

ON THE CORRELATION OF ROTATIONALLY INELASTIC RATES: A SCALING THEORETICAL ANALYSIS

R. RAMASWAMY*, A.E. DEPRISTO and H. RABITZ**

Department of Chemistry, Princeton University, Princeton, New Jersey 08540, USA

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The recently measured rates for the rotationally inelastic process $(A^1\Sigma_u)Na_2(j) + Xe \rightarrow (A^1\Sigma_u)Na_2(j') + Xe$ are analyzed and correlated with a scaling theory that explicitly accounts for the adiabaticity of the collision. A brief discussion of previous scaling theories (which neglect this effect) is presented.

An a-priori scaling relationship between rotationally inelastic rates [1-3] has been shown to allow the extraction of state-to-state information from vibration-rotation linewidth data [1]. It is the purpose of this letter to show that such a scaling relationship has an important *additional* application as a means of data correlation, reduction and prediction. This method of data analysis has an extremely desirable property: the collisional information is contained in a single column of the physically measurable rate matrix.

Consider the case of rotational relaxation. The standard method of data compaction that has been employed by several investigators [4] involves the fitting of the measured inelastic rates, $k_{jj'}$, to a function of the so-called natural variables. In rotational relaxation, the transition energy is nearly always used, and a common choice for the function is an exponential [4,5],

$$k_{jj'} = k_{jj'}^0 B \exp(-\theta|\epsilon_j - \epsilon_{j'}|). \quad (1)$$

Here ϵ_i denotes the energy of the i th state, $k_{jj'}^0$ is a prior (statistical) rate, and the parameters B and θ are determined by yielding the best fit to a large amount of data. Note that eq. (1) reduces all the unknown rates to knowledge of just two parameters that have no

simple or direct physical significance.

A general scaling relationship has recently been developed for vibrationally and rotationally inelastic processes and a detailed account will appear elsewhere [6]. For rotational inelasticity in atom-linear molecule collisions, the general expression relating kinetic rates reduces to the simple form

$$k_{jj'}(T) = [j'] \sum_{L=j-j'}^{j+j'} [L] \begin{pmatrix} j & j' & L \\ 0 & 0 & 0 \end{pmatrix}^2 |A_L^j|^2 k_{L0}(T), \quad (2)$$

with the restriction $\epsilon_j > \epsilon_{j'}$. In the above expression $[L] = 2L + 1$, $\begin{pmatrix} j & j' & L \\ 0 & 0 & 0 \end{pmatrix}$ is a 3- j symbol, and A_L^j is an adiabaticity factor, which is given in terms of an effective collision length l_c as

$$A_L^j = \left[\frac{6 + [(\epsilon_L - \epsilon_{L-1})l_c/2v\hbar]^2}{6 + [(\epsilon_j - \epsilon_{j-1})l_c/2v\hbar]^2} \right], \quad (3)$$

where $v = (8kT/\mu\pi)^{1/2}$ is the average projectile speed. (For homonuclear molecules, $L-1$ and $j-1$ are replaced by $L-2$ and $j-2$ respectively.) Note that the restriction of eq. (2) to downward transitions does not limit its applicability since upward transition rates are related to these by detailed balance.

An understanding of the adiabaticity factor in eqs. (2) and (3) is especially important for the proper analysis of experimental data. Physically, A_L^j specifically accounts for the finite collision time, $\tau_c = l_c/v$. For appropriate kinetic energies in systems with a small

* Present address: Department of Chemistry, California Institute of Technology, Pasadena, California 91125, USA.

** Alfred P. Sloan Fellow, Camille and Henry Dreyfus Teacher-Scholar.

collisional reduced mass and/or cases having closely spaced energy levels (e.g., He-CO), A_L^j is nearly unity and thus can be safely neglected. In the limit that $A_L^j = 1$ and as $(\epsilon_j - \epsilon_{j'})/kT \rightarrow 0$, eq. (2) reduces to the infinite order sudden (IOS) scaling formula of Goldflam et al. [3]. For cases with larger reduced mass (such as $\text{Na}_2^* - \text{Xe}$ which is considered later) or at sufficiently high j , the adiabaticity factor plays a crucial role in determining the variation of the rates $k_{j'j-\Delta}$ with j for fixed Δ . In this regard, note that all of the variables except l_c in eq. (3) are explicitly given in terms of static properties of the collision system such as the mass and energy level spacing. Since the physical interpretation of l_c is defined in terms of the average impact parameter for inelastic collisions, it is often easy to adequately estimate l_c . For rotational transitions in neutral atom-molecule collisions, a crude value for l_c can be taken as the hard sphere radius. In many applications of eq. (2) — such as when k_{L0} are known and the other rates are predicted — the estimated l_c is quite adequate and yields good results [6]. When accurate experimental data is available (especially as a function of initial rotor level), l_c no longer need be totally estimated but can be determined more precisely by comparison to the data. We emphasize that l_c still must be *physically reasonable* and is thus not a purely adjustable parameter. In essence, the analysis of experimental measurements can yield both the specific dynamical rates, k_{L0} , and an improved range for the effective collision length, l_c . With this information available, the rates $k_{j'j}$ for all j and j' can be generated from (2).

The relationship in eq. (2) is a specific illustration of a general scaling formula for non-reactive collisions which is fully discussed elsewhere [6]. For this special atom-linear molecule case, two other scaling theories [2,3] are available. First, as discussed above, the IOS formula sets $A_L^j = 1$ and $(\epsilon_j - \epsilon_{j'})/kT = 0$ and thus is a direct limiting form of eq. (2). Second, the dynamic coupling theory [2] (DCT) relationship includes the energy level spacing as in eq. (2) but sets $A_L^j = 1$ and makes an additional assumption about the form of the potential matrix elements. It is not a direct limit of eq. (2) but the DCT scaling expression can be easily modified to incorporate the adiabaticity. The result is

$$k_{j'j}(T) = \frac{[j']! [j-j']!}{[j]!} \frac{N(kT)}{N(kT + \epsilon_j - \epsilon_{j'})} \times |A_{j-j'}^j|^2 k_{j-j'}(T) \quad (4)$$

for $\epsilon_j > \epsilon_{j'}$ and where $N(E)$ is the number of rotor levels accessible at total energy E . There is a difference between eqs. (2) and (4) in that DCT relates each rate $k_{j'j}$ only to $k_{|j-j'|0}$, while the relationship in eq. (2) includes all higher order effects as well.

As an example of the utility and power of this data analysis procedure, consider the collision system ($A^1\Sigma_u$) $\text{Na}_2^* - \text{Xe}$, in which rotational rates have been experimentally determined [7,8] for 6 initial states and a variety of final states at $T \approx 450$ K. We choose as input the set $k_{j'16}$ $j' = 18, 20, \dots, 48$, which are derived from $k_{16j'}$ by detailed balance. Then, if we adopt the relationship embodied in eq. (2), the rates k_{L0} are obtained as the solution to the linear equations

$$k_{j'16}(T) = [16] \sum_{L=j'-16}^{j'+16} [L] \begin{pmatrix} j' & 16 & L \\ 0 & 0 & 0 \end{pmatrix}^2 |A_L^j|^2 k_{L0}(T). \quad (5)$$

A multistep procedure is used to solve eq. (5): start with k_{1816} , truncate the sum over L to only the lowest term and solve for k_{20} ; next include k_{1816} and k_{2016} , truncate the sum over L to the two lowest terms and solve for k_{20} and k_{40} ; repeat this procedure up till k_{4816} . The systematic inclusion of the higher j' rates in eq. (5) enables one to determine the convergence of the rates k_{L0} . Following this procedure we found that the rates k_{L0} up to $L = 24$ were converged out of the set k_{20}, \dots, k_{640} using input up to k_{4816} . (The higher rates were unconverged but decreasing rapidly in magnitude and thus are relatively unimportant for all $k_{j'j}$ with $|j' - j| \leq 24$.) Note that eq. (5) can be solved for k_{L0} with any value of l_c . One method for calculating l_c would do a least squares fitting to the data. We have not used this technique but have determined l_c by comparison of the scaling predicted and experimental values of k_{7674} . This was sufficient for the analysis of the present data. We also mention that with the modified DCT scaling relationship, a simpler analysis is possible: the k_{L0} 's are obtained by setting $j' = 16$ in eq. (4).

The above procedure using eq. (5) yields the converged rates shown in table 1 and $l_c = 7$ bohr. A more precise value for l_c is not warranted by the accuracy of the experimental rates, $k_{j'16}$ and k_{7674} . For instance, we note that the values of k_{L0} using $l_c = 5$ (8.5) bohr are almost identical to those in table 1, and that the predicted value of k_{7674} is only slightly too large (small). As expected, a moderate variation of l_c does not signifi-

Table 1
Rate constants from the deconvolution of experimental data on $\text{Na}_2^+ - \text{Xe}$ collisions^{a)}

L	k_{L0}^a	k_{L0}^b
2	0.7891±0.0363	0.5479±0.0123
4	0.2325±0.0280	0.1650±0.0060
6	0.0937±0.0237	0.0811±0.0046
8	0.0802±0.0210	0.0558±0.0035
10	0.0541±0.0190	0.0376±0.0030
12	0.0351±0.0175	0.0269±0.0025
14	0.0367±0.0162	0.0219±0.0021
16	0.0222±0.0150	0.0158±0.0018
18	0.0245±0.0140	0.0136±0.0018
20	0.0222±0.0130	0.0107±0.0016
22	0.0192±0.0121	0.0081±0.0014
24	0.0125±0.0112	0.0058±0.0014

^{a)} The rates k_{L0} obtained from the scaling relationship of eq. (5)^{a)} and the modified DCT^{b)} both using $l_c = 7$ bohr are presented here. The temperature is 450 K, and the units of the rates are $10^{-10} \text{ cm}^3 \text{ s}^{-1}$. The stated uncertainties are due solely to experimental error. Note that the rates in column a using eq. (5) are converged with respect to adding higher input rates $k_{j'}$.

cantly effect the scaling theoretical analysis. However, the neglect of A_L^j (i.e., $l_c = 0$) as in the IOS scaling relationship, will yield rates in upper j levels that are significantly too large. In the analogous DCT procedure the value $l_c = 7$ bohr also reproduced the data accurately. The resulting rates are shown in table 1.

An interesting point is that the matrix of rates $k_{jj'}$

with $j \neq 0, j' \neq 0$ predicted by either eq. (2) with k_{L0} from the first column of table 1 or by eq. (4) and the k_{L0} 's from the second column are in very good agreement. However, the differences between k_{20} and k_{40} derived from the two methods serve to stress the difference in the models as discussed above. We have used a gaussian form for the experimental input rate error to determine the uncertainties in the deconvoluted rates. The non-overlapping of some of the error bars in columns I and II is due to the complete neglect of any model errors. In fact, both scaling relationships are unlikely to be consistently more accurate than $\pm 10\%$ — to judge from previous work [2,6]. As a consequence, the two columns are actually in reasonably good agreement, especially concerning the propensity for multiple quantum transitions.

Due to the easy generalization of eq. (2) to more complicated systems [6], the following discussion is based upon the results using this equation. Similar comments would hold for the results of eq. (4). Using the k_{L0} rates and l_c , any individual rate $k_{jj'}$, including those not experimentally measured can be calculated via eq. (2). These are depicted in fig. 1 for sample cases, along with the measured rates. It can be seen that the agreement between the predicted and measured rates is excellent. Similar agreement is found for all the rates in ref. [7]. Since the values of $k_{54j'}$ with $A_L^i = 1$ would be nearly equal to $k_{16j'}$, it is clear that the adiabaticity factor is quite important in this heavy system and that the analysis based upon eq. (2) is capable of correlating

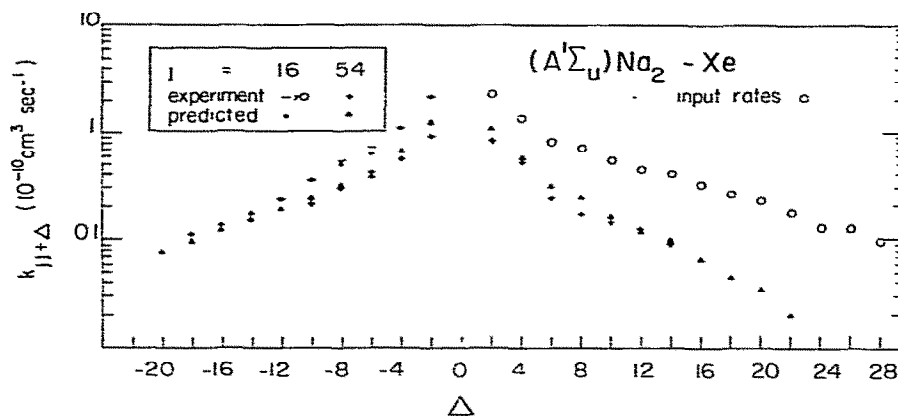


Fig. 1. Scaling predicted and experimental rates: The rates $k_{16\ 16+\Delta}$ (○) are used to determine the k_{L0} in eq. (5). The scaling predicted rates $k_{54j'}$ (▲) and $k_{16\ 16-\Delta}$ (●) agree with the corresponding experimental values $k_{54j'}$ (+) and $k_{16\ 16-\Delta}$ (-) within the experimental uncertainty.

and compacting the data, and predicting the rates. Thus, a purely parametrical fitting of the experimental results is unnecessary [†]. We mention that the adiabaticity factor should be less important for the Na_2^*-He system and consequently the rates in the upper levels should not decrease as rapidly as those in Na_2^*-Xe collisions. An experimental verification of this prediction would be interesting.

The Na_2^*-Xe example illustrates the value of the present procedure as a means of *data-compactation*, since *only* the k_{L0} rates and l_c are needed to obtain *all* other rates. At the same time, such a relationship must not be viewed simply as fitting procedure, since the rates k_{L0} and effective collision length l_c have explicit *dynamical meaning*, and they are obtained by the deconvolution. In this regard, the predictive and non-adjustable nature of eq. (2) allows an in-depth analysis of relaxation effects. In addition, an unsuccessful attempt at a deconvolution would imply that unusual dynamical effects are occurring, and thus would

This point is important for the interpretation of the data. For instance, it has recently been concluded that a propensity for $m_j = m_j'$ exists in the Na_2^*-Xe system [7,9]. Since eq. (2) includes all reorientations, the present analysis shows this conclusion to be an artifact of the assumed functional form and the chosen prior. This is an inherent weakness of any parametrization procedure. Explicitly, the basic dynamical quantities k_{L0} can be fitted equally well by either of the forms $k_{L0} = B[L(L+1)]^S$ or $k_{L0} = (B'/[L])[L(L+1)]^S$. Since the first function assumes a statistical prior, and the second assumes no reorientation, no unambiguous information about reorientations can be obtained with either of the above forms.

point out a system for further study ^{††}. By contrast, a poor fit to the data by an arbitrarily assumed functional form merely warrants a different functional form — no more and no less.

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^{††} See, for example, the deconvolution of linewidth data for near-homonuclear molecules as presented in ref. [1].

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