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Dissociative recombination without curve crossing: study of HeH^+

Baljit K Sarpal[†], Jonathan Tennyson[†] and Lesley A Morgan[‡]

[†] Department of Physics and Astronomy, University College London, London WC1E 6BT, UK

[‡] Computer Centre, Royal Holloway University of London, Egham, Surrey TW20 0EX, UK

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Abstract. We present a new theory for calculating dissociative recombination (and dissociative attachment) cross sections applicable for systems with or without curve crossings. The theory uses the R-matrix method to build up $N+1$ electron 'curves' in an inner region which can be coupled in a full non-adiabatic treatment. We report the first *ab initio* determination of the low-energy dissociative recombination cross section for $^4HeH^+$. The cross section is found to be in good agreement with measurements, now disputed, made in a merged beam experiment.

1. Introduction

The seminal work of Bates [1] recognized the importance of the dissociative recombination (DR) process

$$e^- + AB^+ \rightarrow A + B \tag{1}$$

for systems where a repulsive state of the neutral molecule intersects with the ground electronic state of the ion. This process is often important for the chemistry of plasmas, the upper atmosphere and low-density molecular clouds in the interstellar medium.

There are conventionally two mechanisms by which DR proceeds. First, DR can occur when an incident electron is captured into a repulsive electronic state of the neutral molecule and the nuclei move apart in this potential. The molecule is stabilized against the competing autoionization process when the internuclear separation is such that the potential energy curve of the neutral lies below the ionic ground-state potential energy curve—this is termed the *direct mechanism*. Second, in the *indirect mechanism* for DR [2] the electron is captured into a vibrationally excited Rydberg state, AB*, of the neutral molecule, which then predissociates with the repulsive state. Of the two, the first is normally the dominant process and the interference between the two processes generally results in complicated resonance structure in the cross section.

There are a few cases which do not fall within the picture of DR outlined above. Chief amongst them is the case of HeH^+. As there are no curve crossings between the ground state of the ion and the electronic states of neutral HeH, it had been assumed that the DR cross section for HeH^+ would be very small. Yousif and Mitchell [3] measured the DR cross section of HeH^+ in a merged beam experiment and have, in fact, found it to be of significant magnitude. The cross section displayed window resonance features which have been shown to match accurately with vibrationally excited Rydberg states of HeH [4, 5].

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To date most theoretical treatments of DR have employed the resonant capture mechanism, where the interactions are suitably parametrized within the multichannel quantum defect theory (MQDT) framework [6–8]. R-matrix-based methods [9–11] have been restricted to dissociative attachment, where initially the molecule is neutral and, more significantly, also to cases where the 'direct' mechanism for DR is possible.

Recently a multistep indirect method was proposed by Bates [12, 13] which also considers DR for cases without curve crossings. The mechanism proposed is a series of $\Delta v = 1$ transitions via Rydberg states. Conceptually there are similarities between this approach and the method proposed by us. Our approach, however, is more general. It has no restrictions on the change in vibrational quanta and allows fully for competing autoionization processes. As shown below, the main mechanism for DR is found to be via non-adiabatic coupling of the potentials at short internuclear separation. As yet the method of Bates has not been used for any calculations so it is difficult to make a precise comparison between the two approaches.

Currently there exists no theoretical explanation for the observed DR cross section of HeH^+. All treatments of DR neglect the direct coupling of the electronic and nuclear continua which arises from the nuclear kinetic energy operator. In cases where a favourable crossing of curves is possible the electronic coupling is much more dominant and this non-adiabatic effect can be neglected. In the absence of a favourable crossing it is yet to be seen whether this still remains the case.

In this work we treat DR by generalizing the non-adiabatic R-matrix theory of Schneider *et al* [14] and Gillan *et al* [15]. By considering coupling between R-matrix electronic curves we allow for flux to go from higher states, those describing the electronic continuum, into the lower states which correspond to states involved in the DR process. In our treatment the requirement of a curve crossing is no longer necessary but it is important that there is strong coupling between the different curves over a range of internuclear separations, not necessarily close to the equilibrium separation of the ion. Our approach has the desirable property, in common with other diabatic methods [16–18], that derivatives of electronic wavefunctions with respect to the nuclear coordinate do not arise. There are inevitably other complications, which are discussed below.

In this paper we report our *ab initio* calculations for the DR cross section of $^4\mathrm{HeH}^+$. To our knowledge this is the first time a theoretical determination, *ab initio* or semi-empirical, has been reported for this ion. Atomic units (E_h for energy and a_0 for distance) are used throughout this paper, unless otherwise specified.

2. Theory

As a starting point we take the eigenfunctions

$$\psi_k = \mathcal{A}\sum_{i,j}\phi_i(x_1\cdots x_N;R)u_{ij}(x_{N+1};R)a_{ijk} + \sum_i \chi_i(x_1\cdots x_{N+1};R)b_{ik} \qquad (2)$$

of the electronic Hamiltonian, $H_\mathrm{el}(R)$, diagonalized within an electronic R-matrix sphere of radius a (here 10 a_0) at fixed internuclear separation R. In this expansion ϕ_i are wavefunctions of the N electron target and u_{ij} are continuum functions used to represent the scattering electron. In this case the target states are the three lowest electronic states of HeH^+ ($\mathrm{X}\,^1\Sigma^+$, $\mathrm{a}\,^3\Sigma^+$ and $\mathrm{A}\,^1\Sigma^+$) which were represented by a limited configuration interaction (CI) expansion based on HeH^+ SCF molecular orbitals which, in turn, are linear combinations of atomic Slater type orbitals (see [4]). The second sum in expansion (2) involves putting all $N+1$ electrons in the target orbitals. In calculations such as the one presented here, this term is included primarily to relax the condition which makes the continuum functions, u_{ij}, orthogonal to the target molecular orbitals. The coefficients $\boldsymbol{a}$ and $\boldsymbol{b}$ are obtained as a result of diagonalizing the appropriate configuration interaction (CI) Hamiltonian and will be discussed further below.

Nuclear motion is then introduced by expressing the total wavefunction as

$$\theta_i = \sum_{jk} \psi_k(\boldsymbol{x}_1 \ldots \boldsymbol{x}_{N+1}; R)\eta_j(R)c_{ijk}. \tag{3}$$

In order to determine the vibronic R-matrix [14] it is necessary to diagonalize the full Hamiltonian

$$\langle\theta_i|T_R + H_{\mathrm{el}}(R)|\theta_{i'}\rangle = E_i\delta_{ii'} \tag{4}$$

where T_R is the nuclear kinetic energy operator. It has previously been assumed that T_R is diagonal in the electronic basis in the internal region of the R-matrix [4, 14, 15], which means that electronic states are not coupled. A rigorous treatment for vibrational coupling of adiabatic electronic eigenstates would require one to determine the derivatives of the electronic wavefunctions with respect to the nuclear motion coordinate. For *ab initio* calculations this would be a formidable task.

As the electronic eigenstates, ψ_k, form a complete set at any given geometry we can replace equation (3) by the diabatic expansion

$$\theta_i = \sum_{jk} \psi_k(\boldsymbol{x}_1 \ldots \boldsymbol{x}_{N+1}; R_0)\eta_j(R)c_{ijk} \tag{5}$$

where R_0 is some fixed internuclear distance and the R dependence is present only in η_j. This has the advantage that the nuclear kinetic energy operator in equation (4) acts only on the nuclear basis functions η_j. The disadvantage is that the electronic wavefunctions no longer diagonalize the electronic Hamiltonian H_{el}, except at $R = R_0$. They are orthonormal, so we can reduce equation (4) to the form

$$\sum_{jkj'k'} \langle\eta_j|T_R\delta_{kk'} + \varepsilon_{kk'}(R)|\eta_{j'}\rangle c_{ijk}c_{i'j'k'} = E_i\delta_{ii'} \tag{6}$$

where

$$\varepsilon_{kk'}(R) = \sum_l \langle\psi_k(R_0)|\psi_l(R)\rangle\varepsilon_l(R)\langle\psi_l(R)|\psi_{k'}(R_0)\rangle \tag{7}$$

and the ε_l are the energies of the adiabatic states, i.e.

$$\varepsilon_l(R) = \langle\psi_l|H_{\mathrm{el}}(R)|\psi_l\rangle. \tag{8}$$

The coupling between the diabatic states induced by the electronic Hamiltonian, at R other than R_0, is given by the overlaps $\langle\psi_k(R_0)|\psi_l(R)\rangle$ where $\langle|\rangle$ denotes integration over all electronic coordinates. Thus far we have made no additional approximations in introducing the diabatic representation. However, the evaluation of the overlap integrals is almost as difficult as the original problem of evaluating derivatives with respect to R.

If we can assume that the electronic wavefunction is independent of R at the target SCF molecular orbital level, then its R dependence arises from the electronic correlation and is given by the R dependence of the mixing coefficients $a_{ij,k}$ and $b_{i,k}$ of (2). Using the orthonormality of the electronic wavefunctions, the overlap integrals can be replaced by inner products of the form $\sum_k c_{i,k}(R_0)c_{j,k}(R)$, where we have combined the coefficients $a_{ij,k}$ and $b_{i,k}$ of (2) into a single coefficient matrix $c_{j,k}$. The accuracy of our calculations is dependent on the validity of this approximation.

It is important to note that as the electronic wavefunctions are calculated independently at each R, it is possible that eigenvectors may arbitrarily change sign as a function of geometry. Such a sign change in the CI vector will not affect the matrix (6), because each coupling element occurs twice. However, it will affect the non-adiabatic boundary amplitudes, w', which are given, in the diabatic representation, by

$$w'_k(R) = \sum_l \langle \psi_k(R_0)|\psi_l(R)\rangle w_l(R) \tag{9}$$

where w are the boundary amplitudes within the fixed nuclei approximation.

This has major implications for our calculations because the boundary amplitudes (9) are interpolated, by spline fitting, onto a fine mesh used for integrating over the nuclear coordinate. Any arbitrary sign change on our original grid will then lead to errors in the R averaged amplitudes. There are four points in our calculation where geometry-dependent sign changes are possible: the target SCF orbitals; the target CI wavefunctions ϕ_i; the scattering molecular orbitals after Lagrange orthogonalization [19]; and the scattering CI step (2). At each step in our calculation where phase ambiguity could arise we ensured that wavefunction coefficients were continuous as a function of internuclear separation by following the dominant contribution of each wavefunction.

In choosing our reference geometry, R_0, we have been guided by two requirements: first that the reference geometry should be distanced from any obvious avoided crossing for the adiabatic poles; second that the coupling should be relatively insensitive to the choice of another nearby reference geometry. The most natural choice is the largest internuclear separation used in our calculations, especially if one assumes, as we do in our calculations here, that there is no coupling between neutral nuclear channels at large R. Test calculations showed that we obtained similar results using either of the two largest internuclear separations as the reference geometry.

Once the vibronic eigenfunctions within the two dimensional R-matrix box are determined, the non-adiabatic **R** matrix is generated as described by Schneider *et al* [14]. The **R** matrix is then propagated to 200 a_0 in the electronic coordinate and 4 a_0 in the nuclear coordinate [20]. In the outer region the electronic channels are coupled by the dipole and quadrupole moments of the target but the nuclear channels are not coupled to one another or to the electronic channels. Potential energy curves for the relevant bound states [21] were used for propagating in the nuclear coordinate. **K** matrices were then generated for a range of scattering energies by matching to asymptotic functions [22] and from these cross sections are obtained by standard methods.

The details relevant to our work have been described in an earlier paper [4] and only those aspects which are new to the current calculations are discussed. We repeated these earlier calculations for 14 geometries between $R = 0.8$ and 2.8 a_0, taking note of the phase problem discussed above. In particular two new geometries were considered near the HeH^+ equilibrium as this allowed us to study the effect of removing geometries from the calculation. The lowest 20 R-matrix poles were treated non-adiabatically; of these the lowest 13 were treated within the diabatic formalism described earlier and the remaining seven with the non-coupling formalism of Schneider *et al* [14]. All the higher R-matrix poles, and the Buttle correction, were treated within the adiabatic approximation.

3. Results and discussion

Before discussing final results it is necessary to consider whether the model we use is justified. Particularly we need to examine our assumption that coupling between our SCF orbitals can be neglected. It should be noted that the SCF calculation is performed on the HeH^+ target and any coupling present in HeH, but not HeH^+, will be represented via the CI coefficients of equation (2).

The problem of crossings in the virtual orbitals of HeH and HeH^+ has been considered by Kubach *et al* [23]. These workers found an avoided crossing between their HeH 2σ and 3σ SCF molecular orbitals (MO) at $\sim 0.9\ a_0$. More importantly from our point of view however, they found that for HeH^+ this avoided crossing moved to a much shorter bondlength ($\sim 0.4\ a_0$). Figure 1 shows the behaviour of our 1σ–6σ molecular orbitals as a function of HeH^+ geometry. The only (avoided) crossing in the range of interest ($R \geqslant 0.8\ a_0$) is between the 6σ MO and 7σ MO (which is not included in our calculation) at $R \sim 0.9\ a_0$. This feature is at too high an energy to have a significant influence on our results. In addition we have carried out test calculations using the same basis as Kubach *et al* [23], but omitting the *improved virtual orbital* procedure so that a direct comparison with our calculations could be made. We find that the lowest orbitals are very similar to our own calculations with the higher orbitals using Kubach *et al*'s basis being consistently lower in energy. We ascribe this difference to the larger basis used by Kubach *et al*. It is perhaps pertinent to point out that the virtual orbitals from an SCF calculation do not have a direct correspondence to the real unoccupied MOs of the target HeH^+ molecule but provide a suitable basis for the subsequent CI treatment. Conversely our previous calculations with the wavefunctions used here [4, 24] have clearly shown avoided crossings between states of HeH at internuclear separations of interest to us here, thus demonstrating that such effects are correctly treated within our approach at the CI level.

In principle it is also possible for us to introduce coupling via our numerical continuum orbitals. Prior to orthogonalization, these orbitals are modelled on Coulomb functions and are rigorously independent of HeH^+ geometry, however our Schmidt and Lagrange orthogonalization procedures [4] can, in principle, introduce couplings. Plots equivalent to figure 1 for these orbitals, however, showed little discernible dependence on geometry except for few localized crossings between neighbouring continuum orbitals. In cases where the crossing occurred rather sharply we assumed the curves to be described as diabatic ones. In cases where the interaction is over an appreciable region of internuclear separation the adiabatic curves were taken and in such cases the formalism we described above should yield the correct coupling at the CI level.

In figure 2 we show the diagonal elements of the diabatic energy matrix (7) as a function of R for the lowest 10 R-matrix poles. The six lowest poles, although not identical, are similar in character to the corresponding adiabatic poles [5]. One notes that no crossings are apparent amongst the lowest six poles or between them and the ground state of the ion. A fluctuation for the diagonal energy of the fifth pole is apparent near $R = 1.5\ a_0$ and is discussed later. We find also that the crossing observed for the adiabatic poles 7 and 8 [4] is reproduced in the diabatic treatment, although at a slightly larger internuclear separation. What is different, however, is that the ninth pole makes a crossing with the eighth and seventh poles and for $R \leqslant 1.0\ a_0$ lies below both these poles. In contrast, in the adiabatic

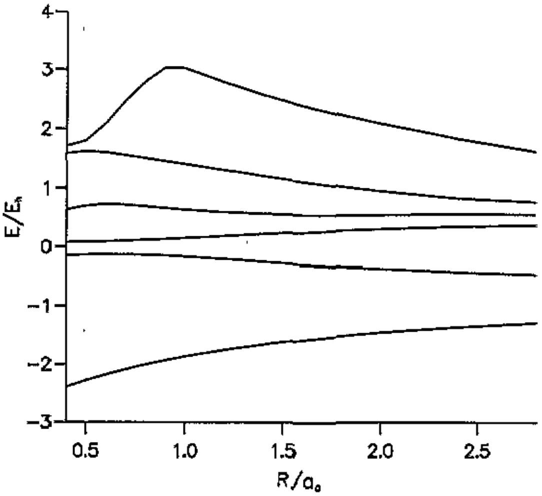

Figure 1. Energies of the HeH^+ molecular orbitals included in our calculation as a function of HeH^+ internuclear separation, R. The lowest curve corresponds to the occupied 1σ orbital, the higher ones are the σ virtual orbitals generated by the SCF calculations. For completeness the behaviour of these orbitals at $R < 0.8\ a_0$ is also shown.

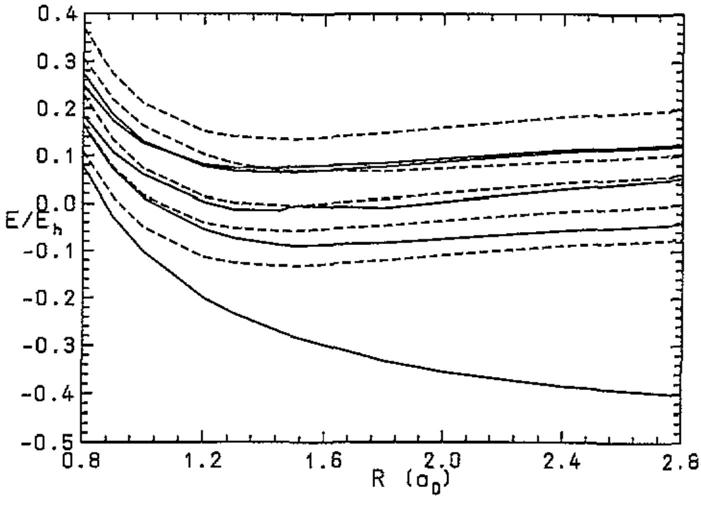

Figure 2. The diabatic potential energy curves, given by the diagonal elements of equation (7), for the lowest 10 R-matrix states as a function of internuclear separation. The zero of the energy scale is the ground-state energy of HeH^+ at $R = 1.455\ a_0$, $-2.951\,208\ E_h$. The full and broken curves are used alternately to aid the eye.

representation, there is no evidence for the ninth pole undergoing an avoided crossing with a lower pole at the internuclear separations considered here [5]. The lowering of the ninth pole is not sufficient to cause a crossing with the potential energy curve for the ionic ground state, within the range of R considered in this work.

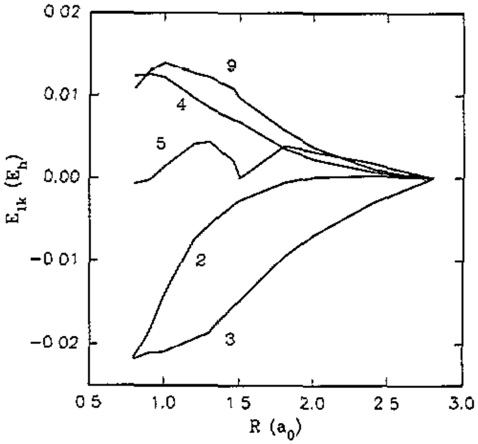

Figure 3. Electronic coupling between the lowest pole and some of the higher lying poles. The reference geometry, R_0, for the diabatization is taken to be 2.8 a_0.

In figure 3 we show the coupling between the lowest diabatic state and some of the other low-lying states as a function of internuclear separation. The coupling terms for states 2 and 3 are similar in character. The large coupling with several of the higher states is evident in figure 3. The largest coupling is found at small internuclear separation, which is consistent with our findings for the bound states of HeH [21] where large interactions at small internuclear separations were most evident in the effective quantum number plots. One should note that all off-diagonal couplings go to zero at our reference geometry by construction, since at this point the electronic wavefunctions are identical to the original adiabatic basis.

These results are in qualitative agreement with those of [17] for HeH bound states calculated with the MRDCI approach in that the coupling terms are largest at small internuclear separation and decrease with increasing R. Quantitative differences can be explained by noting that a different scheme for diabatization is used by them, but a more significant difference is that our adiabatic states do not correspond to real states of HeH but correspond to states of a system confined to a finite spherical region. The real bound states can be expanded in the basis of the R-matrix states, as shown in [21]. We note, however, that a transformation to the real bound states is not appropriate in the context of the present calculations, except for the purposes of projecting onto dissociating channels for the recombined system, because then the advantage of the R-matrix approach in representing the bound states as well as the continuum by a single discrete basis would be lost. The major advantage of our approach is that the coupling matrix contains information not only between bound states but also between both bound and continuum states of electronic and vibrational character.

Figure 3 shows that the matrix element $\varepsilon_{1,5}$ *has a sharp dip around* $R = 1.5\ a_0$ which does not appear to be due to sign changes in the wavefunction near this geometry. This fluctuation has already been noted for the diagonal energy for the fifth pole in figure 2. This feature is related to two MOs which interact strongly near this geometry. As long as both the diagonal and off-diagonal matrix elements are considered consistently such fluctuations pose no problem within our approach. In any case we checked that our results were not too sensitive to this dip, a fact which was verified by manually removing the fluctuation in the

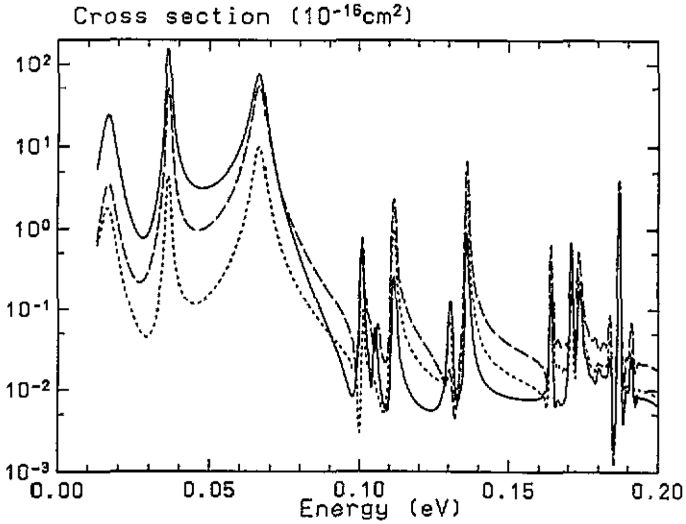

Figure 4. Calculated partial dissociative recombination cross section to the three lowest $^2\Sigma$ states of HeH: full curve, $X\,^2\Sigma$, long dashes, $A\,^2\Sigma$ and short dashes $C\,^2\Sigma$.

diagonal and off-diagonal coupling element. Only small deviations were observed in the very low-energy region, below 0.02 eV.

Figure 4 gives the DR cross section to the three lowest $^2\Sigma$ states of HeH. Below 0.06 eV, the cross section to the ground state, $X\,^2\Sigma$, is largest in magnitude with the cross section to the $A\,^2\Sigma$ being an order of magnitude smaller. The cross section for DR to the $C\,^2\Sigma$ state is smaller still. For higher energies the $A\,^2\Sigma$ channel is the most favoured channel and the ground state has the smallest cross section. The structure in all three partial cross sections is very similar. We note that the window resonance around 0.028 eV is particularly stable to changes in the number of poles coupled or truncation of the summation in (5). The same is also true of the sudden drop in cross section around 0.1 eV which we attribute to large number of Rydberg states lying close together—a list of assignments for the resonances can be found in our earlier work [4, 5]. The fact that DR is due to non-adiabatic coupling was verified by neglecting the couplings between states, i.e. reverting to the formalism of Schneider *et al* [14], when we found that the cross section is effectively zero.

The prediction that the dominant product of DR at low energies is ground state He + H is somewhat counterintuitive. Usually it is assumed that non-adiabatic processes, such as the one considered here, go to the channel nearest in energy. However, it would appear that in this case DR occurs largely as a result of tunnelling through the repulsive wall of the potential curves at short HeH$^+$ bondlengths. At these geometries all the curves correlating with the exit channels (and the infinite number of closed channels) are very close together and it is possible that the usual rules do not apply. However, we should note that our calculation does not include any post dissociation coupling between the exit channels or closed neutral channels and therefore our exact branching ratios should be treated with caution.

Since the completion of this work, a calculation using the MQDT approach has been carried out for ^{3}HeH$^+$ by Guberman [25]. Qualitatively, the total cross section looks similar to that reported for HeH$^+$ here, but it is implied that the main product of DR is $C\,^2\Sigma$ for all energies, although explicitly stated only for 0.001 eV. The recent work of Tanabe *et al* [26] for ^{3}HeH$^+$ reports branching ratios which also appear to suggest the dominance of the H ($n = 2$) channels, but cannot differentiate between the A and C states which have the same asymptote. As can be seen from figure 4, our results show that the branching ratio is a function of scattering energy and for higher energies the $n = 2$ channels are more dominant. The branching ratio given by Guberman is quoted for 0.001 eV scattering energy but the exact energy for which Tanabe *et al* deduce the branching ratio is not reported. Clearly further work is required in order to resolve this discrepancy.

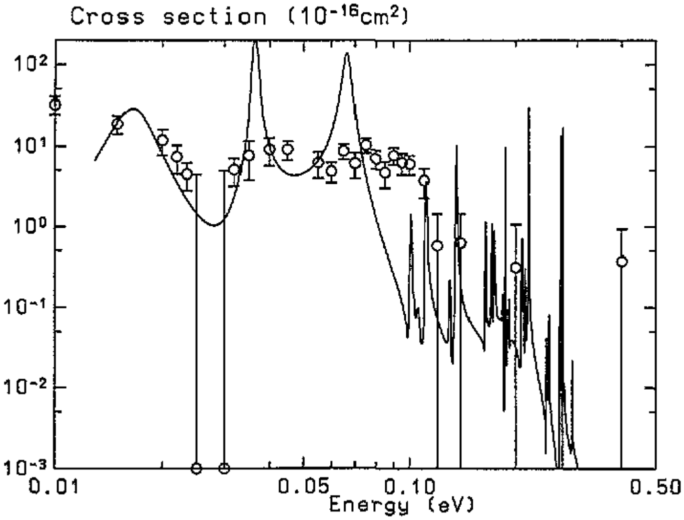

Figure 5. Comparison of our summed calculated dissociative recombination cross section with the experimental results [3].

In figure 5 we compare the summed DR cross section, which is obtained by summing the partial cross sections for the three $^2\Sigma$ states, with the experimental total cross section of Yousif and Mitchell [3]. The agreement between theory and experiment is good, in particular the window resonances are reproduced quite accurately and the cross section displays a sudden decrease around 0.1 eV in both sets of results. Our calculations show more pronounced structure than is apparent in the experimental results, this may be due to (1) energy spread in the experiment which will smooth over resonant features and (2) our neglect of rotational motion, which will be particularly important at lower energies. We have also not yet included the contribution from the $B\,^2\Pi$ state, but we expect this to be much smaller than the Σ contributions since only weak interaction had been observed for the Π symmetry [21].

Recently Yousif *et al* [27] have re-examined the results of Yousif and Mitchell [3] and suggested that the DR cross section is, in fact, due to a metastable $^3\Sigma$ component in their HeH^+ beam. By introducing O_2 into the ion source the triplets are thought to be quenched and they find that the low-energy DR cross section disappears. In a similar experiment on $^3HeH^+$, however, Mowat *et al* [28] and Tanabe *et al* [26] found that oxygen has no effect on the cross section. It is unlikely that quenching should be sensitive to the isotopic species used.

In addition, a survey of ion–molecule reactions by Smith *et al* [29] indicates that the protonating reaction:

$$HeH^+ + O_2 \rightarrow HO_2^+ + He \tag{10}$$

is efficient, with a reaction rate for ground-state HeH^+ almost equal to the collisional rate. One would expect the reaction rate for the excited ion to be even faster due to added exothermiticity making any quenching mechanism less efficient. In the absence of overriding experimental evidence for excited-state quenching we make comparison with the earlier work of Yousif and Mitchell [3] which is supported by other workers [26, 28, 30].

4. Conclusion

We have presented a generalized non-adiabatic R-matrix method which can consider dissociative recombination (DR) for systems without curve crossings. We have calculated *ab initio* the DR cross section for $^4HeH^+$ which is the first ever theoretical determination for this ion. Our results suggest that the DR cross section for species which do not have curve crossings between the dissociating neutral state and the ionic ground state may sometimes be larger than conventionally assumed. For HeH^+, non-adiabatic coupling, which was found to be particularly large at small internuclear separations, has been found to be responsible for this larger than expected cross section.

Qualitatively DR occurs via tunnelling at the inner turning point of the HeH^+ potential where the HeH^+ and HeH curves are close together but do not cross. Tanabe *et al*'s [26] recent experiment observed large isotope effects for DR of HeD^+ as opposed to HeH^+. This is exactly the behaviour we would expect from our tunnelling mechanism and we plan to study DR in both HeD^+ and the $^3HeH^+$ isotopomer studied by Mowat *et al* [28].

Our approximation that adiabatic SCF molecular orbitals are independent of internuclear separation has been shown to be valid in the case of HeH^+, but this may not necessarily be true for many other systems. It may, therefore, be appropriate to work with explicitly frozen molecular orbitals [16] and this will be considered in future work.

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