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RATES FOR THE ELECTRON IMPACT DISSOCIATION OF MOLECULAR HYDROGEN

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ABSTRACT

At astrophysically relevant temperatures (below 15,000 K), electron impact dissociation of H_2 occurs through the excitation of the dissociative $b\ ^3\Sigma_u^+$ state. We have calculated and parameterized the rates of dissociation as a function of electron temperature for the $v = 0$–4 H_2 vibrational states. The assumption that the $v = 0$ rate approximates to the rate at local thermal equilibrium (LTE) is found to be seriously flawed. Instead, the rates are found to depend so critically on the initial vibrational level that dissociation from very high-lying vibrational levels must be included in calculations of the rate at LTE even at low temperature. An extrapolation procedure is used to approximate the rates for all of the higher vibrational levels ($v = 5$–14), which are then used to calculate the LTE rate. The LTE rate is found to be around 2 orders of magnitude greater than the $v = 0$ rate.

Subject headings: molecular data — molecular processes — scattering

1. INTRODUCTION

About half the observable matter in the universe is in the form of molecular hydrogen (H_2), yet information on certain key processes involving molecular hydrogen remains poor. Electron collisions with molecular hydrogen are important in a variety of astrophysical environments such as interstellar shocks (Draine, Roberge, & Dalgarno 1983; Hollenbach & McKee 1989), X-ray–irradiated dense clouds (Tiné et al. 1997), planetary atmospheres (Kim, Fox, & Caldwell 1997), and the aftermath of supernovae explosions (Yan & Dalgarno 1998). In particular, electron impact dissociation of H_2 is thought to have a critical effect in determining the size of the molecular region in clouds near an X-ray source (Tiné et al. 1997). A recent study of collision-induced dissociation of molecular hydrogen (Martin, Keogh, & Mandy 1998) concluded that data on electron impact dissociation of H_2 is particularly poor and, for the case of vibrationally excited H_2, nonexistent.

It is generally agreed that at low energy, electron impact dissociation of H_2 occurs via the first electronically excited state, the dissociative $b\ ^3\Sigma_u^+$ state:

$$e + H_2(v) \rightarrow H_2(b\ \Sigma_u^+) + e \rightarrow H + H + e. \qquad (1)$$

We have recently proposed an "energy balance" model (Stibbe & Tennyson 1998b)[3] that allows the electron impact dissociation via an electronically excited state to be treated, with full allowance for nuclear motion effects, within the adiabatic nuclei approximation. Calculations, using this model, of cross sections for electron impact dissociation of H_2 found that these cross sections showed a strong sensitivity to nuclear motion effects. Tunnelling effects, which were explicitly included in the calculation, were found to be of particular importance near threshold. The onset of electron impact dissociation was found to be at about 8 eV for H_2 in its vibrational ground state, $v = 0$. This is significantly lower than the 8.9 eV that can be estimated from the vertical excitation at the outer classical turning point of the $v = 0$ wave function, or indeed the 10.6 eV vertical excitation energy found at the H_2 equilibrium geometry. Furthermore, vibrational excitation of H_2 was found to lower the effective threshold for electron impact dissociation by far more than the extra vibrational energy involved. Again, this behavior could be explained in terms of the lowered vertical excitation energy at the outer turning point of the vibrationally excited H_2.

Our earlier study did not obtain fully thermal electron impact dissociation rates for H_2. This was because of the limited number of vibrational states studied and the profound effect that the higher vibrational states have on these rates, even at relatively low temperatures where the occupancy of these higher states is very small. However, given the importance of electron impact dissociation of H_2 to astrophysics, we have extended our previous work to obtain accurate estimates for this process. As shown below, this rate is significantly faster in the important 2000–10,000 K region than previous estimates indicated, due mainly to the previously neglected contribution of vibrationally excited states. Furthermore, rapid increase in dissociation rate with vibrational excitation may well lead to H_2 distributions showing subthermal occupation of vibrationally excited states.

2. CALCULATIONS

Calculations of the electron impact dissociation cross section were based on our previous *R*-matrix studies of electron-H_2 collisions at a grid of fixed H_2 bond lengths (Stibbe & Tennyson 1997a, 1997b, 1998a). The geometry-dependent, off-shell fixed-nuclei *T*-matrices corresponding to electron impact excitation to the dissociative $b\ ^3\Sigma_u^+$ state of H_2 were taken from these calculations. These were averaged between wave functions for the ground vibrational states v and nuclear motion continuum functions with appropriate energy to represent the dissociating state. This generalization of the adiabatic nuclei approximation to electron impact dissociation raises difficult issues concerning the various energies in the system and how they are treated within this approximation. Our method incorporates the splitting of the incoming electron energy between the outgoing electron and the dissociating nuclei explicitly and uses an averaging formulation similar in effect to the off-shell *T*-matrix technique suggested by Shugard & Hazi (1975). The general problem and our method are discussed in detail in our previous study (Stibbe & Tennyson 1998b).

The electron impact dissociation cross sections as a function of electron energy and initial vibrational level are shown in Figure 1 for $v = 0$–4, to which our initial calculation was lim-

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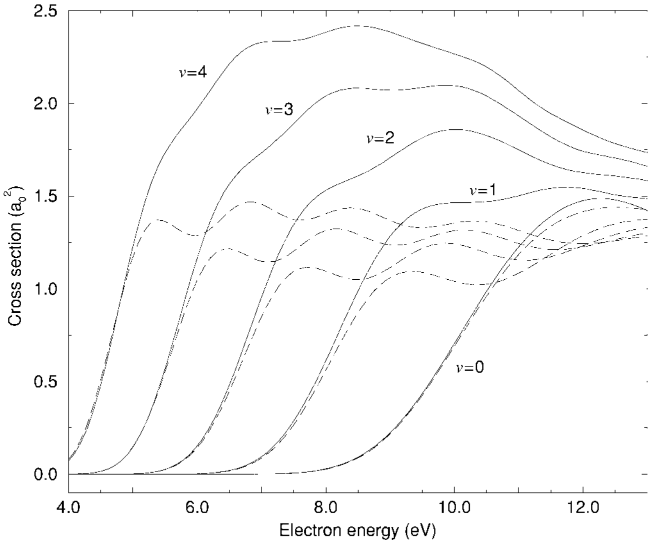

FIG. 1.—Electron impact dissociation cross section as a function of incoming electron energy E and initial vibrational level v. Solid curve: full calculation; dashed lines: Franck-Condon approximation.

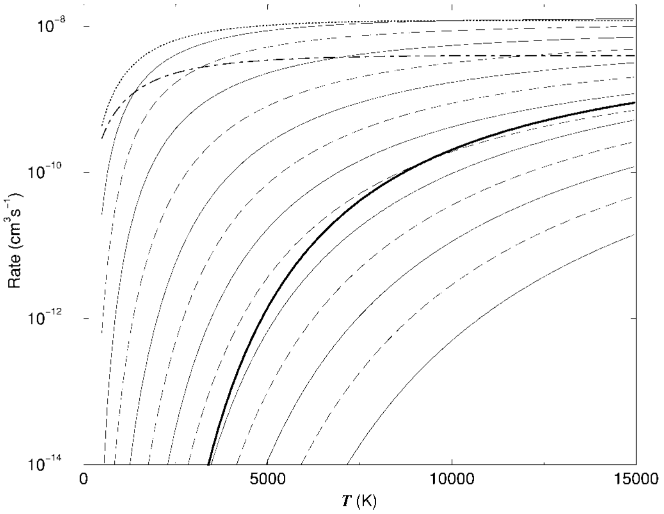

FIG. 2.—Electron impact dissociation rates as function of initial H_2 vibrational state v. Alternating thin solid and dashed lines from the bottom are the rates for $v = 0$–12. Rates for $v = 13$ (*dotted lines*) and $v = 14$ (*dot-dashed lines*) no longer follow the trend of increasing rate with v. The bold line is the LTE rate.

ited. No allowance is made for the possible effect of rotational motion of the H_2.

The rate of electron impact dissociation of H_2 in vibrational state v as a function of electron temperature T_e is calculated from the relevant cross sections using the standard formula

$$q_v(T_e) = \frac{8\pi}{\sqrt{m_e}}\left(\frac{1}{2\pi kT_e}\right)^{3/2}\int_{E=0}^{\infty}\sigma_v(E)e^{-E/kT_e}EdE, \qquad (2)$$

where k is the Boltzmann constant and m_e is the electron mass. For the temperatures under consideration here (up to 15,000 K), the threshold region of dissociation provides by far the most significant contribution to the total rate. Our cross sections are not reliable at high electron energy, and an upper limit for the integral in equation (2) of 15 eV is taken, which should give a sufficiently accurate rate at the relevant temperatures.

Figure 2 shows the calculated rates for the $v = 0$–4 initial H_2 vibrational levels (along with extrapolated $v = 5$–14 levels discussed later). It is clear that the rate is critically dependent on the initial vibrational level, rising several orders of magnitude with v. This is significant when considering total rates for a particular distribution of hydrogen molecules among its vibrational levels. The $v = 0$ value for the rate is often assumed to be a good approximation to the total rate. However, the v-dependence is so critical that this is unlikely to be the case. The rates (in cm^3 s^{-1}) are parameterized to the form

$$q(T) = aT^b \exp\left(-\frac{c}{T}\right) \times 10^{-9} \qquad (3)$$

and are given in Table 1.

At local thermal equilibrium (LTE), the molecules and the electrons each have a Maxwellian distribution associated with the same temperature T. The LTE rate $q_{\rm LTE}$ can be found from the thermally averaged cross section $\bar{\sigma}(E)$,

$$q_{\rm LTE}(T) = \frac{8\pi}{\sqrt{m_e}}\left(\frac{1}{2\pi kT}\right)^{3/2}\int_{E=0}^{\infty}\bar{\sigma}(E)e^{-E/kT}EdE, \qquad (4)$$

where

$$\bar{\sigma}(E) = \frac{1}{z}\sum_{v=0}\sigma_v(E)e^{-\gamma(v)/kT}, \qquad (5)$$

with z the partition function, $z = \sum_{v=0} e^{-\gamma(v)/kT}$, and $\gamma(v)$ the vibrational energy levels, with the sums running over the finite number of vibrational states. Alternatively, the rates themselves can be thermally averaged:

$$q_{\rm LTE}(T) = \frac{1}{z}\sum_{v=0} q_v(T). \qquad (6)$$

The LTE rate can be calculated using equation (6) with the summation cut off at $v = 4$, the highest vibrational level for

TABLE 1
RATES OF ELECTRON IMPACT DISSOCIATION OF H_2

Rate	T(min) (K)	a	b	c
$v = 0$	7200	3.730	0.1121	99430
$v = 1$	5900	5.049	0.0905	82860
$v = 2$	5000	5.181	0.0949	69890
$v = 3$	4100	5.194	0.1002	58960
$v = 4$	3500	5.458	0.1005	49540
LTE	3400	241600	−0.9120	55800

NOTE.—Electron dissociation rates from initial H_2 vibrational levels $v = 0$–4 assuming a thermal electron distribution, and the LTE rate. T(min) is the cutoff temperature below which each rate is under 10^{-14} cm^3 s^{-1} and effectively zero. The parameterization below T(min) is not accurate for the $v = 0$–4 rates, but is accurate for the LTE rate.

which we have cross sections found using the full calculation. The rate, shown in Figure 3, is more than an order of magnitude greater than the $v = 0$ rate. The figure also shows the contribution of each vibrational level to the total thermal equilibrium rate. It is immediately apparent that the higher vibrational levels contribute more to the total rate than the lower levels and that the sum is diverging. This means that including only the first five states is inadequate.

That the contributions of each vibrational level to the total rate should rise with v should not be so surprising. The contributions are determined by the balance between the rate rising with v, as the Franck-Condon (F-C) threshold reduces, and the population dropping as $\gamma(v)$ increases with v. As v increases, the population decreases exponentially. However, the rate has a more or less exponential dependence on the F-C threshold, at least at the low temperatures discussed here. Since the F-C threshold decreases faster than $\gamma(v)$ increases with increasing v (because of the rapidly falling dissociative curve), the rising rate overcomes the dropping population and the contributions increase with v.

In order to obtain an accurate figure for the thermal equilibrium rate, it is clearly necessary to include the higher vibrational states. However, to calculate the cross sections accurately for these states, T-matrices must be calculated over a much wider range of bond length. Our present calculation cannot provide these T-matrices because of basis set limitations and because, at long bond length, the target electronic wave function will leak out of the R-matrix boundary. Figure 1 suggests a method of approximating the cross sections instead. The shape of the cross section curves at threshold for all values of v is extremely consistent. As v increases, the F-C threshold is reduced and the curves are shifted to the left but keep the same shape. The reason for the consistency is that, at threshold, the F-C factor is responsible for the shape of the curves. Slightly above threshold, the variation in the fixed-nuclei T-matrix elements as a function of bond length and energy becomes important.

The dashed lines in Figure 1 are F-C calculations that attempt to reproduce the shapes without the need for further fixed-nuclei T-matrix calculations. Here the nuclear motion-averaged T-matrix is approximated to

$$\boldsymbol{T}_{v_i\rightarrow\text{cont.}}(E_{\text{in}}, E_{\text{out}}) = \langle \Xi_c(E_{\text{ke}}, R)|C|\ \Xi_{v_i}(R)\rangle\ , \qquad (7)$$

where Ξ_c and ψ_v are the normalized final continuum and initial vibrational wave functions, respectively, and E_{in} is the incoming electron energy, which is shared among the outgoing electron (E_{out}), the asymptotic kinetic energy of the nuclei (E_{ke}), and the dissociation energy (see Stibbe & Tennyson 1998b). C is a constant, put in place of the fixed-nuclei T-matrices T_{FN} used in the full calculation, and hence assumes that the T-matrices do not vary with energy or bond length.

A single constant C was found by fitting the F-C $v = 0$–4 results to those of the full calculation as closely as possible. The F-C cross sections give an excellent fit to the cross sections of the full calculation at energies below threshold and are a very close approximation at threshold. Above threshold, the F-C cross section consistently underestimates the full calculation cross section as the variation in fixed-nuclei T-matrices becomes significant and the approximation of constant T-matrices breaks down.

Equation (5) for the averaged cross section $\overline{\sigma}(E)$ underlies the usefulness of the scaled F-C factors. Because of the exponential factor in the summation, which tends to suppress the contributions from higher values of v, the contribution from the $v = n$ level, $\sigma_{v=n}$, is only significant in the $v = n$ threshold region when the $v = (n - 1)$ cross section is negligible. At higher electron energy, the $\sigma_{v=(n-1)}$ is not negligible and, since it is scaled by a larger Boltzmann factor, begins to dominate. In other words, moving left to right as the energy increases, each vibrational level contributes until it is replaced by the next lowest level. The F-C cross sections are therefore a reasonable representation of the true cross sections in the electron energy regions where they make an important contribution to the thermal rate constant.

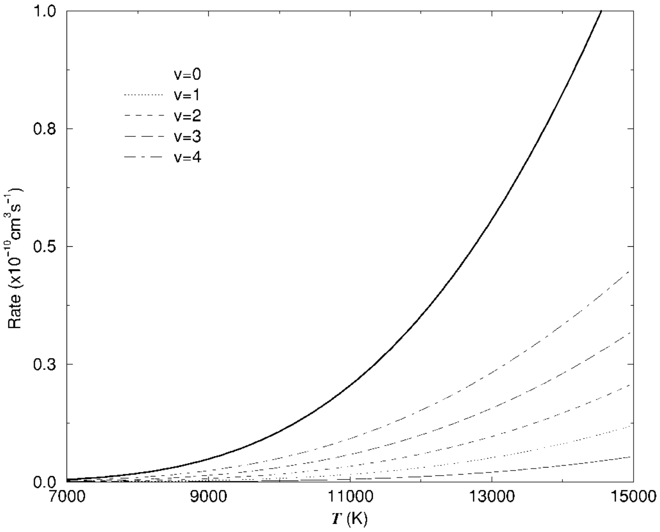

FIG. 3.—Total electron impact dissociation rate of H_2 calculated from the first five vibrational levels (*bold line*) and contribution to this rate from each of the vibrational levels (*thin lines*).

The F-C cross sections were calculated using an accurate H_2 potential curve (Schwartz & Le Roy 1987) for all of the vibrational states up to $v = 14$, the highest state discernible by the LEVEL program, which was used to find the vibrational wave functions (Le Roy 1996). Rates were calculated from the $v = 5$–14 F-C factor cross sections and, along with the rates for $v = 0$–4 from the full calculation, are shown in Figure 2. The rates stop increasing for $v = 12$ and drop slightly by $v = 14$. These rates were put into equation (6) to find the LTE rate, which is also shown in Figure 2. The LTE rate is parameterized in Table 1.

3. CONCLUSIONS

There is little data available for the low-energy electron impact dissociation of H_2 and none for dissociation from vibrationally excited states. We have calculated accurately the rate of dissociation from the lowest five vibrational levels and found that the rate increases so dramatically with v that all of the initial vibrational levels must be included in a calculation of the rate at local thermal equilibrium.

From the $v = 0$–4 results, we used a procedure to estimate the rates of dissociation from the remaining vibrational levels, $v = 5$–14. The LTE rate was calculated from these rates and found to be almost 2 orders of magnitude greater than the $v = 0$ rate. The fact that the LTE rate is so much higher than the $v = 0$ rate is important given that, with the lack of any alternative, the $v = 0$ rate is likely to be used as an approximation to the LTE rate.

Finally, it is worth noting that the greatly increased electron impact dissociation rates for vibrationally excited states of H_2 will, under some circumstances, result in vibrationally hot states of the molecule being preferentially dissociated. This could lead to subthermal vibrational populations of H_2, something not usually achieved by radiative cooling because of the unusually long lifetimes of vibrationally excited H_2.

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REFERENCES

Draine, B. T., Roberge, W. G., & Dalgarno, A. 1983, ApJ, 318, 379
Hollenbach, D., & McKee, C. F. 1989, ApJ, 342, 306
Kim, Y. H., Fox, J. L., & Caldwell, J. J. 1997, Icarus, 128, 189
Le Roy, R. J. 1996, University of Waterloo Chemical Physics Research Report, CP-555R, 1
Martin, P. G., Keogh, W. J., & Mandy, M. E. 1998, ApJ, 499, 793
Schwartz, C., & Le Roy, R. J. 1987, J. Mol. Spectrosc., 121, 420
Shugard, M., & Hazi, A. U. 1975, Phys. Rev. A., 12, 1895
Stibbe, D. T., & Tennyson, J. 1997a, J. Phys. B, 30, L301
———. 1997b, Phys. Rev. Lett., 79, 4116
———. 1998a, J. Phys. B, 31, 815
———. 1998b, New J. Phys., 1, 2
Tiné, S., Lepp, S., Gredel, R., & Dalgarno, A. 1997, ApJ, 481, 282
Yan, M., & Dalgarno, A. 1998, ApJ, 500, 1049