

ential cross sections for  $\text{HD} + \text{H}_2$  at the same beam energy. This measurement agreed with a calculation for a spherical potential<sup>10</sup> and indicates a contamination of less than 0.05 at  $\theta = 30^\circ$ . The neglect of HD was further confirmed by D atom discharge beam experiments on  $\text{D}_2$  as target gas in place of  $\text{H}_2$ ; no elastic scattered mass 3 signal was observed.

For comparison, classical trajectory calculations were performed on the SLTH potential hypersurface<sup>1</sup> for ten translational energies up to  $E_{\text{CM}} = 2.0 \text{ eV}$  and were averaged over the apparatus distributions. The calculated total reactive cross section increases from threshold at 0.28 eV to a nearly constant value at  $E_{\text{CM}} = 1.4 \text{ eV}$  of  $1.8 \text{ \AA}^2$ . The differential cross section broadens with increasing energy from a backward distribution at threshold to a nearly constant distribution disappearing abruptly at some small angle, e.g.,  $10^\circ$  at  $E_{\text{CM}} = 2.0 \text{ eV}$ . A constant fraction of about 78% of the total energy minus the zero point energy of the product molecule goes into translational degrees of freedom for backward scattering. With increasing energy and decreasing angle, more energy goes into rotations leaving, e.g., at  $E_{\text{CM}} = 2.0 \text{ eV}$  and the smallest scattering angle only 43% for the translation. At the average reaction energy of  $E_{\text{CM}} = 1.0 \text{ eV}$  the trajectories probe the hypersurface in the collinear saddle point region up to about 0.85 eV which is high up on the repulsive wall in the equal stretch configuration ( $r_1 = r_2 = 0.8 \text{ \AA}$ ). The center-of-mass flux divided by the square of the center-of-mass velocity, which can be compared directly with the measured contour in Fig. 1(b) is shown in Fig. 1(c).

The general agreement between experimental and theoretical contour plots confirms the observed predominantly sideways scattering. Moreover, the theoretical absolute reaction cross section of  $1.4 \text{ \AA}^2$  is roughly in agreement with

the experimental value which is estimated from the comparison of measured and calculated  $\text{D}_2 + \text{H}_2$  elastic scattering. Thus the SLTH potential provides a good description of our experiment which probes the repulsive region at energies similar to those of the  $v = 1$  kinetic experiments.

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## Fourier transform pure nuclear quadrupole resonance by pulsed field cycling

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We report the observation of Fourier transform pure nuclear quadrupole resonance (NQR) with high field detection by pulsed field cycling. This introduces the possibility of very high resolution magnetic resonance spectroscopy for structural studies of polycrystalline or disordered materials. The method is essentially that described previously for zero field nuclear magnetic resonance<sup>1</sup> and employs magnetic field cycling.<sup>2</sup> In our modification, the field is cycled in two steps, one adiabatic and one sudden. It is ideally suited to the detection of low frequencies, where standard NQR techniques are not applicable.<sup>3</sup>

As an example, Fig. 1 shows the Fourier transform spectrum of polycrystalline perdeuterated dimethoxyben-

zene<sup>4</sup> obtained by our technique at room temperature. The sample was polarized in a large static field (4.2 T) and pneumatically shuttled to an intermediate field (0.03 T) where the nuclear Zeeman energy remains larger than the quadrupolar energy. The intermediate field was then reduced to zero by electronically switched coils. Coherent evolution under the pure quadrupolar Hamiltonian will occur when the field is switched in a time shorter than the inverse of the characteristic frequencies of the spin system. For deuterons, where the frequencies may be as large as hundreds of kilohertz, the switching time should be on the order of a microsecond. In practice, the field transitions were nearly exponential with a time constant of  $1.3 \mu\text{s}$ ,<sup>5</sup> which proved sufficiently rapid.

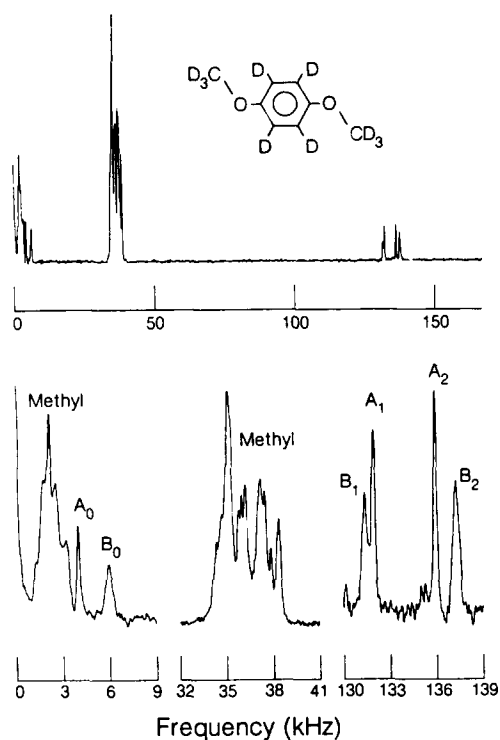


FIG. 1. Fourier transform zero field  $^2\text{D}$  NQR spectrum of polycrystalline perdeuterated 1,4 dimethoxybenzene obtained as explained in the text. The upper plot shows the full spectrum. Data was sampled at  $3\ \mu\text{s}$  intervals in  $t_1$ . The lower plot shows expanded views of the three resonance regions assignable to aromatic deuterons, aliphatic deuterons and  $\nu_0$  lines. Total acquisition time was 9 ms. Different quadrupole couplings and asymmetry parameters are seen for the aromatic deuterons due to the solid state molecular conformation.

Free evolution was allowed to continue for a time  $t_1$ , at which time the intermediate field was reapplied and the sample returned to the large field where the  $^2\text{D}$  magnetization was sampled. The experiment was repeated for regularly incremented values of  $t_1$ , yielding a zero field free precession interferogram. Upon Fourier transformation, this produces the pure NQR spectrum. The shuttle and switchable magnet systems are logic compatible and their timing is directly controlled by a standard NMR pulse programmer.<sup>6</sup>

The spectrum shows resolved lines in three distinct spectral regions; methyl deuterons (near 40 kHz), aromatic deuterons (near 135 kHz), and low frequency lines corresponding to the  $\nu_0$  resonances<sup>7</sup> which are rarely observed in deuterium NQR by any other technique. Because of the *trans* conformation of the molecule in the solid state,<sup>8</sup> two inequivalent groups of aromatic deuterons might be expected (i.e., the pair "near" the methoxy groups and the pair "far from" the methoxy groups). Indeed, these pairs clearly correspond to the two doublets ( $A_1, A_2$  and  $B_1, B_2$ ) with different quadrupole coupling constants and asymmetry parameters.<sup>9</sup> This illustrates the chemical sensitivity and resolution of this type of spectroscopy. The doublet assignment is confirmed by the  $A_0$  and  $B_0$  lines at the difference frequencies. The different linewidths, as well as the splittings of the methyl resonance, arise from interdeuteron dipolar couplings.

There are some significant advantages of this experiment over double resonance field cycling methods for low

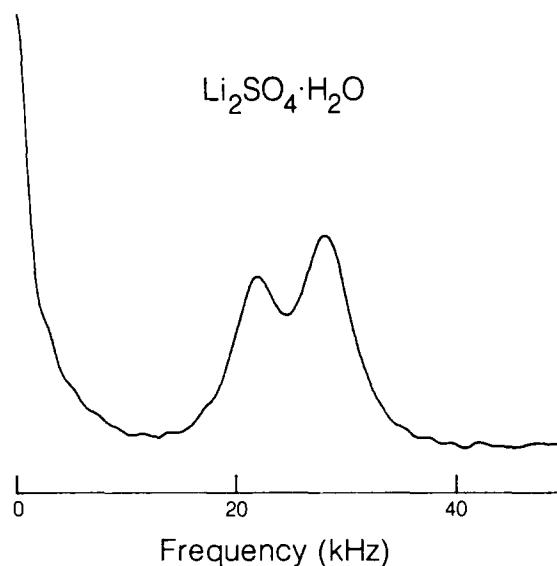


FIG. 2. Fourier transform zero field  $^7\text{Li}$  NQR spectrum of polycrystalline  $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ . The magnetization was sampled at  $10\ \mu\text{s}$  intervals for a total of  $630\ \mu\text{s}$ . For a spin  $3/2$  nucleus, one resonance is expected for each crystallographically inequivalent site and two such sites are resolved.

frequency NQR<sup>3</sup>: (a) Since the deuteron magnetization is detected directly, there is no proton dipolar absorption to obscure the low frequency  $\nu_0$  lines. The presence of protons introduces little complication since, in zero field, the proton-deuteron coupling is effectively quenched;<sup>10</sup> (b) No zero field irradiation is required, thus eliminating saturation broadening. This allows very high resolution determined only by relaxation and the uniformity of the zero field. Furthermore, the zero field line intensities do not fall off with  $\nu^2$  as with continuous wave irradiation; (c) This is a Fourier transform method. As such it makes possible experiments with a wide range of initial conditions<sup>11</sup> and will allow zero field pulsed experiments such as spin-decoupling<sup>12</sup> and two-dimensional spectroscopy.<sup>13</sup> The latter introduces, for polycrystalline samples, the possibility of high resolution spectroscopy of the type one is accustomed to for isotropic liquids.<sup>14</sup> The quadrupole couplings label particular molecular sites, while the dipolar couplings measure correlations and distances between those sites.

Other quadrupolar nuclei with low frequencies can also be observed by this technique. Typical candidates include  $^7\text{Li}$ ,  $^{11}\text{B}$ ,  $^{14}\text{N}$ ,  $^{23}\text{Na}$ , and  $^{27}\text{Al}$ . As an example, Fig. 2 shows the Fourier transform NQR spectrum of  $^7\text{Li}$  in polycrystalline  $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ . The two inequivalent Li sites are clearly resolved, in agreement with quadrupole perturbed NMR experiments on single crystals.<sup>15</sup>

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<sup>5</sup>The intermediate field was produced by a 55-turn solenoidal coil of 8 mm length and 10 mm diam., with 27 Ω series resistance. The coil was powered by a homebuilt high-speed switchable 170 V power supply.

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$(e^2qQ/h)_B = 179.1 \text{ kHz } \eta_B = 0.067.$

It is reasonable to assign the *B* resonances to the deuterons near the methyl groups because of the dipolar broadened lines.

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## Anomalous increase of the time lag in nucleation near the critical point

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In the traditional phenomenological approach,<sup>1</sup> the relaxation of a metastable state is described by the distribution function  $W(r,t)$  of nuclei of size  $r$  at time  $t$ . The variation of  $W(r,t)$  is related to the flux  $J(r,t)$  of nuclei along the size axis by the continuity equation

$$\frac{\partial W(r,t)}{\partial t} = -\frac{\partial J(r,t)}{\partial r}, J(r,t) \equiv -FW - D\frac{\partial W}{\partial r}. \quad (1)$$

Equation (1) contains two unknown functions,  $F$  and  $D$ , describing the systematic and diffusive growth of the nucleus. One usually assumes<sup>1</sup> some model expressions for these functions.

Following the general approach of Refs. 2 and 3, we show that near critical points the properties of the metastable state (and thus of the functions  $F$  and  $D$ ) are determined completely by critical dynamics. We then obtain that, for so-called "fast" quenches, the time lag associated with the approach to steady state is increased drastically, resulting thereby in a much longer time of decay of a metastable state.

Consider the simplest case of a system having only one hydrodynamic mode: The scalar nonconserved order parameter  $\phi(r,t)$ . The equation of motion of the order parameter is<sup>4,5</sup>:

$$\frac{\partial \phi}{\partial t} = \Gamma \left( -\frac{\delta \mathcal{H}}{\delta \phi} + f_r(r,t) \right); \quad (2)$$

$$\mathcal{H}\{\phi\} = \int d^3r \left( \frac{c}{2} |\nabla \phi|^2 + U(\phi) \right),$$

where  $\Gamma$  is the transport coefficient, the Gaussian random force  $f_r(r,t)$  comes from the small-scale degrees of freedom (with respect to the correlation length  $\xi$ ) and plays the role of a thermal bath, and  $\mathcal{H}\{\phi\}$  is the Landau-Ginzburg free-energy functional.

The evolution of a nucleus of a new phase is described by the quasistationary solution  $\phi(r,t)$  of Eq. (2), where  $\phi(r,t)$  is almost everywhere close to the values  $\phi_1$  and  $\phi_2$  in the two coexisting planes, except at the boundary of the nucleus. The order parameter depends upon time only through the variation of the boundary of the nucleus, i.e.,

$$\partial \phi / \partial t = (\partial \phi / \partial r)(dr/dt).$$

Substituting the latter expression into Eq. (2), and using the kind of approximations usually made in considerations of so-called solitons, kinks, domain walls, etc., one finds

$$\frac{dr}{dt} = -\Gamma \left( 2c \left( \frac{1}{r} - \frac{1}{r_c} \right) + \chi \right), \quad (3)$$

where  $\chi = (\partial \phi / \partial r)^{-1} f$  is the part of the random force  $f$ , that determines the radial fluctuations of the boundary. For a Gaussian random force  $f$ , with mean deviation of  $2kT\Gamma$ , the time-correlation function for  $\chi(t)$  is equal to

$$\langle \chi(r,t) \chi(r',t') \rangle = \frac{2D_0 c \Gamma}{r^2} \delta(t-t'); \quad D_0 = \frac{kT}{4\pi\sigma}, \quad (4)$$

where the well-known formula for the surface energy<sup>6</sup>

$$\sigma = c \int (\partial \phi / \partial r)^2 d^3r,$$