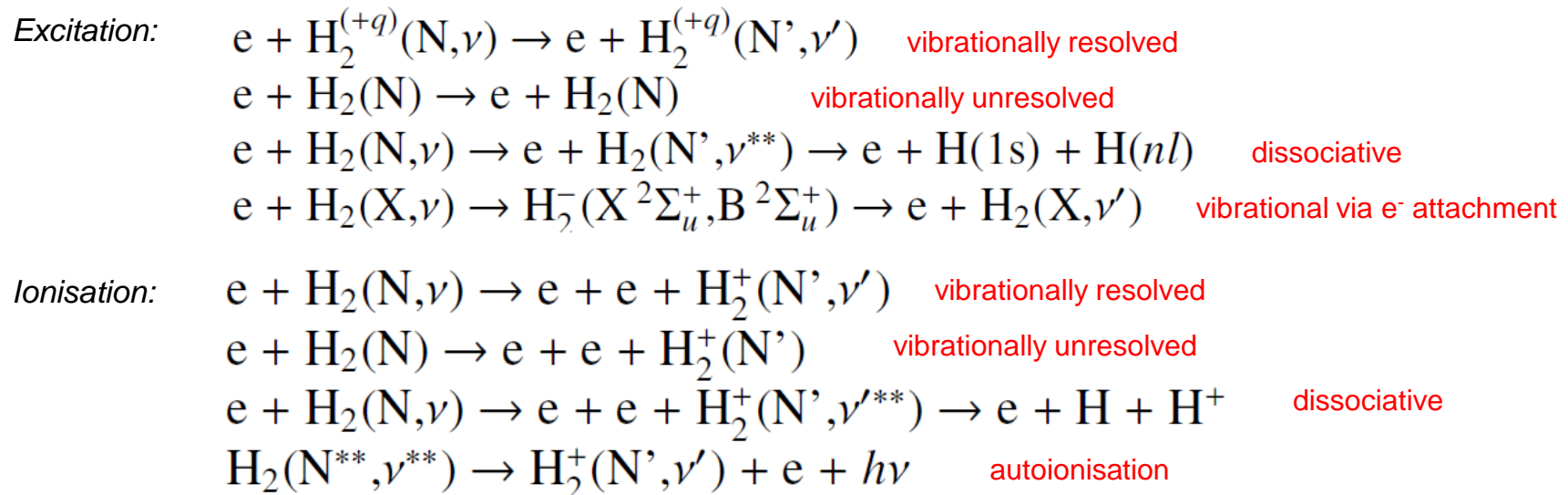
2.1 Electron impact processes with the H₂ molecule

The electron collision processes with the H₂ molecular system has been studied for many years and compilations of reaction cross-sections assembled. A major revision has taken place by Janev, Reiter and Guzman linked to the ADAS-EU project to put these data in a form suitable for ADAS collisional-radiative modelling.

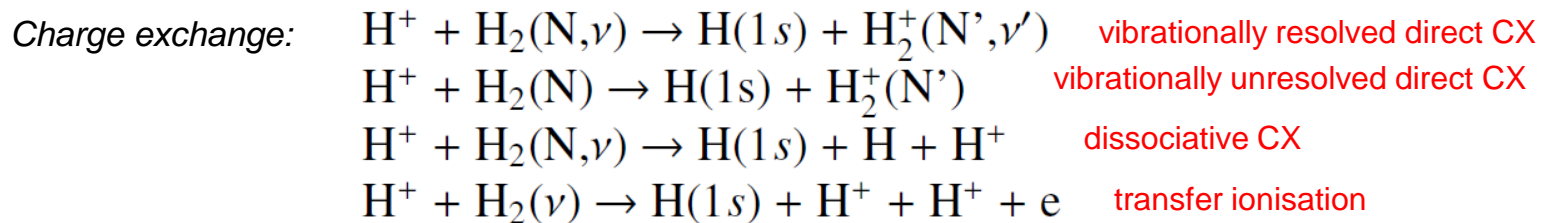
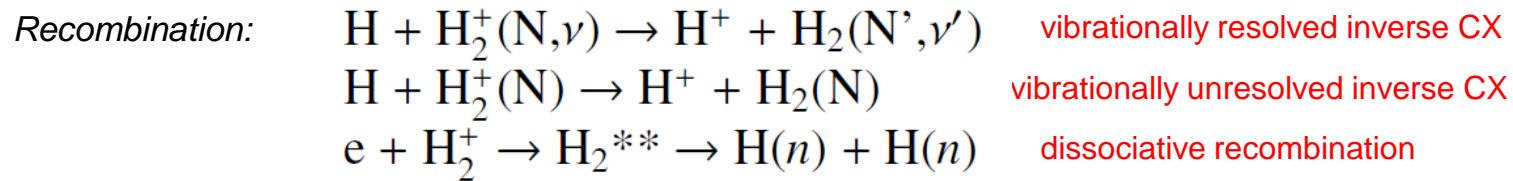
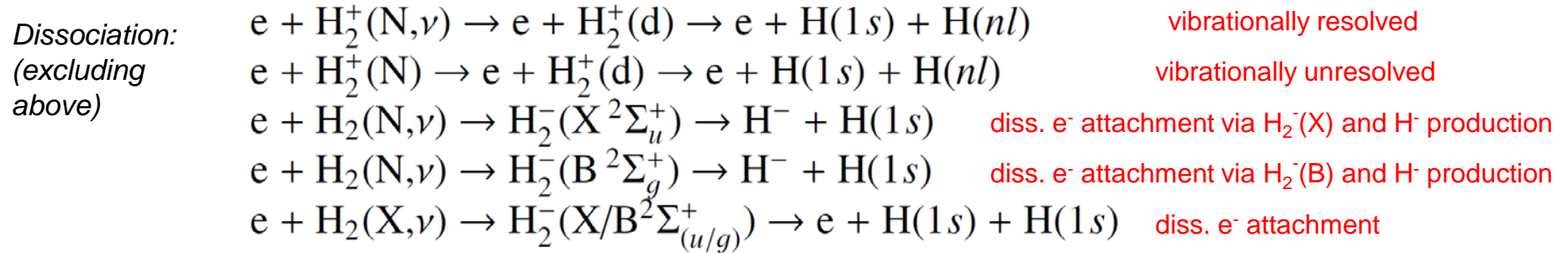
Fundamental data in ADAS data formats are archived as preferred numerical tabulations, with specified asymptotic behaviour. In the molecular collision area, algebraic forms are often used (in certain cases multiple forms) with some lack of clarity in preferment. The ADAS database seeks to correct this.

The ADAS impact process molecular data format is *mdf02* and it has been designed to have both numerical values and the parameters of the formulaic representation (if available) of each transition.

The primary dataset for electron impact with H₂ is *mdf02/fg13_h2#e.dat*. The groups of processes are summarised below.



2.2 Electron impact processes with the H₂ molecule (contd.)



There is a corresponding dataset for H⁺ impact processes with H₂ called *mdf02/fg13_h2#p.dat*

2.3 H₂ system excitation data of format *mdf02*

```

system → H_2 / electron impact mdf02
/
species
/-----
/ ind_s identity e-config e-coupling ch_ion bwno_i ch_dis bwno_d
/-----
1 H_2 dia-ua dia-term 1->2 124418. 1->4+4 36117.00
1 H_2 dia-ua dia-term 1->2 124418. 1->5+6 36117.00
2 H_2^+ dia-ua dia-term 2->5+5 5386. 2->4+5 21380.21
3 H_2^- dia-ua dia-term 3->1 0. 3->4+6 00000.00
4 H atm atm-term 4->5 109691. N 00000.00
5 H^+ atm atm-term N 0. N 00000.00
6 H^- atm atm-term 6->4 427. N 00000.00
/
process
/-----
/ ind_p path description
/-----
1 e+H_2(^+q) (N,v) -> e + H_2(+q) * (N',v') excitation
11 e+H_2(N,v) -> e + H_2*(N',v') vib resolved exc.
53 H^+ + H_2(N,v) -> H(1s) + H + H^+ dissociative CX
54 H^+ + H_2(v) -> H(1s) + H^+ + H^+ + e transfer ion.
55 other CX processes
/
states
/-----
/ ind_s ind_e e-con-ua e-con-sa coupled state (wt.-1)/2 wno wno_d comments
/-----
1 1 1ssg1ssg 1s1s (1)S(+) (g) 0.0 0.0 38292.98 ground state X
1 2 1ssg2psu 1s2p (1)S(+) (u) 0.0 91691.69 120595.97 B
. . . . .
1 29 1ssg4dpg 1s3d (3)P( ) (g) 2.5 118509.87 135837.26 r
2 1 1ssg (2)S(+) (g) 0.5 124418.00 148030.30
2 2 2psu 1s (2)S(+) (u) 0.5 274666.12 274666.12 dissociative state
2 3 2ppu 2s (2)P( ) (u) 0.5 318289.02 318289.02 dissociative state
4 1 1s (2)S 0.5 148030.30 148030.30
5 1 0.0 ion H^+
/
values

```

species list with characterisations →

process list with descriptions →

electronic level list →

2.4 Transition data and the ADAS901 processing screen

<pre> /ch_in /----- s e v 1 1 0 </pre>	<pre> ind_p ----- 14 </pre>	<pre> ch_out ----- s e v 1 1 0 </pre>	<pre> ch_dis ----- </pre>	<pre> parameters & values ----- categ=4 tcode=1 form=201 par=6 numer=28 DE=0.0000e+00 EX te= 1.000 1.200 1.400 1.600 1.800 2.000 2.200 2.400 2.600 2.800 3.000 4.000 5.000 6.000 7.000 8.000 9.000 10.00 15.00 20.00 30.00 40.00 50.00 60.00 70.00 80.00 90.00 100.0 rate= 0.6124E-07 0.5456E-07 0.4877E-07 0.4380E-07 0.3953E-07 0.3586E-07 0.3267E-07 0.2989E-07 0.2746E-07 0.2531E-07 0.2341E-07 0.1650E-07 0.1224E-07 0.9436E-08 0.7480E-08 0.6063E-08 0.5004E-08 0.4191E-08 0.2019E-08 0.1147E-08 0.4829E-09 0.2487E-09 0.1444E-09 0.9086E-10 0.6057E-10 0.4218E-10 0.3041E-10 0.2255E-10 par_val= -7.5980 -1.5006e-1 -2.3448 1.0147 -8.0412 7.9813e-2 </pre>	<p style="color: red;">codes and information</p>
transition data	transition state details	T_e or energy range		rate coefft. or xsect.	fit form parameters

It is helpful to be able to interrogate *mdf02* data and graph the collision data.

The interactive ADAS code **ADAS901** provides this facility. A numerical tabulation at the user's choice of range may also be returned.

The processing screen is shown on the right.

process type selector

transition

details of selected transition

2.5 Text and graphical output from ADAS901

The familiar outputs are available on the output screen of **ADAS901**.

output
tabulation

output
graph

MOLECULAR COEFFICIENT VERSUS ENERGY/TEMPERATURE :

ADAS RELEASE: v4.0 PROGRAM: ADAS901 v1.0 DATE: 24/05/13 TIME: 08:07

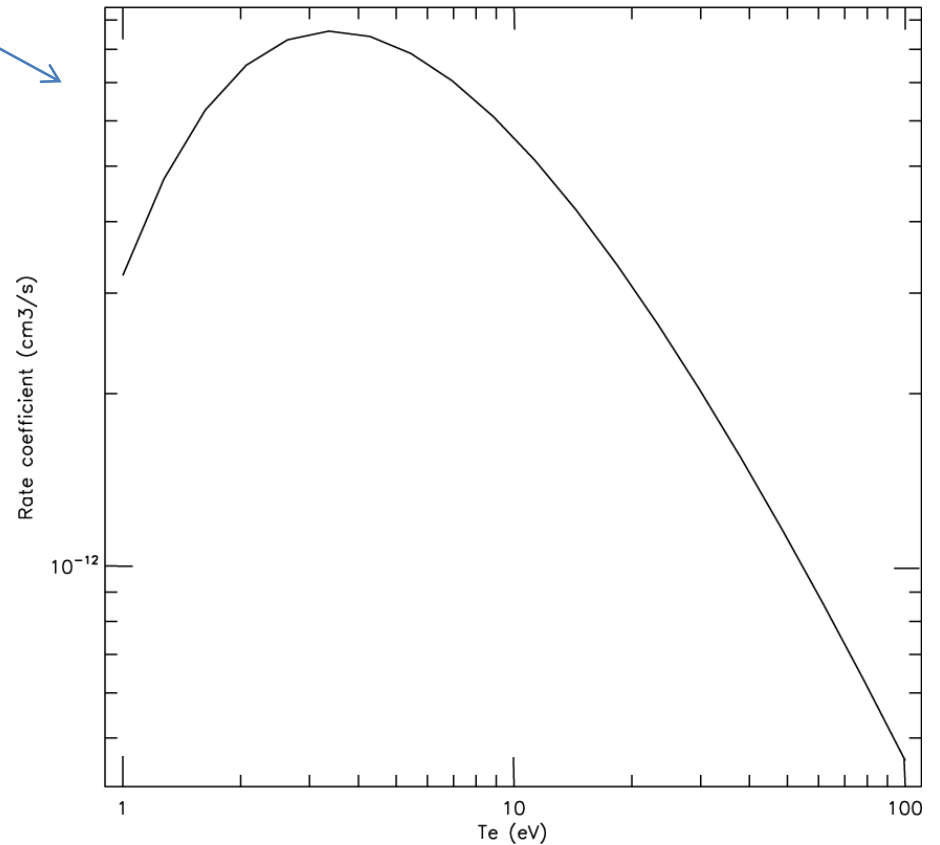
mdf02 file : /home/adas/adas/mdf02/h2/fg13_h2#e.dat

Transition : in : 0, 0, ; out : 0, 0, ; process : 11 ; diss ch :

Energy/Te	Coefficient
1.00	3.221e-12
1.27	4.752e-12
1.62	6.266e-12
2.07	7.510e-12
2.64	8.315e-12
3.36	8.611e-12
4.28	8.429e-12
5.46	7.866e-12
6.95	7.049e-12
8.86	6.101e-12
11.29	5.125e-12
14.38	4.198e-12
18.33	3.361e-12
23.36	2.639e-12
29.76	2.038e-12
37.93	1.549e-12
48.33	1.161e-12
61.58	8.603e-13
78.48	6.300e-13
100.00	4.567e-13

MOLECULAR COEFFICIENT VERSUS ENERGY/TEMPERATURE :

ADAS : ADAS RELEASE: v4.0 PROGRAM: ADAS901 v1.0 DATE: 24/05/13 TIME: 13:22
FILE : /home/adas/adas/mdf02/h2/fg13_h2#e.dat
TRANSITION : in : 0, 0, ; out : 0, 0, ; process : 11 ; diss ch :
KEY : (CROSSES - INPUT DATA) (FULL LINE - FORMULA FIT)



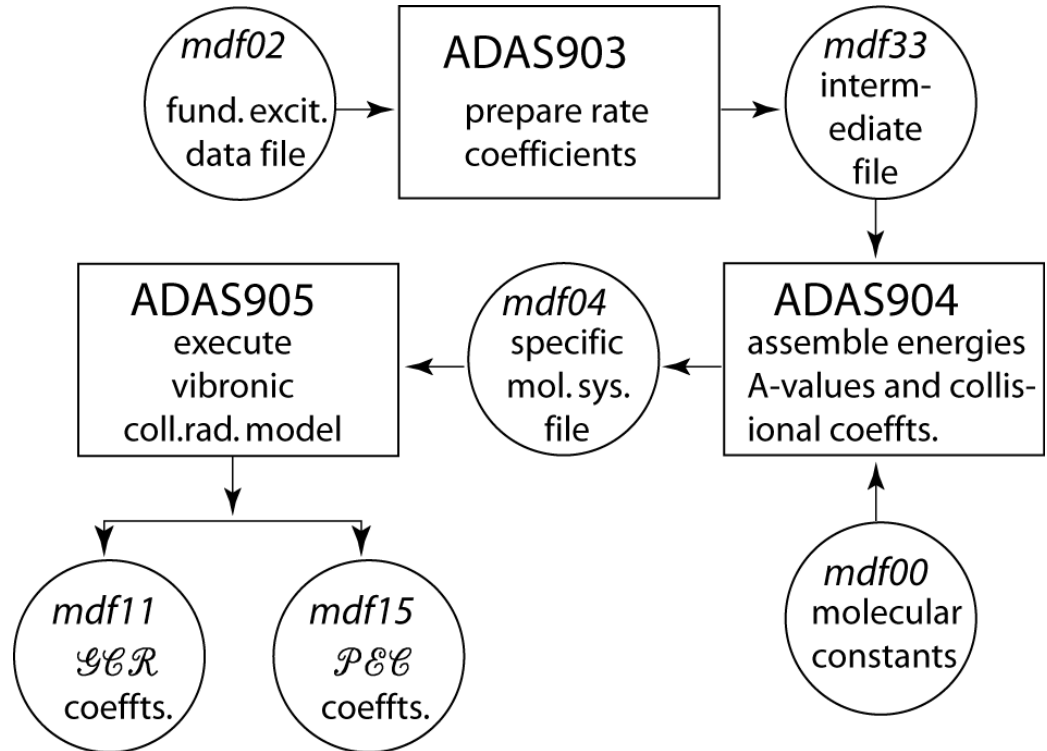
3.1 H₂ vibronic collisional-radiative

The ADAS codes **ADAS903** and **ADAS904** operate in sequence. From *mdf02*, **ADAS903** converts cross-sections to rate coefficients. It prepares an intermediate dataset of format *mdf33* structurally similar to *mdf02*.

ADAS904 gathers the level list and reaction data from *mdf33* and includes A-values and vibrational energies from *mdf00* to prepare the vibrationally-resolved specific molecule file *mdf04*.

Formally, *mdf04* is similar to *adf04*. It is sufficient to support a vibronic population calculation.

ADAS905 executes the vibronic collisional-radiative model for the population solution. It generates the generalised collisional-radiative coefficients of format *mdf11* which couple metastable states of species together and the associated emissivity coefficients *mdf15*. These names parallel the *adf11* and *adf15* formats for atoms and ions.



3.2 H₂ generalised collisional-radiative algebra

The generalised collisional matrix reductions follow broadly the same path as for atoms and ions. But there are some new coefficients

$$\frac{dN_\rho}{dt} = \mathcal{M}C_{\rho\sigma}N_\sigma + \mathcal{M}Q_{\rho\nu}^{\text{ICX}}N_\nu N_H + \mathcal{M}R_{\rho\nu}N_\nu N_H$$

$$\mathcal{M}C_{\rho\sigma} = [C_{\rho\sigma} - C_{\rho j}C_{ji}^{-1}C_{i\sigma}] / N_e \quad \text{M2CD}$$

$$\mathcal{M}R_{\rho\nu} = r_{\rho\nu} - C_{\rho j}C_{ji}^{-1}r_{i\nu} \quad \text{MAD}$$

$$\mathcal{M}Q_{\rho\nu}^{\text{ICX}} = Q_{\rho\nu}^{\text{ICX}} - C_{\rho j}C_{ji}^{-1}Q_{i\nu}^{\text{ICX}} \quad \text{MCXAD}$$

The prefix \mathcal{M} is used for the molecular generalised collisional-radiative coefficients.

New **inverse charge exchange recombination coefficient**

$$\mathcal{M}S_{\nu\sigma} = S_{\nu\sigma} - S_{\nu j}C_{ji}^{-1}C_{i\sigma} \quad \text{MSD}$$

New **charge exchange ionisation coefficient**

$$\mathcal{M}Q_{\nu\sigma}^{\text{CX}} = Q_{\nu\sigma}^{\text{CX}} - Q_{\nu j}^{\text{CX}}C_{ji}^{-1}C_{i\sigma} \quad \text{MCXD}$$

New **dissociative** coefficients.

$$\mathcal{P}D_{\mu\sigma} = D_{\mu\sigma} - C_{\mu j''}C_{j''i''}^{-1}D_{i''\sigma} \quad \text{PDD}$$

$$\mathcal{P}AD_{uv} = -D_{ui}C_{ii}^{-1}Q_{iv}^{\text{ICX}}N_H - D_{ui}C_{ii}^{-1}r_{iv}N_e \quad \text{PADD}$$

$$\mathcal{P}DS_{\mu^+\sigma} = -N_e [S_{\mu^+ j''}C_{j''i''}^{-1}D_{i''\sigma}] \quad \text{PDDSD}$$

$$\mathcal{P}ADS_{\mu^+\nu} = -N_e S_{\mu^+ j''}C_{j''i''}^{-1}D_{i'' j}C_{ji}^{-1} [Q_{iv}^{\text{ICX}}N_H + r_{iv}N_e] \quad \text{PADSDSD}$$

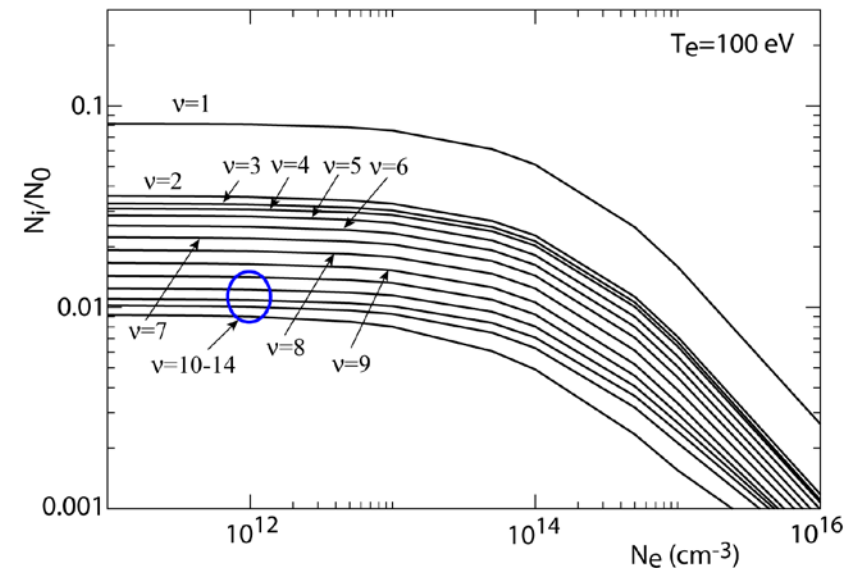
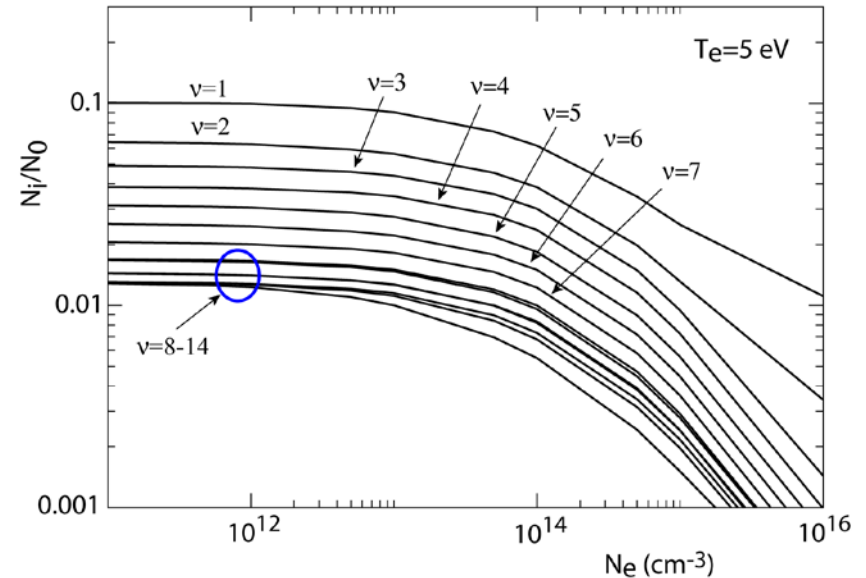
3.3 H₂ ground state vibrational population structure

In the H₂ system, **all** the vibrational states of the ground electronic state H₂ (X ¹S_g⁺) are **metastable**, since they cannot radiate to the lowest vibrational state.

The figures to the right show the vibrational sub-state populations of the ground state in equilibrium.

The vibrational states of the excited electronic states are not metastable. They are **ordinary** states in the generalised collisional-radiative description.

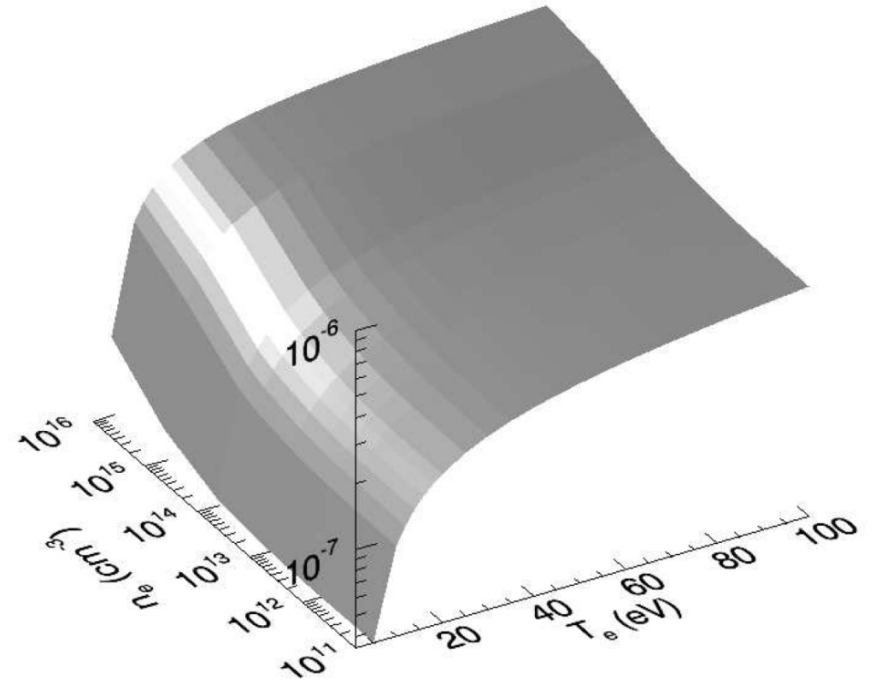
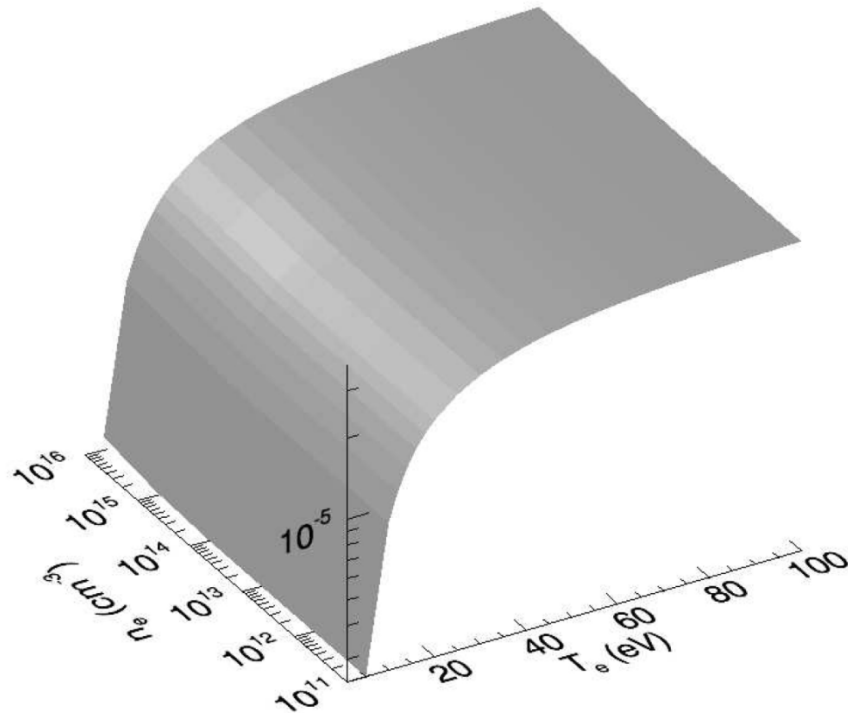
The set of generalised collisional-radiative coefficients is therefore **much larger** for the molecular case. This can be a bit overwhelming for basic studies, so the coefficients are often summed and averaged over the vibrational sub-states of the ground electronic state.



3.3 H₂ collisional-radiative coefficients

The coefficients shown here have been summed over the ground vibrational substates. In the most consistent practice the separate vibrational sub-states of the H₂ (X ¹S_g⁺) ground electronic state are all metastable and should be explicit.

Dissociation coefficient \mathcal{PDCD} for the effective dissociation pathway:
H₂ (X ¹Σ_g⁺) → H + H(H⁺)



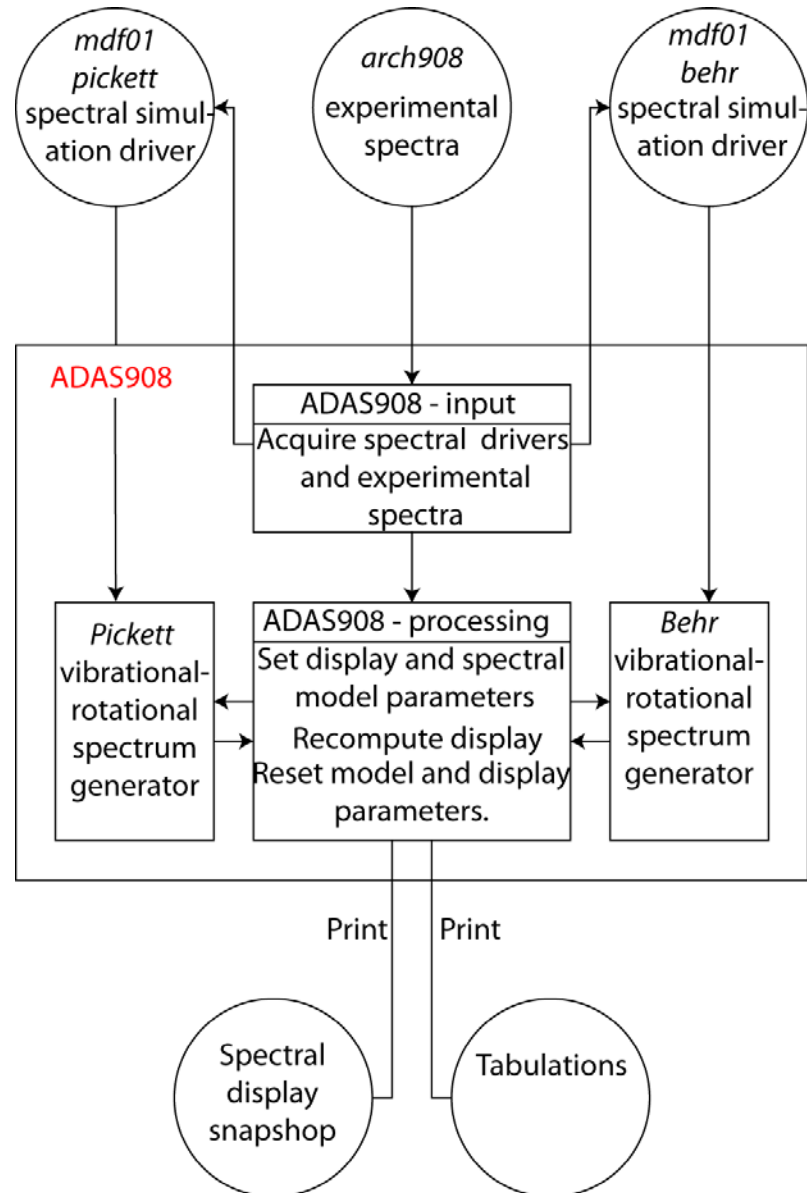
Ionisation coefficient \mathcal{MSCD} for the pathway :
H₂ (X ¹Σ_g⁺) → H₂⁺ (X ²Σ_g⁺) + e

4.1 Spectral analysis using ADAS908

Practical spectral analysis for complex molecular rovibrational spectra often proceeds by comparison and matching of theoretical and experimental spectra over wavelength intervals.

If a convincing match can be obtained, then the variation of relative intensities as a function of effective rotational and vibrational temperatures can be exploited.

ADAS908 is provided to assist in such investigation. It can work with several spectra (experimental and theoretical) simultaneously. Control values appropriate to the experimental spectra and to the theoretical spectra and to the display can be adjusted giving substantial flexibility.



4.2 Some theoretical issues

The usual parametric expansion of a rovibrational level energy is written as:

$$\begin{aligned} T_{\nu,J} &= G(\nu) + F_{\nu}(J) \\ &= \omega_e(\nu + 1/2) - \omega_e x_e(\nu + 1/2)^2 + \omega_e y_e(\nu + 1/2)^3 + \dots \\ &\quad + B_{\nu}J(J + 1) - D_{\nu}J^2(J + 1)^2 + H_{\nu}J^3(J + 1)^3 + \dots \end{aligned}$$

where the rotational parameters may have the supplementary expansions:

$$\begin{aligned} B_{\nu} &= B_e - \alpha_e(\nu + 1/2) + \beta_e(\nu + 1/2)^2 + \dots \\ D_{\nu} &= D_e - \gamma_e(\nu + 1/2) + \dots \end{aligned}$$

If there is no upper electronic state vibrational sub-population collisional-radiative model, then upward projection of the ground and/or metastable thermal vibrational distributions is assumed according to Franck-Condon factors. This can be handled by adjusting B_{ν} values and populations as

$$\begin{aligned} \bar{B}'_{k,\nu'} &= \left[\sum_{\nu_g} B_{g,\nu_g} F_{g\nu_g}^{k,\nu'} N_{g,\nu_g} + \sum_{\nu_m} B_{m,\nu_m} F_{m\nu_m}^{k,\nu'} N_{m,\nu_m} \right] / \left[\sum_{\nu_g} N_{g,\nu_g} + \sum_{\nu_m} N_{m,\nu_m} \right] \\ N_{k,\nu',J} &= \omega_J \exp(-\bar{B}'_{k,\nu'} J(J + 1)/kT_r) N_{k,\nu'} / \sum_J \omega_J \exp(-\bar{B}'_{k,\nu'} J(J + 1)/kT_r) \end{aligned}$$

which most conveniently is presented as a modified rotational temperature $T'_r = B'_{k,\nu'} T_r / \bar{B}'_{k,\nu'}$

4.3 The mdf01/behrr driver for H₂

The *mdf01/behrr* drivers have been specially tuned to the H₂ molecular case.

The nuclear spin specification is required for homonuclear systems so that the intensity alternation of successive rotational transitions may be correctly determined.

Specific rotational parameters for vibrational substates support the high wavelength precision needed for H₂ rovibrational identification.

```

HH; mdf01 Behringer format; etrans = all; vtrans = all
KS1   = 0.5 ] nuclear spins
KS2   = 0.5 ]
  1 X singlet Sigma g           0.000 ]
  2 B singlet Sigma u           91700.000 ] electronic
  3 a triplet Sigma g           95936.1   ] states
  4 d triplet Pi    u           112700.3 ]
-1
  1 e=1 v= 0           1      2179.586 ] 59.3634 0.0455 0.0000465
    .      .      .
 15 e=1 v=14           1      38154.391 ] 8.7701 0.08467 0.0
 16 e=2 v= 0           2      682.321   ] 19.4563 0.0156 0.0000163
    .      .      .
 30 e=2 v=14           2      16139.337 ] 11.375 0.0035 0.0000127
 31 e=3 v=*            3          0.     ]
 32 e=4 v=*            4          0.     ]
-1
  1  2  1 ] electronic transition pairs
  2  4  3 ] for spectral generation
-1
state = "X" ]
vmax  = 14 ]
jmax  = 20 ]
om    = 4401.2654 ]
omx   = 120.602 ]
omy   = 0.7242 ]
Be    = 60.8477 ]
De    = 0.04653 ]
alp   = 3.0513 ]
bet   = 0.0 ]
He    = 5.168E-05 ]
Te    = 0.0 ]
]
base rovibrational
parameter set for
each electronic state

+++ . . .
-1

```

vibrational states

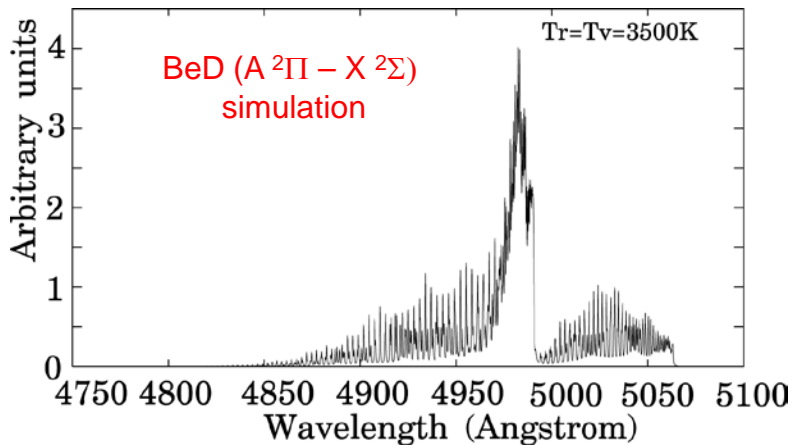
improved rotational parameters for specific vibronic states

4.4 The mdf01/pickett driver for BeD

The method is best suited to diatomics with heavier nuclei than H₂ for which vibrational and rotational energy separation is better.

Examination and selection of parameters was carried out by Duxbury for JET experiments. ADAS has such special data for CH, CD, C₂, BeH, BeD and BeT.

The capabilities of the Pickett package are very large, but expert knowledge is required for full utilisation. The ADAS *mdf01/pickett* database will be extended as needed.



```
BeD; mdf01 Pickett format; etrans = 2 Sigma - 2 Pi
1 doublet Sigma 0.000
2 doublet Pi 20037.910
-1
1 e=1 v=0 1 0.000
. . .
7 e=1 v=6 1 8292.458
8 e=2 v=0 2 0.000
. . .
14 e=2 v=6 2 8320.162
-1
1 8 1
2 9 2
3 10 3
4 11 4
```

Pickett
int
data

Pickett
par
data

```
beryllium deuteride 2pi-2sig 14-Oct-2003
1010 79002 494.139 0 120 -45.0 -45.0 600000 TTTT
013 0.0100
---
Beryllium deuteride 0-0 band 2pi-2sigma 14 Oct 2003
16 600 3 0 1.1220000E-10 1000.000 1.000
'a' -2 2 0 0 0 2 1 1 -1 1
-2 1 1 1 0 2 1 1 0 1
11 20037.68838 .05 ! E' (Band Centre)
100 5.62479800 9.59E-8 ! Bbar'' (1sig)
111 5.69574400 9.59E-8 ! Bbar' (1pi)
200 -3.1176800E-4 2.00E-10 ! DJ'' (1sig)
211 -3.1670100E-4 2.00E-10 ! DJ' (1pi)
300 1.6238000E-8 2.00E-10 ! HJ'' 1sig)
311 1.5743000E-8 2.00E-10 ! HJ' (1pi)
400 -0.8746000E-12 2.00E-10 ! LJ'' 1sig)
411 -0.9078000E-12 2.00E-10 ! LJ' (1pi)
40011 2.1096000e-3 2.00e-10 ! q/2 lambda
40111 -4.5860000e-7 2.00e-10 ! dq/2 lambda
40211 2.6995000e-11 2.00e-10 ! hq/2 lambda
10010011 2.1592000 2.00e-10 ! Aso 2pi
1000011 -0.801500e-2 2.00e-10 ! gamma 2pi
1000111 0.806900e-5 2.00e-10 ! dgamma 2pi
1000211 -2.218000e-9 2.00e-10 ! hgamma 2pi
+++
```

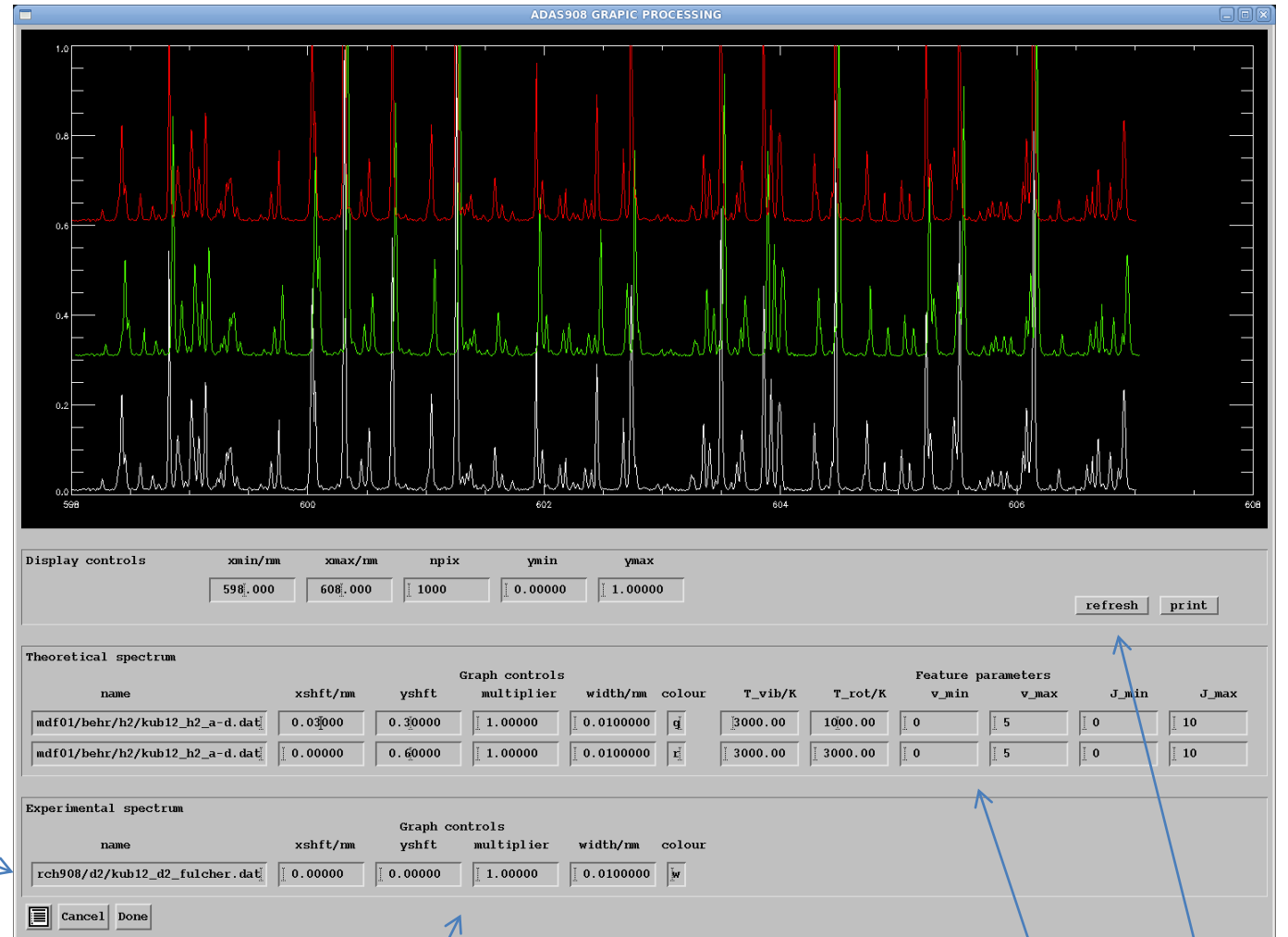
Pickett
datablock
for each
vibronic
pair

parameter
codes parameter
values

4.5 ADAS908 plot and analyse window

The processing window of ADAS908 adjusts according to the number of spectra being handled.

Refreshing, re-evaluates the spectra by repixelation or by model re-computation according the parameters modified.



Selected theoretical spectra from model calculation

selected experimental spectra

x-y shifting, scaling, resolutions and colour manipulation

model parameters

refresh

5.1 Conclusions

- A revision and update of the reaction process for the H₂ molecular system has been carried out and assembled in a new ADAS molecular data format *mdf02*.
- Supplementary molecular vibrational energy levels, A-values, Franck-Condon factors and other fundamental data have been assembled in molecular data format *mdf00*.
- A code machinery has been set up in ADAS series **ADAS9xx** to prepare the specific molecule dataset of format *mdf04*.
- A generalised collisional-radiative model of the H₂ system in vibronic resolution has been implemented called **ADAS905**.
- The rovibrational relative spectral prediction of diatomic band structure has been set based on two models the *Behringer model* and the *Pickett model* suited to the H₂ system and non-homogenous diatomics respectively. These use driver datasets of molecular data format *mdf01*.
- A code **ADAS908** has been set up for comparative assessment of experimental diatomic spectra and theoretical spectra created with *mdf01/beh*r and *mdf01/pickett* drivers.