**Letter**

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 [Zawadzki *et al.*, Phys. Rev. A **98**, 062704 (2018)]. 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 [Trevisan *et al.*, Plasma Phys. Contr. Fusion **44** 1263 (2002); **44**, 2217 (2002)], 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:

$$e^- + H_2(X\,^1\Sigma_g^+, v) \rightarrow H_2(b\,^3\Sigma_u^+) + e^- \rightarrow 2H + e^-. \quad (1)$$
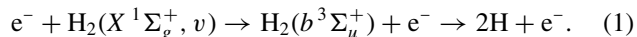
Cross sections and rate coefficients for this process are needed to accurately model astrophysical, scientific, and technological plasmas where hydrogen is present in its molecular form [1–3]. The importance of the reaction (1) and the relative simplicity it presents to theory and experiment has led 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 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 cross sections, but the situation was resolved 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 with the same formalism used for bound excitations, by simply replacing the bound final vibrational wave function with an appropriately normalized dissociative wave function. 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.* [25,26] come from the *R*-matrix calculations of Trevisan and Tennyson [27,28] (hereafter referred to collectively as TT02). 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$_2$ [29,30], 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 both the electronic and nuclear dynamics, but differ in their fundamental definitions of the dissociation cross section, leading to conflicting isotopic and vibrational-level dependencies in the calculations. The formalism applied by TT02 was previously developed by Trevisan and Tennyson [17] (TT01).

Here we compare the standard method adopted in the MCCC calculations with the alternative formulation suggested by TT01, and determine the origin of the disagreement between the two approaches. It is important to note that this paper is not concerned with analyzing the validity of the often-used adiabatic-nuclei (AN) approximation, or variants such as the energy-balanced AN approximation of Stibbe and

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Tennyson [15]. Instead, we aim only to discuss the definition of the dissociation cross section, which is independent of the method utilized to incorporate the nuclear dynamics, and provide a set of accurate cross sections for low-energy dissociation of H_2 and its isotopologues. We will argue in favor of the standard formulation and the MCCC results, which will be of some interest to those who have previously recommended the data of TT02 [25,26,31,32], or implemented it in their models [1–3,33–47]. We limit the discussion here to dissociation through the $b\,^3\Sigma_u^+$ state, but note that we have previously [48] performed more detailed dissociation calculations for vibrationally excited H_2 including all important 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 treatment of dissociation, which is a straightforward adaption of the method for nondissociative excitations. We use SI units throughout for consistent comparison with TT01's formulas. For simplicity, we assume the AN approximation has been applied according to the definitions in the review of electron-molecule collisions by Lane [49], but note that the following discussion would remain valid if the energy-balanced AN method [15] or even full electronic and vibrational close coupling was used. In terms of the electronic partial-wave T-matrix elements defined by Lane [49], the expression for the energy-differential cross section for dissociation of the vibrational level v into atomic fragments of asymptotic kinetic energy E_k in the standard formulation is

$$\frac{d\sigma}{dE_{\text{out}}} = \frac{\pi}{k_{\text{in}}^2} \sum_{\substack{\ell'm' \\ \ell m}} |\langle v_{E_k}|T_{\ell'm',\ell m}(R; E_{\text{in}})|v_v\rangle|^2, \qquad (2)$$

where E_{in} and k_{in} are the incident projectile energy and wave number, and v are the vibrational wave functions. The convergence of Eq. (2) with respect to the maximum ℓ included in the projectile plane-wave expansion is relatively fast for the spin-exchange $X\,^1\Sigma_g^+ \to b\,^3\Sigma_u^+$ transition (previous MCCC studies have found $\ell_{\text{max}} = 6$ to be sufficient at all energies [4]). However, when the partial-wave method is applied to direct (nonexchange) transitions, larger expansions are required, along with the analytical Born completion technique to account for the infinity of terms $\ell > \ell_{\text{max}}$ [4]. The energies of the scattered electron and dissociating fragments are related by

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

where D_v is the threshold dissociation energy of the vibrational level v [15], and E_{out} is the outgoing projectile energy. This relationship makes it possible to treat the energy-differential cross section as a function of either E_{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 [49] for the nondissociative vibrational-excitation cross section. The only difference is the replacement of the final bound vibrational wave function with an appropriately normalized continuum wave function $v_{E_k}(R)$. In principle the continuum normalization is arbitrary

so long as the density of final states is properly accounted for. According to standard definitions [50], the density of states ρ for the vibrational continuum satisfies the following relation:

$$\int_0^\infty v_{E_k}(R)v_{E_k}(R')\rho(E_k)\,dE_k = \delta(R - R'), \qquad (4)$$

giving a clear relationship between the continuum-wave normalization and density. Since the formulas presented by Lane [49] for nondissociative excitations are written in terms of bound vibrational wave functions, with a density of states equal to unity (by definition), the most straightforward adaption to dissociation simply replaces them with continuum wave functions normalized to have unit density as well. Indeed, many of the previous works [13,15,21,24,51,52], which have applied the AN method to dissociation explicitly state that the continuum wave functions are energy normalized, which implies unit density and the following resolution of unity:

$$\int_0^\infty v_{E_k}(R)v_{E_k}(R')\,dE_k = \delta(R - R'). \qquad (5)$$

The works that have applied the fixed-nuclei (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 v_{E_k} have dimensions of $1/\sqrt{\text{energy} \cdot \text{length}}$. The bound vibrational wave functions are normalized according to

$$\int_0^\infty v_v(R)v_{v'}(R)\,dR = \delta_{v'v}, \qquad (6)$$

and hence they have dimensions of $1/\sqrt{\text{length}}$. The electronic T-matrix elements defined by Lane [49] 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 approach to calculating dissociation cross sections has been applied extensively in the literature [8–24]. It is 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:

$$\frac{d\sigma}{dE_{\text{out}}} = \frac{m_H}{4\pi^3 m_e}\frac{E_k}{E_{\text{in}}} \sum_{\substack{\ell'm' \\ \ell m}} |\langle v_{E_k}|T_{\ell'm',\ell m}(R; E_{\text{in}})|v_v\rangle|^2. \qquad (7)$$

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 [27]. 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: first, 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 second, TT01's expression for the energy-differential cross section has dimensions of

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

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

$$\xi^2 = 2\hbar\left(\frac{E_k}{m_H}\right)^{1/2} = \frac{\hbar p_k}{\mu} \qquad (9)$$

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) wave number normalization [56]. The density of states for this choice of normalization is

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

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 nuclear 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 Supplemental Material [57].

The novelty of TT01's reformulated approach to dissociation has been acknowledged numerous times and the results have been widely adopted. Perhaps in part due to being recommended by Yoon *et al.* [25,31] and included in the Quantemol database [58], the cross sections and rate coefficients given by TT02 have been applied in a number of different plasma
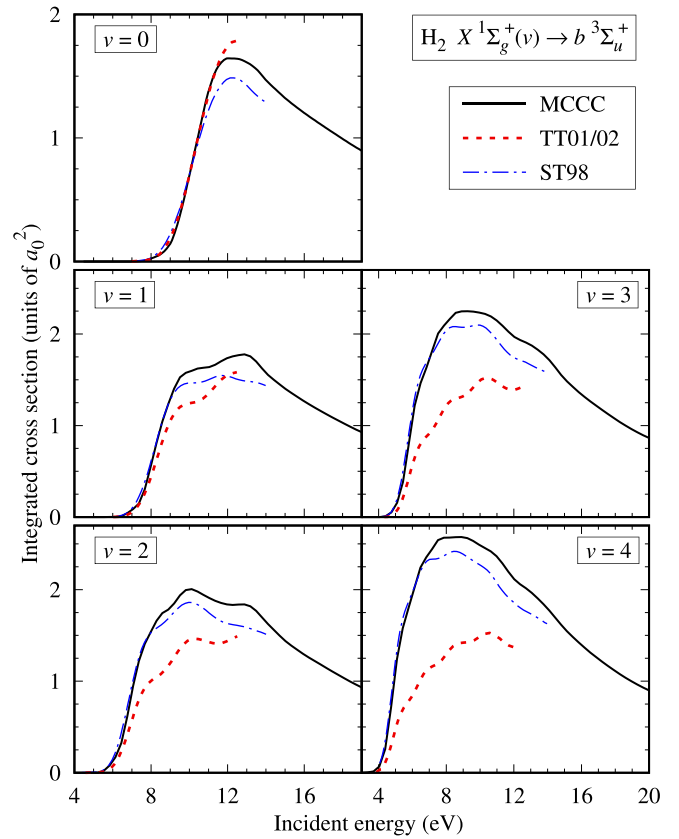

FIG. 1. Comparison of the $X\,^1\Sigma_g^+(v) \to b\,^3\Sigma_u^+$ dissociation cross sections calculated by Stibbe and Tennyson [15] and Trevisan and Tennyson [17,27] (ST98 and TT01/02, respectively), with the molecular convergent close-coupling (MCCC) calculations [29,30] for scattering on the $v = 0$–4 levels of H_2.

models, most notably in the astrophysics community [1–3,33–47]. The formalism of TT01 was also used by Gorfinkiel *et al.* [59] to study the electron-impact dissociation of H_2O, and it has been reiterated a number of times that this method is necessary to accurately treat dissociation in the AN approximation [60–62]. Gorfinkiel *et al.* [59] found in particular that for some dissociative transitions in H_2O 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. [63,63–65]. 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 formulation (2). Both sets of R-matrix calculations used the same underlying T-matrix elements, calculated previously in an investigation into H_2^- resonances [66], so the differences between them is only due to TT01's alternative cross-section formula. The energy-balancing modification to the AN method, which slightly modifies the incident energy at which the T-matrix elements are evaluated, was used by ST98 and TT01/02, and we have implemented it in the MCCC calculations to ensure consistent comparisons between the three sets of calculations. The ST98
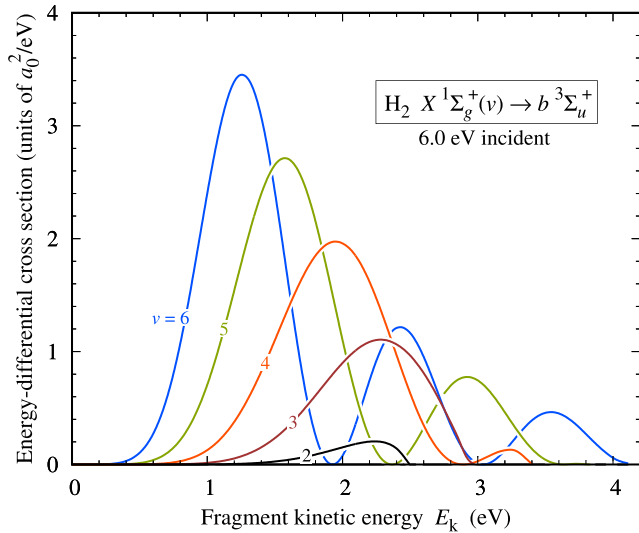
FIG. 2. Molecular convergent close-coupling (MCCC) energy-differential dissociation cross section as a function of the fragment kinetic energy E_k for 6.0-eV electrons scattering on the $v = 2$–6 vibrational levels of H_2.

FIG. 3. Comparison of the $X\,^1\Sigma_g^+(v = 0) \rightarrow b\,^3\Sigma_u^+$ dissociation cross sections calculated by Trevisan and Tennyson [27] (TT02), with the molecular convergent close-coupling (MCCC) calculations [29,30] for scattering on H_2, D_2, and T_2.

and MCCC cross sections are in good agreement, with small differences near the cross-section maximum 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 scattering on 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
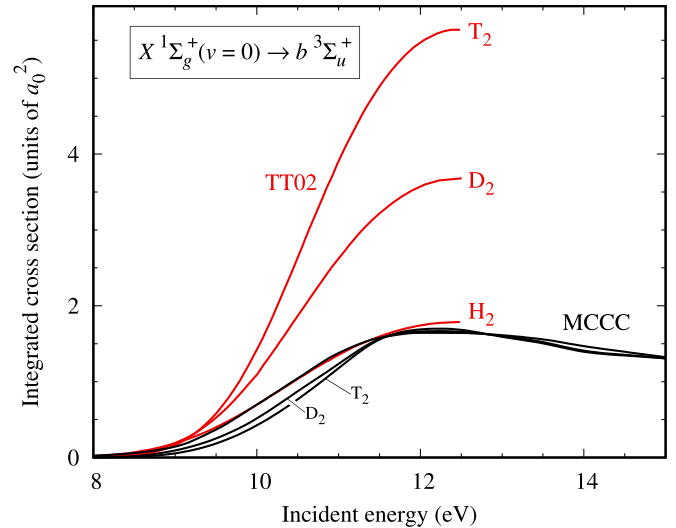
cross sections with isotopic mass should be expected for all dissociative processes. We suggest that this is purely an artefact of the incorrect formalism they have applied. Furthermore, there is no substantial isotope effect in the measurements of El Ghazaly *et al.* [67] for dissociation of vibrationally hot H_2^+ and D_2^+, which are in good agreement with previous MCCC calculations [20] using the standard formulation. The MCCC calculations are also in good agreement with the measurements of Andersen *et al.* [68] 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 [69–75]. Each of Refs. [69–75] cite TT02's factor-of-two H_2/D_2 isotope effect as the likely cause of this, with one [75] 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 [69,72,73], 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 and 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 discrete vibrational spectrum in the initial electronic state, rather than an explicit mass dependence in the cross-section formula. Increasing the nuclear mass has two competing effects: a shift of the vibrational 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
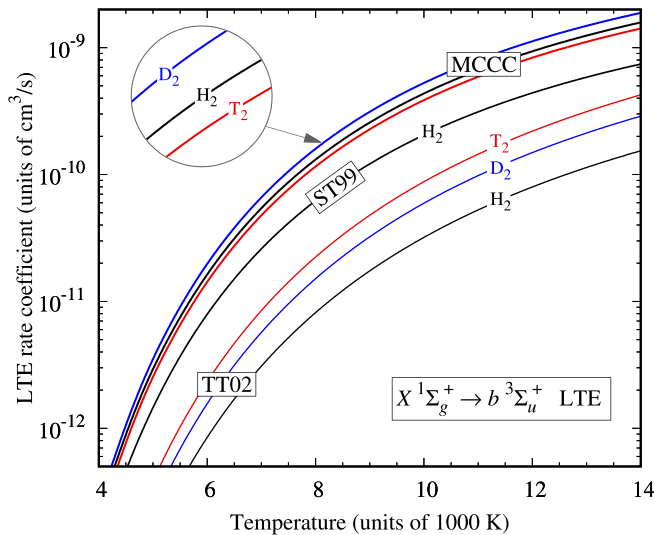
FIG. 4. Local thermodynamic equilibrium (LTE) dissociation rate coefficients for H_2 (black), D_2 (blue), and T_2 (red). Comparison is shown between the calculations of Trevisan and Tennyson [27] (TT02), Stibbe and Tennyson [76] (ST99), and the present molecular convergent close-coupling (MCCC) calculations.

FIG. 5. Comparison of the $X\,^1\Sigma_g^+(v) \to b\,^3\Sigma_u^+$ dissociation cross sections calculated by Celiberto *et al.* [16] with the molecular convergent close-coupling (MCCC) calculations [29]. The cross section increases with initial vibrational level from $v = 0$–14 (Celiberto *et al.* include only up to $v = 13$).

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 [76] (ST99) and TT02 with those obtained from the MCCC cross sections. The ST99 rates are available only for H_2 and 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 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 semiclassical calculations of Celiberto *et al.* [16], which utilized the Gryzinski method to treat the electronic dynamics, and the standard dissociation formalism with the Franck-Condon (FC) approximation to treat the nuclear dynamics. The FC approximation assumes the electronic excitation cross section is independent of R, making it 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
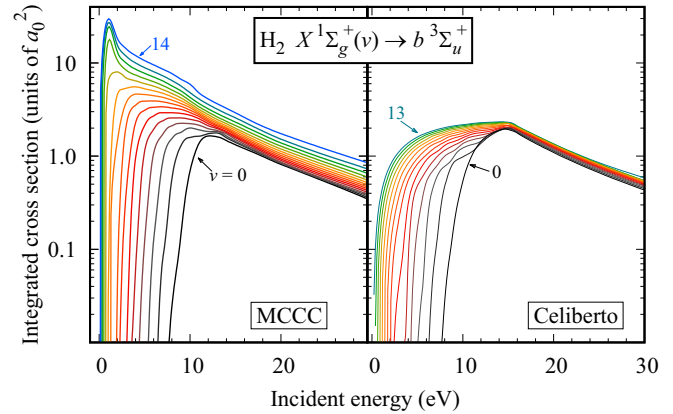
definition of the dissociation cross sections, the approximate methods utilized by Celiberto *et al.* [16] do not correctly model the significant dependence on vibrational level. The comparison is essentially the same for D_2.

We have shown that the standard dissociation formalism is valid, and the cross-section formula derived and applied by TT01/02 [17,27,28] is incorrect. For this reason, we recommend that the MCCC cross sections, which apply the standard formalism, should be used in place of the results of TT01/02 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. [29,30]. This includes dissociation through the $b\,^3\Sigma_u^+$ state over a much wider range of incident energies than previously available, as well as cross sections for 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.

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