Molecular treatment of single (dissociative and non dissociative) and double electron capture in He^{2+} + H$_2$ collisions.

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Abstract. We present close-coupling calculations of total cross sections for single and double electron capture in He^{2+} + H$_2$ collisions in the range of 0.5 - 25 keV/amu, which are compared with experimental data. We confirm the experimental finding that the dominant process for $E \gtrsim 3$keV/amu is the non dissociative capture: He^{2+} + H$_2$ $\rightarrow$ He$^+$(2l) + H$_2^+$(1σ_g), while at lower energies is the dissociative capture leading to He$^+$(1s) +H$^+$+ H. Our calculations also show that He(1s2l) is the main output of the two-electron capture process.

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He^{2+} + H$_2$ collisions have been studied in many experimental works (Graham *et al* 1974, Shah and Gilbody 1976, Shah and Gilbody 1978, Nutt *et al* 1978, Afrosimov *et al* 1980, Shah *et al* 1989, Kusakabe *et al* 1990, Okuno *et al* 1992, Sato *et al* 1994, Hoekstra *et al* 1994, Hodgkinson *et al* 1995, Lubinski *et al* 2001, Juhász *et al* 2002) and model calculations(Shingal and Lin 1989, Saha *et al* 1991, Fritsch 1992, Shikamura *et al* 1993). A reason for this interest is their relevance in fusion plasmas (see (Janev 2001)), and in the interaction of solar wind with comets and planetary atmospheres (see (Cravens 2002) and references therein), where, in both cases, He^{2+} ions are important components of the plasmas. A second reason is that He^{2+}-H$_2$ is a benchmark system for ion-molecule collisions. Besides, cross sections for ion-H$_2$ collisions have been used in plasma modeling (e.g. (Häberli *et al* 1997)) for ion collisions with more complex targets (CO, H$_2$O), whose cross sections are unknown. In particular, recent experiments for He^{2+} collisions with CO of Kearns *et al* (2001) and O$_2$ (Kamber *et al* 2002) targets, have concluded that

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dissociative electron capture is the dominant process at low energies, as previously found for He^{2+}-H$_2$ (Afrosimov *et al* 1980, Hoekstra *et al* 1994, Hodgkinson *et al* 1995).

As a conclusion of He^{2+}-H$_2$ experiments, it is known that, for impact energies below 20keV/amu, the most important processes are:

- Non dissociative single electron capture (NDSEC):

$$\text{He}^{2+} + \text{H}_2 \rightarrow \text{He}^+ + \text{H}_2^+ \tag{1}$$

- Dissociative single electron capture (DSEC):

$$\text{He}^{2+} + \text{H}_2 \rightarrow \text{He}^+ + \text{H} + \text{H}^+ \tag{2}$$

- Two-electron capture (TEC):

$$\text{He}^{2+} + \text{H}_2 \rightarrow \text{He} + \text{H}^+ + \text{H}^+ \tag{3}$$

However, sizeable discrepancies exist between different experiments; this is in contrast with the situation for He^{2+} + H collisions, which seems surprising since most of the data for He^{2+} collisions with H and H$_2$ were measured in the same works. An explanation for this difference could be the lack of reliable calculations for He^{2+} + H$_2$. In particular, at low energies, we can only mention the model calculation of Shikamura *et al* (1993), where the H$_2$ molecule was approximated by two atoms with an average ionization potential. This work, did not include DSEC channels, and this approximation, lead to the conclusion that TEC is the dominant process at low energies. It also suggested that He(1s3l) is the main product of TEC at energies below several keV. Until now, no *ab initio* calculations have been carried out, which also seems surprising given that the HeH$_2^+$ system has only two electrons. However, it must be noted that, for infinite He^{2+} H$_2$ distances, the energy of the entrance channel is above that of He$^+$(1s) + H$_2^{2+}$ + e$^-$ which is the limit of the two Rydberg series He(1snl) + H$_2^{2+}$, and He$^+$(1s) + H$_2^+$($n\lambda$). Moreover, an important difference of He^{2+}-H$_2$ with other ion-H$_2$ collisions (e.g. H$^+$+ H$_2$) is the dominance of DSEC (2) at low v.

The aim of this work is to present the first *ab initio* cross sections for processes (1)-(3), and compare them to the experimental data. We do not include in this letter either a detailed description of the methodology or a discussion of the mechanisms. These lengthly details, together with an explanation of the limits of validity of our techniques will be presented elsewhere (Errea *et al* 2003). Nevertheless, we point out here that our analysis indicates that presence of the vibrational degrees of freedom and the competition between different process prevent us to attain a similar high accuracy as in the case of ion-atom collisions (see e.g. (Errea *et al* 1999*a*)).

Our calculation employs an eikonal, Franck-Condon (FC) treatment. At low energies ($E \lesssim 5$keV/amu), our treatment is similar to that of the calculation of Errea *et al* (1999*b*) for C^{2+}+H$_2$ collisions, where the dynamical wavefunction is expanded in a set of *ab initio* three-centre functions. Here our basis set includes the following 10 electronic states of the HeH$_2^{2+}$ quasimolecule:

(i) The entrance channel, which dissociates into He^{2+}+H$_2$(X$^1\Sigma_g^+$).

(ii) Three NDSEC states, which dissociate into $He^+(2s,2p)+ H_2^+(1\sigma_g)$.

(iii) Three DSEC states, which dissociate into $He^+(1s)+ H_2^+(2\sigma_g, 1\sigma_u, 3\sigma_g)$.

(iv) Three TEC states, which dissociate into $He(1s2s, 1s2p)+ H^+ + H^+$.

At high energies, where ionization starts to be competitive with electron capture ($E \gtrsim 5keV/amu$ in this system), the molecular expansion becomes inaccurate (see (Errea *et al* 2002) and references therein). In this energy range we have employed the IPM-OEDM treatment, based on the following approximations: 1) A two-centre potential is defined by substituting the H_2^+ core by an effective charge (1.0995), obtained by fitting the H_2 ionization potential. 2) The eikonal equation is solved for this potential in a basis of 14 molecular orbitals (OEDM) and 96 Gaussian pseudostates (Errea *et al* 1998). 3) Transition probabilities are obtained by applying the independent particle model (IPM) with the equivalent electron interpretation (see (McGuire and Weaver 1977, Sidorovich 1981, Lüdde and Dreizler 1985)). As it is well known, although the IPM approach is in general not appropriate to describe two-electron processes (in particular, DSEC and TEC), it provides accurate cross sections for one-electron processes, such as NDSEC and single ionization (see (Errea *et al* 2001) and references therein).

Our cross sections for DSEC, NDSEC and total capture (the sum of DSEC and NDSEC) cross sections are plotted in fig 1, compared with the experimental ones of (Nutt *et al* 1978, Shah *et al* 1989, Hodgkinson *et al* 1995, Okuno *et al* 1992). Our results agree with the conclusions of the experimental works of Hodgkinson *et al* (1995) and Shah *et al* (1989)(see fig. 1), which pointed out that DSEC is the dominant process at low energy, and NDSEC at $E \gtrsim 10keV$. In view of the inappropriateness of the IPM-OEDM treatment to obtain DSEC cross sections, we have extended the *ab initio* results for this process in figure 1 up to E=20keV/amu. These agree with the experimental data of (Shah *et al* 1989). Then, for $E >$5keV/amu, we have estimated the total single electron capture, by adding up what we deem to be the most accurate values that we have obtained: IPM-OEDM cross section for NDSEC and *ab initio* ones for DSEC; this also shows good agreement with the experimental data of Shah and Gilbody (1978).

The comparison of figure 1 shows that our total cross section overestimates the experimental values of refs. (Nutt *et al* 1978, Kusakabe *et al* 1990, Okuno *et al* 1992) for $E \lesssim 3keV/amu$. We have studied this point in detail and concluded that what may be at stake is a limitation of our FC method. In this respect, we have carried out a test calculation of the DSEC cross section by using a model (called vibrational excitation model in figure 1). This model, which is explained in (Errea *et al* 2003), includes two electronic states (the entrance channel and the state which correlates to $He^+(1s)+ H_2^+(2\sigma_g)$ when $R \to \infty$), and assumes that non adiabatic transitions take place from a vibrational wavepacket built up by allowing vibrational excitation in the electronic entrance channel. We can see in fig. 1 that the approximate inclusion of vibrational effects in this model leads to a noticeable decrease of the single capture cross section, which points to a limitation of the FC approximation.
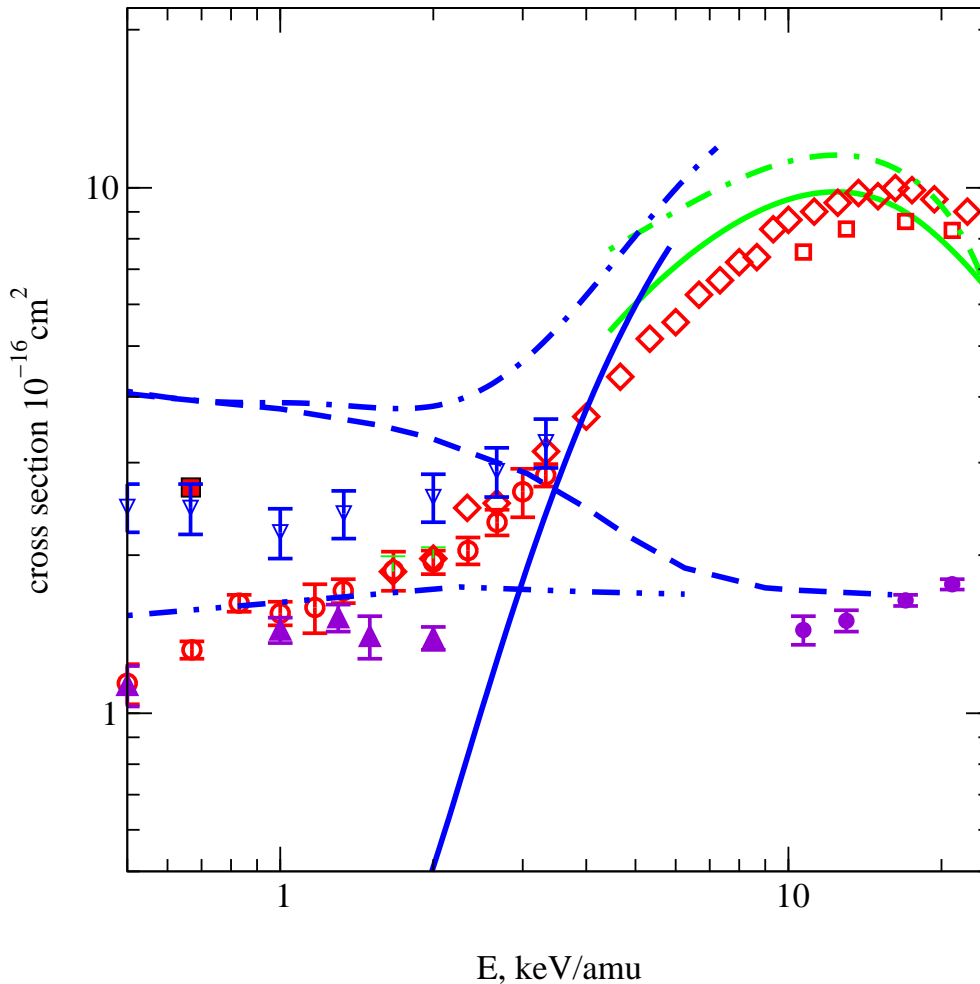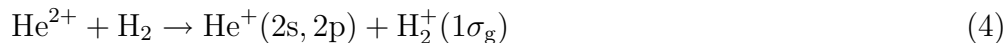
Figure 1. Total cross sections for single electron capture: Dashed-dotted line, present results; ◇, Shah and Gilbody (1978) ; ◯, Nutt *et al* (1978); ◁,Kusakabe *et al* (1990); ■, Okuno *et al* (1992). Total cross sections for NDSEC: Full line, present results; □, Shah *et al* (1989). Total cross sections for DSEC: Dashed line, present results; -·· -, vibrational excitation model; •, Shah *et al* (1989); ▲, Hodgkinson *et al* (1995). Black lines (blue in the electronic version), *ab initio* calculation; gray lines (green in the electronic version), IPM-OEDM calculation.

We present in figure 2 our calculated cross sections for the reactions

$$\mathrm{He}^{2+} + \mathrm{H}_2 \rightarrow \mathrm{He}^+(2\mathrm{s}, 2\mathrm{p}) + \mathrm{H}_2^+(1\sigma_\mathrm{g}) \qquad (4)$$

along with experimental data (Shah and Gilbody 1976, Hoekstra *et al* 1994, Hodgkinson *et al* 1995, Juhász *et al* 2002). In this figure, our cross sections for $E < 5\mathrm{keV/amu}$ were calculated using *ab initio* molecular states and for higher energies with the IPM-OEDM method. At low energy ($E \lesssim 2.5\mathrm{keV/amu}$)our results agree with those of (Hodgkinson *et al* 1995) for total cross section to $\mathrm{He}^+(2l)$; at higher energies, the calculated partial cross sections show a reasonable agreement with those of Shah and Gilbody (1976) for $\mathrm{He}^+(2\mathrm{s})$ and Hoekstra *et al* (1994) for $\mathrm{He}^+(2\mathrm{p})$, respectively. To further illustrate the accuracy of our IPM calculation, we have extended the energy range in figure
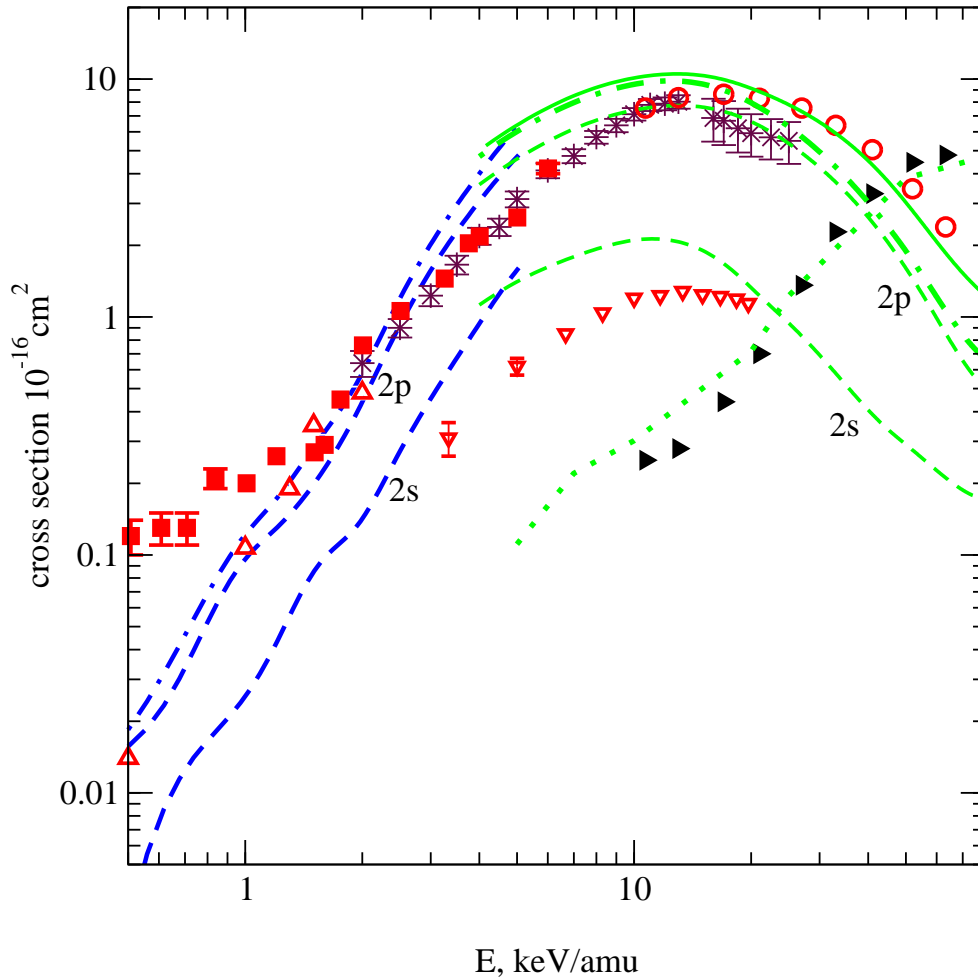
Figure 2. Cross sections for NDSEC into $He^+(2l) + H_2^+(1\sigma_g)$: Dashed-dotted, present results; $\triangle$, experimental data of Hodgkinson *et al* (1995). Cross sections for NDSEC into $He^+(2s) + H_2^+(1\sigma_g)$: Dashed line labelled 2s, present results ; $\triangledown$, experimental data of Shah and Gilbody (1976). Cross sections for NDSEC into $He^+(2p) + H_2^+(1\sigma_g)$: Dashed line labelled 2p, present results; $\star$, (Hoekstra *et al* 1994); $\blacksquare$, (Juhász *et al* 2002) . Total cross section for NDSEC: Full line, present results; $\bigcirc$, experimental values of Shah *et al* (1989) Total cross secion for nondissociative ionization: dotted line, present results; $\blacktriangleright$, experimental data of Shah *et al* (1989). In all cases black lines (blue in the electronic version) correspond to *ab initio* results; gray lines (green in the electronic version)to the IPM-OEDM ones.

2 up to $E=75$keV/amu, and we have included the cross section for non-dissociative ionization, calculated from the one-electron ionization probabilities, which are given by the population of the Gaussian pseudostates after the collision. On the other hand, as mentioned before, ionizing processes such as transfer ionization and dissociative ionization, which involve two-electron transitions are not accurately described by this method, and therefore not given.

Total cross sections for reaction (3) have been calculated using the *ab initio* method; they are compared with the experimental values of Kusakabe *et al* (1990) and Shah and

Gilbody (1978) in figure 3a. Our cross section shows a two-peak structure, similar to that obtained by joining the cross sections from both experiments. We have found that the shape of this cross section is a consequence of the two-step mechanism of this reaction, where the two electrons are consecutively exchanged. At low E, TEC channels are populated from the DSEC ones, and the decrease of the TEC cross section at $E \simeq 1\text{keV/amu}$ reflects that of the DSEC cross section (see fig 1). The higher energy mechanism involves transitions from both DSCE and the NDSEC channels dissociating into $He(2l)+ H_2^+$, which explains the increase of the TEC cross section for $E \gtrsim 2\text{keV/amu}$ as a consequence of the corresponding increase of the NDSEC cross section. On the other hand, the agreement of our calculation, which only includes TEC states dissociating into $He(1s2l)+ H^++ H^+$, with the experimental data, indicates that the main product of TEC is $He(1s2l)$. Moreover, prospective calculations adding the molecular state disssociating into $He(1s3s) + H^++ H^+$ to our basis showed that this state is not significantly populated. An additional illustration is included in fig. 3b, where we compare our results for population of $He(1s2p)$ with the experimental ones of (Juhász *et al* 2002).

By comparing the cross sections of figures 2 and 3 with the total cross section of figure 1, it can be noted that the limitations of the FC approximation are only significant for the largest cross section (the DSEC cross section), while we achieve a better accuracy for the subdominant data. The explanation for this apparent paradox, will be presented in ref. (Errea *et al* 2003) in terms of the mechanisms. The main conclusion of this analysis is that NDSEC takes place independently of the other reactions, and for trajectories with relative large impact parameters, in which the initial vibrational wavefunction has not significantly changed. Although TEC takes place at small ion-H_2 distances, the fact that it mainly occurs in the way in of the collision, also reduces the effect of the distortion of the vibrational wavefunction.

To summarize, we have calculated total cross sections for single and double electron capture in $He^{2+}+H_2$ collisions using *ab initio* and IPM-OEDM methods. In our calculation, which is the first one with both reactions simultaneously taken into account, we have shown that cross sections for NDSEC can be calculated independently from those for DSEC and TEC, and we obtain general agreement with the experimental data. Our cross sections for TEC allow to join the results of two sets of measurements ((Shah and Gilbody 1978) and (Kusakabe *et al* 1990)). We have found that the two-peak structure of this cross section is a consequence of the consecutive mechanism of the TEC process. Further work is required to accurately describe DSEC at low energies, where vibrational effects are important.

Acknowledgments

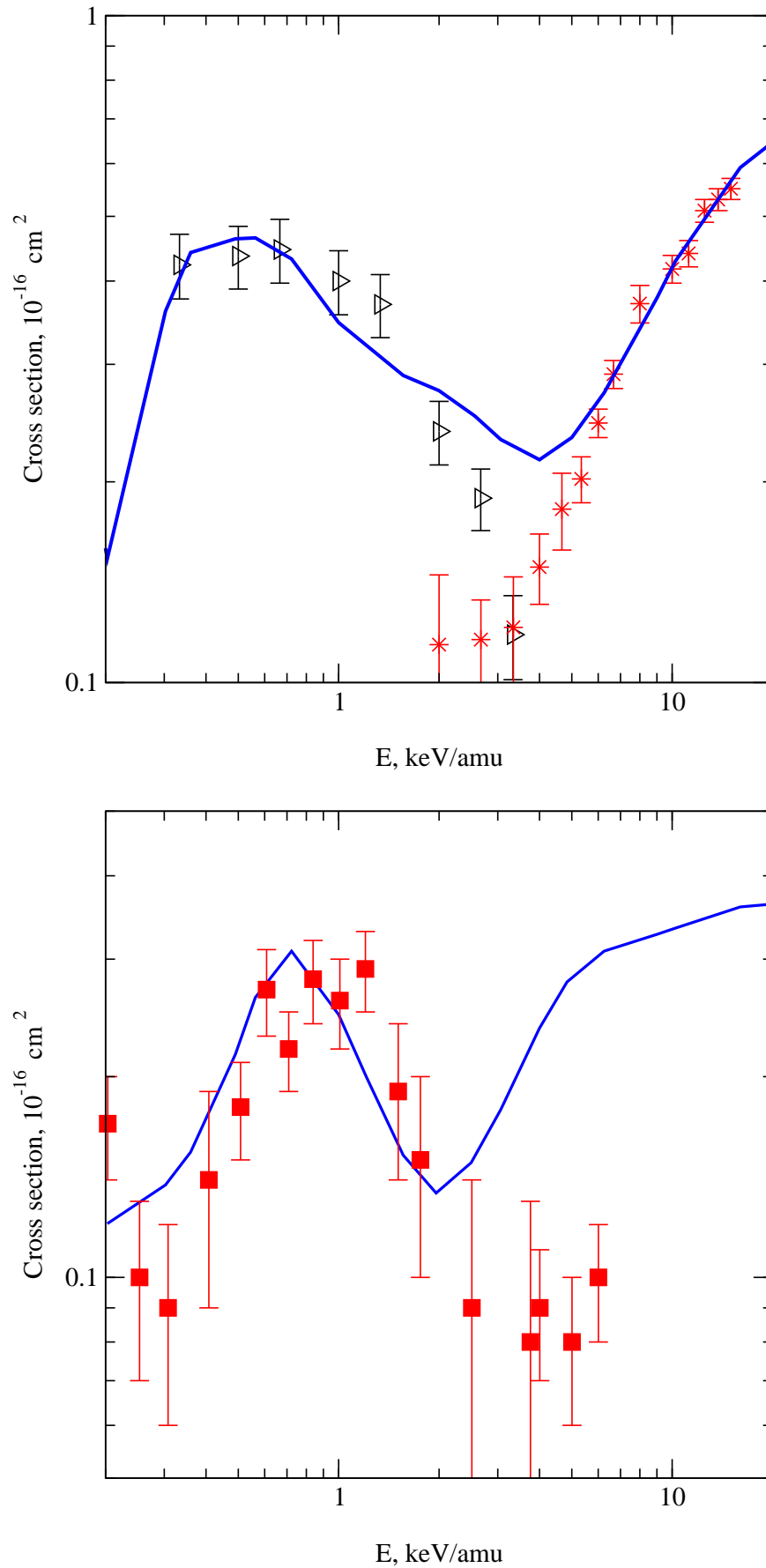**Figure 3.** (a) Cross sections for two-electron capture: — , present results. Experimental data: ▷, (Kusakabe *et al* 1990) ⋆, (Shah and Gilbody 1978). (b)Partial cross section for TEC into He(1s2p): — , present results; ■, results of ref. (Juhász *et al* 2002)

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