

Comments on developments in the theory of dissociative recombination over the past 60 years

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Abstract. Since the proposal, sixty years ago, of the direct dissociative recombination (DR) mechanism by Bates, there have been many important theoretical advances, especially within the past 30 years. Space limitations preclude the review of all significant theoretical contributions. Instead, I comment upon a few selected developments. Highlights of the early scattering theory of DR and of the powerful Multichannel Quantum Defect Theory (MQDT) are discussed. Enhancements to the latter approach have included the addition of second and all order K matrices, ion rotational motion, Rydberg states with excited cores and spin-orbit coupling between Rydberg states. Also discussed are DR by Born-Oppenheimer breakdown, angular product distributions in diatomic DR and oscillations in DR cross sections.

1. The beginning

It was a mild evening on December 31, 1949 in Times Square, New York City as 750,000 [1] gathered to celebrate the arrival of the New Year. But this was no ordinary crowd. Struggling to make his way to a hotel, through the throngs of celebrants, was a British physicist of 33 years who held a one year U. S. Navy fellowship that started at 12:01 AM. [2] David Bates had just arrived by air from London and with no room to carry his suitcase at his side, he had to hug it. Already an important contributor to our understanding of atmospheric physics, he would soon be recognized as one of the most talented molecular physicists of his generation. In the coming year, he would propose a mechanism for a fundamental but poorly understood process in molecular physics, dissociative recombination. This process would eventually be found to be omnipresent in the ionospheres of the Earth, other planets and their moons, in interstellar clouds and necessary to the interpretation of many new laboratory experiments. After a brief stay in Pasadena, “I spent a month at Princeton University at the invitation of Lyman Spitzer.... In that stimulating environment, I also perceived the mechanism of dissociative recombination. This remains my most original contribution in atomic physics...Before 1950 ended, I fully appreciated what a marvellous country the United States is for scientific research ... I sometimes wonder if I should have stayed here. Perhaps I would have stayed except for one factor, one vital factor: Nobody offered me a job [2].”

The inspiration for the proposed mechanism came from the 1949 paper of Biondi and Brown [3]. Using a microwave afterglow in He, they reported measurements of the ambipolar diffusion coefficient. There is no mention of dissociative recombination (DR) in the title or abstract. In what can only be described as an exceedingly bold step, they also reported the measurement of the dissociative recombination rate coefficient, $1.7 \times 10^{-8} \text{ cm}^3/\text{sec}$, i.e. the coefficient for $\text{He}_2^+ + e^- \rightarrow \text{He} + \text{He}$. At that

time, no firm theoretical foundation for such a process existed and in fact both the noncrossing rule and the great mass mismatch between the incoming electron and the nuclei made it appear unlikely. DR had been mentioned previously in attempts to understand the green glow of the ionosphere [4] and the magnitude of the electron concentration in the ionosphere [5]. In the experiment, the rate coefficient was determined by plotting the inverse electron density versus time. For a binary process, as for DR, the slope of the straight line should give the recombination coefficient. In fact, although Biondi and Brown had raised the pressure in order to suppress diffusion, we now know that the measurement was for ambipolar diffusion and not recombination. Had they extended the plot to longer times, it is possible that they may not have obtained a straight line. Bates argued [6], in a one page paper, that the recombination observed by Biondi and Brown could not be atomic because that process was known to have a much smaller rate coefficient than that reported [3]. Instead, the recombination had to be molecular ion recombination [6]. From the vantage point of 60 years, it is clear that the prediction of Bates was based upon an incorrectly interpreted experiment. Another microwave discharge afterglow experiment [7] in Ne gas obtained a DR rate coefficient of $1.1 \times 10^{-7} \text{ cm}^3/\text{sec}$. In this case, the inverse electron density was plotted over a much shorter time than in the He afterglow. One needs to remember that in these first pioneering experiments many other factors, including impurities, may have contributed to the magnitude of the reported rate constants [8]. However, the rate constant for Ne_2^+ is in reasonable agreement with more modern measurements [9]. Moved by the experimental results, another one page paper by Bates [10] gave an expression for the direct DR rate coefficient by writing it as the product of a capture rate constant and a probability for dissociation competing with autoionization. He claimed that the expression gave rate constants consistent with the experimental measurements although the necessary theoretical input data was only poorly known at that time. In the direct mechanism, the electron is captured into a dissociative state in which the atoms separate before autoionization can play a significant role. This seminal paper has received only 128 citations according to the American Physical Society and 144 citations according to Google. The author is tempted to conclude, but cannot prove, that these citation counts are not accurate and are much too low.

By the 1960s, there was enough experimental and theoretical evidence to conclude that the DR of He_2^+ was not observed in the original He afterglow experiments [11]. However, careful experiments on other rare gases, where the rate constants are higher than for He_2^+ , indicated that DR was indeed occurring and the mechanism of Bates seemed plausible.

Fifty nine years after the first experiment on the DR of $^4\text{He}_2^+$, a storage ring study [12] found a rate coefficient of $1.7 \pm 1.0 \times 10^{-9} \text{ cm}^3/\text{sec}$ at 300K for 95% $v=0$ [12]. The rate coefficients for excited v are much higher than for $v=0$ and the ions must be relaxed since a small admixture of $v>0$ can significantly change the reported $v=0$ rate constant. For $^4\text{He}^3\text{He}^+$, another storage ring study [13] found a rate constant of $6.0 \pm 3.0 \times 10^{-10} \text{ cm}^3/\text{sec}$ at 300K. The heavier isotopomer should have the lower rate constant because the $v=0$ level will lie lower in the potential well and the wave function will be more contracted than that for the lighter isotopomer. However, the error bars on the experimental values are too large for an accurate comparison. A theoretical study [14] found a rate constant of $6.1 \times 10^{-11} \text{ cm}^3/\text{sec}$ at 300 K from $v=0$.

The first ab initio DR cross section calculation was reported by Bauer and Wu in 1955 [15] for H_2^+ . Because of the primitive nature of computational facilities at the time, many compromises were necessary. They ignored electron-electron repulsion in the calculation of the potential curves and used plane waves instead of coulomb waves for the free electron. Also an incorrect DR cross section expression was derived.

The role of capture into Rydberg states that are not dissociative channels was first explored by Stabler [16]. This was not a study of DR but of rotational capture and served as the inspiration for Bardsley's later proposal of the indirect DR mechanism. Surprisingly, Stabler found that rotational capture rate coefficients were high, i.e. $10^{-7} - 10^{-8} \text{ cm}^3/\text{sec}$, even though energetic considerations require

capture into high n Rydberg states and $\alpha_{\text{cap}} \propto 1/n^3$. He also found that $\alpha_{\text{cap}} \propto T_e^{-3/2}$ (where T_e is the electron temperature) exactly as would be found later by Bardsley for DR through rovibrationally excited intermediate states.

2. Scattering theory of DR

The first detailed application of scattering theory to DR, appropriate for low energy electrons, was given by Bardsley [17,18] in pioneering papers in which he showed that the direct recombination cross section from $v=0$ could be written as the product of a capture term and a survival factor, S_f , i.e. $\sigma_{\text{DR}} = \sigma_{\text{cap}} * S_f$ where $S_f = 1/|\beta_{0E}G_{00}|^2$. The evaluation of β involves a principal part integral and G is an integral over a Green function. These terms were not evaluated explicitly and it was assumed that the survival factor was unity in many later applications. The direct cross section for $v=0$ is given by [17]

$$\sigma_{\text{direct},v_0} = \frac{\pi^2 r}{k^2 2} \Gamma_c \frac{|\zeta_0(R_c)|^2}{|E'_d(R_c)|} S_f \quad (1)$$

where r is the ratio of the multiplicity of the repulsive state to the ion state, k is the electron wave number ($\varepsilon=k^2/2m_e$), R_c is the internuclear distance at which the separation of the ion and neutral curves is ε , Γ_c is the electronic width at R_c , $\zeta_0(R_c)$ is the amplitude of the ground state ion wave function at R_c and E'_d is the dissociative curve slope at R_c . Bardsley showed that the rate constant for direct recombination varies as $T_e^{-1/2}$.

In a second paper [18], indirect DR by vibrational and rotational capture into bound Rydberg states was introduced. The mechanism was based upon Stabler's [16] earlier discussion of indirect capture but now coupled with the predissociation of the Rydberg state by the dissociative state of the direct mechanism. Bardsley showed that the indirect cross section for an electron of energy ε takes the Breit-Wigner form:

$$\sigma_{\text{indirect}} = \sum_s \frac{\pi \hbar^2 r}{2m\varepsilon} \frac{\Gamma_{sa} \Gamma_{sd}}{2(E - E_s)^2 + \frac{1}{4}\Gamma_s^2} \quad (2)$$

where E is the total energy, s is the index denoting a resonance (a vibrationally excited Rydberg level), Γ_{sa} and Γ_{sd} are the widths for autoionization and dissociation respectively, $\Gamma_s = \Gamma_{sa} + \Gamma_{sd}$ and E_s is the resonance energy. Note that there is no coupling term between two resonances. This expression is often referred to as the isolated resonance approximation because it assumes that the individual resonances do not interact with each other, i.e. they are narrow and nonoverlapping. The indirect rate constant corresponding to (2) has a $T_e^{-3/2}$ temperature dependence in agreement with Stabler's result.

3. Multichannel quantum defect theory

Because direct and indirect recombination provide for two different pathways to the product atoms, there is interference between these paths. However, Bardsley's approach, providing two independent expressions for direct and indirect recombination does not account for this interference. This problem was solved with the application of Multichannel Quantum Defect Theory (MQDT) to DR first by Lee [19] and later by Giusti [20]. These pioneering contributions were in part based upon the earlier development of MQDT due to Seaton, Fano, Jungen, Greene and coworkers. The reader is referred to the volume of Jungen [21] where many of these papers are collected. The details of this approach will not be discussed here other than to say that the theory is formulated so that all electronic interactions between channels are included in a K matrix which is based upon the Lippmann-Schwinger equation and calculated perturbatively. Each channel is generally defined as a state of the ion coupled to a free or bound electron. The innovation of Lee and Giusti was the inclusion of the dissociative state as one

of the channels. With this change, direct and indirect DR could be treated on an equal basis and interference between these mechanisms could be described accurately. In addition, this approach took advantage of the capability of MQDT to describe entire Rydberg series, each characterized by a quantum defect, μ , where $\mu = n - (2E)^{-1/2}$. Here n is the principal quantum number and E is the energy of the Rydberg level relative to the ionization limit. This advantage is of major importance since a scattering theory approach requires the separate treatment of each individual Rydberg state.

The papers of Lee and Giusti did not lead to the same results. Indeed Lee did not treat the dissociative channels and the ionization channels equivalently. This was corrected in the approach of Giusti who showed that Lee's direct cross section expression was incorrect. Giusti showed that the direct cross section expression did not require evaluation of the complex integrals found in the survival factor of equation (1). Instead, she found that the total cross section for $v=0$ reduced to the following direct form if the quantum defects are set to be independent of the internuclear distance, R , and only a single dissociative channel is included:

$$\sigma_{\text{direct},v_0} = \frac{\pi r}{k^2} \frac{4\xi_{v_0}^2}{(1 + \sum_v \xi_v^2)^2} \quad (3)$$

In Eq (3), r and k have the same definitions as for Eq (1) and $\xi_v = \pi \int \chi_v(R) V_{\text{el}}(\epsilon, R) F_d(R) dR$ where $\chi_v(R)$ is the ion vibrational wave function for level v , $F_d(R)$ is the dissociative wave function and $V_{\text{el}}(\epsilon, R) = \langle \{\Phi_i(R)\phi(\epsilon, R)\} | H | \Phi_d(R) \rangle$. In V_{el} , the curly brackets indicate that the product of the ion wave function, Φ_i , and the coulomb wave function, ϕ , is antisymmetrized, H is the electronic Hamiltonian, Φ_d is the wave function of the dissociative state and the integration is over the electronic coordinates. Remarkably, the same expression has been derived by Flannery [22] by simply requiring unitarity for the capture cross section. In equation (3), the summation in the denominator is over all open vibrational levels at the electron energy corresponding to k^2 . The direct cross section including the survival factor is now easily calculated.

Using the MQDT approach, it was shown later [23] that the interference between direct and indirect DR could be described in the same way that Fano [24] originally described the interference of a photoionization continuum with a resonance.

Near a resonance, the DR cross section can be written as $\sigma = \sigma_D (q_v^d + e)^2 / (1 + e^2)$ where σ_D is the background (direct) cross section and e is the energy, taken to be zero at the resonance center. q_v^d is the Fano profile index for a Rydberg resonance in vibrational level v which is predissociated by state d . q_v^d can be calculated from the K matrix elements and quantum defects that enter the MQDT approach. As in Fano's original treatment [24], if q_v^d is zero, a dip occurs in the cross section at the resonance. A peak occurs if $|q_v^d| \gg 0$. Constructive and destructive interference occur for $q_v^d = -1$. For $q_v^d = 1$, the cross section is a reflection of the shape for $q_v^d = -1$. Figure 1 shows two dissociative routes of N_2 , 2 and $4^3\Pi_u$. The $2^3\Pi_u$ potential curve crosses the ion between the turning points of $v=0$ and $4^3\Pi_u$ crosses between $v=1$ and $v=2$. Figure 2 illustrates the cross section shape for $q_1^d \approx 0$ and for $|q_1^d| \gg 0$ [25]. Both cross sections are for DR from $v=0$ and only the $v=1$

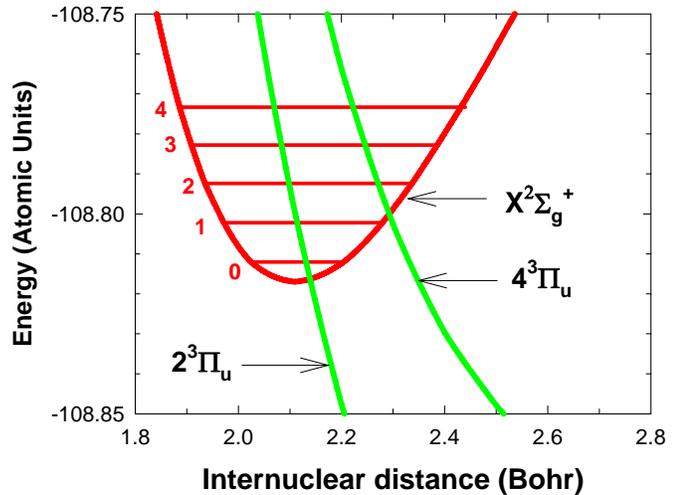


Figure 1. The 2 and $4^3\Pi_u$ potential curves of N_2 shown with the N_2^+ ground state.

resonances are included. The Fano profile index is given by [23] $q_1^d = (1/\pi)(V_1^{\text{capt}}/V_{0d}V_{1d})$ where $V_1^{\text{capt}} = -\langle\chi_0|\mu(\mathbf{R})|\chi_1\rangle$ and $d=2$ or 4 for the two $3\Pi_u$ states. V_1^{capt} does not contain the dissociative state since it describes capture into the $3\Pi_u$ Rydberg states (not shown figure 1) by Born-Oppenheimer break down. V_{vd} is the same as the matrix element for ξ_v (without π) shown below equation 3 for dissociative state d . V_{02} is much greater than V_{04} . The result is that $q_1^2 \approx 0$ leading to dips in the cross section along

$2^3\Pi_u$ and $q_1^4 \gg 0$ giving peaks along $4^3\Pi_u$. This is a general rule

for DR: when direct DR is negligible, the cross section will have only peaks due to the resonances unless interference can occur between different Rydberg series. When direct DR is strong, the cross section will have only dips due to the resonances unless interference can occur between different Rydberg series, i.e. series having different ion vibrational levels as the series limit.

When there is more than one dissociative curve of the same electronic symmetry, as in the case of N_2^+ DR, dissociation can become complicated. [26] For example, in figure 1, capture by $v=0$ can occur into the $2^3\Pi_u$ state which has a non-zero electronic matrix element with an intermediate Rydberg state. The Rydberg state is in turn connected to the $4^3\Pi_u$ state by a similar matrix element. Dissociation along $4^3\Pi_u$ completes DR. So DR can occur along a dissociative route that does not have a large direct matrix element for DR from the $v=0$ level. The same result ensues from capture by the $v=0$ ion into a $v=1$ Rydberg state (not shown in figure 1) by Born-Oppenheimer breakdown. The $v=1$ Rydberg state is predissociated by the $4^3\Pi_u$ state. The MQDT approach allows both mechanisms to interfere with each other.

4. MQDT extensions

The MQDT approach [20] is now the most commonly used approach for calculating low electron energy DR cross sections and rate constants. Since its introduction, many improvements and new capabilities have been added. The scattering matrix, S , is now calculated using Seaton's channel elimination method [27], an approach that ensures the unitarity of the S matrix.

The MQDT approach originally [20] used only a first order K matrix, i.e. the matrix elements were identical to the ξ_v (without π) given under equation 3 above (for the case of a single dissociative state). The method was later revised to include second order matrix elements [23]. Electronic matrix elements between ionization channels, which had been set to zero in the first order approach, were now calculated. These new matrix elements describe the electronic interaction of vibrationally excited Rydberg levels through their mutual interaction with an intermediate dissociative state. This interaction was shown to be quite important for O_2^+ [23]. In addition, the second order interaction was described with a Fano profile index and played an essential role in determining the cross section shape near a resonance [23]. Similar interactions had been explored previously by O'Malley [28] and Hickman [29]. The calculation of the K matrix was later revised so that it could be determined to all orders [30]. These full K matrix calculations have been applied to the DR of H_2^+ , HeH^+ and isotopomers.

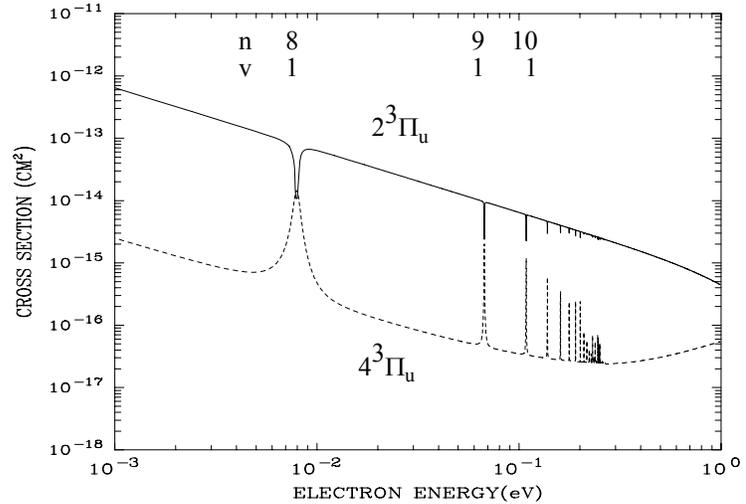


Figure 2. DR cross sections for N_2^+ [25].

Rotational motion was first included in the MQDT approach by Takagi [31] and later by Schneider et al. [32,33]. Valcu et al. [33] found that rotation is important for light ions and in cases where indirect recombination is important and it is not important where the dominant process is direct recombination. This is consistent with the comments at the end of section 3.

Another improvement to the MQDT approach involved the inclusion of intermediate Rydberg states having an excited ion core. [34] These states play a similar role to the ground state core Rydberg states first studied by Stabler and Bardsley. However, these states are also fundamentally different from those with the ground state core. First, an incoming electron can be captured into an excited core state by an electronic matrix element and not by Born-Oppenheimer breakdown as is required for the ground core states. Second, the $v=0$ level of a core excited Rydberg state may exist at an energy above the ion $v=0$ level. On the contrary, all ground core Rydberg $v=0$ levels lie below the ion $v=0$ level. Since the first mention of this process (in the DR of N_2^+) [34], additional studies [35,36] of N_2^+ DR have found that for dissociative states that have large direct DR rate coefficients, the effect of excited core states on the rate coefficient is small, i.e. about 10%. However, in cases where the direct DR rate coefficient is small, excited core states have been shown to increase the DR rate coefficient by a factor of 4 [35] and to decrease it by a factor of 20 [36]. Additional studies of excited core states in DR have been reported for CD^+ [37, 38, 39, 40], CH^+ [38, 39, 40], and OH^+ [41].

Spin-orbit coupling between Rydberg states was incorporated into the MQDT approach in order to account for an important atomic emission in the Earth's ionosphere [42]. The green line of atomic oxygen at 5577 Å is known to arise from the DR of O_2^+ but the only dissociative route that leads to the upper state, $O(^1S)$, does not intersect the ground vibrational level of O_2 . Because of the lack of a favorable intersection, the calculated [23] DR quantum yield of $O(^1S)$ was much lower than the measured yield. This mystery continued for several years until it was shown [42] that the mixing of Rydberg states of different symmetries via spin-orbit coupling could account for the observed yield. The impetus for the study of spin-orbit mixing in DR grew out of the spectroscopic observations of the interaction between the $f^1\Sigma_u^+$ and $E^3\Sigma_u^-$ Rydberg states of O_2 [43]. However, before the theoretical calculations [42] were completed, it was not obvious that spin-orbit coupling could indeed be important for DR. The mechanism is shown in figure 3. The only dissociative route that leads to $O(^1S)$ from the lowest vibrational levels is the $1^1\Sigma_u^+$ valence state shown in the figure. This state has a negligible DR rate coefficient from $v=0$. Spin-orbit coupling mixes the Rydberg states of $1^1\Sigma_u^+$ and $3^3\Sigma_u^-$ symmetries and each of these Rydberg states is connected to the repulsive states of the same symmetry by an electronic coupling. The net result is that electron capture from $v=0$ can occur into the $3^3\Sigma_u^-$ state which has a favorable crossing with $v=0$. Rather than dissociating entirely along the $3^3\Sigma_u^-$ dissociative state, some of the flux exits through the $1^1\Sigma_u^+$ state via the intermediate mixed Rydberg state. The quantum yield for $O(^1S)$ from DR of $v=0$ is in agreement with laboratory and atmospheric measurements. The mechanism is similar to that illustrated by figure 2 except that in that case all curves are of the same symmetry and spin-orbit coupling does not play a role.

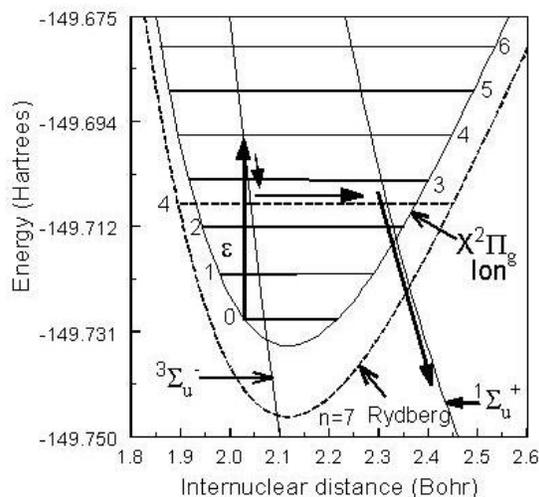


Figure 3. The potentials curves for the ground state of O_2^+ with the lowest 6 vibrational levels (solid line), an $n=7$ Rydberg state (dashed line) and the dissociative $1^1\Sigma_u^+$ and $3^3\Sigma_u^-$ states (solid lines).

5. DR by Born-Oppenheimer breakdown

Since the proposal of the direct mechanism [10] of DR, it was assumed for over 40 years that a favorable crossing of a dissociative potential curve within the turning points of an ion vibrational level was required for a high rate coefficient. In 1994, a calculation [44] on ${}^3\text{HeH}^+$ was reported which showed that a high DR rate coefficient was possible even in a case where there is no crossing of the ion potential by a neutral dissociative curve. The calculation was done with a revision of the first order MQDT approach incorporating derivative couplings. The rate constant was determined to be $2.6 \times 10^{-8} \times (T_e/300)^{-0.47} \text{ cm}^3/\text{sec}$. The main dissociative route at low electron energies was identified as the C state leading to $\text{He} + \text{H}(n=2)$. The identity of the dissociation products was later confirmed in a storage ring experiment [45]. These results had implications for the DR of H_3^+ where it was also known [46,47] that no neutral surface crossed the ion at low electron energies. Both studies [46,47] found that the potential curves were too far apart for the indirect mechanism to play a role. In the absence of a crossing, it was assumed for many years that the DR of H_3^+ had to have a low rate coefficient. However, the ${}^3\text{HeH}$ results indicated that if the DR of H_3^+ proceeded by Born-Oppenheimer breakdown, the rate coefficient could indeed be high. Later calculations showed that this indeed was the case [48].

6. Angular distributions

The angular distributions of the products of DR are needed for the determination of product quantum yields in storage ring experiments. The products of DR are detected by the flash that they make when impacting a phosphor plate. In diatomic DR, the distribution of the distances between the two flashes for each DR event is dependent upon a number of factors of which one is the angular distribution of the two products relative to the space fixed electron beam. An excellent discussion of the experimentally derived angular distributions is given in a paper [49] on CH^+ DR. It has been shown [50] that the angular distribution of products is dependent upon the symmetry of the Coulomb partial wave that is captured in DR. Indeed, if only a single partial wave is dominant and if it is assumed that DR takes place before the molecule has a chance to rotate, the angular distribution of the products will be identical to the angular symmetry of the incoming electron partial wave. The allowed capture symmetries for the electron are determined by selection rules that are based upon the electronic symmetry of the ion ground state and that of the state that governs the motion of the product atoms. Surprisingly, it has only been recently [51] that angular distributions for $\ell > 1$ electrons (where ℓ is the angular momentum quantum number for the electron partial wave) have been used in the derivation of quantum yields. This is especially surprising since $\ell = 2$ is the dominant partial wave in H_2^+ DR. The recent analysis [51] for HD^+ DR has indeed shown the importance of the $\ell = 2$ partial wave. For HD^+ , it was found that the predissociation time of the Rydberg resonances ($\approx 0.2 \times 10^{-12}$ sec) can be comparable to the rotational period, $\approx 0.8 \times 10^{-12} \times 1/J$ sec, where J is the capture state rotational quantum number. In this case, indirect DR is important and the slow rotation approximation is not entirely valid. (For HD^+ , the dissociative curve does not cross within the turning points of the $v=0$ vibrational level). However, at energies where direct DR is important, the slow rotation approximation should be adequate since dissociation is much faster ($\approx 10^{-15}$ sec) than for indirect recombination. Also, in heavier molecules made up of first row atoms the rotational periods are longer than for HD^+ and the slow rotation approximation may be valid. For O_2^+ , the rotational period is $\approx 10^{-11} \times 1/J$ sec. For molecular ions where direct DR is dominant, the slow rotation approximation will be valid unless the ion is highly rotationally excited or the dissociative route has an unusually low slope. Clearly, the validity of the slow rotation approximation should be assessed separately for each molecular ion.

7. Cross section oscillations

For cases where there are multiple dissociation routes that lead to the same products, interference between these routes can cause oscillations in the cross sections. These oscillations were found in

a DR experiment [52] on HD^+ and have been confirmed with theoretical calculations [53]. The products of DR in this case are $\text{H}^+ + \text{D}^-$ and $\text{H}^- + \text{D}^+$. The only dissociative state included in the calculation is the lowest doubly excited $^1\Sigma^+$ state which dissociates directly to the ion pairs. This state has two crossings each with Rydberg states of the same symmetry arising from the $\text{H}(n=2, 3, 4) + \text{D}(n=1)$ and $\text{D}(n=2, 3, 4) + \text{H}(n=1)$ asymptotes. The dissociating flux can enter the Rydberg states at the first crossing and return to the doubly excited $^1\Sigma^+$ state at the second crossing. Wave packet propagation was used to calculate the cross sections. The multiple pathways generate the oscillations in the cross section. Oscillations have also been predicted for the $\text{H}(1s) + \text{H}(2s) \rightarrow \text{H}_2^+ + e^-$ associative ionization reaction [54]. The latter calculation was done with an MQDT approach using coupled equations for the nuclear motion. The interference in the cross section is due to the same process described for DR except that here only the $\text{H}(1s) + \text{H}(2s)$ channel and the doubly excited $^1\Sigma_g^+$ channel are included at low energies.

8. Polyatomic DR

Significant advances have been made in the calculation of the DR cross section of the simplest polyatomic ion, H_3^+ [48, 55]. For further discussion of these advances, the reader is referred to a recent critical review [56].

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