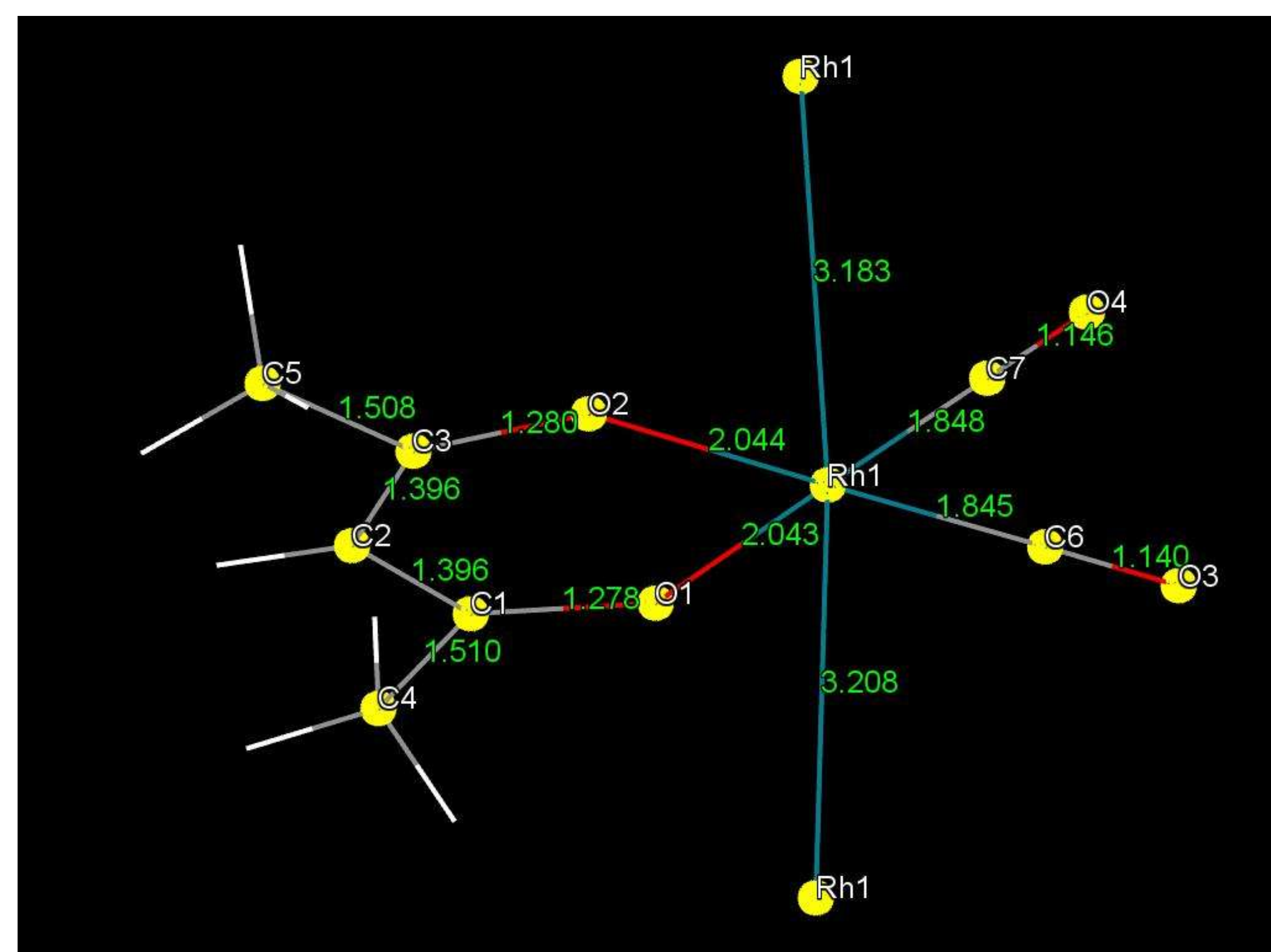


^{13}C NMR and X-ray study of crystalline $[\text{Rh}(\text{Acac})(\text{CO})_2]$: no C_{2v} molecular symmetry in the solid state?

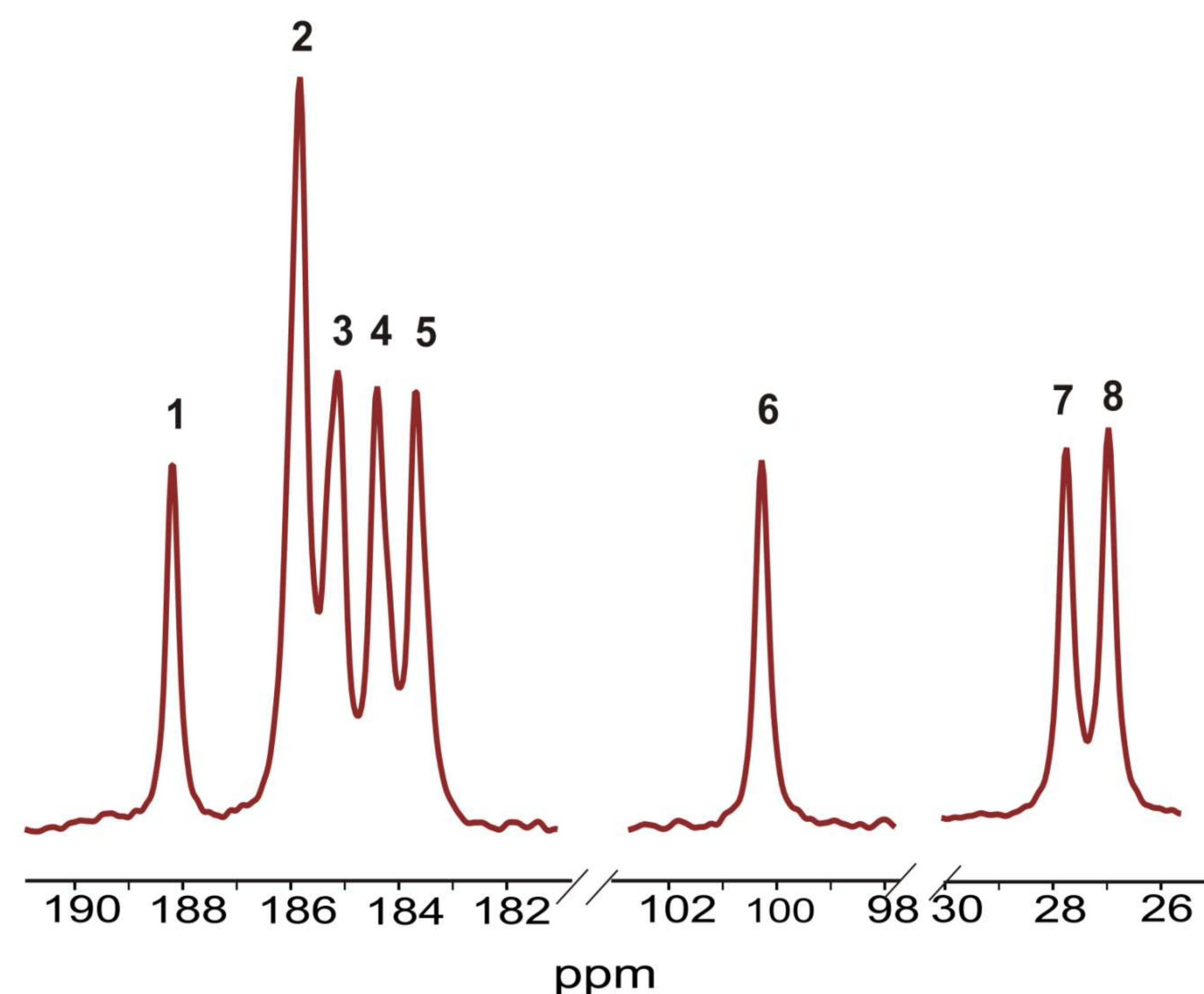
Yuri Varshavsky, Tatiana Cherkasova, Margarita Galding, Alexander Korlyukov, Ivan Podkorytov, Vladimir Gindin, Sergey Smirnov, Anatoliy Rubaylo, Anton Mazur

ST. PETERSBURG STATE UNIVERSITY, ST. PETERSBURG, RUSSIA

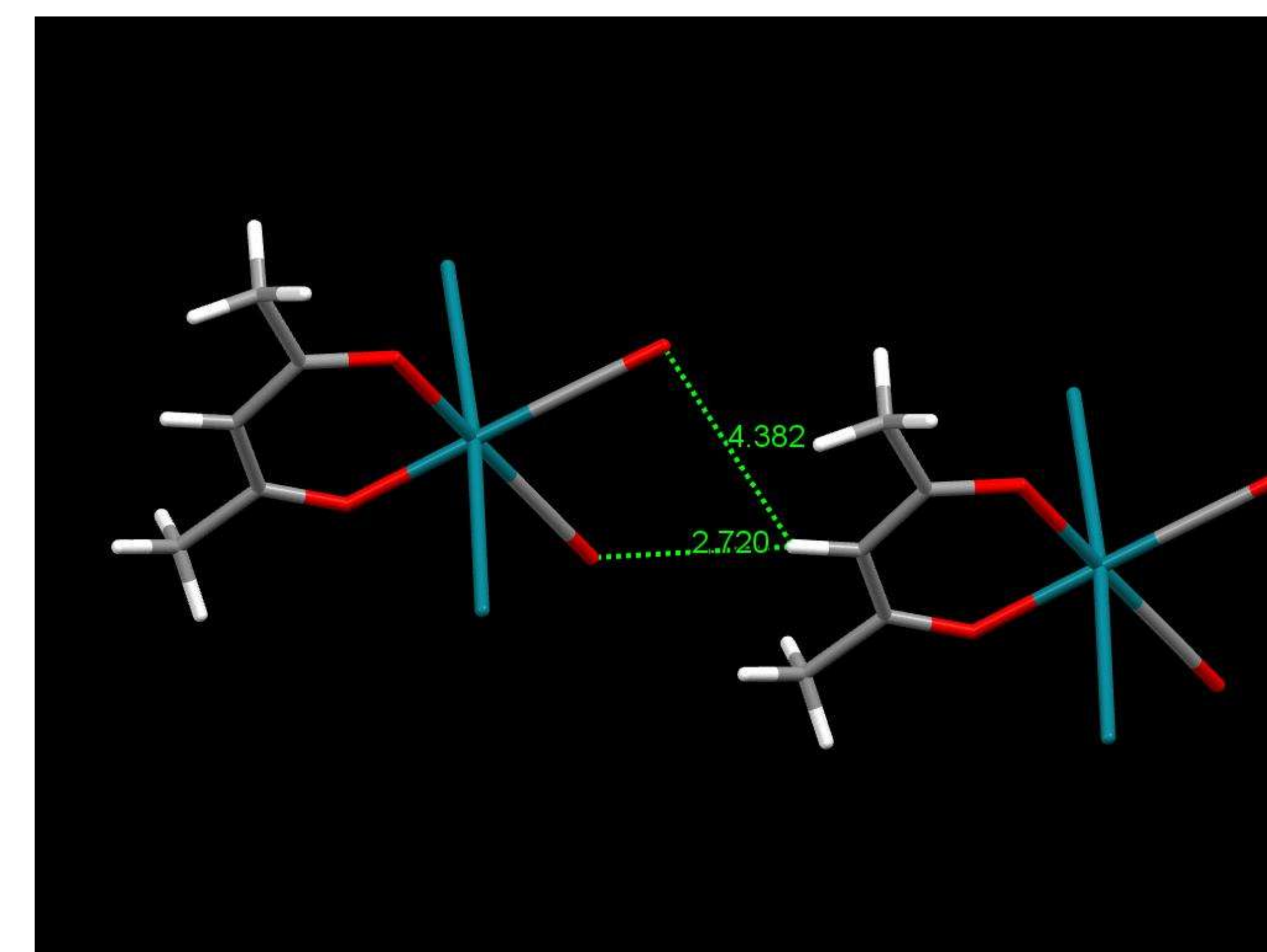


Our X-Ray data on the structure of $[\text{Rh}(\text{Acac})(\text{CO})_2]$ agree well with the data [1,2].

1. F. Huq, A. C. Skapski. J. Cryst. Mol. Struct. (1974) 4, 411
2. C. Pretorius. Ph.D. Thesis. Bloemfontein, 2015



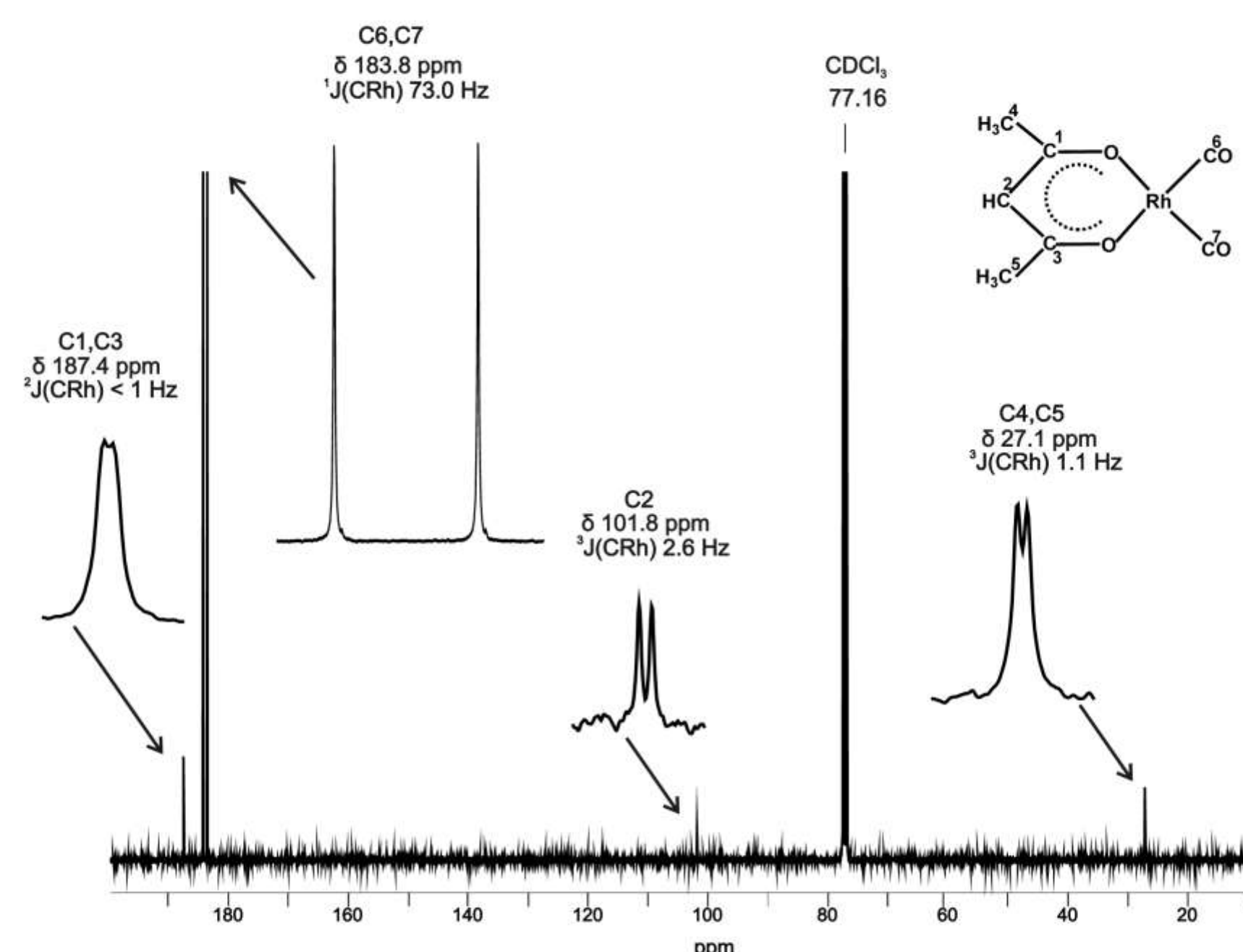
^{13}C MAS NMR spectrum of crystalline $[\text{Rh}(\text{Acac})(\text{CO})_2]$



Inequivalence of carbonyl ligands in the molecule may result from difference in their close surroundings in the crystal. In particular, the contacts $\text{O}\cdots\text{H}-\text{C}$ of two carbonyl oxygens, O3 and O4, to methine and methyl protons of the neighbouring molecules are markedly different. Illustrative is a comparison of the O3 and O4 contacts to the same partner, methine group of the adjacent molecule (its atoms are marked with prime):

(O3) \cdots (H2)' 2.72 Å; (O3) \cdots (C2)' 3.65 Å; $\angle(\text{O3})(\text{H2}')(\text{C2}')$ 164.9°
(O4) \cdots (H2)' 4.38 Å; (O4) \cdots (C2)' 5.00 Å; $\angle(\text{O4})(\text{H2}')(\text{C2}')$ 126.4°

Due to transmission of electronic effects through the central atom, the correlative carbons of Acac ligand, (C1 and C3), (C4 and C5), also become inequivalent.



$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $[\text{Rh}(\text{Acac})(\text{CO})_2]$ (^{13}C enrichment ~ 20%) in CDCl_3 solvent

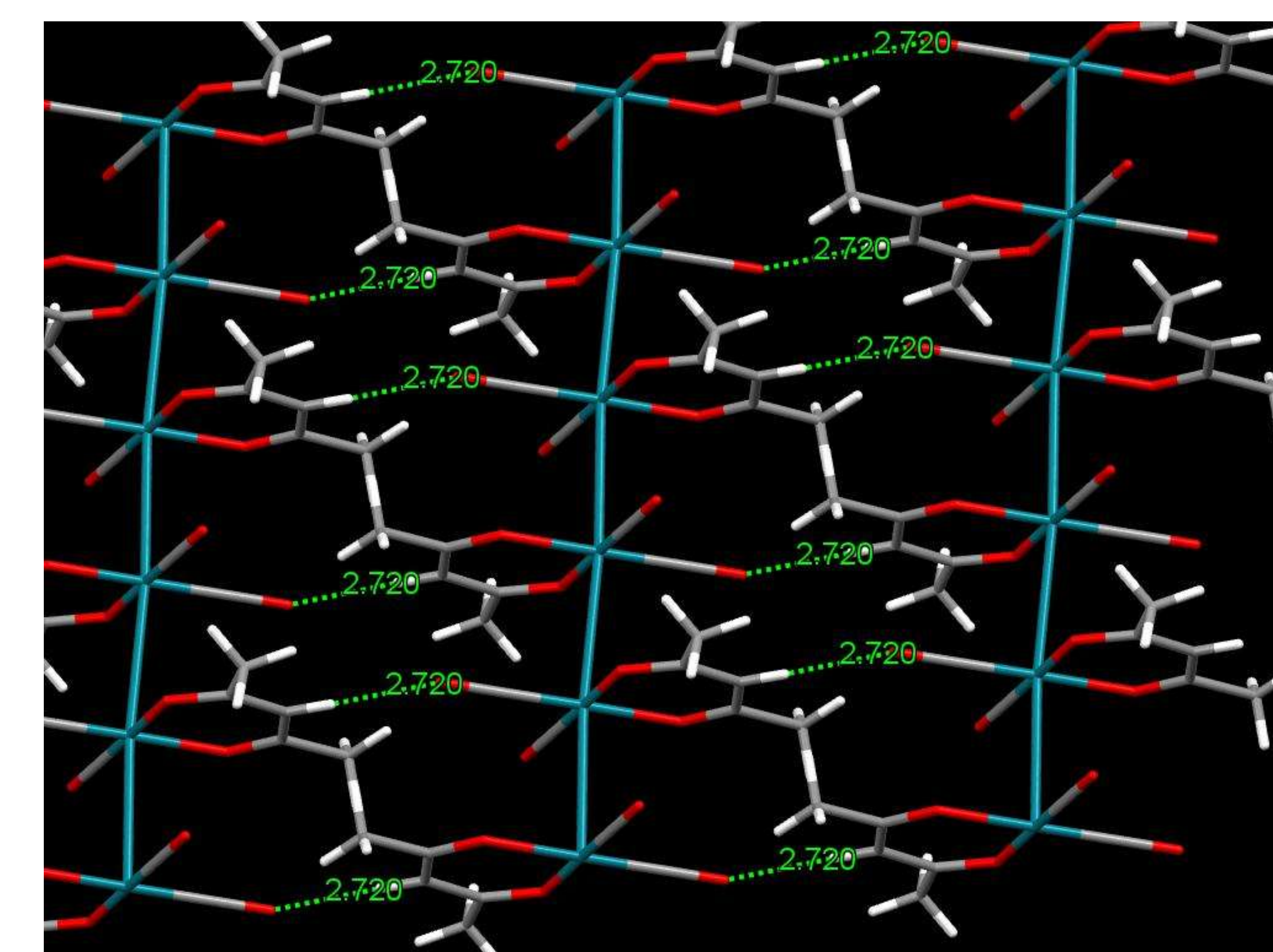
Carbons (1 and 3), (6 and 7), (4 and 5) are pairwise equivalent to one another (one doublet from each pair). In the quasi-isotropic solution medium, molecule $[\text{Rh}(\text{Acac})(\text{CO})_2]$ evidently belongs to the C_{2v} point group symmetry.

Peak assignments

- 1 – singlet from one of carbonyl groups in Acac ligand, $\text{CO}(\text{Acac})$
- 2 – superimposed signals: singlet from the other $\text{CO}(\text{Acac})$ group + low-field component of doublet from one of carbonyl ligands, $\text{CO}(\text{Rh})$
- 3 – high-field component of that doublet
- 4 and 5 – doublet from the other carbonyl ligand, $\text{CO}(\text{Rh})$
- 6 – singlet from methine group, $\text{CH}(\text{Acac})$
- 7 and 8 – two singlets from methyl groups, $\text{CH}_3(\text{Acac})$

The most probable reason for the duplication of the ^{13}C NMR resonances may be loss of the C_{2v} molecular symmetry on passing $[\text{Rh}(\text{Acac})(\text{CO})_2]$ molecule from the solution into the crystal. Two doublets from carbons of CO ligands and five singlets from Acac carbons should give in total nine peaks. Due to coincidence of two peaks, eight peaks are observed actually, one of them being of double intensity – see the figure above.

NMR studies were performed at the Centre for Magnetic Resonance, St. Petersburg State University.



Weak hydrogen bonds form an infinite network in the crystal lattice of $[\text{Rh}(\text{Acac})(\text{CO})_2]$