PERTURBATION FACILITATED OPTICAL OPTICAL DOUBLE RESONANCE INVESTIGATION OF THE QUINTET MANIFOLD OF C$_2$ BY APPLYING TWO-COLOR FOUR-WAVE MIXING

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Perturbation effects open ways to observe dark states (with small transitions moments) on optically more accessible bright states. The spectroscopically dark states can be dynamically active and they can play an important role in energy flow processes governing intra- and intermolecular energy redistribution.
C₂ role not well understood in contrast to other diatomic OH, CH
\[ X^1\Sigma_g^+ \] more reactive than \[ a^3\Pi_u \] (diff: 700 cm⁻¹)
molecular build-up reactions in flames (not included in present combustion models)
relative importance of \[ X^1\Sigma_g^+ \] and \[ a^3\Pi_u \] not established
chemistry of excited C₂*? (chemiluminescence is important to characterize combustion, i.e. local stochiometry, heat release, low-cost sensors for active combustion control)
highly localized: flame front marker as CH but in a different wavelength range
distinguish four C₂ species: \[ X^1\Sigma_g^+ \], \[ a^3\Pi_u \], \[ d^3\Pi_g \], \[ 1^5\Pi_g \]
Experimental
double-resonant four-wave mixing
Discharge source

Cathodes
Ceramic insulator
Grounded anode
Ceramic insulator
Multi-channel body
Pulsed valve

Results
Swan-band around 467 nm (omitting perturbation)

\[ d^3\Pi_g, v' = 4 \]

\[ \delta E \]

\[ \Delta E \]

\[ \delta E \]

\[ b^3\Sigma_g^-, v' = 16 \]

- \[ E = \frac{1}{2}(E_1 + E_2) \pm \frac{1}{2}\sqrt{4W_{12}^2 + \Delta E^2} \]

- \[ \delta E = \pm \frac{1}{2}(\sqrt{4W_{12}^2 + \Delta E^2} - \Delta E) \]

- The spectral separation observed between perturbed and perturbing transitions is given by \[ 2\delta E + \Delta E \], where \( \Delta E \) is the separation of the two levels in the absence of perturbation and \( \delta E \) is the displacement of the levels resulting from the perturbation.
Example: Deperturbation of the $v' = 4$ level
Deperturbation by TC-RFWM

\[ v' = 2 \]

\[ v'' = 3 \]

\[ J''' = 3, F_3''' \]
Deperturbation by TC-RFWM

\( d^3 \Pi_g \)

\( v' = 4 \)

\( v' = 2 \)

\( v'' = 3 \)

\( (2, 3) R_3(4) \)

\( (4, 3) R_3(4) \)

\( J'' = 3, F'' \)
Deperturbation by TC-RFWM

\[ d \, ^3\Pi_g \]
\[ v' = 4 \]

\[ b \, ^3\Sigma_g^- \]
\[ v' = 16 \]

\[ v' = 2 \]

\[ \nu'' = 3 \]

\[ (2, 3) R_3(4) \]

\[ (4, 3) R_3(4) \]

\[ (16, 3) \, ^3\Pi_3 \]

\[ J'' = 3, F_3'' \]
<table>
<thead>
<tr>
<th>R₁(J)</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₂(J)</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>R₃(J)</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>9</td>
<td>10</td>
</tr>
</tbody>
</table>

DFWM

21380  21400  21420
wavenumber (cm⁻¹)
| R_{3}(J) | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| R_{2}(J) | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| R_{1}(J) | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |

DFWM

Simulation w/o perturbation

wavenumber (cm\(^{-1}\))

21380

21400

21420
$R_s(J)$
$R_a(J)$
$R_i(J)$

$\nu' = 2$
$\nu'' = 3$

$J'' = 3, F_3''$

$21380$  $21400$  $21420$

wavenumber (cm$^{-1}$)

DFWM

Simulation w/o perturbation

$R^3\Pi_o$
$\nu' = 4$

$b^3\Sigma_g^-$
$\nu' = 16$

$(2,3)R_3(4)$
$(4,3)R_3(4)$
$(16,3)y_2(4)$

ISMS, Champaign - 2014
$d^3\Pi_g, v' = 4$

$b^3\Sigma_g^-, v' = 16$
Table 2
Optimized molecular constants for the perturbing $b^3 \Sigma^+_g, \nu = 16$ state and parameters resulting from the interaction with the $d^3 \Pi_g, \nu' = 4$ state. All values are in cm$^{-1}$. The origin, T, is relative to the $a^3 \Pi_u, \nu^u = 0$ level. Numbers in parenthesis are one standard deviation.

<table>
<thead>
<tr>
<th>State</th>
<th>Parameter</th>
<th>Optimized w/o extra lines</th>
<th>Optimized value</th>
<th>Extrapolated$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b^3 \Sigma^+_g, \nu' = 16$</td>
<td>$T$</td>
<td>26192.081(72)</td>
<td>26191.865(14)</td>
<td>26187.074</td>
</tr>
<tr>
<td></td>
<td>$B$</td>
<td>1.22508(98)</td>
<td>1.22858(15)</td>
<td>1.22824</td>
</tr>
<tr>
<td></td>
<td>$D \times 10^6$</td>
<td>6.4351$^b$</td>
<td>6.4351$^b$</td>
<td>6.4351$^b$</td>
</tr>
<tr>
<td></td>
<td>$\lambda$</td>
<td>0.32(11)</td>
<td>0.172(18)</td>
<td>0.155</td>
</tr>
<tr>
<td>$\langle d^3 \Pi_g, \nu' = 4</td>
<td>H_{SO}</td>
<td>b^3 \Sigma^+_g, \nu' = 16 \rangle$</td>
<td>$-0.6120(167)$</td>
<td>$-0.6401(86)$</td>
</tr>
<tr>
<td>$\langle d^3 \Pi_g, \nu' = 4</td>
<td>B_{L+}</td>
<td>b^3 \Sigma^+_g, \nu' = 16 \rangle$</td>
<td>0.2459(13)</td>
<td>0.24737(61)</td>
</tr>
</tbody>
</table>

$^a$ Ref. [37].

$^b$ Fixed at the extrapolated value.
Deperturbation by TC-RFWM

- **Spectral simplification by intermediate level labeling** provides a powerful tool to assign complex one-color spectra.

- **High dynamic range** up to S/N of $10^9$ allows observation of the extremely weak perturbing levels.
the $d^3\Pi_g, v' = 6$ state

fixed laser at 18319.49 cm$^{-1}$

(4,5)R1(5)

DFWM
$5 \pi_g$

fixed laser at 18319.49 cm$^{-1}$

(4,5)R1(5)

DFWM
Symmetry (Jeven/Jodd): \( \oplus \): \( (+/-) \)  \( \ominus \): \( (-/+\) \)

Measured energy levels

\[ b^3 \Sigma_g^- \]

\[ d^3 \Pi_g \]

\[ 1^5 \Pi_g \]
# Optimized molecular parameters

<table>
<thead>
<tr>
<th>State</th>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1^5 \Pi_g)</td>
<td>T</td>
<td>29258.5922(48)</td>
<td>29941.99&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>1.14413(11)</td>
<td>1.012&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>8.9450(47)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\lambda)</td>
<td>-0.0428(23)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>o</td>
<td>-0.0744(39)</td>
<td></td>
</tr>
<tr>
<td>(b^3 \Sigma_g^-), (v = 19)</td>
<td>T</td>
<td>29442.1348(843)</td>
<td>29434.25&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>1.179368(214)</td>
<td>1.178804&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>(D \times 10^6)</td>
<td>6.5066&lt;sup&gt;c&lt;/sup&gt;</td>
<td>6.5066&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>(\lambda)</td>
<td>0.142(22)</td>
<td>0.1548&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>(d^3 \Pi_g), (v = 6)</td>
<td>T</td>
<td>29259.3736(32)</td>
<td>29259.704&lt;sup&gt;a&lt;/sup&gt;(14)</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>-12.8223(90)</td>
<td>-13.082&lt;sup&gt;a&lt;/sup&gt;(35)</td>
</tr>
<tr>
<td></td>
<td>p</td>
<td>0.00467(91)</td>
<td>0.00104&lt;sup&gt;a&lt;/sup&gt;(65)</td>
</tr>
<tr>
<td></td>
<td>q</td>
<td>-0.000964(44)</td>
<td>-0.001514&lt;sup&gt;a&lt;/sup&gt;(17)</td>
</tr>
</tbody>
</table>

\(<d^3 \Pi_1\), \(v = 6|H_{so}|1^5 \Pi_1\>)

\(<d^3 \Pi_1\), \(v = 6|H_{so}|b^3 \Sigma_g^-\), \(v = 19\>)

\(\frac{1}{\sqrt{x}}<d^3 \Pi_0\), \(v = 6|B_{L+}|b^3 \Sigma_g^-\), \(v = 19\>)

<sup>a</sup>Reference 17.

<sup>b</sup>Listed values are for \(v = 0\) in Ref. 31.

<sup>c</sup>Extrapolated from the results in Ref. 51.

Gateway states

\[
\sigma_{E,J;E',J'} \sim \sigma_{E,J;E,J'} C_{E,E'}(J')^2 \\
+ \sigma_{E',J;E',J'} C_{E,E'}(J)^2
\]

where \(\sigma_{E,J;E',J'}\) and \(\sigma_{E',J;E',J'}\) are the \(J \rightarrow J'\) purely rotation-changing cross-sections within the \(E\) and \(E'\) electronic states, resp., and \(C_{E,E'}\) is the isolated-molecule \(E\), \(J \sim E', J\) mixing coefficient.

Quintet Character

Rotational Quantum Number $J$

F<sub>1</sub> F<sub>2</sub> F<sub>3</sub>

- $c$
- $f$
Gateway Mediated Intersystem Crossing of $\text{C}_2$ by Two-Color Resonant Four-Wave Mixing
$1^5 \Pi_u, v = 0$  

$1^5 \Pi_g, v = 0$

$d^3 \Pi_g, v = 6$

$\alpha^3 \Pi_u, v = 5$

PROBE/SIGNAL

PUMP

$|f\rangle$

$|i\rangle$

$|g\rangle$
$1^5\Pi_u, v = 0$

$1^5\Pi_g, v = 0$

$d^3\Pi_g, v = 6$

$a^3\Pi_u, v = 5$
Measured Energy Levels

\[ \nu = 0 \]

\[ 1^5\Pi_u, \nu = 0 \]

Rotational Quantum Number \( J \)

Relative energy - \( 1.75(J+1) \) cm\(^{-1} \)

T, B, A, \( \lambda \), \( \delta \), D
Ab initio: MRCI + Davidson and Core-Valence
Double-resonance investigations by Two-Color Resonant Four-Wave Mixing is advantageous to disentangle complex spectra:

- Characterization of perturbations in $C_2$ (and $C_3$)
- Observation of dark states
- Intersystem crossing via gateway states to investigate states that cannot be accessed by direct optical transitions due to the stringent $\Delta S = 0$ selection rule