

# Cross-sections for creation of long-lived molecular hydrogen anions $\text{H}_2^-$ in binary collisions

Ivan A. Pshenichnyuk, Martin Čížek, Jiří Horáček

*Institute of Theoretical Physics, Faculty of Mathematics and Physics, Charles University in Prague,*

*V Holešovičkách 2, 18000 Prague, Czech Republic*

(Received: )

## Abstract

The cross sections of the creation of the long-lived molecular hydrogen anions  $\text{H}_2^-$  in binary collisions of  $\text{H}+\text{H}^-$  or  $\text{H}_2 + e^-$  are calculated within the framework of the nonlocal resonance model. Additionally, the branching ratios for the decay of  $\text{H}_2^-$  into  $\text{H}+\text{H}^-$  and  $\text{H}_2(v) + e^-$  are calculated for all available vibrational levels  $v$ .

*Introduction.* The existence of the long-lived molecular hydrogen anions has recently been proved in several experiments [1–3]. The lifetimes reach the order of microseconds and even miliseconds for  $\text{D}_2^-$  [4,5]. We have studied these states within the nonlocal resonance model [1,6] developed for the description of  $\text{H}+\text{H}^-$  [8] and  $e^-+\text{H}_2$  [9,10] collisions. Previously, we have shown that  $\text{H}_2^-$  in its ground electronic state  $^2\Sigma_u^+$  can be stabilised due to the rotation of the molecule, which prevents the nuclei to get close enough for autodetachment to happen. The autodetachment can however still proceed via quantum tunnelling. Since the tunnelling through the potential barrier is suppressed for the heavier systems, the lifetimes of other isotopic variants of the system  $\text{HD}^-$ ,  $\text{D}_2^-$ ,  $\text{T}_2^-$  are gradually growing [6]. For the highest rotational quantum numbers  $J$  the system can also decay to  $\text{H}+\text{H}^-$  by tunnelling through the outer barrier. This barrier is very low but long-ranged, which makes the calculation of exact lifetimes extremely sensitive to the values of the potential energy for the adiabatic

potential of  $\text{H}+\text{H}^-$  system [6]. Although we used the very accurate data of Senekowitsch et al. [11], the uncertainty of few meV in the potential energy can still lead to uncertainty by several orders of magnitudes in the lifetime of some states. This applies only to few of the long-lived states and we did not stress this uncertainty in our first calculation [1], where the results for some  $\text{D}_2^-$  states were additionally spoiled with numerical instability. The lifetimes of some states were therefore somewhat underestimated. The experiments [4,5] measuring the lifetimes consequently questioned our interpretation of the observed states as the rotationally stabilised  $^2\Sigma_u^+$  states. They suggested alternative interpretation of  $\text{H}_2^-$  being electronically high spin states, stabilised due to the spin-forbidden transitions. Our later calculations [6] have shown, that the lifetimes of the rotationally stabilised  $^2\Sigma_u^+$  states can reach the experimentally measured values (in a consistent way for all the measured states), if we vary the model within its uncertainty of few meV. Furthermore, we predict that the lifetime of  $\text{T}_2^-$  can reach the fraction of second.

The above mentioned problems with the sensitivity of the lifetimes to the model parameters apply only to the states with the highest angular momenta. On the other hand, the states with lower  $J$  undergo a smooth transition (with decreasing  $J$ ) into boomerang oscillations which can be observed in vibrational excitation cross sections [7]. In [12] we investigate this phenomenon in more details. The relation between the long-lived states stabilised by rotation and boomerang oscillations is further more elucidated on the case of  $\text{HCl}^-$  and  $\text{HBr}^-$  [13].

Another interesting issue is the mechanism of the creation of the metastable  $\text{H}_2^-$ . In most of the above mentioned experiments the ions were produced by sputtering of a hydrogen rich surface with fast ions — that creates a hot cloud from which the ions emerge. The most likely mechanism is thus some few-body (counting the atomic nuclei) process like



The creation in a two body process like the ion-atom collision

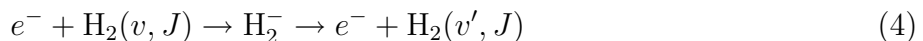


or the electron-molecule collision



is much less likely. Although the cross sections for the processes (2) and (3) can be quite high, the reaction rate would be very small for any realistic collision-energy distribution. That is because the respective cross section has a shape of a peak with a narrow width  $\Gamma$ , resulting from the long lifetime  $\tau = \hbar/\Gamma$ . Nevertheless, for some experiments, with a low background, the small number of emerging ions could still be detected in two body experiments. Such experiments are planned [14] to improve the only existing value for the rate constant of associative detachment in  $\text{H}+\text{H}^-$  collisions [15]. In this communication we present the theoretical data for the cross sections of the creation of the metastable  $\text{H}_2^-$  states in the two body collisions (2), (3) which can be used for designing such experiments or for plasma modelling.

*Theory.* Like in our previous works on  $\text{H}^-+\text{H}$  collisions [8] and  $e^-+\text{H}_2$  scattering [9,10] the dynamics of the system is described within the nonlocal resonance model [8]. The theory is based on the model for the interaction of a discrete state with the one-electron continuum. If the proper diabatic discrete state is chosen [16,17], the theory can describe the broad range of phenomena resulting from the transition of the bound discrete state into the continuum with a changing molecular geometry — including the formation of resonances and virtual states [18]. To find the cross section for the creation of the anions, we first calculated the cross sections for all energetically accessible processes



i. e. vibrational excitation (4), dissociative attachment (5), elastic ion-atom collisions (6) and associative detachment (7) in the relevant energy range close to the energies of  $\text{H}_2^-$  states

with the longest lifetimes. Then we separated the direct contribution from the resonant contribution proceeding through the formation of  $\text{H}_2^-$  state localised in the outer potential well. Finally the cross section for the creation of the anion is found as the sum of the resonant contributions over all accessible final states. For the narrow resonances like here, the separation of the direct and the resonance contribution can be done in a rather simple way. We fit the cross sections for all of the involved processes with the multichannel Fano formula [19]

$$\sigma_{\alpha',\alpha}(E) = \frac{\pi}{2m_\alpha E} \left[ (d_{\alpha',\alpha}^R)^2 + (d_{\alpha',\alpha}^I)^2 + \frac{(\gamma_{\alpha'}\gamma_\alpha)^2 + 2(E - E_R)d_{\alpha'\alpha}^R\gamma_{\alpha'}\gamma_\alpha - \Gamma_R d_{\alpha'\alpha}^I\gamma_{\alpha'}\gamma_\alpha}{(E - E_R)^2 + \Gamma_R^2/4} \right], \quad (8)$$

where  $m_\alpha$  is a reduced mass in the initial channel,  $d_{\alpha'\alpha} = d_{\alpha'\alpha}^R + id_{\alpha'\alpha}^I$  is a complex background term and  $\gamma_{\alpha'}\gamma_\alpha$  is factorised substitution matrix (multichannel scattering matrix  $S_{\alpha'\alpha}(E)$  at the pole  $\bar{E} = E_R - i/2\Gamma_R$ ). The collision energy  $E$  must be taken in the vicinity of the known energies of  $\text{H}_2^-$  states [6]. The parameters for the different processes involving the same channels are not independent and their mutual relations can be used to check the consistency of the assumption, that the processes are all proceeding through one resonance state. For example, the parameters  $\gamma_\alpha$  are directly related to the total width of the resonance

$$\Gamma_R = \sum_\alpha |\gamma_\alpha|^2. \quad (9)$$

The value of  $|\gamma_\alpha|^2$  thus gives partial width of the  $\text{H}_2^-$  state to the individual decay channel  $\alpha$  and the ratio  $r_\alpha = |\gamma_\alpha|^2/\Gamma_R$  is the relative probability for the decay into the specific state. The pure resonant contribution is then given by Breit-Wigner formula

$$\sigma_{\alpha',\alpha}(E) = \sigma^M \frac{\Gamma_R^2}{4(E - E_R)^2 + \Gamma_R^2}, \quad (10)$$

where the peak value of the cross section reads  $\sigma_{\alpha',\alpha}^M = \frac{2\pi}{m_\alpha E_R} r_\alpha r_{\alpha'}$  and the sum over the final decay channels  $\alpha'$  gives the total cross section for the creation of the molecular anion in the form of Breit-Wigner formula (10) with  $\sigma_\alpha^M = \frac{2\pi}{m_\alpha E_R} r_\alpha$ .

*Results and discussion.* We have performed the above described analysis for the six most prominent resonances for  $\text{H}_2^-$ . The resonances can be classified according to the rotational

quantum number  $J$  of the orbiting nuclei and the number of nodes  $\bar{v}$  of the wave function in the outer potential well (see figures 1 and 2 in [6] for the shape of the adiabatic potential). There are three available decay channels for these resonances:  $\text{H}+\text{H}^-$  and  $\text{H}_2(v) + e^-$ , with  $v = 0, 1$ . The quantum number  $v$  characterises the vibrational state of the neutral molecule created in the autodetachment process. The rotational quantum number is approximately conserved (it changes by  $\pm 1$ , but we neglect this change in the current description) [9]. In table I we give the values of the total width  $\Gamma$  for each resonance and the values of parameters  $E_R$ ,  $r_\alpha$  and  $\sigma_M$  for each resonance and each creation/decay channel.

We observe, that the decay of all resonances is entirely dominated either by detachment or dissociation process. The peak value of the cross section  $\sigma_\alpha^M = \frac{2\pi}{m_\alpha E_R} r_\alpha$  for the creation of the anions can then rather well be estimated if we can decide which channel is dominant. In the case of dissociation as a dominant channel we can take  $r_\alpha \simeq 1$ . If the detachment channel dominates we can assume the equal sharing of the all open channels as the first approximation. The question of the dominant decay channel can be resolved roughly just by looking into figures 3,4 in [6], where we already discussed the resonances with dissociation as a dominant channel, because the lifetime of these resonances turns out to be very sensitive to small changes in the model. Especially the resonances (26,0) and (27,0) were analysed in [6], where we found that a small change of the adiabatic potential energy curve for  $\text{H}+\text{H}^-$  has no dramatic effect on (26,0) resonance, but it can completely change the character of the (27,0) resonance by changing its dominant decay channel from dissociation to detachment. This suppression of the dissociation-channel reduces the width of the resonance by more than three orders of magnitude increasing the lifetime accordingly. Keeping this sensitivity in mind, we must read the last line of the table I with caution. From comparison with the experimental data [4], we expect that this modified (27,0) resonance is more likely observed. For such resonance the dissociation channel  $\text{H}+\text{H}^-$  will be greatly reduced, while the peak in the cross section for creation of  $\text{H}_2^-(27,0)$  in electron collisions with rotationally excited molecule will reach the value close to  $\sigma_\alpha^M = \frac{2\pi}{m_\alpha E_R} \simeq 2000 a_0^2 \simeq 500 \text{\AA}^2$ .

## ACKNOWLEDGMENTS

We thank Daniel Savin for encouraging this work. This work has been supported by GACR 105-13/201227, Charles University grant no. GAUK 143107 and by "Výzkumný záměr" grant no. MSM 0021620860 MŠMT.

TABLES

$R = (J, \bar{\nu})$	$\Gamma_R$	H+H <sup>-</sup>			H <sub>2</sub> <sup>-</sup> ( $v = 0$ ) + e <sup>-</sup>			H <sub>2</sub> <sup>-</sup> ( $v = 1$ ) + e <sup>-</sup>		
		$E_R$	$r_\alpha$	$\sigma_M$	$E_R$	$r_\alpha$	$\sigma_M$	$E_R$	$r_\alpha$	$\sigma_M$
(25,0)	2.2e-9	-	-	-	0.0146	0.443	190	2.6e-3	0.556	1365
(25,1)	7.5e-9	2.3e-4	2e-15	3e-14	0.0156	0.356	144	3.5e-3	0.638	1142
(25,2)	1.6e-7	7.4e-4	0.96	4.6	0.0161	0.015	6	4.0e-3	0.030	48
(26,0)	9.3e-11	2.0e-4	9e-19	1.5e-17	8.9e-3	0.715	508	-	-	-
(26,1)	6.6e-8	8.7e-4	0.99	4.2	9.5e-3	0.002	1.5	-	-	-
(27,0)	1.1e-8!	1.0e-3	1.0!	3.6!	3.0e-3	2.9e-4!	0.6!	-	-	-

TABLE I. Parameters of the most stable resonances (all parameters given in atomic units). The values with exclamation mark are the most likely corrupted due to extreme sensitivity to H+H<sup>-</sup> interaction potential (see the discussion at the end of the paper).

## REFERENCES

- [1] R. Golser, H. Gnaser, W. Kutschera, A. Priller, P. Steier, A. Wallner, M. Čížek, J. Horáček, and W. Domcke, *Phys. Rev. Lett.* **94**, 223003 (2005).
- [2] H. Gnaser and R. Golser, *Phys. Rev. A* **73** 021202 (2006).
- [3] R. Golser, H. Gnaser, W. Kutschera, A. Priller, P. Steier, and A. Wallner, *Nucl. Instrum. Meth. Phys. Res.* **259**, 71 (2007).
- [4] O. Heber, R. Golser, H. Gnaser, D. Berkovits, Y. Toker, M. Eritt, M. L. Rappaport, and D. Zajfman, *Phys. Rev. A* **73**, 060501 (2006).
- [5] W. G. Wang, Y. Xu, A. M. Zhu, Z. W. Liu, X. Liu, and X. F. Yang, *J. Phys. B* **40**, 921 (2007).
- [6] M. Čížek, J. Horáček, and W. Domcke, *Phys. Rev. A* **75**, 012507 (2007).
- [7] M. Allan, *J. Phys. B* **18**, 451 (1985).
- [8] M. Čížek, J. Horáček, and W. Domcke, *J. Phys. B* **31**, 2571 (1998).
- [9] J. Horáček, M. Čížek, K. Houfek, P. Kolorenč, and W. Domcke, *Phys. Rev. A* **70**, 052712 (2004).
- [10] J. Horáček, M. Čížek, K. Houfek, P. Kolorenč, and W. Domcke, *Phys. Rev. A* **73**, 022701 (2006).
- [11] J. Senekowitsch, P. Rosmus, W. Domcke, and H.-J. Werner, *Chem. Phys. Lett.* **111**, 211 (1984).
- [12] K. Houfek, M. Čížek, and J. Horáček, *Chem. Phys.* **347**, 250 (2008).
- [13] M. Čížek and J. Horáček, *Int. J. Mass Spectrom.* (2008), *In press*, doi:10.1016/j.ijms.2008.07.034.
- [14] D. W. Savin 2007. *Private communication*.



- [15] A. L. Schmeltekopf, F. C. Fehsenfeld, and E. E. Ferguson, *Astrophys. J.* **148**, L155 (1967).
- [16] K. Houfek, T. N. Rescigno, C. W. McCurdy, *Phys. Rev. A* **73**, 032721 (2006).
- [17] K. Houfek, T. N. Rescigno, C. W. McCurdy, *Phys. Rev. A* **77**, 012710 (2008).
- [18] W. Domcke, *Phys. Rep.* **208**, 97 (1991).
- [19] J. R. Taylor, *Scattering Theory: The Quantum Theory on Nonrelativistic Collisions*, Wiley 1972.