Direct-Potential-Fit (DPF) Analyses of Diatomic Data are Becoming "Routine"

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Objectives of Spectroscopic Data Reduction

1. To represent experimental data compactly within uncertainties.

   - *Should simultaneously treat all types of data (MW, IR, electronic), and data for all isotopologues and multiple connected electronic states in a single analysis.*

2. To be able to interpolate reliably for missing observations within the data range.

3. To provide realistic predictions in the 'extrapolation region' outside the data range.

   - *In effect, this presumes that the analysis provides a realistic global potential energy curve.*

4. To provide reliable estimates of physical interesting properties

   - e.g., r_e , $\mathfrak{D}_e$, *force constants, long-range potential coefficients*

   - *expectation values, matrix elements and transition intensities.*

     { Again, this presumes that the analysis yields a realistic global potential energy curve. }

   - *collisional and dilute (atomic) gas properties* (e.g., virial coefficients)

Conventional Approaches

Band Constant Fits

- Represent level energies using an independent set of band constants $\{G_v\,,\ B_v\,,\ -D_v\,,\ H_v\,,\ \ldots\ \}$ for each vibrational level of each isotopologue.

Problem: *no extrapolation ability or vibrational interpolation ability*!

Dunham-Type Fits

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

$$E^{(\alpha)}(v,J) = T_e^{(\alpha)} + \sum_{m=0}\sum_{l=0}{}' Y_{l,m}^{(\mathrm{ref})} \left(\frac{\mu_{\mathrm{ref}}}{\mu_\alpha}\right)^{m+l/2} (v+\tfrac{1}{2})^l\ [J(J+1)]^m$$

with Born-Oppenheimer breakdown corrections for minor isotopologues

$$\delta E_{\mathrm{BOB}}^{(\alpha)}(v,J) = \sum_{X=A,B} \frac{\Delta M_X^{(\alpha)}}{M_X^{(\alpha)}} \sum_{m=0}\sum_{l=0}{}' \delta_{l,m}^X \left(\frac{\mu_{\mathrm{ref}}}{\mu_\alpha}\right)^{m+l/2} (v+\tfrac{1}{2})^l\ [J(J+1)]^m$$

Problems: • *very limited extrapolation ability*

- the RKR method can generate a potential from the fitted $\{Y_{l,0}\}$ and $\{Y_{l,1}\}$ constants, *but* it is based on the first-order semiclassical approximation, which *has limited accuracy* for small-reduced-mass systems, &
- *point-wise potentials are inconvenient to work with*

Direct Potential Fits

- Simulate level energies as numerically (or algebraically) determined eigenvalues of some parameterized analytic potential energy function $V(r;\{p_j\})$.

- Partial derivatives of observables w.r.t. parameters p_j required for fitting are generated readily by the Hellmann-Feynmann theorem:

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

- Compare with experiment and iterate the least-squares fit to convergence.

Advantages

- satisfies all four 'objectives of spectroscopic data reduction'!
- full quantum mechanical accuracy
- readily takes account of Born-Oppenheimer breakdown (BOB), Λ-doubling, and/or $^2\Sigma$ splittings, in terms of radial strength functions

Challenge

- to develop flexible potential function forms which
  - ∗ are robust and 'well behaved' (no spurious behaviour in extrapolation regions)
  - ∗ can incorporate physical constraints and limiting limiting behaviour

Program `DPotFit` (*'Diatomic Potential Fits'*)

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

performs direct potential fits to spectroscopic data and can :

- simultaneously treat any combination of microwave, infrared, electronic, fluorescence series & photo-association data
- for one or multiple isotopologues
- for one or multiple electronic states
- taking account of atomic-mass dependent Born-Oppenheimer breakdown effects
- taking account of Λ-doubling of singlet states or $^2\Sigma$ splittings
- can use "*sequential rounding and refitting*" to automatically yield fitted parameters with a minimum number of significant digits and no loss of precision in representing data
- and can 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.

Potential Function Forms

Polynomial expansion $V(r) = c_0\,\xi^2\left(1 + \sum_{i=1} c_i\,\xi^i\right)$ in radial variable

- Dunham $\xi_{\rm D} = \dfrac{r - r_e}{r_e}$
- Ogilvie-Tipping $\xi_{\rm OT} = \dfrac{r - r_e}{r + r_e}$
- Simons-Parr-Finlan $\xi_{\rm SPF} = \dfrac{r - r_e}{r}$
- Šurkus ('GPEF') $\xi_{\rm Sur} = \dfrac{r^p - {r_e}^p}{a_S\,r^p + b_S\,{r_e}^p}$

Global Analytic Function such as

Expanded Morse oscillator (EMO):

$$V_{\rm EMO}(r) \;=\; \mathfrak{D}_e\left[1 - e^{-\phi(r)\,(r-r_e)}\right]^2$$

in which $\phi(r) = \phi_{\rm EMO}(r) = \sum_{i=0} \phi_i\; y_p(r)^i$ and $y_p(r) = \dfrac{r^p - {r_e}^p}{r^p + {r_e}^p}$

Morse/Lennard-Jones oscillator (MLJ):

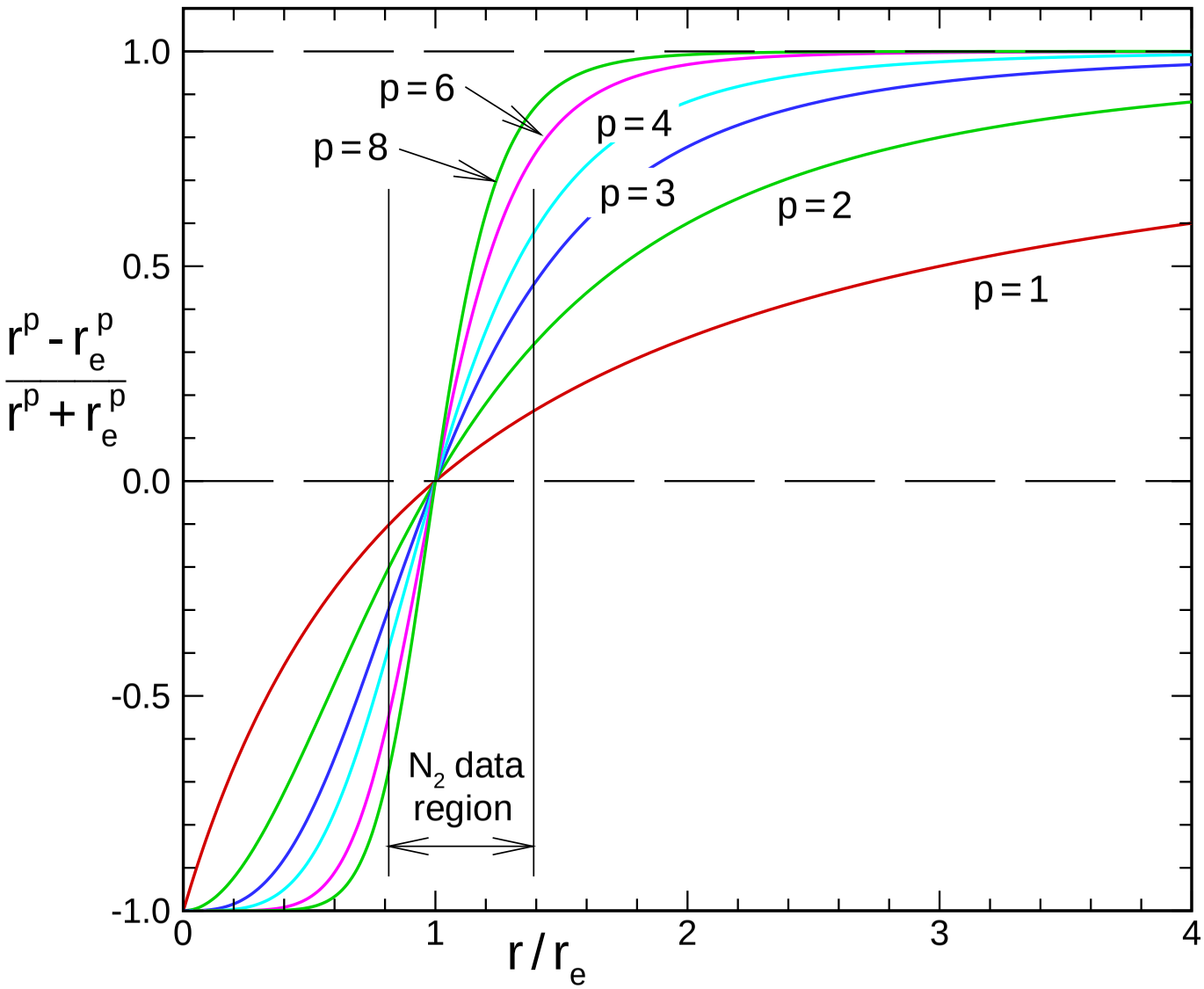
$$V_{\rm MLJ}(r) \;=\; \mathfrak{D}_e\left[1 - \left(\frac{r_e}{r}\right)^n e^{-\phi(r)\,(r-r_e)}\right]^2 \;\xrightarrow{r \gg r_e}\; \mathfrak{D}_e \;-\; \frac{\left[2\,\mathfrak{D}_e(r_e)^n\,e^{\phi_\infty}\right]}{r^n}$$

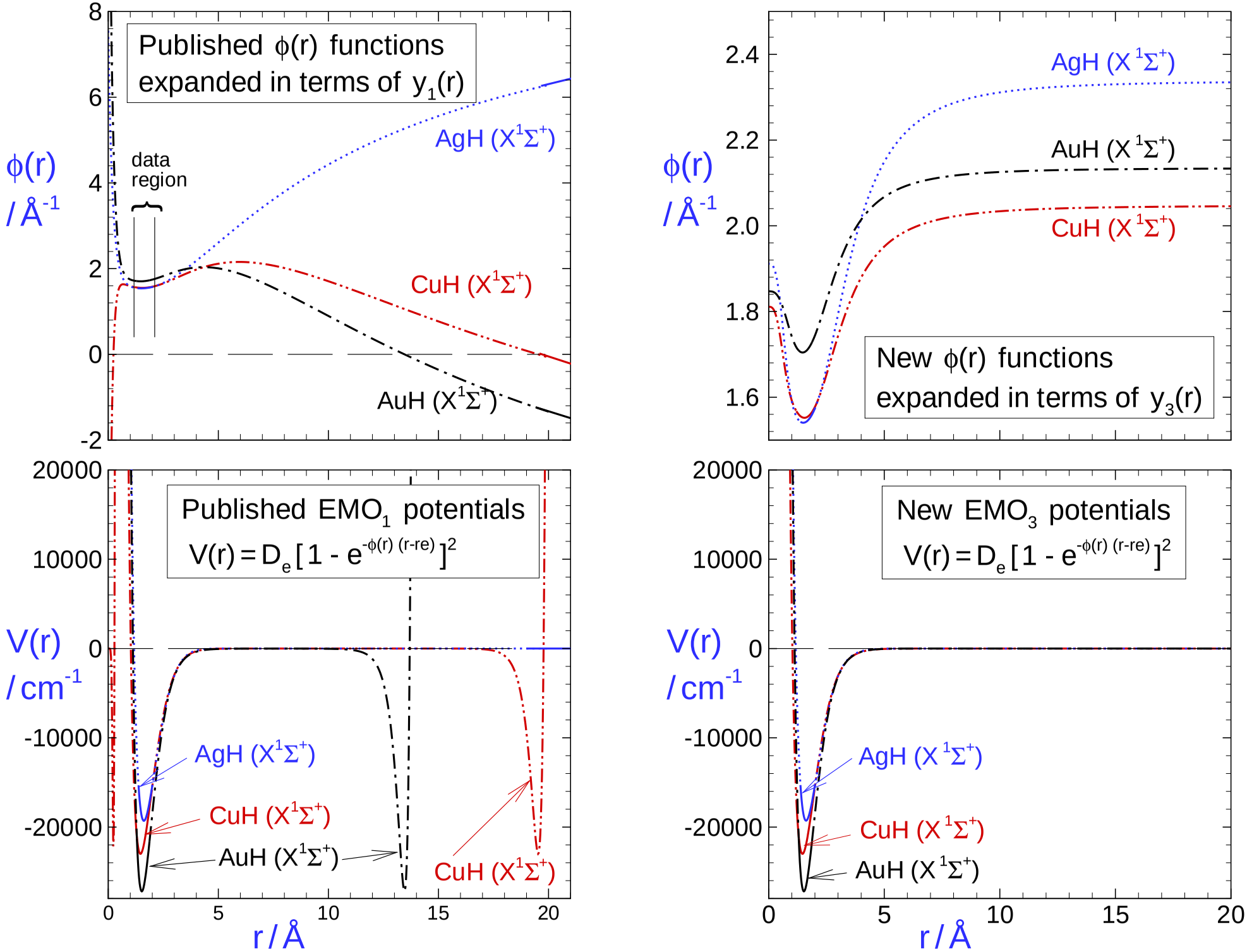
in which $\phi(r) = \phi_{\rm MLJ}(r) = \phi_\infty\; y_p(r) + [1 - y_p(r)]\,\sum_{i=0} \phi_i\; y_p(r)^i$

and $\phi_\infty \equiv \phi(r = \infty)$ with $y_p(r)$ defined as above.

The power p in the expansion variable $y_p(r)$ is very important!

- for p *too small*, most of the domain of $y_p(r)$ is outside the region where the polynomial in $y_p(r)$ is determined, so polynomial 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.




Published ϕ(r) functions expanded in terms of y1(r)
ϕ(r) / Å-1
data region
AgH (X1Σ+)
CuH (X1Σ+)
AuH (X1Σ+)
New ϕ(r) functions expanded in terms of y3(r)
Published EMO1 potentials
V(r) = De [1 - e-ϕ(r) (r-re)]2
V(r) / cm-1
New EMO3 potentials
r / Å

Application to Ground-State N_2

Fit the best available data

[669 Raman data, 37 quadrupole, 525 electronic]

for all three isotopologues

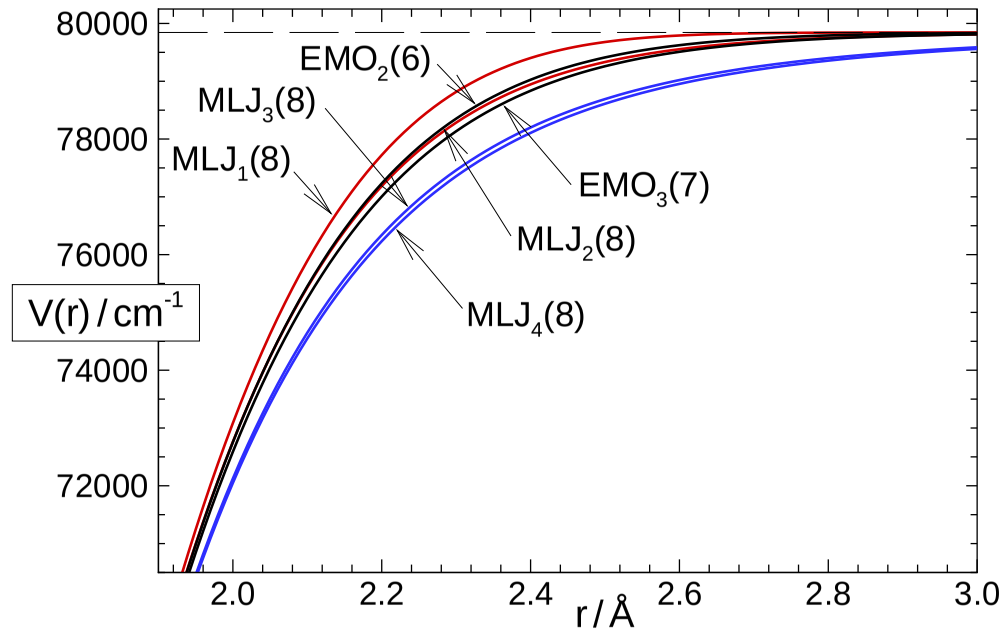
[861 $^{14,14}N_2$ data, 115 for $^{14,15}N_2$ & 245 for $^{15,15}N_2$]

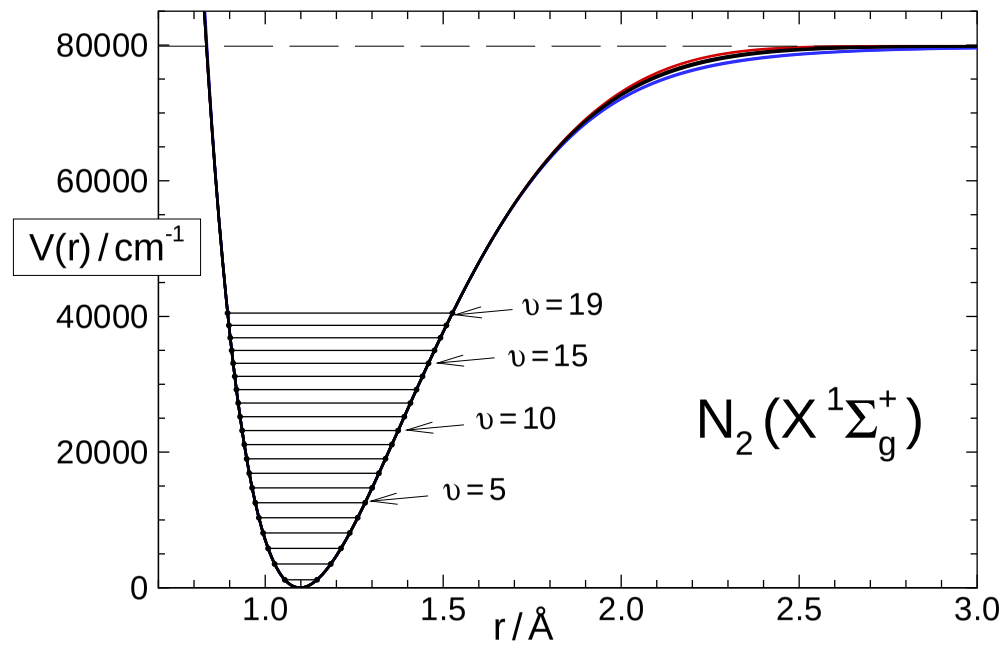
to EMO and MLJ model potentials

for various values of p

RMS error $\overline{dd}$ for fits using various potential models.

exponent order :		4	5	6	7	8
EMO	$p = 1$	3.58	1.48	1.43	1.43	1.42
	$p = 2$	6.00	1.44	**1.43**	1.43	1.42
	$p = 3$	11.0	2.30	1.45	**1.44**	1.42
	$p = 4$	24.5	5.47	1.70	1.56	1.41
	$p = 5$	48.1	12.1	3.62	2.41	1.45
MLJ	$p = 1$	14.2	1.46	1.43	1.43	**1.42**
	$p = 2$	41.9	3.64	1.59	1.45	**1.42**
	$p = 3$	20.4	6.62	3.18	1.74	**1.43**
	$p = 4$	—	26.3	6.97	1.58	**1.42**
	$p = 5$	—	—	—	29.7	11.6





Behaviour of these N_2 potentials outside the 'data region'

A. At long range

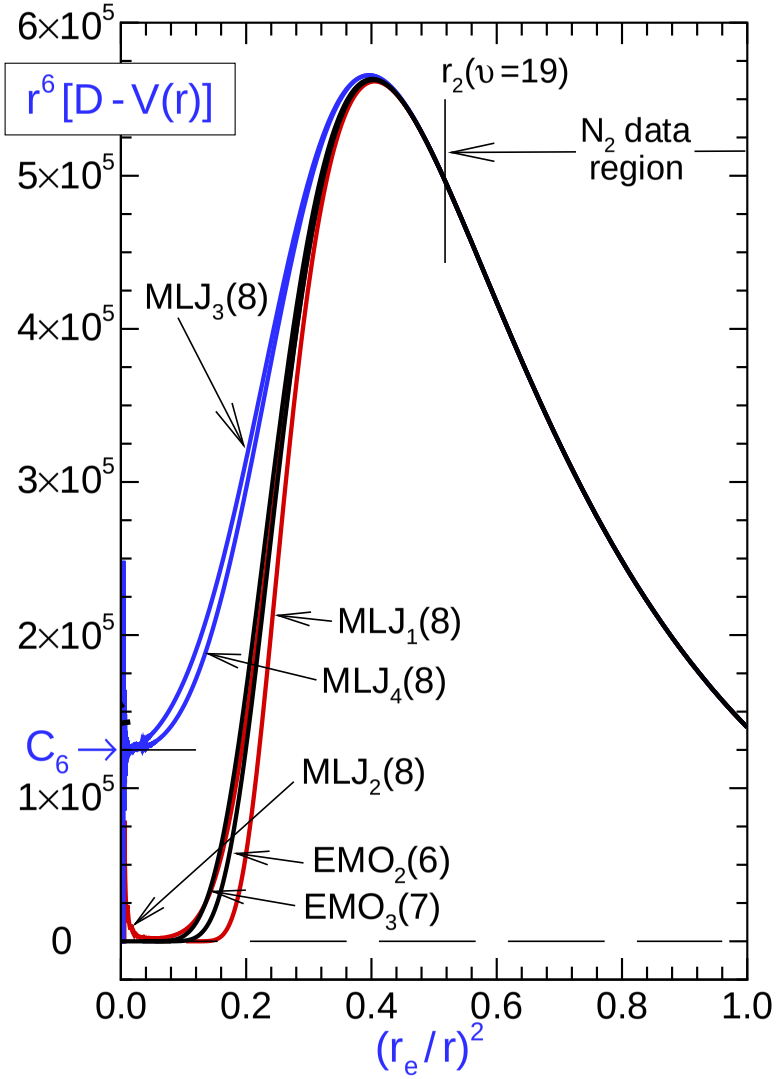
$$V(r) \simeq \mathfrak{D} - \frac{C_6}{r^6} - \frac{C_8}{r^8} - \frac{C_{10}}{r^{10}} + \ \ldots$$

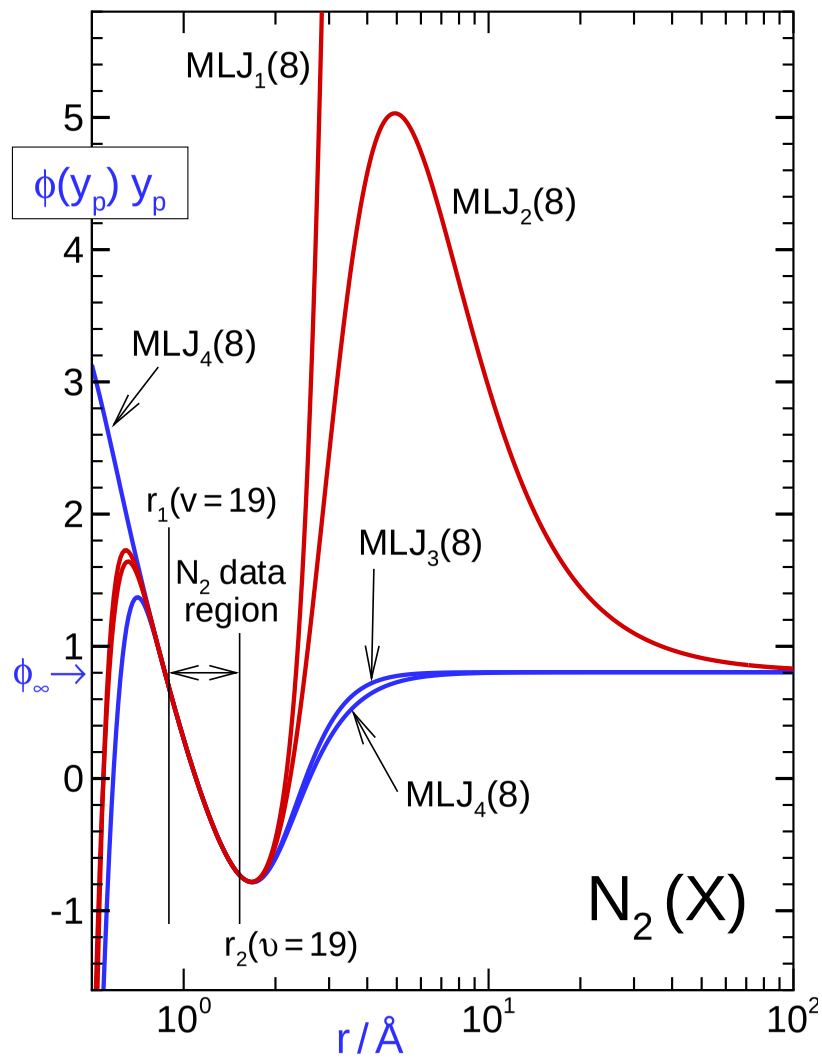
so $\quad r^6\,[\mathfrak{D} - V(r)] \xrightarrow{r\to\infty} C_6$

B. This means that as $r \to \infty$,

the MLJ exponent $\to \phi_\infty = \ln\left\{2, \mathfrak{D}_e(r_e^6)/C_6\right\}$.

Cases $p=1$ & 2 extrapolate implausibly !





Comparing with Experiment

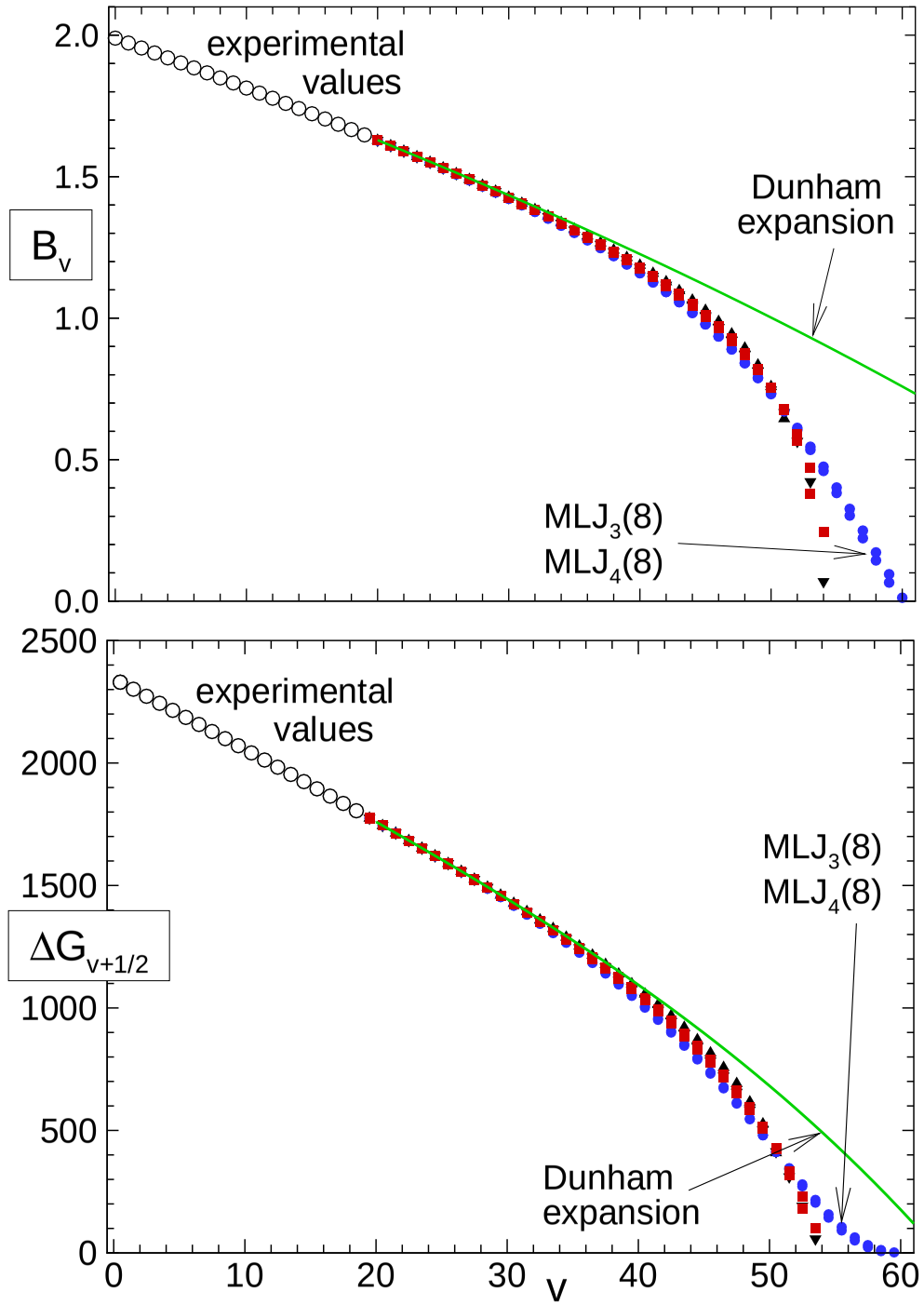
Although $\mathrm{MLJ}_4(8,8)$ model is preferred,

all 6 fitted potentials give very

similar predictions up to $v \approx 50$.

This approximate model independence attests

to the reliability of the predictions.



Program `DPotFit` (*'Diatomic Potential Fits'*)

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

performs direct potential fits to spectroscopic data, ***but***

it requires as input a realistic set of initial trial parameters !

Fortunately, they can readily be generated using

Program `phiFIT`

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

which can fit any of the polynomial, EMO or MLJ forms discussed here

[plus an additional form, the "double-exponential/long-range" (DELR) model]

to some set of approximate initial trial potential function values generated from

- an RKR calculation using Dunham $\{Y_{l,0}\}$ and $\{Y_{l,1}\}$ from a 'parameter-fit' analysis
- *ab initio* calculations
- guesswork !

Thus, direct potential fitting of the type described here may now be considered to be a "routinely" tool in a spectroscopists' toolkit.