

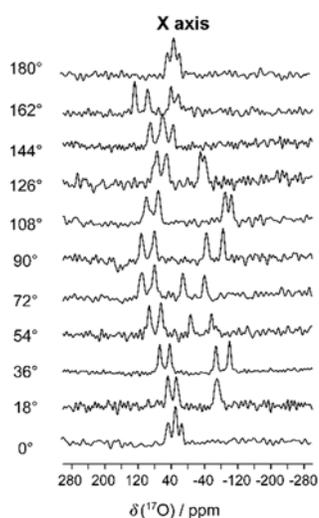
# Structure, Dynamics, and Symmetry. Electrophilic Interactions and Chemical Bonds in Solid Materials Studied by Multinuclear Magnetic Resonance

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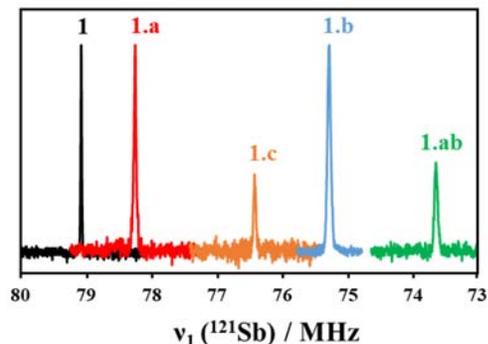
Recent advances from our laboratory are described in the context of two broad research themes: (a) non-covalent electrophilic interactions studied via solid-state NMR spectroscopy and (b) dynamics and equivalence from  $J$  splittings arising from pairs of quadrupolar nuclei in solids.

Over the past several years, a number of non-covalent bonding interactions, named after the electrophilic site, have taken on increased prominence in chemistry, biochemistry, materials science, and crystal engineering. These are akin in many respects to the ubiquitous hydrogen bond. For example, the halogen bond results from the donation of electron density from a Lewis base (Y) toward the electron-deficient  $\sigma$ -hole found on the halogen atom opposite a covalent bond, i.e., R-X $\cdots$ Y. We report on multinuclear powder and single-crystal solid-state magnetic resonance studies of a range of cocrystals and materials featuring halogen bonds, chalcogen bonds, pnictogen bonds, and tetrel bonds. The work involves the examination of a range of nuclides including  $^{13}\text{C}$ ,  $^{17}\text{O}$ ,  $^{31}\text{P}$ ,  $^{35/37}\text{Cl}$ ,  $^{79/81}\text{Br}$ ,  $^{127}\text{I}$ ,  $^{77}\text{Se}$ ,  $^{207}\text{Pb}$ ,  $^{121/123}\text{Sb}$ , etc.



**Figure 2.** Example of  $^{17}\text{O}$  single-crystal NMR data for an isotopically enriched halogen-bonded cocrystal.

Beyond the establishment of relationships between the various NMR tensor magnitudes and the nature of these electrophilic interactions, we also describe several other case studies of particular interest. These include: (i) real-time in-situ kinetic monitoring via  $^{31}\text{P}$  CP/MAS NMR of mechanochemical halogen bond formation in the NMR rotor [1], (ii) the implementation of deuterium NMR to discover and characterize dynamic processes which are catalyzed by halogen bonds [2], (iii) the application of single-crystal  $^{17}\text{O}$  and  $^{31}\text{P}$  SSNMR studies of halogen-bonded solids to reveal how the relevant chemical shift and quadrupolar coupling tensor orientations are affected by the non-covalent interaction (Figure 1); (iv) nuclear quadrupole resonance studies of the quadrupolar halogens participating in halogen bonds ( $^{35/37}\text{Cl}$ ,  $^{79/81}\text{Br}$ ,  $^{127}\text{I}$ ) and  $^{121/123}\text{Sb}$  NQR studies of antimony in pnictogen-bonded cocrystals (Figure 2) [3,4]. The latter work has led to a rudimentary implementation of 'NQR crystallography'.



**Figure 1.** Antimony-121 NQR spectra of pure  $\text{SbF}_3$  (**1**) and a series of pnictogen-bonded cocrystals [4].

In the final part of the talk, I will describe two-dimensional double-quantum filtered  $J$ -resolved solid-state NMR experiments applied to homonuclear pairs of quadrupolar nuclei.

These experiments provide valuable

information on crystallographic symmetry, bond order, electronic structure, and molecular dynamics. Results for  $^{11}\text{B}$ - $^{11}\text{B}$  and  $^{71}\text{Ga}$ - $^{71}\text{Ga}$  spin pairs in singly, doubly, and triply-bonded systems will be presented [5,6]. The central role of dynamics in the interpretation of the experimental data will be emphasized for a series of synthetically important electron-precise dianionic diboranes featuring two-centre two-electron bonds [7].

## References

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