Isotopic and vibrational-level dependence of H$_2$ dissociation by electron impact

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The low-energy electron-impact dissociation of molecular hydrogen has been a source of disagreement between various calculations and measurements for decades. Excitation of the ground state of H$_2$ into the dissociative $b \, ^3\Sigma_u^+$ state is now well understood, with the most recent measurements being in excellent agreement with the molecular convergent close-coupling (MCCC) calculations of both integral and differential cross sections (2018 Phys. Rev. A 98 062704). However, in the absence of similar measurements for vibrationally-excited or isotopically-substituted H$_2$, cross sections for dissociation of these species must be determined by theory alone. We have identified large discrepancies between MCCC calculations and the recommended $R$-matrix cross sections for dissociation of vibrationally-excited H$_2$, D$_2$, T$_2$, HD, HT, and DT (2002 Plasma Phys. Contr. F. 44 1263–1276, 2217–2230), with disagreement in both the isotope effect and dependence on initial vibrational level. Here we investigate the source of the discrepancies, and discuss the consequences for plasma models which have incorporated the previously recommended data.

In low temperature plasmas, electron-impact dissociation of molecular hydrogen into neutral fragments proceeds almost exclusively via excitation of the dissociative $b \, ^3\Sigma_u^+$ state:

$$e^{-} + H_2(X \, ^1\Sigma_g^+, v) \rightarrow H_2(b \, ^3\Sigma_u^+) + e^{-} \rightarrow 2H + e^{-}. \quad (1)$$

Cross sections and rate coefficients for this process are needed to accurately model astrophysical, scientific, and technological plasmas where hydrogen is present in its molecular form [1–3]. The importance of the reaction (1) and the relative simplicity it presents to theory and experiment has led to it being one of the most studied processes in electron-molecule scattering. Despite this, for decades there was no clear agreement between any theoretically- or experimentally-determined cross sections. The largest molecular convergent close-coupling (MCCC) calculations [4] for scattering on the ground vibrational level ($v = 0$) of H$_2$ were up to a factor of two smaller than the recommended when newer measurements were found to be in near-perfect agreement with the MCCC results [5, 6]. Recent $R$-matrix calculations have also confirmed the MCCC results for scattering on the $v = 0$ level of H$_2$ [7].

It is also important to determine accurate cross sections for dissociation of vibrationally-excited and isotopically-substituted hydrogen molecules, due to their presence in fusion and astrophysical plasmas. For these species, however, the absence of experimental data means it is up to theory to make recommendations alone. The primary distinguishing factor between the numerous calculations of the $b \, ^3\Sigma_u^+$-state cross section [8–24] is the treatment of the electronic dynamics. There is generally a consensus in the literature that the nuclear dynamics of the dissociative transition can be treated using the standard adiabatic-nuclei (AN) approximation (as reviewed by Lane [25]). We have taken this approach previously to study the dissociation of vibrationally-excited H$_2^+$ and its isotopologues, finding good agreement with measurements of both integral and energy-differential (kinetic-energy-release) cross sections [20, 21].

The cross sections for dissociation of vibrationally-excited H$_2$, HD, and D$_2$ recommended in the well-known reviews of Yoon et al. [26, 27] come from the $R$-matrix calculations of Trevisan and Tennyson [28, 29] (hereafter referred to collectively as TT01). The results of TT02, which also include HT, DT, and T$_2$, have long been considered the most accurate dissociation cross sections for H$_2$ and its isotopologues, and are widely used in applications. During our recent efforts to compile a comprehensive set of vibrationally-resolved cross sections for electrons scattering on vibrationally-excited and isotopically-substituted H$_2$ [30, 31], it has become apparent that there are major discrepancies between the MCCC calculations and the $R$-matrix calculations of TT02. Interestingly, the two methods are similar in their treatment of the electronic dynamics and differ primarily in their treatment of the nuclear dynamics, leading to conflicting isotopic and vibrational-level dependencies in the calculated cross sections. The formalism applied by TT02 was previously developed by Trevisan and Tennyson [17] (TT01).

Here we compare the standard AN method adopted in the MCCC calculations with the alternative formulation suggested by TT01, and determine the origin of the disagreement between the two approaches. We will argue in favour of the MCCC results, which will be of some interest to those who have previously recommended the $R$-matrix data [26, 27, 32, 33] or implemented it in their models [1–3, 34–48]. We limit the discussion here to dissociation through the $b \, ^3\Sigma_u^+$ state, but note that we have previously [49] performed more detailed dissociation calculations for vibrationally-excited H$_2$ including all im-

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portant pathways to dissociation into neutral fragments from low to high incident energies. These calculations can be readily extended to include the isotopologues in the future.

We first describe the standard AN treatment of dissociation, which is a straightforward adaption of the method for non-dissociative excitations described by Lane [25]. We use SI units throughout for consistent comparison with TT01’s formulas. In terms of the electronic partial-wave $T$-matrix elements defined by Lane [25], the expression for the energy-differential cross section for dissociation of the vibrational level $\nu$ into atomic fragments of asymptotic kinetic energy $E_k$ in the standard AN method is

$$ \frac{d\sigma}{dE_{\text{out}}} = \frac{\pi}{k_{\text{in}}} \sum_{\nu'_{m'}} \left| \langle \nu_{E_k} | T_{\nu'_{m'} \ell m}(R; E_{\text{in}}) | \nu_{\nu'} \rangle \right|^2, \quad (2) $$

where $E_{\text{in}}$ and $k_{\text{in}}$ are the incident projectile energy and wavenumber, and $\nu$ are the vibrational wave functions. The energies of the scattered electron and dissociating fragments are related by

$$ E_k = E_{\text{in}} - D_v - E_{\text{out}}, \quad (3) $$

where $D_v$ is the threshold dissociation energy of the vibrational level $\nu$ [15]. This relationship makes it possible to treat the energy-differential cross section as a function of either $E_{\text{out}}$ or $E_k$. When this method has been applied in previous work [8–16, 18–24], Eq. (2) is not derived explicitly for the case of dissociation since the derivation follows exactly the same steps summarized by Lane [25] for the non-dissociative vibrational-excitation cross section. The only difference is the replacement of the final bound vibrational wave function with an appropriately-normalized continuum wave function $\nu_{E_k}(R)$. In principle the continuum normalization is arbitrary so long as the density of final states is properly accounted for. Indeed, many of the previous works [13, 15, 21, 24, 51, 52] which have applied the AN (rather than FN) method to dissociation explicitly state that the continuum wave functions are energy normalized, which implies unit density and the following resolution of unity:

$$ \int_0^\infty \nu_{E_k}^*(R) \nu_{E_k}(R') dE_k = \delta(R - R'). \quad (5) $$

The works which have applied the FN method also implicitly assume energy normalization, since the FN approximation utilizes Eq. (5) to integrate over the dissociative states analytically. Note that Eq. (5) implies the functions $\nu_{E_k}$ have dimensions of $1/\text{energy}$-length. The bound vibrational wave functions are normalized according to

$$ \int_0^\infty \nu_{E_k}^*(R) \nu_{\nu'}(R) dR = \delta_{\nu \nu'}, \quad (6) $$

and hence they have dimensions of $1/\sqrt{\text{length}}$. The electronic $T$-matrix elements defined by Lane [25] are dimensionless, and the integration over $R$ implied by the bra-kets in Eq. (2) cancels the combined dimension of $1/\text{length}$ from the vibrational wave functions, so it is evident that the right-hand side of Eq. (2) has dimensions of area/energy as required (note that $1/k_{\text{in}}^2$ has dimensions of area).

The standard AN/FN approaches to calculating dissociation cross sections have been applied extensively in the literature [8–24]. They are also consistent with well-established methods for computing bound-continuum radiative lifetimes or photodissociation cross sections, which replace discrete final states with dissociative vibrational wave functions. The latter are either energy normalized [53], or normalized to unit asymptotic amplitude with the energy-normalization factor included explicitly in the dipole matrix-element formulas [54, 55].

TT01 criticized the standard technique, claiming that a proper theoretical formulation for dissociation did not exist, and suggested that a more rigorous derivation for the specific case where there are three fragments in the exit channels is required. We have performed our own derivation following the ideas laid out by TT01 and found that they lead directly to Eq. (2). However, TT01 arrived at an expression which is markedly different:

$$ \frac{d\sigma}{dE_{\text{out}}} = \frac{m_H}{4\pi^3 m_e} \frac{E_k}{E_{\text{in}}} \sum_{\ell m_{\ell m}} \left| \langle \nu_{E_k} | T_{\nu'_{m'} \ell m}(R; E_{\text{in}}) | \nu_{\nu'} \rangle \right|^2. \quad (7) $$

Here $m_H$ is the hydrogen nuclear mass, which is replaced with the deuteron or triton mass in their later investigation into dissociation of $D_2$ and $T_2$ [28]. Comparing Eqs. (2) and (7), we see that TT01’s formula is different by a factor of $m_H E_k/2\pi^4\hbar^2$ (the $T$-matrix elements here are the same as those in Eq. (2)). The distinguishing feature of TT01’s approach and the reason for the mass-dependence in their formula was said to be the explicit consideration of the density of dissociating states. We have two major concerns here: firstly, the energy-normalized wave functions used in Eqs. (2) and (7) have unit density so it is unusual that taking this into account
should have any effect, and secondly, TT01’s expression for the energy-differential cross section has dimensions of

$$\text{dim} \left[ \frac{d\sigma}{dE_{\text{out}}} \right] = \frac{1}{\text{energy}}, \tag{8}$$

which suggests an error in the derivation. As a result, the integral cross sections for scattering on H$_2$(v = 0) presented in TT01 and for vibrationally-excited H$_2$, HD, D$_2$, HT, DT, and T$_2$ presented in TT02 using the same method appear to be incorrect.

TT01’s derivation uses a density of states corresponding to (three-dimensional) momentum normalization. However, rather than calculating momentum-normalized vibrational wave functions, TT01 use energy-normalized functions and apply a correction factor

$$\xi^2 = 2\hbar \left( \frac{E_k}{m_H} \right)^{1/2} = \frac{\hbar p_k}{\mu} \tag{9}$$
to the cross section to account for a conversion from energy to momentum normalization. Since the vibrational wave functions are one-dimensional, it is not obvious how to normalize them to three-dimensional momentum. Although TT01 do not state explicitly how they choose to define the momentum normalization, Eq. (9) corresponds to a conversion from energy normalization to (one-dimensional) wavenumber normalization [56]. The density of states for this choice of normalization is

$$\rho(E_k) = \frac{\mu}{\hbar p_k}, \tag{10}$$

which cancels exactly with the correction factor (9). This is to be expected since Eq. (4) shows clearly that any factors applied to the continuum wave functions to change the normalization must lead to the inverse factor (squared) being applied to the density of states. It is the mismatch between continuum normalization and density of states which leads to some of the additional factors, such as the molecular mass, in TT01’s final cross section formula. Using a consistent normalization and density of states it is possible to follow the remaining steps taken by TT01 in their derivation and arrive at an expression identical to the standard formula (2). We have provided our own derivation in the supplementary materials.

The novelty of the reformulated R-matrix approach has been acknowledged numerous times and the results have been widely adopted. Perhaps in part due to being recommended by Yoon et al. [26, 32] and included in the QuanTemol database [57], the cross sections and rate coefficients given by TT02 have been applied in a number of different plasma models, most notably in the astrophysics community [1-3, 34-48]. The formalism of TT01 was also used by Gorfinkiel et al. [58] to study the electron-impact dissociation of H$_2$O, and it has been reiterated a number of times that this method is necessary to accurately treat dissociation in the AN approximation [59-61]. Gorfinkiel et al. [58] found in particular that for some dissociative transitions in H$_2$O the formalism of TT01 gives results up to a factor of two different to the FN method even 10 eV above threshold. If correct this result would invalidate the use of the FN method in dissociation calculations, for example in the R-matrix calculations of Refs. [62-64].

In Fig. 1 we compare the MCCC and TT01/02 results for dissociation of H$_2$ in the initial vibrational states v = 0–4. We also compare with the earlier R-matrix results of Stibbe and Tennyson [15] (ST98), which were performed using the standard AN method. Both sets of R-matrix calculations used the same underlying T-matrix elements, calculated previously in an investigation into H$_2$ resonances [65], so the differences between them is only due to TT01’s alternative cross-section formula. ST98 proposed an “energy-balancing” correction to the AN method, which slightly modifies the incident energy at which the T-matrix elements are evaluated. This method was also used by TT01/02 and we have implemented it in the MCCC calculations to ensure consistent comparisons between the three sets of calculations. The ST98 and MCCC cross sections are in good agreement, with small differences near the cross section max-
minimum likely due to the use of different electronic scattering models. TT01’s cross section for the $v = 0$ level of H$_2$ is only about 10% different from ST98’s results at the maximum, and up to around 10 eV the two are essentially the same. It is perhaps puzzling that the additional factor of $m_H E_k/2\pi^4\hbar^2$ in Eq. (7) has only a small effect, but we note that the average value of this factor is fortuitously close to 1 (in Hartree atomic units) in the 0–6 eV range of $E_k$ corresponding to incident energies up to 10 eV (see TT01’s Fig. 8). This coincidence disappears for scattering on excited vibrational levels, where the formulation of TT01 predicts significantly different results. The cross sections for dissociation of excited vibrational levels presented in TT02 are up to a factor of 2 smaller than the MCCC and ST98 results. To explain this, in Fig. 2 we present the MCCC energy-differential cross section as a function of $E_k$ for 6-eV electrons scattering on the $v = 2–6$ levels of H$_2$, showing that the cross section peaks at progressively smaller values of $E_k$ as the initial vibrational level is increased. In TT01’s formalism, the suppression in this region caused by the smaller value of their additional factor in Eq. (7) for small $E_k$ leads to a substantial reduction in the integrated cross section for higher vibrational levels.

Further to the different vibrational dependence, the mass factor in Eq. (7) leads to an unusually large isotopic dependence in the dissociation cross sections. In Fig. 3 we compare the MCCC and TT02 cross sections for dissociation of H$_2$, D$_2$, and T$_2$ in the $v = 0$ level. TT02’s results for D$_2$ are two times larger than for H$_2$, and for T$_2$ they are three times larger. Our calculations show only a small isotope effect at low energies due to the slightly higher dissociation thresholds of the heavier targets. Further discussion of the isotope effect in MCCC calculations of low-energy H$_2$ dissociation (including the mixed isotopologues HD, HT, and DT) can be found in Ref. [22]. TT02 stated that their predicted scaling of cross sections with isotopic mass should be expected for all dissociative processes. We suggest that this is purely an artifact of the incorrect formalism they have applied. Furthermore, there is no substantial isotope effect in the measurements of El Ghazaly et al. [66] for dissociation of vibrationally-hot H$_2^+$ and D$_2^+$, which are in good agreement with the previous MCCC calculations [20] using the standard AN method. Additionally, the MCCC calculations are in good agreement with the measurements of Andersen et al. [67] for dissociation of HD+ in its $v = 0$ level.

Although we claim that the large isotope effect predicted by TT02 is unphysical, higher rates of dissociation for D$_2$ compared to H$_2$ have in fact been observed in real plasmas [68–74]. Each of Refs. [68–74] cite TT02’s factor-of-two H$_2$/D$_2$ isotope effect as the likely cause of this, with one [74] even repeating the argument that the density of states is responsible for the higher rate of dissociation in D$_2$. Optical-emission spectroscopy measurements have shown a higher ratio of atomic to molecular densities in deuterium plasmas than in hydrogen plasmas [68, 71, 72], although given the error bars on the measurements the isotope effect could range from being insubstantial to a factor of 2 difference. Of course these measurements are indirect and the atomic/molecular densities are governed by a number of factors, only one of which is the direct dissociation rate.

If there is indeed an isotope effect in the rate of dissociation, we argue that it can result from the mass-dependence of the $X^1\Sigma_g^+$-state discrete vibrational spectrum alone, rather than an explicit mass dependence in
the cross section. Increasing the nuclear mass has two competing effects: a shift of the spectrum to lower energies which increases dissociation thresholds, and the appearance of more bound levels near the dissociative limit of the electronic potential well. It is not obvious what isotope dependence (if any) will arise in a plasma from these effects, but for an approximate idea we can compare the local-thermodynamic-equilibrium (LTE) rate coefficients for different isotopologues. Since LTE assumes a Maxwellian population of the initial vibrational levels this is a useful way to investigate the overall isotope effect with excited vibrational levels included. In Fig. 4 we compare the LTE rate coefficients given by Stibbe and Tennyson [75] (ST99) and TT02 with those obtained from the MCCC cross sections. The ST99 rates were obtained using the cross sections from ST98. The MCCC results show an approximately 10% enhancement for dissociation of D$_2$ compared to H$_2$, but a slightly lower rate for T$_2$. The difference between the MCCC rate for H$_2$ and ST99’s rate can be explained partly by their somewhat lower cross sections around the maximum (see Fig. 1), and their proper treatment of only the $v = 0$–4 levels (with the remaining cross sections extrapolated). The much larger difference with the TT02 results is caused by their substantially smaller cross sections for scattering on excited levels. Importantly, we have shown that the results of the standard AN formalism are consistent with the experimental evidence of a higher dissociation rate for D$_2$.

Aside from TT01/02, the only previous calculations of low-energy dissociation of vibrationally-excited H$_2$ and D$_2$ are the semi-classical calculations of Celiberto et al. [16], which utilized the Gryzinski method to treat the electronic dynamics and the standard AN approach with the additional Franck-Condon (FC) approximation to treat the nuclear dynamics. The FC approximation assumes the electronic excitation cross section is independent of $R$, making it is more inaccurate for the higher vibrational levels with more diffuse wave functions. In Fig. 5 we compare the MCCC b $3\Sigma_u^+$ cross sections for scattering on all bound vibrational levels of H$_2$ with the results of Celiberto et al. [16]. It is evident that even with the correct definition of the dissociation cross sections, the approximate methods utilized by Celiberto et al. [16] do not correctly model the significant dependence on vibrational level at low incident energies. The comparison is essentially the same for D$_2$.

We conclude that the MCCC calculations of low-energy dissociation have treated the nuclear dynamics correctly (within the AN approximation) and recommend that MCCC cross sections should be used in place of the R-matrix results [17, 28, 29] in all applications. The full set of MCCC cross sections for scattering on all bound levels in H$_2$, D$_2$, T$_2$, HD, HT, and DT are discussed in Refs. [30, 31], and are available online at mccc-db.org. This includes dissociation through the b $3\Sigma_u^+$ over a much wider range of incident energies than previously available, as well as a large number of other inelastic transitions (both bound and dissociative). A complete set of rate coefficients for dissociation of each isotopologue will be provided elsewhere, with the hope that they will be of interest to those who have previously utilized the data of TT02, and of use in future models of hydrogenic plasmas.

FIG. 5. Comparison of the $X^1\Sigma_g^+(v) \rightarrow b^3\Sigma_u^+$ dissociation cross sections calculated by Celiberto et al. [16] with the molecular convergent close-coupling (MCCC) calculations [30]. The cross section increases with initial vibrational level from $v = 0$ to 14 (Celiberto et al. include only up to $v = 13$).

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