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## **in theory Dissociative recombination of H<sub>3</sub><sup>+</sup>: progress**

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A. E. Orel, I. F. Schneider and A. Suzor-Weiner

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# $\frac{12000.0659}{\text{Dissociative recombination of H}_3^+}$  $\frac{+}{3}$ : tive recombination of<br>progress in theory

**progress in theory**<br>BY A. E. OREL<sup>1</sup>, I. F. SCHNEIDER<sup>2,3</sup> AND A. SUZOR-WEINER<sup>3,4</sup>

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 $F$ -19254 Furts, France<br>Dissociative recombination is the main destruction process for ground-state  $H_3^+$  in<br>diffuse interstellar medium. Experiments agree on relatively large cross-sections for Dissociative recombination is the main destruction process for ground-state  $H_3^+$  in diffuse interstellar medium. Experiments agree on relatively large cross-sections for this reaction. Time-dependent two-dimensional ca Dissociative recombination is the main destruction process for ground-state  $H_3^+$  in diffuse interstellar medium. Experiments agree on relatively large cross-sections for this reaction. Time-dependent two-dimensional ca diffuse interstellar medium. Experiments agree on relatively large cross-sections for this reaction. Time-dependent two-dimensional calculations confirm the experimental results at high energy as well as the observed pred this reaction. Time-dependent two-dimensional calculations confirm the experimental results at high energy as well as the observed predissociation rates of  $H_3$  Rydberg states, due to non-adiabatic interactions. However, tal results at high energy as well as the observed predissociation rates of  $H_3$  Rydberg states, due to non-adiabatic interactions. However, the value for low-energy cross-section, deduced from the predissociation rates states, due to non-adiabatic interactions. However, the value for low-energy cross-<br>section, deduced from the predissociation rates by an extrapolation procedure, is<br>about four orders of magnitude lower than the measured o section, deduced from the predissociation rates by an extrapolation procedure, is<br>about four orders of magnitude lower than the measured one. A calculation based on<br>multichannel quantum defect theory suggests that an indir about four orders of magnitude lower than the measured one. A calculation based on multichannel quantum defect theory suggests that an indirect non-adiabatic process may prevail in this case. The cross-section increases by multichannel quantum defect theory suggests that an indirect non-adiabatic process<br>may prevail in this case. The cross-section increases by orders of magnitude com-<br>pared with the extrapolated value when indirect couplings may prevail in this case. The cross-section increases by orders of magnitude compared with the extrapolated value when indirect couplings via apparently ineffective channels are properly considered. We discuss how this cha pared with the extrapolated value when indirect couplings via apparently ineffective<br>channels are properly considered. We discuss how this channel-mixing mechanism<br>can be effective in the case of  $H_3^+$ , and show encoura channels are properly considered. We discuss how this channel-mixing mechanism<br>can be effective in the case of  $H_3^+$ , and show encouraging results stressing the role<br>of Rydberg series or 'closed channels'. We also discu can be effective in the case of  $H_3^+$ , and show encourage of Rydberg series or 'closed channels'. We also discusseffects that could enhance the process at low energy.

S that could enhance the process at low energy.<br>Keywords: Rydberg states; interstellar molecules; dissociative recombination;<br>non-adiabatic interactions: predissociation: molecular ion nd childred the process at is a energy.<br>Rydberg states; interstellar molecules; dissociative recombinan-adiabatic interactions; predissociation; molecular ion

### 1. Introduction

The dissociative recombination reaction,

 $M^+ + e^- \rightarrow$  neutral fragments, (1.1)

 $M^+ + e^- \rightarrow$  neutral fragments, (1.1)<br>is the dominant destruction process of molecular ions  $M^+$  in cold plasmas with high<br>electron densities. Such plasmas occur in diffuse interstellar clouds of molecules is the dominant destruction process of molecular ions  $M^+$  in cold plasmas with high<br>electron densities. Such plasmas occur in diffuse interstellar clouds of molecules,<br>planetary atmospheres, supernovae, as well as at th is the dominant destruction process of molecular ions  $M^+$  in cold plasmas with high<br>electron densities. Such plasmas occur in diffuse interstellar clouds of molecules,<br>planetary atmospheres, supernovae, as well as at th electron densities. Such plasmas occur in diffuse interstellar clouds of molecules, planetary atmospheres, supernovae, as well as at the walls of fusion devices (Larsson *et al.* 2000). The neutral fragments produced by t M<sup>+</sup> is a polyatomic ion) molecules usually in an excited state and may initiate chains<br>of reactions that would be energetically forbidden with ground-state reactants. The<br>dissociative recombination (DR) thus appears as a etary atmospheres, supernovae, as well as at the walls of fusion devices (Larsson<br>i. 2000). The neutral fragments produced by the reaction (1.1) are atoms or (if<br>is a polyatomic ion) molecules usually in an excited state a *et al.* 2000). The neutral fragments produced by the reaction (1.1) are atoms or (if  $M^+$  is a polyatomic ion) molecules usually in an excited state and may initiate chains of reactions that would be energetically forbi of reactions that would be energetically forbidden with ground-state reactants. The dissociative recombination (DR) thus appears as a key reaction for the chemistry of ionized media, in particular for astrochemistry.

2445

<sup>2446</sup> *A. E. Orel,I.F.SchneiderandA. Suzor-Weiner*

46 *A. E. Orel, I. F. Schneider and A. Suzor-Weiner*<br>The case of  $H_3^+$  has been, and still is, an enigma. The experimental history is<br>scribed in this issue by Larsson. A very small upper limit was assigned to the rate The case of  $H_3^+$  has been, and still is, an enigma. The experimental history is described in this issue by Larsson. A very small upper limit was assigned to the rate for  $H_2^+$  DR around 1984, based on experimental in The case of  $H_3^+$  has been, and still is, an enigma. The experimental history is<br>described in this issue by Larsson. A very small upper limit was assigned to the rate<br>for  $H_3^+$  DR around 1984, based on experimental in described in this issue by Larsson. A very small upper limit was assigned to the rate<br>for  $H_3^+$  DR around 1984, based on experimental investigation using the FALP tech-<br>nique (Smith & Adams 1984). It was estimated to be for H<sup>+</sup><sub>3</sub> DR around 1984, based on experimental investigation using the FALP technique (Smith & Adams 1984). It was estimated to be less than  $10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> at low temperature, that is about four orders of magnitu nique (Smith & Adams 1984). It was estimated to be less than  $10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> at low<br>temperature, that is about four orders of magnitude less than most usual DR rates.<br>This small value was supported by theoretical est temperature, that is about four orders of magnitude less than most usual DR rates.<br>This small value was supported by theoretical estimates based on the unfavourable<br>Franck–Condon overlap between the ion ground state and an the neutral molecule  $H_3$  (Kulander & Guest 1979; Michels & Hobbs 1984). However, in 1989, a single-pass merged-beams experiment (Yousif & Mitchell 1989) the neutral molecule H<sub>3</sub> (Kulander & Guest<br>ever, in 1989, a single-pass merged-beams e<br>measured a much faster rate  $(ca.10^{-8} \text{ cm}^3 \text{ s}^-$ <br>faster  $(ca.10^{-7} \text{ cm}^3 \text{ s}^{-1})$  a few years later by u  $(s^{-1}),$ 979; Michels & Hobbs 1984). How-<br>periment (Yousif & Mitchell 1989)<br>), which was then found to be still<br>ulti-pass storage-ring measurements ever, in 1989, a single-pass merged-beams experiment (Yousif & Mitchell 1989)<br>measured a much faster rate  $(ca. 10^{-8} \text{ cm}^3 \text{ s}^{-1})$ , which was then found to be still<br>faster  $(ca. 10^{-7} \text{ cm}^3 \text{ s}^{-1})$  a few years later by m faster  $(ca. 10^{-7} cm^3 s^{-1})$  a few years later by multi-pass storage-ring measurements measured a much faster rate  $(ca.10^{-8} \text{ cm}^3 \text{ s}^{-1})$ , which was then found to be still faster  $(ca.10^{-7} \text{ cm}^3 \text{ s}^{-1})$  a few years later by multi-pass storage-ring measurements (Laubé *et al.* 1993) as well as in flowin faster  $(ca. 10^{-7} \text{ cm}^3 \text{ s}^{-1})$  a few years later by multi-pass storage-ring measurement (Laubé *dl.* 1998). Most of the experiments finally agreed on a value close to *ca*.  $10^{-7} \text{ cm}^3 \text{ s}^{-1}$  at  $T = 100 \text{ K}$ , which  $s^{-1}$ (Larsson *et al.* 1993) as well as in flowing afterglow discharge experiments (Laubé *et al.* 1998). Most of the experiments finally agreed on a value close to  $ca$ .  $10^{-7}$  cm<sup>3</sup> s<sup>-1</sup> at  $T = 100$  K, which has been used i at. 1998). Most of the experiments finally agreed on a value close to  $ca. 10^{-7}$  cm<sup>3</sup> s<sup>-1</sup> at  $T = 100$  K, which has been used in interstellar modelling. However, some plasmatype studies (Smith & Španel 1993; Gougousi *e* at  $T = 100$  K, which has been used in interstellar modelling. However, some plasma-<br>type studies (Smith & Španel 1993; Gougousi *et al.* 1995) measured rates smaller by<br>one order of magnitude. Some doubts still persist (G type studies (Smith & Spanel 1993; Gougousi *et al.* 1995) measured rates smaller by<br>one order of magnitude. Some doubts still persist (Gougousi *et al.* 1995) about the<br>influence of the inherent electric fields on the re one order of magnitude. Some doubts still persist (Gougou<br>influence of the inherent electric fields on the recombinati<br>result in an overestimation of the field-free thermal rates.<br>The merged-beams experiments have also mea influence of the inherent electric fields on the recombination process, which could result in an overestimation of the field-free thermal rates.<br>The merged-beams experiments have also measured branching ratios between the

three-body  $(H + H + H)$  and two-body  $(H + H<sub>2</sub>)$  dissociation. The three-body dissociation path represents 75% of the total DR cross-section at thermal energies, three-body  $(H + H + H)$  and two-body  $(H + H<sub>2</sub>)$  dissociation. The three-body dissociation path represents 75% of the total DR cross-section at thermal energies, decreasing progressively to *ca*. 30% around 6 eV and becoming sociation path re<br>decreasing progre<br>higher energies.<br>Surprisingly, the creasing progressively to  $ca. 30\%$  around  $6 \text{ eV}$  and becoming dominant again at gher energies.<br>Surprisingly, the  $H_3^+$  column densities in both diffuse and dense interstellar regions are found to be large and of the

higher energies.<br>Surprisingly, the  $H_3^+$  column densities in both diffuse and dense interstellar regions<br>were found to be large and of the same order of magnitude. This is hard to explain<br>with a fast DR rate, since much Surprisingly, the  $H_3^+$  column densities in<br>were found to be large and of the same or<br>with a fast DR rate, since much less  $H_3^+$  sh<br>dense ones due to a much higher electron of s in both diffuse and dense interstellar regions<br>  $\frac{1}{3}$  e order of magnitude. This is hard to explain<br>  $\frac{1}{3}$  should survive DR in diffuse clouds than in<br>
ron density This is part of the enjoma around were found to be large and of the same order of magnitude. This is hard to explain<br>with a fast DR rate, since much less  $H_3^+$  should survive DR in diffuse clouds than in<br>dense ones, due to a much higher electron density  $H_3^+$  DR ith a fast DR rate, since much less  $H_3^+$  should survive DR in diffuse clouds than in<br>ense ones, due to a much higher electron density. This is part of the enigma around<br> $\frac{1}{3}$  DR. Another unsolved puzzle is the lack dense ones, due to a much higher electron<br> $H_3^+$  DR. Another unsolved puzzle is the<br>to date for the fast DR rate measured.<br>In  $\delta$  2 we summarize the results of cross EXECT DR. Another unsolved puzzle is the lack of theoretical quantitative explanation<br>date for the fast DR rate measured.<br>In § 2 we summarize the results of cross-section calculations for recombination with<br>the electrons

to date for the fast DR rate measured.<br>In  $\S 2$  we summarize the results of cross-section calculations for recombination with<br>fast electrons (1-12 eV) using a time-dependent approach (Orel 2000). In this energy In § 2 we summarize the results of cross-section calculations for recombination with<br>fast electrons  $(1-12 \text{ eV})$  using a time-dependent approach (Orel 2000). In this energy<br>region, DR may proceed by its most usual (and m fast electrons  $(1-12 \text{ eV})$  using a time-dependent approach (Orel 2000). In this energy<br>region, DR may proceed by its most usual (and most efficient) mechanism, with a<br>direct electronic interaction between the ion-plus-e region, DR may proceed by its most usual (and most efficient) mechanism, with a direct electronic interaction between the ion-plus-electron initial complex and a dissociative surface of the neutral molecule. Experiment and direct electronic interaction between the ion-plus-electron initial complex and a dis-<br>sociative surface of the neutral molecule. Experiment and theory agree on relatively<br>large values for the DR cross-section and rate. Se sociative surface of the neutral molecule. Experiment and theory agree on relatively<br>large values for the DR cross-section and rate. Section 3 deals with the low-energy<br>region, close to the ionization threshold and far fro large values for the DR cross-section and rate. Section 3 deals with the low-energy<br>region, close to the ionization threshold and far from any dissociative valence state.<br>Here, we have to rely on non-adiabatic interaction region, close to the ionization threshold and far from any dissociative valence state.<br>Here, we have to rely on non-adiabatic interactions between non-crossing potential<br>surfaces, much as for the case of HeH<sup>+</sup> DR, which Here, we have to rely on non-adiabatic interactions between non-crossing potential surfaces, much as for the case of  $HeH^+$  DR, which has been studied theoretically for the last few years (Guberman 1994; Sarpal *et al.* 1 surfaces, much as for the case of HeH<sup>+</sup> DR, which has been studied theoretically for<br>the last few years (Guberman 1994; Sarpal *et al.* 1994). A non-adiabatic coupling<br>with the dissociative ground-state surface of H<sub>3</sub> e the last few years (Guberman 1994; Sarpal *et al.* 1994). A non-adiabatic coupling<br>with the dissociative ground-state surface of  $H_3$  explains well the predissociation<br>observed for various Rydberg states below threshold with the dissociative ground-state surface of  $H_3$  explains well the predissociation<br>observed for various Rydberg states below threshold (Schneider & Orel 1999), but<br>extrapolation of this mechanism into the continuum lea observed for various Rydberg states below threshold (Schneider  $\&$  Orel 1999), but extrapolation of this mechanism into the continuum leads to a much lower value for the cross-section than in the experiments. Section 4 e extrapolation of this mechanism into the continuum leads to<br>the cross-section than in the experiments. Section 4 explores<br>indirect interaction with a series of bound Rydberg states. indirect interaction with a series of bound Rydberg states.<br>2. The high-energy region

2. The high-energy region<br>Quantum chemistry calculations (Kulander & Guest 1979; Michels & Hobbs 1984;<br>Orel & Kulander 1993) have shown that doubly excited dissociative states cross the Quantum chemistry calculations (Kulander & Guest 1979; Michels & Hobbs 1984;<br>Orel & Kulander 1993) have shown that doubly excited dissociative states cross the Orel & Kulander 1993) have shown that doubly excited dissociative states cross the *Phil. Trans. R. Soc. Lond.* A (2000)

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Dissociative recombination of  $H_3^+$  2447<br>ionic electronic potential more than 1 eV *above* the  $H_3^+$  ground vibrational state<br>(threshold) in  $C_{2v}$  geometry. The lowest of the corresponding potential surfaces corionic electronic potential more than  $1 \text{ eV}$  *above* the  $H_3^+$  ground vibrational state (threshold) in  $C_{2v}$  geometry. The lowest of the corresponding potential surfaces correlates diabatically to the ion-pair  $(H_2^$ ionic electronic potential more than  $1 \text{ eV}$  *above* the  $H_3^+$  ground vibrational state (threshold) in  $C_{2v}$  geometry. The lowest of the corresponding potential surfaces correlates diabatically to the ion-pair  $(H_2^$ (threshold) in  $C_{2v}$  geometry. The lowest of the corresponding potential surfaces correlates diabatically to the ion-pair  $(H_2^+ + H^-)$  limit and adiabatically to the lowest  $(H_2 + H (n = 2))$  limit, situated 0.974 eV above th relates diabatically to the ion-pair  $(H_2^+ + H^-)$  limit and adiabatically to the lowest  $(H_2 + H (n = 2))$  limit, situated 0.974 eV above threshold. Electrons with at least efficient electronic couplings, as in the case of most diatomic ions.<br>The strengths of these couplings have been evaluated by Orel & Kulander  $(1993)$ this kinetic energy may, thus, recombine directly into dissociative states through

efficient electronic couplings, as in the case of most diatomic ions.<br>The strengths of these couplings have been evaluated by Orel & Kulander (1993)<br>and, together with the energies of the relevant states, have been used t The strengths of these couplings have been evaluated by Orel & Kulander (1993) and, together with the energies of the relevant states, have been used to perform a time-dependent wave packet (TDWP) calculation (Heller 1978 and, together with the energies of the relevant states, have been used to perform a<br>time-dependent wave packet (TDWP) calculation (Heller 1978; Kulander & Heller<br>1978; Orel & Kulander 1989) of the DR cross-section above 1 1993). 78; Orel & Kulander 1989) of the DR cross-section above 1 eV (Orel & Kulander<br>93).<br>The wave packet method proceeds by the direct integration of the time-dependent<br>brödinger equation Using the Jacobi coordinates  $(r, B, \theta)$ 

The wave packet method proceeds by the direct integration of the time-dependent Schrödinger equation. Using the Jacobi coordinates  $(r, R, \theta)$  and working within the The wave packet method proceeds by the direct integration of the time-dependent<br>Schrödinger equation. Using the Jacobi coordinates  $(r, R, \theta)$  and working within the<br> $C_{2v}$  symmetry,  $\theta = 90^{\circ}$ , this equation becomes, fo Schrödinger equation. Using the Jacobi coordinates  $(r, R, C_{2v}$  symmetry,  $\theta = 90^{\circ}$ , this equation becomes, for the excited dissociative state of potential energy  $U_{\text{diss}}(r, R)$ : excited dissociative state of potential energy  $U_{\text{diss}}(r, R)$ :

d dissociative state of potential energy 
$$
U_{\text{diss}}(r, R)
$$
:  
\n
$$
i\hbar \frac{\partial}{\partial t} \Psi(r, R; t) = \{ \mathbf{T}(r, R) + U_{\text{diss}}(r, R) - i\pi [V^{(\text{el})}(r, R)]^2 \} \Psi(r, R; t).
$$
\n(2.1)

 $i\hbar \frac{\partial}{\partial t} \Psi(r, R; t) = \{ \mathbf{T}(r, R) + U_{\text{diss}}(r, R) - i\pi [V^{(\text{el})}(r, R)]^2 \} \Psi(r, R; t).$  (2.1)<br>Here,  $\mathbf{T}(r, R)$  is the nuclear kinetic energy operator,  $V^{(\text{el})}(r, R)$  is the electronic cou-<br>pling between the ionization and dissoci Here,  $T(r, R)$  is the nuclear kinetic energy operator,  $V^{(el)}(r, R)$  is the electronic coupling between the ionization and dissociation continua, and the complex imaginary term appearing in the Hamiltonian accounts for auto Here,  $T(r, R)$  is the nuclear kinetic energy operator,  $V^{(el)}(r, R)$  is the electronic coupling between the ionization and dissociation continua, and the complex imaginary term appearing in the Hamiltonian accounts for auto state. The initial wave packet is given by the action of the electronic coupling on the continual electronic of the target ion.

state.<br>The initial wave packet is given by the a<br>vibrational eigenfunction of the target ion: Figure is given by the<br>tion of the target ion<br> $\Psi(r, R; t = 0) = V^{\text{(el)}}($ (el)(r, R) $\chi_{v_{\rm s}}(Q_{\rm s})\chi_{v_{\rm b}}(Q_{\rm b}),$  (2.2)

$$
\Psi(r, R; t = 0) = V^{(\text{el})}(r, R) \chi_{v_{\text{s}}}(Q_{\text{s}}) \chi_{v_{\text{b}}}(Q_{\text{b}}), \tag{2.2}
$$

the latter being approximated as the product of the harmonic oscillator wave functhe latter being approximated as the product of the harmonic oscillator wave func-<br>tions  $\chi_{v_{\rm s}}(Q_{\rm s})$  and  $\chi_{v_{\rm b}}(Q_{\rm b})$  in the symmetric stretch and bending normal modes of<br> $H_{\rm s}^+$  $H_3^+$ . ons  $\chi_{v_{\rm s}}(Q_{\rm s})$  and  $\chi_{v_{\rm b}}(Q_{\rm b})$  in the symmetric stretch and bending normal  $\frac{1}{3}$ .<br>The DR cross-section is evaluated using the formula (in atomic units)

The DR cross-section is evaluated using the formula (in atomic units)

$$
\sigma = (2\pi^3/\varepsilon)(\frac{1}{2}g)S(E),\tag{2.3}
$$

where  $\varepsilon$  is the energy of the incident electron, E is the total energy, i.e. the sum of  $\varepsilon$ where  $\varepsilon$  is the energy of the incident electron, E is the total energy, i.e. the sum of  $\varepsilon$ <br>and the initial energy of the target ion, and g is the ratio of the multiplicities of the<br>neutral and ion states. S is calcu where  $\varepsilon$  is the energy of the incident electron,  $E$  is the total energy, i.e. the sum of  $\varepsilon$  and the initial energy of the target ion, and  $g$  is the ratio of the multiplicities of the neutral and ion states.  $S$  is and the initial energy of the target ion, and g is the ratio of the multiplicities of the<br>neutral and ion states. S is calculated by projecting the propagated wave function<br> $\Psi(r, R; t)$  for large times on the asymptotic cha neutral and ion states. S is calculated by projecting the propagated wave function  $\Psi(r, R; t)$  for large times on the asymptotic channel eigenfunctions (Kulander & Heller 1978). When the final products of the dissociation  $\Psi(r, R; t)$  for large times on the asymptotic channel eigenfunctions (K<br>Heller 1978). When the final products of the dissociation are an atom and<br>molecule in the vibrational level v, we can define  $S_2(E)$  (two-body) as

$$
S_2(E) = \frac{m_R}{2\pi k} \sum_v \lim_{t \to \infty} \left| \iint \phi_v(r) e^{ikR} \Psi(r, R; t) \, dr \, dR \right|^2, \tag{2.4}
$$

where  $\phi_v(r)$  is a vibrational wave function of  $H_2$ ,  $e^{ikR}$  is the plane wave describing<br>the relative motion along the *R* coordinate between H and H<sub>2</sub>, and  $m_P$  is the reduced where  $\phi_v(r)$  is a vibrational wave function of  $H_2$ ,  $e^{ikR}$  is the plane wave describing<br>the relative motion along the R coordinate between H and  $H_2$ , and  $m_R$  is the reduced<br>mass associated to this motion. Once the where  $\phi_v(r)$  is a vibrational wave function of  $H_2$ ,  $e^{ikR}$  is the plane wave describing<br>the relative motion along the R coordinate between H and  $H_2$ , and  $m_R$  is the reduced<br>mass associated to this motion. Once the the relative motion along the R coordinate between H and  $H_2$ , and  $m_R$  is the reduced mass associated to this motion. Once the sum in equation (2.4) is extended to include the continuum states of  $H_2$ , the result is th ass associated to this motion. Once the sum in equation (2.4) is extended to include<br>e continuum states of  $H_2$ , the result is the total DR cross-section.<br>This formalism allowed the first successful modelling of the  $H_3$ 

the continuum states of  $H_2$ , the result is the total DR cross-section.<br>This formalism allowed the first successful modelling of the  $H_3^+$  and  $D_3^+$  DR, and the main results are shown in figure 1. The theoretical cro *Phil. Trans. R. Soc. Lond.* A (2000) **Phil.** The theoretical cross-sections, including the *Phil. Trans. R. Soc. Lond.* A (2000)

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<sup>2448</sup> *A. E. Orel,I.F.SchneiderandA. Suzor-Weiner*



energy (eV)<br>Figure 1. (a)  $H_3^+$  and (b)  $D_3^+$  DR cross-section. Circles denote experimental data obtained with<br>CRYRING (Larsson et al. 1993–1997). The solid line denotes theoretical results for high energy Figure 1. (a)  $H_3^+$  and (b)  $D_3^+$  DR cross-section. Circles denote experimental data obtained with<br>CRYRING (Larsson *et al.* 1993, 1997). The solid line denotes theoretical results for high energy,<br>based on the TDWP m CRYRING (Larsson *et al.* 1993, 1997). The solid line denotes theoretical results for high energy, based on the TDWP method (Orel & Kulander 1993) (see text).

based on the TDWP method (Orel & Kulander 1993) (see text).<br>contribution of four doubly excited states, reproduce the experimental peaks around<br>10 eV quite well. However, they fall dramatically outside the peak region, lea 20 contribution of four doubly excited states, reproduce the experimental peaks around<br>10 eV quite well. However, they fall dramatically outside the peak region, leaving the<br>large experimental cross-sections unexplained in contribution of four doubly excited states, reproduce the experimental per 10 eV quite well. However, they fall dramatically outside the peak region, large experimental cross-sections unexplained in the low-energy range.

# 3. The low-energy region (*a*) *Which mechanism?*

 $(a)$  Which mechanism?<br>Since the doubly excited states are closed for dissociation below 0.974 eV, the only<br>available dissociation channel at low energy is the ground state, whose potential Since the doubly excited states are closed for dissociation below  $0.974 \text{ eV}$ , the only available dissociation channel at low energy is the ground state, whose potential surface *does not cross* that of the ion. For man Since the doubly excited states are closed for dissociation below  $0.974 \text{ eV}$ , the only available dissociation channel at low energy is the ground state, whose potential surface *does not cross* that of the ion. For man available dissociation channel at low energy is the ground state, whose potential<br>surface *does not cross* that of the ion. For many years, this fact has been considered<br>as an indication of a very low DR rate at thermal en surface *does not cross* that of the ion. For many years, this fact has been considered<br>as an indication of a very low DR rate at thermal energies due to a small overlap<br>of the nuclear wave functions, in contradiction wit as an indication of a very low DR rate at thermal energies due to a small overlap<br>of the nuclear wave functions, in contradiction with the high measured rates. In<br>addition, no electronic interaction may couple the H<sub>3</sub> gr of the nuclear wave functions, in contradiction with the highlarities addition, no electronic interaction may couple the  $H_3$  ground inization continuum, which differ by only one spin-orbital.<br>However, an example has rec addition, no electronic interaction may couple the  $H_3$  ground state and the lowest<br>ionization continuum, which differ by only one spin-orbital.<br>However, an example has recently been found of relatively fast DR in a simi

ionization continuum, which differ by only one spin-orbital.<br>
However, an example has recently been found of relatively fast DR in a similar<br>
situation, for the HeH<sup>+</sup> ion. Here also, no low-lying valence state may dissoc However, an example has recently been found of relatively fast DR in a similar situation, for the HeH<sup>+</sup> ion. Here also, no low-lying valence state may dissociate the molecular system formed by the ion ground state and a situation, for the HeH<sup>+</sup> ion. Here also, no low-lying valence state may dissociate<br>the molecular system formed by the ion ground state and a slow electron, but non-<br>adiabatic interaction with dissociative Rydberg states the molecular system formed by the ion ground state and a slow electron, but non-<br>adiabatic interaction with dissociative Rydberg states has proved to be effective.<br>Although their potential curves do not cross the ion cur adiabatic interaction with dissociative Rydberg states has proved to be effective.<br>Although their potential curves do not cross the ion curve, three independent calculations (Guberman 1994; Sarpal *et al.* 1994; Tanabe *et* Although their potential curves do not cross the ion curve, three independent calculations (Guberman 1994; Sarpal *et al.* 1994; Tanabe *et al.* 1998) have shown that these Rydberg states lead to a relatively fast DR process, in good agreement with merged-beam measurements (Yousif & Mitchell 1989; Strö these Rydberg<br>merged-beam<br>*et al.* 1998). *Phil. Trans. R. Soc. Lond.* A (2000)

**IATHEMATICAL,<br>HYSICAL**<br>< ENGINEERING

THE ROYAL<br>SOCIETY

**PHILOSOPHICAL**<br>TRANSACTIONS

IYSICAL<br>ENGINEERING **ATHEMATICAL** 

## $Dissociative\ recombination\ of\ H_3^+$  $Dissociative\ recombination\ of\ H_3^+$  $Dissociative\ recombination\ of\ H_3^+$ Downloaded from rsta.royalsocietypublishing.org

*Dissociative recombination of*  $H_3^+$  2449<br>Based on these studies, we have explored the same mechanism for the case of  $H_3^+$ <br>R. Since the DR of a ground-state ion is strongly related to the predissociation of Based on these studies, we have explored the same mechanism for the case of  $H_3^+$ <br>DR. Since the DR of a ground-state ion is strongly related to the predissociation of<br>Rydberg states converging to the same ion state (see Based on these studies, we have explored the same mechanism for the case of  $H_3^+$ <br>DR. Since the DR of a ground-state ion is strongly related to the predissociation of<br>Rydberg states converging to the same ion state (see DR. Since the DR of a ground-state ion is strongly related to the predissociation of Rydberg states converging to the same ion state (see  $\S 3c$ ), we started by studying the predissociation of H<sub>3</sub> Rydberg states—for whic Rydberg states converging to the same ion state (see  $\S 3c$ ), we started by studying<br>the predissociation of H<sub>3</sub> Rydberg states—for which many experimental data are<br>available (Helm 1993; Müller & Cosby 1996)—in view of a available (Helm 1993; Müller & Cosby 1996)—in view of a later extension of the same formalism to the DR calculation.

 $+$ 

 $\frac{1}{3}$  2449

#### (*b*) *The predissociation of*  $H_3$

Predissociation is a non-radiative transition from a bound to a dissociative state. Predissociation is a non-radiative transition from a bound to a dissociative state.<br>In the case of the low Rydberg states of  $H_3$ , this transition is attributed to the (dissociative) ground state. It results from a break Predissociation is a non-radiative transition from a bound to a dissociative state.<br>In the case of the low Rydberg states of  $H_3$ , this transition is attributed to the (dissociative) ground state. It results from a break In the case of the low Rydberg states of H<sub>3</sub>, this transition is attributed to the (dissociative) ground state. It results from a breakdown of the Born-Oppenheimer approximation, due to a kinetical coupling between the a (dissociative) ground state. It results from a breakdown of the Born–Oppenheimer<br>approximation, due to a kinetical coupling between the adiabatic molecular states.<br>If we label two of these electronic states by  $\Psi_i$  and approximation, due to a kinetical coupling be<br>If we label two of these electronic states by<br>adiabatic coupling is given by the operator adiabatic coupling is given by the operator

$$
\boldsymbol{V}_{i,j}^{(\text{na})} = -\frac{\hbar^2}{m_r} \langle \Psi_i | \frac{\partial}{\partial r} | \Psi_j \rangle \frac{\partial}{\partial r} - \frac{\hbar^2}{m_R} \langle \Psi_i | \frac{\partial}{\partial R} | \Psi_j \rangle \frac{\partial}{\partial R} - \frac{\hbar^2}{I} \langle \Psi_i | \frac{\partial}{\partial \theta} | \Psi_j \rangle \frac{\partial}{\partial \theta}, \tag{3.1}
$$

where the matrix elements represent integration over electronic coordinates only. In where the matrix elements represent integration over electronic coordinates only. In<br>the above formula,  $m_r$  is the reduced mass associated to the internuclear motion<br>along r, and I is the momentum of inertia. where the matrix elements represent integrat<br>the above formula,  $m_r$  is the reduced mass<br>along r, and I is the momentum of inertia.<br>We have applied the analytic gradient to e above formula,  $m_r$  is the reduced mass associated to the internuclear motion<br>ong r, and I is the momentum of inertia.<br>We have applied the analytic gradient technique (Lengsfield & Yarkony 1992)<br>evaluate the non-adiabat

along r, and I is the momentum of inertia.<br>We have applied the analytic gradient technique (Lengsfield & Yarkony 1992)<br>to evaluate the non-adiabatic matrix elements, i.e. the bra-kets in equation (3.1), relevant for the couplings between the  $2p(^{2}E')$  ground state of H<sub>3</sub> and the 2s, 3s, to evaluate the non-adiabatic matrix elements, i.e. the bra-kets in equation (3.1),<br>relevant for the couplings between the  $2p(^{2}E')$  ground state of H<sub>3</sub> and the 2s, 3s,<br>4s(<sup>2</sup>A<sup>1</sup>) and  $3p(^{2}E')$  Rydberg states. The cal relevant for the couplings between the  $2p(^2E')$  ground state of H<sub>3</sub> and the 2s, 3s,  $4s(^2A'_1)$  and  $3p(^2E')$  Rydberg states. The calculations were carried out on a three-<br>dimensional grid that spanned the Franck–Condon re  $4s(^{2}A'_{1})$  and  $3p(^{2}E)$ <br>dimensional grid t<br>state of the  $H_{3}^{+}$  io:<br>The non-adiaba  $<sup>+</sup>$  ion.</sup> dimensional grid that spanned the Franck–Condon region for the ground vibrational state of the  $H_3^+$  ion.<br>The non-adiabatic coupling being determined, we used the technique described in

<sup>x</sup> 2 to solve the time-dependent Schrodinger equation for propagation on the *ground-*The non-adiabatic coupling being determined, we used the technique described in  $\S 2$  to solve the time-dependent Schrödinger equation for propagation on the *ground-*<br>*state* surface in two dimensions, i.e. for  $\theta = 90^{\$  $\S 2$  to solve the time-dependent Schrödinger equation for propagation on the *ground-*<br>state surface in two dimensions, i.e. for  $\theta = 90^{\circ}$ ,  $C_{2v}$  symmetry, and for the case of<br>zero total angular momentum (Schneider state surface in two dimensions, i.e. for  $\theta = 90^{\circ}$ ,  $C_{2v}$  symmetry, and for the case of zero total angular momentum (Schneider & Orel 1999). More specifically, in equation (2.2) the vibrational wave function of the zero total angular momentum (Schneider & Orel 1999). More specifically, in equation (2.2) the vibrational wave function of the predissociating H<sub>3</sub> Rydberg state was approximated with that of the H<sub>3</sub><sup>+</sup> ion corresponding tion (2.2) the vibrational wave funct<br>approximated with that of the  $H_3^+$  i<br>tum number, and the function  $V^{(el)}$ <br>(equation (3.1)) corresponding to t unction of the predissociating H<sub>3</sub> Rydberg state was<br> $H_3^+$  ion corresponding to the same vibrational quan-<br> $\frac{(\text{el})}{(r, R)}$  was replaced with the operator  $\mathbf{V}^{(\text{na})}(r, R)$ <br>to the non-adiabatic interaction between th approximated with that of the  $H_3^+$  ion corresponding to the same vibrational quan-<br>tum number, and the function  $V^{(el)}(r, R)$  was replaced with the operator  $V^{(na)}(r, R)$ <br>(equation (3.1)), corresponding to the non-adiaba tum number, and the function  $V^{(el)}(r, R)$  was replaced with the operator  $V^{(na)}(r)$  (equation (3.1)), corresponding to the non-adiabatic interaction between the F berg and the ground states (the indices *i* and *j* will b quation (3.1)), corresponding to the non-adiabatic interaction between the Ryd-<br>rg and the ground states (the indices *i* and *j* will be omitted from now on).<br>The rate  $\alpha$ , lifetime  $\tau$  and width  $\Gamma$  for the predissoc

berg and the ground states (the indices *i* and *j* will be omitted from now on).<br>The rate  $\alpha$ , lifetime  $\tau$  and width  $\Gamma$  for the predissociation of a state having the total (electronic plus vibrational) energy  $E$  ar

$$
\alpha = \frac{1}{\tau} = \frac{\Gamma}{\hbar} = \frac{2\pi}{\hbar}S(E),\tag{3.2}
$$

where  $S(E)$  is given either by equation (2.4), or by performing the Fourier transform  $\begin{array}{cc} \tau & h & h \\ \text{where } S(E) \text{ is given either by equation (2.4), or by performing the Fourier transform of the overlap between the propagated and initial wave function (Heller 1978):} \end{array}$ 

\n Ween the propagated and initial wave function (Heller 1978):\n 
$$
S(E) = \int_{-\infty}^{\infty} e^{iEt/\hbar} \langle \Psi(r, R; t = 0) | \Psi(r, R; t) \rangle \, \mathrm{d}t. \tag{3.3}
$$
\n

 $S(E) = \int_{-\infty} e^{iEt/\hbar} \langle \Psi(r, R; t = 0) | \Psi(r, R; t) \rangle dt.$  (3.3)<br>We have evaluated predissociation rates for the ground vibrational levels of the  $(^{2}A')$  3s( $^{2}A'$ ) and 3p( $^{2}E'$ ) states and for the first excited symmetric stretc  $2s(^{2}A'_{1})$ ,  $3s(^{2}A'_{1})$  and  $3p(^{2}E')$  states, and for the first excited symmetric stretch mode have evaluated predissociation rates for the ground vibrational levels of the  $(3, 3s(2A_1')$  and  $3p(2E')$  states, and for the first excited symmetric stretch mode

*Phil. Trans. R. Soc. Lond.* A (2000)

**MATHEMATICAL,<br>PHYSICAL**<br>& ENGINEERING<br>SCIENCES

PHILOSOPHICAL THE ROYAL

<sup>2450</sup> *A. E. Orel,I.F.SchneiderandA. Suzor-Weiner*

			theory		experiment	
	state <sup>a</sup>	energy $(eV)^{b}$	two-body rate $(10^7 \text{ s}^{-1})$	three-body rate $(10^7 \text{ s}^{-1})$	two-body rate $(10^7 \text{ s}^{-1})^{\circ}$	total decay rate $(10^7 \text{ s}^{-1})^d$
$H_3$	$2s^{2}A'_{1}(0,0)$	5.449	$5.7 \times 10^{4}$			$5.65 \times 10^{5}$
	$3p^2E'(0,0)$	7.194	$7.9 \times 10^{2}$	$1.77 \times 10^{3}$		
	$3s^{2}A_{1}^{\prime}(0,0)$	7.634	8.2	4.2	7.1	$\cdot \cdot$ < 9.4
						$1.0 < \cdot \cdot \cdot < 5.0$
						$2.5 < \cdots < 12.5$
	$3s^{2}A'_{1}(1,0)$	8.031	44	29	$4 - 40^\circ$	
$D_3$	$2s^{2}A_{1}^{\prime}(0,0)$	5.348	$8.65 \times 10^{3}$			
	$3p^2E'(0,0)$	7.093	21	38		
	$3s^{2}A'_{1}(0,0)$	7.533	0.2	0.06		
	$3s^{2}A_{1}^{\prime}(1,0)$	7.819	1.6	0.4		

Table 1. *Predissociation rates of* <sup>H</sup><sup>3</sup> *and* <sup>H</sup><sup>3</sup> *Rydberg states*

<sup>a</sup>The vibrational quantum numbers of the symmetric stretch and bending mode are indicated in the parentheses; the angular quantum numbers are  $N = 1$  and  $K = 0$ .<br><sup>b</sup> Relative to H<sub>2</sub><sup>1</sup> $\Sigma_g^+$  ( $v = 0$ ) + H ( $n = 1$ ).<br><sup>c</sup> From Müller & Cosby (1996).

 $^1\Sigma_g^+$  (v

<sup>d</sup>The total decay rate is the sum of the rates for radiative decay and two- and three-body predissociation.

<sup>e</sup> According to U. Müller (personal communication).



vibrational quantum numb<br>Figure 2. Relative vibrational populations in the  $H_2^{-1} \Sigma_g^+ (v)$ <br>sociation of the  $(v_+ = 1, v_+ = 0)$  vibrational states of the 3 mumber v<br>  $y = \frac{y + y}{y}$ <br>  $y = \frac{y + z}{y}$ <br>  $y = \frac{z - z}{y}$ Figure 2. Relative vibrational populations in the  $H_2^{-1}\Sigma_g^+(v)$  fragments produced by the predissociation of the  $(v_s = 1, v_b = 0)$  vibrational states of the 3s<sup>2</sup>A'<sub>1</sub> Rydberg level of H<sub>3</sub> ( $N = 1$ ,  $K = 0$ ). The present cal sociation of the  $(v_s = 1, v_b = 0)$  vibrational states of the 3s<sup>2</sup>A'<sub>1</sub> Rydberg level of H<sub>3</sub> ( $N = 1$ ,  $K = 0$ ). The present calculations are marked with solid bars, calculations with the non-adiabatic sociation of the  $(v_s = 1, v_b = 0)$  vibrational states of the 3s<sup>2</sup>A<sub>1</sub><sup>2</sup> Hydberg level of H<sub>3</sub><sup>2</sup> ( $N = 1$ ,  $K = 0$ ). The present calculations are marked with solid bars, calculations with the non-adiabatic coupling operator  $K = 0$ ). The present calculations are marked with solid bars, calculations with the non-adial coupling operator equal to unity are marked with grey bars. The open bars represent the resolutioned by Müller & Cosby (1996) (

*Phil. Trans. R. Soc. Lond.* A (2000)

**MATHEMATICAL,<br>PHYSICAL<br>& ENGINEERING<br>SCIENCES** 

THE ROYAL<br>SOCIETY

**PHILOSOPHICAL**<br>TRANSACTIONS ŏ  $Dissociative\ recombination\ of\ H_3^+$  $Dissociative\ recombination\ of\ H_3^+$  $Dissociative\ recombination\ of\ H_3^+$  $+$  $\frac{1}{3}$  2451

Dissociative recombination of  $H_3^+$  2451<br>
of the 3s( ${}^2A_1'$ ) state. The computed rates, shown in table 1, are in satisfactory agree-<br>
ment with the measured ones (Müller & Cosby 1996). of the  $3s(^{2}A'_{1})$  state. The computed rates, shown in table<br>ment with the measured ones (Müller & Cosby 1996).<br>Even more encouraging is the reasonable agreement by the 3s( ${}^{2}A'_{1}$ ) state. The computed rates, shown in table 1, are in satisfactory agreement with the measured ones (Müller & Cosby 1996).<br>Even more encouraging is the reasonable agreement between our estimations and<br>e

ment with the measured ones (Müller & Cosby 1996).<br>Even more encouraging is the reasonable agreement between our est<br>the experimental data on the vibrational distributions of the  $H_2$ <sup>1</sup> $\Sigma$ <br>product. As shown in figure 2  ${}^{1}\Sigma_{g}^{+}$  dissociation Even more encouraging is the reasonable agreement between our estimations and<br>the experimental data on the vibrational distributions of the  $H_2 \,^1\Sigma_g^+$  dissociation<br>product. As shown in figure 2, the present theory qua the experimental data on the vibrational distributions of the  $H_2^{-1}\Sigma_g^+$  dissociation<br>product. As shown in figure 2, the present theory qualitatively confirms the relative<br>populations of the low vibrational levels, as w product. As shown in figure 2, the present theory qualitatively confirms the relative populations of the low vibrational levels, as well as the overall shape of this distribution. The theoretical predictions assuming a con bution. The theoretical predictions assuming a constant non-adiabatic coupling are (*c*) *The direct DR of* <sup>H</sup>

## $\frac{+}{3}$

The predissociated states studied above belong to Rydberg series that can be The predissociated states studied above belong to Rydberg series that can be<br>extended into the ionization continuum. In particular, for high principal quantum<br>numbers *n*, these couplings scale (in atomic units) as The predissociated states studied above belong to lextended into the ionization continuum. In particular, numbers  $n$ , these couplings scale (in atomic units) as

these couplings scale (in atomic units) as  
\n
$$
\langle \Psi_{\text{continuum}} | \frac{\partial}{\partial R} | \Psi_{\text{gd}} \rangle = \langle \Psi_{\text{Rydberg}} | \frac{\partial}{\partial R} | \Psi_{\text{gd}} \rangle (n - \mu(r, R, \theta))^{1.5},
$$
\n(3.4)

 $\langle \Psi_{\text{continuum}} | \frac{\partial}{\partial R} | \Psi_{\text{gd}} \rangle = \langle \Psi_{\text{Rydberg}} | \frac{\partial}{\partial R} | \Psi_{\text{gd}} \rangle (n - \mu(r, R, \theta))^{1.5}$ , (3.4)<br>where  $\mu(r, R, \theta)$  is the quantum defect and  $\Psi_{\text{gd}}$ ,  $\Psi_{\text{Rydberg}}$  and  $\Psi_{\text{continuum}}$  are the elec-<br>tronic wave functions associa where  $\mu(r, R, \theta)$  is the quantum defect and  $\Psi_{\text{gd}}$ ,  $\Psi_{\text{Rydberg}}$  and  $\Psi_{\text{continuum}}$  are the electronic wave functions associated with the ground state, the Rydberg predissociated state, and a state from the ionization co where  $\mu(r, R, \theta)$  is the quantum defect and  $\Psi_{\text{gd}}$ ,  $\Psi_{\text{Rydberg}}$  and  $\Psi_{\text{co}}$ <br>tronic wave functions associated with the ground state, the Ryd<br>state, and a state from the ionization continuum, respectively.<br>Consequen onic wave functions associated with the ground state, the Rydberg predissociated<br>ate, and a state from the ionization continuum, respectively.<br>Consequently, for each of these series, we can evaluate the contribution of the

consequently, for each of these series, we can evaluate the contribution of the corresponding partial wave of the incident electron to the *direct* DR, where the incident electron is directly captured into a dissociative s Consequently, for each of these series, we can evaluate the contribution of the corresponding partial wave of the incident electron to the *direct* DR, where the incident electron is directly captured into a dissociative corresponding partial wave of the incident electron to the *direct* DR, where the incident electron is directly captured into a dissociative state of the neutral molecule, the ground state in the case of H<sub>3</sub>. The DR cros dent electron is directly captured into a dissociative state of the neutral molecule,<br>the ground state in the case of H<sub>3</sub>. The DR cross-section is evaluated using equa-<br>tion (2.3),  $S(E)$  being obtained as described in § the ground state in the case of H<sub>3</sub>. The DR cross-section is evaluated using equation (2.3),  $S(E)$  being obtained as described in § 3b, the main difference with respect to the predissociation study being the use of the tion (2.3),  $S(E)$  being obtained as described in §3b, the mainto the predissociation study being the use of the *scaled* noments (equation (3.4)) in formula (3.1). The 'scaled'  $V^{(\text{na})}$  same role as the electronic one main difference with respect<br> *d* non-adiabatic matrix ele-<br>  $\binom{(\text{na})}{r, R}$  operator plays the<br>
the high-energy region (8.2). to the predissociation study being the<br>ments (equation (3.4)) in formula (3.<br>same role as the electronic one  $V^{(el)}$ <br>Note however that at low energy the g the use of the *scaled* non-adiabatic matrix ele-<br>(3.1). The 'scaled'  $V^{(na)}(r, R)$  operator plays the<br>(el)(r, R) relevant for the high-energy region (§2).<br>y the autoionization of the dissociative state cansame role as the electronic one  $V^{(el)}(r, R)$  relevant for the high-energy region (§2).<br>Note, however, that at low energy, the autoionization of the dissociative state cannot be accounted for by a complex imaginary term added to the actual potential Note, however, that at low energy, the autoionization of the dissociative state cannot be accounted for by a complex imaginary term added to the actual potential energy  $U_{\text{diss}}(r, R)$ , since  $V^{\text{(na)}}(r, R)$  is a *non-loca*  $V^{(el)}(r,R)$  is. We therefore disregarded autoionization at this stage of our analysis. of the accounted for by a complex imaginary term added to the actual potential<br>hergy  $U_{\text{diss}}(r, R)$ , since  $\mathbf{V}^{(\text{na})}(r, R)$  is a non-local operator, rather than a function as<br> $\frac{(\text{el})}{(r, R)}$  is. We therefore disregar ergy  $U_{\text{diss}}(r, R)$ , since  $V^{(\text{na})}(r, R)$  is a non-local operator, rather than a function as<br>  $F_{\text{ell}}(r, R)$  is. We therefore disregarded autoionization at this stage of our analysis.<br>
Following this procedure, we have o

 $V^{(el)}(r, R)$  is. We therefore disregarded autoionization at this stage of our analysis.<br>Following this procedure, we have obtained for  $H_3^+$  and  $D_3^+$  the DR cross-sections<br>displayed in figure 3 (only the s and p seri Following this procedure, we have obtained for  $H_3^+$  and  $D_3^+$  the DR cross-sections displayed in figure 3 (only the s and p series have been treated, since the non-<br>adiabatic couplings corresponding to the d series a displayed in figure 3 (only the s and p series have been treated, since the non-<br>adiabatic couplings corresponding to the d series are significantly smaller). Whereas<br>for predissociation our results agree well with the mea adiabatic couplings corresponding to the d series are significantly smaller). Whereas<br>for predissociation our results agree well with the measurements, in the case of DR<br>we face a disagreement of orders of magnitude! Howev for predissociation our results agree well with the measurements, in the case of DR we face a disagreement of orders of magnitude! However, this result is not surprising: the position of the neutral dissociative state with we face a disagreement of orders of magnitude! However, this result is not surpris-<br>ing: the position of the neutral dissociative state with respect to the molecular ion<br>surface (Kulander & Guest 1979; Michels & Hobbs 1984 ing: the position of the neutral dissociative state with respect to the molecular ion<br>surface (Kulander & Guest 1979; Michels & Hobbs 1984) corresponds to a very low<br>Franck–Condon factor, much lower than in the case of He surface (Kulander & Guest 1979; Michels & Hobbs 1984) corresponds to a very low<br>Franck–Condon factor, much lower than in the case of HeH<sup>+</sup> DR, which was found<br>to be relatively fast (Guberman 1994). Here, the direct DR *h* Franck–Condon factor, much lower than in the case of  $HeH^+$  DR, which was found<br>to be relatively fast (Guberman 1994). Here, the direct DR has to be slow, and our<br>calculation is just one of the necessary steps towards its to be relatively fast (Guberman 1994). Here, the direct DR has to be slow, and our calculation is just one of the necessary steps towards its complete modelling. We have to consider other mechanisms that, in the case of t calculation is just one of the necessary steps thave to consider other mechanisms that, in the cefficient than direct DR in the  $C_{2v}$  symmetry. efficient than direct DR in the  $C_{2v}$  symmetry.<br>4. The role of the indirect process

4. The role of the indirect process<br>Besides the direct capture of the incident electron into a repulsive state of the neu-<br>tral molecule DR may also proceed by a two-step mechanism, called *indirect* DR tract capture of the incident electron into a repulsive state of the neutral molecule, DR may also proceed by a two-step mechanism, called *indirect* DR. *Phil. Trans. R. Soc. Lond.* A (2000) **Phil.** *Phil. Trans. R. Soc. Lond.* A (2000)

**HYSICAL**<br>ENGINEERING<br>CENCES **ATHEMATICAL** 

THE ROYAL

**PHILOSOPHICAL**<br>TRANSACTIONS

<sup>2452</sup> *A. E. Orel,I.F.SchneiderandA. Suzor-Weiner*



energy (eV)<br>Figure 3. DR of (a)  $H_3^+$  and (b)  $D_3^+$  at low energy, modelled within a wave packet approach. Lines<br>denote computed direct cross-sections, corresponding to  $s^2A_1$  (dot-dashed)  $n^2A_2$  (dashed) and Figure 3. DR of (a)  $H_3^+$  and (b)  $D_3^+$  at low energy, modelled within a wave packet approach. Lines<br>denote computed direct cross-sections, corresponding to  $s^2A_1$  (dot-dashed),  $p^2A_1$  (dashed), and<br> $p^2B_2$  (soli  $p^2B_2$  (solid) continua of the 'ion-plus-electron' system, described in the  $C_{2v}$  symmetry. Circles igure 3. DR of (a)  $H_3^+$  and (b)  $D_3^+$  at low energy, modelled within a wave packet approach. Lines<br>enote computed direct cross-sections, corresponding to s<sup>2</sup>A<sub>1</sub> (dot-dashed), p<sup>2</sup>A<sub>1</sub> (dashed), and<br><sup>2</sup>B<sub>2</sub> (solid) denote computed direct cross-sections, corresponding to s<br>p<sup>2</sup>B<sub>2</sub> (solid) continua of the 'ion-plus-electron' system, d<br>denote CRYRING measurements (Larsson *et al.* 1997). denote CRYRING measurements (Larsson *et al.* 1997).<br>First, a bound state (usually a Rydberg state) is populated by electron capture into

First, a bound state (usually a Rydberg state) is populated by electron capture into<br>an excited energy level lying above the ionization threshold. Fragmentation of the<br>neutral molecule then occurs by predissociation of thi First, a bound state (usually a Rydberg state) is populated by electron capture into<br>an excited energy level lying above the ionization threshold. Fragmentation of the<br>neutral molecule then occurs by predissociation of thi an excited energy level lying above the ionization threshold. Fragmentation of the<br>neutral molecule then occurs by predissociation of this state. Both electron cap-<br>ture and predissociation may involve various types of int neutral molecule then occurs by predissociation of this state. Both electron cap-<br>ture and predissociation may involve various types of interaction (electronic, non-<br>adiabatic, spin-orbit, etc.), much as for the direct pr ture and predissociation may involve various types of interaction (electronic, non-<br>adiabatic, spin-orbit, etc.), much as for the direct process. The two mechanisms,<br>direct and indirect, usually coexist and interfere. Wit adiabatic, spin-orbit, etc.), m<br>direct and indirect, usually coe<br>(Guberman 1994) and  $He<sub>2</sub><sup>+</sup>$  (C<br>order of magnitude of the cros %), much as for the direct process. The two mechanisms,<br>  $\chi$  coexist and interfere. With notable exceptions (e.g.  $HeH^+$ <br>  $\chi^+$  (Carata *et al.* 1999)), the fast direct DR is setting the<br>
cross-section while the indirec direct and indirect, usually coexist and interfere. With notable exceptions (e.g. HeH<sup>+</sup> (Guberman 1994) and He<sup>+</sup> (Carata *et al.* 1999)), the fast direct DR is setting the order of magnitude of the cross-section, while (Guberman 1994) and  $He_2^+$  (Carata *et al.* 1999)), the fast direct DR is setting the order of magnitude of the cross-section, while the indirect process is responsible for resonance structures that hardly affect the val order of magnitude of the cross-section, while the indirect process is responsible for<br>resonance structures that hardly affect the value of the DR rate. However, if the<br>direct DR is very slow, the cross-section may actuall nitude (Guberman 1994; Schneider *et al.* <sup>2000</sup>a; b; Schneider & Suzor-Weiner 2000) direct DR is very slow, the cross-section may actually increase by orders of magnitude (Guberman 1994; Schneider *et al.* 2000*a*, *b*; Schneider & Suzor-Weiner 2000) when *indirect* couplings are included in a multichann nitude (Guberman 1994; Schneider *et al.* 2000*a*, *b*; Schneider & Suzor-Weiner 2000)<br>when *indirect* couplings are included in a multichannel calculation. We show below<br>that such a situation could help explain the fast at such a situation could help explain the fast DR cross-section measured for  $H_3^+$ <br>low energy.<br>It has often been suggested that the indirect DR should play an important role<br> $H_2^+$  DR. Mechanisms involving temporary c when *indirect* contains that such a situ<br>at low energy.<br>It has often b

at low energy.<br>It has often been suggested that the indirect DR should play an important role<br>in  $H_3^+$  DR. Mechanisms involving temporary capture of the incident electron into<br>'low-n high-n' or 'high-n low-n' Rydberg H<sub></sub> It has often been suggested that the indirect DR should play an important role<br>in  $H_3^+$  DR. Mechanisms involving temporary capture of the incident electron into<br>'low-n, high-v', or 'high-n, low-v' Rydberg  $H_3$  states, in H<sub>3</sub><sup>+</sup> DR. Mechanisms involving temporary capture of the incident electron into 'low-*n*, high-*v*', or 'high-*n*, low-*v*' Rydberg H<sub>3</sub> states, subsequently predissociated by the ground state (Helm 1993; Canosa *et a* 'low-*n*, high-*v*', or 'high-*n*, low-*v*' Rydberg H<sub>3</sub> states, subsequently predissociated by the ground state (Helm 1993; Canosa *et al.* 1992), have been proposed, as well as a multi-step indirect DR process involving the ground state (Helm 1993; Canosa *et al.* 1992), have been proposed, as well as a multi-step indirect DR process involving a series of  $\Delta v = 1$  transitions (Bates *et al.* 1993). However, until now no quantitative acco a multi-step indirect DR process involving a series of  $\Delta v = 1$  transitions (Bates *et al.* 1993). However, until now no quantitative account of this effect has been given. At very low energy we are in the situation descr al. 1993). However, until now no quantitative account of this effect has been given. At very low energy we are in the situation described above, with a very slow direct process (see figure 3) but rather strong non-adiabati At very low energy we are in the situation described above, with a very slow direct

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Figure 4. DR of  $H_3^+$  at low energy, modelled within a combined MQDT-wave packet approach.<br>The dashed black line denotes the computed direct cross-section. The grey line denotes the<br>computed total (direct and indirect) The dashed black line denotes the computed direct cross-section. The grey line denotes the computed total (direct and indirect) cross-section. Circles denote CRYRING measurements The dashed black line denotes the computed direct cross-section. The grey line denotes the computed total (direct and indirect) cross-section. Circles denote CRYRING measurements (Larsson *et al.* 1997). The solid black li computed total (direct and indirect) cross-section. Circles denote CRYRING measurements<br>(Larsson *et al.* 1997). The solid black line denotes the computed total cross-section, convoluted<br>according to the anisotropic Maxwe according to the anisotropic Maxwell distribution characterizing the ions in the CRYRING experiment (Larsson *et al.* 1997). The computations are performed in the  $C_{2v}$  symmetry and according to the anisotropic Maxwell distribution characterizing the ions in the CRYRII experiment (Larsson *et al.* 1997). The computations are performed in the  $C_{2v}$  symmetry are restricted to the contribution of the

are restricted to the contribution of the  $p^2B_2$  continuum of the 'ion-plus-electron' system.<br>states and the repulsive ground state on the other hand. Since the dissociative nuclear<br>wave function has a large overlap wit states and the repulsive ground state on the other hand. Since the dissociative nuclear<br>wave function has a large overlap with highly excited vibrational wave functions<br>of bound Rydberg states, the indirect process via 'cl wave function has a large overlap with highly excited vibrational wave functions wave function has a large overlap with highly excited vibrational wave functions<br>of bound Rydberg states, the indirect process via 'closed' ionization channels (i.e.<br>Rydberg series) may cause a spectacular enhancement of t of bound Rydberg states, the indirect process via 'closed' ionization channels (i.e.<br>Rydberg series) may cause a spectacular enhancement of the DR process. Using the<br>DR approach (Giusti-Suzor 1980) based on the multichann Rydberg series) may cause a spectacular enhancement of the DR process. Using the DR approach (Giusti-Suzor 1980) based on the multichannel quantum defect theory (MQDT), such an effect was demonstrated for similar situatio HeH<sup>+</sup> (Guberman 1994) and HD<sup>+</sup> (Schneider *et al.* 2000*a*, *b*; Schneider & Suzorproach (Giusti-Suzor 1980) based on the multichannel quantum defect theory  $\Gamma$ ), such an effect was demonstrated for similar situations in diatomics, e.g. (Guberman 1994) and  $HD^+$  (Schneider *et al.* 2000*a*, *b*; Schne (MQDT), such an effect was demonstrated for similar situations in diatomics, e.g. HeH<sup>+</sup> (Guberman 1994) and HD<sup>+</sup> (Schneider *et al.* 2000*a*, *b*; Schneider & Suzor-Weiner 2000).  $E^{\text{H}}$  (Guberman 1994) and  $HD^+$  (Schneider *et al.* 2000*a*, *b*; Schneider & Suzor-<br>einer 2000).<br>The MQDT treatment of the DR (Giusti-Suzor 1980) is not yet adapted for the<br>plyatomic case, and the TDWP case is not ye

Weiner 2000).<br>The MQDT treatment of the DR (Giusti-Suzor 1980) is not yet adapted for the polyatomic case, and the TDWP case is not yet able to account for the indirect<br>process. Therefore, we have used a hybrid treatment a polyatomic case, and the TDWP case is not yet able to account for the indirect process. Therefore, we have used a hybrid treatment as a first modelling of total polyatomic case, and the TDWP case is not yet able to account for the indirect<br>process. Therefore, we have used a hybrid treatment as a first modelling of total<br>(i.e. direct and indirect) DR of  $H_3^+$ . Specifically, the process. Therefore, we have used a hybrid treatment as a first modelling of total (i.e. direct and indirect) DR of  $H_3^+$ . Specifically, the direct non-adiabatic couplings between the ionization channels, open and closed (i.e. direct and indirect) DR of  $H_3^+$ . Specifically, the direct non-adiabatic couplings<br>between the ionization channels, open and closed, and the dissociative ground state<br>were evaluated using the TDWP technique, while between the ionization channels, open and closed, and the dissociative ground state were evaluated using the TDWP technique, while the vibrational couplings between ionization channels were introduced via the channel mixing coefficients:

$$
\langle \chi_{v_{\rm s}} \chi_{v_{\rm b}} | \cos[\pi \mu(r, R, \theta = 90^\circ)] | \chi_{v_{\rm s'}} \chi_{v_{\rm b'}} \rangle
$$

and

$$
\langle \chi_{v_{\rm s}} \chi_{v_{\rm b}} | \sin[\pi \mu(r, R, \theta = 90^{\circ})] | \chi_{v_{\rm s'}} \chi_{v_{\rm b'}} \rangle.
$$

*Phil. Trans. R. Soc. Lond.* A (2000)

<sup>2454</sup> *A. E. Orel,I.F.SchneiderandA. Suzor-Weiner*

Here,  $\mu(r, R, \theta)$  is the quantum defect surface previously computed (Krause *et al.*) Here,  $\mu(r, R, \theta)$  is the quantum defect surface previously computed (Krause *et al.* 1992; Schneider & Orel 1999), and  $|\chi_{v_s}\chi_{v_b}\rangle$  a two-dimensional ion vibrational wave function. An MODT calculation of the low-energy Here,  $\mu(r, R, \theta)$  is the quantum defect surface previously computed (Krause *et al.* 1992; Schneider & Orel 1999), and  $|\chi_{v_s}\chi_{v_b}\rangle$  a two-dimensional ion vibrational wave function. An MQDT calculation of the low-energy 1992; Schneider & Orel 1999), and  $|\chi_{v_s}\chi_{v_b}\rangle$  a two-dimensional ion vibrational wave<br>function. An MQDT calculation of the low-energy total cross-section has been per-<br>formed, restricted for now to the contribution of t function. An MQDT calculation of the low-energy total cross-section has been per-<br>formed, restricted for now to the contribution of the  $p^2B_2$  symmetry of the 'ion-<br>plus-electron' system. The indirect process was accoun plus-electron' system. The indirect process was accounted for through the inclusion of the *closed* channels (Giusti-Suzor 1980). The result is shown in figure 4: although the initial discrepancy between theory and experiment illustrated by figure 3 is not yet removed, the computed cross-section increases by two orders of magnitude, on average, when the indirect process is included. This cle vet removed, the computed cross-section increases by two orders of magnitude, on yet removed, the computed cross-section increases by two average, when the indirect process is included. This clearly *constructive* role in the case of the low-energy DR of  $H_3^+$ .

#### 5. Conclusions and perspectives

Important progress has been made in the theoretical study of the dissociation dynamics of  $H_3$  and its isotopomers. The calculated predissociation rates and the vibrational Important progress has been made in the theoretical study of the dissociation dynamics of  $H_3$  and its isotopomers. The calculated predissociation rates and the vibrational distributions of the dissociation products agre ics of  $H_3$  and its isotopomers. The calculated predissociation rates and the vibrational<br>distributions of the dissociation products agree well with the existing experimental<br>data. We have estimated the magnitude of the  $+$  n distributions of the dissociation products agree well with the existing experimental data. We have estimated the magnitude of the *direct*  $H_3^+$  DR, and we have shown that this process is slow, as expected. MQDT modelli data. We have estimated the magnitude of the *direct*  $H_3^+$  DR, and we have shown that this process is slow, as expected. MQDT modelling relying on the inclusion of the closed channels has shown that the *indirect* proc that this process is slow, as expected. MQDT modelling relying on the inclusion of<br>the closed channels has shown that the *indirect* process is orders of magnitude more<br>efficient than the direct one, a fact that might expl the closed channels has shown that the *indirec*<br>efficient than the direct one, a fact that might<br>cross-sections at low *and* moderate energies.<br>Much work remains to be done for a satisfact cross-sections at low *and* moderate energies.<br>Much work remains to be done for a satisfactory understanding and modelling of

 $H_3^+$  DR 3 oss-sections at low *and* moderate energies.<br>
3 Much work remains to be done for a satisfactory understanding and modelling of  $\frac{1}{3}$  DR. Besides the account of the indirect process, other mechanisms, such as the stu Much work remains to be done for a satisfactory understanding and modelling of  $H_3^+$  DR. Besides the account of the indirect process, other mechanisms, such as the actual opening of the doubly excited states for low-ene  $H_3^+$  DR. Besides the account of the indirect process, other m<br>actual opening of the doubly excited states for low-energy D<br>coupling to the ground state, should be carefully examined.<br>A major approximation in our calcul actual opening of the doubly excited states for low-energy DR through an efficient coupling to the ground state, should be carefully examined.<br>A major approximation in our calculation is the restriction to two dimensions,

coupling to the ground state, should be carefully examined.<br>A major approximation in our calculation is the restriction to two dimensions,<br> $\theta = 90^{\circ}$ , i.e.  $C_{2v}$  symmetry. For the high-energy calculations, where the d A major approximation in our calculation is the restriction to two dimensions,  $\theta = 90^{\circ}$ , i.e.  $C_{2v}$  symmetry. For the high-energy calculations, where the dissociation proceeds via doubly excited states of the neutra  $\theta = 90^{\circ}$ , i.e.  $C_{2v}$  symmetry. For the high-energy calculations, where the dissociation<br>proceeds via doubly excited states of the neutral, this is justified, since the dissocia-<br>tive potential energy surfaces are re proceeds via doubly excited states of the neutral, this is justified, since the dissociative potential energy surfaces are relatively flat with respect to changes in  $\theta$ , but fall steeply in energy as r and R are increas steeply in energy as r and R are increased. However, in the low-energy case this is steeply in energy as  $r$  and  $R$  are increased. However, in the low-energy case this is<br>not true. Consequently, the Franck–Condon overlaps could change considerably when<br>passing from two to three dimensions  $(C_s$  symmetry) not true. Consequently, the Franck–Condon overlaps could change considerably when<br>passing from two to three dimensions  $(C_s$  symmetry), the corresponding change of<br>couplings being quite able to alter the computed DR crosscouplings being quite able to alter the computed DR cross-section, direct and total.<br>Moreover, the actual vibrational structure corresponding to a system described by<br>three coordinates is much more dense than that accounte couplings being quite able to alter the computed DR cross-section, direct and total.<br>Moreover, the actual vibrational structure corresponding to a system described by<br>three coordinates is much more dense than that accounte Moreover, the actual vibrational structure corresponding three coordinates is much more dense than that accounted lations, where only two vibrational modes were available.<br>Another consequence of extending our calculations Another consequence of extending our calculations to the three-dimensional case

would be the more realistic and general account of the various available couplings. Another consequence of extending our calculations to the three-dimensio<br>would be the more realistic and general account of the various available co<br>For example, in the equilateral  $(D_{3h})$  configuration, the s states are o symmetry would be the more realistic and general account of the various available couplings.<br>For example, in the equilateral  $(D_{3h})$  configuration, the s states are of  ${}^{2}A'_{1}$  symmetry<br>and are coupled by the non-adiabatic coup  $E'$  stat r example, in the equilateral  $(D_{3h})$  configuration, the s states are of  ${}^2A_1'$  symmetry<br>d are coupled by the non-adiabatic coupling operator to the degenerate ground<br>d state, whereas within  $C_{2v}$  symmetry these stat and are coupled by the non-adiabatic coupling operator to the degenerate ground  ${}^{2}E'$  state, whereas within  $C_{2v}$  symmetry these states are of  ${}^{2}A_{1}$  symmetry and are coupled only to the  ${}^{2}A_{1}$  sheet of the g  ${}^{2}E'$  state, whereas within  $C_{2v}$  symmetry these states are of  ${}^{2}A_{1}$  symmetry and are coupled only to the  ${}^{2}A_{1}$  sheet of the ground state, which converges asymptotically to the H + H<sub>2</sub> limit, and not to th coupled only to the  ${}^2A_1$  sheet of the ground state, which converges asymptotically<br>to the H + H<sub>2</sub> limit, and not to the  ${}^2B_2$  sheet, which goes to the H + H + H limit.<br>Similarly, the p states should couple to the Similarly, the p states should couple to the degenerate ground state, but, in  $C_{2v}$ , one couples to the  ${}^2A_1$ , the other to the  ${}^2B_2$  sheet. Recent calculations performed to explain the optical emission spectra of one couples to the  ${}^{2}A_1$ , the other to the  ${}^{2}B_2$  sheet. Recent calculations performed to explain the optical emission spectra of  $H_3$  and its isotopomers (Mahapatra & Köppel 1998a, b) have shown that the asymmetr 1998*a*, *b*) have shown that the asymmetric stretch, that is changing  $\theta$ , can produce *Phil. Trans. R. Soc. Lond.* A (2000)

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 $Dissociative\ recombination\ of\ H_3^+$  2455<br>significant effects. Such calculations must include both ground-state sheets and take<br>into account the counling between these sheets. These calculations are underway significant effects. Such calculations must include both ground-state sheets and take<br>into account the coupling between these sheets. These calculations are underway.

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<sup>2456</sup> *A. E. Orel,I.F.SchneiderandA. Suzor-Weiner*

**MATHEMATICAL,<br>PHYSICAL**<br>& ENGINEERING<br>SCIENCES

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### *Discussion*

*Discussion*<br>J. B. A. MITCHELL (*PALMS, Université de Rennes, France*). There was a question<br>concerning possible field effects due to the downstream electric field in merged-beam  $\sigma$  is an extended to the downstream electric field in merged-beam concerning possible field effects due to the downstream electric field in merged-beam experiments. If the H<sup>+</sup> recombination proceeds via a rotational in J. B. A. MITCHELL (*PALMS, Université de Rennes, France*). There was a question concerning possible field effects due to the downstream electric field in merged-beam experiments. If the H<sub>3</sub><sup>+</sup> recombination proceeds via concerning possible field effects due to the downstream electric field in merged-beam<br>experiments. If the  $H_3^+$  recombination proceeds via a rotational interaction and pro-<br>duces a high n ( $n \approx 30$ ) Rydberg state that i experiments. If the  $H_3^+$  recombination proceeds via a rotational interaction and produces a high  $n$  ( $n \approx 30$ ) Rydberg state that is sufficiently long-lived (10s of seconds) to reach the bending magnet in a storage ri duces a high  $n (n \approx 30)$  Rydberg state that is sufficiently long-lived (10s of seconds) to reach the bending magnet in a storage ring, or the electrostatic beam deflector in a single-pass merged-beam apparatus, then such states would be field ionized and the recombination event would not be seen. Such states would also be affected by the recombination event would not be seen. Such states would also be affected by collisions in afterglow experiments. If the recombination proceeds by a vibrational interaction, this could produce an  $n = 7$  Rydberg state collisions in afterglow experiments. If the recombination proceeds by a vibrational<br>interaction, this could produce an  $n = 7$  Rydberg state that would not be field ion-<br>ized in the bending magnet nor in the electrostatic interaction, this could produce an  $n = 7$  Rydberg state that would not be field ion-<br>ized in the bending magnet nor in the electrostatic beam deflector  $(3 \text{ kV cm}^{-1} \text{ field})$ .<br>It could, however, be field dissociated by the b ized in the bending magnet nor in the electrostatic beat<br>It could, however, be field dissociated by the bending<br> $10^5 \text{ V cm}^{-1}$ ). This might affect the branching ratio.