Characterization of $Mo(CO)_6$ by ^{95}Mo Single-Crystal NMR Spectroscopy

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Single-crystal ^{95}Mo NMR spectra for a crystal of $Mo(CO)_6$ have been acquired for the central and satellite transitions at a high magnetic field (14.1 T). The spectra are analyzed in terms of the quadrupole coupling and chemical shielding tensors. Parameters of high precision for the magnitudes, relative, and absolute orientations of these tensors are determined. The orientations of the two tensors are obtained without any a priori knowledge on the crystal symmetry of the $Mo(CO)_6$ octahedron. The optimized Euler angles, describing the relative orientation of the two tensors, are in accordance with the location of the Mo atom in a crystallographic mirror plane as also seen from the crystal structure of $Mo(CO)_6$ (orthorhombic, *Pnma*). The data from single-crystal NMR fully confirm the magnitudes and relative orientation of the quadrupole coupling and chemical shielding tensors determined in a recent ^{95}Mo static-powder NMR study of $Mo(CO)_6$. Thus, uncertainties about the reliablility of particularly the three Euler angles, describing the relative orientation of the tensor for the very small chemical shielding anisotropy and the quadrupole coupling tensor, have been clarified. Finally, it is shown that slow-speed spinning ^{95}Mo MAS NMR at a high magnetic field (14.1 T) allows determination of the NMR parameters with good precision for the two tensorial interactions, despite the small chemical shielding anisotropy.

Introduction

^{95}Mo (spin $I = 5/2$) NMR of molybdenum compounds in solution has formed an attractive, useful, and quite common analytical method for almost three decades, as evidenced by a recent review on ^{95}Mo NMR spectroscopy.[1] In contrast, much less attention has been paid to ^{95}Mo (or ^{97}Mo) NMR studies in the solid state, e.g., as judged from the overview given in a recent solid-state ^{95}Mo NMR study by Eichele et al.;[2] we note that a few other studies[3,4] may be added to this overview. The apparent lack of interest in solid-state ^{95}Mo NMR may be attributed to the low gyromagnetic ratio (γ) and low natural abundance (15.72%) for this nucleus. Recently, we extended our general interests in the determination of quadrupole coupling and chemical shielding tensors to include low-γ quadrupolar nuclei studied at high magnetic field, e.g., by a report of a quite small ^{67}Zn chemical shielding anisotropy (CSA) in a highly distorted octahedral environment.[5] In a continuation of these studies to ^{95}Mo, an important nucleus for our research related to industrial heterogeneous catalysts, we observed that the ^{95}Mo spin−lattice relaxation times (T_1) for a variety of inorganic molybdates are generally quite long,[6] as recently also observed for other molybdenum species.[4] Thus, in addition to the standard problems associated with a low-γ and low naturally abundant nucleus, i.e., low sensitivity and acoustic probe ringing, the long T_1 values may be an important characteristic which has hampered the flourishing of ^{95}Mo NMR of solids.

Prompted by the recent ^{95}Mo NMR study on a powder sample of molybdenum hexacarbonyl, $Mo(CO)_6$, by the Halifax group,[2] we found it of interest to apply single-crystal (SC) NMR techinques to this material. From a static-powder spectrum of the central and satellite transitions at 9.4 T, Eichele et al.[2] determined the relative orientation of the quadrupole coupling and chemical shielding (CS) tensor, in addition to the quite small magnitudes of these tensors, from the somewhat featureless line shape of the spectrum. Considering the difficulties generally encountered in retrieving all eight parameters describing the magnitude and relative orientations of these tensorial interactions from static powders,[7−9] it appeared somewhat surprising to us that all eight parameters could be obtained with good precision in the case of the extremely small magnitudes for the two tensor interactions in $Mo(CO)_6$. Especially this holds for the three Euler angles describing the relative orientation for the two tensors. For example, using the reported values for the quadrupole coupling and chemical shielding as fixed parameters we find that for a series of simulated static-powder ^{95}Mo spectra (9.4 T) the line shape of the overall spectrum changes only slightly for different combinations of the three Euler angles.

Considering our recent improvements in sensitivity for SC NMR probes using small rf coils and with the goniometer outside the coil (i.e., high filling factor),[10] it seems that a natural abundance ^{95}Mo NMR investigation of a single crystal of $Mo(CO)_6$ would be quite a challenge in testing the low-γ nuclei performance of the probe. This should simultaneously provide highly precise parameters for the two ^{95}Mo interactions, particularly for the three Euler angles, which serve useful for comparison with the ^{95}Mo static-powder data.[2] Here we report the results of such a ^{95}Mo SC NMR study including the determination of the absolute orientations for the two tensors with respect to the molecular frame. Finally, we have undertaken the challenge of studying the possiblility of slow-speed spinning ^{95}Mo MAS NMR at high magnetic field (14.1 T) as a method

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for determination of all eight parameters with high precision despite the apparently small CSA which may easily be averaged by MAS.

Experimental Section

Crystals of $Mo(CO)_6$ were obtained by sublimation of a commercial powder (Aldrich) at 15 mmHg and at a temperature of 35 °C. The selected crystal ($\sim 2 \times 2 \times 2$ mm^3) was glued onto a glass pin with an arbitrary orientation and covered by a film of epoxy to prevent the crystal to sublime.

^{95}Mo NMR experiments were performed at 39.0 MHz using a Varian INOVA 600 spectrometer equipped with a wide-bore 14.1 T magnet. The SC NMR spectra were recorded employing a two-axis goniometer SC NMR probe recently developed in our laboratory and designed particularly for improving the sensitivity of the NMR response from small crystals.[10] The new design uses only two axes of rotation (*a* and *b*) which are separated by an angle of ~39°. Rotation of the crystal is fully automated and controlled by the host computer of the spectrometer via a home-built interface.[10,12] This setup ensures a high precision (±0.3°) in setting the rotation angle (θ). For each rotation axis, 16 spectra were recorded following an incrementation in rotation angle of 24° and employing single-pulse excitation ($\tau_p = 4$ μs for $\gamma B_1/2\pi \approx 30$ kHz), a spectral width of 100 kHz, and 1100 scans with a repetition delay of 8 s ($T_1 = 15.9 \pm 0.5$ s at 14.1 T). The MAS NMR spectrum was recorded employing a CP/MAS probe for 7 mm o.d. rotors (Doty Scientific Inc). A stable spinning frequency of 900 ± 1 Hz was obtained using a Varian spinning-speed controller. ^{95}Mo chemical shifts are in ppm relative to an external 2.0 M aqueous solution of Na_2MoO_4.

The quadrupole coupling and CSA parameters are defined by

$$C_Q = \frac{eQV_{zz}}{h} \quad \eta_Q = \frac{V_{yy} - V_{xx}}{V_{zz}} \tag{1}$$

$$\delta_{iso} = \frac{1}{3}\mathrm{Tr}(\delta) \quad \delta_\sigma = \delta_{iso} - \delta_{zz} \quad \eta_\sigma = \frac{\delta_{xx} - \delta_{yy}}{\delta_\sigma} \tag{2}$$

using the convention

$$|\lambda_{zz} - \frac{1}{3}\mathrm{Tr}(\lambda)| \geq |\lambda_{xx} - \frac{1}{3}\mathrm{Tr}(\lambda)| \geq |\lambda_{yy} - \frac{1}{3}\mathrm{Tr}(\lambda)| \tag{3}$$

for the principal elements ($\lambda_{\alpha\alpha} = V_{\alpha\alpha}$, $\delta_{\alpha\alpha}$) of the two tensors. The relative orientation of the two tensors is described by the three Euler angles (ψ, χ, ξ) which correspond to positive rotations of the CSA tensor around δ_{zz} (ψ), the new δ_{yy} (χ), and the final δ_{zz} (χ) axis.[11] The assignment of the individual resonances in the SC NMR spectra and the subsequent analysis, including calculation of 95% confidence intervals, were performed using the software package *ASICS* (Analysis of Single-Crystal Spectra) developed in our laboratory,[12] while the analysis of the MAS NMR spectrum was performed using the program *STARS* also developed in our laboratory.[11,13]

Results and Discussion

A typical ^{95}Mo SC NMR spectrum of $Mo(CO)_6$ is shown in Figure 1. Generally the ^{95}Mo SC spectra display a maximum of 10 resonances corresponding to two pairs of outer and inner satellites and two central transitions. This observation reveals the presence of two magnetically nonequivalent ^{95}Mo sites. We note that the resonances for the central transitions overlap in the particular spectrum shown in Figure 1. As a result of the effect from the first-order quadrupolar interaction, the resonances from the satellite transitions make excursions over a frequency range of approximately 40 kHz. Figure 2 illustrates rotation plots for the satellite transitions corresponding to the two rotation axes *a* and *b*. We note that the rotation patterns for the two

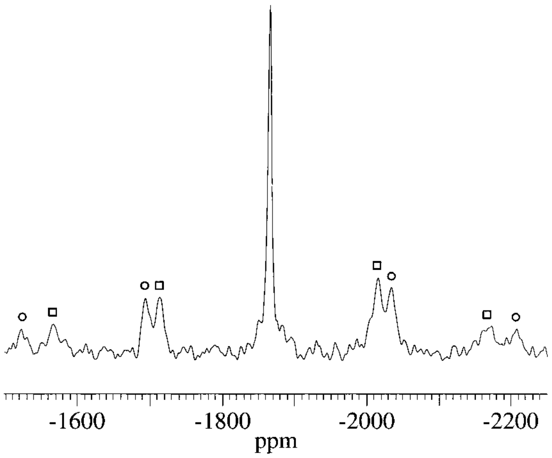

Figure 1. Single-crystal ^{95}Mo NMR spectrum (14.1 T) of a crystal of $Mo(CO)_6$ recorded using a 45° pulse, a relaxation delay of 8 s, and 1100 scans. The resonances from the inner and outer satellite transitions are marked by circles and squares for the two magnetically nonequivalent Mo sites.

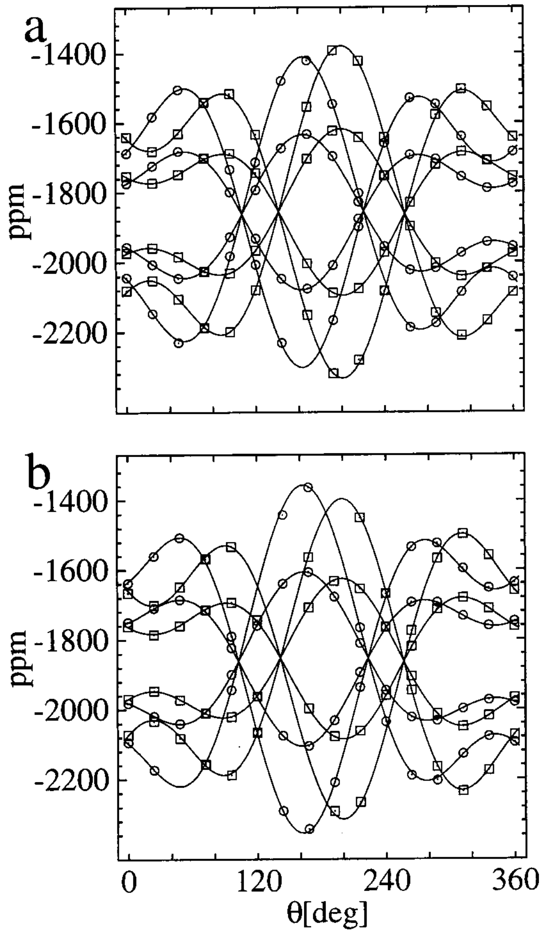

Figure 2. Rotation plots of the ^{95}Mo single-crystal resonance frequencies from the inner and outer satellite transitions for the two magnetically nonequivalent Mo nuclei in $Mo(CO)_6$. The resonances from the two sites are marked with circles and squares while (a) and (b) correspond to rotations about the *a* and *b* axes, respectively, for the two-axis goniometer SC probe.[10]

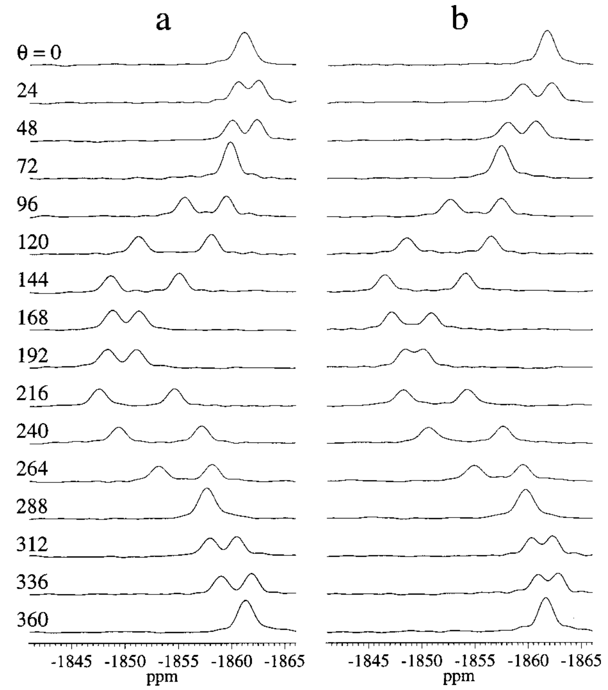

Figure 3. Expansions of the single-crystal ^{95}Mo NMR spectra illustrating the central transitions for the two magnetically nonequivalent nuclei in Mo(CO)$_6$. The spectra were recorded at 14.1 T following a 24° increment for the rotation about the two axes (*a* and *b*) of the two-axis goniometer SC probe.[10]

sites are quite similar, which suggests that the two sites are related by symmetry. A preliminary analysis of the resonances for the two sites, considering the quadrupole coupling interaction only, gives the parameters $C_Q = 89 \pm 1$ kHz and $\eta_Q = 0.15 \pm 0.01$ for both sites. This supports the supposition that the two magnetically nonequivalent ^{95}Mo sites are related by symmetry and do not arise from crystallographically different sites, i.e., the quadrupolar coupling tensors for the two ^{95}Mo sites have the same magnitude but different orientations. This is further supported by the observation of only one site in the static-powder and MAS NMR spectra of Mo(CO)$_6$.[2]

Figure 3 shows expansions of the experimental ^{95}Mo spectra of Mo(CO)$_6$ for the region of the central transitions. These resonances are observed over a frequency range of only 25 ppm (900 Hz) and have line widths between 50 and 80 Hz. At the present field strength of 14.1 T, the second-order quadrupolar shift for the central transition is less than 8 Hz. Thus, the displacement of the resonances is ascribed to the ^{95}Mo CSA. Analysis of the rotation plots for the resonances of the central transition in Figure 3, employing fixed values for the quadrupole coupling parameters (as determined from the satellite transitions), gives the parameters $\delta_\sigma = -11.5 \pm 0.3$ ppm and $\eta_\sigma = 0.95 \pm 0.04$ for both magnetically nonequivalent sites. Figure 4 shows the rotation plots for the central transitions with the experimental frequencies shown as circles and squares while the optimized quadrupole coupling and CSA parameters are represented by solid lines. In the absence of a second-order quadrupolar shift the correlation of the two sets of central-transition resonances to the two magnetically nonequivalent sites is not straightforward. Thus, it is not possible to determine the values for the three Euler angles (ψ, χ, and ξ describing the relative orientation of the quadrupole coupling and CSA tensors), since each of the two possible correlations results in identical values for two of the three Euler angles ($\psi = \xi = 90°$) while the remaining angle takes values of $\chi = 14°$ or $\chi = 50°$.

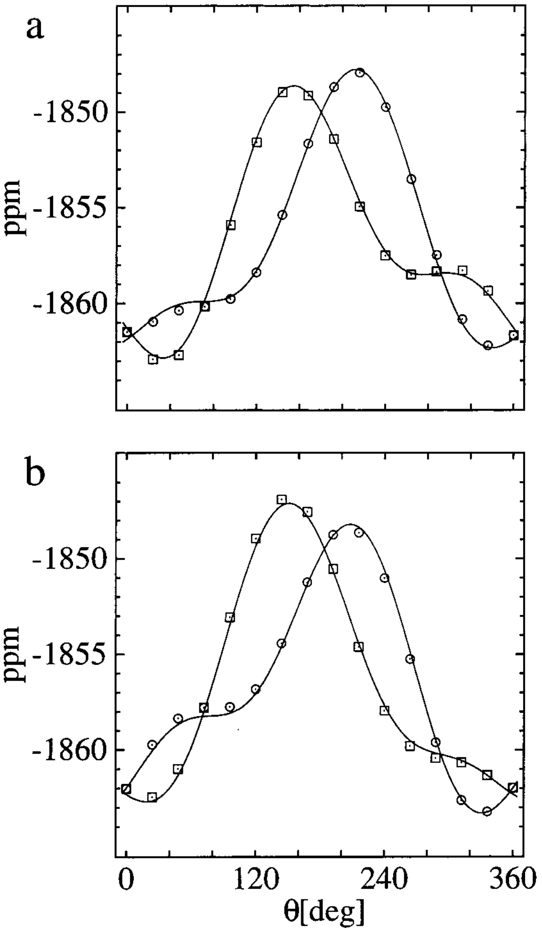

Figure 4. Rotation plots of the central-transition ^{95}Mo frequencies for Mo(CO)$_6$ with the experimental resonance frequencies for the two magnetically nonequivalent Mo atoms marked with circles and squares. Here, (a) and (b) correspond to rotations about the two axes (*a* and *b*) of the two-axis goniometer SC probe.[10]

An unambiguous assignment of the resonances for the central transition may be performed by investigating the influence of the ^{95}Mo CSA on the satellite transitions. By including the effect of the ^{95}Mo CSA on the satellite transitions (only the inner satellites are considered), the values $\delta_\sigma = -11.5 \pm 1$ ppm, $\eta_\sigma = 0.9 \pm 0.2$, $\psi = 90 \pm 4°$, $\chi = 49 \pm 5°$, and $\xi = 90 \pm 2°$ are obtained. These are in excellent agreement with the CSA parameters determined from the central transitions. To ensure the value $\chi = 49 \pm 5°$ represents a global minimum for the *rms* (χ^2_{opt}) function, Figure 5 shows a plot of χ^2_{opt} for different fixed values of χ, i.e., for each value of χ the following ten parameters have been optimized: C_Q, η_Q, δ_σ, η_σ, δ_{iso}, ψ, ξ, and the three Euler angles describing the absolute orientation of the quadrupole coupling tensor. These data demonstrate a well-defined minimum for χ^2_{opt} close to $\chi = 50°$.

Following the unambiguous assignment of the central-transition resonances, a refinement of all parameters is performed using (i) the rotation plots for the satellite transitions in an optimization of the quadrupole coupling parameters for fixed values of the CSA parameters and (ii) the rotation plots for the central transitions in an optimization of the CSA parameters for fixed C_Q and η_Q values. This procedure is repeated until convergence of all parameters is reached. The resulting ^{95}Mo parameters for the two tensorial interactions are summarized in Table 1 along with their error limits evaluated as 95% confidence intervals for the individual parameters.

TABLE 1: ^{95}Mo Quadrupole Coupling (C_Q, η_Q), Chemical Shielding Parameters (δ_σ, η_σ, δ_{iso}), and Relative Orientation (ψ, χ, ξ) for the Two Tensors for $Mo(CO)_6$ from ^{95}Mo Single-Crystal, Static-Powder, and MAS NMR

method	C_Q (kHz)	η_Q	δ_σ (ppm)	η_σ	δ_{iso}[a] (ppm)	ψ (°)	χ (°)	ξ (°)	ref
single-crystal	89.3 ± 0.2	0.151 ± 0.005	−11.5 ± 0.2	0.96 ± 0.03	−1854 ± 1	90.7 ± 0.6	49.6 ± 0.8	90.4 ± 0.3	this work
static-powder[b]	91	0.142	−11.0 ± 1.4	0.91 ± 0.17	−1854 ± 1	90	50	90	2
MAS	91.3 ± 0.8	0.15 ± 0.01	−12.5 ± 1.0	0.43 ± 0.26	−1854.2 ± 0.8	90[c]	40 ± 10	90[c]	this work

[a] Isotropic chemical shift relative to an external sample of an aqueous 2.0 M Na_2MoO_4 solution. [b] The parameters are given in accordance with the conventions used in this work (eqs 1−3). [c] Parameter fixed in the optimization (see text).

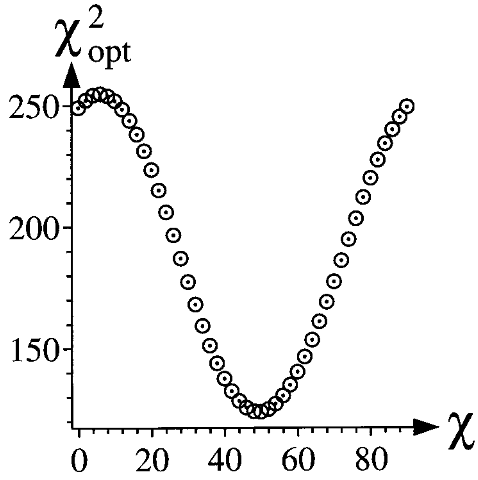

Figure 5. Plot of the χ^2_{opt} function for different fixed values of the Euler angle χ. Each point corresponds to a least-squares fitting of the calculated to the experimental resonance frequencies for the inner satellite transitions employing the parameters C_Q, η_Q, δ_{iso}, δ_σ, η_σ, ψ, ξ, α, β, and γ (see text) as variables. The plot illustrates a well-defined minimum for χ^2_{opt} about $\chi = 50°$.

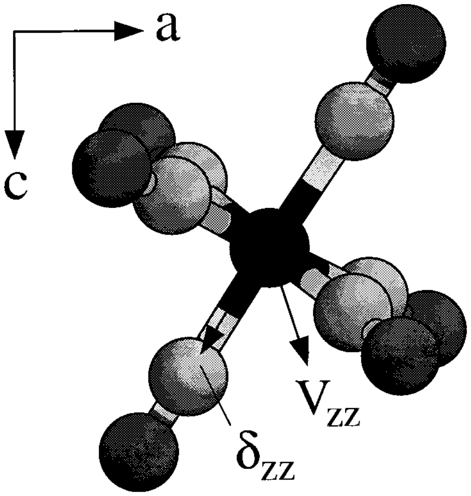

Figure 6. Projection of the $Mo(CO)_6$ unit in the orthorhombic crystal structure onto the *ac* plane (i.e., the mirror plane is in the plane of the paper) illustrating the orientation for the principal elements V_{zz} and δ_{zz} of the quadrupole coupling and chemical shielding tensor. The V_{xx} and δ_{xx} elements of the two tensors are perpendicular to the *ac* plane (cf., Table 2).

TABLE 2: Direction Cosines Describing the Orientation of the Principal Elements of the ^{95}Mo Quadrupole Coupling and Chemical Shielding Tensor for $Mo(CO)_6$ with Respect to the Crystal Frame

	a	*b*	*c*
V_{xx}	0.009	1.000	−0.008
V_{yy}	−0.942	−0.138	0.306
V_{zz}	0.307	0.005	0.952
δ_{xx}	0.007	−1.000	0.012
δ_{yy}	0.851	0.012	0.526
δ_{zz}	−0.526	0.007	0.851

As opposed to NMR of powders, SC NMR allows determination of the orientation of the quadrupole coupling and CS tensors with respect to the crystal/molecular frame. This has been achieved by performing an XRD study of the crystal, using the same crystal setup as for the NMR experiments[7,11] and gives the orientation of the crystallographic axes relative to the tenon frame. Thereby, an unambiguous assignment of the *a* and *c* axis was obtained from the XRD results. For the orthorhombic $Mo(CO)_6$ crystal of space group *Pnma* ($Z = 4$),[15] we may also take advantage of the relative orientation of the tensors for the two magnetically nonequivalent ^{95}Mo nuclei for determination of the orientation of the crystallographic axes according to the procedure previously described.[16] However, the determination of the absolute orientation for the tensors requires assignment of the two pairs of tensors to the two magnetically nonequivalent ^{95}Mo nuclei in the crystal structure. This is done by comparison of the orientation of the experimentally determined quadrupole coupling tensors with the estimated electric field gradient (EFG) tensor resulting from a point−monopole calculation.[17] In the calculation we have included the six carbonyl groups surrounding each molybdenum atom and employed effective atomic charges for C ($q_{eff} = +0.14e$ to $+0.17e$) and O ($q_{eff} = -0.46e$ to $-0.50e$) obtained from a Hatree-Fock calculation.[18]

Comparison of the orientations for the calculated EFG tensor and the experimentally determined quadrupole coupling tensors shows that the unique (V_{zz}) principal element for the calculated EFG tensor deviates by only 2° from that of one of the quadrupole coupling tensors while the deviation to the V_{zz} element of the other quadrupole coupling tensor is 34°. This allows assignment of the quadrupole coupling tensors, and the resulting orientations of the quadrupole coupling and CSA tensor are illustrated in Figure 6 and given by the direction cosines in Table 2. We note that the unique principal element of the CSA tensor (δ_{zz}) is aligned (within ±2°) along the two Mo−CO bonds located in the mirror plane, which possess the shortest and longest Mo−C bonds of the six carbonyl groups octahedrally coordinated around the central Mo atom.

At this stage it seems appropriate to make a comparison of the eight ^{95}Mo parameters (in particular the three Euler angles) for $Mo(CO)_6$ determined here from ^{95}Mo single-crystal NMR with those recently reported by Eichele et al.[2] from static-powder NMR. To properly compare these data, the relations between the two sets of conventions used to express the anisotropic interactions in this and earlier studies (see Experimental Section) and by the Halifax group must first be established. For the Halifax convention we note that $\delta_{xx} \geq \delta_{yy} \geq \delta_{zz}$ for the principal elements of the shielding tensor, while $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$ for the principal elements of the electric field gradient (quadrupole coupling) tensor, i.e., a reversal of the order for the two latter elements as compared to that in eq 3. For the three Euler angles (α, β, γ) used by Eichele et al.[2] to describe the relative orientation of the chemical shielding (CS) and quadrupole interaction (QI) tensor, we note that the convention $\delta^{QI}_{CS} = R_{z''}(\gamma)R_{y'}(\beta)R_z(\alpha)\delta^{PAS}_{CS}$ is used,[2,19] i.e., similar to the convention used in our work for ψ, χ, and ξ. Using the values $\delta_{xx} = -1843 \pm 1$ ppm, $\delta_{yy} = -1855 \pm 1$ ppm, $\delta_{zz} = -1865 \pm 1$ ppm, and $\delta_{iso} = -1854 \pm 1$ ppm reported by Eichele et al.[2] for $Mo(CO)_6$, we obtain the values in Table 1 ($\delta_\sigma = -11.0 \pm 1.4$ ppm and $\eta_\sigma = 0.91 \pm 0.17$) for the CS tensor. Because of the differences in the conventions for the principal elements of the CS and electric field gradient tensor, we find that the three Euler angles ψ, χ, and ξ in our nomenclature correspond to α, γ, and β, respectively, used by the Halifax group.[2,16] Thus, the values $\alpha = 90°$, $\beta = 90°$, $\gamma = 50°$ determined by Eichele et al.[2] convert to $\psi = 90°$, $\chi = 50°$, $\xi = 90°$ for the definitions used here and elsewhere. Comparison of the results in Table 1 for the present single-crystal study with those of the static-powder study shows an excellent agreement between the two sets of data. However, from the error limits listed in Table 1 we note that the single-crystal data are obtained with a high degree of precision; in particular this holds for the Euler angles ψ, χ, and ξ. The χ angle demonstrates a complete agreement between the single-crystal and static-powder value. This result came somewhat surprisingly to us as can be seen from the introduction.

Finally, we investigate the possibility of employing slow-speed ^{95}Mo MAS NMR at high magnetic field (14.1 T) to $Mo(CO)_6$ for determination of all eight parameters characterizing the ^{95}Mo CSA and quadrupole coupling interaction, a method that has proven successful at 9.4 T in studies of the somewhat larger ^{133}Cs interactions for some cesium salts.[20] A slow-speed spinning ($\nu_r = 900$ Hz) ^{95}Mo MAS NMR spectrum of the central and satellite transitions for $Mo(CO)_6$ recorded at 14.1 T is shown in Figure 7a. Apparently, this spectrum differs significantly from the ^{95}Mo MAS spectrum (9.4 T, $\nu_r = 1122$ Hz) reported by Eichele et al.,[2] because asymmetries within the manifold of spinning sidebands (ssbs) from the satellite transitions are clearly observed in Figure 7a. These asymmetries arise because of the CSA interaction and thus show that this interaction is not completely averaged by MAS under the present experimental conditions. In this context we note, as shown elsewhere,[13] that rf excitation/detection of the manifold of ssbs from the satellite transitions in MAS NMR does not perturb the overall relative intensity distribution within the ssb envelope to the same degree as in the case for the line shape of a static powder spectrum. Least-squares eight-parameter optimization of simulated to experimental ssb intensities reveals that reliable values for the three Euler angles cannot be obtained from the spectrum in Figure 7a because of the small CSA. Thus, taking advantage of the crystal structure for $Mo(CO)_6$ (orthorhombic, *Pnma*),[15] i.e., the Mo atom is located in the crystallographic mirror plane,[12] this implies that one axis for each of the two tensors is perpendicular to this plane. This constraint is fulfilled when two of the Euler angles (ψ, χ, ξ) equal 0° modulo 90°. Using different combinations of these values (fixed) for the Euler angles in least-squares optimizations gives the lowest *rms* deviation between simulated and experimental ssb intensities for $\psi = \xi = 90°$. These values are subsequently employed as fixed parameters in a six-parameter least-squares optimization, which gives the parameters for the two tensors and the χ-angle listed in Table 1. The error limits correspond to 95% confidence intervals and are calculated using the procedure given elsewhere.[20] The simulation corresponding to the optimized parameters is illustrated in Figure 7b which shows that the asymmetries within the manifold of experimental ssb intensities are convincingly reproduced. Comparison of the ^{95}Mo MAS NMR data with those from single-crystal NMR shows that the parameters C_Q, η_Q, δ_σ, and δ_{iso} are obtained with high precision. Somewhat lower precision is observed for η_σ and the Euler angle χ, which is most likely the results of the very small ^{95}Mo CSA in comparison to the quadrupole coupling. Improved precision of these parameters may be obtained for larger CSA interactions as demonstrated elsewhere.[20] The present MAS NMR results show that employing a combination of high magnetic field and slow-speed spinning, small CSA interactions for low-γ quadrupolar nuclei may be retrieved with a precision at least as good as obtained from static-powder NMR.

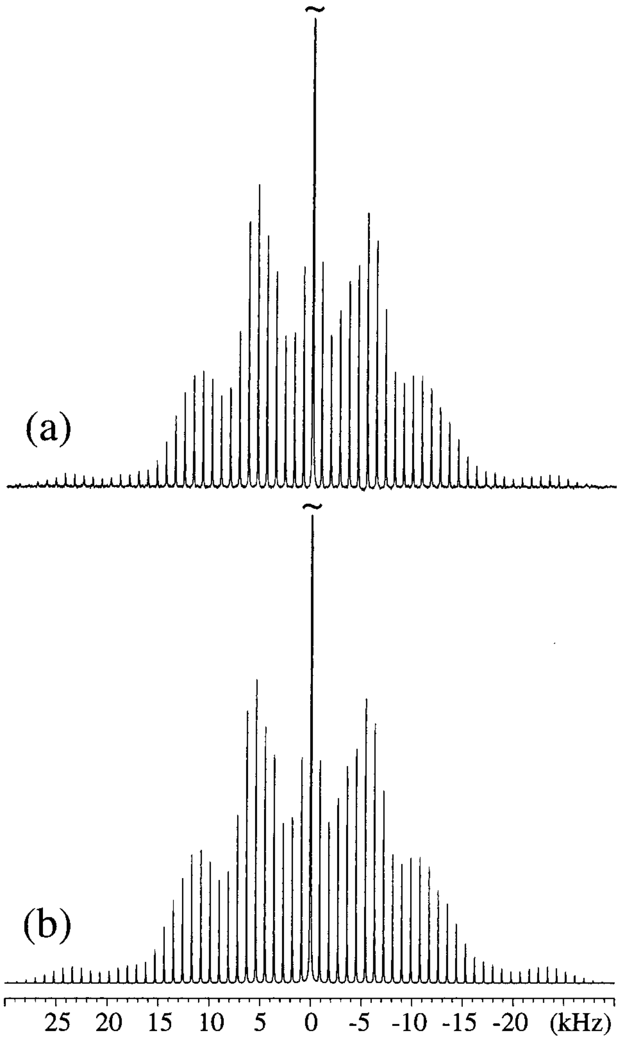

Figure 7. (a) ^{95}Mo MAS NMR spectrum (14.1 T) of the central and satellite transitions for $Mo(CO)_6$ obtained using a spinning speed of $\nu_r = 900$ Hz, a relaxation delay of 10 s, and 7778 scans. (b) Optimized simulation of the spectrum in (a) employing the quadrupole coupling and CSA parameters listed in Table 1. For both spectra the central transition is cut off at 1/6 of its total height and the kHz scale has been referenced to the center of gravity of the central transition.

We should note that solid-state ^{95}Mo NMR spectra and quadrupole coupling parameters for $Mo(CO)_6$ have earlier been obtained by other research groups.[21−24] A discussion of these spectra and parameters has been given by Eichele et al.[2] who observed that the reported parameters showed large deviations from those determined from their static-powder NMR study at 9.4 T.[2]

Conclusions

The new two-axis goniometer single-crystal NMR probe[10] with the goniometer outside a small rf coil has proven particularly useful in studies of low-γ quadrupolar nuclei of low natural abundance. For ^{95}Mo in $Mo(CO)_6$ a single-crystal study has resulted in the determination of parameters for the quadrupole coupling and chemical shielding tensors along with the three Euler angles describing the relative orientation of these tensors; all parameters are determined with an exceptionally high precision. These data fully support the results of a recent static-powder NMR study[2] and those of the MAS investigation reported here for $Mo(CO)_6$, although these powder data are obtained with somewhat lower precision.

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