

# ROTATION OF METHYL RADICALS IN MOLECULAR AND ATOMIC SOLIDS

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## Introduction

CH<sub>3</sub> radicals trapped in cryogenic crystals (of polycrystalline quality = powder spectra) exhibit all (3) features of anisotropy in terms of a dipolar coupling of magnetic moments.

1. Rhombic species: three axial components resolved  $\{A_1, A_2, A_3\} \{g_1, g_2, g_3\}$
2. Axial species: parallel and perpendicular species  $\{A_{\parallel}, A_{\perp}\} \{g_{\parallel}, g_{\perp}\}$
3. Symmetric species: isotropic parameters  $\{A_{iso}\} \{g - g_n\}$

The changes from case to case are connected with different degrees of CH<sub>3</sub> rotation, which depend on trapping site symmetry, volume, and sample temperature.

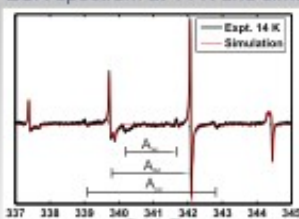
The ESR method can resolve the two different nuclear spin states  $I = 3/2$  and  $I = 1/2$  of CH<sub>3</sub>.

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].

## Solid CO<sub>2</sub>

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

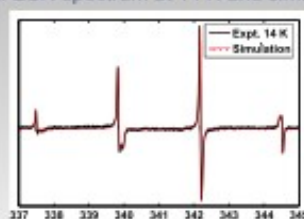


Axial parameters (Line width 0.035 mT):  
 $A_{\parallel} = -2.203$  mT,  $g_{\parallel} = 2.00165$   
 $A_{\perp} = -2.247$  mT,  $g_{\perp} = 2.00215$

Rhombic parameters (minor component, stable < 20 K):  
 $A_{\parallel} = -1.5$  mT,  $A_{\perp} = -2.3$  mT,  $A_{\parallel} = -3.8$  mT

## Solid CO

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

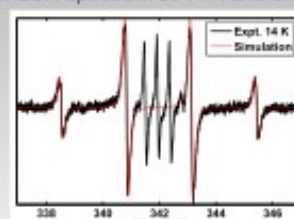


Axial parameters (Line width 0.03 mT):  
 $A_{\parallel} = -2.241$  mT,  $g_{\parallel} = 2.00193$   
 $A_{\perp} = -2.346$  mT,  $g_{\perp} = 2.00232$

A wider magnetic field scan reveals also the HCO radical.

## Solid N<sub>2</sub>

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



Isotropic parameters (Line width 0.12 mT):  
 $A_{\parallel} = -2.303$  mT,  $g_{\parallel} = 2.001475$

The central triplet is due to trapped N atoms.

## Temperature dependence

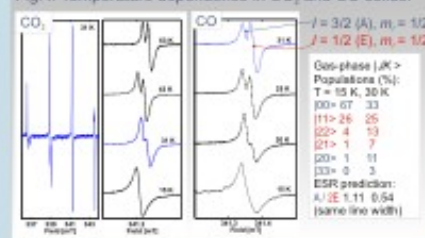
At 14 K, the CO<sub>2</sub> and CO solids exhibit a quartet structure mainly due to the symmetric spin state with  $J = 3/2$  of the lowest rotational state. The three proton couplings in-plane average out rotationally leading to the overlapping two-component (axial) spectra, see above.

Thermal population of excited rotational states  $|JKM\rangle \Rightarrow |11M\rangle, |22M\rangle, \dots$ , appears as increasing  $m_l = +1/2, -1/2$  resonance part, which is spectrally shifted from the central, symmetric-state resonance doublet, see to the right where  $m_l = +1/2$  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\*\*\* (we have yet to simulate them for the final result) to behave interestingly as follows:

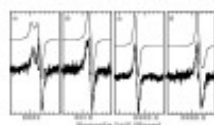
1. CO seems to show an increase reaching the 1:2 thermal equilibrium already at 30 K, which could be due to lowered energy levels.
2. CO<sub>2</sub> seems to show an increase up to 65 K, indicating the opposite effect as compared to CO (and gas phase)!
3. Peculiarly, N<sub>2</sub> seems to be equilibrated already at 14 K, possibly representing an extreme squeezing of energy levels. It seems both massively perturbed (large line width) and a free rotor (isotropic spectrum) at the same time!

Fig.4: Temperature dependence in CO<sub>2</sub> and CO solids.



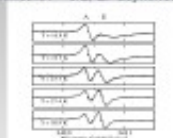
## Solid rare gases Ar and Kr

Fig.5: The quartet structure spectrum at 14 K originates primarily from the lowest rotational state with  $J = 3/2$ .



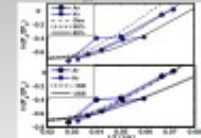
The low-temperature ESR spectra exhibit **axial symmetry in Ar** [1]. The radical is free to rotate about the C<sub>2</sub> axis which is oriented in the <100> crystallographic directions. C<sub>2</sub>-type rotation activates above 15 K.

Fig.6: The  $m_l = 1/2$  resonance portion, A: symmetric  $J = 3/2$ , E: asymmetric  $J = 1/2$ .



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.

Fig.7: Population analyses yield the energy level reductions.



## Summary

Both CO and CO<sub>2</sub> solids contain radicals that rotate only about the C<sub>2</sub> axis.

CO<sub>2</sub> has also a nonrotating 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.

[1] E. Popov, T. Kiljunen, H. Kunttu, and J. Eloranta, *J. Chem. Phys.* **126**, 134504 (2007).

[2] T. Kiljunen, E. Popov, H. Kunttu, and J. Eloranta, *J. Chem. Phys.* **130**, 164504 (2009).