# ISIS Experimental Report

## Rutherford Appleton Laboratory

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**Title of Experiment:** Quantum Breathers

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**Affiliation:** Cambridge

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**Local Contact:** O.Petrenko

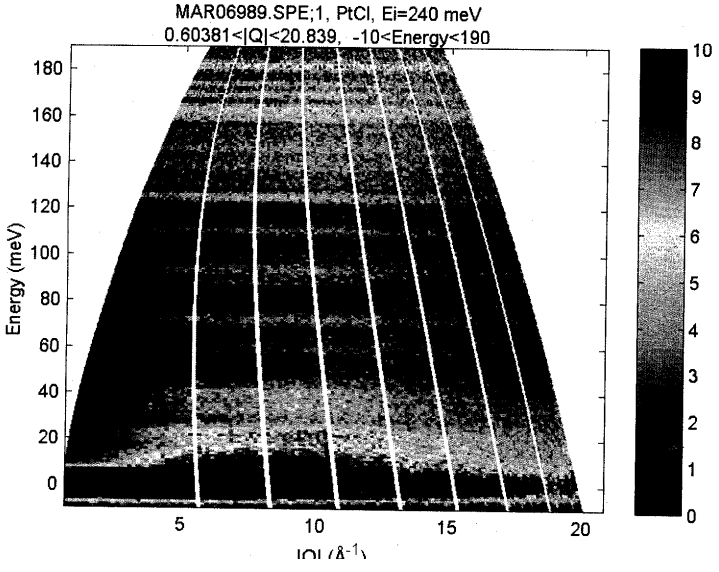
**Instrument:** MARI

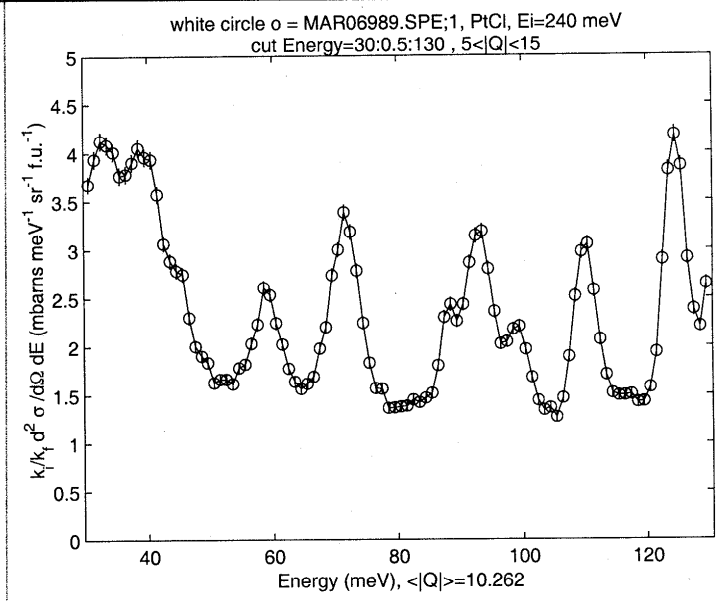
**Date of Experiment:** 30 Jun 99 and 9 Feb 00

The aim was to test the feasibility of observing quantum breathers in $Pt(en)_2Pt(en)_2Cl_2(ClO_4)_4$ by neutron scattering, where *en* is ethylenediamine. Quantum breathers are vibrations of molecular crystals which are localised by strong anharmonicity compared to intermolecular coupling. Evidence for quantum breathers in this material, attributed to symmetric stretches of the $PtCl_2$ "molecules" in the dimerised $PtCl$ chains, was obtained by Raman scattering [S], but no direct evidence for their spatial localisation was given. Our goal was to see whether a spatial coherence length could be inferred by neutron scattering. Translating [S], the excitation and its first overtone have energies 38.7 and 77.2 meV, so 90 meV neutrons would be expected to excite both. These have a wavenumber $6.6A^{-1}$ which although larger than ideal could still permit modulations at the reciprocal lattice vector of $0.58A^{-1}$ along the $PtCl$ chains to be measured in a single crystal by MARI, such as observed in theoretical simulations of a model in [W]. To suppress scattering from other parts of the material, the plan was to fully deuterate it. To enhance the scattering from $Cl$, in particular to render it more coherent, it was planned to make the sample $^{35}Cl$-pure; this would also eliminate interpretations in terms of localisation by isotopic randomness, as made by [L] for the antisymmetric stretch of the $PtCl_2$ molecules. There was a substantial risk, however, that even if these isotopic enhancements were carried out, we might still not be able to see the $PtCl_2$ modes because the recoil curve for $Cl$ ($E = 0.058Q^2$) would be too close to the elastic regime.

Thus to save doing complicated isotopic substitutions for no good use, this initial test was carried out on a natural isotope sample. 5g was prepared by the method of [K]; this was estimated to be the maximum for acceptable multiple scattering (15%). Since [S] saw up to the 7th overtone (at 266 meV), and to allow large enough $Q$ to place the $PtCl_2$ stretch energy near the $Cl$ recoil curve, this feasibility study looked at a big picture, using incident energy 240 meV. The results are shown in Fig. 1. To identify excitation energies more precisely, Fig. 2 shows a cut along energy. Although the data does show an excitation near 39 meV, there is very little evidence for the 77.2 meV and higher overtones (expected at 115.5, 154, 192 and 229 meV), the objects of real interest.

The question arises whether we can identify the excitations evident in Fig. 1. Since they seem to peak around the recoil curve for $H$ ($E = 2.07Q^2$), but have energies much less than a $CH$ or $NH$ stretch or bend, it is reasonable to associate them with modes of ethylenediamine generated by scattering from an $H$ (including possibly twisting of $CH_2$ or $NH_2$ groups). This would fit with infrared data of [L] showing absorption peaks at 26.6, 32.0, 36.6, 38.9, 41.2 and 45.0 meV which they attribute to *en* modes. [L] also observe IR absorption at 43.7, 44.1 and 44.5 meV, which they attribute to antisymmetric $PtCl_2$ stretches, the triple peak




reducing to a single 44.5 meV peak on using a $^{35}Cl$ pure sample. This might perhaps correspond to the small knee in Fig. 2 at this energy.

Deuteration would reduce the excitation of *en* modes by a factor of 7.2 (the bulk of the remainder being due to scattering from $C$ or $N$), which would make a significant improvement to the chances of seeing the $PtCl$ modes. $^{35}Cl$ enrichment of the $PtCl$ chains would enhance the $PtCl_2$ peaks by increasing the $Cl$ scattering by 30% and by reducing the isotopic spread. $^{37}Cl$ substitution of the $ClO_4$ would reduce their scattering by a factor of 1.8. Even with all three isotopic changes, however, the scattering from *en* would still be 5.8 times stronger than that from the $PtCl$ chains (and that from $ClO_4$ 10% stronger). Since there was little evidence for $PtCl_2$ modes in Figures 1 and 2, the prospects for substantial improvements by isotopic substitution look slim. As they would have to be substantial to give a hope of studying the $Q$-dependence, and there were problems with obtaining the reagents in the desired isotopic forms, and to see modulation on the $Q$-profile would require a single crystal, and to get onto the $Cl$ recoil curve would require higher incident energies and consequently poorer resolution at the desired energies of 39 and 77 meV, it was decided not to pursue the goal further at this time. This negative result is somewhat disappointing, but it has been an educational experience and the experiment inspired a rigorous mathematical approach to quantum breathers [M].

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