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The maximum amount of rotational energy transfer in F_2-He system and hard ellipsoid potential model.

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Abstracts: *The importance of the classical limit of the maximum rotational energy transfer, $(\Delta E)_{max}$, has been reviewed for a two dimensional hard ellipsoid potential model over a wide range of energies, reduced mass of the system, potential functions and potential parameters for the F_2-He system. It has been found that $(\Delta E)_{max}$, predicted by the hard ellipsoid potential is comparable to a well-known parameter $l\Delta El^*$ given by the two parameter Power- gap law. The numerical equivalence of $(\Delta E)_{max}$ and $l\Delta El^*$ has been verified for various types of potential surfaces, collision energy and the mass of the system. Such equivalence suggests that the value of $(\Delta E)_{max}$ can be used as one parameter $l\Delta El^*$ of the power -gap law.*

I. Introduction

The study of rotational inelastic scattering between molecules and neutral atoms at low collision energies is a fast developing field in collision dynamics [1-5].The nature of rotational energy transfer (RET) in collisions of molecules with He, Ar and Ne were studied experimentally [6-8] and theoretically [9-11] .

In several papers Mc caffery and co-workers [12-15] explored various aspects of the RET by treating the conversion of orbital angular momentum to the angular momentum of the molecule at the repulsive wall of anisotropic intermolecular potential. However they point out that the maximum change in rotational momentum might be limit either by energy conservation or by momentum conservation, developing on detail of the particular collision system. They obtain the maximum classical limit of RET by using a hard ellipsoid potential model. This model treats a molecule as a hard core ellipsoid and the collision between the atom and the hard core ellipsoid.

The relationship between the shape of the potential surface and the energy transfer is crucial for understanding collision processes of molecules and atoms. The link between the two is provided by the general quantum theory of collision for hard shapes. The problem of the rotationally inelastic collision of a particle with a hard ellipsoid potential [16-17] can be solved by using the three principles of conservation; the total energy conservation, linear momentum conservation and the angular momentum conservation. Agrawal and co-workers [18-21] have noted that the classical limit of rotational energy transfer $(\Delta E)_{max,}$ predicted by the hard ellipsoid model is comparable to a well known parameter $l\Delta El^*$ given by power -gap law [22] and the RET cross –sections computed on the real potentials.

It would be important to perform an elaborate test of the expression for the maximum limit of angular momentum transfer so obtained, such a test would be useful for the RET cross- sections computed using the realistic potential.

In this study, in addition to the validity of the hard ellipsoid potential model we shall also reconfirm that the division between the classically allowed and forbidden transitions given by the power-gap law is excellent. Further, we show that the equivalence of the $l\Delta El^*$ and $(\Delta E)_{max,}$ not only provide the physical meaning to $l\Delta El^*$ given by the RET data and the power -gap law but is also valuable for determination of some features of intermolecular interaction potential from knowledge of RET data.

In Section 2, we formulate the procedure for determination of $l\Delta El^*$ and $(\Delta E)_{max}$. The results are presented and discussed in Section 3. Finally the conclusions are summarised in Section 4.

II. Formulation

2.1. Determination of $l\Delta El^*$

The parameter $l\Delta El^*$ is determined with the help of cross sections obtained from scattering calculations and the power gap law.

For the computation of cross sections the homonuclear diatomic molecule, F2, is treated as a rigid rotor and the interaction between the molecule and the atom, He, is taken as a pairwise sum of the potential terms,

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

where r_1 and r_2 are the F^1-He and F^2-He distances, respectively, as shown in Fig.1.

For $V(r_i)$ the general form of the Lennard–Jones (L-J) potential is taken with different values of n and m:

$$V(r_i) = \varepsilon[\{m/(n-m)\}(r_o/r_i)^n - \{n/(n-m)\}(r_o/r_i)^m], \quad (i = 1, 2), \qquad (2)$$

where r_0 and ε are taken [23, 24] as 1.4178 Å and 1.8259 meV, respectively .

The variation in the potential function is obtained by putting n=9, 12 and 18 in Eq. (2), keeping m=6, giving the potential functions which we shall denote as V (9, 6), V (12, 6) and V (18, 6).

In addition to the above-mentioned potential functions, purely repulsive terms of the potential functions have also been investigated. It is convenient to denote such potentials by the notation $V_R(n)$, which has been obtained by deleting the attractive term from the potential V (n, m). The cross sections have been computed using the modified infinite order sudden approximation method (IOSAM), [25]. The phase shifts have been computed using a 10- point Gauss – Mehler quadrature of the WKB phase shift equation as described by Pack [26].

According to the power gap law [22] the cross sections, $\sigma(j_i \rightarrow j_f)$ can be expressed as

$$\sigma(j_i \rightarrow j_f) = a(2j_f + 1)(T_f/T_i)^{1/2} |\Delta E|^{-\gamma}, \qquad (3)$$

where j_i and j_f are the initial and final rotational quantum numbers, a and γ are the fitting parameters, T_f and T_i are the final and initial translational energies and $|\Delta E|$ is the energy gap between initial and final rotational levels. Eq. (3) gives the following equation which can be used to separate the two regions.

$$Y = -\gamma X + \ln a, \qquad (4)$$

where

$$Y = \ln[\sigma(j_i \rightarrow j_f)(T_i/T_f)^{1/2}/(2j_f + 1)], \qquad (5)$$

and

$$X = \ln |\Delta E|. \qquad (6)$$

A typical X-Y plot which shows the existence of two straight lines signifying the two regions is given in Fig. (2). The location of the critical point has been marked as $|\Delta E|^*$ in the figure. For all sets of the computed cross sections, $|\Delta E|^*$ has been obtained by such plots.

2.2. Determination of $(\Delta E)_{max}$

For the maximum limit of angular momentum transfer the hard ellipsoid potential model was discussed in detailed by Agrawal and co-workers [18-20]. He found the following relation for the classical limit of the angular momentum transfer

$$(\Delta J)_{max} = \sqrt{(2\mu)}(\sqrt{E} + \sqrt{E'})(A-B), \qquad (7)$$

where μ is the reduced mass of the colliding system, E and E' are the initial and final translational energies of the system, respectively and A and B are the lengths of the semi – major and semi-minor axes of ellipsoid, respectively.

From the above expression the limit of the rotational energy transfer in the molecule can easily be obtained. For simplicity, if the diatomic molecule is considered initially in the ground state, then the expression for the maximum amount of rotational energy transfer would be

$$(\Delta E)_{max} = [(\Delta J)_{max}]^2 / 2I,$$

$$(\Delta E)_{max} = (\mu/I)(A-B)^2 [E + E' + 2\sqrt{(EE')}] \qquad (8)$$

where I is the moment of inertia of the diatomic molecule. Eq. (8) together with the following energy conservation equation

$$E' = E - (\Delta E)_{max}, \qquad (9)$$

can be used to compute $(\Delta E)_{max}$ from knowledge of E, A, B, μ and I.

III. Results and discussion

3.1. Effect of mass

Table 1 gives the results for F_2-X system having r_0 and Є value of F_2-He system and the masses of X_2 are 2.0, 4.0, 8.0, 12.0, 16.0, 20.2 and 39.95 amu for the potential V(12,6) at different collision energies. A very good agreement between the $(\Delta E)_{max}$ values given by the hard ellipsoid model and scattering calculations is seen from Table 1. Further a decrease in $(\Delta E)_{max}$ values with increase in mass of the atomic molecule, X, is also seen from the table.

For a system to exhibit angular momentum constraint the final rotational state of the molecule must be energetically accessible to eliminate any energetic restrictions. Thus the $(\Delta E)_{max}$ values must be smaller than the available translational energy E. This gives

$$(\Delta E)_{max}/E < 1,$$

or

$$(\mu/I)(A-B)^2 < 1, \qquad [\text{using Eq. (8)}]$$

or

$$(\mu/\mu_m)[(A-B)/R_e]^2 < 1, \qquad (10)$$

where μ_m and R_e are the reduced mass and bond length of the molecules. Thus the ratio μ/μ_m is an important factor in determining whether a collision system is momentum or energy constrained. In F_2-He system the order

of (A-B) is 0.65 and the bond length of F_2 is R_e = 1.4178 Å. Hence $[(A-B) / R_e]^2$ is ≈ 0.2. Therefore the ratio μ/ μ_m should be smaller than 5 for the inequality in Eq. (10) to hold. In other cases all the transitions permitted by the energy conservation constraint would be possible.

3.2. Effect of energy

Table 2 list γ_{low}, γ_{high} and $l\Delta El^*$ given by the scattering calculations for the potential V (12, 6) and V_R (12) as a function of the initial translational energy for F_2- He system. For comparison the value of $(\Delta E)_{max}$ given by Eq. (8) are also shown in the Table 1. A comparison of the values of $(\Delta E)_{max}$ given by the hard ellipsoid model and $l\Delta El^*$ given by the scattering method shows that they are in very good agreement. This excellent agreement shows that $l\Delta El^*$ can be considered as $(\Delta E)_{max}$.

The data reported in Table 2 also shows that $(\Delta E)_{max}$ is approximately proportional to E : $(\Delta E)_{max}$ / E varies from 0.28 to 0.265 as E increases from 0.1 to 0.4 eV. The variation of $(\Delta E)_{max}$ / E with E can be analyzed by the two factors $(A-B)^2$ and $[E+E' + 2\sqrt{(EE')}]$ / E, occurring in Eq. (8). The factor $(A-B)^2$ decreases from 0.7082 to 0.5015 and letter factor increases from 2.309 to 2.445 as E increases from 0.1 to 0.4 eV. For a perfectly hard ellipsoid potential, $(A-B)^2$ would not depend on E and as such the variation in $(\Delta E)_{max}$ / E would be given by the later factor only. Another important parameter is, γ. For a given potential we see that γ_{low} is insensitive to the change in the collision energy. The values of γ_{high}, however, shows a different trend. The energy dependence of these parameters is a matter of further studies.

3.3. Effect of potential parameters r_0 and □

The parameters A and B do not appreciably change with energy E. For example, for $V_R(12)$ potential, A decreases from 3.6592 to 3.3370 and (A-B) increases from 0.6172 to 0.6458, as E increases from 0.1 to 0.4 eV, respectively.

Therefore, to study the dependence of $(\Delta E)_{max}$ on (A –B) as given by Eq. (8) we have varied the potential parameter $\mathbf{r_0}$ from 1.0 R_0 to 2.5 R_0, where R_0= 1.4178 Å. The so obtained results for F_2-He system at E = 0.1 eV for $V_R(12)$ potential are given in Table 3. With such a change in the range parameter now A varies from 3.6592 to 4.4256 and (A –B) ranges from 0.6172 to 2.2436 as r_0 varies from 1.0 R_0 to 2.5 R_0, respectively, for $V_R(12)$ potential. Thus the data presented in Table 3 exclusively demonstrate the effect of variation of (A –B) on $(\Delta E)_{max.}$. Here again we see that a very good agreement between the scattering results and those given by Eq. (8) for $(\Delta E)_{max.}$

Unlike the effect of r_0, the parameter ε has small effect on (A – B). Such an effect of varying ε from 0.5 ε_0 to 4.5 ε_0, where ε_0 = 1.8259 meV, is shown in Table 4 at E=0.1 eV. Here (A –B) decreases by about 7 % as Є increases from 0.5 ε_0 to 4.5 ε_0 for $V_R(12)$ potential. The data presented in Table 4 also show a very good agreement between the scattering results and those given by the hard ellipsoid potential model.

IV. Conclusions

The maximum amount of rotational energy transfer in collisions of F_2 with He has been investigated over a wide range of energies, reduced mass of the system, potential functions and potential parameters. Further, the classical limit of maximum rotational energy transfer has been reviewed for a hard ellipsoid potential model.

The $l\Delta El^*$ values obtained by scattering results are compared with those given by $(\Delta E)_{max.}$ values predicted by the hard ellipsoid potential model. The good agreement between $l\Delta El^*$ and $(\Delta E)_{max}$ values over the wide range of energies and different potential functions suggest that the parameter $l\Delta El,^*$ given by power-gap law has a physical significance, $l\Delta El^*$ is nothing but the classical limit of the rotational energy transfer. Further, the equivalence of $l\Delta El^*$ and $(\Delta E)_{max}$ also suggest that the classical limit of angular momentum transfer given by the hard ellipsoid potential model is meaningful even for the cross sections computed on the real potentials provided the classical turning point surface of the soft potential is assumed as the hard potential surface.

Such a study also leads the systematic decrease in $(\Delta E)_{max}$ with the increase in the reduced mass of the system has been verified for X_2-He system, where the diatom X_2 has all properties of F_2 except the mass, which is taken as 24.0, 28.0, 32.0 and 38.0 amu. The $l\Delta El^*$ values given by the scattering results are also found to be in good agreement with the $(\Delta E)_{max}$ values obtained by using the hard ellipsoid model.

Similarly, the dependence of $(\Delta E)_{max}$ for F_2-He system has been investigated for different types of potential surfaces over a wide range of initial collision energy and potential parameters. In all cases it is found that the agreement between $(\Delta E)_{max}$ and $l\Delta El^*$ is good to excellent. The agreement, however, is not so good for the potentials having large well depth.

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References

[1] M. T. Bell and T. P. Sotley, Molecular Physics **107,** (2009) 99.
[2] W. M. Smith, Angew. Chem. Int. Ed. **45,** (2006) 2842.
[3] Smith, ed., Low Temperatures and Cold Molecules (Imperial college press, 2008).
[4] R. Krems, W. Stwalley and B. Friedricheds. ,Cold molecules, Theory, Experiment Applications (Taylor and Francis,2009).
[5] M. Kriste, L. Scharfenberg, J. Klos, F. lique, M. H. Alexander, G. Maijer, and S. Y. T. Vande Meerakker, phy. Rev. **A 82,** (2010) 42717.
[6] P. J. Dagdigan, Annu. Rev. Phys. Chem. **48,** (1997) 95.
[7] M. T. Sun, J. Liu, W. Z. Sun, X. L. Chen, B. Jiang, G. H. Sha, Chem. Phys. Lett. **365,** (2002) 244.
[8] P. A. Barrass, P. Sharkey, I. W. M. Smith, Phys. Chem. Phys. **5,** (2003) 1400.
[9] J. Mc Caffery, M. J. Whitaker, Annu. Rev. Phys. Chem. **37,** (1986) 223.
[10] Schiffman, D. W. Cchandler, Int. Rev. in Phys. Chem. **14,** (1995) 371.
[11] M. T. Sun, Y. Q. Lee, F. C. Ma, G. H. Sha, Chem. Phys. Lett. **371,** (2003) 342.
[12] J. Mc Caffery, Z. T. Alwahabi, M. A. Osborne, C. J. Williams, J. Chem. Phys. **98,** (1993) 4586.
[13] M. A. Osborne, A. J. Mc Caffery, J. Chem. Phys. **101,** (1994) 5604.
[14] M. A. Osborne, A. J. Mc Caffery, J. Chem. Phys.**100** ,(1996) 13346.
[15] S. Clare, A. J. Marks, A. J. Mc Caffery J. Phys. Chem. **104,** (2000) 7181.
[16] J. A. Serri, R. M. Bilotta, D. E. Pritchard, J. Chem. Phys. **77,** (1982) 2940.
[17] S. D. Bosanac, N. Petrovic, Phys. Rev. **A 41,** (1990) 5909.
[18] P. M. Agrawal, S. Tilwanker, N. K. Dabkara, J. Chem. Phys. **108**, (1998) 4854.
[19] P. M. Agrawal, S. Tilwanker, Acta Phys. Pol. **A 93,** (1998) 451.
[20] N. K. Dabkara, P. M. Agrawal, Chem. Phys. Lett. **299,** (1999) 125.
[21] N. K. Dabkara, Acta Phys. Pol. **A 100,** (2001) 41.
[22] J. M. Huston, Annu. Rev. Phys. Chem. **41,** (1990) 123.
[23] D. E. Gray (Ed.), American Institute of Physics Handbook, Mc Graw Hill, New York, **1957**, P.4.129.
[24] R. A. Svehla, NASA Tech. Rep. **TR R-132**, 1962.
[25] P. M. Agrawal, L. M. Raff, J. Chem. Phys. **74,** (1981) 3292.
[26] R. T. Pack, J. Chem. Phys. **60,** (1974) 633.

Table 1

Comparison of maximum amount of rotational energy transfer $(\Delta E)_{max}$ values given by the hard ellipsoid potential model and those obtained by using the scattering result for the F_2-X system, as a function of mass of the atom at different collision energies. Potential parameters of X are taken as of He . Potential V(12,6) is used.

Mass of X (amu)	μ	μ / μ_m	γ_{low}[a]	γ_{high}[a]	$(\Delta E)_{max}$ (eV)	
					Ellipsoid Model	**Scattering**
2.0	**1.9**	**0.21**	**0.860**	**9.25**	**0.018**	**0.019**
4.0	**3.6**	**0.40**	**0.800**	**8.99**	**0.027**	**0.028**
8.0	**6.6**	**0.73**	**0.761**	**7.34**	**0.049**	**0.044**
12.0	**9.1**	**1.01**	**0.752**	**6.22**	**0.060**	**0.059**
16.0	**11.3**	**1.26**	**0.746**	**3.75**	**0.068**	**0.064**
20.2	**13.2**	**1.47**	**0.749**	**2.66**	**0.074**	**0.072**
39.95	**19.95**	**2.17**	**0.738**	**1.06**	**0.086**	**0.067**

Table 2

Comparison of maximum amount of rotational energy transfer $(\Delta E)_{max}$ values by the hard ellipsoid potential model and those obtained by using the scattering cross sections and the power- gap law for the F_2-He system.

Potential	**Energy (eV)**	γ_{low}[(a)]	γ_{high}[(a)]	**(□ E)$_{max}$ eV.**	
				Ellipsoid Model	**Scattering**
V (12 ,6)	**0.10**	**0.80**	**8.99**	**0.027**	**0.028**
	0.15	**0.83**	**8.50**	**0.041**	**0.039**
	0.20	**0.79**	**8.61**	**0.055**	**0.050**
	0.25	**0.84**	**10.04**	**0.069**	**0.068**
	0.30	**0.82**	**10.86**	**0.084**	**0.082**
	0.35	**0.82**	**10.84**	**0.098**	**0.095**
	0.40	**0.82**	**10.19**	**0.127**	**0.106**
V_R(12)	**0.10**	**0.96**	**8.88**	**0.025**	**0.025**
	0.15	**0.81**	**7.60**	**0.039**	**0.030**
	0.20	**0.83**	**7.99**	**0.052**	**0.043**

	0.25	**0.86**	**9.39**	**0.066**	**0.059**
	0.30	**0.85**	**10.36**	**0.080**	**0.073**
	0.35	**0.85**	**10.74**	**0.087**	**0.086**
	0.40	**0.85**	**10.28**	**0.109**	**0.098**

(a) The unit of γ_{low} and γ_{high} are such that in Eq. (3) cross section is in (Å) ^{2} and ΔE is in eV.

Table 3

Comparison of maximum amount of rotational energy transfer $(\Delta E)_{max}$ values given by the hard ellipsoid potential model and those obtained by using the scattering results for the F_2-He system, as a function of Potential parameter, $r_{0,}$ at collision energy E =0.1 eV ($r_{0,}$ = 1.4178Å) . Potential $V_R(12)$ is used.

r_0/R_0	A (Å)	B (Å)	(A-B) (Å)	$(\Delta E)_{max}$ (eV)	
				Ellipsoid Model	Scattering
1.00	3.6592	3.0420	0.6172	0.025	0.025
1.25	3.8352	2.9952	0.8400	0.029	0.027
1.50	4.0118	2.9368	1.0750	0.032	0.032
1.75	4.1888	2.1888	2.0000	0.036	0.033
2.50	4.4256	2.1820	2.2436	0.046	0.042

Table 4

Comparision of maximum amount of rotational energy transfer $(\Delta E)_{max}$ values given by the hard ellipsoid potential model and those obtained by using the scattering results for the F_2-He system, as a function of Potential parameter, $\varepsilon_{0,}$ at collision energy E =0.1 eV ($\varepsilon_{0,}$ = 1.8259 meV), Potential $V_R(12)$ is used.

$\varepsilon / \varepsilon_0$	**A** (Å)	**B** (Å)	**(A –B)** (Å)	**$(\Delta E)_{max}$ (eV)**	
				Ellipsoid model	Scattering
0.5	3.4932	2.8616	0.6316	0.026	0.026
1.0	3.6592	3.0420	0.6172	0.025	0.025
1.5	3.7610	3.1520	0.6090	0.025	0.024
2.0	3.8352	3.2324	.6028	0.024	0.022
4.5	4.0546	3.4688	0.5858	0.023	0.021

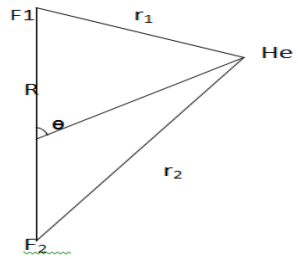

Fig. (1) Coordinates for the rigid rotor F_2-He system.

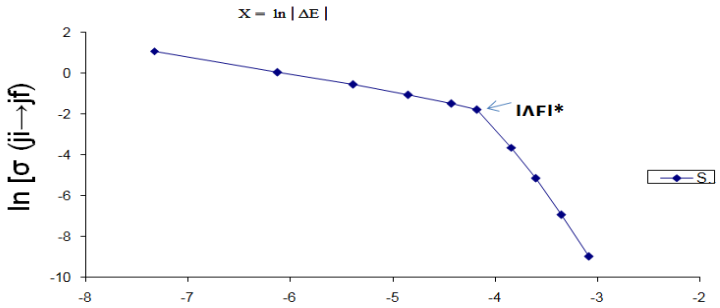

Fig. (2) ln [σ ($j_i \rightarrow j_f$) (T_i/T_e)$^{1/2}$/ (2 j_f +1) versus ln |ΔE| for j_i=0 at E= 0.1 eV for V_R(12) potential. |ΔE|* point is shown by an arrow. The unit of ΔE and σ are eV and Å , respectively.