Manifestation of Berry's Phase in Nuclear Quadrupole Resonance Spectra of Rotating Powder Samples

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Z. Naturforsch. **63a,** 81 – 87 (2008); received August 1, 2007

The effect of Berry's phase on the nuclear quadrupole resonance (NQR) spectra of rotating powder samples is studied experimentally, and its application for the determination of the electric field gradient asymmetry η is demonstrated. The NQR frequency splittings, which are observed for the spin 3/2 nucleus of ^{35}Cl in powder samples of *p*-dichlorobenzene ($C_6H_4Cl_2$) and cyanuric chloride ($C_3N_3Cl_3$), are interpreted as a manifestation of Berry's phase, associated with the adiabatically changing Hamiltonian due to sample rotation. The accumulation of Berry's phase during the rotation process is responsible for the observed dependence of the NQR line shape on the rotation frequency and the asymmetry parameter. The proposed method for the determination of η involves the analysis of the NQR powder patterns of the rotating samples.

Key words: Berry's Phase; Nuclear Quadrupole Resonance; Electric Field Gradient Tensor; Asymmetry Parameter.

1. Introduction

The evolution of a quantum-mechanical system under an adiabatically changing Hamiltonian has important consequences in magnetic resonance. Consider an nuclear quadrupole resonance (NQR) experiment on a crystal sample containing nuclear spins I with the quadrupole coupling constant ν_Q that is rotated with an angular velocity ν_R. Provided that $\nu_R \ll \nu_Q$, the nuclear spin Hamiltonian changes adiabatically. However, only the eigenstates but not the energies change with time since the NQR frequencies in the absence of external static fields are independent of orientation. Berry has shown that in a cyclic adiabatic process via a closed path a quantum state may acquire a geometrical phase factor [1]. Any observed rotational effects in NQR arise from Berry's phase. The NQR signal phase is shifted by the phase acquired during the adiabatic rotation. Since a continuously increasing phase shift is equivalent to a frequency shift, Berry's phase is observable as a frequency shift.

The publication of Berry's famous work [1] has caused an inexhaustible flow of publications. Since then, the concept of a geometrical phase (Berry's phase) has been substantially extended and it has penetrated into various sections of physics. A review of the basic ideas can be found, for example, in [2]. In the literature there are many reports, mostly theoretical ones, devoted to Berry's phase in NMR and NQR spectroscopy.

A pure NQR experiment was performed by Tycko [3], using a crystal of sodium chlorate. In this case the quantization axis, along which the spins of the chlorine nuclei were aligned, was the symmetry axis of the crystal. The nuclei were excited by a radio frequency (r. f.) pulse, generating a superposition of two spin states. By rotation of the crystal about some axis different from the quantization axis, the two spin states acquired geometric phases that increased with time, producing a difference in the frequency of the two states. In other words, the periodic time-dependent phase shift was detected as a change in the NQR frequency of the nuclei, measured using standard phase-sensitive detection techniques.

An example of a non-adiabatic geometric phase in NMR spectra was observed by Suter et al. for a system of a coupled proton pair [4]. A two-level subspace of this quantum system with total spin $I = 1$ was made to undergo a cyclic evolution of the Hamiltonian by applying a time-dependent magnetic field. The geomet-

0932–0784 / 08 / 0100–0081 $ 06.00

ric phase was measured by observing the interference between these two states and the third, unperturbed level. Lisin et al. [5] investigated a geometrical phase in NMR on a two-level system, where the cyclic evolution was created by an off-resonance 2π pulse. Furthermore, it was suggested to observe effects of Berry's phase without any macroscopic rotation of the sample. For example, the adiabatic evolution of a spin system may be achieved by a rotation of the nuclear magnetization in the spin space through the application of special r. f. pulse sequences [6, 7]. Zee [6] has suggested to extend Tycko's experiment to the rotation not only around one, but around two axes, and has shown the occurrence of a non-Abelian Berry phase. Such an experiment was carried out by Zwanzinger, Koenig and Pines [7]. Zwanzinger also described the measurement of the geometric component of the transition probability in a two-level NMR system by sweeping the r. f. irradiation frequency [8]. In [9] it was shown that in the off-resonance case the NMR frequency shift consists of two parts: a Bloch-Siegert shift and a shift due to a Berry phase. Appelt, Waeckerle and Mehring [10], using optically detected ^{131}Xe NQR spectroscopy, extended the experiment by Tycko to the non-adiabatic regime and analyzed the Berry phase, using a rotating frame. Berry dephasing due to diffusion in optically detected NQR of gaseous ^{131}Xe was investigated in [11]. The non-trivial mixing of the spin states during the rotation of an NQR system around two axes and the formation of a non-Abelian Berry phase was shown in [12]. Berry's phase has been used in NMR spectroscopy of strongly dipolar coupled nuclear spins to implement controlled phase shift gates for quantum-information processing [13]. Recently, Tycko's experiment of pure NQR was extended to the case of powders for nuclei with spins $I = 3/2$ and $I = 1$ and an asymmetry parameter, η, not equal to zero [14].

However, mainly theoretical treatments without any relation to practical application have been published. In spite of plenty of publications about a Berry phase in NMR and NQR, experimental verifications are scarce. In particular, no experiment demonstrating a Berry phase in pure NQR, except for the one by Tycko on a monocrystal with $\eta = 0$, has been carried out, to our knowledge. The work presented here is, in essence, the first attempt to make practical use of the manifestation of a Berry phase in pure NQR for obtaining the asymmetry parameter of the electrical field gradient (EFG) tensor of nuclei with spin $I = 3/2$ in powders.

In this paper, the effect of Berry's phase on the NQR spectrum of rotating powder samples is examined experimentally and applied for the determination of the asymmetry of the EFG. The method proposed is particularly important for quadrupolar spins with $I = 3/2$. For spin 3/2 nuclei it is not possible to determine the second-rank quadrupolar tensor from conventional one-dimensional zero-field NQR spectra, since the transition frequency depends on both the quadrupolar coupling constant and the asymmetry parameter η. The theoretical framework of the experiment presented here has been described in [14], where Berry's phases for the eigenstates associated with an adiabatically changing quadrupole Hamiltonian were calculated for nuclei with spin $I = 3/2$ as a function of the asymmetry parameter, and the effect of Berry's phase on the NQR spectra of rotating powder samples was described. The method involves the numerical analysis of the frequency singularities in the NQR powder patterns of the rotating samples. The suggested NQR experiment can be conducted on a standard NMR spectrometer equipped with a magic angle sample-spinning (MAS) probe head. Thus, this new method of sample rotation for the determination of the asymmetry parameter can easily be realized experimentally, whereas conventional Zeeman-effect NQR studies require special additional equipment.

2. Experimental

Experimental ^{35}Cl NQR spectra were observed with a Tecmag Apollo 300 MHz solid state NMR spectrometer equipped with a Bruker MAS probe head. The probe head covered the frequency range from 30 MHz to 80 MHz, making it suitable for the rather low resonance frequencies of the samples chosen, but it contained a non-standard bearing and drive gas system and was not optimized for high and stable rotation frequencies. A standard sample container (rotor) of 7 mm diameter was used. To avoid an influence of the magnetic field on the NQR spectra, the probe head was placed at a distance of 5 m from the magnet. The NQR signal was obtained with a simple one-pulse experiment. The 90° pulse length was 5 μs and the number of scans 4096. ^{35}Cl NQR was observed for polycrystalline samples of p-dichlorobenzene ($C_6H_4Cl_2$) and cyanuric chloride (2,4,6-trichloro-1,3,5-triazin, $C_3N_3Cl_3$) at room temperature ($T = 296$ K).

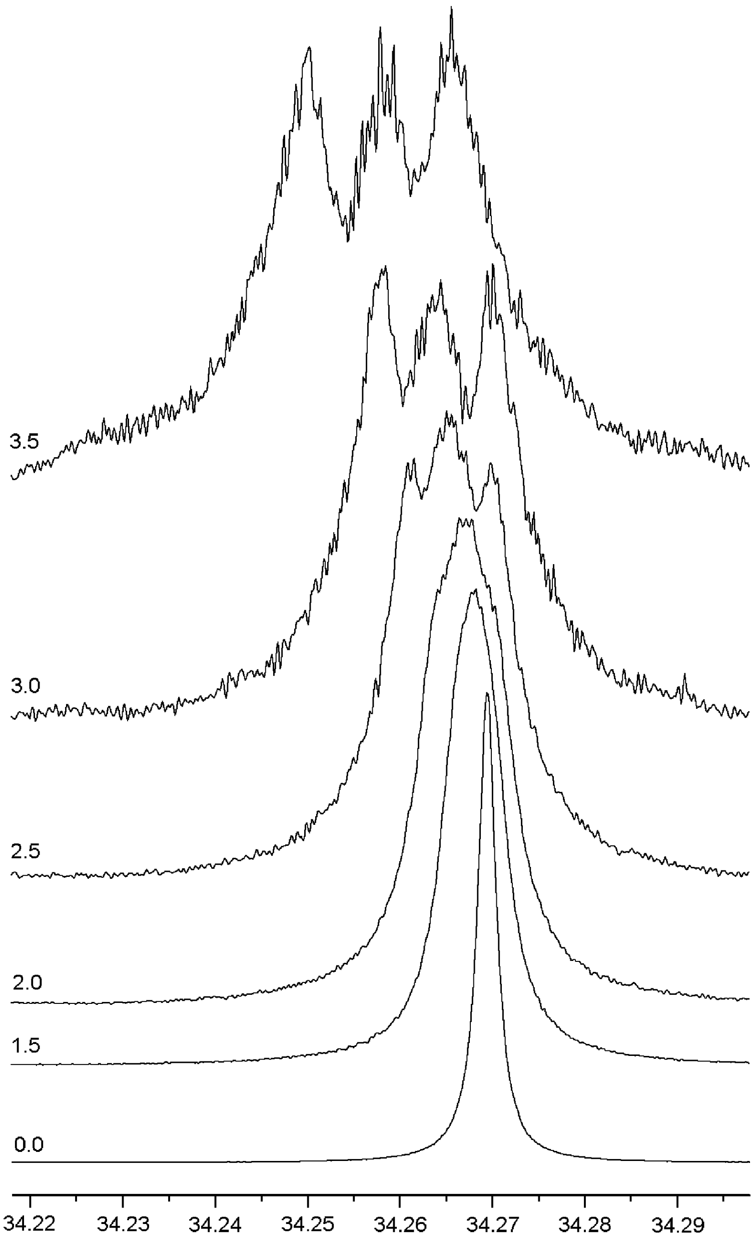

Fig. 1. ^{35}Cl NQR powder patterns of $C_6H_4Cl_2$ at various sample rotation frequencies ν_R, given next to each spectrum (in kHz). The signal intensities of each spectrum are normalized to its intensity maximum.

3. Results and Discussion

When the spectrometer frequency is set at the NQR frequency of the static sample $\nu_Q{}^0$, the NQR line at ν of the rotating sample is detected with the frequency offset $\Delta\nu = \nu - \nu_Q{}^0$. For a nuclear spin $I = 3/2$ the intensity of the NQR line at ν following an r. f. pulse of length t_w for any particular crystallite orientation was calculated in [15]. In a polycrystalline powder, all orientations occur with equal probability, and the total value is then calculated numerically by a weighted average over all orientations. As predicted in [14], each NQR line of the rotating sample displays three pairs of frequency singularities (ν_1, ν_2 and ν_3), distributed symmetrically with respect to the centre line corresponding to the NQR frequency of the static sample.

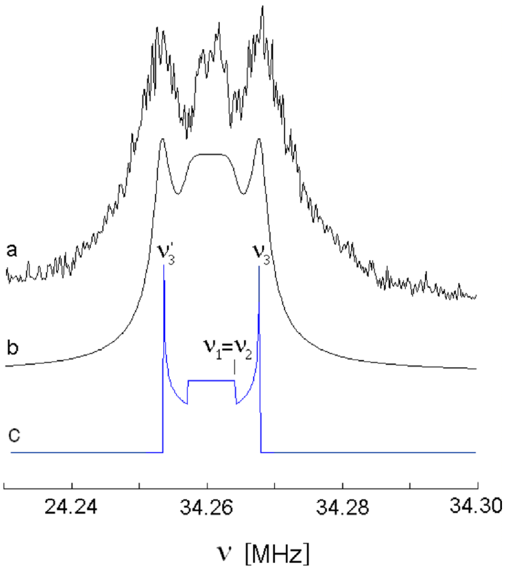

Fig. 2. (a) Experimental NQR powder pattern of a $C_6H_4Cl_2$ sample rotating at $\nu_R = 3.35$ kHz, (b) simulation and (c) idealized calculated spectrum for $\eta = 0$.

The frequencies of the singularities in the powder pattern (ν_1, ν_2 and ν_3) correspond to crystallite orientations of ($\theta = \pi/2$, $\phi = 0$), ($\theta = \pi/2$, $\phi = \pi/2$), and $\theta = 0$, respectively. Here, the angles θ and ϕ are the polar and azimuthal angles of the rotation axis (the symmetry axis of the r. f. coil) in the principal axes system of the EFG tensor. The frequency singularities depend on the value of the asymmetry parameter and on the angular velocity of the rotating sample. Thus, from the measured positions of the frequency singularities the value of the asymmetry parameter η may be determined in powder samples for spin $I = 3/2$.

As a first example, the ^{35}Cl NQR line shapes of a rotating powder sample of $C_6H_4Cl_2$, which contains a single chlorine site with a resonance frequency of 34.2940 MHz at 289.9 K [16, 17], are shown in Fig. 1 as a function of the rotation frequency. At rotation frequencies higher than 2 kHz the NQR line displays the pair of frequency singularities ν_3 and $\nu_3{}'$, shifted symmetrically with respect to the centre line corresponding to the NQR frequency of the static sample. The resolution of the frequency singularities improves considerably with increasing rotation frequency. In addition to the splittings, an overall shift of the resonance is apparent in Figure 1. This is an artifact due to a change in the sample temperature caused by sample spinning. With increasing temperature the NQR frequency shifts towards lower values, and the NQR spectrum becomes broader. The observed decrease of the quadrupole resonance frequency with increasing temperature can be attributed to increasing molecular vibrations [18], and the increase of the line width may be due to temperature gradients in the sample and instabilities of the rotation frequency.

The ^{35}Cl NQR line shape of $C_6H_4Cl_2$ rotating at $\nu_R = 3.35$ kHz is shown in Fig. 2a and compared with the simulated and calculated idealized spectra (Figs. 2b, c). The idealized spectrum has been calculated assuming an asymmetry parameter $\eta = 0$ and without taking into account the real line width. As predicted by the theory [14], for $\eta = 0$ the frequency singularities ν_1 and ν_2 ($\nu_1{}'$ and $\nu_2{}'$) of the powder pattern coincide and are not distinguishable.

The static ^{35}Cl NQR spectrum of the second substance, $C_3N_3Cl_3$, at $T = 303$ K consists of two lines at frequencies 36.261 MHz and 36.279 MHz with an intensity ratio of 2 : 1, respectively [17, 19]. The NQR line shapes of rotating powder samples measured at 296 K are shown in Fig. 3 as a function of the rotation frequency. The frequency singularities ν_3 and $\nu_3{}'$ are clearly visible at rotation frequencies higher than $\nu_R = 2.5$ kHz. The resolution of these frequency singularities increases with the rotation frequency; they are visible as satellites of the central line. The line shapes of the satellites and the central lines are different. According to the theory [14], for $\eta \neq 0$ the frequency singularities ν_1 and ν_2 ($\nu_1{}'$ and $\nu_2{}'$) are different.

Figure 4a shows the ^{35}Cl NQR line shape of $C_3N_3Cl_3$ rotating at $\nu_R = 3.35$ kHz. In Fig. 4b the simulated spectrum ($\eta_1 = \eta_2 = 0.3 \pm 0.1$) and in Fig. 4c the idealized calculated spectrum, assuming the asymmetry parameters $\eta_1 = 0.222$ and $\eta_2 = 0.231$, are shown for comparison. These values, determined by another method, were taken from the literature [17]. As shown in Fig. 4a, the predicted maxima corresponding to the frequency singularities ν_1 and ν_2 ($\nu_1{}'$ and $\nu_2{}'$) cannot be discerned in the experimental spectrum. The central line of the experimental spectrum shows only a broad maximum, making an accurate spectral analysis and precise determination of the singularities difficult.

The calculated dependence of the frequency singularities of the NQR powder patterns for $I = 3/2$ on the asymmetry parameter η at $\nu_R = 3.35$ kHz is shown in Figure 5. Unfortunately, the frequency singularity ν_3, which is clearly visible in the experiment, is only weakly dependent on the asymmetry parame-

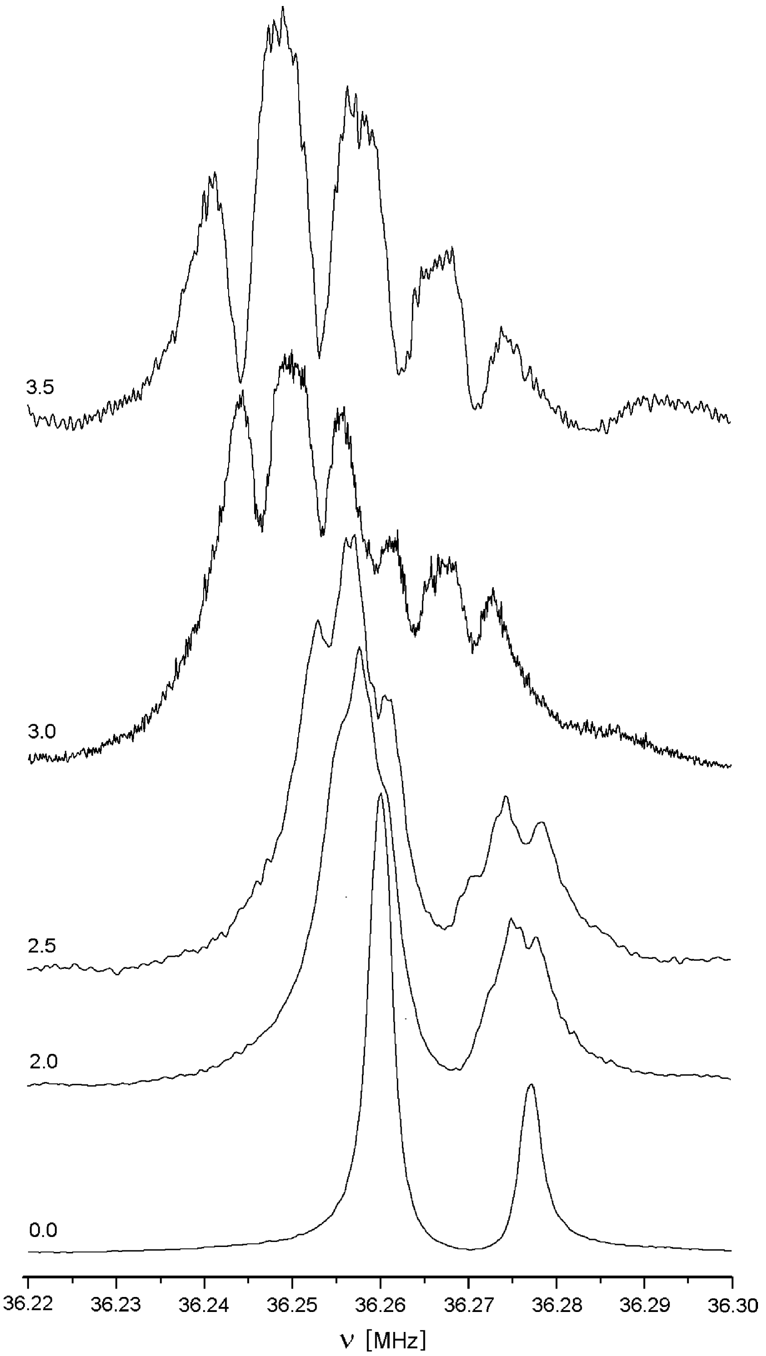

Fig. 3. ^{35}Cl NQR powder patterns of $C_3N_3Cl_3$ at various sample rotation frequencies ν_R, given next to each spectrum (in kHz). The signal intensities of each spectrum are normalized to its intensity maximum.

ter. The frequency singularities ν_1 and ν_2 are, in principle, much more sensitive to the asymmetry parameter, but they are not resolved in the experimental spectra. Therefore, a computer analysis of the overall spectrum was performed. The calculated line shape, assuming a Gaussian line broadening, was compared with the experimental one, and the minimum of the mean-square deviation was determined. Using this method, we obtained $\eta_1 \approx \eta_2 = 0.3 \pm 0.1$ for $C_3N_3Cl_3$. Under the given experimental conditions, the accuracy of this

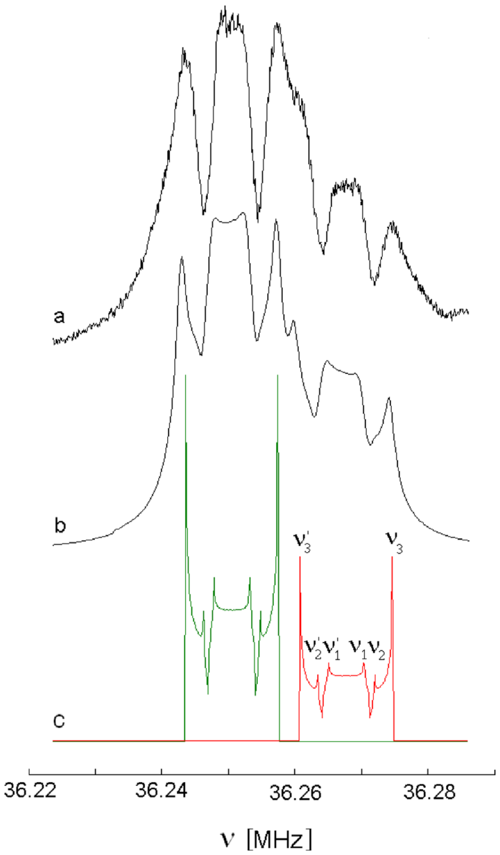

Fig. 4. (a) Experimental NQR powder pattern of a sample of $C_3N_3Cl_3$ rotating at $\nu_R = 3.35$ kHz, (b) simulation for $\eta_1 = \eta_2 = 0.3 \pm 0.1$, and (c) idealized calculated spectrum for $\eta_1 = 0.222$ and $\eta_2 = 0.231$.

method is rather low for small asymmetry parameters. It could be improved considerably by applying a higher and stable rotation frequency.

4. Conclusions

The experimentally observed frequency splittings in NQR spectra of rotating powder samples were interpreted as a manifestation of Berry's phase, associated with an adiabatically changing Hamiltonian. This effect of Berry's phase on the NQR spectrum of rotating powder samples can be applied for the determination of the electric field gradient asymmetry parameter. The proposed new method is simple in its experimental realization and may be conducted on standard NMR spectrometers equipped with a sample-spinning probe head.

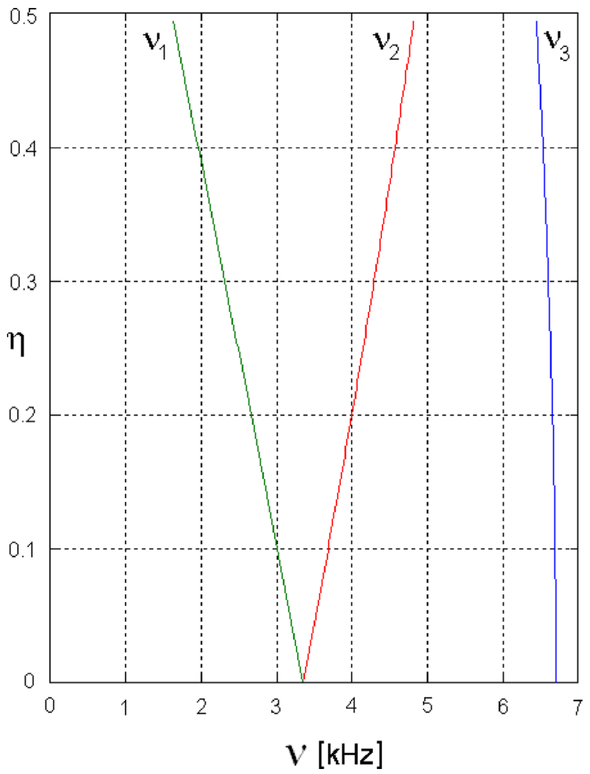

Fig. 5. Dependence of the frequency singularities (ν_1, ν_2 and ν_3) of the NQR powder patterns for $I = 3/2$ on the asymmetry parameter η at $\nu_R = 3.35$ kHz.

Acknowledgements

The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged for funding the research visit of N. S. in Paderborn (436 RUS 17/85/06).

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