Inelastic cross sections for low-energy Mg + H collisions

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Abstract. Quantum calculations of cross sections for the inelastic processes in Mg + H collisions are improved. It is shown that the largest cross section among the endothermic processes with the value of approximately 80 Å² corresponds to the process of the ion-pair formation: Mg(3s4s¹S)+H → Mg⁺ + H⁻. The mechanism of the process is based on nonadiabatic transitions between the MgH(2Σ⁺) molecular states, which provide the main mechanism for inelastic processes in Mg + H collisions. On the other hand, nonadiabatic transitions between MgH(2Π) states affect some cross sections rather significantly. For example, transitions between the MgH(2Π) states increase the cross section for the excitation process Mg(3s3p¹P)+H → Mg(3s3d¹D)+H almost by an order of magnitude as compared to the cross section obtained within the MgH(2Σ⁺) symmetry.

1. Introduction

The measurement of abundances of chemical elements in stellar atmospheres, as interpreted from stellar spectra, is of fundamental importance in modern astrophysics, see, e.g., [1, 2, 3, 4]. Inelastic processes in collisions of different atoms with hydrogen atoms are important for the non-local thermodynamic equilibrium modeling of stellar atmospheres in determining spectra line shapes which is the main tool for relative and absolute chemical abundances, see, e.g., [2, 4]. Magnesium is an element of significant astrophysical importance, see [5, 6] and references therein. Thus, the need for investigation of inelastic collisions of hydrogen atoms with magnesium atoms is well justified.

In the earlier works, Ref. [7, 8], the quantum dynamical calculations have been performed for the three MgH(2Σ⁺) plus two MgH(2Π) molecular states, as well as for the eight lowest-lying MgH(2Σ⁺) states, respectively, based on the accurate ab initio quantum chemical data [9]. In Ref. [7] it was shown that among the low-lying states the transitions between 2Σ⁺ molecular states dominate over transitions involving states of other symmetries. For this reason, the inelastic cross sections were calculated in Ref. [8] by taking into account only the transitions between the eight lowest-lying MgH(2Σ⁺) states. In the present paper, we extend the earlier calculations to include nonadiabatic transitions between MgH(2Π) states.
work in Ref. [8] through a calculation including nine $^2\Sigma^+$ states up to and including the ionic channel, and the five lowest $^2\Pi$ states based on the improved ab initio quantum-chemical data.

2. MgH interaction potentials, related couplings and cross sections

2.1. Ab initio quantum-chemical calculations

The adiabatic potentials and nonadiabatic couplings were calculated using large active spaces and basis sets since avoided crossings occur due to the $Mg^+ + H^-$ ionic configuration [9]. All $^2\Sigma^+$, $^2\Pi$, $^2\Delta$, $^4\Sigma^+$, and $^4\Pi$ electronic molecular states arising from Mg + H for energies up to about 6 eV above the lowest atomic asymptote Mg ($^1S$) + H ($^2S_g$) were calculated at the MRCI level, as well as the couplings between these states. The details are described in Refs. [7, 9] and will be described elsewhere.

The nine lowest MgH($^2\Sigma^+$) molecular states treated in the present work are collected in Table 1, including their asymptotic atomic limits. The corresponding potential energy curves (PECs) are represented on Fig. 1 as a function of the internuclear distance. A series of avoided crossings for the $^2\Sigma^+$ states is clearly seen. The background of these avoided crossings is an interaction of covalent states with the Mg$^+$ + H$^-$ ionic state. For the high-lying molecular states the avoided crossings occur at large distances with small adiabatic splittings (for details see Fig. 2). These avoided crossings provide the main mechanism for inelastic processes in low-energy Mg + H collisions, that is, for the processes of excitation, de-excitation, ion-pair production, and mutual neutralization. The nonadiabatic couplings needed for performing quantum dynamical calculations are depicted in Fig. 3. They clearly confirm the presence of the nonadiabatic regions, where nonadiabatic transitions take place.

It is worth emphasizing that the five lowest MgH($^2\Sigma^+$) molecular states have practically the same adiabatic potentials and nonadiabatic couplings as in the previous calculations [7, 8, 9]. The improvement mainly concerns the higher-lying states, starting from $j = 6$. Thus, inelastic cross sections obtained with the present more accurate quantum-chemical data may be expected to deviate more substantially for partial processes with participation of high-lying states.

Table 1. The MgH molecular channels, the corresponding asymptotic atomic states and the calculated and experimental (NIST [10] weighted average values) asymptotic energies with respect to the ground state. Some calculated asymptotic values were adjusted to fit the experimental data.

| $j$ | Molecular states | Atomic asymptotic states | Asymptotic Calculation | Asymptotic energies (eV) |
|-----|------------------|--------------------------|------------------------|--------------------------|
| 1   | 1 $^2\Sigma^+$   | Mg($^3s^2\,^1S$) + H     | 0.0                    | 0.0                      |
| 2   | 2 $^2\Sigma^+$   | Mg($^3s3p\,^3P$) + H     | 2.7142                 | 2.7142                   |
| 3   | 3 $^2\Sigma^+$   | Mg($^3s3p\,^1P$) + H     | 4.3894                 | 4.3458                   |
| 4   | 4 $^2\Sigma^+$   | Mg($^3s4s\,^3S$) + H     | 5.1342                 | 5.1078                   |
| 5   | 5 $^2\Sigma^+$   | Mg($^3s4s\,^1S$) + H     | 5.4237                 | 5.3937                   |
| 6   | 6 $^2\Sigma^+$   | Mg($^3s3d\,^1D$) + H     | 5.7532                 | 5.7532                   |
| 7   | 7 $^2\Sigma^+$   | Mg($^3s4p\,^3P$) + H     | 5.9321                 | 5.9321                   |
| 8   | 8 $^2\Sigma^+$   | Mg($^3s3d\,^3D$) + H     | 5.9460                 | 5.9459                   |
| 9   | 9 $^2\Sigma^+$   | Mg$^+$($^3s\,^2S$) + H$^-$ | 6.8916                 | 6.8916                   |
Figure 1. (Color online) Potential energy curves for the lowest nine MgH(2Σ⁺) states.

Figure 2. (Color online) Zoom on the highest calculated potential energy functions.

2.2. Nonadiabatic nuclear dynamics
The nonadiabatic nuclear dynamical calculations are carried out within the standard adiabatic Born-Oppenheimer approach by means of the multi-electron reprojection method [11] (see also
references therein) to account for the so-called electron translation problem. The method takes into account non-vanishing asymptotic nonadiabatic matrix elements, provides the correct incoming and outgoing asymptotic total wave functions, and removes nonadiabatic transitions between atomic-state channels in the asymptotic region. First, the nuclear dynamics was performed for the three low-lying \( ^2\Sigma^+ \) and the first two \( ^2\Pi \) states \cite{7}. It was concluded that the main mechanism for nonadiabatic transitions between molecular states at low energies is due to the radial couplings associated with the avoided ionic crossings in the \( ^2\Sigma^+ \) symmetry. The same mechanism, though in the \( ^1\Sigma^+ \) symmetry, was found to be dominant in calculations for Li+H and Na+H low-energy collisions \cite{12, 13, 14, 15, 16, 17}. Based on this conclusion, the nonadiabatic dynamics is then studied for the nine lowest molecular states in the \( ^2\Sigma^+ \) symmetry including the ionic channel, as the astrophysical applications \cite{6, 18, 19, 20} show the importance of ion-pair production processes.

The calculated cross sections for the endothermic processes are presented in Fig. 4 for each particular initial channel. The collision energy \( E \) is the kinetic energy in a given initial channel. The cross sections shown in Fig. 4 are the result of the calculation accomplished within the \( ^2\Sigma^+ \) symmetry. The comparison of the present cross sections with those obtained in Ref. \cite{8} shows...
that the calculations are stable, but some cross section deviate due to the new and more accurate quantum chemical data. It is seen that the process of the ion-pair formation: Mg(3s4s1S)+H → Mg⁺ + H⁻ has the largest cross section of approximately 80 Å² among the endothermic processes. The previously calculated cross section for the same process had a value of 100 Å² [8], that is, the deviation is around 20%. This is within the expected accuracy.

![Cross sections](image)

**Figure 4.** (Color online) The inelastic cross sections $\sigma_{jk}(E)$ for transitions $j \rightarrow k$ ($k > j$) in low-energy Mg + H collisions. The label $j$ of the initial state from which transitions occur is indicated in each panel. The key for the final states $k$ is given in the bottom right panel.

Nonadiabatic transitions between MgH(2Π) states may affect significantly the excitation (but not ion-pair formation or mutual neutralization) cross sections due to transitions between highly excited states of magnesium atoms colliding with hydrogen (see Fig. 5). The labels for the processes within the MgH(2Π) is the same as in the MgH(2Σ⁺) symmetry (see Table 1), but one should keep in mind that not all atomic channels collected in Table 1 can produce MgH(2Π) molecular channels. For example, in the case of the excitation process Mg(3s3p1P)+H → Mg(3s3d1D)+H accounting transitions between the MgH(2Π) states increases the cross section almost by an order of magnitude as compared with the cross section obtained within the MgH(2Σ⁺) states.

The physics for the inelastic processes in the treated collisions was carefully studied in Ref. [8] and several mechanisms were found. The present calculations confirm the previous conclusions. It is shown that some of the mechanisms are determined by interactions between adjacent molecular states due to interactions between ionic and covalent configurations. However, mechanisms at short distances, not restricted to adjacent states, are found to be important.
Figure 5. (Color online) The inelastic cross sections $\sigma_{jk}(E)$ for transitions $j \rightarrow k$ ($k > j$) in low-energy Mg + H collisions calculated within the $^2\Sigma^+$ symmetry (solid lines) and within the $^2\Pi$ symmetry (lines plus symbols).

for some partial processes. These mechanisms explain the relatively large cross sections for excitation of highly excited states.

3. Concluding remarks
In the present study the cross sections for the inelastic processes in Mg+H collisions are calculated based on the improved quantum-chemical data and on estimates of accounting nonadiabatic transitions not only in the MgH($^2\Sigma^+$) symmetry, but also in the MgH($^2\Pi$) symmetry. It is shown that the process of the ion pair formation: Mg(3s4s $^1S$)+H $\rightarrow$ Mg$^+$ + H$^-$ has the largest cross section of approximately 80 Å$^2$ among the endothermic processes. This process occurs due to the nonadiabatic transitions between the $^2\Sigma^+$ states. On the other hand, nonadiabatic transitions between MgH($^2\Pi$) states affect significantly some excitation cross sections due to transitions between highly excited states of magnesium atoms colliding with hydrogen. As an example, accounting transitions between the MgH($^2\Pi$) states increases the cross section for the excitation process Mg(3s3p $^1P$)+H $\rightarrow$ Mg(3s3d $^1D$)+H almost by an order of magnitude as compared with the cross section obtained within the MgH($^2\Sigma^+$) symmetry.
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References
[1] Lambert D L 1993 Phys. Scr. T 47 186
[2] Asplund M 2005 A&A 43 481
[3] Barklem P S. 2007 A&A 466 327
[4] Barklem P S 2012 J. Phys.: Conf. Series 397 012049
[5] Arnone E, Ryan S G, Argast D, Norris J E and Beers T C 2005 A&A 430 507
[6] Mashonkina L 2013 A&A 550 A28
[7] Guitou M, Belyaev A K, Barklem P S, Spielfiedel A and Feautrier N 2011 J. Phys. B 44 035202
[8] Belyaev A K, Barklem P S, Spielfiedel A, Guitou M, Feautrier N, Rodionov D S and Vlasov D V 2012 Phys. Rev. A 85 032704
[9] Guitou M, Spielfiedel A and Feautrier N 2010 Chem. Phys. Lett. 488 145
[10] Ralchenko Y, Kramida A E and Reader J (NIST ASD Team), NIST Atomic Spectra Database (version 3.1.4), Gaithersburg, MD,USA: National Institute of Standards and Technology, 2008 [http://physics.nist.gov/asd3].
[11] Belyaev A K 2010 Phys. Rev. A 82 060701(R)
[12] Belyaev A K, Grosser J, Hahne J and Menzel T 1999 Phys. Rev. A 60 2151
[13] Croft H, Dickinson A S and Gadéa, F X 1999, J. Phys. B 32 81
[14] Croft H, Dickinson A S and Gadéa F X 1999, MNRAS 304 327
[15] Dickinson A S, Poteau R and Gadéa F X 1999 J. Phys. B 32 5451
[16] Belyaev A K and Barklem P S 2003 Phys. Rev. A 68 062703
[17] Belyaev A K, Barklem P S, Dickinson A S and Gadéa F X 2010 Phys. Rev. A 81 032706
[18] Barklem P S, Belyaev A K and Asplund M 2003 A&A 409 L1
[19] Lind K, Asplund M and Barklem P S 2009 A&A 503 541
[20] Lind K, Asplund M, Barklem P S and Belyaev A K 2011 A&A 528 A103