# The ammonia dimer revisited

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# Ammonia dimer, a surprising structure

- MBER spectrum, $^{14}$N quadrupole splittings
  $\Rightarrow$ nearly cyclic structure

- Small dipole moment: 0.75 Debye ($NH_3$ monomer 1.47 D)

- *Ab initio* calculations had predicted a nearly linear N–H$\cdots$N hydrogen-bonded structure

- Equivalent H-bonded structures with donor/acceptor interchanged vibrational averaging ?

- Structure similar for $^{14}NH_3$-$^{14}NH_3$, $^{14}ND_3$-$^{14}ND_3$, $^{15}NH_3$-$^{14}NH_3$
  $\Rightarrow$ nearly rigid

# NH$_3$-NH$_3$
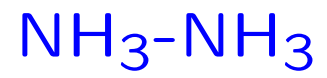
### Hydrogen-bonded structure
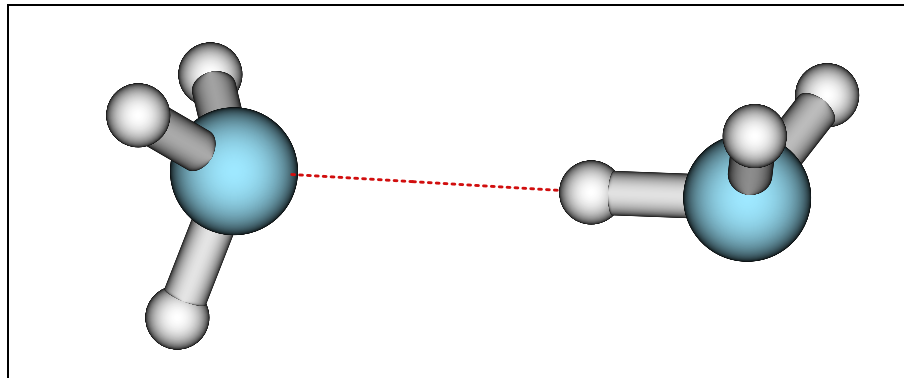


### Structure of Klemperer *et al.*
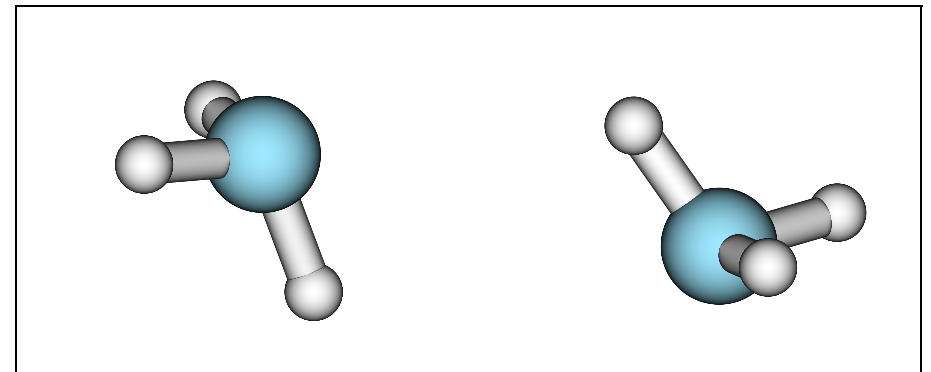
# Contradictory evidence

Havenith, Cohen, Busarow, Gwo, Lee, and Saykally

J. Chem. Phys. 94,4776 (1991)

Loeser, Schmuttenmaer, Cohen, Elrod, Steyert, Saykally, Bumgarner, and Blake

J. Chem. Phys. 97,4727 (1992)

- Large tunneling splittings observed in THz spectra
  $\Rightarrow$ $NH_3$-$NH_3$ must be floppy

## Our approach

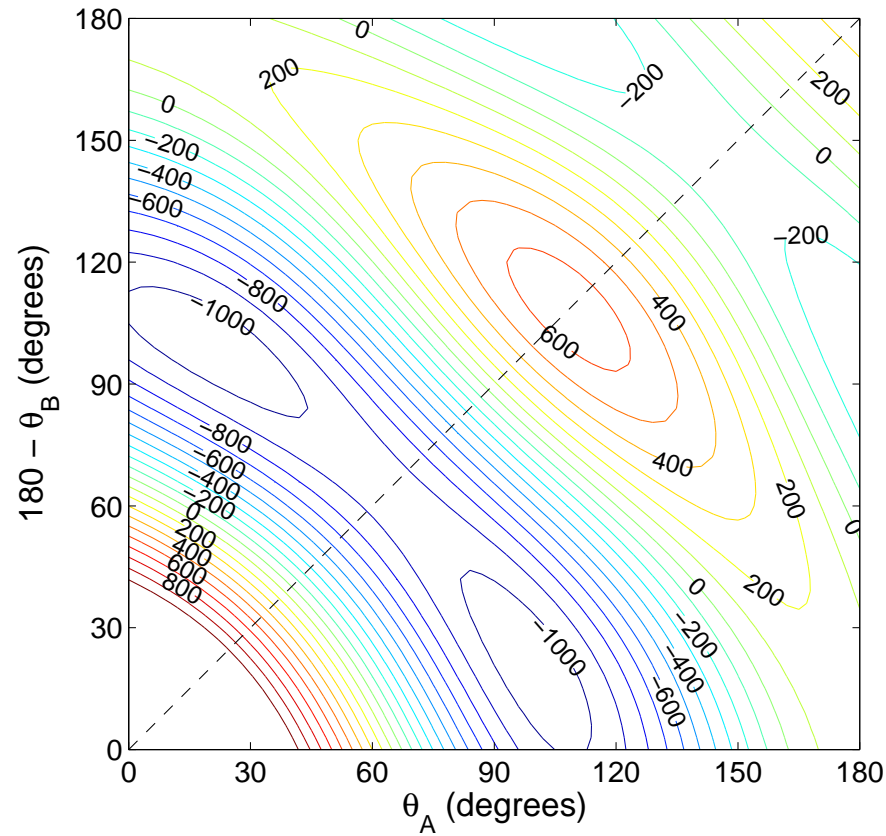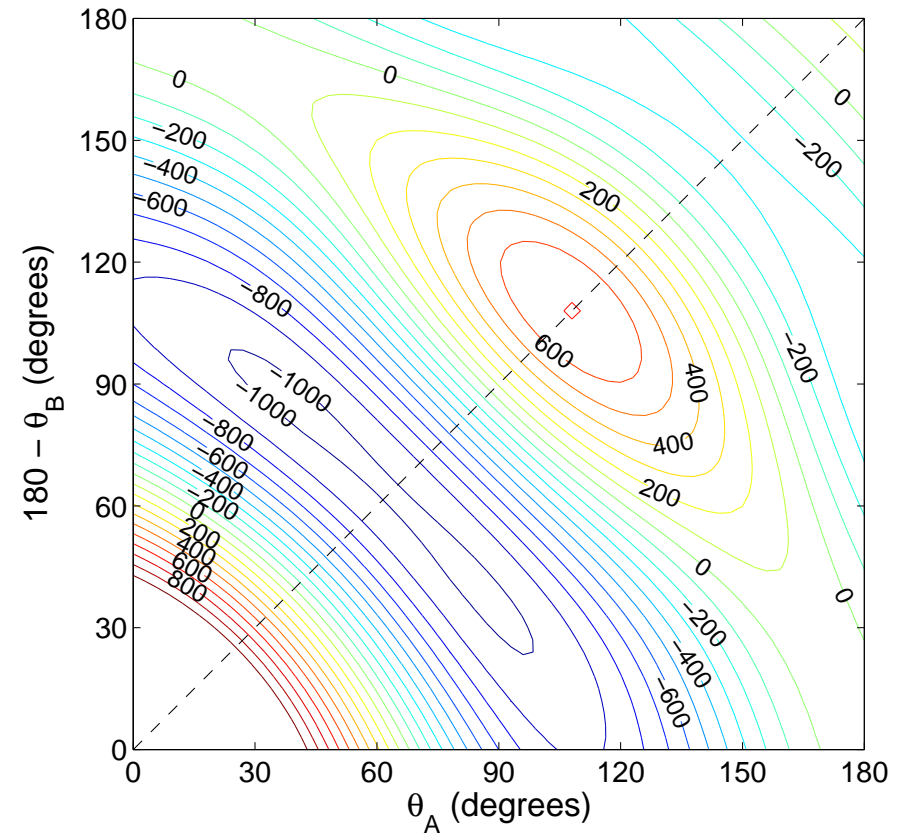| Global potential surface | $\Rightarrow$ | Dimer VRT levels | $\Rightarrow$ | Dimer spectrum |
|---|---|---|---|---|

Compare with high-resolution THz and microwave spectra

# Empirical model potential

Electrostatic interactions
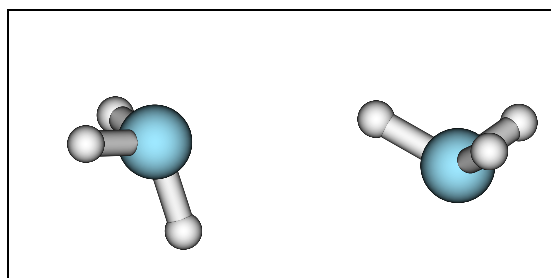favor H-bonded structures
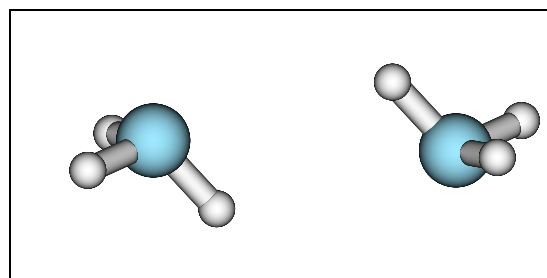
Dispersion and exchange
interactions added

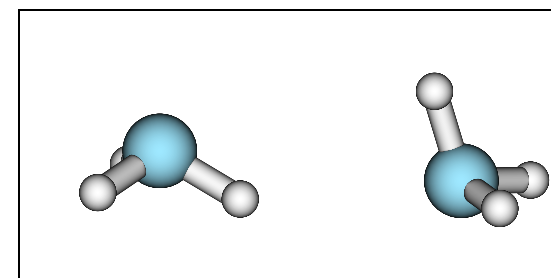# Donor-acceptor interchange pathway

minimum                saddle (cyclic)                minimum



Barrier $\approx 6$ cm$^{-1}$ (after fit to THz spectra)

# Calculation of VRT states

$$H = \left[Aj_{A_a}^2 + Bj_{A_b}^2 + Cj_{A_c}^2\right] + \left[Aj_{B_a}^2 + Bj_{B_b}^2 + Cj_{B_c}^2\right]$$
$$-\frac{\hbar^2}{2\mu_{AB}R}\frac{\partial^2}{\partial R^2}R + \frac{1}{2\mu_{AB}R^2}\left[J^2 + j_{AB}^2 - 2\boldsymbol{j}_{AB}\cdot\boldsymbol{J}\right] + V(R,\boldsymbol{\omega}_A,\boldsymbol{\omega}_B)$$

**Analytic basis**

$$\chi_n(R)\sum_{m_A m_B} D_{m_A k_A}^{(j_A)}(\boldsymbol{\omega}_A)^* D_{m_B k_B}^{(j_B)}(\boldsymbol{\omega}_B)^* \langle\, j_A m_A; j_B m_B \mid j_{AB} K \,\rangle D_{MK}^{(J)}(\alpha,\beta,0)^*$$
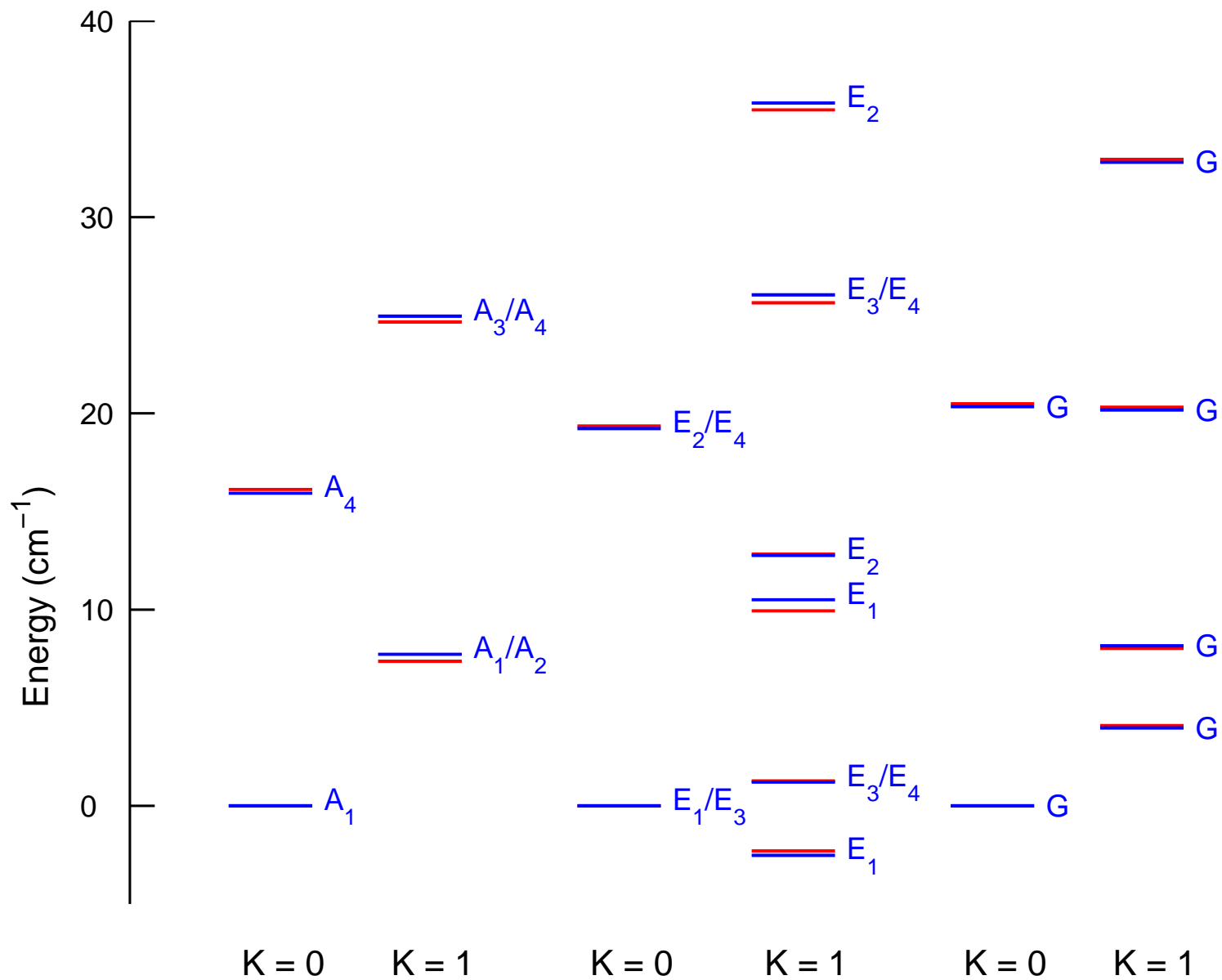
    contracted DVR for $\chi_n(R)$

**Basis adapted to irreps of PI group $G_{36}$**

## Permutation-inversion symmetry group $G_{36}$

| $G_{36}$ irrep | dim. | statistical weight $(NH_3)_2$ | $(ND_3)_2$ |
|---|---|---|---|
| $A_1$ | 1 | 66 | 561 |
| $A_2$ | 1 | 78 | 528 |
| $A_3$ | 1 | 66 | 561 |
| $A_4$ | 1 | 78 | 528 |
| $E_1$ | 2 | 36 | 576 |
| $E_2$ | 2 | 36 | 576 |
| $E_3$ | 2 | 30 | 600 |
| $E_4$ | 2 | 42 | 552 |
| $G$ | 4 | 144 | 1584 |

Calculated and measured energy levels ($J = 0, 1$)

# Wave functions of oNH$_3$-oNH$_3$ ($J = 0$)
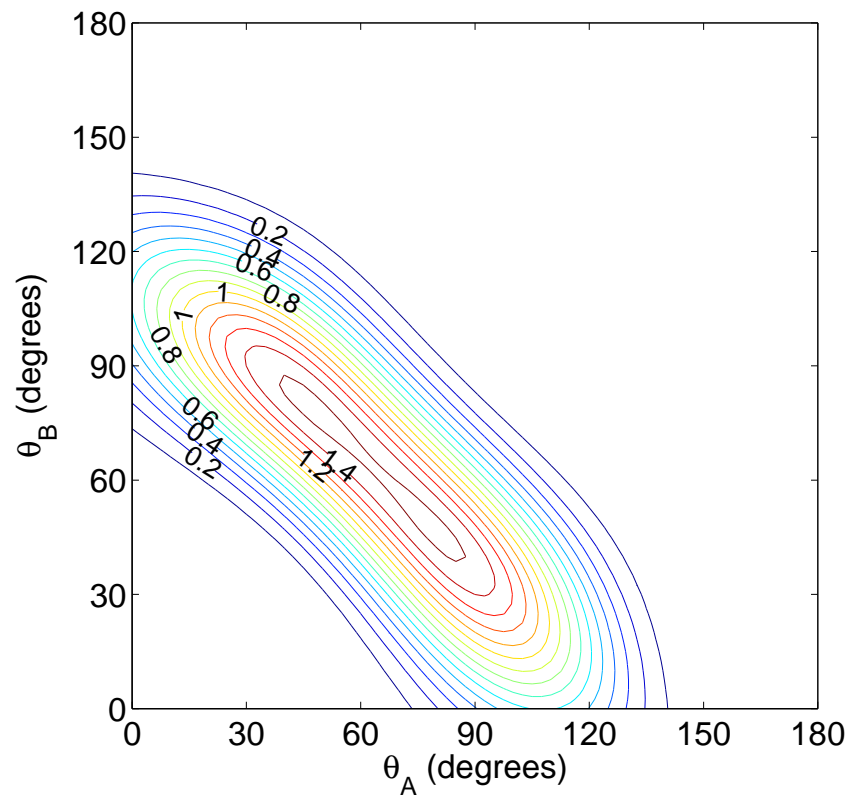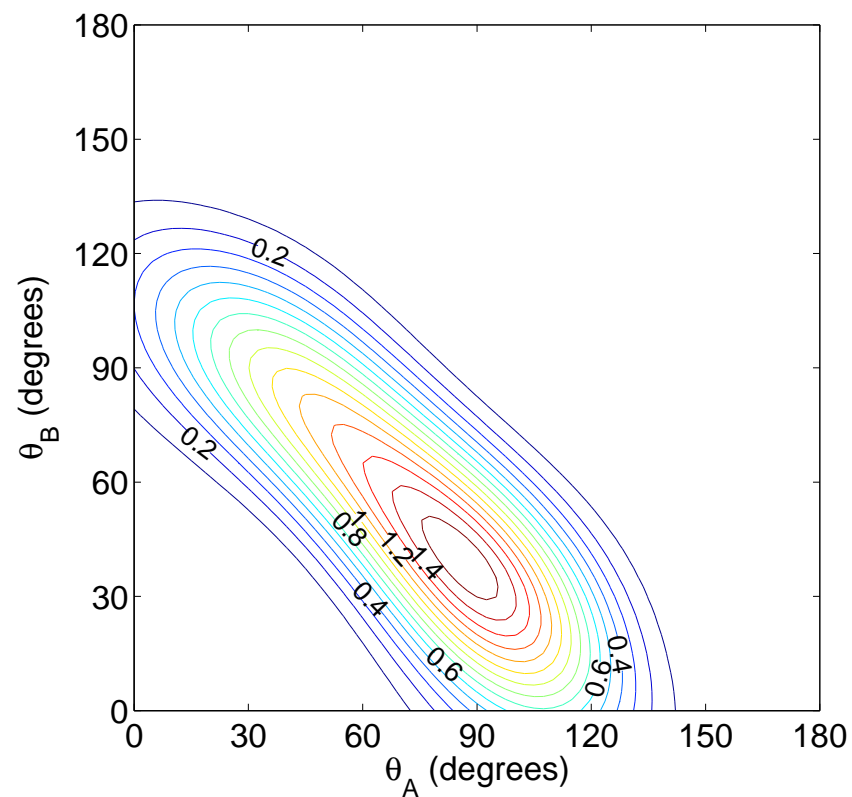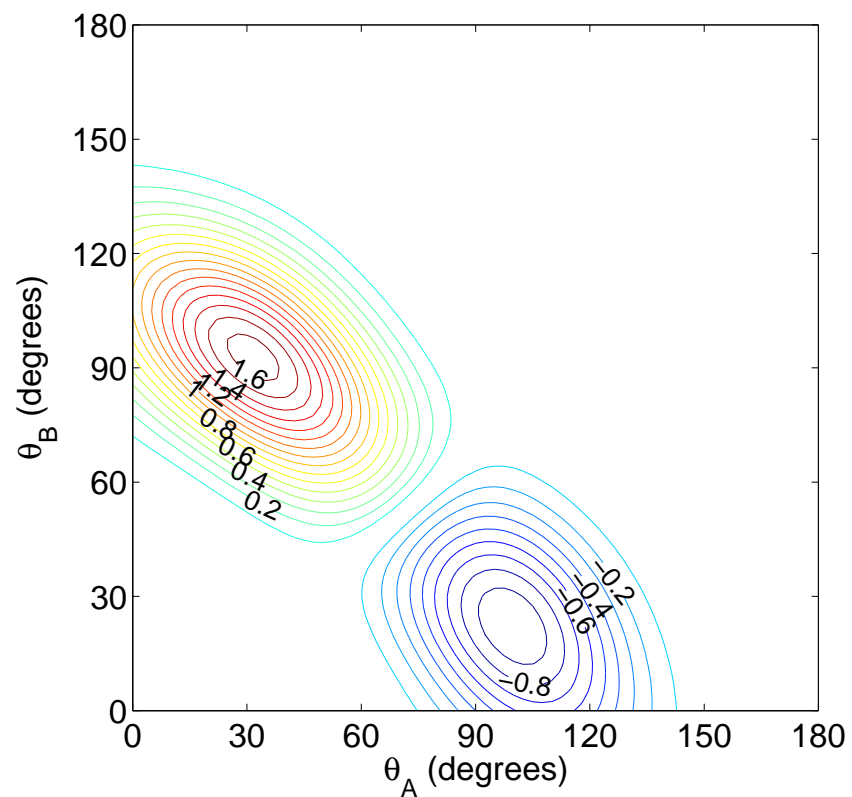


symmetry $A_1$ — symmetry $A_4$
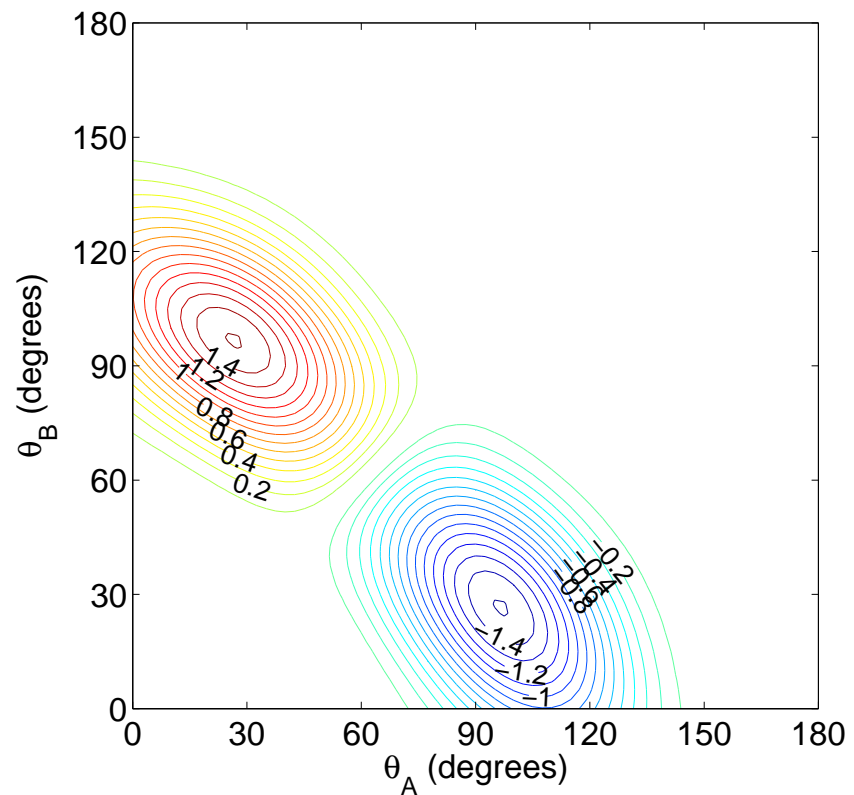
# Wave functions of pNH$_3$-oNH$_3$ ($J = 0$)

## symmetry $G$, lowest state



## symmetry $G$, second state

# Conclusions

- Good agreement with both MBER and THz spectra

- Dipole moment also agrees with experiment

- Ammonia dimer is very floppy

- Isotope substitution effects explained

## Large amplitude internal motions

Why does the vibrationally averaged structure not change by isotope substitution?

## Explanation

Only states of $G$ symmetry observed by Klemperer *et al.* mixed ortho $NH_3$ - para $NH_3$, non-zero dipole moment

### Two effects working in opposite direction

1. $ND_3$ orientations more localized in well region than $NH_3$
   $\Rightarrow$ larger dipole moment

2. ortho-para difference smaller for $ND_3$ than for $NH_3$
   $\Rightarrow$ more symmetric behavior of mixed ortho-para dimer
   $\Rightarrow$ smaller dipole moment

### Result: near cancelation of isotope effects on geometry

# Revisiting

- Accurate potential surface calculated *ab initio* by Richard Dawes

- CCSD(T)-F12b(AE)/VTZ-F12 method;
  more than 22 000 geometries for $R = 2.5 - 20$ A

- $D_0$ measured by Crim *et al.*: 660 ±20 cm$^{-1}$

*Ab initio*:

Minimum $-1111.9$ cm$^{-1}$ ($\theta_A = 43°$, $180° - \theta_B = 87°$)
($-1018$ cm$^{-1}$ in model potential, at nearly the same geometry)

Cyclic saddle point $-1107.5$ cm$^{-1}$ ($\theta_A = 180° - \theta_B = 67°$)

Interchange barrier: 4.4 cm$^{-1}$, very similar to model potential

## Current status:

- VRT levels calculated from fitted potential surface

- First results: $D_0 = 665$ cm$^{-1}$ (for oNH$_3$-oNH$_3$)
  experiment 660 $\pm 20$ cm$^{-1}$

- VRT level pattern OK, tunneling splittings too small

- Splittings depend very sensitively on the potential;
  role of NH$_3$ umbrella mode dependence?

- Global fit of the *ab initio* data to accurate site-site model
  cf. water dimer CCpol-8s potential, which produced accurate
  tunneling splittings and intermolecular vibrational frequencies

# Acknowledgement