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Double Resonance Spectroscopy of the $D^{1}\Pi_{u}^{+}$ and $B''\bar{B}^{1}\Sigma_{u}^{+}$ States Near the Third Dissociation Threshold of $H_2$

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Abstract.

Double-resonance laser spectroscopy via the $E,F^{1}\Sigma_{g}^{+}, v'=6, J'$ state was used to probe the energy region below the third dissociation limit of molecular hydrogen. Resonantly-enhanced multi-photon ionization spectra were recorded by detecting ion production as a function of energy using a time of flight mass spectrometer. Energies and line widths for the $v=14-17$ levels of the $D^{1}\Pi_{u}^{+}$ state of $H_2$ are reported and compared to experimental data obtained by using VUV synchrotron light excitation [G.D. Dickenson et al., J. Chem. Phys. 133, 144317 (2010)] and fully ab initio non-adiabatic calculations of $D^{1}\Pi_{u}^{+}$ state energies and line widths [M. Glass-Maujean et al., Phys. Rev. A 86, 052507 (2012)]. Several high vibrational levels of the $B''\bar{B}^{1}\Sigma_{u}^{+}$ state were also observed in this region. Term energies and rotational constants for the $v=67-69$ vibrational levels are reported and compared to highly accurate ro-vibrational energy level predictions from fully ab initio non-adiabatic calculations of the first six $^{1}\Sigma_{u}^{+}$ levels of $H_2$ [L.Wolniewicz, T. Orlikowski, and G.Staszewska, J. Mol. Spec. 238, 118 (2006)]. While additional observed transitions can be assigned to other states, several unassigned features in the spectra highlight the need for a fully integrated theoretical treatment of dissociation and ionization to understand the complex pattern of highly vibrationally excited states expected in this region.

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1. Introduction

Dissociation by photoabsorption is an important phenomenon in many physical environments. Observations of the $(3p\pi)D^{1}\Pi_{u}^{+}$ state of molecular hydrogen in particular
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has played an important role in the development of our understanding of molecular
dissociation and has provided a benchmark example for testing theoretical approaches
[1–5]. An excellent summary of the experimental observations of the $D^1\Pi_u$ state
preformed to date [6–12] and the theoretical techniques used to calculate predissociation
rates has been provided by Glass-Maujean et al. [13]. There they report on new \textit{ab initio}
non-adiabatic calculations and compare their results to previous measurements,
including the most recent ones obtained by using photoabsorption of synchrotron
radiation [14].

Here, we report results obtained by using a complementary technique: resonantly
enhanced, multiphoton ionization. Measurements of the line widths for the highest
vibrational levels of the $D^1\Pi_u$ state are reported and compared to the recent
experimental and theoretical results [13, 14]. The work presented here updates our
previous results on the $v = 12$ and 13 levels [15] and provides new measurements of the
$v = 14 - 17$ levels. The term energies and widths in general compare favorably and in
some cases additional assignments of higher angular momentum states can be made to
extend the tests of the latest theoretical treatments. In the course of our study of the
$v = 16$ and 17 levels of the $D^1\Pi_u$ state several transitions to the highest vibrational
levels of the $B^\prime\prime\tilde{B}^1\Sigma_u^+$ state could be identified, including the $J = 3, v = 69$ level, bound
by only 8.8 cm$^{-1}$.

2. Experiment

Double resonance spectroscopy via the $J' = 0 - 2$ rotational levels of the $E, F^1\Sigma_g^+, v' = 6$
state was used to probe the energy region below the H(1s) + H(3l) dissociation
threshold. Ionization spectra were obtained by monitoring the production of atomic
hydrogen ions using a time of flight mass spectrometer. The experimental arrangement
has been described in detail previously [16]. Briefly, two pulsed Nd:YAG-pumped dye
lasers and a vacuum chamber housing a pulsed-valve molecular beam source and a time
of flight mass spectrometer were used to obtain double-resonance ionization spectra.
Pump light with a wavelength near 193 nm is used to excite $E, F^1\Sigma_g^+, v' = 6, J' = 0 - 2 \leftarrow X^1\Sigma_g^+, v'' = 0, J'' = 0 - 2$ two-photon transitions. This light was generated by
sum-frequency mixing in BBO the fourth harmonic of Nd:YAG laser light at 266 nm
with the output of a pumped dye laser operated at $\sim 705$ nm. Probe laser output at
665 – 695 nm from the second dye laser was frequency doubled in BBO and then used
to excite single photon transitions from the $E, F^1\Sigma_g^+$ state to the states of interest as
depicted in Figure 1.

A collision-free beam of molecular hydrogen is produced by using a supersonic
expansion of pure H$_2$ from a solenoid-driven pulsed valve. Counter-propagating pump
and probe light pulses crossed the molecular beam in an interaction region located
between two electric field plates. The pump light pulses were typically on the order of
50 $\mu$J, and focused into the chamber with a 50-cm lens. Probe light pulses were focused
into the chamber with a 30-cm lens to a spot size of $\sim 100$ $\mu$m. Ions generated by
Double Resonance Spectroscopy Near the Third Dissociation Threshold of $H_2$

Figure 1. Probe excitation scheme and adiabatic potential energy curves of the states of interest [18].

The two-colour process were accelerated into the time of flight mass spectrometer by a pulsed electric field of 125 V/cm applied across the plates. A time delay of 40 ns was introduced between the pump and probe laser pulses to distinguish ions produced by the pump beam alone, and those produced by two-colour resonant excitation. Spectra are produced by scanning the frequency of the probe light while monitoring the production of $H^+$ ions by using a boxcar integrator with a timed gate set to collect the ions. The optogalvanic effect in argon provides reference transitions at known energies and an etalon provides an independent measure of the linearity of the wavelength scans. Both are used to provide calibrated probe laser wavelengths. The energy and width uncertainties reported in the next section are standard deviations observed from data taken from multiple scans. They reflect the uncertainty associated with the calibration peaks, the statistical uncertainties of peak fits to the spectral features, and remaining scan energy nonlinearities in the spectra. Reported total energies are referenced to the $X^1\Sigma^+_g, v'' = 0$ state ground state by using the known $E, F^1\Sigma^+_g, v' = 6$ transition energies [17].

3. Results and Discussion

In Figure 2 spectra excited from the $J' = 0, 1, \text{and } 2$ rotational levels of the $E, F^1\Sigma^+_g, v' = 6$ state in the energy region just below the third dissociation limit are shown. The predominant features in the spectra are $R(J')$ transitions to the $B''B^1\Sigma^+_g$ state, which are expected for a $\Sigma-\Sigma$ transition and are characterized by small rotational constants. In comparison, transitions to the $D^1\Pi_u^+$ state are relatively weaker and in several cases obscured by other transitions, due in part by their broad widths, especially for higher $J$-values. Also seen in the spectra are transitions to vibrationally excited electronic Rydberg states.

Figure 3 displays higher energy resolution spectra just below the threshold. Here several blended peaks in Figure 2 are resolved. Energies and line widths for the $D^1\Pi_u^+$ state were extracted by making fits of a Beutler-Fano profile to the observed peaks [20].
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Figure 2. $H^+$ ion yield as a function of total energy in the region below the third dissociation limit at 133610.15 cm$^{-1}$. The three spectra correspond to signals obtained via excitation of the $E, F^1\Sigma^+_u, v'=6, J'=0-2$ levels, respectively.

Figure 4 provides an example. Reported line widths are corrected to account for the bandwidth of the probe laser light measured to be 0.34 cm$^{-1}$. Profiles were measured at multiple probe pulse intensities in the range of 30 $\mu$J to 1 mJ per pulse by using neutral density filters to attenuate the probe laser beam. The behaviour of the line width as a function of the probe laser intensity was used to find an equivalent zero-intensity line width by linear extrapolation.

Measured term energies and predissociation widths for the $D^1\Pi_u^+, v = 14-17$ levels are given in Table 1. Comparisons are made to the calculations and measurements of Glass-Maujean et al. and Dickenson et al. [13, 14]. Also presented are results obtained earlier for the $v=12$ and 13 states [15]. We have reanalyzed that data and have provided updated values for the widths of those states. The energies for the $v = 12$ and 13 states are less precisely measured than for the $v = 14-17$ levels due to scan nonlinearities that went unrecognized for the spectra taken earlier. Overall, the agreement with previously measured energies is good and within the experimental uncertainties. The agreement with the calculated values is also quite good considering that producing accurate $ab\ initio$ non-adiabatic calculations is challenging. Of interest is the possible peak assignments to the $v = 17, J = 1$ level. In Table 1 an assignment consistent with the VUV synchrotron
Double Resonance Spectroscopy Near the Third Dissociation Threshold of $H_2$

![Figure 3](image)

**Figure 3.** High energy-resolution scan of the $H^+$ ion yield just below the third dissociation limit. The energy offset is with respect to the dissociation limit at 133610.15 cm$^{-1}$. The three spectra correspond to signals obtained via excitation of the $E, F^1\Sigma_g^+, v' = 6, J' = 0 - 2$ levels.

![Figure 4](image)

**Figure 4.** Fano-profile fit to the R(0) transition of the $D^1\Pi_u^+, v = 14$ state. In this example the asymmetry parameter $q = -13$, and the line width $\Gamma = 1.8$ cm$^{-1}$ for a laser pulse intensity of $2.0 \times 10^{14}$ Watts/m$^2$.

Experimental results is made [14]. In the high resolution spectra shown in Figure 3 however, a second peak can be observed nearby at 133586.7 cm$^{-1}$. Note the energy of this feature is closer to the theoretical value of 133586.0 cm$^{-1}$ calculated by Glass-Maujean et al. for the $v = 17, J = 1$ level [13].

In contrast to the energy results, the agreement among the line width values is more variable. This can be seen in Figure 5, which provides a plot of the line width data presented in Table 1. The measured values for the $J = 1$ levels are in general in very good agreement with the calculations and the previously measured widths. For the case of $v = 13, J = 1$ our experimental value is slightly less and for $v = 14, J = 1$ both of the experimental values are less than the calculated value. For the higher $J$ levels, values for $v = 15, 16, and 17$ are in good agreement. For $v = 12$ and 13, $J = 1$ and 2, our measured widths are lower than the previous measurements. There are several significant sources of uncertainty that contribute to the experimental error.
Table 1. $D^1\Pi_u$ term energies and line widths in cm$^{-1}$. Energy uncertainties in the last significant digit are given in parentheses. $\Delta_E = \text{current} - \text{previously reported values.}$

<table>
<thead>
<tr>
<th>$v$</th>
<th>$J$</th>
<th>Term Energy</th>
<th>$\Delta_E^a$</th>
<th>$\Delta_E^b$</th>
<th>$\Gamma_{\text{obs}}$</th>
<th>$\Gamma^a$</th>
<th>$\Gamma^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>1</td>
<td>131485(2)</td>
<td>0.5, 0.7</td>
<td>2.2 ± 0.8</td>
<td>2.76 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>131533(2)</td>
<td>-0.2, 0.7</td>
<td>4.9 ± 1.0</td>
<td>— ± 7.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>131604(2)</td>
<td>1.8 -4.4</td>
<td>9.0 ± 0.8</td>
<td>— ± 13 ± 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>1</td>
<td>132210(2)</td>
<td>-1.9 -2.0</td>
<td>1.2 ± 0.4</td>
<td>2.38 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>132255(2)</td>
<td>1.6, 2.0</td>
<td>4.1 ± 0.4</td>
<td>— ± 5.7 ± 0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>133235(3)</td>
<td>3.9, 2.8</td>
<td>7.3 ± 1.1</td>
<td>— —</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>132792.3(9)</td>
<td>0.7 -0.1</td>
<td>1.5 ± 0.1</td>
<td>2.32 ± 1.5 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>—</td>
<td>— —</td>
<td>— —</td>
<td>— ± 3.7 ± 0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>—</td>
<td>— —</td>
<td>— —</td>
<td>— ± 9.5 ± 1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>133220.1(4)</td>
<td>0.6 0.8</td>
<td>1.4 ± 0.1</td>
<td>0.8 ± 0.3 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>133244.3(2)</td>
<td>0.3 0.8</td>
<td>3.3 ± 0.7</td>
<td>— ± 3.3 ± 0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>133280.5(2)</td>
<td>2.0 —</td>
<td>6.3 ± 0.3</td>
<td>— —</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>1</td>
<td>133485.1(2)</td>
<td>0.1 0.6</td>
<td>1.0 ± 0.1</td>
<td>— ± 0.8 ± 0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>133500.0(2)</td>
<td>-0.5 0.4</td>
<td>1.8 ± 0.6</td>
<td>— ± 1.8 ± 0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>133520.3(2)</td>
<td>-1.3 0.2</td>
<td>1.0 ± 0.8</td>
<td>— ± 2.6 ± 0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>1</td>
<td>133587.7(6)</td>
<td>1.7 -0.1</td>
<td>0.4 ± 1.0</td>
<td>— ± 0.5 ± 0.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Calculated Ref. [13]

$^b$ Measured Ref. [14]. Energy uncertainties reported as 0.35 cm$^{-1}$.

bars. The largest contribution comes from estimating the uncertainty associated with extrapolating the line widths measured at several different probe light intensities to an equivalent zero intensity value. We used a linear extrapolation, appropriate for a one-photon transition. The observed patterns in the width data can also be considered. The predissociation of the $D^1\Pi_u$ state is due to nonadiabatic couplings with the $(3p\sigma)B''^1\Sigma_u^+$ state at short range. This type of coupling scales as $J(J+1)$ and should therefore lead to widths that scale similarly. It appears the two experimental findings agree on the coupling strength for $v = 15$, for example. However, for $v = 12$ and 13, the results reported here indicate a slightly weaker coupling than the results of Dickenson et al. [14]. Calculations of widths for higher $J$ values could help resolve the discrepancy.

Measured term energies and rotational constants for the $B''B^1\Sigma_u^+$, $v = 67 - 69$ are given in Table 2. The total energies for these levels compare well with the theoretical predictions of L. Wolniewicz, T. Orlikowski, and G. Staszewska for the $v = 67$ and 68 vibrational levels, including their rotational dependences [18]. A consistent, small difference of $-3.1$ cm$^{-1}$ on average is observed. While a calculated energy for the $v = 69$ level was not predicted, extrapolation of the lower-$v$ energy values appears to allow for one additional vibrational level below the dissociation threshold, which we indeed observe. To our knowledge, these are the first reported experimental measurements of the highest lying vibrational levels of the $B''B^1\Sigma_u^+$ state. Additional transitions have been observed that can also be attributed to levels of the $B''B^1\Sigma_u^+$ state in the energy region between the new measurements presented here and our previously reported
Figure 5. Observed and calculated linewidths reported in Table 1. Open circles represent calculated \( J = 1 \) values [13], solid symbols represent current observations, and other open symbols represent previous experimental values [14]. Triangles represent \( J = 1 \) (blue) levels, squares represent \( J = 2 \) (red) levels, and diamonds represent \( J = 3 \) (green) levels.

Table 2. \( B''B^1\Sigma_u^+ \) term energies and rotational constants in \( \text{cm}^{-1} \). Energy uncertainties in the last significant digit are given in parentheses. \( \Delta = \text{observed} - \text{theoretical} \) values.

<table>
<thead>
<tr>
<th>( v )</th>
<th>( J )</th>
<th>Term Energy</th>
<th>( B_v )</th>
<th>( \Delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>67</td>
<td>0</td>
<td>133425.7(4)</td>
<td>1.5 ± 0.1</td>
<td>-2.9</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>133427.4(2)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>133433.0(4)</td>
<td>-3.0</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>133442.2(2)</td>
<td>-3.3</td>
<td>—</td>
</tr>
<tr>
<td>68</td>
<td>0</td>
<td>133514.0(3)</td>
<td>1.2 ± 0.1</td>
<td>-3.0</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>133515.0(2)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>133518.8(2)</td>
<td>-3.4</td>
<td>—</td>
</tr>
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<td></td>
<td>3</td>
<td>133526.6(2)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>69</td>
<td>0</td>
<td>133595.4(2)</td>
<td>0.5 ± 0.1</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>133596.3(2)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>133597.2(3)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>133601.4(2)</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

\( ^a \) Ref. [18] and supplementary data files.

measurements for \( v = 17 - 50 \) [19]. The analysis of these intermediate \( v \)-values will be the subject of a separate publication.

Also present in the reported spectra are transitions that can be assigned to various electronic Rydberg states. Proposed assignments were aided by the results of Glass-Maujean et al. [21–23] who made measurements and calculations of the \( J = 1 \) para and \( J = 2 \) ortho levels of the \( v = 0 \) to \( 6, np \) singlet Rydberg series in \( \text{H}_2 \). The assignments are listed in Table 3 along with the term energies of several additional observed transitions, denoted with an asterisk in Figures 2 and 3. Note the broad lineshapes of the transitions assigned to the \( 12p2 \) and \( 11p3, v = 5 \) Rydberg levels. The
Table 3. Additional peak energies and proposed assignments. The first column denotes the \( J' \) value of the intermediate \( E,F^1\Sigma_u^+, v' = 6 \) state. Energies are in cm\(^{-1}\). Energy uncertainties in the last significant digit are given in parentheses. \( \Delta = \text{current} - \text{literature values.} \)

<table>
<thead>
<tr>
<th>( J' )</th>
<th>Term</th>
<th>Energy ( (\text{cm}^{-1}) )</th>
<th>State</th>
<th>( \Delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>133420.4(6)</td>
<td>( D'^1\Pi_u^+ ), ( v = 9, J = 2 )</td>
<td>-5.1(^{\text{c}} )</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>133459.8(2)</td>
<td>12p2, ( v = 5, J = 1 )</td>
<td>-1.9(^{\text{a}} )</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>133471.2(4)</td>
<td>11p3, ( v = 5, J = 2 )</td>
<td>-0.5(^{\text{b}} )</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>133485.4(3)</td>
<td>unassigned</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>0, 2</td>
<td>133493.4(4)</td>
<td>unassigned</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>133508.4(4)</td>
<td>unassigned</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>133553.9(4)</td>
<td>unassigned</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>0, 2</td>
<td>133580.7(2)</td>
<td>( 4^1\Sigma_u^+, v = 13, J = 1 )</td>
<td>2.4(^{\text{d}} )</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>133586.7(2)</td>
<td>unassigned</td>
<td>—</td>
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<tr>
<td>0, 2</td>
<td>133588.9(2)</td>
<td>unassigned</td>
<td>—</td>
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<tr>
<td>2</td>
<td>133590.7(2)</td>
<td>unassigned</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>133591.0(2)</td>
<td>14p1, ( v = 5, J = 2 )</td>
<td>-1.0(^{\text{b}} )</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>133604.9(5)</td>
<td>13p2, ( v = 5, J = 1 )</td>
<td>1.3(^{\text{a}} )</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>133641.1(2)</td>
<td>12p3, ( v = 5, J = 2 )</td>
<td>2.9(^{\text{b}} )</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) Ref. [22]  
\(^{b}\) Ref. [21]  
\(^{c}\) Ref. [18]  
\(^{d}\) Ref. [25]  
\(^{e}\) Ref. [24]

widths compare well with the calculations of Refs [21,22]. The feature observed via the \( J' = 2 \) level of the \( E,F^1\Sigma_u^+, v' = 6 \) state at an energy of 133553.9 cm\(^{-1}\) is quite strong. From the \( J' = 2 \) level transitions to both the \( np2 \) and \( np4 \) Rydberg series are possible. No assignment could be made based on the previous measurements and calculations of the \( np2 \) series however. To investigate whether assignments to members of the \( np4 \) series might be possible we calculated energy levels for this series following the MQDT procedure of Dehmer and Chupka [26], (which is similar to the energy determinations of Glass-Maujean et al. [23], except that a constant quantum defect function for a given \( v \)-value was used). Again, none was found to be satisfactory.

The state observed via the \( J' = 1 \) level of the \( E,F^1\Sigma_u^+, v' = 6 \) state at an energy of 133420.4 cm\(^{-1}\) matches within uncertainties to the \( D'\Pi_u^+, v = 9, J = 2 \) state observed by Glass-Maujean et al. [24]. The \( J = 3 \) level which one would also expect in excitation from the \( J' = 2 \) level may or may not be present. Its energy is expected to be in the region of the \( v = 68, J = 1 \) level of the \( B'' \bar{B}'\Sigma_u^+ \) state and it may be obscured. The transition observed via the \( J' = 0 \) level of the \( E,F^1\Sigma_u^+, v' = 6 \) state at an energy of 133580.7 cm\(^{-1}\) may be an observation of the theoretically predicted \( 4^1\Sigma_u^+, v = 13, J = 1 \) level [25]. If so, it represents an outer well state predicted to have a rotational constant of 1.74 cm\(^{-1}\) with higher rotational levels expected in the region of the \( v = 17, J = 2 \) level of the \( D'\Pi_u^+ \) state, and therefore they too may be unresolved. In general, in this
complex and dense region of the spectrum of H$_2$ definitive assignments of the observed features to the high vibrationally excited states expected in this energy region await the guidance of an integrated theoretical treatment of the non-adiabatic interactions leading to both ionization and dissociation.

4. Conclusion

Double-resonance laser spectroscopy via the $E, F^{1}\Sigma_{g}^{+}, v' = 6, J'$ state was used to probe the energy region below the third dissociation limit of molecular hydrogen. Energies and linewidths for the $v = 14 - 17$ levels of the $D^{3}\Pi_{u}^{+}$ state of H$_2$ are reported and compare favorably to the experimental data of Dickenson et al. [14] and the fully ab initio non-adiabatic calculations of Glass-Maujean et al. [13]. The highest bound vibrational level of the $B''^{2}\Sigma_{u}^{+}$ state was observed and energies and rotational constants for the $v = 67 - 69$ levels are reported for the first time. Additional observed transitions were assigned to electronic Rydberg states; however, the complexities of the spectra in this region and the difficulties associated with precise theoretical calculations at these high energies and large internuclear separations make definitive assignments for all of the observed transitions in this region a challenge. Improved theoretical techniques are needed to address the extreme conditions of high excitation and long-range internuclear separations present near this dissociation threshold.

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6. References

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