Quantum-State-Specific Detection of Molecular Hydrogen by Three-Photon Ionization

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A sensitive method is demonstrated for determining (v'', J'') populations of H_2. Single rotational levels of the $E, F\,^1\Sigma_g^+$ state are prepared by two-photon excitation; absorption of a third quantum causes ionization. Detection of J'' levels of $v'' = 0$, 1, and 2 is possible while scanning the dye laser fundamental over just 5 nm. Measured rotational populations at different temperatures (295 – 750 K) agree well with the corresponding Boltzmann distributions. Rotational line strengths show almost no J'' dependence for this process.

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The determination of the internal state distribution of H_2 is of fundamental importance in numerous applications, ranging from H atom recombination on surfaces,[1] to $H + H_2$ reactive scattering,[2] to hydrogen plasmas.[3] Molecular hydrogen shows only a weak quadrupole-allowed infrared spectrum and its lowest-lying electronic states are located in the deep vacuum ultraviolet ($\leqslant 110$ nm).[4] Consequently, standard methods, like infrared chemiluminescence[5] or laser-induced fluorescence,[6] either are inapplicable or present formidable technical challenges. Although it is possible to detect H_2 in a quantum-state-specific manner by Raman or coherent anti-Stokes Raman scattering (CARS) spectroscopy,[7] or to infer such information from time-of-flight measurements,[8] signal-to-noise limitations presently prevent the use of these techniques at sufficiently low densities that nascent H_2 internal state distributions can be observed. We report in this Letter the three-photon ionization of H_2 whereby, for the first time, individual (v'', J'') levels can be selectively detected at a sensitivity sufficient to allow the measurement of collisionally unrelaxed internal state distributions.

Kligler and co-workers[9,10] were the first to demonstrate resonant two-photon excitation of H_2 to the double minimum $E, F\,^1\Sigma_g^+$ state. The excited molecules were detected by observing the near-infrared emission to the H_2 $B\,^1\Sigma_u^+$ state. The H_2 E, F state has a radiative lifetime of 100 ± 20 ns,[9,10] and under tight focusing conditions photoionization of the E, F state should dominate other removal mechanisms.[10] As ion collection can readily approach unit efficiency, this suggested to us that experiments could be designed so that almost all the pumped molecules in the excited volume can be detected in order to characterize (v'', J'') populations in the ground state.

Figure 1 shows our experimental scheme. A yttrium aluminum garnet (YAlG)–pumped rhodamine 6G dye laser (Quanta-Ray) is frequency doubled and this doubled output together with the residual fundamental are collinearly focused into an H_2 Raman shifter (60 cm long, 100 psi). The various anti-Stokes orders and the undispersed orders of both the doubled dye and the fundamental frequencies are tightly focused via an $f = 10$ cm MgF_2 lens, which also serves as the entrance window of the ionization chamber. By taking advantage of the two-photon energies provided by combinations of identical and different anti-Stokes orders generated in the Raman process, this scheme gives access to a wide range of rovibronic transitions while utilizing only a narrow range (~ 5 nm) of the dye-laser fundamental. Let nAS denote the nth anti-Stokes order of the frequency-doubled dye. By tuning of the dye laser from 568.7 to 573.5 nm, the $v'' = 0$, $J'' = 0-3$ levels are probed by the combination $3AS + 4AS$, $v'' = 1$, $J'' = 0-3$ by $3AS + 3AS$, and $v'' = 2$, $J'' = 0-4$
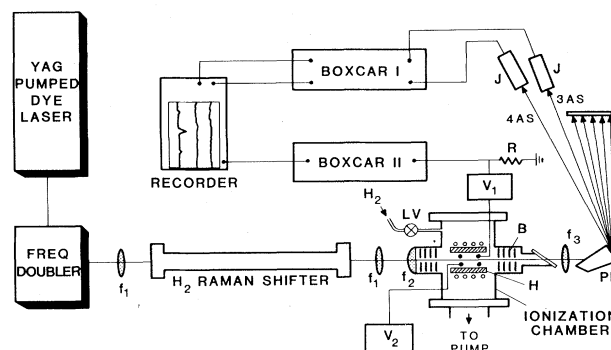

FIG. 1. Experimental scheme. Key: f_1, f_2, f_3 are 50, 10, and 40 cm focal length lenses; PB, Pellin Broca prism; LV, leak valve; B, baffles; H, collecting voltage, $\sim +100$ V; V_2, repelling voltage, ~ -10 V; R, resistor, ~ 1 MΩ; J, Joulemeter.

by 2AS + 3AS. The corresponding two-photon transition frequencies are 98 350–99 156 cm^{-1} [(0, 0) band], 94 995–95 261 cm^{-1} [(0, 1) band], and 90 646–91 074 cm^{-1} [(0, 2) band]. Moreover, the presence of the various orders serves to ionize efficiently the excited molecules.

The photoions are collected by a coaxial electrode and the ion current is measured across a 1-MΩ resistor in series with the same electrode. A dual boxcar integrator (PAR model 162/165) is used to process the ion signal. On emerging from the ionization chamber, the radiation is recollimated and then dispersed using a Suprasil Pellin Broca prism. Pyroelectric Joulemeters (Molectron model J3-05) measure the energy of the anti-Stokes orders via separate boxcar averaging. Both the processed ion signal and the energy of the anti-Stokes orders are displayed on a stripchart recorder.

To minimize spurious photoelectric signals, care must be taken to reduce scattered uv light. Baffles are used at both the entrance and exit arms of the ionization chamber, as shown in Fig. 1. In addition, the voltage on the repeller electrode is varied to ensure the absence of ion multiplication effects.

Figure 2 presents portions of a typical ion spectrum showing the prominent members of the Q branch ($\Delta J = 0$) of the $E, F-X$ (0, 0) band, recorded at room temperature (295 K) and 15 mTorr pressure of flowing H_2. The much weaker members of the O and S branches ($\Delta J = \mp 2$) are not evident at this pressure, but were detected at higher sample densities ($\gtrsim 1$ Torr). The transition frequencies of the Q members were deduced from the experimental assignments of Dieke[11] and correspond to the 3AS + 4AS two-photon excitation scheme. It is readily apparent that the ion signal amplitudes mirror the room-temperature Boltzmann distribution, which is a maximum at $J'' = 1$.

A measurement of the ion current for Q_1 yields an average value of 1.35×10^{-11} A, thus implying
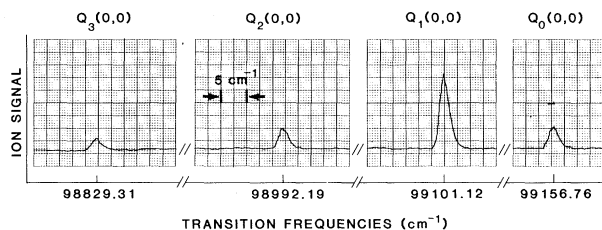
FIG. 2. Room-temperature ion spectrum. The exact line positions of the Q members are indicated (Ref. 11).

production of 8.4×10^6 ions per laser pulse. For the limiting case of total photoionization of the excited-state population (expected for $I > 10^8$ W cm^{-2}), the total number of ions, $i(J'')$, produced during the laser pulse is given by[12]

$$i(J'') = \pi \alpha E_1 E_2 N(0, J'')/(2hct_p), \qquad (1)$$

where α is the two-photon absorption cross section, E_1 and E_2 are the energies of the anti-Stokes orders involved in the transition, $N(0, J'')$ is the rotational population of the ($v'' = 0, J''$) level, and t_p is the duration of the laser pulse. Using the experimentally determined parameters $E_1 = 13$ μJ, $E_2 = 49$ μJ, $N(0, J'') \simeq 2.2 \times 10^{14}$ molecules cm^{-3}, and $t_p = 2$ ns, and a calculated value[12] for α of 1.6×10^{-30} cm^4 W^{-1} (for a measured one-photon laser bandwidth of 0.92 cm^{-1}), we obtain from Eq. (1) about 8.8×10^6 ions per pulse. The excellent agreement between the measured and predicted ion yields indicates that we are indeed ionizing almost all of the excited-state population.

To study the sensitivity of the ion signal amplitudes to variations in the ground-state rotational populations, spectra are recorded at several sample temperatures. A cylindrical stainless-steel tube (5 cm long × 1.5 cm i.d.), heated by a coaxial heating element (Thermocoax) is placed around the electrode assembly to vary the sample temperature. Table I summarizes the results obtained at 295, 560, and 748 K, using a pressure of 100 mTorr and the 3AS + 4AS two-photon excitation scheme with a dye-laser tuning range of 568.7 to 577.5 nm. Ion signals, corrected for laser power, are given for each observed Q branch member normalized to Q_0. Also shown are the corresponding rotational populations given by

$$\frac{N(0, J'')}{N(0, 0)} = (2T+1)(2J''+1)\exp\left[\frac{-F(J'')}{kT}\right], \qquad (2)$$

where $(2T+1)$ is the nuclear spin degeneracy (1 for even J'', 3 for odd J'') and $F(J'')$ is the rotational term energy.[11] Table I shows that the populations of the higher members of the Q branch increase dramatically with increasing temperature.

It is also evident that the normalized ion signals deviate systematically from that predicted by the Boltzmann factor alone. This deviation ensues from the rotational line-strength dependence of each two-photon transition. Relative transition probabilities are obtained by dividing the

TABLE I. Normalized ion signals at different sample temperatures.

| Transition | T = 295 K | | T = 560 K | | T = 748 K | | $R_{J''}$ |
	Ion signal	Boltzmann distribution	Ion signal	Boltzmann distribution	Ion signal	Boltzmann distribution	
Q_0	1	1	1	1	1	1	1
Q_1	4.98 ± 0.14	5.04	6.35 ± 0.5	6.63	7.18 ± 0.5	7.16	0.98 ± 0.03
Q_2	1.01 ± 0.05	0.89	2.12 ± 0.12	2.01	3.11 ± 0.38	2.52	1.14 ± 0.05
Q_3	0.69 ± 0.04	0.67	3.78 ± 0.3	3.42	5.79 ± 0.4	5.39	1.07 ± 0.03
Q_4	$\cdots$	0.03	0.55 ± 0.09	0.44	0.96 ± 0.08	0.94	1.07 ± 0.08
Q_5	$\cdots$	0.006	$\cdots$	0.37	1.6 ± 0.2	1.15	1.39 ± 0.2

normalized ion signals by their Boltzmann counterparts. The last column of Table I lists the average value of this ratio, $R_{J''}$, for each J'' level, obtained by weighting each measurement by the inverse of its uncertainty. Thus when the normalized ion signals are divided by these correction factors ($R_{J''}$), the $N(0, J'')$ populations are determined directly. A measure of the degree of consistency of the $R_{J''}$ values given in Table I is how well they reproduce the sample temperatures. Figure 3 plots the quantity $\ln[i(J'')/R_{J''}(2T+1)(2J''+1)]$ vs $F(J'')$; if the data are described by a rotational temperature, a straight line results [see Eq. (2)]. From the slopes of these plots we obtain (using linear regression analysis) temperatures of 291 ± 5, 582 ± 19, and 730 ± 24 K. These are in reasonable agreement with the measured sample temperatures of 295, 560, and 748 K, respectively, considering that these measured temperatures are only known to $\pm 2\%$ because of calibration uncer-

tainties.

The normalized rotational line strengths, $R_{J''}$, can be compared to those predicted for a Q branch of a Σ-Σ two-photon transition.[13,14] For linearly polarized light this expression reduces to

$$R_{J''} = (S_{J'J''}/S_{00})/(2J''+1)$$
$$= 1 + \frac{(\mu_S/\mu_I)^2 J''(J''+1)}{[5(2J''-1)(2J''+3)]}, \qquad (3)$$

where the ratio of the transition dipole factors $(\mu_S/\mu_I)^2$, as defined in Ref. 13, varies according to the nature of the intermediate state. Best agreement with our experimentally determined rotational line strengths is obtained by using in Eq. (3) a value of $(\mu_S/\mu_I)^2 \simeq 1$. This suggests that the predominant intermediate state must have Π rather than Σ character. The $C^1\Pi_u$ state is the most likely candidate. Corroboration of this conclusion might be accomplished by comparing line intensities for linear and circularly polarized pump photons.

In summary, a sensitive and simple method for detecting molecular hydrogen in a quantum-state-specific manner has been demonstrated in the milliTorr pressure range. By the use of ion particle multipliers and counting techniques, it should be possible to interrogate sample densities down to 10^8 molecules cm^{-3} or less. A large number of vibrational-rotational levels of H_2 and its isotopic analogs can be reached by tuning the fundamental of a pulsed commercial dye laser over a limited wavelength range.[15] Not only will this scheme permit detailed spectroscopic studies of the excited electronic states of molecular hydrogen, but it will also allow the determination of collisionally unrelaxed internal state distributions for a number of dynamical processes of fundamental interest.
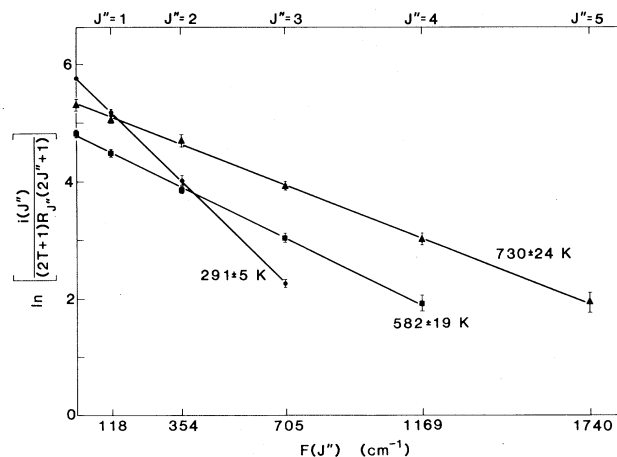
FIG. 3. Rotational temperature plots (see text). Sample temperatures: circles, 295 K; squares, 560 K; triangles, 748 K. The uncertainties represent 3 standard deviations.

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[15]For example, by using the 4AS + 4AS pumping scheme, the $Q_0 - Q_3$ members of both the inner well of the (2, 0) band and the outer well of the (4, 0) band have been observed as well as various O and S members.

Determination of Hyperfine Structures in Ground and Excited Atomic Levels by Level-Crossing Optogalvanic Spectroscopy: Application to 89Y

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This new technique in optogalvanic spectroscopy yields Doppler-free resonances when degeneracies in atomic energy levels are removed by a magnetic field, and also when the interval between levels matches the mode spacing of the laser. g_J factors and magnetic hyperfine interaction constants were determined for lower and upper levels of the transition at 619.2 nm in YI. The value $A = (+)89.6(9)$ MHz for the upper level $4d5s(a\,^3D)5p\,^2D_{3/2}^0$ is new; the remaining determinations agree with published values.

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The change in impedance of a gas discharge caused by irradiation of the plasma with laser light tuned to some atomic transition (the optogalvanic effect) has become an important and sensitive technique for detecting atomic transitions in laser spectroscopy.[1] It has recently been demonstrated that a change in the optogalvanic signal accompanies the removal, by a small magnetic field, of the zero-field degeneracy of Zeeman levels.[2] We report here the location of level crossings at finite fields by the observation of changes in the optogalvanic signal as a function of applied magnetic field. The direction of the magnetic field must be crossed with (or oblique to) the direction of polarization of the laser light.

We apply the phenomenon as a new Doppler-free technique to the determination of hyperfine structures in both ground and excited atomic levels. The experiments were carried out on the $4d5s^2$-$^2D_{3/2} - 4d5s(a\,^3D)5p\,^2D_{3/2}^0$ 619.2-nm transition in atomic yttrium.

The laser is tuned to some frequency within the Doppler absorption profile of the transition. Both upper and lower states have hyperfine structures much smaller than the Doppler width: Both structures undergo decoupling in the magnetic field, and crossings between hyperfine levels occur for the upper and for the lower states. At values of the magnetic field where crossings occur between levels differing by ± 2 in m quantum number, the