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Calculated vibrational excitation rates for electron – H_2^+ collisions

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ABSTRACT

Molecular *R*-matrix calculations are performed at a range of energies to give vibrational excitation cross-sections and hence rates for electron collisions with H_2^+. Results are presented for the $v=0\rightarrow1$, $0\rightarrow2$ and $1\rightarrow2$ excitations for electron temperatures up to 20 000 K. De-excitation rates and critical density are also studied. The vibrational motion is considered within an adiabatic model; an estimate is given for non-adiabatic effects. Our results suggest that the $v=0\rightarrow1$ rate peaks at 7.2×10^{-9} cm^3 s^{-1} for an electron temperature of 8000 K.

Key words: molecular data – molecular processes.

1 INTRODUCTION

Molecular hydrogen is the most abundant species in many parts of the Universe. Where H_2 and ionizing radiation come into contact, the presence of H_2^+ needs to be considered. As some properties of H_2^+, such as its dissociative recombination rate (Dalgarno & Lepp 1987; Mitchell 1990) and its photodissociation rate (Argyros 1974), are strongly dependent on the vibrational state, v, of the ion, vibrational excitation rates are important for modelling (Rawlings, Drew & Barlow 1993). Because of their large collision cross-section, one might well expect electrons to be the major exciting species.

Electron scattering from H_2^+ has been the subject of a number of detailed calculations, including those performed as a function of H_2^+ internuclear separation (e.g. Tennyson & Noble 1985; Shimamura, Noble & Burke 1990; Collins, Schneider & Noble 1992). To our knowledge, there have been only two previous calculations of the vibrational excitation cross-sections of H_2^+. Robb & Collins (1980) evaluated these cross-sections within the single-state approximation using the iterative static-exchange technique. Their results agreed with those of Boikova & Ob"edkov (1968), who used the Coulomb–Born approximation. For electron–HeH^+ collisions, our calculations (Sarpal, Tennyson & Morgan 1991) showed that Boikova & Ob"edkov's Coulomb–Born calculation significantly overestimated the vibrational excitation cross-section. As H_2^+ and HeH^+ differ in the leading term in their long-range potentials, the only contribution to the vibrational excitation cross-section in Coulomb–Born calculations, it is not clear whether the excitation rates for the two systems will scale in the same way.

In this paper, we present collision cross-sections for H_2^+ calculated with the molecular *R*-matrix method. We present results for the lowest three vibrational states, as these are likely to be the most important astrophysically. Furthermore, for higher vibrational states, processes such as dissociative recombination become more important than vibrational excitation. As these processes are not included in our treatment, cross-sections for these higher states would not be accurate.

2 CALCULATIONS

Electron–H_2^+ calculations were performed using the wavefunctions developed by Branchett & Tennyson (1992) for the study of transitions to Rydberg states of H_2. Calculations using the molecular *R*-matrix method (see Gillan et al. 1987) were performed on a grid of 12 internuclear separations in the range $(1.0–3.5)\,a_0$ and an *R*-matrix sphere of radius $14a_0$.

We included three SCF orbitals for each of the σ_g, σ_u, π_u and π_g symmetries. The continuum orbital set, with $l\leq6$, consisted of 41 σ_g, 33 σ_u, 32 π_u, 29 π_g, 30 δ_g and 21 δ_u orbitals. The appropriate continuum functions from the above set were coupled with the three lowest target states $^2\Sigma_g$, $^2\Sigma_u$ and $^2\Pi_u$ for the required total symmetry. The Σ, Π and Δ symmetries with both singlet and triplet spin states were considered. Polarization terms were also included by allowing the continuum electron to occupy one of the L^2 target orbitals.

Our scattering calculations as a function of internuclear separation were extensively tested by comparing our resonance positions and widths, and other properties, with results of previous electron – H_2^+ collision calculations (Tennyson & Noble 1985; Shimamura et al. 1990; Collins et al. 1992).

Nuclear motion was considered by using the adiabatic nuclei approximation, i.e. by using vibrational averages of the geometry-dependent **T**-matrices. Vibrational wavefunctions were generated as numerical solutions (Le Roy 1972) of the exact H_2^+ potential (Power 1973). The major omission from this model is the neglect of non-adiabatic effects. Coupling to vibrationally excited Rydberg states of H_2 will result in a rapidly varying cross-section but the averaged value still lies close to the adiabatic cross-section (see Sarpal et al. 1991). Feshbach resonances which converge to the excited states of the ion, on the other hand, are expected to alter the background behaviour of the cross-section, and the adiabatic approximation may no longer be appropriate. We have therefore restricted our calculations to relatively low energies, where Feshbach resonances have little effect.

In our previous calculations of vibrational excitation of HeH^+ by slow electrons, inclusion of non-adiabatic effects was relatively straightforward because there are only a few curve crossings in the system. For electron–H_2^+ collisions the situation is much more complicated, with many curve crossings which are very difficult to unravel (Tennyson, Noble & Burke 1986). We therefore did not attempt a non-adiabatic calculation.

3 RESULTS AND DISCUSSION

In practice, the Σ_g contribution to the scattering cross-section is dominant: it is larger than Σ_u, and the total Π contribution is only about 20 per cent of the Σ contribution. The Δ symmetries contribute only about 1 per cent of the total cross-section. Amongst the Π symmetries, the Π_u contributions are larger than those of Π_g. The relative importance of the various symmetries can be explained by noting that a larger cross-section is found in those symmetries that are obtained by coupling the ground state of H_2^+ ($^2\Sigma_g$) with the lowest allowed partial wave.

We find the vibrational excitation cross-sections for H_2^+ to be slightly larger than the corresponding cross-sections for HeH^+ (Sarpal et al. 1991). This is in complete contradiction to the results of Coulomb–Born calculations (Boikova & Ob"edkov 1968), which produced larger cross-sections for HeH^+ than for H_2^+ (see Fig. 1). The Coulomb–Born results were rationalized by the fact that HeH^+ has a permanent dipole, whereas H_2^+ does not. However, as we observed in our work on HeH^+, the long-range dipole and quadrupole terms do not change the excitation cross-section significantly. This would suggest that the dominant vibrational excitation mechanism is short-range forces. By the term 'short range', we mean the region inside our R-matrix sphere.

For HeH^+, a point-dipole approximation to the potential, as used in the Coulomb–Born approach, will overestimate the potential for small distances, particularly as HeH^+ has a large dipole moment, leading to larger excitation cross-sections. H_2^+, on the other hand, has a much weaker quadrupole moment and the first excited state is relatively close in energy, and therefore one might expect short-range polarization to be of considerable importance. This has been shown to be the case for the Σ and Π symmetries by Tennyson, Noble & Salvini (1984), and for the Δ symmetries by our present calculations. In the Coulomb–Born approximation, as well as in the calculations of Robb & Collins (1980), such polarization terms are not included.

We calculated cross-sections for electron energies up to a maximum value, $E_{\max}$, so that the total energy of the H_2^+ and the incident electron is 0.16 Ryd above the ground state. When evaluating the reaction rates, α, we assumed that at higher electron energies the cross-section follows a $1/E$ law. This assumption is valid for dipole forbidden transitions.

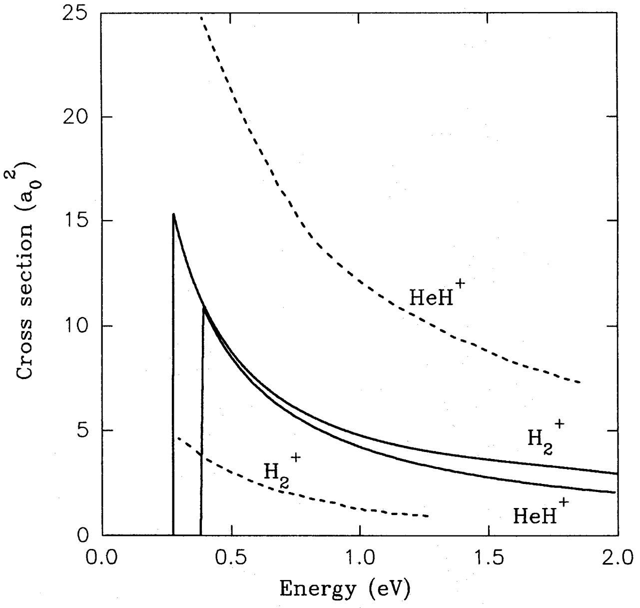

Figure 1. A comparison of the $v=0\rightarrow1$ cross-sections of H_2^+ and HeH^+ in the adiabatic nuclei approximation. Solid lines give our current results for H_2^+ and those of Sarpal et al. (1991) for HeH^+. The dashed lines give the Coulomb–Born results of Boikova & Ob"edkov (1968).

The high-energy tail contribution to the reaction rate can then be evaluated analytically, given the cross-section at the highest calculated electron energy. Assuming a Maxwellian distribution of electron energies at a given temperature, the reaction rate is given by

$$\alpha(T)=8\pi\left(\frac{1}{2\pi kT}\right)^{3/2}\left[E_{\max}\sigma(E_{\max})kT\exp(-E_{\max}/kT)+\int_0^{E_{\max}}E\sigma(E)\exp(-E/kT)\,\mathrm{d}E\right]. \qquad (1)$$

All quantities in (1) are in atomic units.

Table 1 presents vibrational excitation and de-excitation rates for the important transitions between low-lying vibrational states of H_2^+. It should be noted that, at all temperatures considered, $\Delta v=1$ transitions are strongly favoured. Unsurprisingly, as a result of Boltzmann effects, the de-exictation rates are significantly larger than the corresponding excitation rates.

The $v=0\rightarrow1$ excitation rate peaks at 7.2×10^{-9} cm^3 s^{-1} near a temperature of 8000 K. The excitation cross-section for $v=0\rightarrow1$ is almost exactly reproduced, to within 1 per cent, by

$$\alpha_{0\rightarrow1}(T)=3.314\times10^{-7}\,T^{-0.384}\,e^{-3025/T}\ \mathrm{cm^3\,s^{-1}} \qquad (2)$$

in the temperature range $1000\leq T\leq20\,000$ K. The functional form overestimates the rate at lower temperatures, where the absolute value of the rate is very small.

Fits to the de-excitation data in Table 1 are given by

$$\alpha_{1\rightarrow0}(T)=7.0\times10^{-7}\,T^{-0.462}\ \mathrm{cm^3\,s^{-1}}, \qquad (3)$$

$$\alpha_{2\rightarrow0}(T)=1.0\times10^{-7}\,T^{-0.455}\ \mathrm{cm^3\,s^{-1}}, \qquad (4)$$

$$\alpha_{2\rightarrow1}(T)=1.9\times10^{-6}\,T^{-0.486}\ \mathrm{cm^3\,s^{-1}}, \qquad (5)$$

Table 1. Rate coefficient ($cm^3\ s^{-1}$) for vibrational excitation of H_2^+ by thermal electrons. Powers of 10 are given in parentheses.

T (K)	$v=0\rightarrow1$	$v=0\rightarrow2$	$v=1\rightarrow0$	$v=1\rightarrow2$	$v=2\rightarrow0$	$v=2\rightarrow1$
100	9.9(−22)	1.8(−34)	8.5(−08)	2.6(−20)	1.2(−08)	2.0(−07)
200	6.5(−15)	3.4(−22)	6.1(−08)	5.1(−14)	8.9(−09)	1.4(−07)
300	1.1(−12)	8.3(−18)	5.0(−08)	5.9(−12)	7.3(−09)	1.2(−07)
400	1.4(−11)	1.2(−15)	4.3(−08)	6.1(−11)	6.3(−09)	1.0(−07)
500	6.3(−11)	2.4(−14)	3.9(−08)	2.4(−10)	5.7(−09)	9.1(−08)
1000	1.1(−09)	8.5(−12)	2.7(−08)	3.3(−09)	4.1(−09)	6.5(−08)
1500	2.7(−09)	5.5(−11)	2.3(−08)	7.3(−09)	3.4(−09)	5.3(−08)
2000	4.0(−09)	1.4(−10)	2.0(−08)	1.0(−08)	3.0(−09)	4.6(−08)
3000	5.6(−09)	3.2(−10)	1.6(−08)	1.4(−08)	2.5(−09)	3.8(−08)
4000	6.5(−09)	4.7(−10)	1.4(−08)	1.6(−08)	2.2(−09)	3.3(−08)
5000	6.9(−09)	5.9(−10)	1.3(−08)	1.6(−08)	2.0(−09)	3.0(−08)
6000	7.1(−09)	6.8(−10)	1.2(−08)	1.7(−08)	1.9(−09)	2.7(−08)
7000	7.2(−09)	7.5(−10)	1.1(−08)	1.7(−08)	1.8(−09)	2.5(−08)
8000	7.2(−09)	8.0(−10)	1.1(−08)	1.6(−08)	1.7(−09)	2.4(−08)
9000	7.2(−09)	8.4(−10)	1.0(−08)	1.6(−08)	1.7(−09)	2.3(−08)
10000	7.2(−09)	8.7(−10)	9.9(−09)	1.6(−08)	1.6(−09)	2.2(−08)
15000	6.8(−09)	9.3(−10)	8.4(−09)	1.5(−08)	1.4(−09)	1.8(−08)
20000	6.4(−09)	9.4(−10)	7.5(−09)	1.4(−08)	1.3(−09)	1.6(−08)

which agree to within 5 per cent with the calculated values for the entire temperature range considered here. For $v=1$, the de-excitation rate is almost identical to the dissociative recombination rate (Giusti-Suzor, Bardsley & Derkits 1983), whereas for $v=2$ it is more than twice the dissociative recombination rate.

Using our calculated rates and the radiative lifetimes of the $v=1$ and $v=2$ states, 1.92×10^6 and 1.08×10^6 s respectively (Peek, Hashemi-Attar & Beckel 1979), we have estimated the critical electron density for H_2^+ $v=1$ and 2 as a function of electron temperature. The critical density is defined as the electron density at which the collisional de-excitation rate is equal to the radiative de-excitation rate. The results are given in Table 2, and a functional form of the critial density for $v=1$ and 2 is given by

$$N_e(v=1)=0.744\,T^{0.462}\ \mathrm{cm}^{-3}, \tag{6}$$

$$N_e(v=2)=0.465\,T^{0.484}\ \mathrm{cm}^{-3}. \tag{7}$$

Finally, it is important to try to estimate the accuracy of our calculated cross-sections in order to determine the final accuracy of the results we have presented above. To estimate the error introduced by using the adiabatic approximation, we have computed vibrational excitation rates for electron–HeH^+ collisions using the two models. We find that the non-adiabatic approach gives rate approximately 10 per cent higher than the adiabatic ones. At low scattering energies, one can expect a similar contribution to the H_2^+ rates, but for higher energies there may be a large contribution from Feshbach resonances, and the adiabatic approximation will not then be appropriate. For these reasons, we have limited our study to the lowest three vibrational states – in any case, only the lowest few vibrational states are important in astrophysical environments. The neglect of symmetries higher than Δ_u will also lead to an underestimate of the rates. In this case, however, the rapid convergence with symmetries suggests a negligible error of only about 2 per cent.

Table 2. Critical electron density as a function of temperature, assuming a two-level model for the transition.

T (K)	Critical density (cm^{-3})	
	$v=1$	$v=2$
100	6.1	4.3
200	8.6	6.1
300	10.5	7.4
400	12.1	8.6
500	13.5	9.5
1000	18.9	13.4
1500	23.0	16.4
2000	26.4	18.8
3000	31.9	22.9
4000	36.2	26.3
5000	39.8	29.2
6000	42.9	31.8
7000	45.7	34.1
8000	48.2	36.2
9000	50.5	38.2
10000	52.7	40.0
15000	62.0	48.0
20000	69.7	54.6

Undoubtedly, our accuracy drops with temperature. For $T=15\,000$ or $20\,000$ K, the estimated contribution from the tail is more than 25 per cent of that actually evaluated by integration. An anomalously large tail contribution would be particularly evident if there were a resonance at higher energy which had not completely disappeared at the highest energy calculated. Our approximation for the tail contribution would in such a case overestimate the contribution from higher energies. Our results do not show resonance features in the calculated energy range.

4 CONCLUSIONS

We have calculated reaction rates and critical electron densities for a range of temperatures. These data will be useful for the modelling of chemical reactions where H_2^+ abundance is significant. Because of the long lifetime of excited vibrational states against radiative decay, electron-collision-induced de-excitation is most likely in conditions where the electron density is greater than 50 cm^{-3}, and where particle densities are low so that two- and three-body collisions can be neglected.

A major result of our calculations is that the vibrational excitation cross-section of H_2^+ is in fact slightly larger than that of HeH^+, whereas a much smaller cross-section had been anticipated. In the case of H_2^+, short-range polarization is found to enhance the cross-sections significantly. One can only conclude that, for positively charged hydrides, or possibly for positive ions in general, short- and medium-range potentials play the most important role. The long-range dipole and higher multipole potentials play a lesser role in vibrational excitation.

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