The Electron Donor-Acceptor Nature of the Ethanol-CO_2 Dimer

Marie-Aline Martin-Drumel
CNRS

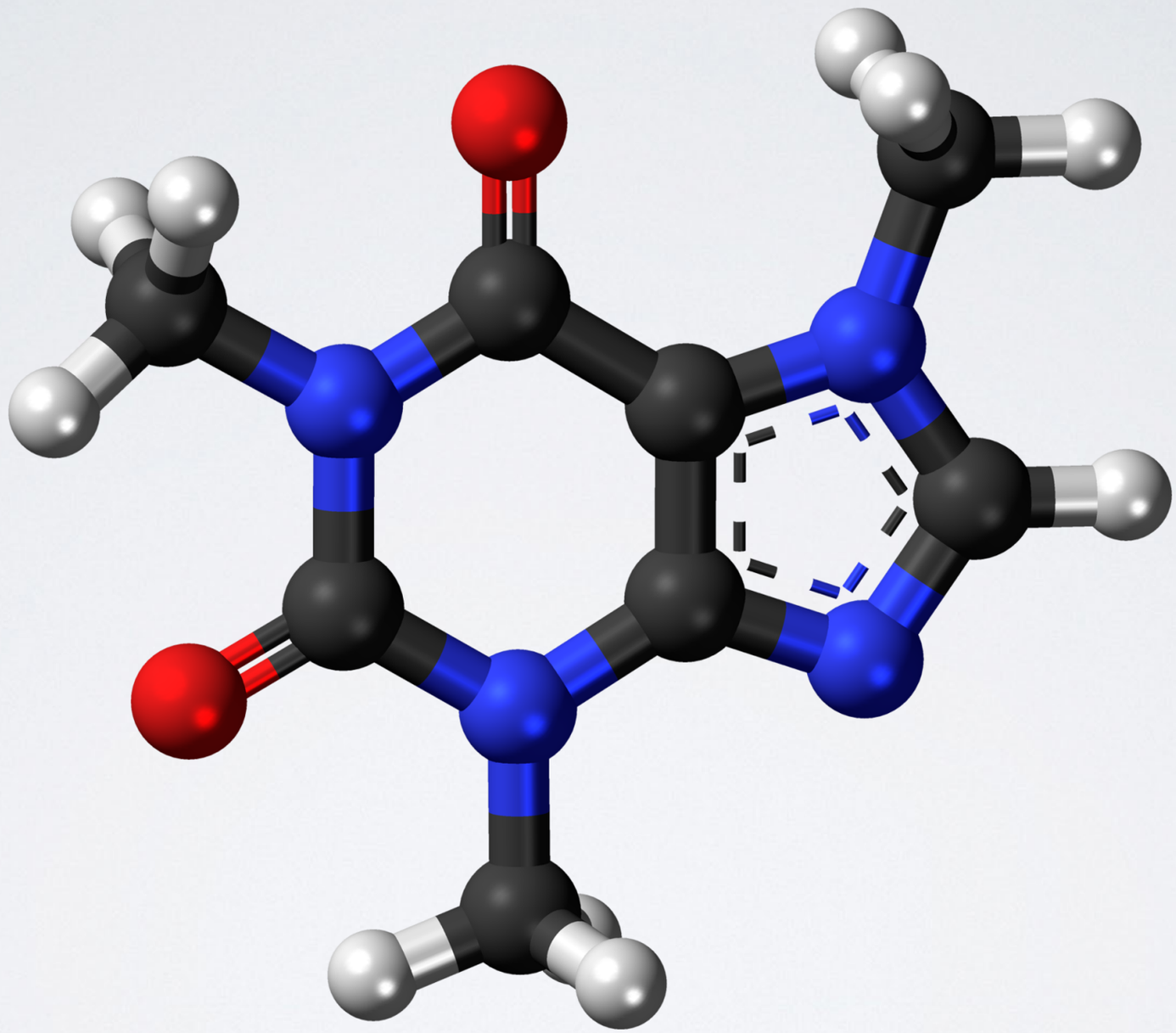
Michael McCarthy
Harvard-Smithsonian CfA

Special thanks to: Kelvin Lee, Geoff Blake

Brett A. McGuire

Jansky Postdoctoral Fellow, NRAO

A BEGINNING



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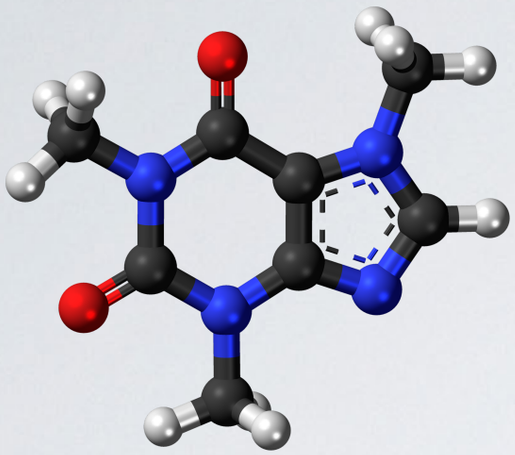

UNITED STATES PATENT OFFICE.

JOHANN FRIEDRICH MEYER, JR., LUDWIG ROSELIUS, AND KARL HEINRICH WIMMER, OF BREMEN, GERMANY, ASSIGNORS TO THE KAFFEE-HANDELS-AKTIENGESELLSCHAFT, OF BREMEN, GERMANY.

PREPARATION OF COFFEE.

No. 897,840. Specification of Letters Patent. Patented Sept. 1, 1908.

Application filed May 4, 1906. Serial No. 315,180.

REISSUED

To all whom it may concern:

Be it known that we, JOHANN FRIEDRICH MEYER, Jr., LUDWIG ROSELIUS, and KARL HEINRICH WIMMER, subjects of the German Emperor, residing at Bremen, Germany, have invented certain new and useful Improvements Relating to the Preparation or Treatment of Coffee, of which the following is a specification.

The present invention has for its object, to deprive coffee beans of caffein, without destroying their other valuable properties. Numerous attempts made for this purpose have been unsuccessful, and especially the treatment of the beans with volatile solvents for caffein has produced unsatisfactory results. The reason for failure seems to have been in the cellular tissue or organic structure of the coffee beans, which renders a sufficient penetration of the solvent almost impossible. Moreover, the caffein is contained in the beans in the shape of salts, which are hardly soluble at all in the volatile solvents. Finally there is the defect, that after prolonged treatment of the beans with the solvent it is exceedingly difficult to remove the solvent completely from the cells, even if the solvent had penetrated only into the outer cellular layers of the beans.

According to the present invention the coffee beans are first subjected to a preliminary treatment which causes the beans to swell and loosens the structure or cellular tissue of the same, preferably by exposing them to dry steam of about 1½–2 atmospheres in a closed receptacle. Subsequently gases or vapors having an acid or alkaline reaction are introduced into the apparatus, in order to decompose the salts of caffein. Ammonia, sulfurous acid, hydro-chloric acid and similar chemicals have been found specially suitable for this purpose. The caffein liberated by this treatment can be extracted more easily than its salts, and in case minute quantities of caffein have remained in the beans after the extraction, they are volatilized by the subsequent roasting, because at the temperature of roasting coffee caffein in its free state is capable of sublimation, although this is not the case with its salts.

The beans treated as described are extracted with a solvent of caffein, preferably one which dissolves only the latter, but as little as possible of the other constituents of the beans. We have found that benzene (also called benzol) is eminently suitable for this purpose, because an extract made with it leaves on evaporation almost pure caffein. In using other solvents, such as alcohol or chloroform, it would be necessary, to restore to the coffee-beans the extract, which has been relieved of caffein. Instead of a single solvent, such as benzene, mixtures of volatile solvents, may, of course, be employed for extracting the coffee beans.

The extraction of caffein is very energetic and leaves only minute traces undissolved, while the solvent action of the mixture for other constituents of coffee is comparatively weak. The boiling point of the mixture is lower than that of the individual components, and the extraction therefore takes place at a lower temperature.

It is useful to subject the coffee, after extraction, to the influence of dry steam at a pressure of about 1½ atmospheres, while keeping the beans continually in motion by stirring, or by causing the apparatus to revolve. An agitation of the beans is useful also during the extraction. In case traces of the extracting liquid remain in the beans in spite of this treatment with steam, these traces may be removed by subjecting the beans alternately to steam of different pressures, or alternately to pressure and vacuum. This treatment also serves to expel the traces of furfurol contained in the coffee, and to relieve the coffee of this constituent, which recent investigations have shown to be injurious.

Example. 100 kilograms of coffee beans are placed in a cylinder with a double jacket, the cylinder is heated indirectly by steam, in order to avoid as much as possible the condensation of the dry steam to be introduced. Subsequently, after the cylinder has been hermetically closed, steam is introduced until the pressure has risen to about 1½–2 atmospheres. This pressure is allowed to act for about half an hour, after which gaseous ammonia is admitted. When the space is filled with this gas, benzene (or a mixture of benzene and alcohol) is admitted and heated, the immediate effect of this being, that the escaping benzene vapors will carry with them any moisture that may be present and also the excess of ammonia. The heating is then continued for about 2 to 3 hours, and the ben-

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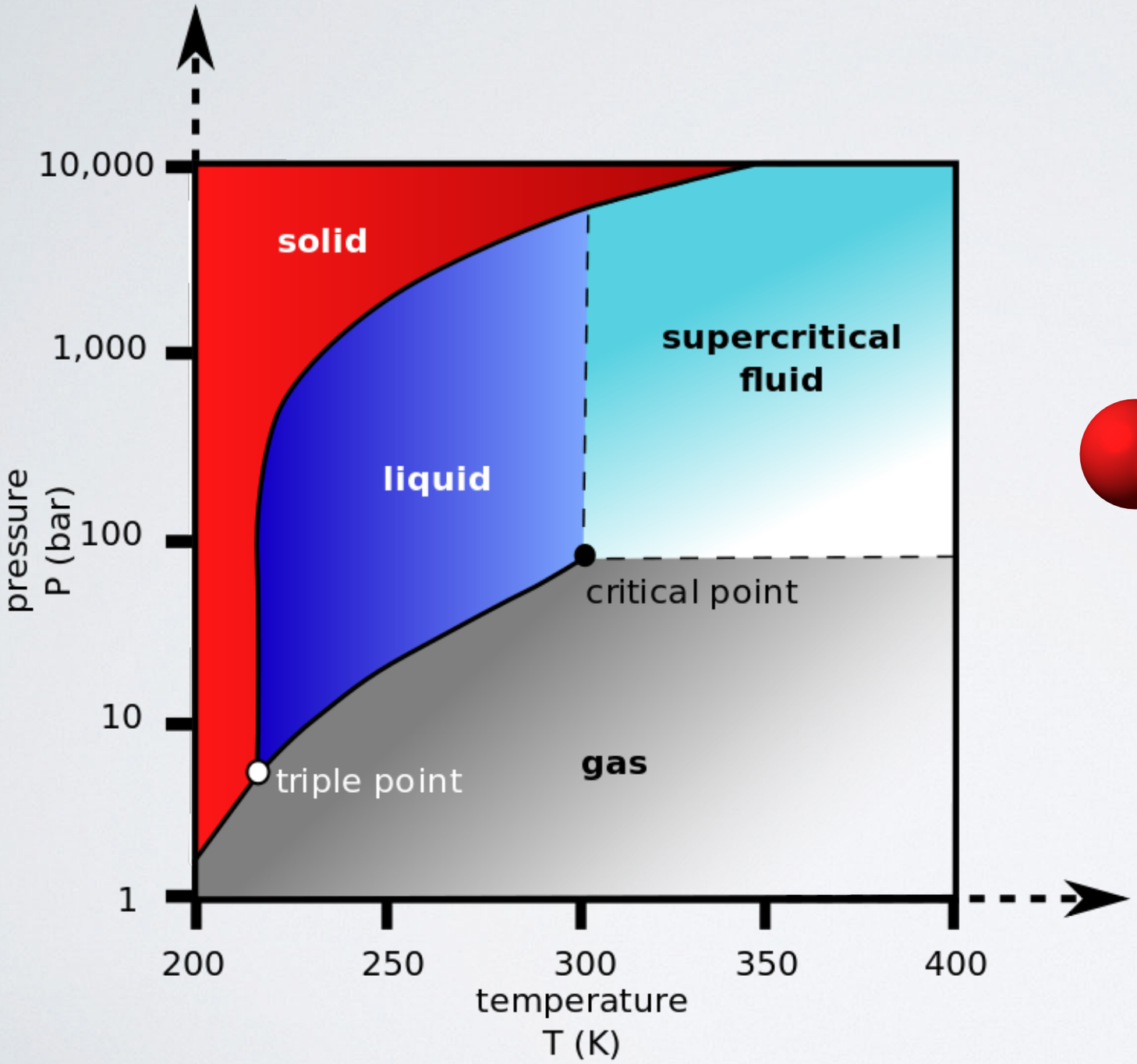


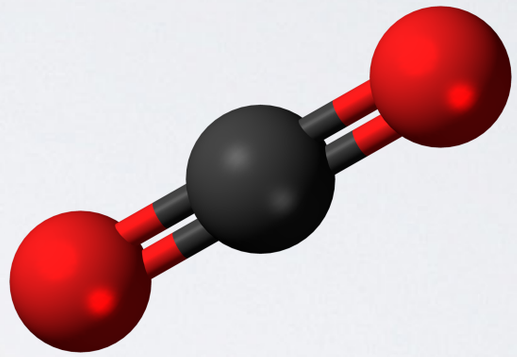
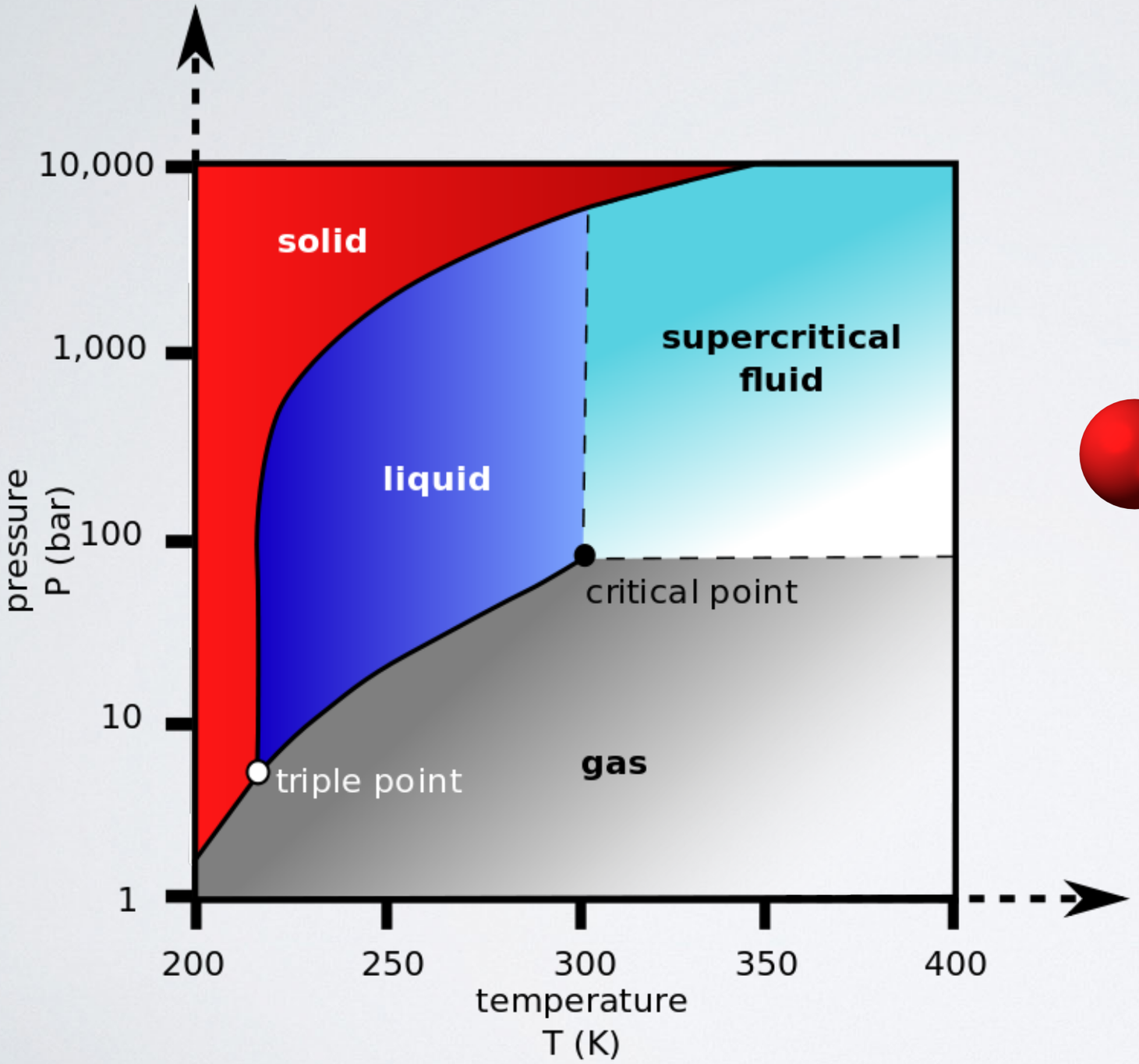
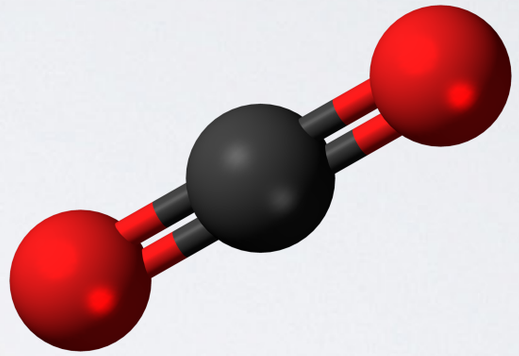


Image Credit: Wikipedia

DECAFFEINATION





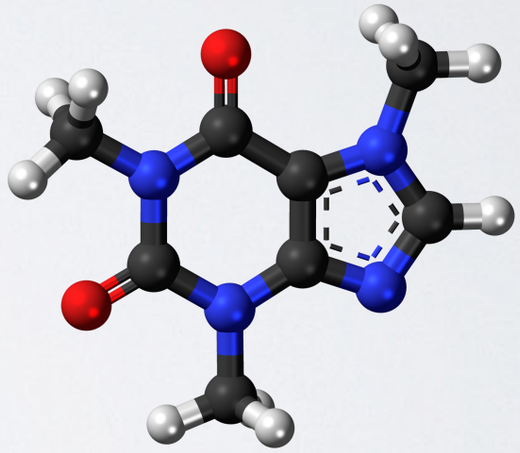
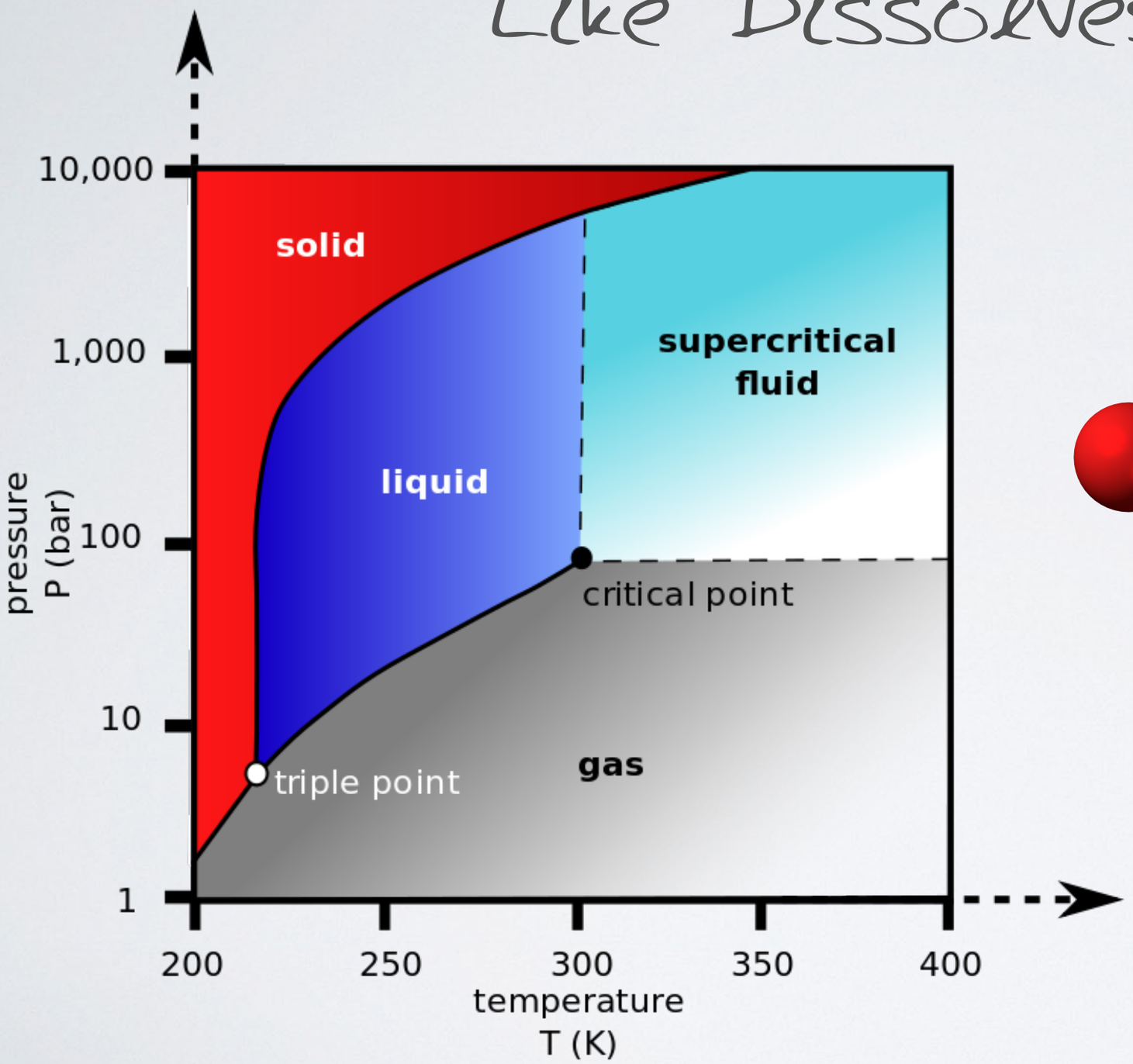
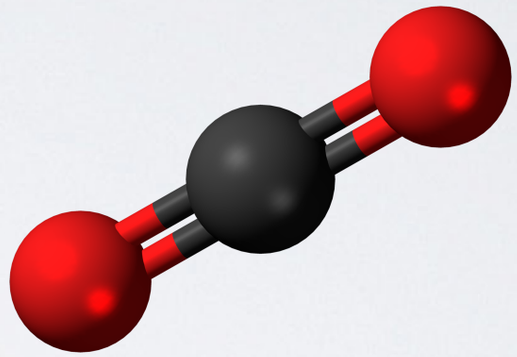
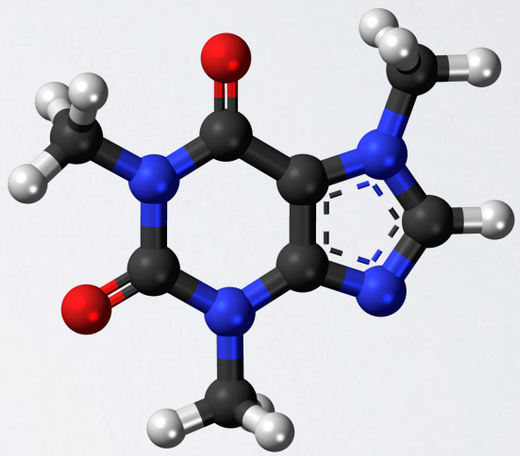


Image Credit: Wikipedia

Like Dissolves Like







United States Patent [19]
Katz

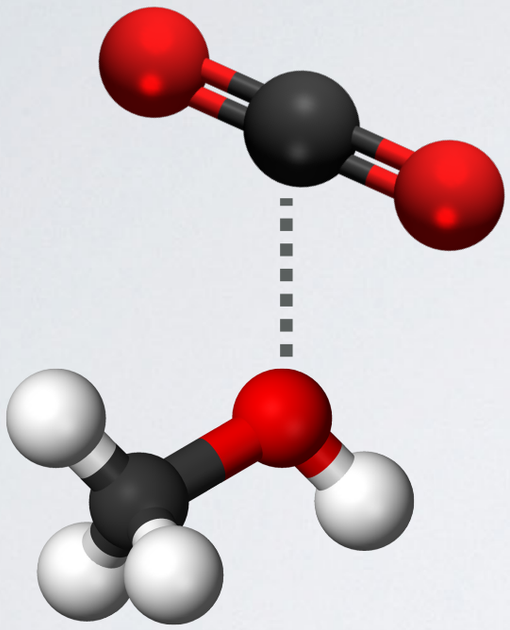
[11] **Patent Number: 4,820,537**
[45] **Date of Patent: Apr. 11, 1989**

In addition, a so-called enhancer may be added to the supercritical fluid to improve the solvent characteristics of the supercritical fluid. The most useful enhancers are the low to medium boiling alcohols and esters. Typical enhancers include methanol, ethanol, ethyl acetate and the like. The enhancers may be added to the essentially caffeine-free supercritical fluids at proportions of between about 0.1% and 20.0% by weight. The enhancers contemplated for use herein are most typically not supercritical fluids at the disclosed operating conditions but rather, the enhancers are simply dissolved in the supercritical fluid, improving its solvent properties.

HOW DOES THIS WORK?

Chatzis et al. 2003 *Chem Phys Lett* 374, 187
Illyushin et al. 2006 *J Mol Spec* 239, 94

Gas-Phase



Supercritical CO_2

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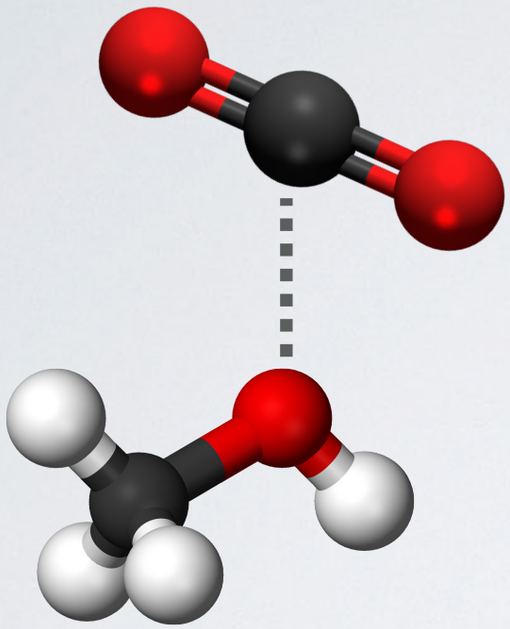

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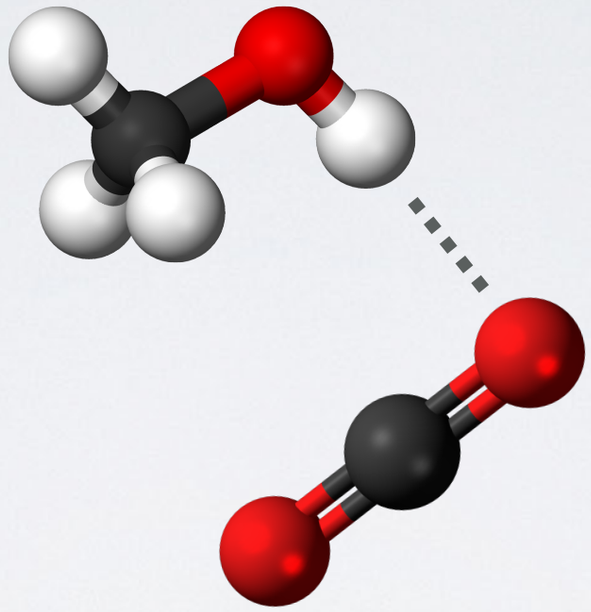

"… a molecular network seems to be formed by MeOH molecules at rather low concentrations and the CO_2 molecules were found to participate partially in this."

HOW DOES THIS WORK?

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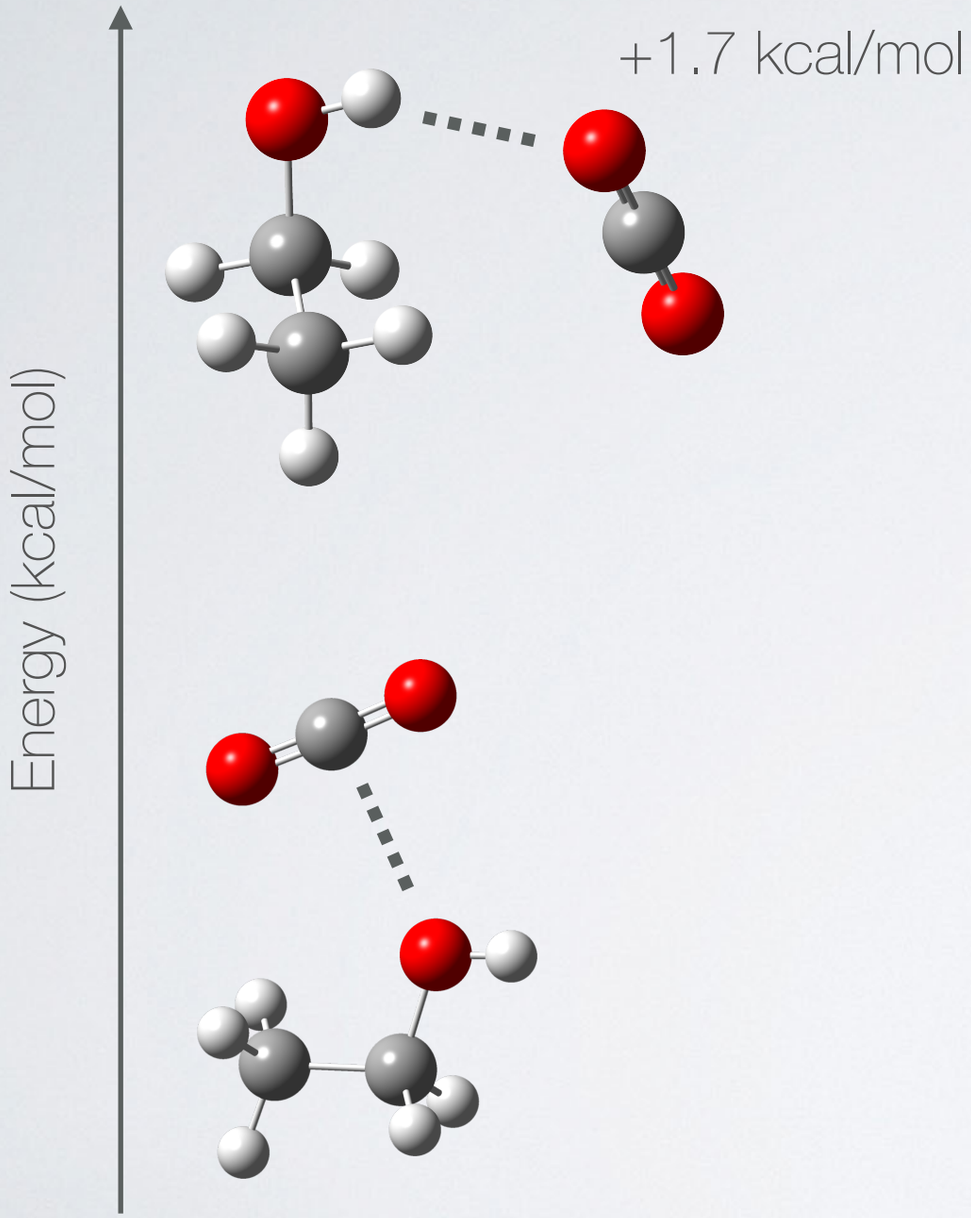

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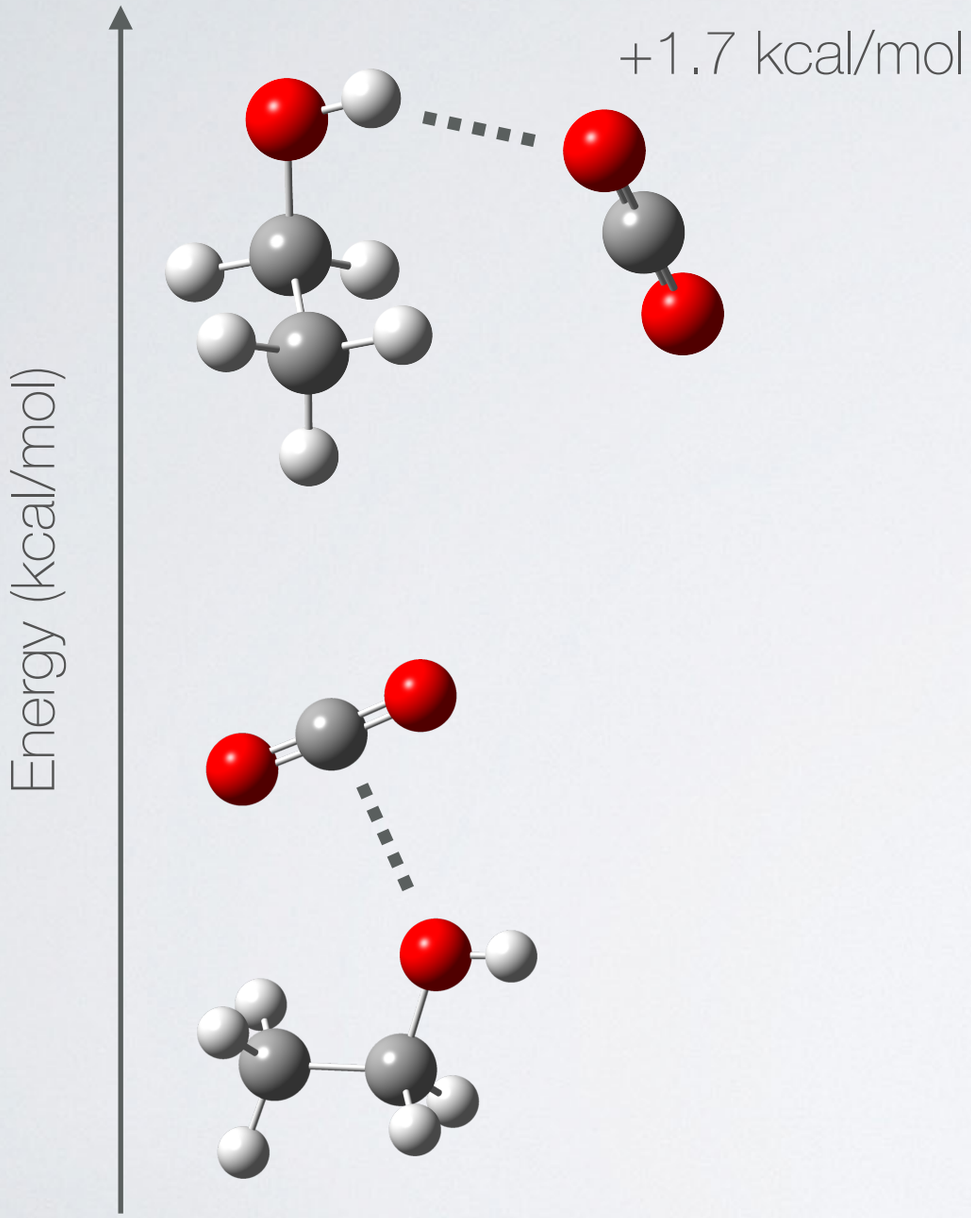

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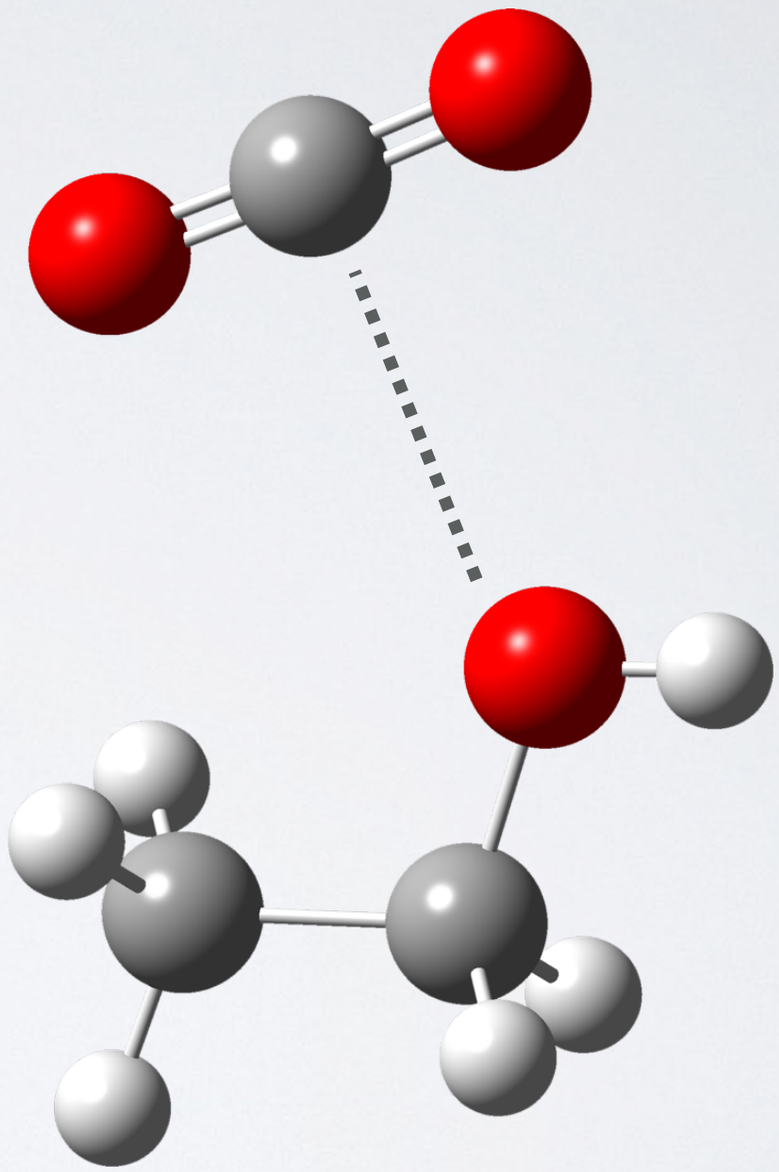

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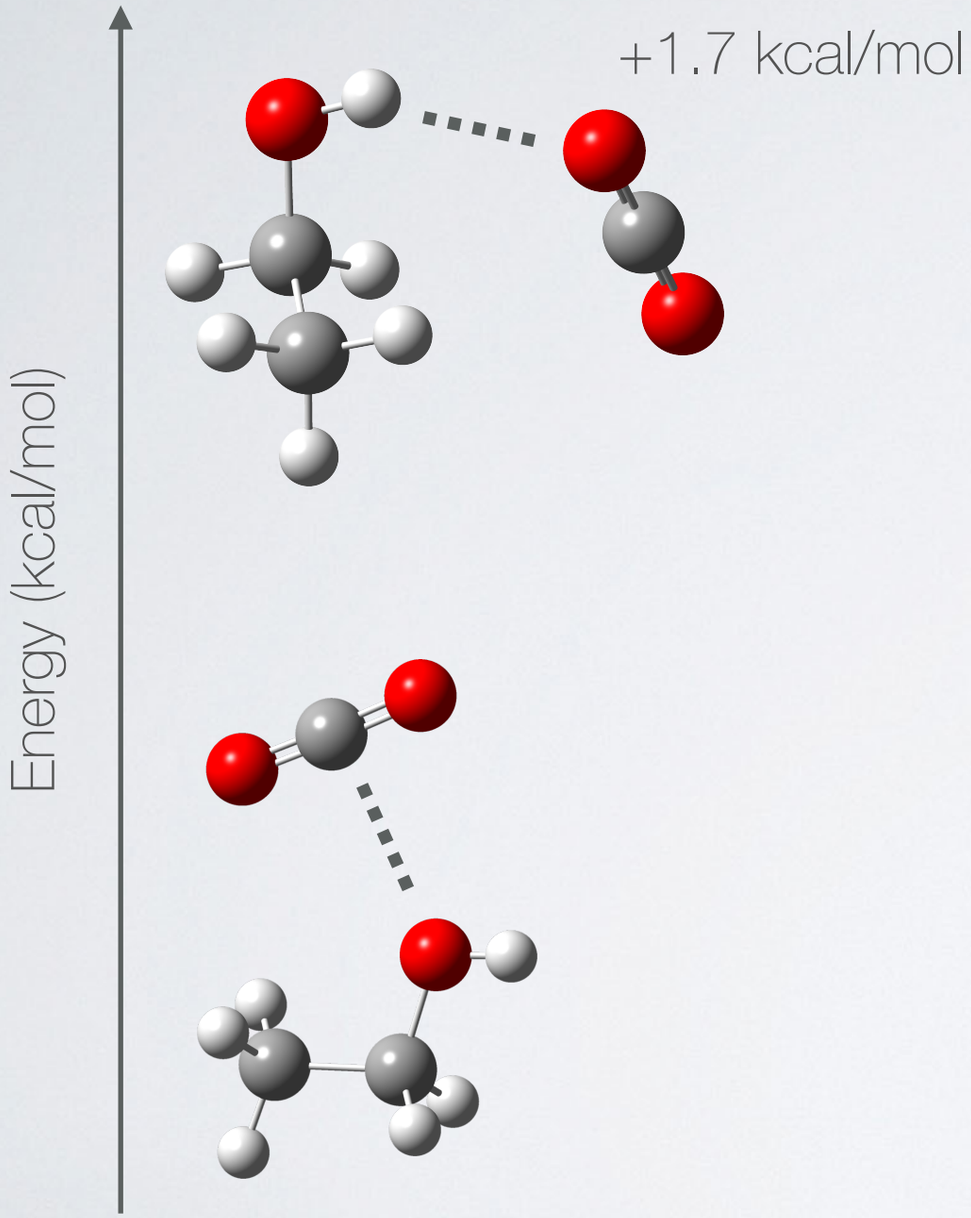

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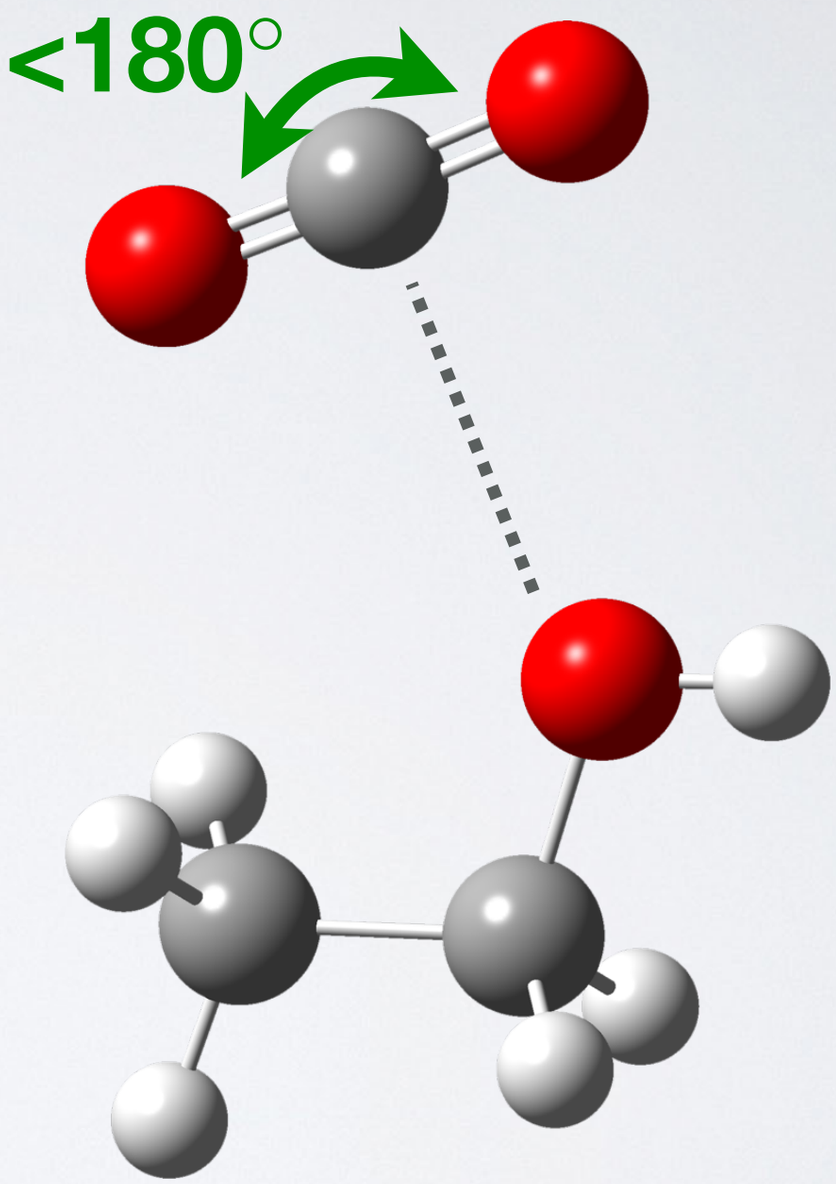
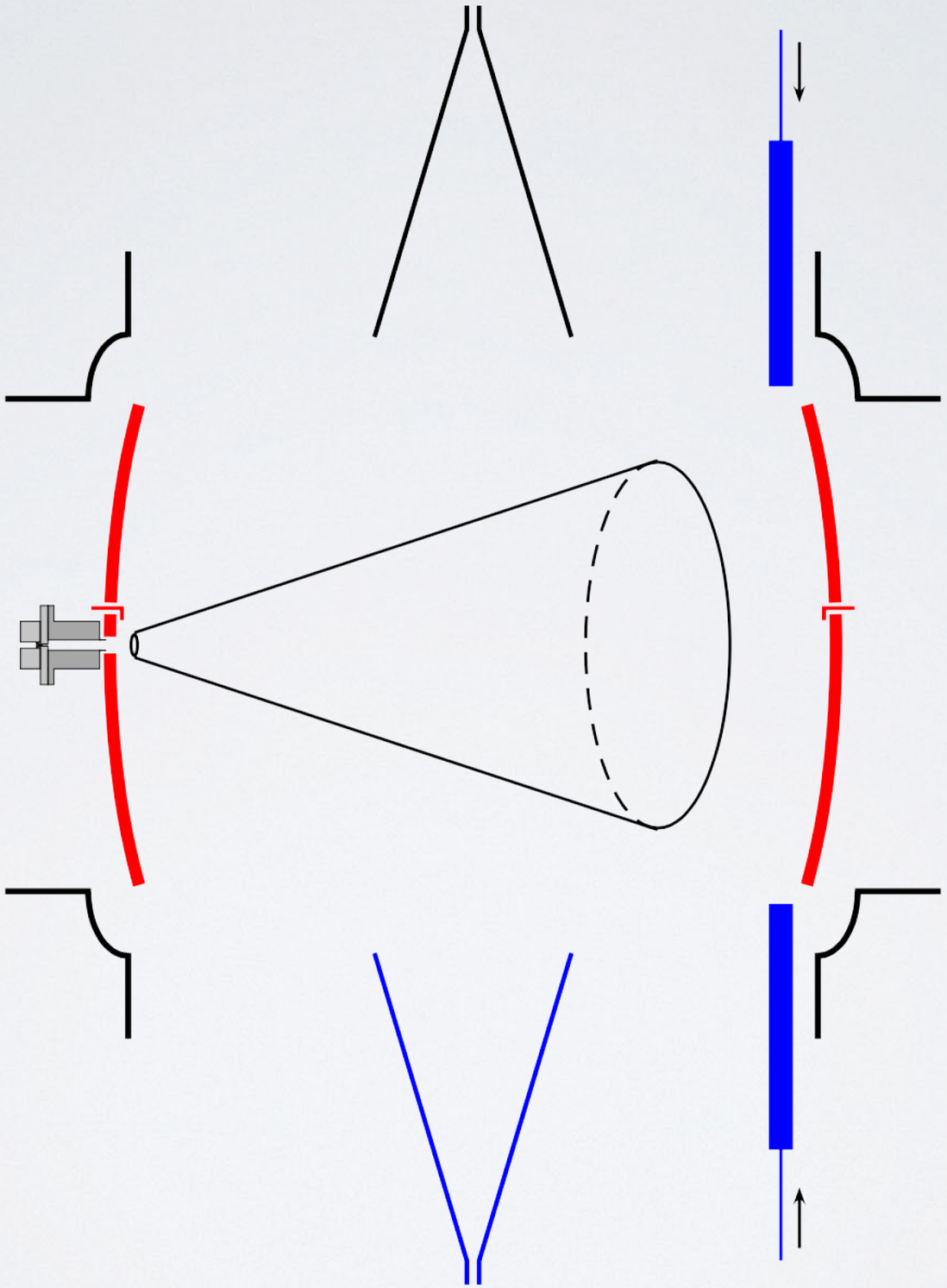


THE EXPERIMENT

Crabtree et al. 2016 *J Chem Phys* 144, 124201



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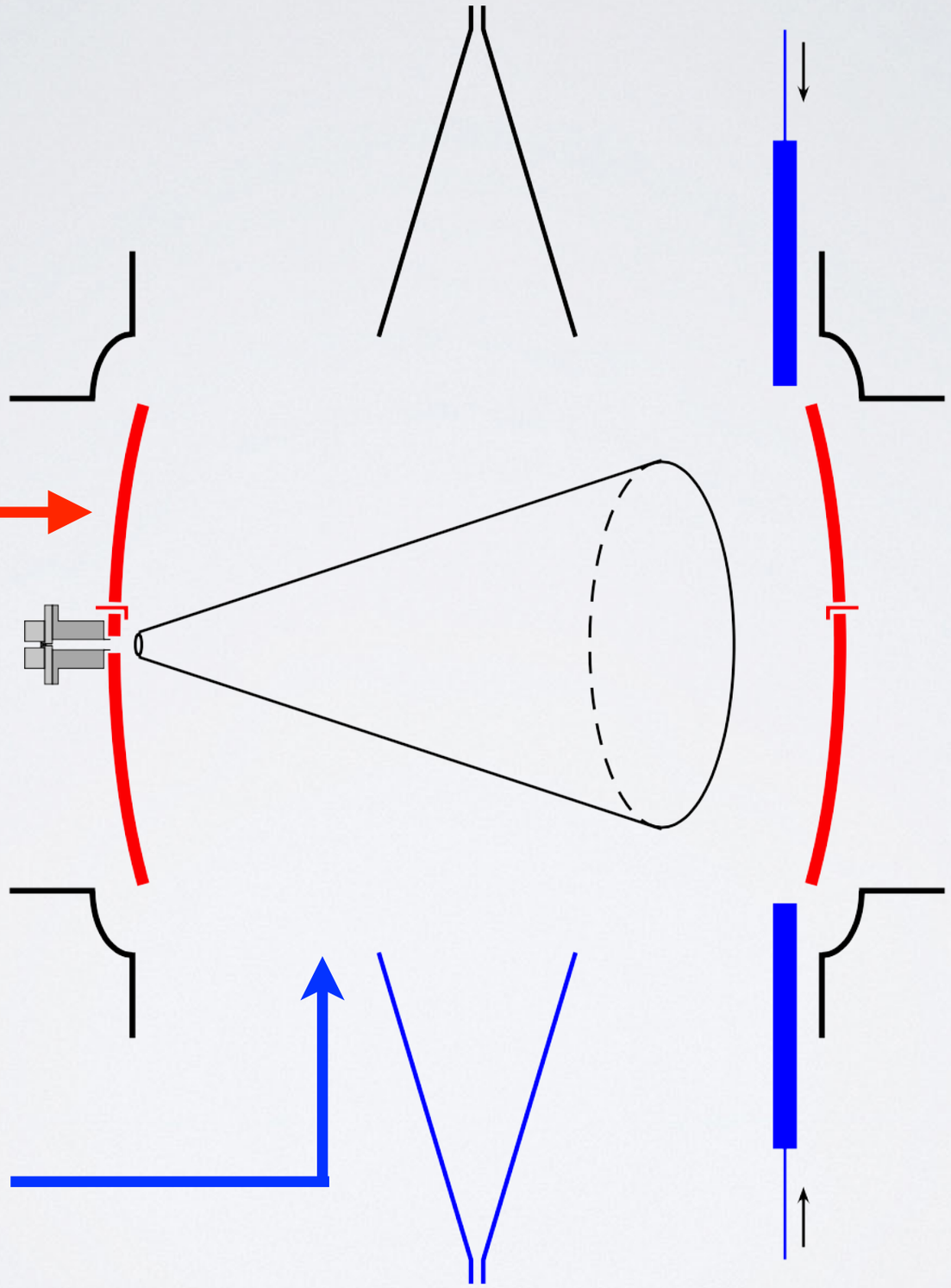
Cavity FTMW



CP-FTMW

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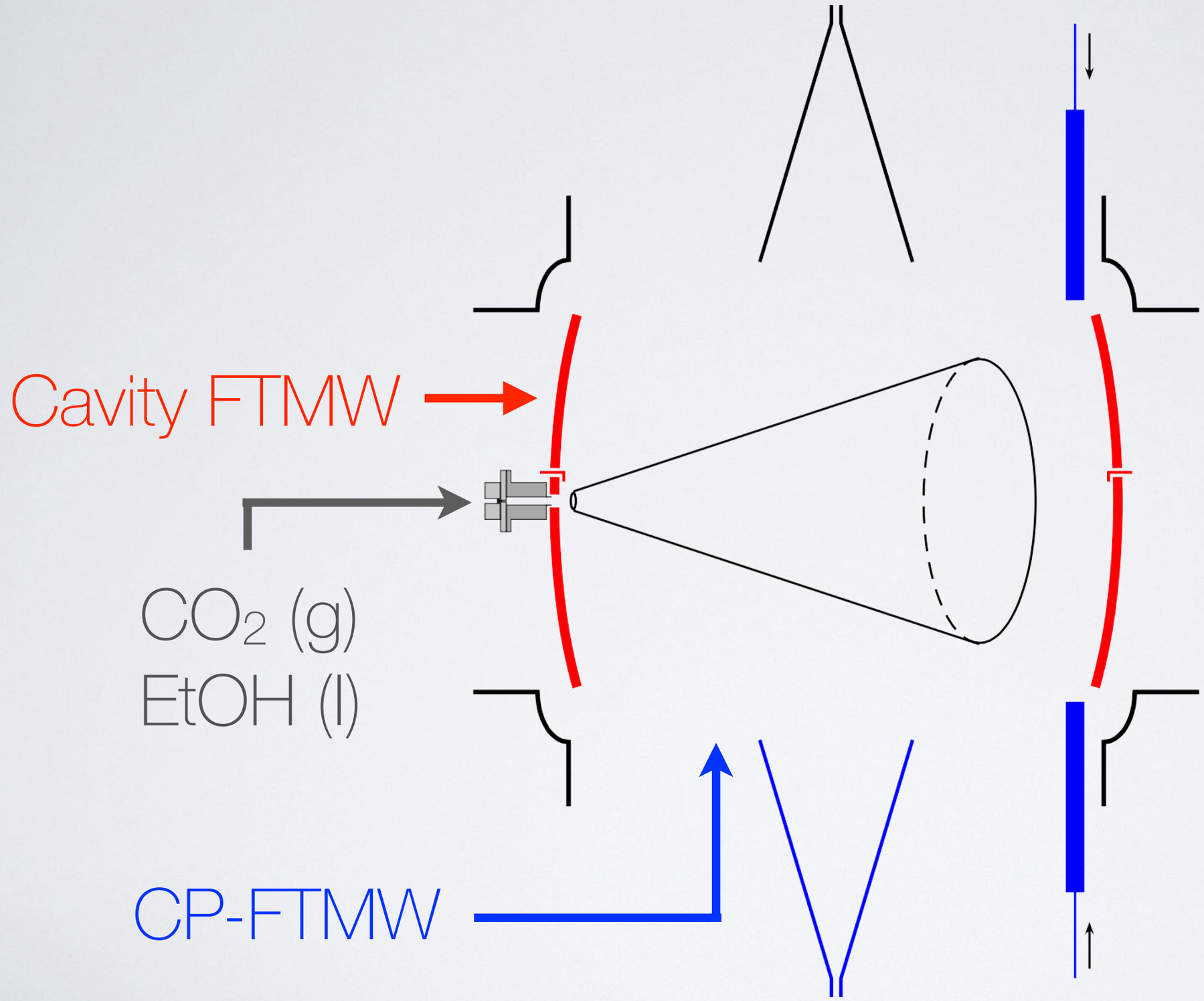

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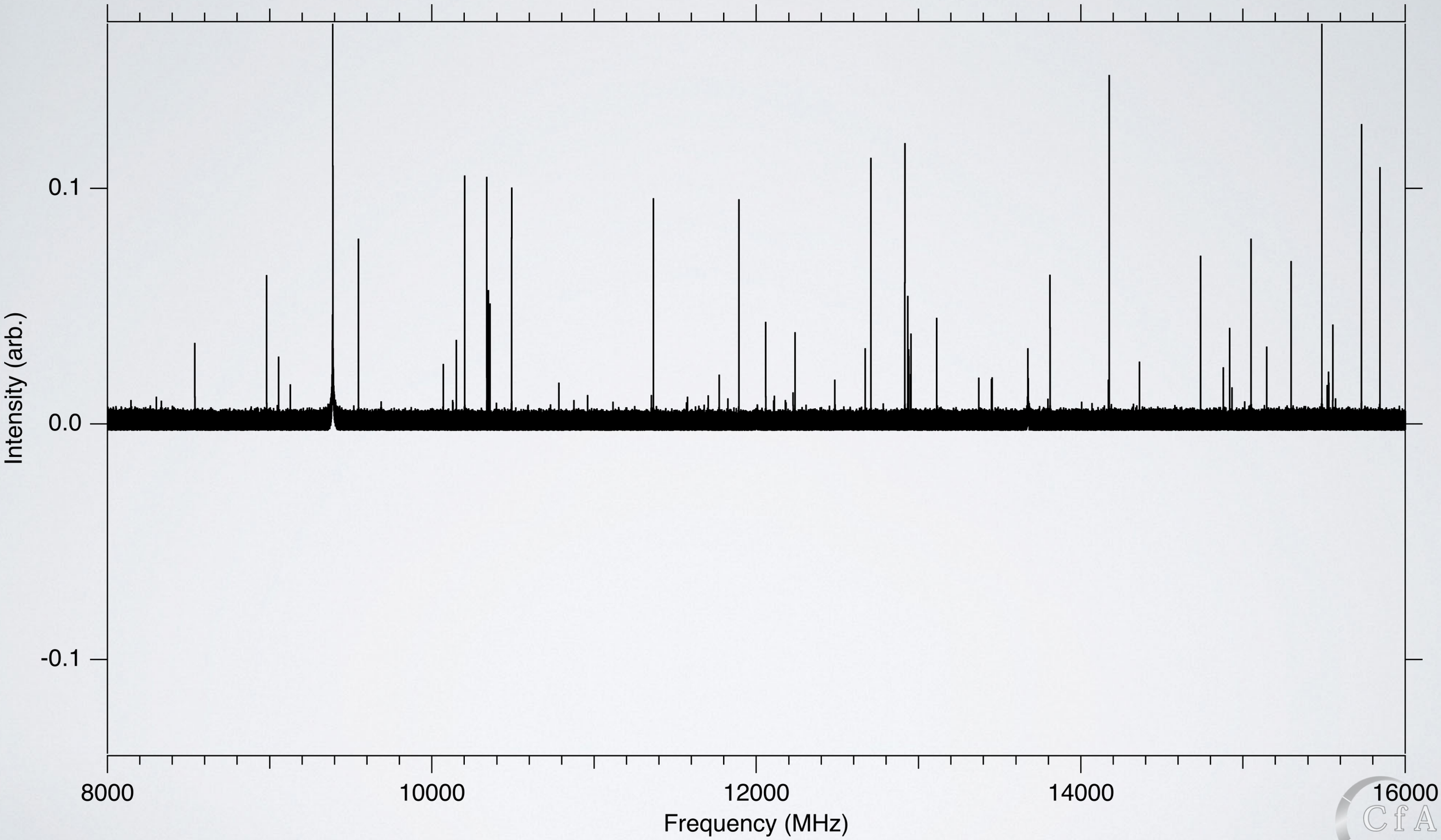

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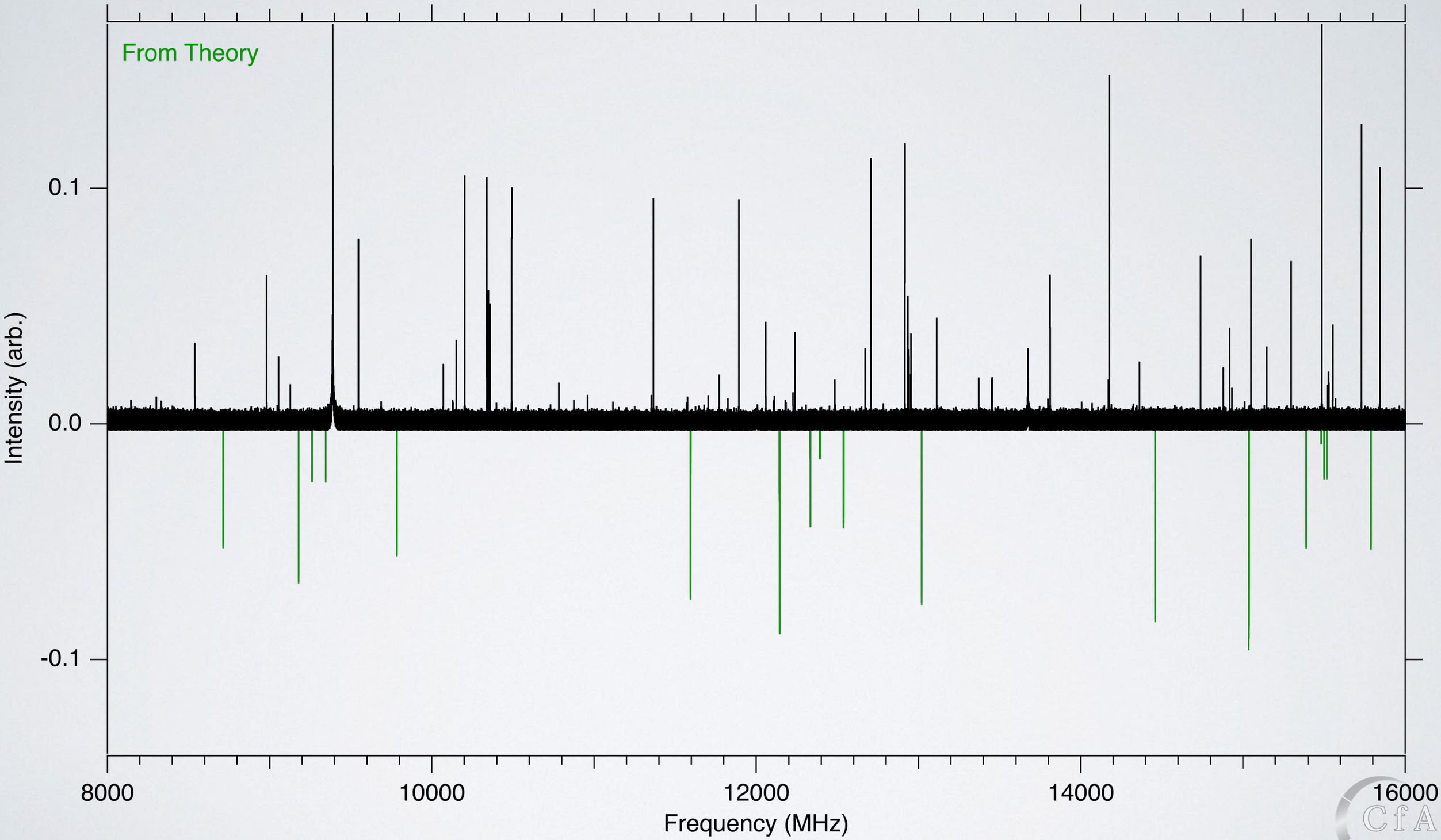


From Theory

THE JOURNAL OF CHEMICAL PHYSICS **144**, 124201 (2016)

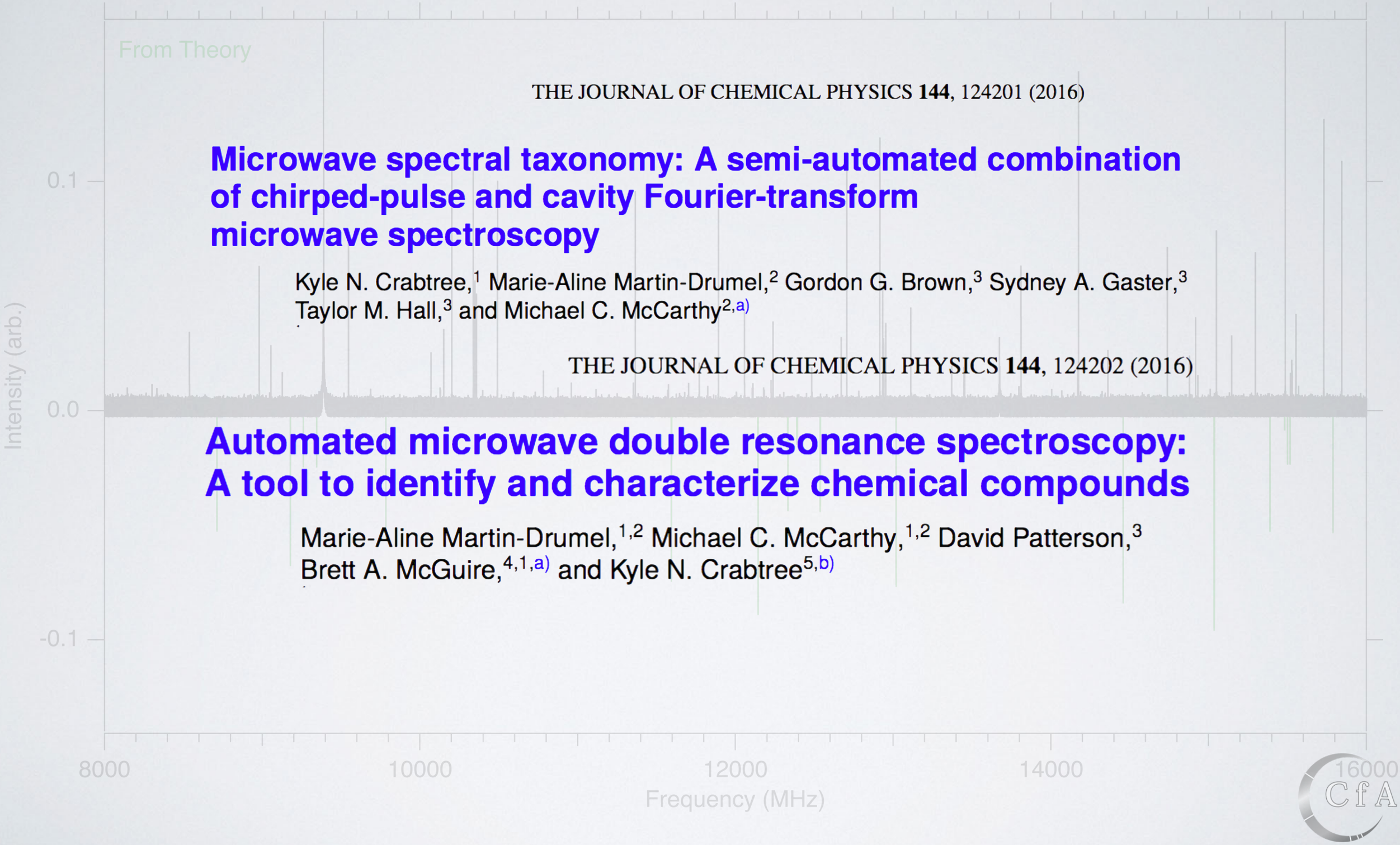
Microwave spectral taxonomy: A semi-automated combination of chirped-pulse and cavity Fourier-transform microwave spectroscopy

Kyle N. Crabtree,[1] Marie-Aline Martin-Drumel,[2] Gordon G. Brown,[3] Sydney A. Gaster,[3] Taylor M. Hall,[3] and Michael C. McCarthy[2,a)]

THE JOURNAL OF CHEMICAL PHYSICS **144**, 124202 (2016)

Automated microwave double resonance spectroscopy: A tool to identify and characterize chemical compounds

Marie-Aline Martin-Drumel,[1,2] Michael C. McCarthy,[1,2] David Patterson,[3] Brett A. McGuire,[4,1,a)] and Kyle N. Crabtree[5,b)]



CfA

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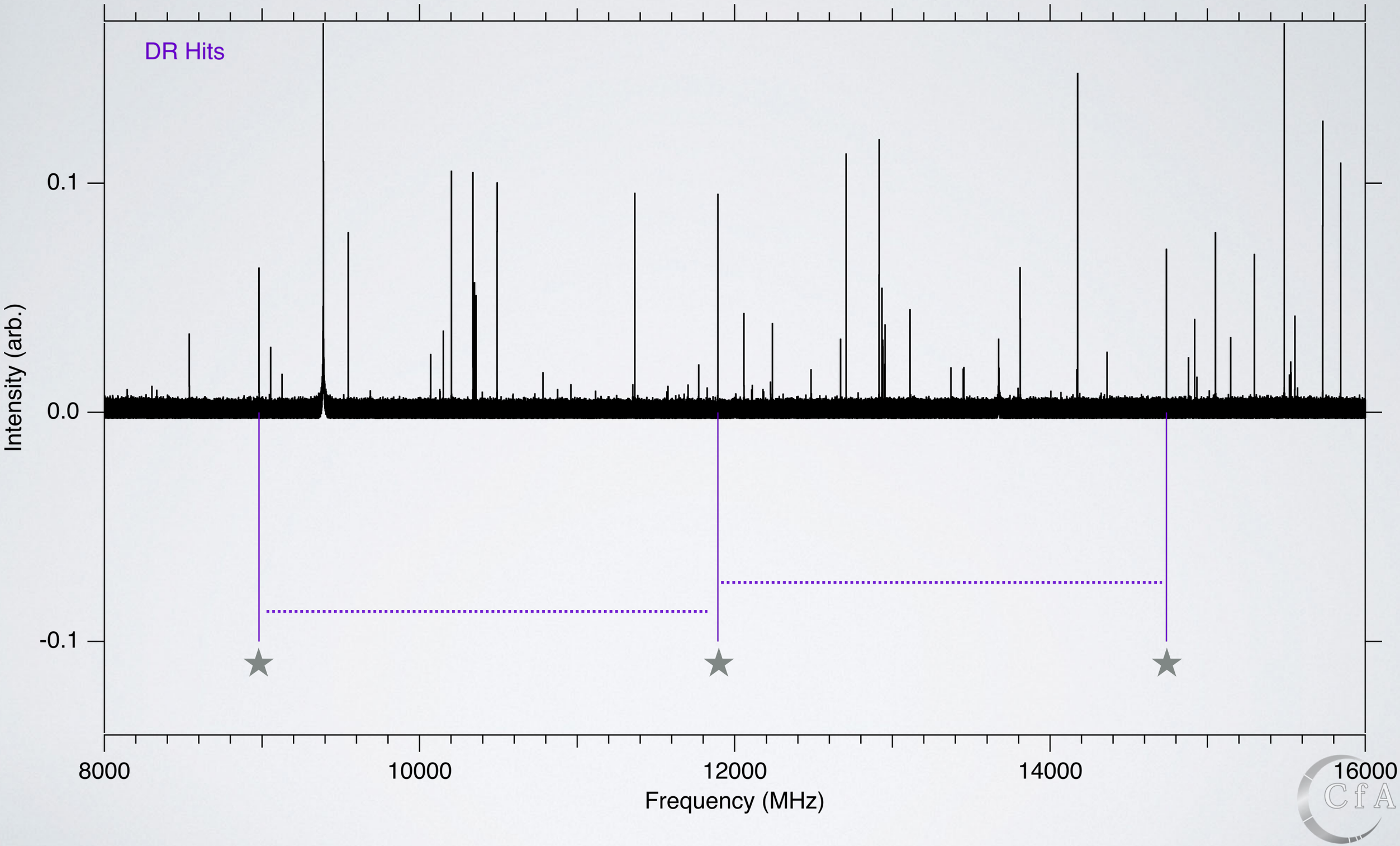

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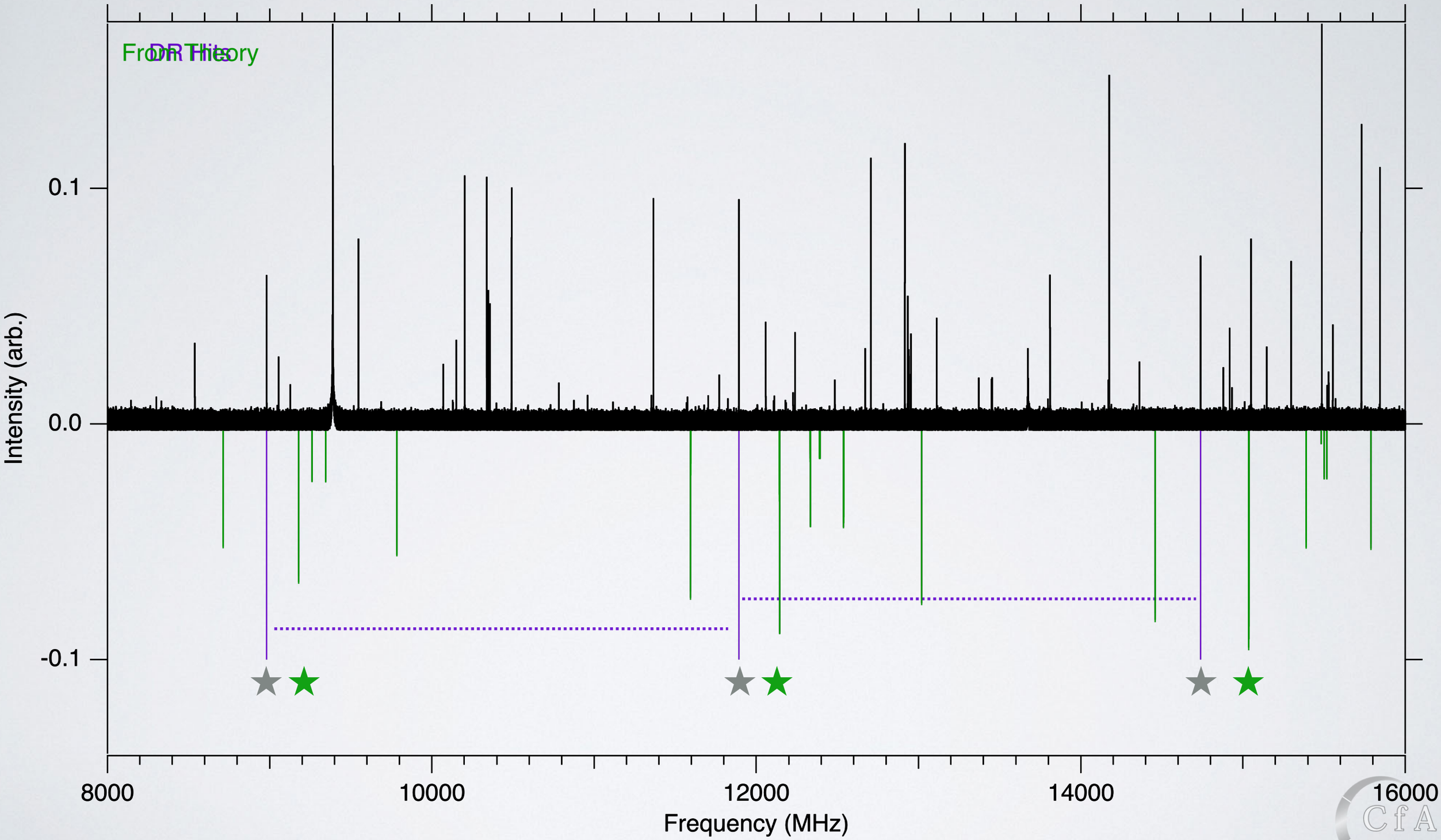

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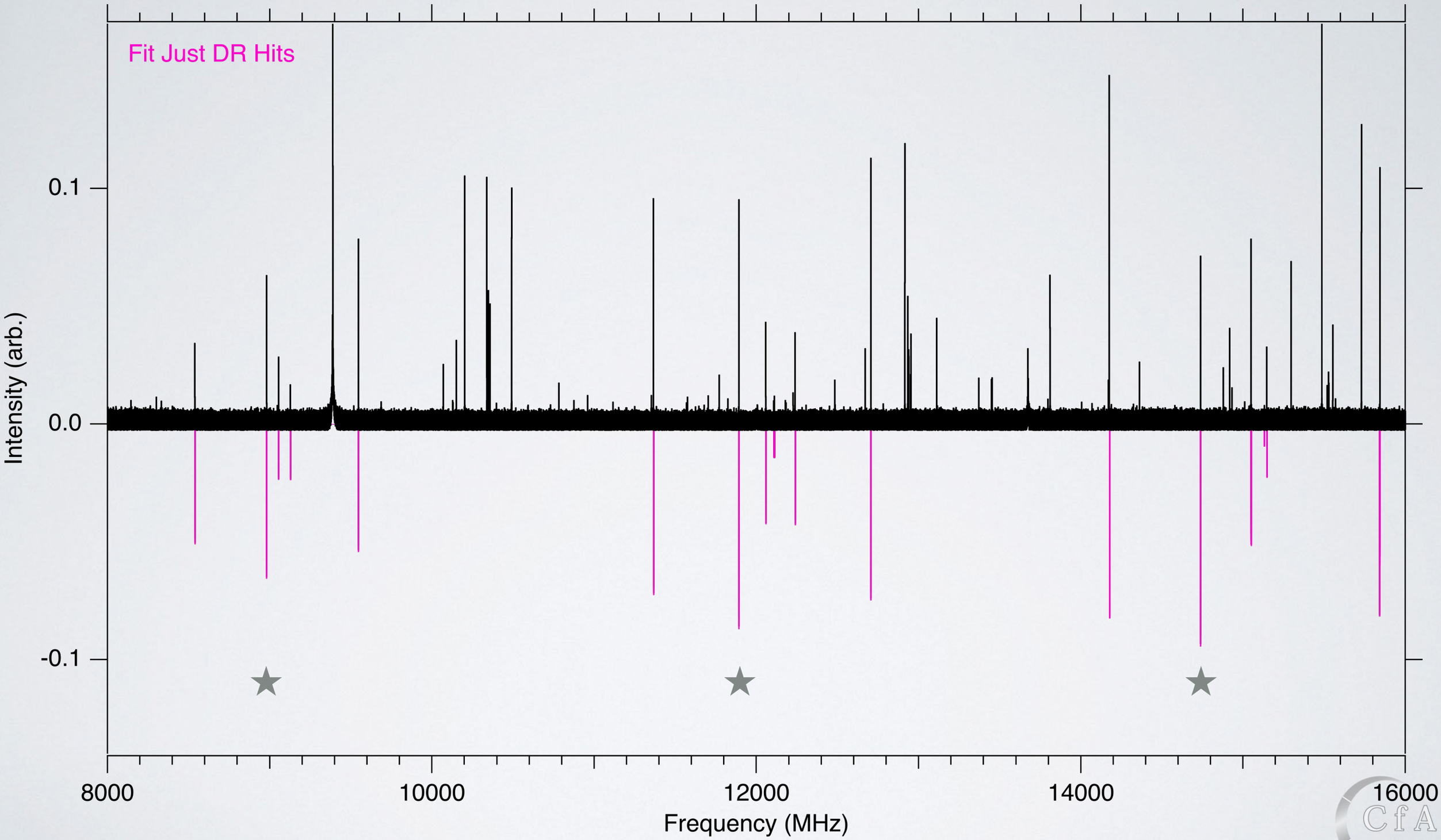

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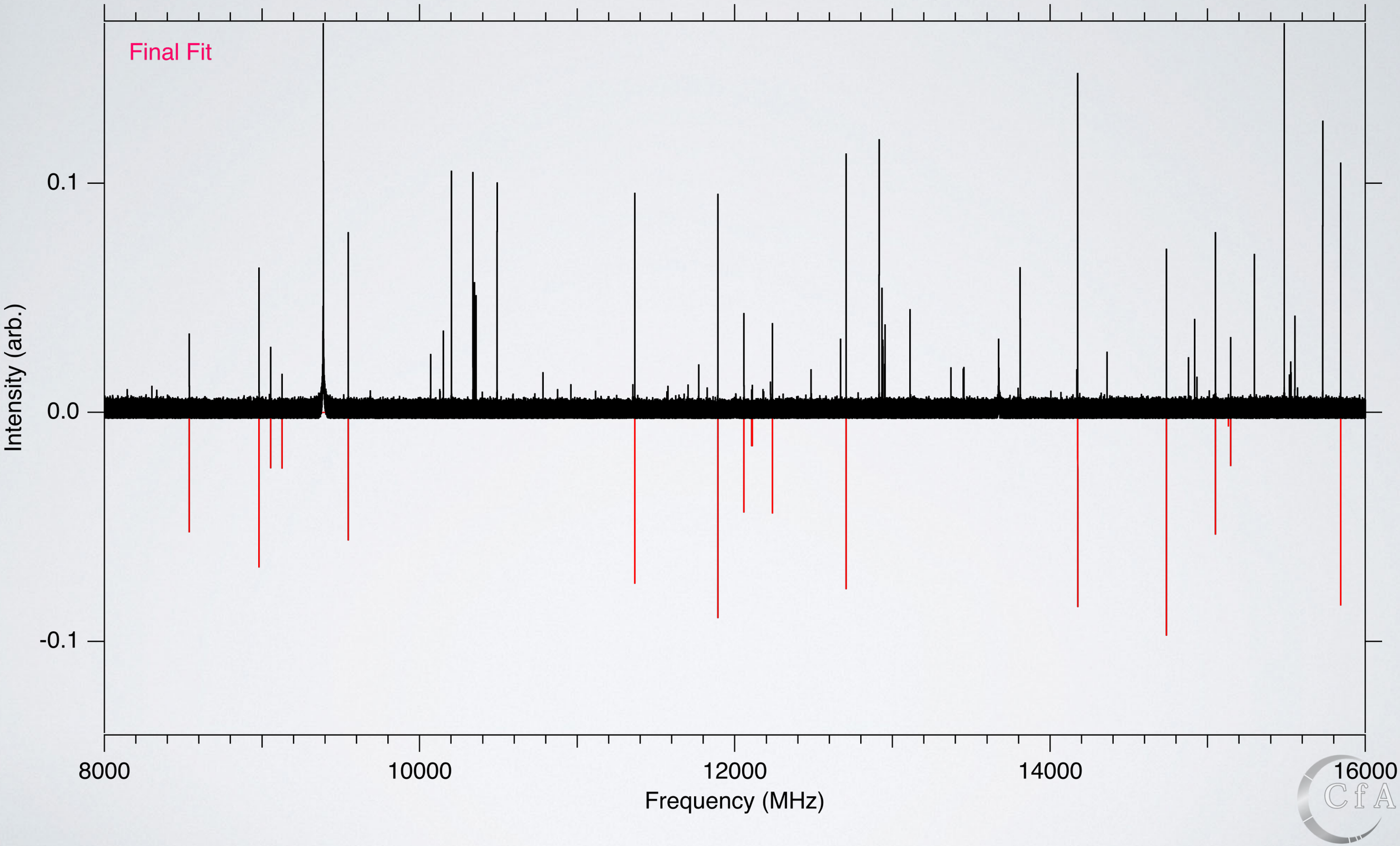

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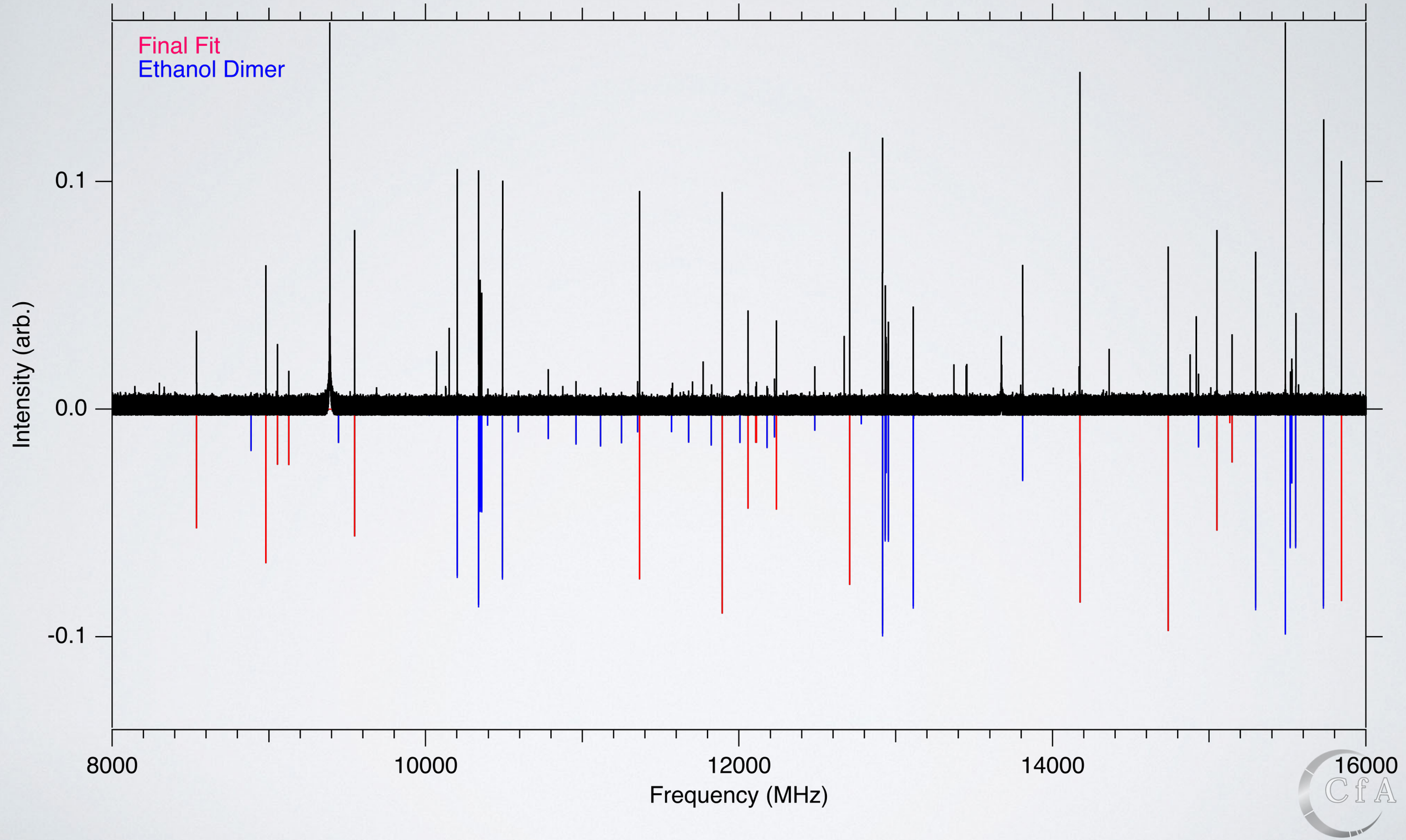
Loru et al. 2017 *JMS 335, 93*



HOW DO THESE COMPARE?

McGuire et al. 2017 *JPCA*, submitted

WB97XD/aug-cc-pVDZ

Constant	H-Bond	EDA	Experiment
A (MHz)	5220	6089	6128.018(1)
B (MHz)	1591	1722	1677.2492(2)
C (MHz)	1406	1365	1340.84697(8)
μ_a	-1.34	-0.93	
μ_b	1.18	1.87	
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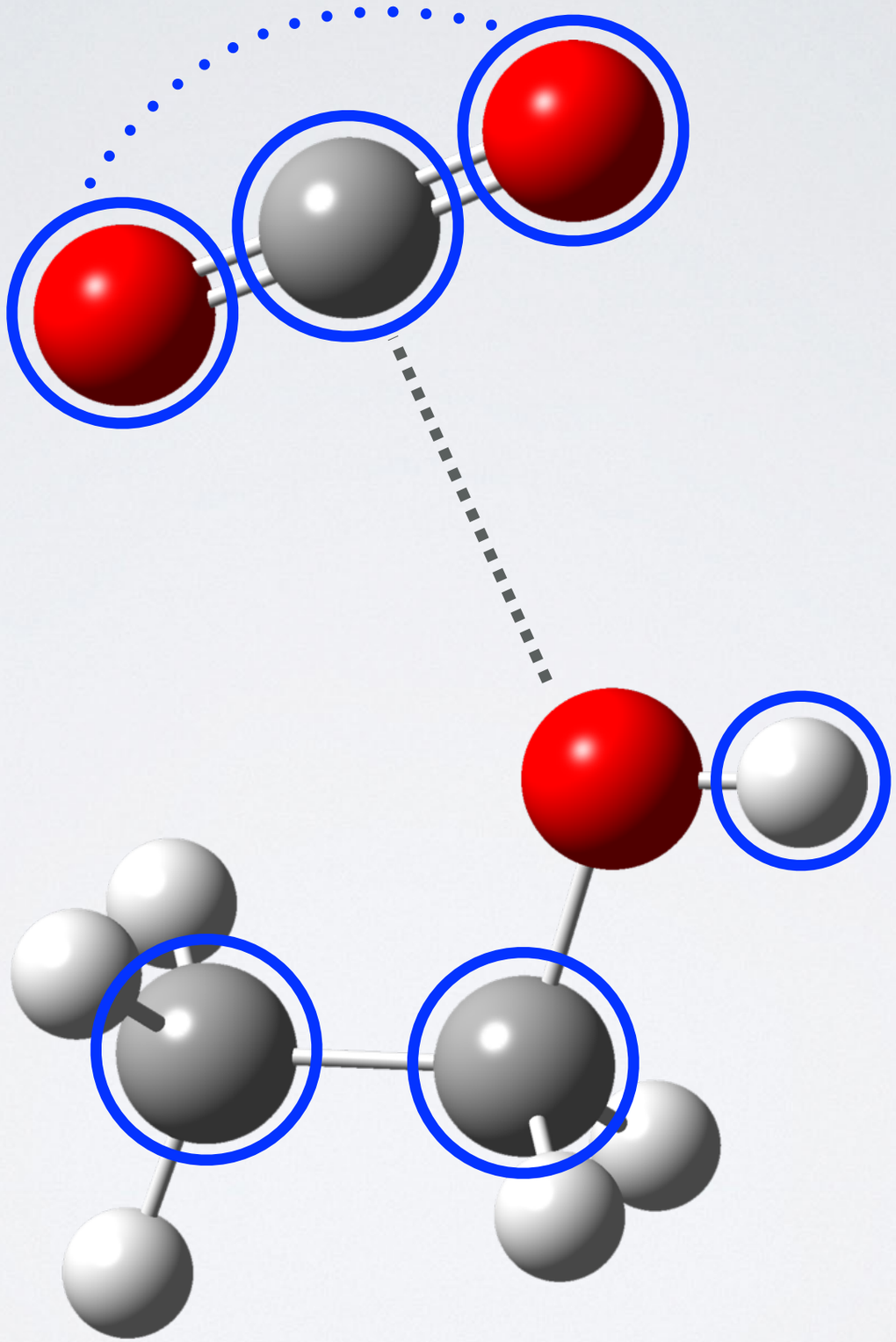

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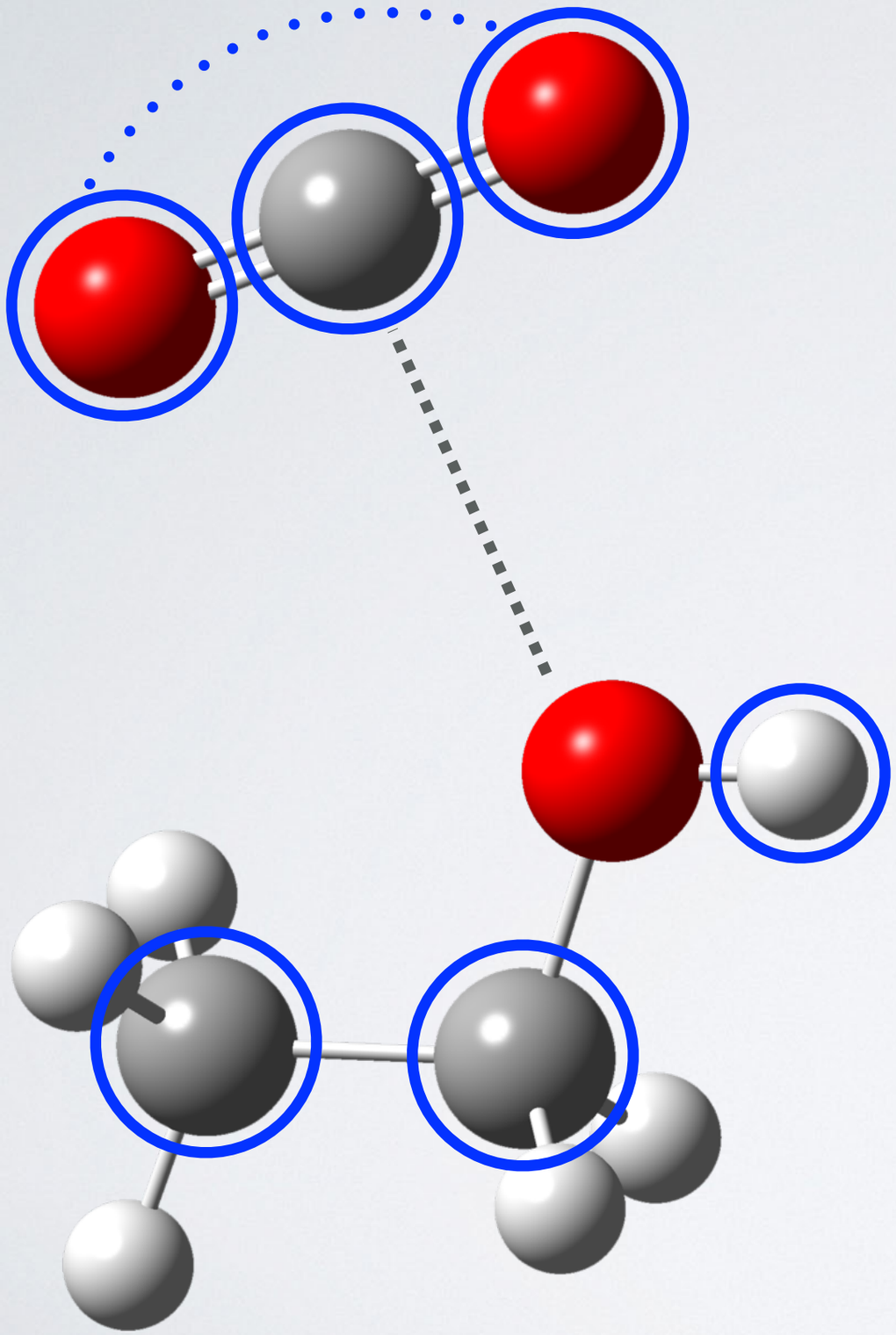

$^{13}CH_3CH_2OH\text{-}CO_2$

$CH_3{}^{13}CH_2OH\text{-}CO_2$

$CH_3CH_2OD\text{-}CO_2$

$CH_3CH_2OH\text{-}{}^{13}CO_2$

$CH_3CH_2OH\text{-}{}^{18}OC^{18}O$

CONFIRMING THE STRUCTURE

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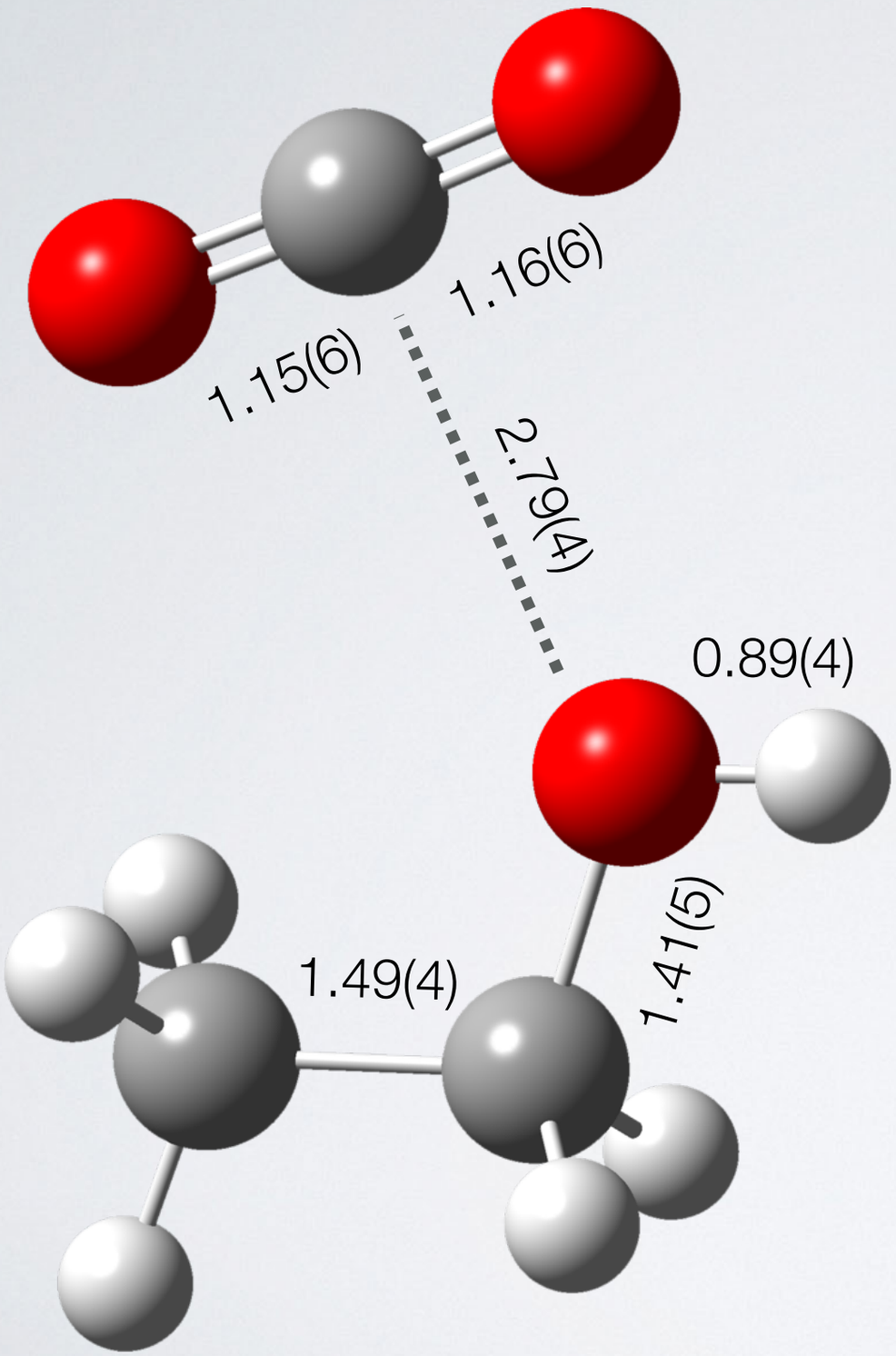

$^{13}CH_3CH_2OH$-CO_2

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CH_3CH_2OD-CO_2

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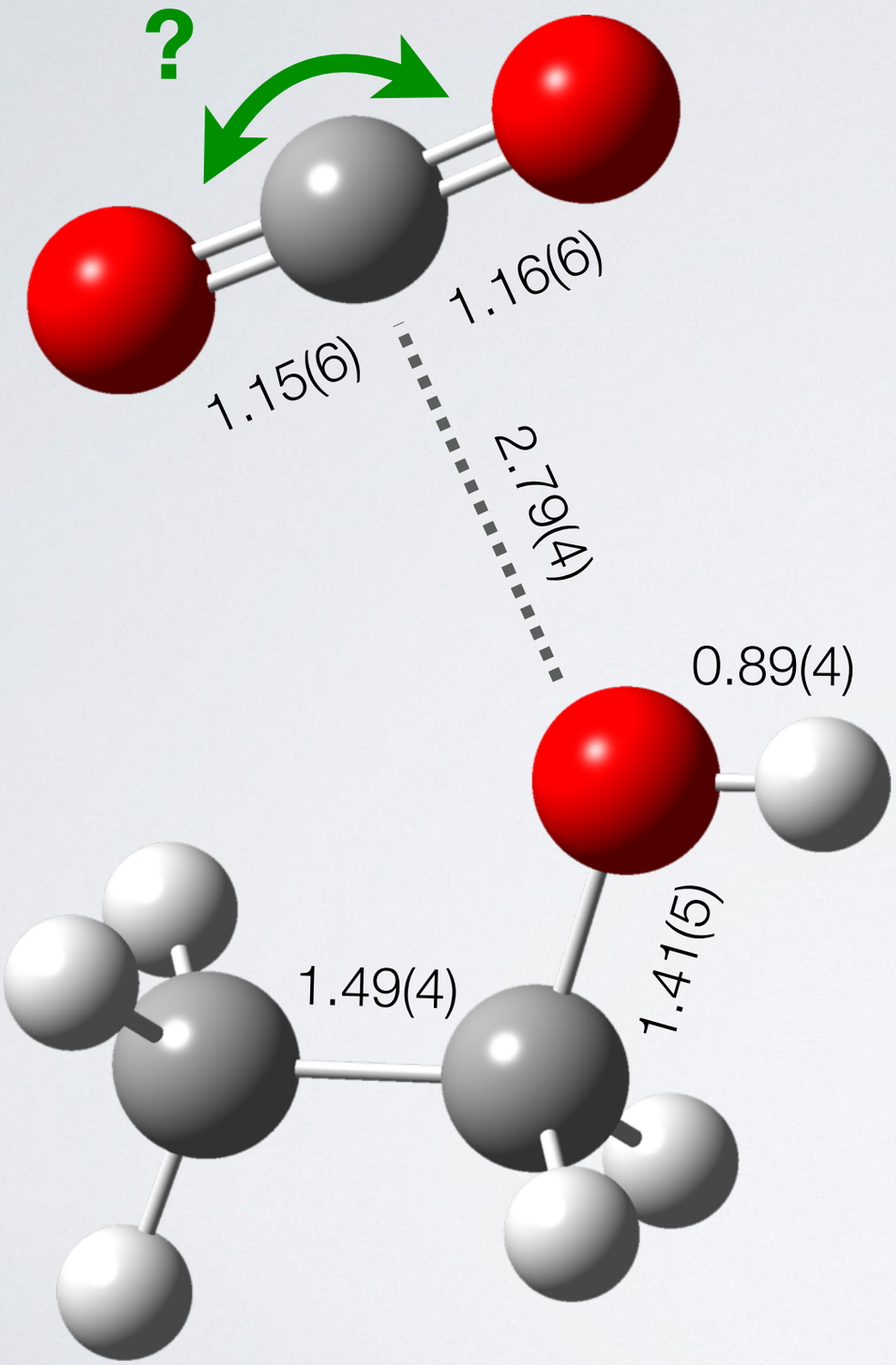

$^{13}CH_3CH_2OH$-CO_2

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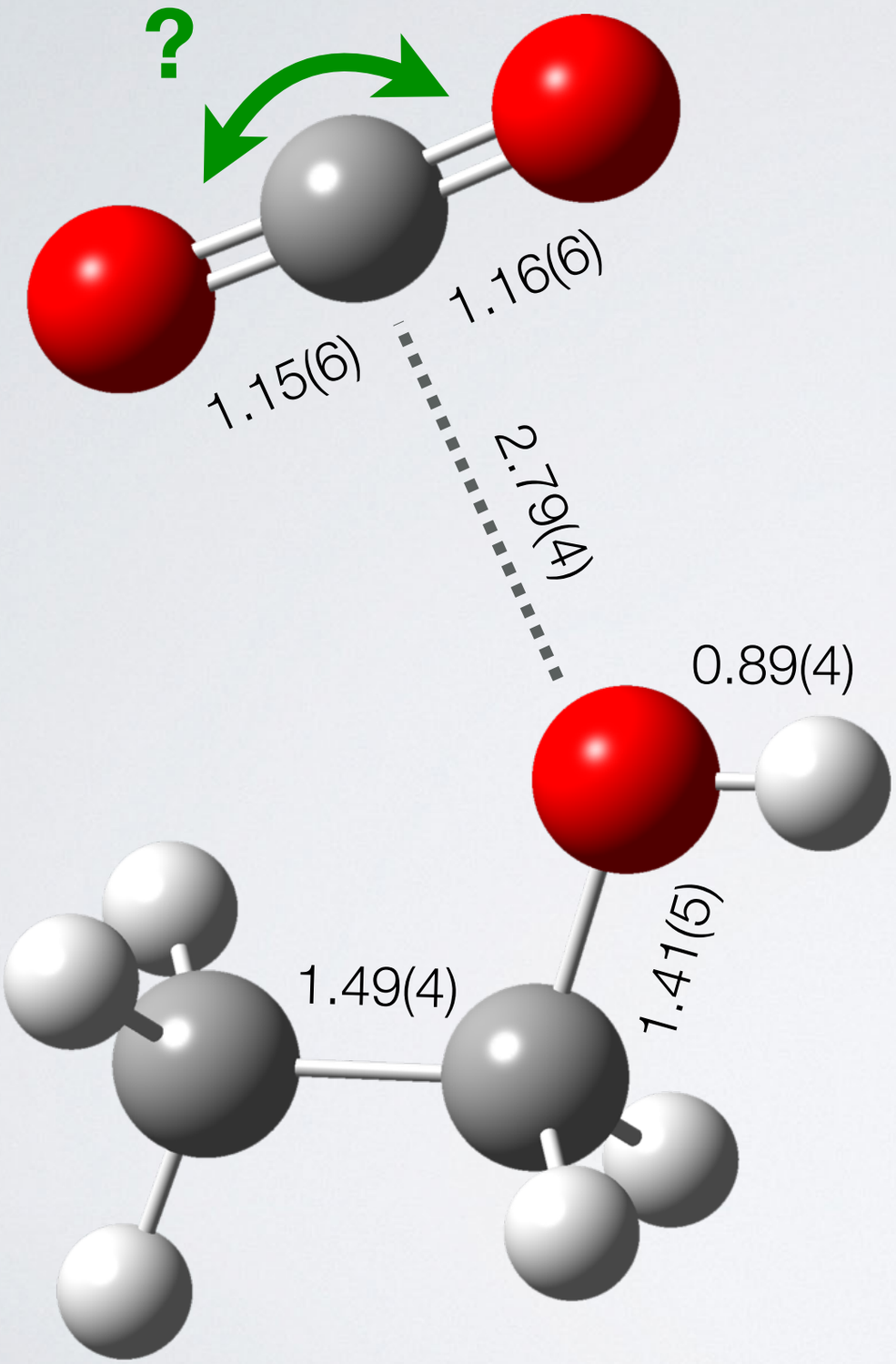
CONFIRMING THE STRUCTURE

McGuire et al. 2017 *JPCA*, submitted



$^{13}CH_3CH_2OH$-CO_2

$CH_3{}^{13}CH_2OH$-CO_2

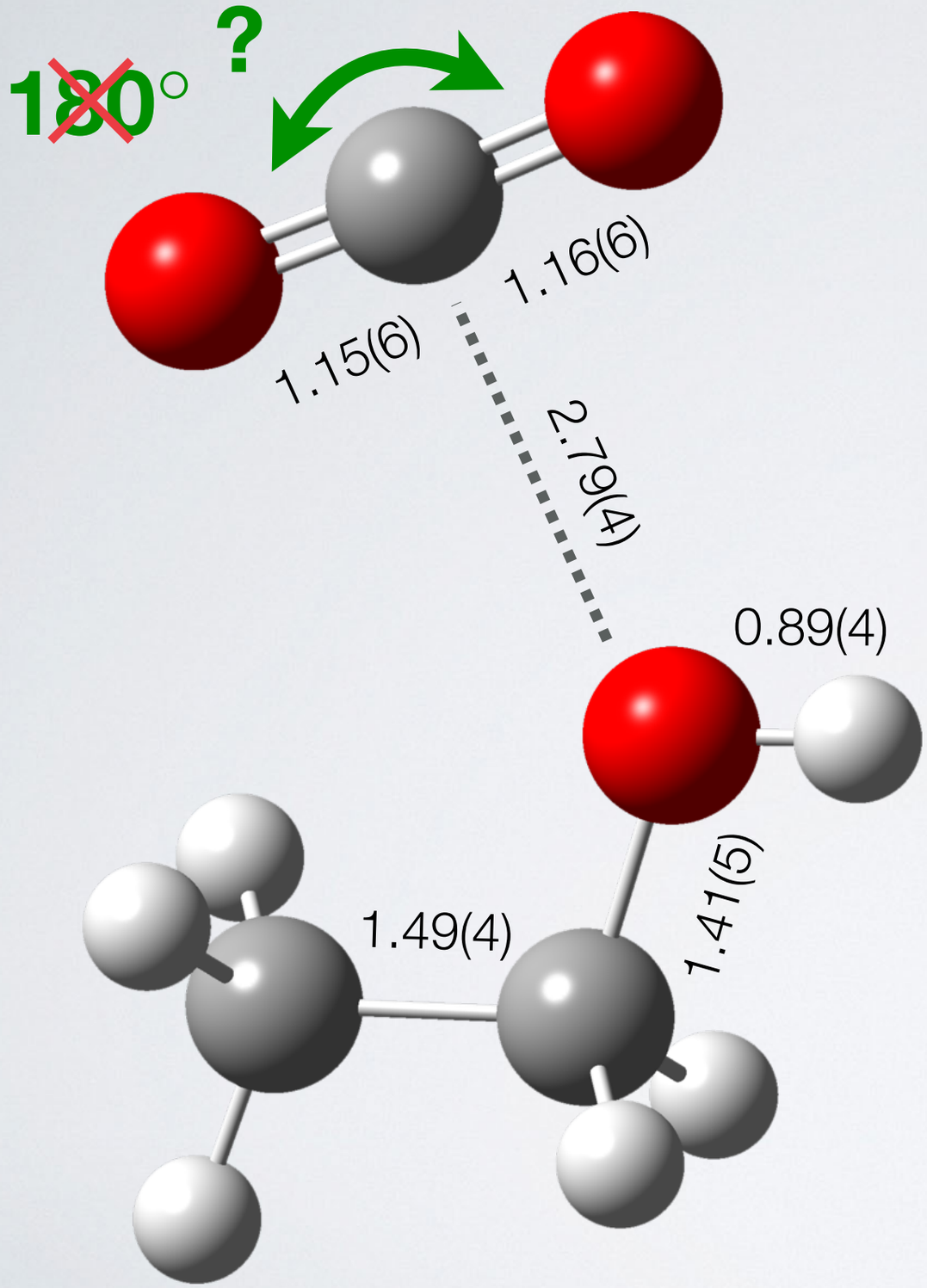
CH_3CH_2OD-CO_2

CH_3CH_2OH-$^{13}CO_2$

CH_3CH_2OH-$^{18}OC^{18}O$

CONFIRMING THE STRUCTURE

McGuire et al. 2017 *JPCA*, submitted



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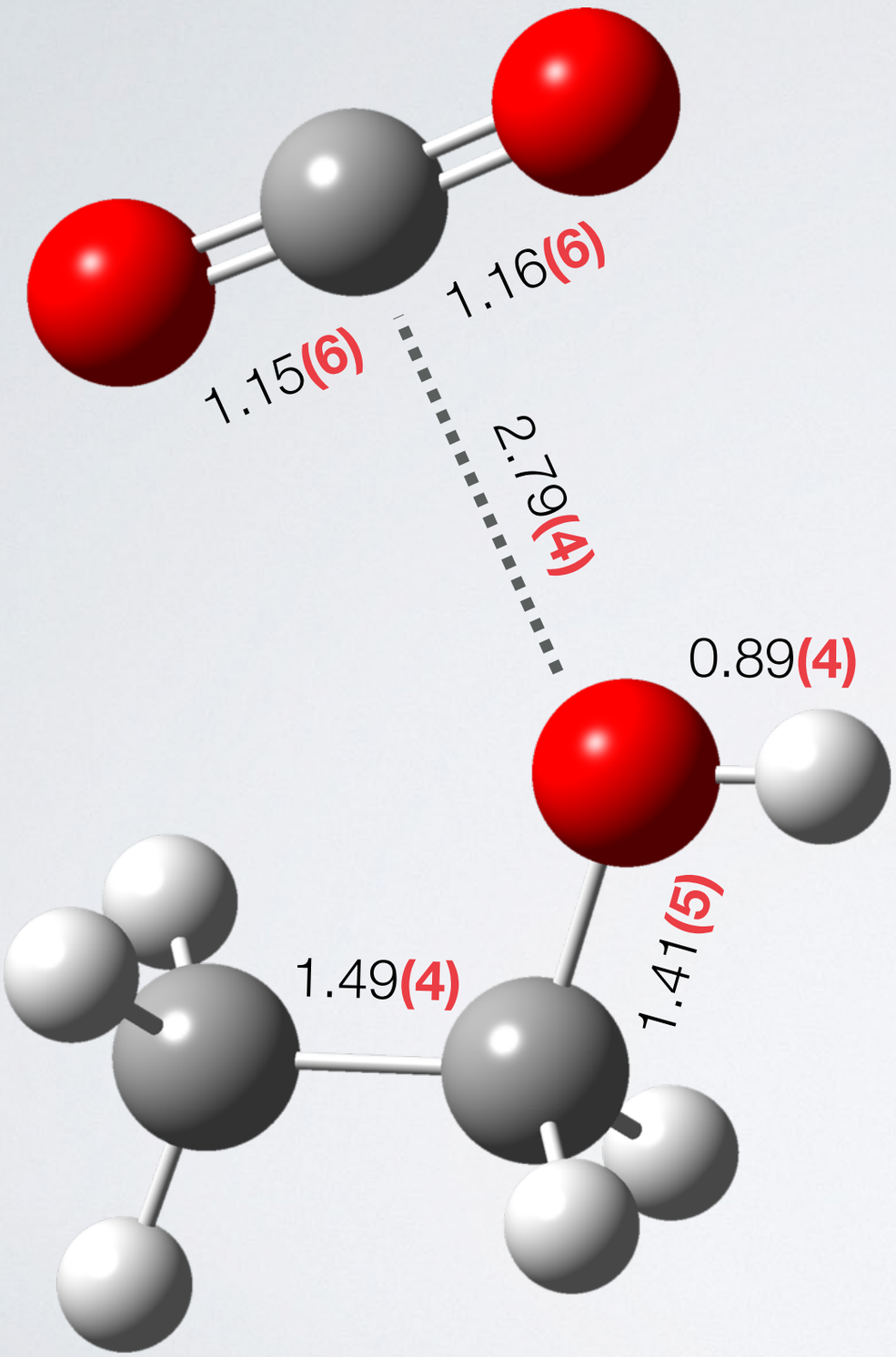

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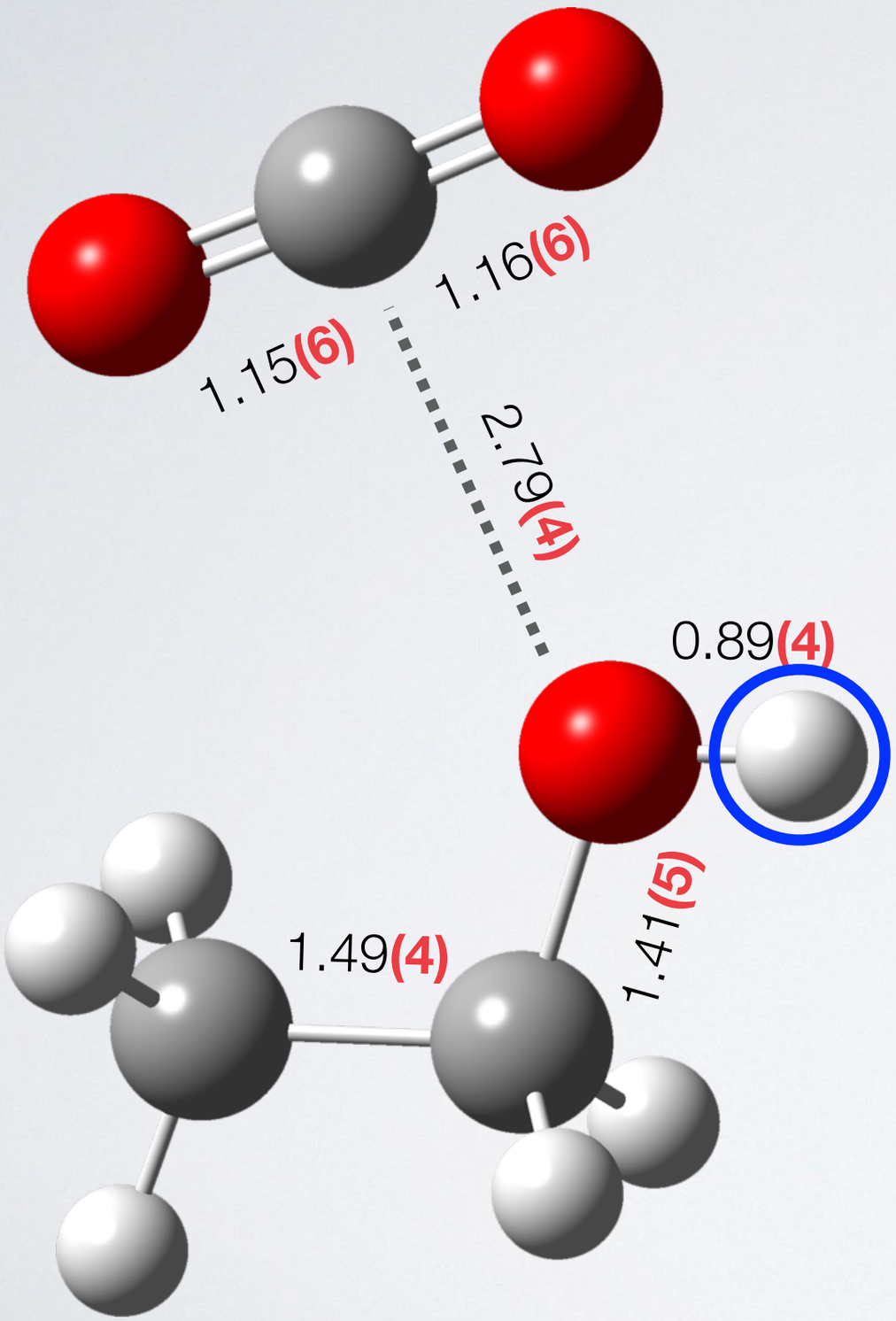

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McGuire et al. 2017 *JPCA*, submitted

Can we find the hydrogen-bonded complex (+1.7 kcal/mol)?

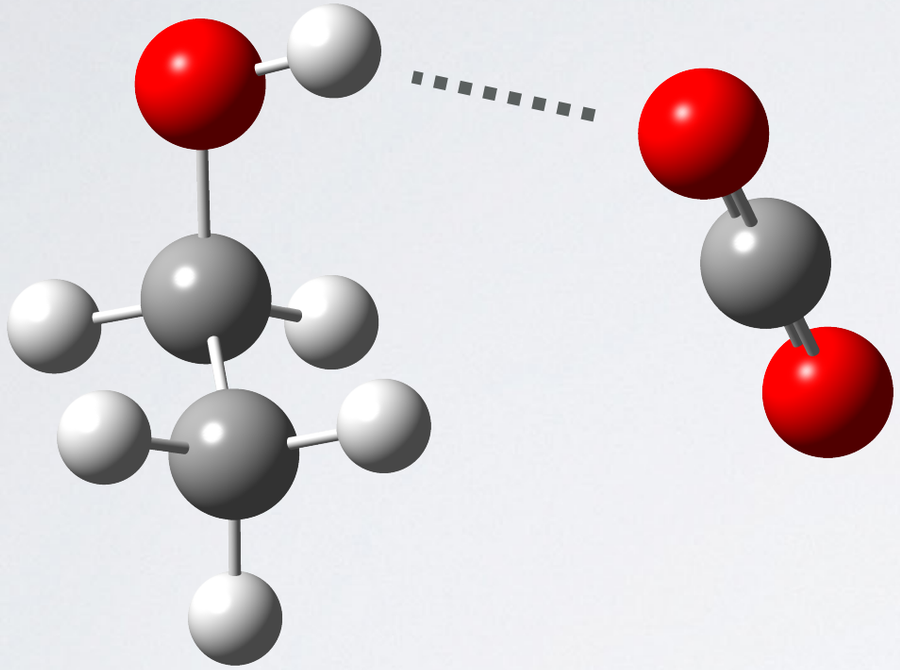
A BIT OF A WITCH HUNT

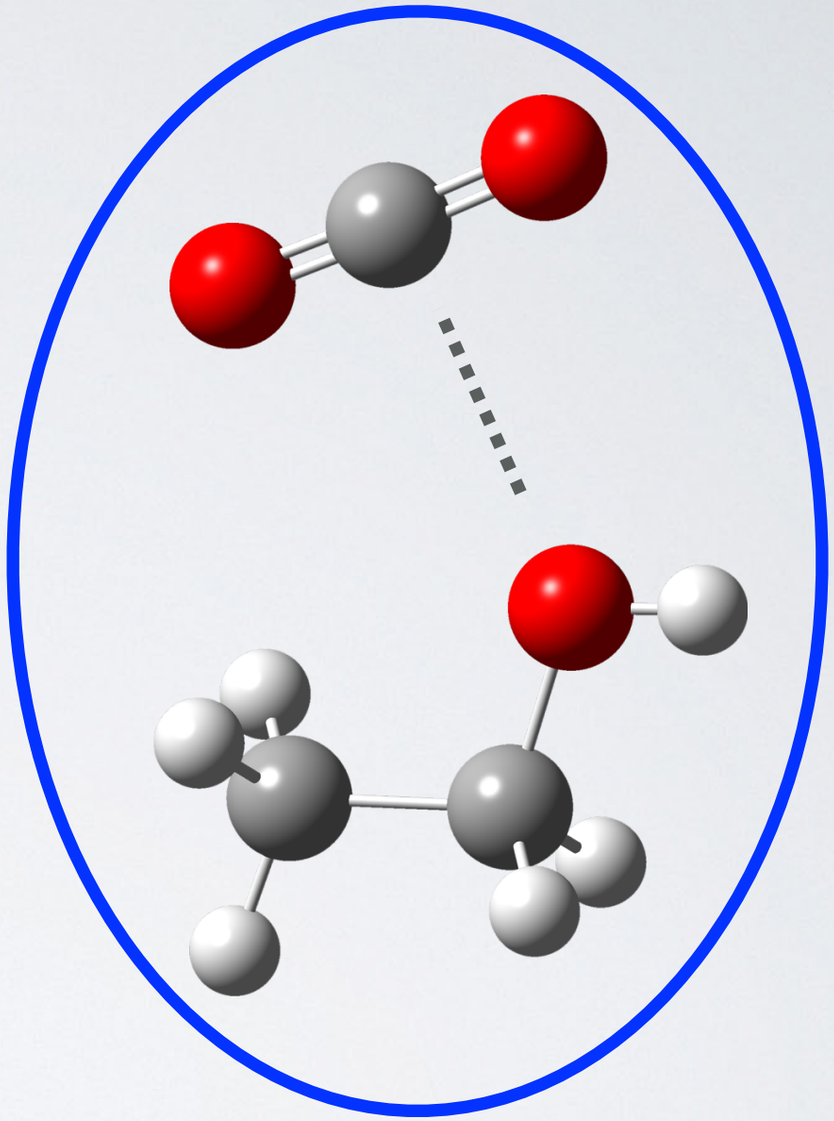
McGuire et al. 2017 *JPCA*, submitted

No

TAKE-HOME MESSAGE

McGuire et al. 2017 *JPCA*, submitted





State-of-the-art microwave spectroscopy can provide insight into chemical physics with everyday applications