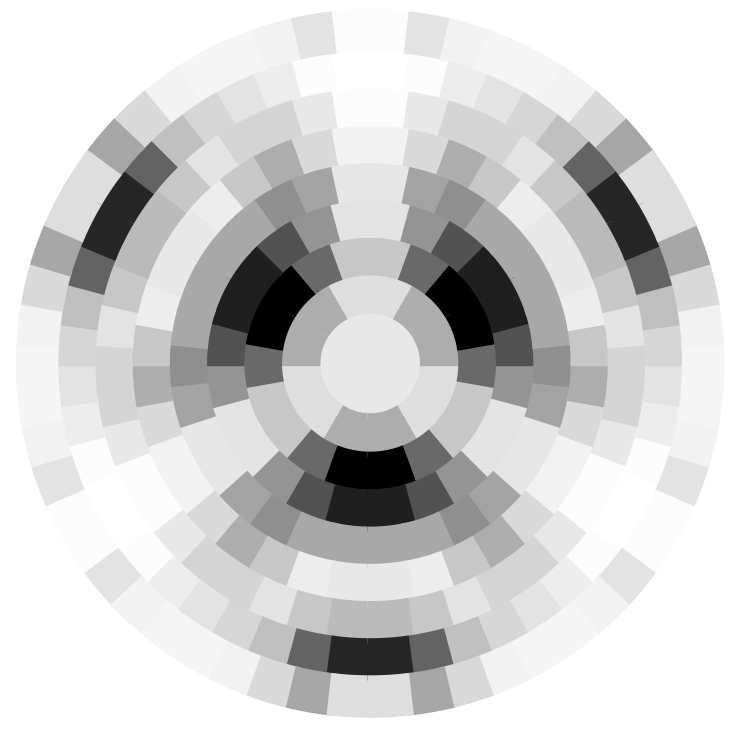# Dalitz plots of 2s-vibrational states in H_3 and D_3 : experiment and theory

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We examine the **decay** of the isotopologues H_3 and D_3 into three hydrogen atoms. Collecting temporal and spatial information of all fragments, allows us to deduce the full **momentum-vector-correlation** of such a decay. The probability-distribution is represented in so-called **Dalitz plots** and sensitively depends on the rovibronic level of the decaying molecule. An **explanation** of the observed **patterns** in the Dalitz plots can be partly found by simply considering the **symmetries** of the involved **wavefunctions** and **nonadiabatic couplings** which induce such dissociations and guide the molecule on different decay-paths. In this way the Dalitz plots contain information on the **complex intra-molecule dynamics** finally leading to the molecule-breakup.

Our measurements are conducted by means of two different methods, one relying on the state-mixing **Stark effect**. Here we present some selected **measured 2s-state Dalitz plots** [3,7] and compare them with results obtained in a simplified version of the model by Galster [3], which concentrates on the symmetry of initial vibrational wavefunction and nonadiabatic coupling operator leading to a dissociation on the upper groundstate-sheet in the triatomic hydogen-molecule.

On this poster we will not give any introduction to the neutral species of triatomic hydrogen nor will we give details on the **experimental setup** we use for measuring the momentum-vector-correlations but refer to sections 1. and 2. on the poster by **Kai Mozer et. al.** with title **"Electric field induced predissociation of H_3 and D_3"**

1. Coordinate Systems and Dalitz plot

We use Jakobi vectors **r**, **R** to define **cartesian coordinates** $v=\{v_1,v_2,v_3\}$, which describe the shape of our triatomic molecule:

$$v_1 = |\mathbf{r}|^2 - |\mathbf{R}|^2 = \rho^2 \cos\vartheta \,\cos\varphi$$
$$v_2 = 2\mathbf{r}\cdot\mathbf{R} = \rho^2\cos\vartheta \sin\varphi$$
$$v_3 = 2|\mathbf{r}\times\mathbf{R}| = \rho^2\sin\vartheta$$

An alternative set are **hyperspherical coordinates** (ρ,ϑ,φ):

$$\rho = (v_1^2 + v_2^2 + v_3^2)^{1/2}$$
$$\vartheta = \arcsin\frac{v_3}{(v_1^2+v_2^2+v_3^2)^{1/2}}$$
$$\varphi = \arctan(v_2/v_1)$$

In Fig.1 (left) one sees which configuration belongs to which hyperspherical-coordinate set.

An X_3 molecule which forms an **equilateral triangle** in equilibrium geometry features three vibrational modes (a single symmetric ν_1 and a doubly degenerate asymmetric vibration ν_2). The **normal-coordinates** describing these vibrations can be either $Q=\{Q_1, Q_{2a}, Q_{2b}\}$ or $Q=\{Q_1, Q_r, \varphi\}$ and their connection to hyperspherical coordinates is given by:

$$Q_{2a} = A\,\rho\,\cos\tilde\vartheta\,\cos\varphi = Q_r\,\cos\varphi$$
$$Q_{2b} = A\,\rho\,\cos\tilde\vartheta\,\sin\varphi = Q_r\,\sin\varphi$$
$$\tilde Q_1 = A\,\rho\,\sin\tilde\vartheta$$
$$Q_r = A\,\rho\,\cos\tilde\vartheta$$
$$Q_r^2 = Q_{2a}^2 + Q_{2b}^2$$
$$\varphi^* = \varphi = \arctan(Q_{2b}/Q_{2a})$$

With $A = 3^{-1/4}\sqrt{m}$, $\tilde Q_1 = Q_1 + \sqrt{m}\,r_e$,
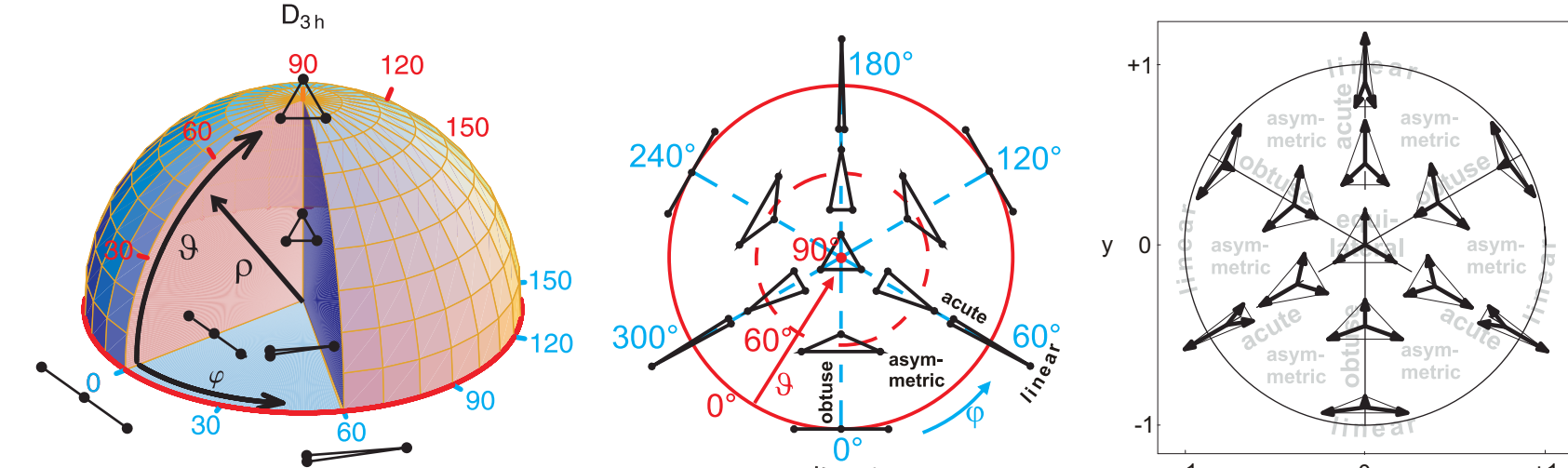$\tilde\vartheta = \frac{\vartheta}{2} + \frac{\pi}{4}$

Fig.1 hyperspherical coordinates (left), "spatial" Dalitz plot (center) and Dalitz plot in momentum-space (right)

Using hyperspherical coordinates we show in Fig.1 which spatial configuration belongs to the different coordinates. All introduced coordinates can equivalently be **introduced for momentum space**. Compare Fig.1 center and right.

The measured momentum-vector-correlations (**MVCs**) in our experiment can be mapped in so-called **Dalitz plots**: in momentum space the sphere of constant radius ρ belongs to a specific energy W. If this sphere is projected into the equitorial plane spanned by v_1 and v_2, the Dalitz plot appears. As **Dalitz coordinates** we define:

$$x = 3(\varepsilon_2 - \varepsilon_1)/\sqrt{3} \quad\text{and}\quad y = 3(\varepsilon_3 - 1/3)$$

Where $W = \sum_i m\mathbf{u}_i^2/2$ is the total released kinetic energy and $\varepsilon_i = m\mathbf{u}_i^2/(2W)$ are the single fragment energies normed to W. The connection between Dalitz-coordinates and v-momentum-coordinates is given by:

$$\begin{Bmatrix} x \\ y \end{Bmatrix} = -\frac{1}{2\,3^{3/2}\,m\,W} \begin{Bmatrix} v_1 \\ v_2 \end{Bmatrix}$$

2. Preparing 2s-vibrational states

- So far **theory** is **only** able to predict Dalitz plots for **2s rovibrational levels** [1,2]. In section 3 we describe a symmetry model based on [2].
- We have developed **two distinct methods** in order to **measure** 2s-Dalitz plots.

A) via laser excitation

starting off with molecules in the **metastable 2p**, **excitation** of states with **n=3**, followed by **radiative cascading** to vibrationally excited 2s-states (see Fig.2), for example :

$$2p''(0,0,0,0) + h\nu \rightarrow 3s'(0,0,1,0)$$
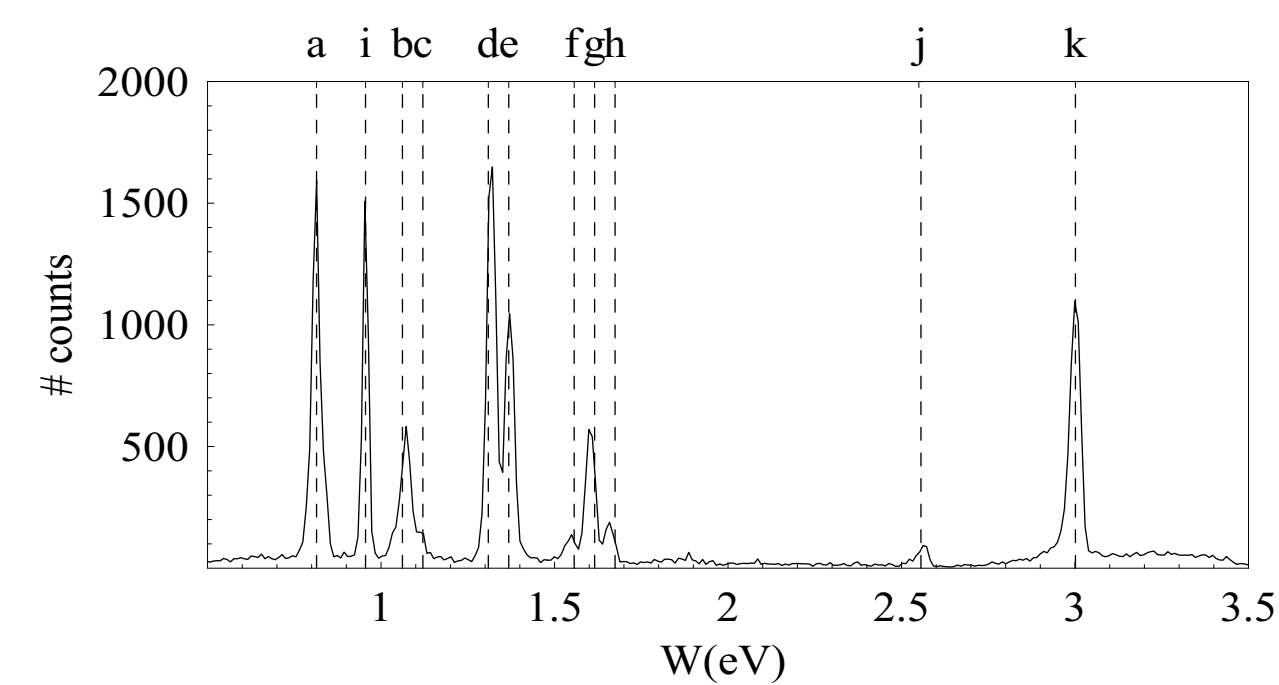$$\downarrow$$
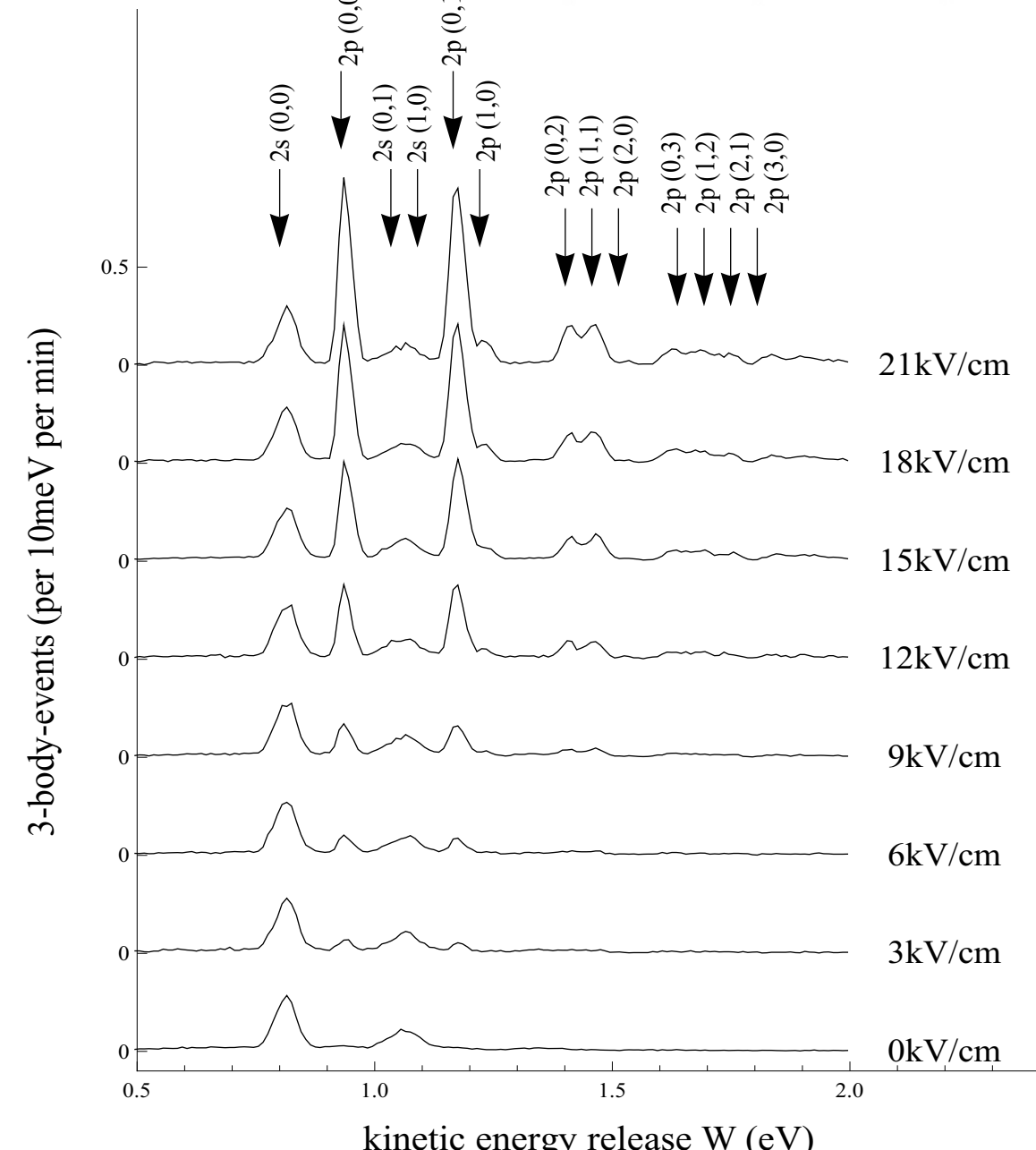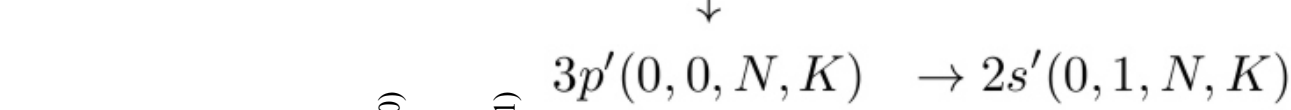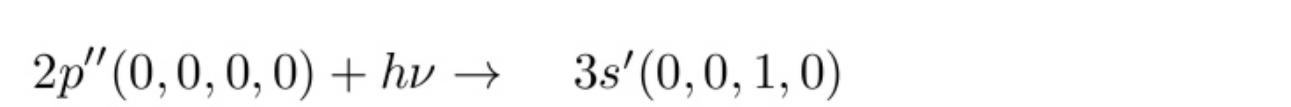$$3p'(0,0,N,K) \rightarrow 2s'(0,1,N,K)$$

Fig.2 Kinetic energy release spectrum in D_3 with laser tuned to transition $2p \rightarrow 3s$, taken from [8]

B) via Stark effect

Molecules in metastable 2p, subject to electric field, formally obtain a low **admixture of 2s-character** (perturbation theory):

$$|\Psi\rangle = |2p\rangle + \alpha\,|2s\rangle \qquad (\alpha_{20kV/cm} = 0.0026)$$

Because of very **high lifetime-difference** between 2p and 2s, the **dissociation-rate** is increased:

$$R_{2p}(\alpha) = 1/\tau_{2p} + \alpha^2\,1/\tau_{2s} \quad (D_3: \tau_{2p} = 800ns,\ \tau_{2s} = 850fs)$$

Decays out of 2p are then governed by the **2s-dissociation-pattern**! (details given in [4])

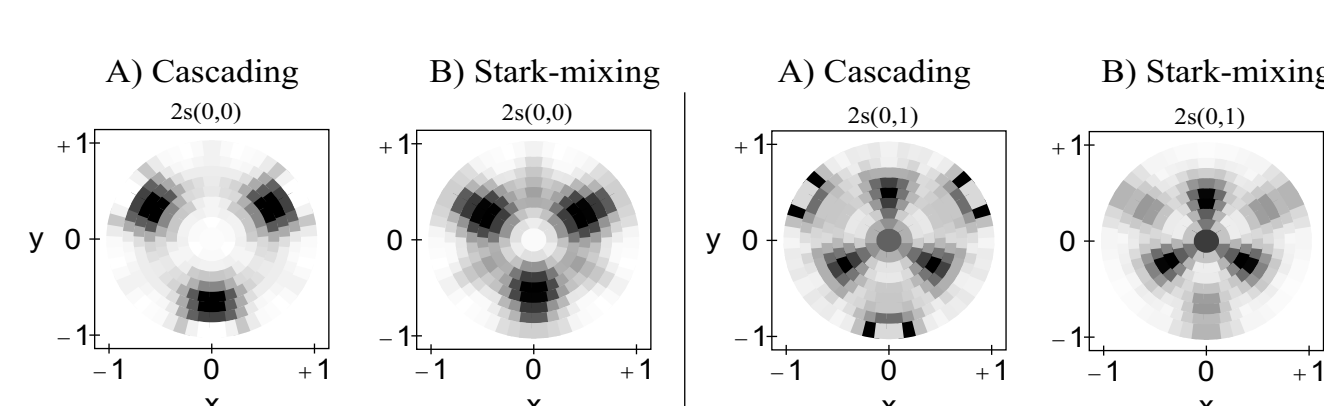Both methods yield the **same features** in the Dalitz plots:

Fig.3 Kinetic energy release spectrum in D_3 at different Stark-fieldstrengths, taken from [7]

3. Simple symmetry model

We have rebuilt Galster's theoretical model for predicting the Dalitz plots of vibrational states in $2sA_1'$ [2]. Different to the original model, we limit ourselves to discuss only the **symmetry properties** of the **intial wavefunction** and the **nonadiabatic coupling operator**, to derive a probability distribution, in which **spatial configuration** the triatomic hydrogen molecules enter the **upper groundstate** sheet. A **propagation** on the upper sheet or any influece of the **lower sheet** is not accounted for in our model for 2s. **Rotational coupling** is neglected.

The vibrational wavefunction χ_{2s} of the bound molecular state may be taken as a product of a **1D- and a 2D-degenerate** harmonic oscillator, described by quantumnumbers (ν_1, ν_2, l_2) and polar normal-coordinates:

$$\chi^{\nu_1,\nu_2,l_2}(q_1,q_r,\varphi) = \zeta^{\nu_1}(q_1)\cdot\eta^{\nu_2,l_2}(q_r,\varphi)$$
$$\zeta^{\nu_1}(q_1) = N_1\cdot e^{-q_1^2/2}\cdot H_{\nu_1}(q_1)$$
$$\eta^{\nu_2,l_2}(q_r,\varphi) = N_2\cdot q_r^{|l_2|}\,e^{il_2\varphi - q_r^2/2}\cdot L_j^{|l_2|}(q_r^2)$$

$a_0 = \sqrt{\hbar/m\omega_1}$, $\lambda = \sqrt{\omega_2/\omega_1}$, $q_1 = Q_1/a_0$, $q_r = \lambda Q_r/a_0$, $j = \frac{\nu_2 - |l_2|}{2}$, N_1 and N_2 normaliz.-constants

$H_n(x)$, $L_n^k(x)$ are the Hermite polynominals and the generalized Laguerre polynominals.

The **vibrational nonadiabatic coupling operator** leading to dissociation of bound molecules via the upper ground-state sheet is given in polar normalcoordinates by:

$$\Lambda_{2s,u} \propto A_u \cos\left(\frac{3\varphi}{2}\right)\cdot\frac{\partial}{\partial q_r} + B_u \sin\left(\frac{3\varphi}{2}\right)\cdot\frac{1}{q_r}\frac{\partial}{\partial\varphi}$$

A_u and B_u control the absolute prediss.rate but only the ratio $\delta = B_u/A_u$ is of importance.

The effect of the nonadiabatic coupling of the bound state to the dissociation continuum is a **steady transfer** of the 2s-wavefunction into the space of the upper sheet: $d\chi_u = \Lambda_{2s,u}\,\chi_{2s}(t)\,dt$

Any fraction $d\chi_u$ is subject to a **nearly monotonic propagation** into the limit of three seperate atoms. Galster has shown that this process is faster then the phase-modulation of $d\chi_{2s}(t)$ and as a result, two fractions $d\chi_u$ will only **weakly interfere** with each other, so we can actually sum all fractions in order to have the transferred wavefunction leaked from the initial 2s-vibrational state to the upper sheet:

$$\chi_u(q_1,q_r,\varphi) \approx \Lambda_{2s,u}(q_r,\varphi)\,\chi_{2s}(q_1,q_r,\varphi)$$

Looking at the **structure** of the nonadiabatic coupling and the initial vibrational wavefunction we see, that the **transferred wavefunction** consists in general of **4 terms** which depend on the initial quantumnumbers of the dissociating state:

$$\chi_u(q_1,q_r,\varphi) \propto \cos(3/2\varphi)\cdot(I + II + III) + \delta_u\cdot\sin(3/2\varphi)\cdot IV$$

Terms I, II, III, IV and their symmetry govern the final probability distribution $|\chi_u(q_1,q_r,\varphi)|^2$ in spatial configuratiion space. Transformation from polar normalmodes **q** to cartesian coordinates **v** and projecting the probability distribution $|\chi_u(\mathbf{v})|^2$ onto the v_1-v_2-plane finally leads to "spatial" plot. This is not the actual Dalitz plot as this would be in momentum space. The results presented in the next section, which were derived in spatial configuration space, show that there seems to be a very close connection between spatial- and momentum-space and that **patterns** from one space are **preserved** in the other.

4. Model compared to experiment

Following the procedure based on [2] and depicted in section 3, we have calculated "spatial" Dalitz plots for **numerous** $2sA_1'$ (ν_1, ν_2, l_2) vibrational levels in H_3 and D_3. In Fig. 4 and 5 we compare the results with experimental MVC obtained with the methods described in section 2.
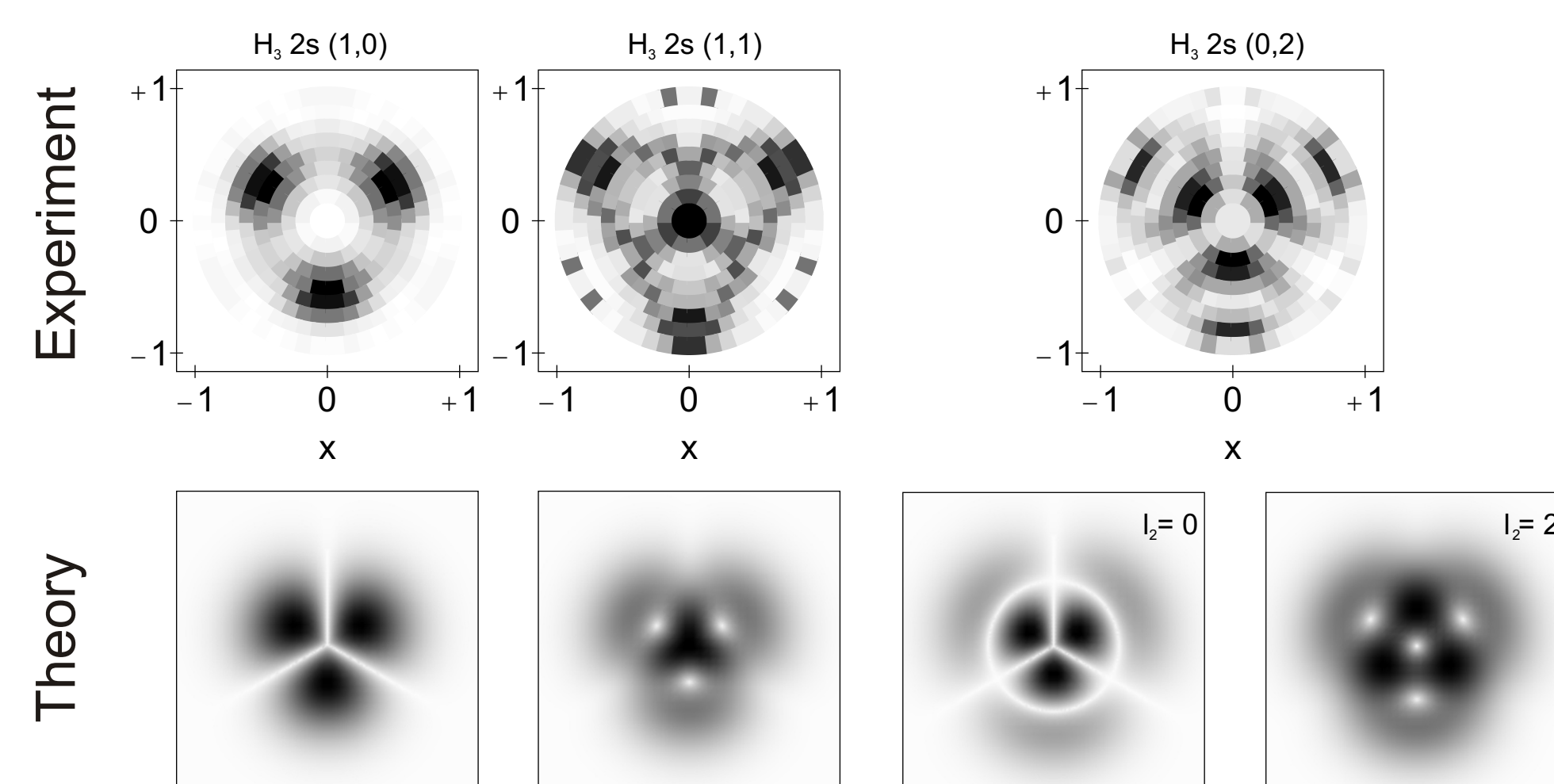

Fig.4 Experimental MVCs of different $2sA_1'(\nu_1,\nu_2)$ in H_3 (upper row) compared to calculated "spatial" Dalitz plots (lower row). Experimental resolution doesn't suffice to resolve a l_2-splitting. Comparison with theoretical results leads to the conclusion that for the (0,2)-state, mainly the $l_2=0$ state contributes to the MVC.
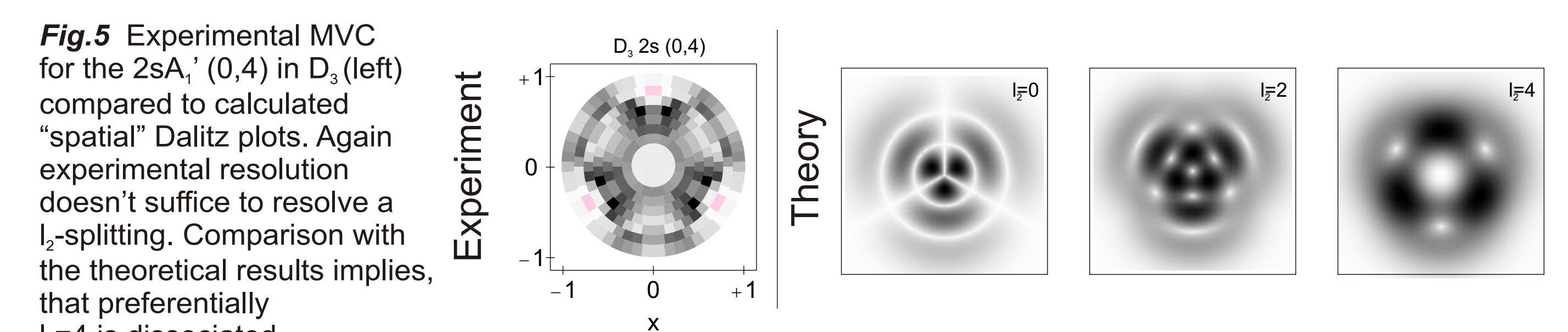

Fig.5 Experimental MVC for the $2sA_1'$ (0,4) in D_3 (left) compared to calculated "spatial" Dalitz plots (right). Again experimental resolution doesn't suffice to resolve a l_2-splitting. Comparison with the theoretical results implies, that preferentially $l_2=4$ is dissociated.

Comparing for example the experimental and theoretical results on the 2s(1,0) and 2s(1,0) states in Fig.4, we see that there is an **excellent agreement** between the observed patterns in the Dalitz plots for momentum and spatial space, the last beeing obtained with the symmetry model.

The experiment isn't able to resolve the l_2-splitting. Comparing the measurements with the model leads to **identification** of l_2-states which seem to contribute **preferentially** to the MVCs, see Fig.4 (right) and Fig.5 .

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