

# **‘Potentiology’ in Spectroscopy: It Matters !**

**Robert J. Le Roy<sup>a</sup>**

*in collaboration with*

*MSc students* **Jenning Seto** *and* **Yiye Huang**,  
*with Research Associates* **Photos Hajigeorgiou** *and* **Hui Li**,  
*and with Undergraduate Research Assistants*  
**Calvin Jary, Robert Henderson, Nikesh Dattani,**  
**Yan-Rong Wu, Carl Haugen, and Jason Tao**

[Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada]

*gratefully acknowledging helpful discussions with colleagues*

**John A. Coxon** *and* **Asen Pashov**

*and inspired by challenging data analysis problems presented by*

**Robert McKellar, Peter Bernath, Aanda Ross, Colan Linton,**  
**Eberhardt Tiemann, Claude Amiot, and Michael Heaven**

---

<sup>a</sup> Research supported by the Natural Sciences and Engineering Research Council of Canada

## *Objectives of Spectroscopic Data Analysis*

1. To provide an accurate, compact, and comprehensive representation of experimental data.
2. To be able to interpolate reliably for missing observations within the data range.
3. To be able to provide realistic predictions in the 'extrapolation region' outside the range of existing data.
4. To provide reliable estimates of physically interesting molecular properties (e.g., bond lengths, force constants, intensities).

## *Objectives of Spectroscopic Data Analysis*

1. To provide an accurate, compact, and comprehensive representation of experimental data.
2. To be able to interpolate reliably for missing observations within the data range.
3. To be able to provide realistic predictions in the ‘extrapolation region’ outside the range of existing data.
4. To provide reliable estimates of physically interesting molecular properties (e.g., bond lengths, force constants, intensities).

*Since the dawn of quantum mechanics, the central paradigm of spectroscopic data analysis has been to explain the patterns of observed transition energies in terms of expressions for molecular level energies as functions of vibrational and rotational quantum numbers.*

## Traditional Methods for Representing Spectroscopic Data

- A. ‘band constants’ – a set of vibrational, rotational, and (when appropriate) angular momentum splitting parameters for each observed vibrational level of each isotopologue in each electronic state:  $\{ G_v, B_v, D_v, H_v, L_v, \dots, q_v, p_v, \dots \}$
- B. Dunham-type expansion representing each band constant as a power series in  $(v + \frac{1}{2})$ :

$$E(v, J) = \sum_{m=0} \sum_{\ell} Y_{\ell,m} (v + \frac{1}{2})^{\ell} [J(J + 1)]^m$$

### *Advantages:*

- both usually able to satisfy Objectives #1 & 2:  
*accurately represent the data and allow reliable interpolation*
- for Dunham-type expansions, the first-order semiclassical mass-scaling relates coefficients for different isotopologues  
 $Y_{\ell,m}^{(2)} = Y_{\ell,m}^{(1)} \times \left( \frac{\mu_1}{\mu_2} \right)^{m+\ell/2}$  allows realistic *extrapolation* to predict properties of other isotopologues (except for hydrides).
- *friendly, familiar forms!*

## *Shortcomings:*

### A. Band Constant representations:

- no direct way of making predictions for other isotopologues
- no way of making vibrational extrapolations
- empirical fitted centrifugal distortion constants  $\{D_v, H_v, L_v, \dots\}$  become increasingly irregular with increasing order
- require a *tediously large* number of parameters:  
e.g., for the  $A^3\Pi_{1u}$  state of  $\text{I}_2$

$v$	$E$	$B_v$	$10^8(-D_v)$	$H_v$	$L_v$	$M_v$	$N_v$
0	46.0795	0.0272593851	-0.98428246	-1.3743252×10 <sup>-14</sup>	-4.7933709×10 <sup>-20</sup>	-1.8483116×10 <sup>-25</sup>	-8.2346821×10 <sup>-31</sup>
1	135.9734	0.0269679400	-1.0557747	-1.5747448×10 <sup>-14</sup>	-5.8947261×10 <sup>-20</sup>	-3.4871892×10 <sup>-25</sup>	-2.1324188×10 <sup>-30</sup>
2	222.7265	0.0266700992	-1.1341137	-2.0454280×10 <sup>-14</sup>	-8.7034087×10 <sup>-20</sup>	-4.6955112×10 <sup>-25</sup>	-2.9537892×10 <sup>-30</sup>
3	306.3178	0.0263555029	-1.2257198	-2.5886882×10 <sup>-14</sup>	-1.2101539×10 <sup>-19</sup>	-6.6113717×10 <sup>-25</sup>	-4.5880897×10 <sup>-30</sup>
4	386.6397	0.0260218436	-1.3304250	-3.1825510×10 <sup>-14</sup>	-1.6563507×10 <sup>-19</sup>	-1.0268860×10 <sup>-24</sup>	-7.1247557×10 <sup>-30</sup>
5	463.5987	0.0256692406	-1.4496585	-3.8855155×10 <sup>-14</sup>	-2.2047451×10 <sup>-19</sup>	-1.5799454×10 <sup>-24</sup>	-1.2580217×10 <sup>-29</sup>
6	537.1214	0.0252977620	-1.5845645	-4.7712666×10 <sup>-14</sup>	-2.9447211×10 <sup>-19</sup>	-2.2419026×10 <sup>-24</sup>	-1.9390085×10 <sup>-29</sup>
7	607.1547	0.0249068471	-1.7367998	-5.8460452×10 <sup>-14</sup>	-3.9072880×10 <sup>-19</sup>	-3.1813912×10 <sup>-24</sup>	-2.7633013×10 <sup>-29</sup>
8	673.6615	0.0244960858	-1.9073347	-7.1098056×10 <sup>-14</sup>	-5.0194818×10 <sup>-19</sup>	-4.3423369×10 <sup>-24</sup>	-4.0881042×10 <sup>-29</sup>
9	736.6258	0.0240657540	-2.0944341	-8.5397349×10 <sup>-14</sup>	-6.2789956×10 <sup>-19</sup>	-5.5442184×10 <sup>-24</sup>	-5.5698737×10 <sup>-29</sup>
10	796.0638	0.0236171696	-2.2942257	-1.0060281×10 <sup>-13</sup>	-7.6533353×10 <sup>-19</sup>	-6.8845864×10 <sup>-24</sup>	-6.8034959×10 <sup>-29</sup>
11	852.0325	0.0231529316	-2.5014240	-1.1587759×10 <sup>-13</sup>	-8.9891698×10 <sup>-19</sup>	-8.3168914×10 <sup>-24</sup>	-8.2227098×10 <sup>-29</sup>
12	904.6337	0.0226767642	-2.7094647	-1.3050206×10 <sup>-13</sup>	-1.0178539×10 <sup>-18</sup>	-9.5428796×10 <sup>-24</sup>	-9.6238430×10 <sup>-29</sup>
13	954.0121	0.0221930918	-2.9115738	-1.4376869×10 <sup>-13</sup>	-1.1172109×10 <sup>-18</sup>	-1.0539983×10 <sup>-23</sup>	-1.0789711×10 <sup>-28</sup>
14	1000.3480	0.0217065598	-3.1020262	-1.5525981×10 <sup>-13</sup>	-1.1959529×10 <sup>-18</sup>	-1.1341509×10 <sup>-23</sup>	-1.2332091×10 <sup>-28</sup>
15	1043.8462	0.0212215309	-3.2770050	-1.6499421×10 <sup>-13</sup>	-1.2660178×10 <sup>-18</sup>	-1.2145133×10 <sup>-23</sup>	-1.4068153×10 <sup>-28</sup>
16	1084.7228	0.0207416546	-3.4353239	-1.7343466×10 <sup>-13</sup>	-1.3455042×10 <sup>-18</sup>	-1.3574141×10 <sup>-23</sup>	-1.6412040×10 <sup>-28</sup>
17	1123.1932	0.0202695855	-3.5785503	-1.8154162×10 <sup>-13</sup>	-1.4515954×10 <sup>-18</sup>	-1.6043256×10 <sup>-23</sup>	-2.1401103×10 <sup>-28</sup>
18	1159.4618	0.0198068610	-3.7104644	-1.9057594×10 <sup>-13</sup>	-1.6045881×10 <sup>-18</sup>	-1.9469816×10 <sup>-23</sup>	-2.9591790×10 <sup>-28</sup>
19	1193.7149	0.0193539427	-3.8362674	-2.0171913×10 <sup>-13</sup>	-1.8245047×10 <sup>-18</sup>	-2.3840172×10 <sup>-23</sup>	-3.9193593×10 <sup>-28</sup>
20	1226.1161	0.0189103967	-3.9617164	-2.1585494×10 <sup>-13</sup>	-2.1211579×10 <sup>-18</sup>	-2.9453899×10 <sup>-23</sup>	-4.9565736×10 <sup>-28</sup>
21	1256.8059	0.0184751665	-4.0922228	-2.3363195×10 <sup>-13</sup>	-2.5035441×10 <sup>-18</sup>	-3.6960486×10 <sup>-23</sup>	-6.1701912×10 <sup>-28</sup>
22	1285.9016	0.0180467706	-4.2325703	-2.5527617×10 <sup>-13</sup>	-2.9514984×10 <sup>-18</sup>	-4.5587698×10 <sup>-23</sup>	-8.1498197×10 <sup>-28</sup>
23	1313.5007	0.0176236403	-4.3862653	-2.8117919×10 <sup>-13</sup>	-3.4917716×10 <sup>-18</sup>	-5.6342294×10 <sup>-23</sup>	-1.0830847×10 <sup>-27</sup>
24	1339.6835	0.0172041835	-4.5561592	-3.1170669×10 <sup>-13</sup>	-4.1496255×10 <sup>-18</sup>	-7.0382190×10 <sup>-23</sup>	-1.4365327×10 <sup>-27</sup>
25	1364.5162	0.0167868906	-4.7447884	-3.4750735×10 <sup>-13</sup>	-4.9621850×10 <sup>-18</sup>	-8.9544801×10 <sup>-23</sup>	-1.9264312×10 <sup>-27</sup>
26	1388.0536	0.0163703479	-4.9548514	-3.8968536×10 <sup>-13</sup>	-5.9828517×10 <sup>-18</sup>	-1.1627555×10 <sup>-22</sup>	-2.6526764×10 <sup>-27</sup>
27	1410.3413	0.0159532052	-5.1896703	-4.3992364×10 <sup>-13</sup>	-7.2815604×10 <sup>-18</sup>	-1.5228014×10 <sup>-22</sup>	-3.6253173×10 <sup>-27</sup>
28	1431.4178	0.0155341227	-5.4533410	-5.0002734×10 <sup>-13</sup>	-8.8950035×10 <sup>-18</sup>	-1.9696972×10 <sup>-22</sup>	-4.9564681×10 <sup>-27</sup>
29	1451.3149	0.0151117697	-5.7498252	-5.7125342×10 <sup>-13</sup>	-1.0895651×10 <sup>-17</sup>	-2.6032922×10 <sup>-22</sup>	-7.3329899×10 <sup>-27</sup>
30	1470.0598	0.0146848958	-6.0830640	-6.5636630×10 <sup>-13</sup>	-1.3510090×10 <sup>-17</sup>	-3.4763642×10 <sup>-22</sup>	-1.0074305×10 <sup>-26</sup>
31	1487.6759	0.0142522936	-6.4583316	-7.5842343×10 <sup>-13</sup>	-1.6798952×10 <sup>-17</sup>	-4.6573049×10 <sup>-22</sup>	-1.5251123×10 <sup>-26</sup>
32	1504.1839	0.0138128081	-6.8809051	-8.8136218×10 <sup>-13</sup>	-2.1189984×10 <sup>-17</sup>	-6.4322123×10 <sup>-22</sup>	-2.2207780×10 <sup>-26</sup>
33	1519.6027	0.0133653231	-7.3582216	-1.0315598×10 <sup>-12</sup>	-2.6983703×10 <sup>-17</sup>	-8.9648247×10 <sup>-22</sup>	-3.4866448×10 <sup>-26</sup>
34	1533.9500	0.0129087006	-7.8993425	-1.2171930×10 <sup>-12</sup>	-3.4927601×10 <sup>-17</sup>	-1.2727229×10 <sup>-21</sup>	-5.2982575×10 <sup>-26</sup>
35	1547.2430	0.0124417441	-8.5162192	-1.4488797×10 <sup>-12</sup>	-4.5731958×10 <sup>-17</sup>	-1.8375376×10 <sup>-21</sup>	-8.4152663×10 <sup>-26</sup>
36	1559.4984	0.0119632037	-9.2224850	-1.7399208×10 <sup>-12</sup>	-6.0594429×10 <sup>-17</sup>	-2.6724809×10 <sup>-21</sup>	-1.3318330×10 <sup>-25</sup>
37	1570.7336	0.0114717994	-1.0033054	-2.1030457×10 <sup>-12</sup>	-8.0495240×10 <sup>-17</sup>	-3.8856485×10 <sup>-21</sup>	-2.1343853×10 <sup>-25</sup>
38	1580.9672	0.0109665909	-1.0960017	-2.5528005×10 <sup>-12</sup>	-1.0668470×10 <sup>-16</sup>	-5.4004000×10 <sup>-21</sup>	-2.6245185×10 <sup>-25</sup>
39	1590.2208	0.0104472488	-1.1999350	-3.0428281×10 <sup>-12</sup>	-1.2229180×10 <sup>-16</sup>	-3.6009180×10 <sup>-21</sup>	6.6108389×10 <sup>-26</sup>
40	1598.5231	0.0099168922	-1.3028931	-3.4136038×10 <sup>-12</sup>	-2.4052883×10 <sup>-16</sup>	-8.9362531×10 <sup>-20</sup>	-4.1382182×10 <sup>-23</sup>
41	1605.9165	0.0093688077	-1.6150213	-2.1592789×10 <sup>-11</sup>	-1.0788030×10 <sup>-14</sup>	-5.3284789×10 <sup>-18</sup>	-2.4849228×10 <sup>-21</sup>
42	1612.2555	0.0085958174	-2.4707854	3.5381670×10 <sup>-12</sup>	1.7945157×10 <sup>-14</sup>	4.6237225×10 <sup>-18</sup>	-8.5641230×10 <sup>-22</sup>

## Shortcomings:

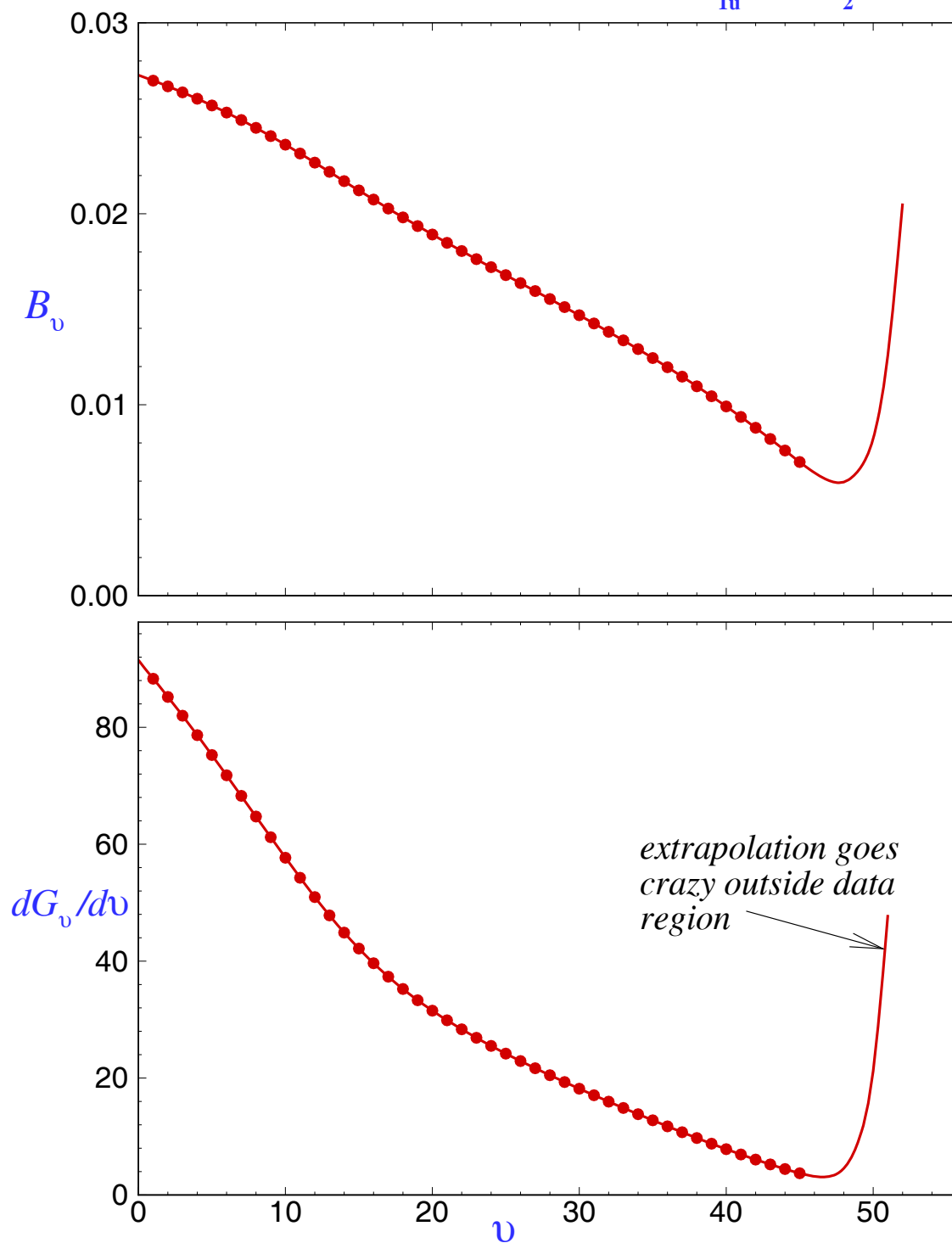
### A. Band Constant representations.

- no direct way of making predictions for other isotopologues
- no way of making vibrational extrapolations
- empirical fitted centrifugal distortion constants  $\{D_v, H_v, L_v, \dots\}$  become increasingly irregular with increasing order
- require a *tediously large* number of parameters:  
e.g., for the  $A^3\Pi_{1u}$  state of  $\text{I}_2$

### B. Dunham-type expansions in $(v + \frac{1}{2})$

- data sets involving many vibrational levels often require sufficiently high-order polynomials that the least-squares fits become unstable.
- polynomials are *notoriously unreliable for extrapolation!*  
e.g., for the  $A^3\Pi_{0u^+}$  state of  $\text{I}_2$
- an inconveniently large number of fitting parameters is often still required: e.g., for the  $X^1\Sigma_g^+$  state of  $\text{Rb}_2$

# Results of Dunham fit for A $^3\Pi_{1u}$ state I<sub>2</sub>





# $Y_{\ell,m}$ 's for $X(^1\Sigma_g^+)$ -state $\text{Rb}_2$ from a fit to 12148 data for levels $v=0-113$

$Y_{1,0}$	$57.7891594(\pm 1.2 \times 10^{-03})$	$Y_{0,2}$	$-1.35672 \times 10^{-8}(\pm 5.6 \times 10^{-11})$
$Y_{2,0}$	$-0.13955803(\pm 4.8 \times 10^{-04})$	$Y_{1,2}$	$-5.711 \times 10^{-11}(\pm 1.9 \times 10^{-11})$
$Y_{3,0}$	$-3.967991 \times 10^{-4}(\pm 1.1 \times 10^{-4})$	$Y_{2,2}$	$-1.5734 \times 10^{-12}(\pm 3.4 \times 10^{-12})$
$Y_{4,0}$	$3.432253 \times 10^{-5}(\pm 1.6 \times 10^{-5})$	$Y_{3,2}$	$-4.7516 \times 10^{-13}(\pm 3.3 \times 10^{-13})$
$Y_{5,0}$	$-3.7913646 \times 10^{-6}(\pm 1.5 \times 10^{-6})$	$Y_{4,2}$	$7.19687 \times 10^{-14}(\pm 2.0 \times 10^{-14})$
$Y_{6,0}$	$2.6921523 \times 10^{-7}(\pm 9.7 \times 10^{-8})$	$Y_{5,2}$	$-4.61312 \times 10^{-15}(\pm 7.9 \times 10^{-16})$
$Y_{7,0}$	$-1.3614188 \times 10^{-8}(\pm 4.5 \times 10^{-9})$	$Y_{6,2}$	$1.66068 \times 10^{-16}(\pm 2.1 \times 10^{-17})$
$Y_{8,0}$	$5.0267882 \times 10^{-10}(\pm 1.5 \times 10^{-10})$	$Y_{7,2}$	$-3.65461 \times 10^{-18}(\pm 3.8 \times 10^{-19})$
$Y_{9,0}$	$-1.3783277 \times 10^{-11}(\pm 3.8 \times 10^{-12})$	$Y_{8,2}$	$5.0119 \times 10^{-20}(\pm 4.5 \times 10^{-21})$
$Y_{10,0}$	$2.8320989 \times 10^{-13}(\pm 7.2 \times 10^{-14})$	$Y_{9,2}$	$-4.1762 \times 10^{-22}(\pm 3.3 \times 10^{-23})$
$Y_{11,0}$	$-4.369351 \times 10^{-15}(\pm 1.0 \times 10^{-15})$	$Y_{10,2}$	$1.933 \times 10^{-24}(\pm 1.4 \times 10^{-25})$
$Y_{12,0}$	$5.032431 \times 10^{-17}(\pm 1.1 \times 10^{-17})$	$Y_{11,2}$	$-3.81 \times 10^{-27}(\pm 2.5 \times 10^{-28})$
$Y_{13,0}$	$-4.26008 \times 10^{-19}(\pm 8.7 \times 10^{-20})$		
$Y_{14,0}$	$2.57191 \times 10^{-21}(\pm 4.9 \times 10^{-22})$	$Y_{0,3}$	$1.129 \times 10^{-14}(\pm 2.2 \times 10^{-15})$
$Y_{15,0}$	$-1.0477 \times 10^{-23}(\pm 1.9 \times 10^{-24})$	$Y_{1,3}$	$-1.7728 \times 10^{-15}(\pm 6.7 \times 10^{-16})$
$Y_{16,0}$	$2.58 \times 10^{-26}(\pm 4.3 \times 10^{-27})$	$Y_{2,3}$	$3.0291 \times 10^{-16}(\pm 9.6 \times 10^{-17})$
$Y_{17,0}$	$-2.9 \times 10^{-29}(\pm 4.5 \times 10^{-30})$	$Y_{3,3}$	$-2.0947 \times 10^{-17}(\pm 7.4 \times 10^{-18})$
		$Y_{4,3}$	$5.3849 \times 10^{-19}(\pm 3.5 \times 10^{-19})$
$Y_{0,1}$	$2.2404336 \times 10^{-2}(\pm 6.1 \times 10^{-7})$	$Y_{5,3}$	$7.162 \times 10^{-21}(\pm 1.0 \times 10^{-20})$
$Y_{1,1}$	$-5.58167 \times 10^{-5}(\pm 2.4 \times 10^{-7})$	$Y_{6,3}$	$-8.042 \times 10^{-22}(\pm 2.2 \times 10^{-22})$
$Y_{2,1}$	$-3.35513 \times 10^{-7}(\pm 5.3 \times 10^{-8})$	$Y_{7,3}$	$2.1403 \times 10^{-23}(\pm 3.1 \times 10^{-24})$
$Y_{3,1}$	$1.37264 \times 10^{-8}(\pm 6.3 \times 10^{-9})$	$Y_{8,3}$	$-2.811 \times 10^{-25}(\pm 2.9 \times 10^{-26})$
$Y_{4,1}$	$-1.702632 \times 10^{-9}(\pm 4.5 \times 10^{-10})$	$Y_{9,3}$	$1.867 \times 10^{-27}(\pm 1.6 \times 10^{-28})$
$Y_{5,1}$	$9.85778 \times 10^{-11}(\pm 2.1 \times 10^{-11})$	$Y_{10,3}$	$-5. \times 10^{-30}(\pm 3.7 \times 10^{-31})$
$Y_{6,1}$	$-3.520313 \times 10^{-12}(\pm 6.5 \times 10^{-13})$		
$Y_{7,1}$	$8.07427 \times 10^{-14}(\pm 1.4 \times 10^{-14})$	$Y_{0,4}$	$-5.37 \times 10^{-20}(\pm 3.0 \times 10^{-20})$
$Y_{8,1}$	$-1.20993 \times 10^{-15}(\pm 1.9 \times 10^{-16})$	$Y_{1,4}$	$2.348 \times 10^{-20}(\pm 9.2 \times 10^{-21})$
$Y_{9,1}$	$1.17177 \times 10^{-17}(\pm 1.8 \times 10^{-18})$	$Y_{2,4}$	$-4.472 \times 10^{-21}(\pm 1.2 \times 10^{-21})$
$Y_{10,1}$	$-7.023 \times 10^{-20}(\pm 1.1 \times 10^{-20})$	$Y_{3,4}$	$3.847 \times 10^{-22}(\pm 8.4 \times 10^{-23})$
$Y_{11,1}$	$2.347 \times 10^{-22}(\pm 3.8 \times 10^{-23})$	$Y_{4,4}$	$-1.7873 \times 10^{-23}(\pm 3.4 \times 10^{-24})$
$Y_{12,1}$	$-3.3 \times 10^{-25}(\pm 5.8 \times 10^{-26})$	$Y_{5,4}$	$4.765 \times 10^{-25}(\pm 8.0 \times 10^{-26})$
		$Y_{6,4}$	$-7.29 \times 10^{-27}(\pm 1.1 \times 10^{-27})$
		$Y_{7,4}$	$5.94 \times 10^{-29}(\pm 8.4 \times 10^{-30})$
		$Y_{8,4}$	$-2.0 \times 10^{-31}(\pm 2.6 \times 10^{-32})$

### *What else is missing ?*

- spectroscopic intensity calculations requires a knowledge of the *potential energy function* within the ‘data range’ of interest
- calculating collisional properties of molecular systems requires a knowledge of *the whole potential energy function*
- *ab initio* potential energy calculations inconvenient to use unless summarized as a *compact, well-behaved, analytic function*

## What else is missing ?

- spectroscopic intensity calculations requires a knowledge of the *potential energy function* within the ‘data range’ of interest
- calculating collisional properties of molecular systems requires a knowledge of *the whole potential energy function*
- *ab initio* potential energy calculations inconvenient to use unless summarized as a *compact, well-behaved, analytic function*

## *Some ‘traditional’ solutions . . . . .*

- Lennard-Jones(m,6):  $V_{\text{LJ}}(r) = \mathfrak{D}_e \left[ \frac{6}{m-6} \left( \frac{r_e}{r} \right)^m - \frac{m}{m-6} \left( \frac{r_e}{r} \right)^6 \right]$
- Exponential-6:  $V(r) = \mathfrak{D}_e \left[ \frac{6}{\alpha-6} e^{-\alpha(r-r_e)/r_e} - \frac{\alpha}{\alpha-6} \left( \frac{r_e}{r} \right)^6 \right]$
- Morse:  $V(r) = \mathfrak{D}_e \left[ 1 - e^{-\beta(r-r_e)} \right]^2$
- Hulbert-Hirschfelder:  $V(r) = \mathfrak{D}_e \left\{ \left[ 1 - e^{-\beta(r-r_e)} \right]^2 + c \beta^3 (r - r_e)^3 e^{-2\beta(r-r_e)} [1 + b \beta (r - r_e)] \right\}$
- ... etc. ...

## *but these forms . . . . .*

- all have limited flexibility
- most lack correct theoretical inverse-power long-range behaviour
- most are mathematically ‘ugly’

## Old Solution for diatomics (1960 – 1990)

- Represent level energies as power series in  $(v + \frac{1}{2})$  and  $[J(J + 1)]$  :

$$E(v, J) = T_e + \sum_{m=0} \sum_{l=0}' Y_{l,m} (v + \frac{1}{2})^l [J(J + 1)]^m$$

- Use the semiclassical “RKR” method to determine a pointwise potential

$$\begin{aligned} r_2(G_v) - r_1(G_v) &= 2\sqrt{\frac{\hbar^2}{2\mu}} \int_{v_{min}}^v \frac{1}{[G_v - G_{v'}]^{1/2}} dv' \\ \frac{1}{r_1(G_v)} - \frac{1}{r_2(G_v)} &= 2\sqrt{\frac{2\mu}{\hbar^2}} \int_{v_{min}}^v \frac{B_{v'}}{[G_v - G_{v'}]^{1/2}} dv' \end{aligned}$$

Yields a very precisely defined and smooth potential!  
( $\approx$  to machine precision)

## Old Solution for diatomics (1960 – 1990)

- Represent level energies as power series in  $(v + \frac{1}{2})$  and  $[J(J + 1)]$  :

$$E(v, J) = T_e + \sum_{m=0} \sum_{l=0}' Y_{l,m} (v + \frac{1}{2})^l [J(J + 1)]^m$$

- Use the semiclassical “RKR” method to determine a pointwise potential

$$\begin{aligned} r_2(G_v) - r_1(G_v) &= 2\sqrt{\frac{\hbar^2}{2\mu}} \int_{v_{min}}^v \frac{1}{[G_v - G_{v'}]^{1/2}} dv' \\ \frac{1}{r_1(G_v)} - \frac{1}{r_2(G_v)} &= 2\sqrt{\frac{2\mu}{\hbar^2}} \int_{v_{min}}^v \frac{B_{v'}}{[G_v - G_{v'}]^{1/2}} dv' \end{aligned}$$

Yields a very precisely defined and smooth potential!  
( $\approx$  to machine precision)

### *Problems:*

- *incorporates no natural extrapolation capability*
- based on the first-order semiclassical approximation, so *accuracy is limited* for small-reduced-mass systems
- a potential defined as a large, irregular array of points with distances specified to *many* significant-digits *is quite inconvenient to work with !*

## *‘Direct Potential Fits’*

*{For 3-D Van der Waals molecules since 1974, and diatomics since ~ 1990 }*

- Simulate level energies as eigenvalues of some parametrized analytic potential energy function  $V(r; \{p_j\})$
- Partial derivatives of observables w.r.t. parameters  $p_j$  required for fitting are generated readily using the Hellmann-Feynmann theorem:

$$\frac{\partial E(v, J)}{\partial p_j} = \left\langle \psi_{v,J} \left| \frac{\partial V(r; \{p_j\})}{\partial p_j} \right| \psi_{v,J} \right\rangle$$

- Compare predicted transition energies with experiment, and optimize potential parameters via an iterative least-squares fit

## *‘Direct Potential Fits’*

*{For 3-D Van der Waals molecules since 1974, and diatomics since ~ 1990 }*

- Simulate level energies as eigenvalues of some parametrized analytic potential energy function  $V(r; \{p_j\})$
- Partial derivatives of observables w.r.t. parameters  $p_j$  required for fitting are generated readily using the Hellmann-Feynmann theorem:

$$\frac{\partial E(v, J)}{\partial p_j} = \left\langle \psi_{v,J} \left| \frac{\partial V(r; \{p_j\})}{\partial p_j} \right| \psi_{v,J} \right\rangle$$

- Compare predicted transition energies with experiment, and optimize potential parameters via an iterative least-squares fit

### *Advantages*

- final result is a global analytic potential energy function
- allows realistic predictions in ‘extrapolation’ region outside the data range, and of non-spectroscopic properties
- yields full quantum mechanical accuracy
- readily accounts for Born-Oppenheimer breakdown (BOB),  $\Lambda$ -doubling, and/or  $^2\Sigma$  splittings, in terms of radial functions



# Extracting Potentials from Spectra

Peter F. Bernath

For most elements, we know whether they can form a diatomic molecule, especially for light atoms that have few electrons and can be treated readily by theory. But for one such light element, surprises are still in store. For most of the 20th century, experimental and theoretical studies agreed that the beryllium dimer ( $\text{Be}_2$ ) did not exist. The Be atom has filled electron shells and—like the inert gases such as helium—was expected to form at most a weak van der Waals dimer at very large internuclear distances. Yet, as shown experimentally by Merritt *et al.* on page 1548 of this issue (1),  $\text{Be}_2$  does exist and has a relatively short bond (2.45 Å), relative to the anticipated van der Waals complex with a bond length of about 5 Å. Its unusually flat potential curve limits the number of vibrational levels and provides the rare opportunity to study the highest vibrational state of a molecule just at its dissociation limit.

Experiments with beryllium are difficult because the metal is refractory (it has a low vapor pressure even at very high temperatures) and because beryllium-containing compounds are generally extremely toxic. However, Be vapor can be created through laser ablation of a Be metal target. Rapid cool-

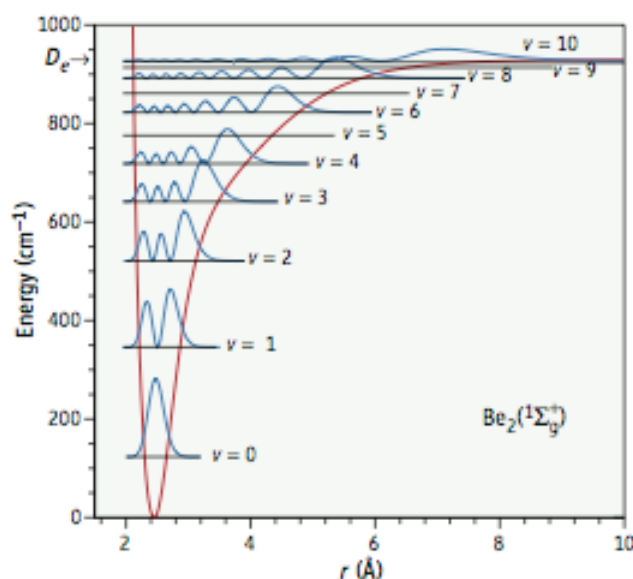
ing of the vapor during supersonic expansion through an orifice into vacuum allows preparation of the dimer. The rovibrational states of the dimer are then probed with a double-resonance method: One laser excites the molecule into an excited electronic state where the

An analysis of the spectra of the elusive beryllium dimer, aided by ab initio calculations, characterizes the molecule near its dissociation limit.

atoms are still bound; stimulated emission pumping (2) by a second laser returns the molecule back into each of the bound vibrational levels of the ground state.

The data analysis performed by Merritt *et al.* is noteworthy because it allows a better connection to theory than standard methods. Vibration-rotation energy levels are usually reduced to spectroscopic constants that are parameters in a power series expansion that uses the relevant quantum numbers of the states (3, 4). However, an excessively large number of expansion terms are needed, particularly for a potential with an unusual shape such as  $\text{Be}_2$ , and these fitting parameters have lost their physical meaning. In contrast, a parameterized potential function (see the figure) requires far fewer fitting parameters and makes a direct connection with ab initio quantum chemistry.

Merritt *et al.* adopted a more powerful analysis method that bypassed traditional constants in favor of a parameterized potential energy function obtained from a direct fit of the energy levels using the vibration-rotation Schrödinger



**Shallow potentials with deeper implications.** The potential energy function for  $\text{Be}_2$  as a function of interatomic distance  $r$  was determined by Merritt *et al.* from a fit to the experimental observations. The levels become more congested as the energy nears the dissociation limit  $D_e$ . The bound vibrational energy levels and the square of the vibrational wave functions were calculated by LeRoy with his program LEVEL (6).

Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK. E-mail: pfb500@york.ac.uk



*Challenge* ... to develop analytic potential function forms

- \* flexible enough to fully represent extensive high-resolution data
- \* robust and ‘well behaved’ (no spurious extrapolation behaviour)
- \* incorporate appropriate physical limiting behaviour
- \* compact and portable – defined by ‘modest’ no. of parameters

*Challenge* ... to develop analytic potential function forms

- \* flexible enough to fully represent extensive high-resolution data
- \* robust and ‘well behaved’ (no spurious extrapolation behaviour )
- \* incorporate appropriate physical limiting behaviour
- \* compact and portable – defined by ‘modest’ no. of parameters

### *Traditional Approach*

*Polynomial expansions*  $V(r) = c_0 \xi^2 \left( 1 + \sum_{i=1} c_i \xi^i \right)$  in variables:

- |                         |                                      |                      |                                                       |
|-------------------------|--------------------------------------|----------------------|-------------------------------------------------------|
| • Dunham                | $\xi_D = \frac{r - r_e}{r_e}$        | • Simons-Parr-Finlan | $\xi_{SPF} = \frac{r - r_e}{r}$                       |
| • Ogilvie-Tipping       | $\xi_{OT} = \frac{r - r_e}{r + r_e}$ | • Šurkus (‘GPEF’)    | $\xi_{Sur} = \frac{r^p - r_e^p}{a_S r^p + b_S r_e^p}$ |
| • Tiemann <i>et al.</i> | $\xi_T = \frac{r - r_e}{r + b r_e}$  |                      |                                                       |

*Problems with such polynomial potentials . . . . .*

- good fits require a relatively large numbers of terms
- polynomials *always* behave badly outside the ‘data region’
- correct theoretical long-range behaviour not readily imposed

*Instead ... consider ‘global’ analytic functions ...*

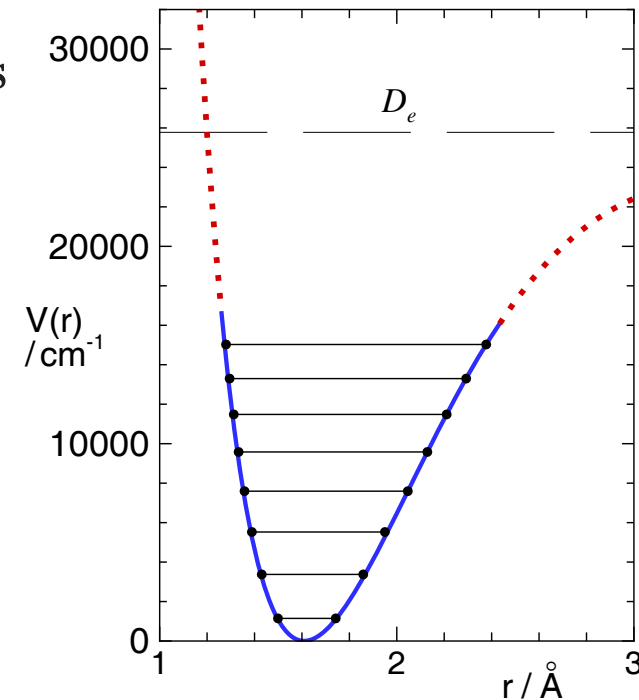
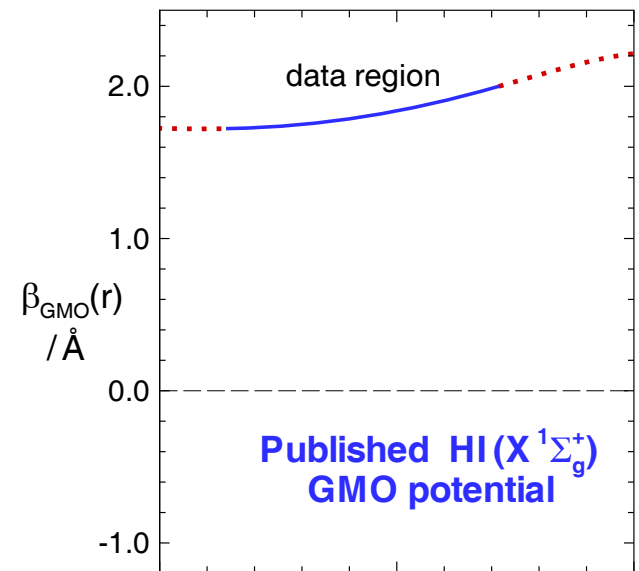
# Coxon-Hajigeorgiou ‘Generalized Morse Oscillator’ (GMO)

$$V_{\text{GMO}}(r) = \mathfrak{D}_e \left[ 1 - e^{-\beta(r) \cdot (r - r_e)} \right]^2$$

with 
$$\beta(r) = \sum_{i=0} \beta_i (r - r_e)^i$$

- algebraic structure defines basic potential shape
- modest changes in exponent coefficient  $\beta(r)$  suffice to define detailed shape
- very effective for data analysis
  - e.g. for  $\text{CO}(^1\Sigma^+)$
  - \* data precision  $0.0005 \text{ cm}^{-1}$
  - \* data span  $> 75\%$  of  $\mathfrak{D}_e$
  - \* more than 10000 data fit within uncertainties
  - \* potential requires only 10 fitted  $\beta_i$  parameters

- *but . . . . .*



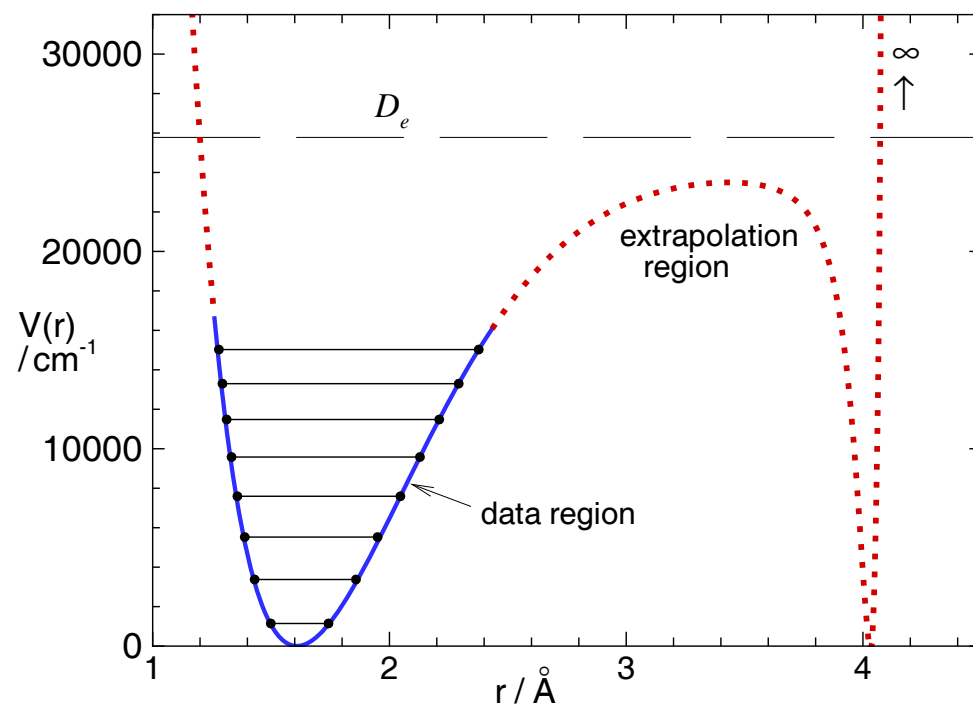
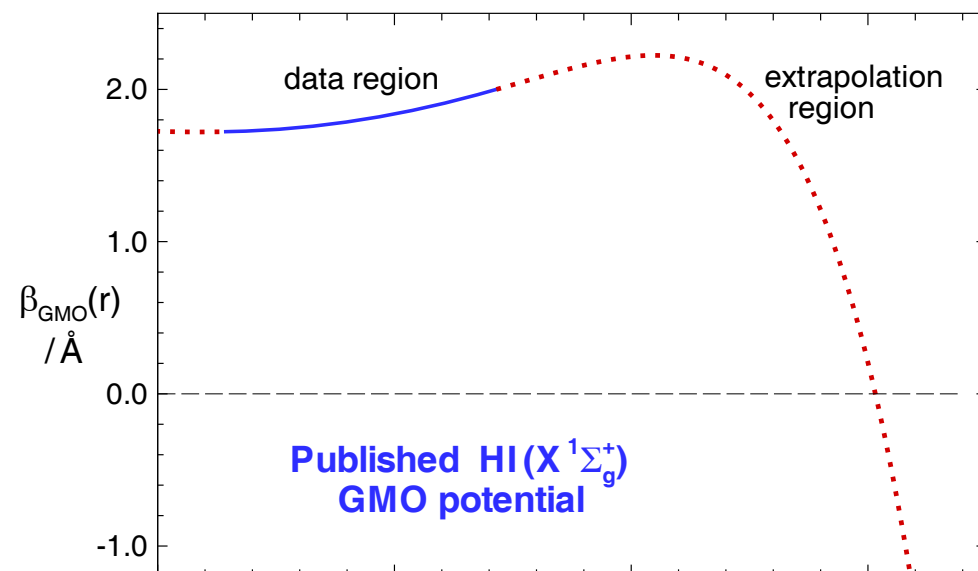
# Coxon-Hajigeorgiou 'Generalized Morse Oscillator' (GMO)

$$V_{\text{GMO}}(r) = \mathfrak{D}_e \left[ 1 - e^{-\beta(r) \cdot (r - r_e)} \right]^2$$

with 
$$\beta(r) = \sum_{i=0} \beta_i (r - r_e)^i$$

- algebraic structure defines basic potential shape
- modest changes in exponent coefficient  $\beta(r)$  suffice to define detailed shape
- very effective for data analysis  
e.g. for  $\text{CO}(^1\Sigma^+)$

- \* data precision  $0.0005 \text{ cm}^{-1}$
- \* data span  $> 75\%$  of  $\mathfrak{D}_e$
- \* more than 10000 data fit within uncertainties
- \* potential requires only 10 fitted  $\beta_i$  parameters



- *but ... problems at large  $r$  !*

***Blame the problem on the expansion variable !!***

If  $\beta(r)$  is simple polynomial, as  $r \rightarrow \infty$ , necessarily  $\beta(r) \rightarrow +\infty$  or  $-\infty$

Introduce the ***‘Extended Morse Oscillator’ (EMO)***

$$V_{\text{EMO}}(r) = \mathfrak{D}_e \left[ 1 - e^{-\beta(r) \cdot (r - r_e)} \right]^2$$

replacing  $\beta(r) = \beta_{\text{GMO}}(r) = \sum_{i=0} \beta_i (r - r_e)^i$

with  $\beta(r) = \beta_{\text{EMO}}(r) = \sum_{i=0} \beta_i \left( \frac{r - r_e}{r + r_e} \right)^i = \sum_{i=0} \beta_i [y_1(r)]^i$

*Blame the problem on the expansion variable !!*

If  $\beta(r)$  is simple polynomial, as  $r \rightarrow \infty$ , necessarily  $\beta(r) \rightarrow +\infty$  or  $-\infty$

Introduce the *‘Extended Morse Oscillator’ (EMO)*

$$V_{\text{EMO}}(r) = \mathfrak{D}_e \left[ 1 - e^{-\beta(r) \cdot (r - r_e)} \right]^2$$

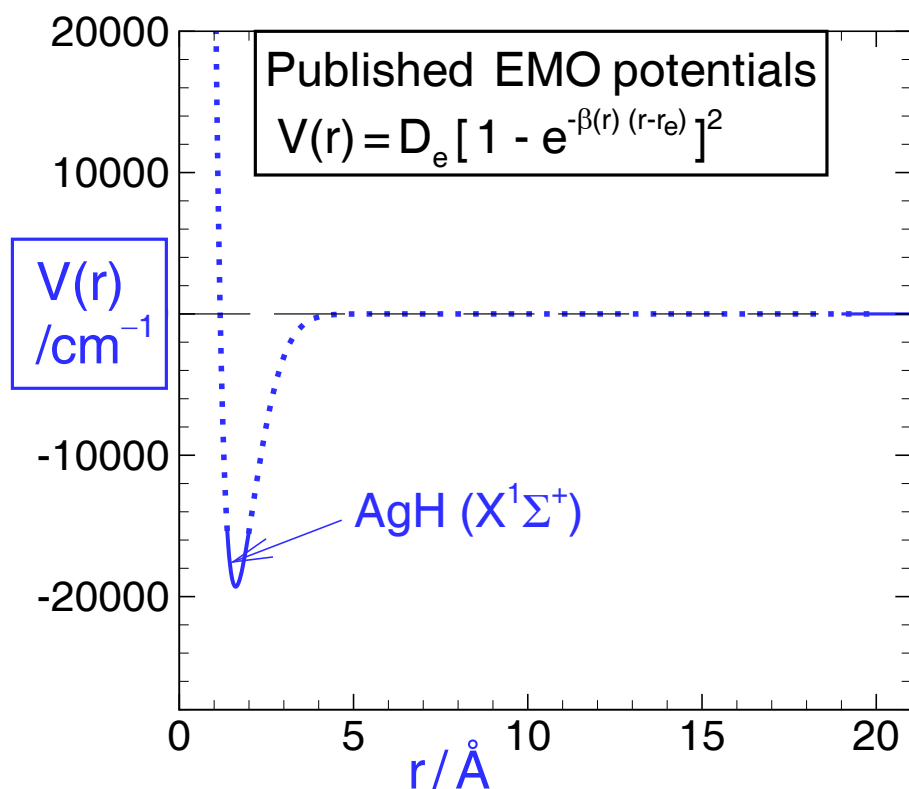
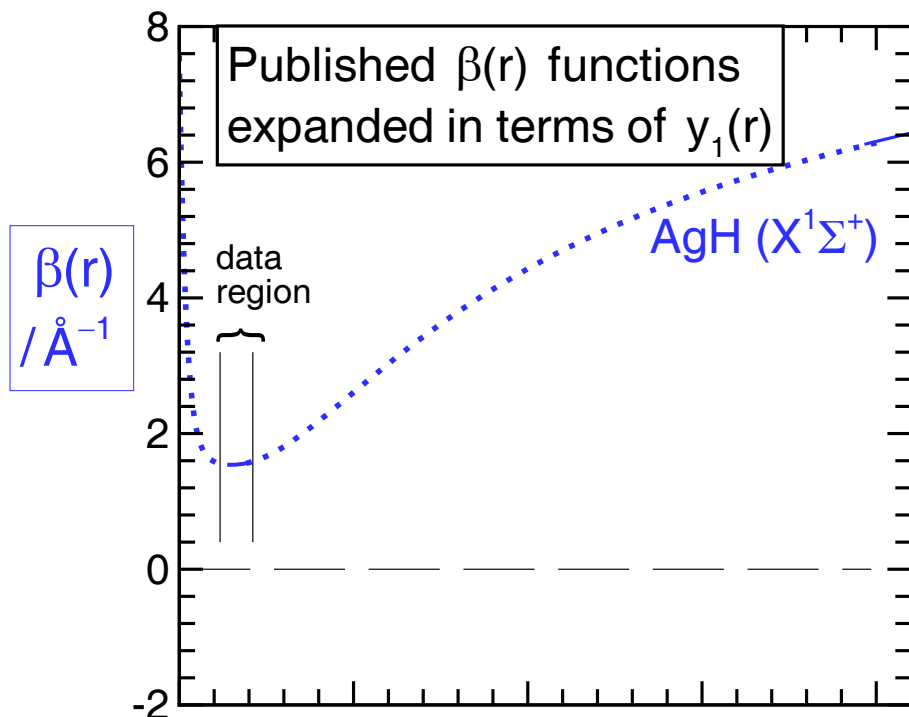
replacing  $\beta(r) = \beta_{\text{GMO}}(r) = \sum_{i=0} \beta_i (r - r_e)^i$

with  $\beta(r) = \beta_{\text{EMO}}(r) = \sum_{i=0} \beta_i \left( \frac{r - r_e}{r + r_e} \right)^i = \sum_{i=0} \beta_i [y_1(r)]^i$

Since  $y_1(r) = \left( \frac{r - r_e}{r + r_e} \right) \longrightarrow +1$  as  $r \rightarrow \infty$  ,  
 $\longrightarrow -1$  as  $r \rightarrow 0$  ,

*shouldn't we expect the exponent polynomial,  
and hence also the potential, to be well behaved?*

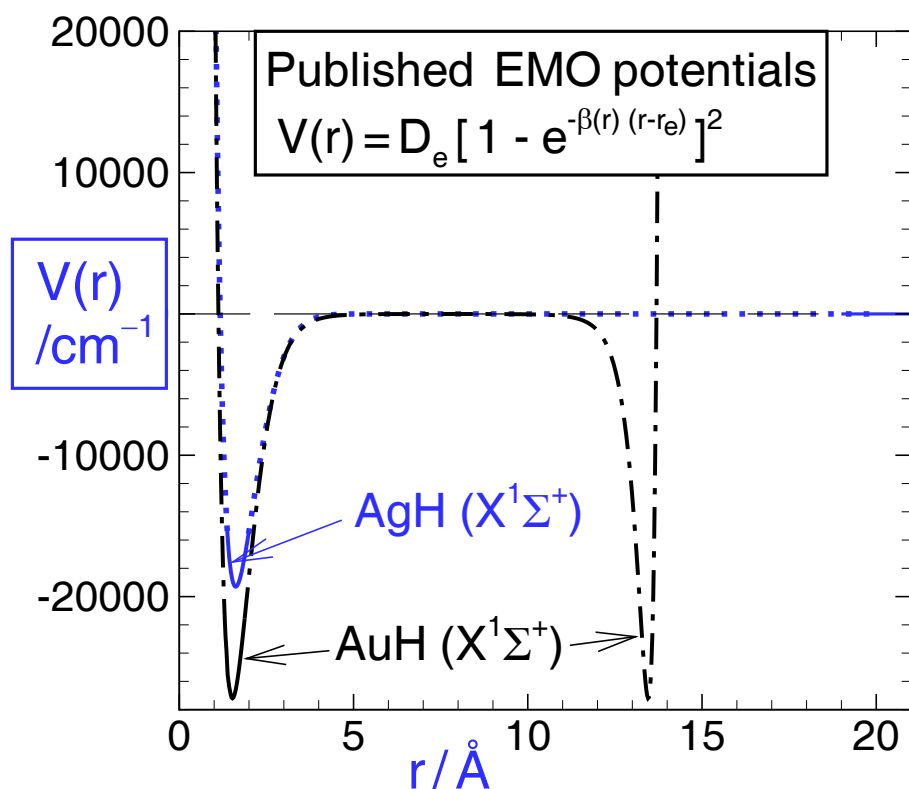
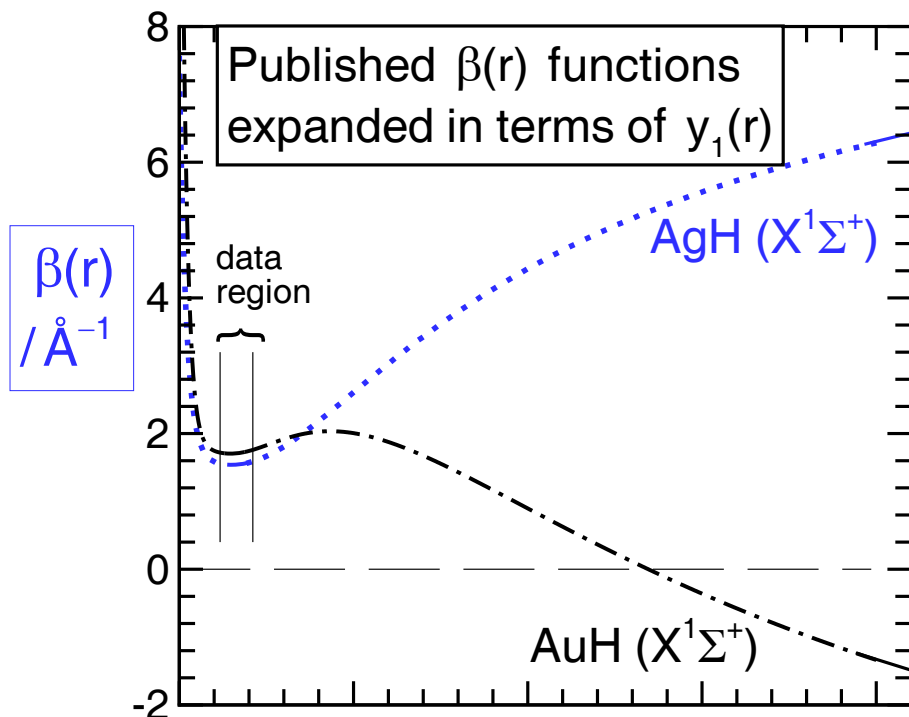
Consider our published EMO potentials for CuH, AgH & AuH determined from direct fits to high resolution IR data.



$$V_{\text{EMO}}(r) = D_e [1 - e^{-\beta(r)(r-r_e)}]^2$$

Expanding  $\beta(r)$  as a power series in  $y_1(r)$

- For AgH EMO exponent coefficient always positive, so potential is 'well-behaved' in extrapolation region at both large & small  $r$

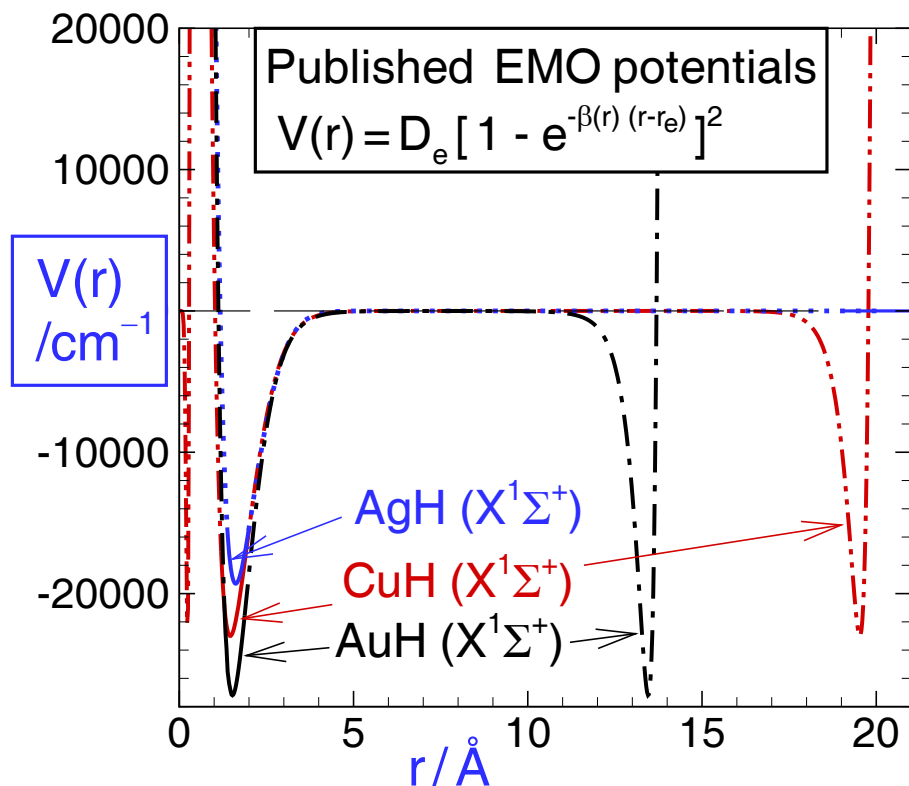
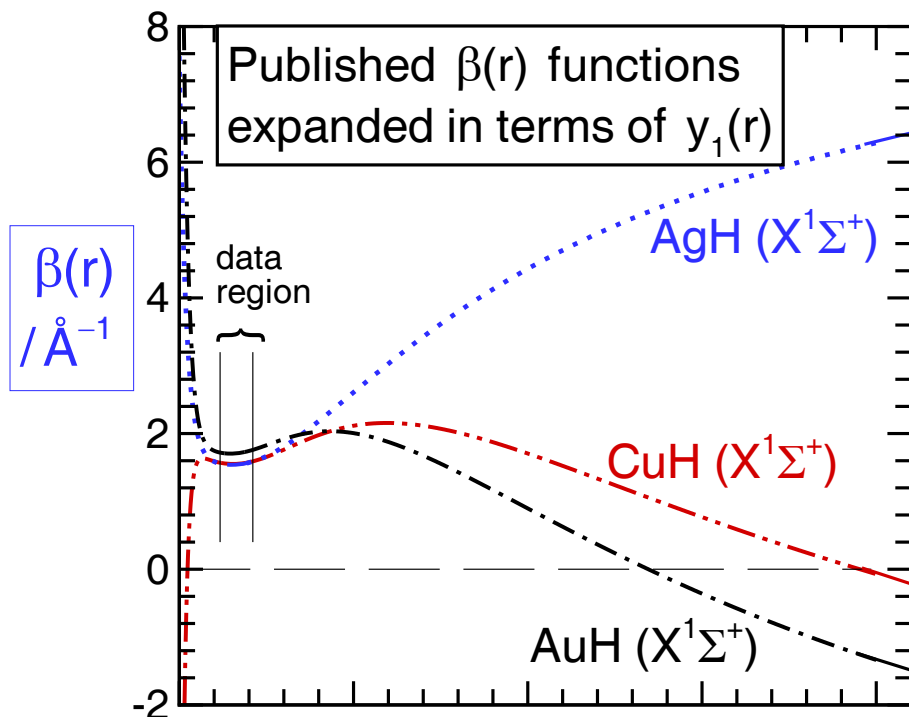


$$V_{\text{EMO}}(r) = D_e [1 - e^{-\beta(r)(r-r_e)}]^2$$

Expanding  $\beta(r)$  as a power series in  $y_1(r)$

- For AgH EMO exponent coefficient always positive, so potential is 'well-behaved' in extrapolation region at both large & small  $r$
- For AgH exponent coefficient  $\beta(r)$  changes sign at large  $r$ , so potential turns over there!





$$V_{\text{EMO}}(r) = D_e [1 - e^{-\beta(r)(r-r_e)}]^2$$

Expanding  $\beta(r)$  as a power series in  $y_1(r)$

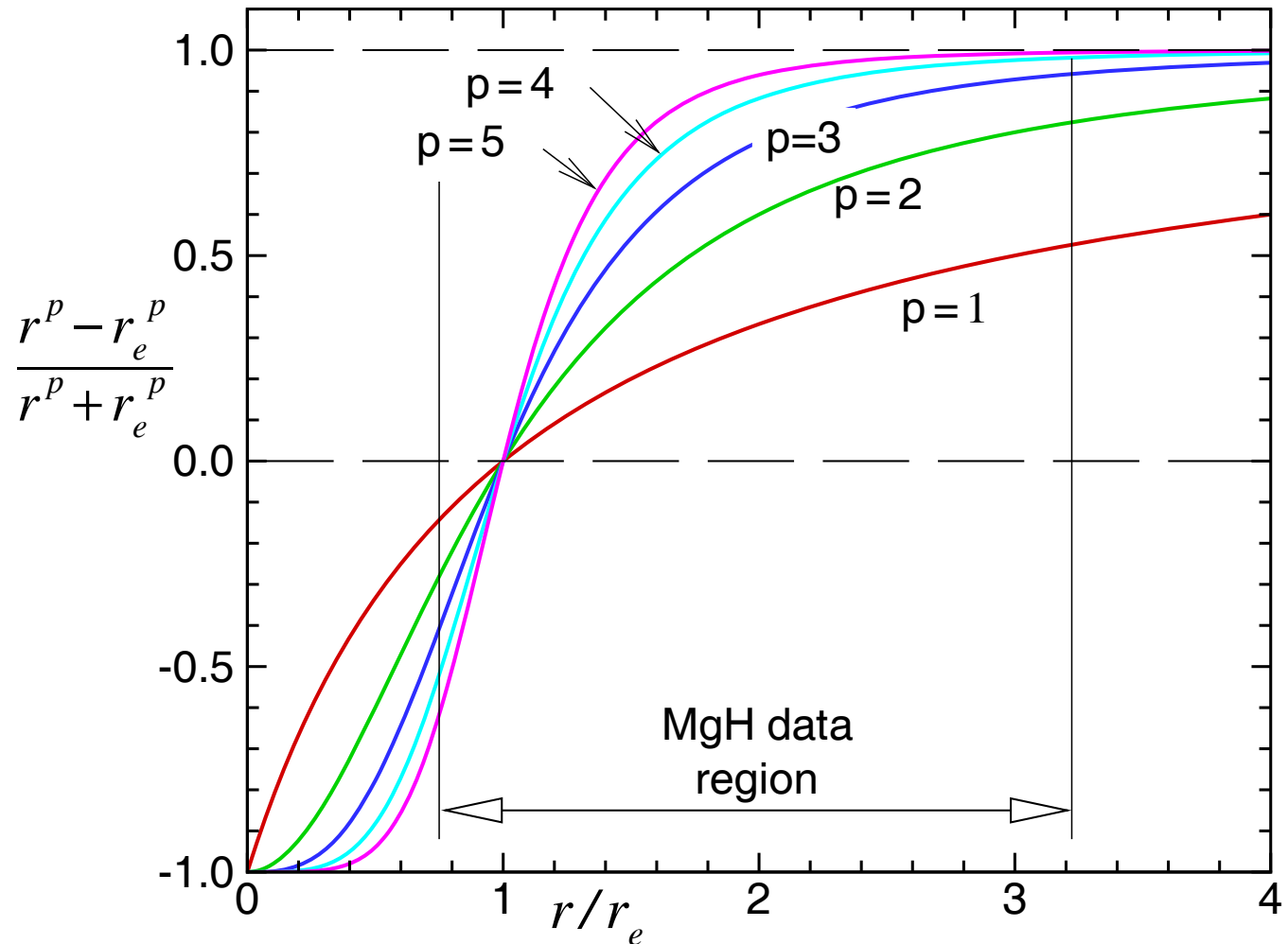
- For AgH EMO exponent coefficient always positive, so potential is 'well-behaved' in extrapolation region at both large & small  $r$
- For AgH exponent coefficient  $\beta(r)$  changes sign at large  $r$ , so potential turns over there!
- For CuH coefficient  $\beta(r)$  changes sign in both large and small  $r$  regions, so potential turns over at both large and small  $r$ !

Again ... *blame the problem on the expansion variable!*

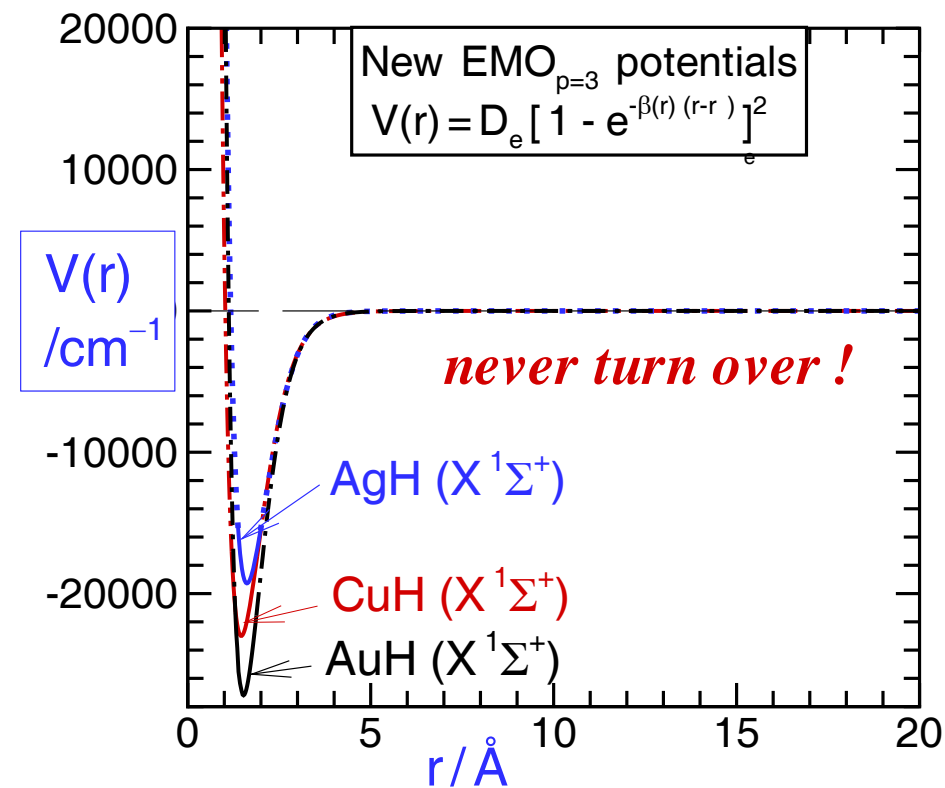
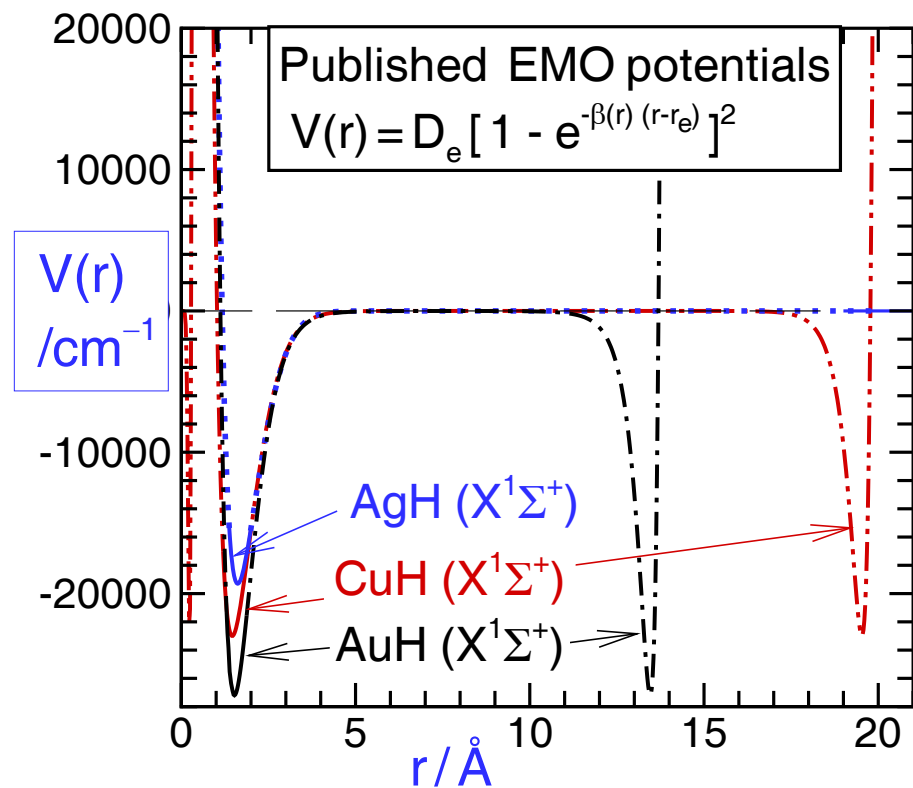
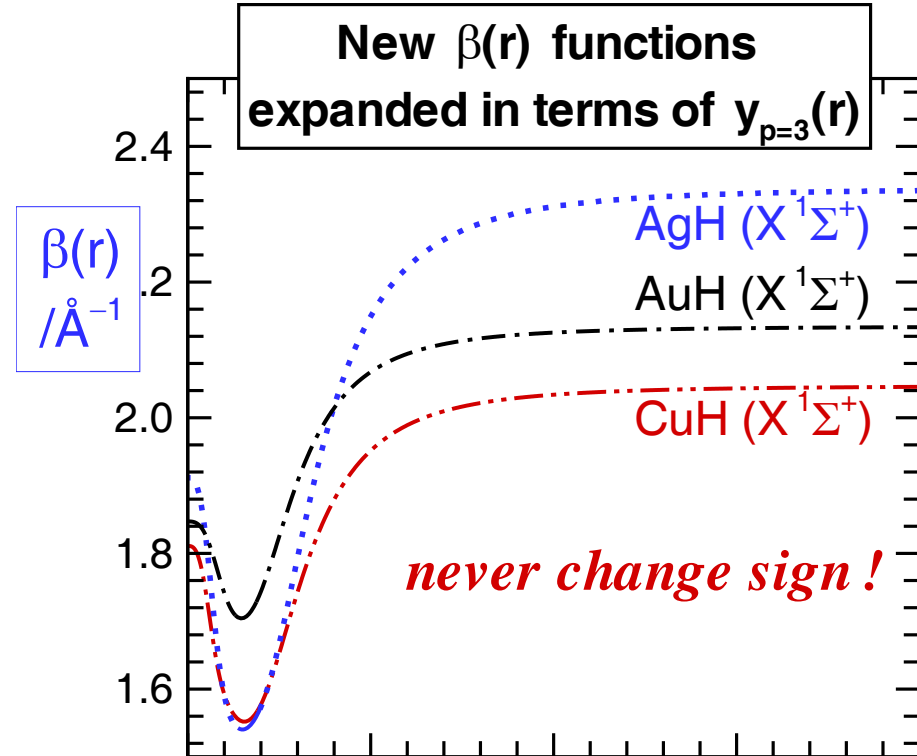
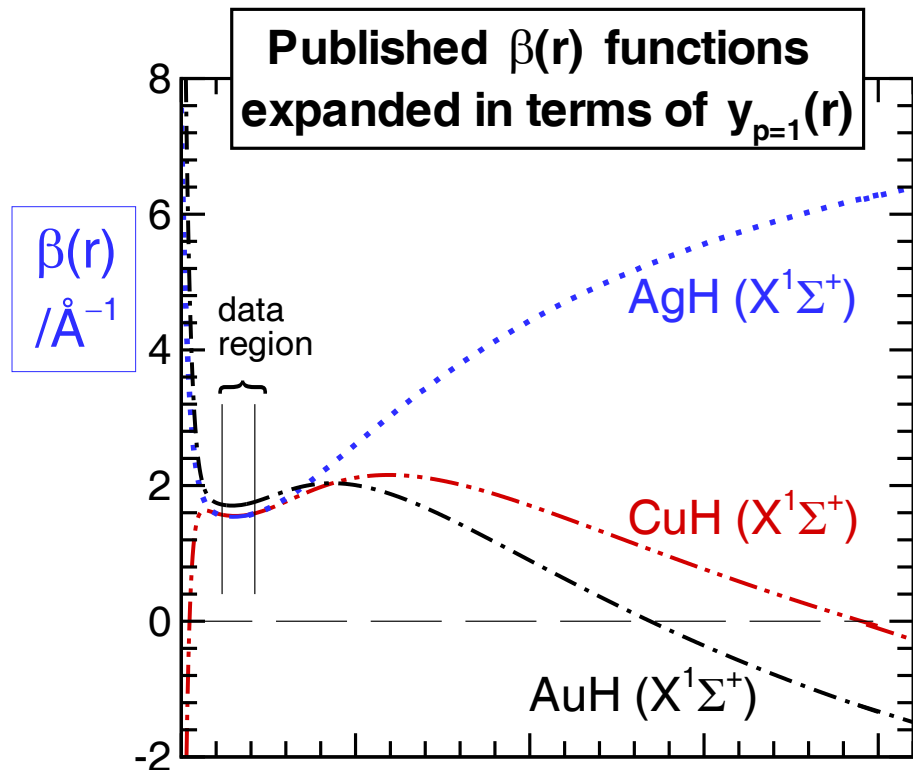
Consider:

$$y_p(r) = \left( \frac{r^p - r_e^p}{r^p + r_e^p} \right)$$

*The power  $p$   
in  $y_p(r)$  is  
very important!*



- for  $p$  too small, much of the range of  $y_p(r)$  is outside the region where the polynomial  $\beta(y_p(r))$  is determined, so  $\beta(r)$  (and the potential) may misbehave there!
- for  $p$  too large,  $y_p(r)$  is too ‘flat’ in the outer parts of the data region to allow a good fit to the data (e.g., MgH for  $p > 5$ ).



*Recall the challenge* ... to develop analytic potential function forms:

- \* able to accurately represent extensive high-resolution data ✓
- \* robust and ‘well behaved’ (no spurious extrapolation behaviour) ✓
- \* *incorporating appropriate limiting long-range behaviour!*

At long range, all molecular interactions become

$$V(r) \simeq \mathfrak{D} - \frac{C_n}{r^n} - \frac{C_m}{r^m} - \dots$$

so we want a function which incorporates this behaviour.

*Recall the challenge* ... to develop analytic potential function forms:

- \* able to accurately represent extensive high-resolution data ✓
- \* robust and ‘well behaved’ (no spurious extrapolation behaviour) ✓
- \* *incorporating appropriate limiting long-range behaviour!*

At long range, all molecular interactions become

$$V(r) \simeq \mathfrak{D} - \frac{C_n}{r^n} - \frac{C_m}{r^m} - \dots$$

so we want a function which incorporates this behaviour.

### *Morse/Long-Range (MLR) Potential*

If we define  $u_{\text{LR}}(r) = \frac{C_{m_1}}{r^{m_1}} + \frac{C_{m_2}}{r^{m_2}} + \dots$  we can write

$$V_{\text{MLR}}(r) = \mathfrak{D}_e \left\{ 1 - \frac{u_{\text{LR}}(r)}{u_{\text{LR}}(r_e)} e^{-\beta(r) \cdot y_p(r)} \right\}^2$$

$$\xrightarrow{r \gg r_e} \mathfrak{D}_e - \left[ \frac{2\mathfrak{D}_e e^{-\beta_\infty}}{u_{\text{LR}}(r_e)} \right] u_{\text{LR}}(r) = \mathfrak{D}_e - \frac{C_{m_1}}{r^{m_1}} - \frac{C_{m_2}}{r^{m_2}} - \dots$$

in which  $\beta(r) = \beta_{\text{MLR}}(r) = \beta_\infty y_p(r) + [1 - y_p(r)] \sum_{i=0}^N \beta_i y_p(r)^i$

where  $\beta_\infty \equiv \beta(r=\infty) = \ln\{2\mathfrak{D}_e/u_{\text{LR}}(r_e)\}$

## Consider Ground-State $N_2$

Fit all available (reliable) data

[Raman, quadrupole, and electronic]

for all three isotopologues

[ $^{14,14}N_2$ ,  $^{14,15}N_2$ , and  $^{15,15}N_2$ ]

to  $EMO_p(N)$ , and  $MLR_p(N)$

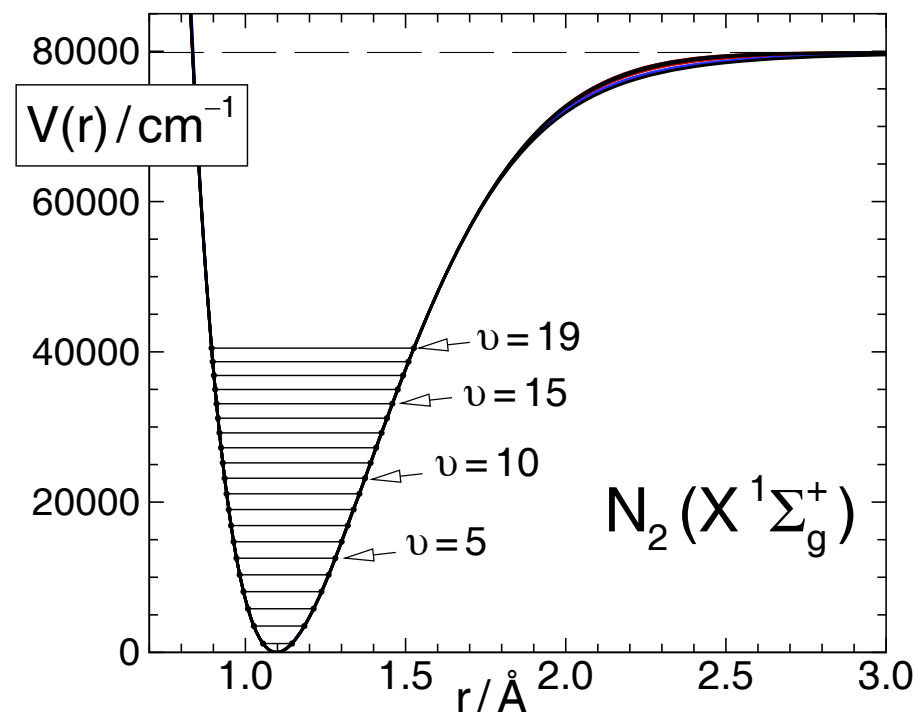
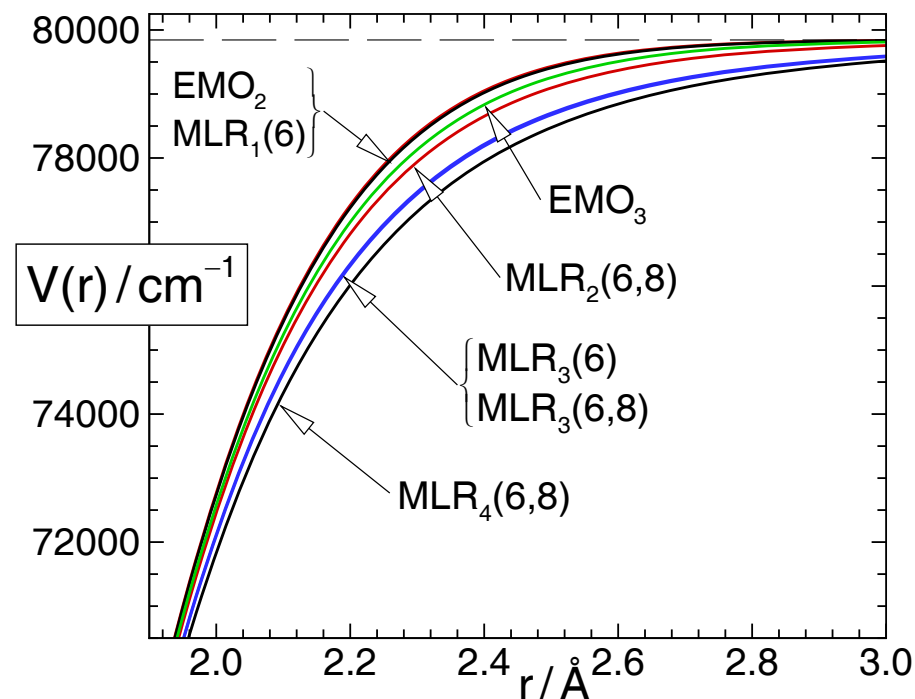
potentials for various values of  $p$

and exponent polynomial order  $N$

[ $\mathcal{D}_e$  fixed at accurate known value.]

Obtain excellent fits for  
a variety of models.

*How do we choose the best!*



## Compare behaviour of these $N_2$ potentials outside the 'data region'

Can write overall potential as

$$V(r) = \mathfrak{D} - \frac{C_6^{\text{eff}}(r)}{r^6}$$

Since at long range

$$V(r) \simeq \mathfrak{D} - \frac{C_6}{r^6} - \frac{C_8}{r^8} - \dots$$

then

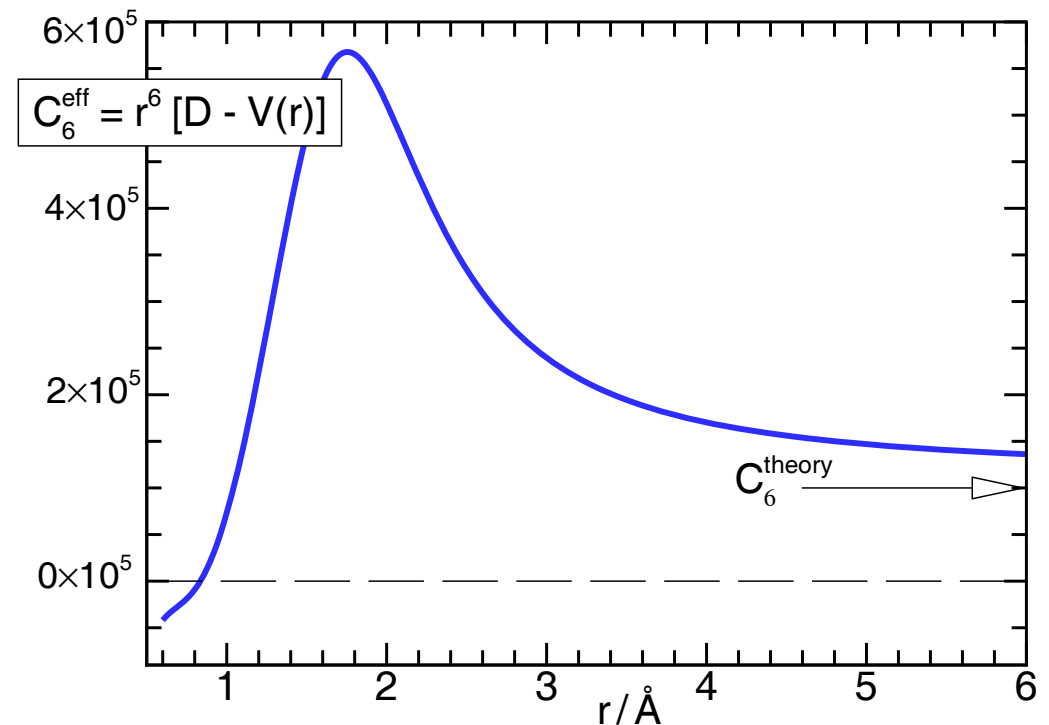
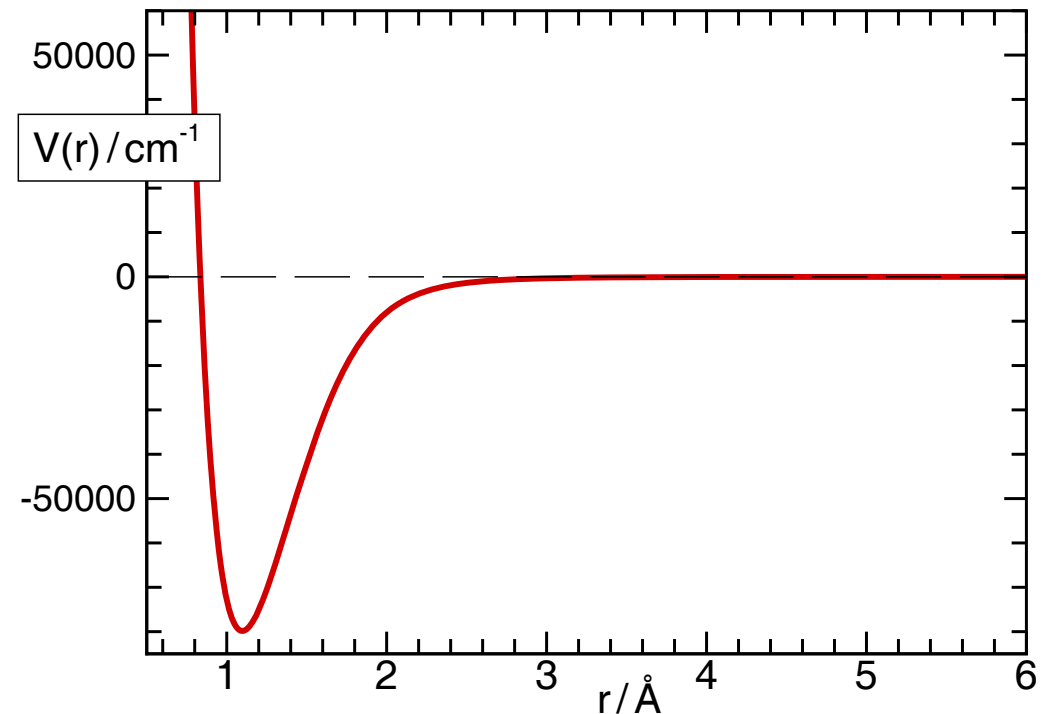
$$C_6^{\text{eff}}(r) \equiv r^6 [\mathfrak{D} - V(r)]$$

$$\xrightarrow{r \rightarrow \infty} C_6 + \frac{C_8}{r^2} + \dots$$

So a plot of  $C_6^{\text{eff}}(r)$  vs.  $1/r^2$

should approach

- an intercept of  $C_6^{\text{theory}}$
  - with a slope of  $C_8^{\text{theory}}$
- from above !*



## Compare behaviour of these $N_2$ potentials outside the 'data region'

Can write overall potential as

$$V(r) = \mathfrak{D} - \frac{C_6^{\text{eff}}(r)}{r^6}$$

Since at long range

$$V(r) \simeq \mathfrak{D} - \frac{C_6}{r^6} - \frac{C_8}{r^8} - \dots$$

then

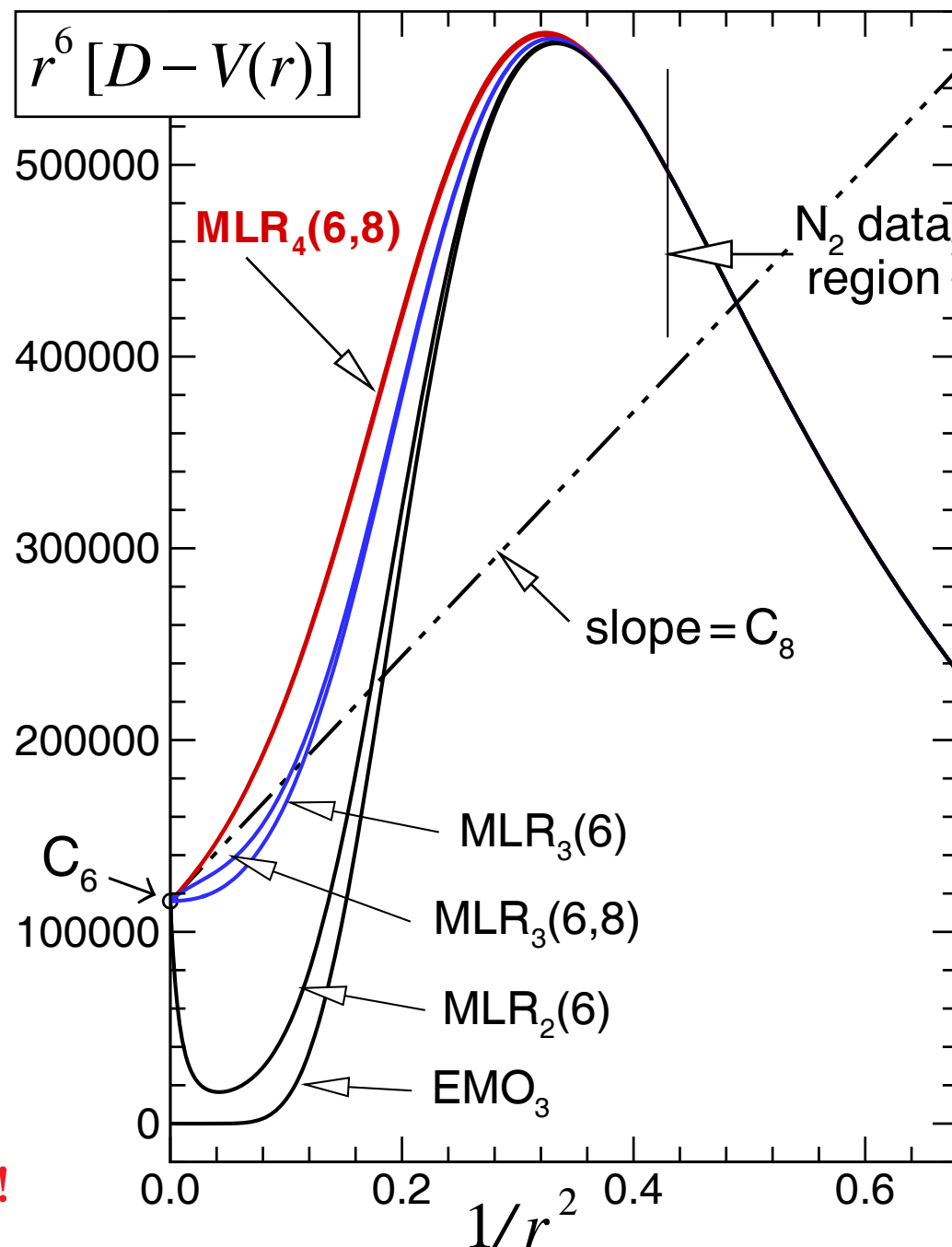
$$C_6^{\text{eff}}(r) \equiv r^6 [\mathfrak{D} - V(r)]$$
$$\xrightarrow{r \rightarrow \infty} C_6 + \frac{C_8}{r^2} + \dots$$

So a plot of  $C_6^{\text{eff}}(r)$  vs.  $1/r^2$

should approach

- an intercept of  $C_6^{\text{theory}}$
  - with a slope of  $C_8^{\text{theory}}$
- from above !*

⇒ **Criterion for the best model !**





*Recall the challenge* ... to develop analytic potential function forms:

- \* able to accurately represent extensive high-resolution data ✓
- \* robust and ‘well behaved’ (no spurious extrapolation behaviour) ✓
- \* incorporating appropriate limiting long-range behaviour! ✓
- \* *compact and ‘portable’ – defined by a ‘modest’ number of parameters*

# *Compare MLR with other current model potential forms*

## 1. **Tiemann-type polynomials**

- potential in ‘data region’ is a polynomial in  $\left( \frac{r - r_e}{r + b r_e} \right)$
- attach repulsive-wall function at some chosen inner bound  $r_m$
- attach an inverse-power long-range tail at some chosen outer bound  $r_{\text{out}}$

## 2. **Pashov’s Spline Pointwise Potential (SPP)**

- potential in ‘data region’ is cubic spline function on a selected radial mesh: potential-fit parameters are energies of those spline points
- attach an inverse-power long-range tail at some chosen outer bound  $r_{\text{out}}$

# *Compare MLR with other current model potential forms*

## 1. **Tiemann-type polynomials**

- potential in ‘data region’ is a polynomial in  $\left(\frac{r - r_e}{r + b r_e}\right)$
- attach repulsive-wall function at some chosen inner bound  $r_m$
- attach an inverse-power long-range tail at some chosen outer bound  $r_{\text{out}}$

## 2. **Pashov’s Spline Pointwise Potential (SPP)**

- potential in ‘data region’ is cubic spline function on a selected radial mesh: potential-fit parameters are energies of those spline points
- attach an inverse-power long-range tail at some chosen outer bound  $r_{\text{out}}$

## **Consider data analysis for ground-state $\text{Ca}_2(X^1\Sigma_g^+)$**

- 3553 data – typical uncertainty  $0.006 - 0.015 \text{ cm}^{-1}$
- data span 99.97% of  $\mathcal{D}_e$
- highest observed level ( $v=38$ ) bound by only  $\sim 0.3 \text{ cm}^{-1}$

Tiemann polynomial (2003)	
$\mathfrak{D}_e$	1102.074
$r_e$	
$C_6$	$1.0030 \times 10^7$
$C_8$	$3.87 \times 10^8$
$C_{10}$	$4.41 \times 10^9$
$b$	-0.5929
$a_0$	0.00043
$a_1$	-2.57153863528197002
$a_2$	$3.79611687289805877 \times 10^3$
$a_3$	$3.82947943867555637 \times 10^2$
$a_4$	$-2.74470356912936631 \times 10^3$
$a_5$	$-3.23378807398046092 \times 10^3$
$a_6$	$3.70205119299758223 \times 10^2$
$a_7$	$6.35318559107446436 \times 10^3$
$a_8$	$-7.39783474312859562 \times 10^3$
$a_9$	$-1.90759867971015337 \times 10^4$
$a_{10}$	$5.41779135173975228 \times 10^4$
$a_{11}$	$4.40527349765557083 \times 10^4$
$a_{12}$	$-1.55406021572582802 \times 10^5$
$a_{13}$	$-8.35826911941128783 \times 10^4$
$a_{14}$	$2.13873243831604603 \times 10^5$
$a_{15}$	$1.56022970979522303 \times 10^5$
$a_{16}$	$-1.56329579530082468 \times 10^5$
$a_{17}$	$-1.46822446075956163 \times 10^5$
$a_{18}$	$2.74480910039127666 \times 10^4$
$a_{19}$	$7.11882274192053592 \times 10^4$
$a_{20}$	$-7.63044568335207146 \times 10^2$
$r_m$	4.277277 Å
$r_{\text{out}}$	9.5

Spline pointwise potential (2003)			
$\mathfrak{D}_e$		1102.060	
$C_6$		$1.0023 \times 10^7$	
$C_8$		$3.808 \times 10^8$	
$C_{10}$		$5.06 \times 10^9$	
$r/\text{\AA}$	$U/\text{cm}^{-1}$	$r/\text{\AA}$	$U/\text{cm}^{-1}$
3.096980	9246.6895	5.678571	636.3741
3.188725	6566.7325	5.809524	684.9589
3.280470	4525.7282	5.940476	728.9235
3.372215	3090.9557	6.071429	768.5976
3.463960	2134.2175	6.202381	804.2551
3.555705	1475.2425	6.333333	836.2419
3.647450	1004.5043	6.464286	864.8746
3.739195	661.4123	6.595238	890.4666
3.830940	410.6117	6.726191	913.2923
3.922685	234.0001	6.857143	933.6417
4.014430	116.0996	6.988095	951.7718
4.106174	44.5437	7.119048	967.8632
4.197920	8.6885	7.250000	982.2159
4.289664	0.1760	7.500000	1005.2497
4.381409	11.9571	7.750000	1023.6698
4.500000	48.5948	8.000000	1038.3262
4.630952	106.9081	8.358974	1054.3861
4.761905	175.7311	8.717949	1066.0579
4.892857	248.8199	9.076923	1074.5969
5.023809	322.3873	9.435897	1080.8961
5.154762	393.7222	9.794872	1085.5974
5.285714	461.4555	10.303419	1090.2990
5.416667	524.6311	10.811966	1093.5160
5.547619	582.9870	11.611111	1096.6870

<b>MLR<sub>5,3</sub></b> (2009)	
$\mathfrak{D}_e$	1102.076
$r_e$	4.27781
$C_6$	$1.046 \times 10^7$
$C_8$	$3.0608 \times 10^8$
$C_{10}$	$8.344 \times 10^9$
$r_{\text{ref}}$	5.55
$\beta_0$	-1.4672501
$\beta_1$	-0.20012
$\beta_2$	-0.72633
$\beta_3$	0.1229
$\beta_4$	-0.2763
$\beta_5$	0.506
$\beta_6$	0.357
$\beta_7$	1.022

- Fits with *all three models account for all data within uncertainties, but ... polynomial and SPP potentials*:
  - \* require *many* more parameters
  - \* long-range tail is ‘attached’ at a chosen (*ad hoc*) point, and not a natural component of the potential
  - \* irregular short-range behaviour requires inward extrapolation outside the ‘data region’ to use an *ad hoc* function attached at a chosen (*ad hoc*) point
  - \* slightly poorer quality of fit (i.e., bigger error  $\bar{\sigma}$ ) !

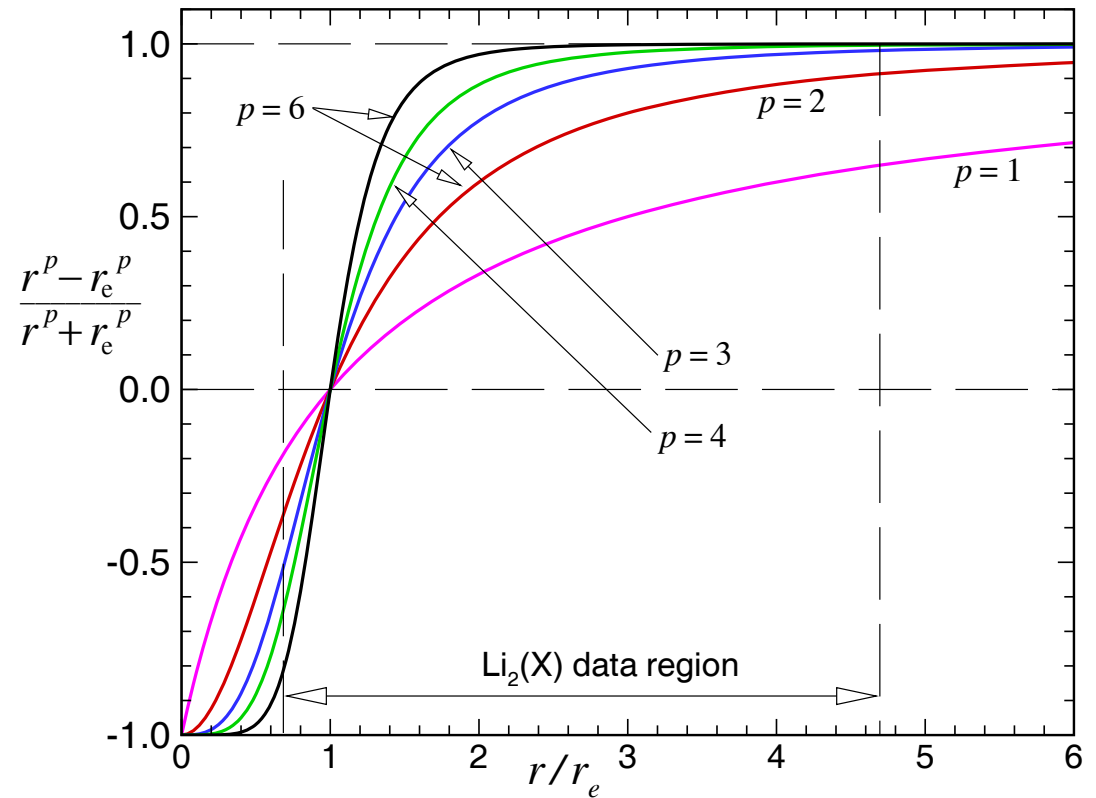
<i>potential function</i>		$\bar{\sigma}$	<i>no. parameters</i>		$10^7 \times C_6$
<i>form</i>	$u_{\text{LR}}(r)$		<i>total</i>	<i>fitted</i>	
<b>Pashov spline</b>	$C_6, C_8, C_{10}$	<b>0.74</b>	<b>52</b>	<b>50</b>	$1.002 (\pm ?)$
<b>Tiemann poly.</b>	$C_6, C_8, C_{10}$	<b>0.69</b>	<b>30</b>	<b>24</b>	$1.003 (\pm 0.033)$
<b>MLR<sub>5,3</sub>(7)</b>	$C_6, C_8, C_{10}$	<b>0.62</b>	<b>16</b>	<b>11</b>	$1.046 (\pm 0.003)$
<b>theory</b> <sup>JCP(2008)</sup>					1.055

*Which experimental  $C_6$  would you trust?*

## Improving the model – minding our $p$ 's and $q$ 's

For  $X(^1\Sigma_g^+)$ -state  $\text{Li}_2$ , including 3 terms in  $u_{\text{LR}}(r)$  ( $C_6$ ,  $C_8$  &  $C_{10}$ ) means we must set  $p \geq 5$ . But in this case:

- $y_p(r)$  is very flat and  $\approx 1.0$  over much of the domain
- so a very high-order exponent polynomial would be required to describe the potential
- and it would have large coefficients of alternating sign!



## Improving the model – minding our $p$ 's and $q$ 's

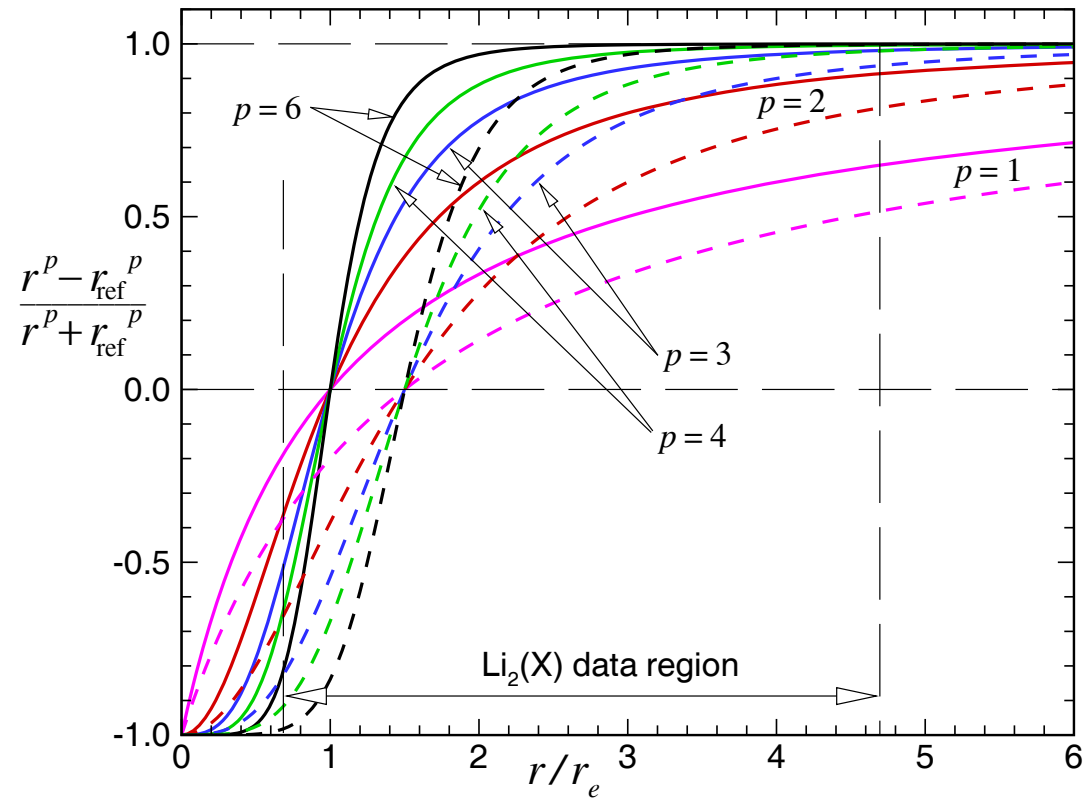
For  $X(^1\Sigma_g^+)$ -state  $\text{Li}_2$ , including 3 terms in  $u_{\text{LR}}(r)$  ( $C_6$ ,  $C_8$  &  $C_{10}$ ) means we must set  $p \geq 5$ . But in this case:

- $y_p(r)$  is very flat and  $\approx 1.0$  over much of the domain
- so a very high-order exponent polynomial would be required to describe the potential
- and it would have large coefficients of alternating sign !

So introduce  $y_p^{\text{ref}} = \frac{r^p - r_{\text{ref}}^p}{r^p + r_{\text{ref}}^p}$   
and then define

$$\beta(r) = \beta_{p,q}^{\text{ref}}(r) \equiv y_p^{\text{ref}}(r) \beta_{\infty} + [1 - y_p^{\text{ref}}(r)] \sum_{i=0}^N \beta_i [y_q^{\text{ref}}(r)]^i$$

$p$  must be bigger than the difference between the highest and lowest inverse powers in  $u_{\text{LR}}(r)$ , and hence is relatively large, but  $q$  can be smaller – giving a better expansion variable !



## Consider NaCs( $X^1\Sigma_g^+$ )

- 5056 data – typical  
uncertainty  $\simeq 0.003 \text{ cm}^{-1}$
- data span 99.96% of  $\mathcal{D}_e$
- highest observed level ( $v=83$ )  
bound by only  $\approx 1.76 \text{ cm}^{-1}$   
outer turning point  $\simeq 14.7 \text{ \AA}$

<i>potential</i>		<i>no. param.</i>	
<i>form</i>	$\bar{\sigma}$	<i>total</i>	<i>fitted</i>
Pashov spline	0.88	55	54
polynomial(29)	0.88	42	32
MLR <sub>4</sub> (6,20)	0.66 <sub>4</sub>	27	24
MLR <sub>5,3</sub> (13)	0.66 <sub>9</sub>	22	17

	MLR <sub>4</sub> (6; 20)	MLR <sub>5,3</sub> (13)
$\mathcal{D}_e/\text{cm}^{-1}$	4954.173(3)	4954.192(3)
$r_e/\text{\AA}$	3.85050(1)	3.850503(3)
$r_{\text{ref}}/\text{\AA}$	$r_e$	5.2
$C_6/\text{cm}^{-1}\text{\AA}^6$	$1.555 \times 10^7$	$1.555 \times 10^7$
$C_8/\text{cm}^{-1}\text{\AA}^8$	$4.89 \times 10^8$	$4.89 \times 10^8$
$C_{10}/\text{cm}^{-1}\text{\AA}^{10}$	—	$1.72 \times 10^9$
$\{p, q\}$	$\{4, 4\}$	$\{5, 3\}$
$\beta_0$	−2.22118251	−0.29786199
$\beta_1$	−1.0553496	−1.2822112
$\beta_2$	−1.546359	−1.116747
$\beta_3$	−1.0359	0.192419
$\beta_4$	−1.51071	1.10351
$\beta_5$	−1.3729	1.28574
$\beta_6$	−1.0316	0.7156
$\beta_7$	$1.0211274 \times 10^4$	1.6298
$\beta_8$	$−2.12300206 \times 10^5$	4.401
$\beta_9$	$2.10449537 \times 10^6$	5.722
$\beta_{10}$	$−1.293897106 \times 10^7$	1.47
$\beta_{11}$	$5.45420478 \times 10^7$	−4.96
$\beta_{12}$	$−1.65568755 \times 10^8$	−6.83
$\beta_{13}$	$3.7115571 \times 10^8$	−3.3
$\beta_{14}$	$−6.2083203 \times 10^8$	
$\beta_{15}$	$7.738836 \times 10^8$	
$\beta_{16}$	$−7.09447 \times 10^8$	
$\beta_{17}$	$4.64693 \times 10^8$	
$\beta_{18}$	$−2.0589 \times 10^8$	
$\beta_{19}$	$5.53 \times 10^7$	
$\beta_{20}$	$−6.8 \times 10^6$	



*MLR structure also works for long-range forms which, e.g.,*

- incorporate ‘damping’ functions:

$$u_{\text{LR}}(r) = D_{m_1}(r) \frac{C_{m_1}}{r^{m_1}} + D_{m_2}(r) \frac{C_{m_2}}{r^{m_2}} + \dots$$

- incorporate inter-state coupling [see **MI-02** for 3-state coupling case]

$$\begin{aligned} u_{\text{LR}}^{\text{A-F}}(r) = & -\frac{A_{\text{so}}}{2} + \frac{C_3^{\Sigma} + C_3^{\Pi}}{2r^3} + \frac{C_6^{\Sigma} + C_6^{\Pi}}{2r^6} + \frac{C_8^{\Sigma} + C_8^{\Pi}}{2r^8} \\ & \pm \frac{1}{2} \left\{ \left( \frac{C_3^{\Sigma} - C_3^{\Pi}}{3r^3} + \frac{C_6^{\Sigma} - C_6^{\Pi}}{3r^6} + \frac{C_8^{\Sigma} - C_8^{\Pi}}{3r^8} - A_{\text{so}} \right)^2 \right. \\ & \left. + 8 \left( \frac{C_3^{\Sigma} - C_3^{\Pi}}{3r^3} + \frac{C_6^{\Sigma} - C_6^{\Pi}}{3r^6} + \frac{C_8^{\Sigma} - C_8^{\Pi}}{3r^8} \right)^2 \right\}^{1/2} \end{aligned}$$

This model has been/is being applied to analyses of data *for diatomics*:

$\text{N}_2(\text{X } ^1\Sigma_{\text{g}}^+)$ ,  $\text{KLi}(\text{a } ^3\Sigma^+)$ ,  $\text{Ca}_2(\text{X } ^1\Sigma_{\text{g}}^+)$ ,  $\text{MgH}(\text{X } ^2\Sigma^+)$ ,  $\text{Cs}_2(\text{a } ^3\Sigma_{\text{u}}^+)$ ,  
 $\text{Cs}_2(\text{X } ^1\Sigma_{\text{u}}^+)$  [see **MI 01**],  $\text{Be}_2(^1\Sigma_{\text{g}}^+)$ ,  $\text{NaCs}(^1\Sigma_{\text{g}}^+)$ ,  $\text{Li}_2(\text{X } ^1\Sigma_{\text{g}}^+)$ ,  $\text{Li}_2(\text{A } ^1\Sigma_{\text{u}}^+)$ ,  
 $\text{Li}_2(\text{a } ^3\Sigma_{\text{u}}^+)$ ,  $\text{Li}_2(\text{c } ^1\Pi_{\text{g}})$  [see **MI 02**] and  $\text{NaRb}(\text{X } ^1\Sigma_{\text{g}}^+)$

and generalized 3-D and 5-D versions have been used to fit to *ab initio* potential energy surfaces for:

$\text{He}-\text{CO}_2$  &  $\text{H}_2-\text{CO}_2$  [see **FB-01** re. superfluidity of  $\text{CO}_2-(\text{H}_2)_n$  clusters]

# Representing *ab initio* Potential Energy Surfaces

For atom-molecule & (small) molecule-molecule systems:

- use an MLR radial function for the  $\{\text{monomer}\} - \{\text{monomer}\}$  interaction
- with parameters  $\{\mathcal{D}_e, r_e, \beta_i\}$  depending on monomer-vibration and relative-orientation coordinates

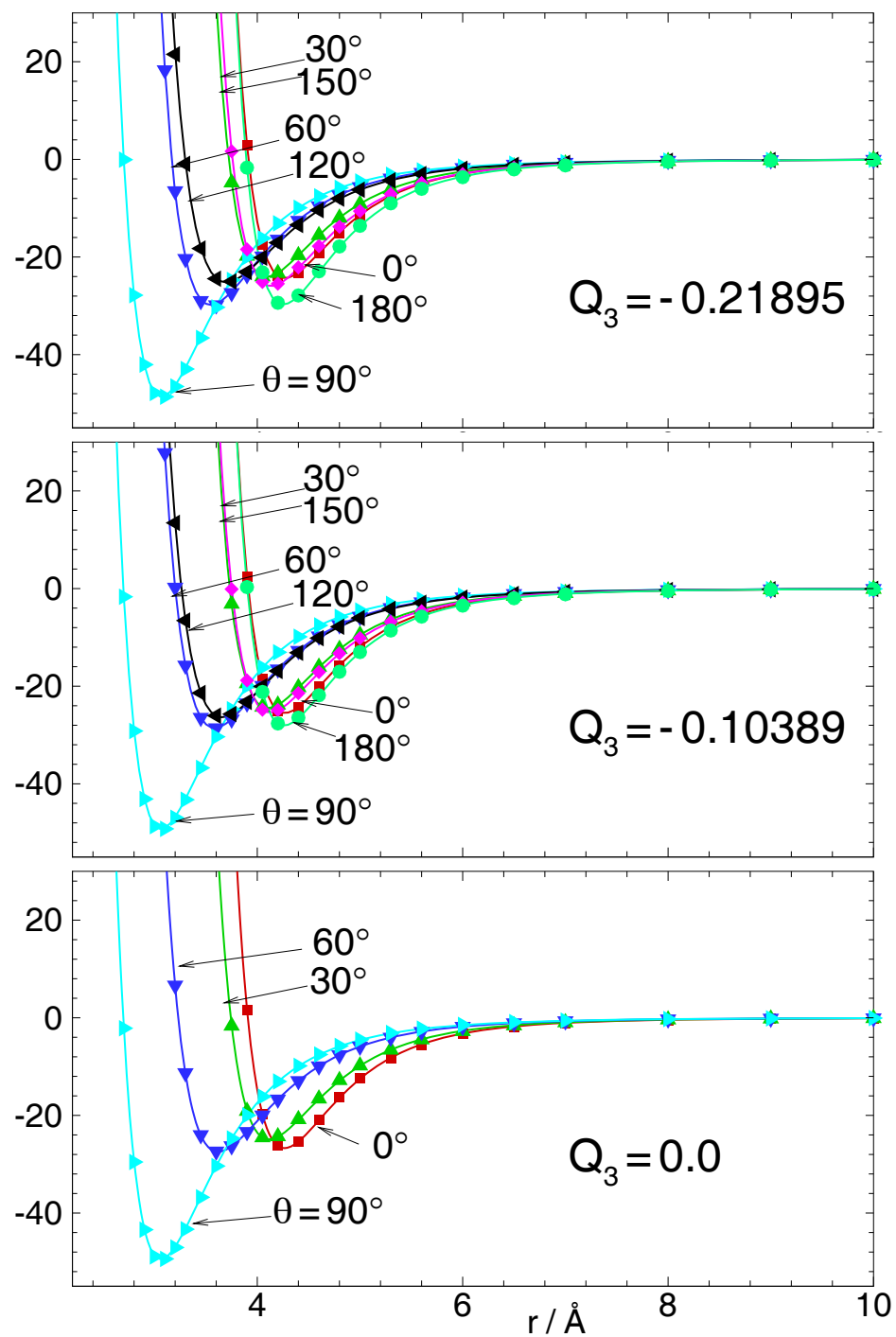
*e.g.*, potential for He–CO<sub>2</sub> depends on

- ⇒ monomer centre-of-mass separation  $r$
- ⇒ CO<sub>2</sub> axis orientation  $\theta$  relative to  $\vec{r}$
- ⇒ CO<sub>2</sub> asymmetric stretch coordinate  $Q_3$

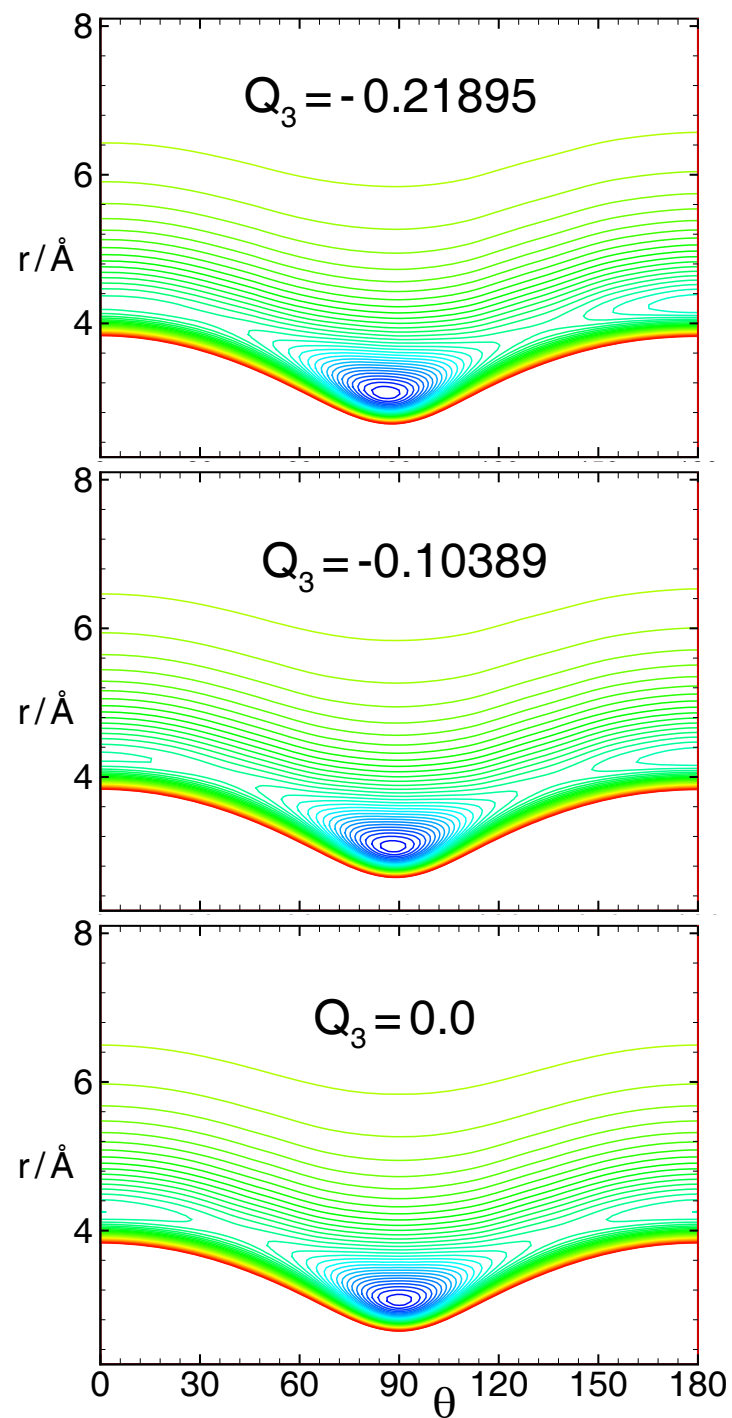
Calculated a 3-D potential surface consisting of 2832 points

- on the domain:  $r = 2.2 - 10 \text{ \AA}$ ,  $\theta = 0 - 180^\circ$ ,  $Q_3 \in [-0.22, +0.22]$
- supermolecule CCSD(T) calculations with full counterpoise correction
- used aug-cc-pVQZ basis supplemented by bond functions

Plot radial cuts through surface at selected  $\theta$  &  $Q_3$



2-D contour plots at selected  $Q_3$



Fit He–CO<sub>2</sub> *ab initio* points to generalized MLR function:

$$V_{\text{MLR}}(Q_3, \theta, r) = \mathfrak{D}_e(Q_3, \theta) \left[ 1 - \frac{u_{\text{LR}}(Q_3, \theta, r)}{u_{\text{LR}}(Q_3, \theta, r_e)} e^{-\beta(Q_3, \theta) \cdot y_p(r, r_e)} \right]^2$$

$$u_{\text{LR}}(Q_3, \theta, r) = \frac{C_6(Q_3, \theta)}{r^6} + \frac{C_8(Q_3, \theta)}{r^8}$$

where  $r_e = r_e(Q_3, \theta)$  and  $y_p(r, r_e) = \frac{r^p - r_e(Q_3, \theta)^p}{r^p + r_e(Q_3, \theta)^p}$

and expand:

$$\mathfrak{D}_e(Q_3, \theta) = \sum_{j=0} \sum_{\lambda=0} b_{j,\lambda} (Q_3)^j P_{\lambda}(\cos \theta)$$

$$r_e(Q_3, \theta) = \sum_{j=0} \sum_{\lambda=0} c_{j,\lambda} (Q_3)^j P_{\lambda}(\cos \theta)$$

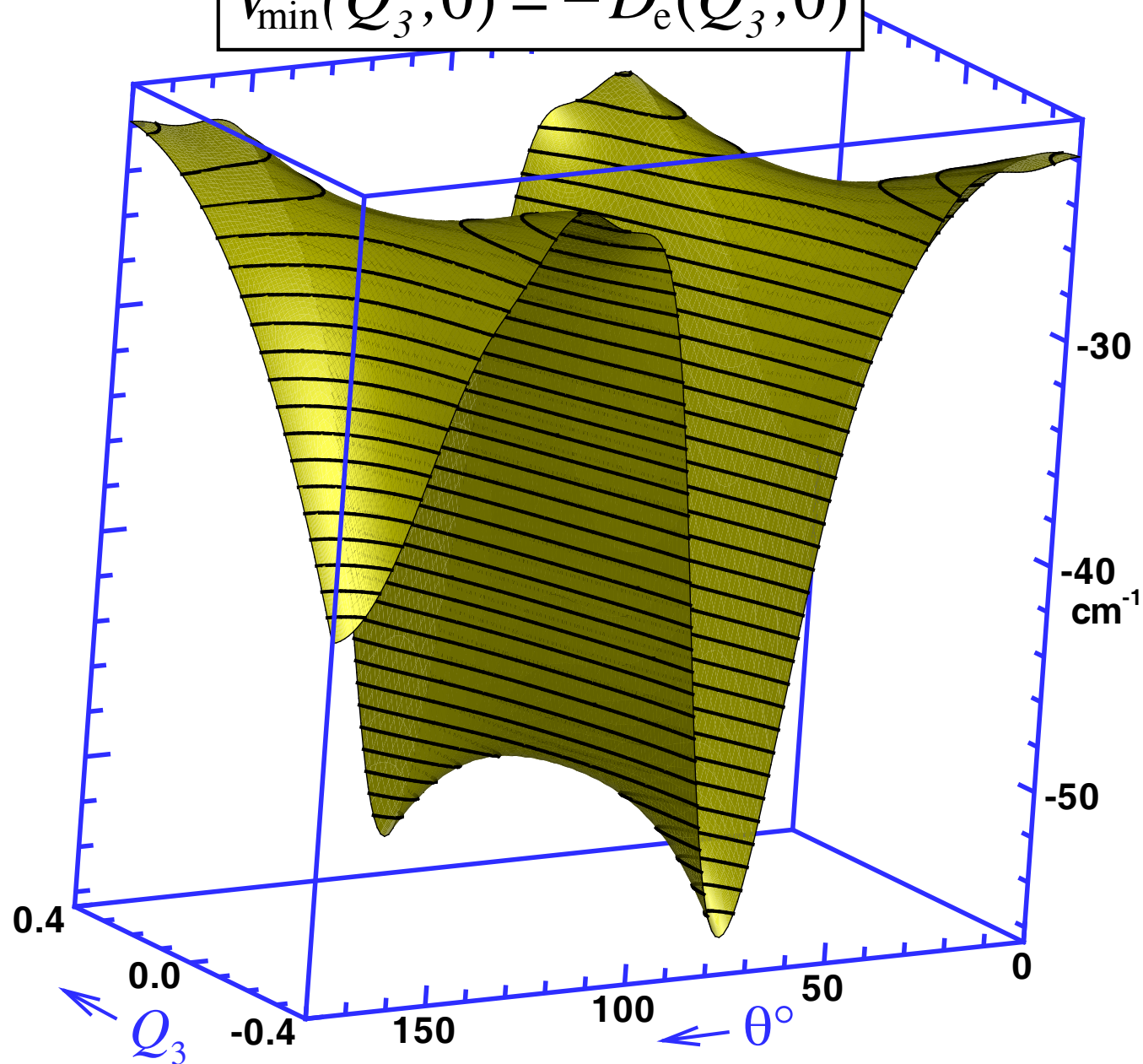
$$\beta_k(Q_3, \theta) = \sum_{j=0} \sum_{\lambda=0} d_{j,\lambda}^k (Q_3)^j P_{\lambda}(\cos \theta)$$

Fit of a 53 parameter function to 2175 points has standard error 0.034 cm<sup>-1</sup> [ 24 parameters for  $\mathfrak{D}_e$ , 13 for  $r_e$ , and 16 for  $\beta_0 - \beta_3$  ]

- eigenvalues of our *fitted surface* agree with those of a *3-D spline surface* to within (on average) 0.003 cm<sup>-1</sup>

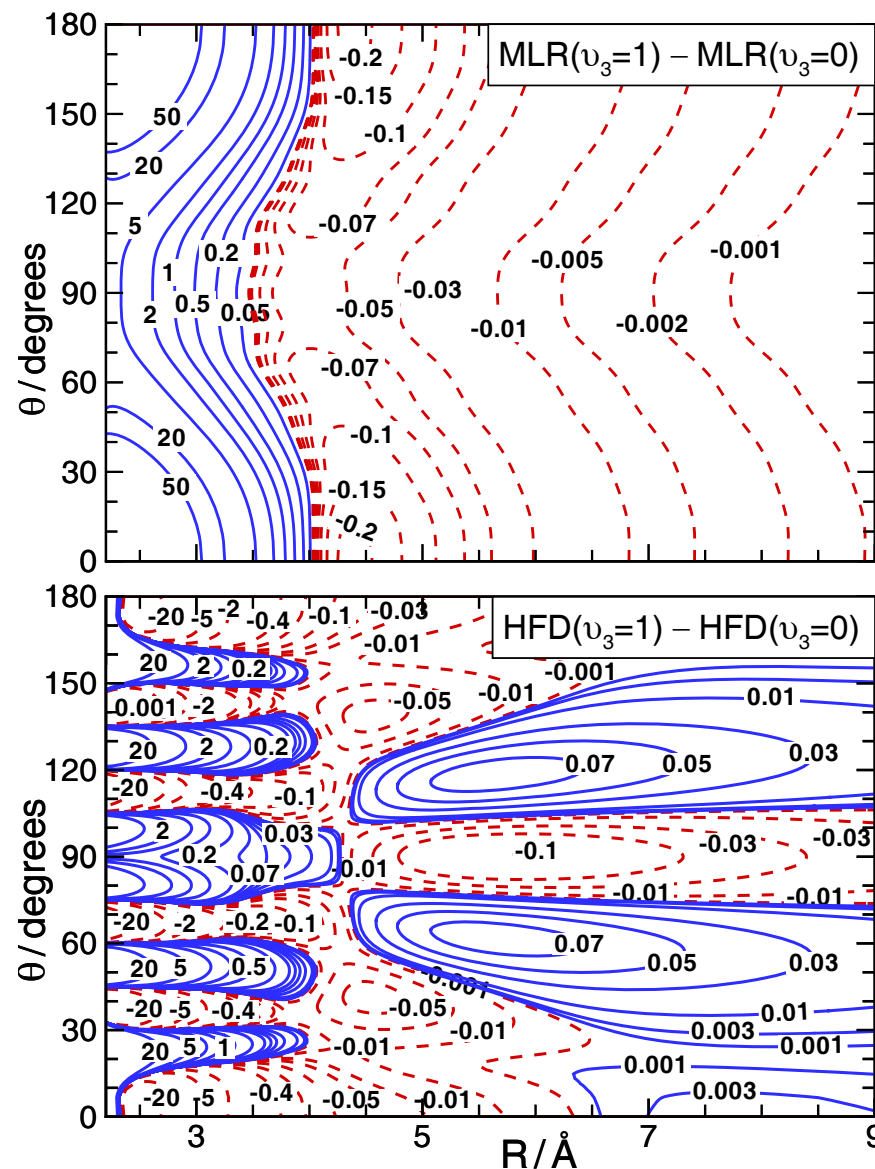
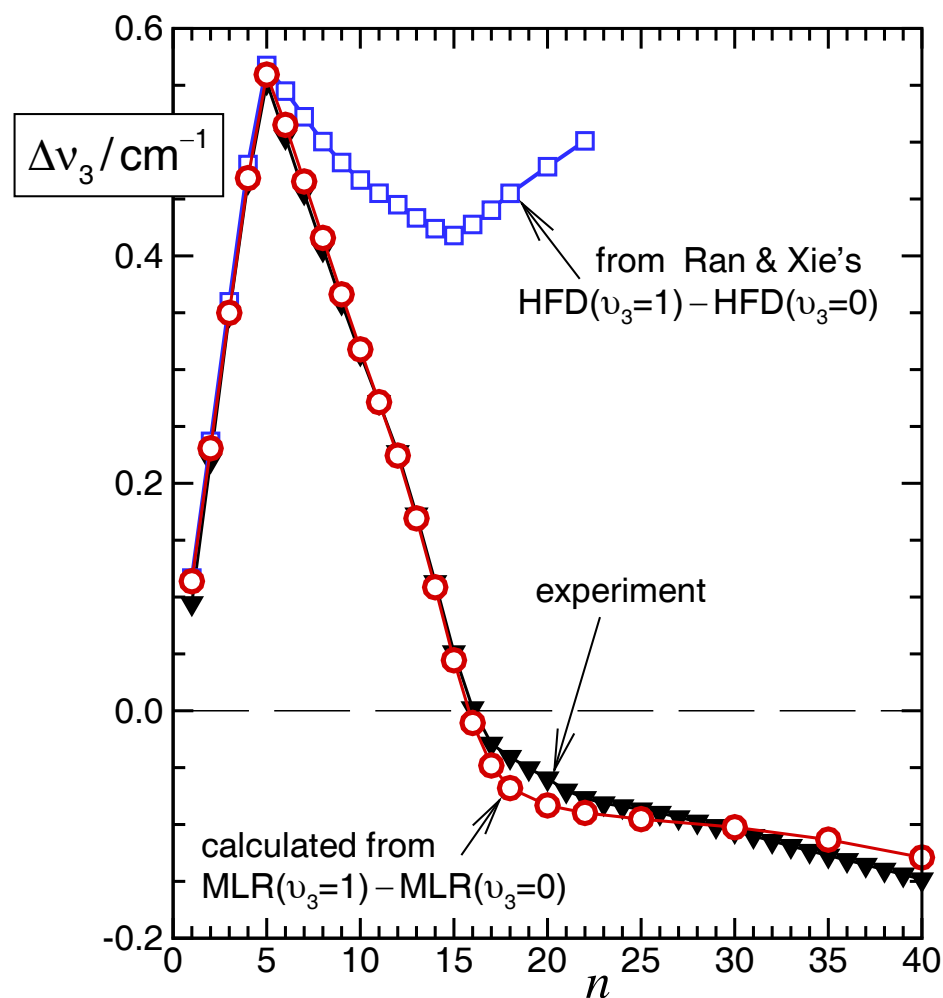
$$V_{\min}(Q_3, \theta) = -D_e(Q_3, \theta)$$

*Dependence of  
the well depth  $D_e$   
on  $Q_3$  and  $\theta$  is  
most dramatic!*



Vibrational frequency shifts for  $\text{CO}_2$  in  $(\text{He})_n$  clusters defined by difference between 2-D vibrationally averaged (over  $Q_3$ ) potentials for  $\text{He-CO}_2(v_3=1)$  and  $\text{He-CO}_2(v_3=0)$

*The quality of the 2-D functional form matters!*



## Conclusions

‘Direct Potential Fits’ are supplanting traditional  
‘parameter fits’ in spectroscopic data analysis

1. They provide as good or better (*and much more compact!*) representations of even very large spectroscopic data sets
2. They readily yield reliable predictions for missing observations within the data range
3. They provide *much more reliable* predictions for the ‘extrapolation region’ outside the data range
4. They can yield reliable equilibrium bond lengths  $r_e$ , bond dissociation energies  $\mathcal{D}_e$ , and long-range potential constants  $C_n$  as parameters of the fitted potential, and the resulting ‘global’ potential functions allow calculation of a host of spectroscopic and collisional properties.

*... but the quality of the result depends  
on the quality of the potential function form!*



## *Keys to successful ‘potentiology’*

- a dimensionless radial expansion variable with a finite range  
such as  $y_p(r) = \left( \frac{r^p - r_e^p}{r^p + r_e^p} \right)$  [J.F. Ogilvie (1981); A. Sürkus (1984)]
- fitting to a exponent coefficient is *much* more efficient than fitting to the function itself [J.A. Coxon (circa 1990)]
- incorporating limiting long-range behaviour *within* the potential model, rather than attaching it at some *ad hoc* point, allows for much more robust extrapolation
- careful selection of the radial expansion variable can yield
  - \* particularly compact (*few-parameter*) and
  - \* particularly robust (*extrapolating sensibly*) potentials, but  
“*mind your  $p$ ’s and  $q$ ’s – and take care with  $r_{\text{ref}}$* ”

## *The MLR radial function*

$$V_{\text{MLR}}(r) = \mathfrak{D}_e \left[ 1 - \frac{u_{\text{LR}}(r)}{u_{\text{LR}}(r_e)} e^{-\beta(r) \cdot y_p(r)} \right]^2$$

*is the best two-body potential function introduced to date!*



*Diatomic DPF analyses may be performed ‘routinely’ using*

**program DPotFit** (*‘Diatomic Potential Fits’*)

{ available with manual from <http://leroy.uwaterloo.ca/programs/> }

*which performs DPF fits to spectroscopic data and can:*

- simultaneously treat any combination of microwave, infrared, electronic, fluorescence series, tunneling level widths, & photo-association data
  - \* for one or multiple isotopologues
  - \* for one or multiple electronic states
- take account of atomic-mass dependent Born-Oppenheimer breakdown
- take account of  $\Lambda$ -doubling of singlet states or  $^2\Sigma$  splittings
- use “*sequential rounding and re-fitting*” to automatically yield fitted parameters with a minimum number of significant digits and no loss of precision in representing data
- use Watson’s “*robust*” data weighting technique to damp the effect of “outlier” observations which give anomalously large discrepancies with the model, and might unreasonably mislead a fit.
- use four types of potential forms: EMO, MLR, DELR, or polynomials.

## *The MLR radial function*

$$V_{\text{MLR}}(r) = \mathfrak{D}_e \left[ 1 - \frac{u_{\text{LR}}(r)}{u_{\text{LR}}(r_e)} e^{-\beta(r) \cdot y_p(r)} \right]^2$$

*is the best two-body potential function introduced to date!*

- \* able to accurately represent large, high precision data sets
- \* robust and ‘well behaved’ (no spurious extrapolation behaviour!)
- \* compact and ‘portable’, requiring a relatively ‘modest’ number of parameters
- \* incorporates correct theoretically known long-range behaviour in a natural way
- \* allows use of a variety of form for the long-range function  $u_{\text{LR}}(r)$
- \* continuous and smooth everywhere
- \* *compact and elegant!*

**Consider: full 3-D PES for BeH<sub>2</sub> as a function of coordinates:**

$$r_s = r_1(\text{BeH}) + r_1(\text{BeH})$$

$$r_d = r_2(\text{BeH}) - r_1(\text{BeH})$$

$$\theta = \cos^{-1}(\vec{r}_1 \cdot \vec{r}_2)$$

$$U(r_s, r_d, \theta) \equiv V(r_s, r_d, \theta) - V_{\text{H}_2}(r_{\text{H}_2})$$

