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# An infrared study of CO<sub>2</sub> activation by holmium ions, Ho<sup>+</sup> and HoO<sup>+</sup>†

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We report a combined experimental and computational study of carbon dioxide activation at gas-phase Ho<sup>+</sup> and HoO<sup>+</sup> centres. Infrared action spectra of Ho(CO<sub>2</sub>)<sub>n</sub><sup>+</sup> and [HoO(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> ion–molecule complexes have been recorded in the spectral region 1700–2400 cm<sup>-1</sup> and assigned by comparison with simulated spectra of energetically low-lying structures determined by density functional theory. Little by way of activation is observed in Ho(CO<sub>2</sub>)<sub>n</sub><sup>+</sup> complexes with CO<sub>2</sub> binding end-on to the Ho<sup>+</sup> ion. By contrast, all [HoO(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> complexes  $n \geq 3$  show unambiguous evidence for formation of a carbonate radical anion moiety, {CO<sub>3</sub><sup>•-</sup>}. The signature of this structure, a new vibrational band observed around 1840 cm<sup>-1</sup> for  $n = 3$ , continues to red-shift monotonically with each successive CO<sub>2</sub> ligand binding with net charge transfer from the ligand rather than the metal centre.

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## 1. Introduction

CO<sub>2</sub> is one of the most abundant greenhouse gases in the earth's atmosphere, and its capture, sequestration or chemical transformation into industrial feedstocks and fuel is a matter of great interest. Recent reviews have shown that both metal atoms<sup>1</sup> and extended metal surfaces<sup>2</sup> can activate molecular CO<sub>2</sub> effectively, the first mechanistic step in its transformation. Of particular interest to this study, Schwarz<sup>1</sup> has highlighted the crucial role that metal ions play in CO<sub>2</sub> reduction and the formation of new bonds involving carbon.

CO<sub>2</sub> has been shown to bind molecularly to charged metal species in at least four characteristic binding motifs: M( $\eta^1$ -OCO), M( $\eta^1$ -CO<sub>2</sub>), M[ $\eta^2$ -(C,O)O], and M[ $\eta^2$ -(O,O)C], representing varying degrees of molecular activation.<sup>3</sup> The natural limit of activation, dissociative binding (or insertion reaction), leads to formation of the metal oxide and a CO molecule.<sup>4–11</sup> Metal anions have a greater capability to activate and dissociate CO<sub>2</sub> compared with their cationic counterparts as they are able to donate electron density into the antibonding 2 $\pi_u^*$  LUMO of CO<sub>2</sub> molecules. This is reflected in the wider range of binding motifs for M<sup>-</sup>(CO<sub>2</sub>) species.<sup>12–22</sup> As well as activating and dissociating CO<sub>2</sub>, metal anions have been shown to promote dimerization of CO<sub>2</sub> forming

oxalate-like structures in which two of the CO<sub>2</sub> ligands form a single chelating ligand.<sup>18</sup> Size-selected metal clusters provide a way to tune the degree of activation with CO<sub>2</sub>. Only larger Co<sub>n</sub><sup>-</sup> ( $n > 8$ ) clusters bind CO<sub>2</sub> at all<sup>5</sup> whilst CO<sub>2</sub> binds molecularly to small Pt<sub>n</sub><sup>-</sup> clusters ( $n < 5$ ) but dissociatively on larger ones.<sup>6</sup>

Metal cations necessarily donate electron density less effectively than anions and M<sup>+</sup>(CO<sub>2</sub>) binding is usually M( $\eta^1$ -OCO),<sup>4,23–28</sup> dictated by the dominant charge–quadrupole interactions and  $\sigma$ -donation. The typical spectroscopic signature of such binding is a weak blue shift in the CO<sub>2</sub> asymmetric stretch around 2349 cm<sup>-1</sup>.<sup>29</sup> There are, however, notable exceptions to this  $\eta^1$  binding; Jiang and coworkers observed M[ $\eta^2$ -(C,O)O] motifs in M<sup>+</sup>(CO<sub>2</sub>)<sub>7</sub> complexes (where M = V, Cr and Mn) resulting from charge transfer from the additional ligands,<sup>26</sup> a phenomenon also observed in other systems, such as [MgCO<sub>2</sub>(H<sub>2</sub>O)<sub>n</sub>]<sup>+</sup> complexes.<sup>30</sup> In rare cases, metal cations have also been shown to lead to oxalate-type structures.<sup>7</sup> Room temperature reactivity experiments have shown that some early transition metal cations undergo direct O-atom transfer reactions with CO<sub>2</sub>.<sup>31</sup> CO<sub>2</sub> reacts with Ta<sup>+</sup> cations under single-collision conditions to form TaO<sup>+</sup> which can, in turn, react with a further CO<sub>2</sub> to produce TaO<sub>2</sub><sup>+</sup>.<sup>32</sup> Direct spectroscopic evidence of dissociatively bound CO<sub>2</sub> was observed in Ti<sup>+</sup>(CO<sub>2</sub>)<sub>n</sub> ( $n = 3–7$ ), V<sup>+</sup>(CO<sub>2</sub>)<sub>5</sub><sup>+</sup> and inferred on Ni<sup>+</sup>(CO<sub>2</sub>)<sub>n</sub><sup>+</sup> ( $n = 1–12$ ) complexes.<sup>7–10</sup> Little work has been performed on CO<sub>2</sub> reactivity with naked metal cluster cations although Ta<sub>n</sub><sup>+</sup> ( $n = 1–16$ ) clusters show size-selective reactivity towards CO<sub>2</sub>.<sup>11</sup>

Metal oxides can, in principle, provide the possibility for more interesting and extensive chemistry to occur. Duncan and co-workers have investigated structures of NiO<sub>2</sub>(CO<sub>2</sub>)<sub>n</sub><sup>+</sup>

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complexes and only found evidence of molecularly bound  $\text{CO}_2$  as did Lang and coworkers in  $\text{Mn}_x\text{O}_y(\text{CO}_2)_z^+$ .<sup>33</sup> We found similar binding in  $\text{TaO}_2(\text{CO}_2)_n^+$  and  $\text{NbO}_2(\text{CO}_2)_n^+$ .<sup>34</sup> Jiang and co-workers, however, found evidence for  $\{\text{CO}_3\}$  moiety formation in infrared studies of  $\text{YO}(\text{CO}_2)_n^+$  ( $n \geq 4$ ) complexes.<sup>35</sup>

Here we report an infrared photodissociation (IR-PD) study of gas-phase  $\text{Ho}(\text{CO}_2)_n^+$  and  $\text{HoO}(\text{CO}_2)_n^+$  ion-molecule complexes in order to elucidate the binding behaviour of  $\text{CO}_2$  to  $\text{Ho}^+$  and  $\text{HoO}^+$  ions. Like most lanthanide metals, holmium typically adopts a +3 oxidation state in solution, the result of (relatively) facile removal of electrons from outer orbitals and larger enthalpies of hydration of higher charge states. Based on their ability to stabilize higher oxidation states,  $\text{Ho}^+$  cations were selected for this work in order to investigate whether they might activate  $\text{CO}_2$  more effectively than transition metal cations.

## 2. Experimental/computational methods

The bespoke instrument used for these experiments has been described in detail previously<sup>25,36–38</sup> and only essential details are given here. Two conceptually different experiments have been performed and the differences are illustrated in Fig. 1. The laser ablation source, Fig. 1a is common to both experiments and is a variation of the cutaway source of Duncan and co-workers.<sup>39</sup>  $\text{Ho}(\text{CO}_2)_n^+$  and  $[\text{HoO}_m(\text{CO}_2)_n]^+$  ion-molecule complexes are produced by pulsed laser ablation of a rotating holmium disc in the presence of Ar carrier gas seeded with 0.75–5%  $\text{CO}_2$ . Varying partial pressures and backing pressures provides some control over the size distribution of ion-molecule complexes produced. Ablation is performed in the throat of a supersonic expansion designed to arrest metal cluster formation and promote the formation of metal ion-ligand complexes entrained within a molecular beam.

Fig. 2 shows a typical time-of-flight mass spectrum of the species generated in the source. The distribution is dominated by the target  $\text{Ho}(\text{CO}_2)_n^+$  and  $[\text{HoO}_m(\text{CO}_2)_n]^+$  complexes and their Ar-tagged equivalents. Here, we employ square brackets,  $[\text{X}]$ , to

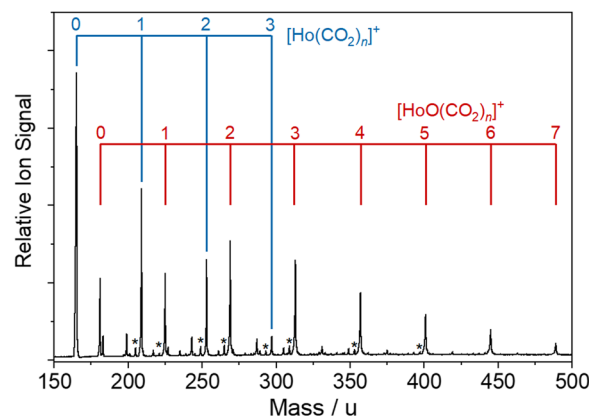
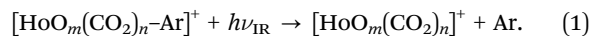


Fig. 2 Representative time-of-flight mass spectrum obtained following the laser ablation of a Ho target in the presence of a backing gas mixture of ca. 2.5%  $\text{CO}_2$  in Ar.  $\text{Ho}(\text{CO}_2)_n^+$  and  $[\text{HoO}(\text{CO}_2)_n]^+$  complexes are formed in high number density, together with Ar-tagged species (marked with asterisks). Other, unmarked peaks result from background  $\text{H}_2\text{O}$  adsorption to the clusters.

indicate complexes for which different chemical structures are plausible. The  $\text{Ho}(\text{CO}_2)_n^+$  complex signal falls rapidly with increasing  $n$  with little signal apparent by  $n > 4$ . By contrast, strong  $[\text{HoO}(\text{CO}_2)_n]^+$  signals are observed well beyond  $n = 15$ . The holmium target, as with many metals, contains enough surface oxide to generate the oxide complexes without any additional oxidant though we cannot rule out the possibility that  $\text{Ho}^+$  ions and/or small  $\text{Ho}(\text{CO}_2)_n^+$  complexes react with the  $\text{CO}_2$  itself to generate the  $\text{HoO}^+$  species.

Two variants of infrared dissociation experiments have been performed. Employing the in-line arrangement in Fig. 1c, target complexes are Ar-tagged, permitting the IR-PD spectra of a wide range of complexes to be recorded simultaneously in depletion of the parent  $[\text{HoO}_m(\text{CO}_2)_n\text{-Ar}]^+$  signal:<sup>25,34</sup>



In what follows, such spectra, recorded in depletion mode, are denoted  $[-\text{Ar}]$  and shown as blue data points. These spectra

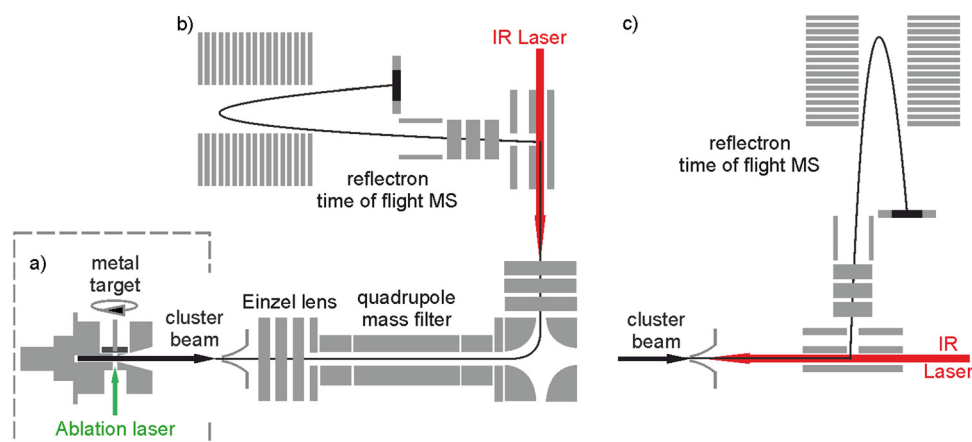


Fig. 1 Schematic of the instruments used for infrared action spectroscopy of  $[\text{HoO}_m(\text{CO}_2)_n]^+$  complexes. The cutaway source, (a), is common to both experiments. In variant (b) a quadrupole mass filter–bender assembly (Extrel) provides parent ion mass selection. In (c) IR-induced depletion of a wide range of Ar-tagged complexes is recorded simultaneously. In both cases infrared excitation occurs before detection.

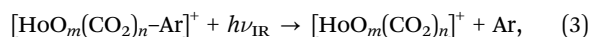


have been normalised to the largest fractional depletion signal in the spectrum.

We have recently added the ability to mass select the parent ion with the addition of a quadrupole mass filter as shown in Fig. 1b.<sup>36</sup> This configuration has been used to record spectra for mass-selected ion–molecule complexes individually *via* loss of either a CO<sub>2</sub> ligand or an Ar messenger depending on complex size:



or



spectra for which are labelled  $-\text{CO}_2$  (red data points) or  $-\text{Ar}$  (green), respectively. The advantage provided by parent ion mass-selection is that spectra can be recorded in enhancement in the daughter fragment mass channel. Since, this is a zero background these spectra have superior signal-to-noise. In all experiments, ions are extracted orthogonally into a reflectron time-of-flight mass spectrometer to be detected.

Tunable infrared radiation between 1650 and 2450 cm<sup>-1</sup> is provided by a pulsed optical parametric oscillator/optical parametric amplifier (OPO/OPA, LaserVision, employing an AgGaSe<sub>2</sub> crystal). Infrared action spectra are recorded either in parent ion depletion or daughter ion enhancement by comparing mass spectra recorded with and without infrared excitation as a function of infrared wavenumber. The data reported as cross-sections,  $\sigma$  where

$$\sigma = \frac{1}{\Phi} \ln \left( 1 - \frac{N_f}{\alpha N_0} \right), \quad (4)$$

in which  $N_f$  is the daughter ion signal,  $N_0$  is the parent ion signal in the absence of excitation,  $\alpha$  is a measure of the overlap between laser and cluster beams (assumed to be 1) and  $\Phi$  is the IR photon flux. For ease of comparison we report these as normalised to the strongest spectral band observed.

Ar-tag depletion experiments (process (1)) provide an effective way to record a consistent series of spectra for all complexes simultaneously. However, the signal-to-noise ratio of such spectra is often poor. Spectra recorded in fragment ion channels, processes (2) and (3), have better signal to noise provided a single photon is sufficient to cause ligand loss – usually the case for all but the very smallest complexes.

In order to aid the interpretation of the infrared spectra obtained, energetically low-lying structural isomers have been calculated using density functional theory (DFT) using the Gaussian 16 program<sup>40</sup> in combination with a modified Kick3 algorithm.<sup>41,42</sup> The UB3P86/Def2-TZVP functional/basis set was used.<sup>43,44</sup> Other basis set and functional combinations were tested but minimal differences were found except for the relative energy ordering of some low-lying isomers and predicted vibrational band positions. Our interest here lies in better understanding the vibrational spectra recorded and thus we focus on the geometrical structures. We have not undertaken full spin-orbit calculations and structures are labelled according to their spin quantum number within a Russell–Saunders

coupling scheme. Calculated vibrational frequencies have been scaled by a factor of 0.96 to better match with experiment, this number determined from the ratio of the experimental CO<sub>2</sub> asymmetric stretch fundamental band at 2349 cm<sup>-1</sup>,<sup>29</sup> and that calculated, 2441 cm<sup>-1</sup>. Line spectra have been convoluted with a Lorentzian function with a full width at half-maximum (FWHM) of 8 cm<sup>-1</sup> to aid comparison with experimental spectra.

## 3. Results and discussion

### 3.1 Ho(CO<sub>2</sub>)<sub>n</sub><sup>+</sup> infrared spectra

Fig. 3 shows the infrared action spectra for Ho(CO<sub>2</sub>)<sub>n</sub><sup>+</sup> complexes. In all cases, only a single feature is observed, between 2350 and 2400 cm<sup>-1</sup>, close to the  $\nu_3$  fundamental in free CO<sub>2</sub> and indicative of essentially unperturbed CO<sub>2</sub> molecules bound in an M( $\eta^1$ -OCO) fashion.<sup>4,23–28</sup> As well as being slightly more blue-shifted (by *ca.* 20 cm<sup>-1</sup>), the spectral features recorded in the  $[-\text{Ar}]$  depletion channel (blue data points, right hand panel) are markedly narrower than the same bands recorded in the  $-\text{CO}_2$  channel (red points, left hand panel). This is commonly observed, has been discussed by the Duncan group,<sup>45</sup> and likely results from a combination of the fact that: (i) fewer IR photons are required to remove the weakly-bound Ar atom than a CO<sub>2</sub> ligand and (ii) that the process of Ar-tagging preferentially selects the cooler complexes. The DFT simulations do not fully recover the blue-shift induced by the Ar tag and the structures with and without tags are essentially identical (see ESI†). It is interesting that the same band red-shifts slightly with increasing  $n$  in the spectra of the Ar-tagged species, while in the non-tagged

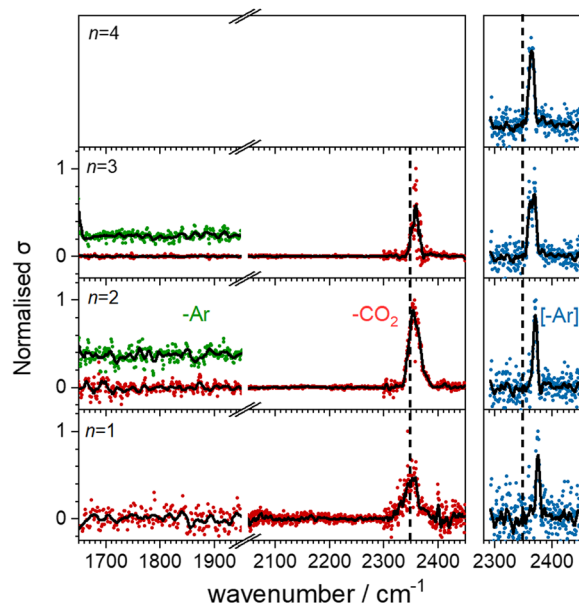


Fig. 3 Infrared action spectra of Ho(CO<sub>2</sub>)<sub>n</sub><sup>+</sup> ( $n = 1-4$ ) complexes with and without Ar-tagging. Spectra were recorded in the daughter fragment channels of Ho(CO<sub>2</sub>)<sub>n</sub><sup>+</sup> ( $n = 1-3$ , red data points) and Ho(CO<sub>2</sub>)<sub>n</sub><sup>+</sup>-Ar ( $n = 2-3$ , green) as well as the parent ion depletion of Ho(CO<sub>2</sub>)<sub>n</sub><sup>+</sup>-Ar ( $n = 1-4$ , blue, right panel). The vertical dashed line indicates the  $\nu_3$  band of free CO<sub>2</sub> at 2349 cm<sup>-1</sup>.



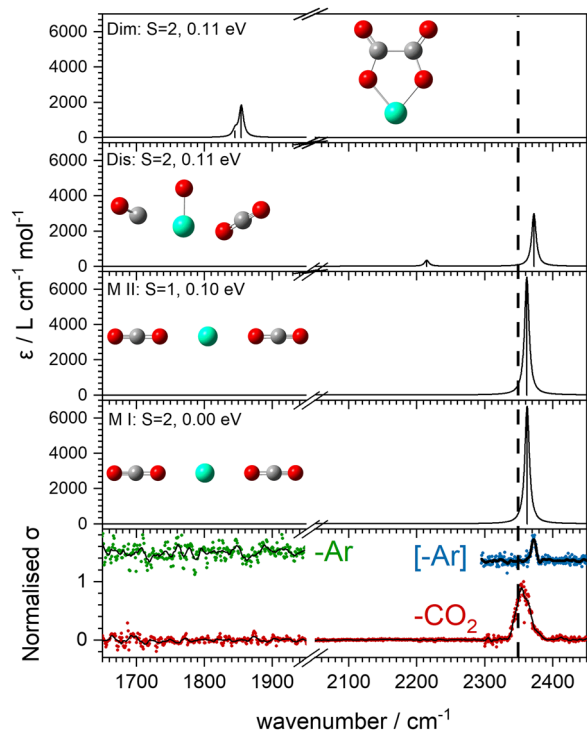


Fig. 4 Comparison of experimental and simulated spectra of energetically low-lying structures (UB3P86/Def2-TZVP) for  $\text{Ho}(\text{CO}_2)_2^+$ . The vertical dashed line indicates the asymmetric stretch ( $\nu_3$ ) fundamental of free  $\text{CO}_2$  at  $2349 \text{ cm}^{-1}$ . Ho blue, C grey, O red.

complexes, the band instead shifts *ca.*  $7 \text{ cm}^{-1}$  to the blue between  $n = 1$  and 3.

Our search of the potential energy surfaces reveals different distinct binding motifs with characteristic vibrational spectra with which to compare the experimental spectra. For example, Fig. 4 shows several structures identified for the  $\text{Ho}(\text{CO}_2)_2^+$  complex. The global minimum structure, MI, is a quintet spin state, linear, ( $D_{\infty h}$ ) structure with one strong infrared allowed band. A similar triplet state structure lies 0.1 eV higher in energy. Two additional quintet structures, Dis and Dim, lie 0.11 eV higher in energy but no experimental evidence for either of these structures is obtained. Instead, the single spectral feature, near  $2350 \text{ cm}^{-1}$ , is assigned to structure, MI. Substantial rearrangements and/or bond breaking would be required to form structures Dim and Dis and it is likely that formation of these is kinetically hindered.

Comparisons of experimental and simulated comparisons for other complex sizes are available in the ESI.† It is clear that  $\text{CO}_2$  only binds to the bare  $\text{Ho}^+$  ion in a simple  $\text{M}(\eta^1\text{-OCO})$  fashion for  $n = 1\text{--}4$  consistent with many transition metal cations investigated previously.<sup>4,23–28</sup> This simple electrostatic binding with negligible back donation from the cation accounts for the lack of  $\text{CO}_2$  activation.

### 3.2 $\text{HoO}(\text{CO}_2)_n^+$ infrared spectra

Fig. 5 shows the experimental infrared spectra of  $\text{HoO}(\text{CO}_2)_n^+$  ( $n = 1\text{--}11$ ) with and without Ar tagging in the  $1650\text{--}1950 \text{ cm}^{-1}$

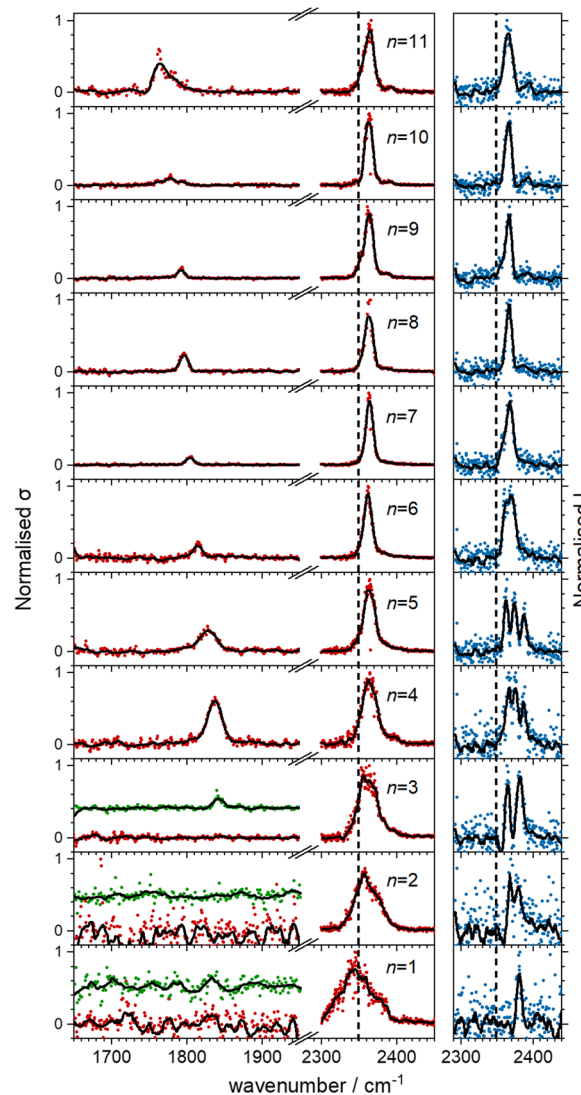


Fig. 5 Infrared action spectra of  $[\text{HoO}(\text{CO}_2)_n]^+$  complexes. The spectra were recorded in the  $-\text{CO}_2$  and  $-\text{Ar}$  daughter fragment channels of  $[\text{HoO}(\text{CO}_2)_n]^+$  ( $n = 1\text{--}11$ , red) and  $[\text{HoO}(\text{CO}_2)_n^+ - \text{Ar}]$  ( $n = 1\text{--}3$ , green), respectively (left hand panel) as well as the depletion of  $[\text{HoO}(\text{CO}_2)_n^+ - \text{Ar}]$  ( $n = 1\text{--}11$ , blue), right hand panel. The vertical dashed lines indicates the fundamental ( $\nu_3$ ) band in free  $\text{CO}_2$  at  $2349 \text{ cm}^{-1}$ .

and  $2300\text{--}2450 \text{ cm}^{-1}$  regions. The signal to noise is poor in the  $n = 1, 2$  spectra as only weak fragmentation is observed which may arise from multiple photon processes. It is an artefact of normalising spectra to the strongest spectral feature even when it is weak, that results in poor spectra in the lower wavenumber region.

By contrast with the spectra of the  $\text{Ho}(\text{CO}_2)_n^+$  complexes, most  $[\text{HoO}(\text{CO}_2)_n]^+$  spectra exhibit two spectral features. All spectra exhibit features in the region of the  $\text{CO}_2$  asymmetric stretch ( $2350\text{--}2400 \text{ cm}^{-1}$ ) which are assigned to simple molecular  $\text{M}(\eta^1\text{-OCO})$  binding. The better resolved spectra recorded in the  $[-\text{Ar}]$  depletion channel (right hand panel, Fig. 5) exhibit clear spectral structure for  $n = 2\text{--}6$  and, as for the  $\text{Ho}(\text{CO}_2)_n^+$  spectra, these Ar-tagged peaks are blue shifted by around  $10\text{--}15 \text{ cm}^{-1}$ . For  $n \geq 4$  complexes, additional features are observed



in the 1850–1760  $\text{cm}^{-1}$  in the  $\text{CO}_2$  loss channel of mass-selected complexes. This same feature is also observed in the Ar loss channel for  $\text{HoO}(\text{CO}_2)_3\text{-Ar}^+$ . Jiang and coworkers assigned similar features in the spectrum of  $\text{YO}(\text{CO}_2)_n^+$  complexes, to a C–O stretch in a  $\{\text{CO}_3\}^{\delta-}$  moiety bound in a  $\text{M}(\eta^2\text{-O},\text{O}(\text{CO}))$  fashion<sup>35</sup> and we have investigated the possibility of this type of structure in our  $[\text{HoO}(\text{CO}_2)_n]^+$  complexes.

The computational potential energy surface search reveals two distinct structural motifs for each cluster size, the relative energies of which are shown in Fig. 6 for the  $[\text{HoO}(\text{CO}_2)_n]^+$  ( $n=1-4$ ) complexes. For each complex an energetically low-lying  $\text{Ho}(\text{CO}_3)(\text{CO}_2)_{n-1}^+$  type structure is calculated. These are labelled C isomers, in which C represents the presence of a carbonate radical anion like moiety  $\{\text{CO}_3^{\delta-}\}$ . In these structures one  $\text{CO}_2$  molecule reacts with the  $\text{HoO}^+$  forming a  $\text{C}_{2v}$   $\text{Ho}(\text{CO}_3)^+$  substructure in which two O-atoms bind to the metal ion ( $\text{M}(\eta^2\text{-O},\text{O}(\text{CO}))$ ) as observed by Jiang and co-workers in the  $\text{YO}^+$  analogues. Zhao *et al.* labelled this a “carbonate structure” but, according to our calculations, the charge on the  $\{\text{CO}_3\}$  group never exceeds  $-1$  so we prefer a “carbonate radical anion” description. Our calculations predict this structure to be the lowest energy isomer for all  $n > 1$ . This  $\text{Ho}(\text{CO}_3)^+$  forms a core structure to which we calculate additional  $\text{CO}_2$  molecules bind at the  $\text{Ho}^+$  centre in a  $\text{M}(\eta^1\text{-OCO})$  configuration.

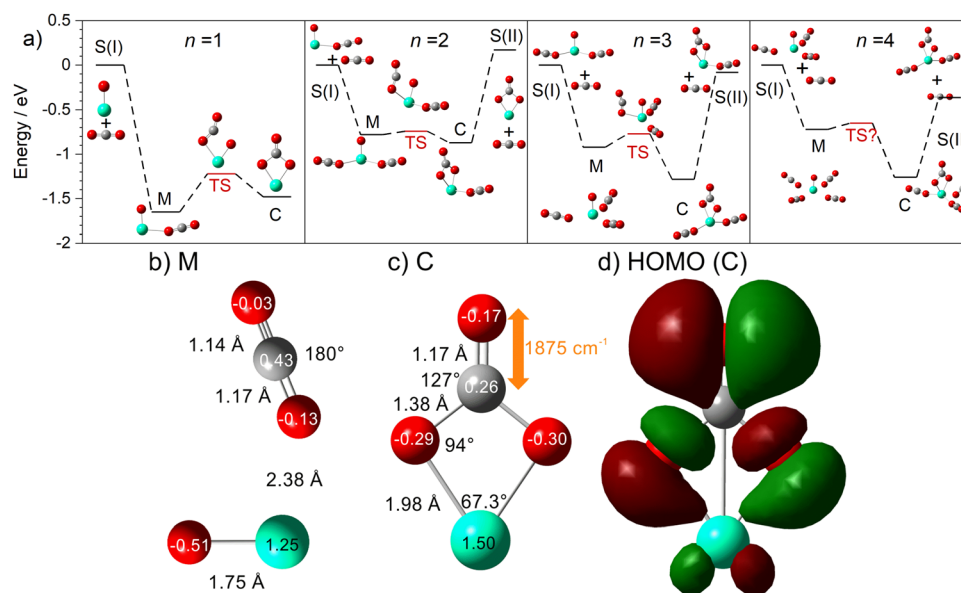
The second type of structure found is a conventional  $\text{HoO}(\text{CO}_2)_n^+$  type structure in which all  $\text{CO}_2$  molecules are molecularly-bound to the Ho end of  $\text{HoO}^+$  in  $\text{M}(\eta^1\text{-OCO})$  fashion. These structures (M isomers) exhibit spectral bands only in the 2350–2400  $\text{cm}^{-1}$  region.

In all  $[\text{HoO}(\text{CO}_2)_n]^+$  ( $n=1-4$ ) complexes, both M and C isomers are strongly bound, by 0.9–1.5 eV, relative to their

respective dissociation limits. In  $n=1$ , the molecularly bound isomer, M, is found to be more stable than the carbonate radical anion, C form whereas for  $n=2$ , both structures are found to be essentially isoenergetic. For all complexes  $n > 2$ , the C isomer is markedly lower in energy than the M isomer making the presence of the  $\text{Ho}(\text{CO}_3)^+$  moiety the likely dominant structural motif.

We have identified plausible barriers to the  $\text{M} \leftrightarrow \text{C}$  interconversion in the case of  $n=1-3$ . According to Jiang,<sup>35</sup> the formation of  $\{\text{CO}_3^{\delta-}\}$  proceeds *via* a 2 + 2 cycloaddition transition state from the molecularly-bound form. This requires a nucleophilic attack upon the carbon atom in  $\text{CO}_2$  by the electron-rich oxygen in  $\text{HoO}^+$ . The transition state energy is stabilized (relative to the M isomer minimum) with increasing complex size, as the charge donated by each successive  $\text{CO}_2$  ligand is localised on the oxide, but in all cases remains submerged below any relevant dissociation threshold. We have little direct information on the internal energy distribution of our complexes but, due to the nature of the molecular beam expansion, it is not uncommon for us to see entrance channel complexes trapped behind submerged barriers on potential energy surface.

The calculated structures and charge distributions of both  $n=1$  isomers are shown in Fig. 6(b and c) and for larger complexes in the ESI.† For the  $n=1$  C isomer, significant charge is donated from the Ho atom (leaving it +1.50 e, compared with +1.41 e in the  $\text{HoO}^+$  ion) to the  $\text{CO}_3$  moiety. The terminal C=O bond length, at 1.17 Å, is almost unchanged from free  $\text{CO}_2$  but the other two C–O bonds are markedly elongated at 1.38 Å reflecting significant activation. In the M isomer the  $\text{CO}_2$  ligand donates electron density, reducing the



**Fig. 6** (a) Potential energy surfaces for  $\text{HoO}(\text{CO}_2)_n^+$  ( $n=1-4$ ) generated at the UB3P86/Def2-TZVP level of theory showing the relative energies of  $\text{Ho}(\text{CO}_3)(\text{CO}_2)_{n-1}^+$  (labelled C-isomers) and  $\text{HoO}(\text{CO}_2)_n^+$  (M-isomer) structures. The surfaces show the transformation between species. S(i) represents the  $\text{HoO}(\text{CO}_2)_{n-1}^+$  isomer and free  $\text{CO}_2$  and S(ii) represents the  $\text{Ho}(\text{CO}_3)(\text{CO}_2)_{n-2}^+$  isomer with free  $\text{CO}_2$ . (b and c) structural details and (Hirshfeld) partial charges of the M and C isomers, respectively for the  $n=1$  case and (d) the C isomer HOMO.



Ho partial charge slightly to +1.25 e but with minimal effect on structure of the CO<sub>2</sub> moiety.

These potential energy surface calculations account qualitatively for the observations in Fig. 5. The lower wavenumber band, assigned to the C isomers appears persistently from  $n = 3$  onwards by which stage the C isomer is calculated to lie significantly lower in energy than the M isomer. For the  $n = 3$  complex itself, the band is clearly observed but only in -Ar loss from the tagged species, presumably because the CO<sub>2</sub> binding energy exceeds the single photon energy. For similar reasons, we cannot exclude the presence of the carbonate radical anion for  $n = 1, 2$  but there is no direct spectroscopic evidence for it.

It is noteworthy that CO<sub>2</sub> loss is the only fragmentation channel observed in the untagged species. At no point was loss of CO<sub>3</sub> observed for any species, this threshold lying at considerably higher energy.

In the CO<sub>2</sub> loss spectra in Fig. 5 (red data points) the main bands around 2350 cm<sup>-1</sup> narrows considerably between  $n = 1$  and  $n = 4$ . The smaller complexes have higher ligand binding energies reflecting direct binding to the metal centre in the inner coordination shell. As a result more infrared photons are required to cause fragmentation. Beyond  $n = 4$ , CO<sub>2</sub> molecules bind more weakly in a second solvation shell (see structures in the ESI†) and single photon absorption leads to facile ligand loss.

With this qualitative understanding of the action spectra on the basis of expected structures, Fig. 7 shows a comparison of experimental and simulated spectra for the [HoO(CO<sub>2</sub>)<sub>n</sub>]<sup>+</sup> ( $n = 2-4$ ) complexes based on the M and C isomers predicted. The main 2330–2380 cm<sup>-1</sup> band is of limited use in identifying the structure as almost all calculated isomeric forms contain one or more molecularly-bound CO<sub>2</sub> with  $\nu_3$  fundamental band in this region (M( $\eta^1$ -OCO)). By contrast, the band between 1850 and 1900 cm<sup>-1</sup> is a clear and unambiguous signature of the C isomer in each case and is clearly visible in the spectra of the  $n = 3, 4$  complexes. This spectral band arises from the unique C=O stretch in {CO<sub>3</sub><sup>δ-</sup>} as shown by the vectors in Fig. 6c. As seen in Fig. 5, this band red shifts approximately linearly with increasing complex size from 1840 cm<sup>-1</sup> ( $n = 3$  complex) to 1760 cm<sup>-1</sup> by  $n = 11$  (see Fig. 8).

It is tempting to interpret two partially resolved peaks in the [-Ar] depletion spectrum (blue data points) of the [HoO(CO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complex (at 2367 and 2378 cm<sup>-1</sup>, bottom panel, Fig. 7a) as the two components of the CO<sub>2</sub> stretches in the M isomer (at 0.09 eV). This would be consistent with the absence of any band to the red, even in the -Ar loss daughter channel despite the calculated Ar binding of only 0.23 eV. It is dangerous, however, to draw conclusions from the absence of a band and we cannot rule out the possibility of both M and C isomers being present in the beam.

The -Ar loss spectrum (in green) of the tagged HoO(CO<sub>2</sub>)<sub>3</sub><sup>+</sup> complex (Fig. 7b) provides the first unambiguous evidence for the presence of the {CO<sub>3</sub>} moiety, its presence reproduced well in the simulated spectrum of the putative global minimum structure around 1850 cm<sup>-1</sup>. The calculated Ar binding energy to this complex is only 0.12 eV making it an ideal tag. Similarly, the two resolved features in the Ar depletion spectrum (blue) at

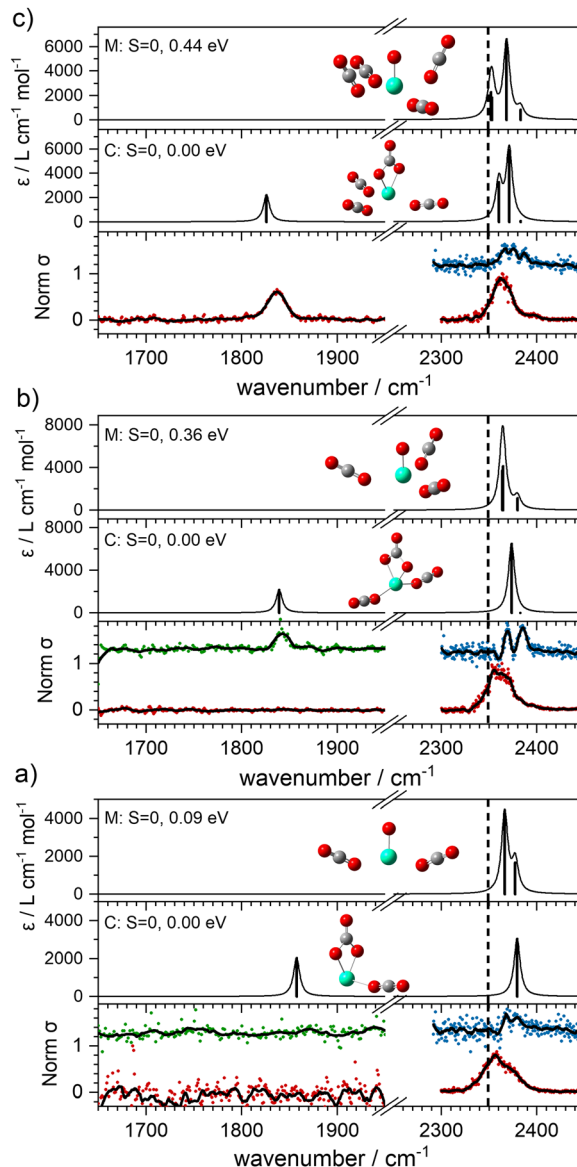


Fig. 7 Comparisons between simulated (UB3P86/Def2-TZVP) experimental spectra of HoO(CO<sub>2</sub>)<sub>n</sub><sup>+</sup> ( $n = 2-4$ , (a)–(c), respectively). Red (green) data points represent spectra recorded in -CO<sub>2</sub> (-Ar) daughter channels, respectively. Blue data was recorded in [-Ar] depletion. The dashed line indicates the vibrational frequency of the asymmetric stretch ( $\nu_3$ ) of free CO<sub>2</sub> at 2349 cm<sup>-1</sup>.

2364 cm<sup>-1</sup> and 2382 cm<sup>-1</sup> can be interpreted as a combination of both the M and C isomers with the latter not observed in the -CO<sub>2</sub> daughter channel due to the higher CO<sub>2</sub> binding energy (see Fig. 6). The signature of the {CO<sub>3</sub>} moiety is observed in the spectrum of all complexes  $n \geq 4$ , though this doesn't mean the presence of the M isomer can be ruled out. Several complexes (notably  $n = 4, 5, 6$ ) exhibit detailed structure in the [-Ar] depletion spectra around the CO<sub>2</sub>  $\nu_3$  fundamental which could be interpreted as indicating the presence of multiple isomers and we have often seen such examples in our ablation source. Equally this structure could indicate different Ar binding sites and/or a reduction in symmetry. For complexes  $n \geq 7$ , only one,



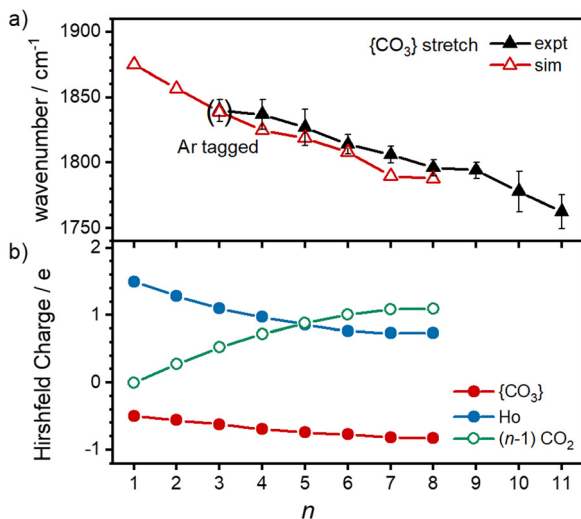


Fig. 8 (a) Observed and calculated wavenumber of the C=O stretch in the {CO<sub>3</sub>} moiety of C-isomers as a function of complex size. Uncertainties represent the half-width at half maximum of the experimental peaks. (b) Trends in the Hirshfeld charges on the {CO<sub>3</sub>} moiety (red), Ho atom (blue, solid) and the CO<sub>2</sub> ligands (green, open circles) with increasing complex size.

narrow feature is seen in the [-Ar] depletion spectra suggesting a dominance of a single isomeric form.

The characteristic {CO<sub>3</sub>} stretch red-shifts as additional CO<sub>2</sub> ligands bind (Fig. 5 and 8). Rather than reflecting increasing donation from the holmium atom, calculations show that this instead arises from increasing  $\sigma$ -donation from successive CO<sub>2</sub> ligand addition. This serves to further activate the terminal C=O bond, reduce the net charge on the Ho atom from 1.7 e ( $n = 1$ ) to +1.3 e ( $n = 8$ ) and reduce the barrier to M  $\leftrightarrow$  C isomer interconversion.

## 4. Conclusions

Infrared action spectra of CO<sub>2</sub> binding to gas-phase Ho<sup>+</sup> ions reveals weak interactions with minimal perturbation of the CO<sub>2</sub> structure consistent with previous studies of CO<sub>2</sub> binding to atomic cations. Each CO<sub>2</sub> ligand undergoes  $\sigma$  donation towards the Ho<sup>+</sup> ion making subsequent CO<sub>2</sub> coordination weaker and no complexes beyond  $n = 4$  were observed for Ho(CO<sub>2</sub>) <sub>$n$</sub> <sup>+</sup>. CO<sub>2</sub> binds to HoO<sup>+</sup> both molecularly and forms a radical carbonate anion structure the latter being the more stable form for [HoO(CO<sub>2</sub>) <sub>$n$</sub> ]<sup>+</sup> ( $n \geq 2$ ). The  $\sigma$  donation from the CO<sub>2</sub> ligands results in electron density being localised on the oxygen atom rather than the Ho<sup>+</sup> making it susceptible to attack *via* the electrophilic carbon in the CO<sub>2</sub> ligands forming {CO<sub>3</sub> <sup>$\delta$ -</sup>}<sub>3</sub>. This structural motif is clearly identifiable by its signature C=O stretch between 1750 and 1850 cm<sup>-1</sup> depending on the number of ligands attached. Each successive CO<sub>2</sub> ligand donates additional charge which ends up localised in this moiety activating the terminal C=O. In this sense, the degree of activation is controllable and in this regard [HoO(CO<sub>2</sub>) <sub>$n$</sub> ]<sup>+</sup> complexes behave very similarly to the YO(CO<sub>2</sub>) <sub>$n$</sub> <sup>+</sup> complexes reported by Jiang and coworkers.<sup>35</sup>

## Conflicts of interest

There are no conflicts to declare.

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