

## Direct Lifetime Measurement of Laser-Excited $n = 3$ Levels in Para- $H_2$

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This paper reports measurements of the lifetimes of fourteen levels in the  $3s, 3d$  complex of para- $H_2$  by a delayed coincidence method. A collimated beam of metastable hydrogen molecules was selectively excited by light pulses from a cw dye laser and fluorescent radiation was detected by a vacuum ultraviolet photomultiplier. The observed lifetimes range from 11.1 to 48.8 nsec. Similar methods can be used to determine the structure and lifetimes in other excited states of  $H_2$  and in a variety of other systems.

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Despite their fundamental importance there are very few measurements of the lifetimes of the excited triplet states of molecular hydrogen.<sup>1-5</sup> The forbidden aspect of singlet to triplet transitions makes optical excitation of triplet levels from the ground state difficult.<sup>6</sup> The density of closely spaced levels with similar decay channels makes it difficult to use pulsed electron excitation as a source of excited molecules for lifetime measurements. This paper reports the use of a new method which employs electron bombardment to produce metastable hydrogen molecules<sup>7-8</sup> and laser pulses to excite molecules from the metastable state to the triplet  $3s$  and  $3d$  states. Measurements of the lifetimes of fourteen levels in this complex are reported.

Figure 1 shows a schematic diagram of the apparatus. The dye laser is a Coherent model No. 599-03 single-mode scanning laser using rhodamine 6G dye, which is stabilized to an external scannable reference interferometer (Burleigh model No. CFT-25P IR). A short-term stability of 10 MHz and a long-term stability of 100 MHz are routinely attained by using a galvanometer-driven Brewster-angle window with a 125 Hz bandwidth to change the cavity length. The laser frequency is determined by first measuring its wavelength to 0.05 nm with a  $\frac{1}{2}$ -m monochromator, and then taking a short scan of the fluorescent lines from an  $I_2$  cell and comparing the lines with the  $I_2$  atlas compiled by Gerstenkorn and Luc.<sup>9</sup>

Parahydrogen diffuses through a 100- $\mu$ m slit into a differentially pumped beam apparatus, and a fraction of the hydrogen is excited to the  $c(2p)^3\Pi_u^+$  metastable state by bombardment in the source slit with 10 mA of 18-eV electrons. The beam is collimated by roughly 60:1 with a vertically oriented slit, and passes through a series of light baffles into the interaction chamber. The molecular beam is crossed transversely by the light from the dye laser and excited to selected

$n = 3$  states with a linewidth of about 100 MHz, which is determined primarily by the residual transverse Doppler width. This linewidth is chosen to yield the maximum resolution consistent with the need to keep the laser frequency within the linewidth for the 1-h data collection time used to measure lifetimes. Since the excited  $ns$  and  $nd$  states of  $H_2$  decay partially to the lower-lying  $b(2p)^3\Sigma_u^+$  dissociative state, a broadband vacuum ultraviolet photomultiplier tube with a fast dynode structure (EMI G24H314LF) is used to detect the continuum fluorescence to this level.

A typical cw scan showing the iodine lines and the fine structure of the Q2 branch of the transition to the  $i(3d)^3\Pi_g^+$  state ( $v' = 0$ ) is shown in Fig. 2. The counting rate at the top of the  $J' = 3$  peak

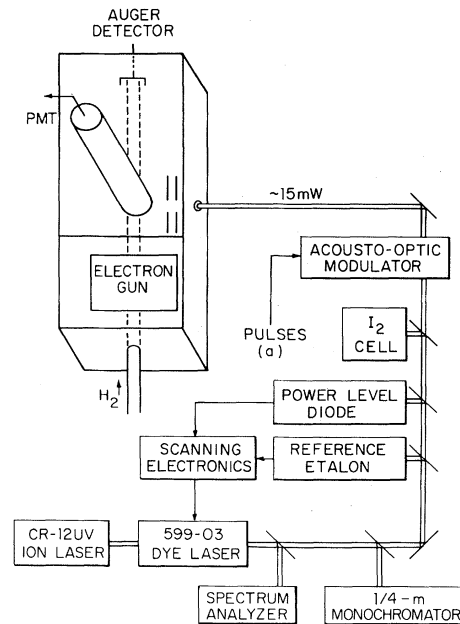


FIG. 1. Apparatus for optical spectroscopy of excited triplet states of  $H_2$ . (a) denotes pulses to modulator from fast electronics.

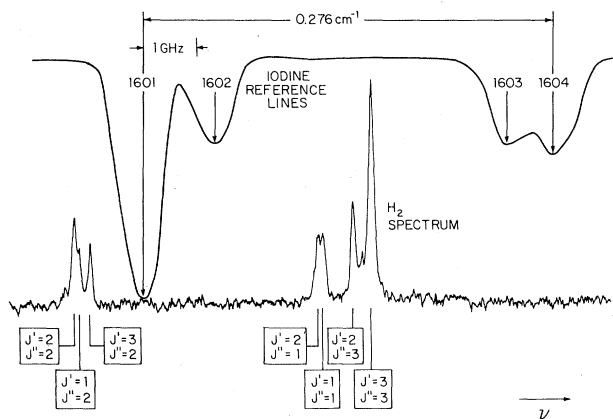


FIG. 2. 5-min cw scan showing  $I_2$  lines and Q2 branch of transition from  $c(2p)^3\Pi_u^+$ ,  $v''=0$  to  $i(3d)^3\Pi_g^+$ ,  $v'=0$ .  $J'$  denotes total angular momentum of upper state;  $J''$  denotes lower state.  $I_2$  lines are labeled with identification numbers of Ref. 9; line 1601 is at  $17\,248.4188(28)$   $\text{cm}^{-1}$ .

is 11 000 counts/sec; this includes about 4000 counts/sec of constant background. We believe that the background arises primarily from vibrationally excited metastable molecules with lifetimes of about  $100 \mu\text{sec}^{10-12}$  that decay directly under the photomultiplier. This counting rate implies a signal-to-noise ratio of 60 for a 1-sec counting time.

For measuring excited-state lifetimes, the laser is externally chopped into approximately Gaussian pulses about 10 nsec wide by an acousto-optic modulator (Isomet model No. 1250) with a repetition rate of 3–4 MHz. The fast instrumentation following the photomultiplier is essentially the same as that used earlier in this laboratory.<sup>13</sup> A time-to-amplitude converter (TAC) measures the intervals between laser pulses and single fluorescent decay photons. The TAC output is stored in a Northern NS-600 pulse height analyzer (PHA). A microcomputer system is used to process the data on-line and store them on a floppy disk. To correct for nonlinearities in the TAC and PHA, data are taken for alternate 10-sec intervals with the laser pulsed and with the laser off. After a 1-h acquisition period for a typical run, both the signal and the channel widths are corrected for the observed background on a channel-by-channel basis. Finally the average background level is subtracted from the signal.

The corrected data from a typical run are shown in Fig. 3 together with a least-squares fit by the sum of an exponential and a constant background. Even though the fit is begun at a channel

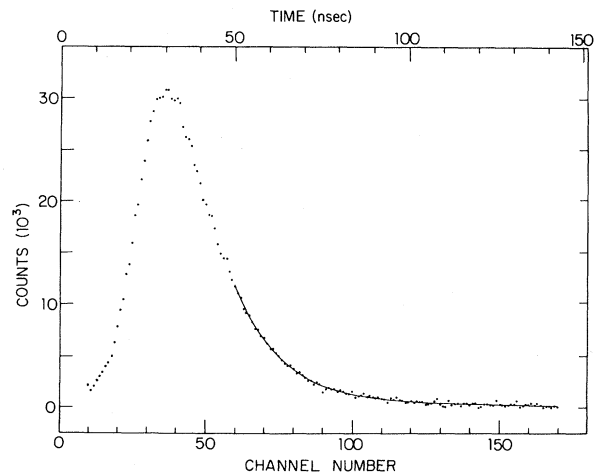


FIG. 3. Normalized fluorescent decay signal for  $i(3d)^3\Pi_g^+$ ,  $v=0$ ,  $N=2$ ,  $J=3$  (largest peak in Fig. 2). Fit is shown starting at channel 60, where laser pulse is at 1% of peak intensity.

where the laser intensity has fallen to 1% of its maximum intensity, it is necessary to correct the data to take into account the tail of the laser pulse. The following procedure was used to correct for the effects of residual laser light. The data for each run were simulated,  $S(t)$ , by numerically convoluting the measured laser pulse shape with an exponential using the expression

$$S(t) = \int dt' f(p(t'))\theta(t-t') \exp[-(t-t')/\tau].$$

Here  $f(p)$  is a function which models the power saturation behavior and  $p(t)$  is the observed average shape of the light pulse. The resulting simulated data were fitted to an exponential and the difference between the decay constant and  $\tau$  was taken as the correction to be applied to the measured lifetime. Not enough information was available to model the saturation behavior in detail for each run, and so we have chosen to use the average of the corrections obtained with no saturation and with the soft saturation expected in a simple two-level system,  $\text{signal} \propto \text{power}/(N + \text{power})$ .  $N$  was chosen to fit the experimental full width at half maximum. The difference between these two extreme models represents a potential systematic error, and is given as the error associated with the corrections. The lifetimes were converted to nanoseconds with use of the PHA calibration scheme described by Baker, Batty, and Williams.<sup>14</sup>

Table I lists the lifetimes for all fourteen levels accessible from the  $N=2$  rotational level of the metastable state in parahydrogen in vibrational

TABLE I. Lifetimes in nanoseconds of fourteen levels in the  $3s, 3d$  complex of para- $H_2$ . All measurements were made on the strongest fine-structure component except as noted. Uncertainties are one standard deviation and apply to the least significant digits shown.

Level	Fit	Correction	Result
$3s^3\Sigma_g^+$ , $\nu=0$ , $N=2$	48.8(28)	0.0(13)	48.8(31) <sup>a</sup>
$3s^3\Sigma_g^+$ , $\nu=1$ , $N=2$	18.1(12)	1.1(11)	17.0(16)
$3d^3\Sigma_g^+$ , $\nu=0$ , $N=2$	12.1( 2)	1.0( 5)	11.1( 5)
$3d^3\Sigma_g^+$ , $\nu=1$ , $N=2$	11.9( 4)	0.4( 2)	11.5( 4)
$3d^3\Pi_g^-$ , $\nu=0$ , $N=1$	14.2(10)	0.8( 1)	13.5(10)
$3d^3\Pi_g^-$ , $\nu=1$ , $N=1$	13.5(11)	0.3( 1)	13.1(11)
$3d^3\Pi_g^+$ , $\nu=0$ , $N=2$	14.0( 2)	0.6( 4)	13.5( 4)
$3d^3\Pi_g^+$ , $\nu=1$ , $N=2$	15.9(13)	0.6( 1)	15.2(13)
$3d^3\Pi_g^-$ , $\nu=0$ , $N=3$	13.6( 1)	0.6( 3)	12.9( 3) <sup>b</sup>
$3d^3\Pi_g^-$ , $\nu=0$ , $N=3$	12.7( 7)	1.0( 7)	11.6(10) <sup>c</sup>
$3d^3\Pi_g^-$ , $\nu=1$ , $N=3$	12.8( 2)	0.8( 6)	12.0( 7)
$3d^3\Delta_g^+$ , $\nu=0$ , $N=2$	16.1( 5)	0.8( 5)	15.4( 8)
$3d^3\Delta_g^+$ , $\nu=1$ , $N=2$	16.2( 8)	0.6( 4)	15.6( 9)
$3d^3\Delta_g^-$ , $\nu=0$ , $N=3$	15.5( 7)	0.7( 4)	14.8( 8)
$3d^3\Delta_g^-$ , $\nu=1$ , $N=3$	13.9(19)	1.2( 8)	12.7(20)

<sup>a</sup>The complete correction algorithm could not be applied to this state for instrumental reasons, but simulations indicate that any correction would be less than 1.3 nsec.

<sup>b</sup> $J = 4$  fine-structure component.

<sup>c</sup> $J = 3$  fine-structure component.

levels  $\nu = 0$  and  $\nu = 1$ . The calculated lifetimes for the  $3^3S$  and  $3^3D$  states of helium, which are the corresponding states in the united-atom limit, are respectively 36.4(10) and 13.9(2) nsec.<sup>15</sup> With the exception of the anomalously short lifetime for the  $\nu = 1$  vibrational level of the  $h(3s)^3\Sigma_g^+$  state, the agreement is reasonable. The fine structure for these  $H_2$  levels was studied by Lichten, Wik, and Miller<sup>8</sup>; the  $g$  factors for the  $3d$  complex were studied by Jost *et al.*<sup>16</sup> The combination of the data reported here with the fine-structure and  $g$ -factor measurements should lead to an improved understanding of the structure of the  $n = 3$  triplet complex for the hydrogen molecule.

We are currently performing a similar experiment on the  $n = 4$  states of  $H_2$ . A level-anticrossing observation of one level of the  $p(4d)^3\Sigma_g^+$  state

suggests that this state is very close to the Rydberg-like Hund's case  $d$  coupling scheme,<sup>17</sup> so that the structure of the  $4d$  states should be quite interesting. Previously no transitions to the  $4s$  state have been observed. We plan in the near future to use a second dye laser to study the  $np$  and  $nf$  Rydberg series of  $H_2$ . The great sensitivity to this technique will make feasible precise measurements on a wide variety of atomic and molecular systems with metastable states.

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