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ION-PAIR PRODUCTION AT 71 nm

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Molecular Spectroscopy By Stepwise Two-Photon Ion-Pair Production at 71 nm

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The Rydberg states of H_2 have been a continuing subject of intensive study by various research groups. [1-4] However, understanding of the high lying electronic states of this molecule has been inhibited by the lack of spectroscopic data in the region < 75 nm. Experimental studies have been difficult because spectroscopic features are generally buried under an intense absorption or photoionization continuum. [5] Intense, high-resolution excitation sources are not easily available. Recent developments on tunable, narrowband, coherent XUV sources [6] provide new means of studying the spectroscopy in this region with high resolution ($\pm .0005$ nm). We have applied the technique of stepwise two-photon excitation to study photoionization of H_2 in a molecular beam using the two lowest excited states of H_2 as the intermediate level. This excitation, coupled with the detection of background-free H^+ ions has enabled us to uncover, for the first time, spectroscopic features that are difficult to observe in positive ion detection. [7] These features have been successfully assigned to new Rydberg series converging to the high vibrations of the H_2^+ ground electronic state.

In this study, the first photon at $\lambda = 96$ nm is derived by frequency tripling of a pulsed tunable dye laser in a pulsed jet of CO. The frequency is tuned on resonance with a ro-vibronic level of H_2 in the Lyman ($B^1\Sigma_u^+$) band with $v'=12, 13$ or the Werner ($C^1\Pi_u$) band with $v'=2$. The excited H_2 molecule absorbs a second photon that is the UV output from a second dye laser (see Figure 1). The frequency of this second photon is chosen such that the sum of the frequencies of the first and the second photons can be higher than

Figure 1: Potential energy diagram of H_2 , showing two-photon excitation scheme.

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Figure 2: H_2 photoionization spectrum following stepwise two-photon excitation. The first photon is fixed at the $C^{1\pi}_{1u}$ ($v'=2$) $Q(1)$ transition frequency.

71.57 nm, the threshold for H^+ ion production. Here, the H^+ ions are formed from H_2 by photopredissociation through H^+ ion-pair channel. Monitoring the negative ions with a quadrupole mass spectrometer and tuning the second laser will show the threshold for ion-pair production followed by a H^+ ion continuum. Interference of this ion-pair continuum by the major, molecular ion production channel will result in structure in the continuum.[8]

Figure 2 is a sample of the resulting spectrum. This spectrum consists of a structured continuum with sharp dips superimposed on the structures. The origin of the gross features is not understood at this point. However, the dips have been successfully assigned. They correspond to previously unobserved Rydberg series of H_2 that converge to the H_2^+ ($v^+=9$, $N=1$) and H_2^+ ($v^+=9$, $N=3$) vibrations as the series limit. By tuning to different intermediate states, we have also observed several preliminary, new Rydberg series converging to the $v^+=9$ vibration of the H_2^+ ion with the rotational quantum number as high as $N=5$. These represent the first observation of large Δv (≥ 9) and ΔJ (≥ 3) transitions in the spectroscopy of H_2 .

In conclusion, we have described a new technique that couples non-linear spectroscopy with negative ion detection for molecular hydrogen spectroscopic studies in the XUV region. The technique should be easily extendable to studies of other diatomics and polyatomic molecules.

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References

1. G. Herzberg, *J. Mol. Spectrosc.* **33**, 147 (1970).
2. G. Herzberg and Ch. Jungen, *J. Mol. Spectrosc.* **41**, 425 (1972).
3. P.M. Delmer and W.A. Chupeka, *J. Chem. Phys.* **65**, 2243 (1976).
4. K.H. Welge, private communication (1995).
5. J. Berkowitz: Photoabsorption, Photoionization, and Photoelectron Spectroscopy, (Academic Press, New York, 1979).
6. C.T. Rettner, E.E. Marinero, R.N. Zare, and A.H. Kung, *J. Phys. Chem.* **88**, 4459 (1984).
7. W.A. Chupeka, P.M. Delmer, and W.T. Jivry, *J. Chem. Phys.* **63**, 3929 (1975).
8. U. Fano, and J.W. Cooper, *Rev. of Mod. Phys.* **40**, 441, (1968).

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