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Reorientational Dynamics of Cyclohexadienyl Radicals in High-Silica ZSM-5

Emil Roduner,* Martina Stolmár, and Herbert Dilger
Institute of Physical Chemistry, University of Stuttgart, D-70569 Stuttgart, Germany

Ivan D. Reid
Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

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The avoided-level-crossing relaxation of a polarized muon spin-label was used to investigate the reorientational dynamics of muonated cyclohexadienyl radicals in NaZSM-5 with SiO_2/Al_2O_3 ratios of 670 and 900 and loadings of one and two benzene molecules per unit cell. It was found that on a critical time scale of about 50 ns the radical performs fast uniaxial rotation about the axis perpendicular to the molecular plane. Superimposed on this there is a two-site jump motion between two orientations that differ by an angle of 110° and 1.0 kJ mol^{-1} in energy. This causes increasing averaging of the orientations above 50 K. It is particularly extensive but still not isotropic in a temperature range between 200 and 450 K. Below 50 K, the uniaxial rotation slows down below the critical time scale of the experiment, and below 20 K any motion is frozen. It is suggested that such a high reorientational mobility is possible only for the radicals occupying sites at the channel intersections. Above ca. 450 K, the reversible appearance of new broad spectral features suggests that new sites with much lower mobility become thermally accessible. These may be located inside the channels.

1. Introduction

The host−guest interactions and the mobility of reactants, intermediates, and products of reactions in zeolites are of paramount importance for the performance of catalytic processes. This holds for the translational mobility, as reactants have to reach the active centers and products have to diffuse out of the porous structures. It is the basis of the efficiency of the catalyst. Reorientational mobility is a measure of similar spatial constraints and of specific interactions. For transient intermediates, in particular, it influences transition-state selectivity and reaction pathways in general.

Reorientational dynamics of diamagnetic molecules in zeolites has been studied mainly by means of nuclear magnetic resonance[1−4] and by quasi-elastic neutron scattering,[5] but Monte Carlo and molecular dynamics calculations[6] have contributed much to a detailed understanding. To reduce complexity, investigations have concentrated on simple molecules of high symmetry and on a few well-defined zeolite structures. One of the best known systems is that of benzene in silicalite I, the siliceous form of ZSM-5 with MFI structure. At least three locations have been suggested as the adsorption site for aromatic molecules in the MFI framework: the zigzag channel, the straight channel, and the intersection between them.[7,8] The benzene molecules fit snugly into the channels which are of slightly elliptical cross section with a diameter of ca. 0.55 nm. At saturation, a maximum of eight molecules can be accommodated per unit cell, but only four intersections are available. The situation is complicated by phase transitions between three subtle polymorphic modifications of the structure which may be monoclinic (MONO) or orthorhombic (in two forms for which the designations ORTHO and PARA have been established). The dependence of these phase transitions on temperature and on the type and the loading of the guest molecule has to be considered when data from different investigations are compared; but also the aluminum content of the ZSM-5 structure plays a role, and the various techniques probe the dynamics on quite different time scales.

The present work is concerned with the reorientational dynamics of the cyclohexadienyl radical which differs from benzene only by an additional hydrogen atom (in the present work by the light hydrogen isotope muonium). It is an open-shell species, but apart from this it is planar like benzene and only slightly elongated in shape; thus, unless there is a specific chemical interaction due to the unpaired electron, one would expect a very similar dynamic behavior as for benzene. The experimental technique is that of avoided-level-crossing muon spin resonance (ALC-μSR), a special variant of magnetic resonance,[9,10] which interprets the relaxation of a polarized muon spin-label in the radical as a function of a longitudinally applied magnetic field which is scanned through avoided crossings of magnetic energy levels. The technique has proven to be very sensitive to reorientational dynamics on a critical time scale of the inverse hyperfine anisotropy, which is typically of the order of 50 ns.[9]

2. Theoretical Background

2.1. Muons and Muonated Species. The positive muon (μ^+) is a spin $^1/_2$ elementary particle with a mass of one-ninth the proton mass. It is available at the ports of suitable accelerators in the form of beams with a spin polarization close to 100%. Like the proton it forms a bound state with an electron. This has been dubbed muonium (Mu $\equiv \mu^+e^-$). Since its reduced mass and its ionization potential are within 0.5% the same as those of H, its chemical behavior is also the same as that of H,

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* To whom correspondence should be addressed. e-mail Roduner@indigo01.chemie.uni-stuttgart.de.

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except when its mass leads to a vastly different dynamics and thus to a large kinetic isotope effect.[11] Mu is thus in a chemical sense a light isotope of hydrogen.[12]

In the experiment, energetic muons are implanted into the sample of interest, where they slow down. They may end up as thermal muons in a diamagnetic environment, or they may capture an electron from the medium or recombine with one of the ionization electrons close to the end of their thermalization tracks to form Mu. Depending on the medium, Mu may be observed directly, or it may react to form a muonated molecule or radical.

Of relevance in the present context is its addition to benzene, forming a cyclohexadienyl radical

$$C_6H_6 + Mu \rightarrow C_6H_6Mu \qquad (1)$$

in which the muon is substituted in the methylene group as a polarized spin-label. It has been used to study the structures of substituted cyclohexadienyl radicals,[13] their reaction kinetics,[14] their translational diffusion on the surface of spherical silica grains,[15] and their interaction with copper ions in ZSM-5 zeolite.[16] Here, it will allow the investigation of the radical reorientation dynamics in high-silica ZSM-5.

2.2. The ALC-μSR Response. The experimental sample is placed in a magnetic field parallel to the orientation of the muon spin in the beam. In general, the spin systems in high fields are represented by pure Zeeman states. Thus, there is no evolution of spin polarization, and the information of interest, the time-integrated muon polarization, is given by the initial muon polarization in the beam. The situation changes near avoided crossings of magnetic energy levels that belong to different muon spin states. The eigenstates are then mixtures of Zeeman states, which leads to oscillation or relaxation of muon spin polarization and hence to a decrease of its time-integrated value. This is the origin of ALC-μSR resonances in a plot of the polarization against field.

Three types of resonances corresponding to different selection rules are expected to occur for a muon−electron−nuclear system with corresponding spin operators I_μ, S, and I_p.[9,10]

(i) Terms of the type $S^+I_\mu^-$ and $S^-I_p^+$ or ($S^-I_\mu^+$ and $S^+I_p^-$) in the spin Hamiltonian lead to muon−proton spin flip-flop transitions in which the spin polarization oscillates between the muon and one of the protons. These terms arise from the isotropic part of the hyperfine interaction, and thus the corresponding Δ_0 resonances (abbreviation for $\Delta m_\mu + \Delta m_p = 0$) are seen for radicals in the solid as well as in the liquid and gaseous phases. They occur at resonance fields given by[14]

$$B_r(\Delta_0) = \frac{|A_\mu - A_p|}{2(\gamma_\mu - \gamma_p)} - \frac{A_\mu + A_p}{2\gamma_e} \qquad (2)$$

where for isotropic media A_μ and A_p are the isotropic muon and proton hyperfine interaction constants in MHz and γ_μ, γ_p, and γ_e are the muon, proton, and electron gyromagnetic ratios (135.5 MHz T^{-1}, 42.57 MHz T^{-1}, and 2.8025×10^4 MHz T^{-1}, respectively). For anisotropic media, A_μ and A_p are the *effective* hyperfine interactions which depend on the orientation of the hyperfine tensor in the external field.

(ii) Terms of the type I_μ^+ or I_μ^-, which are found in the dipolar part of the hyperfine interaction Hamiltonian, give rise to a muon spin flip transition Δ_1 at[10]

$$B_r(\Delta_1) = \frac{|A_\mu|}{2\gamma_\mu} - \frac{A_\mu}{2\gamma_e} \qquad (3)$$

This resonance depends solely on muon hyperfine parameters. It is observed only under anisotropic conditions, where it is most intense, and it is absent in the liquid or gaseous phase where the dipolar interaction is averaged to zero due to the rapid collisional reorientation of the radical. The presence of this resonance is thus a most sensitive indicator for anisotropic conditions and its shape and width for the nature of the averaging motion. The critical time scale for the averaging process is given by the inverse of the hyperfine anisotropy, for axial systems $|2\pi D_\perp|$, where $D_\perp$ is the perpendicular component of the anisotropy in MHz.

(iii) Δ_2 resonances correspond to muon proton spin flip−flip transitions which arise from terms of the type $S^+I_p^+$ and $S^-I_p^-$ in the dipolar part of the Hamiltonian. They are narrow and of low intensity and therefore of no practical importance for disordered systems.

For liquids and static single-crystalline systems, the resonances are of Lorentzian shape. For powders there is a distribution of resonance fields due to the orientation dependence of the effective hyperfine interaction, giving rise to typical powder patterns.

2.3. Hyperfine Interactions in C_6H_6Mu. The Mu adduct to benzene was one of the first muonated radicals to be observed directly.[17] Since then, a large number of singly and multiply substituted muonated cyclohexadienyl radicals were observed so that substituent effects on A_μ are well understood.[14] They follow the same trends as those of H-substituted analogues, and there is a strong correlation between A_μ of the cyclohexadienyl radical and A_p of the α-proton in substituted benzyl radicals, which demonstrates the isoelectronic character of the two species.

Compared with the methylene proton coupling in C_6H_7, the muon coupling in C_6H_6Mu is larger by the ratio of the muon−proton magnetic moments, $\mu_\mu/\mu_p = 3.1833$, and on top of that by a further factor of ca. 1.20. The latter is called the intrinsic isotope effect and ascribed to the C−Mu bond length which, owing to anharmonicity of the potential, is larger than that of C−H by ca. 5% in the vibrational average.[18]

ALC-μSR led to the determination of the isotropic proton hyperfine coupling constants in C_6H_6Mu and, most remarkably, in ^{13}C-enriched samples of the carbon hyperfine couplings, including their temperature dependences.[19,20] Not unexpectedly, a study of the radical in the gas phase led to very similar coupling constants.[21] Significant progress was also made in quantum chemical calculations of the coupling constants, which for delocalized radicals has always been a particular challenge.[22]

An orientation-dependent single-crystal study allowed the determination of the muon hyperfine anisotropy in the Mu adduct to durene, the muonated 2,3,5,6-tetramethylcyclohexadienyl radical.[23] As expected, it was found that a large positive principal component of 8.15 MHz was oriented approximately along the C−Mu bond, at an angle of 25° with respect to the molecular plane. It was nearly balanced by a negative out-of-plane component of −9.05 MHz, leaving only a small in-plane principal component of +0.9 MHz. Considering that the four methyl groups reduce the spin population in the ring by approximately 13%, we arrive at estimated principal values of +9.4, −10.4, and +1.0 MHz for the unsubstituted cyclohexadienyl radical. These numbers agree well with the theoretical values, scaled for the muon, of +9.8, −11.6, and +1.8 MHz, respectively.[22] As well, the theoretical angle of 23° is in perfect agreement with the experimental determination. Knowing the muon and the methylene proton values and their relative angle,

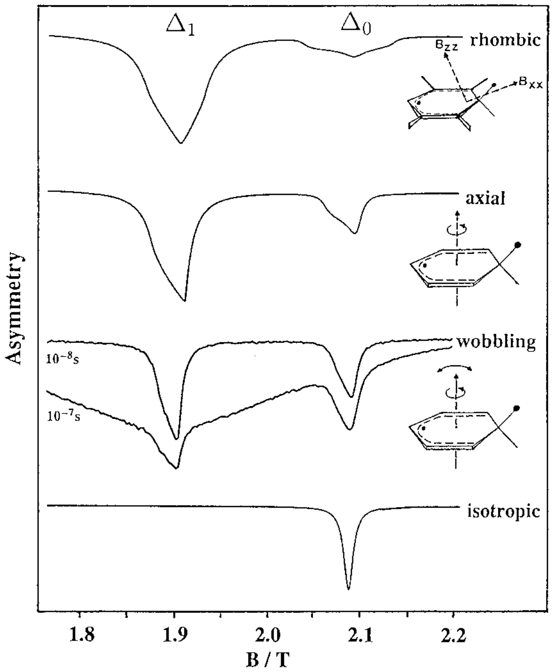

Figure 1. Simulated ALC-μSR spectra, showing the Δ_1 and the methylene Δ_0 resonances for approximate values of the isotropic and the dipolar hyperfine coupling constants for a cyclohexadienyl radical. Note the effect of the dynamics on the line shapes.

we can simulate the powder pattern of the Δ_1 and methylene Δ_0 resonances in the rigid limit. This is shown as the first entry in Figure 1.

Experimental values for the dipolar part of the hyperfine tensor for the cyclohexadienyl ring protons are not available. Quantum chemical calculations show that the components perpendicular to the molecular plane are small ($<$1 MHz for the ortho and para protons, 4 MHz for the meta protons).[22] This agrees qualitatively with the experimental determinations for the ring protons of the benzyl radical.[24]

When the radical is assumed to perform fast uniaxial rotation about an axis perpendicular to the molecular plane, we calculate a parallel axial component $D_{||}$ of -6.8 MHz (or $D_\perp = +3.4$ MHz, second entry in Figure 1). For uniaxial rotation about the long axis of the radical we obtain $D_{||} = +5.8$ MHz. Since this will reverse the high- and low- field sides and change the width of the Δ_1 resonance, we expect to be able to determine the preferred rotational axis from the line shape of the powder spectra. Because the dominant principal components of the dipolar tensor for the ortho and para protons lie in the molecular plane, rotation about the axis perpendicular to the plane will nearly average out the dipolar interaction, whereas a significant anisotropy would survive on rotation about the long axis.

An axial line shape with a further reduced width would indicate a more extensive averaging by a tumbling or wobbling type motion. The effect may be simulated by a Monte Carlo technique, assuming reorientational jumps according to a given model and with a certain correlation time τ_c.[25] An example assuming reorientational jumps with an average tip angle of the axis of 30° is shown in the third entry of Figure 1 for two different correlation times. Most remarkably, a τ_c of 100 ns leads to a very broad feature for Δ_1, resembling a superposition of two lines, whereas for a τ_c of 10 ns only the narrow feature survives, and the baseline is nearly restored. For fast isotropic motion the Δ_1 resonance disappears as expected, and the Δ_0 line is narrow and isotropic (last entry in Figure 1).

So far, experimental examples for the effects of dynamics have been reported for radicals derived by Mu addition to norbornene[26] and to C_{60} and C_{70}.[27,28] It was found that on increasing the temperature the Δ_1 resonance of the dominant MuC_{70} isomer and the Mu adduct to norbornene disappeared as a small narrow vee. This was ascribed to an increase in amplitude of the averaging motion which was always fast on the critical time scale. In contrast, the corresponding resonance of MuC_{60} disappeared by broadening, demonstrating that on warming the correlation time of the averaging motion passed through the critical time scale of the experiment.

3. Experimental Procedures

Experiments were performed at the πE3 beam line of the Paul Scherrer Institute in Villigen, Switzerland, using surface muons with a momentum of 29 MeV/*c* and a polarization close to 100%. A Wien filter removed decay positron contamination from the beam before it was admitted to the sample. At an intensity of the primary proton beam of 1 mA the muon flux was of the order of 2×10^6 s^{-1}. The experimental setup has been described in detail previously,[9,10] but in short it is as follows: The experimental sample was temperature controlled in a flow cryostat or in an oven and mounted in the center of a horizontal superconducting solenoid of 1 m length with a warm bore of 20 cm diameter. The magnetic field was stepped through a given range while being monitored with a Metrolab NMR probe. Decay positrons were counted in two sets of scintillation counters placed in the forward (number of counts: N_f) and in the backward (N_b) direction of the sample with respect to the incoming beam. The muon decay asymmetry, which is proportional to the time-integrated muon polarization, is given by $(N_f - N_b)/(N_f + N_b)$. To compensate for the effects of changing beam optics with field, the spectra were normalized using a reference run obtained with a sample of the same design and mounted in the identical position but containing plain silica powder without organic adsorbate. The Δ_1 resonances were fitted using the MINUIT χ^2 minimization program[29] with a powder line shape function that was described elsewhere.[26]

Two samples of ZSM-5 from CU Chemie Uetikon with SiO_2/Al_2O_3 ratios of 670 and 900 were used. The zeolite was first calcined at 770 K and then filled into a stainless steel cell with a 50 μm foil as an entrance window for the muons. It was then heated again at 600 K until a stable vacuum of the order of 2×10^{-5} mbar was obtained. Loadings of 1.1 wt % in ZSM-5/900, corresponding to approximately one molecule per unit cell, and of 2.3% in ZSM-5/670 were prepared by adsorbing defined amounts of degassed benzene at room temperature before sealing the sample.

4. Results and Discussion

The relevant sections of the ALC-μSR spectrum obtained at 298 K with a loading of two molecules of benzene per unit cell are shown in Figure 2. We find the Δ_1 resonance at 1.8868 T, and three Δ_0 resonances at 2.0808, 2.8962, and 2.9584 T. From these values we deduce isotropic coupling constants of 513.8 MHz for A_μ and 124.9, -26.3, and -37.8 MHz for A_p of the methylene, the ortho protons, and the para protons, respectively. These are in good agreement with those reported for the radical in the gas and liquid phases.[20,21] The Δ_0 meta proton resonance is expected near 2.71 T, but because of the small value of A_p it was too weak to be observed.

In the region of the Δ_1 resonance the upper trace in Figure 2 represents a fit of an axial powder line shape. Besides the resonance position, the important parameter is the anisotropy, determined to be $D_\perp = +0.80(1)$ MHz. The fit is excellent, and

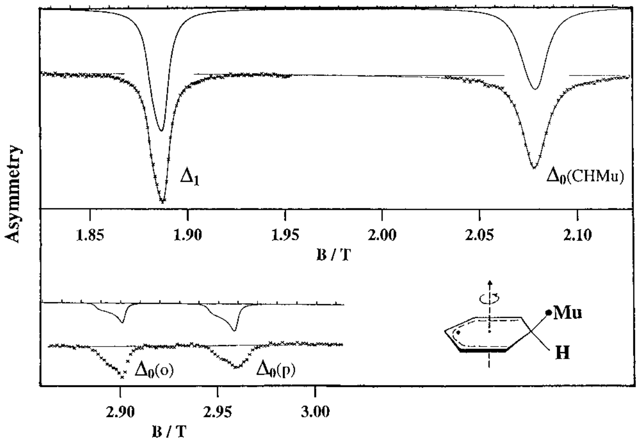

Figure 2. Experimental ALC-μSR spectrum obtained with benzene at $T = 298$ K at a loading of two molecules per unit cell in ZSM-5/670 (lower trace). The upper trace represents a fit of an axial powder line shape in the region of the Δ_1 resonance (near 1.9 T) and a simulation over the remaining lines (see text).

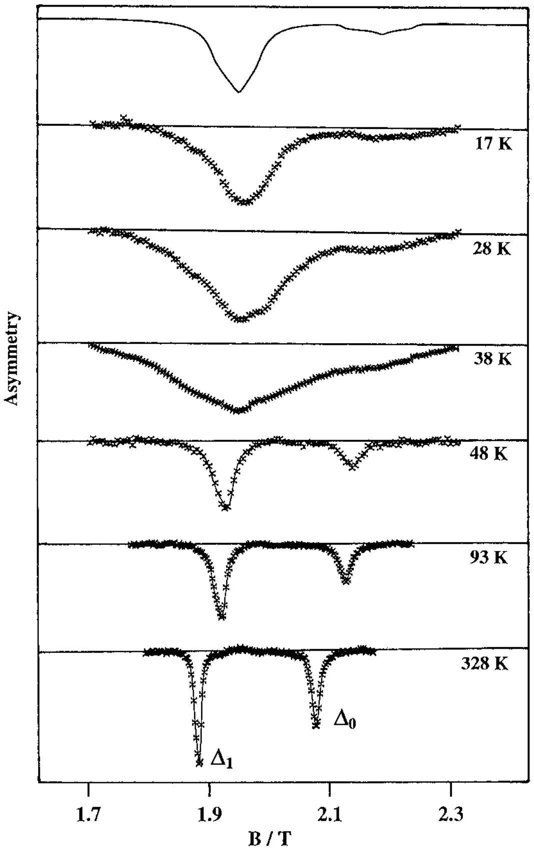

Figure 3. ALC-μSR spectra obtained with benzene at a loading of one molecule per unit cell on ZSM-5/900 at various temperatures. Only the region of the Δ_1 and the methylene proton Δ_0 resonance is shown. The top entry is a simulation based on isotropic coupling constants of 529.5 MHz for the muon and 122 MHz for the proton and for the rhombic dipolar contributions of a radical in the absence of any dynamics. The spectra at 17, 28, and 38 K are raw histograms after subtraction of the experimental background; at the higher temperatures a fitted polynomial with up to cubic terms accounts for background subtraction.

the positive sign of the anisotropy parameter immediately permits the conclusion that the radical performs fast uniaxial rotation about the axis perpendicular to the molecular plane. The magnitude of $D_\perp$ is far below its value for plain fast uniaxial rotation (3.4 MHz), which is an unambiguous indicator for extensive averaging by a tumbling, wobbling, or jump reorientation motion of the rotation axis.

In the region of the three Δ_0 resonances the upper trace is a simulation in which only the isotropic proton hyperfine coupling was varied until the resonances matched the experimental line positions. The anisotropic part for the muon was taken from the fit to the Δ_1 line ($D_\perp = 0.80$ MHz). For the methylene proton, the muon value was scaled by the ratio of proton/muon magnetic moments, giving $D_\perp = 0.25$ MHz. For the aromatic protons, $D_\perp$ was assumed to be zero, as expected based on the orientation of the hyperfine tensors in the radical (section 2.3) and on the motion derived from the Δ_1 line. The quantitative agreement of the line shapes is striking and provides strong support for the above conclusion of fast in-plane rotation.

Figure 3 displays experimental spectra that were obtained with a loading of one molecule per unit cell in ZSM-5/900. At temperatures from 48 K up a fit of axial powder line shapes is also given and shown to represent the data, which means that there is still fast uniaxial rotation of the radical at 48 K. The spectrum at 38 K is dramatically different. The very broad nature of the resonances indicates that the correlation time for rotation corresponds approximately to the critical time scale (47 ns), but the spectrum does not permit a meaningful quantitative analysis. The resonances narrow down again as the sample is cooled further. At 17 K, comparison with a simulation based on the rhombic hyperfine tensor demonstrates that the system is essentially frozen. The line may be slightly affected by inhomogeneous broadening. Qualitatively, the observed behavior is a verification of the prediction in Figure 1.

The Δ_1 resonance fits an axial powder pattern over a large temperature range, and its mere presence confirms that there are no isotropic conditions. The axial muon hyperfine anisotropy, $D_\perp(T)$, is displayed in Figure 4, with the two symbols representing the two loadings. The value of $D_\perp$ for uniaxial rotation in the absence of any wobbling, tumbling, or jump motion corresponds to 3.4 MHz. This value is not quite reached at 48 K. The anisotropy decreases dramatically as temperature rises toward 100 K. The plateau value around room temperature corresponds to only one-fourth of the maximum value, which demonstrates that there is extensive but not isotropic averaging of the orientation. Since it is difficult to imagine such a high mobility of the radical inside a channel, the present observation supports previous conclusions that the favored site for a benzene molecule is at the intersection.[4] The aligning potential corresponds to 100 K, i.e., to about 0.8 kJ mol^{-1}. There is no significant difference between the two loadings, demonstrating that the molecules are isolated and do not interact with each other.

Inspection of Figure 4 reveals a small increase of $D_\perp$ around 300 K. This is roughly where the MONO−ORTHO transition is expected. The effect may thus represent a subtle change in the structure of the host. More obvious is the unexpected but strong increase above 450 K. It is traced back to deviations of the experimental line shape from the axial powder pattern (which fits very well at the lower temperatures). Inspection of the raw data in Figure 5 clearly shows the appearance of broad shoulders at the high-field side of both resonances. They are bearly visible at 398 K but very obvious at 553 K. The effect is reversible; thus, it does not represent a decomposition of the radical. We suggest that a new site with higher hyperfine coupling constants (by about 10 MHz or 2% of A_μ) becomes thermally accessible. From the relative intensities of the two features we estimate an activation free energy of 5 kJ mol^{-1}. This is less than given by the simulation by Snurr et al.,[6] who arrive at 23 kJ mol^{-1} at 553 K for a transition of an isolated benzene molecule from

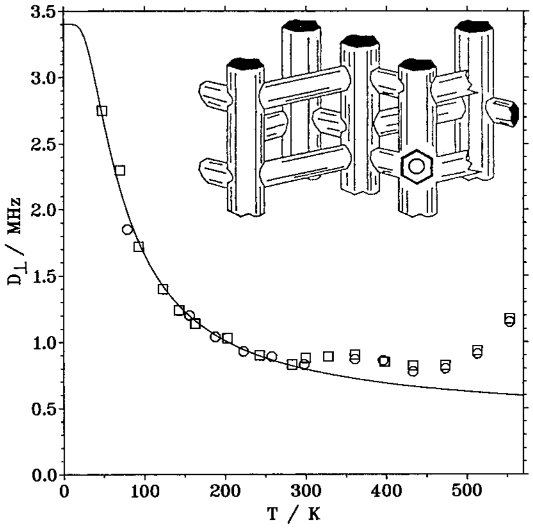

Figure 4. Axial anisotropy of the muon hyperfine interaction as a function of temperature for the cyclohexadienyl radical at a benzene loading of one molecule per unit cell in ZSM-5/900 (squares) and of two molecules per unit cell in ZSM-5/670 (circles). The line corresponds to a fit of a reorientational two-site jump model for points below 300 K. The inset shows the ZSM-5 structure with a benzene molecule roughly to scale at a channel intersection. The zigzag channels are drawn in the horizontal and the straight channels in the vertical direction.

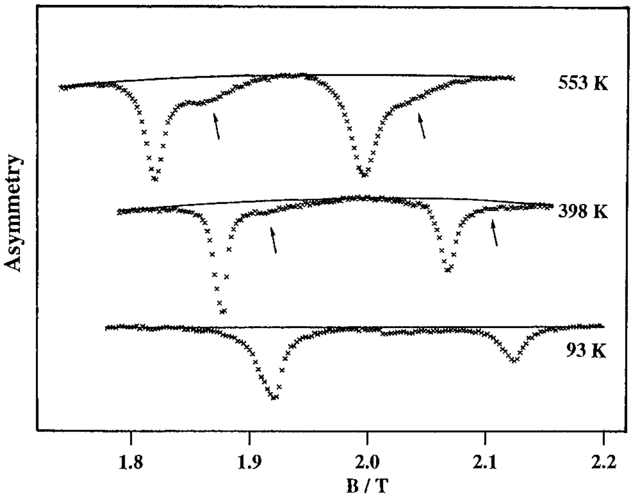

Figure 5. Muon decay asymmetry (raw data after normalization with a background run) obtained with ZSM-5/900 at two molecules per unit cell. A baseline is drawn as a guide to the eye. At the higher temperatures one clearly observes the appearance of shoulders (arrows).

the intersection to a zigzag channel site in the ORTHO structure. The broadness of the features indicates a much lower mobility, and the change in hyperfine coupling points to a certain degree of structural distortion. Both observations are consistent with a population of channel sites that impose some steric constraint. This interpretation is supported by previous results obtained with a near saturation loading of ca. eight benzene molecules per unit cell which showed the broad components superimposed on the narrow lines even at room temperature.[30] At this loading, only 50% of the benzene molecules can occupy a channel intersection; the others have to be inside a channel.

It should be noted that the translational diffusion constant for benzene in silicalite was determined to amount to ca. 7×10^{-14} m^2 s^{-1} at 386 K.[31] This gives a root-mean-square displacement in a muon lifetime that corresponds to the diameter of a benzene molecule. Under these conditions there can be no fast exchange between neighboring channel and intersection sites.

Two models of reorientational motions were tried, aiming at a quantitative interpretation of $D_\perp(T)$. The assumption of a weakly adsorbed radical with the orientation given by a $\cos^2 \alpha$ potential, where α is the angular deviation of the rotation axis from the preferred orientation, did not reproduce the experimental behavior satisfactorily, but a two-site jump model with an energy difference of 1.0 kJ mol^{-1} between the sites and a jump angle of the unique axis of 110° (which is equivalent to 70°) fits the data below 300 K very well. For this jump angle, the asymptotic high-temperature value for $D_\perp$ amounts to 0.4 MHz; for 90° jumps a value of zero would be approached much faster than observed in Figure 4. An estimate based on the universal frequency factor, kT/h, gives a lifetime of the ground state of about 10 ps at 50 K, so that the condition of fast exchange on a critical time scale of 47 ns is well obeyed.

It is interesting to ask why the radical moves the way it does. For this discussion we approximate the moments of inertia of C_6H_6Mu by those of the benzene molecule which are only marginally different. This molecule is a symmetric top which is characterized by the quantum numbers J for its angular momentum and M_J for its z component. Since it is planar, its moment of inertia parallel to the symmetry axis, $I_\|$, is twice the value of $I_\perp$, and high values of $|M_J|$ which belong to nearly pure in-plane rotation with little precession of the symmetry axis are energetically favored. In the Boltzmann average over the subset of all M_J belonging to the same J there is thus an inherent bias for rotation about the axis with the highest moment of inertia. This was found previously for the radical cation derived from tetramethylethylene in ZSM-5 which rotates also about the axis perpendicular to the molecular plane.[32] In the gas phase, there is an isotropic distribution of orientations of this axis, and each molecule will reorient frequently because of collisions (J relaxation). Adsorption on a flat surface excerts a force that aligns the molecules with the rotation axis perpendicular to the surface and thus provides an additional bias for high values of $|M_J|$. Due to the anisotropic nature of the environment, there is no longer isotropic averaging, meaning that J relaxation becomes less efficient.

The size of the energy quantum for the free C_6H_6 rotor, $\hbar^2/2I_\|$, corresponds to 0.14 K. This means that motion at temperatures of interest here can be treated classically and that we should not expect any discrete (quantized) orientations. The two inequivalent sites that were observed here with an orientation differing by 110° must thus be related to two adsorption sites in the zeolite. The high mobility suggests that they are both at the channel intersection, but at this point it is not possible to relate them to details of the microstructure of the environment.

The dynamic model derived here for the cyclohexadienyl radical agrees with the results obtained for benzene molecules.[3−5] Quasi-elastic neutron scattering studies probing the dynamics of the benzene molecule adsorbed on ZSM-5 on a time scale of 10^{-11} s were interpreted in terms of nonisotropic reorientational motion corresponding quite well to uniaxial rotation about the C_6 axis.[5] ^{13}C NMR line shape analysis gave a correlation time for C_6 reorientational jumps of $\ll 100$ μs at 125 K, while ^{2}H NMR lead to a value of $\ll 1$ μs,[3] and for the C_6H_6Mu radical we find $\ll 0.05$ μs here. It was furthermore concluded that superimposed on this reorientation there are jumps between a limited number of sorption sites with distinct orientations of the C_6 axis and that its correlation time amounted to 10−100 μs at 200 K. This is much longer and not compatible with the present finding for C_6H_6Mu, a fact which must be related to the much lower Si/Al ratio of 50 of the NaZSM-5 used in the

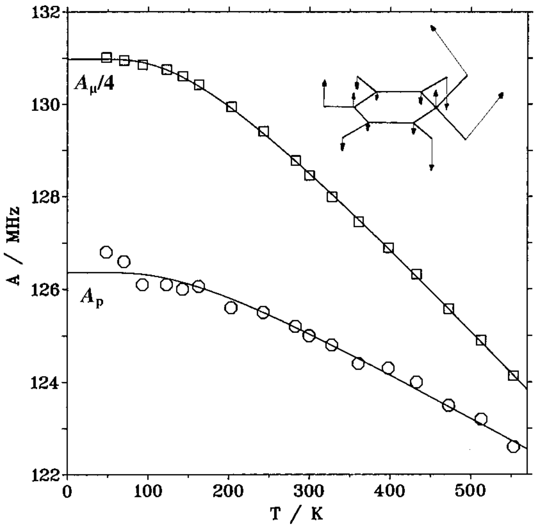

Figure 6. Temperature dependence of the hyperfine coupling constants A_μ (□) and A_p (○) of the methylene nuclei of C_6H_6Mu in ZSM-5 at a loading of one molecule per unit cell. The solid lines are fits of a single-frequency harmonic oscillator model (eq 4). The inset shows the lowest frequency normal mode as calculated using MNDO based on the PM3 parameters.

NMR study. It is clear also from previous ALC-μSR results[16,30] that the cyclohexadienyl radical coordinates strongly with the cation.

A more recent ^{2}H NMR study using a ZSM-5 silicalite[4] concluded that at benzene concentrations below one molecule per channel intersection there are two types of sorption sites: one with fixed benzene molecules which perform uniaxial rotation about the C_6 axis and a second one which is preferred and allows for 98° reorientational jumps superimposed on the fast C_6 rotation. The exchange rate reaches 1 kHz at room temperature. This model approximately matches the present results if the two sorption sites are identified with the channel and intersection sites, and the jump angles which are derived for the species at the intersections differ by only 12° between the two systems and techniques.

It is worthwhile also to have a closer look at the temperature dependence of the hyperfine coupling constants. Since the Δ_0 resonances of the ortho and para protons are weaker and do not warrant sufficient precision at the lower temperatures, we restrict this study to the methylene muon and proton couplings. Their temperature dependence is displayed in Figure 6 where A_μ has been scaled by a factor of 0.25 to facilitate comparison. (The plain ratio of magnetic moments is 0.3141; the rest is an intrinsic isotope effect.) Comparison with the corresponding literature values reported for plain liquid benzene[20] and for the gas phase[21] reveals the same trend, and within 1% or less they agree with the values found in the present work.

The hyperfine couplings measure the vibrationally averaged electron spin density at the nucleus. Therefore, it is expected that the temperature dependence flattens out at lower temperatures where excited vibrational states are no longer thermally accessible. This is clearly observed in Figure 6, in particular for the values of A_μ which are based on a single resonance and therefore more accurate than those of A_p. The solid lines represent fits to a model that assumes that a single normal mode determines the temperature dependence. This assumption is equivalent to the Einstein model for the heat capacities of solids. A corresponding analysis has been performed previously by Yu et al.[20] based on an intuitive normal mode consisting of a bending rotation of the methylene group involving motion of the corresponding nuclei to and from the molecular plane. The fit is to the expression

$$A(T) = A_0[1 - q^{-1}c\sum_{n=0}^{\infty}(^1/_2 + n)\exp(-nhc\tilde{\nu}/kT)] \quad (4)$$

and has the parameters A_0, c, and $\tilde{\nu}$. q is the partition function, A_0 is the hyperfine coupling for an imaginary rigid species in the absence even of zero-point motion, c is a constant which is proportional to $\beta^{-2} = \hbar(mf)^{-1/2}$, the expectation value of the root-mean-square displacement amplitude of the harmonic oscillator (m is the effective mass of the normal mode motion, and f is the force constant), and $\tilde{\nu}$ is the wavenumber of its vibrational transition. $\tilde{\nu}$ determines the temperature at which the plot levels off; c is a strong function of the slope at higher temperatures and A_0 of the intercept. The result of an excellent fit to A_μ is $A_0(\mu) = 540.7$ MHz, $c = 0.062$, and $\tilde{\nu} = 307.6$ cm^{-1}. The data for A_p are more scattered, leading to a strong correlation of the parameters in the fit. Assuming that it is the same normal mode which determines the temperature dependence of both A_p and A_μ, we fixed $\tilde{\nu}$ to the number found from the fit to A_μ, which results in values of 0.035 for c and 128.6 MHz for $A_0(p)$. MNDO calculations based on the PM3 parameter set[33] predict the lowest normal mode at $\tilde{\nu} = 187$ MHz with a reduced mass of 42.75 amu. This high mass and also the displacement vectors identify the mode as a ring puckering motion with a large amplitude for both the methylene H and Mu atoms (inset in Figure 6). Since it is mostly a ring mode, it is not expected to differentiate between H and Mu. The fact that the c values (and the slopes in Figure 6) are different for the two nuclei indicates not unexpectedly that the temperature dependence of the coupling constants cannot be attributed to a single normal mode. There are 33 modes for this 13-atom radical, and the calculation predicts that 12 of them occur below 1000 cm^{-1}.

5. Conclusions

ALC-μSR was found to be well suited and very sensitive in providing detailed information about the structure and reorientational dynamics of cyclohexadienyl radicals in a high-silica ZSM-5 zeolite. The type of information is similar to that obtained from nuclear magnetic resonance and from quasi-elastic neutron scattering, but the critical time scale is of the order of 50 ns and thus quite different from the other methods, rendering μSR complementary to the more conventional dynamic techniques. It was found that the radical behaves much like the benzene molecule in the same environment. This is in accord with expectation since size, shape, and moments of inertia are very similar for the two species, and there is no reason to expect a specific open-shell host−guest interaction of the radical. A high reorientational mobility was found for temperatures down to 50 K, indicating that the radical is located at the channel intersections. Rapid exchange must be present between two inequivalent adsorption sites which differ by 1.0 kJ mol^{-1} in energy and by 110° in the orientation of the normal to the molecular plane. Above 450 K sites in the side channels that are higher in energy by about 5 kJ mol^{-1} become accessible. At the loadings of one and two molecules per unit cell as used in the present experiments, there was no evidence for any interactions between the organic guests or with any remaining sodium cations.

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