EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Proposal to the ISOLDE and Neutron Time-of-Flight Committee

PAC studies of isolated small Cd and Hg molecules: The nuclear quadrupole moments

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H. Haas[1,2], L. Hemmingsen[3], S.P.A. Sauer[3], J.G. Correia[2,4],
J. Schell[2,5], V. Amaral[1], D.C. Lupascu[5], R. Vianden[6]

1 Department of Physics and CICECO, University of Aveiro, 3810-193 Aveiro, Portugal
2 EP Division CERN, 1211Geneve-23, Switzerland
3 Department of Chemistry, University of Copenhagen, 2100 Copenhagen, Denmark
4 C^2TN, Instituto Superior Technico, Universidade de Lisboa, Portugal
5 Institute for Materials Science and Center for Nanointegration, Duisburg-Essen (CENIDE), University of Duisburg-Essen, 45141 Essen, Germany
6 Helmholz-Institut fuer Strahlen- und Kernphysik, Universitaet Bonn, Nussallee 14-16, Bonn, Germany

Spokesperson(s): H. Haas (heinz.haas@cern.ch)
Local contact: J. Schell (juliana.schell@cern.ch)

Abstract

The nuclei ^{111}Cd and ^{199}Hg are among the most widely used Perturbed Angular Correlation (PAC) cases. They have also been extensively used at ISOLDE, in particular for studies of complex molecules of biological relevance. For any quantitative interpretation of such measurements, knowledge of the nuclear quadrupole moment (Q) of the PAC state is necessary. While for ^{199}Hg a fairly reliable value exists, we have recently demonstrated in combining solid-state, molecular, atomic, and nuclear theory that the conventionally accepted value for ^{111}Cd has to be revised. During this work it has become evident, that precise values of the nuclear quadrupole interaction in free molecules is the best route towards higher precision for Q, in particular for ^{111}Cd. The primary purpose of the proposed series of PAC experiments is to obtain such data.

Since Hg and Cd have rather similar chemical properties, we shall attempt measurements of some cases, notably $CdCl_2$, $CdBr_2$, CdI_2, and the corresponding Hg species, as freely rotating molecules in the gas phase. Such PAC experiments have never been successfully performed yet, however. Since they are experimentally and theoretically quite challenging, we will also make complementary 'standard' PAC measurements for comparison purposes. A possible extension of the experiments proposed here could be matrix isolation measurements of the molecules imbedded in rare gas solids. Such experiments would be new for PAC as well, but are in principle straightforward.

Requested shifts: 12 shifts, (split into 4 runs over 2 years)

Motivation

All measurements of nuclear quadrupole interaction primarily determine an interaction frequency $\nu_Q = eQVzz/h$. In order to extract from these the nuclear quadrupole moment Q, the value of the electric field gradient (EFG) Vzz for the system studied has to be known. This then has essentially to come from theory.

Historically atomic systems had to be employed for determining precise values of nuclear quadrupole moments. With the advent of modern quantum chemistry techniques, however, also the accuracy of EFG calculations in molecules has reached the stage of 1% precision in favourable cases [1]. Theoretical calculations for solids, on the other hand, can usually not be trusted below the 10% level.

The primary aim of the present proposal is to obtain reliable values for the ν_Q for some simple molecular Cd systems. In our recent work, where we have determined a new, much revised value for Q of ^{111}Cd ($5/2^+$) in a combination of solid-state, molecular, atomic, and nuclear theory [2] we had to rely on a measurement of Cd-dimethyl in the (molecular) solid state [3] and correct it for the intermolecular interaction according to rather uncertain theory. Nevertheless, we could demonstrate that the linear trend of Q for the $11/2^-$ states in the odd-A Cd nuclei as function of neutron number, so nicely confirmed in recent collinear laser experiments at ISOLDE [4], abruptly ends at mass number 109, in full accord with nuclear covariant density functional theory.
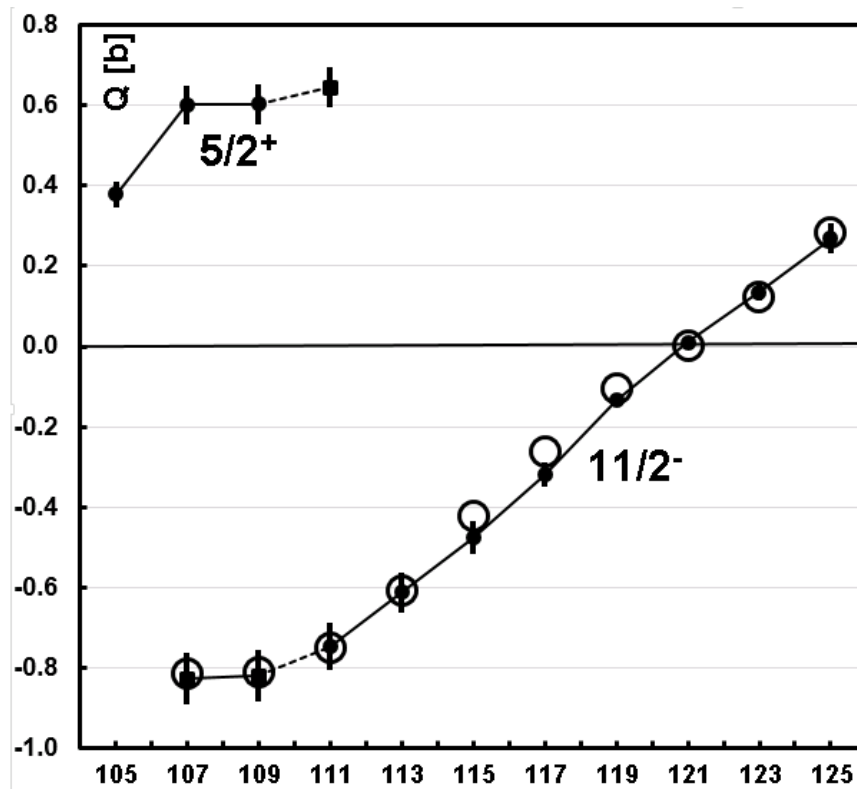

Figure 1: Nuclear quadrupole moments of Cd isotopes from atomic (dots) and solid state (squares) experiments as compared with theory (circles). For visibility the error bars are increased by a factor of 2.

In the present proposal we intend to develop a new technique that will allow to determine ν_Q values for molecules with an accuracy that matches the atomic data, so that the only

remaining uncertainty for Q will come from the corresponding theoretical calculations. It may be hoped that such more precise experimental data would also trigger a more advanced (and also much more complicated) nuclear theory effort to explain the moments of the $5/2^+$ states as well.

To date all PAC measurements have been performed in solids. In liquids the molecular reorientation averages out the EFG, so that at best only relaxation processes have been seen for small molecules. Very large (biological) molecules, not of interest for the present purpose, can in principle be slowed down in viscous liquids to effectively (on the PAC timescale of 100 ns) fixed state. In gases, on the other hand, molecules are freely rotating, and the effective EFG is the projection on the rotation axis. Only for linear molecules, where the rotation axis is always perpendicular to the molecular one, a unique number for Vzz results, -½ the molecular value. Intermolecular (and wall-) collisions, however, will change the rotational axis, again leading to relaxation processes due to motional averaging. In order to avoid these, the free flight time of the molecules has to be on the PAC timescale, requiring pure vacuum conditions. For this reason early attempts of such experiments in the 1970s had to fail. With the availability of pure isotope samples at ISOLDE, however, one should be able to overcome these technical problems.

Since element-changing nuclear decay preceding the PAC cascade will generally lead to a disruption of the molecules, one is essentially limited to isomeric decay cases. ^{111}Cd and ^{199}Hg being by far the most favourable isotopes. In Table 1 their decay properties are summarized.

	$T_{1/2}$ (min)	γ_1 (keV)	γ_2 (keV)	$t_{1/2}$ (ns)	I	A_{22}	Q (mb)	E_{REC} (eV)
^{111}Cd	48.6	151	245	84	5/2	.1786	646	.11
^{199}Hg	42.6	374	158	2.45	5/2	.251	677	.38

Table 1: Half-life of the isotope ($T_{1/2}$), gamma-1 (γ_1) and gamma-2 (γ_2) energies, half-life of intermediate state ($t_{1/2}$), spin (I), gamma anisotropy (A_{22}), nuclear quadrupole moment (Q) and recoil energy (E_{REC}).

Systems chosen

For the proposed studies (relatively) volatile species are required. Since no simple diatomic molecules of Cd with high volatility exist, the choice is limited to linear triatomic cases. These then are the dihalides as listed in Table 2, together with some of their properties. The corresponding Zn compounds have similar structures. Unfortunately they cannot be measured by the PAC technique. The equivalent nuclear quadrupole resonance (NQR) or Mössbauer spectroscopy experiments, however, would be very interesting.

	mp [C]	bp [C]	R [Å]	ν_Q^{mol} [MHz]	ν_Q^{sol} [MHz]	T_{exp} [C]	t_{PAC} [ns]	t_{col} [ns]	p_{max} [hPa]
$CdCl_2$	564	964	2.282	580	49.2	541	34.5	3.10	253
$CdBr_2$	568	863	2.394	526	24.6	509	38.0	3.52	250
CdI_2	388	744	2.582	525	9.7	406	38.1	3.77	232

	mp	bp	R	ν_Q^{mol}	ν_Q^{sol}	T_{exp}	t_{PAC}	t_{col}	p_{max}
HgCl$_2$	276	304	2.252	1272	1235	131	15.7	5.51	490
HgBr$_2$	236	322	2.383	1154	1030	132	17.3	5.68	459
HgI$_2$	259	350	2.554	1152	63	152	17.4	5.42	459

Table 2: Properties of molecules to be used in this study: Melting point (mp), boiling point (bp), internuclear distance (R), ν_Q for molecule (ν_Q^{mol}), ν_Q for solid (ν_Q^{sol}), measurement temperature (T_{exp}), PAC time range (t_{PAC}), collision time at 1 atm (t_{col}), maximum pressure allowed (p_{max}).

Only HgCl$_2$ (HgBr$_2$ approximately) is also present in the (quasi) linear form in the solid state. The other halides are ionic solids. Though their EFG is well known from earlier PAC experiments, these data are of no direct use for the present purpose.

Theoretical basis

For the Hg compounds modern theoretical calculations of the EFG for the molecules in the ground state exist [5]. The preliminary calculations for the Cd halides, made already a long time ago [6], can easily be updated. The small changes to be expected will not influence the present proposal.

In order to perform a full analysis of the expected PAC results additional calculations for the molecules deformed from the equilibrium configuration by stretching or bending will have to be made. The existing preliminary work suggests that the effects expected from stretching vibrations are quite small, those due to bending somewhat larger, however.

1a Free molecule PAC

It is known from electron-diffraction and infrared studies that all the molecules considered here are present essentially as monomers in the gaseous state. If it is then possible to produce them in a clean condition and at sufficiently small pressure that the time between intermolecular (and surface) collisions is longer than the typical PAC observation time one should be able to measure directly the EFG component along the rotation axis. In Table 2 the free flight time necessary t_{PAC} and the maximum molecular density acceptable p_{max} for the cases considered is summarized together with the assumed temperature T_{exp} needed for keeping the molecules in the gas phase, rather than sticking at a container surface, as estimated for a vapour pressure of 100 Pa (.001 atm). Obviously such an estimate will depend on the container material, typically laboratory (Pyrex) glass.

The number of radioactive atoms needed for a PAC experiment with a source half-life of around 1 h, the present case, a representative detector solid angle of .2 steradian, and a count rate of optimally 50000 s^{-1}, amounts to 10^{10}. In a gas volume of 1 cm^3 as example for a typical sample container, this leads to a pressure of $4*10^{-5}$ Pa, well below the assumed vapour pressure of 10^0 Pa and even more so below the estimated maximum allowable pressure from Table 2. Converting the maximum pressures allowed as shown in Table 2 into matter acceptable in a sample gas volume of 1 cm^3 results in 1 to 10 mg amounts. In practice one would like to stay at least a factor of 10 to 100 below these values. Presumably at this relatively large amount of material the rest gas pressure due to other impurity species inevitably present will not be a problem.

1b Vibration and rotation effects

The proposed gas phase PAC experiments will obviously be performed on molecules that are vibrationally and rotationally excited at the measuring temperature. For the strictly linear halide molecules the rotational axis will always be perpendicular to the molecular axis, so that only the effective Vzz will possibly depend on the rotation/vibration state. This will lead to a slight spread of the value, resulting in a damping of the measured precession pattern. This effect, expected to be quite small, can be fairly easily taken into account with modern quantum chemistry techniques.

A further complication in the analysis of the proposed experiments will be due to the recoil effects of the first gamma ray in the PAC cascade. This recoil energy, see Table 1, will lead to additional vibrational excitation to be considered. This may again be estimated to lead to a small further Vzz spread. A full treatment must eventually also consider the correlation of this effect with the gamma-2 angular distribution and presumably result in a slight modification of the actual perturbation pattern observed.

1c Techniques for gas measurements

The production of the gaseous samples needed for this project is expected to be particularly simple for the halides. The isotopes from ISOLDE are collected in an ice sample frozen to a cold-finger, a well-developed technique. A minute amount (typically .1 mg) of the dissolved corresponding solid will be added and the liquid dried in vacuum in a small quartz boat. This will then be introduced in a pre-cleaned glass tube and the material sublimed into another section of the tube using a stream of argon gas and a proper temperature profile as schematically shown in Fig. 2. The part containing the sample will then be sealed off at room temperature (or slightly below) under vacuum. The whole procedure will obviously have to be completed in typically 30 minutes. Another purely technical problem is of course the fact that such small amounts of material cannot be seen optically. The fact that the final sample will be radioactive, however, will allow tracing it by the emitted radiation. The whole procedure, including the temperature profile, will clearly first have to be calibrated with a somewhat larger amount of material. For the PAC measurement the sample container must then be heated to the necessary temperature T_{exp} as given in Table 2.
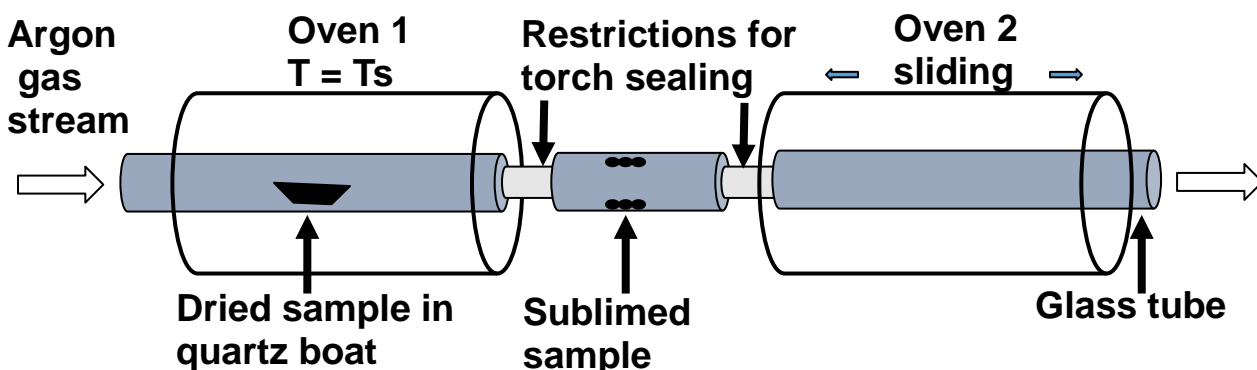

Figure 2: Schematic drawing of procedure to produce the gaseous samples.

2a Complimentary 'standard' PAC measurements

A few quite simple first measurements could already result in the most important data necessary for the determination of the nuclear quadrupole moment of ^{111}Cd (5/2$^+$). These would, however, lead to the precise $\square_Q$ values for the free molecules only in combination with theoretical calculations of the condensed matter involved. We consider:

a: Cadmium halides ($CdCl_2$, $CdBr_2$) as impurities in the corresponding (molecular) Hg solids. The $CdCl_2$ and $CdBr_2$ molecules matrix isolated in the equivalent Hg halide will then be measured at low temperature, typically 77 K being sufficient.

b: Frozen solutions of Cd- and Hg-dimethyl in isopentane, a glass-forming hydrocarbon.

2b Matrix effects

The interpretation of the ν_Q values to be measured within these first experiments will have to be supplemented by solid-state calculations.

a: Early theoretical calculations for solid and molecular $HgCl_2$ show a rather small change of the EFG, less than 2% [7]. They will obviously have to be repeated with more modern techniques also for the impurity system. We expect an even somewhat smaller matrix effect there.

b: For the frozen glass matrix a distribution of lattice sites is to be considered that should manifest itself directly in the PAC data. A small frequency spread is expected for the very large molecular value, however.

2c Chemical techniques

The production of these samples requires much less stringent conditions than for the free molecule experiments. It should thus be quite simple to prepare them.

a: Trace amounts of the corresponding [111]Cd halide in solution will be added to the Hg salt, typically 10 mg, brought to dryness, and then melted.

b: The production of the dimethyl molecules in trace amounts will require a standard chemical technique. Starting with the pure halide (probably bromide), prepared as above, one has to add Grignard reagent ($MgClCH_3$) for this process. The whole procedure will need a high-boiling solvent (probably hexyl ether) out of which the desired compound can be distilled without any other contamination into a glass sample tube that contains the solvent. After torch sealing this will be quickly frozen to 77 K.

Possible future extension: Matrix isolation (MI) experiments

The observation of simple molecules embedded in an inert matrix is a well-developed method for various spectroscopic techniques, Infrared-, Raman-, Ultraviolet-, Mössbauer- and others [8]. It is therefore astonishing that no PAC experiments have yet been reported with this technique. Traditionally rare gas matrices are chosen in this field to have as little as possible interaction with the embedded molecules. This requires very low measuring temperatures, typically 20 K. Obviously in an interpretation of such data the matrix effects would have to be taken into account.

Of particular interest would be a few pioneering PAC experiments using the MI technique. Clearly measurements of the linear Cd and Hg halides in frozen krypton will be prime candidates. For these halide molecules an extensive series of MI experiments has already been performed using infrared spectroscopy [9]. One could thus be rather confident that unexpected difficulties will not arise. Since also non-linear molecules can be studied with this approach, however, many further candidates exist for other PAC isotopes as well. The actual choice of the systems will depend on technical developments.

Summary of requested shifts:

Required isotope	Implanted beam	Probe element	Type of experiment	Approx. Intensity [at/µC]	Target / Ion source	Required atoms per sample	nº of shifts
^{111m}Cd (48 min)	^{111m}Cd	^{111}Cd	γ-γ PAC	10^8	Molten Sn/ VADIS	2×10^{10}	6
^{199m}Hg (43 min)	^{199m}Hg	^{199}Hg	γ-γ PAC	10^9	Molten Pb/ VADIS	2×10^{10}	6

References:

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[3] Haas, H., Shirley, D.A.: Nuclear quadrupole interaction studies by perturbed angular correlations. J. Chem. Phys. **58**, 3339-3355 (1973)

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Appendix

DESCRIPTION OF THE PROPOSED EXPERIMENT

The experimental setup comprises: *(name the fixed-ISOLDE installations, as well as flexible elements of the experiment)*

Part of the experiment	Availability	Design and manufacturing
Part 1: SSP-GLM Biophysics chamber (ISOLDE hall)	☒ Existing	☒ To be used without any modification
	☐ New	☐ Standard equipment supplied by a manufacturer ☐ CERN/collaboration responsible for the design and/or manufacturing
Part 2: Chemical Laboratory (508/R-002)	☒ Existing	☒ To be used without any modification ☐ To be modified
	☐ New	☐ Standard equipment supplied by a manufacturer ☐ CERN/collaboration responsible for the design and/or manufacturing
Part 3: Experimental PAC zone (508/R-008)	☒ Existing	☒ Various PAC spectrometers ☐ To be modified
	☐ New	☐ Standard equipment supplied by a manufacturer ☐ CERN/collaboration responsible for the design and/or manufacturing

HAZARDS GENERATED BY THE EXPERIMENT

(if using fixed installation) Hazards named in the document relevant for the fixed [COLLAPS, CRIS, ISOLTRAP, MINIBALL + only CD, MINIBALL + T-REX, NICOLE, SSP-GLM chamber, SSP-GHM chamber, or WITCH] installation.

Additional hazards:

Hazards	Part 1	Part 2	Part 3
Thermodynamic and fluidic			
Pressure			
Vacuum	.000001 - .1 Bar, .1 l	.000001 - .1 Bar, .1 l	.000001 - .1 Bar, .1 l
Temperature	273 K	293-700 K	77 K
Heat transfer			
Thermal properties of materials			
Cryogenic fluid	Liquid N for SSP-GLM Biophysics collection chamber (20 l) and sample holder cooling (0.1 l)		Liquid nitrogen
Electrical and electromagnetic			
Electricity	230 V, max. 10 A single phase	230 V, max. 10 A single phase	230 V, max. 10 A single phase
Static electricity			
Magnetic field	[magnetic field] [T]		
Batteries	☐		
Capacitors	☐		

Ionizing radiation

Target material	Frozen water		
Beam particle type (e, p, ions, etc)	^{111}Cd ^{199}Hg		
Beam intensity			
Beam energy	60 keV		
Cooling liquids	Liquid nitrogen		Liquid nitrogen
Gases		Argon	
Calibration sources:	☐		
• Open source	☐		
• Sealed source	☐ [ISO standard]		
• Isotope			
• Activity			
Use of activated material:			
• Description	☒ Described in the proposal text. Removal from chamber, transport to chemical laboratory 508/R-002 in standard Pb castle shielding and chemical preparation at 508/R-002.	Chemistry preparation at 508/R-002 as described in Figure 2 and text.	Placed in PAC machine at 508/R-008 for measurement.
• Dose rate on contact and in 10 cm distance	Max. 0.3 µSv/h (Nucleonica gamma dose rate)	Max. 0.3 µSv/h (Nucleonica gamma dose rate)	Max. 0.3 µSv/h (Nucleonica gamma dose rate)
• Isotope	^{111}Cd or ^{199}Hg	^{111}Cd or ^{199}Hg	^{111}Cd or ^{199}Hg
• Activity	Max 6 MBq per sample	Max 6 MBq per sample	Max 6 MBq per sample

Non-ionizing radiation

Laser			
UV light			
Microwaves (300MHz-30 GHz)			
Radiofrequency (1-300MHz)			

Chemical

Toxic		Cd(Hg)-dimethyl, 0.1 mg, $CdCl_2$, $CdBr_2$, CdI_2, 0.1 mg	
Harmful		$HgCl_2$, $HgBr_2$, 10 mg	
CMR (carcinogens, mutagens and substances toxic to reproduction)	[chemical agent], [quantity]		
Corrosive	[chemical agent], [quantity]	$HgCl_2$	
Irritant	[chemical agent], [quantity]		
Flammable	[chemical agent], [quantity]		
Oxidizing	[chemical agent], [quantity]		
Explosiveness	[chemical agent], [quantity]		
Asphyxiant	[chemical agent], [quantity]		
Dangerous for the environment	[chemical agent], [quantity]	$CdCl_2$, $CdBr_2$, CdI_2, $HgCl_2$, HgI_2, $HgBr_2$	

Mechanical

Physical impact or mechanical energy (moving parts)	[location]		
Mechanical properties (Sharp, rough, slippery)	[location]		
Vibration	[location]		
Vehicles and Means of Transport	[location]		

Noise

Frequency	[frequency],[Hz]		

Intensity			
Physical			
Confined spaces	[location]		
High workplaces	[location]		
Access to high workplaces	[location]		
Obstructions in passageways	[location]		
Manual handling	SSP protocol	ISOLDE Chemistry Lab protocol and material safety data sheet	SSP protocol
Poor ergonomics	[location]		

0.1 Hazard identification

3.2 Average electrical power requirements (excluding fixed ISOLDE-installation mentioned above): *(make a rough estimate of the total power consumption of the additional equipment used in the experiment)*