

XUV-multiple resonance excitation of long-range states in molecular hydrogen

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1. Introduction

The binding of atoms in diatomic molecules usually leads to configurations where the internuclear separation nearly equals the sum of the atomic radii. Avoided crossings between diabatic states with the same reflection and inversion symmetry, multiplicity and orbital angular momentum can give rise to double-well structures in the corresponding adiabatic representation. This is the case in the hydrogen molecule, where apart from the celebrated examples of the $EF^1\Sigma_g^+$ and the $GK^1\Sigma_g^+$ states, some double-well structures were predicted but until recently not observed. Now that tunable narrowband XUV-lasers have become mature, they can be implemented in multiple resonance experiments. This allows for bridging the energy gap between the electronic ground state of the H_2 molecule and the first excited singlet states (12 eV), while the internuclear distance can be increased stepwise in subsequent optical transitions making use of wave-function density (Franck-Condon overlap) at the inner and outer classical turning points of intermediate states.

This approach was used to probe, for the first time, a double-well state (referred to as $HH^1\Sigma_g^+$) with bound levels above the ionization potential, for which autoionization is dynamically inhibited due to a barrier at intermediate internuclear distance [1]. For the HD isotopomer a particular case of breaking of the inversion symmetry was found in this state [2]; this also influences the tunneling dynamics. Below the ($n=2$) dissociation limit there exists another outer well state confined to large internuclear separation by a potential barrier. Quantum states pertaining to this state of $^1\Pi_g$ symmetry were observed for the first time, as well as some states pertaining to the $EF^1\Sigma_g^+$ and $GK^1\Sigma_g^+$ states just below the ($n=2$) limit. The results are discussed in the LeRoy and Bernstein's formalism to represent progressions of vibrational quantum states near a dissociation limit. Also the breakdown of this model very close to the limit is discussed, where singlet-triplet interactions as well as u-g symmetry mixing becomes important.

Before going into the details on the observations in the H_2 -spectrum and the comparison with state-of-the-art theoretical calculations some remarks will be made in the next paragraph concerning the current status of tests of theoretical models in the atomic two-electron system, the He atom. The opportunity is taken to use these Proceedings to confront the previously determined experimental values with new calculations of the Lamb shift in He.

2. Retrospective on the Lamb shift measurement in the He ground state

In a series of experiments of increasing accuracy the narrowband XUV-laser source in our laboratory was employed to determine the transition frequency of the first resonance line in He, the $1^1S - 2^1P$ transition at 58 nm. A full account of the experimental methods and the resulting value for the transition frequency, as well as the ^3He - ^4He isotope shift, are given in ref. [3]. Although the energy levels in He cannot be calculated analytically, variational calculations have reached 18-digit accuracy for the non-relativistic energies including the lowest order relativistic corrections. Hence QED-effects, including 2-electron contributions specific to He and also including higher order relativistic corrections, can be determined from a straightforward comparison with the observed transition frequency. At the time of our measurements, performed with an accuracy of 45 MHz (1σ) in the absolute frequency, theory predicted a value with a stated uncertainty of 35 MHz in excellent agreement with experiment. In Fig. 1 one of the final spectral recordings of this first resonance line is presented; some numerical details are given in the caption.

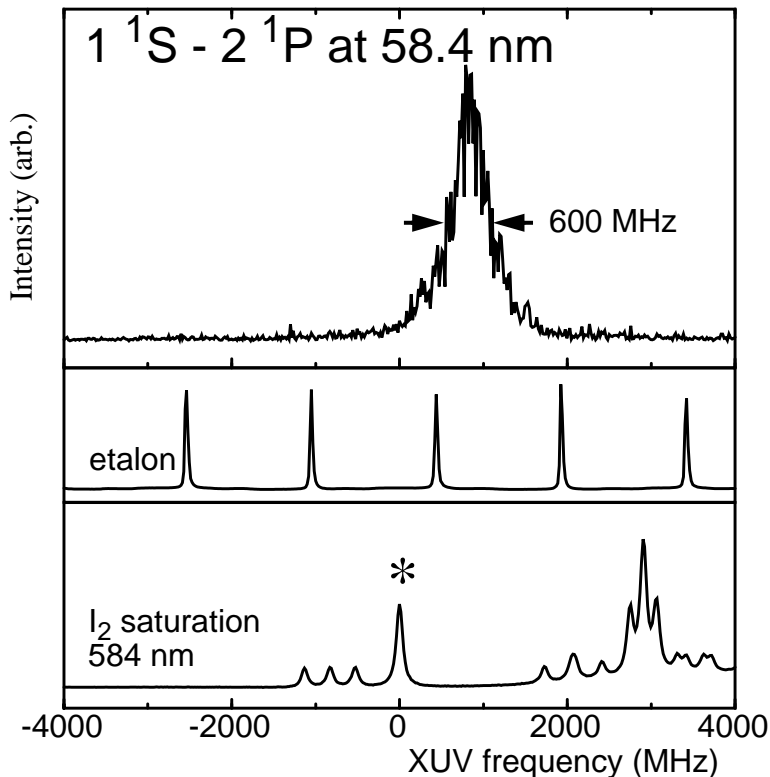


Fig. 1: Recording of the $1^1S - 2^1P$ transition in helium excited with a narrowband tunable XUV-laser. The bandwidth of the XUV source is estimated to be 300 MHz at 58 nm. From comparison with an etalon spectrum as well as a saturated absorption spectrum in I_2 and accounting for systematic effects in the measurements (Doppler shift, AC-Stark effect and frequency chirp) we determined a value of 5130495083 (45) MHz for the transition frequency and of 41224 (45) MHz for the Lamb shift.

The ground state Lamb shift in He was also addressed in a measurement of the $1^1S - 2^1S$ two-photon transition with slightly lower accuracy [4]. Several other experiments were performed using the metastable $1s2s\ ^1S_0$ and 3S_1 states as lower state for an optical transition; since in these experiments cw-lasers can be used typical uncertainties of 0.1 MHz are achieved. All these studies were considered tests

of QED in a low-energy two-electron system. In a recent paper by Drake and Martin [5] a re-evaluation of the status of the theory was given. Some results are reproduced here for convenience. In Table 1 calculated QED-shifts of the lowest S-states are listed.

Quantity	$1s^2\ ^1S$	$1s2s\ ^1S$	$1s2s\ ^3S$
$\alpha^3 Z^4$	-44 702.3	-3356.136	-4265.602
Bethe log corr.	-6.7	269.244	229.394
$\alpha^4 Z^5$	-771.1	-51.995	-67.634
$\alpha^5 Z^6 \ln^2(\alpha)$	83.6	5.639	7.335
$\alpha^5 Z^6 \ln(\alpha)$	-52(52)	-4.9(4.9)	-6.0(6.0)
$\alpha^5 Z^6$	37	2.5	3.3
2-loop	-6.9	-0.464	-0.603
2-loop binding	3.9	0.266	0.346
Finite mass	4.1	0.145	0.215
Subtotal: $\Delta E_{L,1}$	-45 410(52)	-3 135.7(4.9)	-4099.2(6.0)
α^3 : $\Delta E_{L,2}$	4208.1	330.359	36.883
$\alpha^4 \ln(\alpha)$: $\Delta E'_{L,2}$	-30.7	-2.494	0
α^4 : relativistic	0(75)	0(25)	0(25)
Subtotal	4177(75)	328(25)	36(25)
Total	-41 232(91)	-2807(25)	-4062(25)

Table 1:

Calculated QED-shifts for several S-states of the He atom reproduced from ref. [5]. All values in MHz. Note that the largest uncertainty is in the relativistic α^4 term for all three states.

The dominant contribution to the uncertainty is in a term scaling as α^4 , mainly due to uncertainties in the calculation of higher order relativistic effects. This α^4 -term is not yet numerically evaluated for either state and the value itself is set to 0. For the 2^1P state the uncertainty due to this term is estimated to be about 9 MHz, which again implies that it is the dominant contribution. The same holds for the two metastable $1s2s$ states, where the uncertainty in this term is 25 MHz.

In Table 2 values for QED-effects obtained from theory and experiment are compared. For all transitions shown, and also for additional transitions discussed in ref. [5], the uncertainty in the theory is now much larger than in experiments. This situation is unsatisfactory, particularly since the experiments are considered to be stringent tests of QED. The major cause of uncertainty stems from a term that is not in itself a Lamb shift effect. It is remarkable that for nearly all transitions the comparison between theory and experiment yields much better agreement than the estimated uncertainty in the theoretical calculation.

Level	Ionization energy		E-C
	Experiment (E)	Calculation (C)	
1^1S_0	5 945 204 238(45) ^a	5 945 204 226(91)	12(102)
	5 945 204 356(48) ^b		130(103)
2^3S_1	1 152 842 742.87(6) ^c	1 152 842 737.8(25.2)	5.1(25.2)
2^1S_0	960 332 041.01(15) ^c	960 332 039.9(25.0)	1.1(25.0)
2^3P_2	876 110 556.36(9) ^c	876 110 565.2(3.8)	-8.8(3.8)
3P_1	876 108 265.19(9) ^c	876 108 272.2(17.1)	-7.0(17.1)
3P_0	876 078 648.23(9) ^c	876 078 649.0(24.7)	-0.8(24.7)

Table 2: Comparison of experimental and calculated ionization energies for 1S, 2S and 2P levels reproduced from ref. [5]. Note that the uncertainty in the calculations is much larger than the experimental uncertainties.

3. Observation of the $H\bar{H}^1\Sigma_g^+$ long range state

Present day laser technology permits to combine a tunable narrowband source of extreme ultraviolet (XUV) radiation, based on Q-switched solid state laser sources pumping pulsed dye lasers and the techniques of harmonic generation in gas jets, with additional lasers in XUV-double resonance experiments. In Fig. 2 the excitation scheme is shown to study the hitherto unobserved fourth adiabatic state of $^1\Sigma_g^+$ symmetry in molecular hydrogen, referred to as $H\bar{H}^1\Sigma_g^+$.

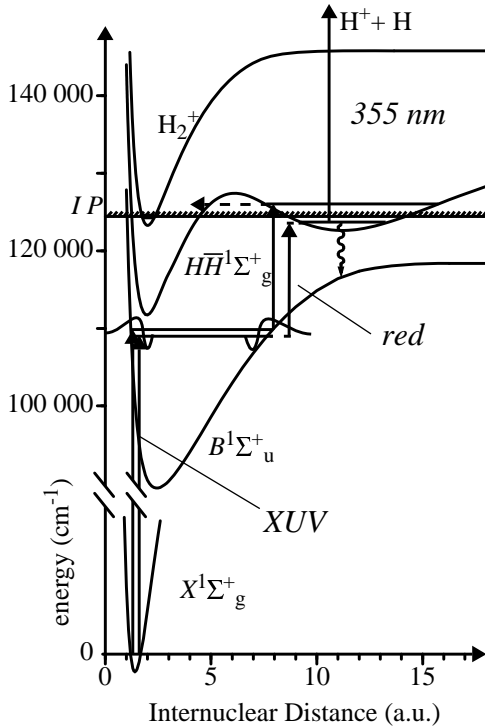


Fig. 2: Scheme showing the two-photon excitation toward the outer-well part of the $H\bar{H}^1\Sigma_g^+$ state. The tunable XUV and red lasers are spatially and temporally overlapped in the interaction region. A third laser at 355 nm is used to probe the \bar{H} -state population; if this laser is delayed in time exponential decay corresponding to the lifetime can be observed. For the study of HD the same scheme is used to also excite the $B''\bar{B}$ state of $^1\Sigma_u^+$ symmetry, which is forbidden in the homonuclear H_2 and D_2 isotopomers. IP is ionization potential.

For various intermediate states, populated with the tunable XUV-laser, double resonance spectra were recorded. While simultaneously scanning the second laser an I₂-calibration spectrum was recorded for frequency calibration, thus yielding level positions with an accuracy of 0.03 cm⁻¹ for $\bar{H}(v,J)$ -levels. Regular spectra were obtained with vibrational progressions of doublets, as to be expected in $^1\Sigma_g^+ - ^1\Sigma_u^+$ transitions. The spectroscopic analysis of the data shows that the outer-well part of the $H\bar{H}$ -potential can be considered as an isolated state that can be treated as a rigid rotor, with only minute centrifugal distortion [1]. Only in a single case in H₂ (none in D₂) small frequency shifts in the form of an avoided crossing were observed; this may be interpreted in terms of an interaction with states of Rydberg type at small internuclear distance. The Rydberg states in this energy region are not yet documented.

Interesting intramolecular dynamics occurs for the levels in the outer well that energetically lie above the ionization potential. In first order the behaviour can be described as non-resonant tunneling through the potential barrier; this process is indicated in Fig. 2 by a dashed arrow. Semiclassical tunneling rates are then given by $\Gamma_v = f_v p(E_v)$ with f_v the classical vibration frequency of the $\bar{H}(v)$ level and $p(E_v)$ the permeability of the potential barrier in the WKB approximation given by:

$$p(E_v) = \exp\left(-2 \int \sqrt{\frac{8\pi^2\mu}{h^2} [V(R) - E]} dR\right)$$

Here $V(R)$ represents the adiabatic potential. An analysis based on this relation shows that the tunneling rate increases by an order of magnitude for each increase of the vibrational quantum number. Although in H₂ the $v=5$ level already lies above the IP the tunneling rate of the $v=10$ level is only 5×10^6 Hz; this value is still smaller than the rate of fluorescence decay. At $v=11$ in H₂ the tunneling becomes significant; for $v < 11$ autoionization is effectively prohibited by the barrier. For the higher v -states ($v=14$ and $v=15$) line broadening can be observed at values that are in reasonable agreement with predictions. However deviations do occur; for different rotational levels a certain spread is observed in the autoionization rate. This may be ascribed to the influence of states localized in the inner region, but not enough is known yet about this region to perform a quantitative analysis.

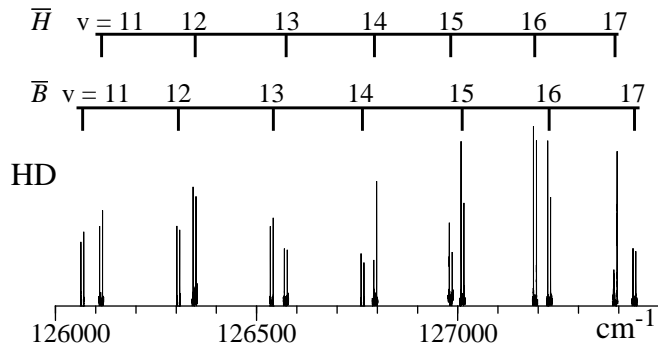


Fig. 3:

Recorded XUV-vis double resonance spectra of the $H\bar{H}$ -state in HD. The phenomenon of $u-g$ symmetry breaking is directly observable in the spectrum; the forbidden transitions to states of u -symmetry are equally strong as the allowed ones.

A remarkable effect of complete breaking of the u-g inversion symmetry was observed in the $\overline{H}\overline{H}$ -state of the HD-isotopomer [2]. The interaction between the \overline{H} outer-well state and another double-well state, usually referred to as $B''\overline{B}^1\Sigma_u^+$, is so strong that an additional vibrational progression of equally intense doublets could be observed, as shown in Fig. 3. For the homonuclear molecules H_2 and D_2 the $B''\overline{B}^1\Sigma_u^+$ state, that was predicted by Kolos in ab initio calculation [6], has never been observed. Based on the accurate spectroscopic analysis of the data for H_2 and D_2 a set of Dunham coefficients was derived from which a prediction was made for the unperturbed level energies $\overline{H}(v,J)$ for HD; it is noted that a mass-dependent adiabatic shift in the potential for each isotopomer was included. By comparing with observed level energies a strong perturbation in the form of an anti-crossing was found near $v=14$ in the \overline{H} -state of HD. The ordering of vibrational levels in both \overline{H} and \overline{B} outer-well potentials (see Fig. 4) is such that the vibrational ladders cross at $v=14$; this can also be observed in the spectra. All perturbations could be modelled by assuming an interaction matrix element of $W_{gu} = 14.1 \text{ cm}^{-1}$ between levels with $v_{\overline{H}} = v_{\overline{B}}$ [2]. The present perturbation is a textbook example of the influence of the symmetry-breaking mass-dependent term in the molecular Hamiltonian:

$$H_{gu} = \left(\frac{h}{2\pi}\right)^2 \frac{M_1 - M_2}{2M_1M_2} \nabla_{R\theta\phi} \sum_j \nabla_j$$

where M_i represent the atomic masses and j summation over all electronic coordinates.

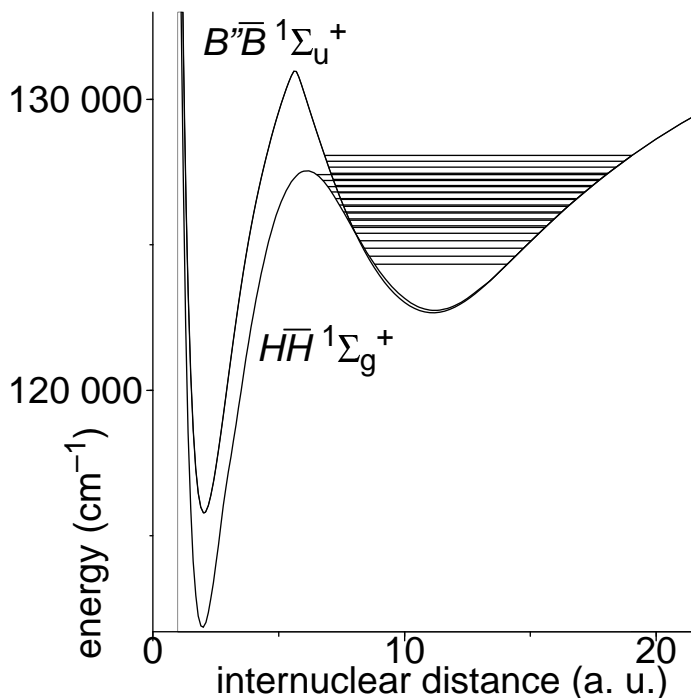


Fig. 4

Potential energy curves of the $\overline{H}\overline{H}^1\Sigma_{(g)}^+$ and $B''\overline{B}^1\Sigma_{(u)}^+$ states, including the mass-dependent adiabatic shifts for HD. Some of the bound levels are depicted as well. The minimum of the $B''\overline{B}$ state is slightly lower, while its potential barrier is higher. As a consequence the vibrational ladders cross.

4. The $I^1\Pi_g$ state and the region near the $n=2$ limit

A second example of a long-range state hidden behind a barrier is that of the $I^1\Pi_g$ state, where the I refers to the outer-well part. This state has a maximum binding energy of only 200 cm^{-1} at $R \sim 8\text{ a.u.}$ The XUV-vis double resonance scheme, with a third laser (355 nm) for probing the excited state population, was again employed to investigate the bound energy levels in this shallow well for H_2 and D_2 [7]. An overview scan in Fig. 5, not at the highest resolution, shows the $v=0-2$ vibrational progression with some additional features and the onset of the dissociation continuum. The third laser promotes the $I'(v,J)$ levels into the dissociative ionization continuum, while the ($n=2$) dissociation fragments are also ionized by this laser; in both cases H^+ -signal is produced and detected with a time-of-flight mass filter.

For the H_2 -isotopomer only $v=0-2$ levels were observed and some perturbed features that might be associated with $v=3$. In D_2 a regular progression $v=0-5$ was observed. The present experiments yield an onset of dissociation (for H_2) at $118377.2(0.1)\text{ cm}^{-1}$, in reasonable agreement with previous studies [8].

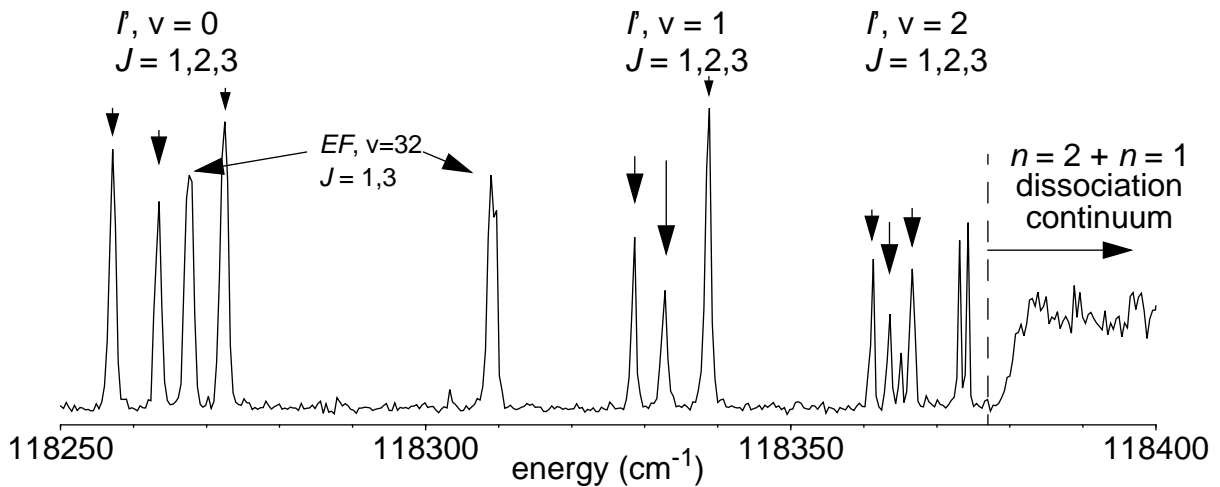


Fig. 5: XUV+IR double resonance spectrum with the XUV laser tuned to the $B^1\Sigma_u^+$, $v=16$, $J=2$ intermediate state.

An interesting question is how many bound quantum levels are supported by the shallow potential. An estimate can be obtained following the method of LeRoy and Bernstein [9]; only the long-range behaviour of the potential curve is needed as an input to extrapolate from the known vibrational structure. The I state correlates with $1s + 2p\pi$ atomic states and approaches the dissociation limit as $V(R)=-C_3R^{-3}$, with $C_3 = 0.554929$ [10]. LeRoy and Bernstein showed that subsequent vibrational levels v have binding energies ϵ_v according to:

$$\approx \epsilon_v^{(n-2)/(2n)} \quad a_n = \frac{2\sqrt{\pi}\Gamma(1/2 + 1/n)\sqrt{2\mu}}{n-2\Gamma(1 + 1/n)} \frac{1}{h} C_n^{1/n}$$

In case of the Γ state $n=3$; v_D is the effective quantum number at threshold. The result of this analysis is shown in Fig. 6 where the data for H_2 and D_2 are included (via scaling with the reduced mass μ).

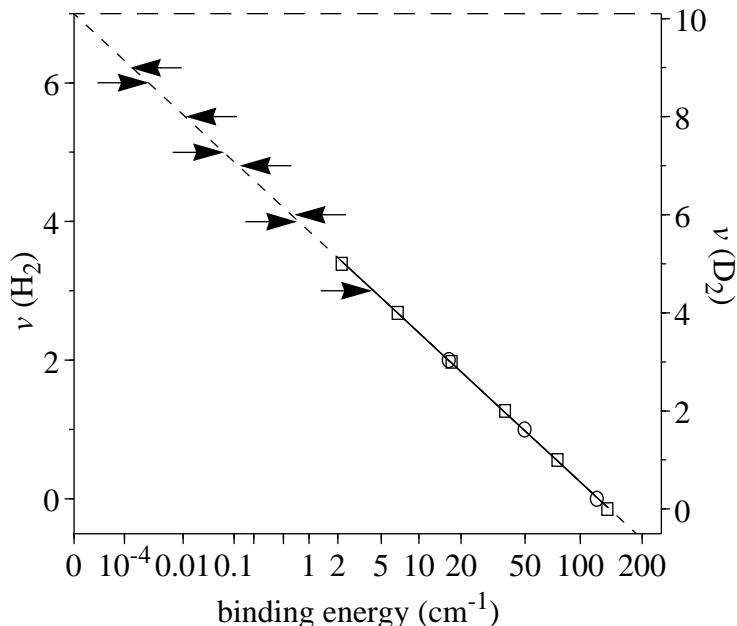


Fig. 6:

Plot of the vibrational quantum number v of Γ levels in H_2 (circles) and D_2 (squares) as a function of the binding energy on an $\epsilon^{1/6}$ scale. Arrows indicate the positions of predicted but unobserved levels. Note that the points for both isotopes fall on the predicted line without further assumptions. In D_2 a $v=9$ level is predicted and in H_2 up to $v=6$.

In an entirely different experiment, via photo-association of cold H-atoms, bound states of triplet character were found recently [11]. A sequence of three vibrational levels, was analysed within the same framework of LeRoy and Bernstein and assigned to the $a^3\Sigma_g^+$ state of H_2 . Similar photoassociation studies with two-photon excitation, for which the equipment is now available at MIT [12] could reveal details on the long-range bound states of triplet-ungerade symmetry.

The energy region near the $H(n=1)+H(n=2)$ dissociation limit is particularly interesting, also in view of the detection of the Bose-condensate of hydrogen [12]; this condensate was detected via a molecular-like collective feature just below the ($n=2$) dissociation limit. Twelve different molecular states converge to this limit, 6 singlets and 6 triplets, 6 of which have gerade symmetry and 6 ungerade; some states converge with positive and some with negative energy. In the molecular language they are: $EF^1\Sigma_g^+$ (a), $GK^1\Sigma_g^+$ (r), $\Pi^1\Pi_g$ (a), $B'^1\Sigma_u^+$ (a), $B^1\Sigma_u^+$ (a), $C^1\Pi_u$ (r), $a^3\Sigma_g^+$ (a), $c^3\Pi_u$ (a), $h^3\Sigma_g^+$ (r), $e^3\Sigma_u^+$ (a), $i^3\Pi_g$ (r), $m^3\Sigma_u^+$ (r), where (a) and (r) indicate whether the potential is attractive or repulsive at large internuclear separation.

Very close to the dissociation limit the molecular spectroscopy becomes complicated due to two symmetry-breaking effects. In the last 0.3 cm^{-1} singlet-triplet mixing occurs, while even closer to the limit u - g symmetry-breaking, induced by the nuclear spins, sets in. In our studies we have found indications of these effects in the Γ state close to threshold, where the $v=3$ level of H_2 was perturbed. In the work of the Eyler group [13] similar perturbations were found in states of singlet-ungerade symmetry. It remains a challenge for future research to unravel the behaviour of the hydrogen molecule near the ($n=2$) dissociation limit.

5. H₂: a test of theoretical calculations on the simplest molecular system

H₂ has a role in molecular physics similar to the one of H in atomic physics. It is the lightest neutral molecule and a test ground for detailed comparisons between *ab initio* theoretical calculations and experiment. A complication is that the approximation, usually made in molecular theory, the Born-Oppenheimer (BO) approximation separating the nuclear and electronic motion, is the least valid in light systems. The procedure to calculate level energies starts with a determination of a BO-potential and BO-wave functions. In perturbation theory on a BO-basis, using the non-BO terms in the Hamiltonian, the diagonal terms can be used to modify the potentials; this gives rise to mass-dependent adiabatic potentials. Non-adiabatic effects can be calculated separately [14]. The accuracy claimed for calculations of level energies in the electronic ground state, with respect to ionization and dissociation limits is 0.01 cm⁻¹ [14].

The new and large set of level energies on the H $\bar{H}^1\Sigma_g^+$ state (82 for H₂ and 107 for D₂) allows for a comparison with renewed state-of-the-art *ab initio* calculations for higher lying states. With inclusion of adiabatic and relativistic effects the agreement is on the order of 1 cm⁻¹ for H₂ and 0.5 cm⁻¹ for D₂ [15]. For HD calculations were performed with inclusion of the u-g symmetry-breaking non-adiabatic term coupling the H $\bar{H}^1\Sigma^+$ to B $\bar{B}^1\Sigma^+$ states, resulting in agreement within 1.5 cm⁻¹, except for some levels close to the tunneling barrier.

At increasing energies in the molecule accurate calculation of energy levels becomes increasingly difficult. For the quantum states at short internuclear distance, strong coupling to the dissociation and ionization continua broaden the resonances into diffuse structures, so that level energies cannot be determined with high precision. Perhaps some additional outer-well states will exist, due to curve crossings with the ion-pair state, near the n=3 and n=4 limits. Recent *ab initio* calculations [16] indicate such behaviour. Such states could then be probed experimentally, using the recently observed outer-well states H $\bar{H}^1\Sigma_g^+$ and II $^1\Pi_g$.

References

- [1] E. Reinhold, W. Hogervorst, W. Ubachs, Phys. Rev. Lett. 78 (1997) 2543
- [2] E. Reinhold, W. Hogervorst, W. Ubachs, Chem. Phys. Lett. 296 (1998) 411
- [3] K.S.E. Eikema, W. Ubachs, W. Vassen, W. Hogervorst, Phys. Rev. A49 (1997) 1866
- [4] S.D. Bergeson, A. Balakrishnan, K.G.H. Baldwin, T.B. Lucatorto, J.P. Marangos, T.J., McIllrath, T.R. O'Brian, S.L. Rolston, C.J. Sansonetti, J. Wen, N. Westbrook, C.H. Cheng, E.E. Eyler, Phys. Rev. Lett. 80 (1998) 3475
- [5] G.W.F. Drake, W.C. Martin, Can. J. Phys. 76 (1998) 679
- [6] W. Kolos, J. Mol. Spectr. 62 (1976) 429
- [7] E. Reinhold, A. de Lange, W. Hogervorst, W. Ubachs, J. Chem. Phys. 109 (1998) 9772
- [8] A. Balakrishnan, V. Smith, B.P. Stoicheff, Phys. Rev. A49 (1994) 2460

- [9] R.J. LeRoy, R.B. Bernstein, *J. Chem. Phys.* 52 (1970) 3869
- [10] T.L. Stephens, A. Dalgarno, *Mol. Phys.* 28 (1974) 1049
- [11] A.P. Mosk, M.W. Reynolds, T.W. Hijmans, J.T.M. Walraven, *Phys. Rev. Lett.* 82 (1999) 307
- [12] D.G. Fried, T.C. Killian, L. Willmann, D. Landhuis, S.C. Moss, D. Kleppner, T.J. Greytak, *Phys. Rev. Lett.* 81 (1998) 3811
- [13] E.F. McCormack, E.E. Eyler, *Phys. Rev. Lett.* 66 (1991) 1042
- [14] L. Wolniewicz, *J. Chem. Phys.* 78 (1983) 6173; *ibid.* 103 (1995) 1792
- [15] E. Reinhold, W. Hogervorst, W. Ubachs, L. Wolniewicz, *Phys. Rev. A* (1999) July issue
- [16] T. Detmer, P. Schmelcher, L.S. Cederbaum, *J. Chem. Phys.* 109 (1998) 9694