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THE PHYSICAL ORIGIN OF FITTING LAWS FOR
ROTATIONAL ENERGY TRANSFER.

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ABSTRACT

An historical overview of the various parameterised forms describing RET processes (fitting laws) is presented. The physical models behind these "laws" are compared. Particular attention is paid to the role of angular momentum constraints and to the energy dependence of the state-to-state cross-sections. Finally it is shown how general trends can be inferred from the topology of the intermolecular potential energy surface.

1. INTRODUCTION

Many of the collision systems in which rotational energy transfer (RET) has been studied are too large for accurate close-coupled quantum calculations. Even though the problem may be somewhat simplified for these heavier systems through the use of the fixed-nuclei or energy sudden (ES)

factorisation ¹, the accurate calculation of the basis cross-sections is still a formidable and often impossible task since the intermolecular potentials, particularly of electronically excited molecules, are not known with any precision.

An alternative approach over recent years has been to look for simple parameterized fitting laws to describe the cross-sections. We describe here below the various forms which have been proposed in historical order.

2. FITTING LAWS

2.1 Exponential gap laws (EGL)

The earliest of these was the exponential gap law (EGL) ^{2,3} which was advanced over a decade ago in order to interpret infrared chemiluminescence experiments. The EGL proposes that the efficiency of a particular rotational transfer channel decreases exponentially as the amount of energy exchanged, compared to the average kinetic energy, increases. Levine, Bernstein and coworkers ^{4,5} later realised that the EGL could be justified from theoretical arguments based on information theory and surprisal analysis. Linear surprisal plots imply :

$$k_{jj'} = C(E) k_{jj'}^{(0)} \exp(-\Theta |\Delta E_{jj'}|/E) \quad (1)$$

where $E = 1/2 \mu u^2 + B_j(j+1)$. $C(E)$ and Θ are (possibly energy dependent) empirical parameters chosen for a best fit to the data. $k_{jj'}^{(0)}$ is the prior

statistical rate constant.

Heller ⁶ and later Sancturary ⁷ were able to approximately describe the energy dependence of the EGL using very simple semi-classical mechanics. However while the information theory and thermodynamic approach can be used to justify expressions such as the EGL it is still by no means clear, on the microscopic dynamical level, why rotationally inelastic cross-sections should be so insensitive to the intermolecular potential as to allow such a simple two parameter reduction of RET data sets. Furthermore the EGL only "agrees" with experimental and numerically calculated data sets in a very broad sense, the detailed comportment of the cross-sections particularly at large energy gaps is not well described.

2.2 Power laws

Some years ago Pritchard and coworkers ⁸ presented a slightly modified form of the EGL in which the scattering amplitude varied as the inverse power of the energy gap. This power gap law (PGL) was found to give somewhat better agreement with experimental data for the $\text{Na}_2(1^1\Sigma^+) + \text{Xe}$ system than the EGL. In a later publication ⁹ they extended their ideas by explicitly including the quantum mechanical factorisation resulting from the sudden approximation to create a combined fitting and scaling law known as the infinite order sudden power law (IOS-P) :

$$k_{j \rightarrow j'} = (2j' + 1) \exp[(E_j - E_{j'})/kT] \times \sum_{\ell} (2\ell + 1) \left(\begin{matrix} j & j' & \ell \\ 0 & 0 & 0 \end{matrix} \right)^2 k_{\ell \rightarrow 0} \quad (2)$$

where the basis rate constants are fitted to the form,

$$k_{\ell \rightarrow 0} = A[\ell(\ell + 1)]^{-\Gamma} \quad (3)$$

by varying the two parameters A and Γ .

In equation (2) the exponential factor takes account of detailed balance - i.e. the Boltzmann averaged expression of microreversibility. ℓ is the Grawert ¹⁰ channel number, E_j is the rotational energy of the state j and $j_{>}$ is the greater of j and j' .

The power gap law, particularly the most recent versions such as the energy corrected power law (ECS-P) ¹¹ has had considerable success in describing RET for a wide variety of diatomic molecules, e.g. Na_2^* , Li_2^* , I_2^* , LiH , HF^\dagger , N_2 in collision with the rare gases and other molecules. Typically the values of the parameter Γ fall in the range 1.1 - 1.3 ¹².

More recently Derouard ^{13,14} has presented a classical expression of the power law, again within the sudden approximation. The classical rate constant for RET between the states j and j' may be written ¹⁵ :

$$k_{j \rightarrow j'} = \int_{|j-j'|}^{j+j'} [(2j'+1)/2\pi jj' \sin \Theta] k_{0 \rightarrow \ell} d\ell \quad (4)$$

where Θ is the in plane angle between the initial and final angular momentum vectors,

$$\cos \Theta = [\ell^2 - (j'^2 + j^2)]/2jj' \quad (5)$$

More generally Derouard ¹³ finds that the multipolar rate constants may be written :

$$k_{j \rightarrow j'}^{(K)} = \int_0^\pi \frac{2j'+1}{\pi(2\ell+1)} P_K(\cos \Theta) k_{0 \rightarrow \ell} d\ell \quad (6)$$

The connection between the quantum mechanical expressions and these latter result is to be found in the large quantum number limits of the Racah coefficients in the ES-factorisation. For the basis rate constants Derouard chooses :

$$k_{0 \rightarrow \ell} = \alpha' (\ell + 1/2)^{-\gamma'} \quad (7)$$

i.e. using the fact that for $\ell \gg 1$, $\ell(\ell + 1) \approx (\ell + 1/2)^2$. Thus Γ and γ' are related by $2\Gamma = \gamma' + 1$. For population transfer these expressions agree with those obtained with the more rigorous factorisation to within 3 % and have the advantage of being very much easier to calculate.

While the basis cross-sections are obtained, as is the case with the EGL, by some justifiable

but nonetheless *ad-hoc* procedure the PG laws have several advantages over the earlier fitting law. In the first place the ES factorisation is rigorously justifiable for most systems of interest, and in the few where this is not the case the addition of an adiabatic correction factor ^{16,17} as in the ECS-P should be a reasonable first order approximation. Secondly they help us understand how it might be possible to reduce data sets to a few parameters since the fitting law only applies to a limited sub-set of the scattering channels.

We still have to tackle the question as to why on the microscopic, quantum dynamical level, RET should follow such simple parameterised fitting laws which so far have no other basis than the empirical observation that they fit the data.

A key set of systems for this understanding has been the study of $I_2^* + {}^3\text{He}$, ${}^4\text{He}$, H_2 , D_2 collisions ¹⁸⁻²⁰ Very complete RET data sets exist for these systems since the ${}^1\Sigma_g^+ - {}^3\Pi_u^+$ electronic band of I_2 is easily accessible with single frequency dye laser radiation. It was found ¹⁸ in the $I_2 + \text{He}$ system the rates of rotational energy transfer fall off very rapidly in the high Δj channels. The rotational constant of I_2^* is $.029 \text{ cm}^{-1}$ and the rovibronic spectrum is consequently fairly dense. This means that at room temperature the number of energetically accessible channels is typically 200. The data however shows that quantum jumps greater than ≈ 40 are extremely unlikely

events ; the cross-section for $\Delta j = + 40$ is three orders of magnitude smaller than that for $\Delta j = +2$ when $j = 41$ of the $v(0-16) \ 1\Sigma_g^+ - 3\Pi_u^+$ band is excited. Dexheimer and coworkers found that it was impossible to fit these data using a power law and that it was necessary to postulate an additional *ad-hoc* constraint on the angular momentum (and another freely adjustable parameter).¹⁸ The best functional form for the basis set was found to be :

$$k_{\ell \rightarrow 0} = A[\ell(\ell + 1)]^{-\Gamma} \exp\{-[\ell(\ell + 1)/\ell^*(\ell^* + 1)]\} \quad (8)$$

Dexheimer et al.¹⁸ called this form "exponential-power" (EP) and interpreted ℓ^* as the maximum transferable angular momentum which can be classically exchanged in a collision between a rigid rotor and a structureless particle, Δj_{\max} .

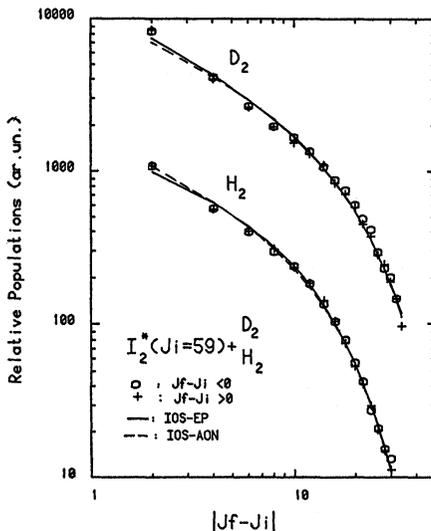


FIGURE 1
Rotational population transfer data from Ref. 19 for $I_2^*(J_i=59) + H_2, D_2$.

This interpretation of the rapid fall off of RET in high Δj channels is supported by the careful and extensive measurements of Derouard and Sadeghi ¹⁹. They studied RET in excited state I_2 for collisions with the isotopic pairs $^3,^4\text{He}$ and H_2, D_2 at fixed thermal energy (see Fig. 1). They conclude that the parameter ℓ^* is proportional to $\mu^{1/2}$ which is consistent with the hypothesis of momentum constraints. Our intuition then suggests that the physical basis for the fitting laws may be found in the conservation of angular momentum rather than in the conservation of energy. Thus the initial ideas of the energy gap laws, such as the EGL, are transposed into an angular momentum language, through the relation $E_j = B_j(j + 1)$ in the power laws, such as the IOS-P and ECS-P, and finally angular momentum constraints are explicitly included in the parameter ℓ^* (IOS-EP). Although it is rather abusive to call eq. (8) "rotational rainbow model" the understanding of RET has gained very much from these experimental findings.

2.3 The AON model

Recently we proposed a new fitting law (the AON) for RET in the energy sudden regime which is analytically derived from a semiclassical theoretical approach to the collision process ^{22,23}. The physical conditions assumed in this derivation are that the anisotropic interaction potential is strongly dominated by a single term, V_λ , or more precisely by terms of a particular parity,

of the Legendre polynomial expansion :

$$V(R, \theta) = \sum_{\lambda'} V_{\lambda'}(R) P_{\lambda'}(\cos \theta) \quad (9)$$

and that the short-range repulsive part of $V_{\lambda}(R)$ is responsible for the large quantum jumps $\Delta j = \ell$ which we have seen to be of particular interest, since it is in these channels that we observe the strongest deviations from statistical energy redistribution.

The basis of the first condition comes from considering the few systems which cannot be constrained to behave according to a power law. For example CO + He, H₂^{24,25} ; NO + Ar²⁶ ; BH + He, Ar²⁷ and ⁶Li⁷Li + He^{28,12}. In these latter systems RET does not decrease uniformly with Δj but oscillates with even and odd Δj changes. The reason for this is simply explained. For example in the ⁶Li⁷Li molecule the separation of the centre of mass from the symmetry centre gives rise to a small $P_1(\cos \theta)$ term in the potential which is absent in the non-isotopically substituted species. The dipolar term makes collisional coupling between the odd Δj states weakly allowed. Similarly CO and NO have small (but non-zero) dipole moment and fairly large quadrupole moments so that the interaction potential cannot be described by terms of a single parity. Indeed accurate *ab-initio* calculations for the CO + He, H₂ systems^{25,29} show that the V_1 and V_2 terms are nearly equivalent. By contrast in the systems for

which the power laws work well the anisotropy is well described by a $P_1(\cos \theta)$ term for the heteronuclear diatomics and a $P_2(\cos \theta)$ term for the homonuclear systems.

The basis of the second condition comes from comparing the average collision energy in thermal cell experiments with the expected anisotropy in the region of the Van der Waals well. Generally in sudden systems the dynamics are expected to be dominated by collisions against the repulsive wall of the intermolecular potential. For instance the beam scattering data of Jones et al.³⁰ clearly illustrate this point. However this may not always be the case, for example in alkali diatomics in collision with the heavier rare gases such as Xe and Kr³¹. Here the collision is adiabatic, indeed there is evidence that some trajectories lead to the formation of a long-lived collision complex, and it is interesting to note that, while the 3 adjustable parameters ECS-P law fits the RET data quite well for these systems, the AON works less well.

The AON is derived from a semi-classical infinite order expansion of the T-matrix, in which the rotational transition is treated as an infinite sum of pathways each made up of a succession of virtual transitions. This approach was first advanced by Smith, Giraud and Cooper³² in the theory of collisional line broadening. With the assumptions about the intermolecular potential

above one obtains the following expression for the basis cross-section :

$$\sigma_{\ell \rightarrow 0} = 2\pi \int_0^{\infty} b J_n^2(K_\lambda) db \quad (10)$$

where b is the impact parameter, $J_n(K_\lambda)$ is a Bessel function of order $n = \ell/\lambda$ and λ is the order of the dominant anisotropy (usually 1 or 2). The term K_λ is essentially the classical path integral :

$$K_\lambda = (2\alpha_\lambda/\hbar) \int_0^{\infty} V_\lambda [R(t)] dt \quad (11)$$

where $\alpha_\lambda = 1$ if $\lambda = 1$ or $3/4$ if $\lambda = 2$. These expressions are similar to others independently obtained by Dickinson and Richards³³, Nyeland and Billing³⁴, and Alhassid and RD Levine³⁵.

The essential step in the derivation of the AON is to assume an exponentially repulsive potential for V_λ . As long as the kinetic energy is limited in range (thermal cell conditions for instance) this approximation is always justified. If we denote the range of V_λ by r_0 the path integral becomes :

$$K_\lambda(b) = (2\alpha_\lambda/\hbar) (A/u) \times \int_{R_0}^{\infty} [1 - (b/R)^2 - 2V_0(R)/\mu u^2]^{1/2} \times \exp(-R/r_0) dR \quad (12)$$

in which R_0 is the distance of closest approach for a particular trajectory on the isotropic potential V_0 , and A is the strength of the

anisotropy.

Assuming rectilinear trajectories the integral can be analytically evaluated for head-on and large impact parameter collisions. The intermediate case can be evaluated numerically and can be shown to be within a factor of two or so of the analytic result. It is important to have the proper asymptotic behaviour. The result is :

$$K_{\lambda}(b) = a \exp(-b/r_0) \quad (13)$$

with :

$$a = 2^{3/2} \alpha_{\lambda} V_c r_0 / \mu u \quad (14)$$

where : $V_c \approx V_{\lambda}(R_0)$. This last result is arrived at by noting that physically realistic potentials will be characterised by range parameters much smaller than R_0 .

The next step is to remark that large changes in the angular momentum occur for small impact parameters. The explanation of this statement can be seen by considering a two dimensional hard ellipse model of the collision ³⁶, where large Δj differential cross-sections fall rapidly to zero in the forward direction. Experimental evidence for this observation has also been reported ³⁰. The physical reason for this is that the

"effective impact parameter" (*), which is actually the parameter responsible for the rotational transition, is a bounded function of b , falling to zero for $b = 0$ and for trajectories which miss the ellipse. In terms of the AON model this follows from approximating the Bessel function of equ. (10) by :

$$J_n(x) = (2/\pi x)^{1/2} \cos(x - n\pi/2 - \pi/4) \quad \text{for } x \geq n \quad (15)$$

$$J_n(x) = 0 \quad \text{for } x < n \quad (16)$$

Thus there is a cut-off to the integral in equ. (10), the only contributing terms being those for which $K_\lambda \geq n$ or equivalently for impact parameters smaller than $r_0 \ln(a\lambda/\ell)$. Since $a \gg \pi$ the cosine oscillates rapidly and its square averages to 1/2. The final result is :

$$\sigma_{\ell \rightarrow 0} = c [(a/n) \ln(a/n) - a/n + 1] \quad (17)$$

where c is an integration constant given by $2r_0^2/a$. In practice the two quantities a and c are treated as free parameters in a fitting procedure. This cross section is obviously a decreasing function of n , which falls to zero for $n = a$.

(*) The effective impact parameter is defined as the shortest distance between the line of the transferred linear momentum of the incoming particle and the centre of mass of the ellipse.

It is important to note that $n > a$ is physically unrealistic since it would imply a negative impact parameter. Then the quantity $\lambda a = \Delta j_{\max}$ represents the maximum transferable angular momentum. Channels for which $\ell/\lambda > a$ are therefore closed by setting $\sigma_{\ell \rightarrow 0} = 0$.

3. PHYSICAL DISCUSSION

3.1 Comparison of AON with power law model

Providing that the channel number is not of the same order as a , the numerical behaviour of the power law and the AON is very similar. The differences between the two are only apparent in the large Grawert channels where the angular momentum constraints become important. In that case the numerical behaviour of the AON can be reproduced by the EP law (eq. 8). Note, however, that the AON does not require the setting of a third independent parameter ℓ^* , and that ℓ^* is usually found markedly different from the fitted values of a . The two laws differ in another respect. According to Brunner et al.³⁷ the physical explanation of the power law behaviour is connected to the shape of the interaction potential at long range. They proposed a simple impulse model based on straight-line trajectories and an anisotropy with a long range attractive tail of the form R^{-p} . According to this model the parameter Γ is related to the potential by :

$$\Gamma = (p + 1) / (p - 1) \quad (18)$$

Thus for a 12-6 potential Γ should be of the order of 1.4, which is at the upper range of the values typically observed. This also explains why the value of Γ does not vary much between different collision systems. However it is not at all clear how one can arrive at Γ values smaller than unity, which have been observed in a few systems most notably LiH + He ³⁸ where the data is best fit by $\Gamma = 0.9$. The AON fits this data well with a χ^2/ν of 0.22 ²³. Similarly in NaH + He a value as low as $\Gamma = 0.75$ has been found by Giroud and Nédelec ³⁹. It is also difficult to see how large Δj changes can be effected by the slowly varying part of the potential.

Very recently Nyeland ⁴⁰ has presented a new dynamically based fitting law which closely resembles a power law in form and overcomes the objections above. He uses a semi-classical version of the effective potential method ⁴¹. Assuming an interaction of the form :

$$V(R, \gamma) = A \exp(-R/r_0) [1 + B P_2(\cos \gamma)] \quad (19)$$

he obtains a fitting law of the form :

$$\sigma_{j' \rightarrow j} = (2j' + 1)/(2j + 1) a (|j' - j|^{-1} - b) \quad (20)$$

for the thermally averaged cross-section. In this very simple law the parameter a is related to the zero-impact parameter distance of closest approach

R_0 through :

$$a = (8kT/\pi\mu)^{1/2} \pi R_0^2 \quad (21)$$

Plots of statistically weighted cross-sections against $|\Delta j|^{-1}$, including data for the $I_2(^3\Pi_u^+) + \text{He}$ system are found to be reasonably linear providing the initial j level is small. Deviations are attributed to the breakdown of the ES approximation, but it is interesting to speculate that better results might be obtained by taking into account the variation of a with the relative velocity.

3.2 Energy dependence

Most recent developments have concentrated on the energy dependence of the cross-sections. Using an original deconvolution procedure Smith et al.⁴²⁻⁴⁴ have been able to measure the velocity dependence of rotationally inelastic cross-sections in cell experiments. The technique relies on velocity selection by Doppler shift (VSDS). For the $\text{Na}_2^* + \text{Xe}$ system the deconvoluted rate constants have been independently fitted to a power law (ECS-P) for each value of the relative velocity u_r ⁴². The exponent Γ varied from 0.93 at low u_r to 1.22 at high u_r ; the total range of relative velocity investigated was from $0.75 (RT/\mu)^{1/2}$ to $3.0 (RT/\mu)^{1/2}$. A plot of Γ versus u_r^{-1} shows a reasonable linear correlation. In the case of $\text{Li}_2^* + \text{Xe}$ collisions Smith et al.

43 observe a very rapid decrease in the cross-sections with increasing u_r , which made it problematical to fit the data with a power law.

The AON has successfully reproduced the velocity dependence of the $\text{Na}_2^* + \text{Xe}$ data²³, but no attempt has been made to fit the lithium data. The energy dependence of the AON is in fact explicit, because the two fitting parameters a and c depend on the relative velocity u . Writing :

$$a(\varepsilon_\ell) = \alpha \varepsilon_\ell^{-1/2} \quad (22)$$

where $\varepsilon_\ell = 1/2 \mu u^2$ is the kinetic energy in the channel ℓ :

$$\varepsilon_\ell = E - B\ell(\ell + 1) \quad (23)$$

the energy-dependent expression of the AON law $\text{AON}(E)$ is :

$$\sigma_{\ell \rightarrow 0} = \frac{2r_0^2}{n} \left[\ln \frac{a(\varepsilon_\ell)}{n} - 1 + \frac{n}{a(\varepsilon_\ell)} \right] \quad (24)$$

It is important to stress that the $\text{AON}(E)$ must be used in conjunction with microreversibility :

$$\sigma_{0 \rightarrow \ell}(\varepsilon_0) = (2\ell + 1) \frac{k_\ell^2}{k_0^2} \sigma_{\ell \rightarrow 0}(\varepsilon_\ell) ;$$

$$k_j^2 = 2\mu \varepsilon_j / \hbar^2 \quad (25)$$

The reason for this arises from the ambiguity in the ES approximation as to whether the kinetic energy in the entrance or exit channel should be used

for the calculation of a particular cross-section. The absence of an energetic threshold for the $\sigma_{\ell \rightarrow 0}$ cross-sections make them a natural choice for the basis functions, but this choice is supported by the fact that the lowest velocity half-collision is more efficient than its high velocity counterpart for transferring angular momentum. The smaller ε_{ℓ} the larger the cross-section. This reflects the increased interaction time.

The energy dependence of the fitting law may be very important, particularly if the cross-sections are measured close to threshold. As an example of this we consider RET in the $\text{CsH}(A^1\Sigma^+) + \text{H}_2$ collisional system, recently measured by Ferray, Visticot, and Sayer⁴⁵. They observed laser excited fluorescence from rotational states up to 0.75 kT away from the initially populated state. In order to deconvolute the effects of multiple collisions they used both the AON and the IOS-P to solve the coupled rate equations. They find that the IOS-P works better than the AON for $\Delta j > 7$ because of the very rapid fall-off of the AON in the high Δj channels. The initial rate of descent is rapid so that the parameter a is small ~ 15.5 . Unfortunately Ferray et al.⁴⁵ do not give the deconvoluted state-to-state cross-sections. However if we use the AON(E) to fit the IOS-P cross-sections resulting from a best fit to the multicollisional data ($A = 8.9 \cdot 10^{-10} \text{ cm}^3 \text{ s}^{-1}$; $\Gamma = 1.22$) we can obtain very good agreement⁴⁶. This is shown in Fig. 2. Physically what happens is this: although in the low Δj channels the a parameter and consequently the maximum transferable angular momentum is small, as the translational energy in the

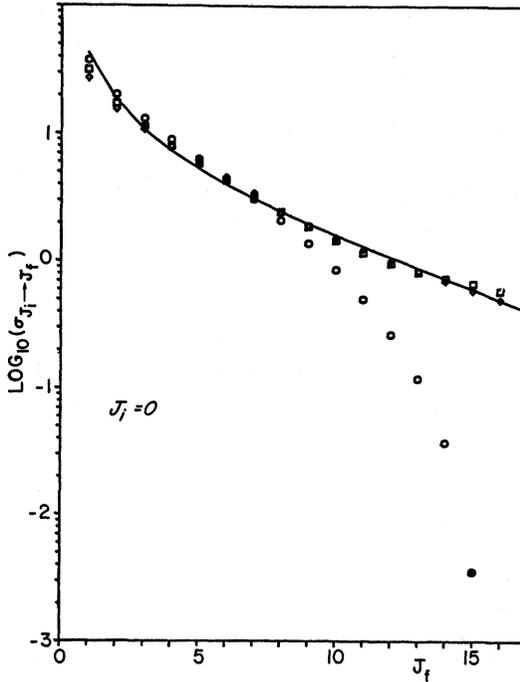


FIGURE 2

Semi-log plots of the $\sigma_{j_i \rightarrow j_f}$ cross sections for CsH-H₂ collisions as a function of j_f for $j_i = 0$. Solid line IOS-P ; o AON ; □ AON(E) ; ◇ <AON(E)> .

final state decreases the collision partners sample the potential further down the "trunk" of the interaction potential where the average distance of closest approach R_0 , and consequently the classical torque, increases. This leads to a larger value of a in the high Δj channels. This variation of a with the kinetic energy is further discussed below.

Indeed, coming back to the hard ellipse model ³⁶, the maximum transferred angular momentum has been found to be :

$$\Delta j_{\max} = 2 (A_1 - B_1) p_0 \quad (26)$$

where A_1 and B_1 are the two arms of the ellipse, and

$$p_0 = \sqrt{2\mu\varepsilon} = \mu u \quad (27)$$

is the linear momentum of the incident particle. As long as the kinetic energy is kept constant, which was the case in the measurements by Derouard and Sadeghi ¹⁹ in $I_2^* + {}^3\text{He}$, ${}^4\text{He}$, H_2 , D_2 , Δj_{\max} scales as $\mu^{1/2}$ (see Fig. 1). This is in agreement with the experiment and with both the IOS-EP and IOS-AON, as shown in Ref. 20. But if the energy ε is changed the effective ellipse will be obtained by various "cuts" of the potential "trunk" at different heights, resulting in a variation of the important quantity $(A_1 - B_1)$ as a function of ε . In most usual systems the isotropic potential $V_0(R)$ is much steeper than the first anisotropic term $V_2(R)$ (as assumed in the derivation of the AON). The consequence of this situation is that $(A_1 - B_1)$ decreases rapidly when ε increases, as it is schematically shown in Fig. 3. In practice the exact description of the energy dependance of Δj_{\max} requires the knowledge of the potential shape. Note that, if it is known, the rather crude approximation $\alpha = \text{cte}$ (Eq. 22) in the AON(E) formula (equivalent to the assumption of a hard sphere for $V_0(R)$) can be replaced by a more realistic variation of α with ε .

The $\text{Na}_2 + \text{He}$ system is an example for which this has been done. The ab initio potential surface calculated by R. Schinke et al ⁴⁷ is such that $V_0(R)$ and $V_2(R)$ have essentially the same R dependence, which seems to be an extreme case (very "soft" molecule). If $V_0(R)$ and $V_2(R)$ are taken exponential with the same range r_0 the parameter $(A_1 - B_1)$ is readily found independent of the energy (see Fig. 3).

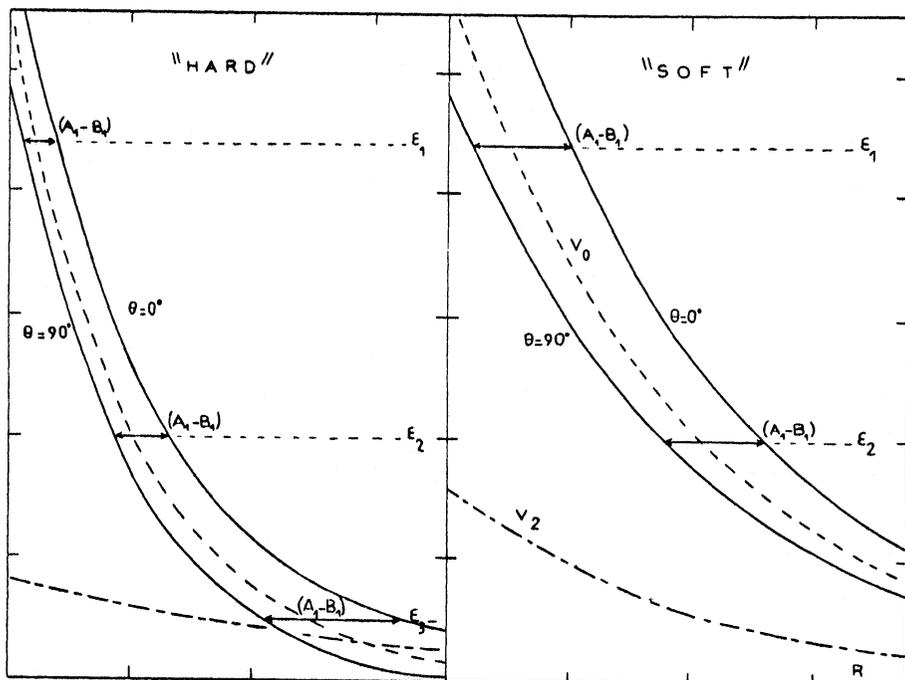


FIGURE 3

Schematic representation of a "hard" potential (left) and of a "soft" potential (right) (see text). $(A_1 - B_1)$ is the difference between the two arms of the effective ellipse.

Then Δj_{\max} scales as $\epsilon^{1/2}$. At the same time the parameter α , like $V_2(R_0)$ is found to scale as ϵ (see Eq. 14) so that $a(\epsilon)$ also scales as $\epsilon^{1/2}$. Thus the AON(E) and the impulsive model predict exactly the same variations, contrarily to some hasty conclusions of Ref. 20. The $\epsilon_1 = 0.2$ eV IOS cross sections of Ref. 47 are best fitted by $a_1 = 22$, while the $\epsilon_2 = 0.05$ eV IOS cross sections are best fitted by $a_2 = 11$, i.e. $a_1 = 2a_2$ as expected.

4. CONCLUSION

Although the very details of the scattering properties in a given atom-molecule system can only be obtained through accurate quantum calculations on a realistic potential, much information on RET can be drawn from simple fitting forms whose physical basis relies on model potentials. More specifically, the content of this review shows that this conclusion holds for the state-to-state integral cross sections and their collision energy dependence.

REFERENCES

1. D.J. KOURI, in "Atom-Molecule Collision Theory : A Guide for the Experimentalists", edit. by R.B. Bernstein (Plenum New York, 1979) p. 301.
2. J.C. POLANYI and K.P. WOODALL, *J. Chem. Phys.* 56, 1563 (1972).
3. A.M.G. DING and J.C. POLANYI, *Chem. Phys.* 39, 10 (1975).
4. R.D. LEVINE, R.B. BERNSTEIN, D. KAHANA, I.A. PROCACCIA and E.T. UPCHURCH, *J. Chem. Phys.* 64, 796 (1976).
5. I.A. PROCACCIA and R.D. LEVINE, *J. Chem. Phys.* 63, 4261 (1975) ; 64, 808 (1976).
6. D.F. HELLER, *Chem. Phys. Lett.* 45, 64 (1977).

7. B.C. SANCTURARY, Chem. Phys. Lett. 62, 578 (1979).
8. T.A. BRUNNER, R.D. DRIVER, N. SMITH and D.E. PRITCHARD, Phys. Rev. Lett. 41, 856 (1978).
9. M. WAINGER, L. ALAGIL, T.A. BRUNNER, A.W. KARP, N. SMITH and D.E. PRITCHARD, J. Chem. Phys. 71, 1977 (1979).
10. G. GRAWERT, Z. Phys. 225, 283 (1969).
11. N. SMITH and D.E. PRITCHARD, J. Chem. Phys. 74, 3939 (1981).
12. T.A. BRUNNER and D.E. PRITCHARD, in "Dynamics of the Excited State", edit. by K.P. Lawley (John Wiley, 1982).
13. J. DEROUARD, Thesis, Université Scient. Méd. Grenoble (1983).
14. J. DEROUARD, Chem. Phys. 84, 181 (1984)
15. S.S. BHATTACHARYYA, A.S. DICKINSON, J. Phys. B12, L521 (1979).
16. A.E. DE PRISTO, S.D. AUGUSTIN, R. RAMASWAMY and H. RABITZ, J. Chem. Phys. 71, 850 (1979).
17. A.M. RICHARD and A.E. DE PRISTO, Chem. Phys. 69, 273 (1982).
18. S.L. DEXHEIMER, M. DURAND, T.A. BRUNNER and D.E. PRITCHARD, J. Chem. Phys. 76, 4996 (1982).
19. J. DEROUARD and N. DADEGHI, Chem. Phys. 88, 171 (1984).
20. J. DEROUARD and N. SADEGHI, J. Chem. Phys. 81, 3002 (1984).
21. J. DEROUARD and N. SADEGHI, Chem. Phys. Lett. 102, 324 (1983).
22. B.J. WHITAKER and Ph. BRECHIGNAC, Chem. Phys. Lett. 95, 407 (1983).
23. Ph. BRECHIGNAC and B.J. WHITAKER, Chem. Phys. 88, 425 (1984).
24. Ph. BRECHIGNAC, A. PICARD-BERSELLINI, R. CHARNEAU, J.M. LAUNAY, Chem. Phys. 53, 165 (1980).
25. A. PICARD-BERSELLINI, B.J. WHITAKER and Ph. BRECHIGNAC, J. Chem. Phys. 79, 1556 (1983).
26. P. ANDRESEN, H. JOSWIG, H. PAULY, R. SCHINKE, J. Chem. Phys. 77, 2240 (1982).
27. O. NEDELEC, J. DUFAYARD, J. Chem. Phys. 76, 378 (1982).
28. R.A. GOTTSCHO, 35th Symp. on Mol. Spectroscopy (1980).
29. L.D. THOMAS, W.P. KRAEMER and G.H.F. DIERCKSEN, Chem. Phys. 51, 131 (1980) ; S. GREEN and L.D. THOMAS, J. Chem. Phys. 73, 5391 (1980).

30. P.L. JONES, U. HEFTER, A. MATTHEUS, J. WITT, K. BERGMANN, W. MULLER, W. MEYER and R. SCHINKE, *Phys. Rev.* A26, 1283 (1982) ; P.L. JONES, E. GOTTWALD, U. HEFTER and K. BERGMANN, *J. Chem. Phys.* 78, 3838 (1983).
31. F.J. AL-IMARAH, A.J. BAIN, M.S. MEHDE and A.J. McCAFFERY, *J. Chem. Phys.* 82, 1298 (1985).
32. E.W. SMITH, M. GIRAUD and J. COOPER, *J. Chem. Phys.* 65, 1256 (1976).
33. A.S. DICKINSON and D. RICHARDS, *J. Phys.* B11, 1085 (1978).
34. C. NYELAND and G.D. BILLING, *Chem. Phys.* 60, 359 (1981).
35. Y. ALHASSID and R.D. LEVINE, *Phys. Rev.* A18, 89 (1978).
36. S. BOSANAC, *Phys. Rev.* A22, 2617 (1980).
37. T.A. BRUNNER, T.A. SCOTT and D.E. PRITCHARD, *J. Chem. Phys.* 76, 5641 (1982).
38. P.J. DAGDIGIAN and B.E. WILCOMB, *J. Chem. Phys.* 72, 6562 (1980).
39. M. GIROUD and O. NEDELEC, *Chem. Phys.* 93, 127 (1985).
40. C. NYELAND, *Chem. Phys. Lett.* 109, 603 (1984).
41. C. NYELAND and G.D. BILLING, *Chem. Phys.* 40, 103 (1979).
42. N. SMITH, T.P. SCOTT and D.E. PRITCHARD, *J. Chem. Phys.* 74, 467 (1981).
43. N. SMITH, T.P. SCOTT and D.E. PRITCHARD, *Chem. Phys. Lett.* 90, 461 (1982).
44. N. SMITH, T.P. SCOTT and D.E. PRITCHARD, *J. Chem. Phys.* 81, 1229 (1984).
45. M. FERRAY, J.P. VISTICOT and B. SAYER, *J. Chem. Phys.* 81, 3009 (1984).
46. Ph. BRECHIGNAC and B.J. WHITAKER, *J. Chem. Phys.*, to be published.
47. R. SCHINKE, W. MULLER, W. MEYER and P. McGUIRE, *J. Chem. Phys.* 74, 3916 (1981).

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