Absolute Sign Determination of Nuclear Quadrupole Couplings by Laser - Radiofrequency Double Resonance

Dieter Suter and Tilo Blasberg

Institute of Quantum Electronics, ETH Zürich, CH-8093 Zürich

The combination of optical and radio frequency is a well-known technique for obtaining spectra of nuclear quadrupole transitions with high resolution and high sensitivity. A new and attractive feature of this technique is, that it allows not only the determination of the strength and orientation of the quadrupole- and Zeeman tensors, but also of the absolute sign of the nuclear quadrupole interaction. This determination of the sign, which is essential for the comparison with calculated EFG tensors, is not possible with purely magnetic methods.

The interaction between the quadrupole moment of nuclear spins and the electric field gradient tensor at the site of the nucleus, known as the quadrupole coupling, shifts the energy of nuclear spin states when the environment of the spins has less than cubic symmetry. The magnitude of this shift depends sensitively on the structural details of the environment and can provide information on average static structure, but also on crystal imperfections or dynamical processes. The measurement of nuclear quadrupole coupling constants is therefore an important tool of solid state physics. The measurements are usually performed by magnetic resonance techniques, which allow precise determinations of the coupling constants and therefore of the electric field gradient tensors. However, they provide only the absolute value of the coupling constant, but are insensitive to the sign of the coupling as long as the high temperature approximation for the spin system holds [1]. The same limitations apply to spectral hole-burning, an alternative method for the determination of quadrupole coupling constants [2]. Nevertheless, a combination of spectral hole-burning and laser-rf double-resonance technique [3] can provide information on both the absolute value and the sign of the nuclear quadrupole coupling.

Figure 1 shows schematically the principle of this method, which we call two beam Raman heterodyne spectroscopy. Our model system consists of three nondegenerate spin states in the electronic ground state and a single electronically excited state. In (1a), a pump laser beam at frequency ν_P saturates the transition from ground state sublevel $|0\rangle$ to the electronically excited state $|e\rangle$. This spectral hole-burning process excites nonthermal populations of the spin states, whose sizes depend on the relevant relaxation processes. The radiofrequency field, which is resonant with transition $|1\rangle \leftrightarrow |2\rangle$, converts this population difference $\rho_{22}-\rho_{11}$ into a coherence. As shown in figure 1b), we detect this coherence optically with a test laser-field at frequency ν_T, which has to be resonant with an optical transition from one of the two sublevels $|1\rangle$ or $|2\rangle$ to the excited state $|e\rangle$. The laser field transforms the coherence from the NQR transition into an optical coherence at frequency $\nu_T \pm \nu_{12}$, which propagates in the same direction as the test laser-field. On the photodetector, the two fields interfere, producing a

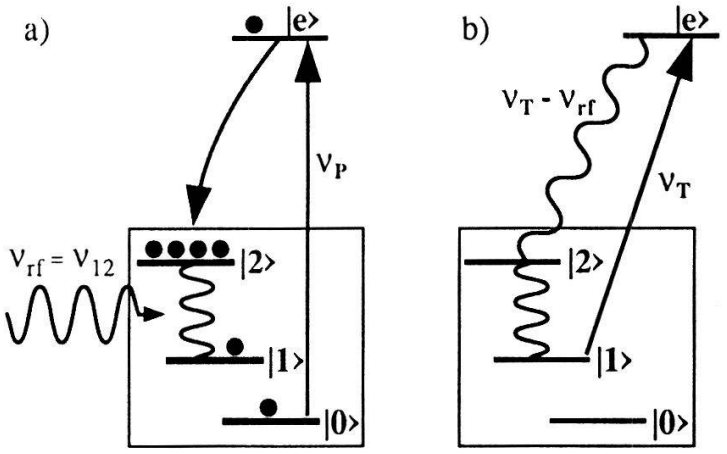

Figure 1: Principle of two beam Raman heterodyne spectroscopy

beat signal with frequency ν_{12}. The resulting signal depends resonantly on the detuning between the rf-frequency ν_{rf} and the NQR transition frequency ν_{12}. The laser frequency difference represents an additional parameter that allows the determination of the absolute sign of the coupling: the detection of the coherence is only possible, if the difference between the frequencies of the pump and test laser beams corresponds to an energy difference between two sublevels.

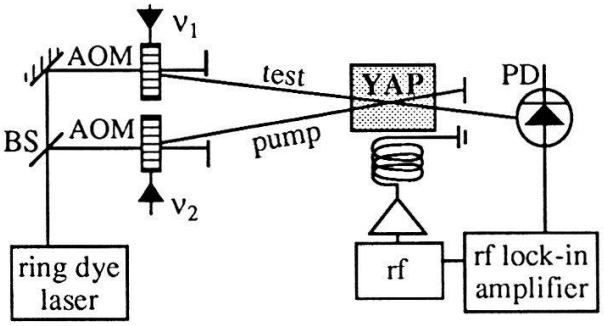

Figure 2: Experimental setup: BS = beam splitter, AOM = acousto-optic modulator, rf = radio-frequency synthesizer, PD = photodiode.

As an example, we have measured the nuclear quadrupole coupling of the impurity ion Pr^{3+} (I= 5/2) in the crystal host lattice $YAlO_3$ (YAP). Figure 2 shows schematically the experimental: two acoustooptic modulators shift the frequencies ν_P of the pump laser beam and ν_T of the test laser beam independently by up to ±30 MHz. The crystal is mounted on the cooling finger of a He flow-cryostat near a rf-coil, which is part of a tuned circuit. The beat signal between the laser- and the coherent Raman-field is detected with a photodiode and a lock-in amplifier.

Figure 3a shows the observed signal as a function of the difference between the pump and test laser frequency. For this experiment, the rf-field was resonant with the transition between the spin states m_I=±1/2 ↔m_I=±3/2 of the electronic ground state. Signal contributions are obtained, when the test laser-field frequency is resonant with the transition from one of the two sublevels |1> or |2> to the excited state |e> and the pump laser frequency with any of the three possible transitions. As shown in figure 3b, c), the five distinguishable frequencies are distributed asymmetrically. Comparison of the experimental spectrum with the two theoretical stick spectra shows clearly, that the quadrupole coupling in this case is negative.

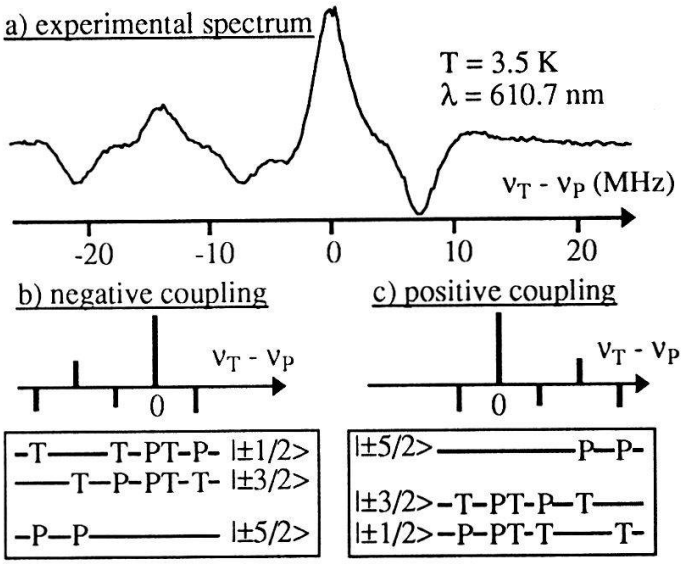

Figure 3: Experimental spectrum (top) compared to the calculated stick spectra

In conclusion, we have demonstrated, that both, the coupling constants and the absolute sign of the nuclear quadrupole interaction can be determined with a laser-radiofrequency double-resonance experiment.

This work was supported by the Schweizerischer Nationalfonds.

References

[1] A. Abragam, *The Principles of Nuclear Magnetism.*, Oxford University Press, Oxford (1961).
[2] S. Völker, Ann. Rev. Phys. Chem. 40, 499 (1989).
[3] N.C. Wong, E.S. Kintzer, J. Mlynek, R.G. DeVoe, and R.G. Brewer, Phys.Rev.B 28, 4993 (1983).