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Approximating Relative Rotational Energy Transfer in Molecular Collisions

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The rotational energy transfer (RET) processes taking place in an atom–diatomic gaseous mixture are analysed in detail by carrying out collision dynamical calculations of the relevant state-to-state cross-sections. Approximate schemes for the dynamics are tested along the series of He, Ne and Ar rare gases in collisions with N_2 molecules, using the IOS and CS approximate models. The corresponding average relative energy transfer (ARET) is found to be a slow function of collision energy and can be used as an efficiency index for the systems at hand. The IOS approximation, however, grossly overestimates this index especially for the more anisotropic interactions. Other dynamical models, like the hard-ellipsoid impulsive model, are also found to have the same shortcomings as the IOSA scheme. It is therefore concluded that approximate treatments of relative rotational energy-transfer processes are capable of only near quantitative predictions for systems that show very low efficiency for such processes, and fail markedly when larger amounts of energy can be transferred during collisions. The present conclusions will be of use in analysing scattering experiments.

1. Introduction

Collision-induced energy-transfer processes in molecular systems are of fundamental importance to several research areas in chemical physics and molecular physics.[1–4] For example, the interpretation of sound absorption effects due to alternate compressions and expansions in the gaseous mixture[5] requires an evaluation of a characteristic rotational relaxation time, τ_{rot}, simply related to one special type of generalised cross-section:[6]

$$\tau_{rot} = [N v_{AB} \sigma(0001/A)_{AB}]^{-1} \quad (1)$$

where N is the number density, v_{AB} the relative velocity of the partners, and the rotational relaxation cross-section $\sigma(0001/A)_{AB}$, further discussed in ref. 7, is related to the amount of relative rotational energy transfer in collisions between the partners A and B.

In this study we have examined a specific series of inert gases interacting with N_2 for which the potential-energy surface (PES) involved has been obtained earlier from an *ab initio* model approach.[8] This PES has been shown to predict successfully several transport properties and dynamical observables.[9,10] It should therefore provide a fairly realistic description of the regions relevant to RET collisional processes. Different dynamical approximations have been considered and used for the production of degeneracy-averaged, partial-integral cross-sections and for the construction of possible indicators of the relative efficiency of RET collisional processes. Such global indices can be used to indicate how well a specific PES is likely to direct energy into rotational motion and how such specific energy deposition effects vary with kinematical conditions dictated by the bath properties and by the partners masses. It is the aim of the present analysis to test the quality of the dynamical approximations for assessing the reliability of such indices.

2. Dynamical Models

A broad range of prescriptions is currently available for computing cross-sections, elastic and inelastic, total and partial, integral and differential, by using quantum, semiclassical or classical methods.[2,9] Various approximations can thus be used to reduce the full dimensionality of the coupled equations (CC) which describe the nuclear relative motion, and their validity for various systems has been extensively tested in the last few years.[11,12]

What has become by now the most common procedure for reducing the dimensionality of the CC equations relies on two distinct physical approximations. (i) The scattering is considered to be dominated by the repulsive part of the intermolecular forces, with the attractive region playing a lesser role, so that the trajectories are distorted mainly by the repulsive potential with little effects coming from coupling of different impact parameters. This approximation is usually called the centrifugal sudden approximation (CSA) of Kouri and McGuire.[13] (ii) The amount of transferred energy is small in comparison with the total energy available to the colliding partners. Thus, the channel wavevectors are assumed not to change in going from one final state to another. This simplification is therefore termed the energy sudden (ES) approximation.[14] The combined use of approximations (i) and (ii) leads to the so-called ISOA decoupling scheme.[15]

The great attraction of such a scheme is its capability of predicting the full ensemble of state-to-state cross-sections from a simple 'golden rule' formula[15] that expresses them as a weighted sum of cross-sections from the initial ground state:

$$\frac{d\sigma}{d\Omega}(j_i \rightarrow j_f | E) = (2j_f + 1) \sum_{j_L} \begin{pmatrix} j_i & j_L & j_f \\ 0 & 0 & 0 \end{pmatrix}^2 \frac{d\sigma}{d\Omega}(0 \rightarrow j_L | E) \quad (2)$$

where j_i, j_f are the initial and final rotational quantum numbers and the j_L index takes on all values which are allowed by the triangular relation required for each of the Clebsh–Gordan coefficients that constitute the weighting factors, these being zero for odd $(j_i + j_L + j_f)$.

For weakly interacting systems, such as He colliding with diatomic targets, the CSA is very good down to collision energies of the order of the well depth, which are typically 20–30 K. Thus, most of the error from computing IOSA inelastic cross-sections is expected to come from the ES assumption, *i.e.* from disregarding the change in relative velocity resulting from the inelastic collision.

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Table 1 BTT potential parameters for rare-gas–N_2 interactions (all values in a.u.)

	$V_{\parallel}$			$V_{\perp}$			$\Delta P = P_{\parallel} - P_{\perp}$		
P	He	Ne	Ar	He	Ne	Ar	He	Ne	Ar
R_m	7.43	7.37	8.15	6.43	6.38	6.89	1.0	0.99	1.26
σ	6.73	6.68	7.36	5.73	5.68	6.14	1.0	1.0	1.22
$\varepsilon \times 10^{-4}$	0.74	1.78	3.00	0.98	2.28	5.10	0.24	0.50	2.1
R_{tp1} [a]	6.50	6.19	6.95	5.54	5.25	5.80	0.90	0.94	1.09
R_{tp2} [b]	6.22	5.80	6.56	5.29	4.87	5.53	0.93	0.93	1.03
R_{tp3} [c]	6.06	5.61	6.41	5.15	4.68	5.41	0.91	0.93	1.00

[a] R_{tp1} = turning point at $E_{coll} = 21.48$ meV. [b] R_{tp2} = turning point at $E_{coll} = 74.24$ meV. [c] R_{tp3} = turning point at $E_{coll} = 124.08$ meV.

Given the capabilities of the approximate IOSA approach, one interesting quantity that could help us to analyse the relation between anisotropic interactions and RET processes is the average relative energy transfer (ARET) defined as follows:

$$\frac{\langle \Delta E_{rot} \rangle_i}{E} = \left(\sum_{j_f} \Delta E_{if}\, \sigma_{i \to f}(E) \Big/ \sum_{j_f} \sigma_{i \to f}(E) \right) E^{-1} \qquad (3)$$

which is referred to a particular initial state $|j_i\rangle$ of the target molecule and where ΔE_{if} is the energy difference between the initial and final states. From an eqn. (3) for each $|j_i\rangle$ one can therefore obtain a relative energy transfer parameter, $\langle \Delta E/E \rangle$, that provides information on the efficiency of the RET process for a particular system and at a specific collision energy E. Note that the state-to-state cross-sections of eqn. (3) provide relative probabilities weighting differently the various ΔE_{if} contributing to the average value. In other words, the cross-sections provide the dynamical factors while the ΔE_{if} represent the structural factors of the RET process.

3. Anisotropic Surface

The reason for choosing He, Ne and Ar colliding with N_2 molecules for this study is related to the established quality of the anisotropic potentials for these systems, which have been tested by us and found to be quite realistic[12] in describing several different transport properties of their gaseous mixtures.[10,11] They have been predicted using the Tang–Toennies potential model[16] which dampens the long-range *ab initio* dispersion terms individually using a universal damping function and adds to it a simple Born–Mayer repulsive form. The resulting potentials will be called BTT potentials[8] and their more relevant features are listed in Table 1, which also contains the values of the classical turning points at three different collision energies and for the two geometries which give rise to the definition of the ellipsoid axes: the corresponding difference values are also listed in the last three columns of the table. It is interesting to note that the general smallness of the deformation is confirmed by these values, as they correspond to *ca.* 12–13% of the average minimum positions R_m for each system. The deformation also varies relatively little with the relative collision energy E, thus suggesting fairly steep walls for all the three repulsive regions, and that the deformation does not increase significantly in going from He to Ne. This somewhat counterintuitive result is confirmed by the R_m values, which also do not increase in going from He to Ne, and by the very similar behaviour found for the three rare gases along the series of interactions with H_2.[17]

4. Average Energy Transfers

Decoupled Quantum Results

One interesting question concerning the quantities defined in section 2, especially that given by eqn. (2) and (3), is to verify the general accuracy of the approximations contained in the computing schemes. We already mentioned that for weakly interacting van der Waals (vdW) systems, where the average well depth is often much smaller than the collision energies, the CS approximation is very realistic especially for comparing partial-integral cross-sections. Thus, one first check is provided by a direct comparison between IOSA and CS calculations for the same quantity. This is shown in Fig. 1 for Ar–N_2, the most anisotropic system we have examined here. Two different collision energies are shown and the relative error, $(\sigma_{IOSA} - \sigma_{CSA})/\sigma_{CSA}$, is plotted as a function of the amount of transferred rotational energy. The partial inelastic cross-sections were computed starting from the $j_i = 2$ level. All open channels and two closed channels were needed for convergence of the cross-sections to within *ca.* 2%. In the case of the IOSA results, all the cross-sections are by definition associated to 'open' channels and therefore the summation in eqn. (3) included all contributions that were necessary to make the partial cross-sections converge to $<1\%$. One clearly sees that the IOSA calculations overestimate the rotational inelasticity and always produce cross-sections that are too large for the present systems.

The consequences of the weighted sum, employed to generate the ARET index of eqn. (3), are shown in Fig. 2 for the same system for $j_i = 0$. The IOSA results are significantly larger than the CSA data at all collision energies, this effect being the greatest at collision energies below 10 meV where the IOSA values are a factor *ca.* 15 larger. This general trend is in keeping with previous comparisons with calculations on similar systems.[18] On the other hand, as the collision energy increases, both sets of calculations are fairly parallel and tend to limiting values nearly independent of the collision energy. This fact underlines the dominance of the purely repulsive features of the interaction at higher energies. It also suggests

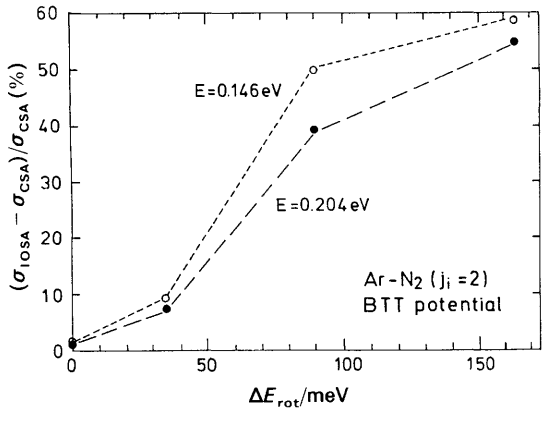

Fig. 1 Percentage deviations between partial inelastic IOSA and CSA cross-sections, as a function of rotational energy transfer. All cross-sections originate from the $j = 2$ rotor state and were calculated for the BTT potential function of ref. 8 for two different collision energies. ○, $E = 0.146$ eV; ●, $E = 0.204$ eV

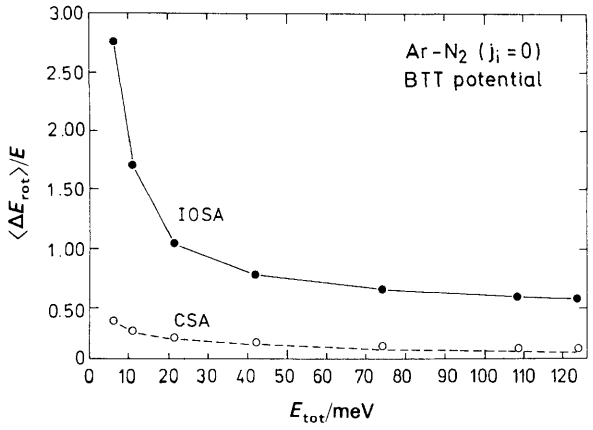

Fig. 2 Computed average relative energy transfers (ARET) as a function of collision energy (in meV) for the Ar–N_2 system. ●, IOSA calculations; ○, CSA calculations. The PES is the BTT function of ref. 18

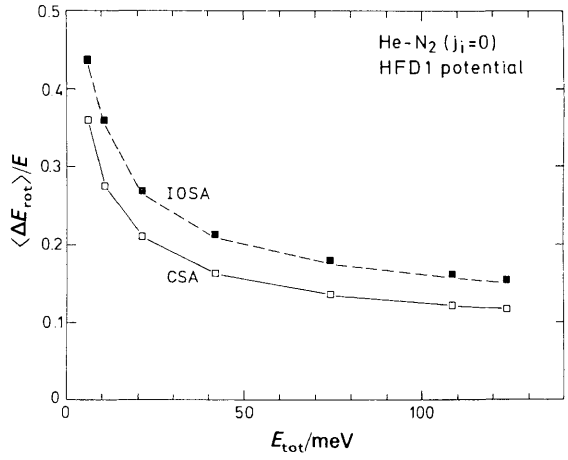

Fig. 4 Same as for Fig. 2 for the He–N_2 system and computed *via* the potential function of ref. 19. ■, IOSA; □, CSA

that in the limit of high energies $\langle \Delta E/E \rangle$ might serve as an indicator of RET efficiency in that particular system.

If one now turns to the weakest of the interaction potentials discussed here, *i.e.* the He–N_2 system, one is able to see that the IOSA model fares much better in yielding inelastic cross-sections as shown in Fig. 3 and 4. Fig. 3 shows the partial-integral cross-sections, computed within the IOSA and CSA scheme, compared in terms of relative percentage error as a function of the amount of rotational energy transferred. The corresponding j_f values are also shown in the upper abscissae. In these calculations the HFD1 potential function of ref. 19 was used. Since this potential shows similar trends as the BTT model but somewhat different magnitudes we also expect similar trends in cross-section error. The main features of both potential functions are listed in Table 2.

The IOSA results consistently overestimate RET efficiency and do so more markedly at lower collision energy and for more anisotropic potentials. Thus, the average energy transfers evaluated by IOSA calculations are all likely to be grossly in error unless the system under consideration happens to exhibit a low efficiency for RET processes through either an unfavourable mass ratio or a weak angular potential anisotropy.

On the other hand, since the IOSA and CSA values of the ARET index from eqn. (3) appear to be scaled by factors largely independent of collision energy, at least in the range examined in Fig. 2 and 4, $\langle \Delta E/E \rangle$ from the simpler dynamical approximation of the IOSA scheme can still be used as a qualitative index of ARET efficiency. The larger its value, in fact, the more likely the system at hand is to require more sophisticated calculations for estimating reliably its relaxation properties. An extensive comparison of different methods for obtaining the latter quantities has been presented elsewhere.[20]

An example of the qualitative value of such IOSA calculations is shown by the results presented in Fig. 5. The relative energy-transfer indices are plotted as a function of total collision energy in meV for a series of projectiles from He to Ar. The interplay of mass factors and anisotropy features of the interactions in producing the three different curves provides some interesting insight: (i) the average relative energy transfer (ARET) changes slowly with collision energy, as discussed before, and therefore the limiting values of the curves could be used to characterize the ARET efficiency in each system. There is a low efficiency for He projectiles (ARET value *ca.* 0.10) and a markedly larger efficiency for Ar–N_2 systems (ARET value *ca.* 0.60); (ii) note that the above values change in going from Ne to Ar by a factor of *ca.* 1.8, which is

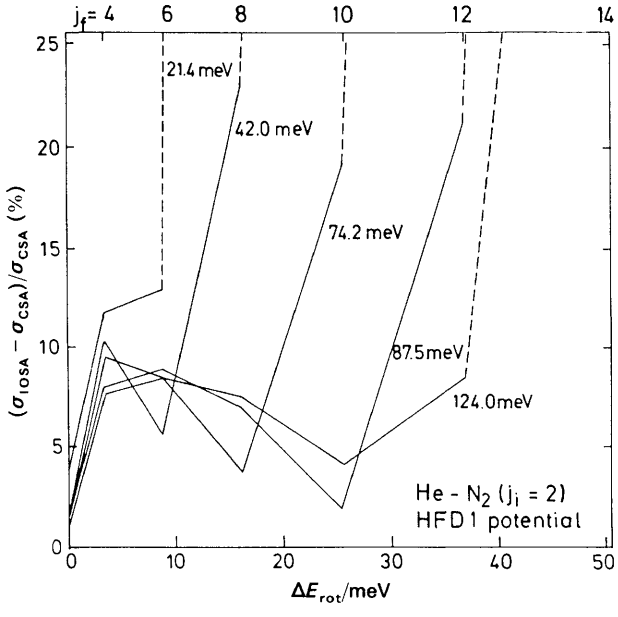

Fig. 3 Same as for Fig. 1, but for the He–N_2 system. The employed PES was that of ref. 19. E_i (in meV) shown on figure

Table 2 Comparison of some characteristic potential parameters for He–N_2 as obtained from two different functional forms (all values in a.u.)

	V_0		V_2		V_4	
	HFD1[a]	BTT[b]	HFD1[a]	BTT[b]	HFD1[a]	BTT[b]
R_m	6.90	7.00	8.05	7.80	—	8.80
σ	6.22	6.10	7.80	7.19	—	8.24
$\varepsilon \times 10^{-4}$	0.79	0.80	0.04	0.13	—	0.003
	turning points					
	$V_{\parallel}$		$V_{\perp}$		ΔR	
R_{tp1}[c]	6.09	6.50	4.84	5.54	1.25	0.96
R_{tp2}[c]	5.57	6.22	4.40	5.29	1.17	0.93
R_{tp3}[c]	5.35	6.06	4.20	5.15	1.15	0.91

a From ref. 19. *b* From ref. 8. *c* R_{tp1} = turning point at E_{coll} = 21.48 meV; R_{tp2} = turning point at E_{coll} = 74.24 meV; R_{tp3} = turning point at E_{coll} = 124.08 meV.

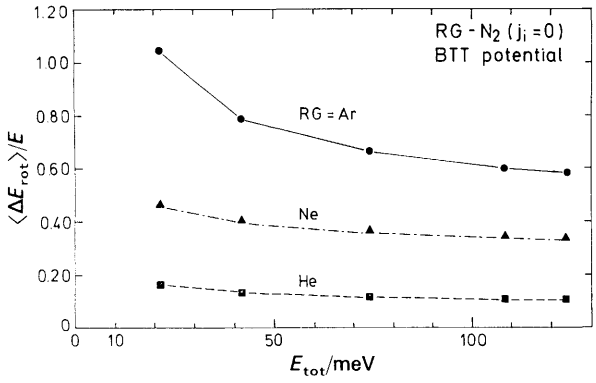

Fig. 5 Average relative energy transfer [eqn. (3)] computed *via* the BTT potential functions of Table 1 for He, Ne and Ar colliding with N_2. The ARET indices are shown as a function of collision energy (in meV). ●, Ar; ▲, Ne; ■, He

larger than the simple increase due to reduced mass changes (1.4). This suggets that the increased anisotropy of the latter system with respect to the former (see Table 1) plays a significant role and makes IOS results correspondingly less reliable; (iii) the visible increase of the ARET index in going from He to Ne, with similar anisotropic interactions, as seen from the features of Table 1. Thus, one expects the changes to be due mainly to mass factor changes with little effect coming from dynamical factors. The reduced mass ratio Ne–N_2/He–N_2 is *ca.* 3.4 and the corresponding ratio of the IOSA limiting values from Fig. 5 is *ca.* 3.3.

Hard-ellipsoid Model

Simpler, approximate procedures which could yield acceptable ARET values for a given system have been used by experimentalists and it is interesting to examine here the classical expressions obtained within the hard-ellipsoid model of anisotropic interaction and the impulsive picture of the RET dynamics.[21–23] Such quantities have often been obtained to make comparisons with experiments.[22]

One important observable determined by scattering experiments is the dimensionless relative recoil velocity g_R^* defined as:

$$g_R^*(j_f) = (1 - \Delta E_{if}/E)^{1/2} \quad (4)$$

for a given relative energy transfer, $\Delta E_{if}/E$ between rotor states j_i and j_f. Within the above classical model one finds that the angular distribution of $g_R^*(j_f)$ is given for $j_i = 0$ by

$$g^*(j_f, \Theta) = [(1 - Q^2 \sin^2 \Theta)^{1/2} + Q \cos \Theta](1 + Q)^{-1} \quad (5)$$

where Θ is the c.m. scattering angle. Although eqn. (5) is strictly correct only for $j_i = 0$ it is only weakly dependent on j_i so long as the impulsive approximation holds. The dimensionless parameter Q is defined as:

$$Q = B_e \frac{2\mu}{h} (\Delta R)^2 \quad (6)$$

where ΔR in this model is simply the difference between the location of the two turning points, in the C_{2v} and $C_{\infty v}$ orientations, at the given collision energy. If one now expresses the constant B_e *via* the moment of inertia of the isolated molecule, I, then eqn. (6) can be rewritten as:

$$Q = \frac{\mu(\Delta R)^2}{I} \quad (7)$$

where all quantities are in atomic units. The above parameter is the ratio between some 'dynamical' moment of inertia for the interacting system, $\mu(\Delta R)^2$, and the 'static' moment of inertia of the isolated molecule, I, which simply provides a structure factor inversely related to the rotational spacings in the target.

It is interesting to note that the Q parameters for the systems at hand tend to a limiting value, as the collision energy increases, which is only slowly dependent on the collision energy itself. In particular, the asymptotic values of Q are very close to the corresponding relative energy-transfer limit values given by the IOSA calculations discussed before and presented in Fig. 5. This surprising result can be gleaned from the quantities shown in Table 3 for the present systems and suggest that, in spite of its ultrasimple evaluation, the parameter Q is roughly related to the ARET index discussed before.

By making use of eqn. (4) and (5) one quickly recovers an expression for the relative energy-transfer value as a function of the scattering angle Θ and the parameter Q:

$$\left(\frac{\Delta E_{if}}{E}\right)(\Theta) = \frac{2Q}{(1+Q)^2} \times [1 + Q \sin^2 \Theta - \cos \Theta(1 - Q^2 \sin^2 \Theta)^{1/2}] \quad (8)$$

The above quantity, within the hard-ellipsoid model for the interaction, classically corresponds to the relative RET when going from j_i to j_f in the target states. It has a maximum at a particular angle Θ_{RB} for which the relative recoil velocity exhibits a rainbow maximum.

The corresponding relative average energy transfer can therefore be obtained by simple integration:

$$\left\langle \frac{\Delta E}{E} \right\rangle = \int_{-1}^{1} \left(\frac{\Delta E_{if}}{E}\right)(\Theta)\, \mathrm{d} \cos \Theta = \frac{4}{3} Q\left(\frac{3 + 2Q}{(1+Q)^2}\right) \quad (9)$$

The quantity given by eqn. (9) does not depend any more on a particular j_i and j_f state since the above integrated value is now taken to represent the overall energy transfer coming

Table 3 Computed Q parameters [eqn. (6)] and computed IOSA average relative energy transfer values [eqn. (3)] for He, Ne and Ar interacting with N_2

	He		Ne		Ar	
E_{coll}/meV	Q	$\langle \Delta E/E \rangle_{IOS}$	Q	$\langle \Delta E/E \rangle_{IOS}$	Q	$\langle \Delta E/E \rangle_{IOS}$
124.08	0.099	0.104	0.34	0.33	0.55	0.58
108.57	0.099	0.106	0.34	0.33	0.56	0.60
74.24	0.101	0.117	0.34	0.35	0.58	0.67
42.01	0.104	0.135	0.35	0.39	0.62	0.79
21.48	0.108	0.165	0.35	0.45	0.67	1.05
10.98	0.111	0.232	0.36	0.55	0.71	1.71
6.21	0.114	0.346	0.37	0.74	0.75	2.76

Table 4 Computed integrated relative energy transfer $\langle \Delta E/E \rangle$, and maximum relative energy transfer, $(\Delta E/E)_{max}$, as given by eqn. (9) and (11) for He, Ne and Ar projectiles interacting with N_2

	He		Ne		Ar	
E_{coll}/meV	$\langle \Delta E/E \rangle$	$(\Delta E/E)_{max}$	$\langle \Delta E/E \rangle$	$(\Delta E/E)_{max}$	$\langle \Delta E/E \rangle$	$(\Delta E/E)_{max}$
124.08	0.35	0.33	0.94	0.76	1.26	0.92
108.57	0.35	0.33	0.94	0.76	1.26	0.92
74.24	0.36	0.33	0.94	0.76	1.29	0.93
42.02	0.36	0.34	0.94	0.76	1.33	0.94
21.48	0.38	0.35	0.95	0.77	1.39	0.96
10.98	0.39	0.36	0.97	0.78	1.44	0.97
6.21	0.39	0.37	0.98	0.79	1.47	0.98

from all scattering angles during the impulsive process and therefore from all possible j_i and j_f values. It is obviously related to the Q parameter for each system under consideration and can be simplified according to the values of Q. Thus when $Q \ll 1$ then

$$\langle \Delta E/E \rangle \approx 4Q \tag{10a}$$

however, for $Q \sim 1$ one obtains instead

$$\left\langle \frac{\Delta E}{E} \right\rangle \approx \tfrac{4}{3}Q^{\frac{5}{4}} = \tfrac{5}{3}Q \approx 1.67Q \tag{10b}$$

and, finally, for very large Q values $(Q \gg 1)\langle \Delta E/E \rangle$ approaches a constant independent of Q,

$$\left\langle \frac{\Delta E}{E} \right\rangle \approx \frac{4}{3} Q\left[\frac{2Q}{Q^2}\right] = \frac{8}{3} \approx 2.67 \tag{10c}$$

A further index of the efficiency of the energy-transfer process can be obtained by taking the value of the relative RET index at the angle at which it is largest. Thus, one can write:

$$\left(\frac{\Delta E}{E}\right)_{max} = 4Q(1 + Q)^2 \tag{11}$$

with the limiting values:

$$\left(\frac{\Delta E}{E}\right)_{max} \approx 4Q(Q \ll 1) \tag{12a}$$

$$\approx 1.0(Q \approx 1) \tag{12b}$$

$$\approx 4/Q(Q \gg 1) \tag{12c}$$

From the above derivations it is seen that the simplified relation for the $(\Delta E/E)_{max}$ given by eqn. (12*a*) in the limit of small Q values[22] coincides with the integrated expression of eqn. (10*a*), the latter being valid also in the limit of small Qs. Thus, the Q parameter turns out to be directly related to the average relative energy transfer index discussed before. The fact that its actual values as a function of collision energy are close to those obtained *via* the IOSA calculations for eqn. (3) confirms more quantitatively this relation. It also tells us, however, that Q must also overestimate the ARET values as is done by the IOSA scheme and that, consequently, its reliability as an efficiency index is greater the smaller its value becomes. The situation of $Q \ll 1$ corresponds in fact to either small reduced masses or to small potential deformations from the spherical shape features for which the IOSA calculations were shown before to be more reliable and closer to the more sophisticated CS results.

The behaviour of the integrated quantity of eqn. (9) and of the maximum value of eqn. (11) as a function of collision energy, is shown in Table 4 for all the systems discussed in the present study.

5. Conclusions

The anisotropic interactions examined above, and the specific systems for which we have computed average relative energy transfer parameters (ARET), have allowed us to look more closely at possible indices of efficiency that could be obtained by approximate dynamical calculations of the ARET values.

As shown by the present results, the energy sudden approximation invariably produces upper bounds to the more correct coupled states calculated inelastic cross-sections. As a result the IOSA average values overestimate the energy transfers. On the other hand, we have shown that the sudden approximation implicit within the IOSA scheme is most sensitive to the short-range anisotropy of the interaction, while including the full anisotropy only indirectly, through the angle-averaging procedure. Thus, when the RET efficiency indices are examined along a series of atom–molecule systems with similar characteristics, their IOSA estimates are increasingly more in error the more the system anisotropy and reduced mass increase along the series.

The alternative index Q was shown to be related to a simple classical model for calculating average energy transfers and was given as a ratio between a 'dynamical' factor and a 'structure' factor in eqn. (6) of section 4. The Q parameter obtained there was, however found to be nearly coincident with the previously examined IOSA quantities of the present systems. Thus, attempts at using it in comparison with experiments[22] must have the same care as that needed to evaluate the general reliability of IOSA cross-sections. This result was never explicitly shown in previous discussions.[20–23]

In conclusion, our study of approximate methods for evaluating average energy transfers in neutral, weakly interacting systems has shown the following features: (i) any of the approximate treatments of the dynamics considered here tends to overestimate inelastic processes and therefore produces ARET indices which are usually too large; (ii) the energy dependence of such approximate quantities is usually correct and tends to change very little with the collision energy E. Thus some fixed limiting value could be chosen to represent a given system and to qualitatively tell us how efficient RET processes are in that system; (iii) for systems where the efficiency is low, either because of the mass factor or of anisotropy features of the interaction, the approximate model discussed here are usually good and provides quantitative estimates of the RET efficiency in thermal and near-thermal collisions.

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