LAM's LAMs

Probing the methyl torsional barriers of the *E* and *Z* isomers of butadienyl acetate by microwave spectroscopy

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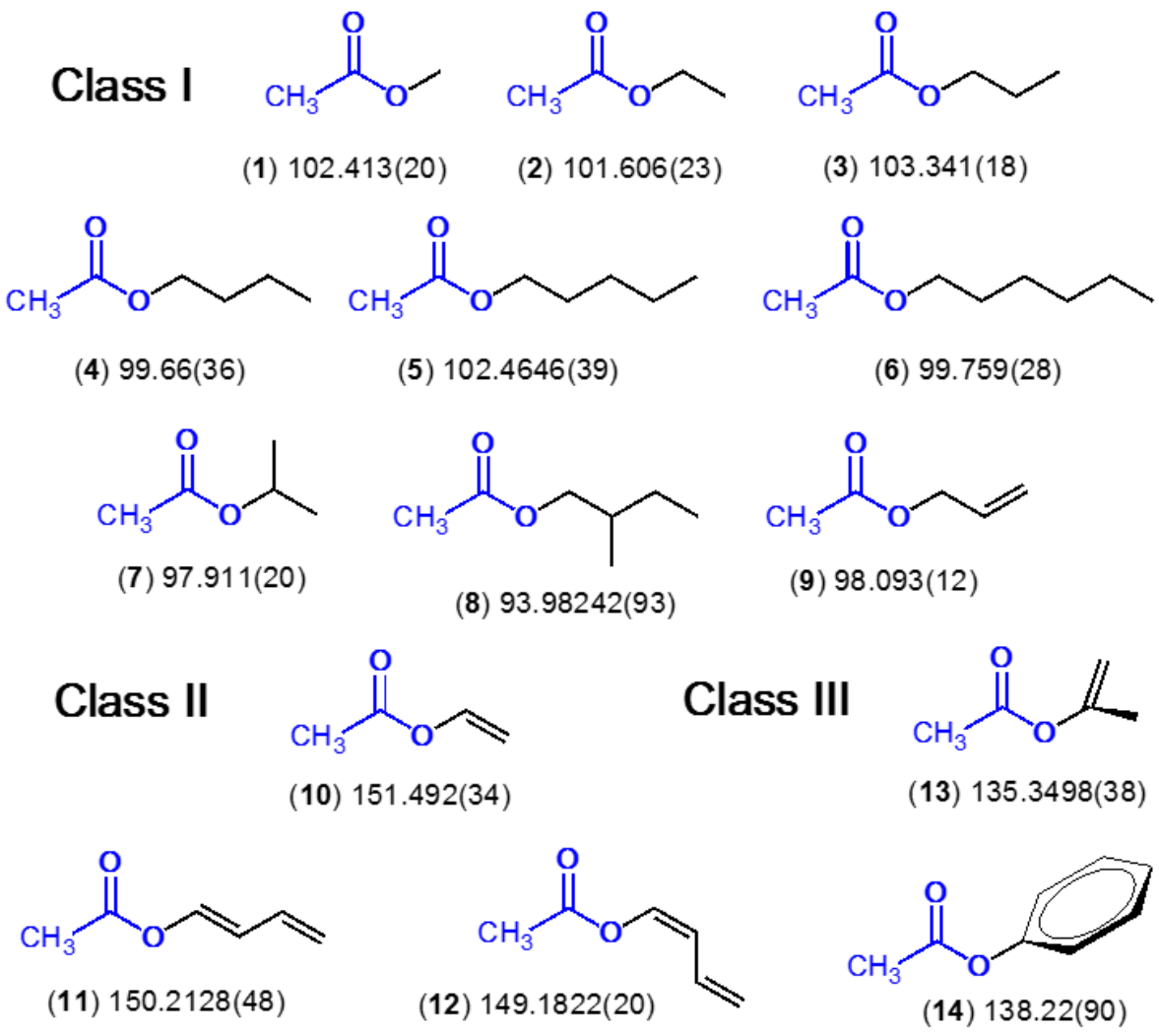
Motivation



- Class I: α,β-saturated acetates (100 cm^{-1})
- Class II: α,β-unsaturated acetates, C=C double bond in the COO plane (150 cm^{-1})
- Class III: α,β-unsaturated acetates, C=C double bond NOT in the COO plane (135 cm^{-1})

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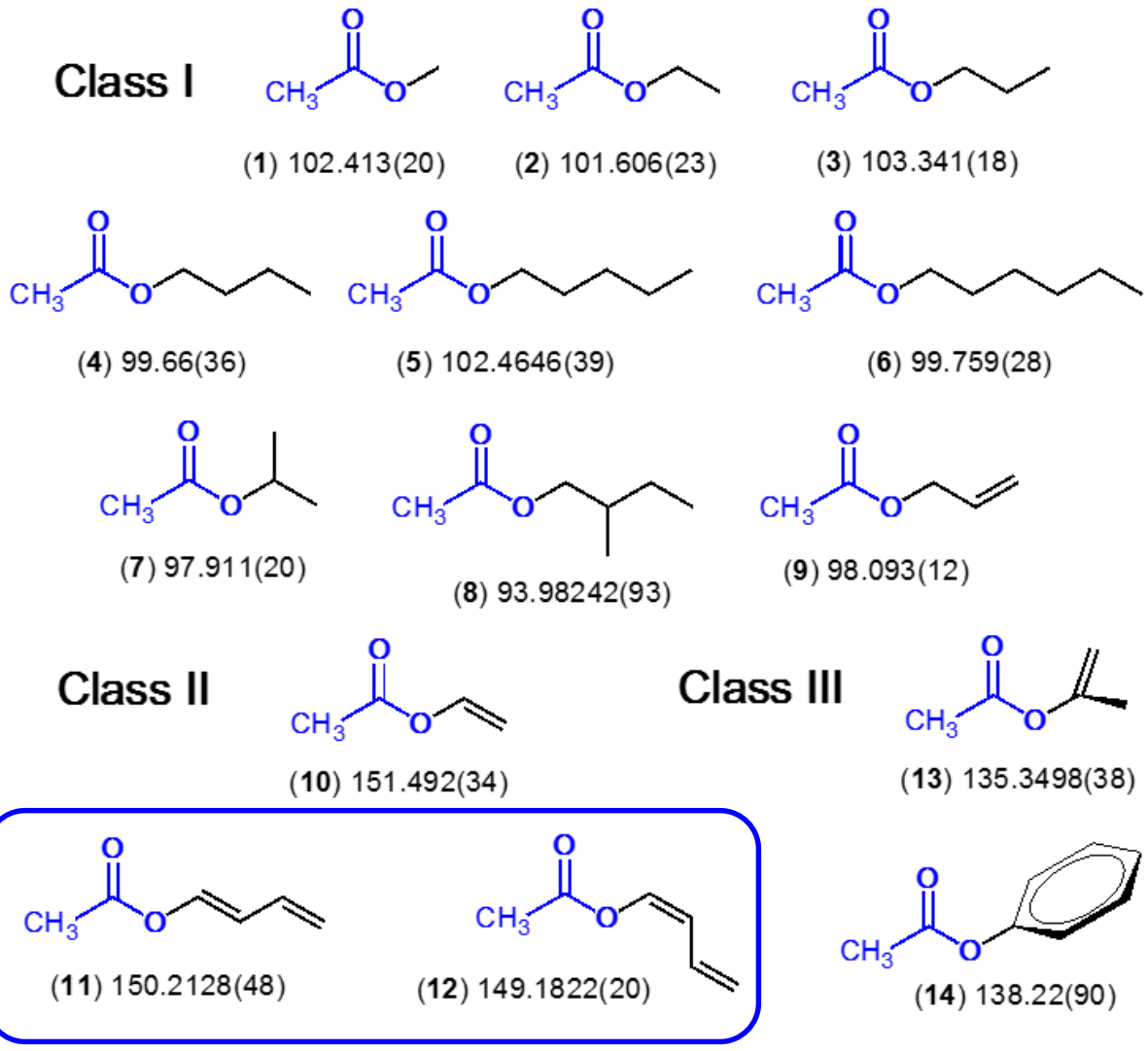

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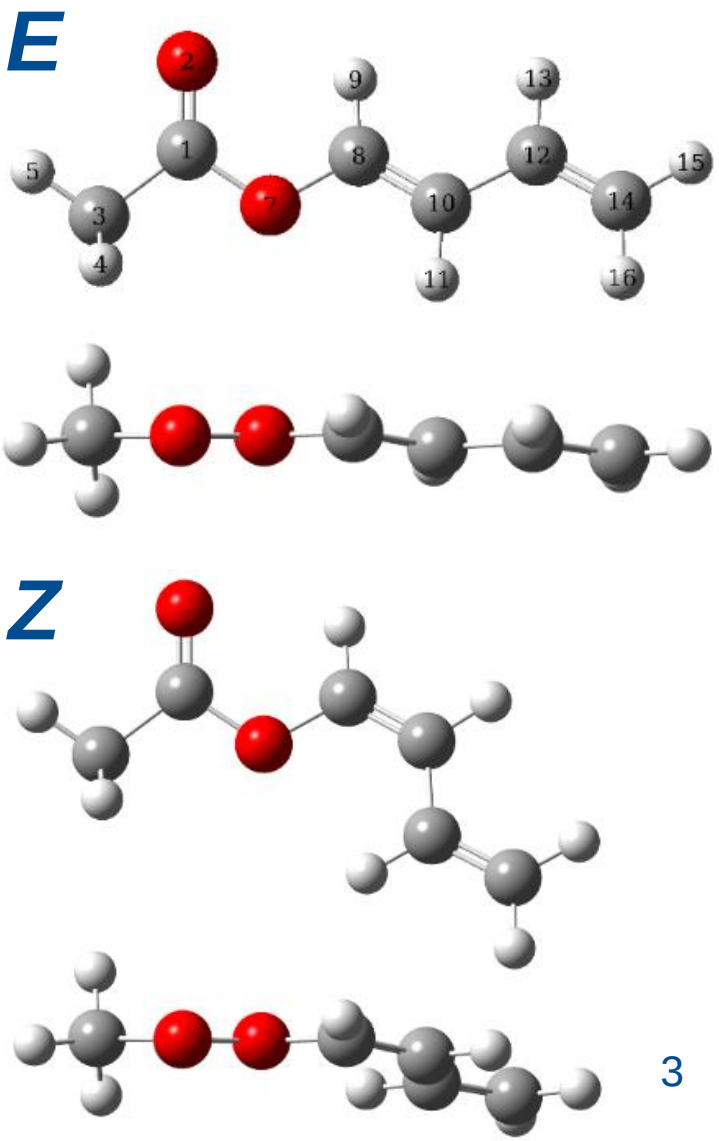
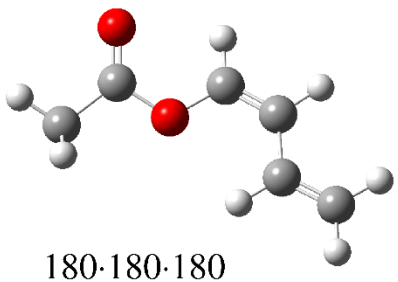
E and *Z* isomers of butadienyl acetate

- E and Z: rotation of 180° about the C_8-C_{10} double bond
- Conformations: rotation about the C_1-O_7, O_7-C_8, and C_{10}-C_{12} bonds
- MP2/6-311++G(d,p) level of theory → 6 *E* and 5 *Z* conformers
- Butadienyl group slightly tilted out of the **CH_3**-COO plane by an angle of about 10°
- Basis set variation

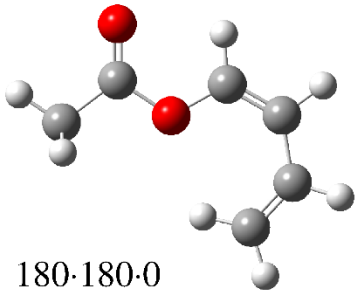


Conformational analysis

E



180·180·180



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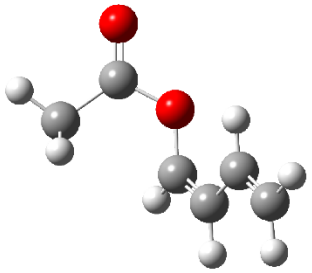

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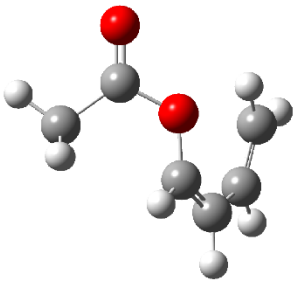

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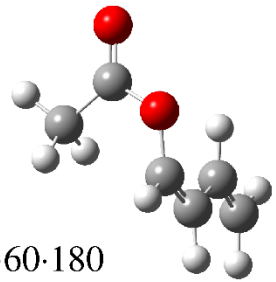

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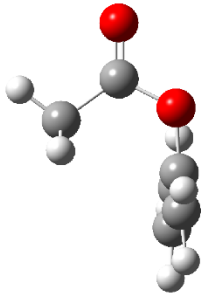
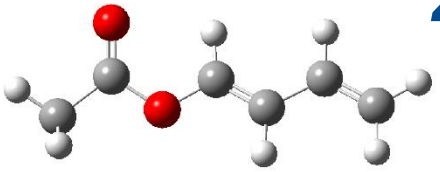


Z



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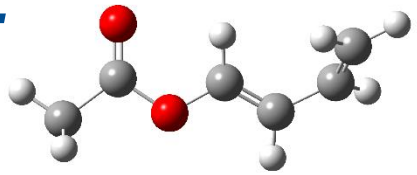

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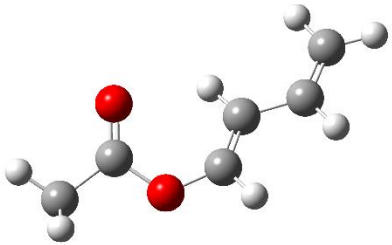

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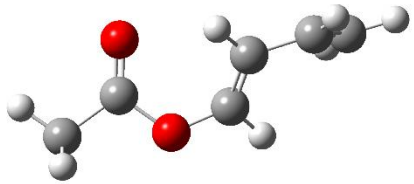

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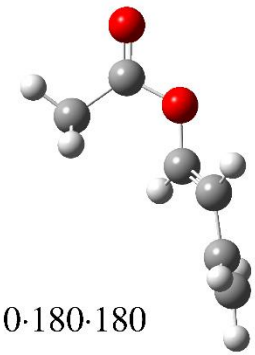

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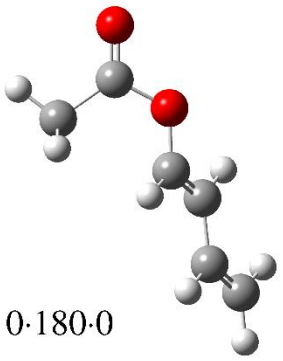


0·180·0

Microwave spectrum

- Molecular beam FT microwave spectroscopy
- 2 – 26.5 GHz Cavity (Aachen) and 26.5 – 40 GHz Cavity (Paris)

High resolution

- Line widths in the range 10 – 25 kHz → measurement accuracy better than 2 kHz
- Doppler effect; carrier gas: helium

Broadband scan

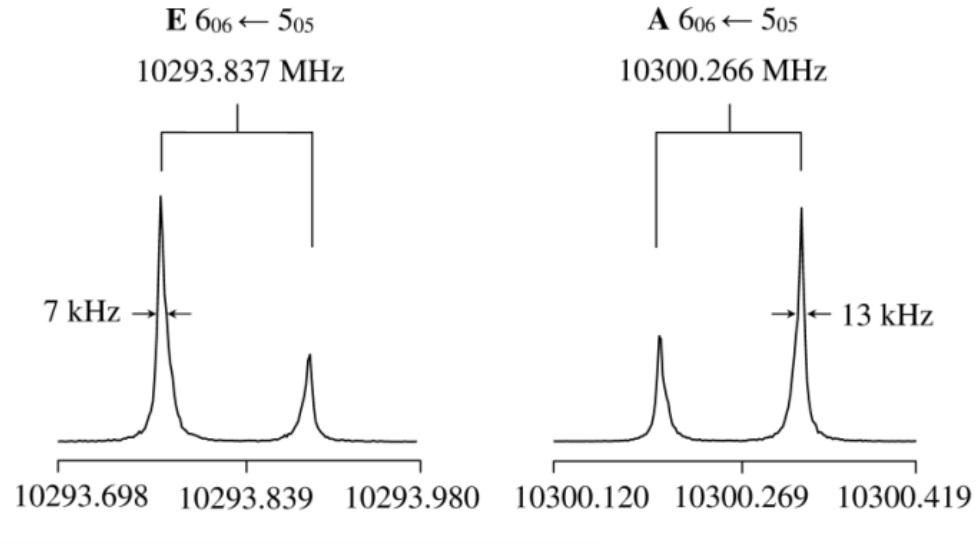
- Series of automatically recorded spectra in the high resolution mode
- 250 kHz step width, 50 decays per step
- Frequency range : 8.0 – 13.3 GHz

Microwave spectrum

High resolution measurements

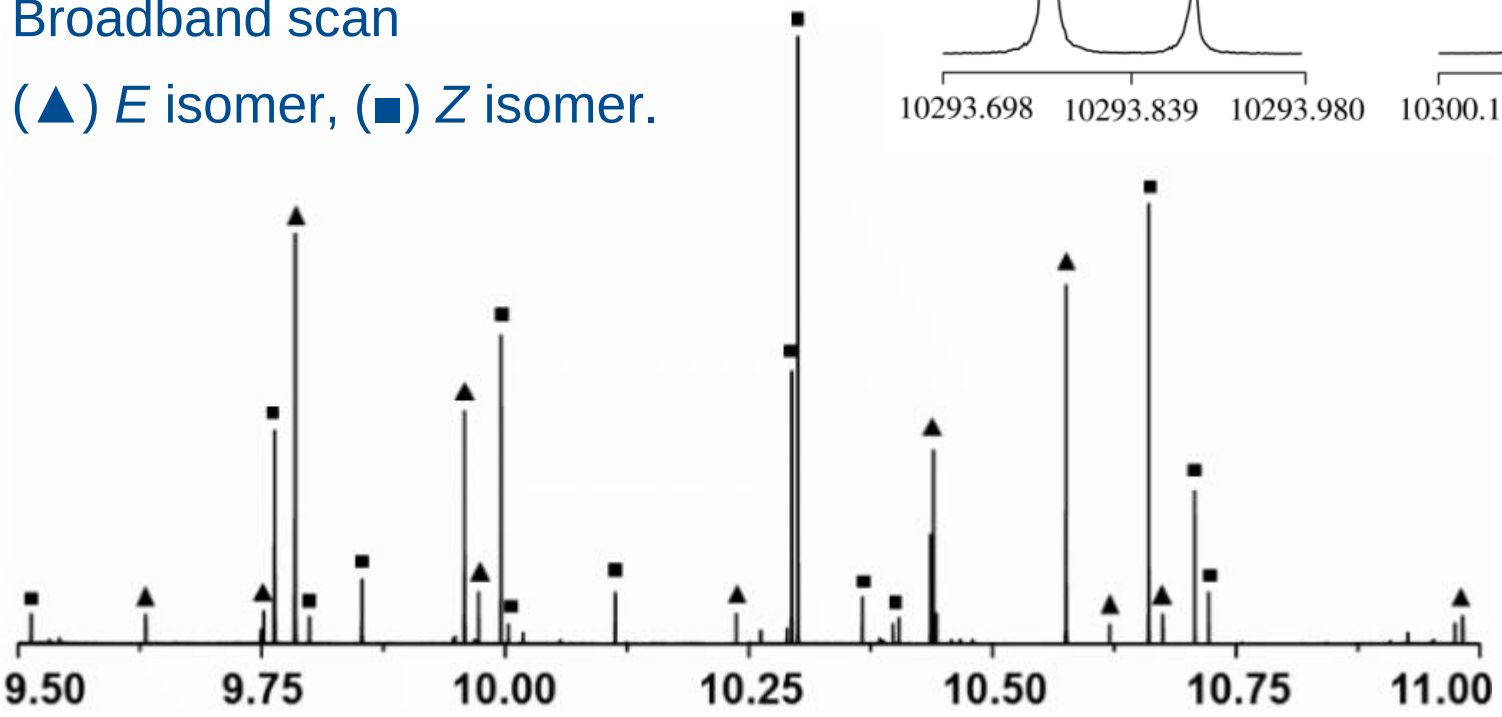
Z isomer

50 decays



Broadband scan

(▲) *E* isomer, (■) *Z* isomer.



Spectral assignment

- First *Z*, then *E* (the *Z* isomer has smaller rotational constants → higher line density in the broadband scan region)
- First *a*-type *R*-branch, then *b*-type
- First rigid-rotor (A species), than methyl internal rotation (E species)
- No A species *c*-type transitions, but E species!
- First XIAM, than BELGI-Cs

Molecular parameters

Parameter[a]	*Z* isomer XIAM	*Z* isomer BELGI-C_s	*E* isomer XIAM	*E* isomer BELGI-C_s
A [MHz]	5891.230(22)	5874.25(20)	8408.726(17)	8375.05(11)
B [MHz]	924.6574(22)	923.643(31)	778.1573(11)	778.59948(82)
C [MHz]	803.8922(19)	804.293(27)	715.8163(11)	716.08363(37)
D_J [kHz]	0.06520(70)	0.22883(53)	0.01567(51)	0.014114(99)
D_{JK} [kHz]	−0.7484(83)		0.5414(90)	
D_K [kHz]	9.24(21)		5.87(36)	
d_1 [kHz]	−0.01394(37)		−0.00109(13)	
d_2 [kHz]	−0.00148(13)		0.0[b]	
V_3 [cm^{-1}]	150.2128(48)	148.165(60)	149.1822(20)	149.2732(67)
F_0[b] [GHz]	158.0		158.0	
F [GHz]	160.1[c]	160.1[d]	163.5[c]	163.5[d]
s[e]	12.50073	12.3303	12.15694	12.16422
I_α[c] [uÅ^2]	3.1986		3.1986	
Δ_c [uÅ^2]	−3.6779	−4.8395	−3.5401	−3.6765
(*i*,*a*) [°]	61.1753(64)	61.21784(19)	39.5131(20)	39.45422(31)
(*i*,*b*) [°]	28.8247(26)	28.78216(71)	50.4869(20)	50.54578(59)
(*i*,*c*) [°]	90.0[b]	90.0[b]	90.0[b]	90.0[b]
D_{pi2J} [kHz]	31.10(26)		20.89(16)	
D_{pi2K} [MHz]	−0.7209(33)		−2.0362(27)	
D_{pi2-} [kHz]	5.23(17)		3.725(51)	
N[e]	134/140	134/140	79/92	79/92
σ[g] [kHz]	15.4	2.1	7.8	1.4

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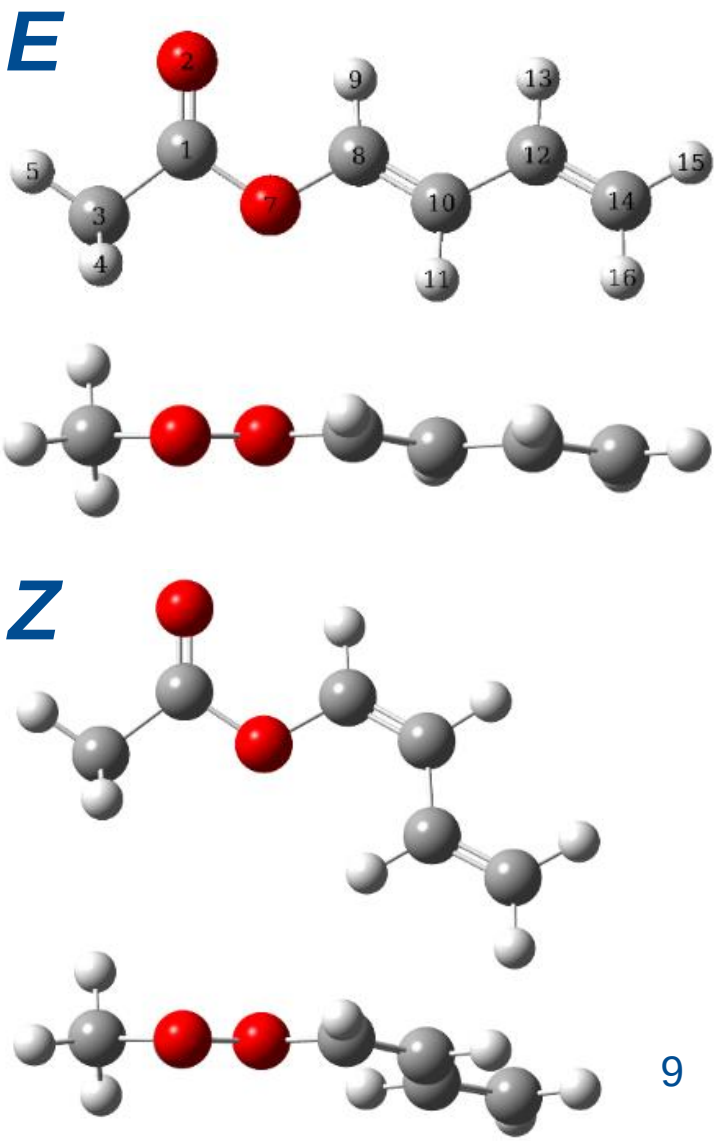
D_{pi2J} [kHz]	31.10(26)		20.89(16)	
D_{pi2K} [MHz]	−0.7209(33)		−2.0362(27)	
D_{pi2-} [kHz]	5.23(17)		3.725(51)	
N[e]	134/140	134/140	79/92	79/92
σ[g] [kHz]	15.4	2.1	7.8	1.4

in or out-of-plane butadienyl group?

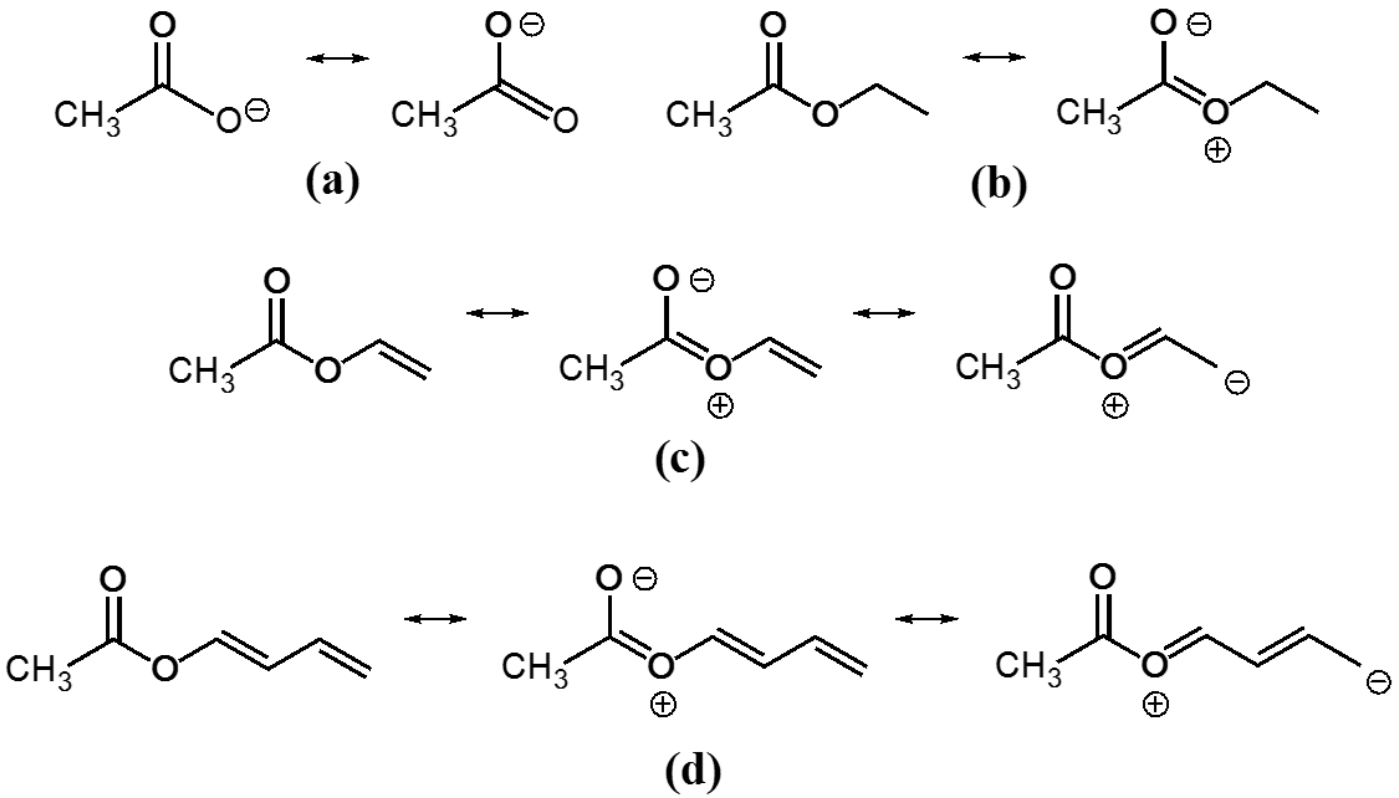
- Non-vanishing dipole moment component in the *c*-direction is predicted at the MP2/6-311++G(d,p) level of theory
- Butadienyl group slightly tilted out of the **CH_3**-COO plane by an angle of about 10°
- Some observed *c*-type transitions, all E species lines
- No A species *c*-type lines



in or out-of-plane butadienyl group?

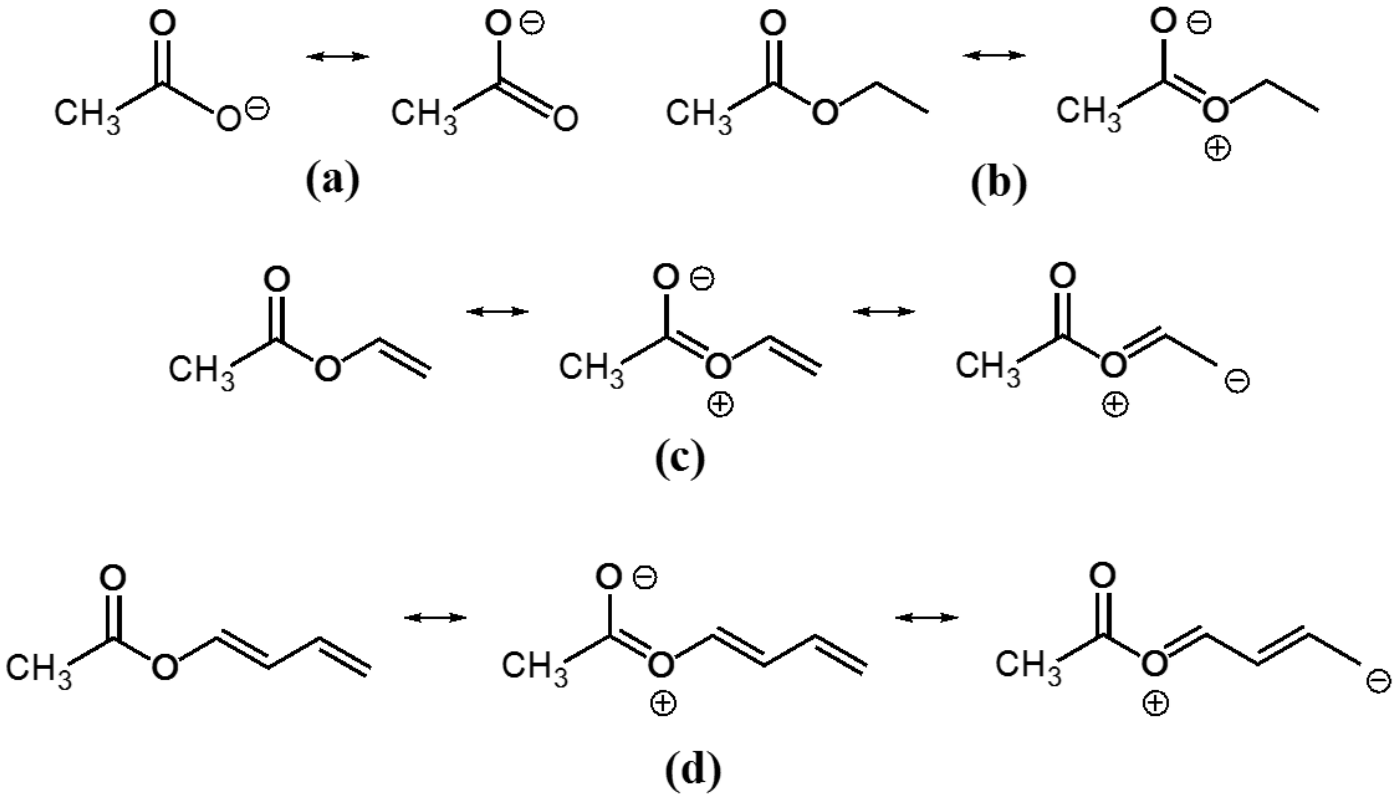
- There is indeed a dipole moment in *c*-direction but our sensitivity is too small to detect the weak *c*-type lines.
- The enantiomers are separated by a low barrier and the tunneling ground state is above this barrier → effective C_s geometry (expectation value of $\mu_c = 0$).
- BELGI-Cs fits did not require any out-of-plan terms.
- Inertial defect $\Delta_c = -3.540$ uÅ^2 (*E*) and -3.680 uÅ^2 (*Z*) → planar heavy atom skeleton (for a comparison: methyl vinyl ketone -3.162 uÅ^2, vinyl acetate -3.491 uÅ^2)
- MP2/6–31+G(d,p), MP2/6–31++G(d,p), MP2/6–311+G(d,p), MP2/6–311++G(d,p), CCSD/6–311++G(d,p)

V_3 potentials



(**a**) C_{3v} methyl group attached to a C_{2v} COO frame → $V_3 = 0$, only small V_6 term, e.g. nitromethane, CH_3NO_2 ($V_6 = 2.1$ cm^{-1}) and toluene CH_3-C_6H_5 ($V_6 = 4.9$ cm^{-1}).

V_3 potentials

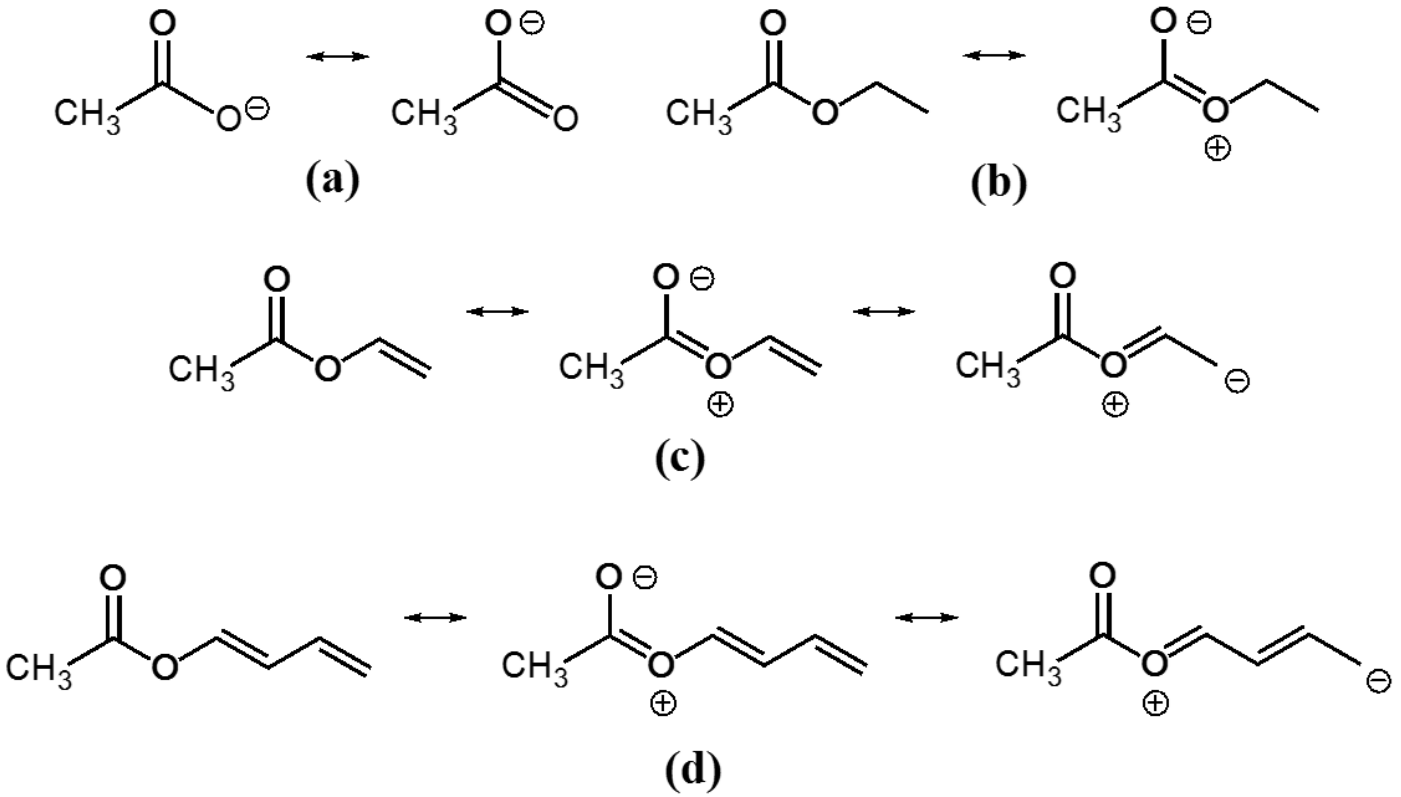


(**b**) C_{3v} methyl group, frame no longer C_{2v} symmetry

→ electronic distribution slightly out-of-balance

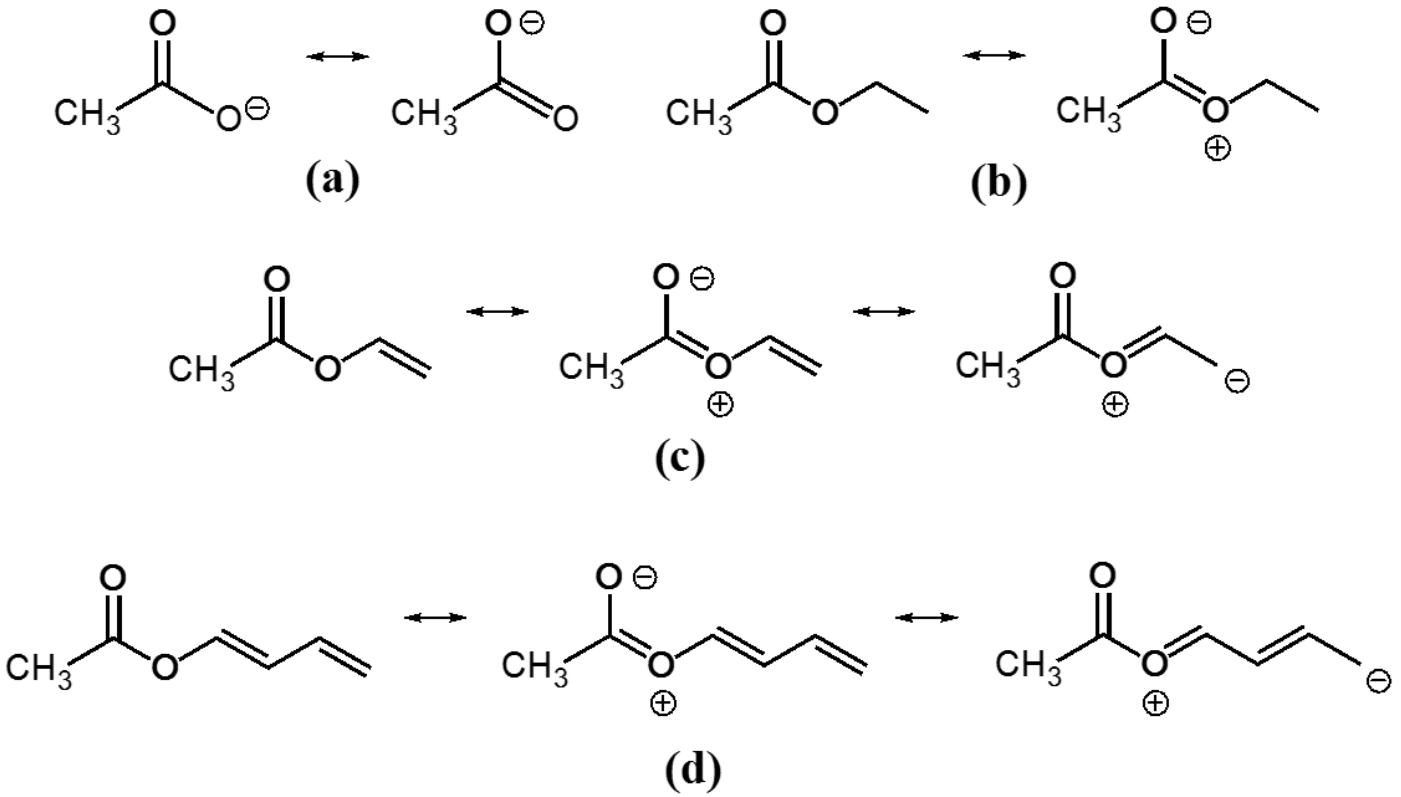
→ V_3 potential term of about 100 cm^{-1}.

V_3 potentials



(**c**) Mesomeric system extended from the carbonyl oxygen atom to the β carbon atom increases the double bond character of the carbonyl bond

V_3 potentials



(**c**) CO stretching vibration blue shifted (vinyl acetate: 1762 cm^{-1}, phenyl acetate: 1765 cm^{-1} vs. methyl acetate: 1736 cm^{-1}, ethyl acetate: 1728 cm^{-1}, *n*-propyl acetate: 1724 cm^{-1})