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Depopulation of Na(8*s*) colliding with ground state He: Study of collision dynamics

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Abstract. A systematic study of the collison dynamics associated with depopulation of Na(8*s*) atom colliding with ground state He has been made by applying the semi-classical impact parameter method using molecular orbital (MO) basis sets of different sizes. The cross-sections for total depopulation of the parent atom as well as those for individual transitions have been calculated. It is shown that the basis set must be large enough so as to include not only the immediate adjacent states coupling with the parent state but also other nearby states, which can affect the overall flux distribution in the reaction.

Keywords. Rydberg atoms; depopulation; collision dynamics.

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1. Introduction

Quenching of low-lying Rydberg states due to the impact of neutral atomic perturbers at very low impact energies (thermal energies) has been subject of both theoretical [1–4] and experimental studies [5–7] in recent past. It has been established beyond doubt that the free-electron model [8] is not suited for such investigations where detailed interactions need to be considered. An impact parameter method using molecular orbital (MO) basis sets of appropriate size has been successfully used by Lane *et al* [3, 4], for the study of depopulation of low-lying Rydberg states of Li and Na colliding with the ground state He. We have also successfully employed the same method for calculating cross-section for depopulation of low Rydberg states of Rb($n = 8$ to 10) colliding with neutral He perturber at thermal energies [9]. Here we arrive at a conclusion that each such pair of Rydberg atom-structureless perturber needs to be investigated separately, specially in the case of low lying states where the energy defects involved are comparatively large. Gallagher and Cooke [7] have also emphasized individual analysis of such interactions. They have observed that the upward transition [ns $\rightarrow (n-1)d$] for Na(ns) + Ar is possible even for 8*s* state for which the available thermal energy $kT(T = 425\,\text{K})$ is just sufficient to overcome the energy defect (asymptotic value). However, similar transition is not reported for Na(ns) + He

before $n = 9$. Obviously, along with this asymptotic value of the energy defect the actual shape of different adiabatic states will have to be considered in explaining these interactions. Complete details of total interactions between the colliding system must, therefore, be considered to account for these findings (see also [3,4,9]).

Such a detailed study is helpful in not only calculating the cross-section for total depopulation but also in understanding the importance of the individual transitions responsible for quenching the parent Rydberg state. An interesting finding of these studies has been the development of $s \rightarrow f$ propensity rule $\Delta l = 3$ as one goes from low ns-state of Na to high ns-state in Na–He collision.

These developments prompted us to undertake a systematic and detailed study of collision dynamics of Na(8*s*)-He interactions in the thermal energy region. The amount of energy available at a collision temperature 425 K for this pair is $1{\cdot}36 \times 10^{-3}$ a.u., which is slightly more than the asymptotic energy defect $\Delta E(R - \infty)$ for upward transition of Na(8*s*) to Na(7*d*). Hence the probability of excitation to higher states is also expected to make a small but finite contribution towards depopulating the parent Rydberg Na(8*s*) state. This also makes the Na(8*s*)-He pair worth investigating. Another advantage of taking He as a perturber is its compact structure. Its orbital electrons are tightly bound to the nucleus and hence He atom as a whole acts as a mere core in our MO calculation.

2. Calculation

For our calculation we make use of the previously discussed semi-classical MO method [3,4] whose suitability for such studies has been discussed in detail by Kimura and Lane [10]. In this approach, the relative nuclear motion is described by a classical trajectory and the active electron by a time dependent wave function expanded in terms of electronic states represented by molecular orbitals (see ref. [10] for details). The molecular orbitals and the corresponding electronic energy curves of the interacting system are calculated by a standard variational procedure. The Rydberg electron's binding in the combined (Na^+–He) core is accounted through the standard pseudopotential approach [11]. In the present calculation we make use of the pseudopotential parameters given by Bardsley [11] and Pascale [12] for Na^+ and He cores respectively. In the expansion of the system's wave function the coefficients (a_n) satisfy a set of linear first order coupled differential equations

$$i\dot{a}_n(t) = \sum_{k \neq n} \mathbf{V}\cdot(\mathbf{P} + \mathbf{A})_{kn} a_k \exp[-i\int^t (E_n - E_k)\mathrm{d}t], \tag{1}$$

where only the first order terms in **V** (relative nuclear velocity) have been considered. In this equation **P** and **A** represent the non-adiabatic coupling (radial and rotational) matrix and its ETF (electron transfer factor) correction terms respectively (see ref. [3] for details). These equations are solved numerically for a sufficiently large number of impact parameters (b) employing the initial boundary conditions

$$a_k(-\infty) = \delta_{ik}, \tag{2}$$

where i represents the initial state and δ_{ik} is the Kronecker delta. The asymptotic values of these coefficients $[a_k(+\infty, b)]$ represent transition amplitudes for various final

states, and the corresponding cross-sections are obtained by integrating the square of the respective transition amplitudes over b.

$$\sigma_k = 2\pi \int b|a_k(+\infty, b)|^2 \, db. \tag{3}$$

3. Collision dynamics

As stated above, in the present method a set of coupled equations, each representing a particular molecular state, are numerically solved for each contributing impact parameter to obtain the probability for transition from the initial state to various final states. This obviously poses a few questions about the convergence of the cross-sections calculated in this way. Since the range of impact parameter required for solving these coupled equations depends on the radius of the Rydberg atom as well as the effective size of the perturber, the calculation is usually carried out up to a certain maximum value of impact parameter. This in turn, requires that all important R dependent couplings are taken into account so that a realistic spectrum of probability is obtained. Hence, the calculated cross-sections are usually checked for convergence with respect to inter-nuclear separation R. By doing calculations up to different R values we have arrived at the conclusion that a maximum limit of $R = 30a_0$ is sufficient to obtain the needful convergence and to provide a realistic picture of the process of depopulation of the parent Na(8s) state due to impact of thermal He. This choice ensures that all important couplings are incorporated when the coupled equations are being solved. It is worth mentioning at this juncture that Kumar *et al* [3] have discussed the convergence of the calculated cross-section with respect to the inter-nuclear separation in a somewhat detailed manner. By repeating their previous calculations and going up to $R = 120a_0$ they have concluded that no significant change is caused in the magnitude of the total depopulation cross-sections; only the details of some individual transitions are found to change.

Another equally important aspect of such a calculation is the convergence of the estimated cross-section with respect to the number of molecular states coupled together. An ideal case should include as many states as possible to have a good convergence. The other choice can be coupling of only immediate neighbouring states of the parent state, because transitions to these states alone are expected to make appreciable contribution towards depopulating the initial Rydberg state. It must be emphasized here that larger the number of coupled equations, greater is the computational effort needed to solve them. This obviously puts a limitation on the number of states one can couple together. But at the same time the calculated individual transition cross-sections must project a realistic picture of the process of depopulation. The above mentioned aspect of convergence of the calculated cross-sections has been the main motivating factor behind the present study of collision dynamics.

In the following section, we present our calculated cross-sections.

4. Results and discussion

The calculated adiabatic potential energies for Na(8s)-He pair is presented in figure 1; for clarity only Σ states have been included in these figures. The calculated adiabatic

Table 1. Comparison between calculated* and experimental** Na energies (a.u.).

nl	Present cal.	Experiment	Difference (%)
3*s*	1·8885 E-1	1·8879 E-1	0·03
3*p*	1·1156 E-1	1·1140 E-1	0·14
4*s*	7·1579 E-2	7·1561 E-2	0·03
3*d*	5·5937 E-2	5·5936 E-2	0·00
4*p*	5·0939 E-2	5·0888 E-2	0·10
5*s*	3·7585 E-2	3·7579 E-2	0·02
4*d*	3·1442 E-2	3·1423 E-2	0·06
4*f*	3·1261 E-2	3·1268 E-2	0·02
5*p*	2·9197 E-2	2·9169 E-2	0·10
6*s*	2·3132 E-2	2·3129 E-2	0·01
5*d*	2·0106 E-2	2·0046 E-2	0·30
5*f*	2·0011 E-2	2·0003 E-2	0·04
6*p*	1·8920 E-2	1·8892 E-2	0·15
7*s*	1·5663 E-2	1·5659 E-2	0·03
6*d*	1·3953 E-2	1·3869 E-2	0·60
6*f*	1·3895 E-2	1·3844 E-2	0·36
7*p*	1·3254 E-2	1·3222 E-2	0·24
8*s*	1·1306 E-2	1·1295 E-2	0·09
7*d*	1·0246 E-2	1·0156 E-2	0·88
7*f*	1·0208 E-2	1·0072 E-2	1·34
8*p*	9·8000 E-3	9·7627 E-3	0·38
9*s*	8·5437 E-3	8·5223 E-3	0·25

*The STO's supplied by Kumar *et al* [3] have been used.
**From ref. [13].

energy values are also compared with the experimental results in table 1 and the two are found to agree each other.

It may be pointed out that the present representation of the electronic states is expected to yield good results except for $R < 2a_0$. At these internuclear separation the charge clouds of the Na core and He atom begin to overlap. But they are of no importance because various states couple strongly only at much larger internuclear separations (see also Saha *et al* [4]). We start with a 3-state calculation in which only $8s\Sigma$, $7p\Sigma$ and $7p\pi$ states are included. This is because the transition Na(8*s*)–(7*p*) is expected to be the most important direct mechanism for depopulating the parent state (see figure 1). The calculated cross-sections is found to have a maximum (figure 2) around $V = 0{\cdot}00075$ a.u. ($3{\cdot}76 \times 10^{-2}$ eV) and nearly the full contribution comes from population of the $7p\Sigma$ state (the rotational coupling between $8p\Sigma$ and $7p\pi$ is very small). However, since thermal impact energies are just sufficient to excite Na(8*s*) to the next higher state Na(7*d*), it is appropriate that the basis set should not exclude these states. Even if the possibility of upward transition at such low energies is very small (due to the threshold effect), virtual (transient) excitation of these states could be important. Indeed, we have found (in a 5-state calculation) that the molecular states $7d\Sigma$ and $7d\pi$ influence the cross-sections for Na(8*s*) depopulation, changing it significantly in magnitude from that obtained from a 3-state calculation (figure 2), although the

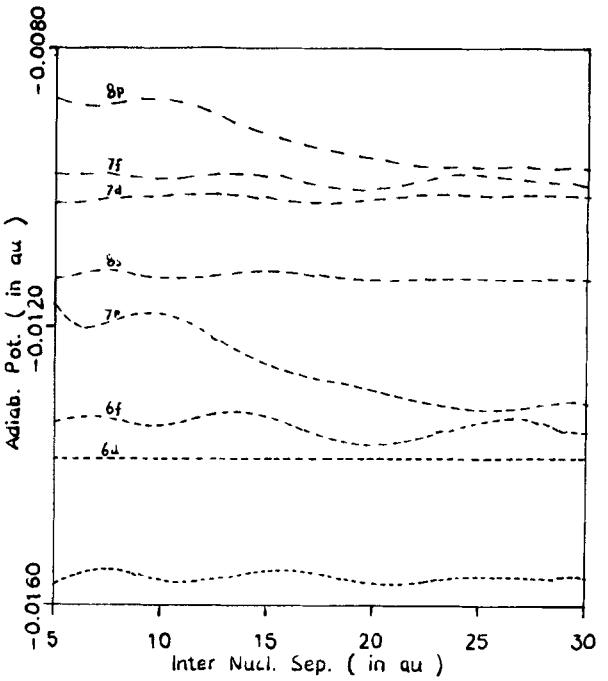

Figure 1. Adiabatic potential curves of 14-state calculations for the Na(8*s*) + He collision. Various states are labelled through the corresponding atomic states of Na.

individual cross-section for excitation to Na(7*d*) remains very small (less than 1% of the total). The 3- and 5-state cross-sections have nearly the same energy dependence except that in the former the cross-section shows a comparatively sharper peak in the investigated energy range. Also when the molecular states correlating with Na(6*f*) (i.e., $6f\Sigma$ and $6f\pi$) are included in a 7-state calculation, the calculated cross-sections (also shown in figure 2) remain nearly unchanged compared with those of the 5-state calculations. The presence of a strong avoided crossing between $7p\Sigma$ and $6f\Sigma$ around $R = 25a_0$, which is manifested by a strong radial coupling between the two in that region, suggests that there should, however, be a probability redistribution in the 7-state calculation with majority of the probability transfer to $7p\Sigma$ eventually passing through to $6f\Sigma$. Here it is found that this holds only at lower energies; for $V > 0{\cdot}00070$ a.u. ($3{\cdot}28 \times 10^{-2}$ eV) the cross-sections for deexcitation to Na(7*p*) again prevail over those for deexcitation to Na(6*f*).

We next enlarged the basis set by including the molecular states $6d\Sigma$ and $6d\pi$, correlating with Na(6*d*). As shown in figure 2, this 9-state calculation results in a significantly different depopulation cross-section not only in magnitude but with the peak shifted to still lower energies ($0{\cdot}00068$ a.u. $= 3{\cdot}09 \times 10^{-2}$ eV). There is also a change in the relative importance of the individual cross-section in that the cross-section for transition to Na(7*p*) is larger than that to Na(6*f*) at low impact energies, whereas the order reverses at high energies. No marked difference is observed when the lower state $7s\Sigma$ is included in a 10-state calculation since there exists no significant coupling (radial or angular) between the molecular states $6d\Sigma$, $6d\pi$ and $7s\Sigma$). We expect

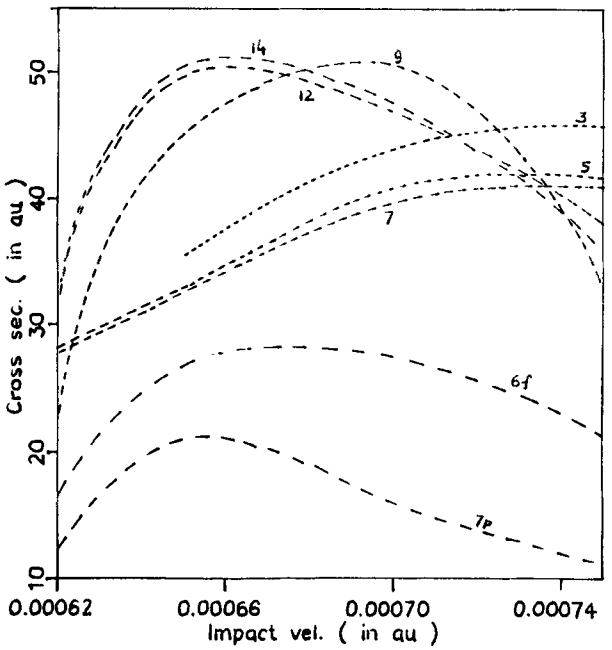

Figure 2. Cross-sections (in a_0^2) for total depopulation of Na(8*s*) colliding with He. Curves labelled as 3, 5, 7, 9, 12 and 14 are the cross-sections obtained through 3-, 5-, 9-, 12- and 14-state calculations. The 8*s*-7*p* and 8*s*-6*f* cross-sections calculated with 14-states are also shown for comparison.

that the molecular states originating from still lower atomic states of Na, such as Na(6*p*), will play essentially no role in depopulating Na(8*s*).

Next, recognizing that the $7f\Sigma$ and $7f\pi$ states correlating with Na(7*f*) couple strongly with $7d\Sigma$ and $7d\pi$, which can be populated from the $8s\Sigma$ parent state at thermal energies, we carried out a 12-state calculation including these states as well. Although there is only a slight change in peak position of the total depopulation cross-section the transition to $6f\Sigma$ is found to dominate transition to $7p\Sigma$ throughout the energy range investigated. Thus, the redistribution of the probability in the 12-state calculation evolves during the collision in such a way that probability transferred to $6f\Sigma$ is permanently trapped there, making the corresponding cross-section the largest at all impact energies studied. The inclusion of two higher states, $8p\Sigma$ and $8p\pi$ does not cause much further change in the depopulation cross-section (figure 2). Since the molecular states correlating with Na(7*f*) and Na(8*p*) interact with one another at large R values their presence probably serves merely to redistribute the small probability transferred to states correlating with Na(7*d*) and Na(7*f*) at smaller R. The inclusion of $9s\Sigma$ and higher states is expected to have no significant effect.

From the aforesaid study of collision dynamics we find that a realistic picture of the process of depopulation emerges only if a fairly large number of molecular states are coupled together. Hence, not only those states that couple directly with the initial channel, but also the neighbouring states that couple strongly with one of the adjacent states should be grouped together in this type of study. By increasing the number of

states in steps we are able to arrive at the conclusion that even though the total depopulation cross-section of a parent state is far less sensitive to the choice of the basis set size, significantly different results are obtained for various individual transitions contributing towards complete annihilation of the initial state. This also helps us in understanding the propensity rule that led to selective population of a particular state. This aspect of collision study can hardly be explained in a simplified model. For example, we found in the present study (Na[8*s*] + He) that all molecular states correlating with various atomic levels of Na lying between 7*s* and 8*p* should be taken into consideration. This not only ensures convergence of the calculated cross-section for total depopulation of the parent Rydberg state, but also explains the propensity rule: ns$\rightarrow(n-2)f(\Delta l=3)$ in downward transition. Obviously as we go up in the Rydberg series individual characteristic of the initial Rydberg state may come into picture. As the energy gaps between adjacent states go on decreasing with increasing n value, more and more molecular states will have to be coupled when considering depopulation of the Rydberg state with larger n value. Beyond a certain limit the MO method will no longer be appropriate and an AO (atomic orbital) method, or even a free electron model can be applied to study their depopulation.

In the end we also compare the present results obtained from a 14-state calculation for Na(8*s*) with the previously reported results on depopulation of Na(9*s*) under similar circumstances [3, 4]. The process of deexcitation rather than excitation is found to be the most important factor in quenching the parent state in both cases. Also for both the systems, the deexcitation to $(n-2)l=3$ [6*f* for Na(8*s*) and 7*f* for Na(9*s*)] attains maximum probability in the investigated (thermal) energy range. However, the two systems differ significantly with regard to the contribution to the total depopulation that comes from upward transitions. In the present Na(8*s*) case, thermal energies are just sufficient to excite Na(8*s*) to the immediate higher state Na(7*d*). However, the cross-sections for upward transitions are very small (less than 10% of the total magnitude). In contrast, for the case of Na(9*s*) thermal impact collision energies are a factor of 2 to 3 above the threshold for excitation and the cross-sections for upward transitions are quite significant and amount to nearly 25% of the total depopulation cross-sections at high collision velocities ($V=0{\cdot}00075$ a.u.). Since a fully quantum mechanical treatment would suppress the excitation cross-sections near threshold, the semi-classical calculations are likely to overestimate these cross-sections and hence, give too large a total depopulation cross-sections for Na(9*s*). In spite of the difference in magnitudes of the contributions from upward transitions in Na(8*s*) and Na(9*s*), we do observe one significant similarity, namely that two-step upward transition is present in both the systems. The probability transferred to $(n-1)d$ from the parent ns-state finally ends up in $(n-1)f$. Thus, both for upward and downward transitions the Rydberg atom tends to occupy the $l=3$ final substate. We would like to emphasize at this point that exclusion of higher m-states from the basis set of the present calculation is not expected to cause any significant change in the magnitudes of the calculated cross-sections. Through a test calculation Kumar *et al* [3] have shown that the flux does not flow primarily to higher m-states; only about 15% of the probability flux is found to pass on to these states through long-range rotational couplings within the nearly degenerate n-manifold. We can, therefore, safely conclude that cross-sections for transition to both 6*f* (downward transition) and 7*f* (upward transition) are representative of

cross-sections for transition to the respective n-manifolds. Hence, both for excitation and deexcitation we expect that a propensity rule $\Delta l \geqslant 3$ should hold good.

It may be pointed out that a 14-state calculation for depopulation of Na(8s) colliding with ground state He has also recently been carried out by Saha *et al* [4] over a large span of collision energy. Thereafter, they calculated the quenching rate by taking a Boltzmann average of relative collision velocity times the cross-section at a temperature of 425 K. Their calculated rate is found to agree with the measured value of Gallagher and Cooke [7] within a factor of 3. We, however, do not attempt to carry out a similar calculation for the reaction rates from our present calculations for basis sets of different sizes. This is because our calculations have been done in a very limited region of impact velocity and therefore it is not advisable to estimate the reaction rate from them. Still we can compare our results with the experimental measurements of Gallagher and Cooke [7] at an impact velocity corresponding to 425 K. The mean Maxwellian velocity corresponding to this temperature [$\upsilon_m = (8kT/\pi\mu)^{1/2}$] turns out to be $7{\cdot}4 \times 10^{-4}$ a.u. Assuming the depopulation cross-section to be energy independent in the thermal region Gallagher and Cooke [7] have estimated its magnitude by taking a ratio of the measured reaction rate and the mean Maxwellian velocity corresponding to 425 K. The cross-section for total depopulation of Na(8s) due to the impact of ground state He, estimated in this way, turns out to be $19{\cdot}64\ a_0^2$ which agrees within a factor of 2 to 3 with our calculated cross-sections at the same temperature. This agreement is more or less same as has been achieved by Saha *et al* [4] through their detailed investigation. A 14-state calculation at an impact velocity $7{\cdot}4 \times 10^{-4}$ a.u. employing the present method estimates the total quenching cross-section to be $33{\cdot}71\ a_0^2$ and its agreement with the experimental observation of Gallagher and Cooke ($\sigma_{ex.} = 19{\cdot}64\ a_0^2$) is within a factor of 2.

In the end we would like to emphasize that the present study has been undertaken with the sole intention of investigating the collision dynamics of the pair: Na(8s) + He. Conclusions drawn from such a study are expected to help probe other similar low Rydberg atom – structureless perturber pairs.

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