

A new fitting law of rovibrationally inelastic rate constants for rapidly rotating molecules

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Abstract

Semiclassical scattering of a particle from a three-dimensional ellipsoid with internal structure is used to model vibration-rotation-translation (VRT) collisional transfer between atoms and diatomic molecules. The result is a very simple analytical expression containing two variable parameters that have a clear physical meaning. Predictions of the model for the $\text{Li}_2 + \text{Ne}$ system are in reasonably good agreement with experimental results.

1. Introduction

Over many years numerous scaling theories have been proposed for reducing the problem of knowing all the state-to-state transition rates to determining several parameters in a simple fitting law [1-6] (and references therein). Considerable progress has been made in the development of successful models for rotationally and vibrationally inelastic cross sections and rate constants in atom-diatom collisions. A different situation takes place when molecular rotation produces significant effect on vibrationally inelastic scattering, i.e., when one has to develop simple scaling laws for rovibrationally rate constants. The energy corrected sudden (ECS) scaling theory [7, 8] and the angular momentum (AM) theory [9, 10] are the exceptions.

Classical scattering of a structureless atom from hard-shell molecules has been employed in many investigations of rotational and vibrational energy and angular momentum transfer [9-

13]. Although this model has many limitations, it is yet able to reproduce a surprising number of complex scattering phenomena, and provides substantial insight into the fundamental principles which govern the collision dynamics. This Letter deals with the analytical approaches to the problem of semiclassical scattering of a particle from a three-dimensional hard ellipsoid, and incorporates the effects of quantized molecular structure that constrains the dynamics of atom-diatom VRT collisions. The basic assumption confirmed by comparison with the experiment is that VRT probabilities are described more adequately by an exponential angular momentum gap (AMG) law.

2. A three-dimensional smooth ellipsoid model

Consider a diatomic molecule that undergoes a vibration-rotation transition $(n_i, j_i) \rightarrow (n_f, j_f)$ due to a collision with another particle. Its energy levels are given by the expression [14]

$$E_{nj} = \omega_e \left(n + \frac{1}{2} \right) - x_e \omega_e \left(n + \frac{1}{2} \right)^2 + B_e j(j+1) - \alpha_e \left(n + \frac{1}{2} \right) j(j+1) \quad (1)$$

Internal state of the molecule is also characterized by the vector of rotational angular momentum, \mathbf{j} , perpendicular to its axis. The atom-diatom potential energy surface is assumed to be represented by a hard ellipsoid [9-13]. For each point of impact on the ellipsoid surface, \mathbf{r} , with coordinates (x, y, z) one can write the equation (in the body-fixed coordinate frame)

$$\frac{x^2 + y^2}{c^2} + \frac{z^2}{a^2} = 1, \quad (2)$$

where a and c are, respectively, the semimajor and semiminor axes. As is known from differential geometry, a unit vector normal to the ellipsoid surface at the point of impact may be represented as

$$\mathbf{n} = \frac{a^2}{c \left[a^4 - (a^2 - c^2) z^2 \right]^{1/2}} \left(x \mathbf{e}_x + y \mathbf{e}_y + \frac{c^2}{a^2} z \mathbf{e}_z \right) \quad (3)$$

Now decompose the relative linear momentum into two components. The first component is parallel to the ellipsoid surface at the point of impact, \mathbf{p}_{\parallel} , and the second one is perpendicular to the surface, \mathbf{p}_{\perp} . Since the ellipsoid is assumed to be smooth, the parallel component is not changed during the momentum transfer process, and energy transfer is caused solely by the component directed along \mathbf{n} , namely, $\mathbf{p}_{\perp} = -p\mathbf{n}$. According to energy conservation law, we have

$$\frac{(p' + p)(p' - p)}{2\mu} = E_{n_i j_i} - E_{n_f j_f} \quad , \quad (4)$$

where μ is the reduced mass of the collisional pair. The change in the relative momentum is given simply by

$$\Delta p = \frac{E_{n_i j_i} - E_{n_f j_f}}{\bar{v}} = \frac{\hbar \omega_{if}}{\bar{v}} \quad , \quad (5)$$

where $\bar{v} = (v + v')/2$ is the arithmetic mean of the initial and final relative velocities.

Due to collisions the initial orbital angular momentum is converted into rotational angular momentum at the repulsive wall of the ellipsoidal intermolecular potential. For an initially non-rotating ellipsoid, the transferred angular momentum $\Delta \mathbf{j}_0$ must obey the equation

$$\Delta \mathbf{j}_0 = -[\mathbf{r} \times \Delta \mathbf{p}] = \Delta p [\mathbf{r} \times \mathbf{n}] \quad (6)$$

To proceed further, one rewrites Eq. (6) in more detail

$$\Delta \mathbf{j}_0 = \left(\frac{\omega_{if} z}{\bar{v}} \right) \frac{a^2 - c^2}{c \left[a^4 - (a^2 - c^2) z^2 \right]^{1/2}} (-y \mathbf{e}_x + x \mathbf{e}_y) \quad (7)$$

Note that $\Delta \mathbf{j}_0$ is written in units of \hbar . Now take into consideration that by definition

$[\mathbf{r} \times \mathbf{n}]^2 = b_n^2$ where b_n is the effective impact parameter [13]. Then

$$\Delta \mathbf{j}_0 = \left(\frac{\omega_{if} b_n}{\bar{v}} \right) \frac{-y\mathbf{e}_x + x\mathbf{e}_y}{\sqrt{x^2 + y^2}} \quad (8)$$

It only remains for us to estimate the total transferred angular momentum, \mathbf{J} . For this purpose, add the change in the angular momentum of rotating ellipsoid, $\Delta \mathbf{j}_1$, to $\Delta \mathbf{j}_0$ by way of [15] (p. 163)

$$\mathbf{J} = \Delta \mathbf{j}_0 - \frac{\mu}{I} [\mathbf{r} \times [\Delta \mathbf{j}_1 \times \mathbf{r}]] , \quad (9)$$

where I is the moment of inertia of the ellipsoid. Assume that vectors $\Delta \mathbf{j}_1$ and $\Delta \mathbf{j}_0$ have the same preferential direction $[\mathbf{r} \times \mathbf{n}]$. Only in this case the z -component of the vector

$[\mathbf{r} \times [\Delta \mathbf{j}_1 \times \mathbf{r}]]$ that has no physical meaning disappears. Obviously, the magnitude of $\Delta \mathbf{j}_1$ is to be proportional to the change in the angular momentum of the molecule, $\Delta \mathbf{j} = \mathbf{j}_f - \mathbf{j}_i$, however,

the coefficient of proportionality remains arbitrary. For the second term in Eq. (9) to be finite at a head-on collision, it is convenient to use a dimensionless quantity of the inertia moment,

$I / \mu r^2$. The above heuristic reasoning gives

$$\Delta \mathbf{j}_1 = \left(\frac{I \Delta \mathbf{j}}{\mu r^2} \right) \frac{-y\mathbf{e}_x + x\mathbf{e}_y}{\sqrt{x^2 + y^2}} \quad (10)$$

So we can simplify (9) by Eq. (10) to give

$$\mathbf{J} = \left| \Delta \mathbf{j} - \frac{\omega_{if} b_n}{\bar{v}} \right| \quad (11)$$

The transferred angular momentum depends on the trajectory of the relative motion via the ‘mean’ velocity and the effective impact parameter. This parameter varies from zero to the

maximum value b_n^{\max} . The appearance of the torque-arm b_n^{\max} in the theory means that instead of two parameters a and c , actually, only one parameter is used. This circumstance enhances significantly the ability of the model to predict and to fit experimental data.

3. Derivation of ‘AMG’ fitting law

Collision-induced RT and VRT inelastic processes are most easily described by the mechanism of the interconversion of linear and angular momenta under constraints imposed by conservation of total energy and of total angular momentum. The AM theory predicts the exponential-like falloff of RT probabilities with the increase in the transferred angular momentum [9, 11]. Calculations based on this theory accurately reproduce results obtained from state-resolved experiments. This idea will serve as a basis for the derivation of simple analytical expressions for inelastic VRT cross sections and rate constants. Accordingly, we assume that the probability of VRT transition for a given trajectory can be represented as

$$P_{n_i j_i \rightarrow n_f j_f} \propto (2j_f + 1) \exp\left(-\frac{\alpha J}{2}\right), \quad (12)$$

where α is the freely adjustable parameter of the model. With such a definition, the quantity $1/\alpha$ is proportional to some upper limit on the number of angular momentum quanta which can be transferred in VRT collisions, and defines the width of the j_f distribution. The proportionality sign in (12) means that the probabilities are not normalized to unity in this expression. This demerit will be eliminated in the expressions for cross sections and rate constants by introducing an appropriate scaling factor.

Cross section of vibration-rotation transition induced by collisions is given by

$$\sigma_{n_i j_i \rightarrow n_f j_f} \propto (2j_f + 1) \int_0^{b_n^{\max}} \exp\left[-\frac{\alpha}{2} \left| \Delta j - \frac{\omega_{if} b_n}{\bar{v}} \right| \right] b_n db_n \quad (13)$$

Though this integral is given by an analytical expression, it is reasonable to use a simple estimate that simplifies noticeably further derivation of the working equation

$$2 \int_0^1 \exp \left[-\frac{\alpha}{2} \left| \Delta j - \frac{\omega_{if} b_n^{\max}}{\bar{v}} t \right| \right] t dt = \exp \left[-\frac{\alpha}{2} \left| \Delta j - \frac{\omega_{if} L}{\bar{v}} \right| \right] \quad (14)$$

The characteristic length L is a new fitting parameter of the model used instead of b_n^{\max} . Eq. (14) is a double-valued representation for L . Two essentially different values of the length satisfy this equation. One such value is roughly equal to $0.7 b_n^{\max}$ in all cases; the other may be less or greater than b_n^{\max} or even has a negative value. It is apparent that these large and negative values of L are of no physical significance, and must be rejected. To gain a better understanding of this derivation, the transition frequency is expressible in terms of vibrational and rotational frequencies of the molecule

$$\omega_{fi} = \omega_V \Delta n + \omega_R \Delta j, \quad (15)$$

where $\Delta n = n_f - n_i$. According to Eq. (1), we have the following expressions for the ‘mean’ vibrational and rotational frequencies, respectively

$$\omega_V = \omega_e \left[1 - x_e (n_i + n_f + 1) - \frac{\alpha_e}{2\omega_e} [j_i(j_i + 1) + j_f(j_f + 1)] \right], \quad (16)$$

$$\omega_R = B_e (j_i + j_f + 1) \left[1 - \frac{\alpha_e}{2B_e} (n_i + n_f + 1) \right] \quad (17)$$

Using the above expressions, one has the resulting equation

$$\sigma_{n_i j_i \rightarrow n_f j_f} = \sigma (2j_f + 1) \exp \left(-\frac{\alpha}{2} \left| \Delta j + (\omega_V \Delta n + \omega_R \Delta j) \tau_c \right| \right), \quad (18)$$

where $\tau_c = L/\bar{v}$ is the collision duration and σ is the amplitude factor which, generally speaking, depends on the relative velocity; more specifically, on \bar{v} . Energy dependence of

rovibrationally inelastic cross sections enters into this equation via the mean velocity. For convenience, this dependence is given below in an explicit form

$$\bar{v} = \frac{1}{\sqrt{2\mu}} \left[E^{1/2} + \left(E + E_{n_i j_i} - E_{n_f j_f} \right)^{1/2} \right] \quad (19)$$

Remember that in this formula $E = \mu v^2 / 2$ where $v = p_{\perp} / \mu$.

Rate constants are obtained from (18) after averaging of the quantity $v\sigma_{i \rightarrow f}$ over kinetic energy before collision. Taking into account that the component of velocity v is directed solely towards the ellipsoid, we immediately get

$$K_{n_i j_i \rightarrow n_f j_f} = \frac{1}{2} \left(\frac{8kT}{\pi\mu} \right)^{1/2} \int_{x_0}^{\infty} e^{-x} \sigma_{n_i j_i \rightarrow n_f j_f} (kTx) dx \quad (20)$$

Here $x_0 = (E_{>} - E_{n_i j_i}) / kT$ where $E_{>}$ is the larger of E_i and E_f . Averaging over kinetic energy made in (20) produces no considerable changes, so one can take the cross section as a function of energy outside the integral sign and take it at some point $x = x_{\theta}$. Then Eq. (20) becomes simply

$$K_{n_i j_i \rightarrow n_f j_f} = A (2j_f + 1) \exp \left[-\frac{\alpha}{2} \left| \Delta j + (\omega_V \Delta n + \omega_R \Delta j) \tau_c \right| - \frac{E_{>} - E_{n_i j_i}}{kT} \right] \quad (21)$$

In the above expression A is the temperature-dependent scaling factor which expresses both the overall magnitude of the rate constant and the units in which it is expressed. At $\alpha \ll 1$ numerical computations by formulae (20), (21) give almost the same results, at least, near the maximum of j_f distribution if the characteristic collision time in this equation is defined as

$$\tau_c = 2L \left(\frac{2\mu}{kT} \right)^{1/2} \quad (22)$$

So we have the dynamically based fitting law, which is called the angular momentum gap (AMG) law.

Let us examine the behavior of rate constants near the maximum of \dot{j}_f distribution. The necessary estimate of the peak shift Δj_{peak} can be made using Eq. (21). The position of the maximum is determined by the minimum of the expression in the exponent. The situation is complicated by the fact that vibrational and rotational frequencies depend both on the initial and final rotational quantum numbers. However, taking these quantities at $\dot{j}_f = \dot{j}_i$ we obtain an ordinary equation instead of transcendental one. Solving it, we get the desired estimate

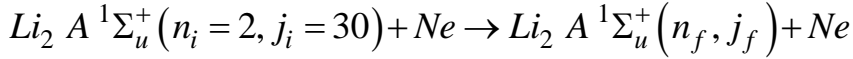
$$(\dot{j}_f - \dot{j}_i)_{peak} = - \left(\frac{\omega_V \tau_c}{1 + \omega_R \tau_c} \right)_{\dot{j}_f = \dot{j}_i} (n_f - n_i), \quad (23)$$

This is a useful relation that makes it possible to find approximately the length L if the value of Δj_{peak} is known from experiment. For rapidly rotating molecules expression (23) is merely the criterion for intramolecular energy conservation. Thus, the systematic shift of the peak away from \dot{j}_i for a given Δn depends solely on the reduced time of collisions both for vibrations and for rotations. These effects are enhanced with decreasing temperature. The dependence on a buffer gas is characterized by the reduced mass of the system only, since the length L is the characteristic of an isolated molecule rather than a collisional pair. Adiabatic effects have a pronounced effect on VRT rate constants. Such effects depend crucially on the reduced time of collisions. As is seen from Eqs. (15) - (17), at high \dot{j}_i , the parameter $\omega_{if} \tau_c$ decreases with the increase in the final \dot{j}_f and goes through zero where ω_V / ω_R is equal to $-\Delta j / \Delta n$. Rate constants rise steeply for transitions with such quantum numbers; in other words, the VRT rate constant rises dramatically as \dot{j}_i increases, and becomes increasingly sharply peaked at a

specific j_f . This effect is known as the quasisonant vibration-rotation transfer in atom-diatom scattering [16]. The above conclusions are confirmed by experiments [16-19].

4. Results and discussion

To compare theory and experiment, we have taken the detailed absolute state-resolved rate constants from [19]



Measurements were made at 690.8 K including $0 \leq n_f \leq 4$ and $0 \leq j_f \leq 84$. Comparison with the experiment for transitions with $\Delta n = -1, -2$ shows that the peak position is determined by the relation $-6.0 \Delta n$ corresponding to the length $L = 1.42 \text{ \AA}$ found by Eq. (23). The position of the peak depends on this length only, and is independent of the maximum transferred angular momentum the value of which specifies the width of j_f distribution. Thus, as the starting point, α and L may be fitted separately. Note that the peak shift decreases with decreasing L and disappears in the limit $L \rightarrow 0$. As a result of the fitting procedure, parameters α and A were found in the AMG fitting law. The results are as follows: $\Delta n = -1$, $\alpha = 0.00664$ and $A = 0.00364 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$; $\Delta n = -2$, $\alpha = 0.004$ and $A = 0.00046 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. The quality of the fit is demonstrated in Fig.1. Remember that the measured rate constants span nearly three orders of magnitude in size. The peak shift is essentially absent in the $\Delta n = 1, 2$ case. Accordingly, experimental data were fitted by the exponential distribution (21) with $\tau_c = 0$. Such an approximation leads to $\Delta n = 1$, $\alpha = 0.071$ and $A = 0.005 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$; $\Delta n = 2$, $\alpha = 0.05$ and $A = 0.00094 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. Comparison with the experiment is shown in Fig. 2. Special attention is required to the case $\Delta n = 1$. Vibration-rotation level $n = 2, j = 30$ is almost coincident with the level $n = 3, j = 20$ ($\omega_{if} = 3.1 \text{ cm}^{-1}$), however, the rate constant of this transition is

approximately twice less than that of the transition with $\Delta j=0$ and $\omega_{if} = -241 \text{ cm}^{-1}$. This is a vivid example showing that the processes of vibration-rotation scattering are defined by angular momentum transfer rather than the energy one; therefore, energy gap relations are not adequate for the description of VRT rates.

Now return to Eq. (18). Semiclassical cross sections of inelastic collisions do not satisfy the detailed balance principle. There exist various receptions for the correction of a semiclassical approximation [5]. In particular, inelastic cross sections $(v_{<}/v)^2 \sigma_{if}(\bar{v})$ will satisfy the detailed balance condition [6]. The scaling factor dependence on relative velocity cannot be established in the framework of our approach, so the choice is arbitrary. The same is true for the scaling factor of temperature-dependent rate constants.

In conclusion we hope that the developed AMG fitting law will find application in the relaxation of gases containing light, rotationally hot molecules.

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Figure captions

Fig. 1. Comparison of measured rovibrationally inelastic rate constants with predictions based on the AMG fitting law for transitions $n_i=2, j_i=30 \rightarrow n_i + \Delta n, j_f$.

Fig. 2. Same as Fig. 1 except $\tau_c = 0$.

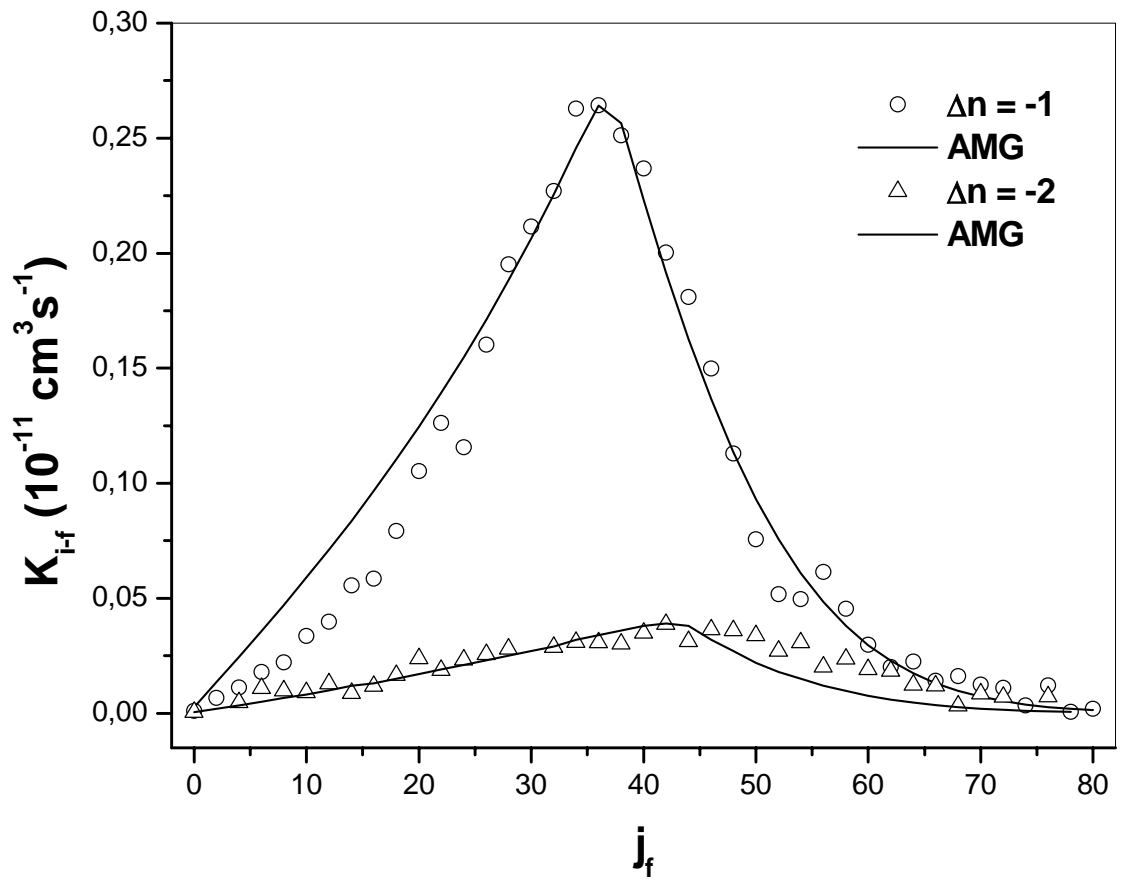


Fig. 1

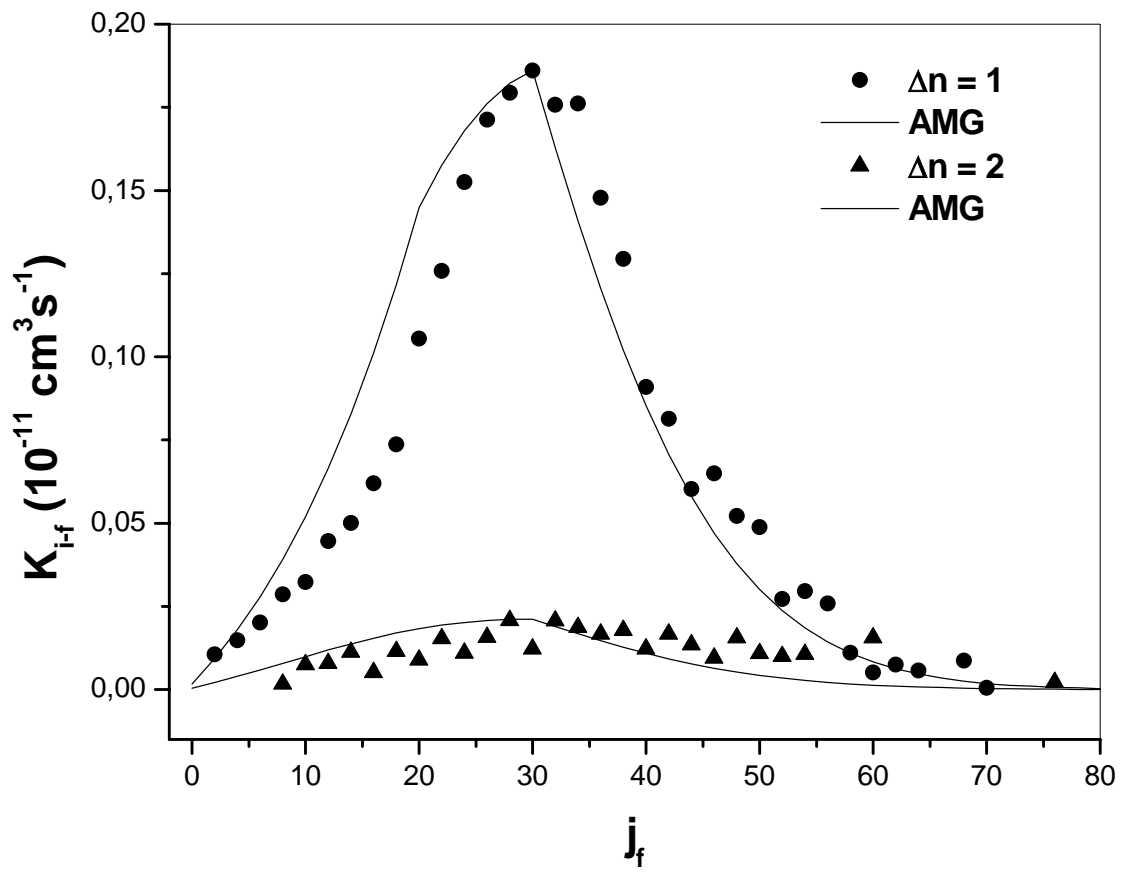


Fig. 2