



Infrared Spectroscopy and Mass Spectrometry of CO₂ Clusters during Nucleation and Growth

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1 **Infrared Spectroscopy and Mass**
2 **Spectrometry of CO₂ Clusters during**
3 **Nucleation and Growth**

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Abstract

CO₂ clusters with 2 to 4300 molecules are characterized with mass spectrometry and infrared spectroscopy in the uniform postnozzle flow of Laval expansions at constant temperatures of ~ 29 K and ~ 43 K. The mass spectra provide independent, accurate information on the cluster size distributions and through magic numbers also on cluster structures. The experimental results are complemented with force field, quantum chemical, and vibrational exciton calculations. We find our data to be consistent with predominantly fcc cuboctahedral structures for clusters with more than about 50 molecules. Infrared spectra of cluster size distributions with average sizes above 140-220 molecules are completely dominated by the features from the larger cuboctahedral clusters in the distribution. For very small clusters, exciton simulations predict a pronounced broadening of the infrared band as soon as the average cluster size exceeds about 5 molecules. The nucleation behavior of CO₂ under the present conditions is found to be barrierless in agreement with similar trends previously observed for other compounds at very high supersaturation.

1 Introduction

Weakly bound molecular aggregates play an important role in atmospheric processes not only in the Earth's atmosphere but also in other planetary atmospheres. This includes their role in the very first steps of aerosol and cloud formation; i. e. in nucleation and early growth processes; which are still rather poorly understood. In the Martian atmosphere, CO₂ clouds are the equivalent of H₂O clouds on Earth^{1,2,3,4}. In laboratory studies, many different techniques have been used to generate and characterize weakly bound molecular aggregates, also with the aim to learn more about nucleation and early cluster growth. Infrared spectroscopy has proven to be particularly useful in this context, not only providing structural information on small clusters but also on the phase and morphology of very large aggregates. Small oligomers are typically generated in free supersonic or slit nozzle expansions and characterized with high resolution infrared or Fourier transform infrared (FTIR) spectroscopy (see refs. ^{5,6,7,8,9,10,11,12,13,14,15,16,17} and references therein). An independent determination of the cluster size is usually not necessary for the very small clusters because the infrared spectra change pronouncedly from cluster size to cluster size thus enabling unambiguous assignments. Very large aggregates, containing billions of molecules, have been studied in collisional cooling cells with FTIR spectroscopy^{1,18,19,20,21,22,23,24,25,26,27,28}. In this size range, the features in the infrared spectra are almost insensitive to the aggregate size so that sizing does not pose a particular issue here^{29,30,31,32}. The formation of aggregates with less than $\sim 10^4$ molecules, however, is very challenging in collisional cooling cells, so that this size range usually remains unexplored. Laval expansions in combination with FTIR spectroscopy provide a mean to bridge the gap between infrared studies of small oligomers and those performed in collisional cooling cells on very large aggregates^{33,34,35,36,37,38,39}. When the expansion is probed with infrared spectroscopy in the uniform postnozzle flow^{34,39} it has the additional advantage that the cluster temperature is well-known, similar to collisional cooling cells. This is not the case in free supersonic or slit nozzle expansions where clusters are not probed under thermal equilibrium conditions. However, the issue in the intermediate cluster size range accessible by Laval expansions is the determination of the cluster size

51 distribution. Here, an independent accurate method for cluster sizing is essential because
52 the expansions produce broad size distributions and the infrared spectra are strongly
53 size-dependent.

54 To account for this, the present work combines Laval nozzle expansions with FTIR
55 spectroscopy and mass spectrometry, both of which probe the expansion in the uni-
56 form postnozzle flow. For CO₂ aggregates, mass spectrometry offers several advantages.
57 Firstly, through the exact mass it provides information on the cluster size distribution; i.
58 e. on the mass and the relative abundance of clusters; and for each size on the number of
59 molecules per cluster. Secondly, magic number clusters appear in the mass spectra and
60 provide information on the cluster structure through geometrical analysis^{40,41,42}. It has
61 been shown in previous studies through the observation of so-called shell and subshell
62 closings that CO₂ clusters with more than about 25-55 molecules form cuboctahedral
63 shapes with an fcc crystal structure^{40,41,42,43,44,45}. Furthermore, CO₂ clusters show very
64 distinct features in the mid-infrared region due to strong dipole coupling between the
65 different CO₂ molecules in the clusters, which is also referred to as vibrational exciton
66 coupling^{31,46}. As a consequence of the dominant dipole coupling, vibrational bands are
67 unusually sensitive to the internal structure and the morphology of the clusters. Here, we
68 focus on the asymmetric stretching band of the CO₂ clusters because it is the strongest
69 vibrational band with the biggest effects from exciton coupling. The experimental results
70 are complemented by vibrational exciton calculations, for which we use the information on
71 the cluster size distribution and cluster structure from mass spectrometry. The mass spec-
72 tra cannot provide structural information for clusters with less than about 55 molecules.
73 In this size range, we use force field (FF) and density functional (DFT) calculations for
74 the determination of the cluster structures.

75 **2 Experiment**

76 Except for the infrared part, the experimental setup (Fig. 1) has been described in
77 detail in previous publications^{47,48,49,50,51}. CO₂ clusters are generated in pulsed Laval

78 expansions and characterized in the uniform postnozzle flow by mass spectrometry and
 79 Fourier transform infrared spectroscopy (FTIR). We use mass flow controllers to regulate
 80 the flow of the carrier gas Ar (PanGas, 5.0) and the condensable gas CO₂ (PanGas, 4.5).
 81 For the nucleation measurements, we add small amounts of CH₄ (Messer Schweiz, 5.5)
 82 to the carrier gas in order to change the flow temperature slightly and thus the super-
 83 saturation in fine steps (see section 4.1). The gas mixture is supplied to the stagnation
 84 volume (stagnation pressure p_0 , stagnation temperature T_0) by two feeding valves (not
 85 shown). The opening times of the valves are 6 ms and 41 ms for the mass spectrometric
 86 and the infrared spectroscopic measurements, respectively. From the stagnation volume,
 87 the gas mixture is then expanded through the Laval nozzle into the first vacuum chamber.
 88 The Laval nozzle generates a uniform flow at the nozzle exit, which is extended into the
 89 postnozzle flow region by matching the pressure in the first vacuum chamber to the flow
 90 pressure p_F . The impact pressure p_I is measured as a function of the axial distance l with
 91 pressure transducers. The flow temperature T_F is determined from p_0 and p_I using the
 92 Rayleigh-Pitot relation, and assuming isentropic relations and ideal gas behavior^{50,51,52}.
 93 In this work, we use two Laval nozzles with flow pressures p_F of 35 Pa and 33 Pa, respec-
 94 tively, and axially averaged flow temperatures of \bar{T}_F of 29.4 ± 1.2 K and 42.6 ± 1.6 K,
 95 respectively. An additional Laval nozzle with $\bar{T}_F = 47.5 \pm 1.2$ K and $p_F = 40$ Pa is used
 96 to record the gas phase spectra (CO₂ concentration 7%) in Figs. 4, 8a, 10a and 11a. The
 97 Laval nozzle is mounted on a translation stage so that the axial distance l can be changed
 98 in steps as small as 1 mm over the whole range of the stable postnozzle flow of $l_{\max} =$
 99 100 mm. This allows us to observe the temporal cluster evolution over a time scale of \sim
 100 200 μ s with a temporal resolution of ~ 2 μ s. The fixed positions of both the mass and the
 101 infrared spectrometers required to perform two consecutive measurements to ensure that
 102 the same region of the postnozzle flow is probed with both methods. For that purpose,
 103 the Laval nozzle is moved between the two measurements so that the distance of the
 104 nozzle exit to the infrared beam is identical to the distance of the nozzle exit to the skim-
 105 mer of the mass spectrometer. In other words, for the infrared measurements the axial
 106 distance l is the nozzle exit to infrared beam distance, while for the mass spectrometric

107 studies l corresponds to the nozzle exit to skimmer distance (see Fig. 1).

108 For the mass spectrometric measurements, the central part of the Laval expansion is
109 sampled by a skimmer (1 mm diameter) into the mass spectrometer, where the neutral
110 clusters are ionized just above the first ionization threshold by single vacuum ultraviolet
111 (VUV) photons from a home-built, low fluence table top VUV laser^{47,48,49,53}. It has been
112 shown that this ionization method is a comparatively soft ionization method even for
113 weakly bound clusters^{54,55,56,57,58}. The VUV light is generated by resonance-enhanced
114 two-color four-wave mixing in a Kr gas expansion at 20 Hz^{50,53}. We use a photon en-
115 ergy of 13.8 eV (89.8 nm) which is close to the ionization threshold of CO₂ monomer
116 (13.778 eV,⁵⁹). The photon flux is on the order of $\sim 10^{11}$ - 10^{12} photons/(cm²pulse). The
117 ions are then accelerated by a Wiley McLaren type mass spectrometer and detected by
118 a multichannel plate (MCP) detector. We use high extraction voltages up to 30 kV to
119 achieve high sensitivity. In addition, for the cluster studies the monomer ion is selectively
120 deflected by a pulsed electric field applied to a plate located in front of the MCP detector
121 to avoid saturation effects^{48,50,51}.

122 The infrared measurements are performed with a Bruker IFS 66v/s FTIR spectrome-
123 ter and a liquid nitrogen cooled HgCdTe (MCT) detector. The spectrometer, the infrared
124 beam path, and the detector chamber are evacuated to ~ 7 mbar and are connected to
125 the first vacuum chamber with two KBr windows (see Fig. 1). The infrared beam is
126 focused onto the center of the Laval expansion to maximize the signal from the clusters
127 located in the cold core of the Laval expansion. The pathlength (distance between the
128 two KBr windows) is ~ 350 mm and the width of the Laval expansion (cluster region)
129 is ~ 10 mm. For the infrared measurements, the pulsed feeding valves are triggered by
130 the FTIR spectrometer. The opening times of the pulsed valves is increased to 41 ms
131 to match the minimum time required for recording an interferogram in the steady state
132 region of the pulsed Laval expansion, and the repetition rate was set to 10 Hz. Note that
133 the flow conditions remain identical to those for the mass spectrometric measurements.
134 The measurements are performed with the RapidScan option with a spectral resolution
135 of 1.5 cm^{-1} . Typically, 9600 interferograms are averaged and then Fourier transformed.

136 The spectra are then converted to absorbance spectra using spectra of the empty chamber
137 as background.

138 The combination of low spectral resolution (1.5 cm^{-1}) and low gas pressures ($<$
139 1 mbar) in the vacuum chamber leads to pronounced artifacts in the CO_2 gas phase
140 infrared spectra. This is exemplified in Fig. 2. The intrinsic line widths of the rotational
141 transitions of gaseous CO_2 are very narrow. Therefore, if spectra are recorded at low
142 total gas pressure, as in our Laval expansions ($< 1\text{ mbar}$), with low spectral resolution
143 this results in false relative intensities of the different rotational transitions in the CO_2
144 gas phase spectra. Two examples for spectral resolutions of 1.5 cm^{-1} and 0.25 cm^{-1} are
145 shown in the top part of Fig. 2. Neither of these two spectra shows the correct intensity
146 distribution of gaseous CO_2 . As the bottom part shows, pressure broadening removes
147 these artifacts when the total pressure is increased to about 1 bar by addition of Ar gas.
148 The maximum resolution and the maximum pressure in the Laval expansion cannot be
149 increased beyond 1.5 cm^{-1} and above 1 mbar (top black trace in Fig. 2) so that the gas
150 phase artifacts cannot be avoided. As a result of the limited resolution, subtraction of
151 gas phase contributions is difficult and (residual) gas phase contributions cannot be easily
152 distinguished from the broad cluster features.

153 3 Calculations

154 3.1 FF and DFT calculations

155 For the force field (FF) calculations, the artificial bee colony (ABC) algorithm is
156 employed by using the ABCluster 1.5 program to generate hundreds to thousands of low
157 energy isomers of $(\text{CO}_2)_n$ clusters with n up to 600 ^{60,61}. The CHARMM force field⁶² is
158 used for the CO_2 molecule (see Table S1 in in the Supporting Information). The struc-
159 ture of the 15 energetically lowest lying isomers for each cluster size up to $n = 38$ is
160 further optimized with density functional theory (DFT). All DFT computations were
161 performed with the Gaussian09 program package⁶³. Three functionals - B3LYP^{64,65,66},
162 B2PLYP-D⁶⁷, and M06-2X⁶⁸ - are tested for $n = 1-4$ (see Table S2 in in the Supporting

163 Information). Pople’s 6-31+G(d) basis set is used for all the atoms up to $n = 25$ and
164 6-31G(d) for larger clusters up to $n = 38$ ⁶⁹. We found the three functionals to result
165 in minimum structures with essentially the same structural characteristics. This is in
166 agreement with the findings of previous studies^{70,71}. Furthermore, Lemke et al.⁷⁰ showed
167 that for $(\text{CO}_2)_n$ clusters with n up to 16, the M06-2X functional provides reliable results
168 compared with benchmark calculations at the CCSD(T) level of theory. Therefore, the
169 M06-2X functional is used here for larger clusters up to $n = 38$. All structures are opti-
170 mized without any symmetry constraint. Harmonic vibrational frequencies are calculated
171 to confirm that the optimized structures are real minima, and to simulate infrared spectra
172 of the clusters for comparison with vibrational exciton calculations (see next subsection).
173 In most cases, the most stable isomer generated from the FF search is also the most
174 stable one after optimization at the M06-2X/6-31+G(d) level. The main change of the
175 structures upon optimization is an overall decrease of the intermolecular distances in the
176 cluster with additional rotations of some specific CO_2 molecules in the cluster. Based on
177 these results, we use the lowest energy structure from FF calculations also for the clusters
178 with $n = 39$ -50, for which DFT/M06-2X optimization is computationally too expensive.
179 We also considered the minimum structures of small $(\text{CO}_2)_n$ clusters studied in refs.^{44,72}.
180 The global minimum structures identified in our study are either the same or more stable
181 structures compared with this previous investigation.

182 The C=O bond distance of linear CO_2 is optimized to be 1.163 Å, which is in excellent
183 agreement with the experimental value of 1.162 Å⁷³. The antisymmetric stretching mode
184 (ν_3) of CO_2 is calculated to be 2468 cm^{-1} . To match the experimentally measured ν_3
185 of 2349 cm^{-1} ⁷⁴, a scaling factor of 0.9518 has to be applied. This scaling factor is also
186 used to scale the calculated vibrational frequencies of clusters with $n = 2$ -25 in the ν_3
187 region, while for clusters with $n = 26$ -38 a scaling factor of 0.9450 is employed. The latter
188 corrects for the difference between vibrational frequencies of $(\text{CO}_2)_{25}$ calculated with the
189 6-31G(d) and 6-31+G(d) basis sets using the M06-2X functional. Note that we do not
190 use different scaling factors for clusters $(\text{CO}_2)_n$ with $n = 2$ -13, for which high resolution
191 IR spectroscopy measurements are available^{5,6,7,75,76,77,78}. Rather, we focus on the general

192 trends of the infrared band shapes as a function of cluster size. Structures and infrared
 193 spectra for the obtained isomers for $(\text{CO}_2)_n$ clusters with $n = 2-4$ are provided in Figs.
 194 S1 and S2 in the Supporting Information. Figs. S3 and S4 in the Supporting Information
 195 present the optimized most stable structures of $(\text{CO}_2)_n$ for $n = 5-38$ from M06-2X and
 196 selected structures for $n = 40-600$ from the FF calculations, respectively. The Cartesian
 197 coordinates of the energetically lowest lying isomers for $n = 2-38$ and $n = 40, 45,$ and
 198 50 are provided in Table S3. Note that the second most stable structures are typically
 199 about 2-4 kJ/mol higher in energy than the most stable ones using the M06-2X method.

200 3.2 Vibrational exciton calculations

201 We have previously shown that infrared spectra of CO_2 clusters are dominated by
 202 contributions from resonant dipole coupling and can thus be reliably simulated using
 203 vibrational exciton calculations^{31,46,79}. The resonant dipole coupling term is dominant
 204 for molecular systems with strong molecular transition dipole moments ($> 0.1-0.2$ D) and
 205 small intermolecular distances ($< 5-7$ Å). The transition dipole moment of CO_2 in the re-
 206 gion of the antisymmetric stretching vibration (ν_3 band) is on the order of 0.32 D^{79,80} and
 207 the intermolecular distances in the clusters are in the range of 3-4 Å^{31,78}. The vibrational
 208 Hamiltonian \hat{H} can be written as^{31,79,81}:

$$\hat{H} = \hat{H}_0 + \hat{H}_D \quad (1)$$

209 \hat{H}_0 is the sum over the vibrational Hamiltonians of the uncoupled molecules and \hat{H}_D
 210 includes all pairwise dipole-dipole interactions between molecules in the cluster. \hat{H}_D is
 211 given by:

$$\hat{H}_D = \sum_{i < j} -\frac{1}{4\pi\epsilon_0} \frac{\vec{\mu}_i \cdot \vec{\mu}_j}{r_{ij}^3} \left[3(\vec{\mu}_j \cdot \vec{r}_{ij}) \cdot \vec{r}_{ij} - (\vec{r}_{ij} \cdot \vec{r}_{ij}) \cdot \vec{\mu}_j \right] \quad (2)$$

212 \vec{r}_{ij} is the displacement vector between the centers of mass of the two molecules i and j and
 213 $\vec{\mu}$ is the dipole moment operator. Up to first order terms in the vibrational coordinates,
 214 the model contains only two input parameters in addition to the cluster structure, which
 215 are the transition wavenumber of the uncoupled molecule $\tilde{\nu}_M$ and the molecular transition

216 dipole moment $\delta\mu = \langle 0|\mu|1\rangle$. For the present calculations, we use $\nu_M = 2355 \text{ cm}^{-1}$ and
217 $\langle 0|\mu|1\rangle = 0.32 \text{ D}^{46}$. The vibrational eigenvalues and eigenfunctions of the cluster are
218 obtained by diagonalization of \hat{H} or through calculation of the autocorrelation function
219 of the dipole moment^{22,31,79}. For the cluster structures, we use the energetically lowest
220 lying structures as obtained from the FF after further optimization with DFT for $n = 2\text{-}38$,
221 while in the size range $n = 39\text{-}50$ we directly use the energetically lowest lying structures
222 from FF calculations. All larger clusters were modeled as cuboctahedral structures with
223 fcc crystal structure in agreement with the results from previous studies^{40,41,43,44,45,72,82}.
224 For this purpose, an fcc crystal structure is constructed by copying a CO_2 unit cell in three
225 directions, from which molecules are removed until a perfect cuboctahedron was obtained.
226 These so-called closed shell cuboctahedra have only very distinct sizes. To model clusters
227 with size between these special closed shell structures, we remove molecules from faces.
228 The removal of complete faces result in subshell closed cuboctahedra. We refer to all
229 these structures simply as fcc cuboctahedral structures.

230 The reliability of the exciton approach for CO_2 clusters was verified in our previous
231 publications^{31,46,79}. Here, we add a more extensive comparison with quantum chemical
232 calculations for the cluster size range $n = 2\text{-}38$ (Fig. 3 and Fig. S5 in the Supporting
233 Information). Fig. 3 shows selected results for $n = 13, 19, 28$ and 38 . The top (black)
234 and the bottom (red) trace are infrared spectra calculated with the exciton approach
235 and with DFT, respectively. The same cluster structures as obtained from optimization
236 with DFT at the M06-2X level of theory are used as input structures for both vibrational
237 calculations. The similar infrared band shapes verify that resonant dipole coupling is
238 able to capture the main features in the infrared spectra (see also Fig. S5 for more data).
239 This is an important result because the exciton approach is the only method that can be
240 applied to even larger clusters containing many thousands of molecules. We mentioned
241 above that the optimization of the FF generated structures with DFT mainly results in a
242 decrease of the intermolecular distances of the molecules in the clusters. To evaluate the
243 influence of this decrease on the infrared spectra we show in the middle (blue) trace of
244 Fig. 3 infrared spectra calculated with the exciton model but this time for FF structures

245 without further optimization by DFT. The agreement with the exciton spectra in the top
246 (black) trace is very good. The shorter intermolecular distances after DFT optimization
247 results in a slightly stronger dipole coupling, which explains the slightly broader overall
248 band width of the spectra in the top trace. This comparison mainly confirms that our
249 approach to use DFT optimized structures for $n < 39$ and FF structures for $n = 39-50$
250 has almost no effect on the infrared spectra. Based on the favorable comparisons in Fig. 3
251 and Fig. S5 in the Supporting Information, we will use throughout the remainder of this
252 work exclusively exciton calculation for the modeling of infrared spectra for all cluster
253 sizes. The cluster sizes and the relative abundances of different cluster sizes will be taken
254 from the experimental mass spectra, and as mentioned above we will use DFT optimized
255 structures for $n < 39$, FF structures for $n = 39-50$, and fcc cuboctahedral structures for
256 larger clusters.

257 4 Results and discussion

258 4.1 Small clusters and nucleation

259 We have recently shown that mass spectrometry in the uniform postnozzle flow of a
260 Laval nozzle allows one to capture the very first steps of gas phase nucleation/condensation
261 at the molecular level^{47,48,49}. Infrared spectroscopy could provide additional information
262 on cluster structures in this size range, where the average cluster size $\langle n \rangle$ and the max-
263 imal cluster size n_{\max} typically lie below about ten and a few ten molecules, respectively.
264 The thermodynamic requirement for nucleation to take place is that the supersatura-
265 tion S is larger than 1, where $S = \frac{p_{\text{cond}}}{p_{\text{eq}}(T_{\text{F}})}$ with the partial pressure of the condensable
266 (here CO₂) p_{cond} and the equilibrium vapor pressure of the condensable $p_{\text{eq}}(T_{\text{F}})$ at the
267 flow temperature T_{F} . However, nucleation can only be observed if it occurs in the time
268 window that is accessible by a given experiment. As explained in refs.^{47,48,49}, we thus
269 refer to conditions where $S > 1$ but nucleation can not yet be observed as *subcritical*, and
270 conditions at which nucleation just becomes observable as *supercritical*. The first steps
271 of nucleation/condensation can then be followed by tuning the conditions in very fine

272 steps from subcritical to supercritical conditions. In the present work this tuning was
273 achieved by adding small amounts of methane gas (maximum of less than 10%) to the
274 argon carrier gas while recording infrared and mass spectra at a constant axial distance.
275 Successive addition of methane gas results in very small (< 0.5 K) increases of T_F , which
276 in turn results in a continuous decrease of the average and maximum cluster sizes until
277 nucleation/condensation is completely inhibited ^{47,48,49}.

278 The middle and the lower traces in Fig. 4 show two example infrared spectra recorded
279 at methane concentrations of 5% and 2.46%, respectively, which correspond to maximum
280 cluster sizes of $n_{\max} = 21$ and $n_{\max} = 33$, respectively (see mass spectra in Fig. 5b).
281 Surprisingly, the two spectra look identical even though the cluster sizes differ substan-
282 tially. This also holds for infrared spectra (not shown) recorded at the other methane
283 concentrations/cluster sizes (see mass spectra in Fig. 5b). For such small clusters one
284 expects substantially different infrared spectra for different cluster sizes; i. e. just the
285 opposite of the experimental results. The observed independence of the infrared spectra
286 from the cluster size can be explained by comparison with the pure gas phase spectrum in
287 the upper trace of Fig. 4. It reveals that the cluster spectra are dominated by gas phase
288 contributions to such an extent that no cluster features are visible. Under nucleation
289 conditions, the cluster number concentrations lies ~ 3 orders of magnitude below the
290 CO_2 monomer number concentration, which is on the order of $\sim 10^{14} \text{ cm}^{-3}$. Given the
291 low infrared monomer signal (low signal-to-noise (S/N) ratio), it is thus not surprising
292 that our infrared experiment is not sensitive enough to detect any cluster signals under
293 these expansion conditions.

294 Even though we cannot record infrared spectra during the first steps of nucleation/condensation,
295 Fig. 5b shows that the higher sensitivity of mass spectrometry allows us to observe the
296 evolution of the cluster size distribution under these conditions. The maximal cluster
297 sizes n_{\max} indicated by black arrows vary over the ranges from about 5 to 38 molecules.
298 Note that at methane concentrations higher than the ones used for the top spectrum in
299 Fig. 5b only monomer is observed (subcritical conditions). The detailed experimental
300 information of the cluster size distributions (size and relative abundance) together with

301 modeling (structure and exciton modeling, see section 3.2) allows us at least to predict
 302 the infrared spectra. As mentioned earlier, the transition to fcc cuboctahedral structure
 303 is expected in the region of $n \sim 25$ -55 molecules^{40,41,42,44,43,45} so that we can safely as-
 304 sume that with an overall largest cluster size of $n_{\max} = 38$ the dominating cluster sizes do
 305 not yet have cuboctahedral structure. We thus used for each cluster size the structures
 306 of the energetically lowest lying isomer as predicted by the FF calculation and further
 307 optimized by DFT (see section 3.1). The corresponding modeling results are shown in
 308 Fig. 5a. The simulated infrared spectra show a pronounced increase by about a factor
 309 of four of the band width with increasing n_{\max} . This broadening can be explained as
 310 follows: in the cluster size range $n < 38$, both the geometrical structure and the infrared
 311 spectra of individual cluster sizes change drastically from one cluster size to another (see
 312 section 3.1). Therefore, the larger n_{\max} becomes, the more different cluster sizes with
 313 different infrared spectra contribute to the overall infrared spectrum. We had already re-
 314 ported on infrared spectra of CO₂ clusters with average sizes of $\langle n \rangle \leq 100$ in a previous
 315 study (see Fig. 5 in ref.³⁴). However, for lack of an accurate sizing method the average
 316 size could only be estimated in that work to be likely below 100 without any further
 317 specification of the lower bound. The largest average cluster size in the present study is
 318 $\langle n \rangle = 9$ (see bottom spectrum in Fig. 5b). The spectral differences (band widths and
 319 structures) between the present infrared spectra and the spectra in Fig. 5 of ref.³⁴ thus
 320 hint that the average size of the latter was above $\langle n \rangle \sim 10$, finally providing a lower
 321 bound for the size estimate of those spectra.

322 In our previous papers on nucleation of water, toluene, and propane^{47,48,49}, we sug-
 323 gested that the type of nucleation behavior can be extracted from graphs showing n_{\max}
 324 as a function of $\ln S$ (see for example Fig. 6a and Fig. 4 in ref.⁴⁷). We found two types of
 325 nucleation behavior: a steplike and a gradual increase of the cluster size with increasing
 326 supersaturation. For water and propane a systematic trend from a steplike behavior at
 327 lower $\ln S$ to a gradual at higher $\ln S$ was found. A steplike increase of n_{\max} with increas-
 328 ing $\ln S$ was considered to be indicative of the presence of a nucleation barrier, while a
 329 gradual increase was suggested to hint at a barrierless condensation process (spinodal

330 decomposition). Our recent study on water nucleation, however, challenges this simple
 331 interpretation, indicating that a steplike increase could also be caused by a kinetic bot-
 332 tleneck other than a free energy barrier⁴⁷. The highest $\ln S$ in all these previous studies
 333 was around 104. The current CO₂ data are recorded at an even higher $\ln S$ around 150.
 334 Thus, from the previously observed trend one would clearly expect CO₂ condensation to
 335 take place in a barrierless regime; i. e. one would expect to observe a gradual increase of
 336 n_{\max} with increasing $\ln S$. Fig. 6a shows that this is indeed the case and CO₂ also seems
 337 to follow the trend observed for the other compounds. It also reveals that the critical
 338 supersaturation for CO₂ condensation under these conditions lies at $\ln S \sim 138$. Cluster
 339 size distributions recorded as a function of $\ln S$ at a constant nucleation/growth time
 340 (constant axial position in the postnozzle flow) provide information on the nucleation
 341 behavior (Fig. 6a) and on critical cluster sizes, which for barrierless condensation is the
 342 monomer. As described in detail in ref.⁴⁷, the nucleation/growth rate J can be extracted
 343 from the total cluster number concentration $N_{\text{cluster,tot}}^{\text{CO}_2}$ recorded as a function of the nu-
 344 cleation/growth time t , where t is varied by varying the axial distance in the postnozzle
 345 flow by fine steps. $N_{\text{cluster,tot}}^{\text{CO}_2}$ is the sum over all cluster number concentrations. Fig. 6b
 346 shows $N_{\text{cluster,tot}}^{\text{CO}_2}$ as a function of t for $\ln S = 160$. At early nucleation times, monomer
 347 depletion and more complex growth processes (cluster agglomeration and coagulation)
 348 are negligible. At these early t , $N_{\text{cluster,tot}}^{\text{CO}_2}$ is proportional to t^{47} . A linear fit to the data
 349 at early t predicts a value of $J \sim 1 - 2 \cdot 10^{15} \text{ cm}^{-3}\text{s}^{-1}$ at $\ln S = 160$, which in the case
 350 of barrierless condensation is rather a growth than a nucleation rate in its usual sense⁴⁷.
 351 To the best of our knowledge these are the first data for CO₂ condensation at such low
 352 temperatures ($\bar{T}_F = 29.4 \pm 1.2 \text{ K}$) and high supersaturations. The uncertainty of the
 353 nucleation rate constants are estimated to be one order of magnitude (for more informa-
 354 tion see⁴⁷). CO₂ nucleation rates have previously been determined to lie in the range
 355 $J \sim 10^{17} - 10^{21} \text{ cm}^{-3}\text{s}^{-1}$ at a supersaturation of $S \sim 10$ and temperatures of 160-190 K⁸³.
 356 These experiments were also performed in Laval nozzles. However, in contrast to our
 357 case condensation most likely takes place in the presence of a nucleation barrier under
 358 the conditions of ref.⁸³.

4.2 Intermediate cluster sizes

In this section, we present infrared and mass spectra of intermediate cluster sizes, which cover the average cluster size range from $\langle n \rangle \sim 20-330$ ($n_{\max} \sim 70-710$). This coincides with the size range where the transition to fcc cuboctahedral structures takes place around $n \sim 25-55$ ^{40,41,42,43,44,45}. The appearance of fcc cuboctahedral clusters is exemplified in the mass spectrum in Fig. 7. For cluster sizes with $n \gtrsim 55$, different minima are observed in the mass spectra, which are labeled with asterisks in the inset in the figure. Such patterns were observed for different substances; e. g. CO₂, SF₆, and rare gases; and were attributed to shell and subshell closings^{40,41,42}. These cluster sizes correspond to particularly stable cluster structures (magic clusters), which in the case of CO₂ appear as local minima in the mass spectra because of their lower ionization efficiency. Note that as a consequence of the latter, the relative abundances of these clusters is underestimated from the ion signals in the mass spectra. We have confirmed the cuboctahedral structure of these special clusters for all mass spectra following the same analysis as proposed in refs.^{40,41,42}; and based on the results from refs.^{40,43,44,45,82} we assume fcc crystalline structures. Using all this information, we make the following assumptions for the vibrational exciton calculations presented in Figs. 8a and 10a (see also section 3.2) : i) The relative abundance of different cluster sizes are taken from the experimental mass spectra. ii) For clusters with $n \leq 50$, the exciton calculations are performed for cluster structures obtained from FF calculations and for $n \leq 38$ from FF calculations with subsequent optimization by DFT, iii) For clusters with $n \gtrsim 50$, we use fcc cuboctahedral structures for the exciton calculations. Based on the additional knowledge on cluster size, abundances, shape and internal structure, this is the best assumption we can make at this point, and to the best of our knowledge also the most detailed compared with previous infrared simulations of CO₂ clusters.

Fig. 8 shows results for the cluster size range $\langle n \rangle \sim 20-60$ ($n_{\max} \sim 70-190$); i. e. the range where the transition to fcc cuboctahedral structures takes place. Panel a contains the experimental (black lines) and the calculated (red lines) infrared spectra together with an experimental CO₂ gas phase spectrum (top trace). The comparison of

388 the experimental spectra with the gas phase spectrum reveals a very high gas phase con-
 389 tribution in the cluster spectra, which decreases with increasing cluster size. The major
 390 gas phase contributions (bands around 2380 cm^{-1} , 2350 cm^{-1} and 2320 cm^{-1}) are labeled
 391 with black arrows in the cluster spectrum with $\langle n \rangle = 21$. We have tried to subtract
 392 gas phase spectra from the cluster spectra to compensate gas phase contributions and
 393 retrieve pure cluster spectra. However, this was not successful because of the the low
 394 S/N ratio of the spectra and the limited spectral resolution (1.5 cm^{-1}). Nevertheless,
 395 cluster features are visible in the spectra in agreement with the predictions from exciton
 396 calculations (red spectra). The clearest cluster feature in the experimental spectra is a
 397 peak at $\sim 2361\text{ cm}^{-1}$, which is labeled with a red arrow in the bottom spectrum. This
 398 peak becomes more prominent with increasing cluster size and at the same time shifts
 399 by $\sim 1\text{ cm}^{-1}$ from $\sim 2361\text{ cm}^{-1}$ to $\sim 2362\text{ cm}^{-1}$. The same trend is also seen in the
 400 exciton simulations, where the peak at 2359.5 cm^{-1} becomes more prominent and shifts
 401 to 2360 cm^{-1} with increasing cluster size. Since these infrared spectra cover the range
 402 of the transition to increasingly higher contributions from fcc cuboctahedral structures
 403 with increasing cluster size we were wondering whether this prominent peak could orig-
 404 inate from fcc cuboctahedral structures. For this purpose we have performed exciton
 405 simulations for cuboctahedral clusters of different sizes (see Fig. 9). These spectra in-
 406 deed show a pronounced peak at $\sim 2361\text{ cm}^{-1}$ for clusters with $n \sim 55-90$, which shifts
 407 from 2359 cm^{-1} to 2362 cm^{-1} with increasing size. Since this cluster size range agrees
 408 with the average cluster size in the experimental spectra (Fig. 8a) we conclude that the
 409 emerging pronounced peak in the experimental infrared spectra is likely a signature of
 410 cuboctahedral cluster structures in this size range.

411 The infrared spectra in Fig. 5 of ref.³⁴ were recorded at the same temperature (\sim
 412 29 K) as those in Fig. 8a, and were estimated to cover a similar cluster size range ($\langle n \rangle \leq$
 413 100). Further above, we have determined a lower bound of $\langle n \rangle \sim 10$ for the smallest
 414 clusters in ref.³⁴ (see top trace in Fig. 5). The spectra in Fig. 5 of ref.³⁴ show indeed
 415 similar features as those in Fig. 8a. This holds in particular for the top two spectra
 416 in Fig. 5 of ref.³⁴ compared with the calculated spectrum for $\langle n \rangle = 21$ in Fig. 8a,

417 which show similar overall band widths and a main broad band below and an additional
 418 pronounced shoulder above 2360 cm^{-1} , respectively. For larger clusters, the shoulder
 419 disappears continuously with increasing cluster size in both studies, and the double band
 420 structures evolves into a single band around 2360 cm^{-1} . In this size range, however, the
 421 overall band widths in Fig. 5 of ref.³⁴ is larger compared with the present spectra. Since
 422 the two different studies were performed at the same temperature in the uniform flows of
 423 Laval nozzles this thus hints rather at a difference in the cluster size (distribution) than
 424 in the cluster structure. While larger clusters do not show further band broadening (see
 425 Fig. 10), a higher contribution of small clusters would explain such a broadening (see e.
 426 g. bottom spectra in Fig. 5a). It seems thus plausible that the upper bound of $\langle n \rangle =$
 427 100 for the largest clusters provided for Fig. 5 of ref.³⁴ was too high, which would not be
 428 surprising in view of the fact that this was a very crude estimate that was not based on
 429 an independent size determination as in the current study.

430 Fig. 10 covers the next higher cluster size range from $\langle n \rangle \sim 40\text{-}330$ ($n_{\text{max}} \sim 110\text{-}$
 431 710). Again, the spectra of the smaller clusters - in particular that for $\langle n \rangle = 41$ in
 432 panel a - are dominated by gas phase contributions (see black arrows and the pure gas
 433 phase spectrum Fig. 8a). For the larger clusters ($\langle n \rangle \geq 138$), however, the gas phase
 434 does no longer dominate and the cluster contribution (broad band around 2360 cm^{-1}) is
 435 clearly visible in the spectra in Fig. 10a, in particular when compared with the exciton
 436 simulations (see red spectra in panel a). Furthermore, the S/N ratio in the experimental
 437 spectra is now high enough to retrieve decent difference spectra, which was not the case
 438 in Figs. 4 and 8. Instead of subtracting the gas phase spectrum (top spectrum in panel a)
 439 from the experimental spectra we choose to subtract the experimental spectrum recorded
 440 for $\langle n \rangle = 41$ from the other experimental spectra for two reasons: i) We found the
 441 subtraction of the pure gas phase spectrum to provide worse results compared with the
 442 subtraction of a small cluster spectrum. This is likely due to the fact that the expansion
 443 conditions must be slightly varied when measuring pure gas phase for which cluster
 444 formation must be avoided. ii) The subtraction of a small cluster spectrum removes
 445 contributions from the cluster size range where fcc cuboctahedral clusters do not yet

446 dominate and thus allows us to clarify at which size the fcc cuboctahedral features start
447 to dominate. The resulting experimental difference spectra (black lines) are shown in
448 Fig. 10b together with exciton simulations for these difference spectra (red lines). The
449 comparison between experiment and simulations shows good agreement, in particular
450 also with respect to the overall band width. It shows that the disagreement of the band
451 width between experiment and simulation in panel a is mainly a consequence of the
452 uncompensated gas phase.

453 The comparison of the exciton calculations in panels a and b of Fig. 10 shows that
454 the full calculations and the ones for the difference spectra look very similar for the same
455 $\langle n \rangle$. Above an average cluster sizes of $\langle n \rangle \sim 217$, they are even identical. This shows
456 that the features from the larger clusters in the size distributions completely dominate
457 these infrared spectra, while the contribution from smaller clusters completely vanishes.
458 Not surprisingly, a comparison with Fig. 9 shows that these spectra are dominated by
459 cuboctahedral features. The simulations for cuboctahedra in this figure shows that the
460 spectral region between $\sim 2355\text{-}2365\text{ cm}^{-1}$ is dominated by a single band for $n \sim 55\text{-}90$
461 (see above) and by a double band for $n > 90$. Even though the spectra in Figs. 10a and b
462 are sum spectra over different cluster sizes, this double band is still visible in the exciton
463 spectra. Also visible is the systematic decrease of the relative intensity of the band at
464 the higher wavenumber with increasing cluster size, in agreement with the simulations
465 in Fig. 9. In the experimental difference spectra (Fig. 10b), the double band structure is
466 not so clearly visible. However, the asymmetric band shape at wavenumbers higher than
467 $\sim 2360\text{ cm}^{-1}$ is consistent with the double band structure.

468 **4.3 Large clusters**

469 Using higher CO_2 concentrations, we were able to record infrared in combination
470 with mass spectra for even larger clusters. The largest cluster size we were able to detect
471 was on the order of $n_{\text{max}} \sim 4300$, which would correspond to a cluster radius of $\sim 3.5\text{ nm}$
472 assuming a spherical shape. These sizes are comparable to the lower cluster size range
473 that can also be reached in collisional cooling cell experiments^{18,19,21,34}. This is a range

474 in which a comparison between different cluster generation methods (e. g. collisional
475 cooling with Laval expansions) is in principle possible as demonstrated in ref.³⁴. A series
476 of infrared spectra recorded in the uniform Laval expansion for the size range $\langle n \rangle \sim$
477 140-760 ($n_{\max} \sim 730-4300$) is shown in Fig. 11. In comparison with the previous cases,
478 the gas phase contribution to these spectra is comparatively small (see top spectrum),
479 so that these spectra are dominated by cluster features and not by the gas phase. The
480 double band structure (main band at about 2360 cm^{-1} and a shoulder at about 2364 cm^{-1})
481 described in Fig. 10 is maintained also for the largest clusters (see also exciton simulations
482 in Fig. 11a). Consistent with the decreasing relative intensity of the shoulder in the
483 exciton spectra with increasing cluster size, the experimental spectra show less structure
484 and a less asymmetric band at wavenumbers higher than $\sim 2360 \text{ cm}^{-1}$. Based on the same
485 arguments as in the previous chapter, we conclude that the infrared spectra of these larger
486 clusters are also dominated by features arising from fcc cuboctahedral clusters.

487 In Fig. 3a in ref.³⁴, Bonnamy et al. reported infrared spectra of clusters in a similar
488 size range as our Fig. 11. Over the whole size range from $\langle n \rangle \sim 100-10000$, they
489 observed an almost identical single band with an almost perfect symmetric band shape,
490 which only showed a minor shift of the maximum and a slight narrowing of the band with
491 increasing cluster size. These spectra best match the bottom spectrum in our Fig. 11a
492 with $n_{\max} \sim 4300$, while the structureless symmetric band shape in ref.³⁴ is not really
493 consistent with our spectra in Fig. 11a for smaller clusters. A major difference between
494 the present study and ref.³⁴ is the lack of an independent accurate size determination in
495 the latter study. A possible explanation could thus be that the average size indicated in
496 Fig. 3a of ref.^{34,39} was not correct for the smaller clusters, and that these smallest cluster
497 had in fact already average size of more than a few thousand molecules (instead of only
498 hundreds of molecules). This would also explain the almost identical symmetric band
499 shape observed for these spectra in ref.³⁴.

5 Summary

We present a common infrared spectroscopic and mass spectrometric investigation of CO₂ clusters generated in pulsed Laval expansions over the average cluster size range from $\langle n \rangle \sim 3-760$ (maximum cluster size $n_{\max} \sim 5-4300$). To the best of our knowledge, this is the first study that simultaneously uses infrared spectroscopy and mass spectrometry for cluster characterization in this size range. Cluster formation in a Laval expansion allows us to cover a broad cluster size range, and by using the uniform postnozzle flow to investigate clusters at known well defined temperatures. A pulsed Laval expansion is required to keep the pressure in the mass spectrometer low enough for sensitive mass spectrometric studies. However, the disadvantage of the pulsed Laval expansions compared with continuous Laval expansions^{34,39} is the limitation it poses on the spectral resolution of the infrared spectra. With our rapid scan infrared spectrometer, we are limited to a resolution of $\sim 1.5 \text{ cm}^{-1}$, which makes subtraction of gas phase contributions in the cluster spectra very challenging.

Mass spectra provide detailed information on the whole cluster size distribution; i. e. the relative abundance of different clusters and the number of molecules in the clusters. This independent size information is used to simulate infrared spectra, which are then compared with experimental infrared spectra. Furthermore, through magic clusters the mass spectra also provide additional information on preferred cluster structures. Consistent with previous studies, the preferred structure for CO₂ clusters with $n \gtrsim 50$ is fcc cuboctahedral. The comparison of calculated and experimental infrared spectra reveals that cluster size distributions with average sizes $\langle n \rangle$ of a few ten molecules show a characteristic band around 2360 cm^{-1} that originates from the larger clusters in the distribution with fcc cuboctahedral structures. For average sizes that exceed the range $\langle n \rangle \sim 140-220$, the infrared spectra are completely dominated by the features of fcc cuboctahedral clusters. Even though we find generally good agreement between simulated and experimental infrared spectra the bands in the experimental spectra tend to be broader compared with the simulations. Uncompensated gas phase contributions are likely one reason for this. Note that the gas phase spectra are not resolved due to our

529 low spectral resolution. Another reasons might include contributions from other crystal
530 structures (not fcc) or from surface molecules^{29,44,84,85,86}, which could become considerable
531 when the ratio of surface to core molecules lies close to one^{25,34,87,88}.

532 We were not able to record infrared spectra during the very first steps of nucle-
533 ation/condensation where the average cluster sizes contain only a few molecules because
534 the number concentration of these nucleation clusters was too low and the gas phase
535 fraction too high. However, because of its higher sensitivity we could record mass spectra
536 under these conditions, which at least allows us to calculate infrared spectra for experi-
537 mental size distributions. These vibrational exciton calculations - based on experimental
538 mass spectra and cluster structures from force field and DFT optimization - predict a
539 pronounced broadening by a factor of about four when the average cluster sizes exceeds
540 $\langle n \rangle \sim 5$ as a consequence of the increasing number of cluster sizes with different infrared
541 spectra that contribute to the overall spectrum. From an analysis of the mass spectra,
542 we have also retrieved the nucleation behavior of CO₂ under these conditions. The barri-
543 erless condensation at the very high supersaturation of $\ln S \sim 140-160$ is fully consistent
544 with previous trends found for other compounds (see Fig. 4 in⁴⁷). In addition, we have
545 also retrieved a nucleation rate for CO₂ of $1-2 \cdot 10^{15} \text{ cm}^{-3} \text{ s}^{-1}$ at this high supersaturation.
546 The general goal behind our studies is to provide more information about nucleation and
547 early growth at a truly molecular level. The extension to infrared spectroscopy in the
548 present contribution has provided valuable additional information on cluster structures
549 in the early growth regime, which cannot be obtained from mass spectra alone.

550 **Supporting Information**

551 In the Supporting Information, we provide the FF parameters for CO₂, the bench-
552 marking of the DFT functional and the Cartesian coordinates of the energetically lowest
553 lying isomers for $n = 2-38$ and $n = 40, 45,$ and 50 . In addition, we give the structures of
554 the CO₂ clusters for $n = 2-38$ from M06-2X and selected structures for $n = 40-600$ from
555 the FF calculations, respectively and analogous figures to Fig. 3 for all cluster sizes with
556 $n = 2-38$.

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References

- [1] Isenor, M.; Escribano, R.; Preston, T. C.; Signorell, R. Predicting the infrared band profiles for CO₂ cloud particles on Mars. *Icarus* **2013**, *223*, 591–601.
- [2] Trainer, M. G.; Tolbert, M. A.; McKay, C. P.; Toon, O. B. Enhanced CO₂ trapping in water ice via atmospheric deposition with relevance to Mars. *Icarus* **2010**, *206*, 707–715.
- [3] Nachbar, M.; Duft, D.; Mangan, T. P.; Martin, J. C. G.; Plane, J.; Leisner, T. Laboratory measurements of heterogeneous CO₂ ice nucleation on nanoparticles under conditions relevant to the Martian mesosphere. *J. Geophys. Res.: Planets* **2016**, *121*, 753–769.
- [4] Nachbar, M.; Duft, D.; Leisner, T. The vapor pressure over nano-crystalline ice. *Athmos. Chem. Phys.* **2018**, *18*, 3419–3431.
- [5] Oliaee, J. N.; Dehghany, M.; Moazzen-Ahmadi, N.; McKellar, A. R. W. Spectroscopic identification of carbon dioxide clusters: (CO₂)₆ to (CO₂)₁₃. *Phys. Chem. Chem. Phys.* **2011**, *13*, 1297–1300.
- [6] Oliaee, J. N.; Dehghany, M.; McKellar, A. R. W.; Moazzen-Ahmadi, N. High resolution infrared spectroscopy of carbon dioxide clusters up to (CO₂)₁₃. *J. Chem. Phys.* **2011**, *135*, 044315.
- [7] Dehghany, M.; McKellar, A. R. W.; Afshari, M.; Moazzen-Ahmadi, N. High-resolution infrared spectroscopy of carbon dioxide dimers, trimers, and larger clusters. *Mol. Phys.* **2010**, *108*, 2195–2205.
- [8] Häber, T. FTIR-spectroscopy of isolated and argon coated (HBr)_{n≤4} clusters in supersonic slit-jet expansions. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1365–1369.
- [9] Häber, T.; Schmitt, U.; Suhm, M. A. FTIR-spectroscopy of molecular clusters in pulsed supersonic slit-jet expansions. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5573–5582.

- 586 [10] Liu, Y.; Weimann, M.; Suhm, M. A. Extension of panoramic cluster jet spectroscopy
587 into the far infrared: low frequency modes of methanol and water clusters. *Phys.*
588 *Chem. Chem. Phys.* **2004**, *6*, 3315–3319.
- 589 [11] Quack, M.; Schmitt, U.; Suhm, M. A. FTIR spectroscopy of hydrogen fluoride
590 clusters in synchronously pulsed supersonic jets. Isotopic isolation, substitution and
591 3-d condensation. *Chem. Phys. Lett.* **1997**, *269*, 29–38.
- 592 [12] Weimann, M.; Fárník, M.; Suhm, M. A. A first glimpse at the acidic proton vi-
593 brations in HCl–water clusters via supersonic jet FTIR spectroscopy. *Phys. Chem.*
594 *Chem. Phys.* **2002**, *4*, 3933–3937.
- 595 [13] Didriche, K.; Lauzin, C.; Macko, P.; Lafferty, W. J.; Saykally, R. J.; Herman, M. On
596 the role of molecular clustering on infrared absorption line shapes of acetylene in a
597 supersonic expansion. *Chem. Phys. Lett.* **2008**, *463*, 345–348.
- 598 [14] Bush, M. F. and Saykally, R. J. and Williams, E. R. Infrared action spectra of Ca^{2+}
599 $(\text{H}_2\text{O})_{11-69}$ exhibit spectral signatures for condensed-phase structures with increasing
600 cluster size. *J. Am. Chem. Soc.* **2008**, *130*, 15482–15489.
- 601 [15] Weida, M. J.; Nesbitt, D. J. Geometric isomerism in clusters: high resolution infrared
602 spectroscopy of a noncyclic CO_2 trimer. *J. Chem. Phys.* **1996**, *105*, 10210–10223.
- 603 [16] Steinbach, C.; Buck, U. Vibrational spectroscopy of size-selected sodium-doped
604 water clusters. *J. Phys. Chem. A* **2006**, *110*, 3128–3131.
- 605 [17] Pradzynski, C. C.; Dierking, C. W.; Zurheide, F.; Forck, R. M.; Buck, U.; Zeuch, T.;
606 Xantheas, S. S. Infrared detection of $(\text{H}_2\text{O})_{20}$ isomers of exceptional stability: a
607 drop-like and a face-sharing pentagonal prism cluster. *Phys. Chem. Chem. Phys.*
608 **2014**, *16*, 26691–26696.
- 609 [18] Lang, K. E.; Knox, K. J.; Momose, T.; Signorell, R. Infrared spectroscopy and
610 phase behavior of n-butane aerosols and thin films at cryogenic temperatures. *J.*
611 *Phys. Chem. A* **2013**, *117*, 11745–11759.

- 612 [19] Lang, K. E.; Knox, K. J.; Signorell, R. Phase behavior of propane and n-pentane
613 aerosol particles under conditions relevant to Titan. *Planet. Space Sci.* **2013**, *75*,
614 56–68.
- 615 [20] Kunzmann, M. K.; Signorell, R.; Taraschewski, M. ; Bauerecker, S. The formation
616 of N₂O nanoparticles in a collisional cooling cell between 4 and 110 K. *Phys. Chem.*
617 *Chem. Phys.* **2001**, *3*, 3742–3749.
- 618 [21] Disselkamp, R.; Ewing, G. E. Large CO₂ clusters studied by infrared spectroscopy
619 and light scattering. *Phys. Chem. Chem. Phys.* **1993**, *99*, 2439–2448.
- 620 [22] Firanescu, G.; Luckhaus, D.; Signorell, R. Phase, shape, and architecture of SF₆ and
621 SF₆/CO₂ aerosol particles: Infrared spectra and modeling of vibrational excitons. *J.*
622 *Chem. Phys.* **2008**, *128*, 184301.
- 623 [23] Wang, C. C.; Zielke, P.; Sigurbjörnsson, O. F.; Viteri, C. R.; Signorell, R. Infrared
624 spectra of C₂H₆, C₂H₄, C₂H₂, and CO₂ aerosols potentially formed in Titan’s atmo-
625 sphere. *J. Phys. Chem. A* **2009**, *113*, 11129–11137.
- 626 [24] Barnes, J. A.; Gough, T. E. Fourier transform infrared spectroscopy of molecular
627 clusters: The structure and internal mobility of clustered carbon dioxide. *J. Chem.*
628 *Phys.* **1987**, *86*, 6012–6017.
- 629 [25] Devlin, J. P.; Joyce, C.; Buch, V. Infrared spectra and structures of large water
630 clusters. *J. Phys. Chem. A* **2000**, *104*, 1974–1977.
- 631 [26] Gough, T. E.; Wang, T. Vibrational spectroscopy of cocrystallized carbon dioxide
632 and acetylene. *J. Chem. Phys.* **1995**, *102*, 3932–3937.
- 633 [27] Ennis, C.; Auchetl, R.; Ruzi, M.; Robertson, E. G. Infrared characterisation of
634 acetonitrile and propionitrile aerosols under Titan’s atmospheric conditions. *Phys.*
635 *Chem. Chem. Phys.* **2017**, *19*, 2915–2925.
- 636 [28] Baurecker, S.; Taraschewski, M.; Weitkamp, C.; Cammenga, H. K. Liquid-helium

- 637 temperature long-path infrared spectroscopy of molecular clusters and supercooled
638 molecules. *Rev. Sci. Instrum.* **2001**, *72*, 3946–3955.
- 639 [29] Sigurbjörnsson, O. F.; Firanescu, G.; Signorell, R. Vibrational exciton coupling as a
640 probe for phase transitions and shape changes of fluoroform aerosol particles. *Phys.*
641 *Chem. Chem. Phys.* **2009**, *11*, 187–194.
- 642 [30] Jetzki, M.; Bonnamy, A.; Signorell, R. Vibrational delocalization in ammonia aerosol
643 particles. *J. Chem. Phys.* **2004**, *120*, 11775–11784.
- 644 [31] Signorell, R. Verification of the vibrational exciton approach for CO₂ and N₂O
645 nanoparticles. *J. Chem. Phys.* **2003**, *118*, 2707–2715.
- 646 [32] *Fundamentals and Applications in Aerosol Spectroscopy*. Signorell, R.; Reid, J. P.;
647 CRC Press, Boca Raton, 2010.
- 648 [33] Tanimura, S.; Okada, Y.; Takeuchi, K. FTIR spectroscopy of UF₆ clustering in a
649 supersonic Laval nozzle. *J. Phys. Chem.* **1996**, *100*, 2842–2848.
- 650 [34] Bonnamy, A.; Georges, R.; Hugo, E.; Signorell, R. IR signature of (CO₂)_N clusters:
651 size, shape and structural effects. *Phys. Chem. Chem. Phys.* **2005**, *7*, 963–969.
- 652 [35] Laksmono, H.; Tanimura, S.; Allen, H. C.; Wilemski, G.; Zahniser, M. S.;
653 Shorter, J. H.; Nelson, D. D.; McManus, J. B.; Wyslouzil, B. E. Monomer, clusters,
654 liquid: an integrated spectroscopic study of methanol condensation. *Phys. Chem.*
655 *Chem. Phys.* **2011**, *13*, 5855–5871.
- 656 [36] Manka, A.; Pathak, H.; Tanimura, S.; Wölk, J.; Strey, R.; Wyslouzil, B. E. Freezing
657 water in no-man’s land. *Phys. Chem. Chem. Phys.* **2012**, *14*, 4505–4516.
- 658 [37] Modak, V. P.; Pathak, H.; Thayer, M.; Singer, S. J.; Wyslouzil, B. E. Experimental
659 evidence for surface freezing in supercooled *n*-alkane nanodroplets. *Phys. Chem.*
660 *Chem. Phys.* **2013**, *15*, 6783–6795.
- 661 [38] Amaya, A. J.; Wyslouzil, B. E. Ice nucleation rates near ~225 K. *J. Chem. Phys.*
662 **2018**, *148*, 084501.

- 663 [39] Bonnamy, A.; Georges, R.; Benidar, A.; Boissoles, J.; Canosa, A.; Rowe, B. R.
664 Infrared spectroscopy of $(\text{CO}_2)_N$ nanoparticles ($30 < N < 14500$) flowing in a uniform
665 supersonic expansion. *J. Chem. Phys.* **2003**, *118*, 3612–3621.
- 666 [40] Negishi, Y.; Nagata, T.; Tsukuda, T. Structural evolution in $(\text{CO}_2)_n$ clusters ($n <$
667 10^3) as studied by mass spectrometry. *Chem. Phys. Lett.* **2002**, *364*, 127–132.
- 668 [41] Ingolfsson, O.; Wodtke, A. M. Electron attachment time-of-flight mass spectrometry
669 reveals geometrical shell closings in van der Waals aggregates. *J. Chem. Phys.* **2002**,
670 *117*, 3721–3732.
- 671 [42] Näher, U.; Zimmermann, U.; Martin, T. P. Geometrical shell structure of clusters.
672 *J. Chem. Phys.* **1993**, *99*, 2256–2260.
- 673 [43] Torchet, G.; de Feraudy, M.-F.; Boutin, A.; Fuchs, A. H. Structural transformation
674 in $(\text{CO}_2)_N$ clusters, $N < 100$. *J. Chem. Phys.* **1996**, *105*, 3671–3678.
- 675 [44] Maillet, J.-B.; Boutin, A.; Fuchs, A. H. From molecular clusters to bulk matter. II.
676 Crossover from icosahedral to crystalline structures in CO_2 clusters. *J. Chem. Phys.*
677 **1999**, *111*, 2095–2102.
- 678 [45] Liu, H.; Jordan, K. D. Finite Temperature Properties of $(\text{CO}_2)_n$ Clusters. *J. Phys.*
679 *Chem. A* **2003**, *107*, 5703–5709.
- 680 [46] Signorell, R.; Jetzki, M.; Kunzmann, R.M.; Ueberschaer, R. Unraveling the origin
681 of band shapes in infrared spectra of $\text{N}_2\text{O}-^{12}\text{CO}_2$ and $^{12}\text{CO}_2-^{13}\text{CO}_2$ ice particles. *J.*
682 *Phys. Chem. A* **2006**, *110*, 2890–2897.
- 683 [47] Lippe, M.; Chakrabarty, S.; Ferreiro, J. J.; Tanaka, K. K.; Signorell, R. Water
684 nucleation at extreme supersaturation. *J. Chem. Phys.* **2018**, *149*, 244303.
- 685 [48] Chakrabarty, S.; Ferreiro, J. J.; Lippe, M.; Signorell, R. Toluene cluster formation in
686 Laval expansions: nucleation and growth. *J. Phys. Chem. A* **2017**, *121*, 3991–4001.

- 687 [49] Ferreiro, J. J.; Chakrabarty, S.; Schläppi, B.; Signorell, R. Observation of propane
688 cluster size distributions during nucleation and growth in a Laval expansion. *J.*
689 *Chem. Phys.* **2016**, *145*, 211907.
- 690 [50] Schläppi, B.; Litman, J. H.; Ferreiro, J. J.; Stapfer, D.; Signorell, R. A pulsed uni-
691 form Laval expansion coupled with single photon ionization and mass spectrometric
692 detection for the study of large molecular aggregates. *Phys. Chem. Chem. Phys.*
693 **2015**, *17*, 25761–25771.
- 694 [51] Ferreiro, J. J.; Gartmann, T. E.; Schläppi, B.; Signorell, R. Can we observe gas
695 phase nucleation at the molecular level? *Z. Phys. Chem.* **2015**, *229*, 1765–1780.
- 696 [52] Atkinson, D. B.; Smith, M. A. Design and characterization of pulsed uniform super-
697 sonic expansions for chemical applications. *Rev. Sci. Instrum.* **1995**, *66*, 4434–4446.
- 698 [53] Forysinski, P. W.; Zielke, P.; Luckhaus, D.; Signorell, R. PFI-ZEKE photoelec-
699 tron spectrum of CH₂F₂, ionisation potential and ionic fragmentation appearance
700 potentials. *Phys. Chem. Chem. Phys.* **2010**, *12*, 3121–3130.
- 701 [54] Yoder, B. L.; Litman, J. H.; Forysinski, P. W.; Corbett, J. L.; Signorell, R. Sizer for
702 neutral weakly bound ultrafine aerosol particles based on sodium doping and mass
703 spectrometric detection. *J. Phys. Chem. Lett.* **2011**, *2*, 2623–2628.
- 704 [55] Litman, J. H.; Yoder, B. L.; Schläppi, B.; Signorell, R. Sodium-doping as a reference
705 to study the influence of intracluster chemistry on the fragmentation of weakly-bound
706 clusters upon vacuum ultraviolet photoionization. *Phys. Chem. Chem. Phys.* **2013**,
707 *15*, 940–949.
- 708 [56] Heinbuch, S.; Dong, F.; Rocca, J. J.; Bernstein, E. R. Single photon ionization of
709 van der Waals clusters with a soft x-ray laser: (CO₂)_n and (CO₂)_n(H₂O)_m. *J. Chem.*
710 *Phys.* **2006**, *125*, 154316.
- 711 [57] Fárník, M.; Lengyel, J. Mass spectrometry of aerosol particle analogues in molecular
712 beam experiments. *Mass Spectrom. Rev.* **2018**, *37*, 630–651.

- 713 [58] Pysanenko, A.; Lengyel, J.; Fárnik, M. Uptake of methanol on mixed HNO₃/H₂O
714 clusters: An absolute pickup cross section. *Mass Spectrom. Rev.* **2018**, *148*, 154301.
- 715 [59] Wang, L. S.; Reutt, J. E.; Lee, Y. T.; Shirley, D. A. High resolution UV photoelec-
716 tron spectroscopy of CO⁺₂, COS⁺ and CS⁺₂ using supersonic molecular beams. *J.*
717 *Electron Spectrosc. Relat. Phenom.* **1988**, *47*, 167–186.
- 718 [60] Zhang, J.; Dolg, M. ABCcluster: the artificial bee colony algorithm for cluster global
719 optimization. *Phys. Chem. Chem. Phys.* **2015**, *17*, 24173–24181.
- 720 [61] Zhang, J.; Dolg, M. Global optimization of clusters of rigid molecules using the
721 artificial bee colony algorithm. *Phys. Chem. Chem. Phys.* **2016**, *18*, 3003–3010.
- 722 [62] MacKerell, A. D.; Bashford, D.; Bellott, M.; Dunbrack, R. L.; Evanseck, J. D.;
723 Field, M. J.; Fischer, S.; Gao, J.; Guo, H.; Ha, S.; et al. All-atom empirical potential
724 for molecular modeling and dynamics studies of proteins. *J. Phys. Chem. B* **1998**,
725 *102*, 3586–3616.
- 726 [63] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheese-
727 man, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian*
728 *09, revision A. 1* Gaussian Inc. Wallingford CT 27, 2009.
- 729 [64] Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange.
730 *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- 731 [65] Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy
732 formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37*, 785–789.
- 733 [66] Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab initio calculation
734 of vibrational absorption and circular dichroism spectra using density functional
735 force fields. *J. Phys. Chem.* **1994**, *98*, 11623–11627.
- 736 [67] Schwabe, T.; Grimme, S. Double-hybrid density functionals with long-range disper-
737 sion corrections: higher accuracy and extended applicability. *Phys. Chem. Chem.*
738 *Phys.* **2007**, *9*, 3397–3406.

- 739 [68] Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group
740 thermochemistry, thermochemical kinetics, noncovalent interactions, excited states,
741 and transition elements: two new functionals and systematic testing of four M06-
742 class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- 743 [69] Dill, J. D.; Pople, J. A. Self-consistent molecular orbital methods. XV. Extended
744 Gaussian-type basis sets for lithium, beryllium, and boron. *J. Chem. Phys.* **1975**,
745 *62*, 2921–2923.
- 746 [70] Lemke, K. H.; Seward, T. M. Thermodynamic properties of carbon dioxide clusters
747 by M06-2X and dispersion-corrected B2PLYP-D theory. *Chem. Phys. Lett.* **2013**,
748 *573*, 19–23.
- 749 [71] Xie, X.; Wu, C.; Liu, Y.; Huang, W.; Deng, Y.; Liu, Y.; Gong, Q.; Wu, C. Identifying
750 isomers of carbon-dioxide clusters by laser-driven Coulomb explosion. *Phys. Rev. A*
751 **2014**, *90*, 033411.
- 752 [72] Takeuchi, H. Geometry optimization of carbon dioxide clusters $(\text{CO}_2)_n$ for $4 \leq n \leq$
753 40 . *J. Phys. Chem. A* **2008**, *112*, 7492–7497.
- 754 [73] Herzberg, G. *Molecular Spectra and Molecular Structure. Vol. 3: Electronic Spectra*
755 *and Electronic Structure of Polyatomic Molecules*. Van Nostrand Reinhold, New
756 York, 1966.
- 757 [74] Shimanouchi, T. *Tables of Molecular Vibrational Frequencies*. National Bureau of
758 Standards, Washington D. C., 1980.
- 759 [75] Weida, M. J.; Sperhac, J. M.; Nesbitt, D. J. High-resolution infrared diode laser
760 spectroscopy of $(\text{CO}_2)_3$: Vibrationally averaged structures, resonant dipole vibra-
761 tional shifts, and tests of CO_2 – CO_2 pair potentials. *J. Chem. Phys.* **1995**, *103*,
762 7685–7699.
- 763 [76] Jucks, K. W.; Huang, Z. S.; Miller, R. E.; Fraser, G. T.; Pine, A. S.; Lafferty, W. J.
764 Structure and vibrational dynamics of the CO_2 dimer from the sub-Doppler infrared
765 spectrum of the $2.7 \mu\text{m}$ Fermi diad. *J. Chem. Phys.* **1988**, *88*, 2185–2195.

- 766 [77] Fraser, G. T.; Pine, A. S.; Lafferty, W. J.; Miller, R. E. Sub-Doppler infrared
767 spectrum of the carbon dioxide trimer. *J. Chem. Phys.* **1987**, *87*, 1502–1508.
- 768 [78] Walsh, M. A.; England, T. H.; Dyke, T. R.; Howard, B. J. Pulsed molecular beam
769 infrared absorption spectroscopy of CO₂ dimer. *Chem. Phys. Lett.* **1987**, *142*, 265–
770 270.
- 771 [79] Signorell, R. Infrared spectroscopy of particulate matter: between molecular clusters
772 and bulk. *Mol. Phys.* **2003**, *101*, 3385–3399.
- 773 [80] Rothman, L. S.; Benedict, W. S. Infrared energy levels and intensities of carbon
774 dioxide. *Appl. Opt.* **1978**, *17*, 2605–2611.
- 775 [81] Bonnamy, A.; Jetzki, M.; Signorell, R. Optical properties of molecular ice particles
776 from a microscopic model. *Chem. Phys. Lett.* **2003**, *382*, 547–552.
- 777 [82] Torchet, G.; Bouchier, H.; Farges, J.; De Feraudy, M. F.; Raoult, B. Size effects in
778 the structure and dynamics of CO₂ clusters. *J. Chem. Phys.* **1984**, *81*, 2137–2143.
- 779 [83] Duff, K. M. Non-equilibrium condensation of carbon dioxide in supersonic nozzles.
780 Ph.D. Dissertation, Massachusetts Institute of Technology, Cambridge, MA, 1966.
- 781 [84] Cardini, G.; Schettino, V.; Klein, M. L. Structure and dynamics of carbon dioxide
782 clusters: a molecular dynamics study. *J. Chem. Phys.* **1989**, *90*, 4441–4449.
- 783 [85] Maillet, J.-B.; Boutin, A.; Buttefey, S.; Calvo, F.; Fuchs, A. H. From molecular
784 clusters to bulk matter. I. Structure and thermodynamics of small CO₂, N₂, and SF₆
785 clusters. *J. Chem. Phys.* **1998**, *109*, 329–337.
- 786 [86] Murthy, C. S.; O’Shea, S. F.; McDonald, I. R. Electrostatic interactions in molecular
787 crystals: lattice dynamics of solid nitrogen and carbon dioxide. *Mol. Phys.* **1983**,
788 *50*, 531–541.
- 789 [87] Häber, T.; Schmitt, U.; Emmeluth, C.; Suhm, M. A. Ragout-jet FTIR spectroscopy
790 of cluster isomerism and cluster dynamics: from carboxylic acid dimers to N₂O
791 nanoparticles. *Faraday Discuss.* **2001**, *118*, 331–359.

792 [88] Kunzmann, M. K.; Bauerecker, S.; Suhm, M. A.; Signorell, R. Spectroscopic char-
793 acterization of N₂O aggregates: from clusters to the particulate state. *Spectrochim.*
794 *Acta A* **2003**, *59*, 2855–2865.

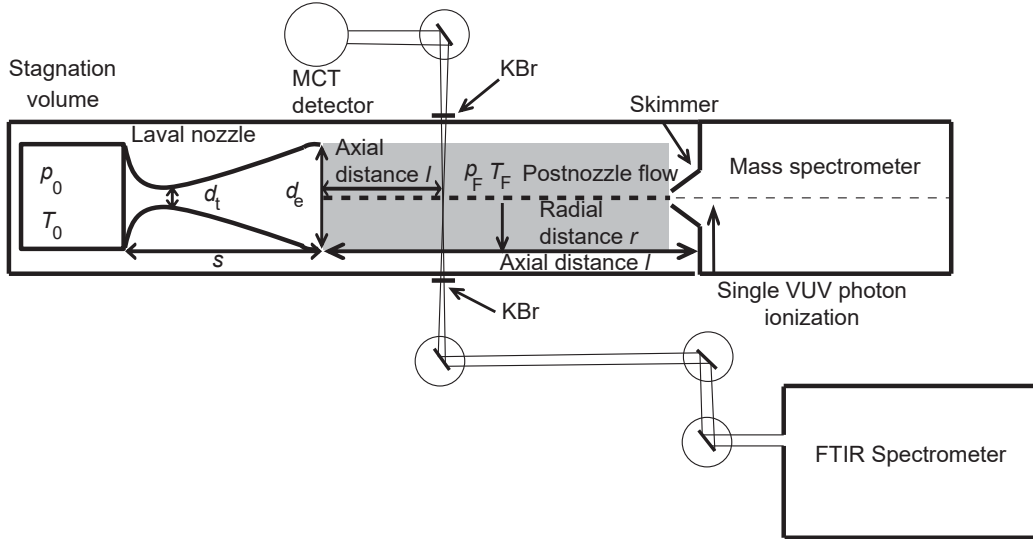


Figure 1: Schematic of the experimental setup^{49,48}. p_0 , T_0 , p_F and T_F are the stagnation pressure, the stagnation temperature, the flow pressure, and the flow temperature, respectively. d_t , d_e , and s is the throat diameter, the exit diameter, and the length of the Laval nozzle, respectively. r is the radial distance from the center of the expansion. The axial distance l is the distance between the nozzle exit and the skimmer. l can be varied, which corresponds to a variation in the growth time t . The central part of the expansion is sampled into the mass spectrometer by a skimmer, where the clusters are ionized and detected. FTIR measurements were performed in the postnozzle flow of the Laval expansion in positions corresponding to the same axial distance as measured with mass spectrometry.

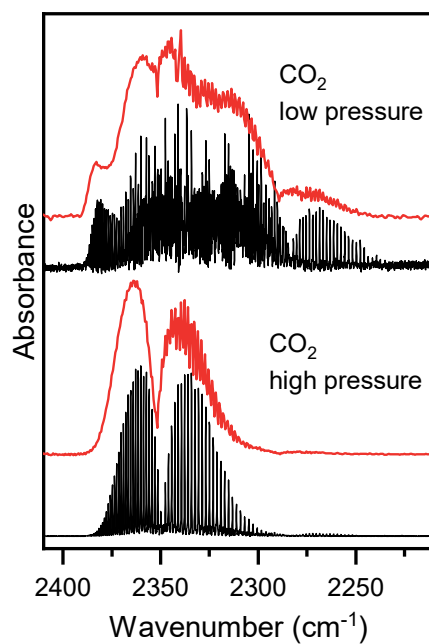


Figure 2: Top: Infrared spectrum of CO₂ at low pressure (< 1 mbar) measured with high (black, 0.25 cm^{-1}) and low (red, 1.5 cm^{-1}) resolution. Bottom: Infrared spectrum of CO₂ at a pressure of about 1 bar measured with high (black, 0.25 cm^{-1}) and low (red, 1.5 cm^{-1}) resolution. The pressure was increased by addition of argon gas. All spectra were measured at room temperature.

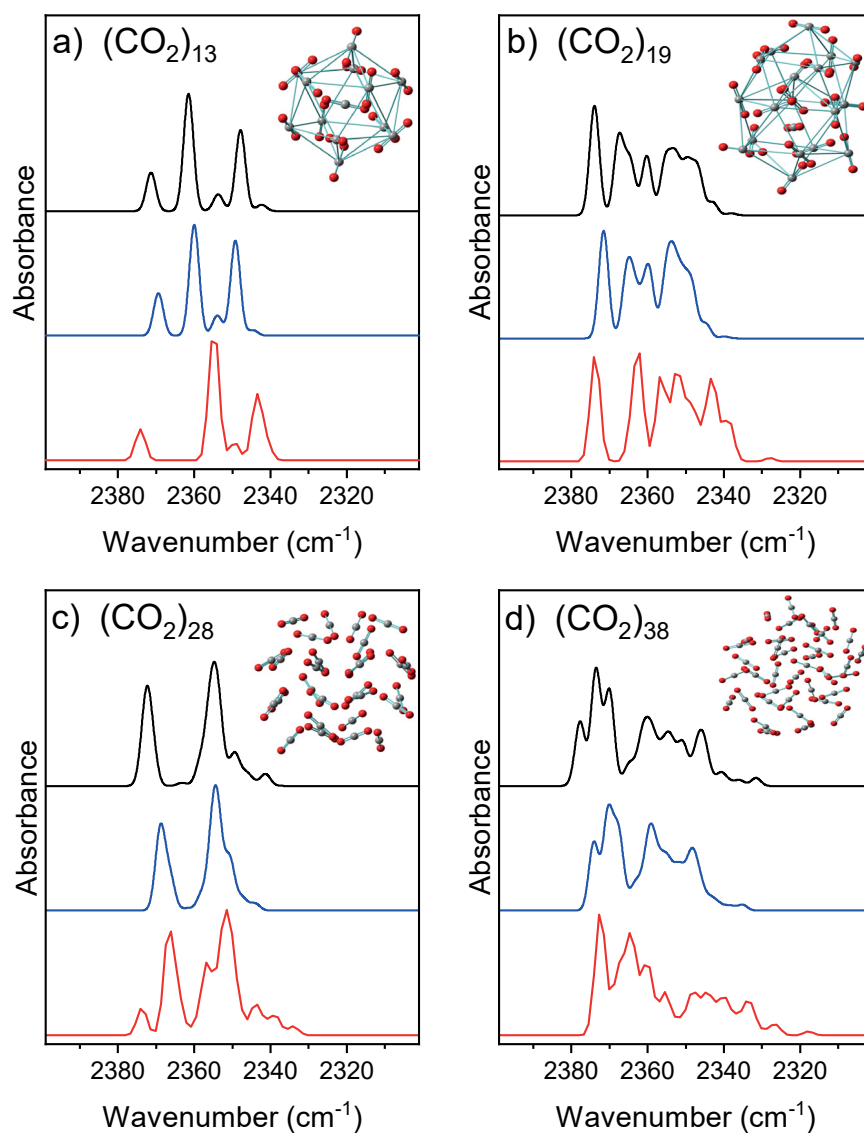


Figure 3: Simulated infrared spectra of the most stable structures of $(\text{CO}_2)_n$ ($n = 13$ (a), 19 (b), 28 (c), and 38 (d)) using Gaussian with optimized M06-2X structures (red, lower), exciton calculations with optimized FF structures (blue, middle), and exciton calculations with optimized M06-2X structures (black, upper) are shown.

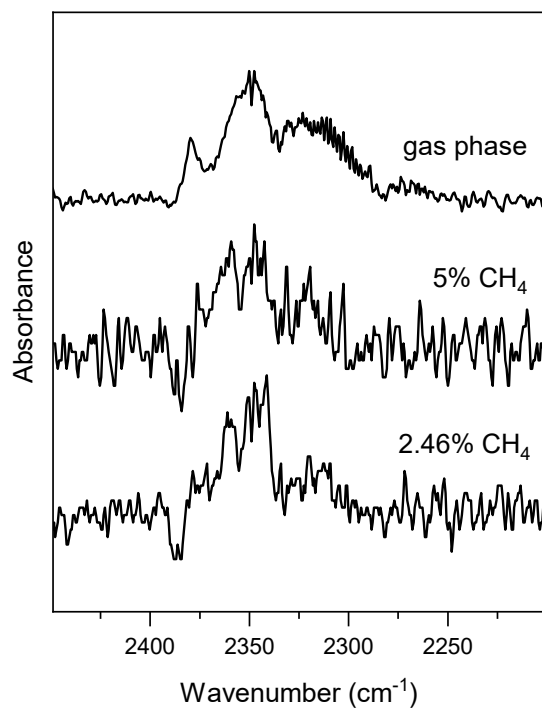


Figure 4: Pure gas phase spectrum (top) and two experimental FTIR spectra under CO₂ nucleation conditions (0.18% CO₂) with 5% (middle) and 2.46% (bottom) methane.

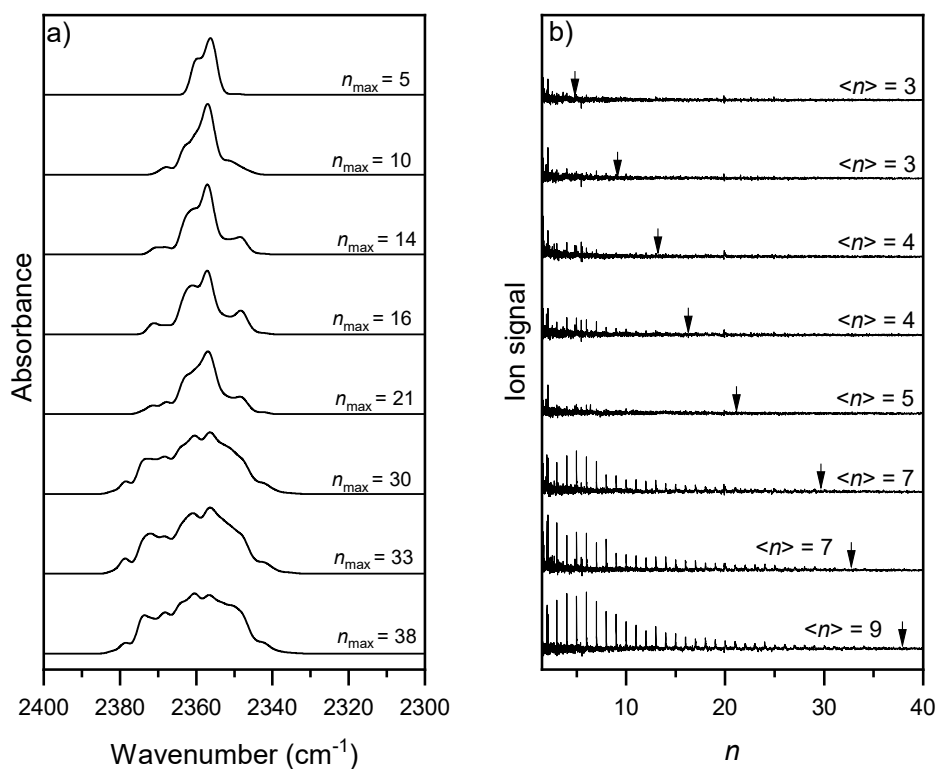


Figure 5: a) Infrared spectra of clusters during nucleation. The spectra are calculated with the exciton model for the cluster size distributions shown in trace b. n_{\max} is indicated in the graph. b) Mass spectra of clusters during nucleation at ~ 29 K and 0.18% CO_2 with methane concentrations between 0 and 8.23%. n_{\max} is indicated by arrows (values see trace a) in addition to the values of $\langle n \rangle$.

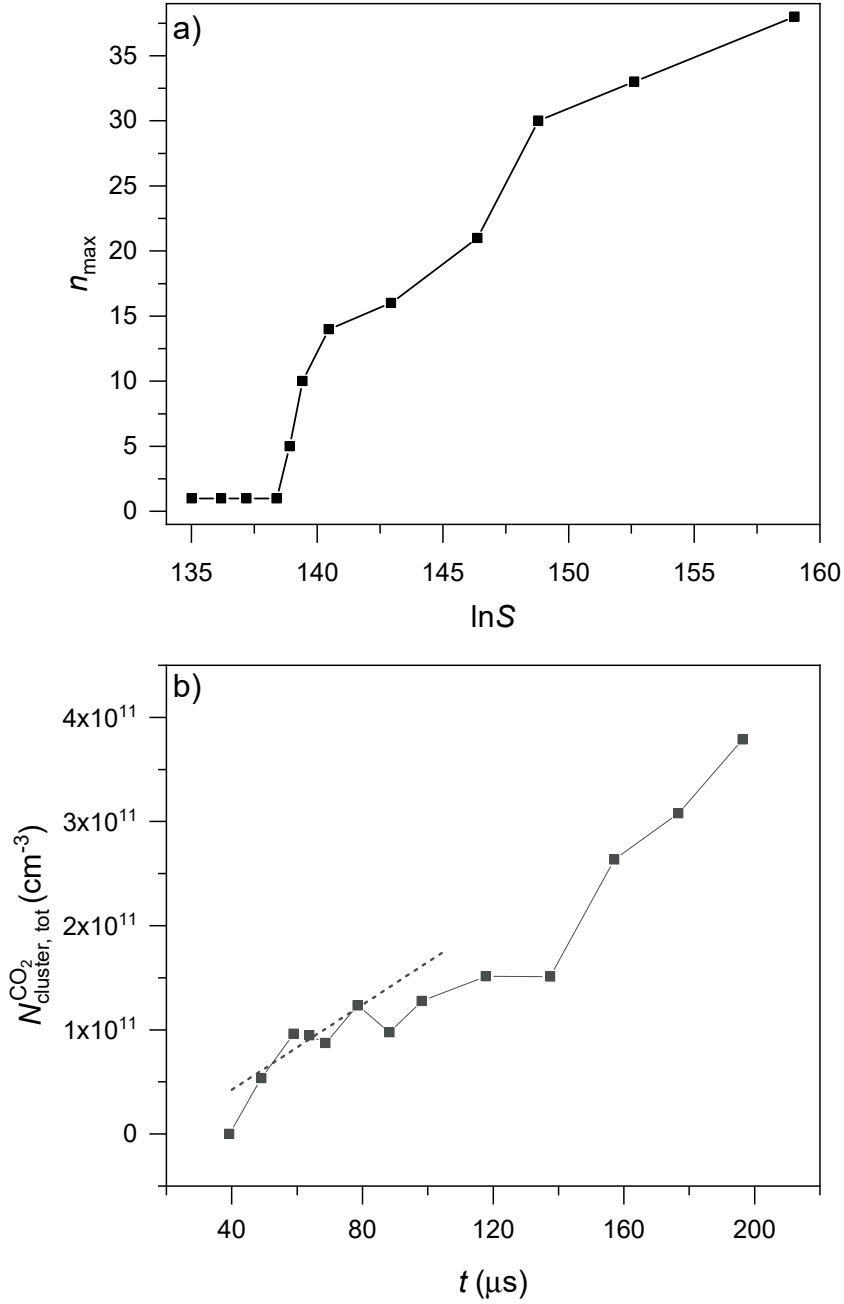


Figure 6: a) n_{\max} from Fig. 5b as a function of $\ln S$. The nucleation behavior hints at a barrierless nucleation process which is consistent with the high S value. b) Total cluster number concentration of CO_2 clusters as a function of the nucleation time at constant supersaturation $\ln S \sim 160$. The nucleation/condensation rate is determined by a linear fit (see dashed line) and is on the order of $1\text{-}2 \cdot 10^{15} \text{ cm}^{-3} \text{ s}^{-1}$.

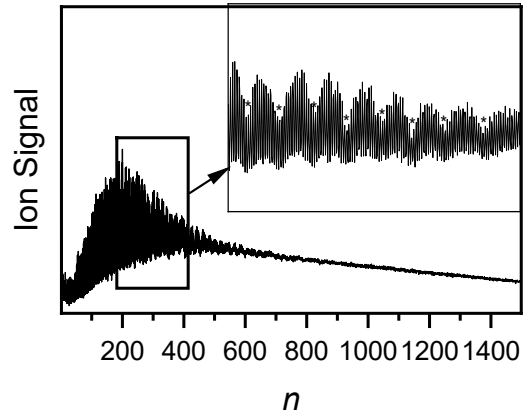


Figure 7: Mass spectrum for 5% CO₂ at ~ 29 K. The inset shows a zoom-in of the part shown by the rectangle. Local minima of the ion signal for cluster sizes $n \gtrsim 55$ are marked with asterisks, these correspond to shell and subshell closings.

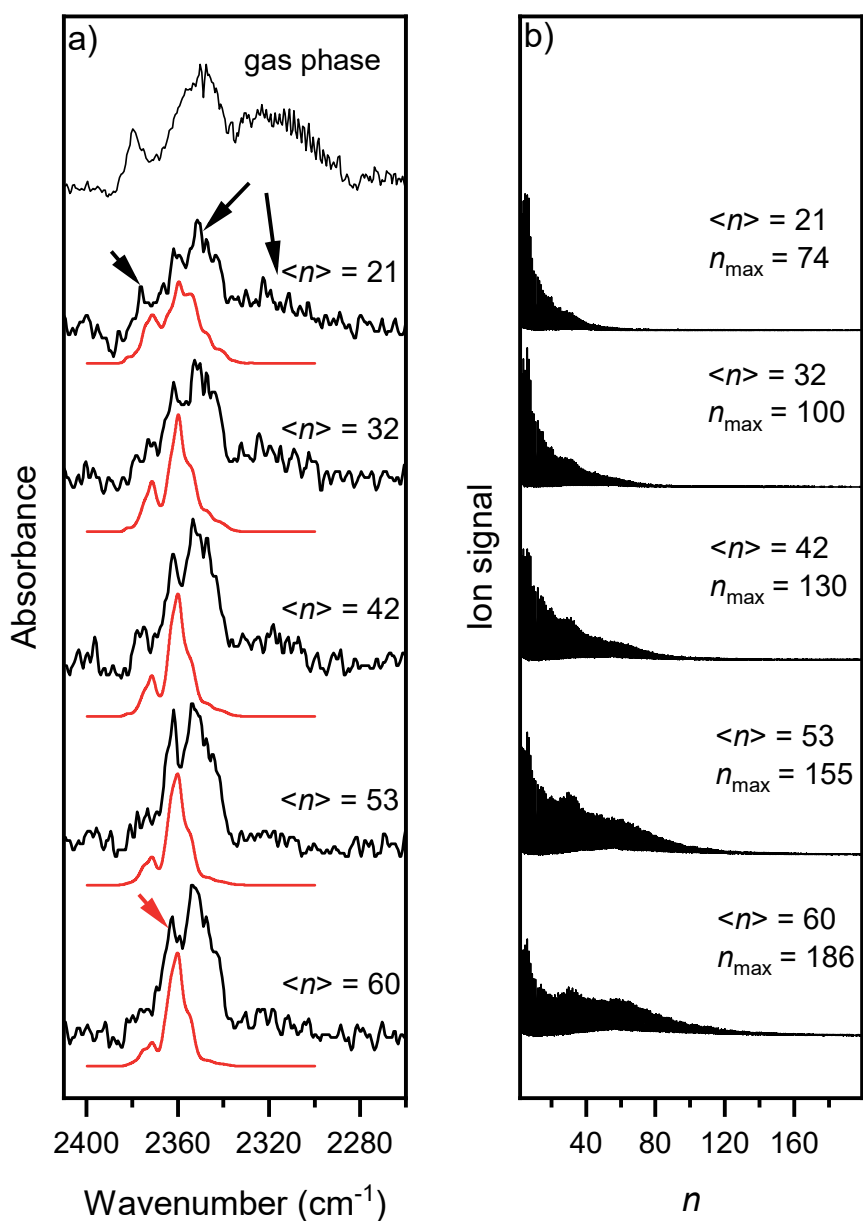


Figure 8: a) Experimental infrared spectra recorded at ~ 29 K for 0.38% CO_2 (black) with respective exciton simulations (red). $\langle n \rangle$ is indicated for each spectrum. The black arrows in the second top spectrum show where we observe mainly gas phase contributions. The red arrow in the bottom spectrum shows where we observe cluster contributions. A pure gas phase spectrum is shown on top. b) Corresponding mass spectra. $\langle n \rangle$ and n_{max} are indicated in the figure.

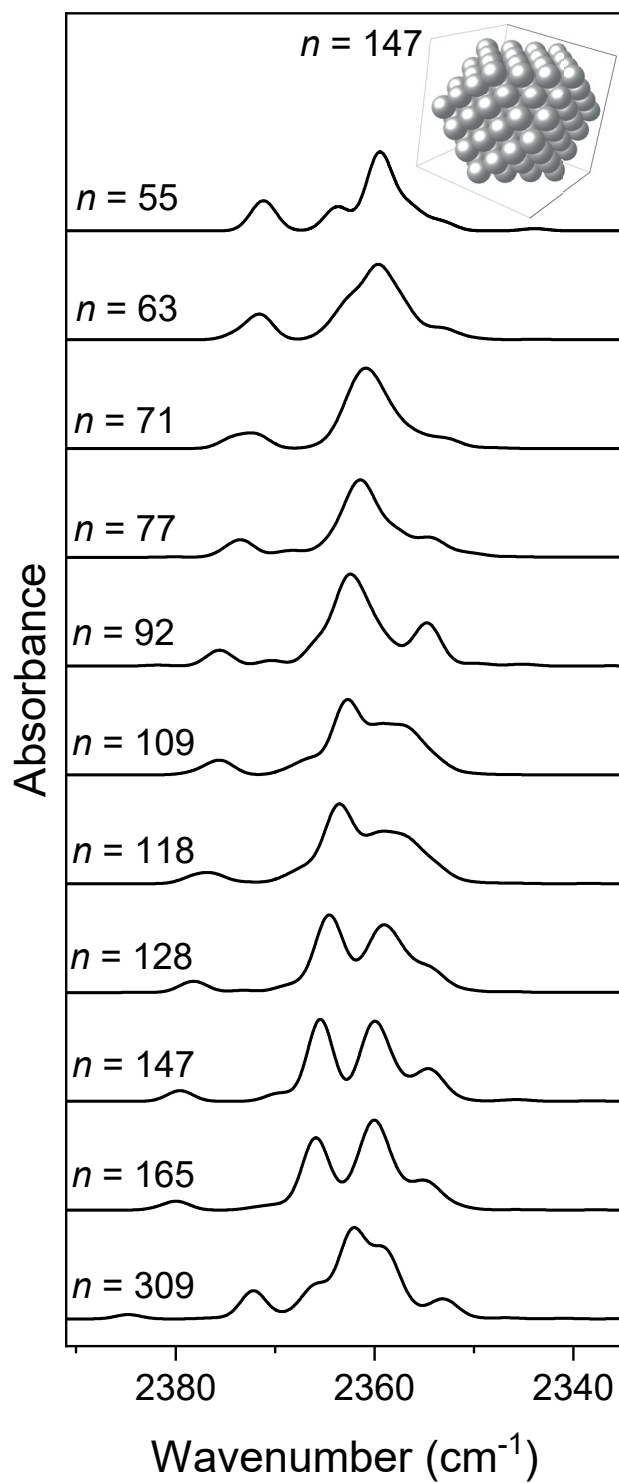


Figure 9: Calculated infrared spectra (exciton calculations) for cuboctahedral structures with n molecules per cluster. A complete shell closed cuboctahedral structure for $n = 147$ is displayed on top of the graph.

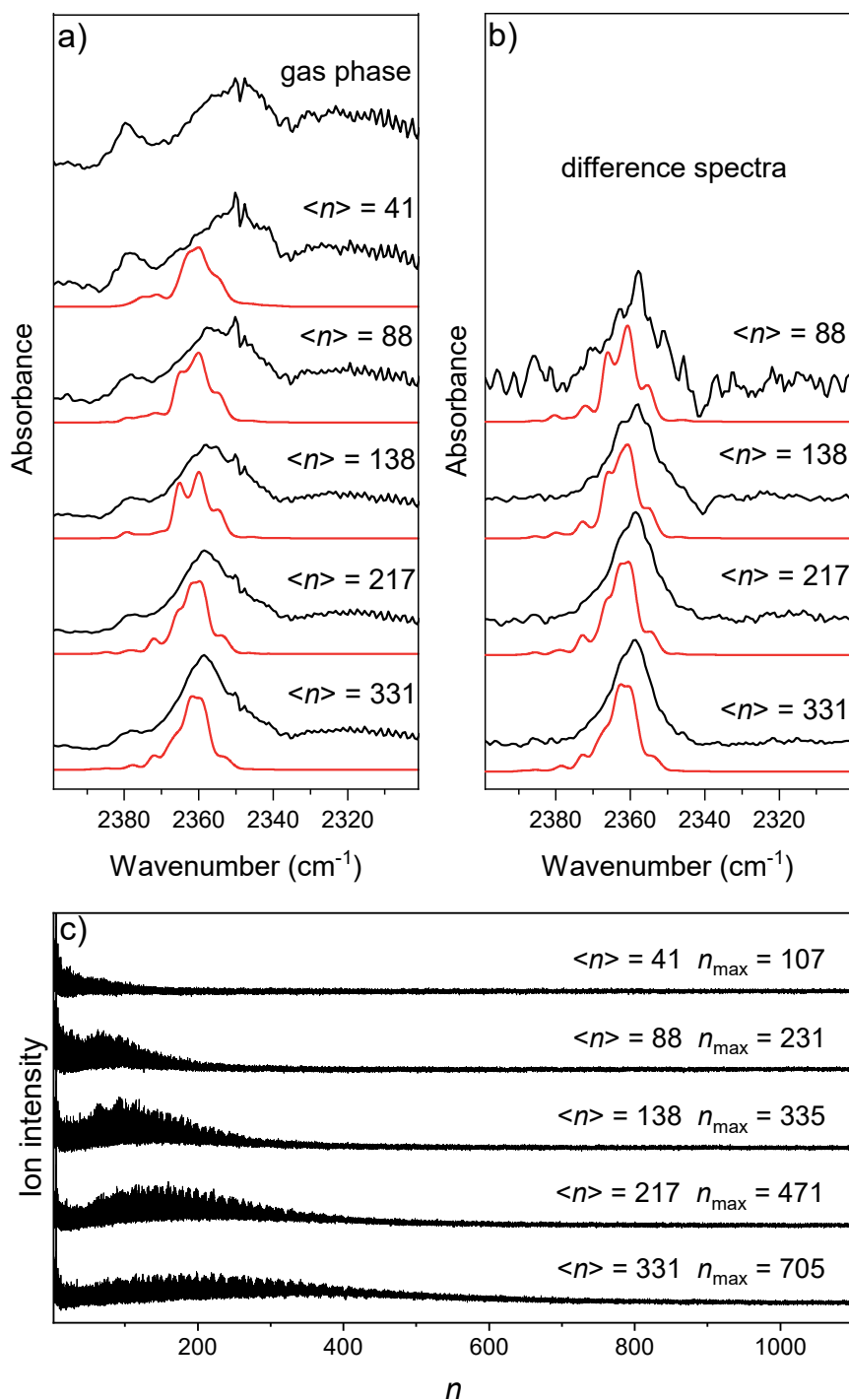


Figure 10: a) Experimental and exciton calculated infrared spectra at ~ 43 K for 2.48% CO_2 for different $\langle n \rangle$ as indicated for each trace. The experimental spectra are shown in black and the exciton calculations in red. A pure gas phase spectrum is shown on top. b) Experimental difference infrared spectra (black) with corresponding difference exciton simulations (red). The difference spectra were obtained by subtracting the cluster spectrum for $\langle n \rangle = 41$ from the spectra with $\langle n \rangle = 88, 138, 217, 331$ (see text). c) Corresponding mass spectra.

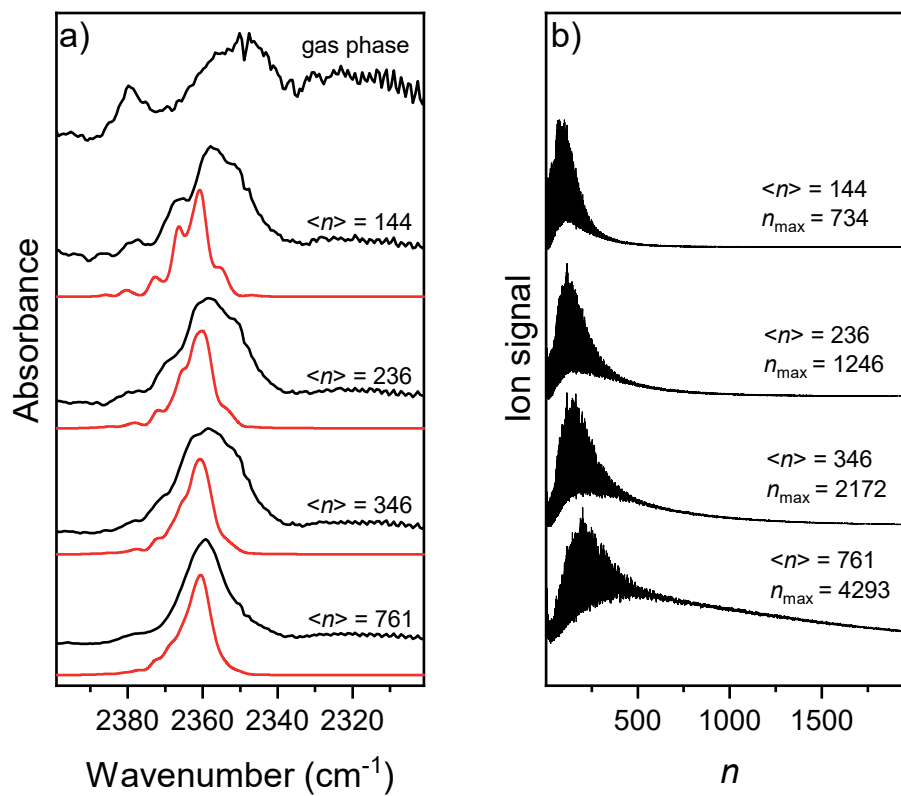
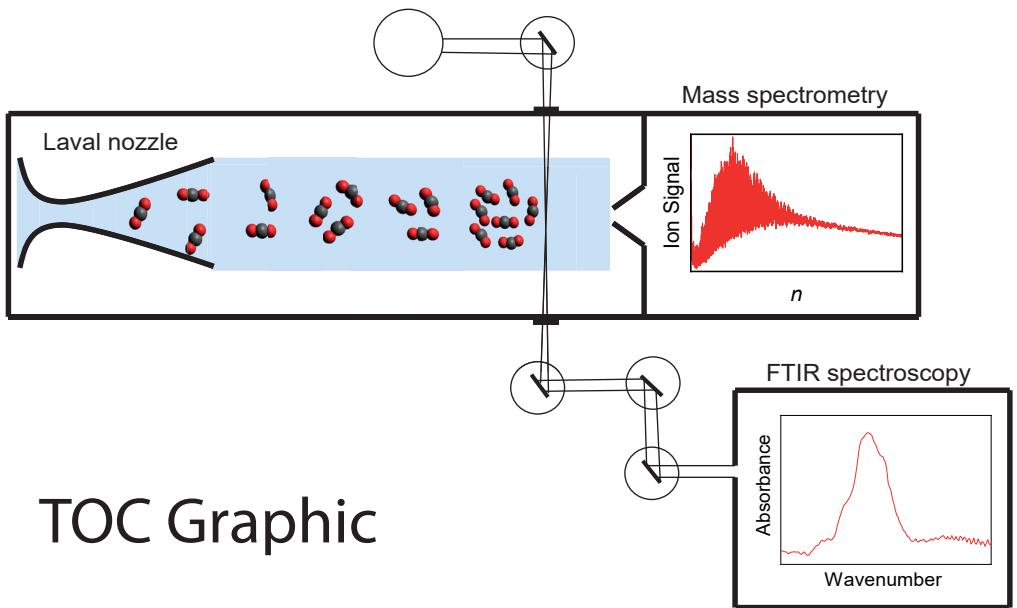


Figure 11: a) Experimental (black) and calculated (red) infrared spectra at ~ 29 K for different concentrations of CO₂ (1, 1.6, 2.3 and 5% from top to bottom). A pure CO₂ gas phase spectrum is shown on top. b) Corresponding mass spectra.



TOC Graphic