Precision spectroscopy of the $X^1\Sigma_g^+$, $v=0 \to 1(J=0-2)$ rovibrational splittings in H₂, HD and D₂

M.L. Niu [a], E.J. Salumbides [a,b], G.D. Dickenson [a,1], K.S.E. Eikema [a], W. Ubachs [a,*]

[a] Department of Physics and Astronomy, LaserLaB, VU University, de Boelelaan 1081, 1081HV Amsterdam, The Netherlands
[b] Department of Physics, University of San Carlos, Cebu City 6000, Philippines

ABSTRACT

Accurate experimental values for the vibrational ground tone or fundamental vibrational energy splitting of H₂, HD, and D₂ are presented. Absolute accuracies of 2×10^{-4} cm^{-1} are obtained from Doppler-free laser spectroscopy applied in a collisionless environment. The vibrational splitting frequencies are derived from the combination difference between separate electronic excitations from the $X^1\Sigma_g^+$, $v=0$, J and $v=1$, J vibrational states to a common $EF^1\Sigma_g^+$, $v=0$, J state. The present work on rotational quantum states $J=1,2$ extends the results reported by Dickenson et al. on $J=0$ [Phys. Rev. Lett. 110 (2013) 193601]. The experimental procedures leading to this high accuracy are discussed in detail. A comparison is made with full *ab initio* calculations encompassing Born–Oppenheimer energies, adiabatic and non-adiabatic corrections, as well as relativistic corrections and QED-contributions. The present agreement between the experimental results and the calculations provides a stringent test on the application of quantum electrodynamics in molecules. Furthermore, the combined experimental–theoretical uncertainty can be interpreted to provide bounds to new interactions beyond the Standard Model of Physics or *fifth forces* between hadrons.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

The first modern explanation of the chemical bond between two neutral hydrogen atoms was put forth in 1927 by Heitler and London [1], and is one of the earliest applications of quantum theory, specifically that of Schrödinger's wave mechanics formulation in 1926 [2]. Heitler and London showed that by accounting for Pauli's exclusion principle [3] in combining atomic hydrogen wavefunctions to construct molecular wavefunctions, the existence of a bound molecular state is explained. Despite their calculated binding energy being off by some 30% from the contemporary experimental value, their pioneering quantum mechanical calculation for the stability of molecular hydrogen ushered the era of quantum chemistry. It is interesting to note that the Born–Oppenheimer approximation [4] was also proposed in 1927, and this approach of separating electronic and nuclear motions has largely shaped molecular theory since. The next breakthrough in *ab initio* potential calculations for H₂ was achieved by James and Coolidge in 1933 in their treatment of the $\left(X^1\Sigma_g^+\right)$ ground state [5]. Using two-electron wave functions with explicitly correlated electrons, an approach introduced by Hylleraas for the helium atom [6], they transcended the concept of electrons being in individual states as used in the Hartree–Fock method. The James-Coolidge solution relied on the variational method to determine the correct nonlinear parameters in combining the wave functions. With a set of only 13 of these wave functions, taken as a truncated basis to represent the total Hilbert space of infinite dimension, they improved the minimum energy in the Born–Oppenheimer potential of the $X^1\Sigma_g^+$ state to 38 300 cm^{-1}. This was a substantial improvement of about 5500 cm^{-1} with respect to the best theoretical values available at the time. Over the years improvements on the accuracy has been obtained [7–12], and important methodical reviews can be found in Refs. [13–17]. The achievement of the initial studies of James and Coolidge [5] can best be appreciated considering that further improvement in the calculated potential has been only 222 cm^{-1} since then, obtained by Wolniewicz in 1995 with essentially the same method but with a basis of 883 wave functions [18]. At present, the Born–Oppenheimer potential energy can be evaluated to accuracies better than 15 digits using more than 22 000 basis functions [19], made possible by developments in numerical procedures and improvements in computing power.

The precision of the calculated Born–Oppenheimer energy may be considered exact for the purpose of comparisons with

experiment. Corrections beyond the Born–Oppenheimer approximation need to be evaluated to improve upon the accuracy of the *ab initio* values. In addition to adiabatic and nonadiabatic effects comprising the non-relativistic Born–Oppenheimer corrections, it is also necessary to account for accurate relativistic and radiative or quantum electrodynamic (QED) corrections. Until up to 2010, the work of Wolniewicz [18] that included estimates of radiative corrections, had constituted the state-of-the-art for calculations of level energies in the $X^1\Sigma_g^+$ ground state of molecular hydrogen. This led to a calculated energy of the actual ground state (or equivalently the dissociation limit) to an accuracy 0.01 cm^{-1}. The recent work of Pachucki, Komasa and co-workers has achieved breakthroughs in the evaluation of nonadiabatic effects [20,21] as well as relativistic and radiative corrections [22,23], resulting in accurate level energies of $X^1\Sigma_g^+$ rovibrational levels [24–26]. In Fig. 1 the different contributions to the level energy of the lowest quantum state $\left(X^1\Sigma_g^+, v = 0, J = 0 \right)$ with respect to the dissociation energy of molecular hydrogen are represented graphically to give an impression of the scale of the corrections.

Theoretical and experimental efforts on the determination of ground state level energies in molecular hydrogen mutually stimulated improvements on both fronts as soon as more accurate values were obtained. As an illustration, consider the dissociation energy of the $X^1\Sigma_g^+$ ground state, a benchmark quantity for the comparison of experiment and theory. The experimental determination of the dissociation energy by Witmer [27] in 1926 already gave results within 3% of the modern value, an order of magnitude better than the Heitler–London calculations as mentioned. The James–Coolidge calculations in 1933 [5] resulted in a dissociation energy that is within 10^{-4} of the present value, matched later by the experimental determination by Beutler in 1935 [28] that was also accurate to within 10^{-4}. This lively dynamics continued through the 1960s–1970s, between the experimental efforts of Herzberg and co-workers [29–31] and theoretical efforts by Kołos and co-workers [9,11]. In the middle of the 1990s, the theoretical result of Wolniewicz [18] for the dissociation energy was expressed in 8 significant digits, although the uncertainty was not explicitly mentioned. Eyler and co-workers determined the dissociation limit to an accuracy of 0.01 cm^{-1} [32] in 2004, improving upon their previous result [33] using the same method. The most

accurate experimental dissociation energy for H_2 was obtained in 2009 by Liu et al. [34], and later extended to D_2 [35] and HD [36]. Remarkably, accurate theoretical values for H_2 and D_2 dissociation energies [24] as well as HD [25] were presented a short time thereafter.

Ab initio theory can also be tested through a comparison with the experimental determinations of level splittings in the rovibrational manifold of the ground state. Herzberg first predicted, in 1938, that it should be possible to record rovibrational transitions in the ground state manifold [37], and later discovered the quadrupole spectrum in 1949 by photographing a total of eight lines in the (2,0) and (3,0) bands [38]. Subsequently the quadrupole spectrum including the fundamental (1,0) band was investigated by several other groups, for example by Rank and co-workers [39,40]. The measurements by Bragg et al. [41] greatly improved the accuracy of the spectroscopy of the quadrupole bands and was until recent years considered as the most accurate work on the direct measurement of the vibrational splittings. Laser-based direct excitation of the weaker (4,0) and (5,0) overtone quadrupole bands was performed in the visible domain [42]. Later investigations using cavity-ring down spectroscopy on the H_2 (3,0) overtone band were carried out by Robie et al. [43] using a pulsed source and Hu et al. [44,45] using a cw source. Campargue and co-workers have recently performed high-resolution determinations of the (2,0) overtone bands of H_2 [46] and D_2 [47] using quantum cascade lasers. Maddaloni et al. [48] performed precision measurements using cavity-ring down techniques for the fundamental band of D_2.

The quadrupole excitations in the ground electronic state described above have very low transition probabilities. The ground state energy splittings can be determined indirectly from appropriate combinations of dipole-allowed transitions between ground state and excited electronic states. For example, the strongest molecular hydrogen transitions in Lyman $\left(B^1\Sigma_u^+ - X \right)$ and Werner $\left(C^1\Pi_u - X \right)$ bands have been used to derive ground state rovibrational constants. Using this approach, Stanke et al. [49] derived accurate ground state molecular constants based largely on the experimental data of Dabrowski [50] but also including quadrupolar transitions. The natural linewidths of transitions in the Lyman and Werner bands ultimately limit the accuracy that can be achieved [51,52].

In contrast, the rovibrational levels of the lowest-lying excited singlet gerade state $EF^1\Sigma_g^+$ of molecular hydrogen have longer natural lifetimes, even up to 150 ns [53], since one-photon transitions to the ground state are forbidden. The gerade states can be accessed from the ground state through two-photon spectroscopies, which also allow for more accurate level energy determinations. This first excited singlet gerade state in molecular hydrogen, the $EF^1\Sigma_g^+$ state, shown to correspond to a double-well potential [54], has been investigated thoroughly over the years. Eyler and coworkers performed a number of laser spectroscopic studies of increasing accuracy [32,55–58]. A determination of frequencies of Q-branch transitions in the lowest $EF^1\Sigma_g^+ - X^1\Sigma_g^+(0,0)$ band was performed with improved accuracy by Hannemann et al. [59]. The lowest rotational levels in the $EF^1\Sigma_g^+$ state derived from the latter study were used as anchor lines, to which a large number of levels in the excited state manifold, obtained from high-resolution Fourier-Transform studies, were connected to the ground state [60,61]. Accurate values for level energies of the high rotational states up to $J = 16$ in the $E^1\Sigma_g^+$, $v = 0$ electronic state were obtained in Ref. [62] using UV two-photon spectroscopy.

In this paper, we present accurate experimental and theoretical values for the fundamental vibrational splitting of H_2, D_2 and HD. This extends a recent report [63] on the *rotionless* ground tone frequencies of hydrogen and its isotopomers, now also including values for $J = 1$ and 2 levels. The experimental determination of
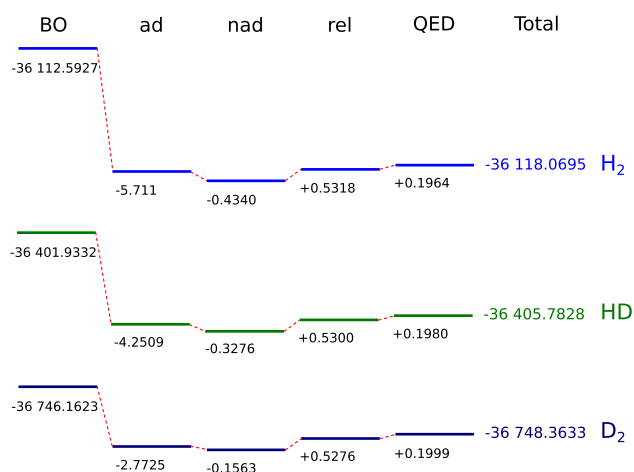

Fig. 1. Graphical representation of the level energy contributions (in cm^{-1}) as corrections to the Born–Oppenheimer approximation level energy, with respect to the dissociation limit, of the $X^1\Sigma_g^+$, $v = 0$, $J = 0$ state for H_2, HD and D_2. BO: Born–Oppenheimer energy; ad: adiabatic; nad: nonadiabatic; rel: relativistic; QED: radiative corrections.