STATE RESOLVED DATA FOR RADIATIVE ASSOCIATION OF H AND H+ AND FOR PHOTODISSOCIATION OF H2

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ABSTRACT

The matrix elements and energies needed to calculate vibrational-rotational state resolved cross sections and rate coefficients for radiative association of H and H+ and for photodissociation of H2 are presented for applications to simulations of chemistry in the early universe and to stellar atmospheres.

Key words: early universe – molecular data – molecular processes – Sun: atmosphere – white dwarfs

Supporting material: machine-readable table

1. INTRODUCTION

Radiative association of H and H+ produces H2 in various vibrational-rotational states. Recent studies of H2 chemistry in the early universe indicated the necessity of accounting for the vibrational-rotational state distribution of the H2 population in the absence of local thermodynamic equilibrium, which accordingly requires “state-resolved,” i.e., vibrational-rotational state resolved, calculations of data for the H + H+ radiative association process and for the inverse process, photodissociation of H2. The absence of such data in the literature was noted by Hirata & Padmanabhan (2006), Coppola et al. (2011), and Glover et al. (2014). In the present paper, the necessary data to calculate radiative association and photodissociation cross sections for each vibrational-rotational level of H2 are presented. Cross sections so assembled can then be summed or averaged as required for particular applications, e.g., rate coefficients for non-local thermodynamic equilibrium models. In addition to being useful for early universe chemistry models, H2 photodissociation cross sections enter in models of the solar atmosphere (Stancil 1994; Mihajlov et al. 2007), where H2 is vibrationally excited, and in models of the atmospheres of DA white dwarfs (Santos & Kepler 2012), and of chemistry in the winds of young stellar objects (Glassgold 1998, p. 168).

The radiative association reaction

H + H+ → H2(v, N) + hν (1)

and its inverse process photodissociation

H2(v, N) + hν → H + H+ (2)

for a photon of energy hν are related through microscopic reversibility (Moses & Wu 1951a 1951b; Light et al. 1969; Hirata & Padmanabhan 2006), where (v, N) denotes the vibrational v and rotational N quantum number of the molecular ion.

The rate coefficients for Equation (1) calculated by Bates (1951), Ramaker & Peek (1976), and Stancil et al. (1993) are in agreement. The cross section summed over all bound states (v, N) of H2 was given by Stancil et al. (1993).

The photodissociation cross sections for Equation (2) were calculated by Oksyuk (1967), Dunn (1968a), Dunn (1968b), Argyros (1974), Stancil (1994), Lebedev & Presnyakov (2002), and Mihajlov et al. (2007). Where individual data for select (v, N) levels and photon energies hν is given there is general agreement between their calculations. A tabulation of the photodissociation cross sections for each of the vibrational states (v, 1) is given in the report of Dunn (1968b). Recently, calculations of the photodissociation cross sections were carried out for applications to DA white dwarfs by Santos & Kepler (2012).

2. THEORY

The cross section for radiative association (1) is (Stancil et al. 1993)

\[ \sigma^r_{v,N}(v, E) = \frac{8 \pi^2 h^3 v^3}{3 h^2 c^3 k^2} p[NM_{v,N-1;k,N}^2 + (N+1)M_{v,N+1;k,N}^2] \]

and \( N_{v,N-1;k,N} \) is the matrix element of the transition dipole moment between the continuum wave function of energy \( E \) and angular momentum \( N \) and the bound vibrational-rotational wave function, \( k^2 = 2 \mu E/h^2, \mu \) is the reduced mass of the colliding system, \( h \) is the photon energy, and \( p = 1/2 \) is the probability of approach in the \( 2p \sigma_g \) electronic state.

The cross section for photodissociation is (Lebedev & Presnyakov 2002)

\[ \sigma^pd_{v,N}(h\nu) = \frac{8\pi^3 v}{3c(2N+1) [(N+1)M_{v,N;k,N+1}^2 + NM_{v,N;k,N-1}^2]}. \]

In Equations (3) and (4), the nuclear spin symmetry weighting is omitted and it can be included later if the cross sections are being folded into a temperature distribution (Stancil 1994; Mihajlov et al. 2007). The effect of centrifugal distortion is negligible for the repulsive \( 2p \sigma_g \) state and it is a good approximation to replace \( N+1 \) and \( N-1 \) by \( N \) in Equations (3) and (4). Then,

\[ \sigma^r_{v,N}(v, E) = \frac{8 \pi^2 h^3 v^3}{3 h^2 c^3 k^2} p(2N+1)M_{v,N;k,N}^2 \]

and the cross section for photodissociation is

\[ \sigma^pd_{v,N}(h\nu) = \frac{4\pi^2 h v}{3hc} M_{v,N;k,N}^2. \]

A comparison of Equations (5) and (6) shows that

\[ \sigma^r_{v,N}(v, E) = p \frac{(h\nu)^2}{\mu c^2 E} \sigma^pd_{v,N}(h\nu). \]
Table 1  
Calculated Values of the Squared Matrix Element, \( M_{v,N,k,N}^2 \), for Bound Vibrational-rotational Levels (\( v, N \)) of the \( 1\sigma_g \) State of \( H_2^+ \) with Eigenvalue \( |E_{v,N}| \) to a Continuum Level of the \( 2p\sigma_u \) State of Relative Kinetic Energy \( E \) for a Photon of Energy \( h\nu \).  

| \( v \) | \( N \) | \( E \) | \( |E_{v,N}| \) | \( c/h\nu \) | \( M_{v,N,k,N}^2 \) |
|-----|-----|-----|------|--------|--------|
| 0   | 0   | 0.7310E+00 | 21375.95 | 55.00 | 0.1333E-03 |
| 0   | 0   | 0.7249E+00 | 21375.95 | 55.41 | 0.1687E-03 |
| 0   | 0   | 0.7188E+00 | 21375.95 | 55.83 | 0.2126E-03 |
| 0   | 0   | 0.7128E+00 | 21375.95 | 56.24 | 0.2667E-03 |
| 0   | 0   | 0.7069E+00 | 21375.95 | 56.65 | 0.3329E-03 |
| 0   | 0   | 0.7011E+00 | 21375.95 | 57.06 | 0.4138E-03 |
| 0   | 0   | 0.6953E+00 | 21375.95 | 57.48 | 0.5122E-03 |
| 0   | 0   | 0.6897E+00 | 21375.95 | 57.89 | 0.6312E-03 |
| 0   | 0   | 0.6841E+00 | 21375.95 | 58.30 | 0.7747E-03 |
| 0   | 0   | 0.6786E+00 | 21375.95 | 58.72 | 0.9469E-03 |
| 0   | 0   | 0.6732E+00 | 21375.95 | 59.13 | 0.1153E-02 |
| 0   | 0   | 0.6678E+00 | 21375.95 | 59.54 | 0.1398E-02 |
| 0   | 0   | 0.6626E+00 | 21375.95 | 59.95 | 0.1689E-02 |
| 0   | 0   | 0.6574E+00 | 21375.95 | 60.37 | 0.2033E-02 |
| 0   | 0   | 0.6523E+00 | 21375.95 | 60.78 | 0.2438E-02 |
| 0   | 0   | 0.6472E+00 | 21375.95 | 61.19 | 0.2914E-02 |
| 0   | 0   | 0.6422E+00 | 21375.95 | 61.61 | 0.3470E-02 |
| 0   | 0   | 0.6373E+00 | 21375.95 | 62.02 | 0.4181E-02 |
| 0   | 0   | 0.6324E+00 | 21375.95 | 62.43 | 0.4872E-02 |
| 0   | 0   | 0.6276E+00 | 21375.95 | 62.84 | 0.5743E-02 |
| 0   | 0   | 0.6229E+00 | 21375.95 | 63.26 | 0.6750E-02 |
| 0   | 0   | 0.6182E+00 | 21375.95 | 63.67 | 0.7907E-02 |
| 0   | 0   | 0.6136E+00 | 21375.95 | 64.08 | 0.9235E-02 |
| 0   | 0   | 0.6091E+00 | 21375.95 | 64.49 | 0.1075E-01 |
| 0   | 0   | 0.6046E+00 | 21375.95 | 64.91 | 0.1248E-01 |
| 0   | 0   | 0.6001E+00 | 21375.95 | 65.32 | 0.1445E-01 |
| 0   | 0   | 0.5956E+00 | 21375.95 | 65.73 | 0.1666E-01 |
| 0   | 0   | 0.5914E+00 | 21375.95 | 66.15 | 0.1920E-01 |
| 0   | 0   | 0.5872E+00 | 21375.95 | 66.56 | 0.2204E-01 |
| 0   | 0   | 0.5829E+00 | 21375.95 | 66.97 | 0.2523E-01 |

Notes. In the table, \( E \) is in atomic units, \( |E_{v,N}| \) is in cm\(^{-1} \), \( c/h\nu \) is in nm, and \( M_{v,N,k,N}^2 \) is in atomic units.

(This table is available in its entirety in machine-readable form.)

in accordance with microscopic reversibility (Light et al. 1969). Thus, tabulation of \( v, N, E_{v,N}, E \), and \( M_{v,N,k,N}^2 \) provides the necessary information for calculations of \( \sigma^\text{pd}_{v,N}(h\nu) \), subject to the requirement \( \delta(h\nu - (|E_{v,N}| + E)) \) for either Equation (5) or Equation (6), where \( E_{v,N} \) is the vibrational-rotational eigenvalue in the \( 1\sigma_g \) state measured with respect to the dissociation limit (taken to be zero here).

3. MOLECULAR STATES

The Born-Oppenheimer potential energy surfaces for the ground \( 1\sigma_g \) state and excited \( 2p\sigma_u \) state were calculated using the methods described by Madsen & Peek (1971) and extended asymptotically as in Stancil et al. (1993). The transition dipole moment was calculated using a variational method (Babb 1994) and extended using the asymptotic formula of Ramaker & Peek (1973). Energy differences and oscillator strengths are in excellent agreement with the recent calculations of Tsogbayar & Banzragch (2010).

There are 423 bound vibrational-rotational levels for \( H_2^+ \) in the \( 1\sigma_g \) state. In the present work, the Born-Oppenheimer potential is used and adiabatic, relativistic, and radiative corrections are ignored. It is worth noting that more precise approaches yield the same number of bound levels (Hunter et al. 1974; Moss 1993), but due to the inclusion of higher-order corrections the resulting

4. CALCULATIONS

The quantities are calculated at a range of energies from the threshold energy \( |E_{v,N}| \) for photodissociation of level \( (v, N) \) to a maximum photon wavelength of 55 nm (22.5 eV or 0.828 a.u.). Only values of \( M_{v,N,k,N}^2 > 1 \times 10^{-9} \) are listed.

Table I gives the vibrational quantum number \( v \), the rotational quantum number \( N \), the relative energy \( E \) in atomic units of energy (27.2114 eV), the eigenvalue \( |E_{v,N}| \) in cm\(^{-1} \), the photon wavelength \( \lambda = c/h\nu \) in nm, and the value of \( M_{v,N,k,N}^2 \) in atomic units.

The photodissociation cross section in units of cm\(^2\) is (el-Qadi & Stancil 2013)

\[
\sigma^\text{pd}_{v,N}(h\nu) = 2.689 \times 10^{-18}(45.563/\lambda)M_{v,N,k,N}^2 \text{ cm}^2, \tag{8}
\]

with \( \lambda \) in nm and \( M_{v,N,k,N}^2 \) in atomic units. The radiative association cross section in units of cm\(^2\) is (Stancil et al. 1993)

\[
\sigma^\text{ra}_{N}(v, E) = 1.475 \times 10^{-20}(45.563/\lambda)^3 \times (2N + 1)E^{-1}M_{v,N,k,N}^2 \text{ cm}^2, \tag{9}
\]

with \( \lambda \) in nm, \( E \) in atomic units, and \( M_{v,N,k,N}^2 \) in atomic units.

Dunn (1968a, 1968b) calculated the photodissociation cross section for \( v = 0 \) to \( v = 18 \) using the potential energy surfaces calculated by Bates et al. (1953). There are slight differences between the accurate potential energy surfaces of the present work and the early calculations of Bates et al. (1953). Nevertheless, agreement is generally good between the current calculations and the tabulated values of Dunn (1968a, 1968b).

In Figure 1 for \( v = 10, N = 0 \), a plot of \( \sigma^\text{pd}_{v,N}(h\nu) \) calculated from the data in Table 1 is presented. The representation is very good and the tabulated data reflect the peaks arising from the \( v = 10 \) bound state wave function. The present tabulated data can be interpolated using cubic splines, but due to the oscillations several intervals should be selected.
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The numerical factor in Equation (9) is incorrect. The correct factor is \(7.797 \times 10^{-26}\). I am grateful to Mark C. Zammit for bringing this to my attention.

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