

Precision Lifetime Measurements in H₂: Disagreement with Theory

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(Received 15 September 1995)

We have measured the lifetimes of three rovibrational levels— $g^3\Sigma_g^+(v=1, N=2)$, $i^3\Pi_g^-(v=0, N=1)$, and $j^3\Delta_g^-(v=1, N=3)$ —in the $n=3$ complex of H₂ with a precision of 2%. On the basis of the first two measurements, we suggest that a previously neglected decay channel should be included in theoretical treatments and may have played an important role in an earlier experiment. Our value for the lifetime of $j^3\Delta_g^-(v=1, N=3)$ agrees well with the earlier experiment; the best theoretical estimate lies almost 50% higher.

PACS numbers: 33.70.Ca

Diatomic hydrogen is the electronically simplest neutral molecule; hence comparisons, and especially discrepancies, between theory and experiment are uniquely important in assessing our physical understanding of molecules. Unexpected discrepancies found in hydrogen necessarily raise serious questions about the reliability of results for more complicated systems. The principal conclusion of this Letter is that there exists a flaw in the understanding of the structure of low-lying bound electronic states of H₂: For at least one radiative lifetime, the best theoretical prediction lies almost 50% above our high-precision measurement.

Bound states of molecular hydrogen are classified by the principal quantum number n of the outer electron. There are two limiting regimes for bound states. For $n \leq 2$, the outer electron is close to the H₂⁺ core. It interacts strongly with the nuclei and inner electron. Such states are in harmony with the mechanical view of molecules as rotating masses connected by springs. In calculating properties of these states, the most important approximation is that both electrons are able to follow the nuclear motions, i.e., these are good “Born-Oppenheimer” states. Computational techniques have proved so successful for such states that meaningful comparisons between theory and experiment can be made to test very small QED effects [1].

The other limiting bound-state regime for H₂ describes electronic states with $n \geq 4$. In these states, the slowly moving outer electron barely interacts with the H₂⁺ core, and a picture of these states as “exotic Rydbergs” is appropriate. The “polarization model” of Eyler and Lundeen [2] starts from this perspective and has successfully described these states.

The $n=3$ states, for which we have measured radiative lifetimes, lie between these two limiting regimes. Because it is a model system for studying the breakdown of the Born-Oppenheimer approximation, the $n=3$ manifold has recently been extensively studied, both experimentally [3] and theoretically [4–7]. Most of this recent work has focused on measuring and calculating energy levels, and the current good agreement between theory and experiment suggests that the essential physics of the

$n=3$ states is fairly well understood. Our lifetime measurements indicate otherwise. The implications of this disagreement may go beyond the fact that we simply do not fully understand some bound states of diatomic hydrogen; the nuclear motion couplings (rotational and vibrational) that are responsible for the breakdown of the Born-Oppenheimer approximation in the $n=3$ manifold are also responsible for reactions in atom-atom collisions when these collisions are described in a molecular basis. Again, molecular hydrogen is the smallest system for which these couplings are important.

The high-precision measurement of radiative lifetimes in atomic systems [8]—some states have now been measured to 1/4% [9]—is a recent development in atomic physics. The advance in precision has been the result of careful attention to systematic effects; the basic techniques have been around for decades. Only recently, however, have atomic theoretical techniques developed to the point that it is worthwhile to make comparisons at the percent level. The present work represents an extension of this effort to molecular systems. While we do not yet rival the precision obtained for atomic systems—we report three values at the 2% level of precision—to our knowledge, these represent the most accurate molecular lifetime measurements to date. They are certainly good enough to identify the problem we discuss below.

In Fig. 1, we show adiabatic (clamped nuclei) potential energy curves for the four molecular electronic states making up the “ $n=3$ triplet gerade complex.” These are the *molecular* states that describe a system with an outer electron in either a $3s$ ($=h^3\Sigma_g^+$) or $3d$ ($=g^3\Sigma_g^+, i^3\Pi_g^\pm$, and $j^3\Delta_g^\pm$) atomic orbital. When nuclear motions, both rotations and vibrations, are included, the electronic states are mixed, and so the electronic character of the spectroscopic or physical rovibration states is usually some combination of Σ , Π , and Δ . The state’s label merely indicates the *dominant* component. The $3p$ molecular states are ignored because their ungerade symmetry allows them to interact with the others only *via* weak hyperfine couplings. However, as we show below, the $e^3\Sigma_u^+$, which corresponds to a $3p$ atomic orbital, is

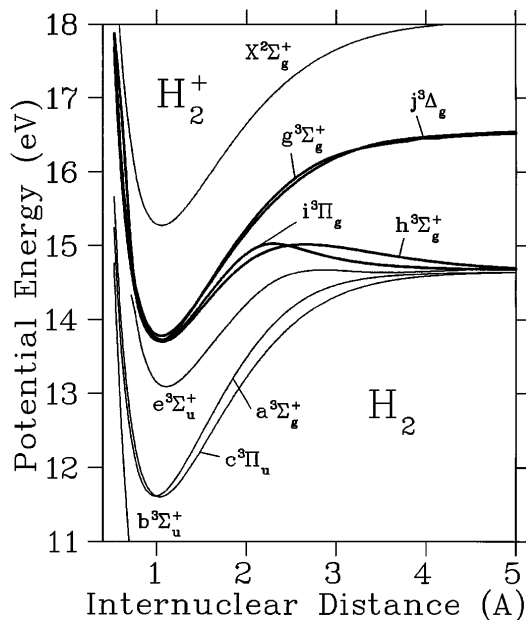


FIG. 1. Adiabatic potential energy curves of triplet H_2 . The left-hand scale gives the energy in eV with respect to the ground state $X^1\Sigma_g^+(v=0, N=0)$. The dark curves are the states in the triplet $n=3$ gerade manifold.

important to the discussion of the radiative properties of the complex.

Our interest in lifetimes in the $n=3$ manifold was piqued by a 1991 work of Schins *et al.* [7] in which high-quality structure calculations were used to “disentangle” dense spectra due to the $n=3$ manifold and to sort out the energy levels of the many individual rovibrational levels. They achieve impressive agreement between theory and experiment—in general, the calculations are able to reproduce experimental energies to better than a wave number. Motivated by the experimental data of Eyler and Pipkin [10], Schins *et al.* reported in the same paper lifetimes for several $n=3$ states. The comparison between calculations and measurements is shown in the left columns of Table I. The measurements have claimed accuracies of (5–10)%. While the calculations do reflect general features of the experimental data, the quantitative comparison is not very satisfying. In the case of the $g^3\Sigma_g^+$ states, for example, the disagreement between theory and experiment reaches almost a factor of 2. Schins *et al.* suggested the largest discrepancies may have been caused by technical limitations in the measurements.

We decided to investigate this by making more precise measurements for three of the states: $g^3\Sigma_g^+(v=1, N=2)$, $j^3\Delta_g^-(v=1, N=3)$, and $i^3\Pi_g^-(v=0, N=1)$. We picked the first two simply because the disagreements between theory and experiment were among the largest. We measured the $i^3\Pi_g^-(v=0, N=1)$ state because it is a “pure Born-Oppenheimer” state; within the

TABLE I. Lifetimes of levels in the $n=3$ triplet gerade complex of H_2 .

| ν | N | State | Experiment [10] (ns) | Theory [7] (ns) | This Work (ns) |
|-------|-----|-----------------|----------------------|-----------------|------------------|
| 0 | 2 | $h^3\Sigma_g^+$ | 48.8 | 58.8 | |
| 1 | 2 | | 17.0 | 16.0 | |
| 0 | 2 | $g^3\Sigma_g^+$ | 11.1 | 6.9 | |
| 1 | 2 | | 11.5 ± 0.4 | 6.2 | 6.05 ± 0.11 |
| 0 | 1 | $i^3\Pi_g^-$ | 13.5 ± 1.0 | 9.1 | 8.66 ± 0.16 |
| 0 | 3 | ($J=4$) | 12.9 | 10.2 | |
| 0 | 3 | ($J=3$) | 11.6 | 10.2 | |
| 1 | 1 | | 13.1 | 8.2 | |
| 1 | 3 | | 12.0 | 8.9 | |
| 0 | 2 | $i^3\Pi_g^+$ | 13.5 | 10.1 | |
| 1 | 2 | | 15.2 | 13.1 | |
| 0 | 3 | $j^3\Delta_g^-$ | 14.8 | 17.4 | |
| 1 | 3 | | 12.7 ± 2.0 | 18.5 | 12.77 ± 0.30 |
| 0 | 1 | $j^3\Delta_g^+$ | 15.4 | 16.4 | |
| 1 | 2 | | 15.6 | 19.2 | |

$n=3$ manifold, symmetry considerations do not allow the nuclear motions to mix this state and other (adiabatic) electronic states. The theoretical problem involves a simple electronic structure calculation. Given the excellent quantum chemistry codes that are available, we felt theoretical estimates should be most reliable for this state.

The basic idea of our experiment is to populate a specific rovibrational level in the $n=3$ manifold and then to measure the rate of decay of that population. A schematic of the experimental apparatus is shown in Fig. 2. The lifetime measurements take place in a molecular beam and use two pulsed dye lasers. The $n=3$ states lie more than 13 eV above the ground state of H_2 . To populate them, a beam of neutral molecular hydrogen passes through a cold-cathode-type discharge [11] that excites about 10^{-5} of the beam into long-lived metastable levels of the $c^3\Pi_u$ electronic state. These metastables serve as a platform

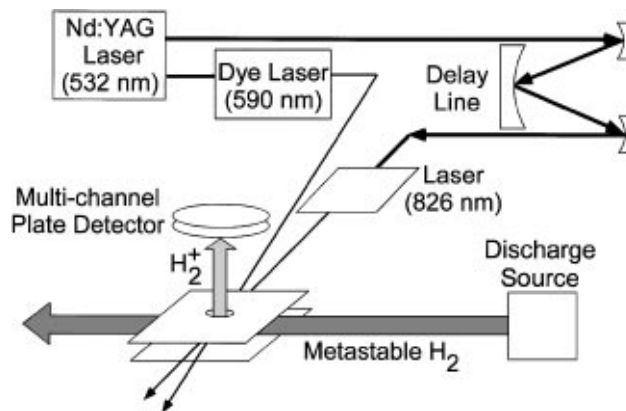


FIG. 2. The experimental apparatus. The second harmonic of a Nd:YAG laser pumps both the exciting and ionizing lasers. The delay is achieved by allowing the YAG pump beam for the ionizing laser to pass multiple times through a White cell.

TABLE II. Excitation frequencies used to populate $n = 3$ triplet gerade levels in H^2 .

| Lower metastable level | Upper $n = 3$ level | Transition frequency (cm^{-1}) |
|----------------------------|-------------------------------|--|
| $c^3\Pi_u^-(v = 0, N = 2)$ | $i^3\Pi_g^-(v = 0, N = 1)$ | 17004.3 |
| $c^3\Pi_u^-(v = 1, N = 2)$ | $g^3\Sigma_g^+(v = 1, N = 2)$ | 16515.5 |
| $c^3\Pi_u^-(v = 1, N = 2)$ | $j^3\Delta_g^-(v = 1, N = 3)$ | 17509.0 |

for laser excitations. A tunable laser with 50 μJ of energy and a wavelength around 590 nm drives a transition from one of the metastable levels and populates the individual $n = 3$ rovibrational level to be measured. The specific transitions we used for this step are recorded in Table II. After a delay that can be varied from 15 to 40 ns, a second laser of 1 to 2 mJ energy and wavelength near 826 nm ionizes a portion of the molecules remaining in the $n = 3$ level. By measuring the ionization yield as a function of the delay time between the two laser pulses, we determine the lifetime of the excited level. Figure 3 shows a representative decay curve.

Table I records the lifetime values we measured. Table III is our systematic error budget. Because our experiment seems to be free of significant sources of systematic uncertainty, we expect our results to be extremely reliable. The 2% precision of the results we report is presently limited by the statistics of the measured ionization yield signal and fluctuations in the metastable source during the measurements. The technique has the potential for making sub-1/2% measurements. To do so requires more careful monitoring of the metastable source and pulse counting of the ionization signal. In this work, we measured the integrated charge created by ions in a charge multiplier, and this signal has relatively large (random) fluctuations due to the statistics in the charge multiplication process.

We discuss our results in comparison with the previous measurements and calculations. First, our value for the pure Born-Oppenheimer state, $i^3\Pi_g^-(v = 0, N = 1)$, lies about 5%—almost three experimental standard deviations—below the theoretical prediction. This lifetime has also been independently computed by Guberman and Dalgarno [5], and the two theoretical estimates agree well. We take this discrepancy to be real and now believe it indicates the importance of a decay channel that has been underestimated in the theoretical treatments and not considered in the previous experiment. As shown in Fig. 1, there are *three* electronic states into which electric dipole radiative decay from an $i^3\Pi_g^-$ level is allowed: $b^3\Sigma_u^+$, $c^3\Pi_u$, and $e^3\Sigma_u^+$. Both theoretical treatments and the analysis of the earlier experiment include only the first two decay channels. Schins *et al.* commented that the transition rate to $e^3\Sigma_u^+$ should be about 1000 times smaller than that to $b^3\Sigma_u^+$ since spontaneous emission rates scale with the third power of the photon energy [12]. However, the $i^3\Pi_g^-(v = 0, N = 1) \Rightarrow e^3\Sigma_u^+$ transition is, to lowest order, a $3d \Rightarrow 3p$ electronic transi-

tion. Hence, the *transition moment* may be exceptionally large. We have estimated the branching ratio of spontaneous emission to $e^3\Sigma_u^+$ using the Coulomb approximation [13], and predict it to be *nearly equal* to that of the $c^3\Pi_u$ branch (which the “theory” calculations include). While our Coulomb approximation is no substitute for a realistic structure calculation, it certainly suggests that this additional radiative branch cannot be discounted.

Next, we consider our measurement of the lifetime of $g^3\Sigma_g^+(v = 1, N = 2)$. The earlier experiment-theory discrepancy was largest for this state. Our result is near, but a little lower, than the theoretical prediction. Again, including the radiative branch to $e^3\Sigma_u^+$ in the theory would improve the agreement. The $e^3\Sigma_u^+$ decay channel may also explain the large lifetime found in the earlier measurement. That experiment proceeded much like ours; an individual rovibrational level was populated by a laser excitation, and its decay in time was measured. But there is an important difference between the two experiments. While we ionize and detect the excited molecules that are left after a delay, the earlier one monitored the excited-state population by observing UV photons that presumably came from spontaneous emissions to $b^3\Sigma_u^+$. However, decay to the $e^3\Sigma_u^+$ channel leads to a slow radiative cascade that can also create an ultraviolet photon within the bandpass of that experiment. Such an alternate, long-lived decay route can have an enormous effect on the measurement of a short lifetime. As time passes, the excited state population that produces the “real” photons is

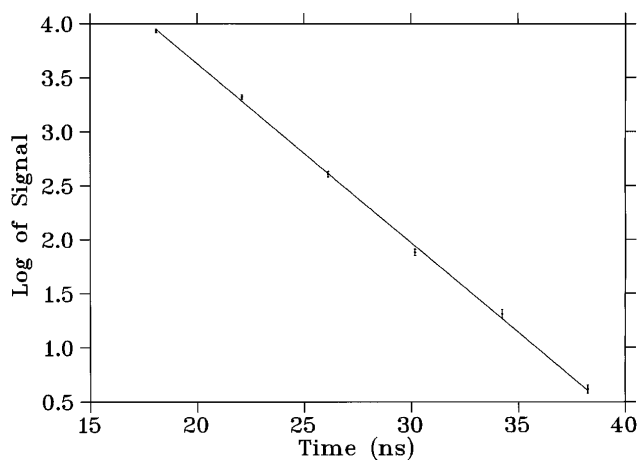


FIG. 3. A representative decay curve. This one is for $g^3\Sigma_g^+(v = 1, N = 2)$.

TABLE III. Sources of systematic error. The magnitude is the fractional contribution of the source to the uncertainty in the measured lifetime.

| Source | Magnitude |
|------------------------------|--------------------|
| Collisional quenching | 10^{-8} |
| Radiation trapping | 10^{-5} |
| Zeeman quantum beats | 10^{-3} |
| Delay line calibration | 2×10^{-3} |
| Ionization by exciting laser | 4×10^{-3} |

rapidly depleted, and the long-lived “false” channel becomes more important.

Finally, our most important result is for $j^3\Delta_g^-(v=1, N=3)$. For this level, our measured lifetime of 12.77 ns agrees very well with the previous experiment, though our error bars are almost an order of magnitude smaller. *The theoretical prediction lies 45% higher.* The agreement with the previous experiment is likely *not* coincidental for this case. The $e^3\Sigma_u^+$ decay branch, which we think proved troublesome for that experiment, may be expected to be relatively unimportant for this state. Within the Born-Oppenheimer approximation, $\Delta \rightarrow \Sigma$ transitions are forbidden; so it is only via the mixings induced by nuclear motion that the $e^3\Sigma_u^+$ channel is even accessible. The *disagreement* with theory is genuinely perplexing. The inclusion of the $e^3\Sigma_u^+$ could reduce the theoretical result a little. But as we have just argued, we expect that channel to be relatively unimportant for this state. Even in a favorable case, the additional branch could account for no more than 1/3 of the discrepancy. If this is simply the best that current theory can do, then it is important to identify the dominant source of theoretical uncertainty. An error this large in calculating the adiabatic electronic states in H_2 would surely have profound implications in theoretical predictions for more complicated systems. For making Born-Oppenheimer corrections to $j^3\Delta_g^-(v=1, N=3)$, only nuclear rotational couplings to $i^3\Pi_g^-$ are necessary, and these are much less controversial [7] than the nuclear vibrational couplings that are needed for other states. It is especially difficult to reconcile how *extremely* well the experimental energies are reproduced with how poorly this lifetime is predicted.

In conclusion, we have measured precision lifetimes to 2% for three states in the $n=3$ triplet gerade manifold of H_2 . For two of the three states, we agree well with theory. If our Coulomb-approximation estimate

of the $e^3\Sigma_u^+$ decay channel is accurate, the agreement improves, and the results of an earlier experiment may be understood. For the third state, both we and the earlier experiment show a large and puzzling disagreement with theory.

This work was supported by NSF via its Presidential Young Investigator’s program and by a seed grant from the Ohio State University. We acknowledge Terry Miller for helpful conversations and E. Hufstедler, T. Barrett, J. Fox, and D. Van Domelen for technical assistance.

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