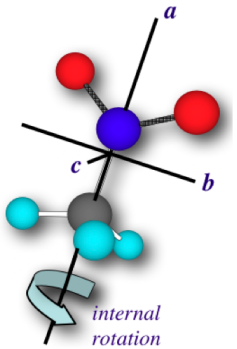
Analysis of the ν_6 Asymmetric NO Stretch Band of Nitromethane

Mahesh B. Dawadi, Lou Degliumberto, David S. Perry,
Howard Mettee, and Robert L. Sams

The University of Akron
Youngstown State University *Pacific Northwest National Laboratory*

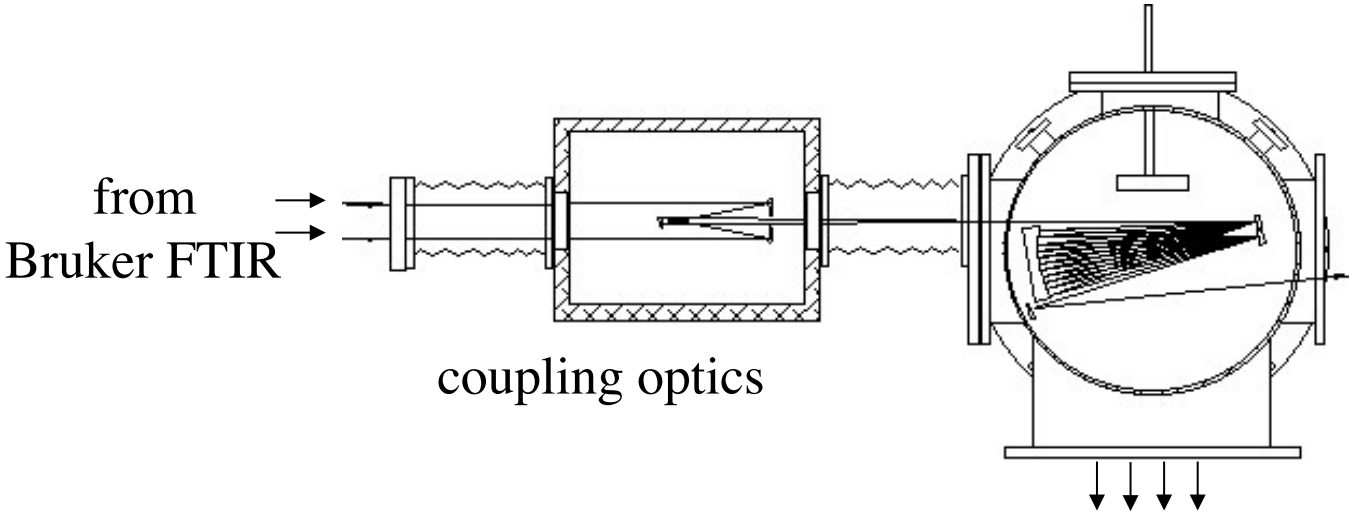


Slit-Jet FTIR Spectroscopy

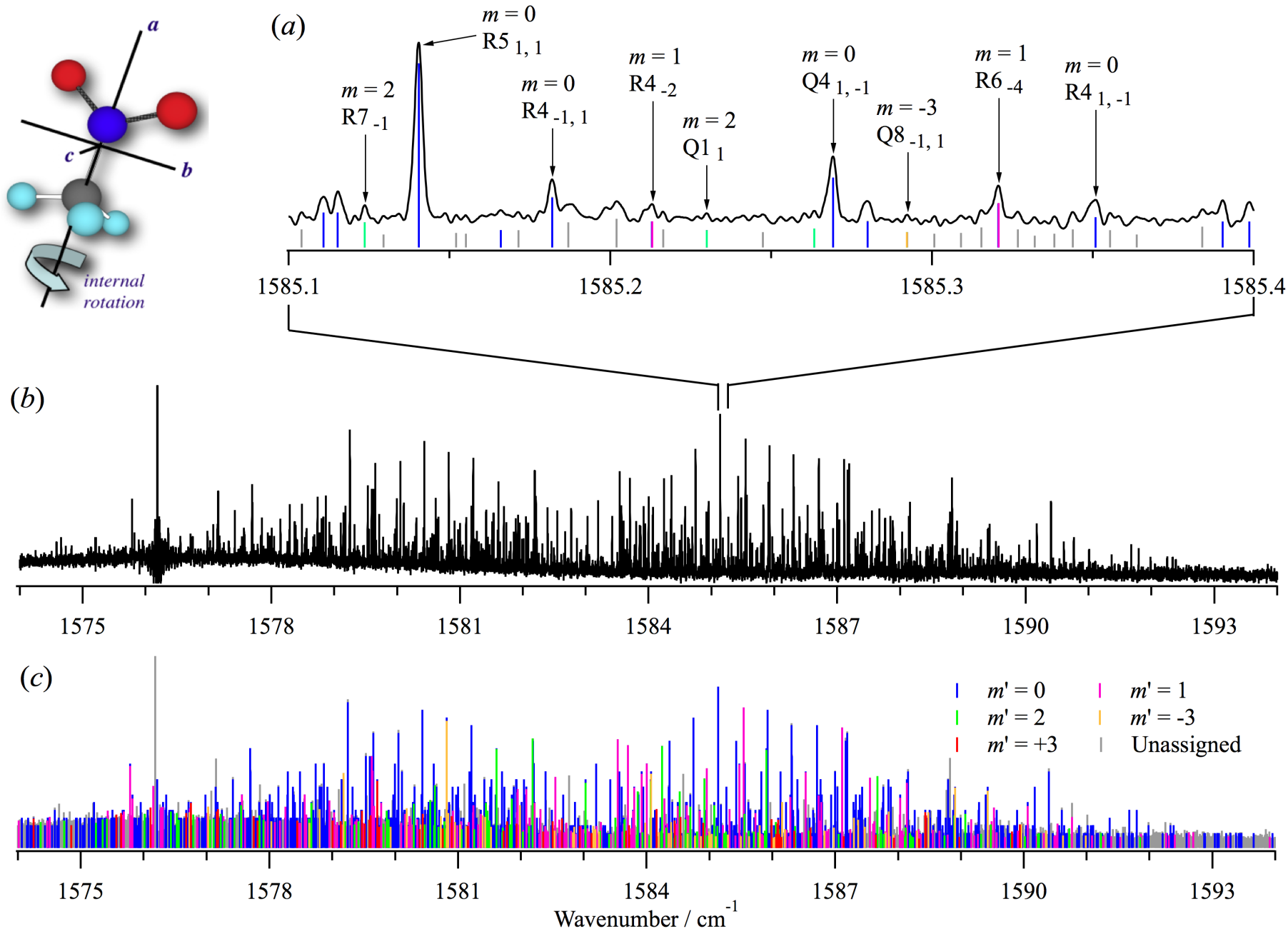
Bob Sams

Instrumental Resolution: 0.0025 cm-1
Cooling to 10 – 35 K

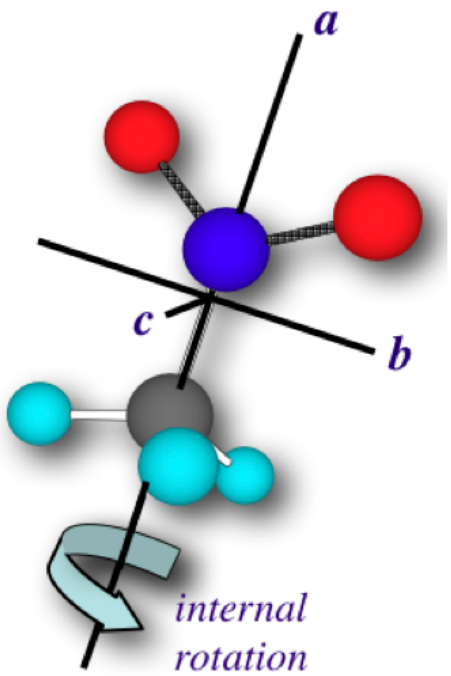
CW slit nozzle



Environmental Molecular Science Laboratory
Pacific Northwest National Laboratory, Richland, WA


a
b
c
internal
rotation
(a)
m = 0
R5 1, 1
m = 2
R7 -1
m = 0
R4 -1, 1
m = 1
R4 -2
m = 2
Q1 1
m = 0
Q4 1, -1
m = -3
Q8 -1, 1
m = 1
R6 -4
m = 0
R4 1, -1
1585.1
1585.2
1585.3
1585.4
(b)
1575
1578
1581
1584
1587
1590
1593
(c)
m' = 0
m' = 1
m' = 2
m' = -3
m' = +3
Unassigned
1575
1578
1581
1584
1587
1590
1593
Wavenumber / cm-1

Nitromethane Asymmetric NO Stretch Band



- Strongly asymmetric rotor

  $\kappa = +0.25$
- Nearly free internal rotation

  $V_6 = 1.049\ \text{cm}^{-1}$

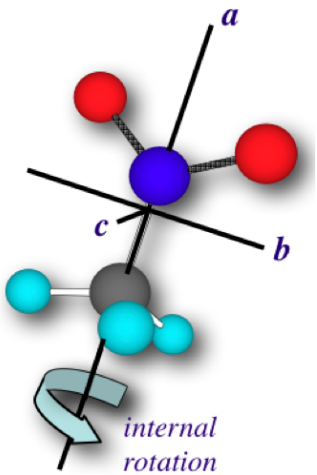
  m is pretty good quantum number
- Only even or odd mK_a due to oxygen atoms
- $\Delta J = 0, \pm 1$; $\Delta K_a = odd$; $\Delta K_c = odd$; $\Delta m = 0$
- Ground state term values thanks to

  G. O. Sorensen

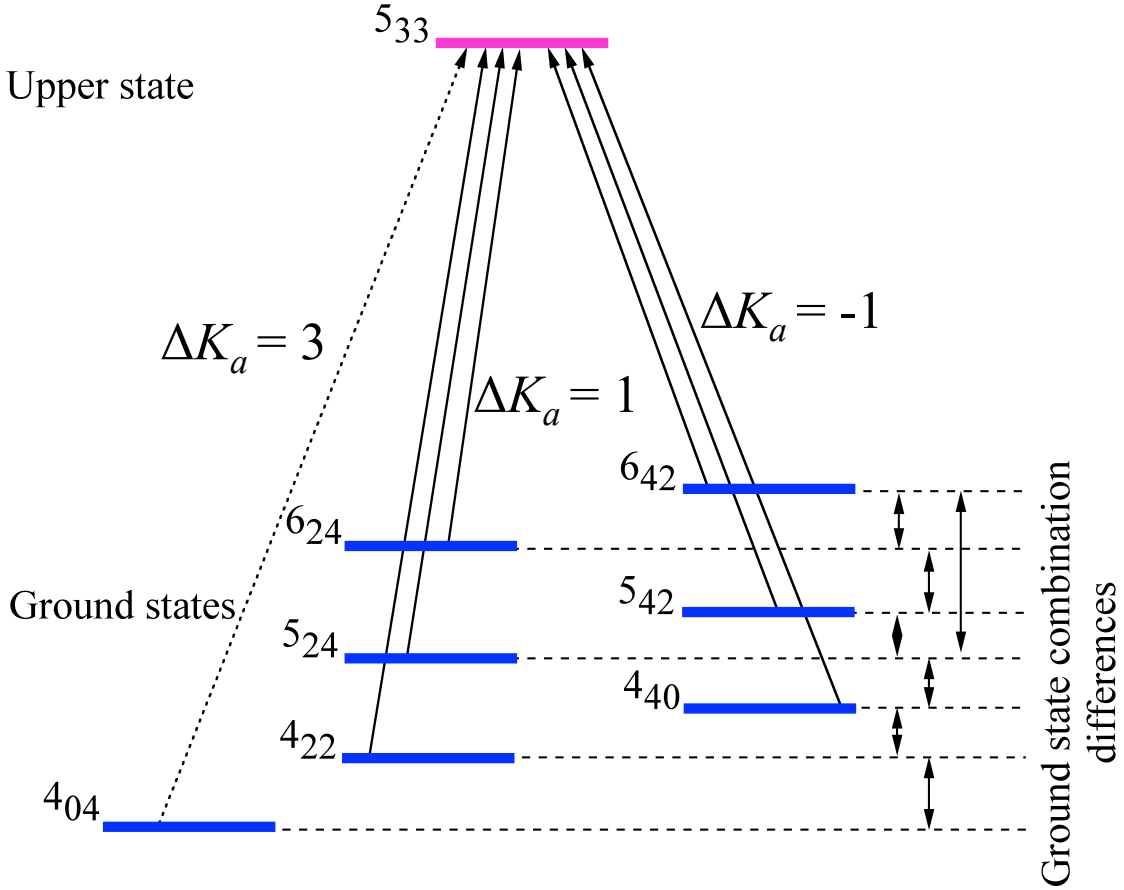
  V. Ilyushin

Lou Degliumberto

Assignments by Ground State Combination Differences



Automated search

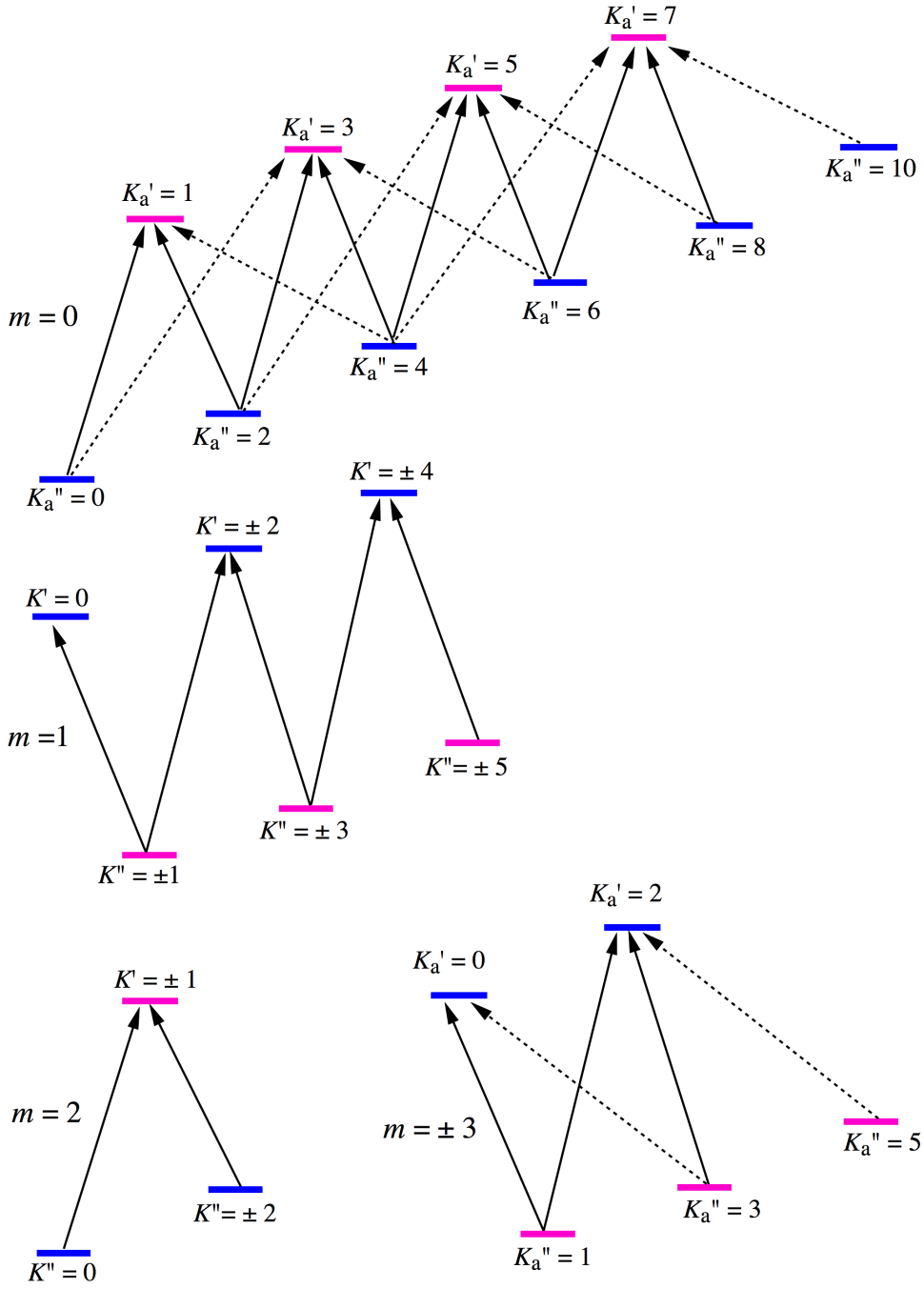


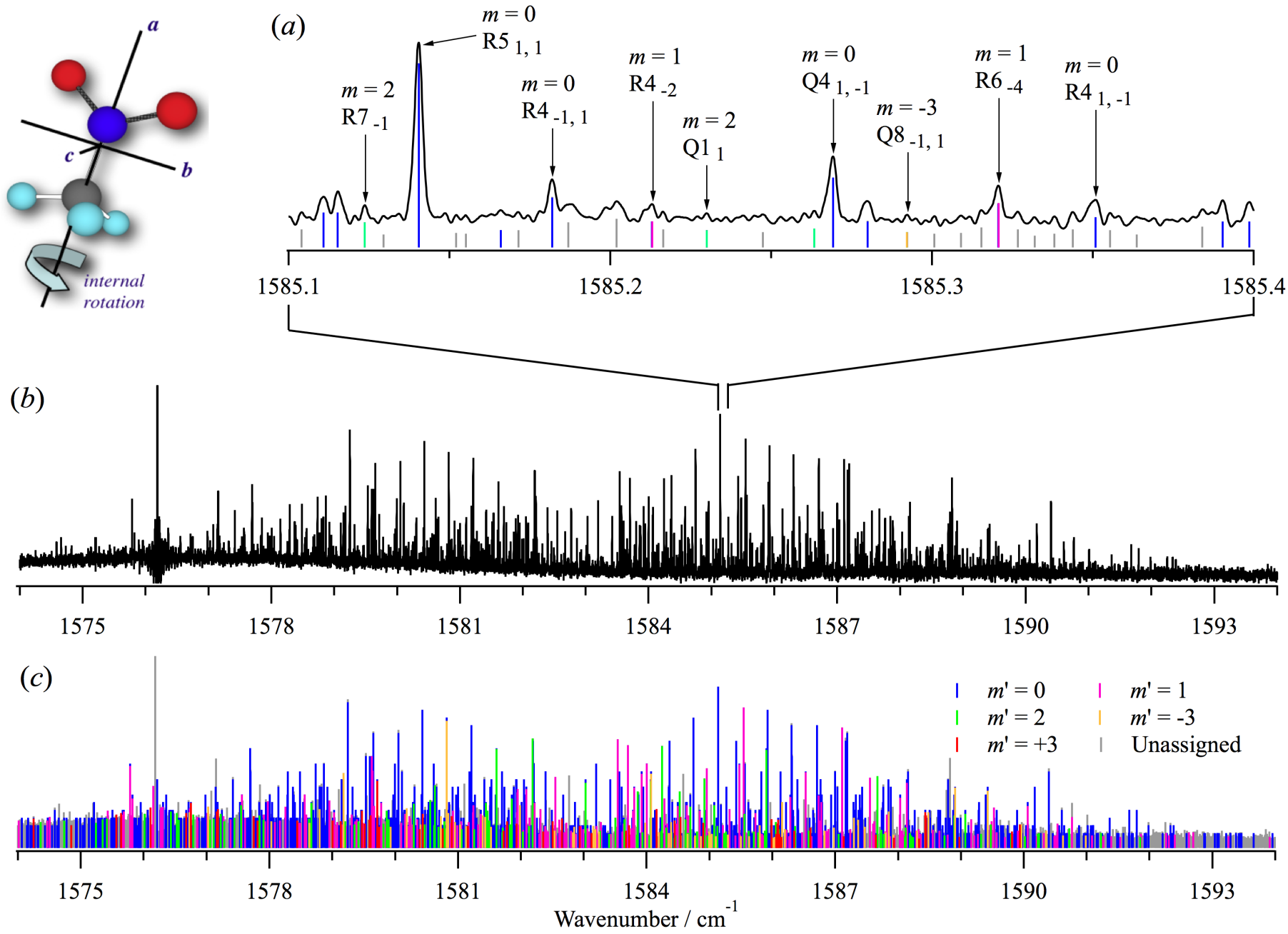
Lou Degliumberto

Mahesh Dawadi

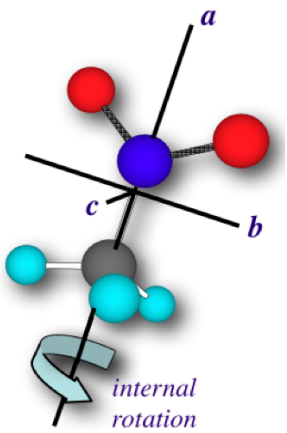
Assigned Subbands

- Confirmed by precise fit of the GSCDs.
- No agreement with previous assignments:
  C. Pal, A. Hazra, P.N. Ghosh, J. Mol. Struct. 407 (1997) 165.




a
b
c
internal
rotation
(a)
m = 0
R5 1, 1
m = 2
R7 -1
m = 0
R4 -1, 1
m = 1
R4 -2
m = 2
Q1 1
m = 0
Q4 1, -1
m = -3
Q8 -1, 1
m = 1
R6 -4
m = 0
R4 1, -1
1585.1
1585.2
1585.3
1585.4
(b)
1575
1578
1581
1584
1587
1590
1593
(c)
m' = 0
m' = 1
m' = 2
m' = -3
m' = +3
Unassigned
1575
1578
1581
1584
1587
1590
1593
Wavenumber / cm-1

Derived Constants



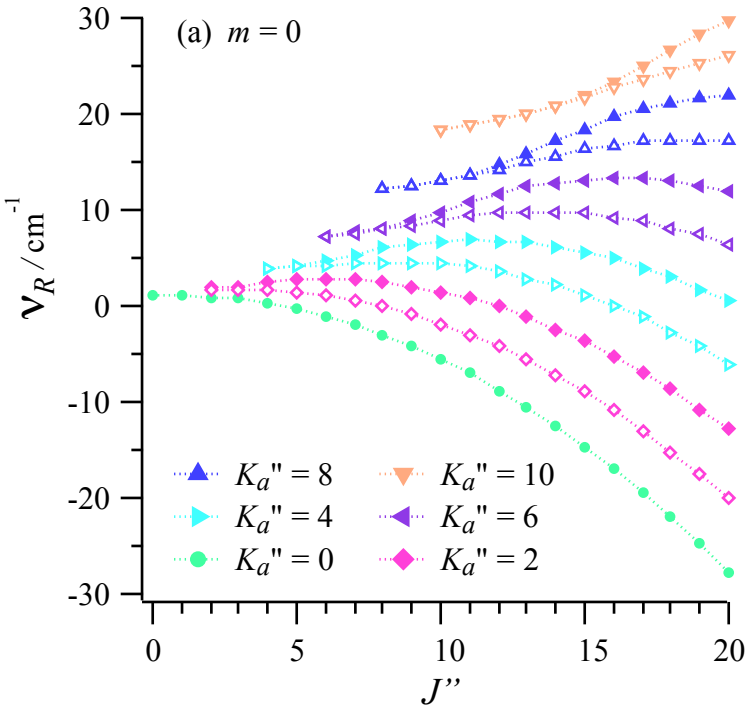
Partial list of nitromethane constants obtained with the RAM36 Program[a]

Operator	Parameter	Ground state cm^{-1}	Excited state cm^{-1}
$(\frac{1}{2})(1+\cos 6\alpha)$	V_6	1.04874(77)	---------
P_a^2	$A_{eff}-(\frac{1}{2})(B+C)$	0.17115(41)	0.17146(57)
P^2	$(\frac{1}{2})(B+C)$	0.273856(14)	0.27666(47)
$P_b^2-P_c^2$	$(\frac{1}{2})(B-C)$	0.077879(13)	0.07703(28)
P_α^2	F	5.56139 (37)	---------
$P_\alpha P_a$	$-2\rho F$	-0.885994 (17)	---------
$-P^4$	Δ_J	$1.859(85)\times 10^{-7}$	$3.10(50)\times 10^{-5}$
$-P^2P_a^2$	Δ_{JK}	$1.30(16)\times 10^{-7}$	$-3.29(13)\times 10^{-5}$
$-P_a^4$	Δ_K	$1.48(35)\times 10^{-7}$	$1.63\ (19)\times 10^{-4}$
$-P^2(P_b^2-P_c^2)$	δ_J	$7.42(37)\times 10^{-7}$	$-2.6(24)\times 10^{-6}$
$-\{P_a^2,(P_b^2-P_c^2)\}$	δ_K	$3.57(10)\times 10^{-7}$	$1.8(07)\times 10^{-6}$
No. of GSCD or USCD		1664	97
RMS deviation		0.00059 cm^{-1}	0.0115 cm^{-1}
m		$0 \le m \le 3$	$m = 0$
J		$0 \le J'' \le 20$	$1 \le J' \le 10$
K_a		0,2,4,6,8,10	1,3,5,7

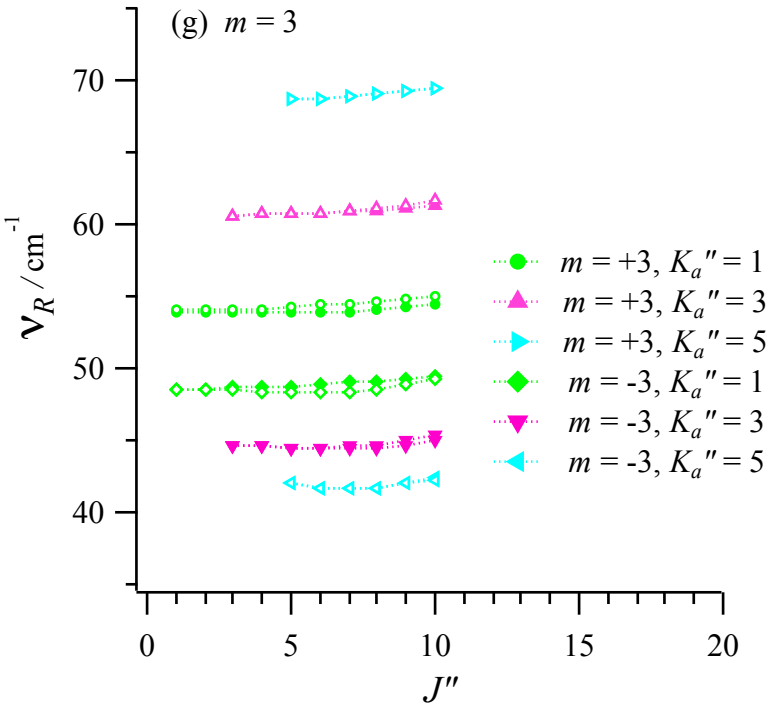
[a] V.V. Ilyushin, Z. Kisiel, L. Pszczokowski, H. Maeder, J.T. Hougen, J. Mol. Spectrosc. 259 (2010) 26.

Ground State Reduced Energies

$m = 0$
Asymmetric rotor limit

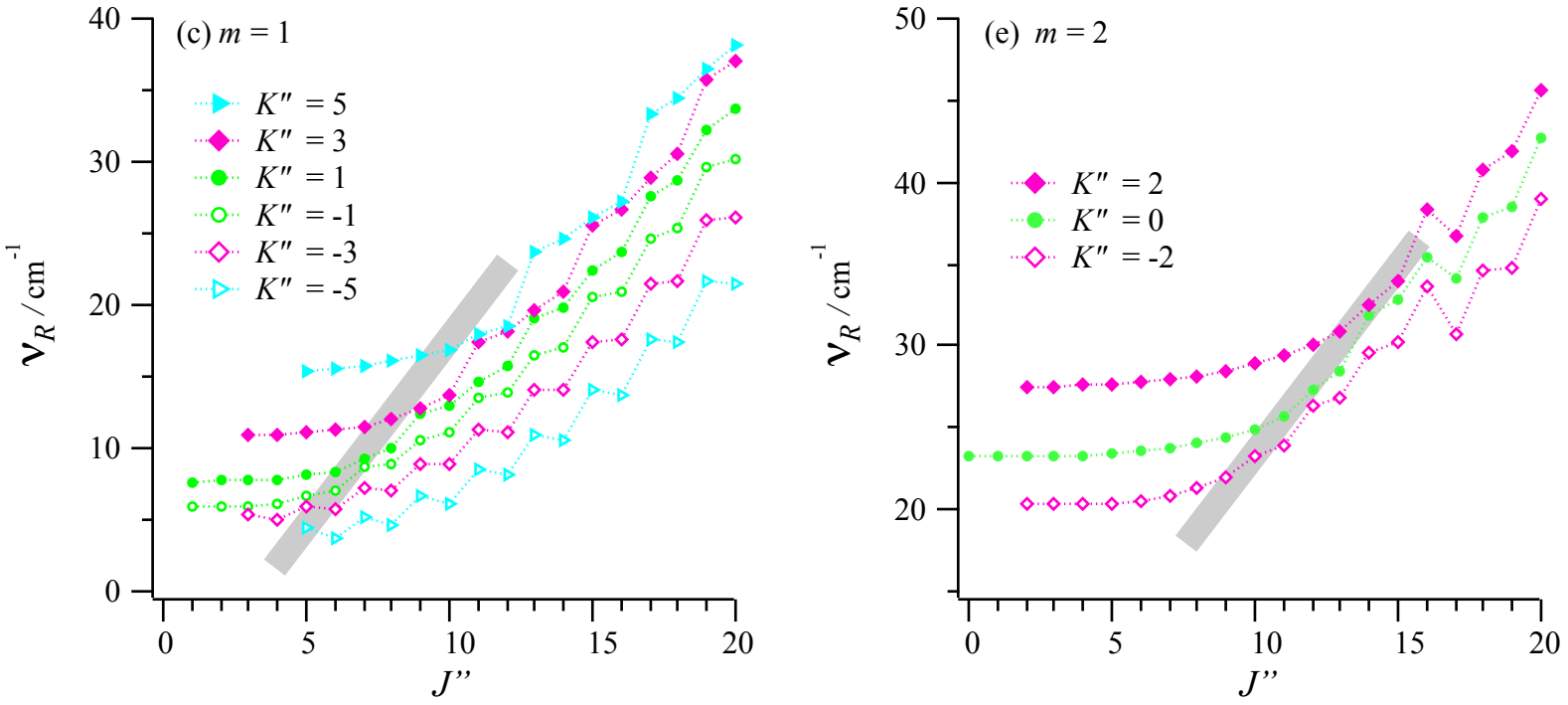


$m = \pm 3$
Angular momentum coupled limit



Ground State Reduced Energies

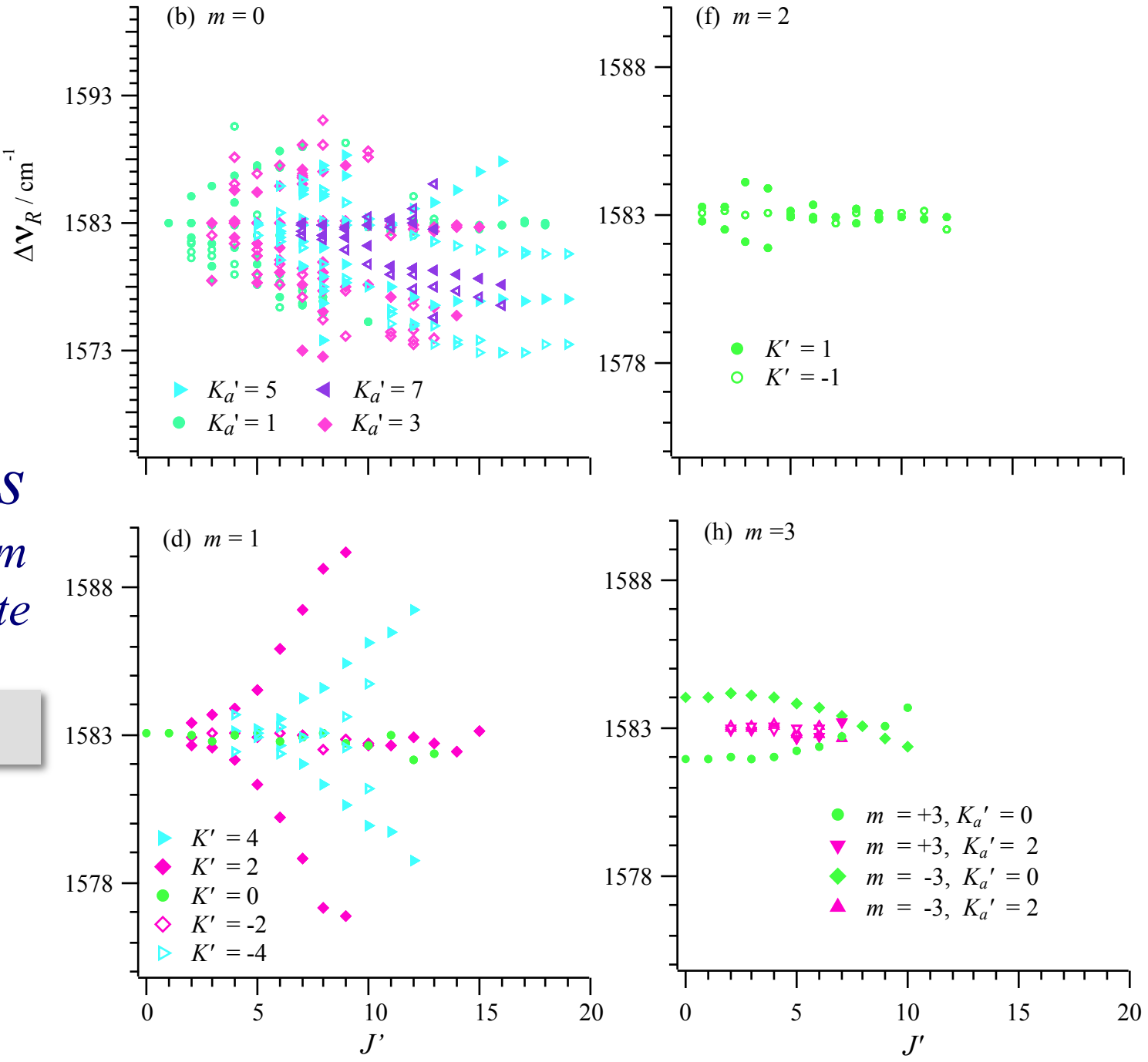
$m = 1$ $m = 2$

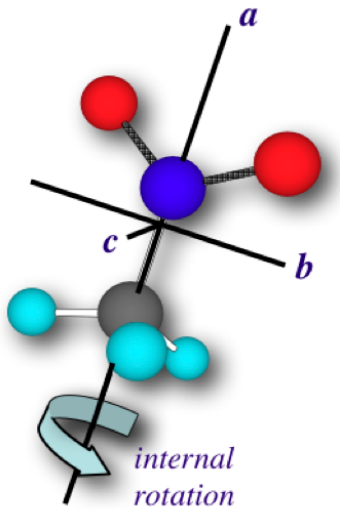


Present *K*-labeling according to: G.O. Soerensen, T. Pedersen, Stud. Phys. Theor. Chem. 23 (1983) 219-236.
"A new scheme of *K*-labeling for torsion–rotation energy levels in low-barrier molecules", V. Ilyushin, J. Mol. Spectrosc. 227 (2004) 140-150.

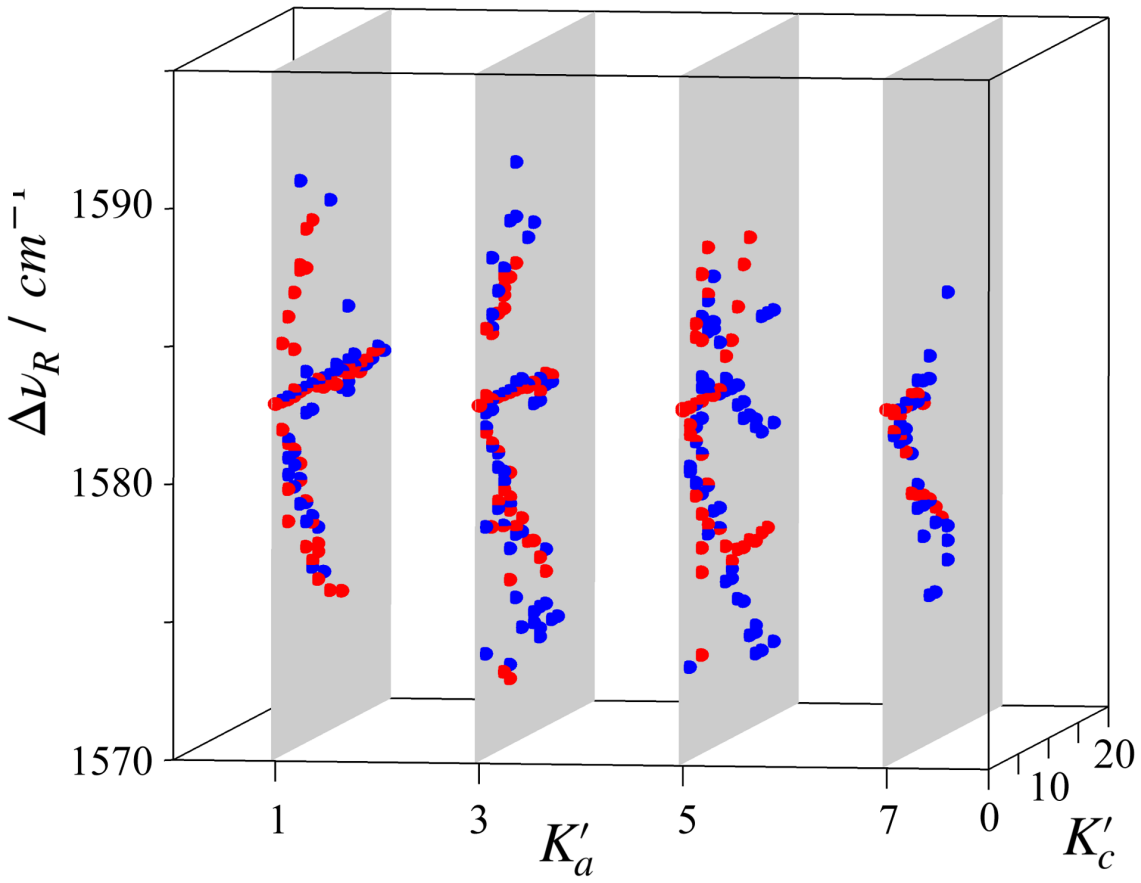
Upper State Energies

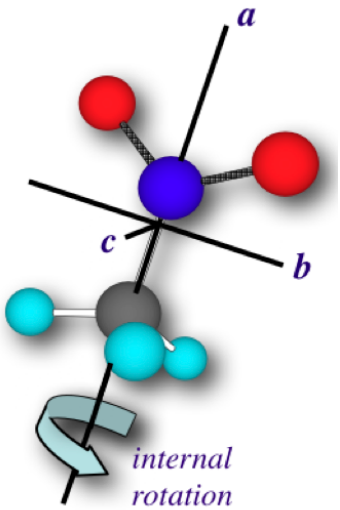
Change from Ground State





Upper State m = 0





Conclusions

Nitromethane Asymmetric NO stretch

- Assignments for the lowest 4 torsional states.
- Confirmed by precise fit of the GSCDs.
- Purely torsional structure is almost identical to the ground state.
- Rotational structure is complicated with multiple perturbations, especially at $m = 0$.
- Fit of USCDs for selected $m = 0$ levels only.