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The molecular structure of phenetole studied by microwave spectroscopy and quantum chemical calculations — Source link

Lynn Ferres, Wolfgang Stahl, Ha Vinh Lam Nguyen

Institutions: RWTH Aachen University, Paris Diderot University

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Topics: Ethyl phenyl ether, Rotational spectroscopy, Conformational isomerism, Ethyl group and Potential energy surface

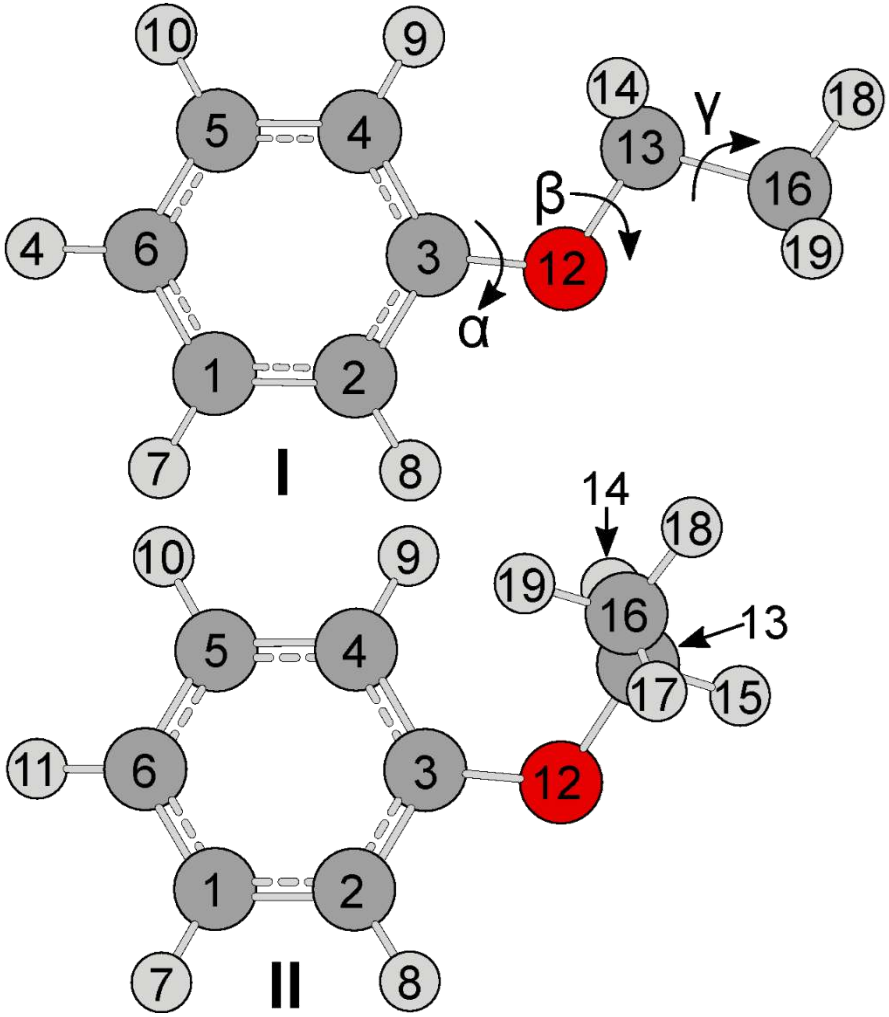
The molecular structure of phenetole studied by spectroscopy and quantum chemical calculations

LAM Nguyen
Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA)
Université Paris-Est Créteil

LYNN Ferres, WOLFGANG Stahl
Institute of Physical Chemistry, RWTH Aachen University

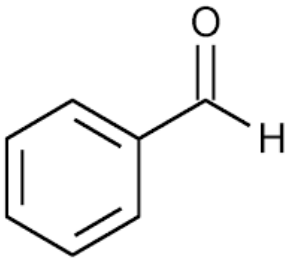
Phenetole

- $C_6H_5OC_2H_5$
- 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



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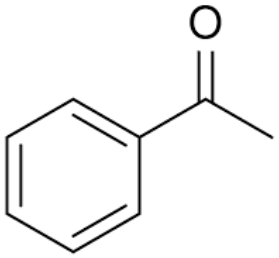

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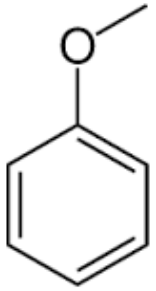

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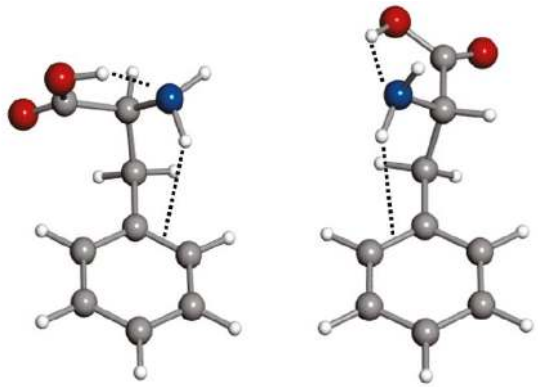
out-of-plane phenyl ring



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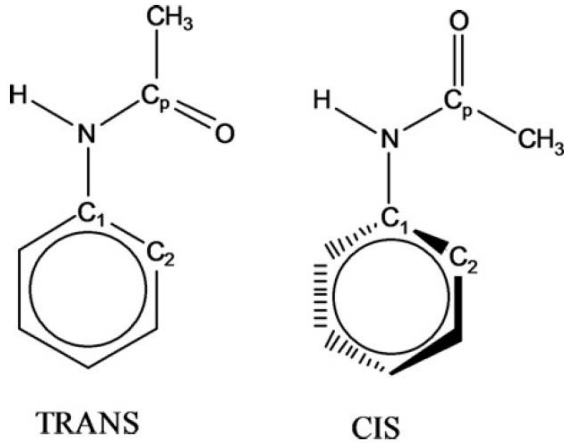

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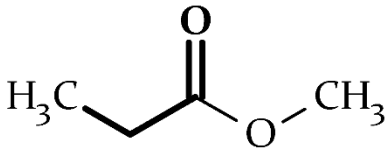
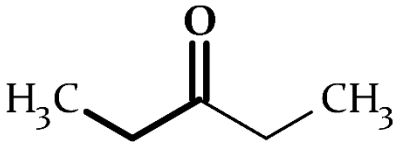
Phenetole

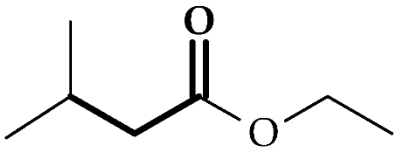
in-plane ethyl group



methyl propionate



diethyl ketone



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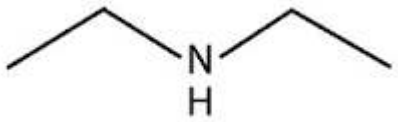
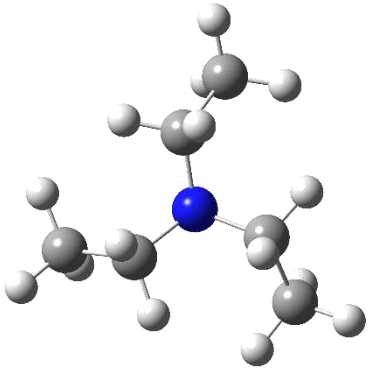


diethyl amine Nguyen *et al.* JCP **135**, 024310 (2011).

out-of-plane ethyl group



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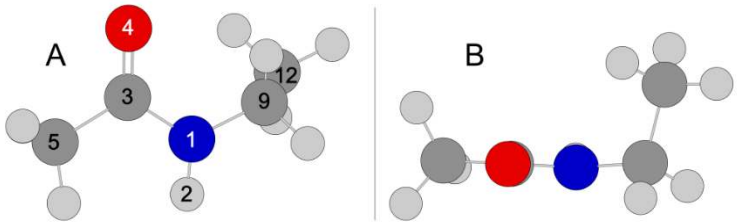

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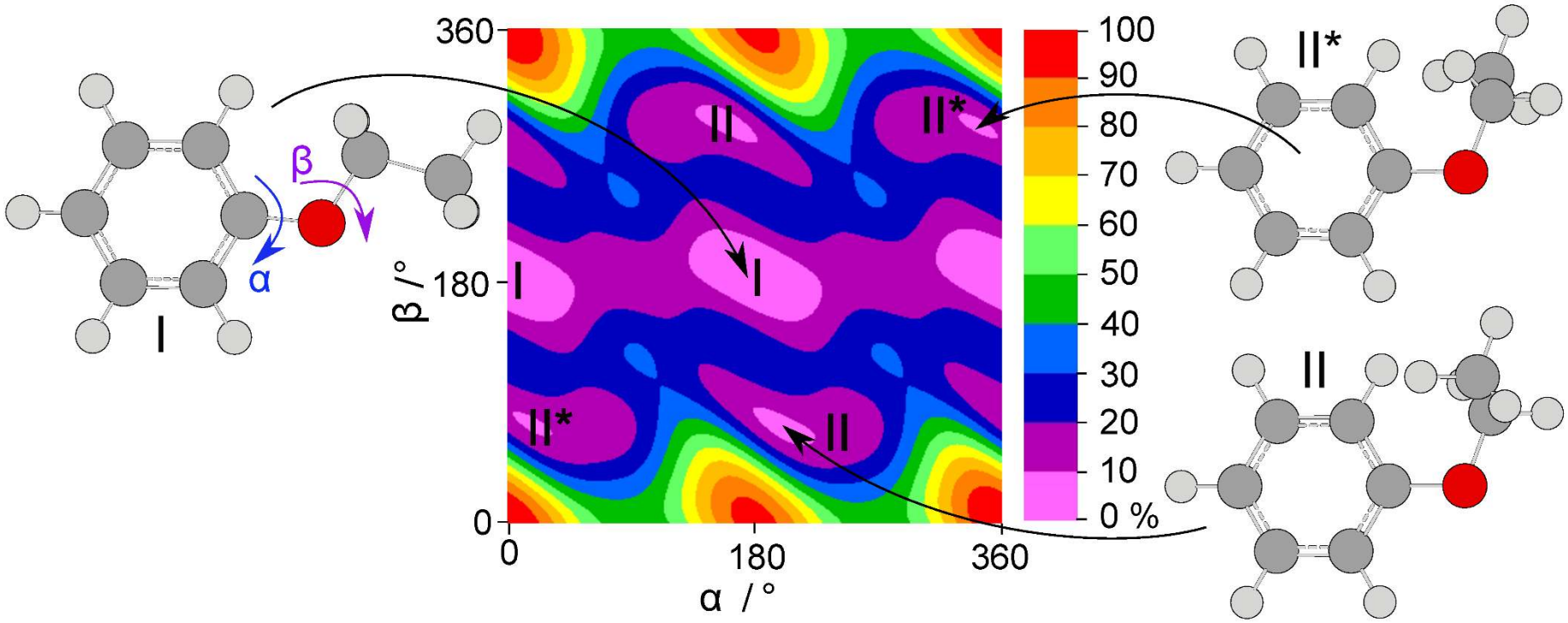
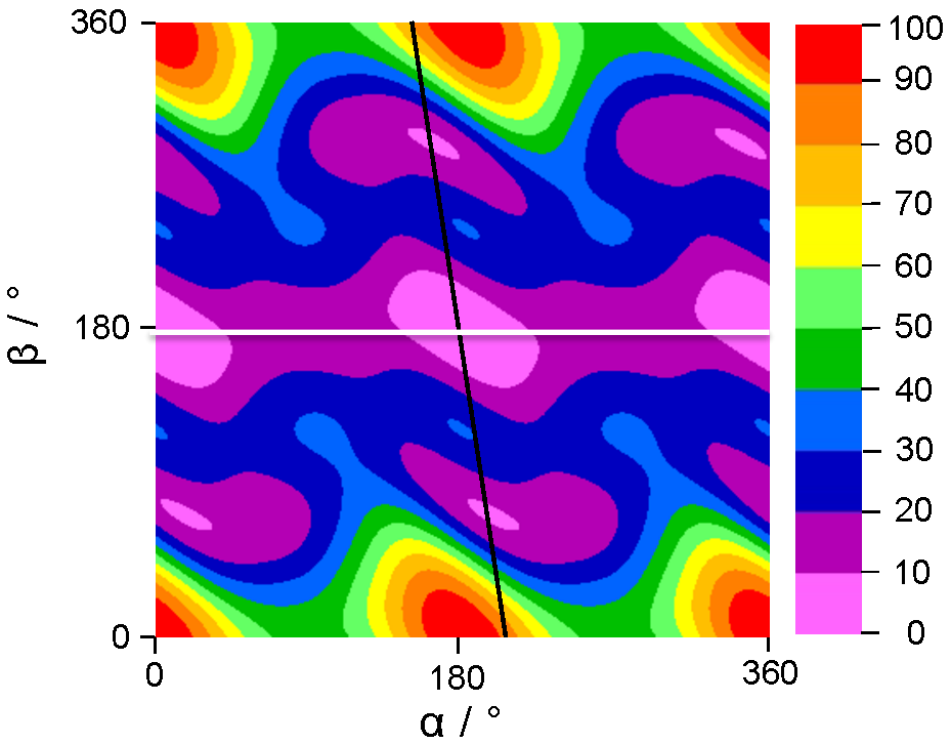
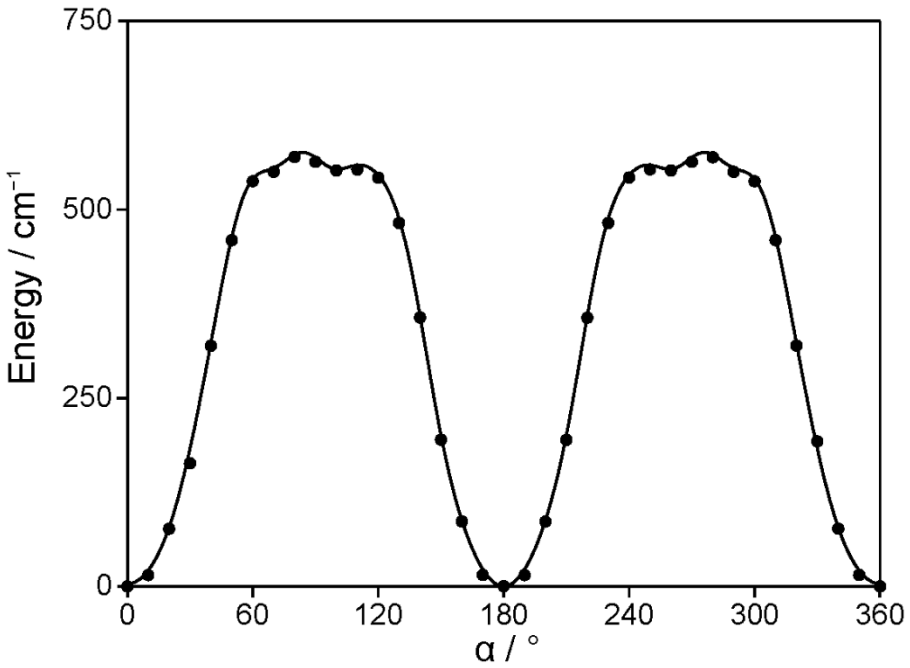
Conformational analysis



- $\alpha = \angle(C_2,C_3,O_{12},C_{13})$: rotation of the phenyl ring
- $\beta = \angle(C_3,O_{12},C_{13},C_{16})$: 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





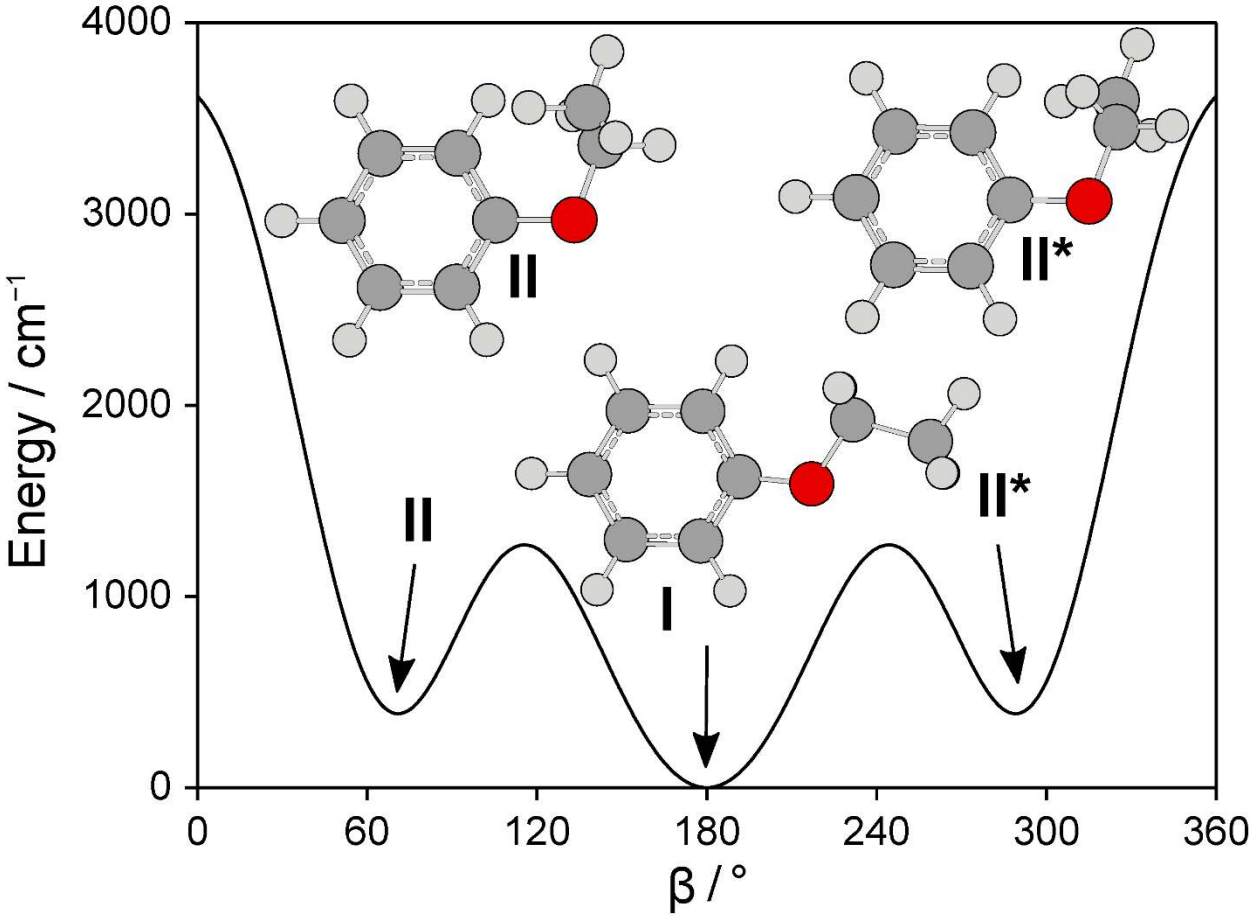
1D energy plot along β = 180°

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

Conformational analysis

- β = 180°: *trans*
- β = ±70.92° : *gauche*,

  > 4 kJ/mol
- *trans* - *gauche* transformation 883 cm^{-1} (barrier to internal rotation of the methyl group in anisole: 735 cm^{-1})



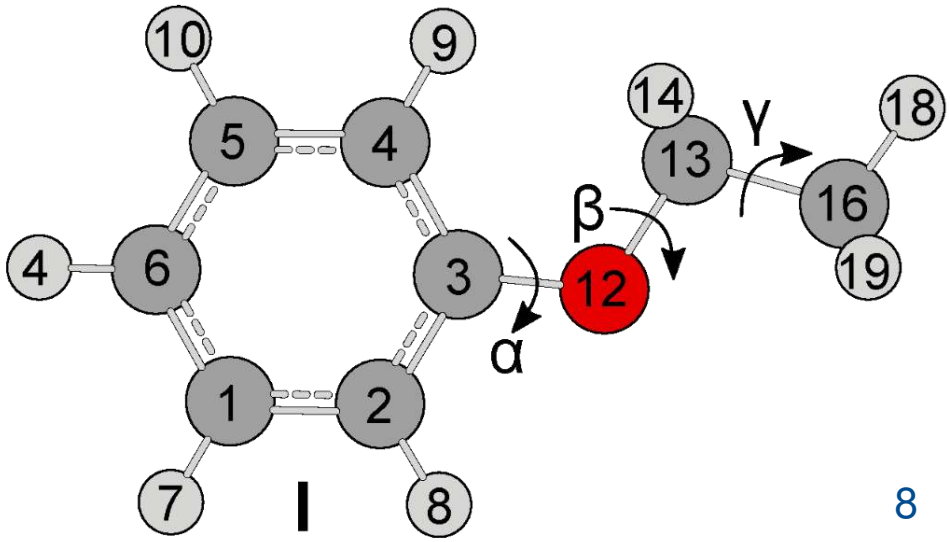
1D energy cut along from β = 0° to 360° (connecting the three minima)

trans conformer

- A = 4837.4 MHz, B = 922.4 MHz, C = 782.4 MHz → *near prolate* top
- μ_a = 0.69 D, μ_b = 1.27 D, μ_c = 0.00 D → *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%)

→ No observable splittings



Microwave spectrum

Molecular beam FT microwave spectroscopy, 2 – 26.5 GHz

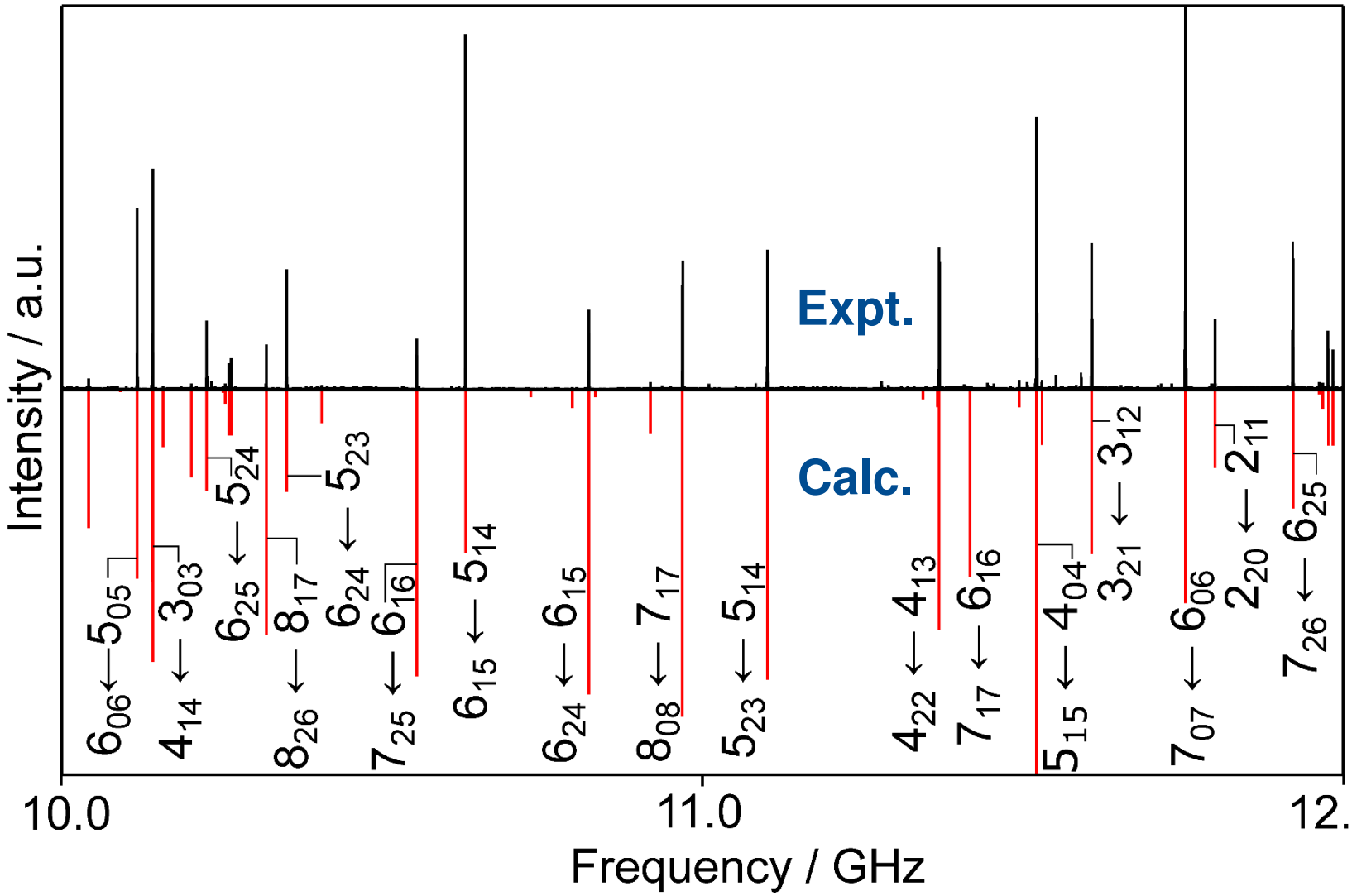
High resolution

- 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
- Frequency range : 10.0 – 14.0 GHz

Microwave spectrum



Molecular parameters

PAR.	Unit	*XIAM**	*MP2*	*XIAM – MP2*
A	MHz	4855.37115(16)	4837.4	18.0
B	MHz	923.288562(38)	922.4	0.9
C	MHz	783.852629(34)	782.4	1.5
D_J	kHz	0.01863(14)		
D_{JK}	kHz	0.1077(10)		
D_K	kHz	0.739(12)		
d_1	kHz	–0.003540(57)		
d_2	kHz	–0.000449(18)		
N		186		
σ	kHz	2.3		

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

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Within the experimental accuracy

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- $\Delta_c = (I_c - I_a - I_b) =$ –6.718 uÅ^2
- *trans* ethyl formate –6.514 uÅ^2; *trans* ethyl nitrate –6.503 uÅ^2)

→ heavy atom skeleton is planar