A Feshbach resonance of the H_3^- anion

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Abstract. Based on a series of *ab initio* calculations a Feshbach resonance of the H_3^- negative ion having $(1sa_1')^2(2sa_1')(2pa_2'')$: ${}^3A_2''$ electronic structure and an estimated lifetime of 10^{-14} s is predicted. This Feshbach state has a potential energy surface roughly parallel to those of the Rydberg states of neutral H_3 with a minimum between the $2pE'$ ground state surfaces of H_3 and the lowest Rydberg state $2sA_1'$. We have determined a number of vibrational levels of the non-rotating molecule.

Mass spectroscopic observation of H_3^- has been reported 30 years ago by Hurley [1] and by Aberth and coworkers [2]. These observations have never been confirmed since.

According to Schultz [3, 4] a temporary negative ion is called a *Feshbach resonance* when its energy is below a "parent" (as a rule Rydberg) state of the neutral system and thus autoionization requires a two-electron process and is relatively slow. In its electronic ground state neutral H_3 is dissociative. The stable positive ion H_3^+ (configuration $(1sa_1')^2$) can bind an electron in the valence orbitals $2pe'$ and in Rydberg orbitals starting with $2sa_1'$, $2pa_2''$. The latter two give rise to the lowest Rydberg states $1^2A_1'$ (or $2sA_1'$) and $1^2A_2''$ ($2pA_2''$) of H_3 with D_{3h} equilibrium geometries and potentials similar to H_3^+. The Rydberg states are only short-lived, the valence states dissociate (for a recent description of H_3^+ and the excited states of H_3 see Ref. [5]).

In the following we shall present theoretical calculations indicating that an electronic $^3A_2''$ state of the anion with configuration $(1sa_1')^2(2sa_1')(2pa_2'')$ is stable with respect to both these Rydberg states of neutral H_3 plus a free electron and thus gives rise to a "two particles-one hole" Feshbach resonance (2p-1h, see [6]), autoionizing to the $2pE'$ ground state plus a free electron in an e'' continuum orbital (because only the direct product $e' \otimes e''$ contains the A_2'' representation). Both Rydberg states can be viewed as parent states of the resonance.

The configuration of this Feshbach state can be related to the atomic systems Be $1s^22s2p\ ^3P$ (1p-1h) [7] or He^- $1s2s2p\ ^4P$ (2p-1h) [8, 9, 10]. Because of the inverted order of the orbitals $2pe'$ and $2s$ the H_3 system cannot directly be compared with its united atom Li. Li^- $1s^22s^2$ is the bound ground state of the negative ion [11]; H_3^- $(1sa_1')^2(2sa_1')^2$ mixed with the configuration $(1sa_1')^2(2pa_2'')^2$ seems to represent another Feshbach state of $^1A_1'$ symmetry which however shall not be discussed here.

The first series of calculations has been carried out using the CEPA ("Coupled Electron Pairs Approximation") program of Fink and Staemmler [12] and basis sets of Widmark and coworkers [13] as well as Rydberg basis sets by Kaufmann et al. [14] (up to $n = 3.5$) and in part of the calculations also continuum functions from Nestmann [15]. In D_{3h} symmetry the preparation of a Hartree-Fock (HF) reference wave function for subsequent use in CEPA is trivial. The specified electron configuration is the lowest one of its orbital symmetry. Both Rydberg orbitals have an orbital radius of about $8a_o$ and do not exhaust the dimensions offered by the basis.

The situation changes somewhat for C_{2v} and C_s arrangements where one or both components of the $2pe'$ valence orbital have the same symmetry as $2sa_1'$ and thus the lowest HF solution of the required symmetry represents a scattering state. With application of level shifting techniques, stationary HF solutions corresponding to the Feshbach configuration could be obtained, in this way avoiding projection operators. Choosing the same hyperspherical coordinates $(\rho, \vartheta, \varphi)$ for the nuclear arrangements as had been used in Ref. [5] the CEPA energies could be obtained at about 100 points on a regular grid surrounding the minimum of H_3^+. At the same time also the energies of the two parent Rydberg states of H_3 have been evaluated with the same method.

With CEPA we find at the equilibrium geometry of H_3^+ (an equilateral triangle of

1.6504 a_o side length) the variational electronic energies of -1.49522 a.u. for the Feshbach state, -1.48280 a.u. for $2sA_1'$ and -1.47746 a.u. for $2pA_2''$. The latter two are slightly lower than previous theoretical results [5, 16, 17] ‡. It turns out that the equilibrium geometry of the Feshbach state is just the average of the equilibria of the two parent Rydberg states (see Table 1).

Table 1. Calculated lowest vibrational energies in cm^{-1} for $J = 0$ (relative to the D_{3h} minima, including zero point energies).

v_1	v_2	H_3^- [a]	H_3 [b]	H_3 [c]	H_3^+ [d]	symmetry
		$^3A_2''$	$^2A_1'$	$^2A_2''$	$^1A_1'$	
0	0^0	4706	4760	4495	4361	A_1(ZPE)
0	1^1	7536	7558	7118	6883	E
1	0^0	8065	8165	7757	7540	A_1
0	2^0	10049	10068	9471	9139	A_1
0	2^2	10325	10309	9698	9359	E
1	1^1	10758	10822	10243	9915	E
2	0^0	11348	11474	10930	10623	A_1

[a] with respect to the minimum at -1.49542 a.u. for $r_{HH} = 1.621\ a_o$

[b] with respect to the minimum at -1.48336 a.u. for $r_{HH} = 1.602\ a_o$

[c] with respect to the minimum at -1.47748 a.u. for $r_{HH} = 1.641\ a_o$

[d] from Ref. [18]

The same type of analytical potential energy surface as used by Jaquet and coworkers [18] in the case of H_3^+ has been fitted to our calculated points for every investigated electronic state. In order to improve the accuracy of this power expansion we have interpolated the difference between the fit and the quantum chemically calculated points by three-dimensional spline functions and added to the fit. For each state a number of vibrational energies of the non-rotating molecule have been evaluated. Interpolation of the Feshbach surface presented more difficulties than the Rydberg surfaces did, and as a consequence its vibrational levels are less precise. Fig. 1a shows cuts of the three surfaces in D_{3h} symmetry and visualizes the order of the first few vibrational levels. A more extensive list is given in Table 1. It is obvious that the vibrational spacings of the Feshbach state are similar to those of the $2sA_1'$ Rydberg state whereas the $2pA_2''$ vibration resembles rather that of the positive ion; the calculated spacings of $2pA_2''$ agree within wavenumbers with the experiment [19]. Including zero point vibration an electron affinity of 0.33 eV is predicted for the $2sA_1'$ state and 0.46 eV for $2pA_2''$. Only the zero point level of the Feshbach state is below all vibrational levels of the neutral parents. From an excited level the Feshbach state can autoionize either by a two-electron process to the dissociative $2pE'$ ground state or by a one-electron jump and a simultaneous change of the vibrational state to a bound Rydberg state (plus a free electron).

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‡ Large scale CI calculations yielded -1.47854 a.u. as a preliminary upper limit for the exact electronic energy of the $2pA_2''$ state at this point.

A second series of calculations has been carried out using the Configuration Interaction (CI) method. In CI the Feshbach configuration is mixed with scattering configurations $(1sa_1')^2(2pe')(ce'')$ where ce'' represents a continuum orbital. Because of the finite basis sets used the scattering solutions appear as single electronic states and the Feshbach state is somewhat shifted up or down depending on the energy distance to the next scattering state, in this way simulating the energy broadening of the resonance with limited lifetime. However we obtain with CI essentially the same potential as with CEPA. With CI we could extend the potential to linear nuclear geometries where it was difficult to obtain HF reference wave functions for the CEPA calculations.

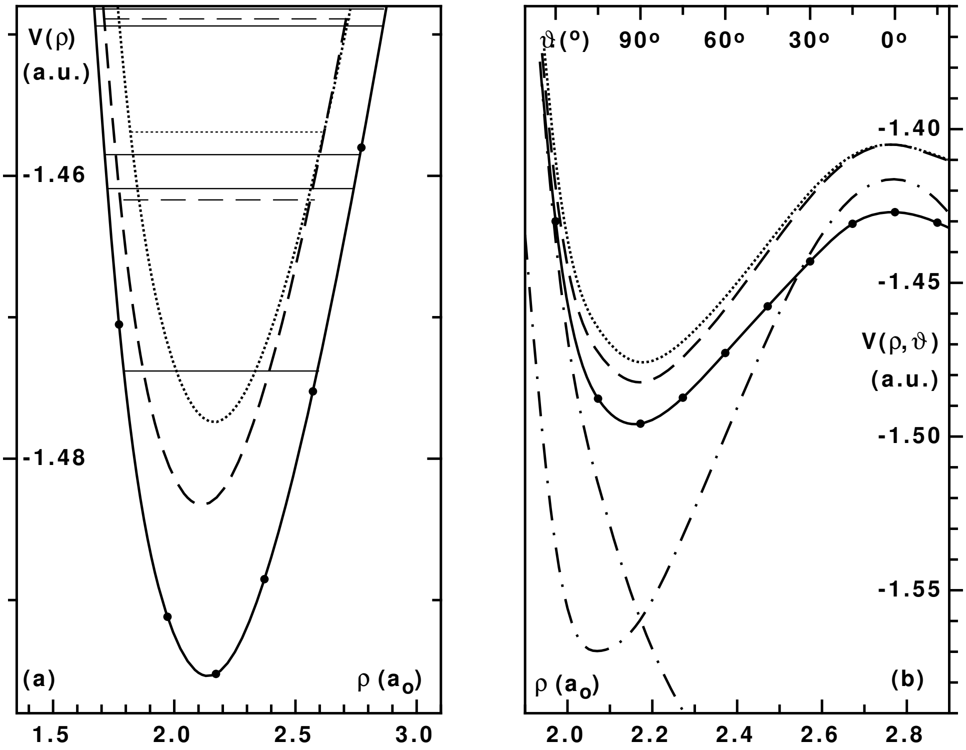

Figure 1. Cuts through the potential energy surfaces using hyperspherical coordinates (see text). $^3A_2''$ ($^3B_1$ in C_{2v} symmetry, solid lines with dots indicating grid points), $^2A_1'$ ($^2A_1$, dashed), $^2A_2''$ ($^2B_1$, dotted), components of $^2E'$ ($^2A_1$ and $^2B_2$, dash-dotted).
(a) CEPA results for D_{3h} symmetry ($\vartheta = 90°$, $r_{HH} = 3^{-1/4}\rho$) and vibrational levels up to -1.45 a.u.
(b) CI potentials. A linear cut varying simultaneously ϑ and ρ is shown (upper and lower coordinate axis; linear structure for $\vartheta = 0°$).

Fig. 1b shows a cut in C_{2v} symmetry connecting the absolute minimum of the Feshbach potential surface with a linear saddle-point for $r_{HH} = 1.49\ a_o$, maximum with respect to ϑ and minimum along the hyperradius ρ. Near this point the Feshbach state penetrates the upper $^2A_1$ ground state surface of neutral H_3, but can still autoionize by a two-electron process into the continuum associated with the lower $^2B_2$ state. This is a region where the $2pa_1$ and $2sa_1$ orbitals of neutral H_3 exchange their angular momentum (see Ref. [5]).

Thus the Feshbach surface stays below the potential of the neutral molecule carrying the $\ell = 0$ orbital character. In linear arrangement the Feshbach state has $(1s\sigma_g)^2(2s\sigma_g)(2p\pi_u)$: ${}^3\Pi_u$ configuration with two degenerate components, the ${}^2A_1$ is its parent $(1s\sigma_g)^2(2s\sigma_g)$: ${}^2\Sigma_g^+$ and the neutral Rydberg states become the components of $(1s\sigma_g)^2(2p\pi_u)$: ${}^2\Pi_u$.

The properties of the wave functions near this saddle-point are fascinating for theory, but probably not very relevant for the observation of the Feshbach resonance.

As the Feshbach potential is everywhere higher than -1.5 a.u. and because the outmost electron occupies a a_2'' orbital, the most probable fate of a H_3^- compound is dissociation to three H atoms and a free electron. We estimate the lifetime of the resonance from the coupling strength of the electronic wave function at equilibrium geometry with the dissociation continuum.

In D_{3h} symmetry the matrix element H_{FC} of the Hamiltonian connecting the Feshbach configuration and a scattering solution reads (using real e orbitals and the conventional quantum chemical notation for electron interaction integrals):

$$\begin{aligned} H_{Feshbach-Continuum} = {} & [(2pe_x' 2sa_1' | 2pa_2'' ce_x'') - (ce_x'' 2sa_1' | 2pa_2'' 2pe_x') \\ & + (2pe_y' 2sa_1' | 2pa_2'' ce_y'') - (ce_y'' 2sa_1' | 2pa_2'' 2pe_y')]/\sqrt{2} \end{aligned}$$

Each integral in this expression contains one continuum orbital and three square-integrable bound state orbitals. Therefore all integrands are confined to the inner region where the bound state orbitals differ essentially from zero and the integrals can be evaluated with quantum chemical methods, provided the continuum orbital can correctly be represented in this inner region without artifacts caused by the finite basis. To this end the system is placed into a spherical "Artificial Well Potential" (AWP) with radius r_o as defined by Guérout and Jungen [20]. Its size corresponds to the diameter of the bound state wave function; the potential vanishes inside of the sphere and rises outside proportional to $(r - r_0)^8$. The strength is chosen such that one of the low-lying scattering solutions of appropriate symmetry (in the present case a ${}^3A_2''$ solution at -1.5110 a.u.) is pushed up to match the energy of the Feshbach state. In this way we obtain a locally correct scattering wave function (subject to the quality of the Gaussian basis set) in the inner region at the desired energy, which can be used for evaluating the integrals.

With this procedure the matrix element H_{FC} becomes half the splitting of the Feshbach configuration interacting with a resonant scattering state. The splitting is interpreted as the energy width Γ of the Feshbach state due to its finite lifetime and is connected with the lifetime by the Heisenberg uncertainty principle.

Using a radius $r_0 = 6a_0$ for the inner region and a potential strength of $2.9 \cdot 10^{-9}$ a.u. we find $\mid H_{FC} \mid = 0.0025$ a.u., corresponding to a lifetime of 400 a.u. or 10^{-14} s. This lifetime is very close to the period of vibration of H_3^- as estimated from the data in Table 1. Therefore the Feshbach compound may survive a few oscillations before autoionization and be observable.

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