Long-lived states of molecular hydrogen anion

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Abstract. The existence of long-lived states (of the order of microseconds) of the molecular hydrogen anion H_2^- is discussed both from theoretical and experimental points of view. The history of experimental search for these states is briefly reviewed and a theoretical explanation based on the use of the nonlocal resonance model offered. Final unambiguous confirmation of the existence by means of the accelerator mass spectrometry and mass spectrometry and the measurement of their lifetimes in electrostatic ion-beam trap is described.

Keywords: Molecular resonances, electron-molecule scattering, molecular hydrogen anion
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INTRODUCTION

It is well known that a stable molecular anion H_2^- does not exist. However, even this simplest and most fundamental molecule has a rather intricate resonance structure involving strong correlation between electron and nuclear motion beyond Born-Oppenheimer approximation. These long-lived (metastable) states are of fundamental importance in the understanding of physical processes in such fields as plasma physics, planetary atmosphere modelling and electrical discharges. It is vital to our understanding of resonance phenomena in molecules to understand these structures.

The calculation of resonance (long-lived) states in molecules is notoriously known to be very difficult because the resonance energy is complex and the resonance wave function, in contrast to the standard bound state calculations of quantum chemistry, is not localised in a finite volume.

The most important state for low-energy processes is the $^2\Sigma_u^+$ state, the lowest resonance of H_2^-, with the lifetime of the order of 10^{-15}s. This resonance dominates the low-energy processes in e^-+H_2 and H^-+H collisions. In the past decade we treated many of the processes within the nonlocal resonance model, which turned out to be the most successful approach to account for the complicated coupling of the electronic and nuclear degrees of freedom within the system. Examples of the cross sections for various processes are shown and compared with experiment in Figures 1-3. It is electron hydrogen elastic scattering [1] (see Figure 1)

$$e + H_2(v_i, J_i) \rightarrow e + H_2(v_i, J_i), \tag{1}$$

vibrational excitation (VE) by electron impact [1] (see Figure 2)

$$e + H_2(v_i, J_i) \rightarrow e + H_2(v_f, J_i), \tag{2}$$

dissociative attachment (DA) of electron to the molecule [5] (see Figure 3)

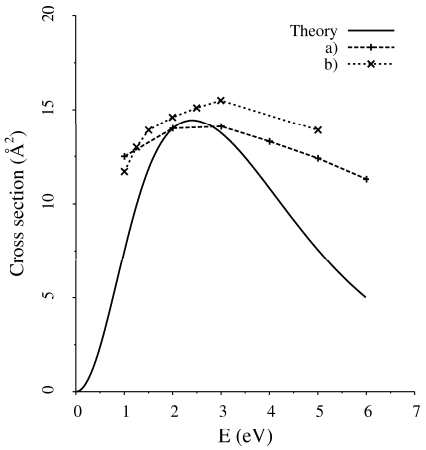

FIGURE 1. Resonance integral elastic electron scattering for the ground rovibrational state of the hydrogen molecule (solid line). Experimental data: a) rotationally resolved measurement of Linder and Schmidt [2], b) measurement of Brunger and Buckman [3]

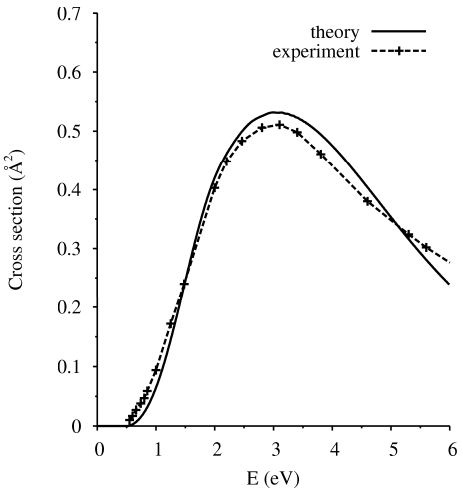

FIGURE 2. Resonance integral $0 \rightarrow 1$ VE cross section - solid line - compared with the measurement of Ehrhardt et al. [4]

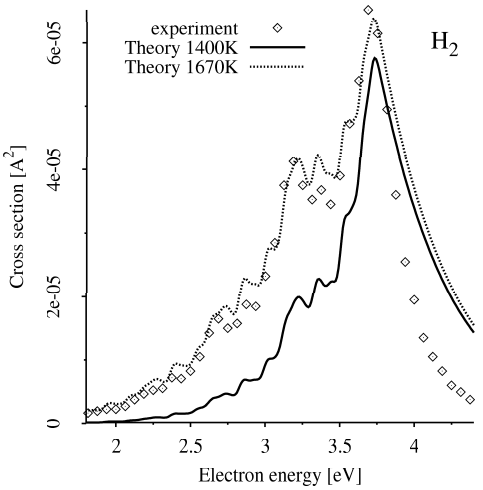

FIGURE 3. Cross sections for dissociative electron attachment to hot molecules. Experimental data: Allan and Wong 1978 [7]

$$\mathrm{e} + \mathrm{H}_2(v_\mathrm{i}, J_\mathrm{i}) \rightarrow \mathrm{H} + \mathrm{H}^-, \tag{3}$$

and associative detachment (AD) of electron [6]

$$\mathrm{H} + \mathrm{H}^- \rightarrow \mathrm{e} + \mathrm{H}_2(v_\mathrm{f}, J_\mathrm{f}). \tag{4}$$

In addition to the $^2\Sigma_u^+$ state there exist many other important resonance states, for example the $^2\Sigma_g^+$ state located around electron energy 8 eV. Generally their lifetime is shorter than 10^{-10} s (for a comprehensive study of these states see [8]). The question however was raised whether states with a longer lifetime (of the order of microseconds) may exist and whether these states can be observed in modern experiments. Starting form 1958 several attempts to see these states were carried out, however, the results were not conclusive. In the next section we give a brief overview of the experimental effort to observe such states.

EXPERIMENT

Experiment before 2004

Despite considerable experimental efforts during the past five decades [9], [10], [11], [12], [13] the possible existence and the lifetime of the molecular hydrogen anions (H_2^- and D_2^-) remained uncertain. The existence of the long-lived states was first reported by Khvostenko and Dukelskii [9] in 1958. They used the recharging method to produce the ion. Water vapour and antimony vapour were introduced simultaneously into an ion source and bombarded by a beam of electrons. The resulting negative ions were mass analysed. When water vapour alone was present in the ion source, H^-, O^- and OH^- were formed but when antimony vapour was subsequently introduced into the source

a negative ion of mass 2 appeared. The height of the peak at mass 2 was only 20-30 times less than that of H^- peak. This was strange because the H^- ion is stable and its flux should be much stronger (by several orders of magnitude) than that of H_2^- ion. And in addition it was not possible to say whether this peak was due to H_2^- or due to the formation of D^-.

A more elaborated experimental attempt to detect H_2^- was published by Hurley et al. [10], using a discharge ion source. Again the results were surprising; the H_2^- ion was reported to be about 5.5 times more abundant than the stable H^- ion, an observation that could not be reproduced later.

Aberth et al. [11] claimed the observation of metastable ($\tau > 10\mu$s) HD^-, D_2^-, D_3^-, and HD_2^- anions, but were unable to detect H_2^-, H_3^-, and H_2D^-, because of mass interferences; in that work, the anion species were produced in a hollow-cathode duoplasmatron source and analyzed in a combination of a Wien filter and 90° magnetic sector (with a resolution of m/Δm$\sim$500).

Barnett has made an extensive search for doublet H_2^- ion formation by simultaneous two-electron capture collisions of H^+ in H_2 and Xe gasses. His careful studies gave completely negative results, [14].

The H_2^- ion was probably observed without any effort to form the ion by people studying interplanetary dust and the H/D ratios for meteors, see e.g. [15].

Later, Bae et al. [12] searched for H_2^- and H_3^- employing a two-step electron capture process, albeit with negative results. Very recently, Wang et al. [13] observed H_3^- produced in a dielectric-barrier discharge plasma; a three-body collision process was proposed as the dominant formation mechanism. The rather moderate mass resolution of the quadrupole mass analyzer did not allow for an explicit identification of H_2^- or D_2^- in that experiment.

High resolution mass spectroscopy

In view of the conflicting results the unambiguous verification of the existence of the (metastable) H_2^- and D_2^- anions was carried out at VERA, the Vienna Environmental Research Accelerator, by means of the accelerator mass spectroscopy. The molecular hydrogen anions were produced by Cs-sputtering of suitable target materials (TiH_2 and TiD_2) and detected by means of highly sensitive and selective mass-spectrometric techniques. VERA is a facility for accelerator mass spectrometry (AMS) based upon a 3 MV Tandem accelerator. For a more detailed description the reader is referred to [16], [17]. AMS allows to literally analyze mass-selected, negatively charged molecules by injecting them into a tandem accelerator and breaking them up into the atomic constituents during the stripping process in the high-voltage terminal. The positively charged atomic ions are further accelerated and are again mass-analyzed after the accelerator; finally their energy is measured. If all atomic constituents of the very same molecule arrive simultaneously in the energy detector, an unambiguous identification of the molecule is accomplished.

These experiments demonstrate conclusively that both H_2^- and D_2^- are formed in the sputtering process; from the respective flight times through the spectrometer, lifetimes

of at least 2.7 μs and 3.9 μs, respectively, can be inferred, for details see [19].

H_2^- anions were detected also recently in a conventional secondary-ion mass spectrometer operated at sufficiently high mass resolution ($m/\Delta m \sim 1500$) to separate H_2^- from D^- [18].

Measurement of the lifetimes

The lifetimes mentioned above are in fact just lower limits of the true lifetimes. To get a real value of the lifetime a direct measurement is necessary. Heber and coworkers [20] measured the lifetime of molecular hydrogen anion by means of an electrostatic ion-beam trap. As expected longer lifetimes were obtained: 8.2$\pm$1.5μs for H_2^-, 50.7 $\pm$1.0 μs for HD^-. The measurement of the lifetime od D_2^- revealed even more interesting feature. In fact there lifetimes were observed: $\tau_1 = 23\pm$ 3μs, $\tau_2 = 84\pm$ 3 μs and a really long one $\tau_3 = 1890\pm$ 80 μs. It was proposed in [20] that more than one electronic state contributes to the overall lifetimes of these states. As suggested by Aberth et al. [11], metastable H_2^- could also exist in a quartet state. According to Bae et al. [12], the most probable configuration would be the $^4\Sigma_g^-$ state. However, to our knowledge, no calculations have yet been reported on quartet states for negative molecular hydrogen ion.

THEORY

The elastic scattering cross section as well as the VE cross sections shown in Figures 1-3 were obtained by means of the nonlocal resonance model (NRM) which is probably the most successful theory of resonance electron molecule scattering [6], [21]. The nonlocal resonance model has been successfully applied to a series of diatomic molecules and yields cross sections for all processes mentioned above, i.e. vibrational excitation, dissociative attachment and associative detachment from first principles with a high accuracy. It will be shown below that NRM offers an explanation of the long lifetimes. First, the basic properties of the model will be introduced.

Nonlocal resonance model

The nonlocal resonance model is based on the assumption that a temporary molecular negative-ion state (resonance) is formed and that this resonance accounts for the coupling of the electronic scattering dynamics with the nuclear motion [21]. The resonance is represented by a square-integrable discrete state $|\varphi_d\rangle$ which interacts with a continuum of scattering states $|\varphi_\varepsilon\rangle$ via coupling matrix elements $V_{d\varepsilon}$. $|\varphi_d\rangle$ and $|\varphi_\varepsilon\rangle$ are assumed to be diabatic states, that is, their wave functions vary smoothly with the internuclear distance R.

The basic equation of the nonlocal resonance theory is the wave equation describing nuclear motion in the short-lived anion state [21]

$$[T_N + V_d(R) - E]\Psi_d(R) + \int d\varepsilon \int dR' V_{d\varepsilon}(R) G_0(R,R';E-\varepsilon) V^*_{d\varepsilon}(R')\Psi_d(R') = -V_{d\varepsilon_i}(R)\chi_{v_i}(R) \tag{5}$$

with

$$G_0(R,R';E) = \langle R \mid (E - T_N - V_0 + i\varepsilon)^{-1} \mid R' \rangle. \tag{6}$$

Here $V_0(R)$ and $V_d(R)$ are the potential energy functions of the target state and the discrete state, respectively. $\chi_{v_i}(R)$ is the wave function of the initial vibrational state of the target molecule, ε_i is the energy of the incoming electron, and E is the total energy of the collision complex. G_0 is the Green's function for nuclei motion in the target state, T_N being the radial nuclear kinetic energy operator.

The second term on the left hand side of Eq.(5) plays the role of a complex, energy-dependent and nonlocal effective potential for the radial nuclear motion. It accounts for the decay of the electronic resonance state through the coupling with the electronic scattering continuum.

From the solution of Eq.(5), cross sections for various processes can be obtained. For example, the integral cross section for electron scattering from initial vibrational state v_i to final state v_f reads [21]

$$\sigma_{v_f v_i}(E) = \frac{4\pi^3}{k_i^2} |\langle \chi_{v_f} | V^*_{d\varepsilon_f} | \Psi_d \rangle|^2. \tag{7}$$

This expression includes only the resonant part of the scattering amplitude, which is dominant for inelastic processes.

High rotational states of hydrogen

As described above the model is based on the assumption that a transient anion is formed in the collision which can be represented by a square-integrable discrete state which interacts with the continuum (autodetachment of an electron) via coupling described by the matrix element $V_{d\varepsilon}$ of the Hamiltonian. In the case of H_2^- it is the formation of the $^2\Sigma_u^+$ resonance that accounts for the strong coupling between electronic and nuclear motion at low energies. Here we will show that for highly rotationally excited hydrogen molecules this resonance generates a series of state with the life time of the order of 10^{-13}-10^{-6} s. In NRM the nuclear dynamics of the transient anion is governed by effective hamiltonian

$$H_{\text{eff}} = T_N + V_d(R) + \int V_{d\varepsilon}(R)[E - \varepsilon - T_N - V_0(R) + i0]^{-1} V^*_{d\varepsilon}(R') d\varepsilon. \tag{8}$$

The last term is the non-hermitian nonlocal potential responsible for autodetachment of the transient anion. The magnitude of the autodetachment width $\Gamma \equiv 2\pi |V_{d\varepsilon}(R)|^2$ is of

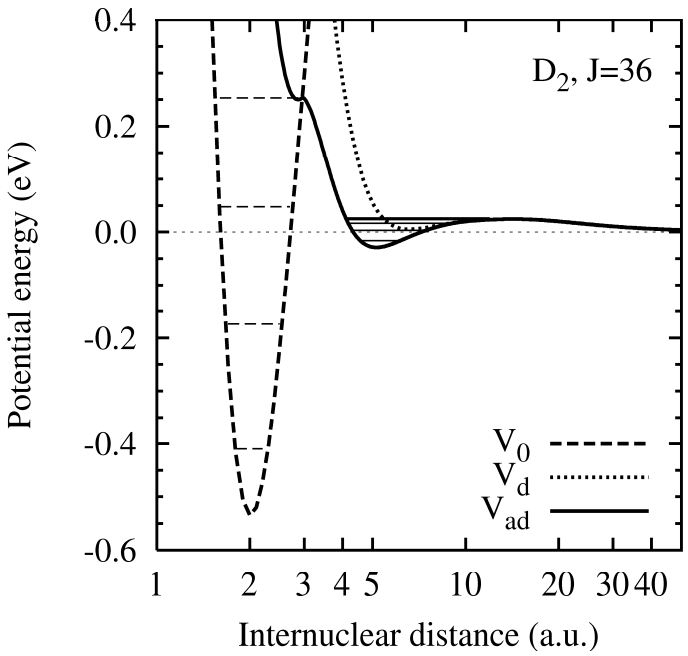

FIGURE 4. Potential-energy curves for hydrogen molecule (dashed line) and its anion (full line). The vibrational states of the neutral molecule and the "outer well resonances" for H_2^- are shown as energy levels in the potentials.

the order of eV for $R < 3a_0$. Since the potential $V_d(R)$ is attractive for $R > 2a_0$ (see for example [6]) the nuclear wave function has a large amplitude in the autodetachment region, which leads to the fast decay of the anion state. If the anion has nonzero angular momentum $J > 0$ the effective hamiltonian (8) is modified by an additional term $J(J+1)/2\mu R^2$. The potentials $V_0^J(R)$ for D_2, $V_d^J(R)$ and the real part $V_{ad}(R)$ of the local complex approximation [21] for D_2^- with $J = 36$ are shown in Fig. 4. For $R > 3a_0$, $V_{ad}(R)$ gives the adiabatic potential for the electronically bound anionic state (for $R < 3a_0$ it is the real pole of the fixed nuclei scattering S-matrix). It is worthwhile to note that for high J the anion potential $V_d(R)$ as well as the adiabatic potential $V_{ad}(R)$ build a repulsive barrier which reduces the amplitude of the nuclear wave function in the autodetachment region increasing thus the autoionization life time. At large internuclear distances the centrifugal barrier $J(J+1)/2\mu R^2$ prevents the particles to escape into dissociative attachment channel. Hence, it make sense to assume that long-lived states are formed in between the two barriers.

To verify the hypothesis we calculated the cross sections for electron impact vibrational excitation and dissociative attachment of H_2 and D_2 molecules using the method described in [6] in the broad range of rotational quantum states J and in the range of energies corresponding to expected states in the outer potential well. We found narrow resonances with energies close (within 0.1 meV) to the adiabatic states in $V_{ad}(R)$. The energies of the states for $J = 36$ in D_2^- are also indicated in the Fig. 4. Widths and positions of the resonances have been analyzed using the Fano formula. The widths spread over a broad region of 10^{-13}–10^{-3} eV. Cross sections for vibrational excitation attain

TABLE 1. Parameters of the most stable resonances for each rotational quantum number J. Resonance energies relative to DA threshold are given in meV.

H_2^- resonances			D_2^- resonances		
J	E_{res}	τ	J	E_{res}	τ
21	-136	2.4 ps	31	-118	0.13 ns
22	-105	12 ps	32	-97	0.68 ns
23	-75	0.11 ns	33	-76	5.6 ns
24	-47	0.9 ns	34	-55	36 ns
25	-20	11 ns	35	-35	0.38 μs
26	5	0.25 μs	36	-16	4.1 μs
27	28	2 ns	37	2	61 μs
			38	19	2.1 ms
			39	34	46 ps

values up to hundreds of square Angsröms at the resonances. The calculated energies and lifetimes of the lowest resonances are collected in Table 1. The J-dependence of the resonance parameters is consistent with the increasing repulsion and decreasing well depth for growing J. The resonances in D_2^- live longer than that for H_2^- as expected because of the tunneling mechanism for the decay.

We have thus demonstrated that the ground $^2\Sigma_u^+$ potential of H_2^- can support quasi-bound states with the lifetimes as long as microseconds if the high angular momentum is assumed. We get for hydrogen the longest lifetime $\tau = 0.25$ μs for $J = 26$ and $\tau = 2.1$ ms for $J = 38$ for deuterium. These long-lived states may survive the path from the sputtering ion source to the stripper (3-5μs) and be observed by the detectors. This explanation is supported by the well known fact that highly rotationally excited states are produced in the sputtering ion sources. Furthermore the observed lifetimes for D_2^- [20] are in full agreement with our values. The longest calculated lifetime for H_2^- is too short by one order of magnitude, but in [22] we show that small changes in potential ($\sim$10meV) can explain this discrepancy. In addition to the $^2\Sigma_u^+$ state explicitly considered in our calculation other electronically excited molecular states combined with rotational excitation may support long lived states of H_2^- and D_2^-. Further experimental and theoretical investigation of the properties and the decay channels of the ions would therefore be highly desirable.

CONCLUSIONS

In this paper it was shown unambiguously that long-lived state of the molecular hydrogen anion H_2^- with the lifetime of the order of μs exist, that can be directly observed in various kinds of experiments. In addition, an explanation of the nature of these states was provided based on the use of the nonlocal resonance model describing the long lived states as states of highly rotationally excited hydrogen molecule. Preliminary results of this work were published in [19**?**]. The more detailed data for long lived resonances in H_2^-, HD_2^-, D_2^- and T_2^- will appear soon [22].

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