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Presented at the 7th International Conference on Laser Spectroscopy, Maui, HI, June 24-28, 1985; and to be published in Laser Spectroscopy VII, Y.R. Shen and T. Hansch, Eds., Springer Verlag, Berlin, Federal Republic of Germany, 1985

MOLECULAR SPECTROSCOPY BY STEPWISE TWO-PHOTON ION-PAIR PRODUCTION AT 71 nm

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June 1985

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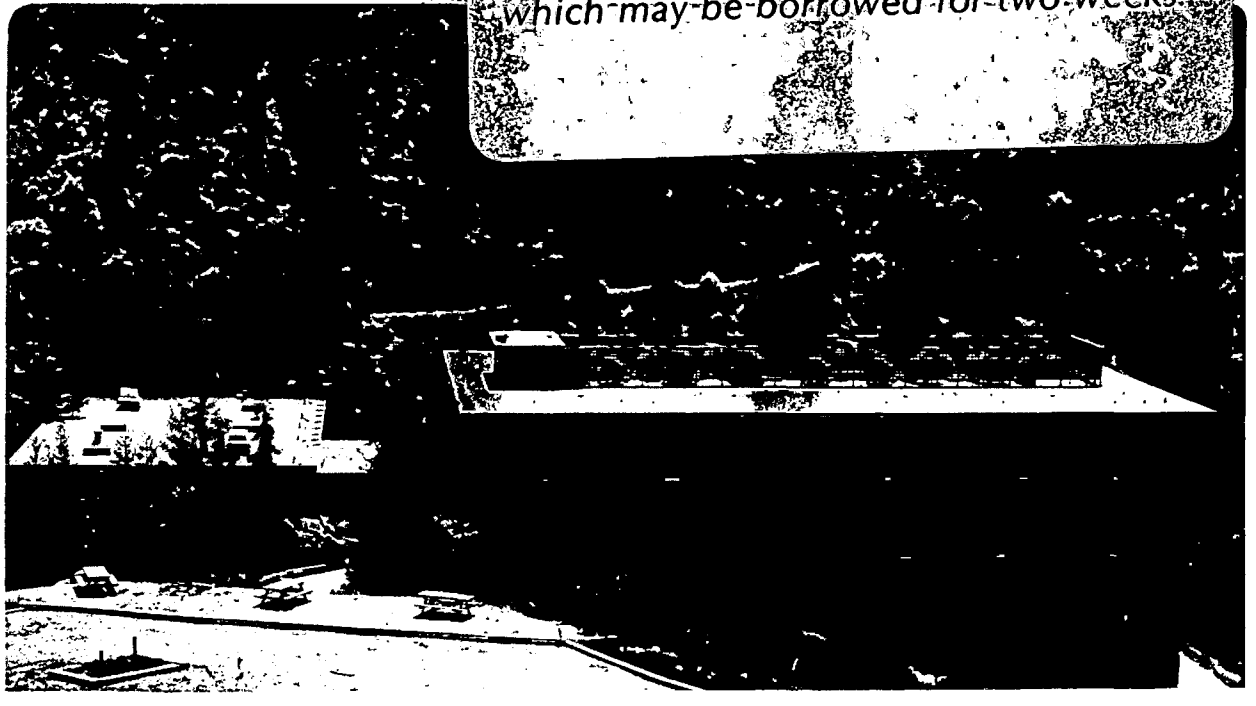

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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To appear in Laser Spectroscopy VII, Editors, Y.R. Shen and T. Hansch, Springer Verlag, 1985.

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 (± .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 ∿ 96 nm is derived by frequence 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

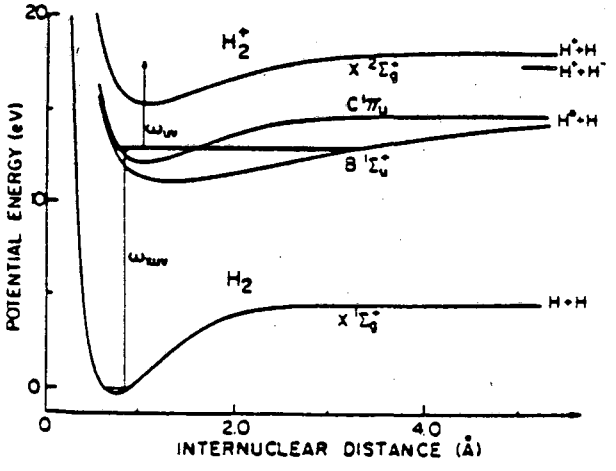

Figure 1: Potential energy diagram of H_2, showing two-photon excitation scheme.

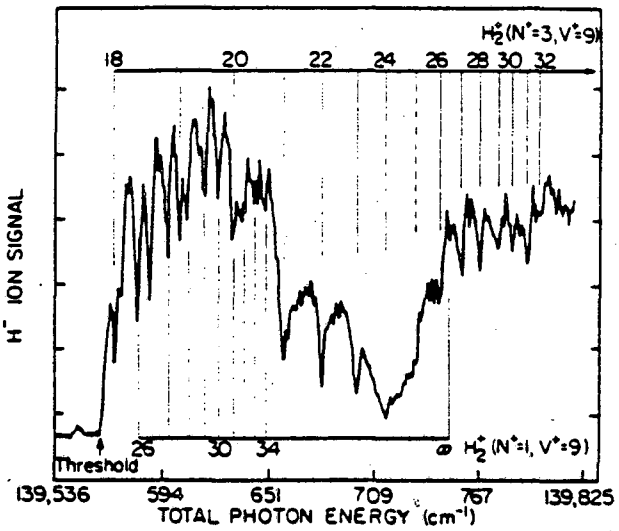

Figure 2: H_2 photoionization spectrum following stepwise two-photon excitation. The first photon is fixed at the $C\,^1\Pi_u$ (v'=2) Q(1) transition frequency.

71.57 nm, the threshold for H^- ion production. Here, the H^- ions are formed from H_2 by photopredissociation through the 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 an example 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.

Acknowledgements This work was supported by the United States Department of Energy under grant DE-AC03-76SF-00098. AHK's work is also supported by the National Science Foundation under grant CHE-8303208.

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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