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First principles model of isotopic fractionation in formaldehyde photolysis: Wavelength and pressure dependence

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Abstract: Experimental studies show large isotope-dependent effects in the photolysis rates of formaldehyde isotopologues, that are both wavelength and pressure dependent. These effects are on the order of 10-20% for ^{13}C and ^{18}O (Feilberg et. al 2004), and 60% for CHDO (Nilsson et. al 2014). We have made a model of the elementary processes involved in the photodissociation including unimolecular dissociation, collisional quenching and crossing between excited state surfaces. Computational chemistry is used to characterize some of these processes. The model is validated by comparison to all existing experimental data and is then used to make predictions about the isotopic fractionation in additional isotopologues (and for conditions not yet addressed by experiment) including fractionation in clumped molecules. The following isotopologues of formaldehyde have been investigated; HCHO, DCHO, DCDO, $D^{13}CHO$, $H^{13}CHO$, $HCH^{17}O$, $HCH^{18}O$, $H^{13}CH^{17}O$ and $H^{13}CH^{18}O$. Rice–Ramsperger–Kassel–Marcus (RRKM) theory was used to calculate the rates for decomposition of the S_0, S_1 and T_1 states with CCSD(T)/aug-cc-pVTZ, ωB97X-D/aug-cc-pVTZ and CASPT2/aug-cc-pVTZ levels of theory. Furthermore, the rates and likelihood of intersystem crossing were investigated by including the spin-orbit coupling between the excited states. The model was able to replicate the experimental pressure trends accurately and was within experimental uncertainty with high energy excitations. We predict a large clumped isotope anomaly in $^{13}C^{18}O$ produced by formaldehyde photolysis.

Introduction

Isotopic analysis can provide insight into many atmospheric mechanisms as trace gas sources and sinks have distinguishable isotopic signatures. In the atmosphere, the oxidation of virtually all hydrocarbons produces formaldehyde, which photolysis via two pathways[1]:

$$HCHO + h\nu \rightarrow H + HCO \ (\lambda \leq 330nm)$$
$$HCHO + h\nu \rightarrow H_2 + CO \ (\lambda \leq 361nm)$$
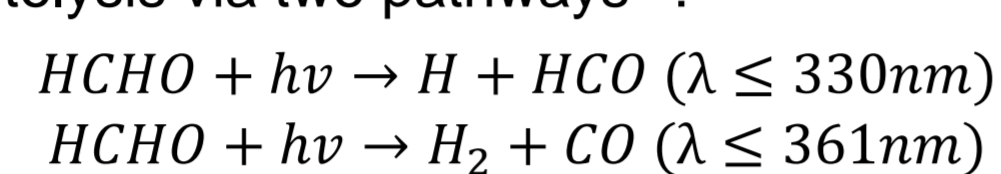
Through the first photolysis reaction, formaldehyde has a large impact on HOx cycle which is key for the oxidative capacity of the atmosphere. The second photolysis reaction produces around half of molecular hydrogen in the atmosphere and a significant fraction of CO.

Understanding isotope effects in formaldehyde photodissociation are therefore at the center of understanding isotopic enrichments in molecular hydrogen and carbon monoxide.
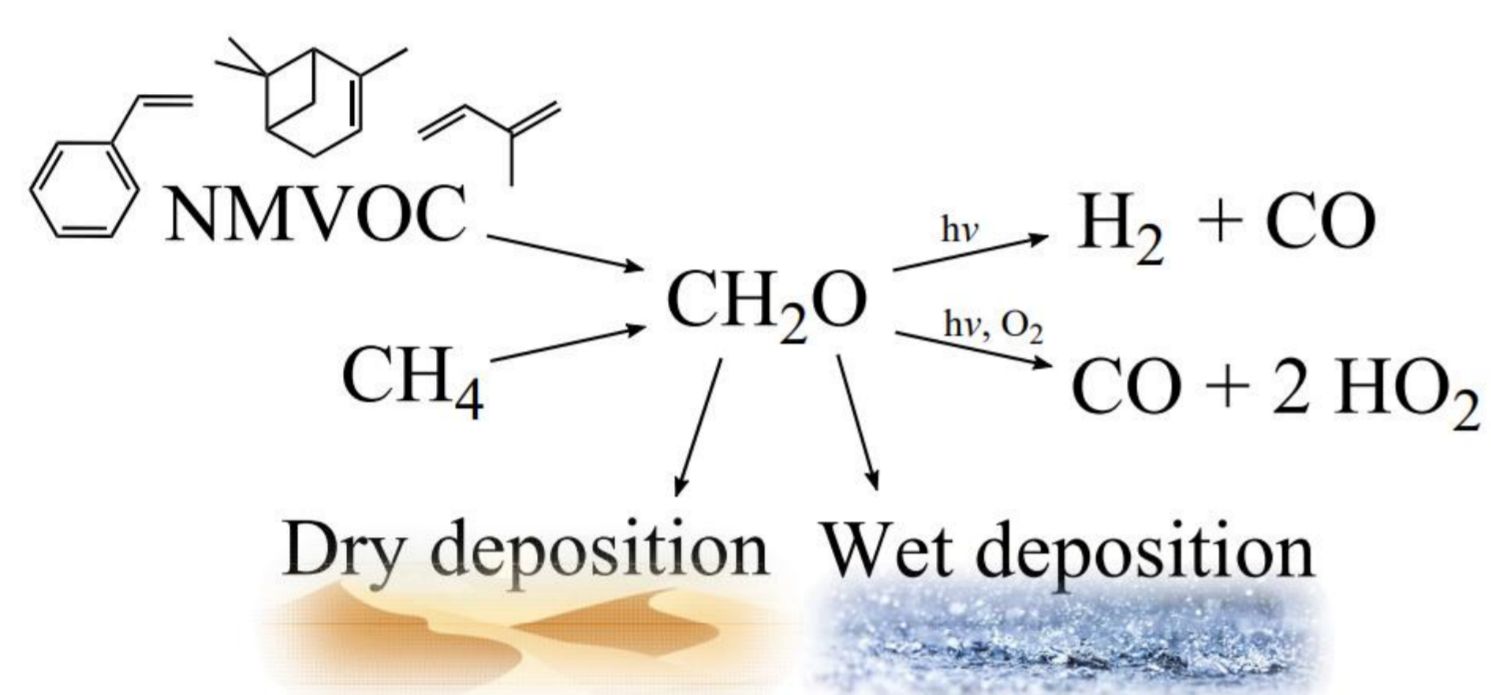

Figure 1: Sources and sinks for atmospheric formaldehyde.

Experimental studies have shown large isotope-dependent effects in the photolysis rates of formaldehyde isotopologues, that are both wavelength and pressure dependent, on the order of 10-20% for ^{13}C and ^{18}O, and 60% for CHDO[2-4].

The UV absorption cross-section of formaldehyde and its deuterated species have been found to be equal within the experimental uncertainty[4]. The observed isotope effects must therefore be due to isotope-dependent changes in the photodissociation dynamics.

Methods

R2-R7 have been determined computationally in this study and R8 has been estimated using hard sphere collision theory. It can be noted that all reactions ultimately lead to the formation of CO, with the exception of deposition. A difference in isotope distribution in CO will therefore originate from the isotope prolonging the atmospheric lifetime and thereby the likelihood of deposition.
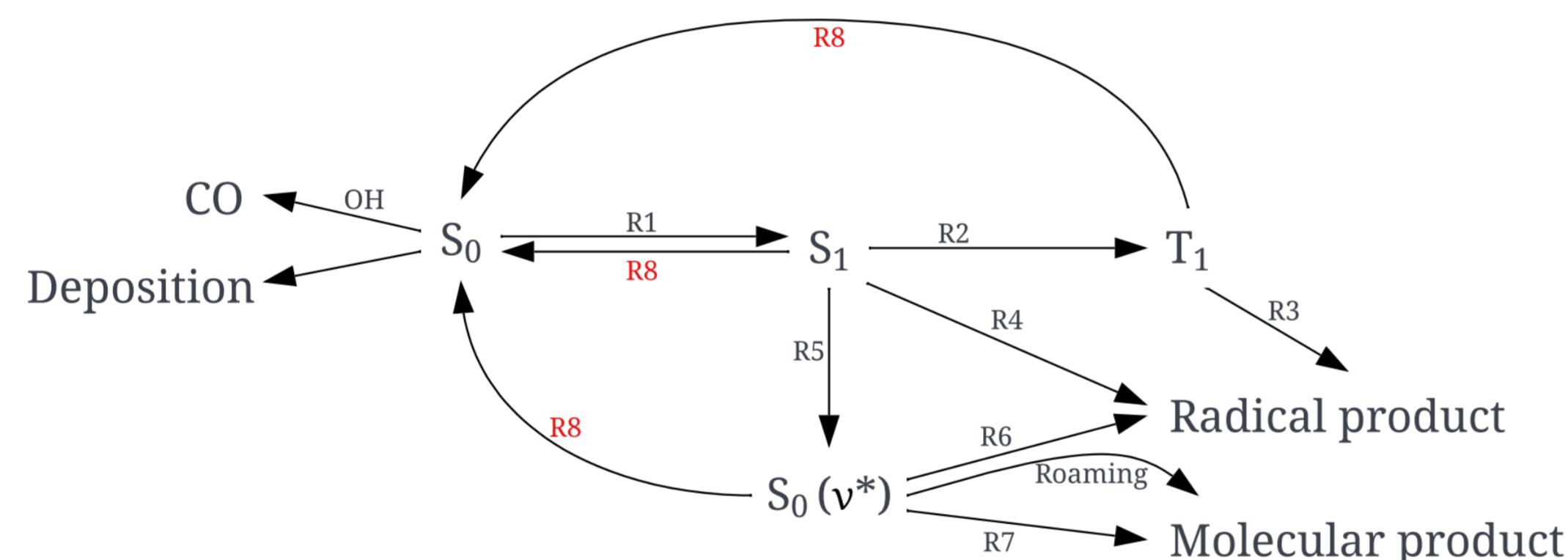

Figure 2: Reaction mechanism for the photolysis of formaldehyde.

RRKM

Rice–Ramsperger–Kassel–Marcus (RRKM) theory[5] was used to calculate the rates for decomposition of the S_0, S_1 and T_1 states and to calculate the rate of intersystem crossing (ISC) and internal conversion (IC) along with spin-orbit coupling (SOC) and Fermi's Golden Rule[6].

The following isotopologues of formaldehyde have been investigated; HCHO, DCHO, DCDO, $D^{13}CHO$, $H^{13}CHO$, $HCH^{17}O$, $HCH^{18}O$, $H^{13}CH^{17}O$ and $H^{13}CH^{18}O$.

Energy barriers and excitation energies from the literature[7-10] have been used and the frequencies and ΔZPE have been calculated with aug-cc-pVTZ and CCSD(T), ωB97X-D and CASPT2 for the S_0, S_1 and T_1 states, respectively.

Kinetic Isotope Effect (KIE)

The quantum yields of the entire process can be determined for the radical, $\phi_R(E)$, and molecular, $\phi_M(E)$, channels as well as quenching to the S_0 state , $\phi_{S0}(E)$,. The photolysis rate is then determined by:

$$j = \int_{250}^{360} F(\lambda)\left(\phi_R(\lambda) + \phi_M(\lambda)\right)d\lambda$$

The absorption cross section can be neglected when determining the KIE, $KIE = {}^j/_{j'}$, as the integrated absorption sections for HCHO and it's isotopologues can be estimated to be equal.
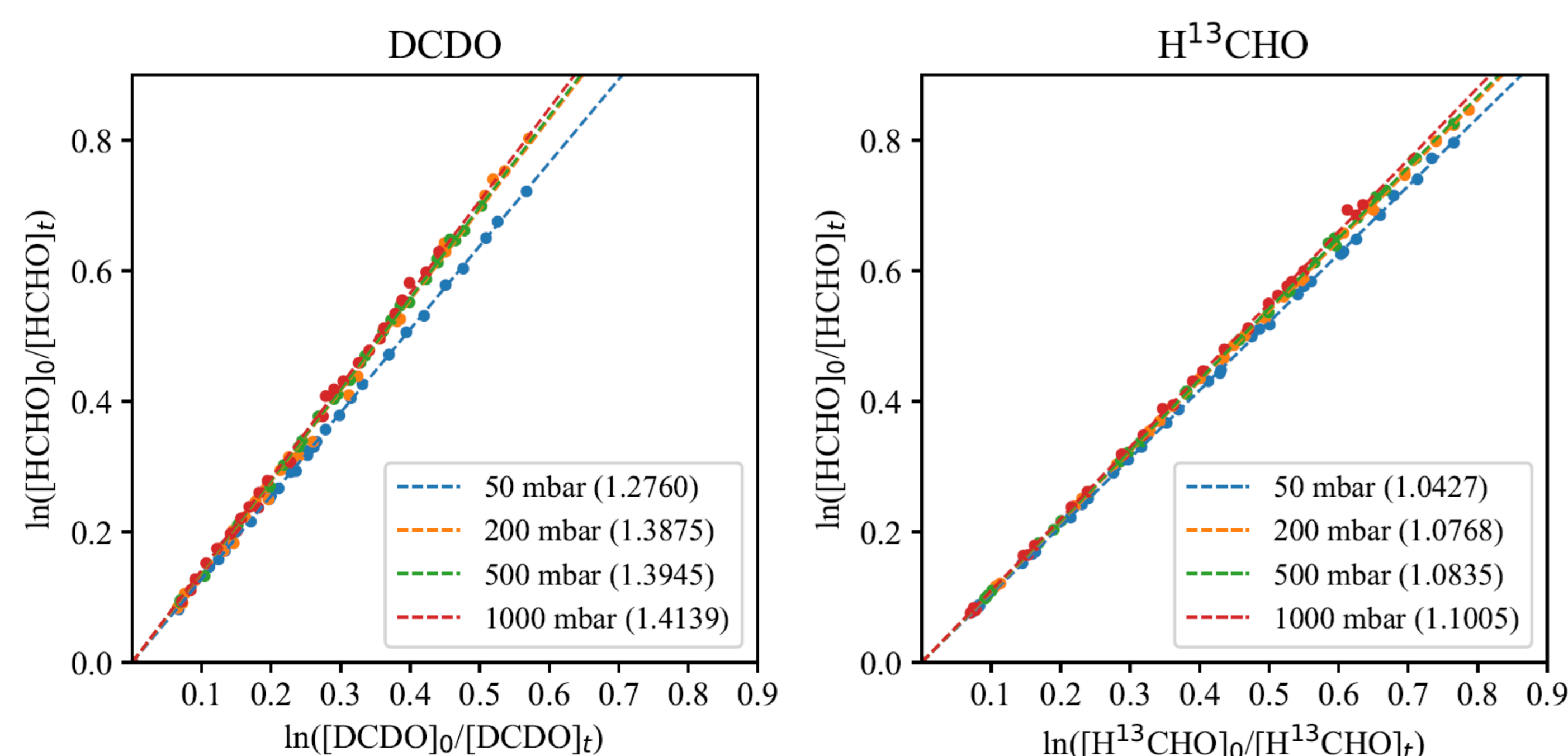
Results
Experiments

Figure 3: Relative rate of DCDO and $H^{13}CHO$ compared to HCHO at various pressures. The KIE is given in the parentheses.

Model

The model is in excellent agreement with experiments when high energy excitations occur, staying within the experimental uncertainty, with the exception of $H^{13}CHO$ which is underestimated. When only low energy excitations are possible, the model overestimates the KIE of deuterium initiated reactions.
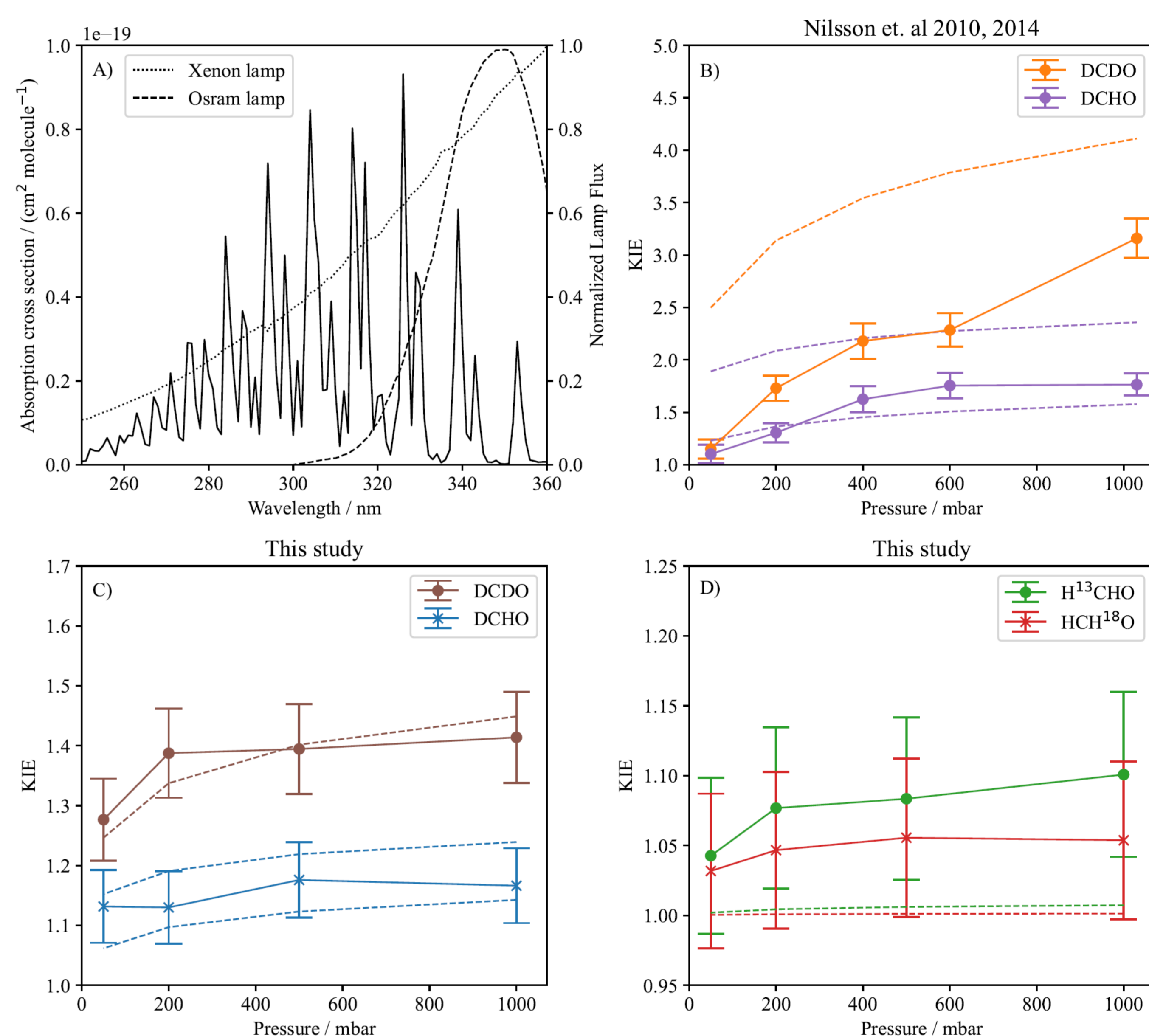

Figure 4: A) Absorption cross section of HCHO (full drawn line) and normalized lamp fluxes of the xenon lamp used in this study (dotted line) and the Osram lamp used by Nilsson et. al 2010, 2014[13,12] (dashed line). **B)-D)** The experimental (full drawn lines) and modelled (dashed lines) KIEs of DCDO, DCHO, $H^{13}CHO$ and $HCH^{18}O$ as a functions of pressure. DCHO and $HCH^{18}O$ have been determined experimentally as single-point relative rates.

This overestimation of deuterium initiated pathways can also be seen when comparing with photolysis by solar flux at surface level and 1030 mbar pressure. The KIE was also modelled for the following: $D^{13}CHO(1.6010)$, $H^{13}CDO(2.2842)$, $HCH^{17}O(1.0029)$, $H^{13}CH^{17}O(1.0286)$ and $H^{13}CH^{18}O(1.0322)$.

Table 1: Modelled KIE of HCDO, DCDO, $H^{13}CHO$ and $HCH^{18}O$ at 1030 mbar and actinic flux at 0 km altitude compared to literature values.

	Model	Feilberg 2005 [2] EUPHORE	Nilsson 2009 [11] EUPHORE	Nilsson 2014 [12] Quartz chamber	Feilberg 2007 [3] EUPHORE	Nilsson 2010 [13] Quartz chamber	Rockmann 2010 [14] SAPHIRE
HCDO	1.5493						
DCHO	2.2037						
DCDO	3.9316	3.003 ± 0607	3.15 ± 0.08	3.16 ± 0.03	3.00 ± 0.5	1.75 ± 0.1	1.63 ± 0.03
$H^{13}CHO$	1.0245	1.195 ± 0.334			1.58 ± 0.03		
$HCH^{18}O$	1.0060	1.205 ± 0.338					

The pressure dependence is described in Figure 5 and will be most pronounced at low energy excitations and for heavy isotopologues, which is illustrated in Figure 4 B) where DCDO has a higher pressure dependence than DCHO.
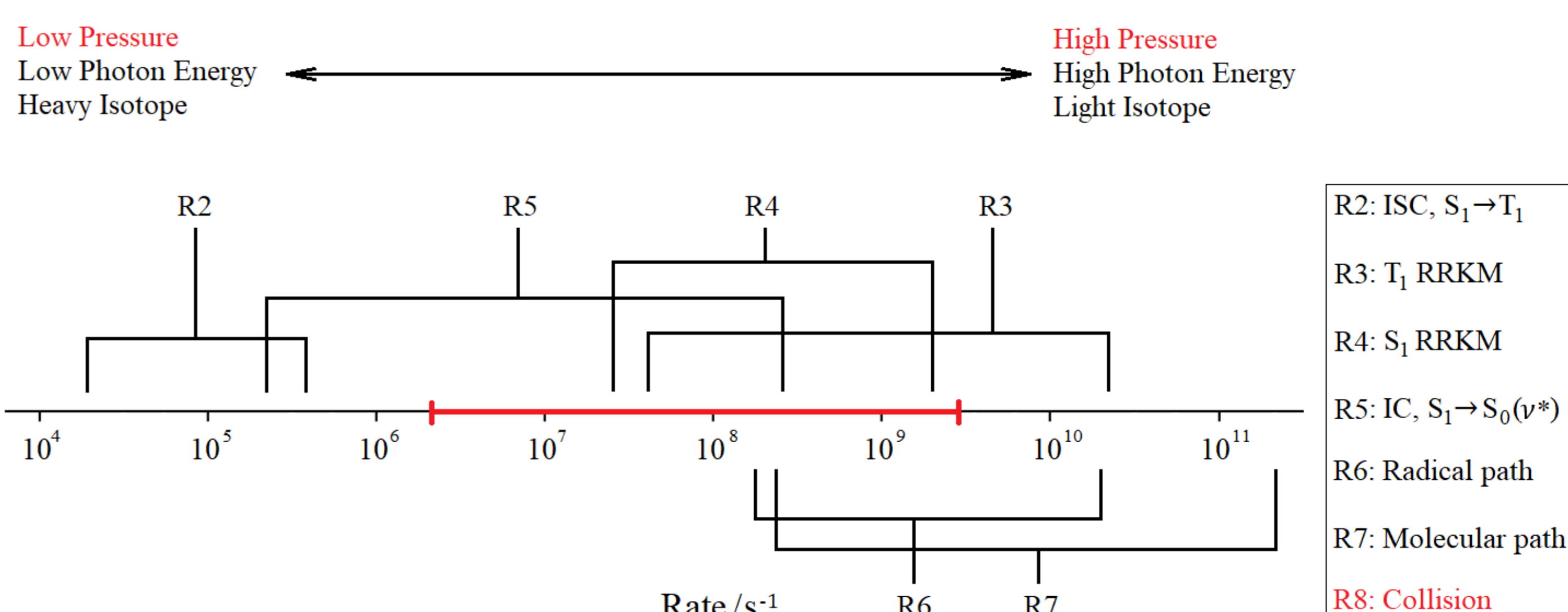

Low Pressure — Low Photon Energy — Heavy Isotope

High Pressure — High Photon Energy — Light Isotope

R2: ISC, $S_1 \rightarrow T_1$
R3: T_1 RRKM
R4: S_1 RRKM
R5: IC, $S_1 \rightarrow S_0(\nu*)$
R6: Radical path
R7: Molecular path
R8: Collision

Rate /s^{-1}

Figure 5: Reaction rates for R2-R8 spanning atmospheric pressures, photon energy and isotopic composition.

Conclusion

- A model has been made of the elementary processes involved in the photodissociation including unimolecular dissociation, collisional quenching and crossing between excited state surfaces.
- The model is validated by comparison to all existing and new experimental data.
- The pressure dependence is highly affected by the excitation energy.
- We predict a large clumped isotope anomaly in $^{13}C^{17}O$ (Δ1.2‰) and $^{13}C^{18}O$ (Δ1.7‰) produced by formaldehyde photolysis.

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