HBA Tool : Delta-family Software for Spinning-Sideband Analysis in Solid-state NMR

In solid-state NMR, MAS (magic-angle spinning) spectra for spin-1/2 dilute nuclei, such as ^{13}C, exhibit resonance lines reflecting isotropic chemical shifts. On the other hand, when the chemical-shift anisotropy (CSA) is larger than the applied sample-spinning frequency, a series of additional lines, called spinning sidebands (SSBs), may appear. SSBs render the MAS NMR spectra complicated and are unnecessary to obtain isotropic chemical shifts.

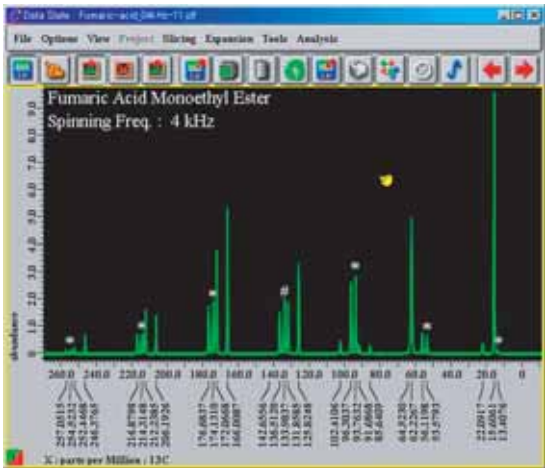
By analyzing SSB intensities, however, we can determine the principal values of CSA tensors, which may provide critical information on microscopic structures and dynamics of materials.

"HBA Tool"† is an application program which works seamlessly with JEOL Delta software and analyzes SSBs based on Herzfeld-Berger method (*J. Chem. Phys.*, **73**, 6021 (1980).). From the MAS NMR spectra presented on Delta, it is easy and straightforward to obtain CSA information by using "HBA Tool".

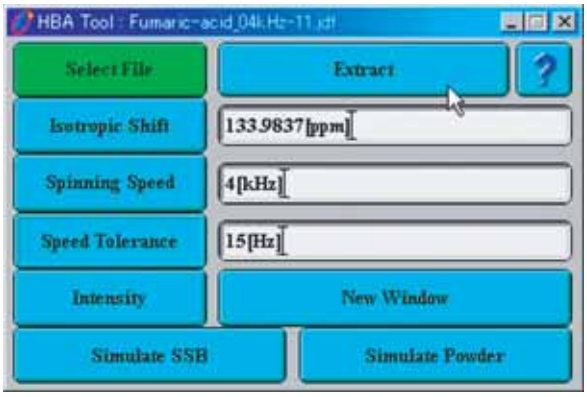
1. When HBA Tool is installed, it is registered in the main window of Delta. At first, click it as shown in the left Figure.

2. Input window of HBA Tool starts. By clicking "Select File" button, the mouse cursor becomes a fingering pointer.

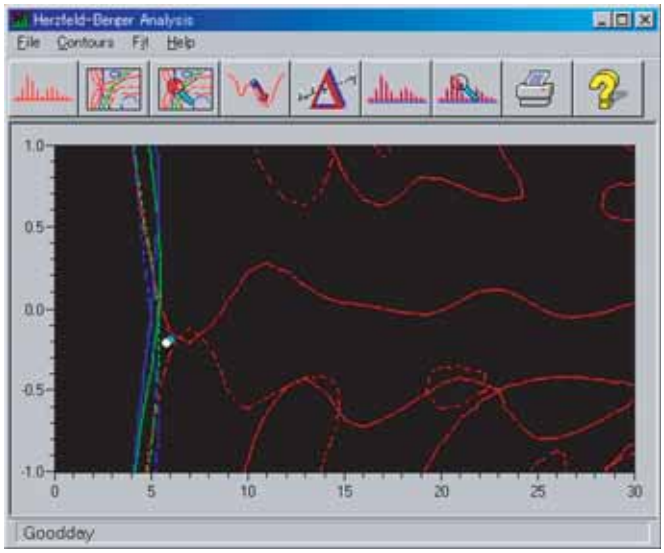
3. With the fingering pointer, touch the MAS NMR spectrum peak-picked on Delta. All information of SSB positions and intensities are loaded on Delta.



† Basic parts of HBA Tool were programmed by Dr. Klaus Eichel and his co-worker: HBA 1.5, K. Eichel and R. E. Wasylishen, Dalhousie Univ., Tuebingen, 2006; http://anorganik.uni-tuebingen.de/klaus/soft/index.php?p=hba/hba



4. Input the isotropic chemical shift (the position of the center peak) to specify a set of the SSB family of interest. Click “Extract” button to start SSB analysis.



5. A window illustrating contour lines appears, informing the end of the analysis.

The horizontal and vertical axes of the graph indicate fitting parameters, μ and ρ, which relate with the principal values of the CSA tensor, δ_{11}, δ_{22}, and δ_{33}:

$\mu = (\delta_{11} - \delta_{33}) / \nu_r$,
$\rho = (2\delta_{22} - \delta_{11} - \delta_{33}) / (\delta_{11} - \delta_{33})$.

The individual contour lines express possible values of μ and ρ. Their cross point manifests the unique values of μ and ρ, consistent with all the SSBs.

The cross point depicted as a white filled circle indicates the final values of μ and ρ.

6. Clicking the printer button in the contour-plot window leads to writing and showing the results of the analysis. The parameters such as Delta_11 signify the principal values of the CSA tensor calculated from μ (Mu) and ρ (Rho):

$\delta_{11} = \delta iso + (1/2)\, \mu\, \nu_r [\, 1 - (1/3)\, \rho\,]$,
$\delta_{22} = \delta iso + (1/3)\, \mu\, \rho\, \nu_r$,
$\delta_{33} = \delta iso - (1/2)\, \mu\, \nu_r [\, 1 + (1/3)\, \rho\,]$,

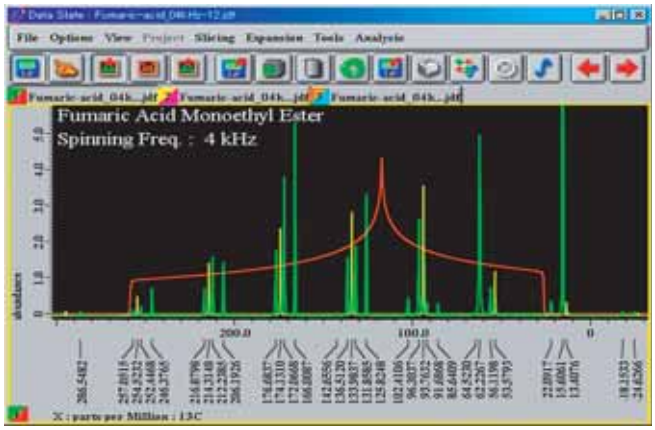
where δiso is the isotropic chemical shift:

$\delta iso = (1/3) (\delta_{11} + \delta_{22} + \delta_{33})$.

HBA Tool has various functions.

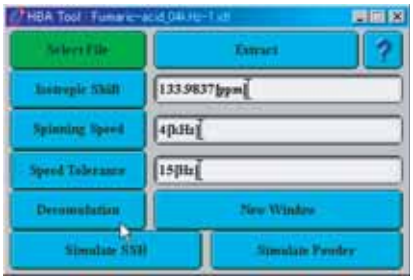
(1) It simulates SSBs and powder patterns.

SSBs and powder patterns are simulated and drawn on Delta by clicking “Simulate SSB” and “Simulate Powder” buttons, respectively.



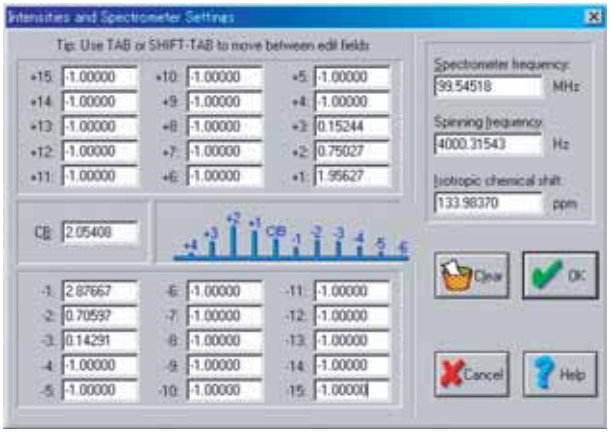
(2) It accommodates deconvolution data.

Peak-height and deconvolution-intensity modes are toggled by clicking “Intensity / Deconvolution” button. The deconvolved spectrum is specified with the fingering pointer after clicking “Select File” button.



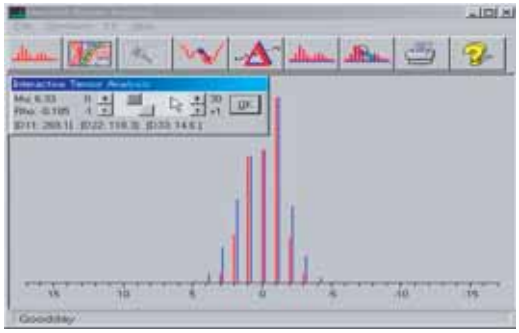
(3) It accommodates manually input data.

Input intensities are shown by clicking  button in the contour-plot window. The intensities can manually be input, modified, or deleted (input a value -1).



(4) It simulates SSBs for an arbitrary CSA tensor.

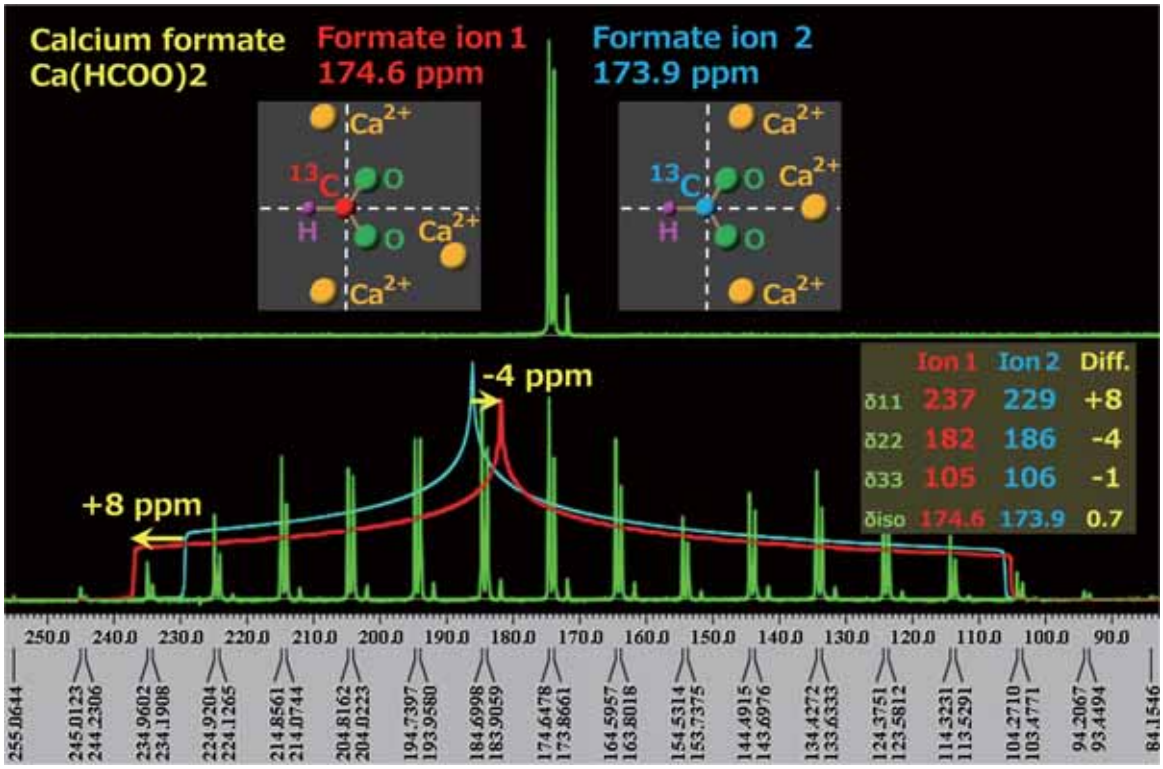
SSB bar graph is shown by clicking  button in the contour-plot window. SSBs are calculated and illustrated in real time by changing μ and ρ with the slide bar. The calculated SSBs (shown in blue) can be compared with observed SSBs (shown in red).



An example: CSA provides structural information of material.

Figure shows ^{13}C CPMAS spectrum for calcium formate $Ca(HCOO)_2$. Its unit cell involves two crystallographically inequivalent formate ions $HCOO^-$; the environments surrounding formate ions are largely different with each other.

However, their ^{13}C isotropic chemical shifts differ only by 0.7 ppm, not sufficiently reflecting the difference of their environments.



A lot of SSBs exhibit themselves in the CPMAS spectrum observed under slow spinning condition. HBA Tool analyzes the SSB intensities, leading to the principal values of CSAtensors as listed in the above Table; if represented as powder patterns, their difference becomes more evident as shown in the above Figure.

In this way, CSA determined using HBA Tool may yield detailed information on the microscopic structure of materials, whereas isotropic chemical shifts only suggest ambiguous information.