NARROW RESONANCES IN DISSOCIATIVE ELECTRON ATTACHMENT AND VIBRATIONAL EXCITATION IN H_2

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This progress report reviews briefly the recent theoretical work of Čížek, Horáček and Domcke[1,2]. Narrow resonances are found in calculated cross sections for various processes in low-energy electron collisions with H_2 molecule. Closer inspection reveals many metastable states of H_2^- with the lifetimes reaching μs values. The properties of these states can qualitatively be understood within the local complex potential approximation. Resonances represent the orbiting states of H+H$^-$ with angular momenta $J = 22 - 27$. The existence of the molecular hydrogen anions has recently been confirmed by experimens[1], where these species are produced by sputtering of TiH_2 and TiD_2 targets with Cs^+ ions with subsequent identification of H_2^- by accelerator mass spectrometry.

1. Introduction

It seems to be well established fact, that the hydrogen molecular anion is a very unstable species. In spite of this it proved to be an important theoretical concept in description of electron collisions with molecular hydrogen and also H+H$^-$ collisions. The lowest H_2^- resonance of the Σ_u^+ symmetry is believed to play the key role in processes below H+H+e$^-$ threshold. This state has the autodetachment width of eV size, corresponding to the lifetime in 1fs range at the internuclear separation of $R = 1.4a_0$, which is equilibrium separation in the neutral H_2 molecule. The time-dependent calculations of Gertischke and Domcke[3] confirm this time-scale. The Σ_u^+ state of H_2^- is stable against autodetachmet for larger R, but the same calculations show that the system will either dissociate or return into autodetachment region within at most 100fs. In this paper we would like to show that there are theoretical reasons to believe that the states with lifetime 7 orders of magnitude higher exist.

In our first paper about H+H$^-$ collisions[4] we found a series of a narrow resonances in some of the partial-wave contributions to the total associative detachment cross section. The resonances are very narrow (with width below 1meV) and the cross section is so small in their vicinity, that they contribute very little to the total sum. The fact that such a narrow resonances are present is surprising in the view of the size of the autodetachment width. The special shape of the H+H$^-$ potential is responsible for this. With increasing angular momentum J the centrifugal term $J(J+1)/2\mu R^2$ modifies the potential so that the outer well is formed[4], in which the system can be trapped shielded by potential barrier against both autodetachment and dissociation. The same resonances can also be seen in dissociative attachment[5]. Closer inspection shows[5] that there must be more such resonances with energies below H+H$^-$ threshold. Such states would not be accessible in associative detachment and dissociative attachment processes but could be seen as narrow resonances in VE cross sections[6]. In this progress report we would like to review briefly the properties of these states. The details of this work are given elsewhere[1]. Preliminary results were also presented on the ECAMP conference last year[2].

2. Brief outline of theory

The dynamics of the collisional complex H_2^- is described within the nonlocal resonance theory as reviewed by Domcke[7]. The specific model for H_2 based on projection-operator formalism was constructed by Berman, Mundel and Domcke[8] and adjusted to treat properly the long range interaction in H+H$^-$ channel[4]. It is outside the scope of this progress report to go into details. In the following paragraphs we will introduce only necessary quantities needed to understand some aspect of the present work.

2.1. *Nonlocal potential versus adiabatic potential*

The main difficulty in theoretical description of the resonant low-energy electron-molecule collision is the failure of adiabatic approximation. In nonlocal resonance theory this difficulty is circumvented by definition of mutually orthogonal discrete state ϕ_d and the electronic continuum ϕ_e, which form basis in the electronic Hilbert space, diabatic with respect to internuclear separation R (for details see review of Domcke[7]). The complete scattering wave-function is expanded in this basis

$$\Psi(R,r) = \psi_d(R)\phi_d(R,r) + \int \mathrm{d}e\ \psi_e(R)\phi_e(R,r), \tag{1}$$

where r stands for all electronic degrees of freedom and e is the energy of the electron released in the autodetachment. It is possible to show that the full information about the dynamics can be extracted from coefficient $\psi_d(R)$ alone[7] which has the interpretation of the probability amplitude for the system to be in the discrete state. This "discrete state" wave-function obeys the Schrödinger-type equation for motion in R-coordinate space, with effective Hamiltonian

$$H_{\rm vib} = T_{\rm N} + V_d(R) + \hat{F}(E), \tag{2}$$

where $V_d(R)$ is the discrete state potential (mean value of electronic Hamiltonian in the state ϕ_d) and $\hat{F}(E)$ is the effective potential resulting from the interaction of the discrete state with the continuum, which in coordinate representation reads

$$\langle R|\hat{F}(E)|R'\rangle = \int {\rm d}e V_{de}(R)\left[E - e - T_{\rm N} - V_0(R) + i0\right]^{-1} V^*_{de}(R'). \tag{3}$$

Here $V_0(R)$ is the neutral molecule potential energy, $V_{de}(R)$ is the coupling matrix element of the electronic Hamiltonian between ϕ_d and ϕ_e, E is the total energy of the system and T_N the kinetic energy of the nuclei. It is possible to show[9] that the partial-wave expansion of the wave-function (1) just produces standard centrifugal term $J(J+1)/2\mu R^2$ which adds to both potentials $V_0(R)$ and $V_d(R)$.

To get the cross sections for associative detachment, dissociative attachment and vibrational excitation the Schrödinger equation (or equivalently the integral Lippmann-Schwinger equation) with the Hamiltonian (2) and boundary conditions corresponding to $H+H^-$ or H_2+e^- intial/final channel is solved. Sometimes the nonlocal interaction $V_d + \hat{F}(E)$ is replaced with local complex potential (LCP) approximation $V_{ad}(R) - \frac{i}{2}\Gamma(R)$. This potential can directly be related to functions $V_0(R)$, $V_d(R)$ and $V_{de}(R)$ defining the nonlocal resonance model[4,7]. For $R \gtrsim 3a_0$ the real part V_{ad} of LCP coincides with adiabatic potential for the ground electronic state of molecular anion at fixed R. The potentials $V_0(R)$, $V_d(R)$ and $V_{ad}(R)$ are shown in Fig. 1 (left). The potential $V_{ad}(R)$ is actually not used in our calculation of cross sections, but it is useful for interpretation of its structure. The quality of the LCP approximation can be understood from the following test. We select some wave-function φ peaked around some $R = R_0$ and write the action of the full interaction operator as multiplication with the constant λ plus some residual vector ρ (making ρ as small as possible)

$$[V_d + \hat{F}(E)]|\varphi\rangle = \lambda|\varphi\rangle + |\rho\rangle. \tag{4}$$

Now we can print $V_{loc}(R_0) \equiv \Re\lambda$ as function of R_0 for some shape of peak φ_{R_0}. We show this test potential in Fig. 1 for energy E close to $H+H^-$

threshold and for φ of Gaussian shape with the width of 0.5a$_0$. It is clear that V_{loc} is very close to V_{ad} for $R \gtrsim 4$bohr[a]. This is an indication that the adiabatic potential can be used for interpretation of features of the dynamics for which this range of R is responsible.

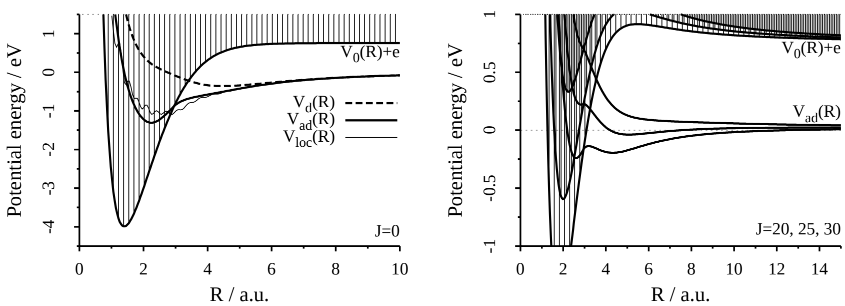

Figure 1. Potential energy curves (including centrifugal term $J(J+1)/2\mu R^2$) for angular momentum $J = 0$ (left) and for $J = 20$, 25, 30 (right).

The dependence of the shape of $V_{ad}(R)$ and $V_0(R)$ on the angular momentum J is shown in the right hand part of Fig. 1 for $J = 20$, 25 and 30. It demonstrates how the outer potential well is build and disappears with growing J. From the previous discussion it is also obvious that the outer well is located in the region where adiabatic potential curve describes satisfactorily the dynamics of the system.

2.2. *Extraction of metastable-state parameters*

To determine the lifetime of the resonances in the H_2^- system we calculate the cross sections for vibrational excitation(VE) and dissociative attachment(DA) processes

$$e^- + \mathrm{H}_2(v_i) \to e^- + \mathrm{H}_2(v_f), \tag{5}$$

$$e^- + \mathrm{H}_2(v_i) \to \mathrm{H} + \mathrm{H}^-, \tag{6}$$

and preform the least squares fit to the famous Fano formula in the vicinity of resonance. The best fit gives values of the resonance energy E_r and the width Γ_r from which we find the lifetime $\tau = \hbar/\Gamma_r$. It turns out that the resonances are very narrow. Sampling the cross section with the constant

[a]Imaginary part of λ and norm of vector ρ are smaller then the difference between V_{loc} and V_{ad}

energy step we can easily miss the resonance. The discussion above shows that the resonances in the scattering cross section have to be located close to bound states in the outer well in the potential V_{ad}. Although we do not use this potential in calculation of the cross sections, we employ it as an auxiliary tool to localise the resonances. Once we know the approximate position of the resonance we can calculate the cross section in a narrow energy interval on a very fine grid and use the Fano formula to find the properties of the respective metastable state.

It is interesting to compare values of the parameters for the states got from this procedure and from the same procedure but using cross sections calculated within LCP approximation. As an example we give parameters for lowest resonance in $J = 23$

$$\begin{aligned} E_r &= -75.294\text{meV}, & \Gamma_r &= 6.020 \times 10^{-6}\text{meV}, \\ E_r^{(\text{LCP})} &= -75.362\text{meV}, & \Gamma_r^{\text{LCP}} &= 1.662 \times 10^{-5}\text{meV}. \end{aligned}$$

The agreement in the position of the resonance is very good in accordance with previous discussion of validity of the LCP potential. On the other hand the decay width is almost factor of three off. This is understood if we remember that the autodetachment responsible for the decay happens at small R where LCP approximation is not very good.

We developed also an alternative strategy to calculate the lifetime of the resonance directly using nonlocal potential given by Eq. (2) and wave-function obtained for outer well in V_{ad} as the (vibrational) discrete state interacting with $H_2 + e^-$ and $H{+}H^-$ continua. The decay width is then found using projection-operator formalism. Detailed description of this procedure is beyond the scope of this brief progress report and will be given elsewhere.

Another possibility, to find the resonance parameters, would be the direct calculation of the poles of the scattering S-matrix as has been done for $J = 0$ within LCP approximation by Narevicius and Moyseyev[10].

3. Meta-stable states — summary

The dissociative attachment cross sections with the narrow resonances are also shown in the paper of Houfek *et al.*[5] The complete summary of potential energy curves V_0 and V_{ad} for $J = 21, 22, ..., 28$ with location of the states in outer potential wells has been given in ECAMP conference in Rennes last year[2] including some VE cross sections in resonance region and values of autodetachment widths. The details will be given elsewhere. It is interesting to remind some details.

The VE cross sections for $J = 21, 22$ are very similar to VE cross sections for $J = 0$ with prominent boomerang oscillations. The shape of the lowest “oscillations” is different, they become narrow and well separated. Such behaviour is known for VE cross section for HCl and was confirmed experimentally by Allan[11]. Looking at Fig. 1 we find that V_{ad} for $J \sim 20$ has a similar shape to the potential for H+Cl$^-$ system. The appearance of boomerang resonances is allowed by low height of the inner barrier which does not shield the autodetachment region for energies close to DA threshold. As the alternative (and equivalent) interpretation, the narrowing of the lowest boomerang oscillations can be understood as an interference effect for multiply reflected waves from the inner barrier in similar way as in optical interferometers. There is thus smooth transition between boomerang oscillations and the outer well resonances. Both can also be understood as the states located in the outer part of the adiabatic potential or as an interference of the wave-packet multiply scattered back by the same potential.

For higher J the VE cross sections are smooth and it is difficult to find resonances without knowing their location. The size of cross section at resonances exceeds 200Å^2 for elastic electron scattering from H_2 molecule with $J = 25$. It goes high above smooth background which is below 1Å^2.

3.1. *Energies and lifetimes*

The summary of all narrow resonances for both H_2^- and D_2^- is given in Fig. 2. The characteristic features can be understood in terms the the shape of the adiabatic potential. For each J the width of resonances grows with the energy[b] which is clearly the quantum tunnelling effect. The decrease of the width and increase of energy with J is associated with the strengthening of the inner barrier and rising of the bottom of the well. Anomalous behaviour for positive energies is due to changes of the shape of the outer well with J. The isotopic effect is more-less trivial. The widths are lower for D_2^- since it is more difficult to tunnel through the barriers for heavier particles and the states are less separated in the energy.

[b]With exception of high resonances for lower J which are better understandable as boomerang oscillations (the inner barrier is too low).

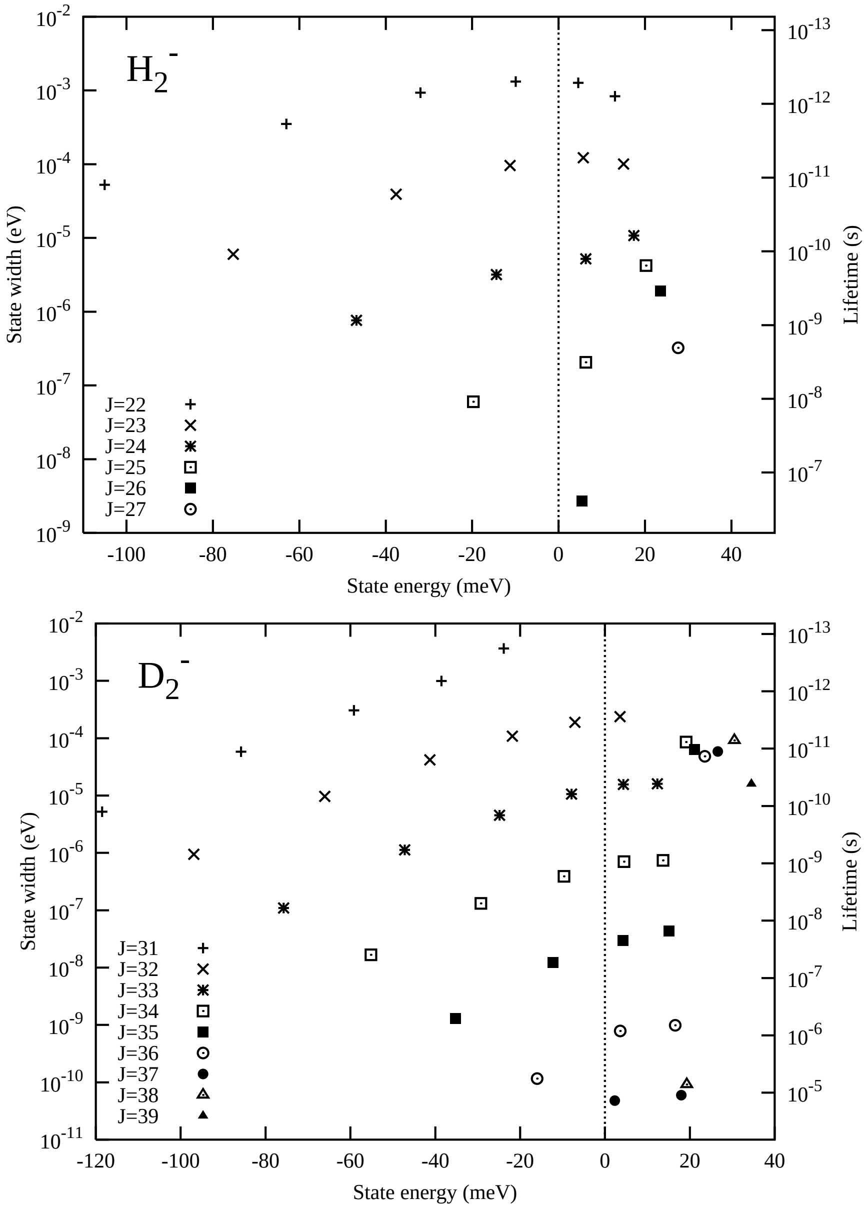

Figure 2. Summary of energies and decay widths/lifetimes of narrow resonances in H_2^- and D_2^-. Energies are given relative to $H+H^-$ $(D+D^-)$ threshold.

4. Conclusions

We have found strong theoretical evidence for the existence of the metastable states of molecular hydrogen anion with lifetimes reaching μs order. The long lifetime can be understood in terms of orbiting H+H$^-$, with angular momentum of $J = 21 - 27$, protected by potential barrier form autodetachment at small R. Local complex potential approximation can not be used to get correct lifetime. The creation of the states in e^-+H$_2$ or H+H$^-$ collisions is difficult although cross sections exceed 200Å^2. With the widths of $10^{-6} - 10^{-9}$eV the production rates with any realistic experimental energy resolution would be very small. This could explain mixed success in experimental efforts to detect such species[12]. Recently the H_2^- with lifetimes of μs order have unambiguously been detected[1]. The species have been produced by sputtering of TiH_2 and TiD_2 surfaces with Cs^+ ions. More experimental evidence is needed to confirm that the anions produced in the experiments are identical with the ones proposed here.

Acknowledgments

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