ENERGY DEPENDENCE OF ROTATIONAL CROSS SECTIONS

B.C. SANCTUARY
Department of Chemistry, McGill University, Montreal, Quebec J3A 2K6, Canada

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A modified exponential model for rotational state-to-state cross sections is proposed which accounts for most of the observed features for Ar–N_2 at large $|\Delta j|$ and large total energy E. This empirical form gives rise to non-linear surprisals, and suggests that the prior transition probability, usually taken as a constant, is proportional to E^{-1}.

1. Introduction

Inelastic collision processes, which lead to energy transfer between molecules, have been studied both experimentally [1,2] and theoretically [3] over recent years. The main interest lies in extracting information about the intermolecular forces. For simple systems (atom–diatom collisions), the theoretical calculations appear to be satisfactory but the situation is hindered for more complicated systems in part by lack of knowledge about the intermolecular forces. Therefore close coupled [4,5] or approximate [6] quantum mechanical calculations are limited to simple systems for which the potential energy surfaces are known accurately enough (e.g. Ar–N_2 collisions).

On the other hand, an empirical approach for the classification of collisional state-to-state transitions is the information theoretic analysis of collision processes [7,8]. This has been actively pursued over the last few years. Essentially the molecular system is treated as a microcanonical ensemble and a purely statistical cross section is calculated based upon density of states arguments. This "prior" collision cross section is compared with either an experimental or numerically calculated cross section with the surprisal being the logarithm of the prior to actual cross section. Physically the surprisal is a measure of the deviation of the transition probability from a given prior probability [8]. The surprisal analysis approach has helped to compact and classify large bodies of data [8,9]. From these it is possible to extract trends which, hopefully, are useful in understanding the processes at play in more complicated systems.

In this paper, a body of data for rotational energy transfer in the N_2–Ar system is examined. A modified exponential model (MEM) which accounts for most of the observed energy dependences of the rotational state to state total cross sections $\sigma_{j'j}(E)$ is presented. The MEM evolved from an attempt to improve the energy gap relation for $\sigma_{j'j}(E)$ introduced by Polanyi and Woodall [11]. That is, the cross section for a collisional transition from state j to j' appears to decrease exponentially as the energy gap increases, viz. [10–14]

$$\sigma_{j'j}(E) = C_S(E)\,\sigma^0_{j'j}\exp(-\theta_R|\Delta E_{j'j}|/E)\,. \qquad (1)$$

Here E is the total energy of the pair $E = p^2/2\mu + E_j$, where p is the relative momentum while $C_S(E)$ and θ_R are (possibly energy dependent) empirical parameters. $\sigma^0_{j'j}$ is a prior statistical cross section.

The energy gap form, eq. (1), leads to linear surprisals which cannot account for the numerical data for the N_2–Ar system [12]. Rotational state-to-state cross sections for this system, calculated by Pattengill and Bernstein [12] and shown to agree well with quantal calculation [3,15], display substantial non-linear surprisals as well as considerable scatter of the points.

In this paper, by introducing an inverse dependence on the energy gap, the MEM for $\sigma_{j'j}(E)$ is obtained from which the shape and scatter of the points are reproduced with some success. Moreover, the exponential

energy gap form employed in ref. [12] uses two parameters for *each* total energy and initial j with no relation being found between data at *different* E. In this work, two parameters describe the non-linear dependence while a term with a simple energy dependence relates the different curves. Hence the MEM fits all the data with three parameters.

The agreement between the calculated cross sections and the MEM in this paper is best for large E and large $|\Delta E_{j'j}|$. In particular $\sigma_{jj\pm2}(E)$ are not well produced being larger than those calculated by Pattengill. This is due to a too steep dependence on ΔE as a consequence of the exponential energy gap form. Thus it is believed that the exponential form is inadequate for small energy gaps and small E.

A further observation is that the MEM cannot distinguish between the different features coming from differences in the two potential energy surfaces used in ref. [12]. However, except for $\sigma_{jj\pm2}$ terms, the form used here fits the data from both surfaces equally well indicating that perhaps only the gross features of the potential are important for rotational relaxation.

2. Energy dependence of rotational cross sections

The total directionally averaged cross section for collisional rotational transitions at fixed total energy E is given by

$$\sigma_{j'j}(E) = \frac{(4\pi)^{-1}}{2j'+1} \sum_{mm'} \int \sigma_E(jmk \to j'm'k')\, \mathrm{d}\hat{k}\, \mathrm{d}\hat{k}' . \quad (2)$$

Here the differential cross section is

$$\sigma_E(jmk \to j'm'k') = (\mu/2\pi\hbar^2)^2 (k'/k) |\langle kjm|t|k'j'm'\rangle|^2 \quad (3)$$

in terms of matrix elements of the transition operator t. The wave vector is related to the momentum by $\boldsymbol{p} = \hbar\boldsymbol{k} = \hbar k\hat{\boldsymbol{k}}$ and the free basis states are

$$\langle R|kjm\rangle \equiv \mathrm{e}^{\mathrm{i}k\cdot R}|jm\rangle . \quad (4)$$

The total energy $E = E_k + E_j$ is conserved during the collision,

$$E_{k'} + E_{j'} = E_k + E_j , \quad (5)$$

where the rotational energy is $E_j = j(j+1)B$ and $E_k = \hbar^2k^2/2\mu$. In terms of the density of translation states,

$$\rho_k = \mu^{3/2}E_k^{1/2}/2^{1/2}\pi^2\hbar^3 , \quad (6)$$

eq. (2) can be written (for later use) as,

$$\sigma_{j'j}(E) = (2\pi\mu/k\hbar^2)\, \rho_{k'}(E)(2j'+1)\, f_{jj'}(kk') . \quad (7)$$

The collision dynamics are contained in

$$f_{jj'}(kk') = \frac{1}{(2j'+1)^2(2j+1)} \left(\frac{\pi\hbar^2}{\mu}\right)^2 \frac{1}{kk'} \times \sum_J (2J+1) \sum_{ll'} P^J_{jlj'l'}(E) . \quad (8)$$

where $P^J_{jlj'l'}$ is the transition probability in the total angular momentum coupling scheme [3,5].

If the function $f_{jj'}(kk')$ is chosen to have an exponential form (based upon experimental data for hydrogen halides [11]), poor agreement is obtained when a fit to the Ar–N_2 data is attempted [12]. This suggests that the energy dependence of eq. (1) is oversimplified. By using a result of Landau [16,17], Heller [14] shows that the momentum gap approximation to the radial integrals, namely,

$$f_{jj'}(kk') \approx K'(E) \exp(-2\pi r_0|k-k'|) \quad (9)$$

can be written as an energy gap relation-by using conservation of energy, eq. (5),

$$\exp(-2\pi r_0|k-k'|) = \exp[-\theta_{jj'}(E)\, r_0|\Delta E_{jj'}/E|] , \quad (10)$$

where $\theta_{jj'}(E)$ is

$$\theta_{jj'}(E) = 2\pi(2\mu E/\hbar^2)^{1/2} \times [(1-E_j/E)^{1/2} + (1-E_{j'}/E)^{1/2}]^{-1} . \quad (11)$$

Heller does not, however, treat the prefactor $K'(E)$ nor attempt a fit of eq. (10) to existing data.

The momentum gap expression of Landau [16], eq. (9) results from assuming that an exponential potential with range r_0 can be fitted to the true potential and that the translational energy is high enough that the repulsive part of the potential plays the dominant role. However, since a stationary phase approximation is used by Landau so that only one point on the potential is important, the exponential potential approximation is not a serious restriction. In particular an inverse R dependent potential also gives a momentum gap expression [18] similar to eq. (9).

On the other hand, if the collisions are weak and do

not result in penetration to the repulsive part of the potential, the momentum gap form is not obtained. Hence it is expected that eq. (9) is only valid for high E and large $|\Delta E_{j'j}|$. Under these conditions, eq. (9) can be physically interpreted as describing a persistence of momentum so that energy transfer from translational to rotational energy is more difficult for larger energy gaps than smaller. In order to account for the non-linear nature of the surprisal plots (see ref. [12] and figures therein), it is necessary to consider the prefactor $K'(E)$. This has been left as a constant in other empirical treatments [11, 12, 14].

From eq. (8) it seems reasonable that $K'(E)$ be at least proportional to $(E_k E_{k'})^{-1/2}$. Moreover, semi-classical approaches using WKB wavefunctions and a stationary phase approximation [19] show an inverse dependence of the radial integrals on $\Delta E_{j'j}$. Based upon these considerations, it is conjectured that an adequate form for the energy dependence of $K'(E)$ is,

$$K'(E) = \frac{K'}{(E_k E_{k'})^{1/2} (\Delta E_{jj'})^{\gamma}}, \tag{12}$$

where γ and K' are constants.

Clearly, the above arguments do not prove that the form eq. (9) with eq. (12) is correct for the general case. It is of interest, therefore, to test the validity of the modified exponential form, namely,

$$\sigma_{j'j}(E) = (2\pi\mu/k\hbar^2)\, \rho_{k'}(E)\, \frac{(2j'+1)K'}{(E_k E_{k'})^{1/2} (\Delta E_{jj'})^{\gamma}} \times \exp[-\theta_{jj'}(E) r_0 |\Delta E_{jj'}/E|] \tag{13}$$

on the existing data.

3. Numerical calculations

The numerical data of Pattengill [12,15] for the Ar–N_2 system are obtained by using classical trajectories on quantum mechanical Ar–N_2 surfaces. The results have been compared with the close coupled calculations of Pack [4] and found to be in good agreement. Pattengill's data is therefore used as a benchmark with which to compare the present work.

The surprisal is defined [9],

$$I_{j'j}(E) = -\ln [\sigma_{j'j}(E)/\sigma^0_{j'j}(E)], \tag{14}$$

where the "prior" statistical cross section is given by

$$\sigma^0_{j'j} = (2\pi\mu/\hbar^2 k)(2j'+1)\, \rho_{k'}(E)\, \mathcal{R}, \tag{15}$$

where $\mathcal{R}$ is usually taken to be a constant [12] (see however, Pollack [20]). The surprisal for the MEM then becomes from eq. (13)

$$I_{j'j}(E) = (1+\gamma) \ln [C(E)E] + \tfrac{1}{2} \ln (E_k E_{k'}/E^2) + r_0 \theta_{jj'}(E) |\Delta E_{jj'}|/E + \gamma \ln (|\Delta E_{jj'}|/E), \tag{16}$$

where $C(E)$ is possible energy dependent and is given by

$$C(E) = (\mathcal{R}/K')^{1/(1+\gamma)}. \tag{17}$$

Comparison of eqs. (13) and (15) with eq. (1) gives the surprisal parameters as,

$$\theta_R = r_0 \theta_{jj'}(E) \tag{18}$$

and

$$C_S(E) = \frac{K'/\mathcal{R}}{(E_k E_{k'})^{1/2} (\Delta E_{jj'})^{\gamma}}. \tag{19}$$

Using $\gamma = 0.6$ and $r_0 = 0.035$ Å and the values of $C(E)$ in table 1, the surprisal plots were calculated and are shown in fig. 1. This should be compared with figs. 12 and 13 of ref. [12]. The values of $\sigma_{j'j}(E)$ are given in table 2 along with the values from tables 1 and 2 of ref. [12].

The dependence of $C(E)$, eq. (17) on E is also reasonable. From table 1 it is seen that $C(E) \propto E^{-0.5}$. This can be accounted for by choosing

$$R = \bar{R}/E. \tag{20}$$

Then with $\gamma = 0.6$ the energy dependence of $C(E)$ is

Table 1
Values of $C(E)$ used in eq. (17) to calculate the surprisals in fig. 1 with $\gamma = 0.6$ and $r_0 = 0.035$ Å

E(K)	$C(E)$	$C(E) \times E^{0.5}$
768	3.35×10^{-3}	0.093
1535	2.31×10^{-3}	0.091
3070	1.72×10^{-3}	0.095
12280	0.92×10^{-3}	0.102

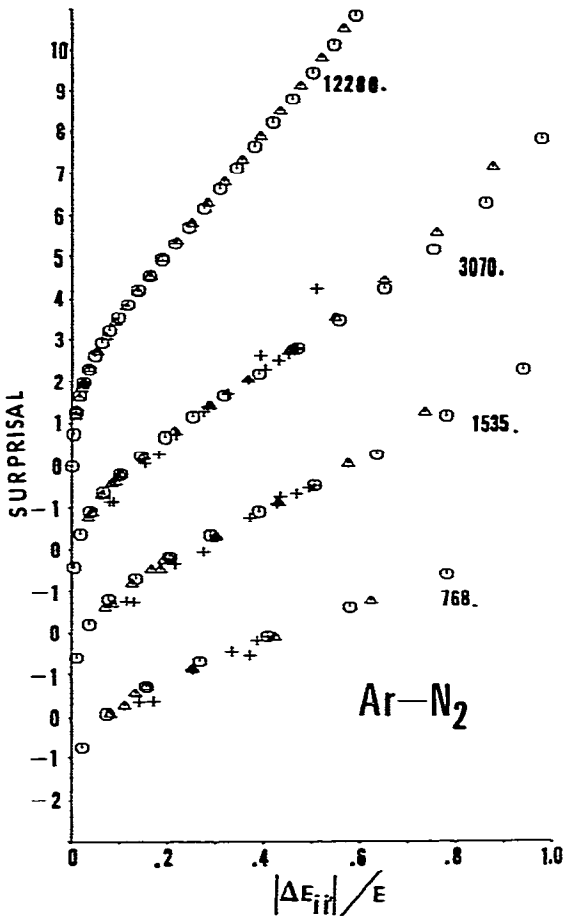

Fig. 1. Combined surprisal plots using $r_0 = 0.035$ Å, $\gamma = 0.6$ and values of $C(E)$ in table 1 as a function of $|\Delta E_{jj'}|/E$. Initial j values are (1) $E = 768$ K; ○, $j = 0$; △, $j = 6$; +, $j = 10$. (2) $E = 1535$ K; ○, $j = 0$; △, $j = 10$; +, $j = 16$. (3) $E = 3070$ K; ○, $j = 0$; △, $j = 10$; +, $j = 22$. (4) $E = 12280$ K; ○, $j = 0$; △, $j = 10$.

$$C(E) = (\hat{R}/K')^{0.63} E^{-0.63} , \qquad (21)$$

which is close to the fitted value of $E^{-0.5}$.

The data in table 2 is seen to agree well with that of ref. [12] for the two potential energy surfaces used (KDV and PBLC) except for the lowest $E = 768$ K and for small ΔE, namely $j' = j \pm 2$. In spite of this, the MEM eq. (13) for $j' > |j \pm 2|$ gives a substantial improvement over the simple energy gap from eq. (1) since the total energy dependence is accounted for.

Not much improvement is obtained if the MEM is restricted to fit each E rather than the 4 different E's simultaneously. To show this the MEM is restricted to each E only and the best fit obtained. The cross sections calculated in this manner are given in table 2 under RMEM.

Although separate fits at fixed E are satisfactory with this model, the ability of the MEM to reproduce the data for different total E without additional parameters is encouraging.

4. Summary

An empirical modified exponential model for rotational state-to-state cross sections, eq. (13), is found to be reasonable for Ar—N_2 at large E and large energy gap. The initial curvature of the surprisal plots are accounted for by the $|\Delta E_{jj'}|^{-\gamma}$ term, while the scatter in the points for each total E in fig. 1 results from variations in

$$(E_k E_{k'})^{1/2} = [(E - E_j)(E - E_{j'})]^{1/2}$$

and $\theta_{jj'}(E)$, eq. (11), for different $j \to j'$ transitions which accidentally have equal energy gaps.

The energy gap form is used here since it has been proposed earlier [11] and can be obtained [14] by an application of Landau's method [16]. However, this is expected to break down for lower E and small energy gaps. Moreover, although quantum scattering calculations [4,5] show that the cross sections do die off for large energy gaps, in the absence of more accurate experimental data it is difficult to distinguish this fall-off from an exponential form. Clearly there is a need for more than the present treatment to justify the MEM, eq. (13), in which the energy dependence is extracted more formally as well as giving dynamical interpretations to the empirical parameters. Also, the form given here has only been tested on the Ar—N_2 system in a specific energy range. It would be of interest to determine if this equation can reproduce other rotational relaxation data.

Table 2
Computed values of $\sigma_{j'j}(E)$ (in Å^2) for Ar–N_2 at different energies for the KDV and PBLC potentials and for the MEM. Columns and rows denote initial and final j states respectively. RMEM is the best fit using the data at the bottom of the table

j'	$j=0$				$j=6$				$j=10$			
	KDV	PBLC	MEM	RMEM	KDV	PBLC	MEM	RMEM	KDV	PBLC	MEM	RMEM
$E=768$ K												
0	–	–	–	–	1.4	0.8	0.5	0.6	0.4	0.1	0.2	0.1
2	14.3	14.9	10.1	15.0	4.6	5.3	3.0	3.7	1.8	1.0	1.0	0.4
4	11.0	12.7	7.7	11.6	10.1	10.4	8.4	12.1	3.5	2.6	2.3	1.0
6	8.3	10.2	5.6	6.5	–	–	–	–	5.9	4.9	5.0	3.2
8	6.7	6.5	3.8	2.6	12.3	11.2	11.8	15.1	10.2	11.5	12.9	13.7
10	4.2	1.2	2.3	0.73	5.9	5.1	5.6	3.6	–	–	–	–
12	2.5		1.2	0.12	2.9	1.8	2.6	0.6	9.5	9.2	14.1	11.1
14	0.3		0.4		0.5		0.9	0.1	2.0	1.3	3.9	0.5
	RMEM $C(E)=1.4\times10^{-3}$ $\gamma=0.36$ $r_0=0.102$ Å											
$E=1535$ K												
0	–	–	–	–	0.1	0.3	0.2	0.2	0.2			0.1
2	11.4	12.0	9.4	11.1	1.4	1.2	1.0	1.0	0.4		0.2	0.3
4	7.9	9.8	7.4	7.5	2.9	2.7	2.2	2.1	0.9		0.5	0.6
6	6.8	7.6	5.9	5.5	4.9	4.8	4.5	4.2	1.2	0.2	0.8	1.0
8	5.7	5.8	4.4	4.1	9.4	8.2	10.3	9 8	1.6	0.8	1.5	1.7
10	4.7	3.8	3.1	3.0	–	–	–	–	1.9	1.8	2.8	3.0
12	3.3	2.1	2.1	2.1	10.1	8.6	12.5	11.9	3.2	3.7	5.9	5.9
14	2.5		1.3	1.4	4.8	4.5	5.7	5.6	8.2	8.6	15.8	15.3
16	1.4		0.7	0.9	2.3	1.7	2.7	2.9	–	–	–	–
18	0.3		0.3	0.5	0.7	0.2	1.2	1.5	6.5	6.4	15.8	15.9
20					0.1		0.4	0.6	1.2	0.7	4.0	4.9
22											0.6	
	RMEM $C(E)=2.83\times10^{-3}$ $\gamma=0.76$ $r_0=0.024$ Å											
$E=3070$ K	$j=0$				$j=10$				$j=22$			
0	–	–	–	–	0.2	0.2	0.2	0.2				
2	9.2	10.5	7.6	10.2	1.1	1.5	0.9	0.8	0.2			
4	6.5	6.4	6.2	6.5	1.6	2.1	1.9	1.7	0.2		0.1	0.2
6	5.7	5.6	5.1	4.8	3.6	3.6	3.7	3.3	0.4		0.2	0.3
8	4.3	4.7	4.2	3.7	7.6	7.1	8.0	7.6	0.6		0.3	0.5
10	4.0	4.7	3.3	2.9	–	–	–	–	1.0	0.2	0.5	0.7
12	3.4	3.4	2.5	2.2	8.1	8.0	10.1	9.3	0.9	0.7	0.8	1.0
14	2.8	2.6	1.8	1.8	4.4	4.4	5.5	4.8	1.5	1.2	1.4	1.6
16	2.1	0.8	1.2	1.0	3.5	2.8	3.3	3.0	1.9	2.1	2.5	2.8
18	1.1		0.8	0.7	2.3	1.8	2.0	2.0	2.7	2.8	5.3	5.3
20	1.4		0.5	0.5	1.8	0.9	1.1	1.3	5.8	6.8	14.0	12.9
22	0.7		0.3	0.3	0.9	0.2	0.6	0.9	–	–	–	–
24	0.3		0.1	0.2	0.3		0.3	0.5	5.9	6.7	14.3	13.6
26					0.2		0.1	0.3	1.8	1.5	4.5	5.1
28									0.3	0.1	1.3	2.2
30											0.3	0.8
32											0.2	0.2
	RMEM $C(E)=2.29\times10^{-3}$ $\gamma=0.83$ $r_0=0.019$ Å											

(to be continued)

Table 2 (continued)

j^*	$j=0$				$j=10$			
	KDV	PBLC	MEM	RMEM	KDV	PBLC	MEM	RMEM
$E=12280$ K								
0	–	–	–	–	0.2	0.1	0.1	0.1
2	7.1	7.6	4.7	7.3	0.7	0.6	0.7	0.6
4	4.4	4.5	4.0	4.6	1.6	1.6	1.4	1.3
6	3.5	3.8	3.5	3.5	2.2	2.7	2.5	2.4
8	3.0	3.2	3.1	2.8	5.0	5.1	5.1	5.2
10	2.3	2.5	2.7	2.4	–	–	–	–
12	2.3	2.4	2.3	2.1	5.3	5.5	6.5	6.4
14	2.0	2.5	1.9	1.8	3.3	3.8	4.1	3.7
16	1.7	1.8	1.6	1.6	2.6	2.4	3.0	2.7
18	1.2	1.6	1.3	1.4	2.1	2.3	2.3	2.1
20	1.1	1.8	1.1	1.2	1.5	1.5	1.7	1.7
22	1.2	1.6	0.8	1.1	1 6	1.4	1.3	1.5
24	1.2	1.2	0.6	1.0	1.3	1.2	1 0	1.2
26	1.0	0.7	0.5	0.8	1.5	1.0	0.7	1.0
28	1.0	0.4	0.4	0.7	1.1	1.0	0.5	0.9
	data in RMEM $C(E) = 1.35 \times 10^{-3}$ $\gamma = 0.7$ $r_0 = 0.0098$ Å							

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