

The molecular structure of phenetole studied by spectroscopy and quantum chemical calculations

LAM Nguyen

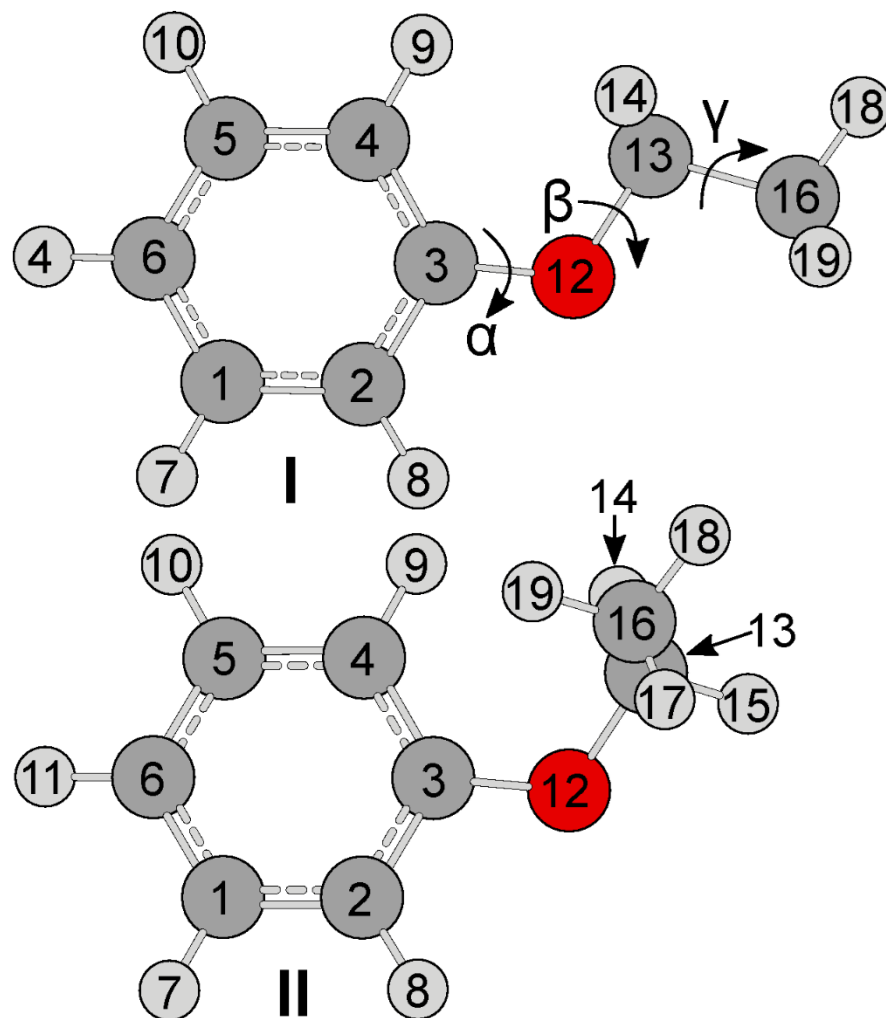
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Institute of Physical Chemistry, RWTH Aachen University

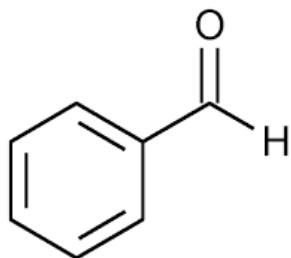
Phenetole

- $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$
- Ethyl phenyl ether or ethoxybenzene
- Colorless liquid with typical aromatic smell
- The conformational landscape is completely determined by the orientations of the phenyl ring and the ethyl group.

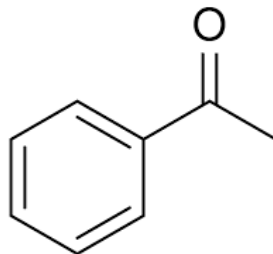


Phenetole

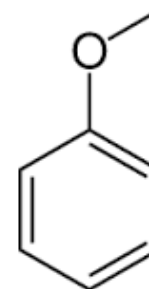
in-plane phenyl ring



benzaldehyde, O.
Desyatnyk *et al.*
PCCP **7**, 1708 (2005).

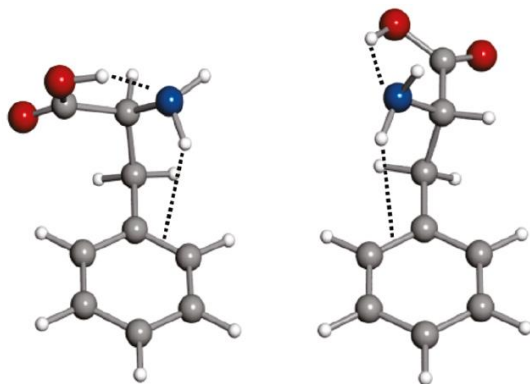


acetophenone, M.
Onda *et al.* J. Mol.
Struct. **442**, 19 (1998).

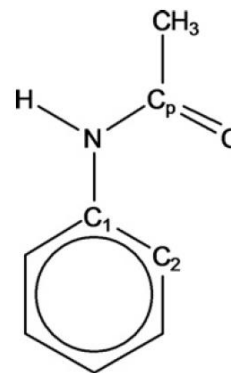


anisole, B. Reinhold *et al.* J. Mol. Spectrosc.
270, 89 (2011).

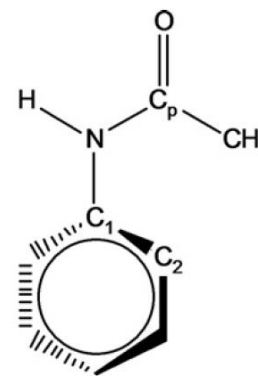
out-of-plane phenyl ring



phenylalanine, C. Pérez *et al.* J.
Phys. Chem. A **115**, 9653 (2011).



TRANS

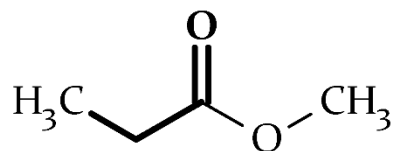


CIS

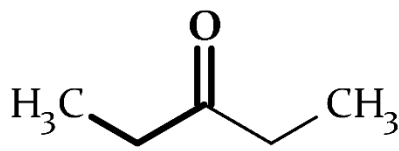
acetanilide, C. Cabezas *et al.* J.
Mol. Spectrosc. **268**, 42 (2011).

Phenetole

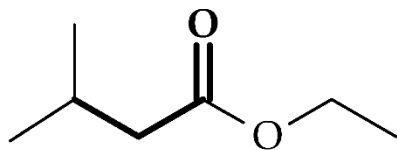
in-plane ethyl group



methyl propionate

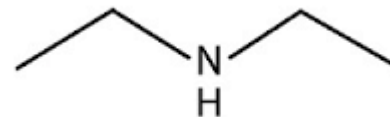


diethyl ketone



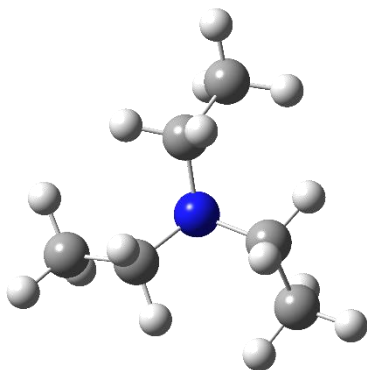
ethyl isovalerate

Nguyen *et al.* Mol.
Phys. **17**, 2035 (2012).

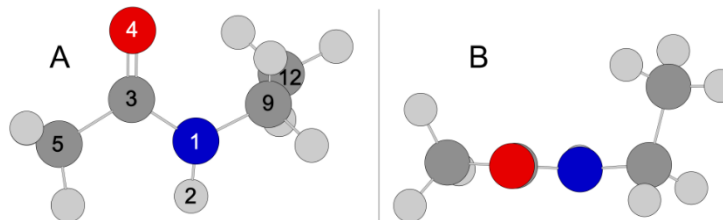


diethyl amine Nguyen *et al.*
JCP **135**, 024310 (2011).

out-of-plane ethyl group

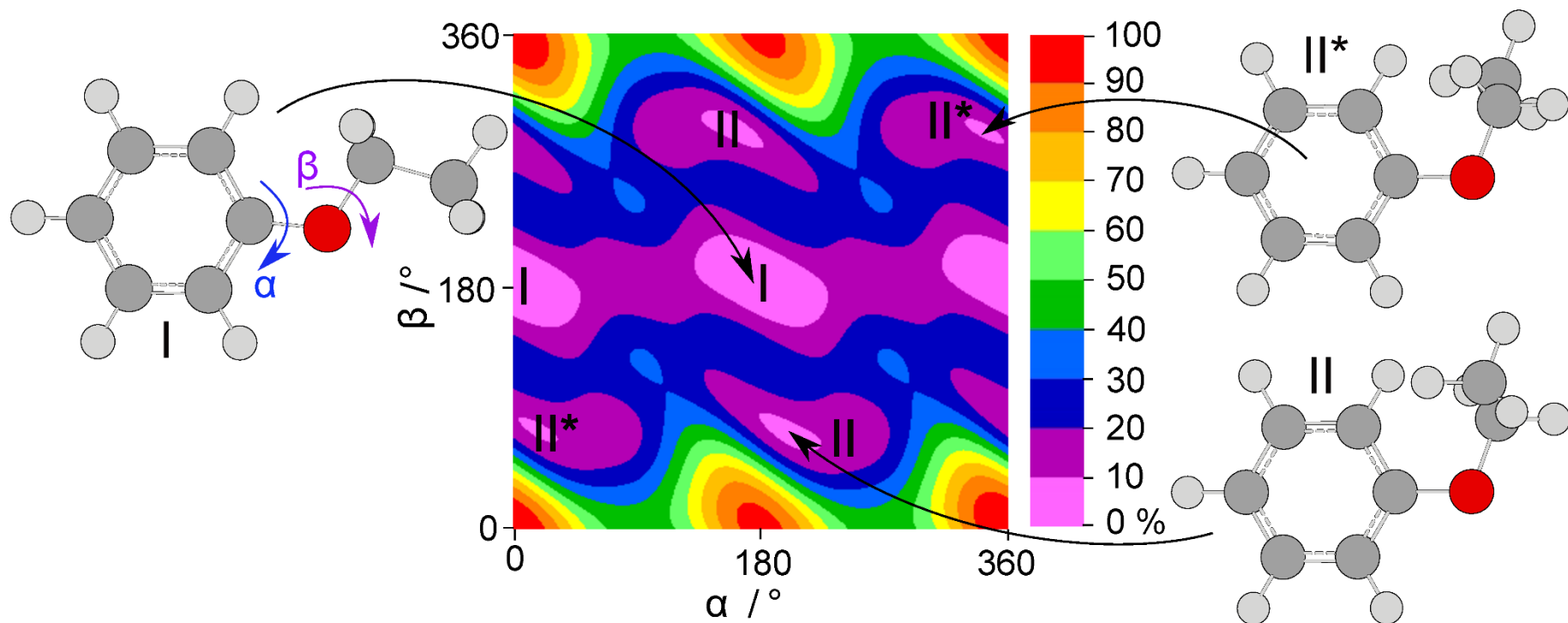


triethylamine, R. Kannengießer
et al. PCCP **14**, 11753 (2012).



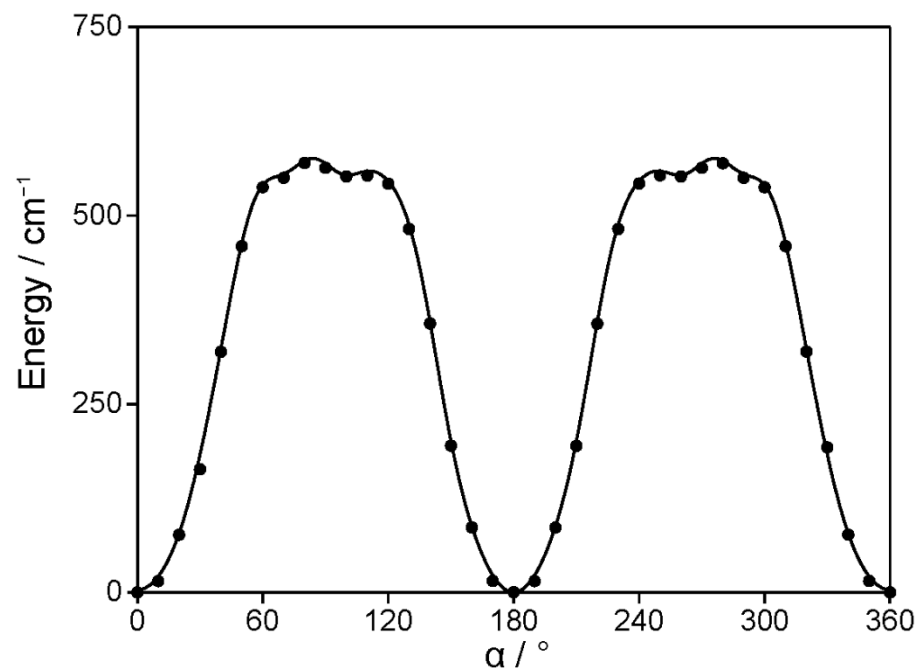
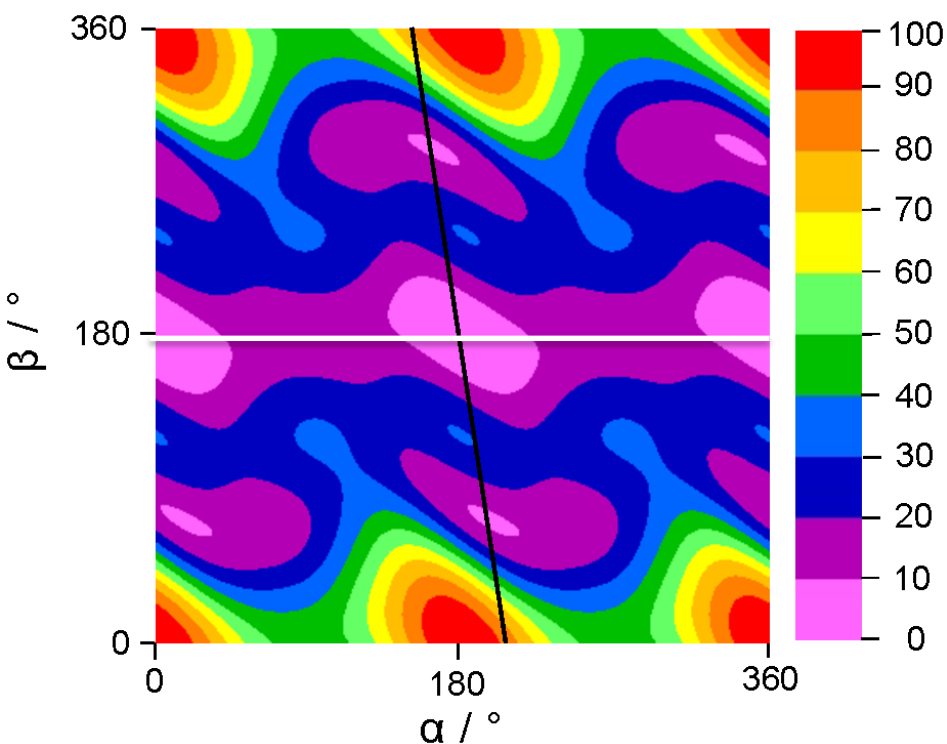
ethylacetamide, R. Kannengießer *et al.* ChemPhysChem **16**, 1906 (2015).

Conformational analysis



- $\alpha = \angle(\text{C}_2, \text{C}_3, \text{O}_{12}, \text{C}_{13})$: rotation of the phenyl ring
- $\beta = \angle(\text{C}_3, \text{O}_{12}, \text{C}_{13}, \text{C}_{16})$: rotation of the ethyl group
- MP2/6-311++G(d,p) level of theory
- (α, β) , $(-\alpha, -\beta)$, $(180+\alpha, \beta)$, and $(180-\alpha, -\beta)$: same potential energy

Conformational analysis

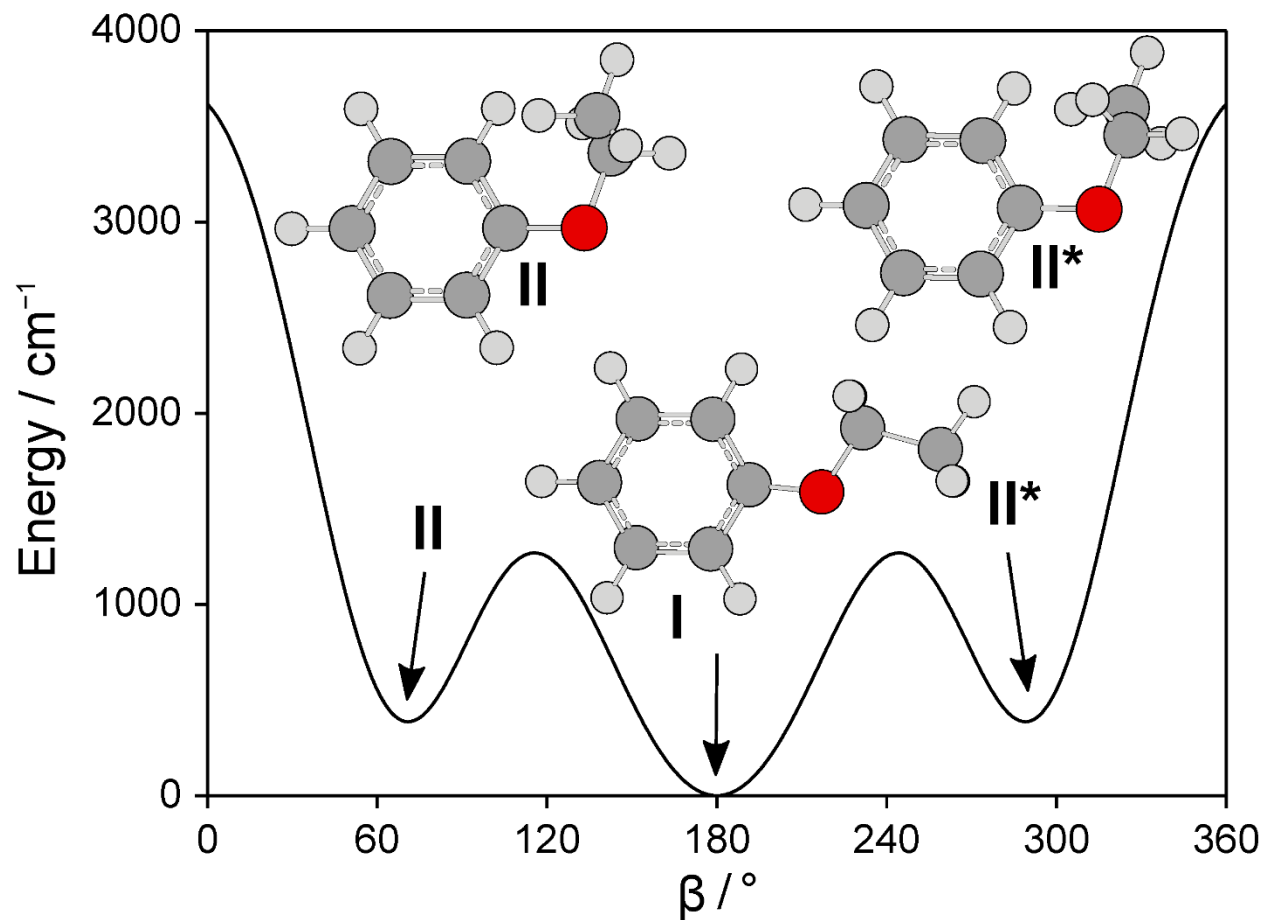


1D energy plot along $\beta = 180^\circ$

- Two narrow minima $\alpha = 0^\circ$ and 180° ,
- Two extremely broad equivalent maxima at about $\alpha = 90^\circ$ and 270°
- V_2 torsional barrier of the phenyl ring : 626 cm^{-1}
- Four other equivalent minima

Conformational analysis

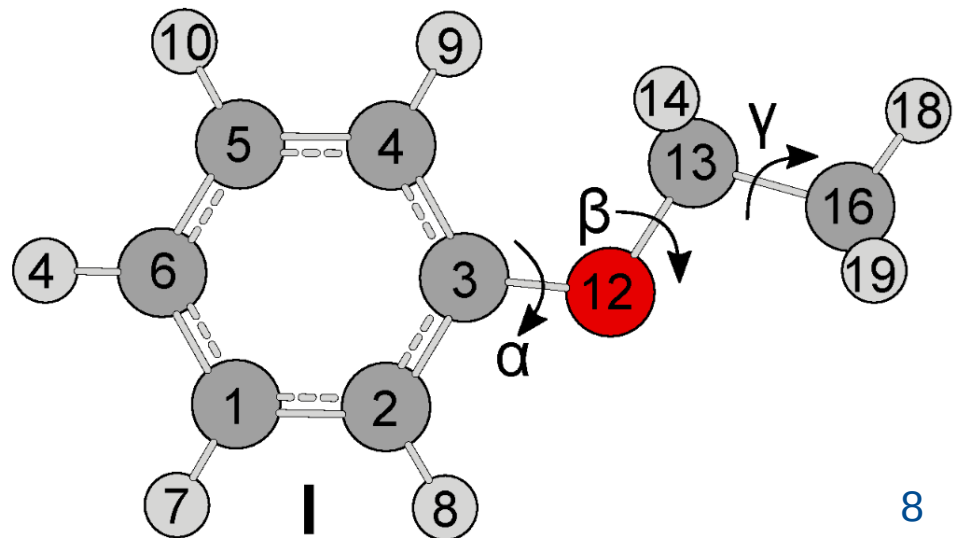
- $\beta = 180^\circ$: *trans*
- $\beta = \pm 70.92^\circ$: *gauche*,
> 4 kJ/mol
- *trans* - *gauche* transformation
883 cm^{-1} (barrier to internal rotation of the methyl group in anisole: 735 cm^{-1})



1D energy cut along from $\beta = 0^\circ$ to 360°
(connecting the three minima)

trans conformer

- $A = 4837.4$ MHz, $B = 922.4$ MHz, $C = 782.4$ MHz $\rightarrow$ *near prolate top*
 - $\mu_a = 0.69$ D, $\mu_b = 1.27$ D, $\mu_c = 0.00$ D $\rightarrow$ *a*- and *b*-type transitions
 - 1 imaginary vibrational mode (bending vibration of the phenyl ring) (well-known spurious result for MP2/6-311++G(d,p) calculations)
 - methyl internal rotation: $V = V_0 + (V_3/2)(\cos 3\gamma) + (V_6/2)(\cos 6\gamma)$
 - V_3 is 1168 cm^{-1}
 - V_6 is 42.5 cm^{-1} (4%)
- $\rightarrow$ No observable splittings



Microwave spectrum

Molecular beam FT microwave spectroscopy, 2 – 26.5 GHz

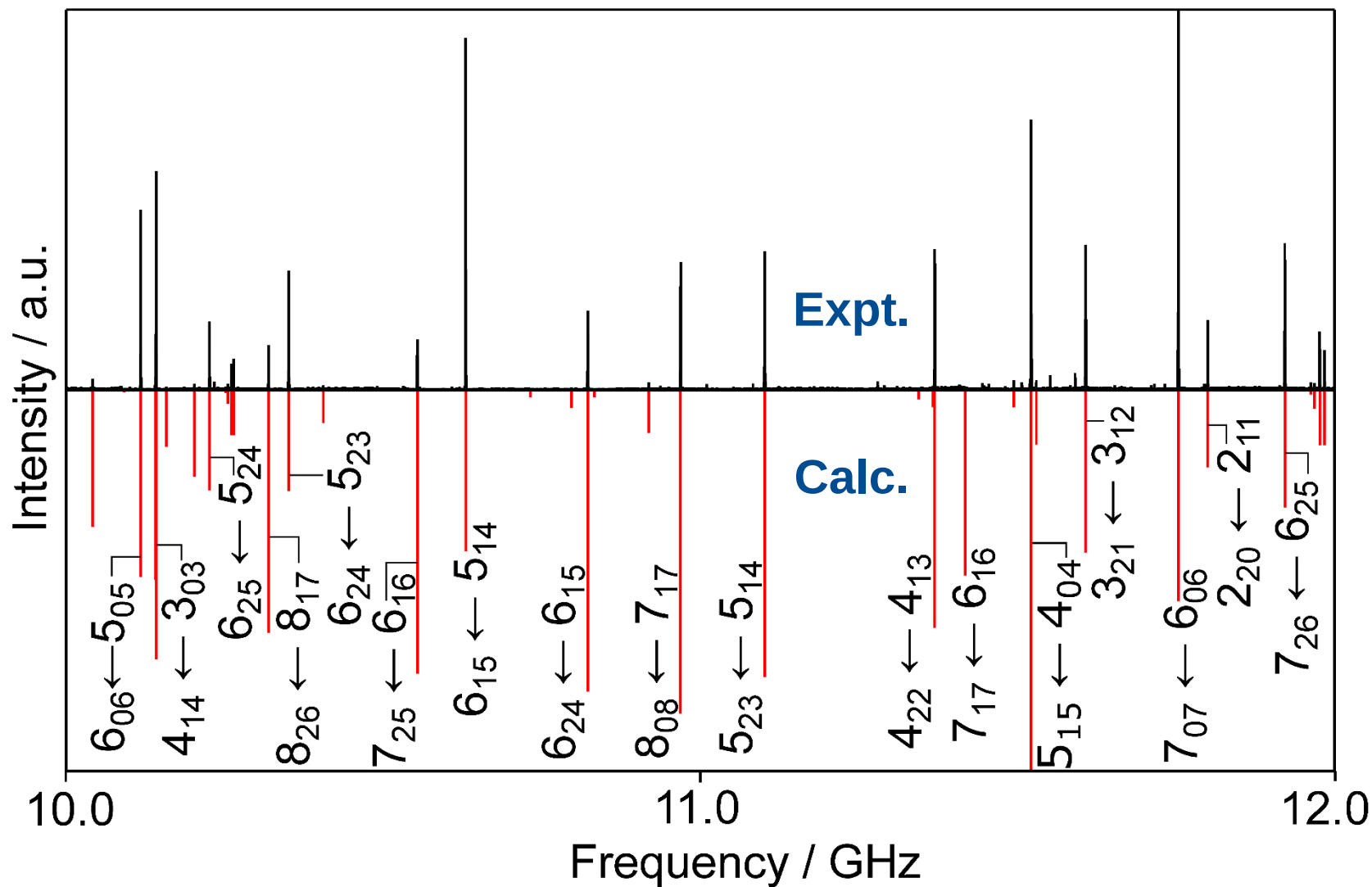
High resolution

- Average value of the line widths is about 20 kHz → measurement accuracy: 2 kHz
- Doppler effect; carrier gas: helium

Broadband scan

- Series of automatically recorded spectra in the high resolution mode
- 250 kHz step width, 50 decays per step
- 2 Frequency range : 10.0 – 14.0 GHz

Microwave spectrum



Molecular parameters

PAR.	Unit	<i>XIAM</i> *	<i>MP2</i>	<i>XIAM</i> – <i>MP2</i>
<i>A</i>	MHz	4855.37115(16)	4837.4	18.0
<i>B</i>	MHz	923.288562(38)	922.4	0.9
<i>C</i>	MHz	783.852629(34)	782.4	1.5
<i>D_J</i>	kHz	0.01863(14)		
<i>D_{JK}</i>	kHz	0.1077(10)		
<i>D_K</i>	kHz	0.739(12)		
<i>d₁</i>	kHz	–0.003540(57)		
<i>d₂</i>	kHz	–0.000449(18)		
<i>N</i>		186		
<i>σ</i>	kHz	2.3		

* asymmetric rotor mode.
Watson's S reduction in I^r representation was used.

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- $\Delta_c = (I_c - I_a - I_b) = -6.718 \text{ uÅ}^2$
 - *trans* ethyl formate –6.514 uÅ²; *trans* ethyl nitrate –6.503 uÅ²)
- heavy atom skeleton is planar