Computer-Kemi: Tidlige visioner og moderne anvendelser

NSM, 14. februar 2014

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Program

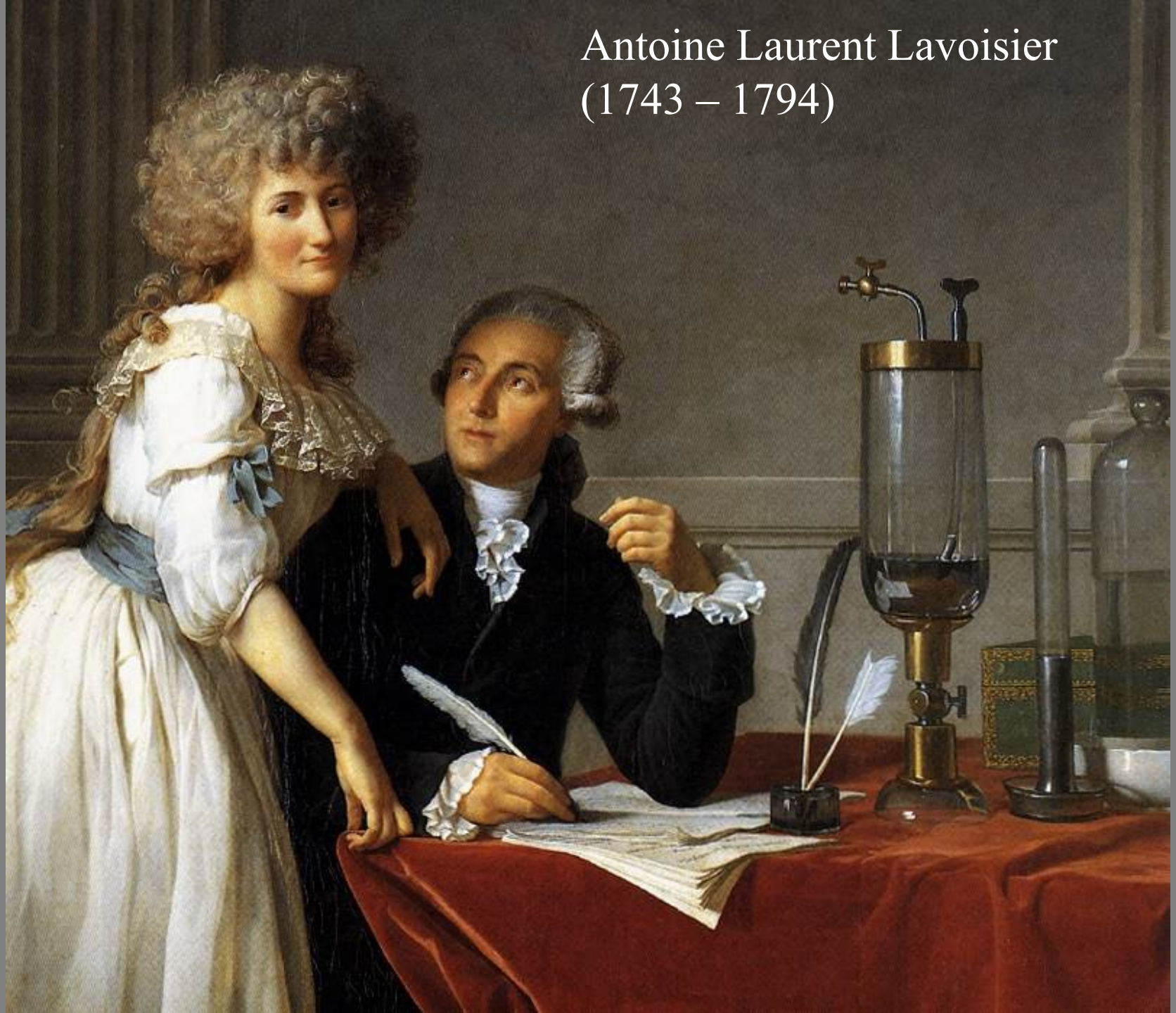
1) Kort kulturhistorisk tilbageblik

   Anvendelser af ”Computer Kemi”:

2) Strukturen af thiodibenzoylmethans fotoprodukt

3) Molekylstruktur af thiosulfonat *S*-estere

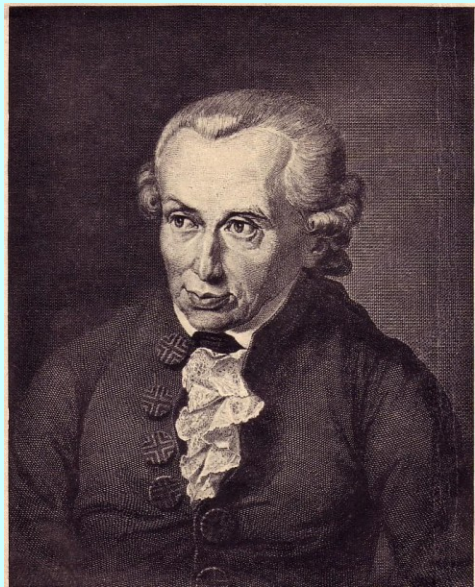
Paulze Lavoisier. Sculp.


Antoine Laurent Lavoisier
(1743 – 1794)

"Så længe vi ikke kender lovene for vekselvirkningerne mellem de kemiske stoffers bestanddele (en indsigt vi nok næppe nogensinde vil opnå), så vil kemi aldrig blive mere end et praktisk eksperimentelt fag.
"Kemien vil aldrig blive en egentlig naturvidenskab, fordi den vil være rent empirisk. En dybere forståelse vil være uopnåelig, fordi matematik ikke kan anvendes."

(forkortet og oversat af JS-L)

Immanuel Kant (1786)
Metaphysische Anfangsgründe der Naturwissenschaft,
Hartknoch, Leipzig



”Alle forsøg på at anvende matematiske metoder i løsningen af kemiske spørgsmål må betragtes, nu og i al fremtid, som totalt fornuftsstridige og i modsætning til kemiens væsen […]

”Hvis matematisk analyse nogensinde skulle få en fremtrædende plads i kemien – en vildfarelse der heldigvis er nærmest utænkelig – så vil det medføre en total undergang af kemien som videnskab”

(forkortet og oversat af JS-L)

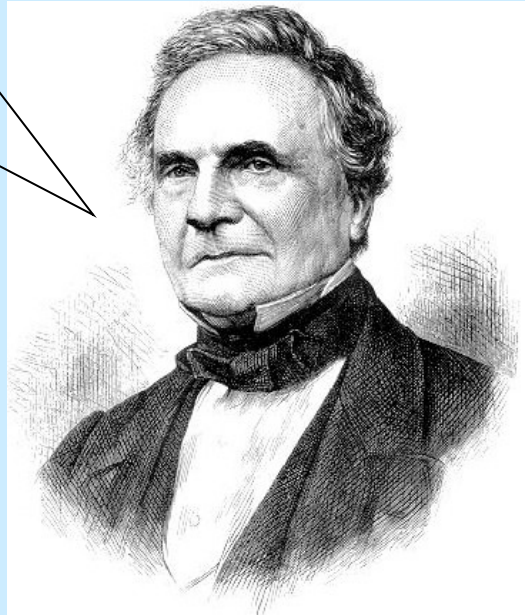
Auguste Comte (1830)

Cours de philosophie positive

Schleicher, Paris

”Hele kemien, og med den krystallografien, vil blive genstand for matematisk analyse […] som vil sætte os i stand til at forudsige egenskaberne af en hvilken som helst ny kemisk forbindelse, og muligvis også hvorledes denne forbindelse kan fremstilles”

(oversættelse JS-L)



Charles Babbage (1838)

Quoted in Faster than Thought, B. V. Bowden, ed.,

Sir Isaac Pitman & Sons, Ltd, London, 1953, p 12.

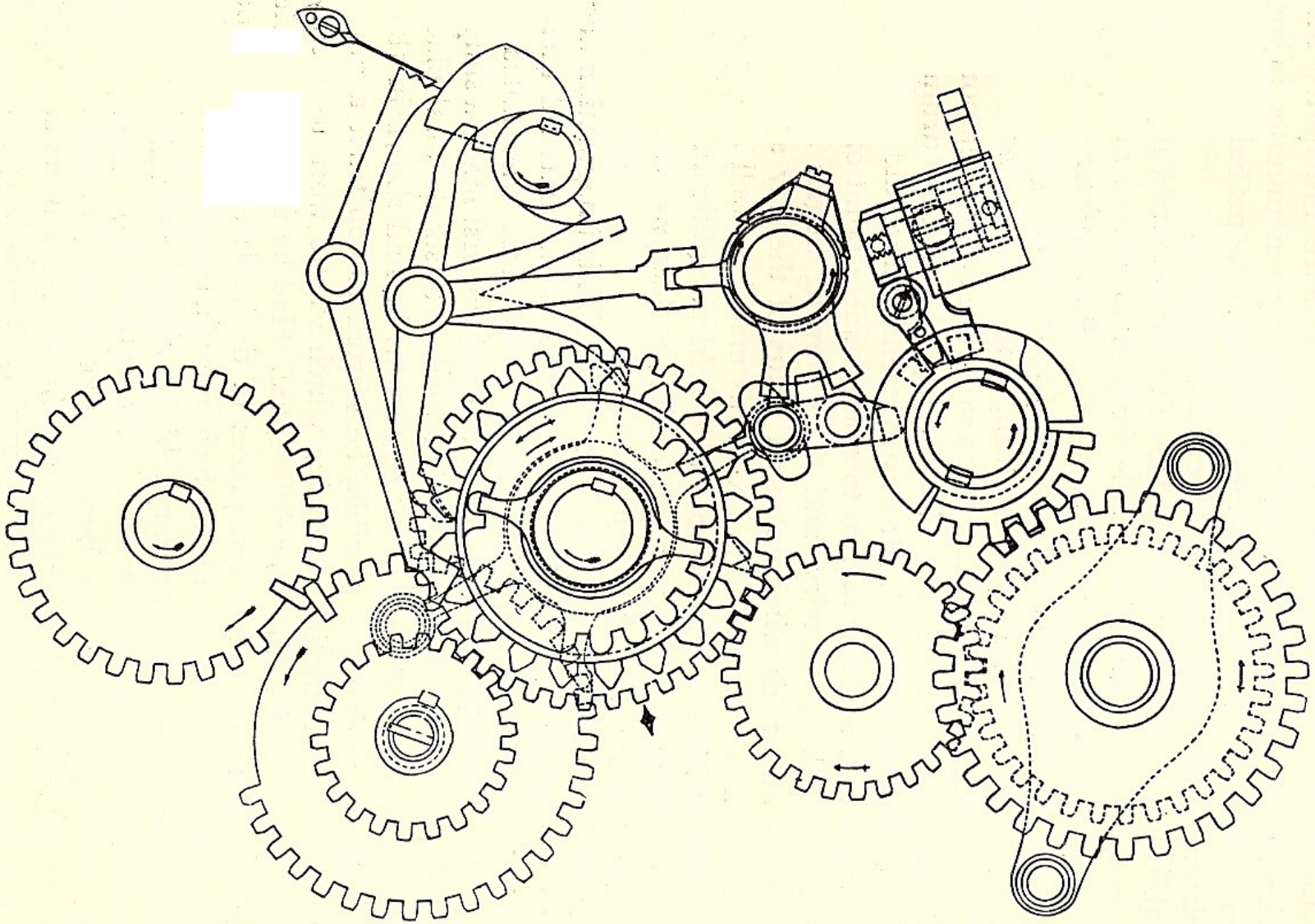
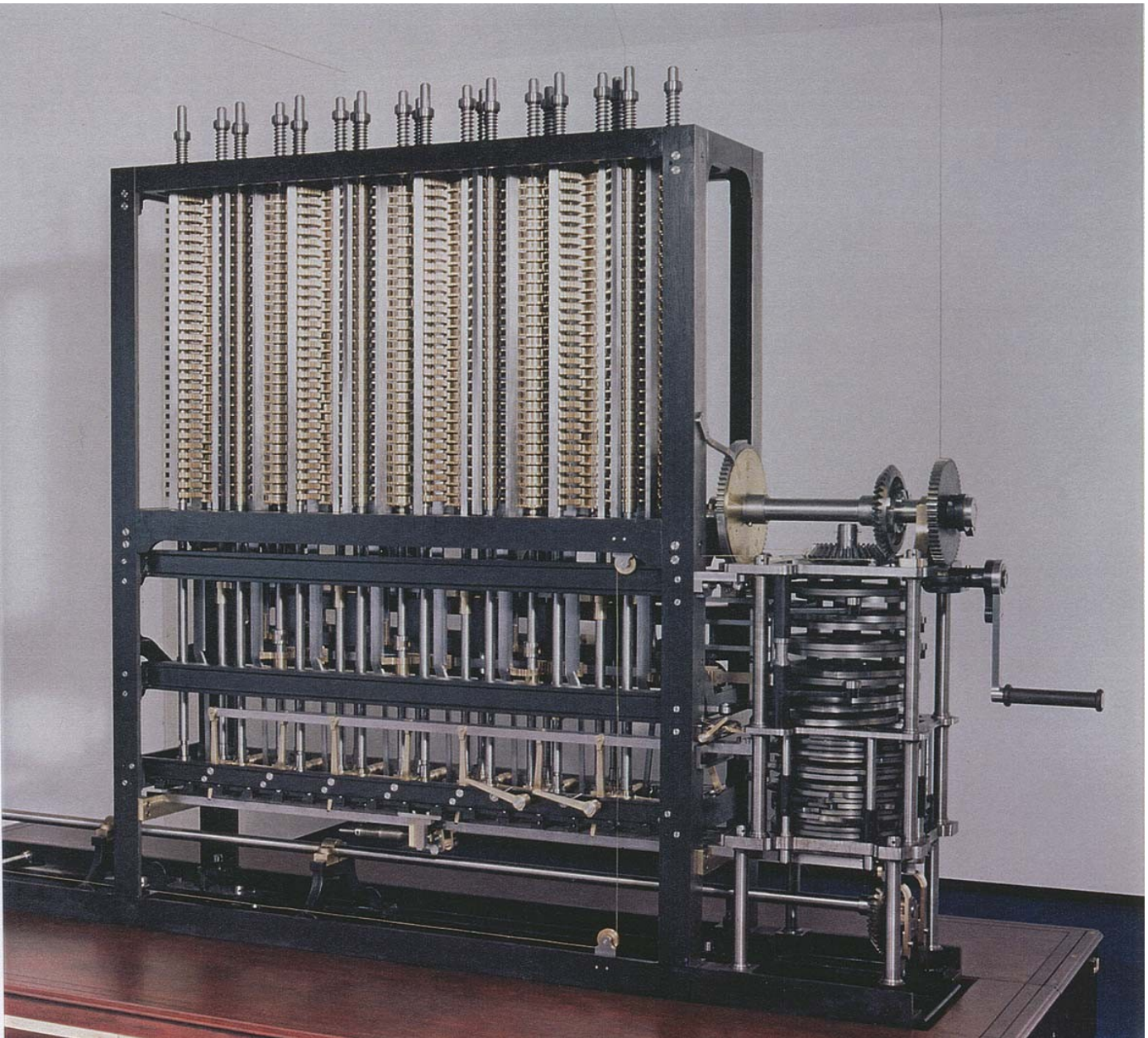
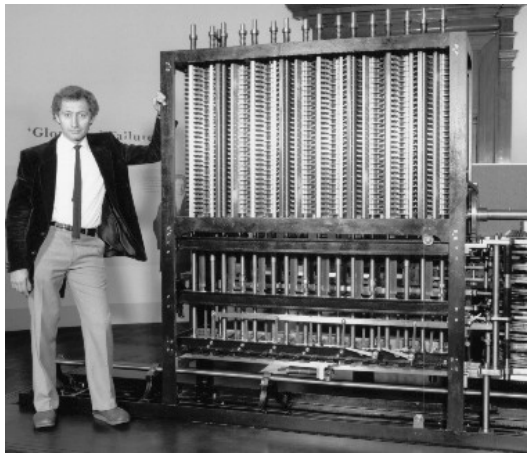


FIG. 1/1. One of Babbage's drawings of part of his engine

Charles Babbage's "Difference Engine No. 2"



Complete replica at the *London Science Museum,* constructed in 1991 from the drawings left behind by Babbage



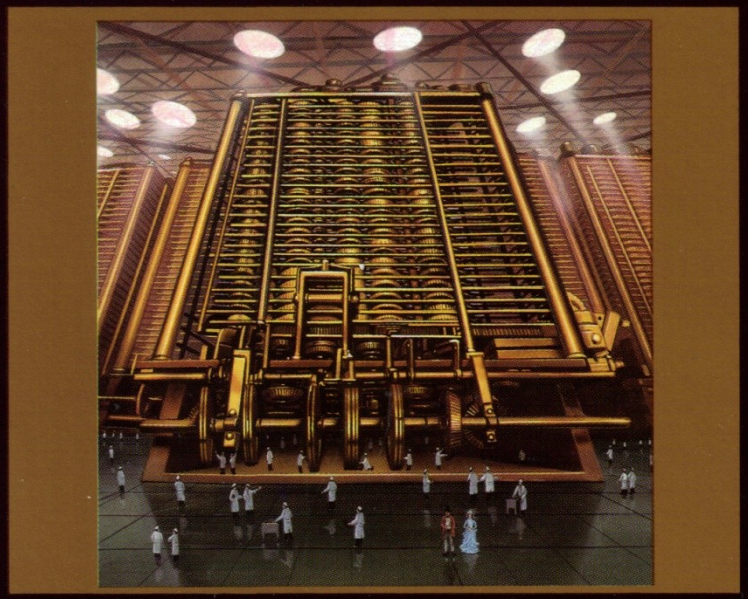
WILLIAM GIBSON

AUTHOR OF VIRTUAL LIGHT

BRUCE STERLING

AUTHOR OF HOLY FIRE

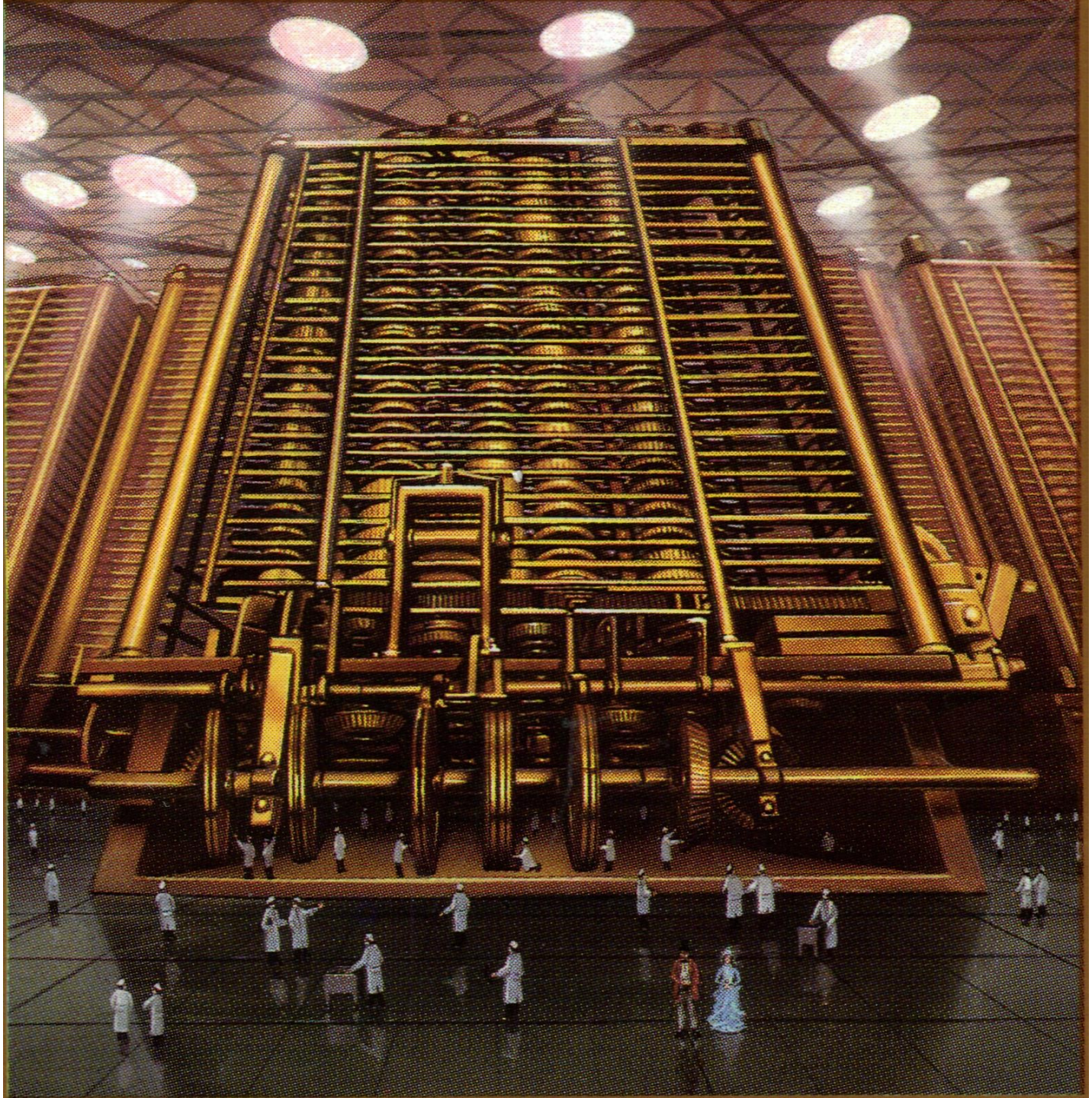
BANTAM BOOKS ®



THE DIFFERENCE ENGINE

"BREATHTAKING." —THE NEW YORK TIMES BOOK REVIEW

SPECTRA SPECIAL EDITIONS



Frontispiece

ADA AUGUSTA
The Countess of Lovelace

Øyvind Burrau: ”Berechnung des Energiewertes des Wasserstoffmolekel-Ions (H_2^+) im Normalzustand”, *Kgl. Danske Vid. Selsk. Math.-fys. Medd.* **7**, 3-18 (1927)

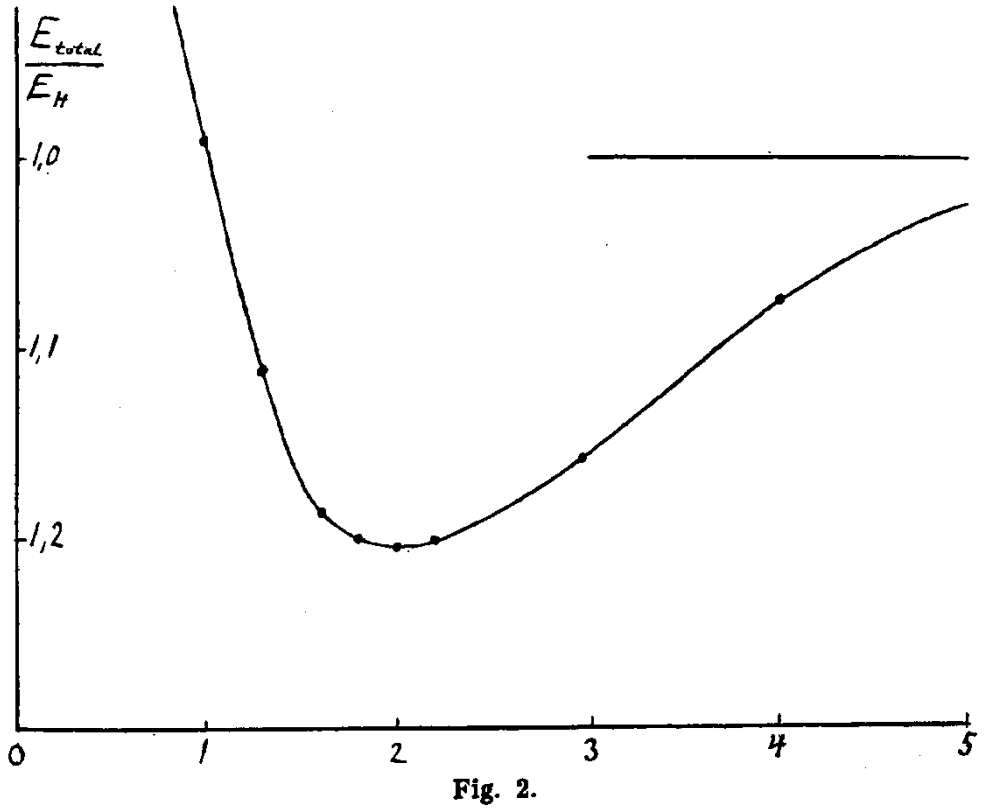


Fig. 2.

Øyvind Burrau: ”Berechnung des Energiewertes des Wasserstoffmolekel-Ions (H_2^+) im Normalzustand”, *Kgl. Danske Vid. Selsk. Math.-fys. Medd.* **7**, 3-18 (1927)

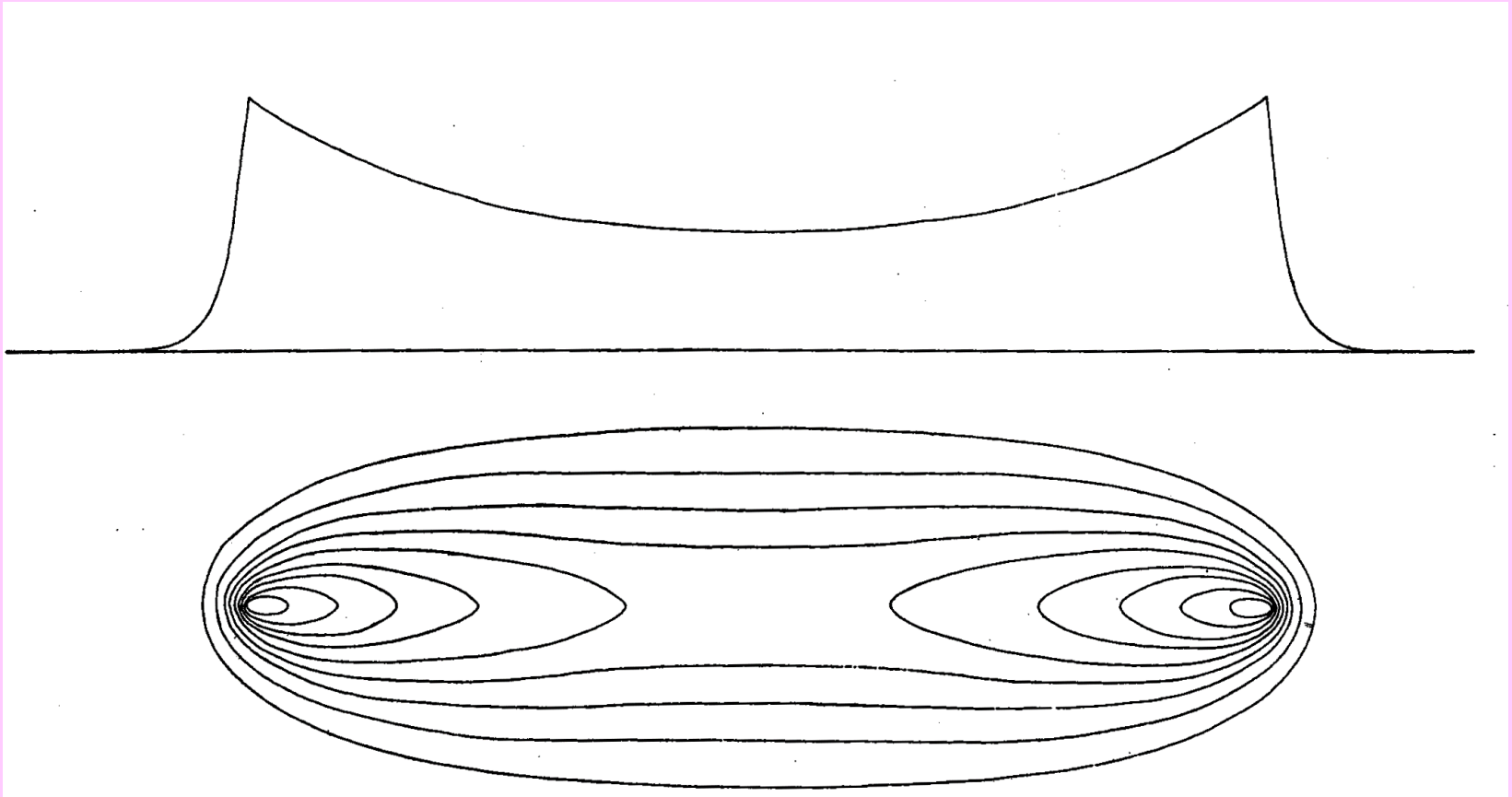
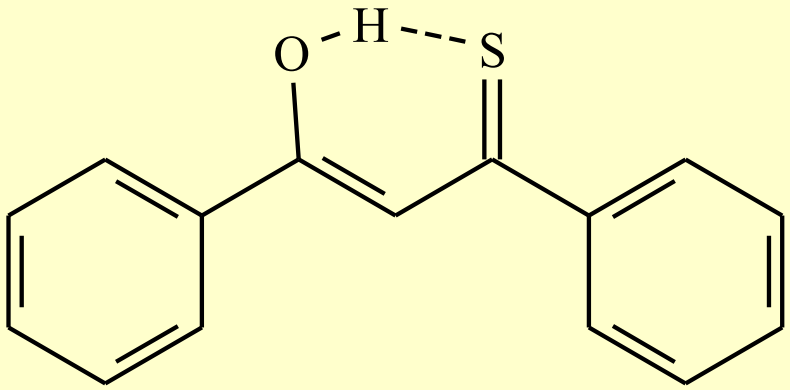
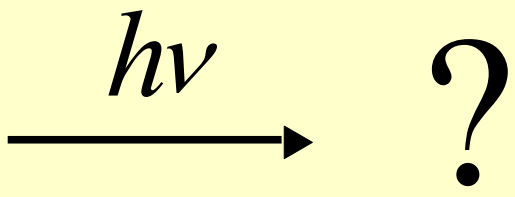


Fig. 3.

Fotoproduktet af thiodibenzoylmethan (TDBM)



TDBM



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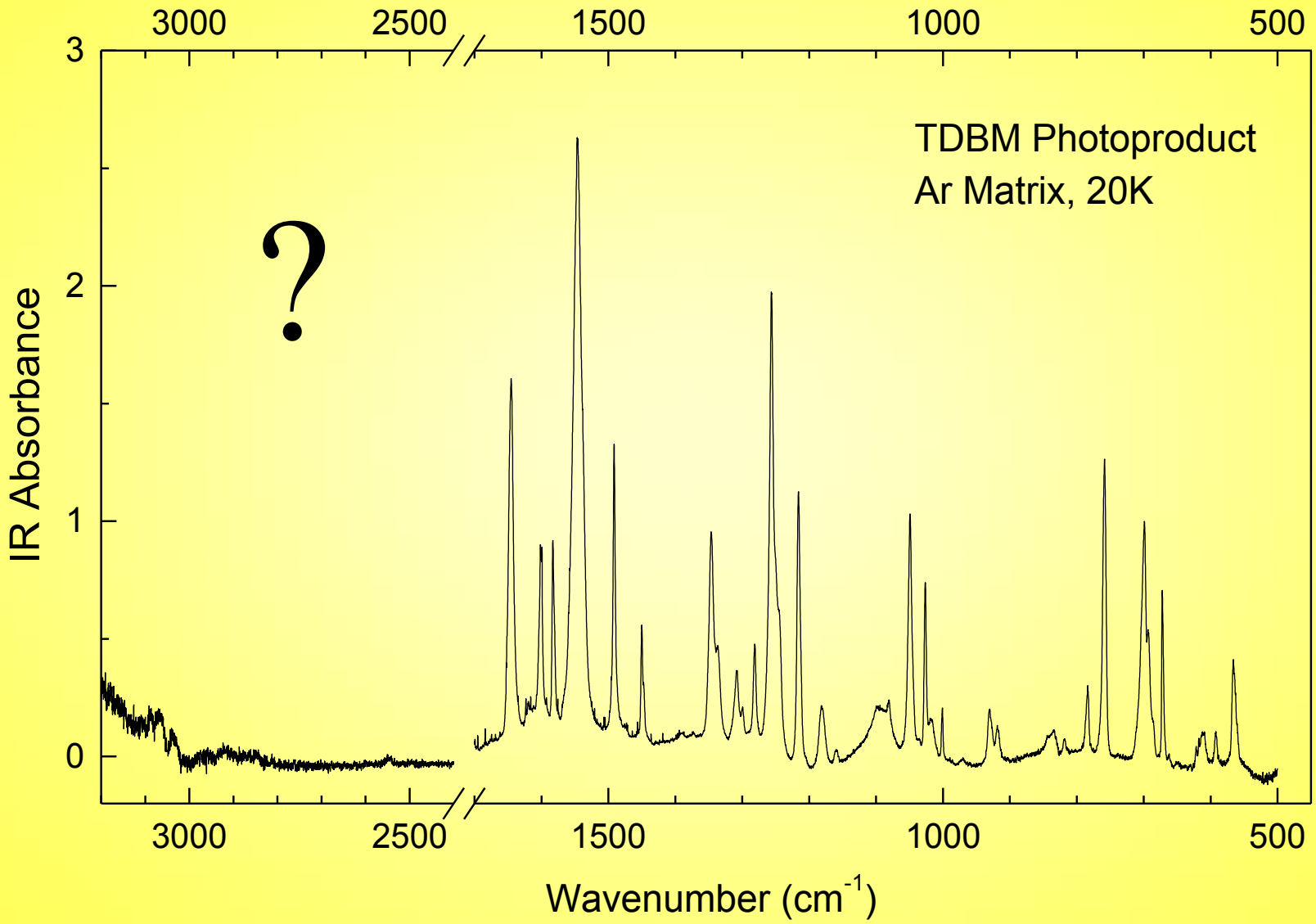
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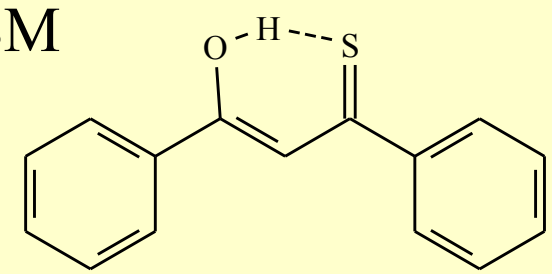
TDBM Photoproduct
Ar Matrix, 20K
Wavenumber (cm-1)

TDBM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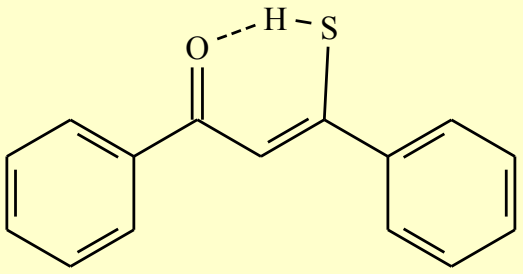
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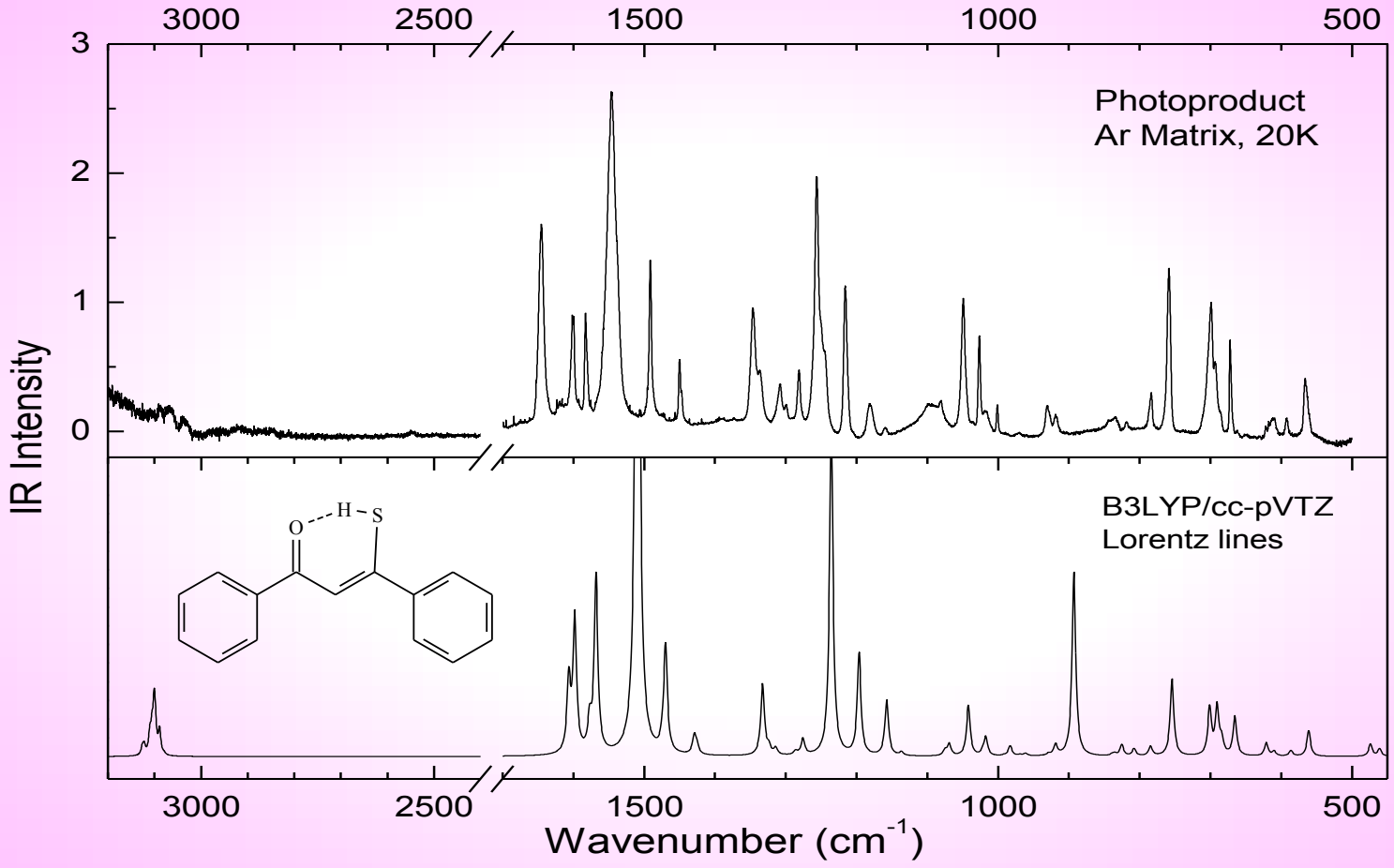
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Photoproduct
Ar Matrix, 20K
B3LYP/cc-pVTZ
Lorentz lines
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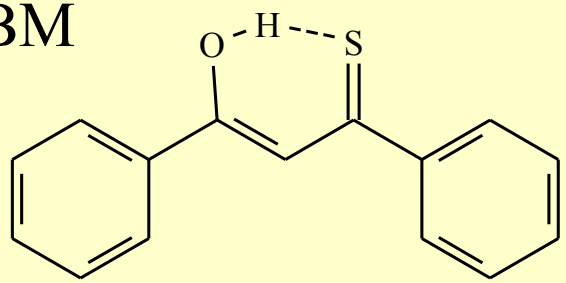
Wavenumber (cm-1)
t-CCC

TDBM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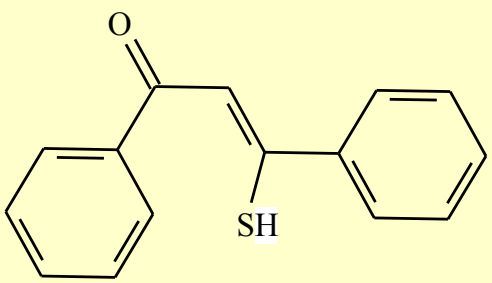
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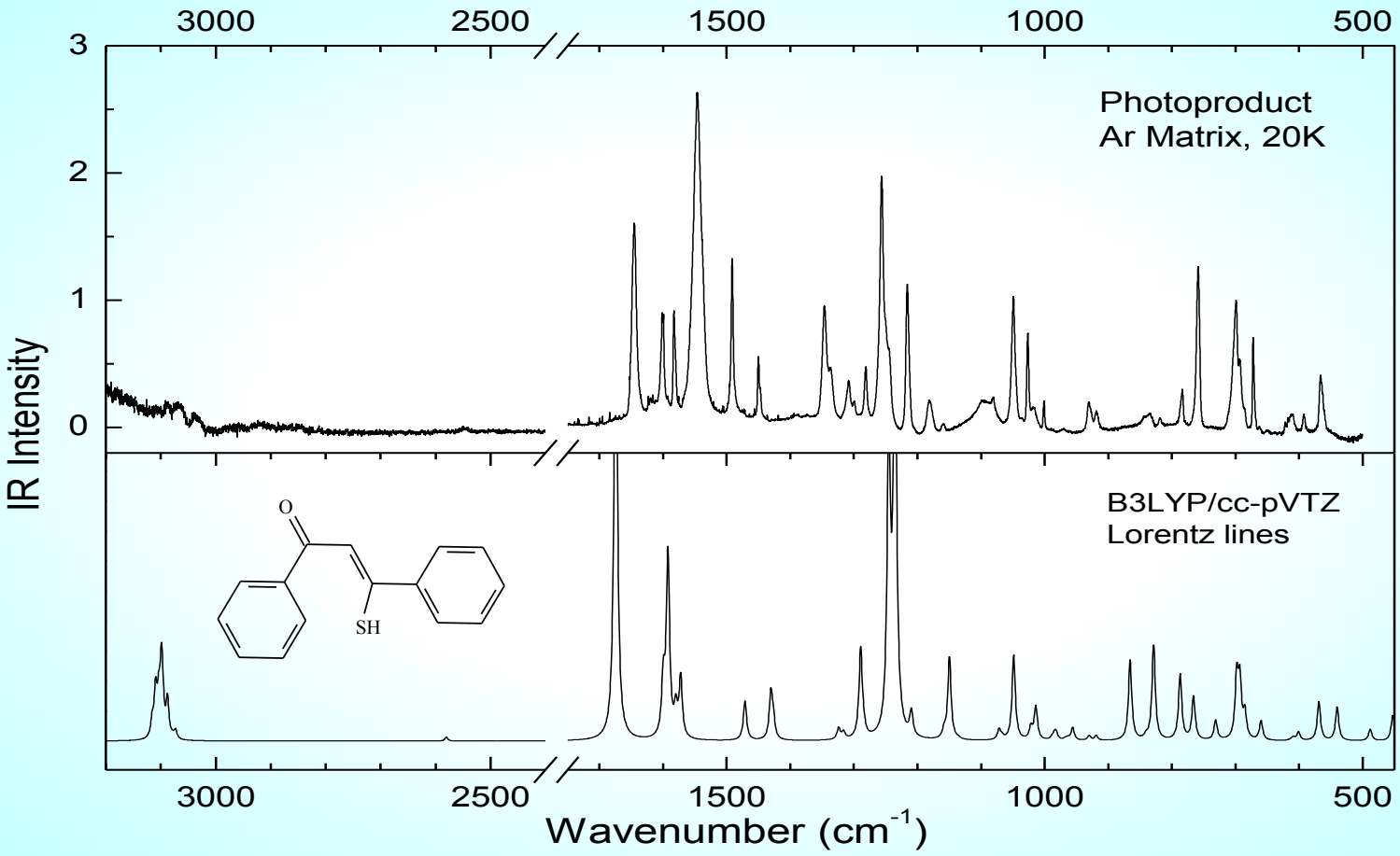
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Ar Matrix, 20K
B3LYP/cc-pVTZ
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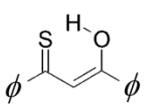
Wavenumber (cm-1)
t-TCT

Enol configurations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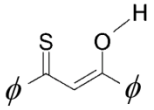
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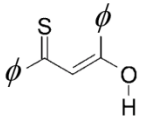
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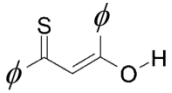
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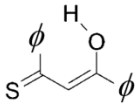
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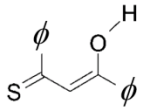
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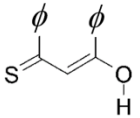
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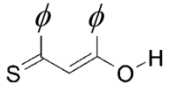
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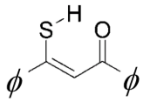
Thiol configurations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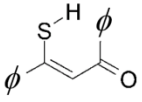
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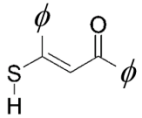
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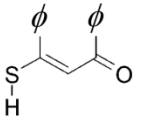
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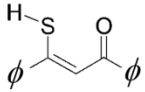
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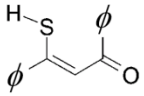
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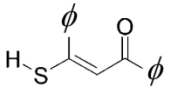
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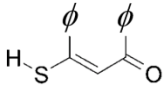
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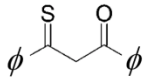
Diketo configurations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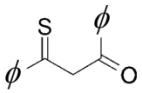
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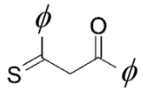
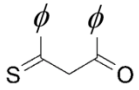

d-TC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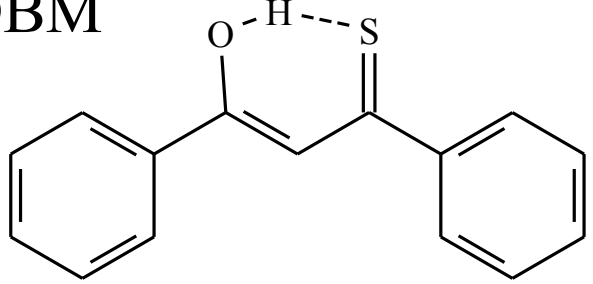
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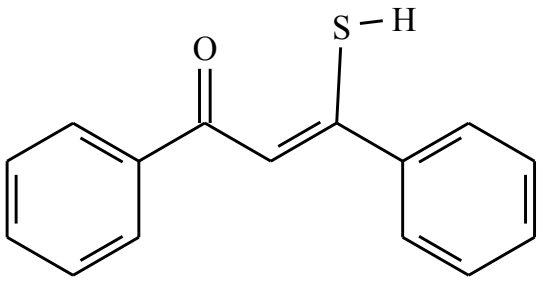
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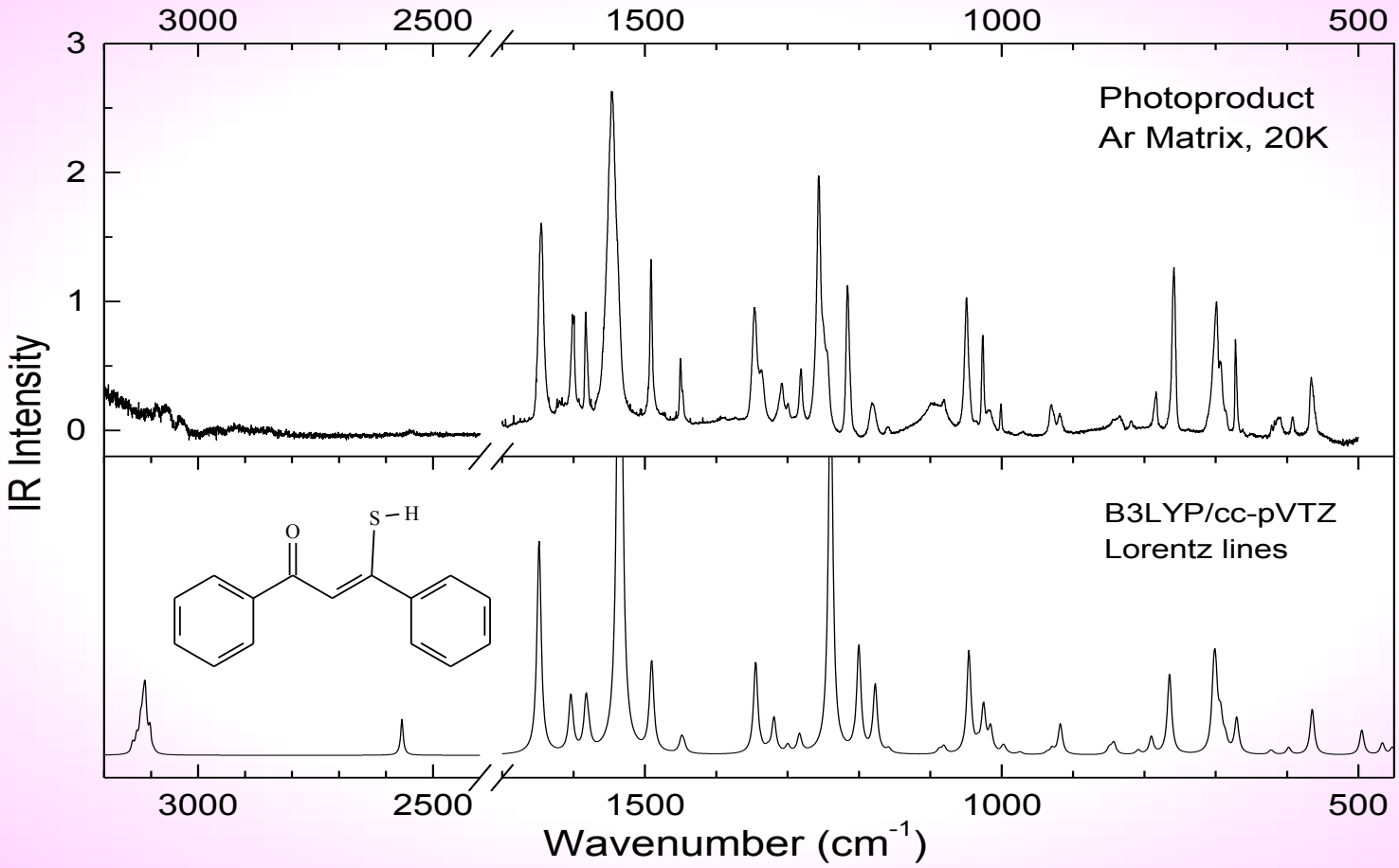
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IR Intensity
Photoproduct
Ar Matrix, 20K
B3LYP/cc-pVTZ
Lorentz lines
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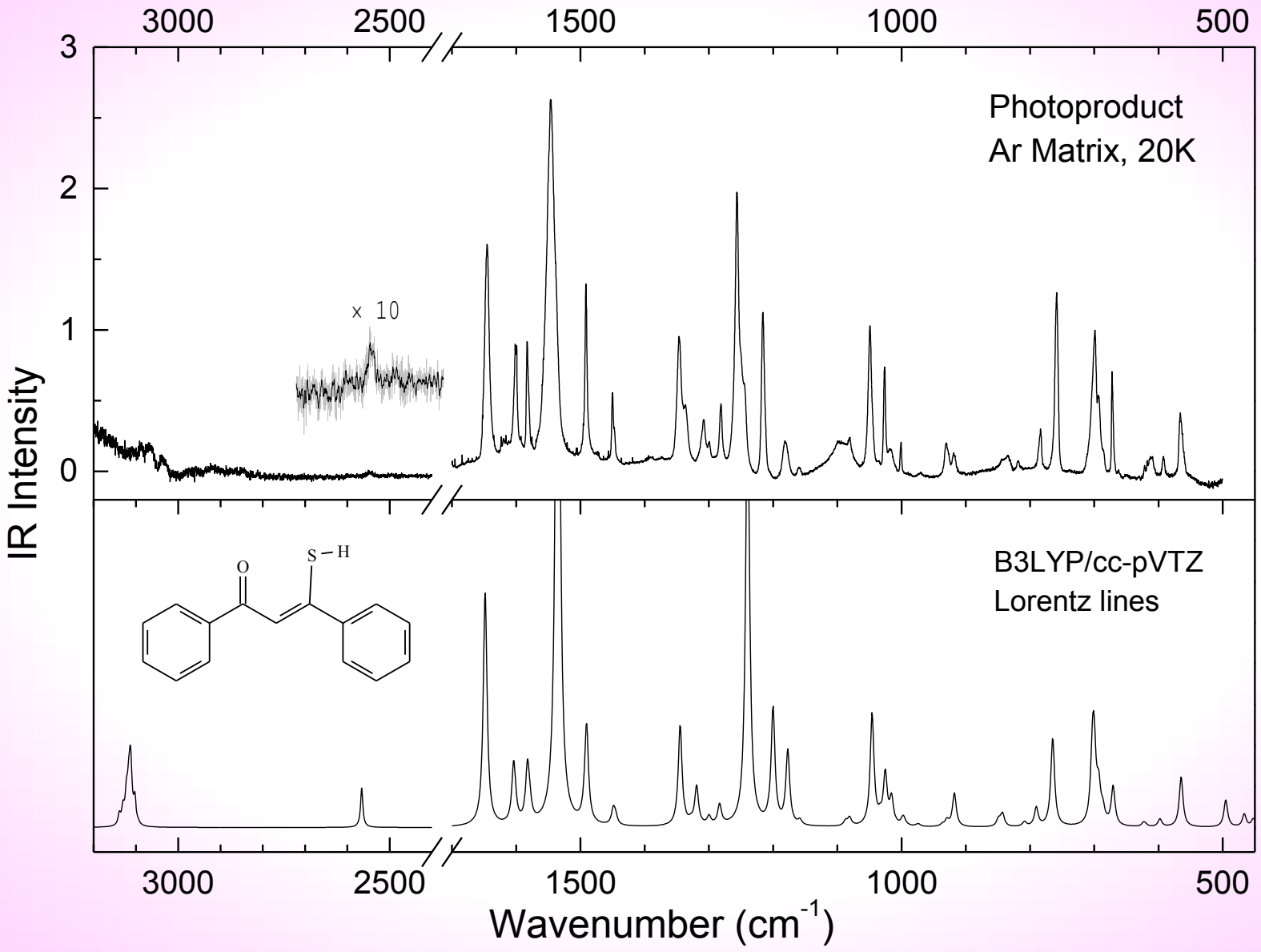
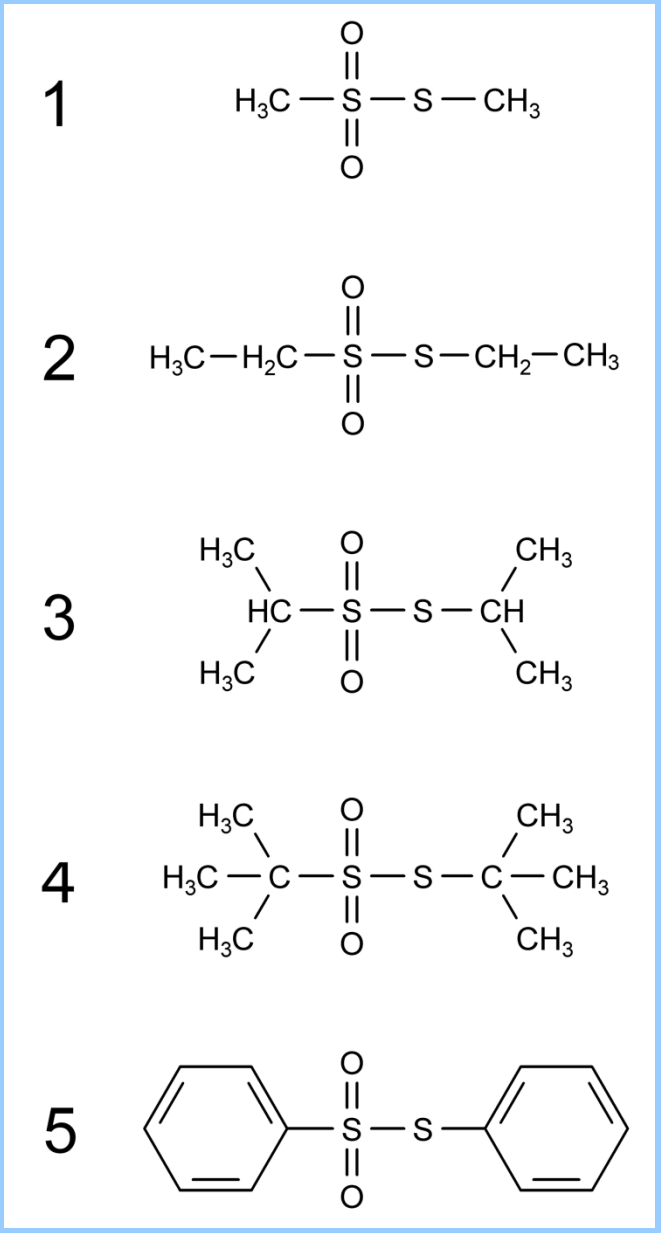
Wavenumber (cm-1)

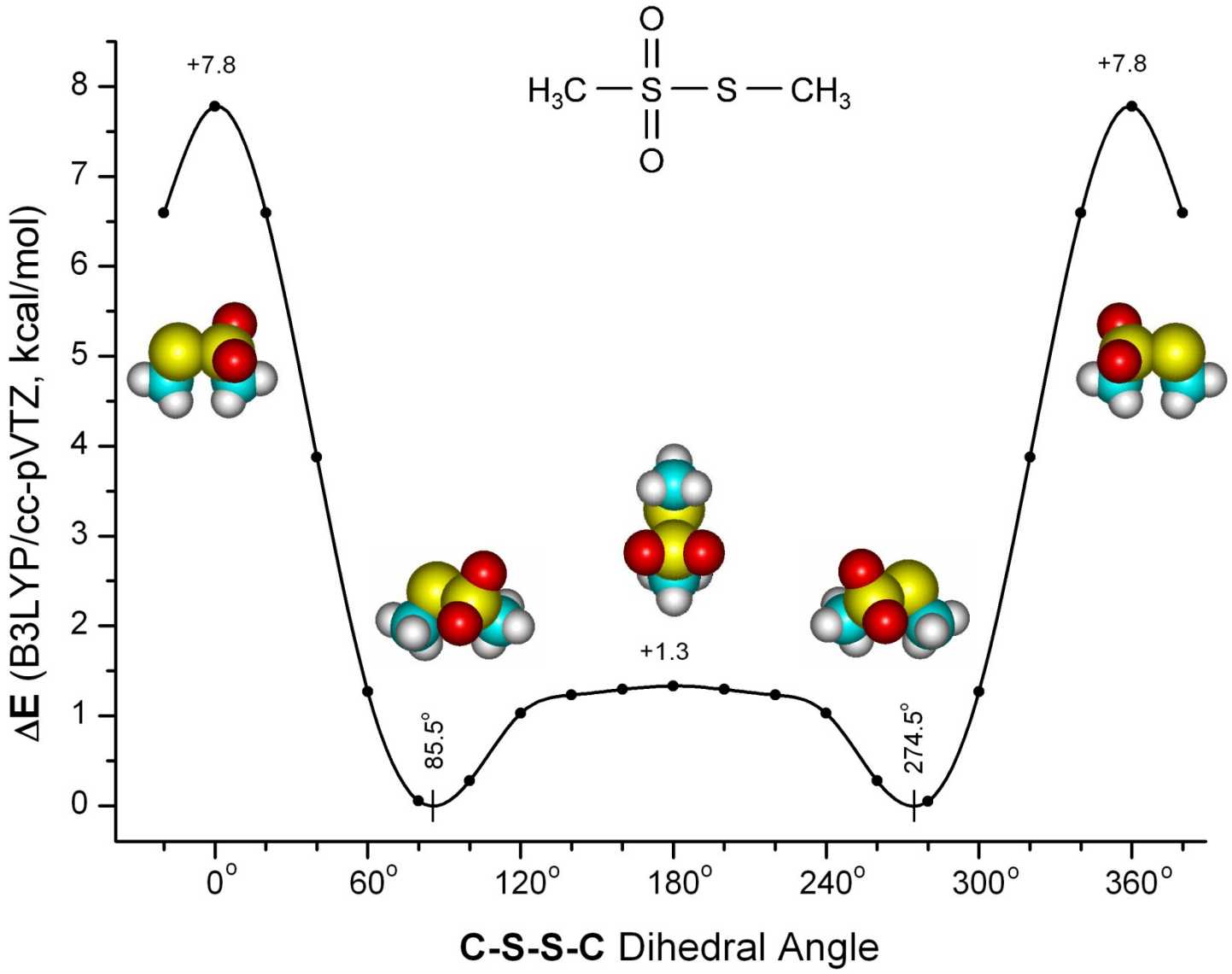
Bjarke K. V. Hansen *et al*., *Vibrational Spectroscopy* (2007)



Molecular and vibrational structure of thiosulfonate *S*-esters

T.X.T. Luu, F. Duus, J. Spanget-Larsen
J. Mol. Struct. 2013




O
H3C — S — S — CH3
O
+7.8
+7.8
+1.3
85.5°
274.5°
ΔE (B3LYP/cc-pVTZ, kcal/mol)
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1
2
3
4
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6
7
8
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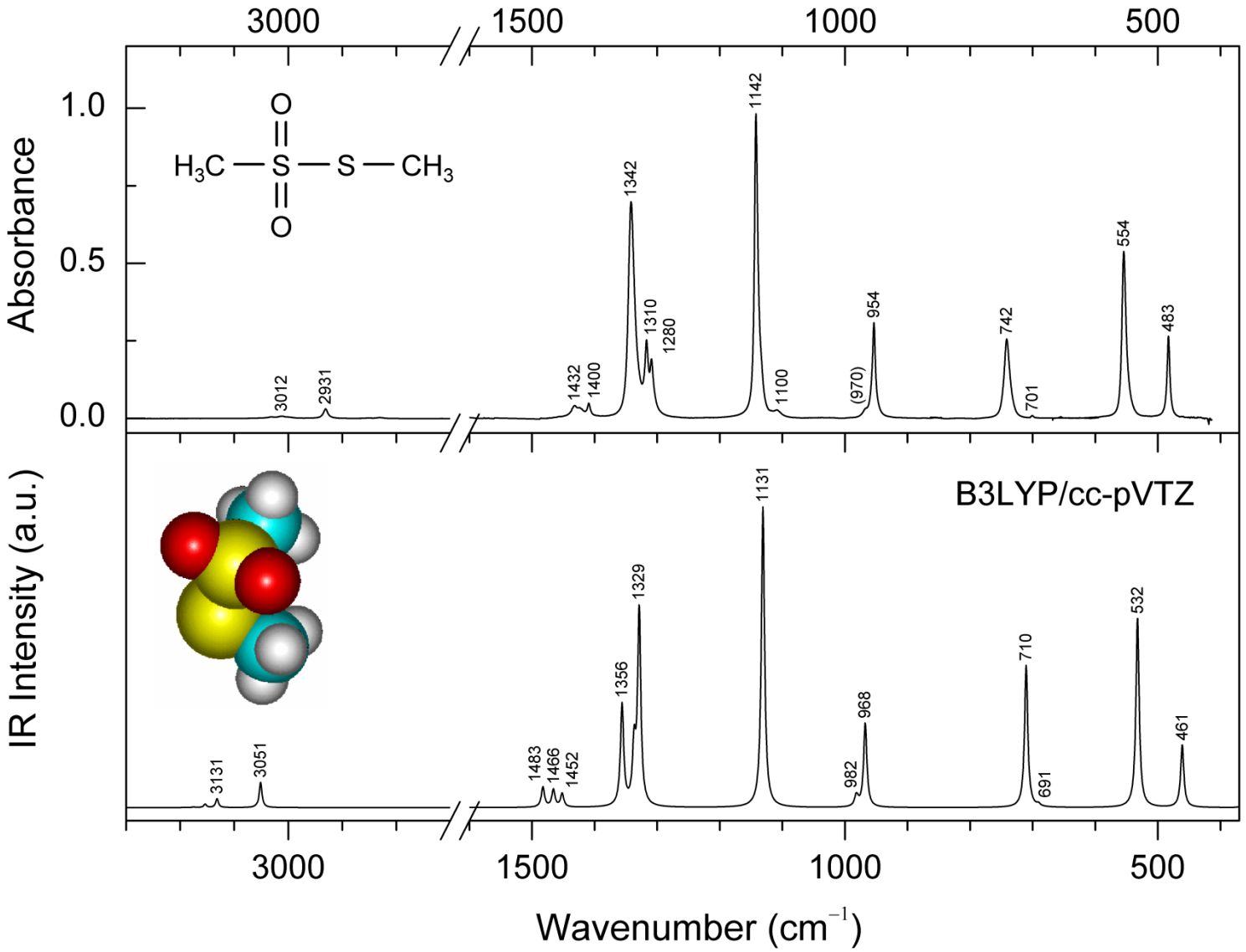
60°
120°
180°
240°
300°
360°
C-S-S-C Dihedral Angle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Absorbance
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H3C — S — S — CH3
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1432
1400
1342
1310
1280
1142
1100
(970)
954
742
701
554
483
B3LYP/cc-pVTZ
IR Intensity (a.u.)
3131
3051
1483
1466
1452
1356
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1131
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968
710
691
532
461
3000
1500
1000
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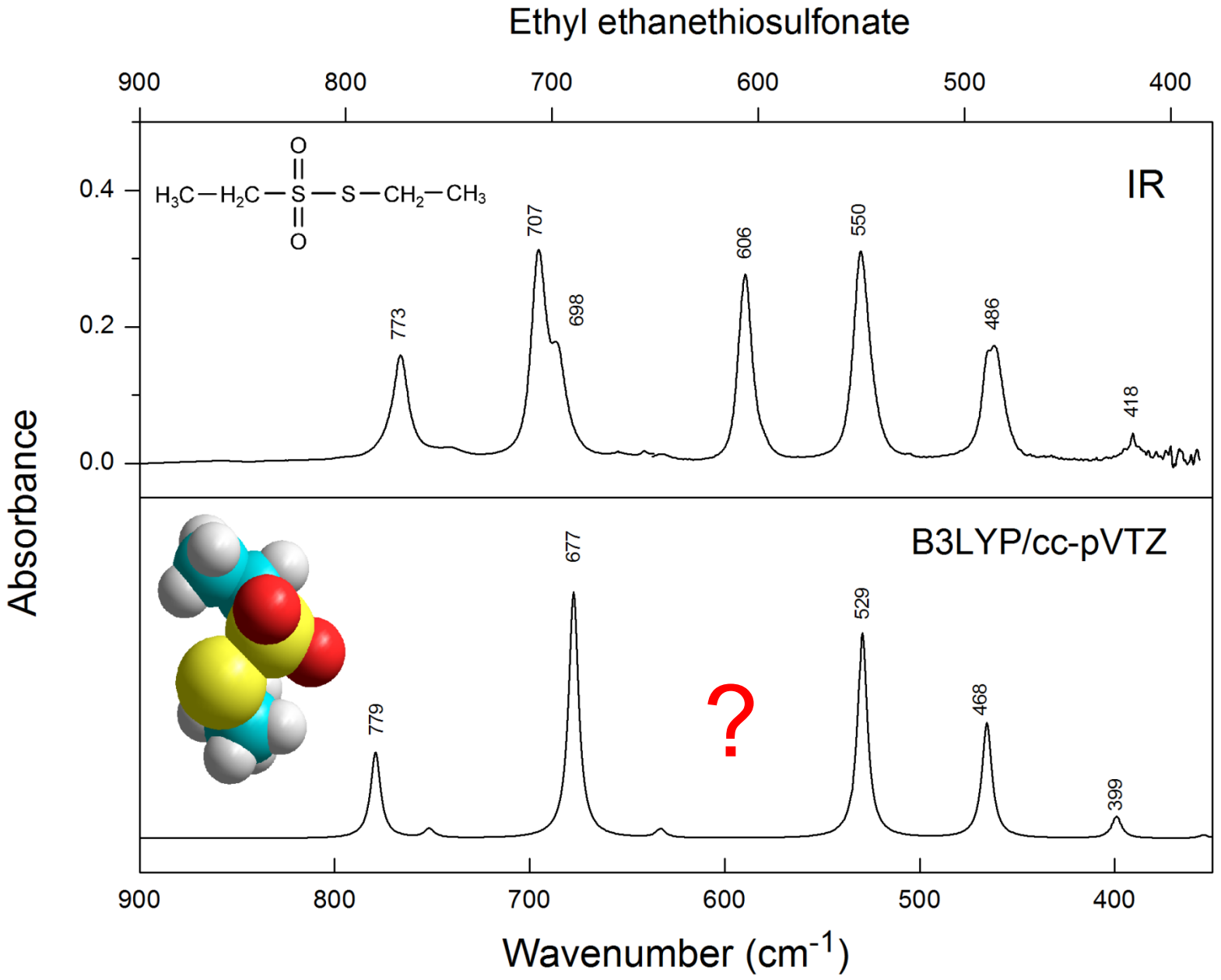
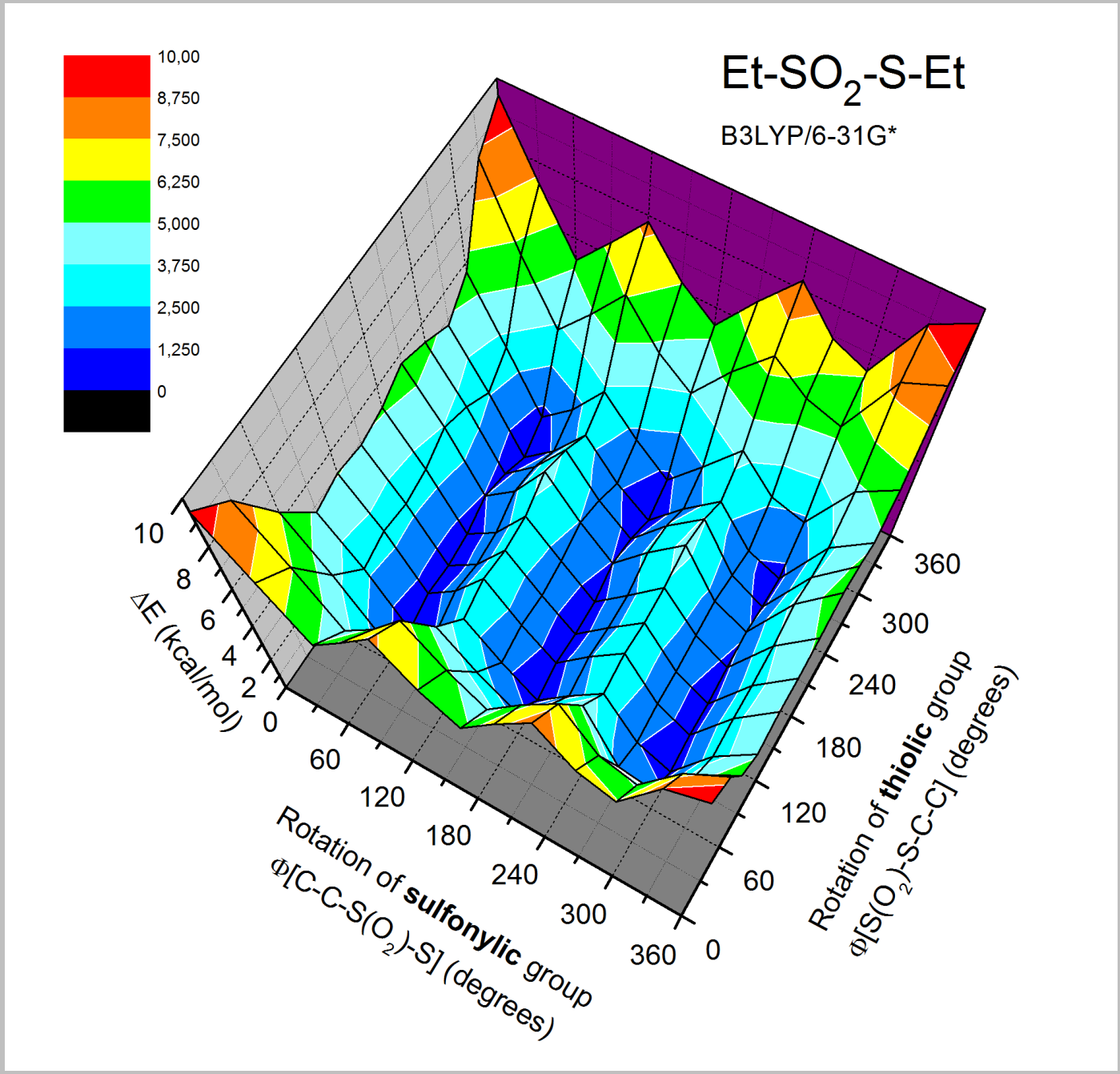
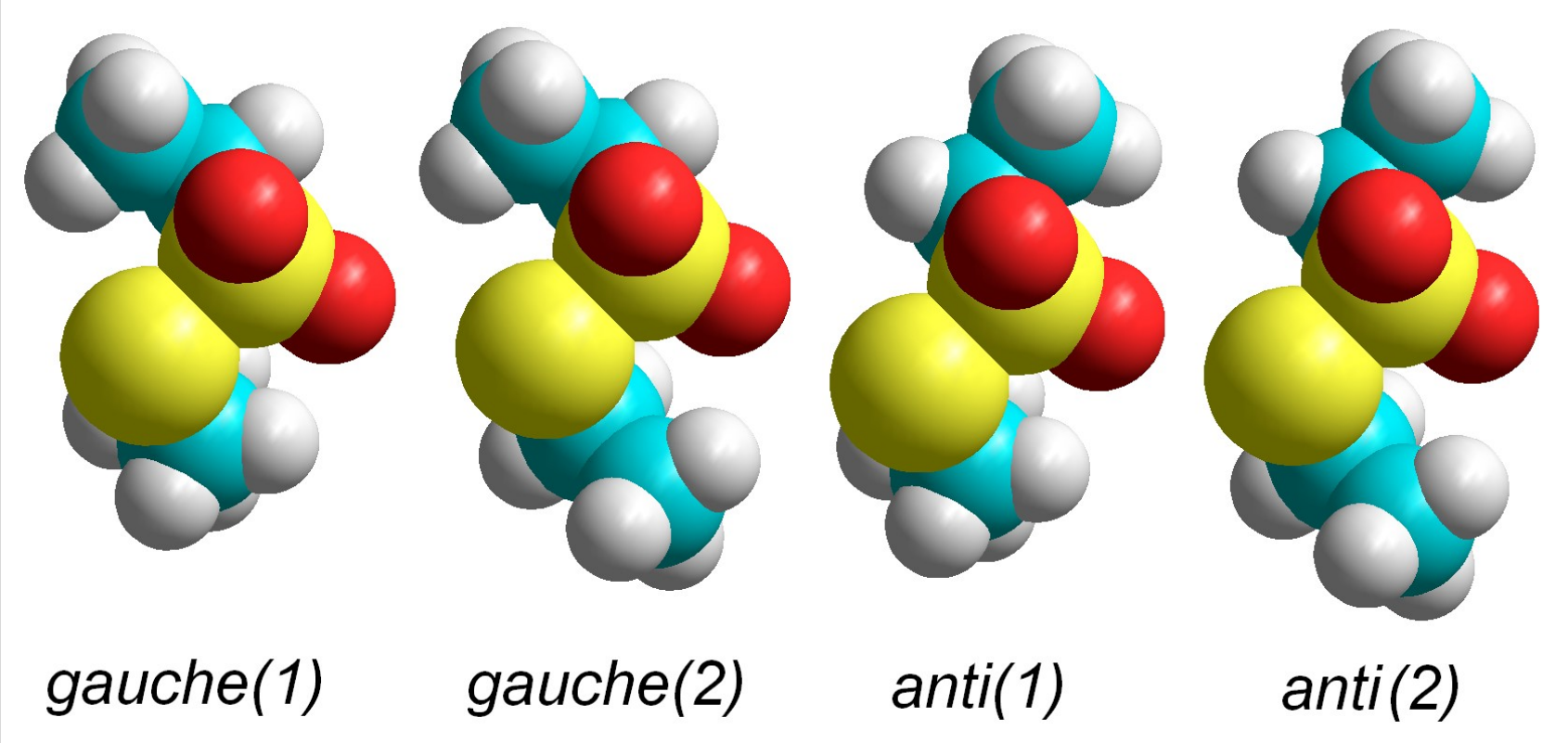
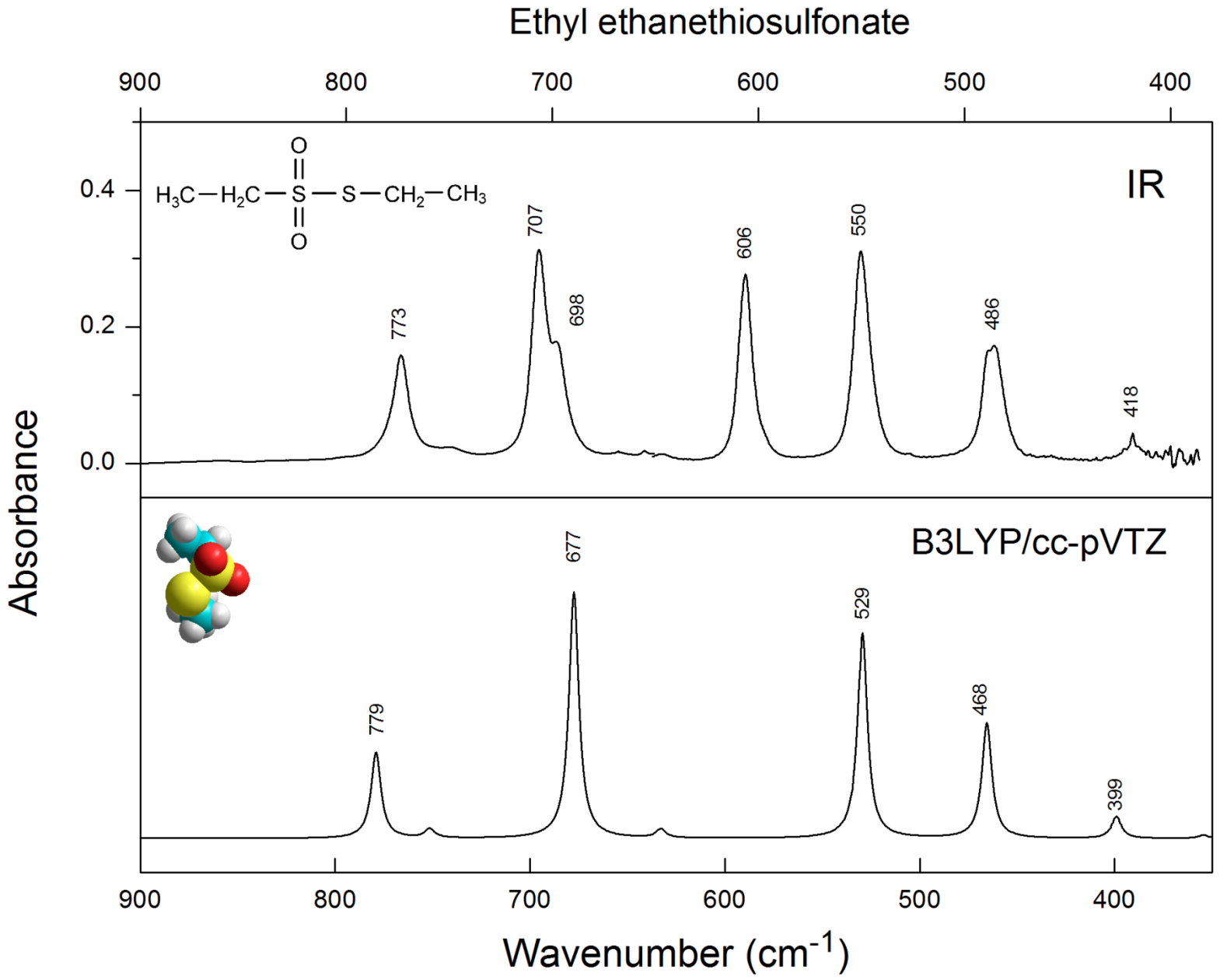
Wavenumber (cm−1)

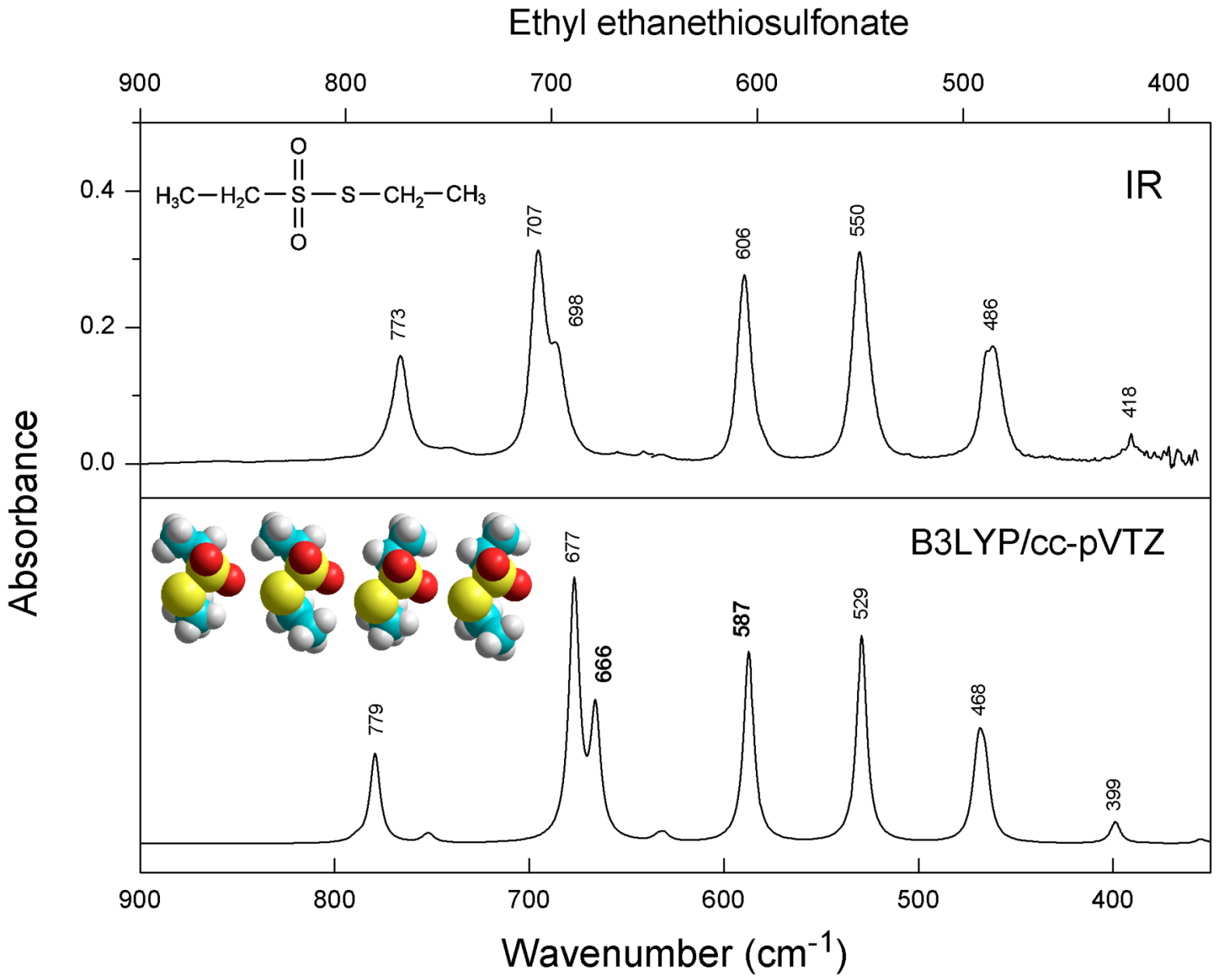

Ethyl ethanethiosulfonate
900
800
700
600
500
400
0.4
0.2
0.0
Absorbance
IR
773
707
698
606
550
486
418
B3LYP/cc-pVTZ
779
677
529
468
399
?
Wavenumber (cm-1)

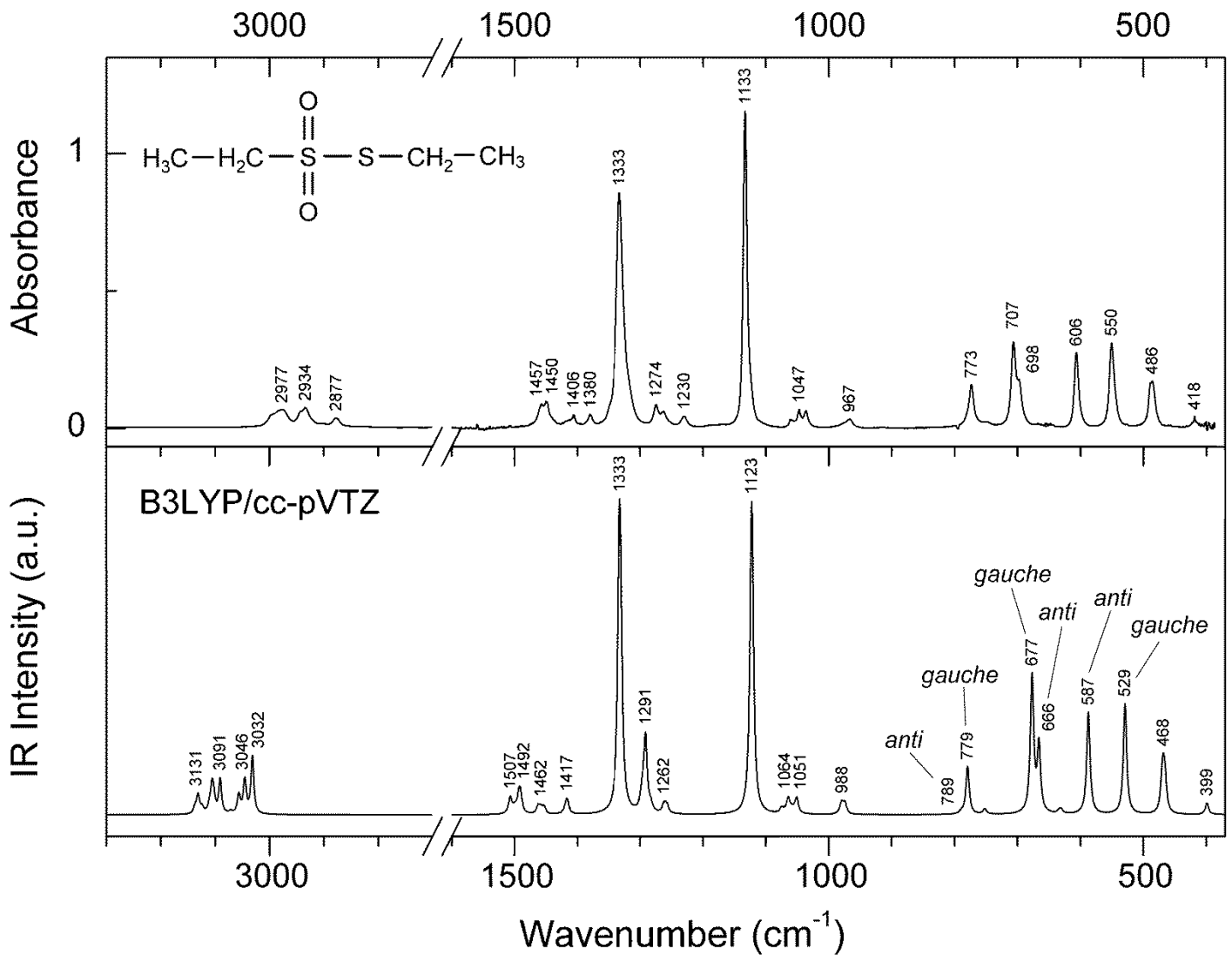

Et-SO2-S-Et
B3LYP/6-31G*
10,00
8,750
7,500
6,250
5,000
3,750
2,500
1,250
0
ΔE (kcal/mol)
10
8
6
4
2
0
Rotation of sulfonylic group
Φ[C-C-S(O2)-S] (degrees)
0
60
120
180
240
300
360
Rotation of thiolic group
Φ[S(O2)-S-C-C] (degrees)
0
60
120
180
240
300
360

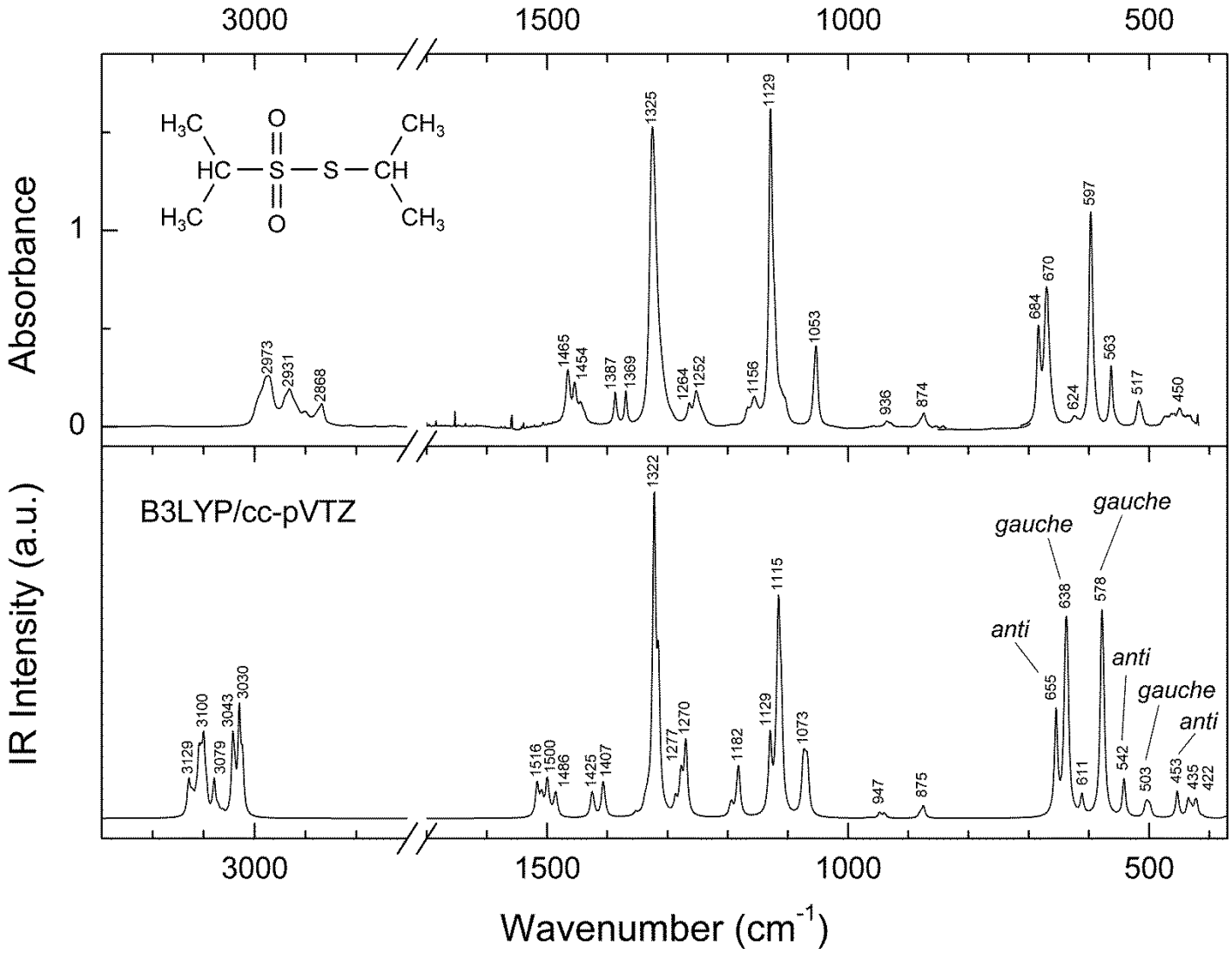
The four rotamers with lowest energy




Ethyl ethanethiosulfonate
900
800
700
600
500
400
0.4
0.2
0.0
Absorbance
IR
773
707
698
606
550
486
418
B3LYP/cc-pVTZ
779
677
529
468
399
Wavenumber (cm-1)


Ethyl ethanethiosulfonate
IR
B3LYP/cc-pVTZ
Absorbance
Wavenumber (cm-1)
900
800
700
600
500
400
0.4
0.2
0.0
773
707
698
606
550
486
418
779
677
666
587
529
468
399


3000
1500
1000
500
Absorbance
1
0
$H_3C-H_2C-S(=O)(=O)-S-CH_2-CH_3$
2977
2934
2877
1457
1450
1406
1380
1333
1274
1230
1133
1047
967
773
707
698
606
550
486
418
B3LYP/cc-pVTZ
IR Intensity (a.u.)
3131
3091
3046
3032
1507
1492
1462
1417
1333
1291
1262
1123
1064
1051
988
anti
789
gauche
779
gauche
677
anti
666
anti
587
gauche
529
468
399
3000
1500
1000
500
Wavenumber (cm^{-1})


3000
1500
1000
500
Absorbance
1
0
2973
2931
2868
1465
1454
1387
1369
1325
1264
1252
1156
1129
1053
936
874
684
670
624
597
563
517
450
B3LYP/cc-pVTZ
IR Intensity (a.u.)
3129
3100
3079
3043
3030
1516
1500
1486
1425
1407
1322
1277
1270
1182
1129
1115
1073
947
875
655
638
611
578
542
503
453
435
422
gauche
gauche
anti
anti
gauche
anti
Wavenumber (cm-1)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IN TRANQUILLO MORS · IN FLUCTU VITA