RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 31, NUMBER 2 FEBRUARY 1985

Three-photon double-resonance spectroscopy of autoionizing Rydberg states in H_2

N. Bjerre,* R. Kachru, and H. Helm

Molecular Physics Department, SRI International, Menlo Park, California 94025

(Received 15 October 1984)

A new three-photon double-resonance excitation scheme for H_2 is combined with time-of-flight ion detection and is used for high-resolution spectroscopy of autoionizing and field-ionizing Rydberg states. Using modest laser powers, we have achieved a Doppler-limited resolution of 0.15 cm^{-1}.

The singlet *np* Rydberg series in H_2 has already been studied extensively by vacuum ultraviolet (vuv) photoabsorption and photoionization spectroscopy from the electronic and vibrational ground state,[1–4] and two-step photoionization via the short-lived $B\,^1\Sigma_u^+$ state has recently been performed with a vuv laser.[5] The energies and autoionization lifetimes of levels in the singlet *np* series have been treated in terms of multichannel quantum-defect theory (MQDT),[3,4,6–9] which in several cases predicts structure in the line shapes beyond the resolution of the vuv photoionization spectra.

In the present experiments we have successfully demonstrated a three-photon double-resonance excitation scheme for H_2 and have achieved a spectral resolution an order of magnitude higher than in the previous photoionization spectra of this molecule.[4] The excitation scheme uses two lasers: An ArF excimer laser two photon excites hydrogen from the ground state to selected levels in the double-well state $E,F\,^1\Sigma_g^+$ (Fig. 1) as first demonstrated by Kligler and Rhodes.[11] These *E,F* levels are subsequently excited to the singlet *np* Rydberg levels by visible light from a neodymium:yttrium aluminum garnet (Nd:YAG) pumped-dye laser. Using ion detection under low-pressure collision-free conditions, we study autoionized as well as field-ionized Rydberg levels.

The apparatus is a simple time-of-flight mass spectrometer where the ions are formed at the crossing between the two laser beams and a jet of H_2 gas effusing from a 0.15-mm nozzle into a vacuum system at a background pressure of 10^{-4}–10^{-5} Torr. The broadband ArF excimer laser provides 12-ns pulses at 193 nm of typically 30 mJ in a focal spot of 0.3×1.7 mm^2 and populates the $v'=6$, $J'=0,1,2,3$ levels in the *E,F* state of H_2 by two-photon excitation.[11–14] These levels are subsequently excited to ionizing Rydberg levels with a 1-ns pulse from an unfocused Nd:YAG pumped dye laser which has a typical output of 500 μJ per pulse. The dye laser has a linewidth ~ 1 cm^{-1} which can be reduced to 0.1 cm^{-1} by means of a pressure tuned intracavity etalon. The ions formed by the lasers are extracted from the source region by an electric field of typically 150 V/cm and detected by an electron multiplier after a drift length of 3 cm.

The excimer laser alone produces H^+, H_2^+, and traces of H_3^+. H_2^+ is formed when a third ArF photon ionizes H_2 in the *E,F* state.[13,15] H_2^+ ions formed in vibrational levels $v\geq 2$ may subsequently photodissociate[16] into H^+ and H by absorbing a fourth ArF photon. H_3^+ is formed in the very fast ion molecule reaction of H_2^+ and H_2.[17] Focusing the ArF laser increases the efficiency of both the two-photon process populating the *E,F* state and the undesired photoionization of that state. In accordance with previous observations[13] we find that a comparatively weak focusing of the ArF laser gives the best yield of H_2 in the *E,F* state.

When the dye laser is temporally coincident with the excimer laser and is on resonance with a transition to a Rydberg level autoionizing to $v=0$ of H_2^+, we observe an increase in the H_2^+ signal and a corresponding decrease in the H^+ signal. This indicates that the dye laser effectively competes with the excimer laser in depopulating the *E,F* state to form H_2^+ $(v=0)$. The decrease in the H^+ signal results because H_2^+ $(v=0)$ cannot be photodissociated by either of the two lasers due to small Franck-Condon factors.

The best signal to noise ratio for H_2^+ from autoionization was obtained with a time delay of 20–40 ns between the excimer- and dye-laser pulses. This delay allows temporal

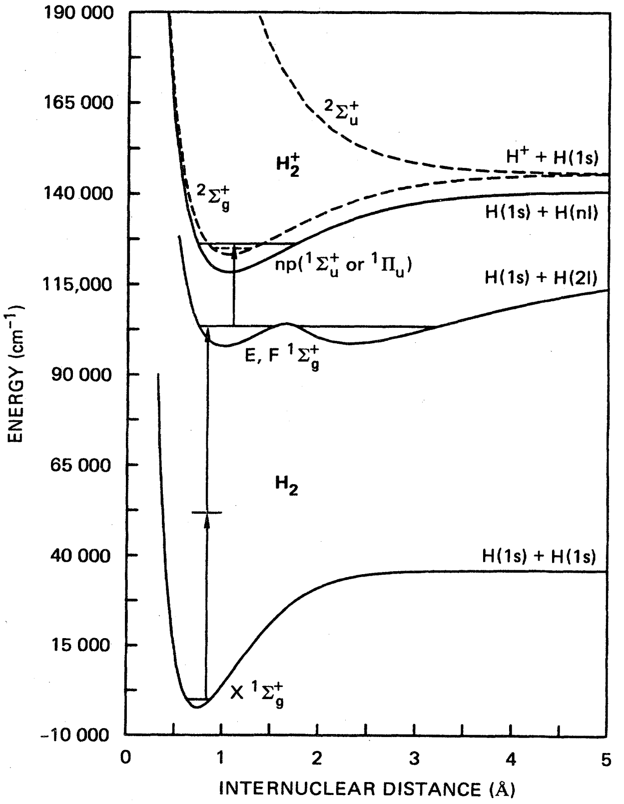

FIG. 1. Potential-energy curves for H_2 and H_2^+ taken from Ref. 10.

separation of the ion signals from the two lasers and eliminates possible ac Stark broadening induced by the excimer laser.

The time delay between the two laser pulses can also be used for measuring the lifetime of the *E,F* ($v'=6$) state. The dye laser is kept on resonance with a Rydberg transition and the intensity of the H_2^+ signal produced by the dye laser is monitored as a function of the delay time. In this way, we obtained a lifetime of 100 ns in agreement with the fluorescence measurements of Kligler, Bokor, and Rhodes.[13]

A portion of the spectrum obtained by scanning the dye laser in its 1-cm^{-1} bandwidth mode is shown in Fig. 2. The transitions are labeled *P,Q,R* for $\Delta J=-1,0,1$ followed by (J'), the total angular momentum for the level in the *E,F* state, and by *np*, the quantum numbers of the Rydberg electron. For levels with high *n*, the upper state is appropriately described in Hunds case (*d*),[3] where the rotational angular momentum of the H_2^+ core, *N*, is a good quantum number, while levels with low *n* are more properly described in Hunds case (*b*) in terms of the projection of the electronic angular momentum on the molecular axis, $\Lambda=\sigma,\pi$. The label ends with the vibrational quantum number of the Rydberg state, *v*.

In all, we have observed 40 transitions to autoionizing levels by scanning the dye laser between 420 and 490 nm. We have assigned 26 of the lines as *Q* and *R np* Rydberg transitions from the $J'=1$, $v'=6$ level of the *E,F* state, which is predominantly excited by the broadband ArF laser.[13] Within the precision of our present wavelength calibration (~ 1 cm^{-1}) the energies of these transitions agree with those obtained from the *np* Rydberg data of Herzberg and Jungen[3] combined with the *E,F* state energy of Dieke[18] corrected by 8.1 cm^{-1}, as suggested by Miller and Freund.[19] Most of the remaining lines are tentatively assigned to *np* Rydberg transitions from the $J'=2$ and $J'=3$, $v'=6$ levels of the *E,F* state, based on the agreement between the transition energies observed and those calculated using the quantum-defect method of Fano.[3,6] Somewhat surprisingly, none of the observed lines can be assigned to transitions from the $J'=0$ level.

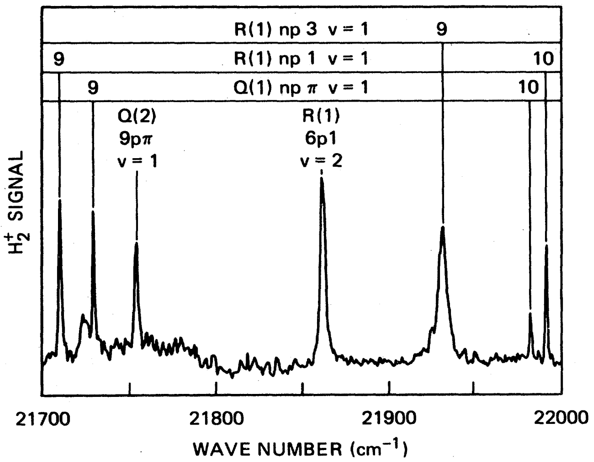

FIG. 2. Portion of the three-photon double-resonance ionization spectrum of H_2 obtained by scanning the dye laser in its 1-cm^{-1} bandwidth mode. The labeling of the transitions is explained in the text.

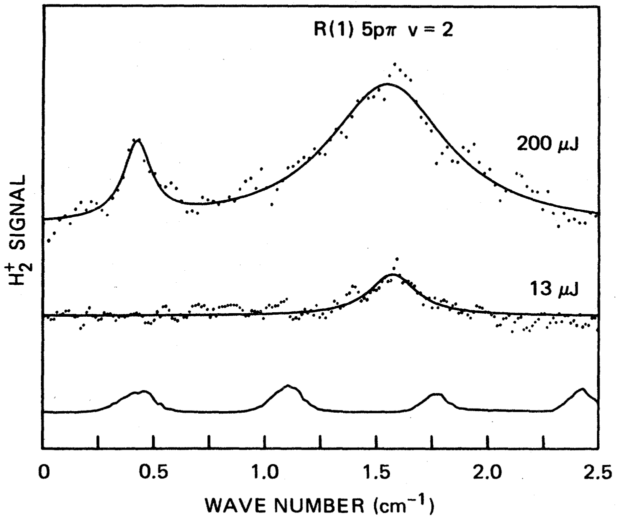

FIG. 3. Two transitions recorded with 0.1-cm^{-1} dye laser bandwidth. Upper trace: dye laser power ~ 200 μJ; middle trace: dye laser power ~ 13 μJ; lower trace: frequency markers from an etalon with free spectra range 0.667 cm^{-1}. The origin of the wavenumber scale is at 21 004.7 cm^{-1}. The solid curves in the two upper traces are Lorentzian fits to the observed spectra; upper trace widths 0.15 and 0.66 cm^{-1}, respectively, middle trace width 0.26 cm^{-1}.

The transitions assigned populate *n* levels up to 15. No Stark splittings due to the extraction field were observed. The splittings are calculated to be less than 0.1 cm^{-1} for the observed transitions.

Figure 3 shows two lines recorded with a dye laser bandwidth of 0.1 cm^{-1} at power levels of 200 and 13 μJ per pulse. The weaker of the two transitions, which is so far unassigned, has a linewidth of 0.15 cm^{-1}, which is close to the Doppler width of H_2 gas at room temperature and constitutes an improvement by an order of magnitude over the resolution of previous photoionization spectra. The intensity of this line is reduced beyond detection in the 13 μJ spectrum. Contrary to the weak line, the stronger of the two lines, $R(1)$ $5p\pi$ $v=2$ at 21 006.2 cm^{-1}, is clearly saturated. Its intensity decreases by a factor of only 3 when the power of the dye laser is reduced from 200 to 13 μJ per pulse. Since the saturation takes place within the 1-ns duration of the dye laser pulse, the Rabi frequency must be several GHz, which is consistent with the broadening of the line with increasing dye laser power. The natural linewidth of the $R(1)$ $5p\pi$ $v=2$ transition is expected to be less than 0.1 cm^{-1} because the autoionization of the upper level proceeds in a $\Delta v=2$ process, which typically occurs on a nanosecond time scale.[4] From the linewidth measured at 200 μJ per pulse, we estimate a transition moment of 0.03 D for the $R(1)$ $5p\pi$ $v=2$ transition. This value compares well with the transition moments calculated for transitions from the ground state.[7]

The two transitions in Fig. 3 illustrate yet another advantage of the present excitation scheme. They were not observed in the vuv excitation spectra from ground state H_2 (Refs. 3 and 4) due to an overlap with a strong transition from the $J''=0$ level of the ground state. Such overlaps are eliminated with the present double-resonance technique.

Field ionization under the present conditions is demonstrated by the appearance of the $R(1)$ $4p\sigma$ $v=4$ transition which ends on a level 22.9 cm^{-1} below the lowest allowed ionization limit and accordingly cannot autoionize. It was shown previously,[20] that this level can be ionized in fields of the order of 15 V/cm, considerably less than the 150 V/cm used to extract the $H_2{}^+$ ions in the present experiments. By varying the extraction voltage, it will be possible to study the onset of field ionization as the effective ionization limit moves across the $4p\sigma$ $v=4$ level.

In conclusion, we have demonstrated an efficient and selective two-step laser excitation scheme for high-lying autoionizing states of H_2. We have obtained a Doppler-limited spectral resolution of 0.15 cm^{-1}, which is an order of magnitude better than that of previous photoionization spectra. The selective nature of the excitation scheme allows the isolation of transitions that overlap in the vuv absorption spectra. The three-photon double-resonance technique is in general very powerful[21] and provides a convenient way of obtaining photoionization spectra with a resolution that allows stringent tests of theories on vibrational and rotational autoionization of Rydberg states.

This research was supported by SRI International through its Independent Research and Development Program. Nis Bjerre gratefully acknowledges financial support from the Danish Natural Science Research Council.

---

[*] Permanent address: Institute of Physics, Aarhus University, DK-8000 Aarhus C, Denmark.

[1] S. Takezawa, J. Chem. Phys. **52**, 2575 (1970).
[2] G. Herzberg, Phys. Rev. Lett. **23**, 1081 (1969).
[3] G. Herzberg and Ch. Jungen, J. Mol. Spectrosc. **41**, 425 (1972).
[4] P. M. Dehmer and W. A. Chupka, J. Chem. Phys. **65**, 2243 (1976).
[5] H. Rottke and K. H. Welge, in *Thirteenth International Quantum Electronics Conference,* Anaheim, 1984 [J. Opt. Soc. Am. B **1**, 485 (1984)].
[6] U. Fano, Phys. Rev. A **2**, 353 (1970).
[7] Ch. Jungen and D. Dill, J. Chem. Phys. **73**, 3338 (1980).
[8] Ch. Jungen, J. Chim. Phys. **77**, 27 (1980).
[9] M. Raoult and Ch. Jungen, J. Chem. Phys. **74**, 3388 (1981).
[10] T. E. Sharp. At. Data **2**, 119 (1971).
[11] D. J. Kligler and C. K. Rhodes, Phys. Rev. Lett. **40**, 309 (1978).
[12] H. Pummer, H. Egger, T. S. Luk, T. Srinivasan, and C. K. Rhodes, Phys. Rev. A **28**, 795 (1983).
[13] D. J. Kligler, J. Bokor, and C. K. Rhodes, Phys. Rev. A **21**, 607 (1980).
[14] W. M. Huo and R. L. Haffe, Chem. Phys. Lett. **101**, 463 (1983).
[15] E. E. Marinero, C. T. Rettner, and R. N. Zare, Phys. Rev. Lett. **48**, 1323 (1982).
[16] R. E. Kutina, A. K. Edwards, R. S. Pandolfi, and J. Berkowitz, J. Chem. Phys. **80**, 4112 (1984).
[17] V. H. Gutbier, Z. Naturforsch. Teil A **12**, 499 (1957).
[18] *The Hydrogen Molecule Wavelength Tables of Gerhard Heinrich Dieke,* edited by H. M. Crosswhite (Wiley-Interscience, New York, 1972).
[19] T. A. Miller and R. S. Freund, J. Chem. Phys. **61**, 2160 (1974).
[20] W. A. Chupka and J. Berkowitz, J. Chem. Phys. **51**, 4244 (1969).
[21] Y. Anezaki, T. Ebata, N. Mikami, and M. Ito, Chem. Phys. **81**, 103 (1984).