Near-threshold electron impact dissociation of H$_2$ within the adiabatic nuclei approximation

Darian T Stibbe†‡ and Jonathan Tennyson†
† Department of Physics and Astronomy, University College London, London WC1E 6BT, UK
‡ NASA Ames Research Center, Moffett Field, CA 94035, USA

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Abstract. At low energies, the major pathway for the electron-impact dissociation of H$_2$ (e + H$_2$ → H(1s) + H(1s)+ e) is through excitation to the b $^3\Sigma_u^+$ dissociative state. We present ab initio calculations of the rate of dissociation as a function of initial vibrational level. The calculations employ an extension to the adiabatic nuclei approximation, balancing the energy between the electrons and the nuclei, for excitation to a dissociation continuum. We find that near-threshold rates show so strong a dependence on the initial H$_2$ vibrational level that the common practice of approximating the total dissociation rate to the $v = 0$ rate is invalid in many situations.

1. Introduction

The electron impact dissociation of molecules is important in various environments, including planetary atmospheres, lasers and plasmas such as those used in fusion reactors and in semiconductor manufacturing. For plasmas, the process was recently described as the most important electron impact cross sections, as it determines the radical densities in the plasma [1].

Electron impact dissociation of molecular hydrogen is particularly important for astronomical studies [2], models of the edge of Tokomak plasmas [3], gas discharges [4, 5] and models of diamond deposition [6]. Martin et al., when discussing astrophysical applications, recently concluded, ‘further work is... needed on electron impact excitation from other than the ground (rovibrational) state’ [7]. Since the vibrational state dependence is difficult to study in the laboratory, the $v = 0$ dissociation rate is often used as an approximation to the total rate, despite the importance of higher vibrational states in all of the different applications; see [8] for example.

The dissociation of H$_2$ for energies below around 12 eV proceeds almost exclusively by the direct excitation of the b $^3\Sigma_u^+$ repulsive state through exchange interaction. The molecule will
The molecule is excited from the $X^1\Sigma^+_g$ to the $b^3\Sigma^+_u$ state and then dissociates as it falls down the potential curve. Also shown are the ground state $v = 0$ nuclear wavefunction (dashed black) and continuum wavefunctions (ranging from red to blue) for different asymptotic kinetic energies of the dissociating molecule ($E_{ke}$). The figure can be downloaded as an XMGR file (see Appendix A) from the article multimedia page.

Figure 1. The molecule is excited from the $X^1\Sigma^+_g$ to the $b^3\Sigma^+_u$ state and then dissociates as it falls down the potential curve. Also shown are the ground state $v = 0$ nuclear wavefunction (dashed black) and continuum wavefunctions (ranging from red to blue) for different asymptotic kinetic energies of the dissociating molecule ($E_{ke}$). The figure can be downloaded as an XMGR file (see Appendix A) from the article multimedia page.

then dissociate as it falls down the potential curve (see figure 1): \[
e + H_2(X^1\Sigma^+_g) \rightarrow H_2(b^3\Sigma^+_u) + e \rightarrow H(1s) + H(1s) + e.\] (1)

For energies above 12 eV, the molecule can be excited to higher triplet states from which it can cascade down to the repulsive state. Another possibility above 12 eV is the excitation of an $H_2^-$ resonance state which can then decay into the $b^3\Sigma^+_u$ [9]. At astrophysically relevant electron temperatures (up to around 10 000 K), only direct excitation is pertinent and this paper concentrates on that process. Dissociative attachment, in which the molecule is excited to a resonant state which then dissociates to $H^+H^-$, occurs at lower energies. This process, which has been much studied [10], is assumed to proceed entirely via resonances.

It is important to differentiate between the two energies conventionally termed ‘thresholds’ involved in the dissociation. The formal threshold is clearly the vibrational state-dependent dissociation energy, $D_v$, which is 4.48 eV for $v = 0$ [11]. In practice, the electron impact dissociation cross section is only detectable experimentally at higher energies. Figure 1 shows nuclear continuum functions for the excited molecule with increasing total energy (i.e. with increasing asymptotic kinetic energy $E_{ke}$), and the ground state $v = 0$ wavefunction. Only when the outgoing nuclei have sufficient energy (somewhere between 2 and 5 eV) does there begin to be significant overlap between the initial and final wavefunctions, thus defining an ‘effective Franck–Condon’ threshold. Naturally, it is this threshold that is seen experimentally and this paper concentrates on that region.

Corrigan [12] made the first quantitative electron impact dissociation measurement by detecting $H(1s)$ products. After making corrections for other processes, such as ionization, the study provided an estimate of magnitude and qualitative form. Electron energy loss experiments,
which should be more accurate, have subsequently been performed by (among others) Hall and Andrić [13], Nishimura and Danjo [14] and Khakoo and Segura [15].

Most previous calculations (e.g. [16, 17, 18, 19, 20]) have been performed at the H₂ equilibrium bond length of $R_e = 1.4 \ a_0$ and do not take into account the nuclear motion. Rescigno and Schneider [21] performed a series of two-state, fixed-nuclei calculations using the Kohn variational method to find $R$-dependent T-matrices which they averaged using an initial vibrational and a $\delta$-function approximation to a final continuum function. However, they made no allowance for the variation in the vertical excitation energy, $\epsilon$, with $R$, and took no account of energy partitioning between the outgoing atoms and the exiting electron. This prevents their method from being used near the effective Franck–Condon threshold.

Celiberto et al used the semiclassical Gryzinski approximation to look at the dissociation of H₂ [22] and D₂ [23], again using a $\delta$-function approximation for the continuum, which they suggest should be useful for qualitative comparison. Gorse et al [24] also used the Gryzinski approximation and by adjustment of parameters within that approximation gained good agreement with experiment at higher energies. The method they used for the nuclear dynamics is not well documented, making it difficult to judge the accuracy of their near-threshold results.

Attems and Wadehra [25] looked explicitly at the contribution of the lowest two H₂− resonances to the dissociation cross section, using a T-matrix averaging method similar to Rescigno and Schneider, with whom they compared results. They concluded that the cross section was dominated by direct excitation.

In this paper we report calculations of the dissociation cross section near the effective Franck–Condon threshold as a function of initial vibrational level. The rate of dissociation as a function of scattering electron temperature and initial vibrational level is also calculated. The calculations employ a new energy-balancing procedure using off-shell T-matrices to extend the adiabatic nuclear approximation to treat the dissociation continuum.

2. The energy balancing method

The body frame adiabatic nuclei (AN) approximation [26, 27] was developed to include the effects of nuclear motion by averaging fixed-nuclei T-matrices using the initial and final nuclear wavefunctions. Extensions have been made for vibrational excitation [28], rotational excitation [29] and electronic excitation [30]. The basic method cannot, however, be used near threshold and several methods have been proposed to treat this region; see the extensive reviews of Lane [31], Morrison [32] and Domcke [10]. Particularly relevant here is the work of Shugard and Hazi [30] who suggested calculating off energy-momentum shell T-matrices to avoid the assumption of degeneracy between entrance and exit channels in electron impact electronic excitation calculations. To our knowledge, their methods have never been implemented.

The inclusion of nuclear motion within the AN approximation in the case of dissociation is complicated by several factors. In the first place, the excess energy of the incoming electron over the dissociation energy can be split between the dissociating nuclei and the outgoing electron in any proportion. Secondly, the fixed-nuclei excitation energy to the dissociating state changes rapidly with bond length, even in the Franck–Condon region. Thirdly, in the effective Franck–Condon threshold region, the effects of tunnelling must be taken into account. No previous studies have attempted to resolve these difficulties.
The first problem is dealt with by calculating, for a given incoming electron energy, energy-differential cross sections as a function of outgoing electron energy $d\sigma(E_{in})/dE_{out}$. The latter two problems are connected and together determine the choice of the fixed nuclei T-matrices to be averaged.

The method used here attempts to adhere as closely as possible to the overall physical picture, given the limitations of the adiabatic nuclei approximation. An incoming and an outgoing electron energy ($E_{in}$, $E_{out}$) are assumed. For the electronic transition in which the fixed-nuclei or vertical target electronic excitation energy is $\epsilon(R)$, the T-matrix to be averaged is the off-shell, fixed-nuclei one, $T_{FN}(E_{out} + \epsilon(R), E_{out}, R)$. The bond-length dependent $E_{out} + \epsilon(R)$ is not exactly the incoming electron energy $E_{in}$. However, this approximation is necessary to allow a well defined energy for the nuclear continuum function. For each fixed bond length $R$, the energy is enough to excite the molecule electronically to the dissociative state $\epsilon(R)$ with $E_{out}$ energy left over for the electron; see figure 2. This formulation is similar in effect to a combination of the off-shell technique suggested by Shugard and Hazi [30] for electronic excitation with the use of the T-matrix with the outgoing kinetic energy, implemented by Chang and Temkin [33] for rotational excitation. A similar discussion of incoming and outgoing electron energies is given by Ficocelli Varracchio [34] for electron impact electronic excitation.

The extra energy, $E_{extra}$, above that required for dissociation, $D_v$, is given by:

$$E_{extra} = E_{in} - D_v = E_{out} + E_{ke}$$  \hspace{1cm} (2)

where $E_{ke}$ is the asymptotic kinetic energy of the dissociating atoms. The energy-balance is illustrated in figure 2. Clearly $E_{out}$ can range from zero to $E_{extra}$ with a corresponding $E_{ke}$ from $E_{extra}$ to zero.
T-matrices including nuclear motion are given by:

\[
T_{v_i \rightarrow \text{cont.}}(E_{\text{in}}, E_{\text{out}}) = 
\langle \Xi_v(E_{\text{ke}}, R) | T_{F,N}(\epsilon(R) + E_{\text{out}}, E_{\text{out}}, R) | \Xi_i(R) \rangle
\]

where \( \Xi_v \) and \( \Xi_c \) are bound and continuum nuclear wavefunctions and the integration runs over \( R \). For each incoming electron energy, the energy-differential cross section is found as a function of outgoing electron energy:

\[
\frac{d\sigma(E_{\text{in}})}{dE_{\text{out}}} = \frac{\pi}{k_i^2} S \sum_{l,l'} |T_{vl,cl'}(E_{\text{in}}, E_{\text{out}})|^2,
\]

where \( k_i \) is the incoming electron energy, \( S \) is a spin multiplicity factor, with \( T_{vl,cl'} \) the T-matrix element connecting the initial state \( i \), partial wave \( l \) with the continuum state \( c \), partial wave \( l' \).

The integral electron impact dissociation cross section \( \sigma(E_{\text{in}}) \) is then:

\[
\sigma(E_{\text{in}}) = \int_{E_{\text{out}}=0}^{E_{\text{extra}}} \frac{d\sigma(E_{\text{in}})}{dE_{\text{out}}} dE_{\text{out}}.
\]

It should be noted that the averaging using nuclear wavefunctions ensures that the cross section approaches zero correctly below the effective Franck–Condon threshold. Vibrational state dependent rates are calculated from the integral cross sections assuming a Maxwellian energy distribution of electrons for a given temperature, but fixing the \( \text{H}_2 \) target in a given vibrational state.

The T-matrices used here were originally calculated in an investigation of \( \text{H}_2^- \) resonances as a function of \( R \) [9, 35, 36]. Calculations were performed for \( R \) equal to 0.8 \( a_0 \) to 4.0 \( a_0 \) in steps of 0.1 \( a_0 \) using the UK Molecular R-matrix suite of programs [37]. Target wavefunctions were represented using a full configuration interaction (CI) within a basis set of 4\( \sigma_g \), 3\( \sigma_u \), 3\( \pi_u \) and 3\( \pi_g \) Slater-type orbitals (STOs) which had been energy optimized [36] for the lowest seven target states (\( X^1\Sigma^+_g \), b \( ^3\Sigma^+_u \), a \( ^3\Sigma^+_g \), B \( ^1\Sigma^+_u \), C \( ^1\Pi_u \), c \( ^3\Pi_u \), E,F \( ^1\Sigma^+_g \)), those retained in our close-coupling expansion. Numerical functions were used to represent the continuum electron in a truncated \( (l \leq 6, m \leq 3) \) partial wave expansion. Our calculations yield full T-matrices linking all the (open) target states included in the calculation; here we are only concerned with the off-diagonal portion of the matrix which links the \( X^1\Sigma^+_g \) and b \( ^3\Sigma^+_u \) states. Full details can be found in [36].

As the excitation is from a singlet to a triplet state, it is exchange dominated and rapidly convergent with total symmetry. Only the lowest four total symmetries, \( ^2\Sigma^+_u \), \( ^2\Pi_u \), \( ^2\Pi_g \) and \( ^2\Sigma^+_g \) were included as higher symmetries were found to give a negligible contribution to the integral cross section, as found in previous calculations (e.g. [17]). In our model, the low-lying \( ^2\Sigma^+_u \) shape resonance does not contribute non-adiabatically, but this omission is not expected to make any measurable difference [25]. Due to its short lifetime (\( \Gamma \sim 1 \) eV), our adiabatic treatment of the B \( ^2\Sigma^+_g \) \( \text{H}_2^- \) resonance associated with the b \( ^3\Sigma^+_u \) dissociative state should be sufficient. In practice, the largest contribution comes from the non-resonant \( ^2\Sigma^+_u \) symmetry in line with previous calculations [21, 25].

Nuclear continuum wavefunctions, \( \Xi_c(E_{\text{ke}}) \), were calculated by directly solving the Schrödinger equation for the dissociating potential, and energy normalized using the asymptotic condition (in atomic units):

\[
\Xi_c(r \to \infty) \sim \sqrt{\frac{2\mu}{\pi k}} \sin (kr + \delta),
\]

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where $\mu$ is the reduced mass, $k$ the momentum and $\delta$ a phase shift. The exact potential of Kolos and Wolniewicz [38] was used in place of that implicit in our T-matrix calculations, which is ($\sim 0.1$ eV) less accurate. The initial vibrational wavefunctions and energies were found with the program LEVEL [39] also using the exact potential. For each value of $E_{\text{out}}$, the appropriate fixed nuclei T-matrices were interpolated over 1000 points between $R = 0.8$ and $4.0$ $\alpha_0$ prior to numerical integration to account for the rapid oscillations of the continuum functions.

3. Results

Figure 3 shows the dissociation cross section as a function of initial vibrational level and incoming electron energy. Although cross sections are shown up to 14 eV, our calculations are expected to be accurate only up to around 12 eV (and less for the higher $v$). Above that energy, there are resonances which can decay into the $b^{3}\Sigma^+_{u}$ state. Our adiabatic model is not valid for these long-lived resonances and cannot model the additional dissociation pathways above 12 eV.

In the region where our model is valid, there are few available experimental results. Those that are available are not consistent and have very wide error bars. The quantitative agreement with the $v = 0$ measurements of Khakoo and Segura [15] (shown in the figure) is good considering the large experimental uncertainties. The qualitative agreement with the cross sections of Hall and Andrić [13] is also good, with their results tracing out the form of our $v = 0$ curve. Although their results are consistently much higher than ours, they estimate their error as at least $\pm 40\%$.

Other experiments do not sample this region but are fairly consistent with the results of Khakoo and Segura at higher energies. As expected, above 12 eV our results are consistently too low in comparison with experiment.

Also shown in the figure are the $v = 0 - 2$ results of Rescigno and Schneider [21] at 12 eV. Their results show similar qualitative behaviour, with the total cross section increasing with initial vibrational level. The cross sections at 12 eV are around 30% higher than ours, but unfortunately their method does not work near threshold and so more extensive comparison at energies below 12 eV is not possible.

Qualitative agreement is also obtained with the semiclassical results of Celiberto et al [22]. A more detailed comparison including differential cross sections will be presented elsewhere [40].

The form of the cross sections is similar for each initial vibrational state but the effective Franck–Condon threshold is shifted lower and the maxima are greater for higher values of $v$. The threshold energy decreases by around 2 eV with each increase in $v$: about 0.5 eV comes from the increase in vibrational energy, but the majority arises from the rapid drop in $\epsilon(R)$ as the Franck–Condon region probes the longer bond lengths sampled by vibrationally excited states. A qualitatively similar picture was obtained by Gorse et al [24].

For $v = 0$, the value of $\epsilon(R)$ at the outer classical turning point using the exact potential curves is 8.7 eV. Within our model, this means that any dissociation found at electron energies below this arises via tunneling, for which our model explicitly allows. Our calculations suggest that the cross section for electron energies below 8 eV is not negligible and will contribute to the rate for low temperature electrons. The effective Franck–Condon threshold region has not been well characterized experimentally, although there are indications in the results of both Nishimura and Danjo [14] and Khakoo and Segura [15] that it lies well below 8.7 eV.

Figure 4 shows the dissociation rates calculated for the lowest five vibrational states of H$_2$ for electron temperatures up to 15 000 K. This temperature range is the most important for modelling
applications and the rates rely heavily on a correct treatment of the effective Franck–Condon threshold region. The rate is critically dependent on the initial vibrational level, $v$, rising several orders of magnitude as $v$ increases. This is a direct consequence of the vibrational dependence of the cross section in the threshold region. Full details of the calculated dissociation rate, along with fits to an analytic form, will be presented elsewhere \cite{41}.

4. Conclusion

The dependence of the rate on initial vibrational state is particularly significant when considering dissociation rates for the H$_2$ molecules in thermal equilibrium with the electrons. Assuming a Boltzmann distribution among the initial vibrational levels, the dissociation of the higher levels contributes far more to the total dissociation cross section than the lower levels despite their unfavourable population. This means that the oft-used practice of taking the $v = 0$ rate as an approximation to the total rate is invalid and, depending on temperature, could give errors of several orders of magnitude. Many molecules have an attractive ground state and a dissociative first excited state, as found in H$_2$. We would therefore expect that the extreme sensitivity found here of the near-threshold electron impact dissociation cross section to initial target vibrational state may be found in many other systems.
Figure 4. Dissociation rate as a function of electron temperature and initial H$_2$ vibrational level. Note the log rate scale. The figure can be downloaded as an XMGR file (see Appendix A) or the data can be downloaded in ascii format from the article multimedia page. (Updated 18 March 1999)

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Appendix A. Note on the use of XMGR

The excellent 2D plotting package XMGR (previously known as ACEGR and soon to be superseded by GRACE), is freely available from http://plasma-gate.weizmann.ac.il/Xmgr/. Your browser can conveniently be set up to run XMGR as a helper application by defining a new application within the browser with the Description ‘XMGR’, MIMETYPE ‘application/xmgr’, Suffixes ‘xmgr,gr’ and with the full pathname of the xmgr binary followed by %s (such as /usr/local/bin/xmgr %s).

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