Carbon Dioxide Diffusivity in Single, Levitated Organic Aerosol Particles

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Supporting Information Available

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1. Rapid refractive index change

![Graph showing exponential decay fitting for the 10 s irradiation period at 0% RH.](image)

\( \tau = 2.20 \pm 0.18 \text{ s} \)

Figure S1: An exponential decay fitting for the 10 s irradiation period at 0% RH.

In Figure S1 we show a close-up of the rapid blue shift in resonance wavelength of the pulsed irradiation experiment under dry conditions. First, the amplitude of the shift during irradiation, \( \Delta \lambda = -0.520 \text{ nm} \) may be compared to a theoretical prediction based
on ideal mixing assumptions. For simplicity, let us assume that there is no water present in the particle under dry conditions and that its density, $\rho_p$, is that of citric acid, i.e. $\rho_p = 1.58056 \text{ g cm}^{-3}$. According to reactions R1 and R2, after irradiation and before CO$_2$ loss to the gas phase, the density of the particle will decrease due to the produced CO$_2$ and the decarboxylated product (here we assume that the C$_5$ product is 3-oxoglutaric acid).

Ideal mixing predicts a density change $\Delta \rho = -(7.06 \pm 0.40) \times 10^{-3} \text{ g cm}^{-3}$ using the known molar ratio of Fe$^{III}$(Cit) to citric acid (0.05), a molar volume for CO$_2$ of 34.2 cm$^3$ mol$^{-1}$ and a molar volume for C$_5$ of (98.9 $\pm$ 0.5) cm$^3$ mol$^{-1}$. A reduction in density alone would lead to a red shift in resonance wavelength. However, the Lorentz-Lorenz relation allows us to calculate the corresponding change in refractive index in terms of the refractivity, $a$, of the solution:

$$n^2 = \frac{1 + 2a}{1 - a},$$

(S1)

$a$, to a good approximation, is a linear superposition of the molar refractivities $A_i$:  

$$a = \frac{\rho_p}{M_p} \sum_i x_i A_i,$$

(S2)

where we take $A_{\text{cit}} = 36.3 \text{ cm}^3 \text{ mol}^{-1}$, $A_{\text{CO}_2} = 6.64 \text{ cm}^3 \text{ mol}^{-1}$, $A_{C_5} = (28.4 \pm 0.3) \text{ cm}^3 \text{ mol}^{-1}$, $x_i$ is molar fraction of species $i$, and $\rho_p/M_p$ is the molar density of the mixture. This calculation yields $\Delta n = -(3.68 \pm 0.36) \times 10^{-3}$. Putting $\Delta n$ and $\Delta \rho$ into Eq. 1 yields a resonance wavelength shift of $\Delta \lambda = -(0.53 \pm 0.21) \text{ nm}$. It is important to note that the second irradiation led to an additional rapid shift in the experiment, see Figure 3, of about $\Delta \lambda = -0.120 \text{ nm}$. The combined observed shift of $\Delta \lambda = -0.640 \text{ nm}$ compares favourably with the predicted shift based on ideal mixing. We conclude that the rapid shift observed in our experiments is due to the combined effect of density and refractive index change caused by the production of CO$_2$ through the rapid decarboxylation of the Fe$^{III}$(Cit) complex upon irradiation.
In addition to the amplitude of resonance wavelength change, we also resolve the decay time of the blue shift \( \tau = (2.20 \pm 0.18) \) s, see Figure S1. The rate of formation of \(^{\cdot}\text{Cit}\) can be written as:

\[
\frac{d[^{\cdot}\text{Cit}]}{dt} = \phi j[^{\text{Fe}^{\text{III}}}\text{(Cit)}],
\] (S3)

where \( j \) is the first-order rate constant for photolysis or the so-called absorption rate of \(^{\text{Fe}^{\text{III}}}\text{(Cit)}\), and \( \phi \) is the quantum yield of reaction R1. Assuming that reaction R1 is followed by reaction R2 instantaneously, then the rate of formation of CO\(_2\) is the same as the one of the radical \(^{\cdot}\text{Cit}\):

\[
\frac{d[\text{CO}_2]}{dt} = \phi j[^{\text{Fe}^{\text{III}}}\text{(Cit)}].
\] (S4)

Since the resonance wavelength shift is due to the refractive index change caused by the formation of CO\(_2\), the time constant, \( \tau \), can be related to the formation rate of CO\(_2\) as:

\[
\tau = \frac{1}{\phi j}.
\] (S5)

On the other hand, \( j \) is determined by the absorption cross section of \(^{\text{Fe}^{\text{III}}}\text{(Cit)}\), \( \sigma \), and the photon flux, \( I \):

\[
j = \sigma I.
\] (S6)

Substituting Eq. S6 into Eq. S5 results in

\[
\tau = \frac{1}{\phi \sigma I}.
\] (S7)

With the laser intensity used in this experiment of \( 470^{+740}_{-240} \) W cm\(^{-2}\), the photon flux \( I \) is calculated to be \( 1.1^{+1.8}_{-0.6} \times 10^{21} \) cm\(^{-2}\) s\(^{-1}\) for the wavelength (473 nm) used in the experiment and the observed \( \tau = (2.20 \pm 0.18) \) s. The derived absorption cross section of \(^{\text{Fe}^{\text{III}}}\text{(Cit)}\) is \( \sigma = 4.1^{+5.8}_{-2.7} \times 10^{-22} \) cm\(^2\), assuming a quantum efficiency of \( \phi = 1 \). This cross section corresponds to a molar absorption of \( 0.11^{+0.15}_{-0.07} \) M\(^{-1}\) cm\(^{-1}\). Pozdnyakov et al.\(^7\) measured the
absorption spectra of \( \text{Fe}^{\text{III}}(\text{Cit}) \) in aqueous solution, yielding an approximately 500 times larger molar absorption of 60.7 M\(^{-1}\) cm\(^{-1}\) at 473 nm. This difference may be due to low quantum yield, which has been observed, for example, to be as low as 0.05 at 436 nm for the mono(malato)-ferrate complex\(^8\). Partly it could be due to not all available iron being present as the \( \text{Fe}^{\text{III}}(\text{Cit}) \) complex. According to reported equilibrium constants\(^9,10\), only about 25\% of \( \text{Fe}^{\text{III}} \) is in \( \text{Fe}^{\text{III}}(\text{Cit}) \) in our system. We also note that this method to deduce quantum yield is rather indirect.

2. Mass-loss retrieval considering density and refractive index change during loss of \( \text{CO}_2 \)

Using the same ideal mixing approach detailed in section 1 above, we can account for density and refractive index changes during \( \text{CO}_2 \) loss in an iterative procedure. The ideal mixing approach should yield reliable estimates for the data of the irradiation experiment under dry conditions, as we may safely ignore changes due to water activity there. Figure S2 shows that this yields a significantly larger amplitude for the normalized mass ratio, but does not have a significant effect on the characteristic diffusion time. This supports our initial simplification of ascribing all changes in resonance wavelength shift to size changes only for the purpose of retrieval of characteristic diffusion times. The mass ratio observed under ideal mixing assumptions yields a 2\% change whereas we expect a 1\% change based on the initial \( \text{Fe}^{\text{III}}(\text{Cit}) \) to citric acid ratio. This difference may be partly due to partial reduction of \( \text{Fe}^{\text{III}} \) to \( \text{Fe}^{\text{II}} \) during preparation of the solution prior to the injection of a particle into the EDB, partly due to our ideal mixing assumption and the neglect of residual water.
Figure S2: Normalized mass ratio profile of the particle at 0% RH and 293 K. Black data repeat the data of Figure 3, neglecting density and refractive index change due to loss of CO$_2$. Grey data: taking into account refractive index and density change, assuming ideal mixing. Grey dotted line marks the initial ratio.
3. Raw data of the experiment under dry conditions

In Figure S3 we show the raw data of the irradiation experiment under dry conditions. Two things are evident from this graph. First, there is slow, residual water loss after more than two days of drying, consistent with Figure 4. Second, after irradiation the shift of resonance wavelength with time increases significantly, indicating faster diffusivity of CO₂ compared to that of H₂O. The data of Figure 3 have been corrected by subtracting a linear fit to the last 25000 s of the data shown here in Figure S3.

![Image](image.png)

Figure S3: Black crosses: Raw data of observed resonance wavelength response at 0% RH before and after irradiation without correction for the residual slow water diffusion. Solid grey line: linear fit to the data prior irradiation, dashed grey line: linear fit shifted to smaller wavelength by by 0.7 nm to show the steepening of resonance shift after irradiation.

4. Experiment at 25% relative humidity

For completeness, we show in Figure S4 the normalized mass data of the experiment at 25% RH together with the linear regression curve to deduce CO₂ diffusivity. Similar to the
experiment at nominally 0% RH, we do not observe significant water uptake here. The particle was irradiated for four times with each one lasting 3 s.

![Graph](image)

Figure S4: Response of normalized mass of the particle to the first irradiation (3 s duration) at 25% RH. Red line: regression curve to deduce CO₂ diffusivity

\[ D_{\text{CO}_2} = 5.01 \times 10^{-15} \text{ m}^2 \text{ s}^{-1} \]
References


