

Chapter 2

Reactivity and Relaxation of Vibrationally/Rotationally Excited Molecules with Open Shell Atoms

Vibrational kinetics is built around detailed data of molecular collisions. One of the most important processes determining vibrational non-equilibrium is the collision of open shell atoms with molecules. In this case, in addition to non-reactive outcome and dissociation, also the reactive channel should be considered, because it can significantly contribute to vibrational non-equilibrium. Historically, state-to-state kinetics has been used long before reliable state-to-state data were available. To this aim, simple models of *non-reactive* rate coefficients have been used for long times, often neglecting the reactive process as well as the dissociation, or using further approximations (Capitelli 1986). These models are essentially based on atom induced small perturbations on *harmonic* oscillators. Of course, this kind of results are limited to low-lying vibrational states, and under the hypothesis of negligible reactive processes. As a matter of fact, comparisons with more accurate data show the unsatisfactory performance of these methods, in particular for atom-molecule collisions, also by orders of magnitude. Accurate quantum mechanical methods are available (Skouteris et al. 2000; Launay 1991; Gray and Balint-Kurti 1998), but their requirements of computational resources are really huge, and they are not free from important drawbacks concerning dissociation (Skouteris et al. 2000; Launay 1991) and low-energy regime (Gray and Balint-Kurti 1998). This is the motivation for using the quasiclassical trajectory method (QCT), which represents a good compromise between reliability of results and feasibility of calculations, and is the most used method for large scale cross section calculations.

2.1 Computational Method

The quasiclassical trajectory method dates back to 1965, with the publication of the paper on $H+H_2$ reaction cross sections by Karplus et al. (1965), using a simple LEPS PES for this system. The method has been refined by many other

authors, and some reviews can be found for example in Porter and Raff (1976) and Pattengill (1979). Here only a brief outline will be presented, with particular emphasis on some practical details of relevance in order to obtain reliable and also affordable results, considering the large amounts of data required in the context of kinetic studies. In QCT method, nuclear dynamics is completely classical on the adiabatic potential energy surface of the scattering problem. The underneath hypothesis is the smallness of the De Broglie length in comparison with the typical dimensions of the problem. However, it is clear from the large amount of comparisons in literature that this criterion alone is not very useful to discriminate reliable results from very approximate ones. It is often the case that averaged quantities, such as cross sections and rate coefficients, are in quite good agreement with accurate theoretical and experimental results, despite significant discrepancies of very detailed results (such as transition probabilities in collinear case or with zero total angular momentum). Of course, QCT is not the method of choice for low total energies, but it can be extremely useful to continue low energy results obtained with accurate methods, considering that these methods require a huge computational effort, rapidly growing as the total energy increases, the reverse being true for quasiclassical trajectories. Characterization of molecular reagents and products is of course a central point in QCT. Concerning the first ones, the common way of performing quasiclassical dynamics is to prepare reagents by pseudoquantizing the initial molecule, in order to obtain a vibrating and rotating classical body whose rovibrational actions can be put in direct relation with the corresponding quantal values by simple pseudoquantization rules (Langer 1937):

$$j_1^{cl} = \sqrt{\ell(\ell + 1)}\hbar \quad (2.1)$$

or

$$j_2^{cl} = (\ell + \frac{1}{2})\hbar \quad (2.2)$$

and

$$v^{cl} = \oint p \, dq = (v + \frac{1}{2})h \quad (2.3)$$

The meaning of these relations is linked to the principle of correspondence, so they can be considered exact in the limit of high quantum numbers (this is the reason for coexistence in literature of two possible angular momentum quantization rules: their values at high rotational quantum numbers tend to be the same). A much more accurate analysis of the correspondences between quantal and classical motion can be found in Miller (1970), where the basis is the classical approximation to the Feynmann path integral. In QCT the operation to perform for reagents is to impose a molecular angular momentum given by Eq. (2.1) or (2.2), and then to prepare the molecule in order to have a classical action given by Eq. (2.3). This is done generally

by pre-computing the whole set of useful quantities for rovibrational states for the given molecule in the proper diatomic asymptote of the PES. This last operation, in turn, can be made by recursively finding the classical inversion points for an initial guess of internal energy, and then calculating the action integral (2.3) and comparing with the searched integer value (the quantized value to be simulated). A trial and error procedure brings the calculus towards the solution with the desired level of approximation. At that point, a complete table of classical inversion points is available for each pseudoquantized couple of rovibrational quantum numbers, therefore the classical motion can always start from one of these two points and a very simple dynamics can be performed for a fraction of the vibrational period, in order to set up the initial vibrational phase. Other operations to complete the preparation of the initial molecule are the setting up of the rotational phase and initial orientation of rotational axis, as well as the impact parameter of the atomic projectile, that is the distance of the initial atom velocity from the parallel line passing through the center of mass of the diatom. The impact parameter can be pseudoquantized or not (more frequently), in the first case it can be obtained by pseudoquantizing the orbital angular momentum. No quantum counterpart exists of rotational and vibrational phase, as well as the precession angle around angular momentum. They are undetermined, being their conjugated momenta quantized, i.e. known without uncertainty. Quasiclassically these coordinates are uniformly distributed, using a vector of independent random variables (the statistics associated to QCT rises from distributions of these random input parameters). Concerning products, an analysis of final properties is needed, because of course no quantization is found after a purely classical dynamics. Therefore a method for pseudoquantizing the final (possible) molecular outcome of the collision is required. Here the problem is more subtle and complex, because a continuous distribution of final rovibrational actions obtained from QCT have to be put in some relation with a discrete quantal distribution. The easiest (and by far the most used) way to treat the problem is to find the nearest integers in final angular momentum and vibrational action, by simply inverting Eqs. (2.1)–(2.3) (histogram binning). The correspondence with quantal motion can be not very accurate, in particular for the first rovibrational levels (in accord with the correspondence principle). The theoretical justification of this procedure is in Miller (1971), where it is possible to recognize that the procedure consists in averaging final actions instead of taking only the exact quantized values (whose calculation would be statistically impossible). In that paper it is possible also to understand the level of approximation of the histogram binning, due to both the action averaging as well as lack of amplitude superposition (this is substituted by superposition of probabilities). Concerning the first issue, the gaussian binning can really improve the quasiclassical result, as explained in Bonnet and Rayez (2004) and Bonnet (2008). It is directly derived from the purely classical probability of Miller, with the substitution of the Dirac delta with a gaussian of suited width (Bonnet 2008). Its application is extremely simple at the trajectory analysis stage, with the only drawback of some increase of statistical noise due to the very low importance attributed to trajectories too far from exact quantized values. Concerning the lack of trajectory interference, on the contrary, the problem

is much more complex, because the classical probability should be replaced by more sophisticated formulations (primitive, or uniform, or initial value representation semiclassical approximations Miller 2001). However, the examples of application of these semiclassical methods in literature are really scarce, and never for systematic calculations of cross sections, as those ones needed in kinetic models. This kind of calculations could be very effective in the ranges of low energy where QCT does not give accurate results for state-to-state cross sections. A very accurate QM calculation is offered by two quite popular codes, ABC (Skouteris et al. 2000) and the code of (Launay 1991). They are both time independent, require a huge amount of computational resources, and are currently limited by total energies below dissociation limit. As a consequence they are insufficient to perform complete calculations for kinetic models, but they are extremely important for assessing lower limits of total energy for the reliability of calculations performed by QCT method. Once the quasiclassical results connect smoothly to exact QM calculations in a restricted range of relatively low energies, it is very likely they will be reliable for higher energies, where the classical approximations get better and better and exact QM calculations become more demanding. In the following paragraphs, some relevant aspects of calculation of cross sections for atom-molecule collisions will be illustrated by using real systems of large theoretical as well as technological interest.

2.2 H+H₂

This is one of the most studied systems, for its relative simplicity and the availability of experimental results, since the 1960 of the past century. Actually, an accurate PES has been obtained for this system only in 1978 (LSTH Truhlar and Horowitz 1978). Important papers have been devoted to presentation of new methods for molecular dynamics tested on this system (Karplus et al. 1965; Schatz and Kuppermann 1976b,a; Althorpe 2001; Hankel et al. 2006). As a consequence, some sparse very accurate results have been obtained, even recently, on new PESs, considering higher order effects (Mielke et al. 2002). When dealing with application of molecular dynamics results to kinetic models, where complete sets of cross sections or rate coefficients are needed, it is practically impossible to apply an accurate method for the entire range of total energy needed (typically from room temperature to many tenths of thousands of Kelvin). In fact, complete sets of cross sections have been obtained only using approximations. Essentially three sets have been obtained by QCT method by Martin and Mandy (1993) on the cited LSTH PES, by Kim et al. (2009) on BKMP2, and by Esposito et al. (1999) and Esposito and Capitelli (2001, 2005) on both surfaces. Approximated quantal methods have been applied to this collisional system spanning the whole vibrational ladder (Krstić and Schultz 1999b). It is important to underline, however, that the use of an *approximated* quantal method *does not guarantee better accuracy* than methods based on classical mechanics. It strongly depends on the level of approximation used in the methods adopted, the range of collisional energy explored in calculations, the (light or heavy)

collisional system, the level of detail that is needed in final results. Dealing with (ro)vibrationally detailed cross sections for atom-molecule collisions to be used in kinetic models, these issues are all present, because the energy range is very large (from 1 meV to 10 eV or more), the whole detailed (ro)vibrational ladder is preferably required, and the systems considered can have very different masses. As an example, the largely used infinite order sudden approximation (Krstić and Schultz 1999a) consists of calculating transition probability for collisions neglecting rotation, both for reagents and products. If it is possible to study kinetic conditions which do not require initial excited rotational states (they are anyway a subset of those ones of interest), it is quite problematic to neglect final rotation in products, because it is the dynamics that should assess its irrelevance, given the initial conditions. In a vibrational transition it could be possible (as it often happens) that final rotation is significant, even if initial rotation does not. Rotation is also extremely important in dissociation and recombination processes, as can be seen in Esposito and Capitelli (2009). Generally speaking, the best strategy would be surely to merge results obtained from different methods in different and partially overlapping ranges of parameters, checking for smooth continuity of data and reasonable accord with available experimental results. This is a challenging task requiring experience in quite different methods for molecular dynamics and a huge availability of computational resources. As an example of application of successful accurate quasiclassical calculations to this light system the reader is referred to Esposito and Capitelli (2009), where collisional three-body recombination is studied by means of two mechanisms, including state-to-state processes. It appears that the final result is quite appreciable, with reliable results with good comparisons with the available data of experimental and theoretical origin. Actually a successful application of QCT needs high accuracy in its implementation when a complete state-to-state database of cross section or rate coefficients is required. In this case, it is not possible to tune the computational parameters of the simulation for a specific process. As a consequence, for some low probability processes it is possible to find a completely misleading result on the base of very few useful trajectories badly calculated. To avoid this effect, it is important to check each trajectory with a systematic method. In Esposito and Capitelli (2002) the choice is simply the reintegration of each trajectory step with a smaller time step, for example one half of the starting value. If the check is positive, a new time step is generated, otherwise only the lower time step result is retained and compared with a new more accurate integration, and so on. Even if this can appear a very expensive method, it allows a fine tuning of the time step along each integration, which has the result of statistically decreasing significantly the total computational time, and avoids integration of useless wrong and very long trajectories when the potential has a deep well, as in case of O+O₂ collisions (Esposito and Capitelli 2002). The present collisional system is of interest in many fields of technological application, in particular considering the lightest isotopes of hydrogen. However, it is much easier to obtain detailed experimental data about non-symmetrical isotopes, as in H+D₂ or D+H₂. As a consequence, the majority of comparisons between computational and experimental results are with that kind of isotopic combinations. Detailed data

for identical isotopes, on the contrary, should be taken from computational results, being their reliability assessed indirectly by means of experimental and theoretical data comparison with other isotope combinations. This is not the right place to digress about the overwhelming literature about these comparisons, the reader is referred to Aoiz et al. (2005) for a wide survey on the topic. The main findings that can be extracted from these comparisons concern the following points:

1. Reliability of the most recent PESs about this system, BKMP2 (Boothroyd et al. 1996) and CC (Mielke et al. 2002). They are very accurate (indeed they are the most accurate PESs ever calculated), and the last one (CC) has negligible differences with the older BKMP2, on which the majority of results has been calculated. This reliability comes from comparisons with many experiments. The famous significant discrepancy of the exothermal reactive rate $v = 1 \rightarrow 0$ (Mayne and Toennies 1981) between theory and experiment is now solved in favor of theoretical results, being the experiment with the excited vibrational state not completely reliable (Götting et al. 1987).
2. Accurate and quasiclassical methods have been applied, and in general the comparisons are quite good for averaged quantities, as initially guessed by Miller (1970) on the basis of his semiclassical theory. Following his explanation, it is clear the effect of neglecting the superposition of amplitudes. In fact, while the probability is “conserved” throughout the distribution in different final rovibrational channels, it is distributed with a sort of unpredictable randomness, due to lack of superposition of each trajectory contribution with the correct phase (which is completely lacking in a quasiclassical calculation).
3. This quasiclassical drawback must anyway obey the correspondence principle: in fact, when higher states are considered, faster oscillations tend to cancel with higher probability in the superposition, and as a consequence QCT results tend to be more accurate.
4. Also the dynamics can influence the importance of lack of correct superposition in QCT. In fact, it is known (Aoiz et al. 2005) that non-reactive results tend to be less accurate than reactive ones when compared with “exact” QM data. Even in this case it is possible to rationalize the effect: a significative part of non-reactive trajectories can come from a recrossing of reactive barrier. As a consequence, there can be a systematic superposition of two sets of trajectories with two quite different paths in the unreactive case, with important phase effects, of course absent for reactive trajectories.
5. Another independent source of errors in QCT is the presence of classically forbidden transitions. When the vibrational phase of reactant molecule is uniformly varied in its whole range, as is normal in a QCT calculation by means of the appropriate random numbers, the final products reach a range of possible values of final vibrational action, that is unquantized vibrational number times \hbar . The range of this vibrational outcome can be smaller than the possible vibrational range of products, therefore there can be some final values of vibrational quantum number never reached by the classical collision at the specified collisional energy: the transition is said “classically forbidden”. This has nothing to do

with energy forbidden transitions, in fact a well known case is found for He+H₂ non-reactive collisions in the exothermal direction (Balakrishnan et al. 1999). In that case, for collisional energies lower than about 1.0 eV the rovibrational cross section drops, contrarily to the accurate quantum mechanical result. Classically forbidden rovibrational transitions are naturally present at a certain low energy value for every collisional system, but a general method to know the lower limit of applicability of classical calculations is not available.

These observations are mainly obtained with calculations and comparisons about H+H₂ collisions, because of the availability of many data about it. However, it is the lightest atom-molecule collisional system, therefore quasiclassical calculations are expected to perform also better on heavier systems.

2.2.1 *Isotopes and Scaling Relations*

For the very light H+H₂ collisional system the isotope effect can be particularly important. In addition, a real interest into heavier isotopes is due to their applications in nuclear fusion technological development. As a consequence scaling relations to obtain rate coefficients for a different set of isotopes have been developed (Krstić and Schultz 1999b). Concerning quasiclassical calculations and simultaneous change of the three atomic masses by the same factor, there is the possibility of obtaining an exact (in the quasiclassical sense) scaling relation, by scaling the time of the simulation proportionally to the square root of the mass ratio, as considered in Capitelli et al. (2007). This can be applied at the level of trajectories (more accurately), or at the level of cross sections. The reader is referred to the literature for the details of the procedure (Capitelli et al. 2007).

2.3 N+N₂

This is one of the most important collision processes in atmospheric kinetics, with technological applications in the field of entry into planetary atmospheres. It has been studied initially only from a non-reactive point of view (i.e., without atom exchange between the projectile and the initial molecule, but only rovibrational energy exchange), because of the application of approximated schemes of calculation (SSH, FHO) (Schwartz et al. 1952; Husimi 1953; Kerner 1958; Treanor 1965). Actually, the reactive part is of large importance, as can be shown, and must be summed to the non-reactive part in order to obtain reliable results for rovibrational energy transfer processes, also at moderate temperatures. The first reliable PES for this collisional system was the semiempirical LEPS (London-Eyring-Polany-Sato) PES by Laganà and Garcia (1994). Many calculations have been done on that PES, with fairly good comparisons with the few experimental

results available. In particular, the same authors provided the first calculations on their PES (Laganà and Garcia 1994; Laganà et al. 1997). Extensive calculations of state-to-state cross sections for vibrational energy exchange and dissociation have been performed, including the whole ladder of rovibrational states in an approximate way (Esposito and Capitelli 1999, 2006; Esposito et al. 2006). Actually, the results of those calculations represent one of the most extensive databases on that system from low (1 meV) to intermediate (10 eV) collisional energy. The limits of this database are the following:

1. The lower energy limit, determined by the problems of quasiclassical method already stressed, as well as the inaccuracy of the large range interaction in the PES calculation, which becomes important at low energies. On the contrary, tunneling problems are probably of negligible importance (Caridade et al. 2010).
2. The upper limit, determined by problems of possible interaction with excited electronic states, which implies the use of a non-adiabatic method for dynamics, and the consequent requirement of larger computational resources. Recently new excited PESs have been proposed in literature (Galvão et al. 2012), of large interest for possible applications. From preliminary calculations in Galvão et al. (2012), it appears that this upper limit could be negligible, at least for energy ranges of some eVs.
3. The huge number of states of the molecule (about 10,000) imposes an approximation strategy. In Esposito and Capitelli (1999) this strategy was based on calculating dynamics starting from a limited number of rotational initial states, including the whole ladder of initial vibrational states. All the possible final states energetically accessible are in principle reached by trajectories, but to have a sufficient statistics for reliable results it is necessary to sum on final rotational states. This strategy allows one to have the whole vibrational ladder, which is fundamental for detailed kinetic studies, but introduces an approximation on initial rotation, that can be relevant (Capitelli et al. 2000). Another possibility is of course to approximate the initial vibrational ladder, considering on the contrary the whole initial rotational ladder, as in Esposito and Capitelli (2006). In this case it is possible to interpolate the rate coefficients in a relatively easy way on vibrational distribution, as in Esposito et al. (2006), but a global interpolation of cross sections is much more challenging, due to the relevant variations among cross sections originating from different vibrational states. If rate coefficients are suitable for the applications, vibrational interpolation of rates can be a good solution, but this not true for DSMC (Direct simulation Monte Carlo) applications, as in Bruno et al. (2002). A better solution for this important case is to try to directly interpolate cross sections on initial rotation, as will be briefly illustrated in Fig. 2.1. In this case, rotationally averaged cross section for collisions of O with $N_2(v, j)$ is obtained, using only one initial rotational state in 15. A simple linear interpolation on j is then used to generate all the lacking initial state cross sections to add into the Boltzmann weighted sum for the rotational temperature:

Fig. 2.1 Rotationally averaged cross sections (*line with markers*) for vibrational energy exchange in collisions of ground state atomic oxygen with ground state molecular nitrogen. (*red*) $T_{\text{rot}} = 300$ K, (*blue*) $T_{\text{rot}} = 10,000$ K; (*lines without markers*) corresponding interpolated cross sections (see text for details)

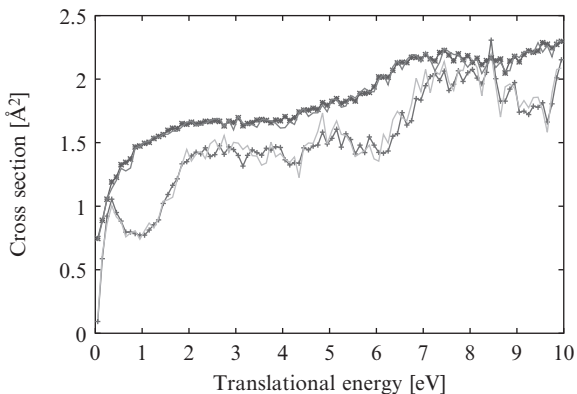
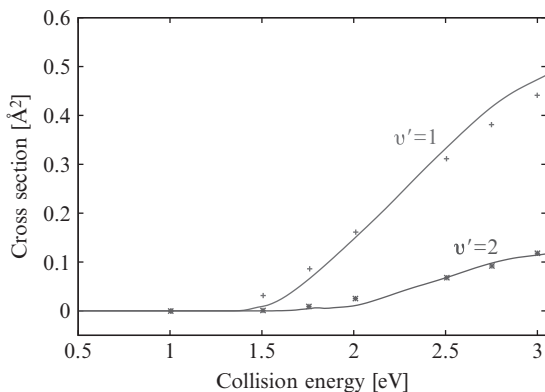


Fig. 2.2 Comparison of (*solid line*) quasiclassical and (*markers*) semiclassical (Balakrishnan et al. 1998) cross section calculations of $\text{N}+\text{N}_2(v=0, j=7)$ to different v' as a function of collision energy



$$\sigma(\varepsilon, T_{\text{rot}}) = \sum_j (\sigma(\varepsilon, j) \exp(-E_{vj}/k_B T_{\text{rot}})) / Q \quad (2.4)$$

being E_{vj} the energy of the (v, j) rovibrational level, k_B Boltzmann constant, Q rotational partition function.

In Fig. 2.1 the comparison is done between interpolated and completely calculated cross sections, at two quite different rotational temperatures, 300 and 10,000 K, for vibrational state-to-state cross sections. The results are quite good and reliable, with a clear gain in computational resources required.

In Fig. 2.2 the cross sections for inelastic vibrational excitation in $\text{N}+\text{N}_2$ collisions from $(v=0, j=7)$ to final $(v'=1,2)$ are shown, as calculated in Esposito and Capitelli (2006) on the LEPS PES (Laganà and Garcia 1994). For comparison the data (Balakrishnan et al. 1998) are shown, calculated on the same PES with a semiclassical method, essentially consisting in a quasiclassical method in which the vibrational degree of freedom of the molecule is treated quantum mechanically, with a feedback on the classical dynamics by means of an average potential (Billing 1984). This method copes with the problem of the quasiclassical inaccuracy in

presence of large spacings of energy levels, as for low-lying vibrational states. The comparison in Fig. 2.2 appears globally good. However, some apparently minor discrepancies in the threshold region could eventually have catastrophic consequences on low temperature rate coefficients. This depends on two reasons. The first one is that for processes with a threshold as in this case rate coefficients are extremely sensitive to tiny details in the threshold region, particularly if the mean energy of the translational energy distribution is lower than the threshold. The statistical errors on the semiclassical calculation in Fig. 2.2 have not been published, therefore it is not possible to appreciate if the discrepancy in the threshold region is due to statistical uncertainty or to a fundamental difference in the application of the quasiclassical and semiclassical methods. The second problem is in the approximation of the cross sections by points. Once the dynamical calculation has been performed in this way, it is hard to guess what analytical function should be used to interpolate the points in order to get a continuous cross section, for example in order to calculate the rate coefficient (but also to use it in a DSMC code). Being not unique, any interpolation could be good, but really in the threshold region this is a catastrophe, and can bring to very large errors on rate coefficients. A better strategy is the one of Aoiz and coworkers in (1997), where the whole energy range is continuously and uniformly scanned, and the cross section is calculated on the whole range using a suitable number of terms of Legendre polynomials, obtained directly from the trajectory results. In this way, no ambiguity is present in the cross section results, because the cross section is *ab initio* represented by a unique functional form. Another possible strategy is presented in Esposito (2011), where a particular kind of interpolation is performed on a very large number of discretized bins along the energy axis of each cross section, obtained with a continuous collisional energy distribution. The large number of bins results in better energy resolution, but of course also in an extremely noisy cross section. A procedure is then applied to perform a “feature extraction” from these noisy results in order to recover in an optimized way the “meaningful” information obscured by the statistical noise. This feature extraction is adaptive, recursive and strictly dependent on the level of statistical error of each point. The first attempt of the algorithm is to find a simple segment that initially approximates the full cross section on the whole range, then the segment is broken in two pieces connected by one point, and the two segments are free to adjust themselves with the constraint of the common point. This point can move both in value (cross section) and in collision energy. The procedure is then iterated with each of the two segments, and so on, with a convergence criterion linked to the statistical noise. In fact, the final number of segments depends on this noise and on the average local curvature of the distribution. The typical final result is illustrated in Fig. 2.3a, where it is possible to note that many small segments are present in the region near the threshold, while long segments are able to accurately describe the cross section in the regions where this one shows a quasi-rectilinear trend.

In Fig. 2.3b the rate coefficient calculated from the cross section interpolated by the polygonal is compared with the same rate obtained directly from the noisy cross section. It is clear the perfect agreement on many orders of magnitude. It is worth

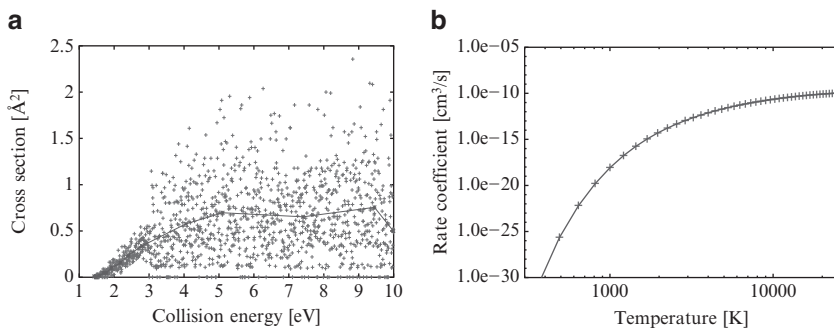


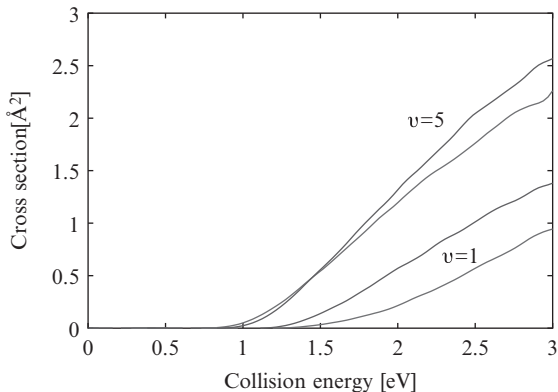
Fig. 2.3 (a) Original (noisy) cross section as a function of collision energy (red markers) and interpolation (blue polygonal line). (b) Comparison of rate coefficient calculated from the original points (red markers) and from the interpolation (blue line)

noting the small number of points used in the polygonal that allow to describe accurately the noisy cross section, retaining all the fundamental details (thresholds, plateaus, linear trends, etc.) and discarding the statistical fluctuations (hence the name “feature extraction”). Reaching the same level of accuracy using only discrete points along the energy axis would require much more calculations, for example in the threshold region. The use of this particular interpolation allows to manage a large mass of cross sections with high level of detail, using very compact data.

Concerning atom-molecule collisions with all atoms of the same species, the sum of reactive and non-reactive processes should be considered when dealing with vibrational energy transfer. On the contrary, old data used in kinetic models are based only on non-reactive data, as well as data coming from recent quantum calculations are often limited to non-reactive processes, because this can be obtained with a relatively simpler method. Any method limited in this way can be safely used only when the reactive channels are really closed, otherwise it is clear that the non-reactive result will be affected by the limitation, in addition to the lack of reactive contribution. But the question is: to what extent reactive processes are significant with respect to non-reactive ones? With quasiclassical calculations it is easy to obtain both contributions, provided the PES is adequate, with the only limitation of classically forbidden transitions (Miller 1970). In the H+H₂ case, the work of Martin and Mandy (1993) has been considered by other authors (Flower and Roueff 1998) to conclude that a ratio of 2 between reactive and non-reactive rates should be considered. The justification given in Flower and Roueff (1998) is quite simple, linked just to selection rule for orto-para states in H+H₂ system. However, a more fundamental reason can explain the general predominance of reactive processes on non-reactive ones in rovibrational energy exchange, as will be explained in the following.

A comparison of reactive and inelastic quasiclassical cross sections for N+N₂ collisions is performed in Fig. 2.4, where the diatom starts from $v=1$ and $v=5$ at a rotational temperature of 300 K, and the removal process is considered (that is

Fig. 2.4 Comparison of cross sections for (*red*) reaction and (*blue*) inelastic processes from $v = 1$ and $v = 5$, with final $v' \neq v$, at a rotational temperature of 300 K, for $N+N_2$ collisions



final $v' \neq v$). It is clear the strong similarity of the two contributions in the whole energy range, with a higher value of the non-reactive cross section for $v=1$ with respect to the reactive one. Considering that $v=5$ energy level is very near to the reaction barrier height, while $v=1$ level is well below, this similarity suggests that the majority of non-reactive trajectories are indeed missed reactive ones (recrossing trajectories). The presence of a threshold for an exothermal process could appear strange (removal process is dominated by de-excitation), and this effect might be ascribed just to a deficiency of the classical method of calculation. Low probability in the exothermal direction for low energy values can be easily justified on the basis of very general considerations. It is possible to consider two extreme conditions, the first one in which the time for traversing the SCR (strong coupling region), t_{SCR} , which depends on energy projectile as well as on potential features, is much higher than the vibrational period t_{vib} (which tends to slightly increase with vibrational quantum number), and the second condition in which t_{SCR} is comparable to or less than t_{vib} . In the first case, translational motion is by definition adiabatic with respect to vibration, so no transition is expected (its probability might be very low). In the second case, on the contrary, it is quite likely that vibration-translation transitions take place, because the characteristic times of the two motions are similar and the interaction of the two degrees of freedom is expected to be strong. Summarizing, vibrational adiabaticity is expected at low collision energy and low initial vibrational quantum number, and viceversa. These considerations (essentially the Massey criterion for adiabatic-diabatic processes applied to vibration-translation exchange (Massey 1949)) are quite general, therefore the same behavior can be expected from a classical as well as a quantum calculation. However, it is clear that this qualitative criterion cannot assure that a given cross section is exactly zero in a range of translational energy, but only that it should be very low. It is well known the inability of QCT to calculate very low probabilities, as well as its inadequacy in describing vibrational quasi-adiabaticity (Bonnet 2008) (i.e. quite low probability of final vibrational outcome different from the initial one in inelastic cases). As a consequence, quasiclassical results can be essentially considered reliable, excluding

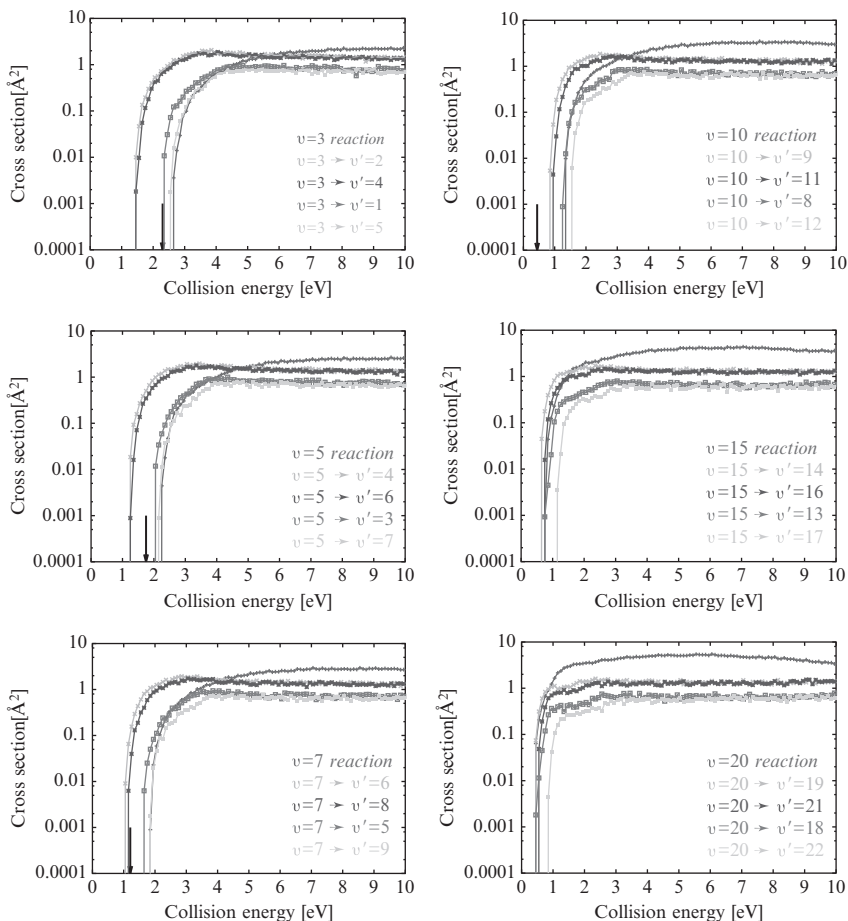


Fig. 2.5 Reactive (*red*) and non-reactive ($v \rightarrow v'$) cross sections of vibrational energy exchange for O+N₂($v, j = 0$) collisions, as a function of collision energy. The *downward arrow*, when present, is the threshold for reactive processes. Non-reactive processes appear quite similar to reactive ones in the threshold region, excluding only mono-quantum processes. See text for comments

the very low energy values, for which quite low values of probability are anyway expected. A better description of this point will be presented in the following, introducing the criterion of discrimination of two- and three-body collisions.

In Fig. 2.5 the collisions of ground state oxygen atom with nitrogen molecule is considered on the $^2A''$ PES of Gamallo et al. (2003). The initial vibrational state is indicated in the panels, while initial rotation is zero. For $v < 12$ the reactive process is endothermic, without a reaction barrier (apart from the purely endothermic step) along this PES (a reaction barrier is present along the C_{2v} minimum, at an energy higher than the endothermic step, see Akpınar et al. 2012). The energy threshold

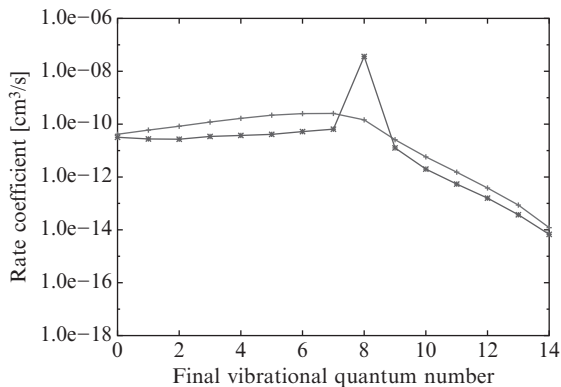
for reaction, which depends on initial (ro)vibrational state considered, is indicated by a downward arrow on the collision energy axis. This system has been chosen because of its high endothermicity (3.3 eV), in order to compare easily the typical behavior of reactive and inelastic cross sections. In Fig. 2.5, the reaction cross section is represented by the red curves, the blue and green curves represent the inelastic mono-quantum deexcitation and excitation, respectively, while the magenta and turquoise are bi-quantum deexcitation and excitation, respectively. The scale is logarithmic, in order to show clearly the threshold behavior. In panel (a), where initial $v = 3$, the inelastic mono-quantum cross sections are clearly dominant on the reaction one and on the bi-quantum ones up to 4 eV. The bi-quantum case (both deexcitation and excitation) is quite similar to the reactive case, with similar thresholds, while the mono-quantum case is significantly under the reactive threshold (about 1 eV). These two trends of mono- and bi-quantum cross section in comparison with reaction continue also for higher initial vibrational quantum numbers, as it is clear in lower panels (b),(c), from $v = 5$ and 7 respectively, but progressively reducing the discrepancy in the thresholds.

In panel (d), with $v = 10$, all the considered cross sections are completely on the right of the energy threshold for reaction. In panel (e) the case from $v = 15$ is shown, which is exothermal. The dynamical thresholds tend clearly to coalesce into a unique value, as stressed also in the last panel (f) from $v = 20$. The reaction cross section starts to be higher than inelastic cross sections at a collisional energy decreasing with initial v . Only for $v \geq 20$ reaction tends to be the dominant process on the whole range explored. The observation to extract from this comparison is that non-reactive processes are indeed quite similar to reactive ones with the exclusion of the elastic and quasi-elastic ones (i.e. mono-quantum deexcitation-excitation processes). Excluding these last processes, it is possible to say that the whole non-reactive processes take place only when reaction threshold is overcome, as one of the possible outcomes of a strong interaction. In fact, it is possible to appreciate that for symmetric systems like $\text{H}+\text{H}_2$ (Fig. 2.6) and $\text{N}+\text{N}_2$ (Fig. 2.8), there are two independent equivalent reactive channels, and the inelastic channel, excluding elastic and quasielastic processes, has a rate coefficient quite near to each reactive channel rate coefficient. This is the origin of the 1:2 ratio between non-reactive and reactive rate coefficients for symmetric collisional systems. It is anticipated here that all the discrepancies between non-reactive and reactive rates, apart from the elastic and quasi-elastic ones, could be attributed to non-reactive non-recrossing trajectories (see below).

On the contrary, it is clear the completely different trend of elastic and quasielastic processes, with a very high elastic peak with two rapidly decaying shoulders of quasielastic transitions. This behavior is typical of a harmonic oscillator perturbed by an atomic projectile, where there is an exponential decay of probability of vibrational energy exchange as a function of vibrational energy ε_{vib} transferred to the classical oscillator. The well known formula for transition probability of a forced harmonic oscillator is:

$$P_{n,m} = n! m! e^{-\varepsilon} \varepsilon^{(m+n)} (S_{n,m})^2$$

Fig. 2.6 Comparison of (red) reactive and (blue) non-reactive rate coefficients as a function of final vibrational quantum number at $T_{\text{coll}} = T_{\text{rot}} = 3,000$ K for collision of H with $\text{H}_2(v = 8)$. The elastic peak is only qualitatively approximated. The non-reactive contribution is doubled to compare with the two reactive channels for this kind of symmetric systems



$$S_{n,m} = \sum_{j=0} \frac{(-1)^j \varepsilon^{-j}}{(n-j)!j!(m-j)!} \quad (2.5)$$

where ε is the ratio of the ε_{vib} to one quantum of energy of the harmonic oscillator, being n, m initial and final vibrational quantum number, respectively. This transition probability has been exploited many times in different approximated methods for molecular dynamics, in particular in FHO (Husimi 1953; Kerner 1958; Treanor 1965) and DECENT (Giese and Gentry 1974) methods. This formula was obtained for a harmonic oscillator by Husimi (1953) and Kerner (1958) for a special potential:

$$U(x) = \frac{1}{2}kx^2 - xF(t) \quad (2.6)$$

This potential has the property of allowing the quantal and classical motion to be put in *exact* correspondence. Once the vibrational energy ε_{vib} transferred to the oscillator, initially at rest, is known from classical mechanics, it is possible to use directly formula (2.5) with this classical value of ε_{vib} , and the probability result is what can be obtained in an exact quantum calculation. Of course, the potential of realistic cases can be quite different from Eq. (2.6), therefore some restrictions must be put on the applicability of the method (even if it is not a perturbation method in principle). In particular, it is clear that during an atom-molecule collision the perturbing force cannot have a spatial dependence on the typical scale of the vibrational motion, otherwise it would not be expressible in the (2.6) way (Treanor 1965). In order to fulfill this condition the R distance between the atom and the center of mass of the diatom should be sufficiently larger than r , the internuclear distance of the diatom. This kind of collision could be indicated as “purely non-reactive” (PNR), essentially a *two body collision* between the atom and the diatom as a whole. Of course, the minimum acceptable value of $z = R/r$ depends on the true atom-diatom interaction potential. In order to correctly apply the formula (2.5), one should only consider PNR trajectories, defined as those ones having a ratio z never less than a certain two-body parameter $z_{2b} \sim 1.5$ during time evolution.

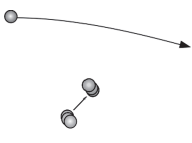
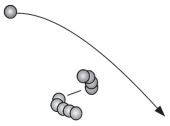
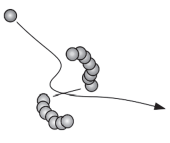
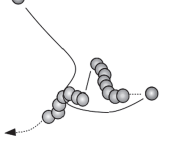
This is done only implicitly and approximately, by limiting the maximum value of collisional energy considered in the calculation. However, the limitation is not stringent, because the model is not a first order perturbation method, as already pointed out. It is clear that the value of z_{2b} is arbitrary to a certain extent, like R_{\max} for the maximum radius of interaction in a collision. If the collisional system has a barrier to reaction, PNR trajectories are those ones with energy sufficiently below the barrier, or trajectories above the barrier but with a sufficiently high impact parameter, so that the atomic projectile is only slightly deviated from the original straight line.

As a consequence, under the conditions of Fig. 2.5 purely non-reactive trajectories are the only ones below the reactive barrier, of course, but give also a contribution above the barrier, with high impact parameter trajectories. The remaining *large* contribution comes from non-reactive but not-PNR trajectories: in this case the collisional system has a significant interaction, that is the encounter is a true *three body collision*, not a simple two body interaction. Non-reactive but not-PNR trajectories are those ones for which $z < z_{2b}$ somewhere along time evolution. In this set there are surely the recrossing trajectories, that could be defined as those non-reactive trajectories for which $z_{\min} < z_{3b}$ (three-body parameter $z_{3b} \approx 1$; a more accurate definition is based on considering the couples of internuclear distances). These trajectories recross the ideal surface dividing reactants from products. It is easy to realize that these trajectories have necessarily entered the strong coupling region. However, it is clear from the preceding discussion that these trajectories should be much more similar to reactive trajectories than to purely non-reactive ones. This is confirmed by the striking similarity of trends in rate coefficients between reactive and non-reactive cases already illustrated in Figs. 2.6 and 2.8.

In Table 2.1 a scheme of the classification is sketched. The subdivision of non-reactive trajectories in recrossing and non-recrossing is necessary because z_{PNR} is obviously arbitrary, and there is an intermediate condition between PNR and recrossing. PNR and non-reactive non-recrossing trajectories take place with a weak interaction, the reverse being true for recrossing and reactive trajectories.

A better illustration of the existence of all these kind of trajectories can be observed in Fig. 2.7, where some trajectories for $\text{O} + \text{N}_2(v = 5, j = 0)$ collisions are monitored for their minimum ratio $z_{\min} = (R/r)_{\min}$ (along time evolution) against their final vibrational actions (the quasiclassical analog of quantum number), at increasing values of collisional energy. At 1.0 eV (Fig. 2.7a) the range of possible z_{\min} values varies only from about 2.0 down to 1.5, with a range of final vibrational number well below 1. This means exactly the existence of a PNR condition for the whole set of trajectories shown, where the vibrational adiabaticity that obviously derives from the application of QCT final analysis is indeed incorrect, because QCT is here unable to see the very low (but not necessarily zero) probability of vibrational exchange. This condition would be perfect for application of forced harmonic oscillator model. When energy is increased, the response changes with a wider final action distribution, in a way that is now correctly detectable by QCT analysis (Fig. 2.7b at 1.5 eV, with a vibrational width greater than 1). The range of z_{\min} now is displaced towards lower values. At 2 eV (Fig. 2.7c) the

Table 2.1 Scheme of the classification for trajectories

purely non-reactive	$z_{\min} > z_{2b}$	2-body collision (weak)	
non-reactive non-recrossing	$z_{3b} < z_{\min} < z_{2b}$	3-body collision (weak)	
non-reactive recrossing	$z_{\min} < z_{3b}$	3-body collision (strong)	
reactive	$z_{\min} < z_{3b}$	3-body collision (strong)	

new element is the presence of few trajectories with z_{\min} near to 1 (essentially recrossing trajectories) with very low values of final vibration. This condition is then replicated with much more trajectories when collisional energy is increased to 2.5 eV (Fig. 2.7d) (beyond the reaction threshold), together with the appearance of reactive trajectories at z_{\min} significantly lower (<0.6). It is important to realize that this kind of analysis stresses the presence of a threshold for accurate quasiclassical calculation of transition probability. In fact, for a collisional energy of 1 eV the O+N₂ system does not produce any vibrational result detectable by a standard binning procedure, while for larger energy values this is feasible. This threshold for quasiclassical vibrational adiabaticity cannot be anticipated from purely energetic considerations, in fact this threshold is lower for He+H₂ collisional system, even if the vibrational quantum is higher than the analogous quantity for O+N₂. This vibrational response to translational energy input is typical of each collisional system and can be studied phenomenologically with the analysis presented here. Under this vibrational threshold, of course, the quasiclassical transition probability is, erroneously, zero, and could be corrected by using for example DECENT method limited to trajectories quasiclassically adiabatic in the vibrational sense.

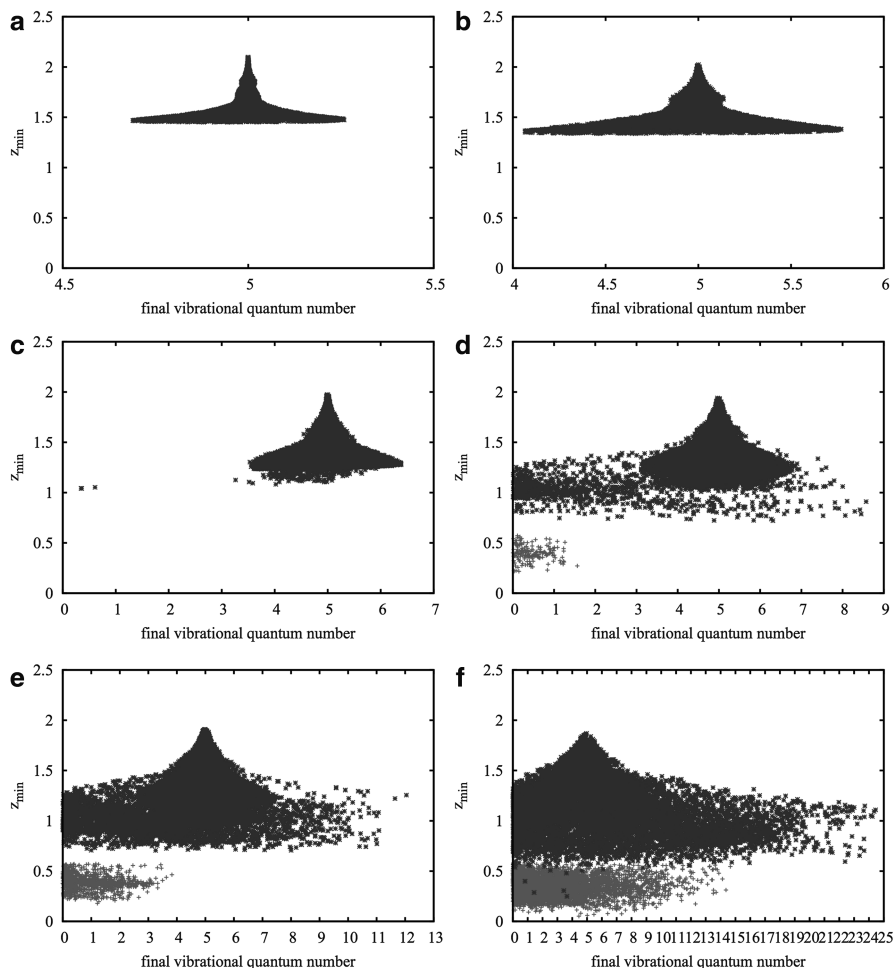
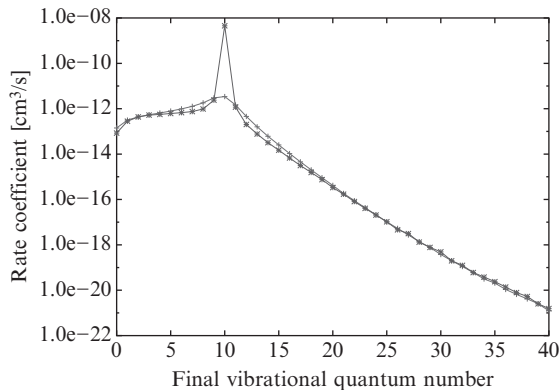


Fig. 2.7 Relation between minimum ratio of R/r along each trajectory, z_{\min} , and final vibrational quantum number (in quasiclassical sense) for $\text{O}+\text{N}_2(v=5, j=0)$ collisions, at various collisional energies (a) 1.0, (b) 1.5, (c) 2.0, (d) 2.5, (e) 3.0, (f) 5.0 eV. In red: reactive, in blue: non-reactive trajectories. At 1.0 eV (a) QCT method is unable to detect any vibrational variation from $v=5$, because final action does not differ more than half quantum from the original value. At 2.0 eV (c) very few trajectories near the $z_{\min}=1$ limit present a very low value of final vibrational action. Many other trajectories present this feature when collisional energy is increased beyond the reaction threshold

It is clear from preceding discussion that recrossing trajectories should not be modeled with harmonic oscillator models like FHO and DECENT, because the simple forced harmonic oscillator model that is the base of these methods is inapplicable for strong interaction of the projectile with the target, as already stressed in Shuler and Zwanzig (1960) and Treanor (1965). Fortunately, recrossing

Fig. 2.8 Comparison of (red) reactive and (blue) non-reactive vibrational energy transfer rate coefficients for N+N₂($v = 10$) collisions as a function of final vibrational quantum number, at $T_{\text{coll}} = T_{\text{rot}} = 3,000$ K. The non-reactive contribution is doubled, in order to show its ratio 1:2 with the reactive contribution



trajectories and reactive trajectories can be successfully treated with QCT. On the contrary, QCT is not accurate on PNR trajectories, as can be seen for example in the already cited He-H₂ collisions in Balakrishnan et al. (1999), where QCT vibrational cross sections in the exothermal direction for collisional energy less than about 1 eV are zero, while the accurate quantum mechanical calculations give values as high as 0.1 \AA^2 . Being the potential of the collisional system completely repulsive, there are no reactive trajectories, but all the possible kinds of non-reactive trajectories are present. In fact, it is clear that the classification presented is valid, because trajectories with sufficient energy will bring the three atoms sufficiently close to classify the encounter as a three body one. Therefore in this important case the same considerations should apply, with a possible cooperation of FHO model with quasiclassical trajectories in low and high energy ranges respectively.

Why reactive and mixed inelastic transitions should be well reproduced by QCT, contrarily to what happens to purely inelastic transitions? The answer is in the approximation introduced by histogram binning in QCT. As clear from the preceding discussion, when less than a vibrational quantum is classically exchanged, QCT is inaccurate. This inaccuracy is present also for reactive trajectories and for inelastic ones passing through transition state (recrossing), but in those cases a quite continuous and smooth distribution of final actions is expected, as can be appreciated in the preceding figures, the opposite of the dramatic elastic peak with quasiselastic exponentially decaying shoulders. In this last case, the inaccuracy on quasiselastic transitions tends to be largely overemphasized, while in the former case it is generally negligible.

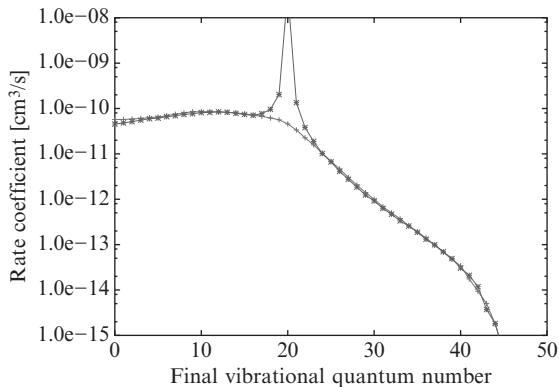
This is also shown in Fig. 2.8, where reactive and non-reactive rate coefficients as a function of final vibrational quantum number are presented from $v = 10$ for the collisional system N+N₂(v). It is clear the similarity of reactive and non-reactive trends, if just the elastic and quasiselastic rates are excluded. This is confirmed by analogous quasiclassical calculations on many other systems (O+N₂, O+O₂, N+O₂) (Esposito and Capitelli 2002, 2007; Laganà et al. 2014). A word of caution should be spent about the quasiclassical elastic cross section. This one should be without convergence, because the method normally is not able to

distinguish between trajectories without interaction and trajectories in which the only modification is in the kinematics of the projectile (and no change in molecular rovibrational actions). As a consequence, the elastic peak shown here is due only to the accumulation of results in the elastic channel, with the convergence due to any other different channel. Therefore, it is only a very rough value to evaluate only qualitatively. It is important, however, to point out that a purely classical elastic cross section is obtainable, by introducing an ad-hoc modification of the final analysis of projectile motion (essentially the Heisenberg uncertainty principle reintroduced in the classical context to eliminate non-interacting trajectories). This has been probably presented for the first time by Polanyi et al. (1977).

From these observations, one could suggest to apply standard QCT method for reactive and recrossing non-reactive trajectories, discarding purely non-reactive trajectories. The non-reactive part of the calculation so obtained should be summed to the results of the application of forced harmonic oscillator method with classical trajectories (like DECENT method Giese and Gentry 1974), limited to purely non-reactive trajectories. In this way the best results of the two methods can be usefully exploited. Some uncertainty remains about the treatment of non-reactive non-recrossing trajectories, however it should not be a major issue, because both methods should be able to treat correctly those trajectories.

New PESs have been recently proposed in literature since the semiempirical LEPS PES. The one of the NASA AMES group (Wang et al. 2003) has introduced an important feature in the barrier region ("Lake Eyring"), potentially capable of significantly changing the reactive properties of the collisional system with respect to the simple LEPS PES. The height of the barrier to reaction is also quite different, about 2 eV against 1.56 of the semiempirical PES. Unfortunately, this PES has been used only by its authors for dynamical calculations, but it has never been publicly available. Other groups (Garcia et al. 2008; Caridade et al. 2010) have calculated accurate PESs for this system, with a particular attention to the barrier region as described by the NASA group. It is likely that the purely non-reactive part of the calculations on these new PESs are quite similar to preceding calculations on LEPS PES, partially because that part of the calculations are poorly treated by QCT method, but also because it should not be too sensitive to the PES features. The significantly new part is surely what is concerned with the *new* transition state. Following the preceding observations, however, this should not affect only the reactive calculations, but also the non-reactive ones, because these last ones are for the most part recrossing ones and not purely non-reactive trajectories. An accurate comparison should be performed in order to assess this point. However, a quite reliable database of quasiclassical cross sections and rate coefficients is available for this collisional system, obtained on the cited LEPS PES with a high degree of accuracy from the statistical point of view, and good comparisons with literature. The reader is referred to the literature for the details and the data (Esposito and Capitelli 1999, 2006; Capitelli et al. 2000; Esposito et al. 2006).

Fig. 2.9 Comparison of (red) reactive and (blue) non-reactive (multiplied by 2) vibrational energy transfer rate coefficients for O+O₂($v = 20$) collisions as a function of final vibrational quantum number, at $T_{\text{coll}} = T_{\text{rot}} = 3,000$ K



2.4 O+O₂

What happens in the case of an attractive potential between the atom and the molecular target, as for O+O₂ collisions? Following the explanation of the preceding paragraph, it should be clear that all the considerations remain unaltered, with the observation that in this case it is much more likely that only a small part of trajectories will be purely non-reactive and, as a consequence, reactive and non-reactive trajectories should behave in a quite similar way. This is confirmed in Fig. 2.9, where rate coefficients for collisions of O+O₂($v = 20$) as a function of final vibrational quantum number are shown, while rotational and translational temperatures are fixed at 3,000 K. The PES used is the one of Varandas and Pais (1988), and the series of calculations have been performed in Esposito and Capitelli (2002, 2007). It is clear the strong similarity of the reactive and non-reactive trends, taking into account the 2:1 ratio and excluding the elastic peak and its surroundings. Another observation is the relatively flat behavior of de-excitation rates, due to the mixing effect of the attractive potential. In this case, in fact, the collisional system is temporarily trapped into the attractive potential, escaping at the end with a statistical distribution of final products. It is important to take into account this behavior when evaluating approximation of rates, because it is clear that in this case simple models of mono-quantum rates are strongly inadequate.

The figure is an important confirmation of the very striking similarity of reactive and non-reactive trajectories, because in this case it would be very easy to see differences due to statistical or non-statistical behavior, differences that are completely absent. On the other side, the elastic and quasielastic peak is anyway present and important, and it could be successfully modelled with forced harmonic oscillator methods, but realizing anyway that in this case only a quite small part of dynamics is captured, while the multi-quantum transitions are due to three body interactions, more correctly modelled by QCT method. The best way of comparing data obtained by various computational procedures is of course to compare with experiments. However, very often there is a problem in this comparison, rarely stressed, that can

significantly alter the conclusions. In fact, it is quite common to obtain vibrational data from shockwave experiments, where the original measured quantity is a slight pressure deviation from equilibrium. The connection between this macroscopic quantity and the state-to-state rate coefficients (Dove and Teitelbaum 1974) is quite laborious and, principally, is based on some very crude approximations, first of all the Bethe-Teller law (Bethe and Teller 1941) for low-lying vibrational states. This law is another model based on transitions in a forced harmonic oscillator, and it is clear from the preceding discussion what can be actually modelled from these models, and what should not. For $\text{O}+\text{O}_2(v)$ this approximation appears completely inadequate, because of the large majority of trajectories coming from strong three body encounters, with a small contribution from weak two body ones. The flat distribution of multi-quantum rate coefficients, on the other side, is another clear indication that forced harmonic oscillator models, with their exponential decay of probability as a function of vibrational energy exchanged, cannot be adequate for this collisional system. As a consequence, also comparisons with experiments based on these simplifications in the deconvolution of data should be considered with caution. The recommended rate coefficients for this system for both vibrational energy exchange and dissociation can be found in Esposito et al. (2008), where complete analytic fits of the relevant quantities are available.

2.5 Future Developments

The increasing computational power available for computational chemistry allows new detailed calculations using accurate methods for molecular dynamics. However, with increasing collisional energy the computational requirements for exact methods scales unfavorably, while in the same conditions quasiclassical calculations scale very efficiently. It is obvious, as a consequence, to search for a correct compromise between the two approaches. This will be the best strategy for obtaining reliable data in a large range of collisional energy. In order to perform this program, it is important to know the lower limits of applicability of quasiclassical method, in particular with respect to vibrational adiabaticity, a relatively less studied aspect, often much more relevant than tunneling in distorting the classical results in comparison to an exact quantum treatment. Some relevant notes about this point have been presented here, with an analysis of molecular collisions based on the distance of closest approach during each classical encounter. As a consequence, a new proposal of merging in a peculiar way the quasiclassical results with forced harmonic oscillator model applied to classical trajectories has been presented, in order to obtain reliable results also for low energy values, useful for kinetic models of technological interest. However, for collisional energies larger than 0.5–1 eV quasiclassical calculations can be considered reliable also for light atoms, and the relevant sets of data have been indicated for some important atom-diatom collisional

systems. The next challenge is now to introduce a more accurate treatment for high energies, which in general implies the consideration of non-adiabatic transitions. The difficulties in this case consist of the construction of excited PESs, the couplings among them and, last but not least, the suited method for performing the dynamics, considering the large number of processes required for a subsequent kinetic study. Trajectory surface hopping (Tully and Preston 1971) is the most natural extension of quasiclassical method for this kind of problems, but many methods (Jasper et al. 2004) based on classical trajectories have been developed, including an original proposal by Esposito (2013).

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