

LETTER TO THE EDITOR

Radiofrequency-Infrared Double-Resonance Spectroscopy of OsO₄ Using Microwave Modulation Sidebands on CO₂ Laser LinesFLAVIO SCAPPINI,¹ WELF A. KREINER,² JOAN M. FRYE, AND TAKESHI OKA*Departments of Chemistry and of Astronomy and Astrophysics,
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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 ν_3 fundamental band of OsO₄ in order to determine the splitting constants in the excited state (Z_i) as well as in the ground state (D_i). 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 ν_3 band of OsO₄ at 961 cm^{-1} overlaps with the CO₂ laser transitions around $10.4\ \mu\text{m}$. 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 C_{3v} cluster transitions. This suggested the possibility of an rf-ir double-resonance experiment. The A_1 and A_2 components of the clusters are connected by the vibration-induced dipole moment in the excited state (10) and by the rotation-induced dipole moment in the ground state (11).

The infrared source used is described elsewhere (3, 5). The absorption cell is 2 m long and contained OsO₄ with a pressure of a few milli Torr. 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 $A_1^{(2)} \leftrightarrow A_2^{(3)}$ $\Delta J = 0$, and $\Delta F = 0$ rf transition in the ν_3 state with $J = 25$ and $R = 24$. Note that ¹⁸⁹OsO₄ with natural abundance (16%) was used for this experiment. Other radiofrequency transitions, i.e., the $\Delta F = \pm 1$ transitions in the excited state which would show the hyperfine pattern and the $A_1^{(3)} \leftrightarrow A_2^{(2)}$ 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 $\sim 10^3$).

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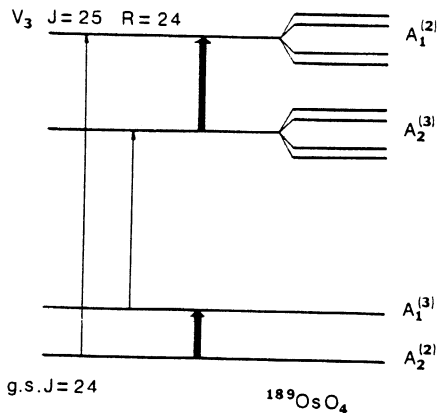


FIG. 1. Energy level scheme involving the $\nu_3 R(24)$ transition of $^{189}\text{OsO}_4$ used for the double-resonance experiment. The quadrupole hyperfine structure in the ν_3 state ($eqQ = 7.1$ MHz (5)) is shown; the structure in the ground state due to rotation-induced eqQ is not shown. The bold arrows indicate rf transitions, of which only the one in the ν_3 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 $^{189}\text{OsO}_4$ and $^{192}\text{OsO}_4$. 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 D_t in the ground state and Z_t in the excited state using the formulae (13, 14)

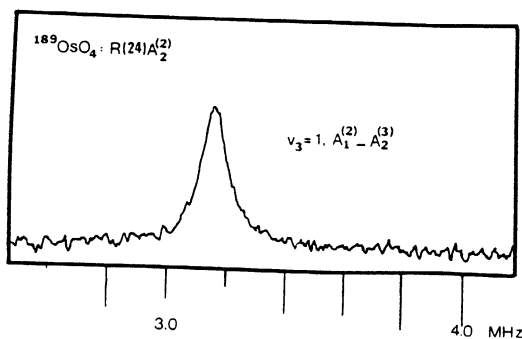


FIG. 2. The double-resonance signal corresponding to the $\nu_3 J = 25 R = 24 A_1^{(2)} - A_2^{(3)} \Delta F = 0$ transitions in $^{189}\text{OsO}_4$. The microwave modulation sideband generated on the 10 $R(8)$ laser line of the CO_2 laser is kept on the $R(24) A_2^{(2)}$ transition, and the amplitude-modulated radiofrequency was swept from 2.6 to 4 MHz. A time constant of 0.3 sec was used.

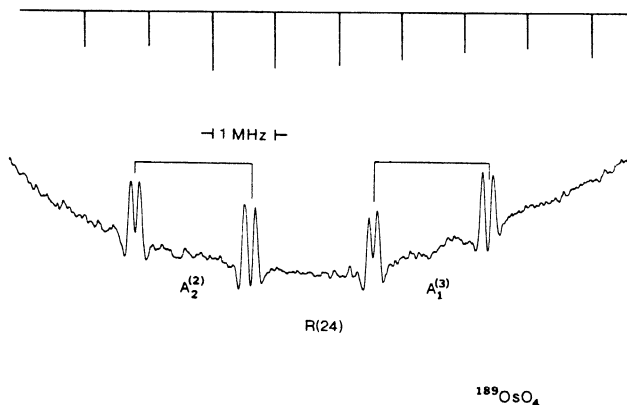


FIG. 3. The sub-Doppler saturation Lamb dips of the $\nu_3R(24)$ $A_1^{(3)}$ and $A_2^{(2)}$ transitions of $^{189}\text{OsO}_4$. The quartet for each transition is caused by the vibration-induced nuclear quadrupole coupling in the ν_3 state (16). The splitting between the $A_1^{(3)}$ and $A_2^{(2)}$ components of the cluster and the excited state splitting observed in Fig. 2 gives the splitting in the ground state.

$$\nu(v=0) = D_i[f(J, \kappa_1) - f(J, \kappa_2)]$$

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

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 $J=R-1$ and $J=R+1$, 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 α_{224} used by Takami (6, 7) by the relation (17)

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

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

$$D_i = \frac{B^3}{5} \left[\frac{1}{\nu_2^2} - \frac{\zeta_{23}^2}{\nu_3^2} - \frac{\zeta_{24}^2}{\nu_4^2} \right],$$

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

$$\zeta_{23}^2 = (1 - \zeta_{24}^2) = \frac{2}{3}(1 - \zeta_3) = 0.582.$$

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 ν_3 and other vibrational states. Takami noted that Z_{3i} differs by a factor of as much as 3 between $^{12}\text{CF}_4$ and

TABLE I

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

		ν_e^b, ν_m^b, ν_r (MHz)	$\nu_e + \nu_m$ (cm ⁻¹)
¹⁸⁹ O _s O ₄	CO ₂ 10 R(8)	29011133.014	967.25437(1)
	ν_3 R(24) A ₁ (2) - A ₂ (2)	-13576.107	967.25424(1)
	A ₂ (3) - A ₁ (3)	-13579.987	967.25424(1)
	Difference	3.879(61)	
	ν_3 J = 25 A ₁ (2) - A ₂ (3)	3.151(7)	
	G.S. J = 24 A ₁ (3) - A ₂ (2)	0.728(61)	
¹⁹² O _s O ₄	CO ₂ 10 P(10)	28566649.209	
	ν_3 P(30) A ₁ (3) - A ₂ (3)	16874.097	953.11012(1)
	A ₂ (3) - A ₁ (3)	16872.133	953.11006(1)
	Difference	1.964(50)	
	ν_3 J = 29 A ₁ (3) - A ₂ (3)	1.502(4)	
	G.S. J = 30 A ₁ (3) - A ₂ (3)	0.426(50)	
CO ₂	10 P(12)	28516026.673	
	ν_3 P(37) A ₂ (3) - A ₁ (3)	15331.311	951.70366(1)
	A ₁ (3) - A ₂ (3)	15321.821	971.70334(1)
	Difference	9.491(50)	
	ν_3 J = 36 A ₁ (3) - A ₂ (3)	6.639(9)	
	G.S. J = 37 A ₁ (3) - A ₂ (3)	2.852(50)	

^aQuoted uncertainties are one standard deviation of over ten measurements for each value.

^bLaser line frequencies are taken from reference 12.

¹³CF₄ due to the perturbation between the ν_3 and the $2\nu_4$ states. Our observed values of Z_{3t} are smaller than that obtained by McDowell *et al.* (8), but this is probably due to their neglect of D_t in the analysis. The observed value of D_t agrees with the calculated value within the uncertainty.

TABLE II

Tetrahedral Splitting Constants in the Excited State (Z_{3t}) and Ground State (D_t)^a

Transitions	Z_{3t} (kHz)	D_t (Hz)
¹⁸⁹ O _s O ₄ R(24)	395 ± 3	72 ± 18
¹⁹² O _s O ₄	P(30)	80 ± 26
	P(37)	72 ± 6
Ref. (8)	514 ± 1	
Theoretical		67

^aQuoted errors are three times the standard deviation.

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.

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