Laborastrophysik
Universität Kassel

Understanding the Internal Torsion and Bending Motion of Dimethyl Ether via Isotopic Studies

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Motivation

Dimethyl Ether (DME) is well suited to study the large amplitude internal motion of two methyl groups. The internal torsion exhibits strong coupling effects of both rotors and also with the C-O-C bending mode. Furthermore DME is of astrophysical interest and the main isotopologue as well as the singly ^{13}C substituted species have been detected in the interstellar medium [1,2]. DME has dense spectra in a broad frequency range, so that accurate predictions of its transition frequencies can help to reduce the line confusion of interstellar spectra. Up to date its abundance and interstellar formation pathway are not fully understood [3]. While the main isotopologue is quite well explored [4] there are open questions concerning ^{13}C substituted species, such as symmetry properties and their influences on rotational spectra.

Spectroscopic Interest

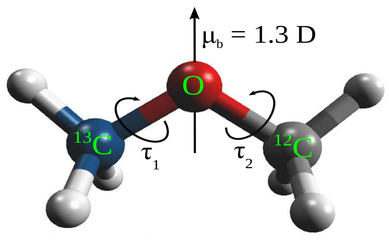

Figure 1: Structure of DME

- Ray asymmetric parameter:

$$\kappa = \frac{2B - A - C}{A - C} = -0.9$$

- Permanent dipole moment $\mu_b = 1.3$ D
- Molecular symmetry group changes from G_{36} to G_{18} for asymmetric substitution of ^{13}C.
- Perpendicular spectra and *b*-type asymmetric top selection rules:

$\Delta J = 0, \pm1,...;\ \Delta k_a = \pm1, \pm3,...;$
$\Delta k_c = \pm1, \pm3,...$

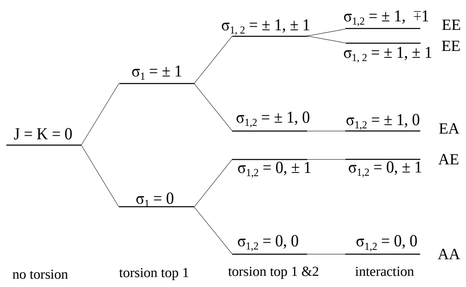

Figure 2: Schematic torsional energy level diagram for J=K=0

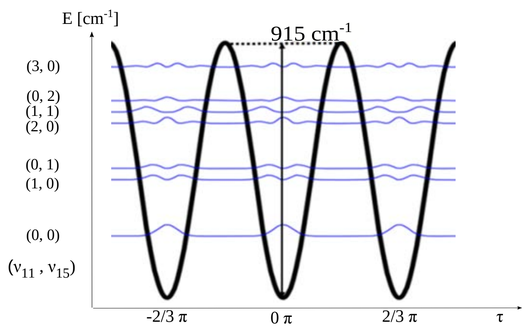

Figure 3: 2π/3 periodic potential function of torsional vibration modes of DME

Vibrational energies of exited modes of DME isotopologues, based on HF/6-31G(d) [HF] and B3LYP/ cc-pVTZ [DTF] calculations.

	$\bar{\nu}_{1212}$ HF $[cm^{-1}]$	$\bar{\nu}_{1212}$ DFT $[cm^{-1}]$	$\bar{\nu}_{1313}$ HF $[cm^{-1}]$	$\bar{\nu}_{1313}$ DFT $[cm^{-1}]$	symmetry	$\bar{\nu}_{1213}$ HF $[cm^{-1}]$	$\bar{\nu}_{1213}$ DFT $[cm^{-1}]$	symmetry
ν_{11}	215, 83	210, 08	215, 63	209, 85	A_3	209, 33	209, 96	A_2
ν_{15}	265, 86	240, 25	265, 27	239, 75	A_2	261, 81	240, 00	A_2
ν_7	443, 81	410, 28	437, 01	404, 12	A_1	440, 42	407, 24	A_1
ν_6	1045, 62	939, 99	1023, 10	919, 07	A_1	1035, 22	929, 10	A_1
ν_{21}	1234, 58	1119, 15	1219, 96	1103, 59	A_4	1227, 46	1111, 59	A_1
ν_{10}	1280, 69	1163, 24	1271, 33	1154, 65	$A_3(G)$	1274, 84	1158, 38	$A_2(E_2)$
ν_{20}	1350, 23	1194, 11	1334, 03	1180, 73	A_4	1343, 19	1187, 39	A_1
ν_{14}	1316, 35	1194, 57	1307, 31	1186, 16	$A_2(G)$	1311, 94	1190, 93	$A_2(E_2)$
ν_5	1402, 49	1267, 66	1389, 63	1255, 41	A_1	1396, 10	1161, 74	A_1
ν_{19}	1612, 41	1459, 54	1606, 08	1455, 22	A_4	1608, 77	1457, 04	A_1
ν_9	1639, 54	1481, 71	1637, 01	1479, 56	$A_3(G)$	1637, 84	1480, 49	$A_2(E_2)$
ν_4	1650, 07	1489, 55	1641, 86	1481, 78	A_1	1646, 57	1486, 05	A_1
ν_{13}	1650, 88	1490, 07	1648, 31	1487, 81	$A_2(G)$	1649, 46	1489, 08	$A_2(E_2)$
ν_{18}	1652, 13	1498, 50	1649, 20	1496, 07	$A_4(G)$	1650, 79	1497, 26	$A_1(E_1)$
ν_3	1670, 71	1517, 57	1665, 97	1514, 82	$A_1(G)$	1668, 54	1516, 21	$A_1(E_1)$
ν_{17}	3163, 52	2955, 30	3159, 94	2951, 86	$A_4(G)$	3163, 60	2953, 33	$A_1(E_1)$
ν_2	3179, 50	2967, 74	3175, 51	2964, 05	$A_1(G)$	3179, 86	2966, 14	$A_1(E_1)$
ν_{12}	3217, 80	2997, 52	3203, 21	2986, 73	$A_2(G)$	3206, 20	2988, 55	$A_2(E_2)$
ν_8	3215, 24	3002, 47	3205, 95	2991, 37	$A_3(G)$	3218, 43	3000, 50	$A_2(E_2)$
ν_{16}	3302, 29	3104, 35	3290, 98	3094, 07	$A_4(G)$	3294, 80	3094, 73	$A_1(E_1)$
ν_1	3304, 84	3105, 85	3293, 45	3095, 49	$A_1(G)$	3306, 42	3105, 15	$A_1(E_1)$

Measurements and Analysis

Parts of the recorded spectra of singly ^{13}C and doubly ^{13}C substituted DME and simulated spectra of the ν_{07} and ν_{15} states. Some lines in the spectrum belong to impurities like e.g. methanol.

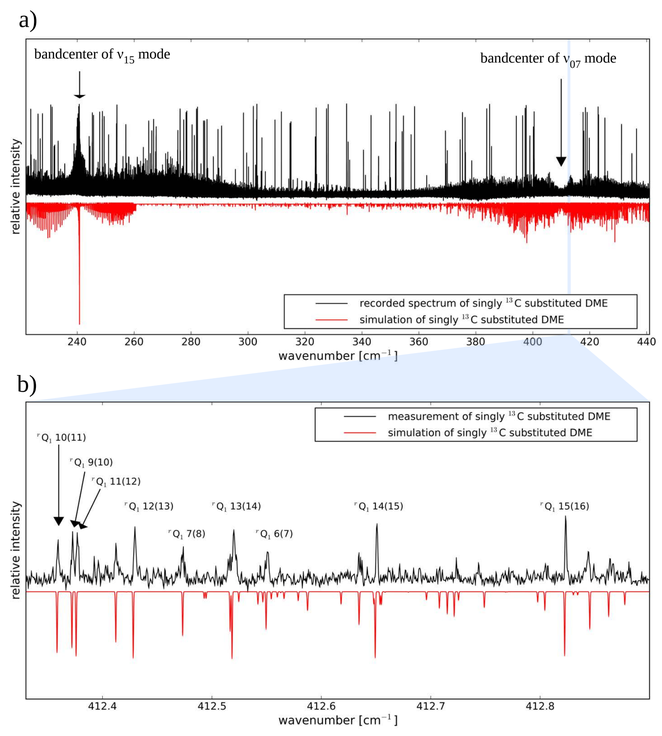

Figure 6: a) Recorded spectra of singly ^{13}C substituted DME
b) Detail of ν_{07} mode of singly ^{13}C substituted DME
c) Detail of ν_{07} mode of doubly ^{13}C substituted DME
compared to simulated spectra using PGOPHER [7].

Predicted and meassured energy values of the first excited ν_{07} and ν_{15} modes of singly ^{13}C substituted DME.
Energy given in $[cm^{-1}]$.

	ν_{15}	ν_{07}
ERHAM [5]	242.112	
MP3+MP2 [5] *		416.5
CCSD(T) [6] -	244.553	418.537
Adjusted [6] +	241.607	409.170
this work	240.866	409.9899

* harmonic approximation on MP3/cc-pVDZ level corrected by anharmonic contributions with MP2/cc-pVDZ
\- CCSD(T)/aug-cc-pVTZ
\+ corrections derived from the definition of α coordinate and from isotopic structural changes

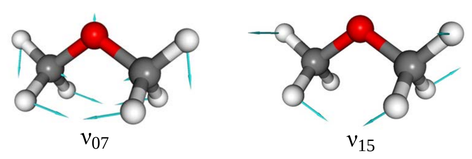

Figure 5: Schematic sketch of ν_{07} and ν_{15} of DME

Derived energy values for first excited ν_{07} mode compared to ground state energy values for all three measured isotopologues of DME.
Energy given in $[cm^{-1}]$

	main	singly	doubly
A_0	1.2938^-	1.2880^+	1.2822^+
$A_{\nu_{07}}$	1.268^*	1.307^*	1.260^*
B_0	0.3354^-	0.3267^+	0.3182^+
$B_{\nu_{07}}$	0.3345^*	0.3257^*	0.3135^*
C_0	0.2964^-	0.2894^+	0.2823^+
$C_{\nu_{07}}$	0.2968^*	0.2875^*	0.2834^*
origin of ν_{07}	412.1485^*	409.9899^*	407.6047^*

* this work
\- [4]
\+ [5]

Experimental Setup

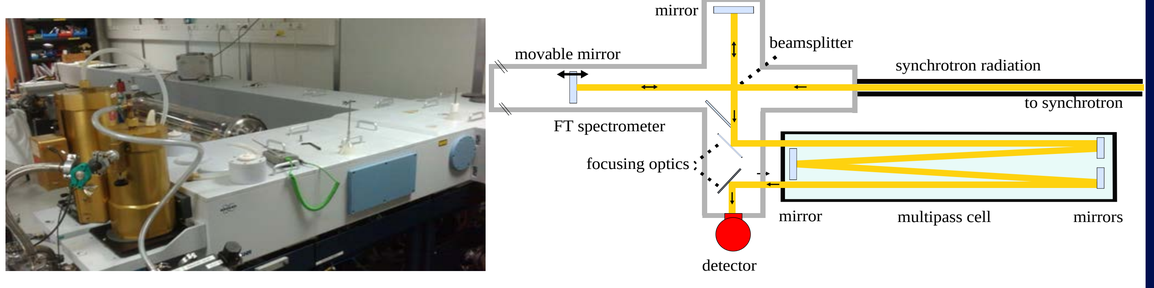

Figure 4: Spectrometer at SOLEIL beam line AILES and sketch of setup

- Bruker IFS 125HR FT spectrometer
- Spectral resolution 0.0001 cm^{-1}
- Radiation source: Synchrotron
- Optical pathway of 36 m

- Recorded frequency range: 70 cm^{-1} to 500 cm^{-1}

a. main isotopologue of DME
b. doubly ^{13}C substituted isotopologue of DME
c. singly ^{13}C substituted isotopologue of DME

Conclusion and Future Prospects

- We obtained the first experimental data of a pure singly ^{13}C and doubly ^{13}C substituted DME in the infrared from 70 cm^{-1} to 500 cm^{-1} with superb signal to noise ratio.
- We could assign the modes ν_{07} and ν_{15}. These data are highly on demand to verify state of the art *ab initio* calculations.
- Further investigation:
  - Pertubations (eg. overlap of ν_{07} and (ν_{11} , ν_{15}) = (11) or (20) or (02)
  - Anomality of Q branch origins for ν_{07} = 1, in singly substituted DME (possible interaction with ν_{11} centered at 421 cm^{-1}).
- Testbed for quantum chemical models and programs like BELGI [8] and TROVE [9].

Further meassurements of singly and doubly ^{13}C substituted DME at Kassel

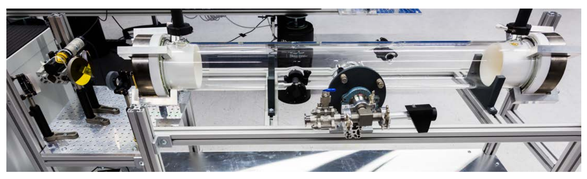

Figure 7: New built multipass spectrometer at Kassel

- Bruker VERTEX 80 FT spectrometer
- Spectral resolution 0.075 cm^{-1}
- Multipass cell, optical base length 1 m

References

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