PRECISION MEASUREMENT OF THE IONIZATION AND DISSOCIATION ENERGIES OF H_2, HD AND D_2

DANIEL SPRECHER, JINJUN LIU, and FRÉDÉRIC MERKT, *ETH Zürich, Laboratorium für Physikalische Chemie, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland*; CHRISTIAN JUNGEN, *Laboratoire Aimé Cotton, CNRS II, Bâtiment 505, Campus d'Orsay, 91405 Orsay Cedex, France*; WIM UBACHS, *Laser Centre, Department of Physics and Astronomy, Vrije Universiteit, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands.*

The ionization and dissociation energies of H_2, HD and D_2 are benchmark quantities in molecular quantum mechanics. Comparison between experimental and theoretical values for these quantities has a long history starting with the early measurement of Beutler[a] and the calculations of James and Coolidge.[b] Transition wave numbers from the $EF\,^1\Sigma_g^+$ $(v = 0, N = 0, 1)$ state to selected np Rydberg states $(n \approx 60)$ below the $X^+\,^2\Sigma_u^+$ $(v^+ = 0, N^+ = 0, 1)$ ionization threshold have been measured in H_2,[c] HD and D_2[d] at a precision better than 10 MHz (0.0003 cm^{-1}). Combining the results with previous experimental and theoretical data for other energy level intervals, the ionization and dissociation energies of H_2, HD and D_2 could be determined at an absolute accuracy of better than 20 MHz. These new results represent an improvement over previous experimental results by more than one order of magnitude and the most precise values of dissociation and ionization energies measured to date in a molecular system. The results therefore offer the opportunity of a comparison with theoretical values. In particular they will be compared to the latest *ab initio* calculations[e] which include nonadiabatic, relativistic and radiative effects. The comparison indicates that relativistic and radiative quantum electrodynamics corrections of order up to α^4 are needed to account for the experimental results.

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