# Ozone Photolysis: strong Isotopologue selectivity in the stratosphere.

F. Gatti[(1)], S. Ndengué[(3)], H.-D. Meyer[(2)], R. Jost[(3)].

(1) CTMM Institut Charles Gerhardt UMR-CNRS 5253
University of Montpellier, France

(2) Institute for Physical Chemistry
University of Heidelberg, Germany

(3) Laboratoire de Spectrométrie Physique
University of Grenoble, France

# Unusual isotopic constitution of Ozone

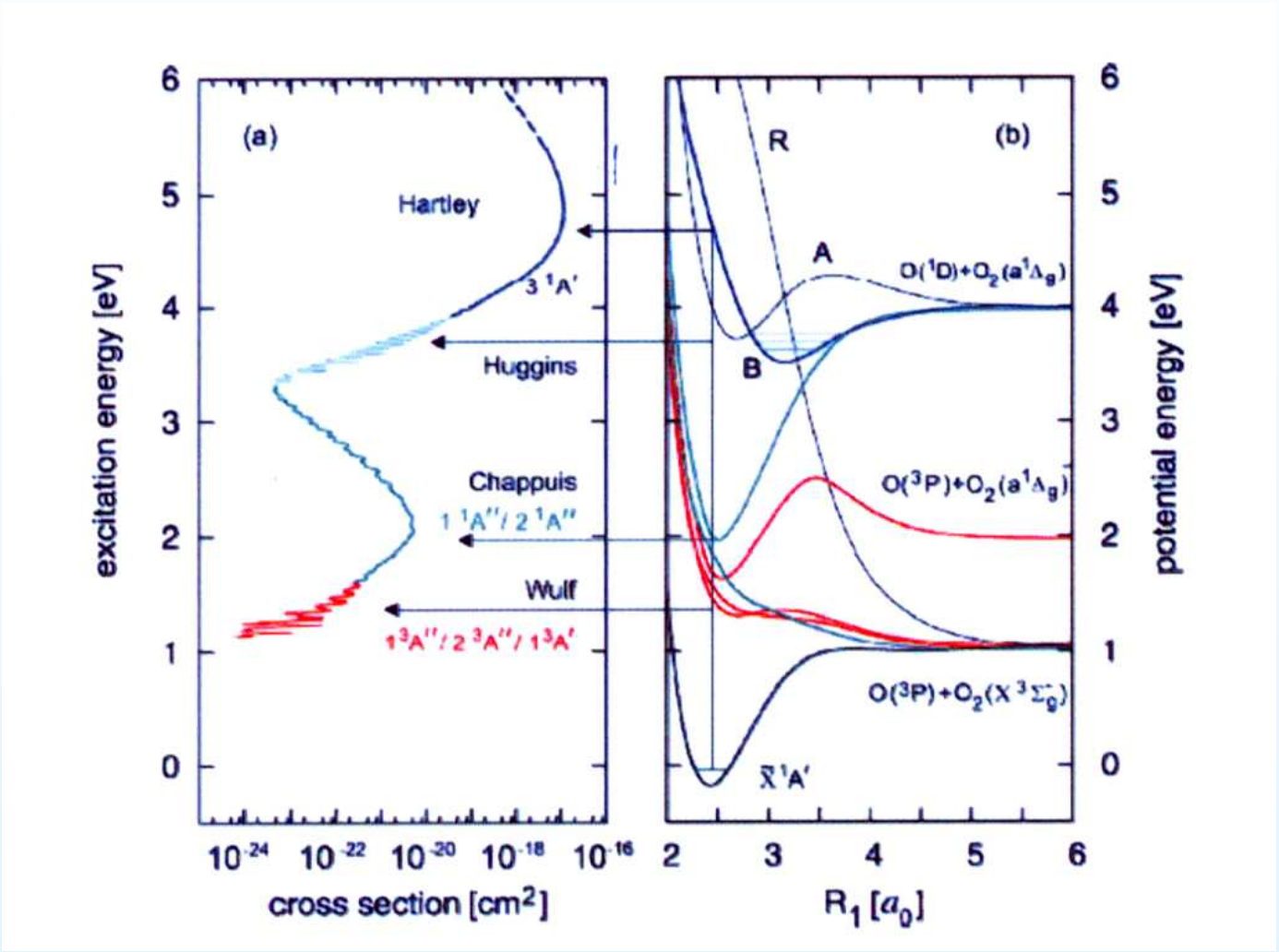
- Ozone has an unusual $^{17}O$ and $^{18}O$ isotopic constitution in the atmosphere
- Due to ozone formation process but also photolysis especially in the stratosphere (estimated previously at 25 $\%$ of the isotopic enrichment)
- Studied previously

  M. C. Liang, F. W. Irion, Weibel, J. D. Blake, C. E. Miller and Y. L. Yung, J. Geophys. Res. **2006**, *111* D02302.

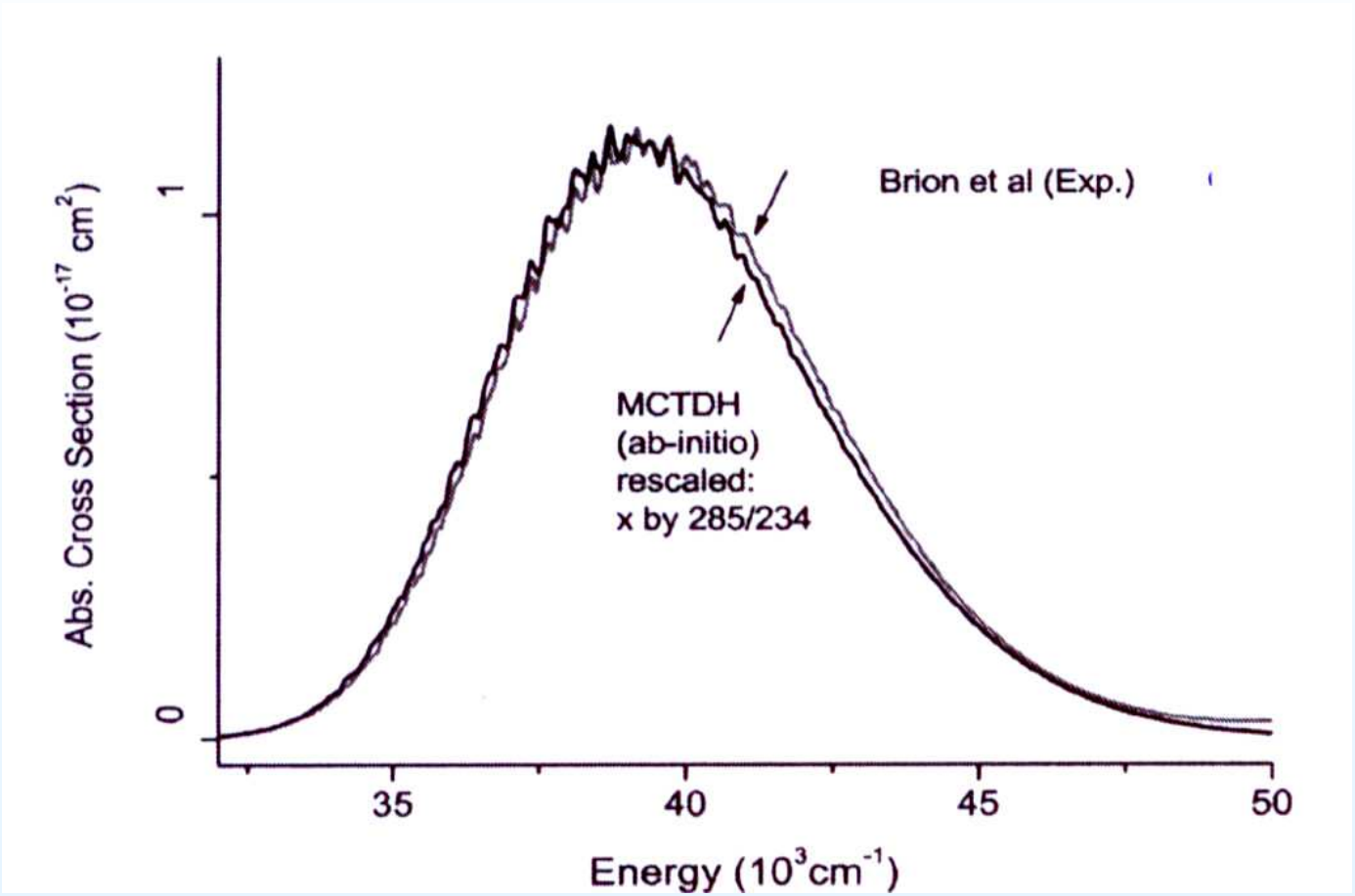
  D. Krankowsky and K. Lämmerzahl and K. Mauersberger and J. Janssen and B. Tuzson and T. Röckmann, J. Geophys. Res. **2007**, *112* D08301.
- New calculations using Potential Energy Surfaces (PESs) and Dipole Moment Surfaces by Schinke and co-workers and the Heidelberg Multi-Configuration Time-Dependent Hartree (MCTDH) package

  http://www.pci.uni-heidelberg.de/cms/mctdh.html

# Focus on the Huggins band



# Calculation of the Hartley band




S. Ndengué and F. Gatti and R. Schinke and H.-D. Meyer and R. Jost, JPCA (2010) *114* 9855.

## Five isotopologues

$^{16}O_3$ (666)

Symmetric $^{16}O^{17}O^{16}O$ (676), $^{16}O^{18}O^{16}O$ (686)

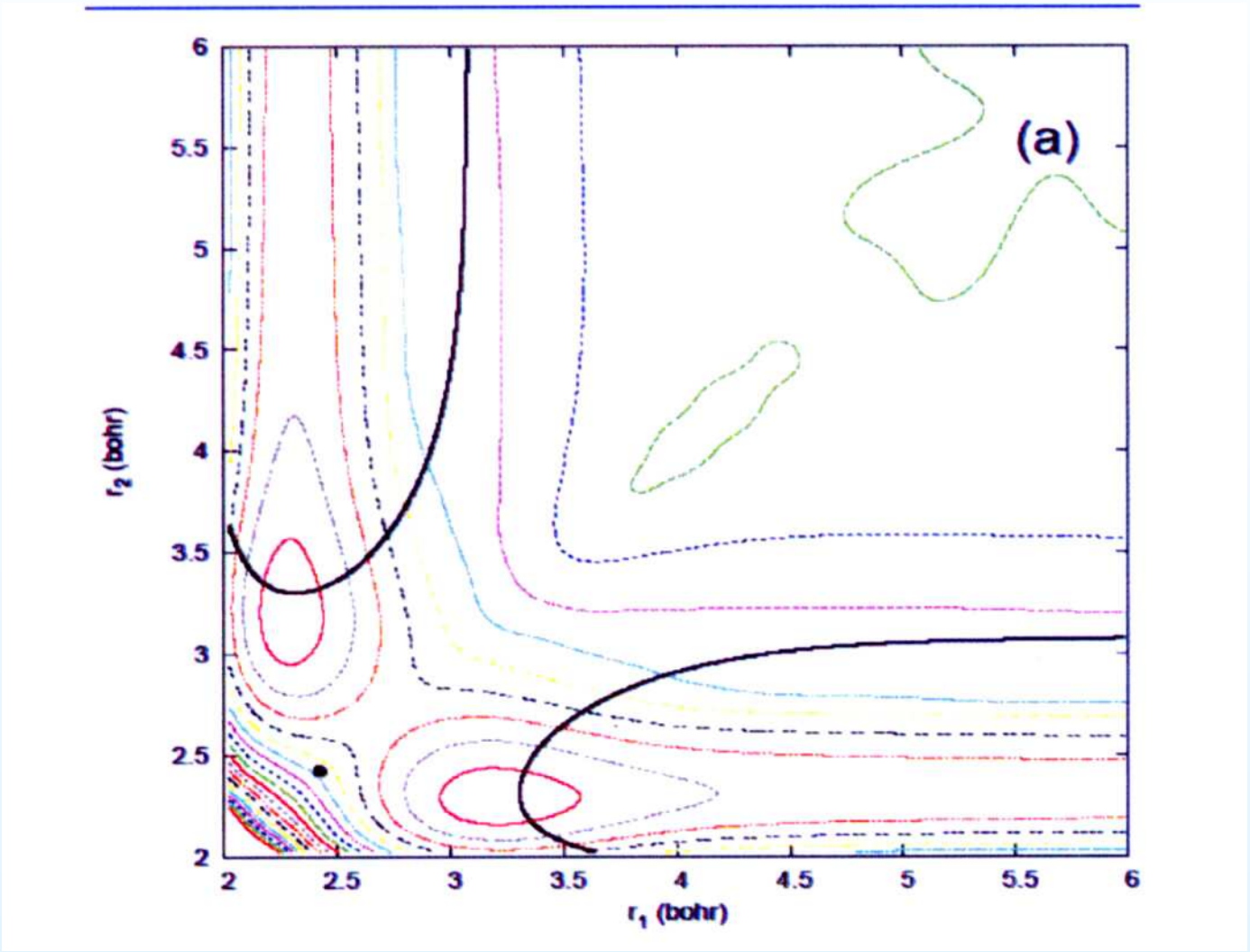
Asymmetric $^{16}O_2{}^{17}O$ (667), $^{16}O_2{}^{18}O$ (668)

668 can dissociate into either 66 + 8 or 68 + 6

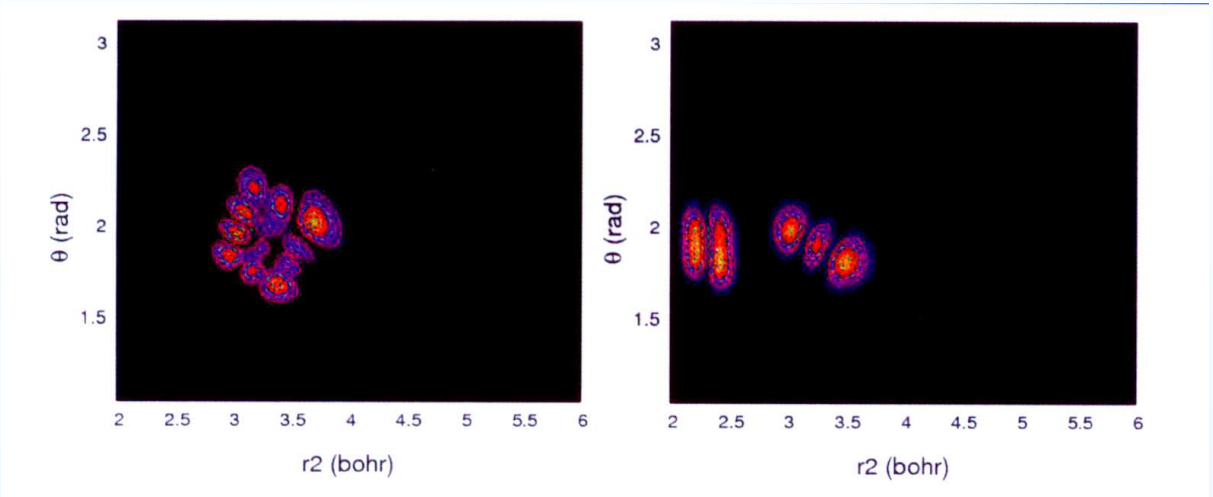
The dissociated Oxygen atom can be triplet or singlet

We neglect the dissociation into three atoms of oxygen

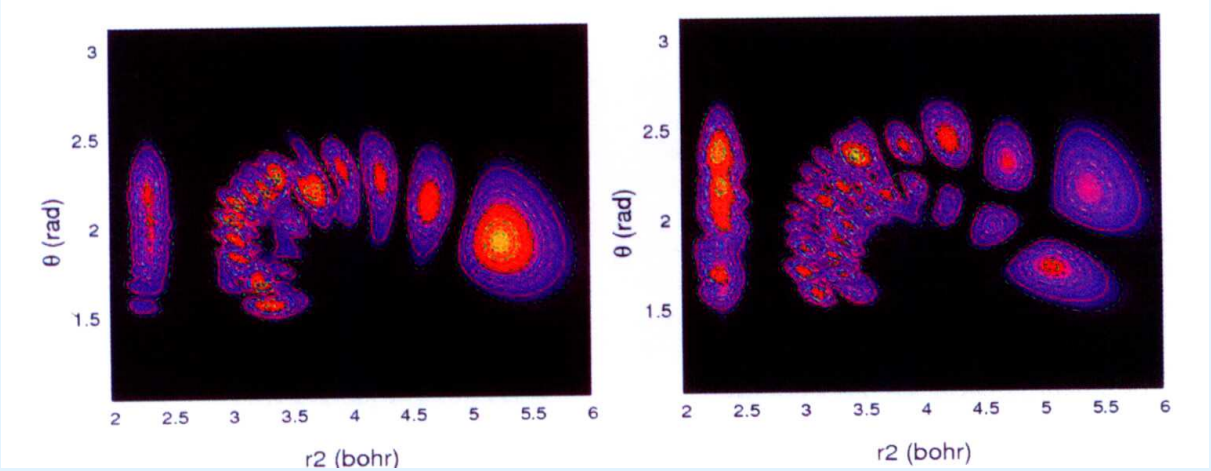
# PES of the B $3^2A'$ state



# Calculation of the vibrational B states

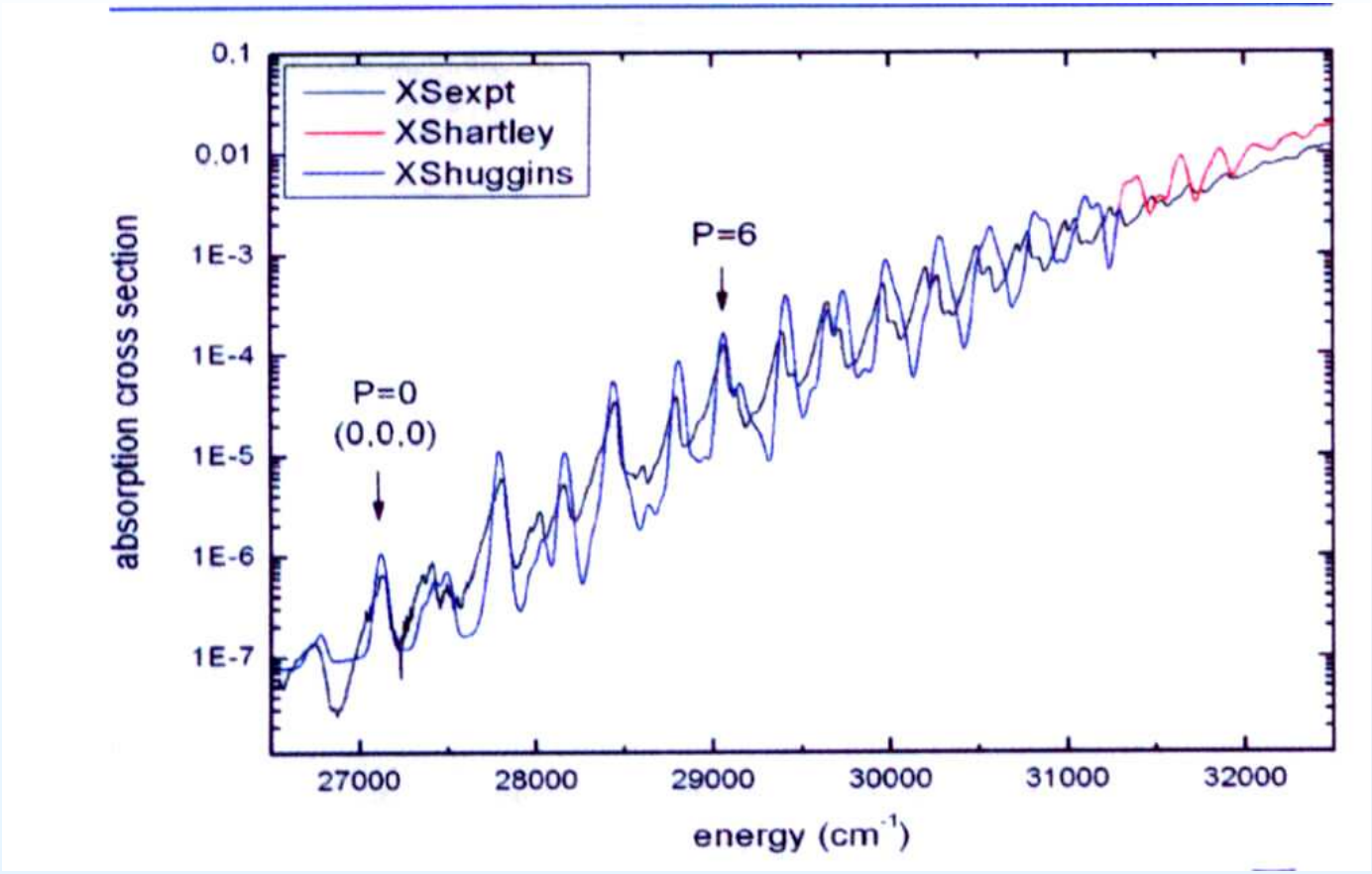



States (2,3,0) and (2,0,1)




States 95 and 100

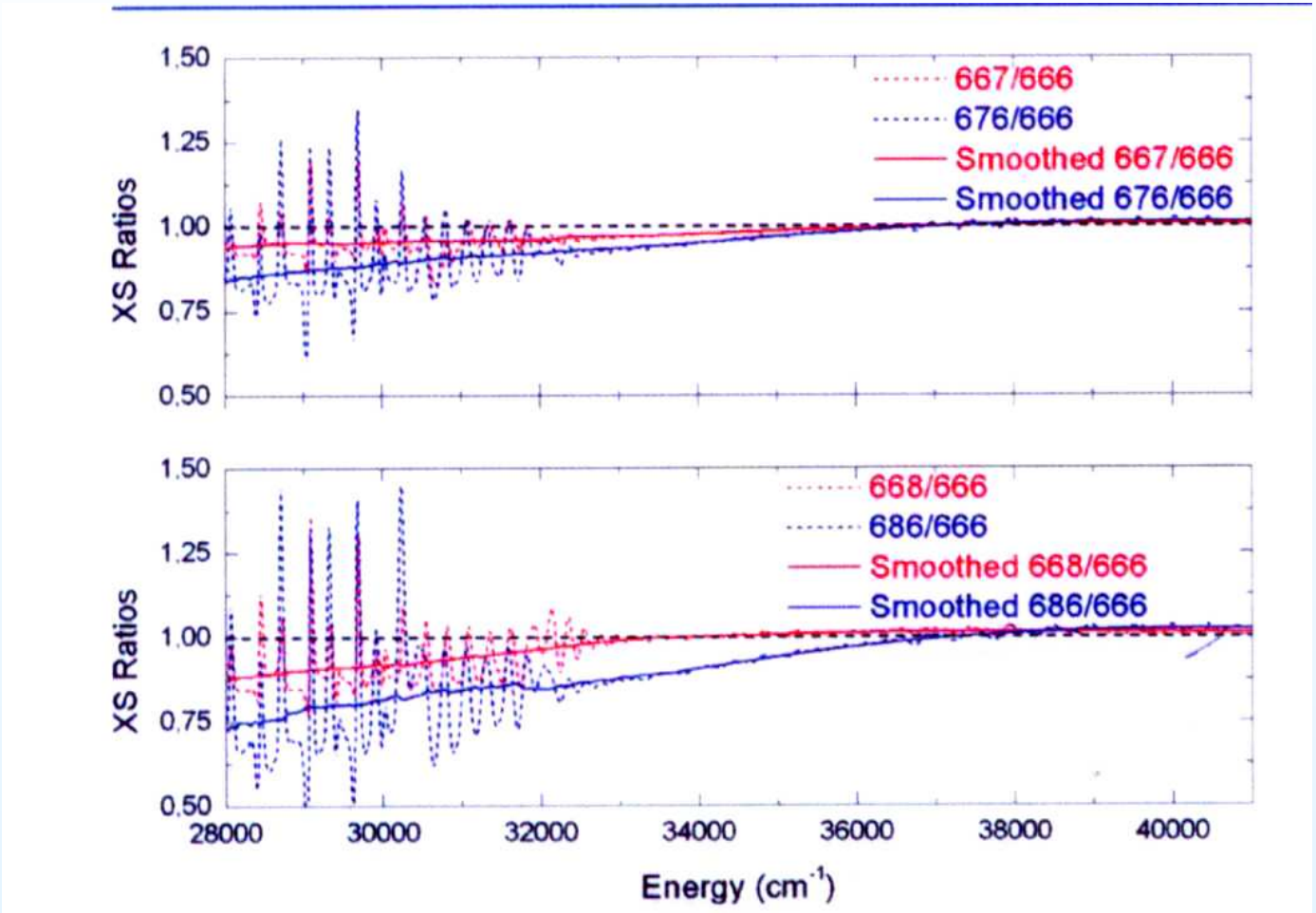
# Absorbed cross sections (Huggins)




Experimental cross section at 218 K : J. Brion (Reims)

Theoretical values energy shift (to lower energy) of 450 $cm^{-1}$ and a 285/234 factor of rescaling.

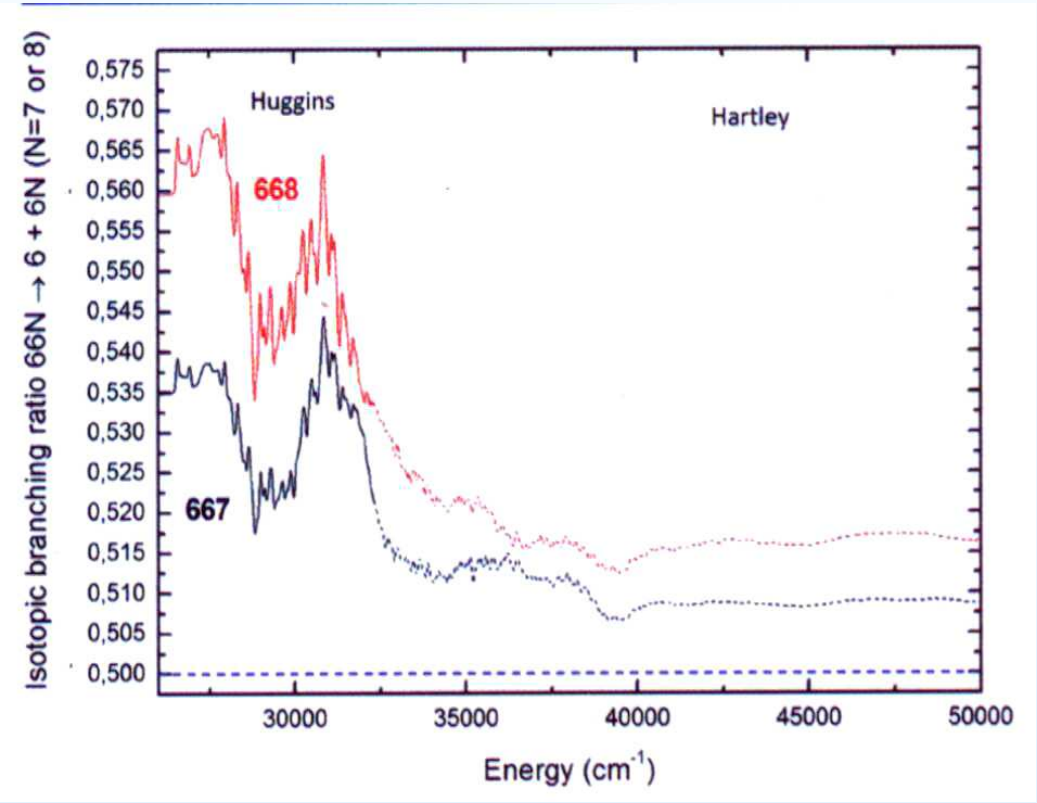
# Cross section ratios



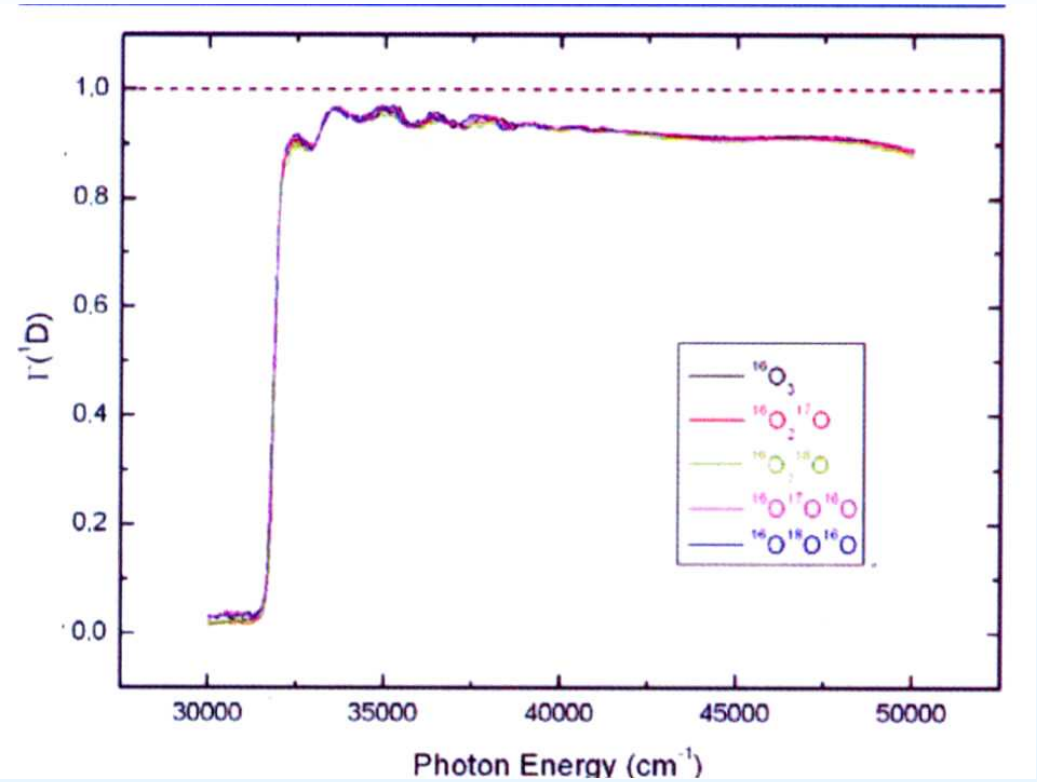

S. Ndengué and R. Schinke and F. Gatti H.-D. Meyer and R. Jost, JPCA (2012) *116* 12260.

# Asymmetric isotopologues

$$66N \rightarrow 6 + 6N$$
$$66N \rightarrow N + 66$$



# Singlet-Triplet Oxygen atom




S. Ndengué and R. Schinke and F. Gatti H.-D. Meyer and R. Jost, JPCA (2012) *116* 12271.

# Isotopic enrichment

Photolysis rate coefficient:

(1) $$J_{abc} = \int XS_{abc}(E) Ac.Flux(E,h) dE$$

Troposferic Ultraviolet-Visible model version 5:

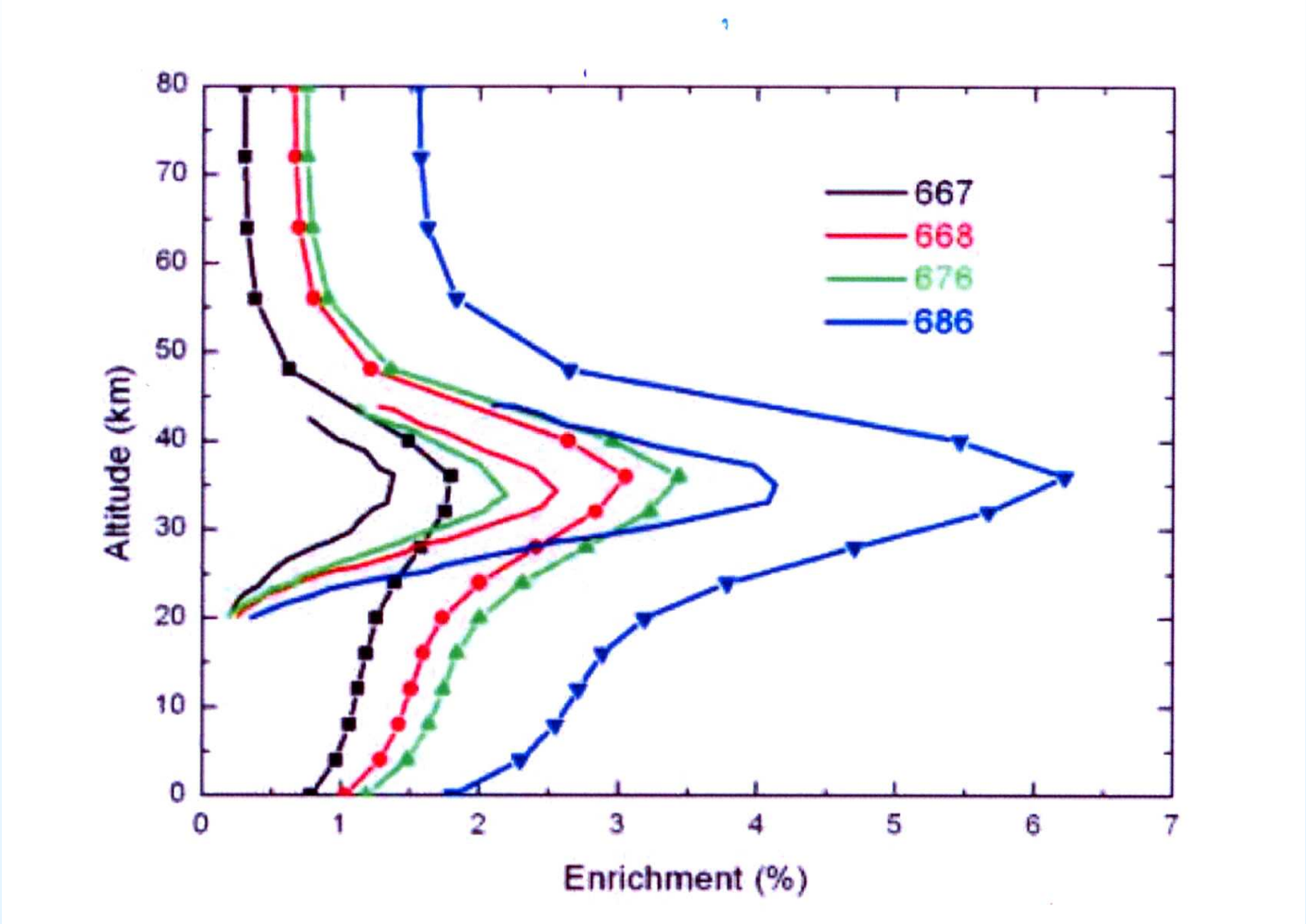
Sasha Madronich and G. Weller, TUV program J. Atmos. Chem. (1990) **10** 289

averaged over latitudes and seasons.

The enrichment of an abc isotopologue :

(2) $$I_{abc} = -100 * (J_{abc}/J_{666} - 1)$$

# Isotopic enrichment




Comparison with

M. C. Liang, F. W. Irion, Weibel, J. D. Blake, C. E. Miller and Y. L. Yung, J. Geophys. Res. **2006**, *111* D02302.

## Conclusion

The contribution of the photolysis process to the ozone and atomic oxygen isotope enrichment should be increased respectively by 25 % and 50 % for the asymmetric and symmetric isotopologues

Necessity to combine these results with the formation process to have the global enrichment

## Acknowledgements:


- **Grenoble: S. Ndengué and R. Jost**
- **Heidelberg: H.-D. Meyer**
- **Göttingen: R. Schinke**
- Funding : ANR IDEO (NT09_436466), DFG