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Dynamically based fitting law for cross-sections of vibrational energy transfer

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A three-dimensional semiclassical analytical model for cross-sections of vibrational energy transfer in collisions between an atom and a diatomic molecule has been developed. The model is based on the Bessel uniform approximation for transition probabilities valid for highly excited states of a molecule represented by the Morse oscillator. Three fitting parameters of the model are expressed in terms of the features characterizing the anisotropic intermolecular potential. The accuracy and validity of this law are tested by comparison with large Δn transitions and isotope effects in the crossed beam inelastic scattering of I_2 from He, H_2 and D_2.

1. Introduction

Vibrationally inelastic atom–molecule collision processes have been studied in detail with different degrees of approximation by solving close-coupled scattering equations [1–11]. In particular, collisions between an atom and a diatomic molecule represented by a Morse oscillator have been analysed using classical [2–4], semiclassical [5–7], and quantum mechanical treatments [8–11]. The references cited include both collinear [3, 5, 7, 8] and three-dimensional studies [1, 2, 4, 6, 9–11]. Recently, the closed form solution for Morse oscillator transition probabilities was proposed [12]. The approach is based on the strong-coupling correspondence principle (SCCP) approximation [13] valid for highly excited states, and involves a semiclassical description of vibrationally inelastic collisions. The approach also incorporates the effects of rotational degrees of freedom in the infinite order sudden (IOS) approximation. In the framework of this analytical model for probabilities, cross-sections of vibrational energy transfer have been calculated numerically. It is possible, however, to simplify the calculations by considering the transferred energy as an exponential function of the impact parameter. The aim of this analysis is twofold. On the one hand, such a model generalizes previous studies and gives the cross-sections in a closed form expression that depends on the interaction potential parameters. On the other hand, if one considers the parameters appearing in the theory as free adjustable parameters, one can derive

a new fitting law for cross-sections $\sigma_{n\to n'}(v)$, which involves the dependence on the relative translational velocity v and on the vibrational quantum numbers n, n'.

Numerous attempts to develop analytical models for vibrationally inelastic atom–molecule collisions are available in the literature (see, for example, [14–20] and references therein). Nevertheless, many of the models are in one way or another based on the perturbation theory, that is, the change in action in adiabatic collisions is considered small, and the transition probabilities are expressed in terms of the transition probability from the ground state to the first excited state. The forced harmonic oscillator model [21] and the correspondence principle approximation [22] are the exceptions. Here we examine moderately non-adiabatic collisions with arbitrary value of the change in action. In this case, our approach makes it possible to derive an analytical formula for cross-sections of vibrational relaxation with three fitting parameters that have a clear physical meaning and are related to intermolecular potential parameters. This derivation gives new insight into mechanisms of energy transfer for highly vibrationally excited molecules, as well as bridging the gap between theoretical methods and their practical applications.

2. Derivation of 'AMBA' fitting law

Consider, for simplicity, vibrationally inelastic collisions in the atom–diatom case. If the diatom is assumed to make no rotation during the collision time, a drastic

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simplification of the expression for the corresponding cross-sections takes place [1]

$$\sigma_{nn'} = \int_{-1}^{1} \frac{d(\cos\gamma)}{2} \int_{0}^{\infty} 2\pi P_{nn'}(b, \mathbf{v}, \gamma) b \, db, \qquad (1)$$

where $P_{nn'}$ is the vibrational transition probability summed over all final rotational states and averaged over all initial states and which depends on the impact parameter b and the relative velocity $\mathbf{v}$; γ is the rotor orientation relative to the intermolecular direction. Recently, the linearly perturbed Morse oscillator problem has been solved within the SCCP approximation [12]. The transition probability is

$$P_{nn'} = \frac{1-w(\bar{n})}{2}\Big[J_{|\Delta n|}^2\Big(2\delta(\gamma)\sqrt{\varepsilon(\bar{n})}\Big) + J_{|\Delta n|+1}^2\Big(2\delta(\gamma)\sqrt{\varepsilon(\bar{n})}\Big)\Big]$$
$$+ \frac{w(\bar{n})\ln\xi(\bar{n})}{2\sqrt{1-w(\bar{n})^2}}J_{|\Delta n|}^2\left(2\delta(\gamma)\sqrt{\varepsilon(\bar{n})}\frac{\ln\xi(\bar{n})}{2\sqrt{1-w(\bar{n})^2}}\right), \quad (2)$$

where $\bar{n}$ is the mean vibrational quantum number, $\delta(\gamma)$ the first-order change in action of the active molecule evaluated along a classical trajectory, $\Delta n = n' - n$, and

$$\varepsilon(\bar{n}) = \bar{n} + \frac{1}{2} - x_e\left(\bar{n} + \frac{1}{2}\right)^2. \qquad (3)$$

In other words, $\varepsilon(\bar{n})$ is given by $E_{\bar{n}}/\hbar\omega_e$ where E_n is the energy level of the Morse oscillator, ω_e the equilibrium oscillation frequency, and x_e the anharmonicity constant. According to the correspondence principle, the transition frequency $\omega_{n'n}$ is to be equal to $(n' - n)\omega(\bar{n})$ where the mean frequency is given by $\omega(\bar{n}) = \omega_e w(\bar{n})$ and

$$w(\bar{n}) = 1 - 2x_e\left(\bar{n} + \frac{1}{2}\right). \qquad (4)$$

For the Morse oscillator $\bar{n}$ is exactly equal to $(n + n')/2$. Finally, in equation (2) $\xi(\bar{n})$ is defined by

$$\xi(\bar{n}) = \frac{1 + \sqrt{1-w(\bar{n})^2}}{1 - \sqrt{1-w(\bar{n})^2}}. \qquad (5)$$

To proceed further, consider more carefully the model potential energy surface (PES) of the form (usually $\lambda = 1$ or 2)

$$V(r, R, \gamma) = V(r)\exp\left(-\frac{R}{L}\right)[1 + qP_\lambda(\cos\gamma)], \qquad (6)$$

where R is the distance from the atom A to the centre of mass of the molecule BC, r the distance between B and C, q the anisotropy parameter, and L the range of interaction. The above PES is, however, sufficient for investigating the influence of the rotational degrees of freedom upon vibrational relaxation. Further, the change in action has been found by the joining of solutions obtained along a head-on collision trajectory and a rectilinear one. Since we have already presented the detailed derivation elsewhere [12], here we shall only give necessary definitions. The change in action is given by the expression

$$\delta(\gamma) = 2C_e\left(\frac{\mu \mathbf{v} L}{\hbar}\right)\frac{\beta b K_1(\beta b)}{(\beta L)^2}[1 + qP_\lambda(\cos\gamma)], \qquad (7)$$

where the dimensionless parameter C_e is proportional to a logarithmic derivative at $r = r_e$

$$C_e = \left(\frac{\hbar}{2M\omega_e}\right)^{1/2}\frac{1}{V(r_e)}\left(\frac{\partial V}{\partial r}\right)_e, \qquad (8)$$

and

$$\beta = \frac{1}{L}\left(\frac{\sinh[\pi\omega(\bar{n})L/\mathbf{v}]}{\pi\omega(\bar{n})L/\mathbf{v}}\right)^{1/2}. \qquad (9)$$

In equations (7) and (8) M is the reduced mass of the molecule BC, μ the reduced mass of the system A + BC and $K_1(\beta b)$ the modified Bessel function of the first order. Thus formulae (2)–(9) give the analytical representation of transition probabilities that depend on all parameters that define the process of excitation/deactivation of a Morse oscillator in collisions with atoms. Then inelastic cross-sections were calculated numerically by equation (1).

To go further, the dependence $\delta(\gamma)$ with the impact parameter has to be considered. The main contribution to cross-sections of transitions with large Δn is made by the trajectories close to a head-on trajectory, thus we replace the function $\beta b K_1(\beta b)$ by $\exp(-\beta b)$ at small and moderate values of βb neglecting its exact behaviour at large βb. Consequently, the argument of the Bessel function from equation (2) is conveniently recast as

$$\delta(\gamma)\sqrt{\varepsilon(\bar{n})} = A\exp(-\beta b). \qquad (10)$$

According to (7)

$$A = a(0)f(\bar{n}, \tau)\sqrt{\varepsilon(\bar{n})}[1 + qP_\lambda(\cos\gamma)]. \qquad (11)$$

For notational convenience we define

$$a(0) = 2|C_e|\frac{\mu \mathbf{v} L}{\hbar} = a\left(\frac{\mathbf{v}}{\mathbf{v}_0}\right), \qquad (12)$$

and

$$f(\bar{n}, \tau) = \frac{w(\bar{n})\tau_V}{\sinh[w(\bar{n})\tau_V]}, \qquad (13)$$

where

$$\tau_V = \frac{\pi \omega_e L}{\mathbf{v}} = \tau\left(\frac{\mathbf{v}_0}{\mathbf{v}}\right). \qquad (14)$$

As is obvious from (12) and (8), the parameter a is expressed in terms of the range of the model potential $V(r)$ and the characteristic value of orbital angular momentum $\mu \mathbf{v} L$. In (14) the parameter τ is the reduced time of collisions (or adiabaticity parameter); $\mathbf{v}_0$ is a reference relative velocity.

Now evaluate the integral over the impact parameter in equation (1). Substituting the probabilities from (2) into (1), we restrict ourselves to the evaluation of this expression with one of the three Bessel functions only, since other integrals are calculated by the same procedure

$$\sigma_{nn'}^{(1)}(\gamma) = 2\pi \int_0^\infty J_{|\Delta n|}^2 (2Ae^{-\beta b}) b \, db$$

$$= -\frac{2\pi}{\beta^2} \int_0^1 \frac{\ln x}{x} J_{|\Delta n|}^2 (2Ax) \, dx. \qquad (15)$$

Inelastic collisions of atoms with highly vibrationally excited molecules are close to impulsive or sudden collisions because of the low frequency of strongly anharmonic vibrations. In addition to that, large values of the mean vibrational quantum number make the perturbation theory inapplicable in this case. So we can simplify (15) with the aid of the approximate expression of the Bessel function averaged over fast oscillations

$$\left\langle J_{|\Delta n|}^2 (2Ax) \right\rangle = \begin{cases} 0, & 2Ax < |\Delta n|, \\ \dfrac{1}{\pi(4A^2 x^2 - \Delta n^2)^{1/2}}, & 2Ax > |\Delta n|. \end{cases} \qquad (16)$$

This approximation to the Bessel function can be considered as the classical limit of transition probabilities $P_{n,n+\Delta n}$ derived from the same change in action with $x = 1$ or $b = 0$ [23]. Substitution of (16) into (15) immediately gives

$$\sigma_{nn'}^{(1)}(\gamma) = \frac{\pi}{\beta^2 |\Delta n|} \left[\ln \frac{A}{|\Delta n|} + F\left(\frac{|\Delta n|}{2A}\right) \right], \qquad (17)$$

where

$$F(z) = \frac{2}{\pi} \int_0^z \frac{\arcsin t}{t} \, dt. \qquad (18)$$

This function increases monotonically from zero to a maximum value $F(1) = \ln 2$. Note that the cross-section is equal to zero at $|\Delta n|/2A > 1$ according to equation (16). As we consider multiquantum vibrational transitions for which $|\Delta n|/2A << 1$, the second term in (17) may be omitted. This reasonable assumption greatly simplifies further calculations. In particular, the integral over γ in (1) is taken in the analytical form. Omitting simple computations, one obtains

$$\sigma_{nn'}^{(1)} = \frac{\sigma f(\bar{n}, \tau)}{|n - n'|} \ln\left[\frac{a(q) f(\bar{n}, \tau)\sqrt{\varepsilon(\bar{n})}}{|n - n'|}\right], \qquad (19)$$

where $\sigma = \pi L^2$. The argument of the logarithmic function is to exceed unity, otherwise $\sigma_{nn'}^{(1)} = 0$, that is the transition $n \to n'$ becomes classically forbidden under such conditions.

The case $\lambda = 1$ (heteronuclear molecules)

$$a(q) = a(0)\left(\frac{1+q}{1-q}\right)^{1/2q} (1 - q^2)^{1/2} e^{-1}. \qquad (20)$$

The case $\lambda = 2$ (homonuclear molecules)

$$a(q)$$
$$= a(0)(1+q)\exp\left[-2 + 2\left(\frac{2-q}{3q}\right)^{1/2} \arctan\left(\frac{3q}{2-q}\right)^{1/2}\right]. \qquad (21)$$

In either case $a(q)/a(0)$ is a monotonically decreasing function of the anisotropy parameter that decreases sharply at $q \to 1$ (or $q \to 2$) attaining its limiting value $2/e = 0.735\ldots$ (or $3/e^2 = 0.406\ldots$ at $\lambda = 2$). Thus the influence of the anisotropy of the intermolecular potential upon vibrational relaxation becomes quite noticeable for multiquantum transitions such that $a(q) f(\bar{n}, \tau)\sqrt{\varepsilon(\bar{n})} \approx |\Delta n|$, that is, in the case of small cross-sections.

So we have obtained a simple expression for $\sigma_{nn'}$ with explicit dependence on all parameters that define inelastic collisions in the case of exponential potential (the remaining two expressions necessary in general formula (29) will be given below). Overall, to develop a realistic model of vibrational energy exchange, one should allow for the contribution of long-range attraction forces and their cancellation with short-range repulsion forces. Although in a general case evaluation

of the effects calls for numerical calculations, here we restrict ourselves to phenomenological consideration sufficient for the derivation of the desired fitting law.

Let us assume that the long-range interaction of the form $C_k(r)R^{-k}$ plays the leading role in vibrationally inelastic collisions. Then equation (15) may be rewritten as

$$\sigma_{nn'}^{(1)}(\gamma) = 2\pi \int_0^\infty J_{|\Delta n|}^2 \left(2A'b^{-k+1}\right)b\,\mathrm{d}b \propto |\Delta n|^{-p}, \qquad (22)$$

where $p = (k+1)/(k-1)$. Since the physical meaning of the quantity A' is wholly immaterial for further discussion, this expression is omitted. It is clear that at very large k we have $p \approx 1$, that is the case of short-range forces. This suggests that equation (19) may be generalized in such a way as to allow for the long-range forces *ad hoc*, namely:

$$\sigma_{nn'}^{(1)} = \frac{\sigma f(\bar{n},\tau)}{|n-n'|^p}\ln\left[\frac{a(q)f(\bar{n},\tau)\sqrt{\varepsilon(\bar{n})}}{|n-n'|}\right]. \qquad (23)$$

With such a definition p is just a fitting parameter of the theory. The case where $p > 1$ and p differs essentially from unity means that attraction forces are dominant; $p \approx 1$ means that the main contribution is made by repulsion forces; the case where p is noticeably less than unity means that the cancellation effect takes place.

Finally, rewrite equation (23) once again to show explicitly the dependence of cross-sections on the relative translational velocity

$$\sigma_{nn'}^{(1)}(\mathbf{v}) = \frac{\sigma_w(\mathbf{v})}{|n-n'|^p}\ln\left[\frac{a_w(\mathbf{v})\sqrt{\varepsilon(\bar{n})}}{|n-n'|}\right], \qquad (24)$$

where

$$\sigma_w(\mathbf{v}) = \frac{\sigma w(\bar{n})\tau(\mathbf{v}_0/\mathbf{v})}{\sinh[w(\bar{n})\tau(\mathbf{v}_0/\mathbf{v})]} \qquad (25)$$

and

$$a_w(\mathbf{v}) = \frac{aw(\bar{n})\tau}{\sinh[w(\bar{n})\tau(\mathbf{v}_0/\mathbf{v})]}. \qquad (26)$$

The subscript w means that the functions σ_w and a_w depend on vibrational quantum numbers n, n' only via $w(\bar{n})$; its definition is given in (4). The contributions to the cross-section $\sigma_{nn'}(\mathbf{v})$ from two Bessel functions remaining in equation (2) are found similarly

$$\sigma_{nn'}^{(2)}(\mathbf{v}) = \frac{\sigma_w(\mathbf{v})}{(|n-n'|+1)^p}\ln\left[\frac{a_w(\mathbf{v})\sqrt{\varepsilon(\bar{n})}}{|n-n'|+1}\right], \qquad (27)$$

$$\sigma_{nn'}^{(3)}(\mathbf{v}) = \frac{\sigma_w(\mathbf{v})}{|n-n'|^p}\ln\left[\frac{a_w(\mathbf{v})\sqrt{\varepsilon(\bar{n})}}{|n-n'|}\frac{\ln\xi(\bar{n})}{2\sqrt{1-w(\bar{n})^2}}\right]. \qquad (28)$$

Eventually we get

$$\sigma_{nn'}(\mathbf{v}) = \frac{1-w(\bar{n})}{2}\left[\sigma_{nn'}^{(1)}(\mathbf{v}) + \sigma_{nn'}^{(2)}(\mathbf{v})\right]$$
$$+ \frac{w(\bar{n})\ln\xi(\bar{n})}{2\sqrt{1-w(\bar{n})^2}}\sigma_{nn'}^{(3)}(\mathbf{v}). \qquad (29)$$

It should be noted that the cross-sections appearing in (24), (27) and (28) are positively defined quantities according to equation (16), thus they are calculated so that in either case the logarithmic function argument exceeds unity. Otherwise, we take $\sigma_{nn'}^{(i)} = 0$ where $i = 1, 2, 3$. When all $\sigma_{nn'}^{(i)}$ are equal to zero, the transition $n \to n'$ is classically forbidden. The dominant contribution to vibrational relaxation cross-sections near the dissociation limit is made by the first two terms, while the last term is the leading one in the limit of the harmonic oscillator.

In a semiclassical approximation, the cross-sections of upward and downward transitions are equal. This relation contradicts the detailed balance principle

$$\mathbf{v}^2\sigma_{n\to n'}(\mathbf{v}) = \mathbf{v}'^2\sigma_{n'\to n}(\mathbf{v}'). \qquad (30)$$

To satisfy the detailed balance condition (30), we modify cross-sections (29)

$$\sigma_{n\to n'}(\mathbf{v}) = \left(\frac{\mathbf{v}_<}{\mathbf{v}}\right)^2\sigma_{nn'}(\bar{\mathbf{v}}), \qquad (31)$$

where $\mathbf{v}_<$ is the smaller of $\mathbf{v}$ and $\mathbf{v}'$, and $\bar{\mathbf{v}}$ is a 'mean relative velocity'. This function must be symmetric in $\mathbf{v}$ and $\mathbf{v}'$ such that $\bar{\mathbf{v}}(\mathbf{v},\mathbf{v}) = \mathbf{v}$. These conditions are sufficient for the explicit form $\bar{\mathbf{v}}(\mathbf{v},\mathbf{v}')$ to be found up to the term proportional to ΔE

$$\bar{\mathbf{v}} = \bar{\mathbf{v}}(\mathbf{v},\mathbf{v}) + \left(\frac{\partial\bar{\mathbf{v}}}{\partial\mathbf{v}'}\right)_{\mathbf{v}'=\mathbf{v}}(\mathbf{v}'-\mathbf{v}) + \cdots$$
$$= \mathbf{v}\left(1 - \frac{E_{n'}-E_n}{2\mu\mathbf{v}^2} + \ldots\right). \qquad (32)$$

Note that the derivative in (32) is equal to 1/2 from symmetry considerations. The ratio of speeds factor is necessary in any semiclassical time-dependent model of collisions. Intensive calculations performed by us for the systems $I_2 + He$, H_2 and D_2 show that the best agreement with experiments is reached when: downward transitions ($n > n'$)

$$\sigma_{n\to n'}(\mathbf{v}) = \sigma_{nn'}(\mathbf{v}); \qquad (33)$$

upward transitions ($n < n'$)

$$\sigma_{n \to n'}(\mathbf{v}) = \left[1 - \frac{2(E_{n'} - E_n)}{\mu v^2} \right] \sigma_{nn'}(\mathbf{v}). \qquad (34)$$

In either case, the mean relative velocity has been taken as the initial velocity. This is no surprise, since in molecular beam studies of vibrationally inelastic collisions [24–26] the condition of the transferred energy smallness in (32) ($\Delta E/4E << 1$) has always been met.

As is seen from the above formulae, cross-sections of vibrational relaxation depend functionally on three parameters a, τ, p and the scaling factor σ. Assuming that these parameters can vary independently from each other, one can consider expression (29) together with (33) and (34) as a systematization or condensation of experimental data in which a small amount of measured data will suffice to determine the entire state-to-state array. So we have the dynamically based fitting law, which is called the analytical model within the Bessel approximation (AMBA).

3. Results and discussion

Before proceeding to a direct comparison of theoretical results and experimental evidence, we should like to make some general remarks. Let us return to equations (24)–(29), (33) and (34). It is easily seen that vibrational energy transfer cross-sections increase monotonically with increasing relative velocity, beginning with zero. The cross-sections of T–V transitions vanish at the threshold. However, even for V–T transitions, the adiabatic effects result in the existence of classical 'dynamical threshold velocities'. Such effects depend crucially on the reduced time of collisions τ ($= \pi \omega(\bar{n}) L/v$). The analysis of equation (15) together with (11) and (12) shows that, along with adiabatic effects, a physical limitation on the maximum angular momentum transfer manifests itself in a rapid drop-off of cross-sections as a function of Δn beyond some characteristic value Δn^* such that $\Delta n^* \geq 2A$. In our approach, such cross-sections are merely taken to be equal to zero. Just for this reason, the threshold behaviour of T–V cross-sections needs refinement. A more careful examination of the case where $\mathbf{v}' \to 0$ shows [12]

$$\sigma_{n \to n'}(\mathbf{v}) \propto \left(1 - \frac{2(E_{n'} - E_n)}{\mu \mathbf{v}^2} \right)^{n'-n} \qquad (35)$$

instead of (34). This is supported by experiments [27]. Nevertheless, taking account of the detailed balance by approximate equations (33) and (34) makes the agreement with experiment much better even far from the threshold. Another peculiarity of the above formulae should be noted. The larger the mean quantum number

$\bar{n} = n + \Delta n/2$ for transitions $n \to n + \Delta n$, the larger the corresponding cross-section at small and moderate values of n. At very large n the cross-sections reach their maximum, and then decrease slightly with decreasing n near the dissociation limit. Note that the maximum is shifted towards the dissociation limit with increasing adiabaticity parameter τ. These conclusions are in full qualitative agreement with exact quantum mechanical calculations done in the breathing sphere approximation [9]. It is pertinent to note in this connection that close to dissociation the Morse potential will give a poor approximation as the vibrational energy spacings become controlled by the long-range form of the B–C potential. In our approach, it is impossible to make definite inferences about the anisotropy parameter value. Comparison with experimental data may give the parameter $a(q)$ but the quantity $a(0)$ remains unknown. Further, we shall make no distinction between these quantities denoting $a(q)$ as a.

Molecular beam studies of collisions between He, H_2, D_2 and I_2 in the $B \, 0_u^+$ highly excited vibrational states (abbreviated I_2^*) [24–26] provide vibrational relaxation data as a function of collision energy and vibrational quantum numbers. For this reason, the results of these studies were used for comparison and predictions of our theory. In the framework of the AMBA fitting law, cross-sections for I_2^* + He are derived from computer fits to experimental values in terms of a statistical goodness-of-fit χ^2/ν solely for the case $n = 35$ and the centre-of-mass collision energy 89 meV. We used the spectroscopic parameters $\omega_e = 133.47$ cm^{-1} and $x_e \omega_e = 1.039$ cm^{-1} found by fitting transition frequencies given in [24] (see table 1). The resulting parameters of the model are

Table 1. Comparison of experimental $10\sigma_{nn'}/\sigma_{n,n-1}$ cross-sections for $I_2^*(n = 35) +$ He inelastic scattering at $E_{\text{c.m.}} = 89$ meV with theoretical values obtained by the AMBA model.

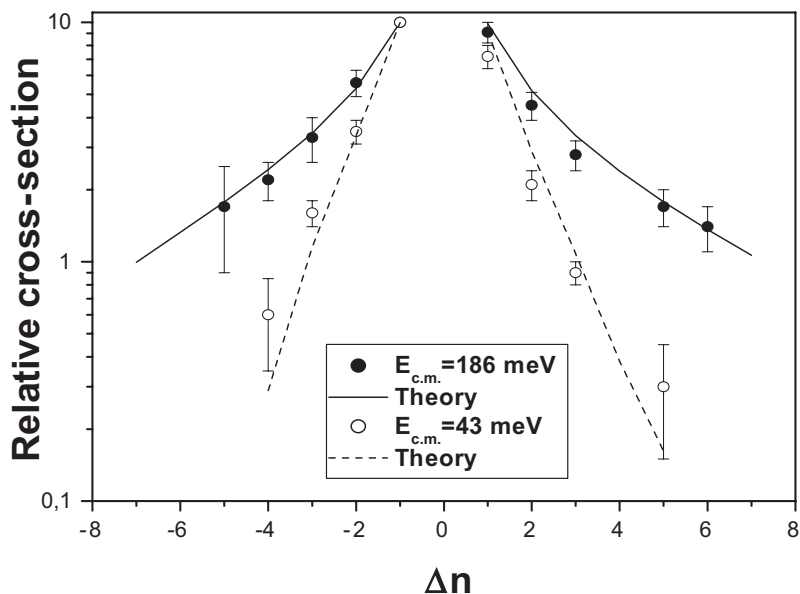| Δn	ΔE_{vib}(cm^{-1})	Experiment[a]	Theory
7	367	0.43 ± 0.10	0.404
6	321	0.66 ± 0.13	0.643
5	272	0.99 ± 0.15	1.005
4	222	1.61 ± 0.32	1.581
3	170	2.60 ± 0.26	2.561
2	115	4.56 ± 0.36	4.48
1	58.6	9.09 ± 0.45	9.635
−1	−60.8	10	10
−2	−124	4.76 ± 0.38	4.757
−3	−189	2.43 ± 0.36	2.737
−4	−256	1.84 ± 0.28	1.655
−5	−325	0.93 ± 0.20	0.983
−6	−396	0.49 ± 0.25	0.555
−7	−469	0.29 ± 0.15	0.305

[a]Data from [24].

Figure 1. Experimental cross-sections (symbols) for inelastic vibrational transitions of $I_2^*(n = 35)$ + He measured at $E_{c.m.} = 43$ and 186 meV. The solid and dashed curves indicate predictions of the AMBA fitting law.

$a = 2.22$, $\tau = 3.8$ and $p = 0.53$. The flexibility and accuracy of this fitting law are illustrated in table 1. Further, the parameters found were employed to test the predicting abilities of the model. Figure 1 shows the calculated and measured relative cross-sections for two kinetic energies differing from the reference energy [25]. Good agreement is observed even for $E_{c.m.} = 43$ meV, when collisions are almost adiabatic ($w(\bar{n})\tau_v = 2$–3). Along with experimental cross-sections [24], we plot in figure 2 the relative cross-sections (from both V–T and T–V processes) for other initial vibrational quantum numbers and the same reference energy. In this case the calculated values are in agreement with the measured ones (except $\Delta n = -3$ at $n = 15$; $\sigma_{15 \to 12} \approx 0$), although cross-sections of T–V transitions are represented better than those of V–T transitions. Therefore, we find that the AMBA model gives a very good description of both vibrational and relative velocity dependences of inelastic cross-sections.

Finally, we tested the ability of the theory to predict isotope effects in the crossed beam inelastic scattering of $I_2^*(n = 35)$ from H_2 and D_2 [26]. The isotopic targets are treated as structureless in our approach. The fitting procedure gave the following results for the system $I_2^* + D_2$ at $E_{c.m.} = 103$ meV: $a = 1.98$, $\tau = 3.5$ and $p = 0.525$. Everything needed for the evaluation of parameters a and τ for collisions $I_2^* + H_2$ at 89 meV is given by equations (12) and (14)

$$\frac{a_1}{a_2} = \frac{\mu_1 \mathbf{v}_1}{\mu_2 \mathbf{v}_2} = \left(\frac{\mu_1 E_1}{\mu_2 E_2}\right)^{1/2} \text{ and } \frac{\tau_1}{\tau_2} = \frac{\mathbf{v}_2}{\mathbf{v}_1} = \left(\frac{\mu_1 E_2}{\mu_2 E_1}\right)^{1/2}. \quad (36)$$

The resulting values are $a = 1.3$, $\tau = 2.67$ and the value of p must be the same for two isotopic targets. Comparison with experimental data is shown in figure 3. As is seen from the foregoing, the difference in angular momentum together with the difference in relative velocity affects the efficiency of vibrational transitions of I_2 molecules from two isotopic targets. Note that for adiabatic collisions the difference in relative velocity will play the leading role, since under such conditions the influence of the adiabatic factor becomes decisive.

Several interesting observations may be made about the magnitudes of some of the parameters appearing in the foregoing. The first observation concerns the reduced collision time. Equation (14) allows one to determine the range of interaction L. For the system $I_2^* + $ He we have 1.0 Å. Although this value seems to be too high, the resulting value of the scaling factor 3 Å^2 is such that it represents adequately absolute values of cross-sections obtained in $n = 43$ bulb studies [28]. On the other hand, if we take that $V(r)$ decreases exponentially at the length L_V, then equations (8) and (12) give a reasonable value 0.37 Å for the range L_V of the B–C potential. It is pertinent to note that the parameter p differs essentially from unity. If only short-range repulsion forces are taken into account ($p = 1$), the goodness of fit is characterized by $\chi^2/\nu = 1.6$ instead of 0.3 in a general case. As is seen, inelastic cross-sections for $I_2^* + D_2$ collisions coincide closely with those for $I_2^* + $ He collisions, thus the fitting parameters of these systems also differ slightly, primarily because of the difference in range parameters (see [29] for detailed discussion).
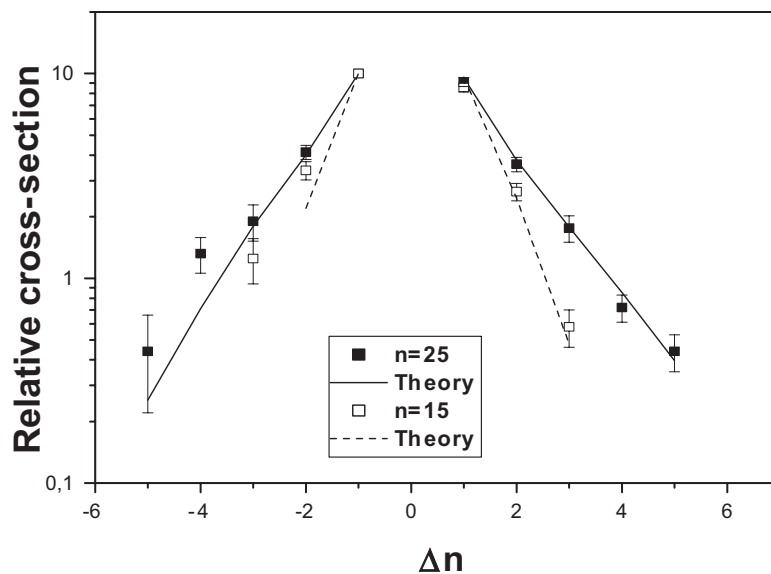
Figure 2. Experimental cross-sections (symbols) for inelastic vibrational transitions of $I_2^*(n)$ + He measured at $E_{c.m.} = 89\,meV$. The curves are corresponding calculations using the AMBA fitting law.
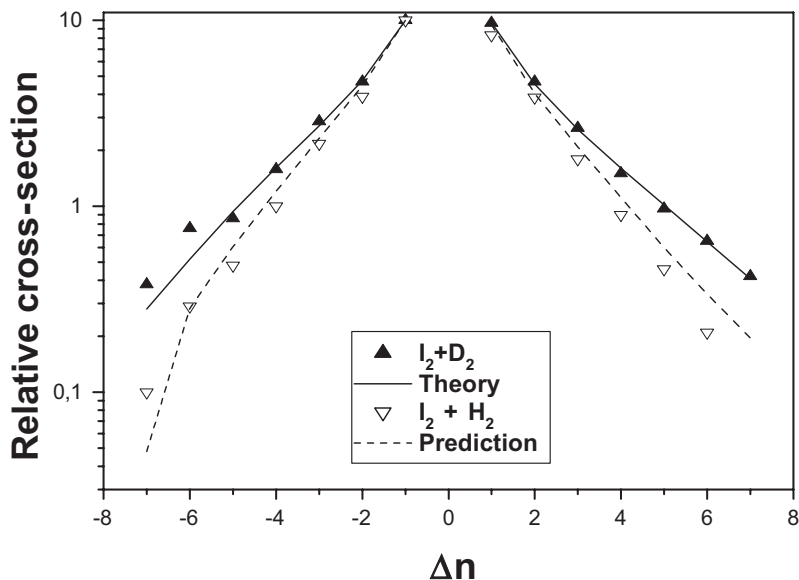

Figure 3. Comparison of experimental cross-sections (symbols) for vibrational energy transfer of $I_2^*(n = 35)$ by H_2 and D_2 with theory and predictions based on the AMBA fitting law.

4. Conclusion

For vibrationally inelastic collisions such that I_2^* + He, the so-called exponential energy gap law (EGL) has often been used to represent the experimental data [4, 25, 26]. The EGL model gave a statistical goodness-of-fit to the data $\chi^2/\nu = 1.2$ indicating that agreement with the data is within the reported experimental standard deviation. For comparison, the AMBA model gave the essentially better fit to the data with $\chi^2/\nu = 0.30$. On the other hand, with such a simplified approach one cannot predict the dependence of the model parameters on relative velocity and the reduced mass, as well as on other parameters characterizing the interaction potential. Thus, the AMBA fitting law derived from a dynamical theory is superior to the EGL for representing these data in a compact form. However, the principal advantage of the AMBA model is that we are able to provide a general physical interpretation of

the log-power law for vibrational energy transfer in highly excited states, for example the behaviour of rotational energy transfer in sudden collisions [30].

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