

# Internal Dynamics of Simple Molecules Revealed by the Superfine and Hyperfine Structures of Their Infrared Spectra

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This paper reports some of the progress achieved with our 10  $\mu\text{m}$  saturation spectrometer since our 1979 FICOLS presentation [1] with a special emphasis on recent results in molecular physics. Let us first summarize the improvements of the spectrometer acquired during that period :

**A. The absolute frequency calibration** is now based : /1/ on a grid of  $\text{OsO}_4$  frequency markers which is connected to the Cesium primary frequency standard with accuracies ranging from 50 Hz to a couple of kHz [2,3] and which has been extended to include many identified lines of the  $\nu_3$  band of various isotopic species : P(30) $A_1^1(\text{g})$  and  $A_1^1(\text{u})$  of  $^{188}\text{OsO}_4$ , P(63) $A_1^1(\text{u})$ , P(56) $A_1^2(\text{g})$ , P(49) $A_1^3(\text{u})$  and  $A_1^3(\text{g})$ , R(26) $A_1^0(\text{g})$  and  $A_1^0(\text{u})$ , R(45) $A_1^0(\text{u})$  and R(64) $A_1^2(\text{u})$  of  $^{189}\text{OsO}_4$ , R(40) $A_1^0(\text{u})$ ,  $A_1^0(\text{g})$  and  $A_1^1(\text{g})$  of  $^{190}\text{OsO}_4$ , P(46) $A_1^2(\text{u})$ , P(39) $A_1^3(\text{u})$  and  $A_1^2(\text{g})$ , R(23) $A_1^1(\text{u})$  and  $A_1^1(\text{g})$ , R(35) $A_1^0(\text{g})$  and  $A_1^1(\text{u})$ , R(55) $A_1^1(\text{g})$  of  $^{192}\text{OsO}_4$  (the previous point group label  $A_2$  is replaced by  $A_1(\text{u})$  where u is the overall parity [4]); Fig.1 illustrates two such  $^{192}\text{OsO}_4$  markers and their positions in the Fourier transform spectrum (a) of the  $\nu_3$  band [5] /2/ on the saturation peaks of  $\text{CO}_2$  itself, observed directly in the absorption cell with a half-width as low as 2.1 kHz.

These two grids have been connected for the P(12)  $\text{CO}_2$  line, as shown in Fig.1, and for the P(14)  $\text{CO}_2$  line, and excellent agreement (within our 1kHz uncertainty) has been found with the values determined by the saturated fluorescence technique [6] .

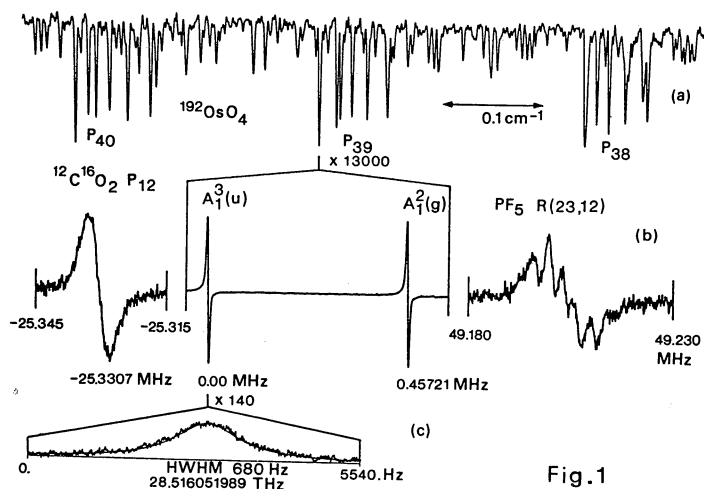


Fig.1

**B. The resolving power times tuning range** product as well as the quality of frequency calibration have benefited from phase-locking waveguide CO<sub>2</sub> lasers to a conventional reference laser, resulting in a 10 Hz spectral purity over 600 MHz tuning ranges [2,7] and also from high quality corner-cube optics (which is a by-product of our Ramsey fringes studies [8] ); the linewidth is transit-limited and corresponds to the 4 cm beam waist radius. Fig.1 illustrates this resolving power for a single OsO<sub>4</sub> line as well as in the case of a typical hyperfine structure of PF<sub>5</sub>.

**C. The detectivity** (S/N) has also benefited : /1/ from long-term computerized frequency control (e.g. the CO<sub>2</sub> saturation peak is obtained by integration over 20 minutes periods in turn with 200 seconds periods for OsO<sub>4</sub> and this process is repeated 6 to 7 times to determine accurately frequency drifts of the reference laser (< 10 Hz/minute)) /2/ in some cases from high frequency modulation applied to the laser piezoelectric transducer (97 kHz in the case of Fig.1c).

### 1. SUPERFINE AND HYPERFINE STRUCTURES IN THE $\nu_3$ BAND OF OsO<sub>4</sub>

The doublet in Fig. 1 is a very simple example of superfine structure : the clustering of these lines results from a spontaneous symmetry-breaking of the point group T<sub>d</sub> into a lower symmetry (C<sub>3v</sub>) and the splitting corresponds to a tunnelling rate between equivalent C<sub>3v</sub> distorted configurations [9] . Other dynamical aspects are visible through hyperfine effects, for which a remarkable test system is the isotopic species with a central <sup>189</sup>Os nucleus, since a spin 3/2 probes both the electric field gradient and the magnetic field at the centre of the molecule. Our previous saturation spectroscopic studies [1] have revealed quadruplet structures which could be attributed to an electric quadrupole interaction. The existence of such structures results from the breakdown of spherical symmetry of the molecule by vibration-rotation distortions which induce an electric field gradient at the Osmium nucleus site. In a first step, these structures have been interpreted as a purely vibrational effect and two corresponding constants (respectively for a scalar and a tensor interaction) were derived in [10] . On the other hand, it was suggested that pure rotation could induce similar effects and two corresponding constants  $\chi_s^R$  and  $\chi_t^R$  were introduced [11] . This effect was confirmed by further theoretical studies [12,13] , but since the observed spectra usually correspond to a difference between excited and ground state structures (  $\Delta F = \Delta J$  transitions), this rotational effect cancels almost completely and requires high precision spectroscopy to be observed experimentally. We have therefore reinvestigated the structures corresponding to the 8 vibration-rotation transitions listed above. The magnetic dipole hyperfine structure of these lines results from purely scalar spin-rotation and spin-vibration interactions and can be easily separated from the symmetric purely quadrupolar quadruplet as shown in [1] . The high accuracy (< 100 Hz) of the measured lines (HWHM  $\sim$  1 kHz) is such that they cannot be fitted with a single eQq in the excited state but require an important value for this quantity, also in the ground state. The set of values for eQq in the ground vibrational state is fully consistent with :  $\chi_s^R \approx -760$  Hz and  $\chi_t^R \approx -35$  Hz. This conclusion has been fully confirmed by a study of crossover resonances for the two R(26) and the two P(49) lines and is illustrated in Fig.2 for R(26)A<sub>1</sub><sup>0</sup>(g). These crossover peaks are less than 1/1000 times weaker than the main peaks and measured with an accuracy of 200 Hz (HWHM  $\sim$  6 kHz). They give a direct and independent access to hyperfine energies in both vibrational levels, and yield an accurate value of the spin-rotation interaction constant in the  $\nu_3 = 0$  state :  $c_a = -21.69$  kHz. The overall analysis of the magnetic dipole interactions also provides values for a change in this constant with vibration :  $\delta c_a \approx 18$  Hz and for a scalar spin-vibration interaction constant :  $A \approx -2.76$  kHz. Finally let us note that the ratio of A and  $c_a$  is quite close to  $\zeta_3 = 0.127$  as could be anticipated.

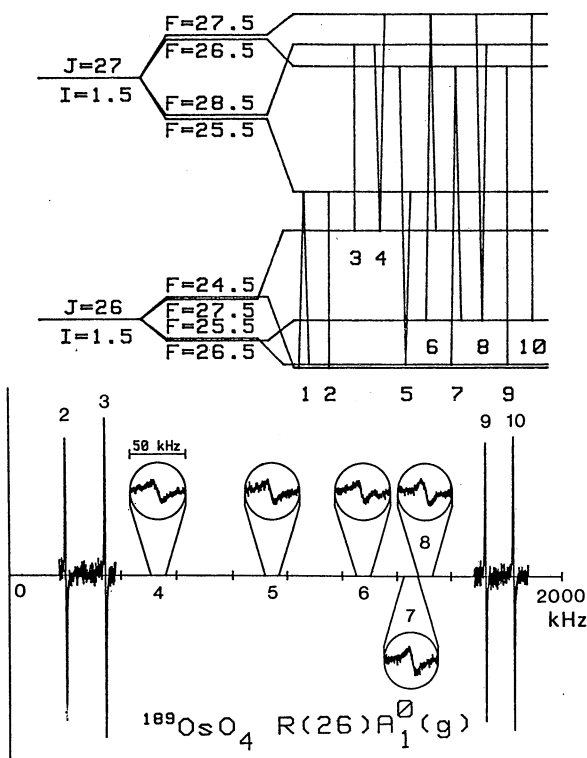


Fig. 2

## 2. SUPERFINE, HYPERFINE AND SUPERHYPERFINE STRUCTURES IN THE $\nu_3$ BAND OF $^{32}\text{SF}_6$

A much richer variety of spectra is offered by  $\text{SF}_6$  for which all possibilities of superfine patterns have been observed [1,14] and fully demonstrate the spontaneous symmetry breaking of  $O_h$  into  $C_3$  or  $C_4$  subgroups, as well as the tunnelling effects described by W. HARTER and coll. [9]. A full account of the fine and superfine structures with a 30 kHz standard deviation has been given recently [16] for 136 transitions ranging from P(84) to R(94). Hyperfine structures themselves display superclusters  $O_h \uparrow S_6$  and have been observed for all symmetry species of the  $O_h$  group. As illustrated in Fig. 3,4,5, the observed spectra agree beautifully with those calculated from the theory presented in [14,15] with the following set of constants (in kHz):

$c_a = -5.27$ ,  $c_d = -4.60$ ,  $A = 4.57$ ,  $A_t = 6.75$  (\*),  $d_1 = 9.82$ ,  $d_2 = 3.47$  respectively for the scalar spin-rotation, tensor spin-rotation, scalar spin-vibration, tensor spin-vibration and spin-spin interactions. In addition, we have determined three coupling constants associated with three formal operators given in [12] and which correspond to vibrational corrections to the scalar and tensor spin-rotation interactions. As a result, 85% of the structures (i.e. for 108 vibration-rotation transitions) have been perfectly reproduced, whereas 15% have still one or two hyperfine components off by quantities of the order of one kilohertz. As studied in detail in previous papers

(\*) with this value the second member of equation Eq. (2) of reference [15] should be multiplied by  $\sqrt{2}$ .

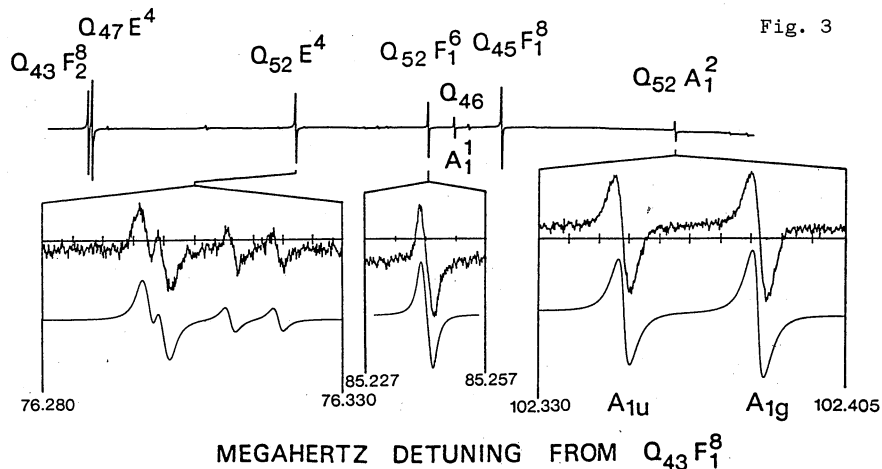


Fig. 3

[14] hyperfine interactions break the point group symmetry. A spectacular manifestation of this mixing can be seen as a splitting of the inversion doublet  $A_{1u} - A_{1g}$  in Fig. 3 (only the tensor spin-rotation interaction in  $v_3=0$  contributes noticeably to this splitting which yields directly a value for  $c_d = -4.63$  kHz). As vibration-rotation states get closer and closer within rovibrational clusters this hyperfine mixing gets stronger and the individual hyperfine structures collapse into a single superhyperfine structure [9]. Fig.4 illustrates this evolution in the case of  $F_1 - F_2$  lines, for which the final stage of this mixing is the complete breakdown of the  $S_6$  symmetry into  $S_4 \times S_2$ . States are then labelled by broken Young tableaux [9]. A remarkable and unpredicted feature is the quadruplet organization of superhyperfine tetragonal clusters, which can be understood from the large difference in axial and equatorial spin-rotation interactions. It can be shown that in the lower state, the two axial and equatorial interaction coupling constants are precisely the  $c_{//} \approx -2.2$  and  $c_{\perp} \approx -6.8$  kHz introduced in [14]. Fig. 5 displays an example of the 4 possibilities of axial spin Young tableaux associated with each choice of equatorial spin Young tableau (the  $S_2$  and  $S_4$  parts of the broken tableaux are respectively given above and below the experimental and theoretical spectra).

### 3. HYPERFINE STUDIES OF SYMMETRIC TOPS

We have undertaken similar hyperfine studies for a number of other molecules belonging to other symmetry groups and whose fundamental bands fall within the  $CO_2$  (or  $N_2O$ ) laser tuning ranges e.g. the  $v_2$  band of ammonia or the  $v_3$  band of  $^{23}PF_5$  (Fig.1). In the case of the  $v_2$  band of ammonia, both electric quadrupole effects [17] and magnetic dipole interactions have been shown to depend strongly on internal degrees of freedom: inversion, rotation [18,19] and vibration. A recent study of the asQ(8,7) line (HWHM  $\approx 7$  kHz) has not only confirmed the important change in eqQ ( $\Delta eqQ \approx -350$  kHz) in good agreement with a theoretical prediction of V. SPIRKO [20] but also revealed important variations in the nitrogen and hydrogen spin-rotation constants R and S with vibration and inversion ( $\Delta R \approx 0.25$  kHz and  $\Delta S \approx -0.59$  kHz). As another example, Fig.6 displays a comparison between theory and experiment for the asR(2,0) line of the same band of  $^{15}NH_3$ . The calculated asR(2,0) spectrum offers a nice confirmation of the low-field theory of intensities in saturation spectroscopy presented in [22].

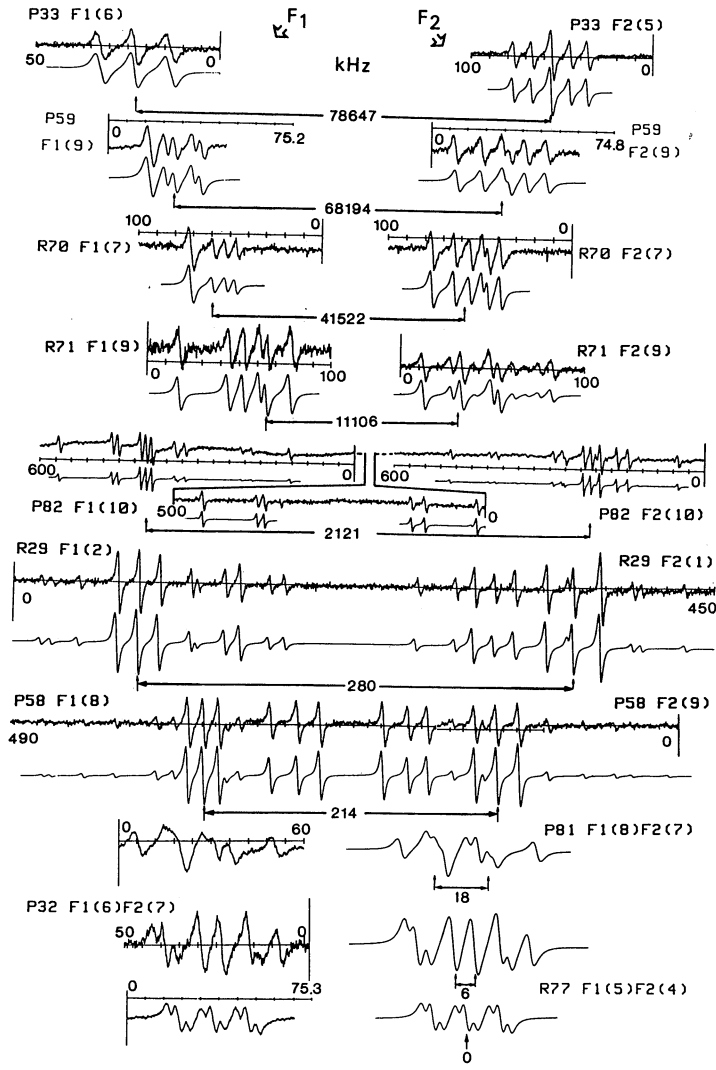


Fig. 4

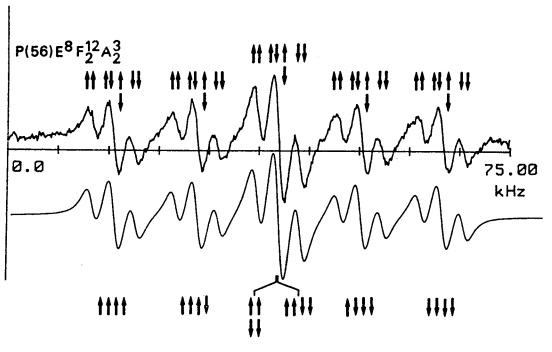


Fig. 5

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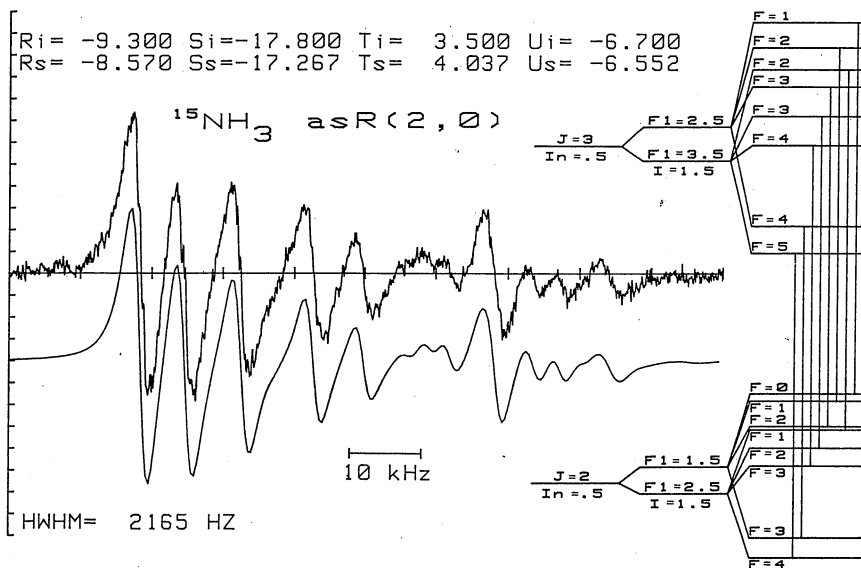


Fig. 6

In this case, the high accuracy of the data requires to introduce also a change in the nitrogen-hydrogen and hydrogen-hydrogen spin-spin interaction constants  $T$  and  $U$  which are directly related to a change in the mean geometry of the molecule. This is another illustration of the role that hyperfine studies can play as a probe of large amplitude motions within molecules.

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