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PRECISE MULTIPHOTON SPECTROSCOPY OF H_2

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ABSTRACT

This paper summarizes our recent progress in the determination of absolute energy levels in the H_2 molecule using two- and three-photon excitation. Several vibrational bands of the E,F+X transition have been measured using two-photon excitation near 220 nm, to an accuracy of 0.01 cm^{-1} , an improvement by nearly an order of magnitude. Three-photon transitions to the B($2p\sigma$) and C($2p\pi$) states have been measured to 0.06 cm^{-1} . The three-photon measurements are somewhat less precise because they are affected by shifts arising from the AC Stark effect and from interference between three-photon excitation and third harmonic generation. Finally, transitions have been measured from the E,F state to the dissociation limit yielding $H(1s) + H(2s\text{ or }2p)$, providing a preliminary new value of $36118.1 \pm 0.2\text{ cm}^{-1}$ for the dissociation energy of H_2 .

TWO-PHOTON SPECTROSCOPY OF E,F+X TRANSITIONS

The hydrogen molecule is the only neutral molecule for which theoretical calculations of the dissociation energy and ionization potential have been performed with an accuracy better than 0.1 cm^{-1} . To test these calculations, absolute wavelengths must be measured for transitions from the ground state to the electronically excited states. The lowest excited state accessible using two photons is the E,F $^1\Sigma_g^+$ state, with a total energy of about $99,000\text{ cm}^{-1}$. This state, which has a double-minimum potential curve, is of particular interest because it can be used as a convenient intermediate level for subsequent excitation to higher states.

We have observed transitions to the $v=0$ and $v=1$ levels of the inner E state well using two-photon resonant, three-photon ionization. To accomplish this, a laser system operating near 210 nm was used to excite a beam of vibrationally excited ground state H_2 . The vibrational excitation was created by a discharge between electrodes placed just outside the exit of a pulsed supersonic nozzle. The laser radiation was obtained by frequency doubling the output of a pulse-amplified cw ring dye laser in a crystal of $\beta\text{-BaB}_2\text{O}_4$. Pulses about 10 nsec in duration with energies of 200-500 μJ were obtained, with a bandwidth of 0.005 cm^{-1} . Collimation of the molecular beam reduced the residual Doppler width to about 0.01 cm^{-1} .

The wavelengths of 22 transitions in the (0,1), (0,2) and (1,2) bands were measured to an absolute accuracy of 0.01 cm^{-1} by comparison with the absorption spectrum of a tellurium cell. A complete table of the results appears in Ref. 1. The accuracy was limited principally by nonlinearity in the laser scans. Minor improvements in the apparatus should result in an improvement to about $0.001\text{-}0.002\text{ cm}^{-1}$.

These new measurements of the E,F state are in good agreement with most previous determinations. They disagree slightly with a recent measurement made using a Raman shifted dye laser, but subsequent work indicates

that the Raman shifting process introduces small shifts that probably account for the discrepancy.²

By combining these results with other measurements, a value of $124417.4 \pm 0.15 \text{ cm}^{-1}$ is obtained for the ionization potential of H_2 .¹ This value is in good agreement both with theory and with other recent experiments, and of about the same accuracy. A value accurate to 0.01 cm^{-1} should be attainable in the near future.

THREE-PHOTON SPECTROSCOPY OF B+X AND C+X TRANSITIONS

An alternative arrangement for determining vacuum ultraviolet intervals in H_2 is the measurement of three-photon transitions. Preliminary measurements of transitions to the B and C states were described at this conference a year ago.³ It was clear from this initial work that measurements to an accuracy of 0.05 cm^{-1} or better are feasible, but that at this level the measurements can be affected by line broadening and shifts that depend both on the laser power and the number density in the molecular beam apparatus. During the past year we have confirmed that most of the frequency shift arises from interference between third harmonic generation and three photon excitation. This process has been observed previously, mainly in atomic systems, and a detailed theoretical treatment has recently appeared.⁴

To confirm this explanation we observed the three-photon excitation with a pair of counterpropagating laser beams. Some of the transition amplitude must then arise from the absorption of two photons from one laser beam and of one from the other, a process that cannot be cancelled by third harmonic generation because momentum conservation is impossible. Thus a large enhancement in the signal size is expected. In the experiment, one of the C+X transitions was studied under conditions such that when only the main beam was present, the line was shifted about 0.2 cm^{-1} to the blue. When the counterpropagating beam was introduced, we observed an enhancement by a factor of 20 of the signal at the unshifted resonance position. We have also observed the dependence of the line shift on number density by varying the voltage that opens the pulsed nozzle.

The obtainable accuracy should be much better for measurements to a level from which single-photon decay is impossible, so that third harmonic generation cannot occur. To investigate this possibility, we are currently undertaking measurements of three photon intervals from the ground state of H_2 to the 4f and 5f Rydberg states.

PHOTODISSOCIATION OF THE E,F STATE

The region near the second dissociation limit of H_2 , to $\text{H}(1s) + \text{H}(2s \text{ or } 2p)$, can be studied with very high resolution by exciting the E,F state and using an additional laser to scan the region near the dissociation threshold. Hydrogen atoms in the 2p state can be detected by their Lyman α fluorescence, and 2s state atoms can be quenched through the 2p state by applying a small electric field. Figure 1 shows preliminary experimental data for this transition, obtained by exciting the $v=2$ level of the E state using an ArF excimer laser at 193 nm, then observing photodissociation produced by a pulse-amplified cw laser operating near 680 nm. Although this data suffers from a very poor signal to noise ratio, the top trace, showing the signal produced by $\text{H}(2s)$ atoms, clearly shows the onset of the threshold at a total

energy of 118377.2 cm^{-1} . The shape of the threshold is easily resolved, but is partially obscured by noise. The bottom trace was taken with much higher laser powers, near 10^6 W/cm^2 , and a different detector arrangement. The signals in this case arise from the absorption of two photons from the E state. The obvious peaks arise from resonances at the one photon level with the highest bound vibrational levels of the B and B' states.

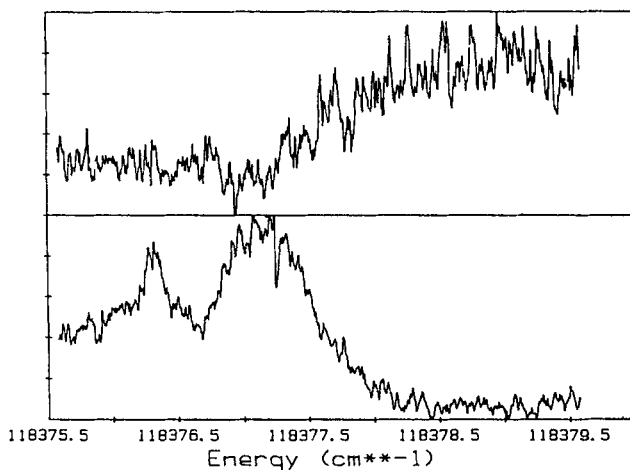


Fig. 1 Top trace: preliminary data showing the $\text{H}(1s) + \text{H}(2s)$ threshold, observed by Lyman α fluorescence. Bottom trace: Scan at higher laser power showing two-photon transitions with resonances through the highest bound levels of the B and B' states. The peak near 118376.3 cm^{-1} is the R(1) branch of the (39,2) band of B+E. The sharp negative signal near the threshold is an experimental artifact.

The threshold can be determined directly from the top trace, or indirectly by extrapolating the highest B state vibrational levels using the procedure of Stwalley.⁵ Finally, it can be determined from the decrease in the two-photon signal above the one-photon threshold. All three methods agree, and yield a preliminary new value of $36118.1 \pm .2 \text{ cm}^{-1}$ for the ground state binding energy. This value is a factor of 2.5 more precise than previous work, and agrees well both with earlier experiments and theory.

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