MODEL DISCRIMINATION FOR ROTATIONAL ENERGY TRANSFER IN THE Ar–N_2 SYSTEM

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The jackknife test of Rothstein et al. is applied to discrimination between several different models used to compute the rotationally inelastic cross sections for the Ar–N_2 system. The modified exponential models are the best models, except for the case where the energy gap is small, when power laws are best.

1. Introduction

Various calculations have produced accurate numerical values for state-to-state collisional rotational energy transfer [1,2]. These results show the well-known trends first noticed by Polanyi and Woodall [3] and gave rise to an exponential rotational energy gap model and the linear surprisal relations [4]. However, the data are not well reproduced by the exponential gap law alone with a different empirical fit being required for each total energy E and each initial j value. This model is

$$\sigma_{j'j}(E) = C(E)\, N_\Delta\, (E'_T/E_T)^{1/2}\, \exp(-\theta_R |\Delta g|), \quad (1)$$

where $\Delta g = (E_{j'} - E_j)/E, E_T = E - E_j, N_\Delta = 2j' + 1, \theta_R$ and $C(E)$ are adjustable parameters.

In 1977, Sanctuary [5,6] proposed a modified exponential model (MEM) which with three parameters, fits the data of ref. [2] for all initial j and all E. Also a restricted exponential model (RMEM) was proposed which is the same as the MEM except that all initial j were fitted with a different parameter for each E. This model is

$$\sigma_{j'j}(E) = \frac{N_\Delta\, [C(E)]^{-(1+\gamma)}}{E_T\, |E_{j'} - E_j|^\gamma} \exp[-r_0 \theta_{j'j}(E) |\Delta g|], \quad (2)$$

where $r_0, C(E)$ and γ are adjustable parameters and

$$\theta_{j'j}(E) = 2\pi(2\mu E/\hbar^2)^{1/2} \times [(1 - E_j/E)^{1/2} + (1 - E_{j'}/E)^{1/2}]^{-1}. \quad (3)$$

In 1979, Pritchard et al. [7] presented a power law model which is

$$\sigma_{j'j}(E) = N(E'_T/E_T)^{1/2} a/|E_{j'} - E_j|^\gamma, \quad (4)$$

where N is N_Δ or $N_0 = (2j_< + 1)/(2j + 1)$, where $j_<$ is the lesser of j' and j. The constants a and γ are adjustable parameters.

Eqs. (1), (2), and (4) represent three models called, respectively: the linear surprisal model (LSR), the modified exponential models (MEM and RMEM) and the power law model (PL). The MEM and the PL appear to give better fits to the data than the LSR. However, in the fitting the MEM and RMEM, statistical uncertainties in the Pattengill data were not included. Moreover, the PL fits the data for $|\Delta g| \lesssim 0.2$. The purpose of this letter is to present results for re-optimization of the models and to compare the ability of the various models to reproduce the data. The comparison is based upon the jackknife statistical test which is described in section 2. We have chosen the Ar–N_2 system for which state-to-state cross sections may be computed from two available potentials: PLBC

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(Pattengill, LaBudde, Bernstein, and Curtiss) [8], and KdV (Kistemaker and de Vries) [9].

2. Statistical analysis

Consider a set of N calculated cross sections for each of two models M = I and II. We are concerned with the quality of fit of the model values (σ_k^M) and "observed" values (σ_k^0) for the cross sections. A measure of the goodness of the fit is

$$\Delta_k^M = w_k^{1/2}(\sigma_k^M - \sigma_k^0) \tag{5}$$

for each model, where the index k denotes the kth member of the set of σ_{jj}^M values. The weight is given by the observed variance,

$$w_k^{-1} = \mathrm{var}(\sigma_k^0). \tag{6}$$

An appropriate mathematical model is to view the set of Δ^M values for the two models as N randomly selected values drawn from an unknown bivariate distribution function with variance–covariance matrix given by

$$\Sigma \equiv \begin{pmatrix} \sigma_{\mathrm{I}}^2 & \sigma_{\mathrm{I,II}} \\ \sigma_{\mathrm{I,II}} & \sigma_{\mathrm{II}}^2 \end{pmatrix}. \tag{7}$$

Note that the σ in (7) are variances and not the cross sections. In other words, we assume that $\sigma_{\mathrm{I}}^2 = \mathrm{var}(\Delta_1^{\mathrm{I}}) = \mathrm{var}(\Delta_2^{\mathrm{I}}) = \ldots$ and $\sigma_{\mathrm{II}}^2 = \mathrm{var}(\Delta_1^{\mathrm{II}}) = \mathrm{var}(\Delta_2^{\mathrm{II}}) = \ldots$ and the covariance is $\sigma_{\mathrm{I,II}}$. The quantity of interest is the unknown ratio of variances for the two models,

$$\tilde{\gamma}^2 = \sigma_{\mathrm{I}}^2/\sigma_{\mathrm{II}}^2. \tag{8}$$

Recently, Rothstein and co-workers [10,11] published a jackknife significance test on $\tilde{\gamma}^2$ with special application to problems in crystallography and structure elucidation using lanthanide shift reagent data [12,13]. This same procedure is applicable to the problem at hand, and the fundamental equations are given by (7)–(20) in ref. [10].

A limitation of the jackknife test is that it cannot take into account differences in the number of parameters in the two models. Thus, we expect to reject II relative to I if II has fewer parameters, but a rejection of I rather than II is unexpected and therefore of interest.

The classical statistical procedures for testing a variance ratio (e.g. the F test) are not applicable. Given the reasonable assumption that models I and II give similar σ^M values, there will be significant covariance ($\sigma_{\mathrm{I,II}}$) for the bivariate distribution (Δ^{I}, Δ^{II}), and thus the "sum of squares" for model I, the "weighted R factor",

$$R_{\mathrm{I}}^2 = \left[\sum_k (\Delta_k^{\mathrm{I}})^2\right]\left[\sum_k w_k(\sigma_k^0)^2\right]^{-1}, \tag{9}$$

is not independently distributed with respect to R_{II}^2. Another significant drawback of classical procedures (e.g. the reduced χ^2 test [7]) is the assumption of bivariate normality. A recently completed Monte Carlo simulation [14] using the jackknife test shows that results are not sensitive to departures from normality and non-zero covariance. The test also shows good "power" properties, which means that it does not tend to accept the null hypothesis under test when it is actually false.

3. Calculations and results

The information theoretic ("linear surprisal") models are LSRS with a pair of parameters for *all j* for a *given E*, and LSRL with a pair for *each j* for a *given E*. Sanctuary's models, denoted MEM and RMEM, have four parameters for *all j* and *all E*, and three parameters for *all j* and a *given E*, respectively. The power law models are PLS and PLL; the former has two parameters for *all j* for a *given E*, and the latter has two for *each j* for *each E*. (We arbitrarily choose to report power law results using N_Δ rather than N_0, having found no difference between them.)

As it is important to consider these models on an equal basis, we re-optimized the parameters for the models, minimizing R^2, (9), being careful to take into account the uncertainties in σ_k^0. The re-optimized parameters appear in table 1.

Given σ_k^0 and σ_k^M for each model, the weighted R factors, R^2, (9), and jackknife statistics Q' ((20) in ref. [10]) are computed. Now, Q' is compared with the upper tail probability for the standard normal distribution z_α, where α is the (nominal) significance level. (The significance level is the probability under the null hypothesis ($\sigma_{\mathrm{I}}^2 = \sigma_{\mathrm{II}}^2$) that an outcome might have occurred which is more extreme than the actual outcome.) The value of z is 1.28 for $\alpha = 0.10$. Thus, a value of Q' greater than or equal to 1.28 occurs with a

Table 1
Optimized parameters for various models

$E(K)$	j	Model [a]									
		LSR [b]		RMEM					MEM [c]	PL [d]	
		$C(E)$ (Å^2)	θ_R	$10^3\,C(E)$	γ		$10^2\,r_0$ (Å)		$10^3\,C(E)$	a (Å^2)	γ
	surface KdV										
768	0	2.20 (3.28)	5.63 (10.8)	– –	– –		– –		– –	(17.6)	(0.723)
	6	1.66 (1.39)	5.90 (4.12)	– –	– –		– –		– –	(6.62)	(0.497)
	10	1.13 –	5.07 –	– –	– –		– –		– –	–	–
	0,6,10	1 67 (3.14)	5.99 (11 2)	3.14 (3.91)	0.658 (0.800)		4 60 (0.700)		3.42 (2.88)	(18.3) [e]	(0.743) [e]
1535	0	1.21 (2.30)	7.26 (16.9)	– –	– –		– –		– –	(14.6)	(0.745)
	10	0.892 (0.859)	7.76 (7.42)	– –	– –		– –		– –	(26.5)	(0.905)
	16	0.568 –	7.74 –	– –	– –		– –		– –	–	–
	0,10,16	1.05 (1.80)	9.87 (14.1)	2.66 (2.76)	0.723 (0.753)		5.06 (2.66)		3.16 (2.30)	(17.3) [e]	(0.807) [e]
3070	0	0.704 (0.905)	9.52 (13.5)	– –	– –		– –		– –	(13.2)	(0.783)
	10	0.446 (0.584)	8.20 (12.1)	– –	– –		– –		– –	(20.4)	(0.898)
	22	0.231 (0.329)	7.58 (10.8)	– –	– –		– –		– –	(117)	(1.36)
	0,10,22	0.438 (0.837)	9.82 (18.1)	2.74 (1.76)	0.915 (0.666)		2.57 (7.00)		2.25 (2.31)	(23.4)	(0.963)
12280	0	0.147 (0.233)	11.7 (19.4)	– –	– –		– –		– –	(13.4)	(0.887)
	10	0.155 (0.181)	11.8 (15.0)	– –	– –		– –		– –	(11.9)	(0.870)
	0,10	0.152 (0.198)	11.9 (16.5)	1.35 (1.45)	0.820 (0.876)		0.818 (0.271)		0.975 (0.989)	(13.0)	(0.884)
	surface PLBC										
768	0	3.22 (3.40)	8.34 (9.25)	– –	– –		– –		– –	(15.0)	(0.640)
	6	1.72 (1.68)	6.71 (6.44)	– –	– –		– –		– –	(18.9)	(0.771)
	10	1.67 –	7.26 –	– –	– –		– –		– –	–	–
	0,6,10	2.32 (3.31)	8.28 (11.5)	2.51 (3.34)	0.577 (0.726)		6.78 (2.94)		3.54 (2.87)	(19.8) [e]	(0.757) [e]
1535	0	1.74 (3.25)	10.9 (15.2)	– –	– –		– –		– –	(15.8)	(0.739)
	10	0.866 (0.728)	8.64 (7.06)	– –	– –		– –		– –	(19.7)	(0.869)
	16	0.844 –	10.4 –	– –	– –		– –		– –	–	–
	0,10,16	1.25 (2.50)	11.7 (12.4)	2.20 (2.69)	0.643 (0.763)		6.97 (3.59)		3.42 (2.39)	(23.5) [e]	(0.884) [e]
3070	0	0.988 (1.03)	14.5 (15.4)	– –	– –		– –		– –	(15.1)	(0.801)
	10	0.535 (0 585)	11.0 (12.3)	– –	– –		– –		– –	(26.6)	(0.961)
	22	0.389 (0.466)	11.3 (13.2)	– –	– –		– –		– –	(588)	(1.59)
	0,10,22	0.705 (0.859)	14.3 (17.2)	2.09 (1.84)	0.779 (0.712)		4.58 (5.95)		2.17 (2.14)	(27.0)	(0.985)
12280	0	0.274 (0.275)	20.7 (20.7)	– –	– –		– –		– –	(15.6)	(0.909)
	10	0.225 (0.229)	19.2 (19.7)	– –	– –		– –		– –	(21.1)	(0.979)
	0,10	0.244 (0.246)	19.7 (20.0)	1.22 (1.25)	0.777 (0.797)		1.85 (1.57)		0.956 (0.957)	(17.1)	(0.935)

a) Values in parentheses pertain to $|\Delta g| \leq 0.2$.
b) Where several j values are listed, the parameters belong to the LSRS model; otherwise they belong to LSRL.
c) $r_0 = 0.035$ Å, $\gamma = 0.6$. d) Where several j values are listed the parameters belong to PLS model; otherwise they belong to PLL.
e) Only the first two j values are considered.

Table 2
Level of significance (α) above which the null hypothesis $\tilde{\gamma}^2 = 1$ can be rejected

	Model [a]			
	LSRL(22)	RMEM(12)	LSRS(8)	MEM(4)
surface KdV				
LSRL	–	0.3435	$<10^{-5}$	0.0078
RMEM	–	–	0.0274	$<10^{-3}$
LSRS	–	–	–	0.3811
R^2 [b]	0 3216	0 3409	0.4073	0.4181
surface PLBC				
LSRL	–	0.4296	$<10^{-4}$	0.0526
RMEM	–	–	0.0547	$<10^{-4}$
LSRS	–	–	–	0.1054
R^2 [b]	0.2698	0 2826	0.3450	0.3984

[a] Parentheses denote the number of parameters in the model.
[b] Eq. (9).

probability equal to 0.10 due to chance when the null hypothesis is in fact true. If in the application of the jackknife test we compute $Q' \geqslant 1.28$ from our data, and we are willing to accept the risk of being wrong 10% of the time, we would reject the null hypothesis and accept the alternative hypothesis (i.e. $\sigma_{\mathrm{I}}^2 > \sigma_{\mathrm{II}}^2$). This is a ground for "rejecting" model I relative to model II at the $\alpha = 0.10$ level of significance, because model I has a larger dispersion.

Levels of significance above which the null hypothesis $\sigma_{\mathrm{I}}^2 = \sigma_{\mathrm{II}}^2$ can be rejected in the comparison of each pair of models are displayed in tables 2 and 3.

The results in table 2 reveal that there is no significant difference between LSRL and RMEM or between LSRS and MEM. As the modified exponential models have fewer parameters than the information theoretic models, we may conclude that RMEM and MEM are the best many-parameter and few-parameter models, respectively, for the Ar–N_2 system.

The results in table 3 pertain to a small energy gap, where the power law models are valid. For this case, PLL is significantly better than all the other models, and PLS is the next best model. It is clear that PLS

Table 3
Level of significance (α) above which the null hypothesis $\tilde{\gamma}^2 = 1$ can be rejected, where $|\Delta g| \leqslant 0.2$

	Model [a]					
	$PLL_\Delta(18)$	$PLS_\Delta(8)$	RMEM(12)	LSRL(18)	MEM(4)	LSRS(8)
surface KdV						
PLL_Δ	–	0.0083	$<10^{-4}$	$<10^{-4}$	$<10^{-12}$	$<10^{-8}$
PLS_Δ	–	–	0.0025	0.0017	$<10^{-9}$	$<10^{-6}$
RMEM	–	–	–	0.1363	0.0033	0.0032
LSRL	–	–	–	–	0.2719	0.0059
MEM	–	–	–	–	–	0.1935
R^2 [b]	0.1060	0.1611	0.2210	0.2771	0.3078	0.3362
surface PLBC						
PLL_Δ	–	$<10^{-5}$	$<10^{-5}$	$<10^{-3}$	$<10^{-8}$	$<10^{-7}$
PLS_Δ	–	–	0.0787	0.0733	$<10^{-4}$	0.0021
RMEM	–	–	–	0.2167	0.0043	0.0142
LSRL	–	–	–	–	0.2795	0.0049
MEM	–	–	–	–	–	0.2065
R^2 [b]	0.1230	0.1981	0.2300	0.2668	0.3018	0.3281

[a] Parentheses denote the number of parameters in the model. [b] Eq. (9).

is a good model, as it has only a small number of parameters. Our methodology does not allow us to determine whether PLL is better than PLS merely because it has more parameters. (Hamilton's test [15] on the R factor may take into account the different number of parameters in competing models, but the models must be at least locally linear in the parameters.)

We conclude that the modified exponential models are better than the information theoretic models, except for the case of a small energy gap, where the power law models are best.

Finally, it is clear that in the limit of small Δg, the modified exponential and power law models become equivalent if the same data set is used. In fact, the RMEM and MEM have been fitted to a considerably larger data set than that of the PL models. Moreover, the parameter r_0 has negligible effect for small Δg.

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