

Dependence Of The Parameters Of The Power–Gap Law On The Collision Energy And The Determination Of The Rotationally Inelastic Cross Sections For N₂-He System

Kavita Agrawal¹, Vinod Garg²

¹ (Department of Physics, Government Polytechnic College, Chittorgarh (Raj.) 312001, India)

² (Department of Physics, Bhagwant University. Ajmer, (Raj.)305001,India)

Abstract: The cross sections, $\sigma(o \rightarrow j_j)$, for the rotational transitions in N₂ due to collisions with He have been computed using the quantum mechanical modified infinite order sudden approximation (IOSAM) method, at six different values of collision energy ranging from 0.1eV to 0.5eV and have been analyzed by using the power-gap law. The parameters of the power-gap law are found to depend on the collision energy through simple equations. It is observed that the equations so obtained for the fitting parameters can lead to the prediction of the cross sections at any value of collision energy, within the range explored, in good agreement with the cross sections computed by the IOSAM method.

Keywords: Atom-diatom molecule collisions, cross-sections, N₂-He system, power-gap law, rotational energy transfer.

I. Introduction

The study of rotational energy transfer of molecules has been a subject of considerable interest for scientists. Because of its importance in several research areas in chemical physics and molecular physics, this field remains a hot topic in the last couple of decades, both in experimental and theoretical studies [1-10]. The evolution of empirical scaling and fitting laws such as power-gap law[11-19] is one of the important outcomes of the experimental and computational efforts in studying rotational energy transfer (RET) in molecular collisions. These laws provide entire matrix of integral inelastic cross-sections (IICS), $\sigma(j_i \rightarrow j_f)$, in terms of a few fitting parameters.

Here we intend to explore the advantages of the power-gap law along with the computation and prediction of rotationally inelastic cross sections in an atom-diatom system such as N₂-He. To achieve this objective, we shall first perform a quantum mechanical computation of cross sections. The computed cross sections will then be employed to test the validity of the power-gap law and its fitting parameters would be determined. These parameters may be a function of collision energy of the system. We would like to explore such functional dependence. We would see that this knowledge of the fitting parameters and their energy dependence can lead us to arrive at the prediction of the cross sections at any value of collision energy within the range explored.

In section 2, we shall describe potential energy surface and the procedure for the computation of the cross sections. The power-gap law is given in section 3, and the results are finally presented and discussed in section 4.

2. Computation and formulation

2.1 Potential energy surface

Assuming the diatomic molecule N₂ as a rigid rotor, the potential energy V of the system is taken as a sum of pair wise interaction terms V (N-He) and V (N-He):

$$V = V(r_1) + V(r_2), \quad (1)$$

where r₁ and r₂ are the N-He and N-He distances respectively as shown in Fig. 1. For V(r_i), (r_i = 1,2), the following form of the Morse potential is taken :

$$V(r_i) = D [\exp \{-2\alpha(r_i-r_0)\} - 2\exp \{-\alpha(r_i-r_0)\}] \quad (2)$$

The values of potential parameters [20] taken for N-He system are as below:

$$D = 0.002328 \text{ eV}; \quad \alpha = 1.668985 / \text{\AA} \quad (3)$$

$$r_0 = 3.5941 \text{ \AA}; \quad R_{\text{bond}} = 1.094 \text{ \AA}, \quad (4)$$

Where R_{bond} denotes the N₂ bond length.

2.2 Computation of cross sections

The cross-sections have been computed by using Agrawal and Raff's modified version [21] of the infinite order sudden approximation (IOSAM). The cross-sections (IOSAM) obtained by this procedure are related to the IOSA cross-section by :

$$\sigma_{\text{IOSAM}} = \sigma_{\text{IOSA}}(T_f/T_i)^{1/2}, \quad (5)$$

where T_f and T_i , respectively represent the final and initial translational kinetic energy and the expression for σ_{IOSA} is as given in Ref.[21]. Such a modification closes the channels which are not allowed by the energy conservation constraints. Depending on the energy of the system, the number of phase shift have been varied in the range 100-300. The phase shifts have been computed using a 10-point Gauss-Mehler quadrature of the WKB phase shift equation as described by Pack [22].

3. Power-gap law

The power-gap law [16] can be expressed in the following form:

$$\sigma(0 \rightarrow j_f) = a'(2j_f + 1)(T_f/T_i)^{1/2} |\Delta E|^{-\gamma}. \quad (6)$$

Rewriting the law in following form so that constants may have good dimensions, we obtain:

$$\sigma(0 \rightarrow j_f) = a(2j_f + 1)(T_f/T_i)^{1/2} |\Delta E/B|^{-\gamma}. \quad (7)$$

Here 'a' and ' γ ' are the fitting parameters, j_f is the final rotational quantum number, $|\Delta E|$ is the energy gap between the initial and final rotational levels, B is the rotational constant, i.e.

$$B = \hbar^2/2I$$

Where $I = \mu R_{\text{bond}}^2$,

with μ as the reduced mass of the diatom-atom system.

The Power-gap "law" given by equation (7) can be expressed as

$$Y = -\gamma X + \ln a, \quad (8)$$

where

$$Y = \ln[(\sigma(T_f/T_i)^{1/2})/(2j_f + 1)]$$

and

$$X = \ln |\Delta E/B|. \quad (10)$$

Thus a graph can be plotted between X and Y and from the knowledge of the intercept and slope of the line the value of the parameters 'a' and ' γ ' can be obtained for a given set of potential parameters and colliding energy.

Several studies [23-25] have shown that for low transitions ($|\Delta E| \leq |\Delta E|^*$) one set of parameters a_{low} and γ_{low} is required and for ($|\Delta E| > |\Delta E|^*$) another set of parameters a_{high} and γ_{high} is required. There have been several studies regarding the dependence of $|\Delta E|^*$ [25-28] on various factors. However, the relationship of these fitting parameters with the energy and the intermolecular potential parameters is still not well understood. One, therefore, needs to know the dependence of the fitting parameters upon the various parameters that describes the colliding system, wherever equation (6) is applicable. In this paper, we have investigated dependence of a_{low} and γ_{low} on the collision energy.

II. Results and discussion

Using the quantum mechanical procedure described in section 2, we first computed state-to-state rotationally inelastic cross sections for N_2 -He system at six values of colliding energy (E) varying from 0.1 to 0.5 eV. Using such computed cross-sections and the power-gap law, the parameter $|\Delta E|^*$ has been evaluated by plotting graph between Y and X as mentioned in equations (9) and (10), respectively. For the sake of further discussion we express $|\Delta E|^*$ in terms of the rotational quantum number j^* defined as

$$|\Delta E|^* = j^*(j^* + 1) \hbar^2/2I.$$

For the determination of j^* for each value of E we have fitted the Y versus X data [see equations.(9) and (10)] by two straight lines – one line corresponding to the linear least square fit of the data corresponding to $j_f \leq j_{\text{trial}}^*$ and another line for $j_f \geq j_{\text{trial}}^*$; where j_{trial}^* is an arbitrary number such that by varying j_{trial}^* we arrive at j^* by the following criteria: j^* equals that value of j_{trial}^* which gives the best fit for both the regions.

The values of j^* so obtained as a function of collision energy E are shown in Table 1. The table also lists the values of $a = a_{\text{low}}$ and $\gamma = \gamma_{\text{low}}$ [see equation(8)] given by the straight line obtained for the data corresponding to $j_f \leq j^*$.

The data reported in Table 1 reveal that a_{low} monotonically decreases from 15.33 to 7.02 as energy E increases from 0.1 to 0.5 eV. Referring to equation (7), one can say that due to the factor 'a' alone ('a' is being denoted as a_{low} here) there is a decrease in the value of the cross section as colliding energy increases. To investigate the dependence of a_{low} on E, we plot a graph between $\ln(a_{\text{low}})$ and $\ln(E)$. The graph so plotted is shown in Fig. 2. The results reveal that the points lie on a straight line described by the following equation:

$$\ln(a_{\text{low}}) = a_1 \ln(E) + a_1' \quad (11)$$

where

$$a_1 = -0.509, \text{ and } a_1' = 1.560. \tag{12}$$

Here units are such that cross sections are in \AA^2 and energy is in eV.

The results for the variation of γ_{low} with E are reported in Table 2. We note that the variation in γ_{low} with E is not as rapid as that for a_{low} with E. γ_{low} decreases from 1.027 to 0.901 as E increases from 0.1 to 0.5 eV. A decrease in γ corresponds to an increase in the value of the cross sections. Therefore, one can say that due to the dependence of γ_{low} on E there is an increase in the cross sections with energy. A smaller change in the value of γ_{low} with energy does not mean that the cross sections are insensitive to the variation in γ_{low} . It may be noted that the value of cross section, $\sigma(0 \rightarrow j_f)$, is very sensitive to γ as it appears in the factor $|\Delta E/B|^{-\gamma}$ [see equation(7)]. Further, to investigate the dependence of γ_{low} on energy E, we have plotted a graph between $\ln(\gamma_{\text{low}})$ and $\ln(E)$. The results are shown in Fig.3. We note that the data satisfy the following equation of a straight line:

$$\ln(\gamma_{\text{low}}) = b_1 \ln(E) + b_1' \tag{13}$$

Where

$$b_1 = -0.0888, \text{ and } b_1' = -0.180 \tag{14}$$

Here again units are such that cross sections are in \AA^2 and energy is in eV.

For $|\Delta E| \leq |\Delta E|^*$, we have seen that the cross sections for $N_2\text{-He}$ at any value of energy in the given energy range can be determined using the following relation provided by the power-gap law:

$$\sigma(0 \rightarrow j_f) = a_{\text{low}}(2j_f + 1)(T_f/T_i)^{1/2} |\Delta E/B|^{-\gamma_{\text{low}}} \tag{15}$$

where a_{low} and γ_{low} are given by equations (11) and (13), respectively. Such an equation is valuable in the sense that one can determine the cross sections at any value of energy in the given range without performing quantum mechanical calculations.

To test the success and usefulness of equation (15), for example, we have computed cross sections at four values of energy: $E=0.12, 0.25, 0.35, \text{ and } 0.45$ eV. The results are reported in Table 3. For comparison, we have also computed the quantum mechanical cross sections using equation (5) and have included the results in the table. A very good agreement between the cross sections given by Equations (15) and (5) demonstrate the success of Equation (15) and the parameters given by equations (11) - (14).

Dexheimer *et al.* [26], and Agrawal and his coworkers[25,27-28] have shown that the existence of two regions - one corresponding to $|\Delta E| \leq |\Delta E|^*$ and another corresponding to $|\Delta E| > |\Delta E|^*$ - is due to a basic aspect of the mechanism of the rotational energy transfer in the molecular collisions: They showed that the region corresponding to $|\Delta E| > |\Delta E|^*$ belongs to the region forbidden by the angular momentum conservation limits, i.e., though the law of conservation of energy allows such rotational excitations, the angular momentum conservation constraints as provided by the hard ellipsoid potential model [25] prevents the transitions with the energy transfer beyond $|\Delta E|^*$. Thus such an investigation of rotationally inelastic cross sections through the power-gap law has been useful in providing a valuable aspect of the mechanism of the rotational energy transfer. The observation of the two regions as noted here in the present study affirms this point.

Earlier, Agrawal *et al.*[25] have reported the results of a study of rotational energy transfer in the similar system with a different kind of interaction potential. They employed a pair-wise Lennard -Jones potential. It is interesting to note that the values of j^* as a function of energy evaluated by them (as shown in Table 1 of Ref. [25]) are almost the same as noted in the present study. However, γ_{low} values for that potential in that study [25] are somewhat lower than that observed here: Against the variation of γ_{low} from 1.027 to 0.901 as noted here (see Table 1) Agrawal *et al.*[25] observed the variation from 0.85 to 0.79 in the same energy range. This difference gives rise to a new avenue of research to find the specific nature of difference in the interaction potential that affects the values of γ_{low} . It is also expected that more studies in the direction of γ_{low} , a_{low} , and j^* for different systems with different kinds of interaction potential, and an exploration of energy dependence equations, such as Equations(11) to (14), as noted in this study, may also reveal some valuable aspects of the mechanism of the rotational energy transfer.

III. Conclusion

The above results reveal that quantum mechanical cross-sections calculated by the IOSAM formulation for $N_2\text{-He}$ system with the pair -wise Morse potential verifies the power -gap law. To our knowledge, the success of the power-gap law for $N_2\text{-He}$ system with the pair- wise Morse potential is being reported for the first time. Further, we have seen that the energy dependence of the parameters of the power-gap law is valuable as it allows us to the determination of the cross sections at any value of energy in the given range: With the help of Eq. (11) to Eq. (15) one can determine various cross - sections for $N_2\text{-He}$ system at any value of energy in the range $E=0.1\text{eV}$ to $E=0.5\text{eV}$ even by a simple calculator. This provides motivation to further investigate the dependence of these parameters of the power-gap law on the parameters of the potential. Such a study may also be extended to other systems.

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Table - 1 Variation of j^* , a_{low} and γ_{low} with the collision energy

Energy (eV)	j^*	$a_{low}^{(a)}$	$\gamma_{low}^{(a)}$
0.10	10	15.3329	1.027
0.15	12	12.3666	0.983
0.20	14	11.4158	0.980
0.30	16	8.3562	0.912
0.40	18	7.3964	0.899
0.50	20	7.0217	0.901

(a) The units of a_{low} and γ_{low} are such that in Equation(7) cross section is in Å² and ΔE is in eV

Table – 2 Comparison of cross sections, $\sigma(0 \rightarrow j_f)$ obtained by using scattering theory (IOSAM) and by empirical relation [Equation (15)] for four values of collision energy for $N_2 - He$

j_f	$\sigma(0 \rightarrow j_f)$ in \AA^2	
	Empirical relation [Equation(15)]	IOSAM
E= 0.12 eV		
2	11.43	9.37
4	6.02	6.39
6	4.01	5.36
8	2.94	4.0
10	2.26	1.96
E= 0.25 eV		
2	8.84	7.46
4	5.07	5.14
6	3.59	4.14
8	2.78	3.18
10	2.25	2.75
12	1.88	2.29
14	1.59	1.42
E= 0.35 eV		
2	7.84	6.89
4	4.65	4.64
6	3.38	3.59
8	2.66	3.05
10	2.20	2.43
12	1.87	2.04
14	1.61	1.83
16	1.41	1.34
E= 0.45 eV		
2	7.16	6.51
4	4.36	4.29
6	3.22	3.34
8	2.57	2.72
10	2.15	2.38
12	1.84	1.94
14	1.61	1.62
16	1.43	1.48
18	1.27	1.17

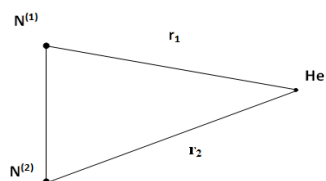


Fig. 1 A diatomic molecule having atoms $N^{(1)}$ and $N^{(2)}$ colliding with He.

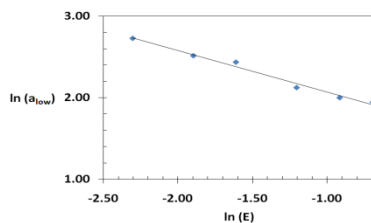


Fig. 2 Variation of a_{low} with collision energy E (eV)

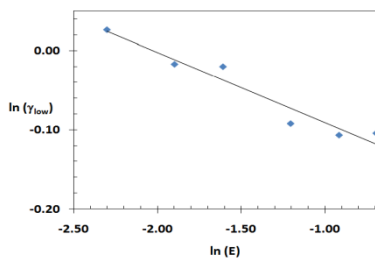


Fig. 3 Variation of γ_{low} with collision energy E (eV)