Infrared Spectroscopy of Size-Selected Hydrated Carbon Dioxide Radical Anions CO2.−(H2O)n (n=2–61) in the C−O Stretch Region

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Published in:
Chemistry - A European Journal

Published: 01/08/2019

Document Version:
Final Published version, also known as Publisher's PDF, Publisher's Final version or Version of Record

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Publication record in CityU Scholars:
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Published version (DOI):
10.1002/chem.201901650

Publication details:
Carbon Dioxide Radical Anions

Infrared Spectroscopy of Size-Selected Hydrated Carbon Dioxide Radical Anions \( \text{CO}_2\cdot\cdot\cdot\text{(H}_2\text{O)}_n \) (\( n = 2–61 \)) in the C–O Stretch Region


Dedicated to Professor Dr. Dr. h.c. mult. Tilmann D. Märk on the occasion of his 75th birthday

Abstract: Understanding the intrinsic properties of the hydrated carbon dioxide radical anions \( \text{CO}_2\cdot\cdot\cdot\text{(H}_2\text{O)}_n \) is relevant for electrochemical carbon dioxide functionalization. \( \text{CO}_2\cdot\cdot\cdot\text{(H}_2\text{O)}_n \) (\( n = 2–61 \)) is investigated by using infrared action spectroscopy in the 1150–2220 cm\(^{-1}\) region in an ICR (ion cyclotron resonance) cell cooled to \( T = 80 \) K. The spectra show an absorption band around 1280 cm\(^{-1}\), which is assigned to the symmetric C–O stretching vibration \( \nu_s \). It blue-shifts with increasing cluster size, reaching the bulk value, within the experimental linewidth, for \( n = 20 \). The antisymmetric C–O vibration \( \nu_a \) is strongly coupled with the water bending mode \( \nu_b \), causing a broad feature at approximately 1650 cm\(^{-1}\). For larger clusters, an additional broad and weak band appears above 1900 cm\(^{-1}\) similar to bulk water, which is assigned to a combination band of water bending and libration modes. Quantum chemical calculations provide insight into the interaction of \( \text{CO}_2\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdot\cdo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gen bonds, and two H$_2$O molecules are independently bound to the oxygen atoms of the CO$_2$" in CO$_2$"(H$_2$O)$_2$. For [(CO$_2$)$_4$(H$_2$O)$_n$]$^-$, additional IR absorption bands appear at $n = 4$, which are assigned to the bending overtone and the hydrogen-bonded O–H vibration of H$_2$O bound to CO$_2$" through a single O–H–O linkage.\[56\]

Liu et al. performed a detailed theoretical study on localization and time evolution of the excess electron in heterogeneous CO$_2$–H$_2$O systems.\[39\] Their calculations show that hydrogen bonds are not only formed with the oxygen atoms of CO$_2$, but also with the carbon atom. Furthermore, they suggest that CO$_2$" is localized inside the cluster with four to seven H$_2$O molecules coordinated to the carbon dioxide radical anion. The reactivity of this species is heavily influenced by the surrounding hydrogen-bond network, which calls for a detailed vibrational spectroscopic analysis of CO$_2$"(H$_2$O)$_n$, clusters.

The details of the interaction between ions and water are ideally investigated through microhydration studies, adding water molecules one at a time. Asmis and co-workers studied how different anions\[46,41\] and dianions\[42,43\] behave upon step-wise hydration by using infrared spectroscopy combined with quantum chemical calculations. Special interest was devoted to the number of water molecules needed to saturate the first solvation shell. In the HCO$_3$"(H$_2$O)$_n$ system, a maximum of five water molecules interact directly with the bicarbonate anion,\[41\] whereas for the SO$_4$"(H$_2$O)$_n$ dianion, twelve water molecules are needed to close the first solvation shell.\[42\] These results show that vibrational spectroscopy is a powerful tool to elucidate the structure of the water network surrounding the ionic core. Williams and co-workers investigated how different core ions influence the hydrogen-bond network in large water clusters up to $n = 550$, far beyond the first solvation shell.\[44–51\] They found that the free O–H band, resulting from the vibration of water molecules with at least one hydrogen atom not involved in hydrogen bonding, redshifts and increases in intensity with increasing positive charge.\[44\] Their work demonstrates long-range solvation effects upon hydration of different ions. In a recent temperature-controlled experiment with SO$_4$"(H$_2$O)$_n$, these ion–water interactions were seen at temperatures that are relevant to Earth’s atmosphere.\[46\] Thermochromical properties\[52–55\] as well as infrared spectroscopic signatures\[56–58\] have been frequently investigated as a function of cluster size to determine the transition to bulk-like behavior of hydrated ions. Along these lines, we investigate size-selected CO$_2$"(H$_2$O)$_n$ clusters, $n \leq 61$, by using infrared photodissociation spectroscopy in the range 1150–2220 cm$^{-1}$ at $T = 80$ K.

**Results and Discussion**

Figure 1 shows the measured IR spectra of CO$_2$"(H$_2$O)$_n$, $n = 2–61$, at $T = 80$ K by using infrared action spectroscopy, assuming single photon absorption for the calculation of relative cross sections. This is correct only for those clusters with a relatively high internal energy, which decay upon absorption of a single photon. The majority of clusters may require two or three IR photons for dissociation, especially at the low-energy end of the spectrum. However, to account for the frequency-depen-

![Figure 1](image-url)
is observed largely developed for CO and several H vibrational frequencies calculated at the B3LYP/6–311 region for some clusters, in particular (50 cm–1 G** level in absorption and bands. a) Position and cluster, 25 atoms are in motion. Instead, several normal modes of T in liquid water (1298 cm–1) is found, albeit only slightly above noise level. For clusters n=5–10, the asymmetry of the peaks indicates contributions of different isomers or from combination bands. Both features are discussed below with the aid of quantum chemical calculations. The irregularities in the 1200–1350 cm–1 region for some clusters, in particular n=30, 49, and 61, could not be assigned to specific isomers or combination bands and may be noise or a weak water absorption. Accidental spatial alignment of oscillators at a specific cluster size may afford intense combination bands. However, at the low-frequency end of the spectral range of the laser system, the power drops, and the noise level goes up substantially. Therefore, and owing to the lower intensity of the symmetric C–O stretching mode, irradiation times of 1–2 s were chosen below 1350 cm–1, compared with 0.5 s for the major part of the spectrum.

The antisymmetric stretching mode of CO2− is observed around 1650 cm–1, strongly coupled to the water bending mode ν2, denoted νs/ν2. The band is strongly asymmetric, with the higher energy components being more blueshifted with increasing cluster size. The overall band position, however, is only mildly affected by cluster size, with a small shift of 10 cm–1 for the measured cluster size range. The νs/ν2 absorption band was fitted with Gaussian functions (see Figure SI-2 in the Supporting Information); in Figure 2b, we show the position and full width at half maximum (FWHM) of the two most prominent contributions to the fits. The individual Gaussian functions, however, cannot be assigned to specific vibrational modes owing to the strong coupling of νs and ν2. In particular, the normal mode analysis of our quantum chemical calculations (see below) does not yield a single mode where only the CO2− atoms are in motion. Instead, several normal modes of the cluster with frequencies around 1650 cm–1 have both CO2− and several H2O molecules oscillating. The strength of this band scales approximately linearly with cluster size, as expected with the increasing number of water bending modes (Figure SI-3 in the Supporting Information).

For larger clusters, an additional broad, weak band appears at approximately 2100 cm–1, which is assigned to a combination band of H2O bending ν1 (1638 cm–1), H2O libration ν2 (395 cm–1), and bending of H2O triplets ν2 (50 cm–1) known from bulk liquid water. Its intensity overall increases with cluster size, with a pronounced exception at n=49, a cluster size with increased stability, see Figure SI-4 in the Supporting Information). In this cluster size region, a strong even–odd os-
cillation of the ion signal is observed. The integrated peak areas are shown in Figure SI-5 (in the Supporting Information) as a function of cluster size. Relative to \( n = 61 \), the area reaches 75\% already at \( n = 30 \), and drops to 31\% at \( n = 49 \), lower than the \( n = 20 \) value of 42\%. This largely parallels the behavior of the water bending/C–O stretching peak in Figure SI-3 (in the Supporting Information), which indicates that, owing to its increased stability, the \( n = 49 \) cluster requires more photons for dissociation than typical. In Figure 1, we also compare the spectrum of the largest cluster (\( n = 61 \)) with the IR spectrum of liquid water measured at room temperature.[60] Both the intense peak at approximately 1650 cm\(^{-1}\) and the broad peak at around 2100 cm\(^{-1}\) converge to the bulk spectrum, whereas the width of the \( \nu_C/\nu_b \) band is still smaller than in the bulk.

To get further insight into the hydration of CO\(_2^+\), we calculated various CO\(_2^+\)(H\(_2\)O)\(_n\) structures, \( n = 0–20 \), at the B3LYP/6–311 + + G** level of theory. In the CO\(_2^+\) ion, the calculations predict two features at 1193 and 1720 cm\(^{-1}\), assigned to the symmetric \( \nu_s \) and antisymmetric \( \nu_is \) stretching vibrations, respectively. The third CO\(_2^+\) vibration at 661 cm\(^{-1}\) corresponds to bending of the ion. Note that for gas-phase CO\(_2^+\), an additional structure with a more loosely bound electron was found, reflecting its metastability.[60] This structure is, however, not relevant here, as CO\(_2^+\) is readily stabilized by water molecules (see above).

For the hydrated species, three hydration motifs were considered: (i) structures with extensively hydrated CO\(_2^+\) created so as to maximize the number of CO\(_2^+\)--H\(_2\)O interactions, preferably including the C–H interaction (further denoted as "solvated"); (ii) structures with CO\(_2^+\) added on the surface of a compact water cluster ("surface"); (iii) clusters in which CO\(_2^+\) is built into the water cluster structure ("incorporated"), that is, with CO\(_2^+\) assuming at a position that would be otherwise reserved for water molecules in a neutral water cluster, without necessarily the C–H interaction present. The latter group can be expected to represent usually the lowest-energy structure at 0 K. Selected cluster sizes are shown in Figure 3, and all results for \( n = 0–20 \) are available in the Supporting Information (Figure SI-7).

Within experimental accuracy, the calculated position of the \( \nu_s \) vibration matches quantitatively with the measured one in the whole \( n = 2–20 \) range (Figure 2c). The "solvated" structures with more pronounced C–H\(_2\)O interaction seem to follow the experimental values more closely compared with the "incorporated" structures with CO\(_2^+\) positioned on the cluster surface (the difference is, however, within error limits). Within the precision of the computational method, mainly with respect to the accuracy of the DFT approach, it cannot be judged which cluster motif is preferred at a finite temperature. The \( \nu_s \) frequency for "surface" structures with CO\(_2^+\) attached to an already formed water cluster, on the other hand, lies outside the error limits of the experimental values. This is more pronounced when the CO\(_2^+\) is incorporated into the water cluster only by one oxygen atom (see clusters with \( n = 5, 7 \) in Figures 2c and 3). Therefore, we can conclude that the IR spectra document a strong interaction between CO\(_2^+\) and water. Note that CO\(_2^+\) is not fully solvated even for the largest cluster considered computationally (\( n = 20 \) owing to the insufficient size of the cluster. However, CO\(_2^+\) in the "solvated" isomer already interacts with a considerable number of water molecules.

The \( n = 2 \) feature at 1310 cm\(^{-1}\), if real, can be assigned to a combination band of the CO\(_2^+\) bending mode at 712 cm\(^{-1}\) with the water libration at 650 cm\(^{-1}\) for the "solvated" structure type. For \( n = 5 \), 7–10, the minority contribution to the symmetric stretching peak is assigned to a different isomer of the solvated type, and candidates for these isomers are present in the calculations. In line with this argument, the contribution is most pronounced for \( n = 9 \), where the calculated energy difference between the two lowest-lying isomers is only 1.1 kJ mol\(^{-1}\). For \( n = 6 \), the situation is different, the peak exhibits a shoulder on its blue end, and we could not find candidate isomers to explain this feature. As the lowest-lying structure is a relatively strained cube, we suggest that this particular geometry facilitates coupling of modes, for example, again the CO\(_2^+\) bending mode at around 700–730 cm\(^{-1}\) with the water librations below 700 cm\(^{-1}\).
To investigate the effect of the C–H₂O interaction on the vibrational frequency, we further optimized 27 different structures for the CO₂⁻(H₂O)ₙ cluster (sampled from a molecular dynamics run at 300 K starting from the lowest-energy structure in Figure 3). The C–H radial distribution function shows a low-intensity peak at about 2.1 Å, indicating a rather weak interaction, compared with 1.9 Å for the O–H radial distribution function (Figure S1-8 in the Supporting Information). More importantly, the optimized geometries show that the position of the ν₁ frequency (an average of 1273 cm⁻¹ with standard deviation of 13 cm⁻¹) is independent of the C–H distance in the respective local minimum (varying within 2.0–2.8 Å, see Figure S1-9 in the Supporting Information). A clear distinction of these two binding motifs cannot be obtained based on the position of the ν₁ band.

**Conclusion**

We have measured the IR spectra of CO₂⁻(H₂O)ₙ, n = 2–61, clusters trapped at a temperature of 80 K. We have shown that the symmetric stretch of the CO₂⁻ anion approaches the bulk value already for n = 20. Analysis of the antisymmetric stretch is hindered by its coupling with the water bending vibration. Its shift, however, seems to be limited within the measured range. The IR spectrum of CO₂⁻(H₂O)ₙ approaches the spectrum of CO₂⁻ in bulk aqueous solution. Quantum chemical calculations reproduce quantitatively the position of the symmetric CO₂⁻ vibration and suggest that the presence of the C–H interaction has a rather limited effect on the IR spectrum in the studied region.

**Experimental and Computational Methods**

The experiments were performed with a modified Bruker/Spectrospin CMS47X FT-ICR (ion cyclotron resonance) mass spectrometer described in detail elsewhere,[68–70] see also the Supporting Information for further details. Hydrated carbon dioxide radical anions CO₂⁻(H₂O)ₙ were generated in a laser vaporization source.[68–70] A gas mixture of helium with traces of CO₂ and water vapor was pulsed into the source region through a piezoelectric valve and expanded into the UHV region (p(UHV) < 3 × 10⁻¹⁰ mbar) of the instrument. The cell was cooled by liquid nitrogen to T ≈ 80 K to minimize blackbody infrared radiative dissociation (BIRD).[71,72] The beam of an EKSPLA NT273-XIR optical parametric oscillator laser system was coupled to the cell covering the 4500–12000 nm region (833–2222 cm⁻¹), linewidth < 1 cm⁻¹, 1000 Hz repetition rate, pulse duration < 10 ns). The wavelength was calibrated by a high-finesse Laser Spectrum Analyzer IR-III. Spectra are recorded by action spectroscopy, reaction (1).

\[ \text{CO}_2^- (\text{H}_2\text{O})_n + m \hbar \nu \rightarrow \text{CO}_2^- (\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} \quad (1) \]

The number of photons that are needed to evaporate a water molecule ranges from one to three, as discussed in the Supporting Information (Figure S1-10).[73,74] For the presentation of a realistic spectrum that accounts for laser energy and irradiation time, the single photon cross-section σ is calculated by a modified Lambert–Beer’s law:

\[ I_d = \left( \frac{t}{\tau} \right) e^{-\sigma \times \lambda} \quad (2) \]

where \( I_d \) is the intensity of the precursor, \( I_l \) is the intensity of the fragments, \( \lambda \) is the wavelength, \( P \) is the laser power, \( t \) is the irradiation time, \( h \) is the Planck constant, \( A \) is the area of the laser beam, and \( k \) is an empirical factor, which corrects for the contribution of BIRD and cell warming effects caused by the laser.

For optimization and harmonic frequency calculations, the B3LYP/6-311++G** method was used. The scaling factor of 0.977 was chosen as to match the experimental frequency of the symmetric CO₂⁻ stretch for n = 3. A molecular dynamics run was performed for CO₂⁻(H₂O)ₙ at a constant temperature of 300 K on the revPBE potential energy surface, employing the Nosé–Hoover thermostat and the time step of 0.5 fs, with the total running time of 15 ps. In total, 30 geometries were picked in the constant interval of 0.5 ps and optimized into 27 different structures. Room temperature, i.e. 300 K was chosen in the MD run to sample the potential energy surface efficiently. All geometry optimization were performed with the Gaussian suite of programs.[75] The MD simulation was performed with the Quickstep module of the CP2K suite of programs.[76] A triple-zeta Gaussian basis set augmented with diffuse functions plus the Goedecker–Teter–Hutter pseudopotential (with charge density cutoff of 280 Ry) for an auxiliary plane wave basis set (TZV2P-MOLOPT-GTH) were used. Dispersion interactions were corrected with the Grimme D3 method (with Becke–Johnson damping). The cluster ion was placed at the center of a simulation box with the parameters of 16 × 16 × 16 Å³, corrected with the Martyna and Tuckerman Poisson solver.

**Acknowledgments**

This work was supported by the Austrian Science Fund (FWF), project No. FP28896 & FP291740, within the DK-ALM W1259-N27, and the doctoral program Reactivity and Catalysis at Universität Innsbruck. The tunable OPO system is part of the Innsbruck Laser Core Facility, financed by the Austrian Federal Ministry of Science, Research and Economy. The computational results presented have been achieved by using the HPC infrastructure LEO of the University of Innsbruck and HPCC of City University of Hong Kong (CityU). Research Grants Council, Hong Kong SAR (RGC) (project no. 11300917) and CityU (project no. 7005101) are gratefully acknowledged. E.G.D. thanks RGC for the award of Hong Kong PhD Fellowship 2018/19.

**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** ab initio calculations · carbon dioxide radical anions · clusters · infrared spectroscopy · mass spectrometry