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Dynamical constraints on the angular momentum transfer in rotationally inelastic molecular collisions

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The rapid decrease in the integral inelastic cross sections, when rotational energy transfer $|\Delta E|$ is greater than a critical value ($|\Delta E|^*$), has been explained quantitatively for the systems CO_2–H_2, CO_2–He, Na_2–He, Na_2–Ne, LiH–He, and N_2–Ar on the basis of the model proposed by Dexheimer *et al.* An expression for $|\Delta E|^*$ has been obtained that shows the increase in $|\Delta E|^*$ with the increase in the reduced mass μ, initial rotational quantum number j_i, and initial relative energy of the translational motion K_i. The predictions of the model for CO_2–X (X = Ne, Ar, Kr, Xe) are also reported.

I. INTRODUCTION

One of the important outcomes of the recent experimental and computational efforts in studying the rotational energy transfer (RET) in molecular collisions has been the evolution of the empirical scaling and fitting laws[1–12] which attempt to fit the entire matrix of the integral inelastic cross sections (IICS), $\sigma(j_i \to j_f)$, and the rate constants in terms of a few parameters. Considerable attention has been focused on the power-gap (PG) law.[1–3,13–27] One of the forms of the PG law states[3]:

$$\sigma(j_i \to j_f) = a(2j_f + 1)(K_f/K_i)^{1/2}|\Delta E|^{-\gamma}, \tag{1}$$

where j_i and j_f are the initial and the final rotational quantum numbers $|\Delta E|$ is the energy gap between the initial and final rotational levels, K_i and K_f, respectively, represent the initial and final kinetic energy of the relative translational motion. a and γ are the fitting parameters. Regarding a and γ, it was noted that these depend on K_i and j_i but do not depend on $|\Delta E|$. The dependence of a and γ on $|\Delta E|$ was first pointed out by Noorbatcha and Sathyamurthy.[13] By analyzing ten sets of data on CO_2–H_2 they found that for $|\Delta E| \leqslant |\Delta E|^*$ one set of parameters a_{low} and γ_{low}, and another set of parameters a_{high} and γ_{high} for $|\Delta E| > |\Delta E|^*$ are needed to fit the data. Their study also indicates that γ_{high} is five to ten times larger than γ_{low}, and $|\Delta E|^*/K_i$ increases with the increase in j_i. The quantitative variation of $|\Delta E|^*$ with K_i has been first revealed by Koura.[14] His analysis of the IICS data on N_2–Ar system gives $|\Delta E|^* \approx \eta K_i^{\lambda}$, where $\lambda = 0.89$ and $\eta \approx 1$ when $|\Delta E|^*$ and K_i are measured in the temperature units (Kelvin). Schinke's[15] work on Na_2–He and Na_2–Ne shows the increase in $|\Delta E|^*$ with the increase in the mass of the collision partner.

The study of the fitting laws is not important only for their ability of expressing the RET data in a compact form but it may also be useful in understanding the mechanism of the RET process. The existence of two regions, one for $|\Delta E| \leqslant |\Delta E|^*$ and the other for $|\Delta E| > |\Delta E|^*$, is interesting. Noorbatcha and Sathyamurthy[13] suggested that perhaps two different mechanisms of the RET process are responsible for the existence of such two regions.

It is also well known that some systems do not exhibit existence of two such regions. One may say that when theoretical value of $|\Delta E|^*$ is greater than the energy available for the excitation then only one region would be observed. It is thus very important to explain the existence of $|\Delta E|^*$ and its dependence on K_i, j_i, and the mass of the collision partner. Recently, Dexheimer *et al.*[1] attempted to explain the existence of $|\Delta E|^*$ in terms of the limitations on the angular momentum transfer.

In Sec. II we present the model given by Dexheimer *et al.*[1] in a more detailed form and obtain an expression for $|\Delta E|^*$ in terms of the parameters of the colliding system. The final section demonstrates the validity of the model for systems CO_2–H_2, CO_2–He, Na_2–He, Na_2–Ne, N_2–Ar, and LiH–He. A few predictions of the model on CO_2–Ne, Ar, Kr, Xe have also been included in the final section.

II. EXPRESSION FOR $|\Delta E|^*$

Let the interaction potential between a diatomic molecule and an atom is of the form

$$V(r,\theta) = V(r)[1 + bP_l(\cos\theta)]. \tag{2}$$

Here r is the distance between the atom and the center of mass of the molecule, θ is the angle between $\mathbf{r}$ and the bond axis, and P_l denotes the Legendre polynomial.

The maximum torque $T_{\max}$ may be taken as the value of $\partial V/\partial\theta$ at the classical turning point ($r = r_0$). Taking $V(r_0) \sim K_i$, one gets

$$T_{\max} \sim bK_i. \tag{3}$$

Now assuming collision duration $\sim 2r_0/V_{\text{rel}}$, we obtain the following expression for the maximum transfer of angular momentum:

$$(\Delta J)_{\max} \sim T_{\max} \times (2r_0/V_{\text{rel}})$$

or

$$(\Delta J)_{\max} \sim br_0(2\mu K_i)^{1/2}, \tag{4}$$

where μ is the reduced mass of the colliding system and V_{rel} denotes the relative incident translational speed.

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If repulsive portion of $V(r)$ varies as $4\epsilon_0(\sigma/r)^n$ [e.g., for the LJ potential, $n = 12$] then one may assume

$$K_i \sim 4\epsilon_0(\sigma/r_0)^n . \tag{5}$$

Eliminating r_0 between Eqs. (4) and (5) one obtains

$$(\Delta J)_{\max} \sim b\sigma(2\mu)^{1/2}(4\epsilon_0)^{1/n} K_i^{(\frac{1}{2}-\frac{1}{n})}. \tag{6}$$

This leads to the following estimate for the maximum rotational energy transfer in the molecule initially in the rotational ground state:

$$(\Delta E)_{\max}(j_i = 0) \sim (\Delta J)^2_{\max}/2I \sim b^2\sigma^2(4\epsilon_0)^{\frac{2}{n}}(\mu/I) K_i^{(1-\frac{2}{n})}, \tag{7}$$

where I is the moment of inertia of the molecule. Thus the probability of the rotational energy transfer greater than $(\Delta E)_{\max}$ would be very small (not zero, due to the nonrigorous nature of this treatment), as compared to that for $|\Delta E| < (\Delta E)_{\max}$. The rapid decrease of $\sigma(j_i \to j_f)$ governed by the slope $\gamma_{\text{high}} \gg \gamma_{\text{low}}$ in the region $|\Delta E| > |\Delta E|^*$ suggests to recognize $|\Delta E|^*$ as $(\Delta E)_{\max}$. We may, therefore, write:

$$|\Delta E|^*(\text{for } j_i = 0) \sim b^2\sigma^2(4\epsilon_0)^{\frac{2}{n}}(\mu/I) K_i^{(1-\frac{2}{n})} \tag{8}$$

or

$$|\Delta E|^*(\text{for } j_i = 0) \sim \eta(0) K_i^{\lambda}, \tag{9}$$

where

$$\lambda = 1 - \frac{2}{n} \tag{10}$$

and

$$\eta(0) = b^2\sigma^2(4\epsilon_0)^{2/n}(\mu/I). \tag{11}$$

We now obtain an expression for $|\Delta E|^*$ when $j_i \neq 0$. Let $|\Delta E|^*$ correspond to the rotational level j^*, i.e.,

$$|\Delta E|^* = |\{j^*(j^*+1) - j_i(j_i+1)\}|\hbar^2/2I. \tag{12}$$

Replacing $j(j+1)$ by $(j+1/2)^2$ and substituting $j^* - j_i$ by $(\Delta j)^*$, Eq. (12) yields

$$|\Delta E|^* = (\Delta j)^{*2}|[1 + (2j_i+1)/(\Delta j)^*]|\hbar^2/2I. \tag{13}$$

Now assuming $\hbar(\Delta j)^*| \approx |(\Delta J)_{\max}$ and by using Eqs. (6) (9)–(11), and (13) we obtain

$$|\Delta E|^* \approx \eta(j_i) k_i^{\lambda}, \tag{14}$$

where

$$\eta(j_i) = \eta(0)|[1 + (2j_i+1)/(\Delta j)^*]|. \tag{15}$$

For $2j_i \gg 1$, Eq. (15) may be written as

$$\eta(j_i) = \eta(0)|[1 + 2j_i/(\Delta j)^*]|. \tag{16}$$

It may be remembered that in Eq. (16) for an excitation, $(\Delta j)^*$ is positive and for a deexcitation, $(\Delta j)^*$ is negative. Further, as $(\Delta j)^*$ depends on k_i, it may be seen that $\eta(j_i)$ depends on K_i but $\eta(0)$ does not.

III. DISCUSSION AND NUMERICAL RESULTS

A. CO_2–H_2

Noorbatcha and Sathyamurthy[13] analyzed quasiclassical trajectory data on the CO_2–H_2 system and noted that at $K_i = 0.0548$ and 0.1548 eV, $100|\Delta E|^*/K_i$ values are, respectively, 9 and 8 when $j_i = 0$ for CO_2 and $j_i = j_f = 2$ for H_2. These two data give $\lambda = 0.87$ and $\eta(0) = 0.066$ (when energy is in electron volt) for this system. We now use these values of $\eta(0)$ and λ as input and predict j^* by using Eqs. (9)–(11), (14), and (16) for eight other observations of Noorbatcha and Sathyamurthy.[13] These observations cover a wide range of j_i ($j_i = 0$, 16 and 30), $K_i (0.0548 \leqslant K_i \leqslant 0.20$ eV), and $\eta(j_i)[\eta(30)/\eta(0) \sim 5]$. The predicted values of j^* are listed in Table I along with the j^* values observed by Noorbatcha and Sathyamurthy.[13] Table I shows the excellent agreement between j^*_{predict} and j^*_{observe}. Out of eight cases, for two cases j^*_{predict} and j^*_{observe} are identical, and for the remaining six cases $|[j^*_{\text{predict}} - j^*_{\text{observe}}]| = 2$, the smallest possible nonzero difference.

The absolute values of $\eta(0)$ and λ can also be used to test the predictions of Eqs. (10) and (11). This may be done by estimating the anisotropy parameter b and the parameter n. Equation (10) together with $\lambda \approx 0.87$ yields $n \approx 16$. For estimating b we need σ and ϵ_0. Svehla[28] gives $\sigma = 3.941$ and 2.827 Å, and $\epsilon_0 = 195.2$ and 59.7 K for CO_2 and H_2, respectively, for the LJ potential. σ and ϵ_0 values for the CO_2–H_2 system may be obtained by the arithmetic mean rule for σ and the geometrical mean rule for ϵ_0. Using these parameters, Eq. (11) estimates $b = 0.45$. This estimate appears to be of the right order of magnitude.

B. CO_2–He

If the parameters b and n for CO_2–He and CO_2–H_2 are assumed equal, then starting from λ and $\eta(0)$ values of CO_2–H_2, Eqs. (10) and (11) yield $\lambda = 0.87$ and $\eta(0) = 0.104$ for CO_2–He. Here again the parameters σ and ϵ_0 given by Svehla[28] have been used.

Recently, Agrawal and Garg[26] have studied RET in the CO_2–He system at $j_i = 19$. The IICS have been computed on the electron-gas surface[29] by Agrawal and Raff's[30] modified version of the infinite order sudden approximation. In addition to these data, the IICS data obtained by Stroud and Raff[31] by the quasiclassical trajectory method have been analyzed to get j^*. The observed values of j^* are given in Table II along with the predictions of this model with the abovementioned values of η and λ. We note, here again, the

TABLE I. The comparison of observed[a] and predicted[b] j^* values for CO_2–H_2. $j_i = j_f = j$ for H_2.

$j_i(CO_2)$	$j(H_2)$	K_i/eV	j^*	
			Observed[a]	Predicted[b]
0	2	0.0548	10	Input
0	2	0.1548	16	Input
0	0	0.10	12	12
0	0	0.20	18	18
16	0	0.0868	26	28
16	0	0.1868	30	32
16	2	0.1416	30	32
30	0	0.0550	36	38
30	0	0.1550	44	46
30	2	0.1097	42	44

[a] Evaluated by using $|\Delta E|^*$ values given by Noorbatcha and Sathyamurthy (Ref. 13).
[b] Evaluated by using Eqs. (14) and (16), $\lambda = 0.87$, and $\eta(0) = 0.066$.

TABLE II. The comparison of observed[a] and predicted[b] j^* values for CO_2–He.

j_i	K_i/eV	J^*	
		Observed[a]	Predicted[b]
19	0.012	11	11
19	0.0159	9	11
19	0.0537	29	31
19	0.1146	37	37
19	0.2009	43	41
16	0.0616	28	30
0	0.0616	20	14

[a] Reference 26. The IICS data for $j_i = 19$ have been computed by the modified infinite order sudden approximation. The IICS data for $j_i = 16$ and 0 are from Ref. 31.
[b] Predicted using Eqs. (14) and (16).

excellent agreement between j^*_{predict} and j^*_{observe} for six out of seven cases.

C. CO_2–Ne, Ar, Kr, Xe

It would be interesting to predict j^* values for the systems with large μ. Starting from $\eta(0)$ and λ for CO_2–H_2 we have computed $\eta(0)$ for CO_2–X (X = Ne, Ar, Kr, Xe) by the method similar to that used for CO_2–He. The value of $\eta(0)$ so obtained are given in Table III. j^* values now can be easily computed using $\lambda = 0.87$ and $\eta(0)$ reported in this table.

Due to high value of η, for large μ, it is possible that $|\Delta E|^*$ computed by Eq. (9) is greater than K_i. Under such situations $|\Delta E|^*$ and hence γ_{high} would be noneffective, i.e., the limitation on the transfer of the angular momentum would not affect the RET process. Let K_c is that value of K_i for which $\eta K_c^{\lambda} = K_c$, i.e.,

$$K_C = \eta^{1/(1-\lambda)}. \tag{17}$$

It can be seen by Eqs. (9) and (17) that only for $K_i > K_c$, the constraint on the transfer of the angular momentum, would be important. For CO_2–Ar, the computed value of K_c according to Eq. (17) is 0.41 eV, therefore, for $K_i \leqslant 0.41$ eV, the limitation on the transfer of the angular momentum would not affect the RET process; and for $K_i > 0.41$, this limitation would affect the process, and the two slopes γ_{low} and γ_{high} would be observed. It may be mentioned here that at $K_i = 0.11$ eV and $1 \leqslant j_i \leqslant 33$ all the computed[27] cross sections for this system on the electron-gas surface[29] by the modified[30] infinite order sudden approximation for $|\Delta E|$ as large as K_i have been found[27] to satisfy Eq. (1) with only one set of parameters a_{low} and γ_{low}.

Equation (17) shows the strong dependence of K_C on η e.g., η values for CO_2–Ne, CO_2–Ar, and CO_2–Kr are 0.46, 0.89, and 1.36, and, accordingly, K_C values are 0.0025, 0.41, and 10.6 eV, respectively.

Table IV gives the predicted values of j^* for a few values of $K_i > K_c$ for CO_2–Ar. Extensive experimental and theoretical data are required to confirm these predictions.

D. Na_2–He, Ne

Schinke's[15] analysis of the data computed by the infinite order sudden approximation gives $|\Delta E|^* \approx 2$ and 4 meV at $K_i = 50$ and 100 meV, respectively, for Na_2–He and $|\Delta E|^* \approx 3.2$ and 8 meV at $K_i = 20$ and 50 meV, respectively, for Na_2–Ne ($j_i = 0$). These data yield $\lambda \approx 1$, for both and $\eta \approx 0.04$ and 0.16 for Na_2–He and Na_2–Ne, respectively. The ratio of these values of η is consistent with Eq. (11): Equation (11) together with the assumption of equality of b for both the systems, and σ and ϵ_0 values listed in Ref. 28 predicts $\eta(Na_2\text{–Ne})/\eta(Na_2\text{–He}) = 4.1$ and 3.9 for n = 20 and ∞, respectively.

E. Na_2–Ar

Koura[14] studied N_2–Ar system at five values of K_i ranging from 768 to 12 280 K and concluded that $|\Delta E|^*$ depends on K_i according to the relation $|\Delta E|^*$ (Kelvin) $\approx K_i^{0.89}$ (Kelvin), $\lambda = 0.89$ leads to $n = 18$.

F. LiH–He

Jendrek and Alexander[16] computed IICS for RET in the LiH–He system. They used coupled states approximation and employed the *ab initio* potential energy surface. We have analyzed their data for $j_i = 0$ and $K_i = 0.2921$, 0.3921, and 0.4921 eV. It is found that $j^* = 9$ at $K_i = 0.2921$ eV. This figure gives $\eta = 0.26$ if $\lambda = 0.9$ is assumed. These values of λ and η, and Eq. (9) predict $|\Delta E|^*$ such that the solution of the equation $|\Delta E|^* = j^*(j^*+1)\hbar^2/2I$ gives $j^* = 10.3$ (≈ 10) and 11.5 (≈ 12) at $K_i = 0.3921$ and 0.4921 eV, respectively. These values of j^* agree with $j^* = 10$ and 12, respectively, obtained by us from the analysis of their IICS data at $K_i = 0.3921$ and 0.4921 eV.

Recently, the limitation on the transfer of the angular momentum due to the dynamical constraints has also been observed experimentally.[1,25,32]

Equation (6) shows independence of $(\Delta J)_{\max}$ on j_i whereas Eqs. (14) and (15) show dependence of $|\Delta E|^*$ on j_i. The validity of these results for several systems discussed here

TABLE III. Predicted $\eta(0)$ values for CO_2-inert gas systems. (Energy in electron volt.)

System	$\eta(0)$
CO_2–He	0.10
CO_2–Ne	0.46
CO_2–Ar	0.89
CO_2–Kr	1.36
CO_2–Xe	1.74

TABLE IV. Predicted j^* values for CO_2–Ar ($j_i = 0$).

K_i/eV	j^*
0.5	100
0.6	108
0.7	116
0.8	124
0.9	130
1.0	136

thus demonstrates that the fundamental physical limitations are on angular momentum $(\Delta J)_{\max}$ not on energy $|\Delta E|$*.

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