ROTATION OF METHYL RADICALS
IN MOLECULAR AND ATOMIC SOLIDS

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Introduction

CH3 radicals trapped in cryogenic crystals (of polycrystalline quality = powder spectra) exhibit all (3) features of anisotropy in terms of a dipolar coupling of magnetic momenta.

1. Rhombic species: three axial components resolved \( A_{\|}, A_{\perp}, A_{v} \) (\( g_{\|}, g_{\perp}, g_{v} \)).
2. Axial species: parallel and perpendicular species \( A_{\|}, A_{\perp} \) (\( g_{\|}, g_{\perp} \)).
3. Symmetric species: isotropic parameters \( A_{v} \) (\( g \approx g_{v} \)).

The changes from case to case are connected with different degrees of CH3 rotation, which depend on trapping site symmetry, volume, and sample temperature.

The ESR method can resolve the two different nuclear spin states \( I = 3/2 \) and \( I = 1/2 \) of CH3.

Coupling of rotational and nuclear spin states can be used to analyze population statistics and molecule-host interactions;

Rotational energy level shifts, rotational barriers, and crystal-field effects [1,2].

Fig.1: ESR spectrum at 14 K and simulation.

Solid CO2

Solid CO

Solid N2

Temperature dependence

At 14 K, the CO and CO solids exhibit a quartet structure mainly due to the symmetric spin state with \( I = 3/2 \) of the lowest rotational state. The three proton couplings in-plane average out rotationally leading to the overlapping two-component (axial) spectra, see above.

Thermal population of excited rotational states follows, appears as increasing \( m = \pm 1/2 \), -1/2 resonance part, which is spectrally shifted from the central, symmetric-state resonance doublet, see to the right where \( m = \pm 1/2 \) is plotted.

This increase of relative intensities can be used to trace crystal-field effects on the rotational energy levels in the solids.

The intensity ratios seem [2] (we have yet to simulate them for the final result) to behave interestingly as follows:

1. CO seems to show a 1:2 ratio reaching the 1:2 thermal equilibrium already at 30 K, which could be due to lowered energy levels.
2. CO3 seems to show an increase up to 65 K, indicating the opposite effect as compared to CO (and gas phase).
3. Particularly, N3 seems to be equilibrated already at 14 K, possibly representing an extreme squeezing of energy levels.

It seems both mass-spectroscopically and free rotor (isotropic spectrum) the same time.

Fig.2: ESR spectrum at 14 K and simulation.

Fig.3: ESR spectrum at 14 K and simulation.

Fig.4: Temperature dependence in CO, and CO solids.

Solid rare gases Ar and Kr

The low-temperature ESR spectra exhibit axial symmetry in Ar [1]. The radical is free to rotate about the C3 axis which is oriented in the <100> crystallographic directions. C3 rotation is activated above 15 K.

The ESR spectra are isotropic in Kr despite the stronger molecule-host interaction [2]. The radical can however rotate about both the axes due to the larger trapping volume.

Summary

Both CO and CO3 solids contain radicals that rotate only about the C3 axis.

CO3 has also a non-rotating radical < 20 K, before rotation activates or the site bleaches. Nitrogen contains fully rotating radicals.

***According to the preliminary spectral fittings, the temperature changes in CO do not modify the intensity ratios (populations). The observed changes are rather due to a nonlinear line width dependence of the excited rotor states on T.

Calculations of the radical-host potentials and crystal fields are also under way.