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# On the classical simulation of unimolecular reaction processes

**Invited Review**

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**Abstract:** The numerical simulation of the internal motions of a molecule undergoing a unimolecular reaction on an assumed potential energy surface requires the step-by-step solution of a set of simultaneous differential equations. After several thousand time steps, due to differences in the handling of rounding errors in different computing systems, the situation often arises that no two computing machines will give the same result for a given trajectory, even when running the identical algorithm.

Such effects are demonstrated for a simple unimolecular isomerisation reaction. In general, it is only when reliance is placed on the integration of a single trajectory, rather than on an ensemble of similar trajectories, that conclusions may be unreliable. Moreover, under certain conditions, small molecules may show signs of chaotic internal motions; conversely, but for a different reason, large molecules may exhibit non-statistical characteristics rather than RRKM behaviour.

The rounding error problem, in a slightly different guise, has come to be dubbed the “butterfly effect” in popular culture, and the original proposition is re-examined using 16- and 32-decimal precision arithmetic.

**Keywords:** *Recrossings • Transition state • Non-RRKM processes • Potential energy surfaces • Computational chaos*

## 1. Introduction

Classical trajectory simulations of the internal motions of single molecules on theoretically-constructed potential energy surfaces have played an important rôle in understanding some aspects of unimolecular reaction processes. The implicit assumption is that as the reacting molecule is in a “high” energy state, the correspondence principle ensures that the computed behaviour will approximate the true quantum solution, provided that such issues as barrier penetration, zero-point energy, curve crossing, *etc*. (which have to be dealt with by other means) can be neglected.

However, when the lifetime of the reacting molecule is far greater than a vibrational period, thus using millions of integration steps before completion, numerical rounding errors occurring at each individual step in the integration will cause any trajectory to deviate from the “true” classical path. Because rounding errors are handled differently in various hardware architectures and/or software applications, the same trajectory may yield different outcomes when run on different computing systems. As an example, for a specific low-energy trajectory in the isomerisation reaction NCNC → NCCN studied on five different machines, three gave similar lifetimes close to 3.3 ps, but the other two gave values of 233 ps and 728 ps; yet for ensembles of trajectories, all machines gave average lifetimes of 125 ps ± 5% [1].

The reason why, despite these large divergences, ensemble averages on different systems agree, more-or-less, is straightforward. In practice, using 16-decimal precision arithmetic, the resulting divergences begin to show up between 10 000 and 20 000 steps, *i.e.*, between 1 and 2 ps when using a typical 0.1 fs step length. In this particular case, with 4 atoms, there are 24 independent variables (12 spatial coordinates and 12 components of momentum) with the chance of a 1-bit rounding error in any or all of them at each 0.1 fs time step. All five trajectories started from the same set of coordinates and momenta[1], but because of the random nature of these errors, began to differ gradually from each other in an unpredictable manner; moreover, within each ensemble, given sufficient time, the configurations will become truly random, regardless of whether the initial configurations were random or regular. It is not clear at what stage we can assume this randomness to be perfect, but it was sooner than 125 ps in this example [1], *i.e.*, somewhat in excess of a million time steps. The common occurrence of random-gap law behaviour in decay from such ensembles [1-3], *i.e.*, the RRKM requirement, usually

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[1] *Likewise, the same potential energy surface and Fortran code [1], but the respective machines, MIPS RC3240, SPARC 1000, home-built, IBM RS/6000 [1], each used a different Fortran compiler; these old machines no longer exist, is not possible.*

gives confidence that decay rates calculated in this manner provide a reasonable classical approximation of the reaction process.

This reasoning implies that a single result is valueless unless it forms part of an ensemble of trajectories whose mean value has a real interpretation. However, some conclusions about unimolecular reaction behaviour derive not from ensemble studies, but from examination of individual trajectories, and it is the purpose of this Communication to examine some such cases, to illustrate the general patterns of behaviour caused by rounding errors in such simulations, and to note their ubiquity in other fields of endeavour.

## 2. Computational procedure

The algorithm used was simply a fourth-order Runge–Kutta start-up procedure followed by a fifth-order Adams–Mouton predictor-corrector [4]. It has been used over the past 20 years to study dissociation and relaxation in ethane, and isomerisations in hydrogen isocyanide, isocyanogen and methyl isocyanide. In most of these studies, a standard time step of 0.1 fs was used, whence the results appeared to be satisfactory. Similar procedures [5] and similar step lengths [5,6] have been used in other molecular dynamic simulations, also with apparently satisfactory results.

The present review is confined to the reaction NCCN ↔ NCNC in the *J*=0 state, using an 870-point MP2/6-31G* potential energy surface [1,7]. For a given value of the energy, trajectories were started from the normal internuclear configuration of either NCCN or NCNC with quasi-random momenta assigned to each of the 12 degrees of freedom. A portable random number generator (ran1.for [4]) was used throughout so that trajectory #*n*, whether run on different machines, or else on the same machine with different compilers, always commenced from, ostensibly, the same set of momenta.

As an example of the effects of cumulative rounding errors in simulations of this kind, Fig. 1 shows results for the same Fortran F77 algorithm run on two different computers, one an Intel processor, the other an AMD 64-bit processor running in 32-bit mode, and of the same F77 compiled module run on these two different machines. For each of the three 1000-point ensembles, population decay obeyed the random-gap law, with the same slopes and with the roughly 200 trajectories having lifetimes below 2.5 ps being identical; also, due to the randomness of the initial conditions, there was no incubation period.

## 3. The classic butterfly effect

The idea of the "butterfly effect" stems from an accidental observation by Edward Lorenz [8] in 1963: an integration similar to those discussed here, but related to weather prediction, carried out in 6-decimal place precision, was restarted part-way through; however, the variables were re-read into the computer to only 3 decimal places, whence the subsequent path of the integration was quite different from the same calculation run without interruption. Following a whimsical talk by Lorenz a decade later [9], this numerical inconsistency became inflated into environmental folklore [10], and even into a motion picture [11].

Subsequently, during the development and testing of the numerical procedures described above [12], we found a similar result, except that the intermediate data were printed out to 16 decimal places and when these same numbers were read back into the same algorithm, the results differed from those of a calculation that had proceeded without interruption.

The effect was first examined using double precision (real*8 Fortran) arithmetic. There are two possible causes for the new paths taken after interruption to be different: one, the truncation and/or rounding errors of the output and input routines; two, a mismatch between the new sequence of variables created on start-up and those that would have been generated if the integration had just been allowed to proceed.

The present calculations were severely constrained by the difference in timings between a conventional double precision implementation of Fortran and the available quadruple precision version. Hence, rather short-lived trajectories had to be chosen for this phase of this study, *i.e.*, the isomerisation of NCNC at an energy *E* above its *v*=0 state of 18 361 cm$^{-1}$, with an average lifetime of 1.8 ps [7]. For this case, an ordinary 2 GHz desktop machine would complete 1000 real*8 trajectories in 50 minutes, whereas the DEC 3000-500 V6.2-1H2 real*16 emulation took about 10 minutes per picosecond, a speed ratio of about 360. Thus, quadruple precision trajectories were usually run in small batches, or else singly when using shorter time steps.

To test the first possibility, at 5 fs (*i.e.*, 50 steps of 0.1 fs) the 12 components of momenta and the 12 values of the coordinates were printed out to 16 decimal places, then re-read immediately to overwrite the existing values, whence the integration was left to continue. Out of an ensemble of 1000 trajectories, 191 lifetimes were changed by 0.1 fs or more beyond about 3 ps, growing to as much as a factor two, larger or smaller, at longer times.

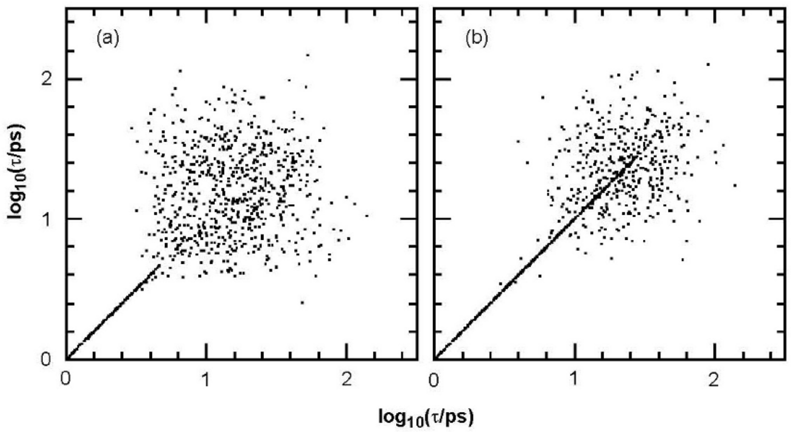

**Figure 1.** Comparison of lifetimes ($\tau$), in ps, for an ensemble of 1000 trajectories representing the isomerisation of NCCN → NCNC at an energy of 18 361 cm$^{-1}$. Horizontal axes: lifetimes calculated using an Intel 80386 processor with Fortran version 2.2.5. Vertical axes: lifetimes calculated using an AMD Athlon 64-bit proceesor in 32-bit mode, (a) with Fortran version 2.6.9, (b) with Fortran version 2.2.5.

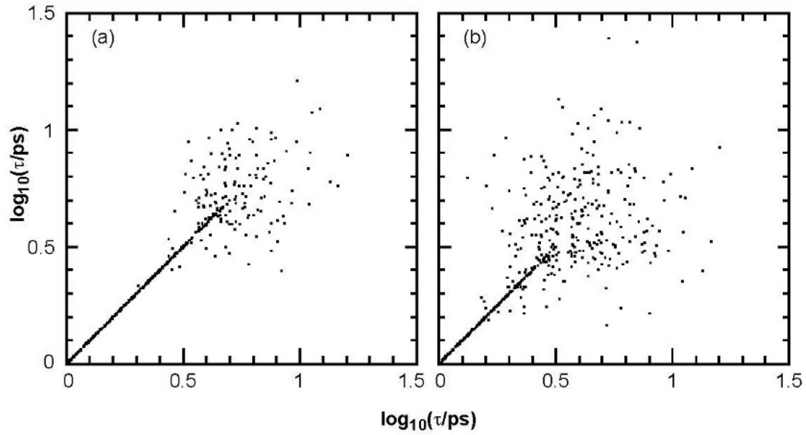

**Figure 2.** Comparison of lifetimes ($\tau$), in ps, for an ensemble of 1000 trajectories representing the isomerisation of NCNC → NCCN at an energy of 18 361 cm$^{-1}$. Horizontal axes: uninterrupted calculation. Vertical axes: (a) simple output and re-input at 5 fs, (b) output at 5 fs followed by full restart.

For the second option, after re-reading the positions and momenta, a new integration was begun, using the Runge–Kutta procedure for the first four steps. Now, there were 380 differences in the lifetimes, of magnitudes between one-fifth and a factor of five, with onset at around 2 ps. These results are shown in Fig. 2.

In other words, truncation errors of 1 in the 16th place of positions and momenta are sufficient to cause divergence in the lifetimes after about 30 000 time steps, On the other hand, the mismatches between the new sequence of numbers generated by the Runge–Kutta module and those that would have been created otherwise are slightly more significant, leading to divergences as early as around 20 000 time steps.

The same two experiments were repeated using quadruple precision arithmetic, with the positions and momenta being printed out at 5 fs to 32 decimal places. For reasons already mentioned, the ensembles were limited to 100 trajectories instead of 1000. On simply re-reading these values, there were only differences in the 3 longest trajectories with (unperturbed value first) 11.2 → 8.4 ps, 9.5 → 9.8 ps, and 9.6 → 9.7 ps. One can surmise that if a lower energy could have been used, where the lifetimes are of the order of 1 ns, or more, every trajectory for which the new input did not replicate the original values exactly would diverge from the original.

Alternatively, invoking the integration upon restart caused major differences: all 35 lifetimes longer than 1.5 ps were changed, sometimes by factors of two or three in either direction. There were too few points with which to make illustrative graphs similar to those

**Table 1.** Results for three selected trajectories after integration and return to zero time, 3 ps in each direction, using real*16 arithmetic: numbers of crossings in each direction, final angles, and energy conservation for various step lengths[a].

| | **step/fs** | **crossings** | **Angles[b]** | ***ΔE/E*** |
|---|---|---|---|---|
| #27 | 0.1000 | 7, 6 | 139 28 | $1.1\times10^{-6}$ |
| | 0.0500 | 2, 1 | 155 15 | $9.3\times10^{-9}$ |
| | 0.0100 | 9, 10 | 69 160 | $5.9\times10^{-14}$ |
| | 0.0050 | 5, 5 | 150 157 | $5.1\times10^{-16}$ |
| | 0.0010 | 2, 2 | 179 179 | $1.0\times10^{-16}$ |
| | 0.0005 | 2, 2 | 180 180 | $3.2\times10^{-18}$ |
| #35 | 0.100 | 6, 7 | 27 144 | $5.6\times10^{-7}$ |
| | 0.050 | 5, 4 | 44 121 | $1.2\times10^{-8}$ |
| | 0.010 | 5, 5 | 114 177 | $1.8\times10^{-13}$ |
| | 0.005 | 5, 5 | 167 136 | $2.5\times10^{-16}$ |
| | 0.001 | 5, 5 | 180 180 | $1.6\times10^{-16}$ |
| #55 | 0.100 | 4, 3 | 23 126 | $1.9\times10^{-6}$ |
| | 0.050 | 10, 10 | 155 103 | $5.5\times10^{-9}$ |
| | 0.010 | 6, 6 | 136 127 | $7.9\times10^{-14}$ |
| | 0.005 | 6, 6 | 153 167 | $2.5\times10^{-15}$ |
| | 0.001 | 6, 6 | 180 180 | $1.0\times10^{-16}$ |

[a] *These data represent approximately 380 hours of DEC 3000-500 CPU time.*

[b] *An angle ≤70° denotes either CNCN or NCNC as the final configuration.*

in Fig. 2. Furthermore, the mean lifetime for the ensemble of 1000 real*8 trajectories was 1.8 ps, as expected, and for the smaller ensemble of 100 trajectories, 1.7 ps in either real*8 or real*16 arithmetic .

The popular notion of the butterfly effect [9-11], that the flap of a butterfly's wings in some remote place could set off a tornado or a hurricane in and around the Gulf of Mexico is clearly apocryphal. At low (butterfly) altitudes, the vortex wakes of a large aircraft, which can sometimes destroy a smaller plane flying too closely behind [13] normally dissipate due to natural atmospheric turbulence within a few minutes [14].

## 4. Estimating accuracy

A simple way to assess the reliability of an integration of this kind is to reverse the direction at some time *t* and see whether the original configuration is restored at time 2*t*. In order to examine trajectories with and without reactive crossings, all of these calculations were started with the four atoms in the NCCN configuration, for which the mean lifetime at 18 361 cm$^{-1}$ is 15.3 ps [7], and in batches of 100. Trajectories were integrated either up to 1 ps or 3 ps, at which point all the components of momenta were reversed in sign and a new integration was launched in the opposite direction. In a previous exercise [15], we had used the departure of the final kinetic (or potential) energy from its initial value as the criterion for failure to return, but this difference does not impart much insight. Hence, for this exploratory survey, return to origin was arbitrarily taken to be both angles within half a degree of linear *and* the rms differences of all six interatomic distances from normal within $10^{-5}$ Å; in fact, simple failure of the two angles to achieve linearity usually gives a clear enough picture.

In real*4 arithmetic (8 decimal places) with a step length of 0.1 fs, after reversal at 1 ps, 67 out of 100 trajectories met these criteria. At 3 ps, no trajectories returned to the origin, even when the step length was reduced to 0.001 fs, and calculations at this level of precision were abandoned.

In real*8 arithmetic, also with a step length of 0.1 fs, 98 trajectories returned to linear after reversal at 1 ps, but only 9 after reversal at 3 ps. The following is a list of successful returns after reversal at 3 ps with the corresponding time step in parentheses: 9 (0.1 fs); 33 (0.05 fs); 64 (0.02 fs); 80 (0.01 fs); 83 (0.005 fs); 80 (0.001 fs). This reduction in success rate at 0.001 fs, together with the fact that many more trajectories exhibted crossings and recrossings than in the preceding set (17 *versus* 8) suggests that further step-length reduction would be counterproductive, due to accumulation of rounding errors; moreover, the mean values of the energy conservation Δ*E*/*E* degraded from $9.6\times10^{-12}$ at 0.01 fs to $1.3\times10^{-11}$ and then to $2.6\times10^{-11}$ for 0.005 and 0.001 fs time steps, respectively.

In this light, a previous diagram [15] representing the return to origin for a set of HNC trajectories, done with 0.1 fs time steps, was of little value except as an example of inconsistent results from the same algorithm on the same machine with different versions of the Fortran compiler.

Next, a series of 100 trajectories in real*16 arithmetic, reversing at 3 ps, was run with a 0.1 fs time step, taking 1 h 5 min per trajectory. The results were very little better than those of the real*8 calculations, 10 returns instead of 9; all of the successful returns exhibited no crossings (*i.e.*, reaction NCCN → NCNC). Crossings were observed in about 25% of the trajectories, sometimes balanced but more often with different numbers of crossings on the forward and return paths. Somewhat unexpectedly, the energy conservation for these 100 trajectories averaged $2.0\times10^{-6}$, exactly the same as for the real*8 calculations.

With the available computing facilities, to repeat these calculations at a time step of 0.001 fs would take around 10 000 hours, and clearly be impracticable. Consequently, using a clue from the above observations, that only trajectories exhibiting no crossings returned to the origin, it was decided to examine a small selection showing multiple recrossings at all step lengths in

**Table 2.** Crossing properties for the three selected trajectories: given are times $t$ from the origin, in ps, the arrows indicating direction of integration, with corresponding energies in kcal mol$^{-1}$, and their differences $\delta E$.

| # & step/fs | | crossing times and energies | | | | | |
|---|---|---|---|---|---|---|---|
| #27 | $t$ = | 0.340 | 2.041 | 2.660 | 2.861 | 2.953 | |
| 0.005 | → | 83.392 | 71.321 | 73.125 | 85.768 | 75.354 | |
| | ← | 83.050 | 71.331 | 73.131 | 85.775 | 75.374 | |
| $\delta E$ | | 0.342 | 0.010 | 0.006 | 0.007 | 0.020 | |
| 0.001 | → | 83.397 | 71.326 | | | | |
| | ← | 83.426 | 71.328 | | | | |
| $\delta E$ | | 0.029 | 0.002 | | | | |
| 0.0005 | → | 83.397 | 71.326 | | | | |
| | ← | 83.400 | 71.327 | | | | |
| $\delta E$ | | 0.003 | 0.001 | | | | |
| #35 | $t$ = | 0.568 | 0.940 | 1.030 | 1.285 | 1.358 | |
| 0.01 | → | 70.474 | 70.387 | 78.951 | 71.387 | 70.809 | |
| | ← | 70.954 | 70.412 | 78.956 | 71.401 | 70.822 | |
| $\delta E$ | | 0.480 | 0.025 | 0.004 | 0.014 | 0.013 | |
| 0.005 | → | 70.465 | 70.387 | 78.951 | 71.386 | 70.809 | |
| | ← | 70.454 | 70.400 | 78.954 | 71.394 | 70.816 | |
| $\delta E$ | | 0.011 | 0.013 | 0.003 | 0.008 | 0.007 | |
| 0.001 | → | 70.460 | 70.387 | 78.953 | 71.391 | 70.815 | |
| | ← | 70.459 | 70.390 | 78.954 | 71.392 | 70.816 | |
| $\delta E$ | | 0.001 | 0.003 | 0.001 | 0.001 | 0.001 | |
| #55 | $t$ = | 0.689 | 1.052 | 1.119 | 1.234 | 1.409 | 1.527 |
| 0.01 | → | 69.553 | 65.248 | 67.552 | 76.534 | 75.359 | 82.145 |
| | ← | 69.540 | 65.254 | 67.560 | 76.535 | 75.369 | 82.123 |
| $\delta E$ | | 0.013 | 0.006 | 0.008 | 0.001 | 0.010 | 0.022 |
| 0.005 | → | 69.553 | 65.251 | 67.552 | 76.535 | 75.360 | 82.121 |
| | ← | 69.547 | 65.254 | 67.556 | 76.535 | 75.365 | 82.110 |
| $\delta E$ | | 0.006 | 0.003 | 0.004 | 0.000 | 0.005 | 0.011 |
| 0.001 | → | 69.549 | 65.253 | 67.554 | 76.535 | 75.360 | 82.121 |
| | ← | 69.548 | 65.254 | 67.555 | 76.535 | 75.361 | 82.119 |
| $\delta E$ | | 0.001 | 0.001 | 0.001 | 0.000 | 0.001 | 0.002 |

real*8 arithmetic. Three trajectories at an energy of 18 361 cm$^{-1}$, #27, #35, and #55 were chosen, and the results of this series of calculations are shown in Table 1[2].

For the standard time step of 0.1 fs, all three trajectories exhibit different numbers of crossings in the two directions. However, by the time the step length is sufficiently short for their numbers to be equal, the times at which the crossings occur agree to the nearest fs in both directions. Nevertheless, the configuration did not converge to being linear until the step length was reduced, in two cases, to 0.001 fs whence the conservation of energy had improved by 10 orders of magnitude, or 0.0005 fs in the other, with an even greater improvement in energy conservation; here, linearity means both angles within 0.05 degrees of 180.

Table 2 analyses the convergence of the crossing energies as the step length is reduced; only data for the three shortest step lengths are shown here, since when the number of crossings is not the same, the energies cannot match; the two energy values for each particular crossing should only be equal in the limit, as the numbers given are for the first time *after* crossing the barrier in either direction. Of the three cases, #55 is the best behaved: at 0.01 fs step length, the energy of the final return crossing is beginning to differ slightly, but as the steps are shortened to 0.005 and then to 0.001 fs, a clean convergence of both the angles and the crossing energies occurs. The same is true for trajectory #35, except that the final two crossing energies on the return trip at 0.01 fs step length are rather poor; however, the final convergence of energies and angles is quite acceptable. Trajectory #27 is the least tractable of the three, requiring a step length of $5\times10^{-4}$ fs before the final angles and the forward/reverse crossing energies agree convincingly.

## 5. Old results revisited

In view of the preceding discussion, some earlier conclusions, dependent in part on single-trajectory behaviour may need re-appraisal; on the other hand, examination of the internal motions of individual trajectories, or the behaviour of pairs with closely adjacent starting points, can yield useful diagnostics. Below are three such cases for which sufficient data are still available.

### 5.1 Rotational disintegration of highly excited ethane molecules

Two studies examining the break-up of quasi-bound states of the ethane molecule as a function of $K$-rotational quantum number and of total internal energy $E$ depended principally on the behaviour of individual trajectories [16,17], without consideration that the onset of computational chaos may have been a contributory factor. Fortunately, monotonic behaviour of trajectories leading to rupture with small changes in either $K$ or $E$ were found [12]; hence, within the limitations of the model potential, the conclusions are probably safe.

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*[2] In retrospect, it would have been slightly more economical to avoid the use of a new Runge–Kutta process, simply by continuing the forward integration several steps beyond the intended reflection point and then reversing this whole stored extra sequence of positions and momenta in order to launch the Adams–Mouton sequence back towards the origin.*

## 5.2 Black-body radiation and randomisation

Figs. 1 and 2 of this paper are very similar to one in [2] which claimed to support the proposition [18] that black-body radiation was capable of affecting the internal motions of a reacting molecule.

In those calculations, and others like them [19], a sinusoidal perturbation of appropriate strength and frequency was imposed on the reacting molecule, either ethane [19] or methyl isocyanide [2], causing significant departures from the unperturbed trajectories. Again, no clear distinction was made between molecular and computational chaos, but the the imposed frequency could readily be extracted from Fourier transforms of the molecular motions, so it seemed reasonable to infer that the presence of black-body radiation would cause randomisation of the internal energy when the densities of states were sufficiently high.

However, the issue was settled soon afterwards with evidence that dissociation caused by black-body radiation can be detected in a mass spectrometer [20].

## 5.3 Recrossings and transition state theory

In calculations on the isomerisation of methyl isocyanide [2] and of cyanogen extending into the nanosecond range [7], as well as others of shorter duration [21-24], recrossings were found to occur on time scales of less than 1 ps. For the NCCN ↔ NCNC reaction at 18 361 $cm^{-1}$, recrossings (defined as a transition there-and-back within 0.2 ps [7]) were quite common, and in an ensemble lasting a total 40 ns, were often bunched together; likewise for ensembles at other energies lasting in excess of 300 ns. However, only about half the transitions were preceded by a gap longer than 0.2 ps, and were therefore true reactive processes, so that the transition state transmission coefficient $\kappa$ should tend towards 0.5 instead of 1, as usually assumed.

**Table 3.** Comparison of isomerisation lifetime ratios with the corresponding state-density ratios for the reactions NCNC ↔ NCCN and $CH_3NC$ ↔ $CH_3CN$ at various energies[a]

| energy/$cm^{-1}$ | $\rho(E)_{CN}/\rho(E)_{NC}$ | $\tau_{CN}/\tau_{NC}$ | ratio |
|---|---|---|---|
| **NCNC ↔ NCCN (1000 trajectories)** | | | |
| 13 814 | 16.2 | 13.9 | 1.16 |
| 15 528 | 13.1 | 11.6 | 1.13 |
| 18 361 | 9.7 | 8.5 | 1.14 |
| 20 809 | 7.8 | 7.5 | 1.04 |
| 26 055 | 5.5 | 4.5 | 1.22 |
| **$CH_3NC$ ↔ $CH_3CN$ (100 trajectories)** | | | |
| 25 019 | 7.3 | 0.53 | 13.7 |
| 33 085 | 4.8 | 0.55 | 8.7 |
| 41 150 | 3.6 | 0.44 | 8.2 |

[a] *see Table II of [27] and Table 1 of [7], the latter using a newer NCCN ↔ NCNC potential energy surface, for full details.*

Although the existence of "basins" in the vicinity of the NCCN ↔ NCNC transition state that might cause such recrossings had been ruled out [7], the extreme variability of any individual trajectory to rounding errors (c.f. Tables 1 and 2), makes it necessary to exclude the possibility that recrossings might occur by accident in this sensitive region of the potential energy surface. Table 2 shows two examples of multiple recrossings: in trajectory #35 there are 4 crossings (2 recrossings) within 0.418 ps, and in trajectory #55, there are 5 crossings within 0.475 ps. This shows that multiple crossings on the sub-picosecond time scale are not an artefact, but persist as the calculations approach convergence.

# 6. Non-RRKM systems

It becomes clear that a small molecule, whose internal motions should be regular, could experience random variations if followed for a very long time, rather as happens for calculated trajectories of planets and asteroids in the solar system [25], and in similar studies noted elsewhere [19]. This would be most likely at energies just above the reaction threshold where the rate is slow, as in the case of the HNC isomerisation reaction, already mentioned above [15]. Plots of population decay are *definitely* not random-gap (*i.e.,* not first order) but even with only a 1 ps forward path, *many* trajectories failed to return to the origin after reversal. So long after the original work, there is no way to know whether these failures represented true chaotic motion, or simply the onset of computational chaos rather earlier than we have found in the present study.

Conversely, examples exist of trajectory calculations in which the complete volume of phase space cannot be accessed, even though the molecules are sufficiently large for conventional RRKM behaviour to be expected. Relevant data [7] from simulations of isomerisation of NCNC and of $CH_3NC$ are collected in Table 3. For a molecule exhibiting statistical behaviour, the densities of states and lifetimes should obey microscopic reversibility, *i.e.*,

$$\rho(E)_{CN} / \tau_{CN} = \rho(E)_{NC} / \tau_{NC}$$

where $\tau$ is the lifetime and $\rho(E)$ is the density of states at energy $E$. Thus, the numbers in columns 2 and 3 of the table should be equal. For the former reaction, this is seen to be reasonably true; one does not expect to find the ratios to be exactly one since the densities of states are harmonic oscillator approximations, they were only reported originally to two significant figures, and NCNC may or may not be a borderline large molecule, and not ideally statistical in the RRKM sense.

On the other hand, Table 3 shows that the $CH_3NC$ forward and reverse reaction rates fail badly to conform to microscopic reversibility. As discussed before [7,26,27], using the Sumpter and Thompson potential energy surface [28], these rates obey the random-gap law [2] but are about a factor of 20 too slow [26], indicating that a large portion of phase space is inaccessible.

Another example is the simulation of the $CH_3$-O-O-N-O radical thermal dissociation [29] into $CH_3O + NO_2$. This system, containing 5 heavy atoms in a single chain, and with 5 stretch or bend frequencies below 500 $cm^{-1}$, would be expected to exhibit random-gap behaviour more perfectly than in the 4-atom NCNC: however, the population depletion of the original ensemble of trajectories [29] resembles very closely that found for the triatomic HNC molecule [15].

These two examples of apparent non-RRKM behaviour in “large” molecules share one factor in common – both use potential energy surfaces containing switching functions. We have speculated on several occasions [7,26,27] that the presence of these artefacts may be the cause of hidden bottlenecks in the $CH_3NC$ case, leading to imperfect ergodic behaviour, and the same may be true in the case of this nitroso radical. We should not abandon one of the cornerstones of unimolecular reaction theory [30,31] until this possibility has been eliminated.

## 7. General comments

Given a sufficiently large ensemble of trajectories, simulations of this kind are generally expected to give acceptable estimates of reaction rates as long as the potential energy surface is reliable and quantal effects are unimportant. For short lifetimes, *e.g*. the 1.8 ps case above, taking fewer than 20 000 time steps, an ensemble of 100 cases yields a result within 5%, whereas if the lifetime is much longer, *e.g*. 125 ps with more than a million time steps, ensembles as few as 30 give acceptable results [1] because the onset of computational chaos mimics the randomisation due to black-body radiation and/or long-range interactions [32]. Nor do the integrations require sufficient precision to return each individual trajectory to the origin upon reversal [5], again because, if energy and angular momentum remain conserved, the cumulative effect of rounding errors helps to achieve and maintain a truly randomised ensemble, in conformity with RRKM theory.

However, deductions made from the examination of single trajectory behaviour require extra consideration. Of the three cases re-analysed here, only case (c) requires further corroboration. There is no doubt that *for this particular model* there are multiple recrossings on the sub-picosecond time scale, as shown in Tables 1 and 2. However, there is still the possibility of an undetected flaw in the potential energy surface and certainty about this particular proposition requires analogous simulations for different reactions, and/or demonstration that the similar calculations by others [21-24] (with time steps of 1.2 fs [21] and 0.2 fs [24] where specified) can survive re-examination with longer word lengths and shorter time steps, and preferably with extension to longer time periods.

The main difficulty is that, as formulated, in a hypothetical field-free space, the model trajectory will always follow the same unique path on any machine if the step length is sufficiently small and the word length sufficiently large; this would appear to echo Lorenz’s final remark in his classic 1964 paper [33] about “using the most powerful computing machine available”. In Fig. 2a, a minuscule perturbation ($1 \pm n\delta$), where $n$ is a small integer (usually 1) and $\delta$ corresponds to a 1-bit difference, is applied to one, or a few, of the 24 variables in the calculation, yielding vastly different outcomes: it simply means that failure to return to the origin after reversal is only a signal of chaotic motion within the molecule if, and only if, the onset of computational chaos has been ruled out.

There have been many studies of the distinction between true chaotic motion and computational chaos, *i.e*., the appearance of chaos due to imperfect representation of numbers in the calculation; in the main, they have concentrated on relatively simple analytic functions [34-37], unlike the present multi-dimensional problem, but also including variation of word length [35]. Likewise, the progression from regular to chaotic behaviour of the internal motions in isolated molecules, including unimolecular reaction processes, has been studied extensively [38,39]. As noted before [2], it is possible to extract an effective Lyapunov constant from the envelope within which points such as shown in Fig. 1 lie, but being really a composite of 24 distinct divergence rates, only to provide a very coarse-grained description of the onset of chaotic motions.

Other single trajectory calculations could include geological studies, both back or forward in time, such as the isolation of nuclear waste, where the models run “over periods from decades to more than millions of years” [40] and, perhaps also climate behaviour: for example, one computer model [41] uses a time step of 7.5 minutes for some aspects of the calculation, but a million of them is only about 15 years. Million-step calculations of this sort should be subjected to both step-length and word-length variation before acceptance. Furthermore, as Tables 1 and 2 show, conservation is an important criterion, but in these multifaceted studies it may be difficult to choose which variable(s) to monitor.

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