

Mechanisms of molecular motion of Mo(CO)₆ in zeolites NaY and HY from ¹³C-NMR lineshapes

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Mechanisms of molecular motion of $\text{Mo}(\text{CO})_6$ in zeolites NaY and HY from ^{13}C -NMR lineshapes

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Abstract

The potential of ^{13}C -NMR spectroscopy of stationary samples for the study of mechanisms of anisotropic molecular motion of $\text{Mo}(\text{CO})_6$ adsorbed in zeolites has been examined. Free diffusional rotation or jump processes about the various symmetry axes of the octahedral complex cause motional averaging of ^{13}C chemical shift anisotropy, allowing for the characterization of the different motional mechanisms. At 110 K a large portion of the $\text{Mo}(\text{CO})_6$ molecules is firmly fixed in zeolites NaY and HY as indicated by a broad (ca. 410 ppm) chemical shift powder pattern. A narrow ^{13}C -NMR component is observed in both zeolites for molecules undergoing isotropic motion or rotation about a three-fold axis. An additional line, which is inverted in shape and reduced in width by a factor of $-1/2$ compared to the rigid case, is only observed for NaY. This line is assigned to molecules undergoing free rotation about the four-fold axis, but it may also be due to $\text{Mo}(\text{CO})_6$ jumping about a two-fold axis. The changes in the distribution of molecules in different motional states was explored between 110 K and ambient temperature. Molecules undergoing rotations or jumps about the four- or two-fold axes only exist in NaY at lower temperatures when stationary $\text{Mo}(\text{CO})_6$ molecules are also present. At 180 K and higher temperatures, rotation about the three-fold axis or isotropic motion are the sole types of molecular motion. © 1997 Elsevier Science B.V.

Keywords: ^{13}C -NMR; HY; $\text{Mo}(\text{CO})_6$; Mobility; NaY

1. Introduction

The inclusion of transition metal complexes by zeolite host frameworks has evolved into a thriving field of current materials research [1–3]. A possible synthetic route for the post-synthetic insertion of

transition elements into a zeolite from the gas or liquid phase is the use of metal carbonyl compounds [4–10]. One example of this class of inclusion compounds is zeolite Y loaded with $\text{Mo}(\text{CO})_6$ molecules. This material is a precursor for heterogeneous catalysts [11], and it offers perspectives to novel materials with special electronic and optical properties [12]. $\text{Mo}(\text{CO})_6$ is only admitted into the supercages of zeolite Y, because it is too bulky to penetrate through the

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six ring windows of the sodalite cages and the hexagonal prisms. The local interactions which determine the location, distribution and mobility of $\text{Mo}(\text{CO})_6$ are of synthetic as well as theoretical interest.

Various methods, for example vibrational, NMR or EXAFS spectroscopies have been employed to characterize metal carbonyls encaged in zeolites [7,13,14]. ^{13}C MAS NMR spectroscopy was applied to zeolites X and Y containing subcarbonyls of $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ [15,16]. The mobility of $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$ in zeolite Y has been studied by ^{13}C -NMR spectroscopy [17,18].

The location and ordering of the molybdenum hexacarbonyl clusters in the supercages of the zeolite Y crystals is a hitherto unsolved question. Molecular dynamics simulations on $\text{Mo}(\text{CO})_6$ loaded in zeolite Y have been carried out for different extra-framework cations [19]. For NaY the $\text{Mo}(\text{CO})_6$ molecules were predicted to assemble pairwise in the vicinity of the 12-membered ring windows at full loading of two molecules per supercage. On the basis of space-filling computer models, Pastore et al. have concluded that $\text{Mo}(\text{CO})_6$ is oriented along its four-fold axis between two sodium cations within the supercage, resulting in an interaction of the two trans-CO ligands with two Na^+ cations [14]. From ^{23}Na -NMR studies it is clear that the $\text{Mo}(\text{CO})_6$ molecules interact with the extra-framework sodium cations in the supercages of zeolite NaY [14,20–22]. A complementary approach to a deeper understanding of the interaction between extra-framework cations and $\text{Mo}(\text{CO})_6$ is the investigation of the molecular motion of the complex.

2. Theoretical section

Anisotropic nuclear spin interactions offer an excellent means for studying anisotropic motions in solids by NMR spectroscopy. The chemical shift tensor, δ , with its three principal components, $\delta_{11} \geq \delta_{22} \geq \delta_{33}$, characterizes the anisotropic nuclear shielding. The isotropic chemical shift (δ_{iso}), the asymmetry parameter (η), and the span (Ω) are

defined by [23]:

$$\delta_{\text{iso}} = 1/3(\delta_{11} + \delta_{22} + \delta_{33}), \quad (1)$$

$$\eta = \frac{\delta_{22} - \delta_{11}}{\delta_{33} - \delta_{\text{iso}}}, \quad (2)$$

and

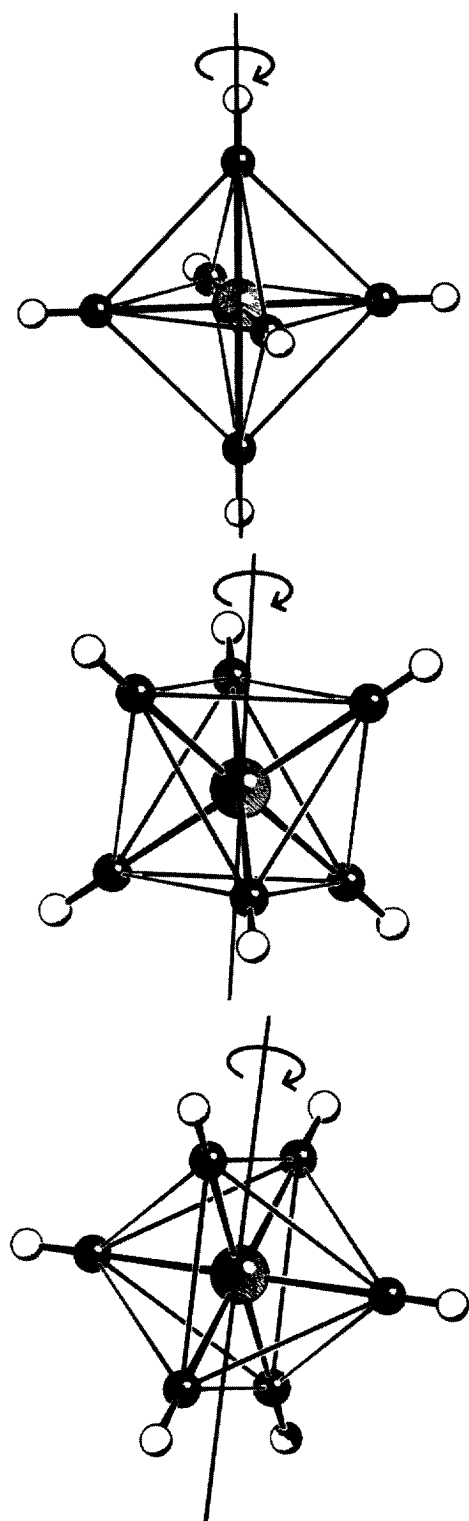
$$\Omega = \delta_{11} - \delta_{33}. \quad (3)$$

In $\text{Mo}(\text{CO})_6$ δ is axially symmetric ($\eta=0$) for the ^{13}C nuclei, and the three chemical shift components are reduced to $\delta_{11} = \delta_{22} = \delta_{\perp}$ and $\delta_{33} = \delta_{\parallel}$. The orientation of the tensor is defined for each carbonyl group with δ_{\parallel} being directed along the C–O bond, while the two degenerate components, δ_{\perp} , are perpendicular to this bond and to each other. As a result of anisotropic shielding, a broad ^{13}C -NMR line is observed for a stationary sample with a typical powder pattern [24,25]. The line-shape can be used to analyse the chemical shift tensor resulting in the parameters $\delta_{\text{iso}} = 201$ ppm, $\eta = 0$ and $\Omega = 410$ ppm for crystalline $\text{Mo}(\text{CO})_6$ [24,25].

In solution fast isotropic reorientation averages the anisotropic part of the chemical shift tensor to zero, and only the isotropic value δ_{iso} is directly available in the ^{13}C -NMR experiment. As opposed to isotropic liquids, anisotropic motional processes can occur in solids leading to only partial averaging of δ . The most probable dynamic processes of $\text{Mo}(\text{CO})_6$, which affect the ^{13}C -NMR linewidth in zeolite Y, are isotropic motion and uniaxial rotations. Fig. 1 shows three different rotation axes for $\text{Mo}(\text{CO})_6$, i.e. rotations about the four-, three- and two-fold axes. The anisotropic dynamic averaging of δ is easy to describe in the fast motional limit, namely the motional correlation time is much shorter than the reciprocal linewidth (ca. $25 \mu\text{s}$ at $B_0 = 9.4$ T). Two anisotropic rotational motions have to be distinguished: free rotational diffusion, and discrete jumps between different orientations. For fast uniaxial rotational diffusion, the averaged span is given by the angle φ between the rotation axis and the C–O bond direction:

$$\bar{\Omega} = \frac{1}{2}(3 \cos^2 \varphi - 1)\Omega. \quad (4)$$

Irrespective of its original value in the stationary molecule, the averaged asymmetry parameter, $\bar{\eta}$,



is zero for all rotation angles φ [26]. The expected ^{13}C -NMR spectra for the different modes of molecular reorientation are summarized below.

A rotation about a four-fold axis [Fig. 1(a)] partially averages the chemical shift powder pattern, and the ^{13}C -NMR spectrum shown in Fig. 2 is expected. The two axial CO ligands do not move, leaving the corresponding ^{13}C -NMR lineshape unchanged [Fig. 2(b)]. Four CO ligands rotate with an angle of $\varphi=90^\circ$ resulting in a narrowing factor of $-1/2$ according to Eq. (4) [Fig. 2(c)]. The negative sign means that the shape of the chemical shift powder pattern is inverted. The expected ^{13}C -NMR spectrum for the entire $\text{Mo}(\text{CO})_6$ molecule is shown in Fig. 2(a) exhibiting a characteristic maximum at $\delta=133$ ppm. Recall

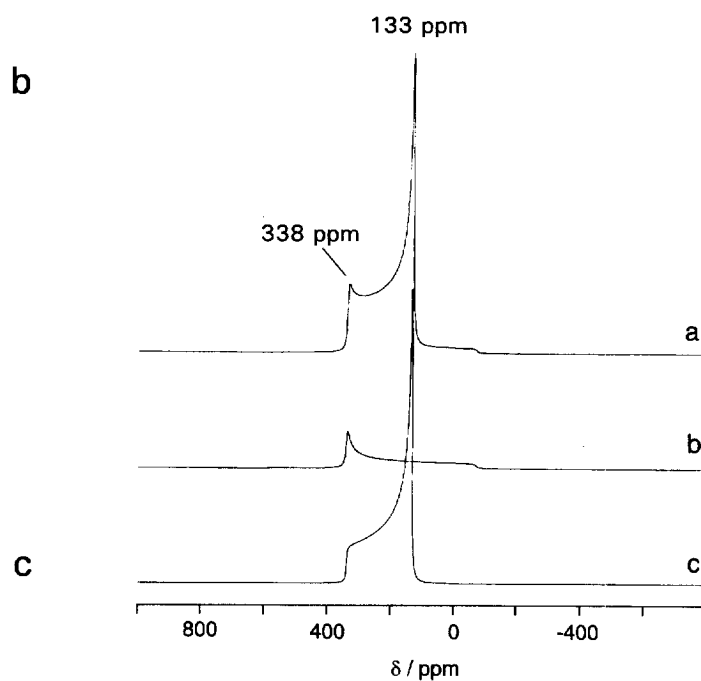


Fig. 2. (a) Calculated ^{13}C -NMR spectrum for $\text{Mo}(\text{CO})_6$ undergoing free rotation about the four-fold axis, or jumping about the two-fold axis; lines (b) and (c) are expected components (see text).

Fig. 1. The principal axes of uniaxial molecular rotation of octahedral $\text{Mo}(\text{CO})_6$: rotation about the (a) four-fold axis, (b) three-fold axis, and (c) two-fold axis; large grey atoms are Mo, small dark atoms are C, and white atoms are O.

that this value indicates the most intense part of the asymmetric lineshape and does not correspond to the isotropic chemical shift. The latter is defined at the centre of gravity of the chemical shift powder pattern. This method has been applied to a $\text{Mo}(\text{CO})_5$ fragment adsorbed on γ -alumina so as to show the rotation about the four-fold axis of the pyramidal geometry of $\text{Mo}(\text{CO})_5$ [24]. The authors concluded that the four-fold axis of the $\text{Mo}(\text{CO})_5$ moiety is oriented perpendicular to the surface. If a $\text{Mo}(\text{CO})_6$ molecule rotates quickly about a fixed three-fold axis [Fig. 1(b)], then φ is the magic angle (54.74°) resulting in $\bar{\Omega}=0$, and a sharp line at $\delta_{\text{iso}}=201$ ppm. This result is also expected for fast isotropic motion. Rotation about the two-fold axis [Fig. 1(c)] would again result in two different types of CO ligands, two with $\varphi=90^\circ$ and four with $\varphi=45^\circ$. The expected features in the ^{13}C -NMR spectrum (Fig. 3) would be a dominant maximum at $\delta=235$ ppm for $\varphi=45^\circ$ [Fig. 3(c)], and a less intense maximum at 133 ppm for $\varphi=90^\circ$ [Fig. 3(b)].

For discrete rotational jumps the situation differs, and the averaged chemical shift tensor,

δ_{avg} , has to be calculated from the contributions of all orientations

$$\delta_{\text{avg}} = \sum_{j=1}^N p_j \delta_j, \quad (5)$$

where p_j are the occupation probabilities [27,28], and N is the number of orientations. δ_{avg} is not necessarily axially symmetric even if the static tensor is. However, for rotational jumps with C_N symmetry, the averaged chemical shift tensor is axially symmetric ($\bar{\eta}=0$) for $N \geq 3$ [27]. The expected lineshape would not differ from the one expected for free uniaxial rotational diffusion about the same rotation axis. On the contrary, the expected lineshapes for free rotation about a two-fold symmetry axis would generally be different from a jump mechanism about the same axis. For such a two-site jump $\bar{\eta}$ and $\bar{\Omega}$ are a function of the angle Φ between the two non-averaged principal tensor orientations [27], i.e. the angle between the exchanging interatomic CO vectors. In Fig. 1(c) two pairs of CO ligands in $\text{Mo}(\text{CO})_6$ would exchange by an angle of $\Phi=90^\circ$, resulting in the averaged values $\bar{\eta}=0$ and $\bar{\Omega}=-1/2\Omega$, and for the two CO ligands with a corresponding angle of $\Phi=180^\circ$ the static tensor would not be altered by the two-site jump process [27,28]. The expected ^{13}C -NMR spectrum of $\text{Mo}(\text{CO})_6$ would actually be the same for such a two-site jump about the two-fold symmetry axis and for the rotational diffusion about the four-fold symmetry axis (Fig. 2). Therefore, a ^{13}C -NMR lineshape analysis cannot distinguish between these two cases.

Here, the ^{13}C -NMR spectra of stationary zeolite NaY and HY samples loaded with $\text{Mo}(\text{CO})_6$ were analysed at a variety of temperatures between 110 K and ambient temperature in view of the dynamic averaging of chemical shift anisotropy due to different mechanisms of molecular motion.

3. Experimental section

3.1. Materials

The dehydration and loading of the zeolites NaY and HY with $\text{Mo}(\text{CO})_6$ have been described previously [22]. The highest achievable loading is

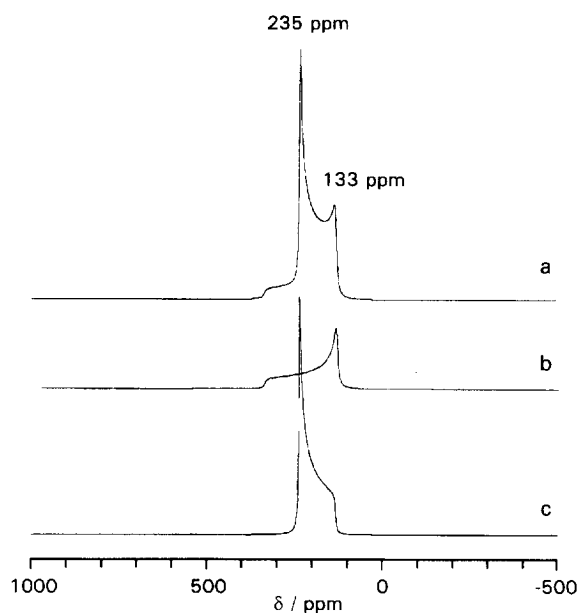


Fig. 3. (a) Calculated ^{13}C -NMR spectrum for $\text{Mo}(\text{CO})_6$ undergoing free rotation about the two-fold axis; lines (b) and (c) are expected components (see text).

two molecules per supercage. Special attention has been paid to avoid partial decarbonylation by dry-mixing the zeolites (0.5 g) with $\text{Mo}(\text{CO})_6$ and annealing the mixtures at 383K in a sealed glass ampoule [22]. The structural integrity of the samples and the absence of H_2O and SiOH defect groups were ensured by ^1H MAS NMR spectroscopy. ^{13}C enrichment of $\text{Mo}(\text{CO})_6$ was carried out in the zeolite by the following procedure. The loaded zeolite was evacuated at 353K for periods between 5 and 45 min. During this treatment the sample turned yellow, indicating partial decarbonylation of the hexacarbonyl complex [8]. Then the ampoule was filled with labelled ^{13}CO gas (Campro Scientific, 99.3% ^{13}C) which caused immediate disappearance of the yellow colour. Evacuation and refilling was repeated twice, and the sample was then kept under a ^{13}CO atmosphere overnight at ambient temperature. Afterwards, the slightly evacuated glass ampoule was sealed under liquid nitrogen. The obtained sample was colourless, and decarbonylated fragments were not observed by ^{13}C -NMR spectroscopy [16]. About 50% of the CO ligands were labelled as estimated from ^{13}C -NMR spectroscopy at room temperature with absolute intensity scaling. The intramolecular ^{13}C - ^{13}C dipole interaction is expected to be small, e.g. it is smaller by at least a factor of 50 as compared to that of ^1H - ^1H spin-pairs in H_2O , considering the different molecular geometries and nuclear gyromagnetic ratios. In addition, any ^{13}C homonuclear dipole interactions are not refocussed by the applied spin-echo-technique (see below), and therefore do not contribute to the observed lineshape.

3.2. NMR spectroscopy

All ^{13}C -NMR experiments were obtained on stationary samples in sealed glass ampoules at a ^{13}C resonance frequency of 100.6 MHz using a Bruker MSL-400 spectrometer. The chemical shift scale is relative to tetramethylsilane. The spin-echo technique ($\pi/2$ - τ - π - τ -acquire) was applied with $\pi/2$ pulse lengths of 8.5 μs and recycle delays of 5 s. A delay of 60 s did not give any results different from the reported experiments. The dwell time was 1 μs in order to digitize sufficient data points in the fast

decaying parts of the time domain signals. No more than 250 free induction decays were necessary to achieve a good signal-to-noise ratio, and Fourier transformation was carried out without exponential line-broadening. A ^{13}C probe background was eliminated by appropriate phase cycling in the spin-echo experiments. The spectra were analysed using the programs WINNMR and WINFIT (Bruker).

4. Results and discussion

The results of NaY loaded with two molecules $\text{Mo}(\text{CO})_6$ per supercage, which is full coverage, are presented first. The ^{13}C spin-echo NMR spectrum of this sample at 110 K is shown in Fig. 4(a). At least three components are readily identified by their characteristic peak maxima at

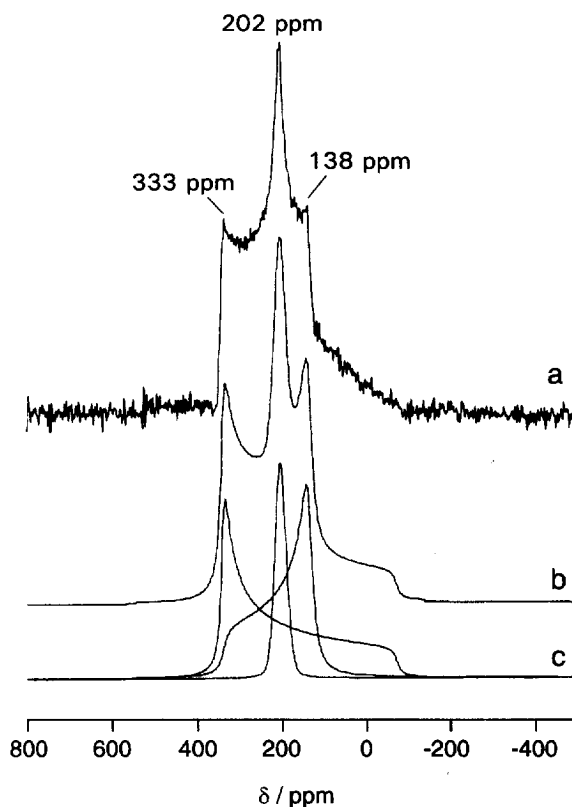


Fig. 4. (a) ^{13}C spin-echo NMR spectrum of $\text{Mo}(\text{CO})_6$ in zeolite NaY at 110K; (b) simulated spectrum; (c) components of (b).

138, 202 and 333 ppm. The simulated components shown in Fig. 4(c) are plotted with the parameters based on the premise that the ^{13}C chemical shift tensor without motion is the same in the zeolite and in bulk $\text{Mo}(\text{CO})_6$ [24]. The results of the spectral analyses show that this assumption is reasonable. The small deviations of the maxima in Fig. 4 from the expected positions (Fig. 2) are probably due to minor variations in nuclear shielding caused by the host–guest interactions in the zeolite, and they are of no concern for the general conclusions here.

The narrow component at 202 ppm in Fig. 4(c) can be due to isotropic motion of $\text{Mo}(\text{CO})_6$ molecules, or it can be caused by moieties rotating or jumping about the three-fold axis [cf. Fig. 1(b)]. The broad powder pattern with a maximum at ca. 138 ppm is caused by $\text{Mo}(\text{CO})_6$ molecules rotating about the four-fold axis, or by molecules which experience a two-fold jump mechanism. In either case another broader component is expected (cf. Fig. 2), and this is observed by the broad chemical shift powder pattern with the maximum at 333 ppm [Fig. 4(a) and (c)]. However, the intensity of this broad component is larger than expected for molecules in the two possible motional states. This observation indicates that a considerable portion of the $\text{Mo}(\text{CO})_6$ molecules are not moving at all on the NMR time scale. These static molecules contribute to the intensity of the expected ^{13}C -NMR spectrum [cf. Fig. 2(b)] which has been reported in Refs [24,25] for bulk $\text{Mo}(\text{CO})_6$.

Upon increasing the sample temperature, the ^{13}C -NMR spectra change considerably (Figs. 5 and 6). A concomitant disappearance of the two broad components is observed when the temperature is increased to 180 K (Fig. 5). From this observation it follows that the static $\text{Mo}(\text{CO})_6$ molecules are becoming mobile when the temperature is increased. Additionally, the disappearance of the inverted component, with the corresponding maximum at 138 ppm, indicates that local diffusional rotation about the four-fold axis or rotational jumps about the two-fold axis have ceased to exist at 180 K. It is probable that other types of motion now contribute to the dynamics, and the ^{13}C -NMR linewidths are further reduced. The possible motional mechanisms at 180 K are a fast

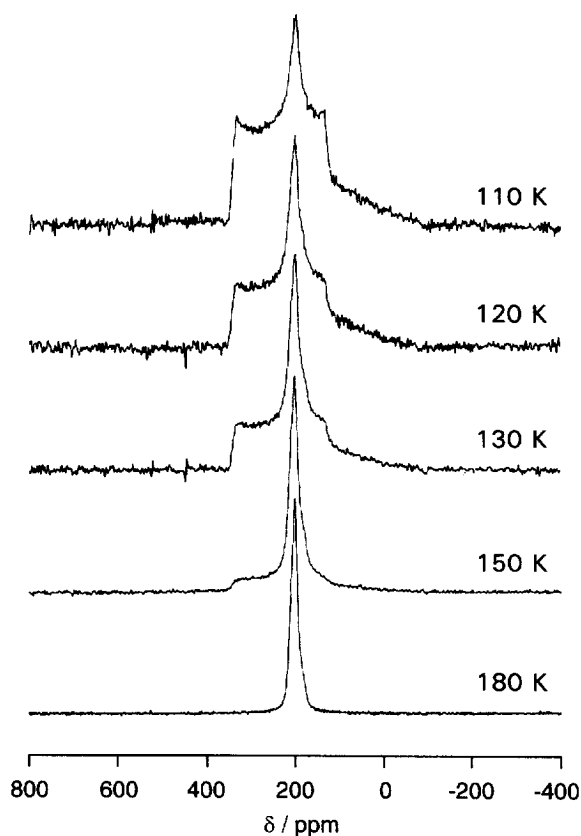


Fig. 5. ^{13}C spin-echo NMR spectra of $\text{Mo}(\text{CO})_6$ in zeolite NaY at the indicated temperatures.

isotropic tumbling or a rotation about the three-fold symmetry axis (free rotation or discrete jumps) with a corresponding narrow ^{13}C -NMR signal at 202 ppm. This feature is further analysed between 180 and 260 K in Fig. 6, where an asymmetric shape of this signal at 202 ppm is apparent at 180 K. A weak shoulder on the left-hand side and a clear shoulder at the high-field side are observed which both decline upon increasing the temperature to 260 K. This observation is rationalized by the components shown in Fig. 6. A gaussian component at 202 ppm and a chemical shift powder pattern with an averaged span $\bar{\Delta}$ of 38 ppm and a chemical shift of $\delta = 202$ ppm are used for a spectral fit. A ^{13}C -NMR spectrum similar to the one shown for 180 K in Fig. 6 has been observed at room temperature in a Na, NH_4 -Y zeolite loaded with $\text{Mo}(\text{CO})_6$ [22]. In that case, the presence of

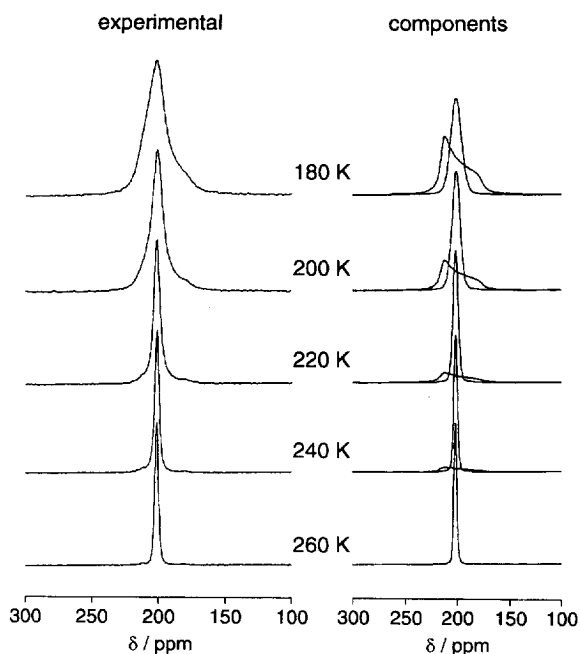


Fig. 6. Experimental ^{13}C spin-echo NMR spectra of $\text{Mo}(\text{CO})_6$ in zeolite NaY at the indicated temperatures (left) and simulated components (right).

the two components was confirmed by magic angle spinning. A small elongation of the octahedral geometry by about $3\text{--}4^\circ$ along the three-fold symmetry axis would result in the averaged span value $\bar{\Omega}$ of 38 ppm according to Eq. (4) [22]. Another possible explanation for the line broadening is an additional motion of the rotational direction by a few degrees, when the undistorted $\text{Mo}(\text{CO})_6$ octahedron rotates close to the three-fold axis. At least one conclusion is unambiguously clear: the broader component at 180 K cannot be explained by molecules undergoing isotropic motion. Rotation of $\text{Mo}(\text{CO})_6$ about an axis close to the three-fold symmetry axis is the only possible mechanism to account for the broad component in Fig. 6.

The gaussian component, which is the only signal remaining at 260 K or higher temperatures, is assigned to $\text{Mo}(\text{CO})_6$ molecules undergoing isotropic motion. This explanation is consistent with ^{95}Mo -NMR relaxation data which suggest high, liquid-like mobility of $\text{Mo}(\text{CO})_6$ in the supercage of zeolite NaY at room temperature [29].

Due to the different rotational directions, all possible orientations of $\text{Mo}(\text{CO})_6$ to the extra-framework sodium cations are likely: in particular, $\text{Mo}(\text{CO})_6$ can interact with Na^+ along the four-, three- and two-fold axes. The ^{13}C -NMR experiments as such do not indicate whether these types of interaction take place on one or on both sides of the rotating complex. However, the high sodium cation concentration {ca. two Na^+ per $\text{Mo}(\text{CO})_6$ in the supercage [22]} makes the latter very likely. For rotations about the four- or two-fold axes, a Na^+ cation interacts with one or two CO ligands, respectively. At temperatures of 180 K and higher these motions are not observed on the NMR time scale. In contrast, the orientation of three CO ligands towards Na^+ along the three-fold axis of $\text{Mo}(\text{CO})_6$ survives at higher temperatures, up to 240 K, indicating higher stability of this mode of interaction. Interestingly, the reorientation along the four- or two-fold axes, which cannot be distinguished by the lineshape analyses, is only observed when stationary $\text{Mo}(\text{CO})_6$ molecules are also present. Steric influences are one obvious explanation for this observation. ^{13}C -NMR experiments with half-loading of one molecule per supercage showed the presence and the same concomitant decrease of the broad components between 110 and 180 K as the experiments with full coverage. This experiment would apparently provide an argument against steric reasons. However, one must bear in mind that one molecule per supercage is an average value, and pairing of two molecules close to each other, as suggested by Brémard et al., could occur [19].

In zeolite HY the $\text{Mo}(\text{CO})_6$ molecules are highly mobile at room temperature. An interaction with the charge-compensating protons (Brønsted sites) in the supercages is indicated by a shift of the corresponding signal in the ^1H MAS NMR spectrum from 3.7 to ca. 4.7 ppm. A similar change of the proton chemical shift of the Brønsted protons in the sodalite cages at 4.2 ppm is not observed as $\text{Mo}(\text{CO})_6$ cannot enter the sodalite cages in order to interact with these sites [22].

At low temperatures the situation in HY is different from zeolite NaY. Fig. 7 shows the ^{13}C -NMR experiments for temperatures ranging from 110 to 298 K. Only two maxima at 331 and

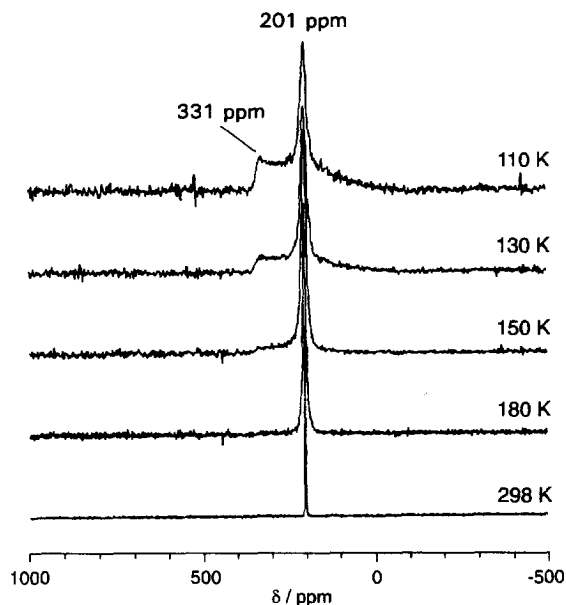


Fig. 7. ^{13}C spin-echo NMR spectra of $\text{Mo}(\text{CO})_6$ in zeolite HY at the indicated temperatures.

201 ppm are observed at 110 K. The broad component with a maximum at 331 ppm can only be due to static $\text{Mo}(\text{CO})_6$ molecules. The narrow component at 201 ppm is assigned to molecules undergoing rotation about the three-fold axis or rotating isotropically. At higher temperatures the narrow component increases in relative intensity, and the broad component has disappeared at 180 K. The peak at 201 ppm can be simulated with a single gaussian line (not shown) with decreasing linewidth upon increasing the temperature. An asymmetric shape of the narrow component in the ^{13}C -NMR spectra of $\text{Mo}(\text{CO})_6$ in HY, as shown in Fig. 6 for NaY, is not observed. Unlike the results for $\text{Mo}(\text{CO})_6$ in NaY, it follows that in HY fast diffusional rotation about the four-fold axis and two-fold jumps of the hexacarbonyl octahedron do not occur. A diffusional rotation about the two-fold axis does not exist in either zeolite, NaY and HY, since the expected maximum at 235 ppm, shown in Fig. 3, is not found.

At least at low temperatures a chemical exchange between CO ligands is not likely to be the reason for the line narrowing effects, since the observed differences between NaY and HY could not be

rationalized. A recent theoretical work [30] and results from laser pyrolysis in the gas phase [31] show that the first Mo–CO bond dissociation energy is ca. 165 kJ mol^{-1} . This finding defines an upper limit for the activation energy of CO ligand exchange between different molecules. It is anticipated that this bond dissociation energy is lower in zeolites due to the electrostatic potential. At room temperature a chemical exchange is deemed to be possible in the zeolite matrix. The ease of the ^{13}C labelling procedure to an exchange level of about 50% implies that a fast redistribution of CO ligands takes place. Another evidence for the CO exchange to be facilitated in the zeolite at higher temperatures is the decarbonylation observed by a yellow colour [8,22]. In a closed ampoule the decarbonylation is effectively suppressed [22]. By simply watching the colour changes of zeolites loaded with $\text{Mo}(\text{CO})_6$ in a glove box, we found qualitatively that decarbonylation in NaY is faster than in HY. This could be due to the different kinds of interactions between $\text{Mo}(\text{CO})_6$ and Na^+ or H^+ .

5. Conclusions

It has been shown that ^{13}C -NMR spectroscopy is a useful method to characterize motional mechanisms of $\text{Mo}(\text{CO})_6$ in zeolites NaY and HY. At 110 K a large portion of molecules does not move on the NMR time scale. However, for the other $\text{Mo}(\text{CO})_6$ species in NaY several motional processes exist. Rotation about the three-fold axis or isotropic motion is observed, along with a second type of motion which can be a fast rotation about the four-fold axis or a jump process about the two-fold axis of the octahedral complex (or both). The ^{13}C -NMR lineshape analysis cannot distinguish between the two latter cases. A free rotation about the two-fold axis is not observed.

Upon increasing the temperature gradual changes become apparent. The disappearance of stationary molecules is accompanied by a change in the distribution of molecules in different motional states. At 180 K all $\text{Mo}(\text{CO})_6$ molecules are more or less mobile by rotating about the three-fold axis or by an isotropic process, but

rotations about the two- or four-fold axes no longer exist at these higher temperatures. The latter are only observed in NaY in conjunction with stationary $\text{Mo}(\text{CO})_6$ at lower temperatures. These motional mechanisms indicate the distribution of local orientations of $\text{Mo}(\text{CO})_6$ toward the extra-framework sodium cations, and the observed changes show that these orientations vary with temperature. From these results it follows that the system is characterized by a complex orientational disorder of $\text{Mo}(\text{CO})_6$. In addition, the rotational degrees of freedom of $\text{Mo}(\text{CO})_6$ in zeolite Y depend on the nature of extra-framework cations. This disorder has also been confirmed by means of ^{23}Na MAS NMR spectroscopy [22].

The differences in molecular motion of $\text{Mo}(\text{CO})_6$ in NaY and HY zeolites are ascribed to differences in local interactions between the adsorbed complex and the extra-framework cations. Sodium cations influence the directions of molecular reorientations of $\text{Mo}(\text{CO})_6$ more so than Brønsted protons do.

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