Radiative transitions in quasimolecules: H⁺H⁻ collisions

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Abstract. The \( H^+H^- \rightarrow H^-H + \hbar \omega \), \( H + H^- + \hbar \omega \rightarrow H + H + e \) reactions give examples of bound-bound and bound-free electron transitions in the \( H + H^- \) quasi-molecules temporally formed during collisions. The present work is aimed at the calculations of spectral profiles produced in the reactions of resonant charge exchange \( H + H^- \). The oscillator strength of photodetachment of quasimolecules has been calculated for the first time.

1. Introduction

The study of radiative transitions in single ions or atoms is a traditional approach in plasma spectroscopy. On the other hand, radiative transitions in collisional quasi-molecules, that is temporary molecules formed during ion or atom collisions, are also of importance. Such transitions are directly connected with the dynamics of ion or atom collisions. The study of the transitions produced in the \( H + H^- \) collisions has been initiated in [1] where bound-bound transitions were analysed. The aim of the present work is to get down to the case of bound-free transitions. Thus, the main new result of the present work is the calculation of the oscillator strengths of bound-free transitions in collisions or, in other words, photodetachment during collisions.

In the frame of the adiabatic approach the process of charge exchange \( H + H^- \) can be regarded as evolution of an atomic system along gerade and ungerade potential energy curves of the adiabatic states of a quasi-molecule formed during collisions. In the adiabatic approach emission is treated as the dipole transition between two quasi-molecular states involved [2].

The main characteristics of the radiative transitions involved in the description of optical transitions in quasi-molecules have been calculated in the frame of the zero-range potential model [3]. In the model the energy state difference and other characteristics of the process can be expressed in a closed form in terms of the Lambert W(z) function [4]. Another type of electron transitions can also be treated in the frame of the zero-range potential model, namely \( H + H^- + \hbar \omega \rightarrow H + H + e \) as an example of bound-free transitions in quasi-molecules. For the first time the spectral profiles in charge exchange reaction \( H + H^- \) are presented the generalization of calculations and the oscillatory strength calculated as a function of momentum the photodetachment in these collisions.
2. **Bound-bound transitions**

The radiation process is treated as a dipole transition between the gerade $U_g$ and the ungerade $U_u$ adiabatic quasi-molecular states produced by the interaction of the ion and the atom in their ground states that is as an optical transition between the two quasi-molecular states formed during the collision.

The spectral profile in the quasi-static approximation is

$$I(\omega) = 4\pi R_c^2 \frac{A(R_c)}{d\Delta U/dR_c} \exp\left(\frac{-U_u(R_c)}{kT}\right),$$

(1)

here $U_u$ - the adiabatic energy of the initial ungerade state, $\Delta U$ is the difference between gerade and ungerade quasimolecular states,

$$A(R_c) = \left(\frac{4}{3g}\right) \left(\frac{\omega^2}{137}\right) D(R_c)^2$$

(2)

is the Einstein coefficient for spontaneous emission of the quasimolecule, $g$ statistical factor, $D$ is the electric dipole moment for transitions between the two states involved [1]. In our case and $R_c$ is the position of the Condon point that is the root of the equation

$$\Delta U(R_c) = \omega$$

(3)

that has the solution at $\alpha R \geq 1$ as

$$R_c = \frac{1}{\alpha \text{LambertW}\left(\frac{2\alpha^2}{\omega}\right)}$$

(4)

The results of the profile calculations are shown in Figures 1 and 2 for two temperatures versus the frequency of the radiation and the interatomic distance, respectively.

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**Figure 1.** Spectral profile produced in the collisions versus frequency of the radiation for two temperatures.

**Figure 2.** Spectral profile produced in the collisions versus the interatomic distance for two temperatures.
It should be stressed that the maxima of the intensities are formed by electron transitions at 7 - 9 \( a_0 \). It means that the radiative transitions are followed by the formation of the unstable \( \text{H}_2^- \) molecules in their high rotational states. The last conclusion seems to support the prediction Golser et al [5]. We emphasize that for the first time a summary of the results presented in this paper

3. Bound-free transitions

In the previous Section the radiative processes produced by charge exchange have been considered as an example of bound-bound transitions in quasi-molecules. Here, we consider bound-free transitions in quasi-molecules or, in other words, photodetachment taking \( \text{H} - \text{H}^- \) collisions as a typical example.

The cross-section of photodetachment is proportional to the density of oscillator strengths which is the main characteristic of the dipole transitions

\[
\sigma(\omega) = \frac{2\pi^2}{c} \frac{d\sigma}{d\omega} = \frac{4\pi^2}{c} \omega_{bc} |X_{bc}|^2
\] (5)

For simplicity, we discuss the one-dimensional case. Then the matrix element is

\[
X_{bc} = \int \langle \Psi_b | x | \Psi_c \rangle \, dx
\] (6)

In the LCAO approximation quasimolecular gerade and ungerade wave functions in the frame of the zero-range potentials model are written as

\[
\Psi_{gu}^b = \sqrt{\alpha_{gu}} \left[ \exp(-\alpha_{gu} |x + R/2|) \pm \exp(-\alpha_{gu} |x - R/2|) \right]
\] (7)

\[
\Psi_{gu}^c = \frac{1}{\sqrt{2\pi k}} \left[ \sin(k |x + R/2|) \pm \sin(k |x - R/2|) \right]
\] (8)

Then the matrix element dipole moments can be expressed by the formula:

\[
X_{b=g,c=u} = \sqrt{\frac{\alpha_g k}{\pi}} \frac{\alpha_u}{\omega^2} \cos \left( \frac{kR}{2} \right) + \sqrt{\frac{\alpha_g \alpha_u R}{\pi k}} 4\omega \sin (kR)
\] (9)

\[
X_{b=u,c=g} = \sqrt{\frac{\alpha_u k}{\pi}} \frac{\alpha_g}{\omega^2} \sin \left( \frac{kR}{2} \right) - \sqrt{\frac{\alpha_u \alpha_g R}{\pi k}} 4\omega \sin (kR)
\] (10)

where \( \omega = (\alpha_{gu}^2 + k^2)/2 \)

Although the quasi-molecular matrix elements increase with increasing \( R \) it does not lead to difficulties at large \( R \). In this case \( U_u = U_g \), and it is obligatory to use the sum of amplitudes of two different ways of detachment [2].

The position of the Condon point that is the root of the equation:

\[
\omega = \frac{\alpha_u^2 (R_u) + k^2}{2}
\] (11)

The Figure 3 shows the results for the oscillatory strength for the radiation transition between gerade and ungerade quasimolecular states as a function of momentum.

Collisions result in a lowering of the threshold of the electron detachment compared with the single ion \( \text{H}^- \) because ungerade quasi-molecular term is repulsive.
4. Conclusion
The spectral profiles in charge exchange reaction $H + H^-$ are presented together with preliminary results related to photodetachment in these collisions. The main results obtained are as follows. First, the emission is produced in the collision $H + H^-$ in the absence of any initial electronic excitation in the colliding particles. Second, quasi-molecular radiative transitions lead to the formation of ro-vibrational states of the $H^{-}_2$ molecules at comparatively large interatomic distances about 8 - 10 a.u. Third, collisions result in a lowering of the threshold of the electron detachment compared with the single ion because ungerade bound quasi-molecular term is repulsive. The results obtained may contribute to the cold and thermal plasma spectroscopy.

References
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Figure 3. Oscillatory strength as a function of momentum.