

# Atomic Data on Inelastic Processes in Calcium–Hydrogen Collisions

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## Abstract

Inelastic cross sections and rate coefficients in Ca + H and Ca<sup>+</sup> + H<sup>-</sup> collisions for all transitions between the 17 lowest covalent states plus one ionic molecular state are calculated based on the most recent ab initio adiabatic potentials for the 11 lowest molecular states, as well as on the model asymptotic potentials for higher-lying states, including the ground ionic molecular state. Nuclear dynamics is treated by the probability-current method and the multichannel formulas for the collision energy range 0.01–100 eV. The rates are computed for mutual neutralization, ion-pair formation, and (de-)excitation processes for the temperature range T = 1000-10,000 K. The calculations single out the partial processes with large and moderate rate coefficients. The largest rates correspond to the mutual neutralization into the Ca(4s5s  ${}^{3}S$ ), Ca(4s5p  ${}^{3}P^{\circ}$ ), Ca(4s5s  ${}^{1}S$ ), and Ca(4s5p  ${}^{1}P^{\circ}$ ) final states; at T = 6000 K the largest value is  $5.50 \times 10^{-8}$  cm<sup>3</sup> s<sup>-1</sup> for Ca(4s5s  ${}^{3}S$ ) transition; at T = 6000 K, the largest rate coefficient corresponds to the Ca(4s5s  ${}^{1}S$ )  $\rightarrow$  Ca(4s5s  ${}^{3}S$ ) transition; at T = 6000 K, the largest rate coefficient corresponds to the Ca(4s5s  ${}^{1}S$ )  $\rightarrow$  Ca(4s5s  ${}^{3}S$ ) transition; at T = 6000 K, the largest rate coefficient corresponds to the Ca(4s5s  ${}^{1}S$ )  $\rightarrow$  Ca(4s5s  ${}^{3}S$ ) transition; at T = 6000 K, the largest rate coefficient corresponds to the Ca(4s5s  ${}^{1}S$ )  $\rightarrow$  Ca(4s5s  ${}^{3}S$ ) transition; at T = 6000 K, the largest rate has the value of  $8.46 \times 10^{-9}$  cm<sup>3</sup> s<sup>-1</sup>.

Key words: atomic data - atomic processes - scattering - stars: abundances

Supporting material: machine-readable table

## 1. Introduction

Non-local thermodynamic equilibrium (non-LTE) modelings of stellar atmospheres are of importance for determining absolute and relative abundances of different chemical elements, for the Galactic evolution, and so on (see, e.g., Asplund 2005; Barklem 2016a, and references therein). Non-LTE modeling of stellar spectra requires detailed and complete information about inelastic heavy-particle collision processes, most importantly ones in collisions with hydrogen atoms and negative ions. The lack of atomic data on inelastic processes due to collisions with neutral hydrogen atoms and hydrogen negative ions, has been a major limitation on non-LTE modeling of stellar spectra.

Calcium is of particular astrophysical importance since it belongs to the  $\alpha$ -elements group (see Drake 1991; Korn et al. 2009; Mashonkina et al. 2017, and references therein). Several non-LTE studies of calcium stellar spectra have been performed (Idiart & Thévenin 2000; Christlieb et al. 2002; Frebel et al. 2005, 2015; Mashonkina et al. 2007; Norris et al. 2007; Caffau et al. 2011; Cohen et al. 2013) by using the classical so-called Drawin formula (Drawin 1968, 1969; Steenbock & Holweger 1984), which is known to be often unreliable (Barklem et al. 2011). The first reliable quantum calculations of inelastic rate coefficients in calcium-hydrogen collisions were performed by Belyaev et al. (2016) based on the asymptotic semi-empirical model approach (Belyaev 2013) for the electronic structure and on the multichannel model approach (Belyaev 1993; Belyaev & Barklem 2003; Belyaev et al. 2014; Yakovleva et al. 2016) for nonadiabatic nuclear dynamics. Later on, the inelastic rates in the same collisions were calculated by the asymptotic Linear Combinations of Atomic Orbitals (LCAO) method (Barklem 2016b, 2017) for the electronic structure and the same multichannel formulas for nuclear dynamics. Both calculations took into account only the

long-range nonadiabatic regions. Comparisons of the results of these two calculations<sup>4</sup> show that the semi-empirical and the LCAO models perform roughly equally well on average. These allowed one to accomplish the improved non-LTE modeling (Mashonkina et al. 2017).

Very recently, the ab initio electronic structure calculations have been published (Mitrushchenkov et al. 2017). These accurate data present a way to take into account not only the long-range, but also short-range nonadiabatic regions. This can be done by the probability-current method (Belyaev 2013) based on the novel formula for nonadiabatic transition probabilities (Belyaev & Lebedev 2011) within the Landau– Zener model. These nonadiabatic nuclear dynamical calculations are performed and reported in the present paper.

#### 2. Model Dynamical Approach

Adiabatic potential energies for the CaH  $(^{2}\Sigma^{+})$  (quasi-) molecule are plotted in Figure 1. The 11 lowest potentials are obtained by the ab initio calculation (Mitrushchenkov et al. 2017), while higher-lying long-range potentials are estimated by the model asymptotic approach (Belyaev et al. 2016). Many avoided-crossing nonadiabatic regions are clearly seen: they include both long- and short-range regions.

A nonadiabatic transition probability in each avoided-crossing region can be calculated within the Landau–Zener model. The conventional Landau–Zener formula expresses a transition probability via diabatic matrix elements. However, diabatization is not uniquely defined and often troublesome. On the other hand, recently the alternative formula within the Landau–Zener model has been derived (Belyaev & Lebedev 2011; Belyaev 2013) that writes a nonadiabatic transition probability in terms of adiabatic potentials only, in particular, via a local

 $<sup>\</sup>frac{1}{4}$  Note the corrections of the results of Barklem (2016b) as described by Barklem (2017).



**Figure 1.** CaH  $(j \, {}^{2}\Sigma^{+})$  adiabatic potential energies, obtained by ab initio (j = 1-11, solid lines) and model asymptotic (j = 12-17 and ionic, dashed lines) calculations as functions of the internuclear distance (in atomic units, au).

minimum of an adiabatic potential splitting and its second derivative with respect to the internuclear distance. This adiabatic-potential-based formula allows one to take into account all avoided-crossing regions: long- and short-ranged.

An inelastic state-to-state transition probability then can be calculated by means of the probability-current method (Belyaev 2013) using the adiabatic-potential-based formula for nonadiabatic transitions between adjacent molecular states in each nonadiabatic region. In the present paper, the probabilistic version of the probability-current method is used.

The general idea of the method is the following: (i) to run an incoming probability current from a particular initial channel *i* as a function of the internuclear distance at a given collision energy E and a given total angular momentum quantum number J; (ii) to allow a current to hop to another molecular state according to a nonadiabatic transition probability, in each nonadiabatic region the current meets both before and after classical turning points; (iii) to determine a final channel where an outgoing probability current occurs; and (iv) to calculate state-to-state transition probabilities for each final channel by repeating many times (122,880 at present) the dynamical calculations with the same incoming probability current. This procedure is somewhat similar to a probabilistic version of the surface-hopping classical trajectory method, but replacing the calculation of time-dependent classical trajectories by the evaluation of probability currents as functions of the internuclear distance.

Known state-to-state transition probabilities allows one to calculate inelastic cross sections and rate coefficients as usual. Cross sections and rate coefficients for exothermic  $[\sigma_{kn}(E)$  and  $K_{kn}(T)$ , for a transition  $k \to n$ ] and endothermic  $[\sigma_{nk}(E)$  and  $K_{nk}(T)$ ] processes (we consider k > n) are calculated by the following formulas,

$$\sigma_{kn}(E) = \frac{\pi \hbar^2 p_k^{\text{stat}}}{2\mu E} \sum_{J=0}^{\infty} P_{kn}(J, E)(2J+1), \quad (1)$$

$$\sigma_{nk}(E) = \sigma_{kn}(E - \Delta E_{kn}) \frac{p_n^{\text{stat}}}{p_k^{\text{stat}}} \frac{E - \Delta E_{kn}}{E}, \qquad (2)$$

$$K_{kn}(T) = \sqrt{\frac{8}{\pi\mu(k_BT)^3}} \int_0^\infty E \ \sigma_{kn}(E) \exp\left(-\frac{E}{k_BT}\right) dE, \quad (3)$$

Table 1Scattering Channels Correlated to CaH  $(j \ ^2\Sigma^+)$  Molecular States, theirAsymptotic Energies with Respect to the Ground-state Level, the ElectronicBound Energies  $E_j$  Measured from the Ionization LimitCa<sup>+</sup>(4s \ ^2S) + H(1s \ ^2S), and the Statistical Probabilities forPopulation of the Molecular States

j	Scattering Channels	Asymptotic Energies (eV)	Bound Energies $E_j$ (eV)	$p_j^{\text{stat}}$
1	$Ca(4s^2 S) + H(1s^2 S)$	0.0	-6.11708	1.0
2	$Ca(4s4p \ ^{3}P^{\circ}) + H(1s \ ^{2}S)$	1.88585	-4.23123	0.11111
3	$Ca(3d4s \ ^{3}D) + H(1s \ ^{2}S)$	2.52317	-3.59391	0.06667
4	$Ca(3d4s \ ^{1}D) + H(1s \ ^{2}S)$	2.70920	-3.40788	0.2
5	$Ca(4s4p \ ^{1}P^{\circ}) + H(1s \ ^{2}S)$	2.93215	-3.18493	0.33333
6	$Ca(4s5s \ {}^{3}S) + H(1s \ {}^{2}S)$	3.91022	-2.20686	0.33333
7	$Ca(4s5s \ {}^{1}S) + H(1s \ {}^{2}S)$	4.13066	-1.98642	1.0
8	$Ca(3d4p \ {}^{3}F^{\circ}) + H(1s \ {}^{2}S)$	4.44114	-1.67594	0.04762
9	$Ca(4s5p \ ^{3}P^{\circ}) + H(1s \ ^{2}S)$	4.53218	-1.58490	0.11111
10	$Ca(4s5p P^{\circ}) + H(1s S)$	4.55395	-1.56313	0.33333
11	$Ca(4s4d \ ^{1}D) + H(1s \ ^{2}S)$	4.62433	-1.49284	0.2
12	$Ca(4s4d \ ^{3}D) + H(1s \ ^{2}S)$	4.68080	-1.43628	0.06667
13	$Ca(3d4p \ ^{3}P) + H(1s \ ^{2}S)$	4.87719	-1.23989	0.11111
14	$Ca(4s6s \ {}^{3}S) + H(1s \ {}^{2}S)$	5.01809	-1.09899	0.33333
15	$Ca(3d4p \ {}^{1}F) + H(1s \ {}^{2}S)$	5.02598	-1.09110	0.14286
16	$Ca(4s6s \ {}^{1}S) + H(1s \ {}^{2}S)$	5.04490	-1.07218	1.0
17	$Ca(4p^2 D) + H(1s^2S)$	5.04854	-1.06854	0.2
ionic	$Ca^{+}(4s \ ^{2}S) + H^{-}(1s^{2} \ ^{1}S)$	5.36308	-0.754	1.0

**Note.** The electronic bound energies are the same as the asymptotic energies, but measured from different levels; the differences between the asymptotic energy values and the bound energy values are equal to the Ca ionization potential.

$$K_{nk}(T) = K_{kn}(T) \frac{p_n^{\text{stat}}}{p_k^{\text{stat}}} \exp\left(-\frac{\Delta E_{kn}}{k_B T}\right),\tag{4}$$

where *E* is a collision energy,  $\Delta E_{kn} = E_k - E_n$  is an energy defect between channels *k* and *n*, *J* is the total angular momentum quantum number, *T* is the temperature,  $p_j^{\text{stat}}$  is the statistical probability for population of the channel *j*, *k*<sub>B</sub> the Boltzmann constant, and  $\mu$  is the reduced nuclear mass.

## 3. Calcium-Hydrogen Collisions

The scattering channels in calcium-hydrogen collisions treated in the present paper are collected in Table 1. These channels correlate to CaH  $(j^{2}\Sigma^{+})$  molecular states. This molecular symmetry makes the dominant contribution for inelastic processes in Ca + H and Ca<sup>+</sup> + H<sup>-</sup> collisions and, hence, transitions within this symmetry lead to large-valued inelastic rate coefficients. Scattering channels, which do not correlate to the CaH  $(j \, {}^{2}\Sigma^{+})$  molecular symmetry, are not included in the present consideration. For instance, the Ca  $(4p^2 {}^{3}P) + H(1s {}^{2}S)$  channel correlates to the CaH  $(2\Sigma^{-})$ molecular symmetry and, therefore, is not listed in Table 1. Transitions between the 11 lowest molecular states are treated by means of the probability-current method, that is, all avoided crossings (both short- and long-range) are taken into account. Transitions between higher-lying molecular states are studied by the multichannel formula, that is, only long-range nonadiabatic regions are taken into account.

Table 2Rate Coefficients in Units  $cm^3 s^{-1}$  for Temperature  $T = 6000 K^a$ 

	$4s^2 {}^1S$	$4s4p \ ^{3}P^{\circ}$	$3d4s$ $^{3}D$	3d4s <sup>1</sup> D	$4s4p \ ^1P^{\circ}$	4s5s <sup>3</sup> S	4s5s <sup>1</sup> S	$3d4p$ $^{3}F^{\circ}$	$4s5p \ ^{3}P^{\circ}$	$4s5p \ ^1P^\circ$	Ca <sup>+</sup> +H <sup>-</sup>
$4s^{2}$ <sup>1</sup> S		1.65e-13	3.37e-14	5.82e-16	8.84e-17	3.93e-16	7.08e-17	1.15e-16	1.06e-17	3.47e-18	4.53e-17
$4s4p \ ^{3}P^{\circ}$	7.04e-13		1.50e-10	8.40e-13	3.03e-13	3.73e-13	6.33e-14	1.20e-13	1.45e-14	6.11e-16	3.09e-14
3d4s <sup>3</sup> D	2.96e-13	3.08e-10		4.47e-12	4.63e-13	4.96e-13	1.01e-13	1.85e-13	5.17e-14	1.52e-15	4.16e-14
$3d4s$ $^{1}D$	2.20e-14	7.43e-12	1.92e-11		1.83e-11	2.61e-11	4.89e-12	7.26e-12	3.29e-12	2.53e-14	1.25e-12
$4s4p \ ^1P^\circ$	8.56e-15	6.89e-12	5.10e-12	4.69e-11		3.03e-11	6.68e-12	2.33e-11	5.69e-12	1.18e-12	4.74e-12
4s5s <sup>3</sup> S	2.52e-13	5.61e-11	3.62e-11	4.44e-10	2.01e-10		1.84e-09	4.18e-10	5.39e-10	9.20e-11	1.10e-09
4s5s <sup>1</sup> S	2.09e-13	4.38e-11	3.39e-11	3.82e-10	2.03e-10	8.46e-09		4.36e-10	2.76e-09	2.02e-10	3.94e-09
$3d4p \ ^{3}F^{\circ}$	2.95e-14	7.21e-12	5.40e-12	4.93e-11	6.17e-11	1.67e-10	3.79e-11		6.07e-11	2.66e-12	4.22e-11
$4s5p \ ^{3}P^{\circ}$	7.52e-15	2.43e-12	4.19e-12	6.20e-11	4.19e-11	5.98e-10	6.67e-10	1.69e-10		3.59e-11	1.07e-09
$4s5p \ ^1P^\circ$	7.73e-15	3.20e-13	3.85e-13	1.49e-12	2.72e-11	3.20e-10	1.53e-10	2.31e-11	1.12e-10		1.67e-09
Ca <sup>+</sup> +H <sup>-</sup>	1.45e-12	2.32e-10	1.52e-10	1.06e-09	1.57e-09	5.50e-08	4.28e-08	5.27e-09	4.82e-08	2.40e-08	

Note.

<sup>a</sup> This table and other tables with calculated rate coefficients for different temperatures are available in their entirety in machine-readable form.

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



Figure 2. Graphical representation of rate coefficients (in units cm<sup>3</sup> s<sup>-1</sup>) for all partial processes of excitation, de-excitation, mutual neutralization, and ionpair formation for the temperature T = 6000 K. The key labels are presented in Table 1.

The inelastic cross sections and rate coefficients for all transitions between the states listed in Table 1 were calculated in the present work for the collision energy range from 0.01 to 100 eV and the temperature range from T = 1000 to 10,000 K, respectively. The calculated rate coefficients are presented in machine-readable form. The example of the calculated data is shown in Figure 2 as a graphical representation for the temperature T = 6000 K. In addition, Table 2 shows the rate coefficients at T = 6000 K for partial processes between the 10 lowest covalent states plus the ionic channel, that is, the rates calculated by the probability-current method. It is seen that the largest rate coefficients correspond to the mutual neutralization processes into the Ca(4s5s  $^{3}S$ ), Ca(4s5p  $^{3}P^{\circ}$ ), Ca(4s5s  $^{1}S$ ), and  $Ca(4s5p \ ^{1}P^{\circ})$  final states. The largest values exceed  $10^{-8}$  cm<sup>3</sup> s<sup>-1</sup> (with the value as large as  $5.50 \times 10^{-8}$  cm<sup>3</sup> s<sup>-1</sup> at T = 6000 K) and are determined by long-range nonadiabatic regions. The next largest rate coefficients with the values exceeding  $10^{-9}$  cm<sup>3</sup> s<sup>-1</sup> correspond to the mutual neutralization, ion-pair formation and a few (de-)excitation processes. The largest rate coefficient for the (de-)excitation processes corresponds to the Ca(4s5s  $^{1}S$ )  $\rightarrow$  Ca(4s5s  $^{3}S$ ) transition with the value of  $8.46 \times 10^{-9} \text{ cm}^{3} \text{ s}^{-1}$  at T = 6000 K. There are also many partial processes with rate coefficients larger than  $10^{-10}$  cm<sup>3</sup> s<sup>-1</sup>.



**Figure 3.** Mutual neutralization rate coefficients  $K_{ij}(T)$  at T = 6000 K as a function of the final-state bound energy. Circles are the results of calculations by the probability-current method, stars by the multichannel formula, dashed curve by the simplified model.

Distribution of the mutual neutralization rate coefficients at T = 6000 K as a function of the final-state bound energy is shown in Figure 3. It is seen that the calculated rates reasonably agree with the general distribution (Belyaev & Yakovleva 2017) obtained by the simplified model plotted by the dashed line. In particular, one can see that the largest rates correspond to the transitions into the final states with bound energies from some vicinity of the value -2 eV (f=6, 7, 9, 10), as predicted by the simplified model. The simplified model estimates a dependence of inelastic rate coefficients on electronic bound energies based on ionic-covalent interactions as a basic mechanism. It is shown (Belyaev & Yakovleva 2017) that optimal parameters correspond to bound energies from a vicinity of -2 eV.

It is worth noticing that the large-valued rate coefficients calculated by the probability-current method agree well with those calculated by the multichannel formula (Belyaev et al. 2016), but low-valued rates may be changed substantially by the inclusion of the short-range avoided crossings. The example is the mutual neutralization into the final channel



Figure 4. Rate coefficients  $K_{if}(T)$  of (de-)excitation processes for the initial channel i = 7 at T = 6000 K as a function of the final-state bound energy. Circles are the results of calculations by the probability-current method, stars by the multichannel formula, dashed curve by the simplified model.

f = 8, which corresponds to two-electron transitions and generally has a low rate coefficient. However, the inclusion of the short-range regions opens another mechanism (the socalled loop mechanism; Belyaev et al. 2012), which increases the rate by several orders. Nevertheless, the two-electron transitions have rate coefficients much smaller than the singleelectron ones.

According to the general role, the distribution of (de-) excitation rate coefficients depends on two electronic bound energies, for the initial and for the final states (Belyaev & Yakovleva 2017): the highest rates correspond to processes for which both bound energies are close to the value -2 eV. In the present case, this corresponds to the processes from and to the scattering channel i, f = 7, see Table 1. The example of these (de-)excitation processes is shown in Figure 4 for the initial channel i = 7, Ca(4s5s <sup>1</sup>S) + H(1s <sup>2</sup>S). It is seen that the largest rate coefficient corresponds to the transition  $i = 7 \rightarrow f = 6$ . One should note that it is roughly an order of magnitude smaller than the largest mutual neutralization rate coefficient, see Table 2.

Temperature dependence of some rate coefficients for the mutual neutralization and their inverse, ion-pair-formation processes are presented in Figures 5 and 6. It is seen that the rates for the exothermic processes weakly vary with the temperature, while for the endothermic processes the dependence is strong. In particular, Figure 5 shows temperature dependence of the rate coefficients for the transitions ionic  $\rightarrow$  6, 7, that is, for the processes with the largest rates. The rates shown were calculated by two methods: by the probability-current method (taking into account both long- and short-range nonadiabatic regions, depicted by lines) and by the multichannel method (taking into account only long-range nonadiabatic regions, depicted by symbols). It is seen that the results of these two calculations for these transitions agree well, which means that the large-valued rates are mainly determined by the long-range nonadiabatic regions. The same Figure 5 shows temperature dependence of the rate coefficients for the transition ionic  $\rightarrow 8$ , the process  $Ca^+ + H^- \rightarrow Ca(3d4p \ {}^3F^\circ) + H(1s \ {}^2S)$ , which corresponds to two-electron transitions. Inclusion of the long-range regions only, the multichannel method, results in low rate coefficients (symbols) due to small long-range exchange



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Rate coefficient, cm<sup>3</sup> s<sup>-1</sup> x10 ionicionic-10<sup>-9</sup> ionic->8 2000 4000 6000 8000 10000 Temperature, K

10

10<sup>-1</sup>

Figure 5. Temperature dependence of the rate coefficients for mutual neutralization processes for the transitions ionic  $\rightarrow 6, 7, 8$  calculated by the probability-current method (solid lines) and by the multichannel method (symbols). Note that the rate coefficient calculated by the multichannel method for the process ionic  $\rightarrow 8$  is multiplied by 10<sup>7</sup>.



Figure 6. Temperature dependence of the rate coefficients for ion-pair formation processes for the transitions 6, 7,  $8 \rightarrow \text{ionic}$  calculated by the probability-current method (dashed lines) and by the multichannel method (symbols). Note that the rate coefficient calculated by the multichannel method for the process  $8 \rightarrow$  ionic is multiplied by  $10^7$ .

coupling matrix elements for two-electron transitions; note that the rate shown in Figure 5 is multiplied by a factor of  $10^7$ . The situation is changed drastically if the short-range nonadiabatic regions are taken into account by the probability-current method (lines): the inclusion of the short-range nonadiabatic transitions increases the rate coefficient by several orders of magnitude. Obviously, these conclusions hold for the inverse, ion-pair formation processes (see Figure 6).

# 4. Conclusion

In the present work, the inelastic rate coefficients in Ca + Hand  $Ca^+ + H^-$  collisions for all transitions between the 17 lowest covalent states plus one ionic molecular state are calculated based on the accurate adiabatic potentials (Mitrushchenkov et al. 2017) for the 11 lowest molecular states, as well as on the model asymptotic potentials (Belyaev et al. 2016) for higher-lying states including the ground ionic molecular state. Other (higher-lying) covalent states have negligible rate coefficients. The nonadiabatic nuclear dynamics is treated by the probability-current method (Belyaev 2013) for the 11

lowest states. This method allows us to take into account both long- and short-range nonadiabatic regions. For transitions between higher-lying states, the multichannel formulas (Belyaev 1993; Belyaev & Barklem 2003; Belyaev et al. 2014; Yakovleva et al. 2016) are used. Nonadiabatic transition probabilities in each of the avoided crossings are computed by means of the adiabatic-potential-based formula (Belyaev & Lebedev 2011; Belyaev 2013). Thus, the present calculations provide the most accurate and complete collision data up to now on low-energy calcium–hydrogen collisions. The calculated rate coefficients are available online. Table 2 shows an example at T = 6000 K.

The present calculations single out the partial processes with large and moderate rate coefficients, first of all, mutual neutralization processes, but also their inverse ion-pair formation as well as (de-)excitation ones. It is shown that the largest rate coefficients correspond to the mutual neutralization into the  $Ca(4s5s^{3}S)$  (with the value as large as  $5.50 \times 10^{-8} \,\mathrm{cm^3 \, s^{-1}}$  at T = 6000 K),  $Ca(4s5p^{-3}P^{\circ})$ , Ca(4s5s <sup>1</sup>S), and Ca(4s5p <sup>1</sup>P°) final states. Among the (de-) excitation processes, the largest rate coefficient at T = 6000 K corresponds to the Ca(4s5s  ${}^{1}S) \rightarrow$  Ca(4s5s  ${}^{3}S)$  transition with the value of  $8.46 \times 10^{-9}$  cm<sup>3</sup> s<sup>-1</sup>. It should not be surprising that the largest de-excitation rate corresponds to a spinforbidden atomic transition, since within the Born-Oppenheimer approach a collision problem is treated in a molecular representation, and from a molecular point of view, there is no difference between singlet-triplet Ca transitions and transitions among triplet or singlet Ca states. The processes with large and moderate rate coefficients calculated in the present work are likely to be important for non-LTE modeling of stellar spectra.

A.K.B., Y.V.V., and S.A.Y. gratefully acknowledge support from the Ministry for Education and Science (Russian Federation), projects No. 3.1738.2017/4.6, 3.5042.2017/6.7. N.F. acknowledges partial support from Paris Observatory council through the "Action Fédératrice Etoiles" and from PNPS stellar program of the CNRS. The authors wish to acknowledge their friend and colleague Annie Spielfiedel who actively participated in building the project leading to the present work. Annie Spielfiedel passed away on 2016 December 14. We dedicate this paper to her memory.

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