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Journal of Molecular Structure 743 (2005) 53–57

Journal of
MOLECULAR
STRUCTURE

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Two-dimensional exchange ^{35}Cl NQR spectroscopy of hexachloroethane

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Received 13 January 2005; revised 3 February 2005; accepted 3 February 2005
Available online 5 April 2005

Abstract

Two-dimensional exchange ^{35}Cl NQR spectroscopy for studies of the CCl_3-group reorientation processes in hexachloroethane has been applied. It has been demonstrated that 2D NQR exchange spectroscopy is appropriate for quantitative studies of exchange processes in molecular crystals containing quadrupole nuclei. The method is of particular value for the detection of exchange networks in systems with many sites. Thus, detailed information on the exchange pathways within a network of structural isomers in hexachloroethane can be deduced and a proper assignment of the NQR lines can be made. Temperature dependence of the exchange rate was studied. The mixing dynamics by exchange and the expected cross-peak intensities have been derived. The very good agreement of the experimental results with theoretical predictions confirms the validity of the motion model.

Keywords: Nuclear quadrupole resonance; 2D spectroscopy; Exchange; Hexachloroethane

1. Introduction

Pure nuclear quadrupole resonance (NQR) spectroscopy is sensitive to structural, as well as dynamic, properties of the investigated system. In particular, NQR provides information on the quadrupolar interaction energy of the nuclear charge distribution with the electric field gradient (EFG) evaluated at the nuclear site. The EFG tensor strongly reflects the symmetry of the site and provides a concise summary of the nature of the charge environment of the nucleus (electronic cloud distortion, crystal field, etc.). This makes the quadrupolar interaction a unique probe for the study of any physical phenomena affecting the charge distribution around a nucleus. Molecular dynamics can be studied by pure NQR methods based on the measurement of spin–lattice relaxation times, lineshape parameters and the temperature dependence of the resonance frequency. However, the amount of information provided by conventional one-dimensional (1D) NQR spectroscopy is very often limited. The 1D NQR method is unable to assign the specific lines of the multiline NQR spectrum to the particular reorienting molecular groups and to provide information on exchange-pathways.

Important improvements were achieved by introducing the two-dimensional (2D) techniques that offer fundamental advantages. The basic principle of 2D-exchange NQR is the measurement of the NQR frequency of one and the same molecular segment at two different times and the detection of slow dynamics through a change in NQR frequency. Experiments can be designed which correlate different spin interactions providing different structural information, or relate various states taken up by the molecular unit during different time periods by exchange, and in this way probe dynamic processes in real time. 2D-exchange spectroscopy involves a combined study of the distribution of nuclear environments, exchange rates, and pathways between the sites, which are distinguishable because of different resonance frequencies. 2D NMR exchange spectroscopy was first suggested by Jeener et al. [1]. Progress in multidimensional NQR has been hampered by experimental and conceptual difficulties, which we try to overcome in this paper. In contrast to NMR, some characteristic problems arise with a 2D-exchange NQR-experiment. The quantization axis is defined by the local direction of the EFG tensor. The direction of quantization changes jumpwise during

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doi:10.1016/j.molstruc.2005.02.020

the exchange process. With powder geometry, corresponding averages must be considered. Moreover, the NQR spectrum is usually spread over several hundreds kHz. Thus, the NQR lines are excited in off-resonance conditions. To our knowledge, only two attempts to use the pulse sequence of Jeener for NQR-exchange studies exist in the literature [2,3]. To explain many unsuccessful attempts we developed the theory, in which the mixing dynamics by exchange and the expected cross-peak intensities as a function of the frequency offset have been derived [4]. Application of this theory has allowed us to obtain 2D-exchange NQR spectra in hexachloroethane, which is a subject of the present paper. The various features and practical applications of the proposed technique are demonstrated with experimental ^{35}Cl 2D-exchange NQR spectra of hexachloroethane. The analysis of 2D spectra presented here allows one to assign the particular molecular groups and to provide information on molecular dynamics.

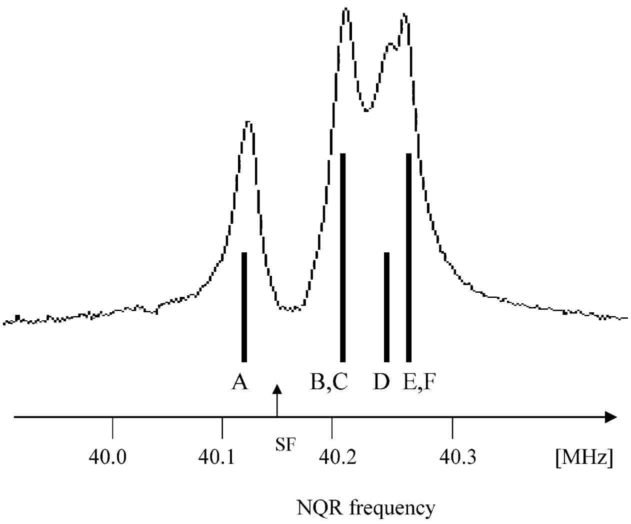

Fig. 1. ^{35}Cl NQR spectrum of hexachloroethane recorded at 233 K. The corresponding stick-spectrum is also shown. The spectrometer frequency is 40.150 MHz.

2. Experimental

2D exchange ^{35}Cl NQR experiments were carried out with polycrystalline hexachloroethane, C_2Cl_6. The sample was purchased from Aldrich Chemical Co. The purity was specified as ‘pro analysi’ (99%). The spectra have been recorded with a digital NMR Bruker spectrometer DSX 200 equipped with a special NQR probehead. The temperature was measured and controlled using the Bruker variable temperature unit BVT 3000. The standard NMR software UXNMR was used. For the 2D exchange experiments the noesytp pulse sequence (equivalent to the 2D homonuclear correlation via dipolar coupling in NMR spectroscopy) was used. The typical length of an RF pulse for the optimum ^{35}Cl signal excitation was 3.5 µs. As shown in our earlier paper [4], for such a short pulse the off-resonance effects preventing detection of the cross-peaks were compensated for.

3. Results and discussion

^{35}Cl Fourier-transformed NQR spectrum of hexachloroethane recorded at 233 K is shown in Fig. 1. The ^{35}Cl NQR spectrum consists of four lines; two of them are double the intensity of the others that correspond to the number of non-equivalent chlorine sites in a molecule [5]. The pure ^{35}Cl NQR frequencies of C_2Cl_6 are $\nu_A = 40.117$ MHz, $\nu_B = \nu_C = 40.206$ MHz, $\nu_D = 40.247$ MHz, and $\nu_E = \nu_F = 40.260$ MHz (at $T = 233$ K). With a frequency separation of 143 kHz, all lines can be excited simultaneously within the bandwidth of conventional RF pulses, but under off-resonance conditions. The chlorine nuclei B and C (and similarly E and F) are located in equivalent surroundings and are subject to the same resonance frequency. The specific NQR lines in the 1D spectrum cannot be assigned to any particular CCl_3-group. This problem can be solved only by 2D exchange spectroscopy, which provides a means to visualise the exchange pathway pattern of a given compound and to distinguish between the possible models of exchange. In C_2Cl_6, two models of exchange have to be considered. In the first case, one can assume that rotational jumps interchange the site of the chlorine nucleus A with one of the two sites of the nuclei B or C (it means that the nuclei A–C belong to one CCl_3-group). The second model considered involves the possible interchange of the site of A with that of E or F that corresponds to another assignment of the CCl_3-group. Other combinations are less probable but in principle cannot be excluded.

Fig. 2 shows the ^{35}Cl 2D exchange NQR spectrum of hexachloroethane recorded at $T = 233$ K. Cross and diagonal peaks are clearly visible. Without exchange, the 2D spectrum consists solely of diagonal peaks. If exchange takes place at the time scale of the mixing period there are two additional cross-peaks at frequency coordinates corresponding to the sites between which the exchange occurs. The mixing interval was $\tau_m = 2$ ms. The transmitter frequency 40.150 MHz was chosen somewhat apart from the centre frequency between the two resonances in order to avoid the coincidence of mirror signals of diagonal peaks and cross-peaks. In our case, the mirror signals were avoided by using the *noesytp* pulse program with suitable phase cycling. The evolution period t_1 was incremented in 128 steps of 1 µs. In the t_2 interval 512 data points in steps of 0.5 µs were taken. The number of accumulations was 6000, the repetition time was 20 ms, and the total time of the experiment was 6 h. The two cross-sectional spectra positioned at the NQR frequencies 40.117 and 40.206 MHz are shown in Fig. 2. The spectra demonstrate the large intensity ratio of diagonal peaks (high) and cross-peaks (low). According to the calculation