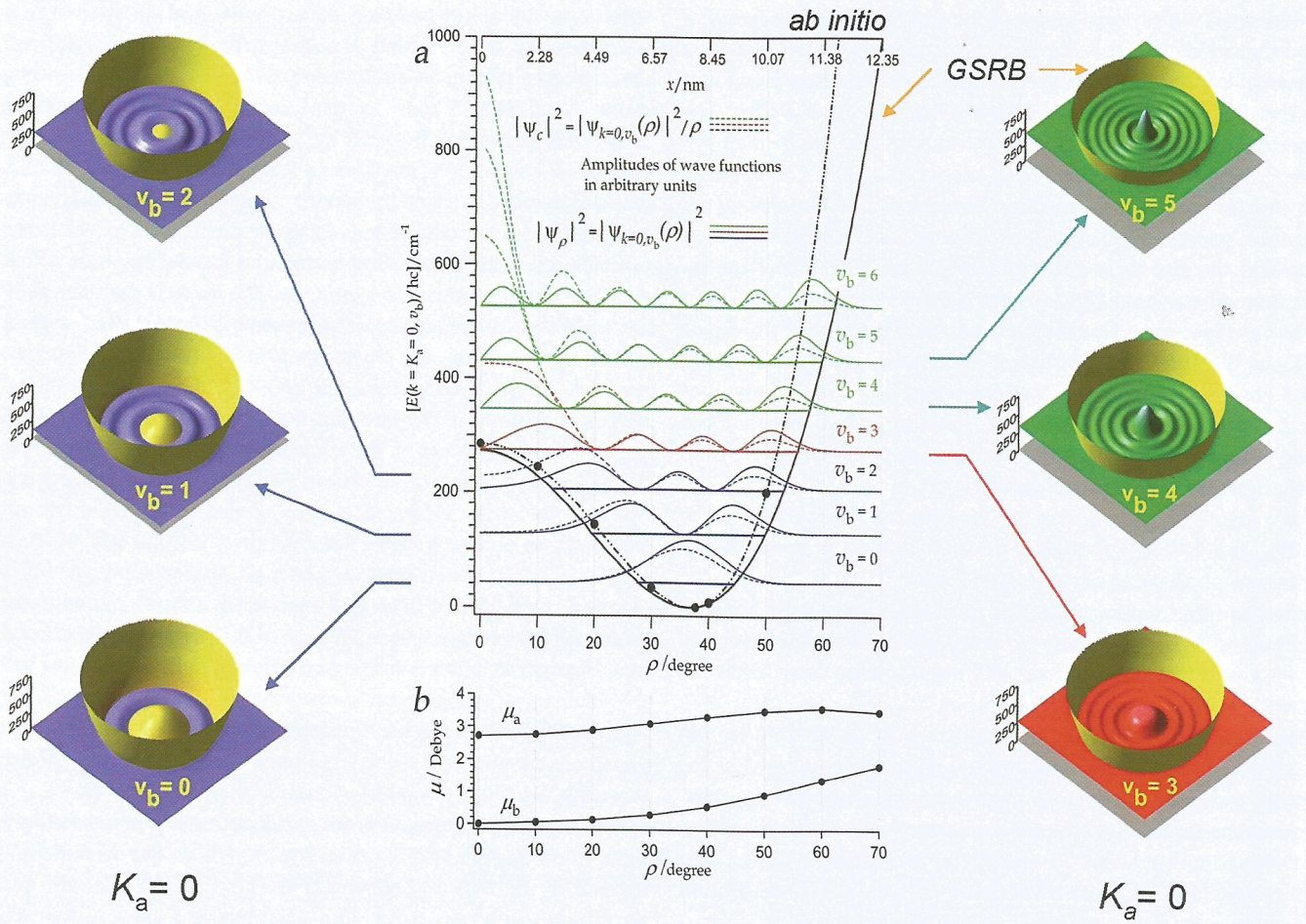

Fig. 3 The central panel with parts a and b of this figure is taken from our recent PCCP paper.[2] The solid black line represents the dependence of the potential energy on the bending coordinate ρ, obtained by fitting the Generalized Semi-Rigid Bender Hamiltonian (GSRB) to our experimental data. The solid black dots are the calculated *ab initio* values. The probability densities $|\Psi_\rho|^2$ and $|\Psi_c|^2$ for v_b and $K_a = 0$ are given in both polar and Cartesian coordinates for all observed values of v_b. We plot $|\Psi_c|^2$ in cartoons for each wave function indicated in the central panel, and obtain a feeling for the stationary state probability density in the Cartesian representation. The champagne bottle potential is plotted in golden color. We clearly see that $|\Psi_c|^2$ has a maximum at the origin (*i.e.* linearity) as soon as we have reached the classical monodromy point which lies slightly below the energy of the $v_b = 3$, $K_a = 0$ vibrational state. Part b of the central panel depicts the dependence on ρ of the *ab initio* calculated electric dipole moment components μ_a and μ_b.

for the product wave function,

$$\Psi_{k,v}(\rho,\chi) = \frac{1}{\sqrt{2\pi}} e^{ik\chi}\psi_{k,v}(\rho), \qquad (3)$$

where k is the quantum number associated with rotation about the z-axis while v corresponds to the large-amplitude bending quantum number. (Note: This corresponds to the definition of v for a bent asymmetric rotor molecule, or the radial quantum number n when using polar coordinates for a linear molecule.) The Euler angle χ describes the rotation about the a-(or z-) axis with the smallest moment of inertia. ρ is the large amplitude bending coordinate defined in Fig. 1 which displays the equilibrium structure of NCNCS in the principal axis system.

In the second step the product basis functions $\Psi_{k,v}(\rho, \chi)$ of eqn (3) are multiplied by "end-over-end" rotational factors, that is by the θ, φ parts, $S_{Jkm}(\theta, \varphi)$, of the normalized symmetric rotor wave functions. This gives the full Semi-Rigid Bender (SRB) basis functions of eqn (14) of Bunker and Stone,[20]

$$\begin{aligned}\Psi_{J,k,m,v}(\theta,\varphi,\chi,\rho) &= S_{j,k,m,}(\theta,\varphi)\Psi_{k,v}(\rho,\chi)\\ &= |Jkm\rangle\psi_{k,v}(\rho),\end{aligned} \qquad (4)$$

where $|Jkm\rangle$ are normalized symmetric top wave functions and where the $\psi_{k,v}(\rho)$ are independent of the sign of k since eqn (29) in ref. 2 depends on k^2. The GSRB Hamiltonian for all 4 degrees of freedom was then diagonalized in this basis yielding wavefunctions and level energies.

The GSRB fitted potential energy function for the large amplitude bending motion is shown in the center of Fig. 3. Also shown, by the round dots, are the *ab initio* potential energy values. The GSRB potential energy function includes the variation with ρ of the zero-point energy of all the small-amplitude vibrations and is not expected to be identical to the *ab initio* function.