The latest revision of the ERHAM code

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Revision R3 of ERHAM

Revision R3 is now available on PROSPE web site

(http://www.ifpan.edu.pl/~kisiel/prospe.htm**)**

Modifications of version R2:

1. Correction of calculated relative intensities
2. Predictions in JPL catalog file format
3. Calculation of rotational partition function
4. Parameter scaling
5. Number of tunneling parameters

   Size of arrays for frequency-ordered list of predictions

1. Correction of Calculated Relative Intensities

Version R2

Formula used $I_{rel} = g_l * S * \mu^2 * \exp(-E_l/kT) * (1 - \exp(-h\nu/kT))$

g_l = spin weight, S = line strength, μ = dipole moment, E_l = lower state energy, ν = transition frequency

Threshold for printing transitions based on $g_l * S * \mu^2$

Version R3

Correct formula $I_{rel} = g_l * S * \mu^2 * \exp(-E_l/kT) * (1 - \exp(-h\nu/kT)) * \nu$

Threshold for printing transitions now based on I_{rel}

2. Predictions in JPL Catalog File Format

Option selected with the IFPR parameter

Previously:

c IFPR = 0 no additional printout

c = 1 prints derivatives, a LOT of printout !!!!

c = 2 prints eigenvectors of rotational energy levels

c = 3 prints eigenvectors and derivatives

New:

c = 4 predictions also in JPL catalog file format

Prints predictions in an additional separate text file, requires on-screen input.

2. Predictions in JPL Catalog File Format (cont'd)

Prints predictions in an additional separate file, requires on-screen input of

* Respond to prompt 'Enter catalog file name !' by typing: FILECAT
  FILECAT = name of catalog file (unit 7, up to 20 characters)
* Respond to prompt 'Enter catalog ID !' by typing: ICATID
  ICATID = catalog ID of molecule (= **TAG**)
* Respond to prompt 'Enter Partition function !' by typing: Q
  Q = partition function at selected temperature TEMP (Input 2)
* Respond to the prompt 'Enter first LOG Intensity Cutoff (LOGSTR0) !' by typing: **LOGSTR0** (as in catdoc.pdf from JPL web site)
* Respond to the prompt 'Enter second LOG Intensity Cutoff (LOGSTR1) !' by typing: **LOGSTR1** (as in catdoc.pdf from JPL web site)

ERHAM prints a summary of this input just before the list of ordered transitions.

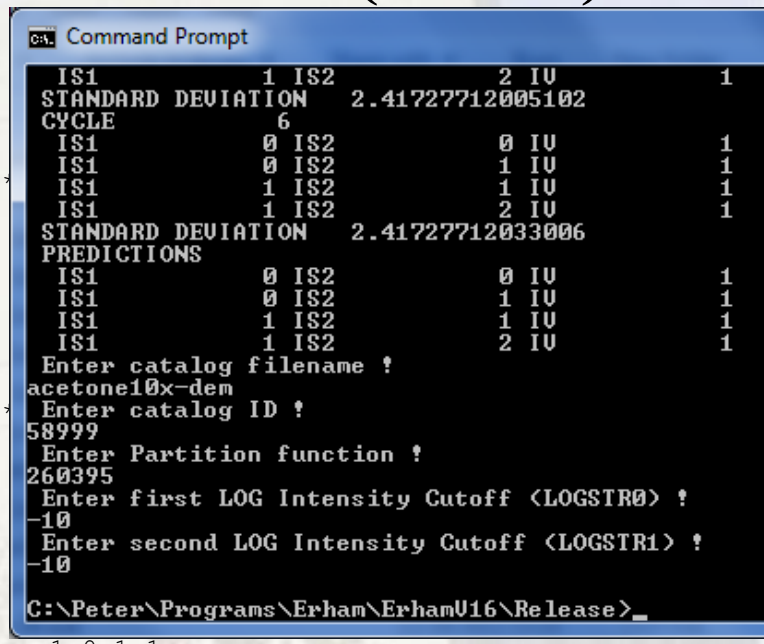
* Please note: The information about degrees of freedom (**DR** = 3) and quantum number format (**QNFMT** = 1404) is coded directly into the program. The 4^{th} quantum numbers for upper and lower state are used to enter the symmetry numbers (IS1 & IS2 = 4th QN of upper & lower state, respectively). Q calculated by ERHAM is NOT used to calculate the catalog entries (allowing adjustment of Q for vibrational contributions).

Red: as in **catdoc.pdf** from JPL web site (http://spec.jpl.nasa.gov)

2. Predictions in JPL Catalog File Format (cont'd)

Screen input echoed in regular ERHAM output

```
*****************************************************************
 CATALOG ENTRY INFORMATION
 Catalog ID                  58999
 PARTITION FUNCTION          0.26039500D+06
 1st INT CUTOFF (LOGSTR0) -0.10000000D+02
 2nd INT CUTOFF (LOGSTR1) -0.10000000D+02
*****************************************************************
```



Begin of catalog output

```
   5105.5348  0.0056 -6.5972 3    1.1992 30  589991404 1 1 0 0
   5690.7499  0.0136 -6.3523 3    0.6252 48  589991404 1 1 0 0
   5758.7514  0.0267 -6.7732 3    0.0742 18  589991404 1 1 0 1     1 0 1 1
   6395.9573  0.0503 -6.8807 3    0.0780 12  589991404 1 1 0 1     1 0 1 2
   6763.8037  0.0411 -6.5723 3    3.6240112  589991404 3 3 1 0     3 2 1 1
   7063.8492  0.0099 -6.4121 3    2.3806 30  589991404 2 2 0 0     2 1 1 0
   7523.7526  0.0665 -6.7758 3   25.2176304  589991404 9 6 4 0     9 5 4 1
   7597.6717  0.1919 -6.8659 3   20.1990 68  589991404 8 6 3 1     8 5 3 2
   7783.7375  0.0446 -6.3413 3    8.6273176  589991404 5 4 2 0     5 3 2 1
   8014.8127  0.0544 -6.4476 3   15.8269240  589991404 7 5 3 0     7 4 3 1
   8090.3185  0.0281 -6.8274 3    1.2696 10  589991404 2 2 0 1     2 1 1 1
   8213.4189  0.3162 -6.7610 3   30.8059 84  58999140410 7 4 1    10 6 4 2
   8451.3493  0.4287 -6.8503 3   43.6182100  58999140412 8 5 1    12 7 5 2
   8634.1684  0.0203 -5.9465 3    1.8176 80  589991404 2 2 0 0     2 1 1 1
  10254.6542  0.1360 -6.8137 3   58.8945464  58999140414 9 6 0    14 8 6 1
  10273.8374  0.0889 -6.4365 3    1.2871 20  589991404 2 2 0 1     2 1 1 2
  10519.9035  0.0092 -5.7461 3    3.8118 70  589991404 3 2 1 0     3 1 2 0
```

3. Calculation of Rotational Partition Function

Calculation of rotational partition function by direct summation

$$Q = \sum g_l * \exp(-E_l/kT)$$

* Q (= Q_{rs} in **catdoc.pdf** from JPL web site http://spec.jpl.nasa.gov) is automatically aquired by direct summation during the prediction, if $J_{min} = 0$, but only up to J_{max}.

* A revised definition of the - signs printed for some energy levels during the prediction is used to ensure that the Q acquisition works with the correct spin weights.

* To assess convergence, two accumulated sums are printed for each symmetry block and each J. The 1st sum is from the levels without the (-) sign mentioned above, the 2nd sum (which may be zero) from the levels with this sign.

* After a blank line follow the sums for J_{max} **adjusted** for the lowest energy level. The final partition function (up to J_{max}) is the sum of all sums in this last row.

3. Calculation of Rotational Partition Function (cont'd)

SUM OF STATES

IS1,IS2 00	00	01	01	11	11	12	12	
5.935	0.000	15.959	0.000	2.011	0.000	4.021	0.000	0
23.614	58.901	158.508	0.000	7.999	35.912	16.008	23.932	1
110.640	155.675	548.560	0.000	37.471	94.901	74.906	63.309	2
229.889	420.373	1295.995	0.000	77.843	256.217	155.785	170.723	
477.576	751.103	2494.940	0.000	161.674	457.687	323.177	305.316	
769.684	1334.278	4219.936	0.000	260.488	812.820	521.291	541.592	5
1230.939	1994.611	6523.182	0.000	416.459	1214.693	832.481	810.267	
1737.277	2956.696	9432.988	0.000	587.557	1799.948	1175.768	1199.345	
2430.642	3986.788	12953.449	0.000	821.738	2426.097	1642.647	1618.254	
3157.660	5328.876	17065.331	0.000	1067.085	3241.463	2135.236	2159.918	
4066.605	6710.913	21728.019	0.000	1373.654	4080.378	2746.011	2721.529	10
4987.773	8379.276	26882.365	0.000	1684.069	5092.501	3369.614	3393.462	
6066.490	10045.921	32454.229	0.000	2047.354	6102.658	4092.937	4070.092	
7130.019	11945.977	38358.436	0.000	2405.195	7253.578	4812.191	4833.734	
8313.760	13796.652	44502.929	0.000	2803.236	8373.556	5604.300	5584.286	
9453.740	15812.283	50792.860	0.000	3186.216	9592.612	6374.420	6392.751	15
24456.994	40761.659	130866.060	0.000	8205.488	24616.466	16410.490	16410.490	55
24458.730	40764.549	130875.323	0.000	8206.068	24618.204	16411.649	16411.649	
24460.050	40766.751	130882.373	0.000	8206.509	24619.528	16412.531	16412.531	
24461.051	40768.418	130887.715	0.000	8206.843	24620.530	16413.199	16413.199	
24461.806	40769.677	130891.745	0.000	8207.095	24621.286	16413.703	16413.703	
24462.373	40770.622	130894.772	0.000	8207.285	24621.854	16414.082	16414.082	60
24332.522	40554.203	130199.956	0.000	8163.719	24491.156	16326.953	16326.953	

4. Parameter scaling

Introduced to improve convergence during least-squares fit

Standard LS

$\Delta\nu = J\,\Delta p$

$J^T\Delta\nu = J^T J\,\Delta p$

$(J^T J)^{-1} J^T \Delta\nu = \Delta p$

$\Delta p = (J^T J)^{-1}\, J^T \Delta\nu$

Matrix $(J^T J)^{-1} J^T$ is calculated by using singular value decomposition (SVD). The singular values are the square roots of the eigenvalues of $J^T J$. If the ratio of the smallest to the largest singular values is of the order of the machine precision ($\approx 10^{-15}$), the smallest singular values are very imprecise which may cause slow convergence, instability of the LS iteration process, and/or error messages by the SVD routine.

4. Parameter scaling

Introduced to improve convergence during least-squares fit

Standard LS	Scaled LS
$\Delta\nu = J\,\Delta p$	$\Delta\nu = (JS)\,S^{-1}\Delta p = K\Delta p'$
	using $K = JS$ and $\Delta p' = S^{-1}\Delta p$
$J^T\Delta\nu = J^TJ\,\Delta p$	$K^T\Delta\nu = K^TK\,\Delta p'$
$(J^TJ)^{-1}J^T\Delta\nu = \Delta p$	$(K^TK)^{-1}\,K^T\Delta\nu = \Delta p' = S^{-1}\Delta p$
$\Delta p = (J^TJ)^{-1}\,J^T\Delta\nu$	$\Delta p = S\,(K^TK)^{-1}\,K^T\Delta\nu$

The matrix $(J^TJ)^{-1}J^T$ is calculated by using singular value decomposition. The singular values are the square roots of the eigenvalues of J^TJ. If the ratio of the smallest to the largest singular values is of the order of the machine precision ($\approx 10^{-15}$), the smallest singular values are very imprecise which may cause slow convergence and/or instability of the LS iteration process.

The parameters are scaled with a diagonal scaling matrix S to reduce these problems. Individual scaling factors of the order of the estimated uncertainty are best. The exact values are irrelevant as long as they are within a factor of 1000 of the uncertainty.

4. Parameter scaling (cont'd)

STATE		OLD PARAMETER		STANDARD ERROR	CHANGE	PREC	SCALE FAC
	1	RHO1	0.625922046020D-01	0.77837D-05	-0.88287D-15	0.16264D-06	0.100D-02
	2	BETA1	0.258749629799D+02	0.13278D-01	-0.20730D-10	0.14437D-03	0.100D+01
1	3	A	0.101772026797D+05	0.42158D-02	-0.15683D-10	0.50799D-03	0.100D+01
1	4	B	0.850284564073D+04	0.36377D-02	0.22177D-10	0.43479D-03	0.100D+01
1	5	C	0.491025168865D+04	0.18968D-02	-0.25040D-11	0.17807D-03	0.100D+01
1	6	DELTA J	0.490825450991D+01	0.10097D-01	0.11909D-09	0.11968D-03	0.100D+01
1	7	DELTA JK	-0.331218147871D+01	0.74693D-01	-0.42713D-09	0.89897D-03	0.100D+01
1	8	DELTA K	0.976551131133D+01	0.93940D-01	0.14142D-09	0.20689D-02	0.100D+01
1	9	DDELTA J	0.207506395483D+01	0.49779D-02	0.48125D-10	0.71923D-04	0.100D+01
1	10	DDELTA K	-0.526383688129D+00	0.25692D-01	0.14539D-09	0.88374D-03	0.100D+01
1	18	1-1 1 0 0 0	0.964869737751D+02	0.43730D-01	-0.17194D-09	0.87879D-02	0.100D+01
1	19	1 0 1 0 0 0	0.554731588602D+04	0.44118D+00	-0.13168D-08	0.14819D-01	0.100D+04
1	20	1 1 1 0 0 0	0.656761152609D+02	0.12562D+00	0.77001D-09	0.39410D-01	0.100D+01
1	21	2 0 1 0 0 0	0.151297612151D+02	0.63391D-01	-0.35455D-09	0.76532D-02	0.100D+01
1	28	1 0 1 0 2 0	0.206624079104D+00	0.54965D-02	-0.11696D-10	0.11004D-03	0.100D+01
1	29	1 0 1 0 2 2	0.434026864959D-03	0.12602D-04	0.16805D-13	0.76531D-06	0.100D+01
1	30	1 0 1 0 4 0	-0.168073465898D-03	0.28209D-05	0.14668D-13	0.87460D-07	0.100D+01
1	31	1 0 1 1 0 1	-0.349612869845D-01	0.86544D-02	-0.68071D-11	0.16861D-02	0.100D+01
1	32	1 0 1 2 0 0	0.674601141191D-01	0.25430D-02	-0.46208D-11	0.54240D-04	0.100D+01
1	33	1 0 1 2 0 2	-0.436468464515D-04	0.89600D-05	-0.27977D-14	0.84547D-06	0.100D-02
1	34	1 0 1 2 2 0	-0.841022541471D-04	0.13907D-05	0.65488D-14	0.49505D-07	0.100D-02
1	35	1 1 1 0 0 2	0.263697563696D+00	0.15312D-02	-0.75217D-11	0.34837D-03	0.100D+01
1	36	1 1 1 0 2 0	-0.683982256717D-01	0.70665D-03	0.38577D-11	0.10231D-03	0.100D+01
1	37	1 1 1 2 0 0	-0.356887453216D-01	0.40079D-03	0.41162D-11	0.58044D-04	0.100D+01
1	38	2 0 1 0 0 2	-0.362001642278D-01	0.95424D-03	-0.46679D-11	0.22916D-03	0.100D+01
1	39	2 0 1 0 2 0	0.361266170617D-01	0.41379D-03	0.59720D-11	0.78553D-04	0.100D+01
1	40	2 0 1 2 0 0	-0.690232129089D-03	0.40573D-03	-0.22291D-11	0.52600D-04	0.100D+01

5. Redimensioned arrays

Some array dimensions have been increased:

To accommodate 37 tunneling parameters per vibrational state (up from 31).

To allow ordering of up to 140000 transitions by increasing frequency (up from 50000)

Summary

1. Correction of calculated relative intensities

   (Error discovered when I started to accommodate point 2 below)

2. Predictions in JPL catalog file format

   (At the request of some users)

3. Calculation of rotational partition function

   (My own idea)

4. Parameter scaling

   (Response to problems encountered when using octic CD constants)

5. Number of tunneling parameters

   Size of arrays for frequency-ordered list of predictions


Thank you