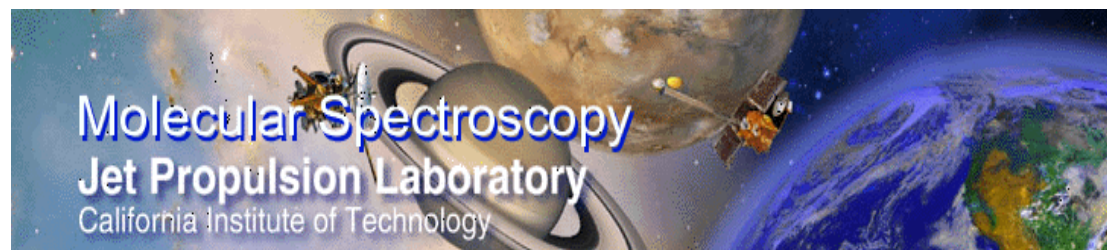


COUPLING OF LARGE AMPLITUDE INVERSION WITH OTHER STATES

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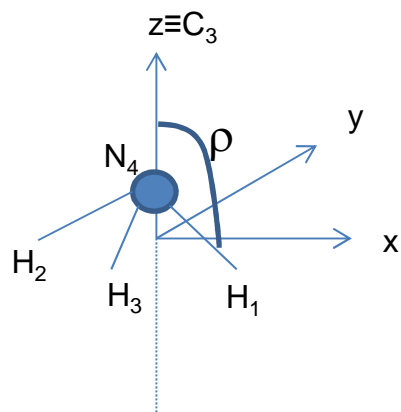


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Motivation

- A Hougen-Bunker-Johns effective Hamiltonian successfully modeled the ground and v_2 states of ammonia to High J
 - Intensities of forbidden $\Delta K=3$ lines remains problematic
- Attempts to model higher lying (but not isolated) states of ammonia did not achieve experimental accuracy
 - Intensities even more problematic (pathological?)
- Effective Hamiltonians of little use in excited ammonia
 - Latest Obs-Calc for intensity used an 8 order of magnitude log scale
- Inversion in C_s molecules is similar
- What is it about inversion that we don't understand?

Ammonia Hamiltonian Set up



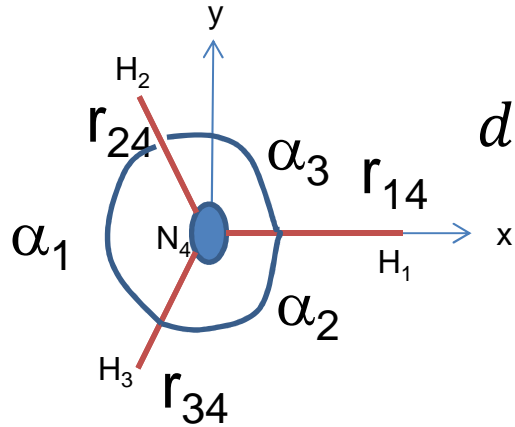
$a_i(\rho)$ Position vector of atom i

$\sum_i m_i a_i(\rho) = 0$ Origin at center of mass

$\sum_i m_i \left[a_i(\rho) \times \frac{da_i(\rho)}{d\rho} \right] = 0$

No reference angular momentum

- Four coordinates x, y, z and ρ
- Require C_3 symmetry at all times
- Everything is a function of ρ the inversion coordinate
- ρ is unique for each vibrational or inversion state
 - Path of inversion is unique



d_i Vibrational displacement vector relative to reference

Eckart and Sayvetz conditions

$$\sum_i m_i d_i = 0 \quad \sum_i m_i [a_i(\rho) \times d_i] = 0$$

$$\sum_i m_i \left[\frac{da_i(\rho)}{d\rho} \cdot d_i \right] = 0$$

- Eckart and Sayvetz conditions are a function of ρ
- Each state has a different internal axis associate with ρ

The Hamiltonian 1/2

$$H = H_{diag} + H_{nondiag}$$

Diagonal is with respect to inversion $\psi_i^s(\rho)$ or $\psi_i^a(\rho)$

$$H_{diag} = H_0 + H_2 + H_{4d} + H_{6d} + \dots$$

$$H_0 = E_i \quad \text{Solution of inversion problem}$$

$$H_2 = B(\rho)J^3 + (C(\rho) - B(\rho))J_z^2$$

$$H_{4d} = -D_J(\rho)(J^2)^2 - D_{JK}(\rho)J^2J_z^2 - D_K(\rho)J_z^4$$

$$H_{6d} = H_J(\rho)(J^2)^3J_z + H_{JK}(\rho)(J^2)^2J_z^2 + H_{KJ}(\rho)J^2J_z^4 \\ + H_K(\rho)J_z^6 + \eta_3(\rho)(J_+^6 + J_-^6)$$

Note constants are different for a and s inversion states

$$H_{nondiag} = H_3 + H_{4nd} + H_5 + H_{6nd} + \dots$$

$$H_3 = i\beta(\rho)(J_+^3 - J_-^3)$$

$$H_{4nd} = \alpha(\rho)[J_+^3 + J_-^3, J_z]_+$$

$$H_5 = i\beta_J(\rho)J^2(J_+^3 - J_-^3) + i\beta_K(\rho)[J_z^2, J_+^3 - J_-^3]_+$$

$$H_{6nd} = \alpha_J(\rho)J^2[J_+^3 + J_-^3, J_z]_+ + \alpha_K(\rho)[J_+^3 + J_-^3, J_z^3]$$

Where $[A, B]_+ = AB + BA$

Ground state and v_2 were solved with $H_3=H_5=0$

Can be solved with $H_{4nd}=H_{6nd}=0$ just as well

One set for each s and a pair

Can make a unitary Transform of the form:

$$\tilde{H} = e^{-iS} H e^{iS}$$

Can define the following

$$S_3 + S_5 = i s_3 [J_+^3 - J_-^3] + i s_{5J} J^2 [J_+^3 - J_-^3] + i s_{5K} [J_+^3 - J_-^3, J_z^2]$$

$$S_4 + S_6 = s_4 [J_+^3 + J_-^3, J_z] + s_{6J} J^2 [J_+^3 + J_-^3, J_z] + s_{6K} [J_+^3 + J_-^3, J_z^3]$$

Where

$$S = S_3 + S_4 + S_5 + S_6$$

$s_3, s_{5J}, s_{5K}, s_4, s_{6J}, s_{6K}$ are chosen according to Watson

The transformed Hamiltonian

$$\tilde{H}_0 = H_0$$

$$\tilde{H}_2 = H_2$$

$$\tilde{H}_3 = H_3 + i[H_0, S_3]_\rho$$

$$\tilde{H}_4 = H_4 + i[H_2, S_3]_R + i[H_0, S_4]_\rho$$

Where H and S are both products for rotation R and inversion ρ

$$H = \cdots + H_\rho(\rho)H_R(R) + \cdots$$

$$S = \cdots + S_\rho(\rho)S_R(R) + \cdots$$

Can choose S_3 or S_4 to make either \tilde{H}_3 or \tilde{H}_4 vanish

If the orders of magnitude of the terms satisfy “smallness”

Ground and ν_2

- Ground and ν_2 fit with $\tilde{H}_3=0$
 - Transformations are different in ground and ν_2
 - Form of transformation: $S_3 + S_5 = i s_3 [J_+^3 - J_-^3] + i s_{5J} J^2 [J_+^3 - J_-^3] + i s_{5K} [J_+^3 - J_-^3, J_Z^2]$ which is $\Delta K=3$
 - Transform scrambles the meaning of “K” in ground state relative to ν_2 results in $\Delta K=3, 6, 9$ contributions
 - Transformed dipoles moment are now needed
- Contact transformation depends on ρ in each state
- Two choices to get intensities right:
 - Transform dipoles or
 - Solve in a common ρ -axis

Other States

- GS and ν_2 do fit but $\Delta K=3$ intensities are poor
- $2\nu_2/\nu_4$ and higher
 - States are no longer isolated
 - Magnitude of inversion very different (path of atoms different)
 - One set of transformations cannot remove H_3 and H_5 in all states
 - “smallness” will be violated in one or more states
 - Fits poor with parameters in H_3 and H_5 set to zero
 - Intensities are worse than fits
- At a minimum one ρ -axis can be defined so that the others are relative. I.e. must fit the H_3 and H_5 terms
- Care must be taken in vibrational bands to use the same axis system or transform the dipoles accordingly

What about other inversions?

Inversion in alcohols and thiols with C_s symmetry is very similar:

$$H = H_{diag} + H_{nondiag}$$

Diagonal is with respect to inversion $\psi_i^s(\rho)$ or $\psi_i^a(\rho)$

$$H_{diag} = H_0 + H_2 + H_{4d} + H_{6d} + \dots$$

$H_0 = E_i$ Solution of inversion problem

$H_2 + H_{4d} + H_{6d} + \dots$ Usual Watson Asymmetric Top but each parameter is a function of the inversion, different in each a or s

Inversion C_s

$$H_{nondiag} = H_1 + H_{2nd} + \dots$$

$$H_1 = F_a(\rho)iJ_z + F_b(\rho)i(J_+ - J_-)$$

$$H_{2nd} = D_{bc}(\rho)(J_+^2 - J_-^2) + D_{ac}(\rho)[J_z, J_+ + J_-]$$

Where the ab-plane is the plane of symmetry

Once again we can make a unitary transformation

$$\tilde{H} = e^{-iS} H e^{iS}$$

To get rid of either H_1 or H_{2nd}

This is the Hamiltonian of Pickett, JCP 56, 1715, 1972.

However, like ammonia this transformation is a function of the inversion path and also affects the dipole

- The C_S inversion state is not isolated if
 - There is a third state i.e. non-threefold internal rotation
 - There is an interacting vibrational state
- Both cases define a relative internal coordinate
 - Dipoles determined in either $H_1=0$ or $H_{2nd}=0$ will be wrong by the “rotation” applied
 - Choices must be made about what part of problem should be solved off diagonal. Easy to end up with both H_1 and H_{2nd}
- Care must be taken to get intensities right in different isolated vibrational states since ρ -axis is different for each

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- The ρ -axis of the inversion problem in the Hougen-Bunker-Johns formalism is unique to each vibrational state (large or small amplitude)
 - Effective Hamiltonians used to model more than one a & s inversion state pair must account for the ρ -axis differences
 - How to choose a reference ρ -axis is not obvious
 - Both the odd (antisymmetric imaginary) and even (symmetric real) off-diagonal in inversion terms will be required. Within each state and where applicable between each state



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