LETTER TO THE EDITOR

Radiofrequency–Infrared Double-Resonance Spectroscopy of OsO₄ Using Microwave Modulation Sidebands on CO₂ Laser Lines

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A mixing of microwave radiation and the infrared radiation from a CO₂ laser in a CdTe crystal generates frequency tunable coherent infrared radiation with medium power (∼0.5 mW) and with high spectral purity (1, 2). Recent successful application of this infrared source for sub-Doppler spectroscopy (3–5) has demonstrated that the radiation is sufficiently powerful to saturate molecular transitions and thus can also be used for double-resonance experiments. This letter reports the first such application to the ν₃ fundamental band of OsO₄ in order to determine the splitting constants in the excited state (Z₃) as well as in the ground state (D₃). This experiment is similar to those conducted by Takami on CF₄ (6) and SiH₄ (7) for which he used a diode laser as the frequency-tunable infrared source.

The infrared active stretching fundamental ν₃ band of OsO₄ at 961 cm⁻¹ overlaps with the CO₂ laser transitions around 10.4 μm. This band was studied extensively by McDowell et al. (8) with tunable diode lasers. More recently, vibrationally induced quadrupole hyperfine structures were observed by Bordé et al. (9) and by Scappini et al. (5). In the course of these studies many vibration–rotation transitions were observed which showed closely spaced C₃ᵥ clusters transitions. This suggested the possibility of an rf–ir double-resonance experiment. The A₁ and A₂ components of the clusters are connected by the vibration-induced dipole moment in the excited state (J₀) and by the rotation-induced dipole moment in the ground state (J₁).

The infrared source used is described elsewhere (3, 5). The absorption cell is 2 m long and contains OsO₄ with a pressure of a few milliTorr. Radiofrequency power of about 1 W, amplitude modulated at 10 kHz, was applied to the molecule. The energy level scheme and the observed double-resonance signal are shown in Figs. 1 and 2, respectively. The signal given in Fig. 2 corresponds to the A₁(3) ↔ A₂(3) ΔJ = 0, and ΔF = 0 rf transition in the ν₃ state with J = 25 and R = 24. Note that ¹⁸⁰OsO₄ with natural abundance (16%) was used for this experiment. Other radiofrequency transitions, i.e., the ΔF = ±1 transitions in the excited state which would show the hyperfine pattern and the A₁(3) ↔ A₂(3) transition in the ground state which would appear at lower rf frequency, were not observed because of their much lower intensity (by a factor of ∼10³).

While we could not determine the signal from the ν₃ transition, we could do so by comparison with the direct infrared transitions (9) with the other hyperfine structures observed in Fig. 3. Table 1 shows the result: the ground state fraction of the excited state splitting is the same as that of Dorney and Watson's convention.

These results give the tensor σ₉ for the excited state using the formula

![Diagram](image-url)

Fig. 1. Energy level scheme involving the ν₃ transition. The quadrupole hyperfine structure of the ν₃ state was observed in Fig. 3 which were observed by the technique.

![Diagram](image-url)

Fig. 2. The double-resonance signal corresponding to the A₁(3) ↔ A₂(3) transition in the ground state which was not observed because of their much lower intensity (by a factor of ∼10³).

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Letter to the Editor

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radiation from a CO₂ laser in infrared radiation with medium l. Recent successful application 3–5] has demonstrated that the r transitions and thus can also reports the first such application mine the splitting constants in D₉. This experiment is similar (7) for which he used a diode 1 of OsO₄ at 961 cm⁻¹ overlaps s band was studied extensively recently, vibrationally induced ordé et al. (9) and by Scappini ation–rotation transitions were transitions. This suggested the The A₁ and A₂ components of dipole moment in the excited nt in the ground state (11).

Fig. 1. Energy level scheme involving the v₁R(24) transition of OsO₄ used for the double-resonance experiment. The quadrupole hyperfine structure in the v₁ state (ėQ = 7.1 MHz (5)) is shown; the structure in the ground state due to rotation-induced ėQ is not shown. The bold arrows indicate r transitions, of which only the one in the v₁ state was observed. The thin arrows show the infrared transitions (shown later in Fig. 3) which were observed by the technique of Lamb dip spectroscopy.

While we could not determine the splitting in the ground state directly from the rf transition, we could do so by combining the rf transition in the excited state with the direct infrared transitions (shown in Fig. 1 with thin arrows). The two transitions with their hyperfine structures observed by the Lamb dip technique (5) are shown in Fig. 3. Table 1 shows the results for three transitions for OsO₄ and OsO₄. It is remarkable that the ground state splitting due to centrifugal distortion is a sizable fraction of the excited state splitting for both cases because of large J values. We use Dorney and Watson’s convention (13) for designating levels.

These results give the tensor splitting constants Dₙ in the ground state and Zₙ in the excited state using the formulae (13, 14)

Fig. 2. The double-resonance signal corresponding to the v₁ J = 25 R = 24 A₁⁽²⁾ - A₂⁽₂⁾ ΔF = 0 transitions in OsO₄. The microwave modulation sideband generated on the 10 R(8) laser line of the CO₂ laser is kept on the R(24) A₁⁽²⁾ transition, and the amplitude-modulated radiofrequency was swept from 2.6 to 4 MHz. A time constant of 0.3 sec was used.

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Fig. 3. The sub-Doppler saturation Lamb dips of the $\nu_5 R(24) A^{(1)}_2$ and $A^{(2)}$ transitions of $^{189}$OsO$_4$. The quartet for each transition is caused by the vibration-induced nuclear quadrupole coupling in the $\nu_3$ state (16). The splitting between the $A^{(1)}_2$ and $A^{(2)}$ components of the cluster and the excited state splitting observed in Fig. 2 gives the splitting in the ground state.

$$\nu(v = 0) = D_{ij}[f(J, \kappa_1) - f(J, \kappa_2)]$$

$$\nu(v = 1) = Z_{3i}[O_{pp33}(J, \kappa_1) - O_{pp33}(J, \kappa_2)].$$

The values of $f(J, \kappa)$ are calculated from Krohn's table (15) using the relation

$$f(J, \kappa) = -[3(2J + 5)/28(2J - 4)!]^{1/2}F(J, \kappa),$$

and $O_{pp33}(J, \kappa)$ are calculated by multiplying $f(R, \kappa)$ with $1/R(2R - 1)$ or $1/(R + 1)(2R + 3)$ for $R = R - 1$ and $R = R + 1$, respectively (16).

The obtained values of $D_i$ and $Z_{3i}$ are summarized in Table II, together with the value of $Z_{3i}$ obtained by McDowell et al. (8) and the calculated value of $D_i$. The Hecht's parameter $Z_{3i}$ is related to the parameter $g_3$ used by McDowell et al. (8) and $a_{224}$ used by Takami (6, 7) by the relation (17)

$$Z_{3i} = \sqrt{7/3}g_3 = 2a_{224}.$$ 

The calculated value of $D_i$ was obtained using Hecht's relation (17)

$$D_i = B^3 \left[ \frac{1}{5} \frac{\xi_2^2}{(\xi_3^2 - \xi_4^2)} \right],$$

with $\nu_2 = 332.9$ cm$^{-1}$, $\nu_3 = 960.7$ cm$^{-1}$, $\nu_4 = 329.0$ cm$^{-1}$, $B = 1.349$ cm$^{-1}$, and

$$\xi_3^2 = (1 - \xi_4^2) = \frac{2}{3} (1 - \xi_3) = 0.582.$$

from McDowell's paper (8).

The values of $Z_{3i}$ for the two isotopic species do not agree with each other within the uncertainty. This may be due to a perturbation between the $\nu_3$ and other vibrational states. Takami noted that $Z_{3i}$ differs by a factor of as much as 3 between $^{12}$CF$_4$ and $^{13}$CF$_4$ due to the perturbation between $Z_{3i}$ and that obtained to their neglect of $D_i$ in the analysis, value within the uncertainty.

Tetrahedral Splitting Constants

<table>
<thead>
<tr>
<th>Transitions</th>
<th>189OsO$_4$</th>
<th>192OsO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R(24)$</td>
<td>$A^{(1)}_2$</td>
<td>$A^{(2)}$</td>
</tr>
<tr>
<td></td>
<td>$A^{(1)}_2$</td>
<td>$A^{(2)}$</td>
</tr>
<tr>
<td>Difference</td>
<td>$\nu_3 J = 25$ $A^{(1)}_2 - A^{(2)}$</td>
<td>$A^{(1)}_2 - A^{(2)}$</td>
</tr>
<tr>
<td></td>
<td>G.S. $J = 24$ $A^{(1)}_2 - A^{(2)}$</td>
<td>$A^{(1)}_2 - A^{(2)}$</td>
</tr>
<tr>
<td></td>
<td>$CO_2$ 10</td>
<td>10 P(10)</td>
</tr>
<tr>
<td></td>
<td>$CO_2$ 10</td>
<td>P(12)</td>
</tr>
<tr>
<td></td>
<td>$CO_2$ 10</td>
<td>P(37)</td>
</tr>
<tr>
<td>Difference</td>
<td>$\nu_3 J = 29$ $A^{(1)}_2 - A^{(2)}$</td>
<td>$A^{(1)}_2 - A^{(2)}$</td>
</tr>
<tr>
<td></td>
<td>G.S. $J = 30$ $A^{(1)}_2 - A^{(2)}$</td>
<td>$A^{(1)}_2 - A^{(2)}$</td>
</tr>
<tr>
<td>$1^{3}$CF$_4$</td>
<td>quoted uncertainties are for each value.</td>
<td></td>
</tr>
</tbody>
</table>
| $^3$Laser line frequencies a

*Quoted errors are the
TABLE I

Infrared Transitions and Differences Obtained from Sub-Doppler Spectroscopy, Radiofrequency Transitions Obtained from Double Resonance, and Ground State Splittings.

<table>
<thead>
<tr>
<th>189 OsO4</th>
<th>CO2</th>
<th>10 R(8)</th>
<th>ν2 - ν3 (MHz)</th>
<th>ν4 - ν3 (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>29011133.014</td>
<td>467.292437(1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>192 OsO4</td>
<td>ν3 P(30) A(3) - A(2)</td>
<td>15331.111</td>
<td>951.70366(1)</td>
<td></td>
</tr>
<tr>
<td>2851626.673</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3) and A(2) transitions of 189 OsO4. The ar quadrupole coupling in the ν3 state and the excited state splitting observed

\[ J = 2I + 1 \]

\[ I^2 F(J, k) \]

\[ h/2R(2R - 1) \] or \( 1/(R + 1)(2R \)

in Table II, together with the e calculated value of \( D_i \). The ed by McDowell et al. (8) and

\[ m, B = 1.349 \text{ cm}^{-1} \]

0.582.

it agree with each other within even the ν3 and other vibrational much as 3 between 12 CF4 and

13 CF4 due to the perturbation between the ν3 and the 2ν4 states. Our observed values of ZNi are smaller than that obtained by McDowell et al. (8), but this is probably due to their neglect of \( D_i \) in the analysis. The observed value of \( D_i \) agrees with the calculated value within the uncertainty.

TABLE II

Tetrahedral Splitting Constants in the Excited State (ZNi) and Ground State (Di).

<table>
<thead>
<tr>
<th>Transitions</th>
<th>ZNi(kHz)</th>
<th>D_i(kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>189 OsO4 R(24)</td>
<td>456 ± 2</td>
<td>72 ± 6</td>
</tr>
<tr>
<td>192 OsO4 P(30)</td>
<td>450 ± 1</td>
<td>80 ± 26</td>
</tr>
<tr>
<td>Ref. (8)</td>
<td>514 ± 1</td>
<td></td>
</tr>
<tr>
<td>Theoretical</td>
<td>67</td>
<td></td>
</tr>
</tbody>
</table>

*Quoted errors are three times the standard deviation.
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In conclusion, this experiment demonstrates the usefulness of the new infrared source for double-resonance experiments. The combination of the rf transitions and the infrared Lamb dip spectroscopy is the new feature of this method.

ACKNOWLEDGMENT

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