Quantum and quasiclassical trajectory studies of rotational relaxation in Ar–N$_2^+$ collisions

Otoniel Denis-Alpizar, Oliver T. Unke, Raymond J. Bemish and Markus Meuwly

The collision of N$_2^+$ with Ar is studied using quantum and classical methods. The dynamics was followed on a new potential energy surface based on ab initio energies computed at the UCCSD(T)-F12a/aug-cc-pVTZ level, using the correct analytical long range behaviour and a reproducing kernel representation. Comparison with multi-reference MRCl+$Q$ calculations establish that UCCSD(T)-F12a is a sufficiently high level of theory for this problem. Results from quantum close coupling and quasiclassical trajectory calculations agree favourably with each other and the rates for inelastic collisions are lower than those from Langevin theory. This differs from previous calculations on a zero point-corrected potential energy surface (PES) and indicates that such corrections, although potentially useful, should not be applied in the present case. Despite the rather large differences between the potential energy surfaces, the computed rates are within one order of magnitude of one another which suggests that the quality of the PES is not the main reason for the remaining disagreement between computation and experiment. Also, the fraction of inelastic rotational collisions exceeds 20% in all cases irrespective of whether quantum or classical dynamics is used. Previous experimental rate coefficients for N$_2^+$(ν = 0, j = 6) colliding with Ar suggest that the rotational quantum number is largely conserved. This can not be confirmed from any of the simulations and calls for new single molecule experiments.

The collision of N$_2^+$ with Ar is a prototypical system to study ion–atom collisions. Previous experiments reported inelastic rate coefficients 50 times smaller than those predicted by Langevin theory. The efficiency of inelastic collisions in removing internal energy from collision partners is essential in experiments where cooling of the molecular ion is important. For the particular case of the (ν = 0, j = 6) state of the N$_2^+$ ion these early experiments indicated that rotational inelastic collisions would be insignificant. Contrary to that, recent quasiclassical trajectory simulations based on a UCCSD(T)/aug-cc-pVTZ and a zero point energy-corrected UCCSD(T)+ZPE potential energy surface, represented as a reproducing kernel Hilbert space (RKHS), suggested that inelastic collisions are non-negligible. However, this computational study was based on single reference electronic structure calculations and QCT simulations which prompted the present work.

Experiments at low collision energies (<1452 cm$^{-1}$, i.e. <0.18 eV)$^3$ and with the collider N$_2^+$(X$^2\Sigma^+$) in the ground vibrational state (ν = 0)$^4,5$ suggest that charge transfer to the Ar atom is improbable. Therefore, assuming the Born–Oppenheimer approximation and following the dynamics on the [ArN$_2$]$^+$ ground state PES correlating with N$_2^+$ (ν = 0) + Ar appears to be a valid approximation at low collisional energies. Only when the first vibrational state of N$_2^+$ is excited, charge transfer from the Ar atom to form N$_3$ occurs.$^6$

It is conceivable that due to the small difference in the electron affinity between Ar(4S) and N$_2$(4$^2\Sigma^-$) multireference effects become important, particularly in the long range of the potential energy surface which is important for the capture process and hence the early stages of the formation of the ion-atom complex. For the N$_2^+$($X^2\Sigma^+$) + Ar(4S) system, the multi-reference character of the complex formed could play an important role, and effects beyond single-reference methods such as UCCSD(T) should be considered. Furthermore, quantum effects on the nuclear dynamics could also influence the rotational rates coefficients. These two aspects are the focus of the present work: the main goal of the present work is to study the N$_2^+$($X^2\Sigma^+$) + Ar(4S) collision at low temperatures using multi-reference CI and UCCSD(T)-F12a electronic structure calculations and including quantum effects in the nuclear dynamics.

In order to quantitatively assess multi-reference effects, electronic structure calculations at the CASSECF/MRCI+$Q$ level for the lowest electronic states using the aug-cc-pVTZ basis set (avtz) were carried out with the MOLPRO suite of codes.$^7$ In this work, Jacobi coordinates ($R, r, \theta$) were used. Fig. 1 shows the lowest electronic states of Ar–N$_2^+$ for the classical turning

---

$^a$ Department of Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland. E-mail: m.meuwly@unibas.ch
$^b$ Universidad Autónoma de Chile, Instituto de Ciencias Químicas Aplicadas, El Llano Subercasueos 2801, San Miguel, Santiago, Chile
$^c$ Air Force Research Laboratory, Space Vehicles Directorate, Kirtland AFB, New Mexico 87117, USA
$^d$ Department of Chemistry, Brown University, Providence, Rhode Island, USA
Fig. 1 Interaction energies at \( r^{(0)} = 1.072 \) Å (panels A and B) and \( r^{(0)} = 1.167 \) Å (panels C and D) and \( \theta = 168^\circ \) and 89° for the three lower electronic states (solid lines to guide the eye) from MRCI+Q/avtz calculations in the \( ^2A' \) symmetry (black lines represent the ground state, and green and blue lines, the excited states in \( C_2 \) symmetry). The open symbols are the \textit{ab initio} energies at the MRCI level for the ground state. Furthermore, interpolated RKHS energies using the UCCSD(T)-F12a PES computed in this work (red dashed lines) is represented. In panels C and D, the UCCSD(T) (green dash-dot lines) and UCCSD(T)+ZPE (blue dashed lines) results from previous work are also shown with the zero of energy at \( R = 100 \) Å at the corresponding angular and diatomic distance.

points \( (r^{(0)} = 1.072 \) Å and \( r^{(0)} = 1.167 \) Å\) of \( N_2^\dagger(\nu = 0) \). For small \( r \) and large \( \theta \) the ground and excited states are very close (see Fig. 1A) and excitation to the charge transfer state \( \text{Ar}^+–N_2 \) may be possible. This is consistent with experimental findings that excitation of the \( N_2 \) to the excited states in \( C_2 \) symmetry is a strong function of \( \nu \). The results suggest that using standard techniques in these two codes yield different asymptotic energies. The energies computed with MOLPRO asymptotically approach zero as it is expected for interaction energies \( V^{\text{int}} = E_{N_2^\dagger} - E_{\text{Ar}^+} \), which is, however, not the case for the interaction energies computed with Gaussian. Further analysis of the Mulliken charges shows that the calculations with MOLPRO follow the lowest-energy \( N_2^\dagger–\text{Ar} \) state as required whereas with Gaussian09 charge transfer to the \( N_2^\dagger–\text{Ar} \) state occurs, see the charge redistribution for the \( \text{Ar}^-\text{N}_2 \) at \( R = 3.0 \) Å and \( R = 4.0 \) Å in Fig. 2B. Because here the potential energy curves appear smooth it is difficult to notice and eliminate such discontinuities (as for the \(^2A\) and \(^4A\) states in systems such as Heme-NO) between the two states occur which can be readily detected. In order to assess the effect of the basis set size, additional calculations were carried out with the aug-cc-pVQZ basis set. The asymptotic energy is 3068 cm\(^{-1}\) (0.38 eV) which compares with 2581 cm\(^{-1}\) (0.32 eV) from calculations with the aug-cc-pVTZ basis set and which both are compatible with the experimentally determined difference in ionization potentials of \( N_2 \) and \( \text{Ar} \) (1452 cm\(^{-1}\), i.e. 0.18 eV). At \( R = 3.0 \) Å the triple- and quadruple-zeta basis sets differ by \( \Delta E_{\text{Molpro}} = 260 \) and \( \Delta E_{\text{Gaussian}} = 262 \) cm\(^{-1}\), respectively. With increasing \( R \) the differences between calculations with the aug-cc-pVTZ and aug-cc-pVQZ basis sets decrease to zero. These comparisons suggest that a larger basis set will not eliminate the problem of
converging to the charge-transfer state found for the calculations with Gaussian.

For the remainder of the present work a fully dimensional PES at the UCCSD(T)-F12a/avtz level of theory was calculated using MOLPRO. The use of this basis set in the UCCSD(T)-F12a method has been shown to give results close to the basis set limit. Even with UCCSD(T)-F12a about 15% of the energies were difficult to converge. They were determined by local interpolation in order to complete the full grid. For the MRCI energies, more than 20% of the points showed convergence problems. The angular grid included an 11-point Legendre quadrature $\theta = 11.98^\circ$, $27.49^\circ$, $43.10^\circ$, $58.73^\circ$, $74.36^\circ$ and $89^\circ$ and their symmetry related values $E(r, R, \theta) = E(r, R, 180^\circ - \theta)$. In order to carry out all calculations in the same symmetry point group $(C_\infty)$, energies for $\theta = 89^\circ$ were actually computed instead of $90^\circ$. For the atom-diatom distance $R$, the 26 values ranged from 1.7 Å to 16 Å and for the diatomic distance $r$ the grid contains 10 values between 0.998 Å and 1.288 Å.

Upon inspection, several ab initio energies for $R > 6$ Å did not converge to the desired ground state. Hence, the long range part of the PES was represented as the known long range part of the interaction potential,$^{13}$

$$V(r, R, \theta) = -\frac{Z_{\text{Ar}}}{2R^4} \frac{I_{\text{Ar}} I_{\text{N}_2} a_{\text{Ar}}}{2(I_{\text{Ar}} + I_{\text{N}_2})} \frac{1}{R^6} \times \left[ z_1(r) + 2z_\perp(r) + 0.5 \left[ z_\parallel(r) - 2z_\perp(r) \right] \left( 3 \cos^2 \theta - 1 \right) \right],$$

(2)

where the parallel ($z_\parallel$) and perpendicular ($z_\perp$) polarizabilities of $\text{N}_2^+$ were obtained by interpolation of the data reported in ref. 14 according to

$$z_\parallel(r) = \sum_{k=0}^{4} a_k (r - r_c)^k,$$

$$z_\perp(r) = \sum_{k=0}^{4} b_k (r - r_c)^k,$$

(3)

The ionization energy$^{15}$ of $\text{N}_2^+$ is $I_{\text{N}_2} = 15.58$ eV, the ionization energy of argon$^{15}$ $I_{\text{Ar}} = 15.76$ eV, and the polarizability of the argon atom is $a_{\text{Ar}} = 11.23 a_0^3$. In summary, for $R < 6$ Å the ab initio energies were used and for $R \geq 6$ Å the energies were computed from eqn (2). Between the two set of grids, there was a radial region (4.5 Å $< R < 6$ Å) of 1.5 Å without points to facilitate the reproducing kernel to interpolate and to avoid using switching functions. This PES is referred to as UCCSD(T)-F12a+LR in the following and its performance is reported in Fig. 3.

The interaction PES was represented by using a reproducing kernel Hilbert space (RKHS)$^{17}$ approach

$$V(x) = \sum_{k=1}^{M} z_k Q(x_k, x)$$

(4)

where $M$ is the number of ab initio points, $x$ is the vector of the internal coordinates $x = (R, r, z)$, with $z = \left( 1 - \cos \theta \right) / 2$, and $x_k$ corresponds to a grid point $x_k = (R_k, r_k, z_k)$. $Q(x_k, x)$ is the reproducing kernel for a multidimensional PES, which corresponds to the multiplication of three 1-dimensional reproducing kernels $q(x_k, x)$

$$Q(x_k, x) = q^{2,4}(R_k, R)q^{2,4}(r_k, r)q^2(z_k, z)$$

(5)

where $q^{2,4}(R_k, R)$ and $q^2(z_k, z)$ are the radial and angular kernels,$^{12}$

$$q^{2,4}(R_k, R) = \frac{7}{15} R^{-5} \left[ 1 - \frac{5R_k}{7R} \right]$$

$$q^2(z_k, z) = 1 + z_{<} z_{>} + 2z_{<} z_{>} \left( 1 - \frac{z_{<}}{3z_{<}} \right)$$

(6)

The subscripts $R_{<}$ and $R_{>}^*$ are, respectively, the greater and smaller of any pair of $R_k$ and $R$, and similar for $z_{<}$ and $z_{>}$. The coefficients $z_k$ are determined from solving the linear system $Q(x_k, x) = zV(x_k)$, where $k$ and $l$ label the different coordinates of the ab initio grid.

The global PES required for the classical trajectories, including the interaction and the diatomic energies, was obtained from adding the $\text{N}_2^+$ energies to the grid at the respective value of $r$.

![Fig. 3](image-url) (A) Contour plot of the potential energy surface (UCCSD(T)-F12a+LR) at $r_{\text{opt}} = 1.122$ Å. Red lines correspond to repulsive energies ($V(r, R, \theta) > 0$). Contour lines are in steps of 1000 cm$^{-1}$ up to $-1000$ cm$^{-1}$, in increments of 200 cm$^{-1}$ up to $-400$ cm$^{-1}$ and from $-400$ cm$^{-1}$ to 0 cm$^{-1}$ in steps of 50 cm$^{-1}$. (B) The long range potential for $r_{\text{opt}} = 1.122$ Å and $\theta = 12^\circ$. Blue triangles are the UCCSD(T)-F12a ab initio energies, the dashed red line the energies from eqn (2), the black solid line is the RKHS PES including the analytical energies in the grid and the green line the RKHS surface from using only the ab initio energies.
and also represented as an RKHS. By construction, reproducing kernels decay to zero for \( R \to \infty \). Therefore, the asymptotic energies need to be adjusted which was done following the procedure described in ref. 2.

The contour plot of the RKHS PES using the UCCSD(T)-F12a+LR grid described in the methods at \( r_{N_N'} = 1.122 \text{ Å} \) is shown in Fig. 3A. The linear [NN–Ar]\(^+\) geometry is the most stable configuration while the T-shaped geometry is a transition state. The global minimum of the RKHS PES is in the linear configuration with \( r_{N_N'} = 1.108 \text{ Å} \) and \( R = 2.73 \text{ Å} \) and a stabilization energy of \(-10.477 \text{ cm}^{-1}\) \((-1.299 \text{ eV})\). The N–N separation for the minimum energy structure of the complex is close to the equilibrium value of isolated \( N_N' (r_{N_N'} = 1.122 \text{ Å}) \). This suggests that the rigid rotor approach in quantum scattering calculations at low collisional energies should be a valid approximation. The two symmetry-related linear minima are separated by a T-shaped transition state \( 4759 \text{ cm}^{-1} \) \((–1.299 \text{ eV})\). The N–N stabilization energy of \( 1.299 \text{ eV} \).

The maximum propagation distance was 26.46 Å \((50 \text{ Å})\). For constructing the RKHS of the \( ab \text{ initio} \) energies, the grid was pruned of unconverted points. Those were replaced by local RKHS interpolation to arrive at a complete grid which was then interpolated using the kernel.

The RKHS representation of the UCCSD(T)-F12a+LR PES was then used in quantum calculations of the inelastic cross sections. For computing the inelastic cross sections for \( N_N'^{+} \) colliding with Ar the close-coupling equations were solved in the space-fixed representation using the log-derivative propagator implemented in the atom–diatom code Newmat,\(^{18}\) which was recently used to study the rovibrational rate coefficients for NO\(^+\) colliding with He.\(^{19}\) The maximum propagation distance was 26.46 Å \((50 \text{ Å})\) and convergence of the cross section as a function of the total angular momentum was checked for each collisional energy from 10\(^{-3}\) cm\(^{-1}\) to 10\(^{3}\) cm\(^{-1}\).

The state to state rate coefficients at temperature \( T \) were computed by averaging over the collision energy \( E_c \) of the corresponding cross sections \( \sigma_{j_j' \to f_f'} \) as

\[
  k_{j_j' \to f_f'}(T) = \sqrt{\frac{8}{\pi \mu k_b T}} \int_0^\infty \sigma_{j_j' \to f_f'}(E_c) E_c^{1/2} \exp\left(-\frac{E_c}{k_b T}\right) \, dE_c, \tag{8}
\]

where \( k_b \) is the Boltzmann constant and \( j \) and \( \nu \) are the rotational and vibrational quantum numbers in the initial states, and the final quantum numbers are \( j' \) and \( \nu' \), respectively.

The initial state for \( N_N'^{+} \) was the \((\nu = 0, j = 6)\) state as was the case in the experiments, and the fine structure of \( N_N'^{+} (2\Sigma^+_v) \) is neglected in the present calculations. Convergence of the calculations with the rotational and vibrational basis set is shown in Table 1 for two collision energies \((100 \text{ cm}^{-1} \text{ and } 500 \text{ cm}^{-1})\). The cross sections do not vary strongly with the number of vibrational basis functions included in the calculations. It is worth remembering that these calculations are performed for \( \text{para-}N_N'^{+} \) which means that including 20 rotational states corresponds to a maximum value of \( j_{\text{max}} = 38 \).

Fig. 4 shows the cross sections as a function of the collision energy from the initial rotational state \( j = 6 \) using the rigid rotor approach (with the \( N_N'^{+} (\nu = 0) \) rotational constant\(^{20}\) \( B_c = 1.93 \text{ cm}^{-1}\)) and two different basis sets \((N_\nu = 2, N_j = 20)\) and \((N_\nu = 4, N_j = 17)\). This figure also shows that the channel with \( j = 8 \) opens at 58 cm\(^{-1}\) above the initial state \((j = 6)\), which corresponds to the energy difference between the \( j = 6 \) and \( j = 8 \) states of \( N_N'^{+} \). For collision energies lower than 0.1 cm\(^{-1}\) the cross-sections are sensitive to the size of the basis used. However, for the energies of interest in the present work assuming a rigid \( N_N'^{+} \) monomer would suffice, see Table 1.

The rate coefficients up to \( T = 150 \text{ K} \) from the initial state \( j = 6 \) are shown in Fig. 5. These rates were computed from cross sections calculated including 20 values of \( j \) in each of the two lower vibrational states. The elastic transition \((6 \to 6)\) is the dominant process for all temperatures considered and the de-excitation rates decrease with increasing \( \Delta j \). Furthermore, the

<table>
<thead>
<tr>
<th>State ( \nu )</th>
<th>( N_\nu )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( j )</td>
<td>( j_f )</td>
</tr>
<tr>
<td>( 14 )</td>
<td>( 16 )</td>
</tr>
<tr>
<td>( 14 )</td>
<td>( 16 )</td>
</tr>
<tr>
<td>( 14 )</td>
<td>( 16 )</td>
</tr>
</tbody>
</table>

Table 1: Cross section in \( a_0^2 \) computed using basis set including 14, 16, and 20 rotational state in each \( \nu \) for the rotational transition \( j_i \to j_f \) at \( E_c = 100 \text{ cm}^{-1} \) and 500 cm\(^{-1}\). The number of vibrational states included in the calculations is \( N_\nu \).
rates for several transitions are reported in Table 2. These values can be used in the analysis of future experiments.

For directly comparing results using the present UCCSD(T)-F12a/avtz and the previous UCCSD(T)/avtz PESs, additional quasiclassical trajectory (QCT) simulations were carried out. This also allows to compare the quantum results with QCT using the same PES (UCCSD(T)-F12a/avtz) and to quantify to what extent quantum effects influence the results. Classical molecular dynamics simulations of the collision between $N_2^+$ and Ar were carried out with CHARMM.\textsuperscript{21} The equations of motion were integrated using the Verlet integrator with a time step of $\Delta t = 0.1$ fs and energies and forces were calculated from the RKHS representation of the PES. Energy conservation had been verified in previous work.\textsuperscript{2} With the present integration scheme and $\Delta t = 0.1$ fs total energy for individual trajectories is also conserved and the fluctuation around the mean is $\Delta E \leq 0.1$ cm$^{-1}$. Initial conditions for $N_2^+$ were generated from a WKB-quantized periodic orbit of the corresponding rotating Morse oscillator\textsuperscript{22,23} for vibrational and rotational quantum numbers $\nu = 0$ and $j = 6$. Relative collision energies were randomly sampled from a Maxwell–Boltzmann distribution at 90 K. Impact parameters $b$ ranged from 0 to 13.23 Å ($25a_0$) and the collision partners are initially separated by at least 7.94 Å ($15a_0$). A total of 250 000 trajectories was run; simulations were stopped when $N_2^+$ and Ar were separated by more than their initial distance.

QCT simulations were carried out at 90 K. As was done previously, different filtering criteria were applied in the final state analysis.\textsuperscript{2} Such filtering at the post-processing stage is necessary to limit the number of classical trajectories to be analyzed to those which correspond to valid simulations within a semi-classical framework. Filtering at the post-processing stage was carried out as follows. The $N_2^+$ vibrational quantum number $\nu$ was determined from the effective potential $V_{\text{eff}}(r) = V(r) + \frac{j(j+1)}{r^2}$. In general, a real, non-integer number is obtained for $\nu$. By applying a binning criterion, only trajectories with $\nu$ within certain thresholds are retained for further analysis. This ensures that only trajectories are analyzed in which vibrational zero-point energy (ZPE) was not leaked into other degrees of freedom during the simulation. As was done before,\textsuperscript{2} three different thresholds were used: $\text{frac}(\nu) = \pm 0.1$, $\pm 0.01$ and $\pm 0.001$, where $\text{frac}(x)$ is the difference of $x$ to the closest integer value. Fig. 6 shows the distribution of the quantum state $j_f$ after the collision. The thresholds used do not influence the shape of the distribution. For $\text{frac}(\nu) = \pm 0.1$ and $\pm 0.01$ the results are almost identical and for both, a statistically significant number of events (43 672 and 4275, respectively), see Fig. 6. For $\text{frac}(\nu) = \pm 0.001$, only 333 out of the 250 000 trajectories fulfilled the binning criterion. This is probably not sufficient for convergence and hence these results should be considered with caution. Comparison with the results from QM calculations suggest that the QCT simulations are representative although they underestimate the elastic channel.

The QM and QCT treatments agree in that the fraction of inelastic collisions is considerably larger than 1 out of 50 ($i.e.$ 2%),\textsuperscript{1} they are larger by one order of magnitude and range from 22% to 67% depending on the method used. This supports the intuitive expectation that due to the strong $N_2^+$–Ar interaction (binding energy of $-10$ 477 cm$^{-1}$ (1.3 eV)) and the long range induced dipole–quadrupole interaction efficient mixing between rotational states should take place. The quantum distribution from the rate coefficients at 90 K is also included in Fig. 6, and the QCT simulations agree quite favourably with them. The major difference concerns inelastic transitions to higher $j$-states ($j > 10$) which are completely suppressed in quantum calculations but occur with appreciable probability in the QCT simulations.

![Fig. 5](image1.png) **Fig. 5** Rate coefficients from the initial state $\nu = 0$, $j = 6$ as function of temperature.

![Table 2](image2.png) **Table 2** Inelastic rate coefficients (in units of cm$^{-3}$ molecule$^{-1}$ s$^{-1}$) for the rotational transition $j_i \rightarrow j_f$ at several temperatures from quantum calculations.

<table>
<thead>
<tr>
<th>State</th>
<th>Temperature</th>
<th>$j_i$</th>
<th>$j_f$</th>
<th>$1$ K</th>
<th>$10$ K</th>
<th>$50$ K</th>
<th>$100$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1$</td>
<td>$2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0$</td>
<td>$0$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0$</td>
<td>$10$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0$</td>
<td>$20$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0$</td>
<td>$30$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0$</td>
<td>$40$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0$</td>
<td>$50$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0$</td>
<td>$60$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0$</td>
<td>$70$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0$</td>
<td>$80$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0$</td>
<td>$90$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$0$</td>
<td>$100$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 6](image3.png) **Fig. 6** Fractional occupation of $j$ states after the collision for different conservation criteria from QCT. The results of the quantum calculation are shown in blue. For the QCT simulations the numbers in bracket show how many of the 250 000 trajectories meet the conservation criterion. Note that the simulations with $\text{frac}(\nu) = \pm 0.001$ are probably not fully converged, see text.
Rotational rates from QCT simulations were calculated according to\(^\text{(9)}\)

\[
k(T) = \frac{8}{\pi \mu \beta} \frac{2\pi h_{\text{max}}}{N_{\text{tot}}} \sum_{i=1}^{N_{\text{tot}}} b_i
\]

where \(\mu\) is the reduced mass of the \(\text{N}_2^+\text{-Ar}\) complex, \(h_{\text{max}}\) is the maximum impact parameter, \(b_i\) the impact parameter of trajectory \(i\), \(N_{\text{tot}}\) the total number of trajectories that meet the filtering criterion, \(N_{\text{tot}}\), the number of trajectories that count as “reactive” and \(\beta = 1/(\epsilon_0 \mu t)^{1/2}\). Rates for inelastic transitions which change the initial angular momentum, i.e. \((j = 6 \rightarrow j' \neq 6)\), are reported in Table 3. Trajectories only count as inelastic if \(j\) changes by more than 2 quantum numbers.\(^2\) The inelastic rates from quantum and QCT calculations on the UCCSD(T)-F12a+LR PES are consistent with one another and all smaller than the Langevin rate as expected. This is also true for the earlier UCCSD(T) PES\(^2\) although the inelastic rate is smaller by about a factor of 4 compared to the rates from the present calculations. Contrary to that, the inelastic rate on the vibrational zero point corrected UCCSD(T)-ZPE PES is largest and even exceeds the Langevin rate. Hence, it is concluded that QCT simulations on a ZPE-corrected PES is deemed unreliable and should not be considered for this system.

One possibility to discuss the topography of all three PESs (UCCSD(T),\(^2\) UCCSD(T)+ZPE\(^2\) and UCCSD(T)-F12a + analytical long range) on an equal footing is to expand the PESs into a Legendre series \(V(r, r, \theta) = \sum_{i} V_i(r) P_i(\cos \theta)\) and to compare the radial strength functions \(V_i(r, R)\). The topography of the isotropic part \(V_0(r, R)\) is comparable for all three PESs with a minimum at \((R = 2.5 \text{ Å}, r = 1.11 \text{ Å})\) but differing well depths \(V_0^{\text{UCCSD(T)}} = -162022.85 \text{ cm}^{-1}, V_0^{\text{UCCSD(T)+ZPE}} = -159375.02 \text{ cm}^{-1}, V_0^{\text{UCCSD(T)-F12a+LR}} = -107463.92 \text{ cm}^{-1}\). However, the well depths appear to be unrelated to the magnitude of the inelastic rates which are \(k^{\text{UCCSD(T)}} = 1.35, k^{\text{UCCSD(T)+ZPE}} = 11.70, k^{\text{UCCSD(T)-F12a+LR}} = 6.96 \times 10^{-10}\), see Table 3.

The next term in the Legendre expansion is \(V_2(r, R)\) which is shown in Fig. 7. It is found that in the long range part of the \(V_2\)-part of the PES a slightly repulsive region appears for \(R > 5.5 \text{ Å} \) and \(r > 1.2 \text{ Å}\). However, this range is outside the classical turning points for the \(v\)-vibration and at least the QCT simulations will not be sensitive to this region. Also, the appearance of this feature in the PES does not correlate with the changes in the inelastic rates because the lowest and highest rates are from the UCCSD(T) and UCCSD(T)+ZPE surfaces which both exhibit the repulsive part in \(V_2\) whereas UCCSD(T)-F12a (intermediate rate) does not. However, upon closer inspection it is found that the well region (around \(-3000 \text{ cm}^{-1}\), and \(1.08 < r < 1.15 \text{ Å}\)) for the UCCSD(T)+ZPE surface (which leads to the highest inelastic rate) differs considerably from the other PESs. The UCCSD(T)+ZPE PES exhibits a minimum around the outer \(r\)-turning point whereas the other two PESs do not.

As a final test of the reliability of the computed rates and occupations of the \(j\)-states, the QM calculations were repeated with the RKHS interpolation using only the \textit{ab initio} energies (see green trace in Fig. 3), i.e. without the analytical long range and without switch between the two grids in the intermediate \(R\)-range. With this PES, \(76%\) of the collisions are elastic, compared with \(77\%\) from the UCCSD(T)-F12a + analytical LR PES.

---

**Table 3** Rate coefficients \(k_{ij}\) in \(10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\) for the transition \((\nu = 0, i j = 6 \rightarrow j' \neq 6)\) at \(T = 90 \text{ K}\) for different cases and conservation criteria. C stands for “complex” (the collision partners formed the complex, lifetime \(\geq 5 \text{ ps}\)) and NC for “no complex” (complex was not formed, lifetime \(\leq 5 \text{ ps}\)). QCT, quantum, Langevin and experimental \(k_{ij}\) are reported. Differences in the rates should be considered in the context of the differences in the PESs, see Fig. 1 and 7.

<table>
<thead>
<tr>
<th>Determination Method</th>
<th>Inelastic rates</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>UCCSD(T)-F12a+LR</strong></td>
<td><strong>C</strong></td>
<td><strong>NC</strong></td>
<td><strong>C + NC</strong></td>
</tr>
<tr>
<td>QCT/(\nu = 0 \pm 0.1)</td>
<td>2.24</td>
<td>3.39</td>
<td>5.63</td>
</tr>
<tr>
<td>QCT/(\nu = 0 \pm 0.01)</td>
<td>2.1</td>
<td>3.24</td>
<td>5.34</td>
</tr>
<tr>
<td>QCT/(\nu = 0 \pm 0.001)</td>
<td>2.91</td>
<td>4.05</td>
<td>6.96</td>
</tr>
<tr>
<td>Quantum</td>
<td></td>
<td></td>
<td>5.69</td>
</tr>
<tr>
<td><strong>UCCSD(T) from ref. 2</strong></td>
<td><strong>C</strong></td>
<td><strong>NC</strong></td>
<td><strong>C + NC</strong></td>
</tr>
<tr>
<td>QCT/(\nu = 0 \pm 0.001)</td>
<td></td>
<td></td>
<td>1.35</td>
</tr>
<tr>
<td><strong>UCCSD(T)+ZPE from ref. 2</strong></td>
<td><strong>C</strong></td>
<td><strong>NC</strong></td>
<td><strong>C + NC</strong></td>
</tr>
<tr>
<td>QCT/(\nu = 0 \pm 0.001)</td>
<td></td>
<td></td>
<td>11.70</td>
</tr>
<tr>
<td><strong>Langvin(^1)</strong></td>
<td></td>
<td></td>
<td>7.4</td>
</tr>
<tr>
<td><strong>Experiment(^1)</strong></td>
<td></td>
<td></td>
<td>0.14</td>
</tr>
</tbody>
</table>

---

**Fig. 7** Comparison of the \(V_2(r, R)\) term from the Legendre expansion (A) of the PES of Unke et al.\(^2\) including ZPE correction, (B) without including ZPE correction, and (C) from the surface of the present work. Contour lines are in increments of 100 cm\(^{-1}\) for \(V_2(r, R) > 0\) (red lines) and in increments of 200 cm\(^{-1}\) for \(V_2(r, R) < 0\) (blue lines). Horizontal lines indicate the inner and outer classical turning points \(r^0\) and \(r^0\) along the \(\text{N}_2^+\) coordinate.
This further confirms that the computed propensities and rates are robust to variations in the PES and their representation and the expected fraction of rotationally inelastic collisions is at least 25%.

One possible reason for the disagreement between calculations and experiment is that nonadiabatic effects play a role. For certain configurations it may be possible that two or more electronic states mix, see Fig. 1A. For the collision considered here the initial dynamics starts on the ground state (black line) PES. When the two partners collide and the N2+ compresses, there is the possibility for crossing to an excited state (blue line) for short N2+ bond lengths such that both, N2+–Ar+ and N2+–Ar, are accessible final states. Another possibility are uncertainties in the modeling of the experiments. Specifically, the analysis is based on a measured overall rate and a population model which, e.g., assumes that the rate for charge exchange is independent on rotational angular moment N or J. As a comparison, a recent quantum study of CrH in collision with He also showed that the calculated ratio of elastic/inelastic cross sections is 5.6 times lower than the experimental value by using a UCCSD(T) PES while this value increases to 18 from simulations on an MRCI surface. The reasons for this disagreement were both due to approximations in the computations and uncertainties in the analysis of the experiment.

Conclusions

In summary, quantum close coupling calculations on a new PES at the UCCSD(T)-F12a level have been performed for the Ar–N2+ system at low (T = 90 K) temperature. Furthermore, QCT calculations have been carried out on the same PES to directly compare with the QM results. For inelastic transitions, the agreement between quantum and classical results is good. However, irrespective of the PES used and whether the nuclear motion is treated with classical or quantum mechanics, the probability and rate for inelastic rotational excitation of the N2+ ion after collision with Ar at 90 K is typically larger by one order of magnitude compared to experiment. Given the rather large differences between the UCCSD(T) and the UCCSD(T)+F12 PES (see Fig. 1C, D and 7) which have only a small effect on the rates (Table 3) it is unlikely that major deficiencies in the PESs are the primary cause for the disagreement between computations and experiment. New single-molecule experiments using quantum controlled initial states as is possible in Coulomb crystals and which are directly sensitive to the final state population would be valuable as there is no collisional mechanism that currently explains the conservation of the rotational quantum number found in the experiments carried out so far for this pivotal system.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Part of this work was supported by the United States Department of the Air Force which is gratefully acknowledged (to ODA). Support by the Swiss National Science Foundation through the NCCR MUST (to MM), and the University of Basel is also acknowledged.

References