

The Pauli Principle and Ultrahigh Resolution Spectroscopy of Polyatomic Molecules

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Abstract. We review some observed consequences of the Pauli principle in ultrahigh resolution spectroscopy of polyatomic molecules with several identical bosonic or fermionic nuclei. An important feature is the link with parity. Several possible tests of the symmetrization postulate come out of this analysis and we discuss in more detail an experiment which is presently conducted with OsO_4 in our laboratory.

INTRODUCTION

Tests of the Pauli symmetrization postulate have, this far, been performed at a very high sensitivity level, only on simple spectra of diatomic or triatomic molecules with two identical spinless nuclei (specifically ^{16}O) [1–7] (see also the contributions of G. Tino and R.C. Hilborn in this book and references therein). Thanks to modern techniques of ultra-high resolution spectroscopy (saturation spectroscopy, two-photon spectroscopy) it is now possible to resolve individual hyperfine components of vibration-rotation lines of molecules having three or more identical nuclei with a high degree of symmetry: spherical tops such as SF_6 [8–14], OsO_4 [9,12,15–17], SiF_4 [18], symmetric tops such as NH_3 [12,19], PH_3 [20], PF_5 [12]...

We have built several generations of saturation spectrometers with very high resolving power, accuracy and sensitivity in the 9–12 μm spectral range [9,21]. Recently, a linewidth of 80 Hz (HWHM) has been achieved for OsO_4 , thanks to the use of slow molecules [22] and the absolute frequency accuracy is now typically better than 100 Hz. The long absorption path (108 m) of our large cell gives access to very high sensitivity. For high contrast, we have also used recently external Fabry-Perot resonators for a spectroscopic test of parity violation in chiral molecules [23,24]. Also, the spectra of some of these molecules are now very well-known e.g. the ν_3 band of SF_6 , which is known to an accuracy better than 40 kHz for J values ≤ 100 [25].

The Pauli principle has important consequences on the hyperfine spectra of these molecules, which we have observed in the course of many studies. We have also

emphasized on several examples that there was a strong link between these consequences and parity [26] and we have shown two spectacular examples where this link leads to a parity doubling in PH_3 [20] and SiF_4 [18].

CONSEQUENCES OF THE PAULI PRINCIPLE ON HYPERFINE SPECTRA

In the ground electronic state of molecules the total internal wavefunction is the tensor product of a vibration-rotation wave function and of a nuclear spin wavefunction. The total nuclear spin wave function is built from products of spin wavefunctions for each nucleus, which are symmetrized in the point group of the molecule [27,28]. Using a double tensor notation in ${}^{(L)}O(3) \times G \subset {}^{(L)}O(3) \times {}^{(M)}O(3)$ [13,28] and the notations of Berger and Landau [29,30], we shall write this wave function $\Psi_{NS}^{(I_+, C_{NS})}$, where I is a value of the total nuclear spin corresponding to the point group symmetry species C_{NS} and where the subscript $+$ corresponds to even parity¹. As an example, for SiF_4 , $I = 2$ for $C_{NS} = A_1$, $I = 1$ for $C_{NS} = F_2$ and $I = 0$ for $C_{NS} = E$. For SF_6 , I can take the two values 1 and 3 for $C_{NS} = A_{1g}$, 1 and 2 for E_g , 0 and 2 for F_{1u} , $I = 1$ for F_{2g} and for F_{2u} and finally $I = 0$ for $C_{NS} = A_{2g}$ or A_{2u} . Similarly, we write the vibration-rotation wave functions $\Psi_{VR}^{(J_\tau, R_\lambda C_{VR})} = [\Psi_R^{(J_\tau, J_\tau)} \otimes \Psi_V^{(0_+, l_\rho)}]^{(J_\tau, R_\lambda C_{VR})}$, where R is the pure rotation angular momentum, which comes from the coupling of the total orbital momentum J with the vibrational angular momentum l and where $\tau, \lambda, \rho = \pm$ are parity indices. The rovibrational states are also characterized by their symmetry species C_{VR} which is obtained from the reduction of the representation $D^{(R_\lambda)}$ in G : $D^{(R_\lambda)} \downarrow G = \sum_j C_j^{(n_j)}$. The rotational wave functions are degenerate with respect to parity.

The total internal wave function in the ground electronic state is obtained by coupling the vibration-rotation and the nuclear spin parts as

$$\Psi_{tot}^{(F_\tau, C)} = [\Psi_{VR}^{(J_\tau, R_\lambda C_{VR})} \otimes \Psi_{NS}^{(I_+, C_{NS})}]^{(F_\tau, C)}.$$

For any molecular system containing identical nuclei, the only allowed states are either totally symmetric with respect to permutations (case of bosons) or totally antisymmetric (case of fermions). The Pauli principle implies therefore that the only populated vibration-rotation states are such that $C = A_1$ for bosons and $C = A_2$ for fermions (A_{2u} for SF_6). This introduces a correspondence between the vibration-rotation symmetry species and the total spin value I and hence the number of allowed hyperfine components $2I + 1$. One can check in Fig.1 that, for SiF_4 , we have indeed five hyperfine components for A_2 lines and three for F_1 lines. This correspondence between the values of I allowed by the Pauli principle and the

¹) This parity, which depends on the intrinsic parity of the nuclei, is fixed and is chosen to be $+$ for simplicity.

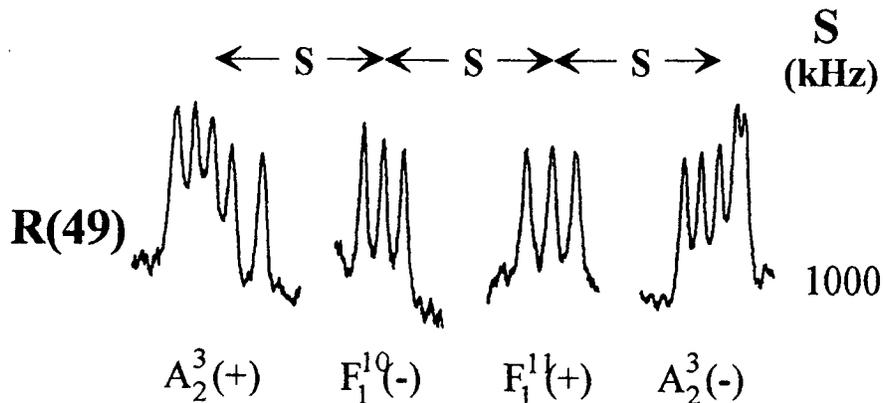


FIGURE 1. Superfine and hyperfine structures of a trigonal ($O_3 \uparrow O$) cluster in the ν_3 spectrum of SiF_4 . The hyperfine structure of each component spreads over a few kilohertz, whereas the superfine splitting S is one MHz in this case.

symmetry species of the vibration-rotation lines is well verified on the hyperfine structure of all the spectra observed this far, in symmetric and spherical tops. A first clear consequence for hyperfine spectra, if other permutation symmetries were allowed, is that one would have extra-components violating this correspondence and one could look for these missing lines, whose positions can be easily calculated from the theory. For example, we have seen that for SF_6 , A_1 lines require $I = 0$ for both the components A_{1u} and A_{1g} and, as a matter of fact, only doublets are observed in this case [12,13], but one could certainly look for additional weak components corresponding to other values of I , which would result from a violation of the Pauli principle. This test will require high resolution, which implies a limited signal-to-noise. A simpler experiment is presently underway which can be performed with very high signal-to-noise and will be presented in the next section. Let us mention another important consequence of the Pauli principle in such spectra and discussed in detail in references [13,18,20,26]. Some lines are parity doublets while others are parity singlets, but states, which differ by their overall parity, differ also by some other part of their wave function, either through their rotational or through their nuclear spin wave functions. Even if inversion is negligible, two states of opposite parity cannot be strictly degenerate owing to rovibrational or hyperfine interactions.

A HIGH SENSIVITY TEST ON A DARK BACKGROUND

In the case of spherical tops, an important consequence of the internal dynamics is that the vibration-rotation lines tend to cluster together in multiplets (doublets, triplets or quadruplets) corresponding to rotation about one of the symmetry axes with a degeneracy equal to the number of equivalent axes [31]. Furthermore these multiplets are split by tunnel effect in a tumbling motion between these equivalent axes giving rise to regular spacings between their components [9,13]. An example is shown in Fig.1 where a typical quadruplet is displayed corresponding to rotation around a three-fold axis in SiF_4 .

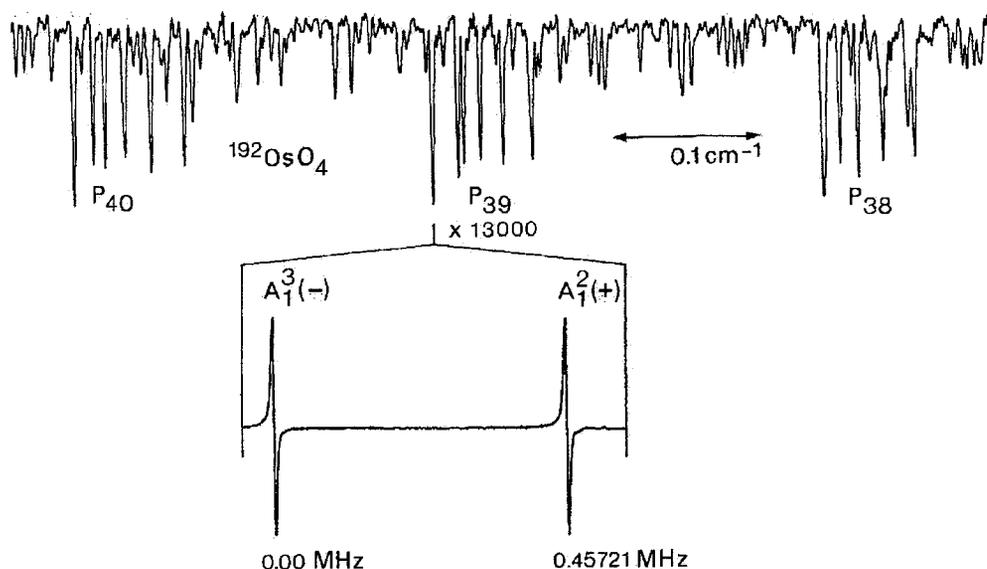


FIGURE 2. Top: Fourier transform spectrum of $^{192}\text{OsO}_4$ showing the fine structure of three J manifolds of the ν_3 band. Bottom: high-resolution derivative saturation spectrum of a superfine doublet. The F lines present in Fig.1 are missing here because of the Pauli principle.

For SiF_4 , the Pauli principle allows the existence of superfine quadruplets $A_2(+)\bar{F}_1(-)\bar{F}_1(+)\bar{A}_2(-)^2$, whereas for $Os^{16}O_4$ it forbids the states with F vibration-rotation symmetry species since $C_{NS} = A_1$ and, as a matter of fact, only $A_1(+)\bar{A}_1(-)$ doublets are observed [12]. In this case, the principle of our test consists in looking for the missing lines of the quadruplet (at one third and two thirds of the splitting) with the ultimate sensitivity that we can reach with our

²⁾ These representations are those of the point group T_d and differ from those of the permutation-inversion group e.g. $A_1(-)$ corresponds to A_2 , $A_1(+)$ to A_1

long absorption cell (108 m) or with our Fabry-Perot resonators. In the past, we have indeed been able to record very weak lines e.g. those corresponding to the CO₂ laser lines themselves [32] or those corresponding to weak crossover resonances [33]. Here, we look for transitions from unpopulated states with a transition moment similar to the strong observed lines. We have thus to optimize the S/N ratio of the observed lines and look for the missing lines in the same conditions. Already, from Fig.2, published in reference [12], we can estimate that these lines are at least a factor 1000 smaller than the allowed ones, but we can certainly improve this result by many orders of magnitude. The intensities of the lines in saturation spectroscopy can be calculated [34–36,22] and the sensitivity can be easily estimated [37]. The linear absorption coefficient is given by [35,21]:

$$k_\nu = \frac{4\pi^2}{3} \alpha \nu \frac{1}{\sqrt{\pi} u/\lambda} \frac{\mu^2 N}{e^2 Z} \exp(-E/kT)$$

where α is the fine structure constant, ν the transition frequency, u/λ the Doppler width, μ the transition moment, e the electron charge, N the number density, Z the partition function and $\exp(-E/kT)$ the Boltzmann factor. In the case of the OsO_4 lines under consideration, we find $0.5 \text{ cm}^{-1}/\text{Torr}$. In order to optimize the contrast of the saturation resonances, we have to use a gas pressure such that the linear absorption satisfies $k_\nu L \sim 1$; with a path length $L = 108 \text{ m}$, this leads to a typical pressure of a few 10^{-4} torr. The pressure broadening is still reasonable (a few kilohertz) and quite compatible with typical $A_1(+)$ $A_1(-)$ splittings.

The maximum laser power that we may then apply to the molecules, is such that the saturation parameter should not exceed a few units, to optimize the size of the saturation peaks. In the transit-time regime, it is given by the π pulse power [21] $1.36 \times 10^{-5} \text{ W}$, but in the collisional regime [37], this power will rise typically up to several milliwatts. Since the photon noise is in the picowatt range, a typical sensitivity of 10^{-8} – 10^{-9} is expected.

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