Infrared spectroscopy of Mg–CO₂ and Al–CO₂ complexes in helium nanodroplets

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The catalytic reduction of CO₂ to produce hydrocarbon fuels is a topic that has gained significant attention. Development of efficient catalysts is a key enabler to such approaches, and metal-based catalysts have shown promise towards this goal. The development of a fundamental understanding of the interactions between CO₂ molecules and metal atoms is expected to offer insight into the chemistry that occurs at the active site of such catalysts. In the current study, we utilize helium droplet methods to assemble complexes composed of a CO₂ molecule and a Mg or Al atom. High-resolution infrared (IR) spectroscopy and optically selected mass spectrometry are used to probe the structure and binding of the complexes, and the experimental observations are compared with theoretical results determined from *ab initio* calculations. In both the Mg–CO₂ and Al–CO₂ systems, two IR bands are obtained: one assigned to a linear isomer and the other assigned to a T-shaped isomer. In the case of the Mg–CO₂ complexes, the vibrational frequencies and rotational constants associated with the two isomers are in good agreement with theoretical values. In the case of the Al–CO₂ complexes, the vibrational frequencies agree with theoretical predictions; however, the bands from both structural isomers exhibit significant homogeneous broadening sufficient to completely obscure the rotational structure of the bands. The broadening is consistent with an upper state lifetime of 2.7 ps for the linear isomer and 1.8 ps for the T-shaped isomer. The short lifetime is tentatively attributed to a prompt photo-induced chemical reaction between the CO₂ molecule and the Al atom comprising the complex. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4919693>]

INTRODUCTION

Currently, interest on the topic of catalytic CO₂ reduction for useful organic compound production is intense. The two most commonly discussed strategies are to reduce CO₂ to usable fuels or to produce compounds that can be converted into fuels through processes that are industrially feasible.^{1–6} The development of efficient catalysts is a key enabler to such technologies, and research in this area is ongoing. Many of the catalysts currently under consideration are metal-doped,^{5,7} with the choice of metal dopant playing a key role in the effectiveness of the resulting catalyst.⁸ Consequently, it is important to understand the chemistry of such materials in detail, with the interactions between active sites and adsorbed CO₂ molecules being of particular interest.⁹

The development of a bottom-up understanding entails a detailed examination of the interactions between an adsorbed molecule and the metal atoms and/or other species composing the active site of a catalyst. Metal cluster investigations, both experimental^{10,11} and theoretical,^{12,13} have repeatedly shown that size can have a profound effect on the chemical and electronic properties of metal clusters. Similarly, size has been

shown to strongly influence the activity and selectivity of active sites,¹⁴ and the addition or subtraction of a single metal atom can often determine whether or not a site is catalytically active. Consequently, it is highly desirable to study how the interactions between the molecules of interest and the metal centers evolve as a function of both the identity of the metal and the size of the metal cluster.

To probe the interactions with adsorbed molecules, vibrational spectroscopy can be particularly informative since the vibrational frequencies associated with the molecule are strongly dependent on the nature of the interaction between the molecule and surface site. Use of techniques such as high-resolution electron energy loss spectroscopy (HREELS) and reflectance-absorbance infrared spectroscopy (RAIRS) to examine surface-bound species is understandably widespread. For the same reasons, high resolution vibrational spectroscopy is often used to examine the interactions in complexes incorporating metal atoms or metal ions^{15–20} and prototype adsorbate molecules. Additionally, complexes of this nature have also been studied theoretically.^{21,22}

In the current investigation, we focus on the assembly and study of complexes between a CO₂ molecule and a single metal atom, in this case either Mg or Al. These two metals represent very different levels of reactivity with respect to many molecules, including CO₂. Magnesium atoms, due to their [Ne]3s²

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electron configuration, have no unpaired electrons and are relatively unreactive, particularly at low temperature. Stable van der Waals (vdW) complexes of Mg atoms with HCN,^{23,24} HCCN,²⁵ HF,²⁶ and HCCH²⁷ have all been previously assembled inside helium droplets at 0.37 K and studied via high resolution infrared (IR) spectroscopy. Theoretical studies of the Mg–CO₂ system have identified a T-shaped vdW complex, along with a MgCO₂ adduct that can be endothermically formed.²⁸ The barrier associated with the reaction is calculated to be ~0.7 eV. Signals attributed to Mg–CO₂ complexes have been observed in matrix isolation experiments,²⁹ but the adduct has not to our knowledge been experimentally observed.

Aluminum, on the other hand, is much more reactive on account of the unpaired electron arising from its [Ne]3s²3p¹ electron configuration. Consequently, the interactions between an Al atom and its complexation partners have been somewhat more varied in nature. The Al–HF, Al–HCN, and Al–CO systems have been previously studied in helium droplets. The results of the Al–HF study³⁰ suggested that an Al atom reacts with HF even at the low temperature of the droplet³¹ (0.37 K). Investigations of complexes involving Al and HCN revealed unreacted Al–HCN complexes, while the HCN–Al structure was found to spontaneously react to form an adduct rather than to assemble a vdW complex.^{32,33} The Al–CO system has also exhibited very interesting behavior.³⁴ Complexes containing an Al atom with up to five CO molecules were assembled and studied, and a photo-induced reaction was observed for the complex containing two CO molecules.

Several groups have previously studied the Al–CO₂ interaction. One study indicated that an AlCO₂ adduct is an important intermediate in the Al + CO₂ → AlO + CO reaction and measured both the reaction barrier and exothermicity associated with formation of the adduct to be in excess of 350 cm^{−1}

and 3150 cm^{−1}, respectively.³⁵ On the other hand, we note that a photoionization investigation of Al–(CO₂)_n clusters found reaction to be spontaneous for $n \geq 5$.³⁶ Another study utilized co-deposition of Al and CO₂ in an argon matrix.³⁷ Unreacted Al–CO₂ complexes were not observed; however, two adduct structures were identified: an OCO–Al species with the Al atom bound to one of the O atoms at low temperature and a cyclic structure with the Al atom bound equally to both O atoms at higher temperature.

The goal of the current investigation is to study Mg–CO₂ and Al–CO₂ interactions by recording the vibrational spectra of the 1:1 vdW complexes. We utilize helium droplet methods to assemble and study these species. Helium droplets serve as an excellent medium for assembling a wide variety of clusters,^{38–41} including pure metal clusters,^{42–49} as well as many of the complexes already mentioned above. The chief advantages of this approach are that virtually, any combination of atoms or molecules can be assembled with fine control over the size of the clusters formed and that the superfluid nature of the droplet permits rotation of the assembled cluster, leading to rotationally resolved IR bands in many cases. As we will discuss below, our results are generally consistent with those from the aforementioned studies but add observation of structures and dynamics not previously reported.

EXPERIMENTAL

The instrument used in the present study, shown in Figure 1, has been described previously.^{50,51} Droplets are formed by supersonic expansion of high-purity helium (99.9999%) through an optically measured 5 μm diameter pinhole nozzle into a vacuum chamber pumped by an 8000 L/s diffusion pump. The supersonic expansion was skimmed by a 1.0 mm

FIG. 1. Schematic representation of the instrument used in the current study. Helium droplets are formed by expanding ultrahigh purity helium from a 5 μm diameter pinhole nozzle into vacuum. The expansion is then skimmed to form a droplet beam. The droplets are doped first with either Mg or Al by passing the droplet beam directly over the mouth of a resistively heated oven, and then with ¹³CO₂ using a pickup cell downstream. The droplets continue to a time-of-flight mass spectrometer where they are ionized and detected. Complexes solvated in the droplets are excited by the output beam of a quantum cascade laser that is counter-propagated with the droplet beam.

skimmer located ~ 20 mm downstream to produce a collimated droplet beam. The temperature of the nozzle is measured using a silicon diode (calibrated from 3 to 77 K) and is variable from 4 to 30 K. It is well known that the resulting droplet beam consists of a lognormal distribution of droplet sizes, the mean value of which can be varied by adjusting either the nozzle pressure or temperature, according to published scaling laws.⁵² For these experiments, the nozzle pressure and temperature were held constant at 50 bars and 19 K, respectively, corresponding to a mean droplet size of ~ 4600 atoms.

The droplet beam then enters a pickup chamber evacuated by a 2000 L/s diffusion pump, where the droplets are first doped by passing the beam over the mouth of a resistively heated ceramic crucible (Ladd Research) filled with either Al wire or Mg turnings. Because the helium droplets are transparent to photons of <20 eV, the radiation from the hot metal oven does not deplete the droplet beam. The temperature of the oven (calibrated with a thermocouple) was adjusted to ~ 375 °C or ~ 785 °C to optimize for the pickup of a single Mg or Al atom, respectively. An effusive pickup cell located downstream of the metal oven was used to dope the droplets with $^{13}\text{CO}_2$. We utilized isotopically substituted $^{13}\text{CO}_2$ rather than $^{12}\text{CO}_2$ due to the fact that the tuning and performance of the laser used in these experiments are significantly better in the vicinity of the absorption lines of the former. For these experiments, the pickup cell was optimized for pickup of a single $^{13}\text{CO}_2$ molecule. The output of the effusive cell was read using an ion gauge located opposite to the cell, and registered an uncorrected $^{13}\text{CO}_2$ pressure of $\sim 1 \times 10^{-6}$ Torr when the pressure was optimized.

We note that for the Al experiments, it was necessary to utilize a particular procedure in order to ensure smooth evaporation of the Al sample and prevent sudden loss of the sample via flash boiling. The crucible was loaded with Al wire and very slowly heated while watching the sample through a shutter-equipped window located directly above the mouth of the crucible. As soon as the Al wire completely melted, the temperature of the crucible was then quickly dropped to re-solidify the sample and mold it to the shape of the crucible interior. The temperature of the crucible was then raised to the desired temperature and operated normally. The presence of a pool of molten Al in the glowing crucible was visually confirmed periodically throughout the course of the experiments. When we were not viewing the crucible, it was necessary to close the shutter to prevent coating the window with Al. In contrast, neglecting this procedure and simply heating the crucible to the requisite Al evaporation temperature nearly always resulted in complete loss of the sample due to the need to somewhat overshoot the required temperature as a result of the poor thermal contact between the crucible walls and the Al wire. However, once the wire melts, the thermal contact improves dramatically. If not careful, the sample had a tendency to violently boil away before stable evaporation of the liquid could be achieved. The procedure above alleviated this difficulty.

After passing through the pickup chamber, the helium droplets are detected when they arrive downstream at a time-of-flight (TOF) mass spectrometer (Jordan TOF Products) equipped with a pulsed electron gun using an incident electron

energy of 100 eV (40 kHz repetition rate, 1 mA current, and $4 \mu\text{s}$ ionization pulse). It has been previously shown that electron bombardment of helium droplets at energies in excess of the ionization potential of helium (24.6 eV) results in ionization of the droplet.⁵³ The probability of ionization occurring depends upon the droplet's ionization cross section, which in turn depends upon the number of atoms in the droplet. The process begins with creation of a He^+ somewhere within the droplet; the charge then rapidly migrates on the fs timescale⁵⁴ until it is either transferred to the embedded dopant⁵⁵ or formation of a He_n^+ ion ($n \geq 2$) occurs.⁵⁶ Either outcome is sufficiently exothermic to desolvate the ion. The desolvated ions are then directed into a flight tube for detection by a multichannel plate (MCP) detector. The output of the MCP detector is simultaneously monitored by an oscilloscope and an ion counter that is interfaced to a lock-in amplifier.

A quantum cascade laser (Daylight Solutions), tunable from ~ 2190 to 2350 cm^{-1} , is used to vibrationally excite the $^{13}\text{CO}_2$ antisymmetric stretch of the molecules and complexes contained within the droplets. The laser frequency was measured using a mid-IR wave meter (Bristol Instruments). Vibrational excitation of an embedded dopant is followed by relaxation to the helium solvent, which results in both the evaporation of several hundred He atoms from the droplet and a concomitant reduction in the droplet's ionization cross section. This is detected as a decrease in the number of ion counts in the mass spectrometer. By amplitude modulating the laser and utilizing phase sensitive detection via the lock-in amplifier, the IR spectra are made background-free.

In order to aid in the assignment of the bands observed in the IR spectra, we made use of optically selected mass spectrometry (OSMS).⁵⁷ The OSMS spectra were obtained by tuning the laser into resonance with the spectral feature of interest. The OSMS signal for a selected ion mass-to-charge was acquired by gating the ion counter to send only the signal corresponding to the selected peak in the TOF mass spectrum to the lock-in amplifier (rather than ion counts from the entire TOF spectrum). The gate is then moved to examine the next mass of interest, and this process is repeated under computer control to acquire the OSMS spectrum over a specified mass range.

RESULTS AND DISCUSSION

CO_2 and its multimers

We begin by examining the IR spectra of $^{13}\text{CO}_2$ and its multimers without any metal atoms present, i.e., when the metal oven is cooled to room temperature. We note that IR spectra of helium-solvated $^{12}\text{CO}_2$ and its $^{16}\text{O}/^{18}\text{O}$ isotopomers have been previously reported.^{58–60} In Figure 2, we show the experimental spectra corresponding to the $^{13}\text{CO}_2$ monomer and several multimers. An expanded view of the monomer and dimer spectra, along with fits, is shown in the Figure 2 inset. For the monomer, we see three peaks in the vicinity of the ν_3 antisymmetric stretch at 2282.55 cm^{-1} , 2283.44 cm^{-1} , and 2283.92 cm^{-1} which we assign to the P(2), R(0), and R(2) lines, respectively. As expected, transitions originating from odd J states in $v = 0$ are missing due to nuclear spin

FIG. 2. IR spectrum of $^{13}\text{CO}_2$ and its multimers embedded in helium droplets. The inset shows the fits (red) for the $^{13}\text{CO}_2$ monomer and dimer using the constants listed in the text and in Table I.

considerations ($I = 0$ for oxygen). Fitting of this band to a linear rotor Hamiltonian (including nuclear spin effects) yielded $\nu_0 = 2283.16(2) \text{ cm}^{-1}$, $B'' = 0.149(2) \text{ cm}^{-1}$, and $B' = 0.137(2) \text{ cm}^{-1}$, where the numbers in parentheses denote the error estimates. Fitting for this spectrum and all subsequent spectra in this paper was accomplished using the Pgopher program.⁶¹ A Lorentzian peak shape with 0.045 cm^{-1} FWHM (full width half maximum) was used for the fit. The small red shift in the vibrational band origin relative to the gas phase value⁶² of 2283.48 cm^{-1} is neither surprising nor is the fact that the rotational constant is reduced from the gas phase value by a factor of ~ 2.7 . For many systems solvated inside helium droplets, rotational following by the helium solvent has been previously shown to increase the effective moments of inertia of the rotating species by a factor⁴⁰ of approximately 2–4. The reduction factors reported for $^{12}\text{C}^{16}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}$ were 2.5 and 2.6, respectively.⁵⁸ The reported vibrational red shift for $^{12}\text{CO}_2$ relative to the gas phase value was also similar to that seen here for the $^{13}\text{CO}_2$ isotopomer.⁵⁸

Consistent with previous $^{12}\text{CO}_2$ studies,^{59,63} we see a dimer band located slightly to the blue of the monomer at $\sim 2284.4 \text{ cm}^{-1}$ in Figure 2. Unfortunately, the individual rotational levels are not resolved and we obtain only the band

contours. We note that other bands corresponding to higher multimers are also visible between 2285 and 2287 cm^{-1} , but these are beyond the scope of the current discussion and were not analyzed further. The $^{12}\text{CO}_2$ dimer has been shown in the gas phase to have a slipped parallel structure with A, B, and C rotational constants of 0.30 , 0.054 , and 0.045 cm^{-1} , respectively, and a vibrational blue shift relative to the monomer⁶³ of 1.6 cm^{-1} . Corresponding theoretical values, calculated at the MP2/6-311++G** level of theory using the GAMESS suite of programs,⁶⁴ are shown in Table I and are in good agreement with the gas phase values. The spectroscopic constants obtained by fitting the band originating from the helium-solvated $^{13}\text{CO}_2$ dimer with a prolate symmetric top Hamiltonian are also found in Table I. The vibrational shift, as well as the rotational constants (modified by the helium following), is in line with our expectations and would seem to indicate that the same slipped parallel structure observed for the CO_2 dimer in the gas phase is also formed in helium droplets.

Mg- CO_2 complexes

We now turn our attention to complexes between Mg atoms and $^{13}\text{CO}_2$ molecules. In Figure 3, we show the spectrum obtained when the Mg oven is heated to $\sim 375 \text{ }^\circ\text{C}$. Two new bands appear concurrently at $\sim 2280.1 \text{ cm}^{-1}$ and at $\sim 2281.2 \text{ cm}^{-1}$ as the oven is warmed. As was the case with $(^{13}\text{CO}_2)_2$, the individual rotational levels are not resolved and only the band contours are obtained. A third feature with low signal intensity is observed at $\sim 2282.9 \text{ cm}^{-1}$ and is due to an impurity (likely water) which we were not able to completely bake off from the oven at this temperature. In any event, this signal does not require any Mg to be present in the oven. The feature at $\sim 2281.2 \text{ cm}^{-1}$ is Mg-related and resembles a parallel band of a symmetric top. The OSMS spectrum of this feature is shown in Figure 4. In addition to the usual distribution of He_n^+ ions ($n \geq 2$) resulting from the ionization of a helium droplet,²⁰ we find a peak at 69 amu , corresponding to $[\text{Mg}-^{13}\text{CO}_2]^+$. We also observe strong signals at 24 , 28 , 40 , and 44 amu . These masses are coincident with those of He_n^+ ions, but we note that the observed peaks are significantly more intense than the neighboring He_n^+ peaks, and we assign the additional intensity to Mg^+ , Mg^+-He , MgO^+ , and MgO^+-He , respectively. The

TABLE I. Spectroscopic constants for the $^{13}\text{CO}_2$ dimer, $\text{Mg}-^{13}\text{CO}_2$ complexes, and $\text{Al}-^{13}\text{CO}_2$ complexes observed in helium droplets. *Ab initio* values for the rotational constants and for the vibrational shifts relative to $^{13}\text{CO}_2$ monomer (in the harmonic approximation) were calculated at the MP2/6-311++G** level of theory for $^{13}\text{CO}_2$ and the $\text{Mg}-^{13}\text{CO}_2$ complexes and at the MRMP2/6-311++G** level of theory for the $\text{Al}-^{13}\text{CO}_2$ complexes.

	$(^{13}\text{CO}_2)_2$		$\text{Mg}-^{13}\text{CO}_2$ linear		$\text{Mg}-^{13}\text{CO}_2$ T-shaped		$\text{Al}-^{13}\text{CO}_2$ linear		$\text{Al}-^{13}\text{CO}_2$ T-shaped	
	Theory	Exp	Theory	Exp	Theory	Exp	Theory	Exp	Theory	Exp
$\Delta\nu$	+2.0	+1.29(2)	-1.0	-1.98(2)	-1.4	-3.11(3)	+0.02	+0.8(3)	-11.2	-5.9(2)
A	0.291	0.116(30)	...	0.020(4)	0.384	0.130(30)	...	...	0.409	...
$A_{\text{theory}}/A_{\text{exp}}$	...	2.5	...	...	...	3.0	...	...	...	...
B	0.052	0.014(3)	0.034	0.012(2)	0.054	0.025(5)	0.048	...	0.042	...
$B_{\text{theory}}/B_{\text{exp}}$	...	3.7	...	2.8	...	2.2	...	...	...	...
C	0.045	0.014(3)	...	0.012(2)	0.047	0.025(5)	...	...	0.038	...
$C_{\text{theory}}/C_{\text{exp}}$	...	3.2	...	...	...	1.9	...	...	...	...
FWHM	...	0.045(10)	...	0.045(7)	...	0.045	...	3.0(5)	...	2.0(5)

FIG. 3. IR spectrum of $\text{Mg-}^{13}\text{CO}_2$ complexes assembled in helium droplets. Fits for the bands at $\sim 2280.1\text{ cm}^{-1}$ (red) and $\sim 2281.2\text{ cm}^{-1}$ (blue) that appear concurrently when the Mg oven is warmed are shown in the inset. The constants used in the fits are listed in Table I.

OSMS spectrum in Figure 4, combined with the fact that the $^{13}\text{CO}_2$ pickup cell pressure dependence (Figure 5) of the feature at $\sim 2281.2\text{ cm}^{-1}$ matches that of the $^{13}\text{CO}_2$ monomer R(0) line, strongly suggests that this band corresponds to a complex with 1:1 $\text{Mg-}^{13}\text{CO}_2$ stoichiometry.

The additional Mg-related band present at $\sim 2280.1\text{ cm}^{-1}$ resembles a perpendicular band of a symmetric top. The presence of a perpendicular band is not unexpected, given the theoretical prediction of a T-shaped Mg-CO_2 complex mentioned above.²⁸ The OSMS spectrum for this band, shown in Figure 6, exhibits an intense peak at 24 amu that is assigned to Mg^+ , but no additional ions (other than He_n^+) are observed. This band does not result from the same species that produced the band at $\sim 2281.2\text{ cm}^{-1}$, but an unambiguous assignment of its identity cannot be made based solely on this OSMS spectrum. However, as mentioned above, this band appears

FIG. 4. OSMS spectrum collected from the band at $\sim 2281.2\text{ cm}^{-1}$. In addition to the He_n^+ ions ($n \geq 2$) located at every 4 amu, we see a prominent peak at 69 amu corresponding to $[\text{Mg-}^{13}\text{CO}_2]^+$. We also observe strong signals at 24, 28, 40, and 44 amu that are significantly more intense than the neighboring He_n^+ peaks. The additional intensity is assigned to Mg^+ , $\text{Mg}^+\text{-He}$, MgO^+ , and $\text{MgO}^+\text{-He}$, respectively.

FIG. 5. $^{13}\text{CO}_2$ pickup cell pressure dependence curves for $^{13}\text{CO}_2$ monomer, dimer, and the bands centered at $\sim 2281.2\text{ cm}^{-1}$ and at $\sim 2280.1\text{ cm}^{-1}$. The curves for the new bands match the $^{13}\text{CO}_2$ monomer curve.

concurrently with the band at $\sim 2281.2\text{ cm}^{-1}$ as the Mg oven is warmed. Given that the $^{13}\text{CO}_2$ pickup cell pressure dependence (Figure 5) of this band also matches that of the $^{13}\text{CO}_2$ monomer R(0) line and that the Mg oven temperature dependence curve (Figure 7) matches that of the band at $\sim 2281.2\text{ cm}^{-1}$, the data suggest that this band also corresponds to a 1:1 $\text{Mg-}^{13}\text{CO}_2$ complex, albeit not the same 1:1 complex that produces the band at $\sim 2281.2\text{ cm}^{-1}$.

In order to provide additional insights into Mg-CO_2 complexes, we performed *ab initio* calculations using GAMESS⁶⁴ at the MP2/6-311++G** level of theory. In Figure 8, we show the angular potential energy surface (PES) as a Mg atom is moved around a CO_2 molecule. None of the molecular degrees of freedom are frozen in the calculation except the Mg-C-O angle. We find two minima for this 1:1 case, namely, a linear isomer bound by 88 cm^{-1} and a T-shaped isomer bound by 98 cm^{-1} . Given that $kT \approx 0.25\text{ cm}^{-1}$ at the droplet temperature, we would not expect the rearrangement barrier evident in Figure 6 to be surmountable in either directions once the

FIG. 6. OSMS spectrum of the band at $\sim 2280.1\text{ cm}^{-1}$. In addition to He_n^+ ($n \geq 2$) appearing at every 4 amu, there is a peak with increased signal intensity at 24 amu, assigned to Mg^+ .

FIG. 7. Mg oven temperature dependence curves for features at ~ 2281.2 cm^{-1} and at ~ 2280.1 cm^{-1} in the $\text{Mg}-^{13}\text{CO}_2$ IR spectrum.

complexes are assembled and cooled. Consequently, we might expect to obtain both structural isomers in the droplet, and this prediction is consistent with our observation of two new bands (one parallel from the linear isomer and one perpendicular from the T-shaped isomer) appearing concurrently as the Mg oven is warmed.

Fits for both $\text{Mg}-^{13}\text{CO}_2$ bands are shown in the Figure 3 inset. The band at ~ 2280.1 cm^{-1} was fit as a perpendicular band of a prolate symmetric top. We note that due to the T-shaped geometry and the nuclear spin considerations imposed by exchange of the O atoms, we would expect transitions originating from odd K_a in $v = 0$ to be missing. The constants used in the fit, along with the vibrational shifts and rotational constants predicted by theory, are listed in Table I. The nuclear spin restrictions on the allowable values of K_a were included in the fit plotted in Figure 3. The band at ~ 2281.2 cm^{-1} was fit as a parallel band, again using a prolate symmetric top Hamiltonian. The fitting constants are also listed in Table I along with the corresponding theoretical values.

In general, the theoretical values are in reasonable agreement with the experimental results. The calculated vibrational

shifts (obtained via harmonic frequency calculations) are consistent with the observed vibrational shifts, not only in magnitude but also in the relative ordering of which isomer should be most strongly red-shifted from the $^{13}\text{CO}_2$ monomer band. The experimental rotational constants are also in good agreement with the calculated values, accounting for the expected reduction resulting from rotational following by the helium solvent.

There is, however, one highly intriguing and very unexpected discrepancy. Namely, although the experimental results for the band at ~ 2281.2 cm^{-1} otherwise compare favorably with the properties of the linear structure calculated, the band exhibits a significant Q branch, whereas we would expect only P and R branches for a parallel transition of a linear species. We note that this phenomenon is not without precedent and has been observed for other linear species such as $(\text{HCCCN})_2$,⁶⁵ $\text{HCCCN}-\text{HCN}$,⁶⁶ and $(\text{HCN})_{n \geq 3}$.⁶⁷ It is interesting that the presence or absence of a Q branch feature is difficult to anticipate even amongst closely related species. The aforementioned species exhibit this spectral feature; however, HCN ,⁶⁸ $(\text{HCN})_2$,⁶⁹ HCCCN ,⁷⁰ and $\text{HCN}-\text{HCCCN}$ ⁶⁶ do not. Nevertheless, theory has made significant advances in understanding this phenomenon in terms of the structure of the helium solvent surrounding the complex.⁶⁶ However, we wish to note that the linear species mentioned above as exhibiting this feature are all significantly more polar than $\text{Mg}-\text{OCO}$, and we would not necessarily expect the same type of Q-branch-inducing excitations of the helium solvent to occur here. Sophisticated theoretical treatments will most likely be required to resolve this issue definitively.

An alternative explanation for the presence of a Q-branch feature is related to the rearrangement barrier going from the linear to the T-shaped isomer in Figure 8. The calculated barrier in this direction is only ~ 5 cm^{-1} . Harmonic frequency calculations of the normal modes of the linear isomer predict the mode involving off-axis motion of the Mg atom to have a zero point energy of ~ 2 cm^{-1} . The low barrier, combined the fact that this bending mode is doubly degenerate, suggests that $\text{Mg}-\text{OCO}$ is able to spend a significant portion of its time in a non-linear geometry. This could certainly explain the presence of a Q-branch, although the magnitude of the A rotational constant (smaller than that for the T-shaped isomer) is still puzzling. On the other hand, this idea would also explain why a linear $\text{Mg}-\text{CO}_2$ isomer was not previously observed in matrix isolation experiments.²⁹ Especially in view of the non-trivial contribution towards bending from zero point energy, the barrier to rearrangement to the T-shaped isomer would be surmountable in all but the lowest temperatures.

$\text{Al}-^{13}\text{CO}_2$ complexes

We begin our exploration of $\text{Al}-^{13}\text{CO}_2$ complexes by showing the angular PES in Figure 9. The surface was calculated with GAMESS⁶⁴ using second-order multi-reference perturbation theory (MRPT2) applied to the complete active space self-consistent field (CASSCF) zeroth-order wavefunctions obtained with the 6-311++G** basis set. It was necessary to employ multireference methods for this system in

FIG. 8. Angular cut through the potential energy surface corresponding to the interaction of a Mg atom with CO_2 .

FIG. 9. Angular cut through the potential energy surface corresponding to the interaction of an Al atom with CO_2 .

order to avoid unphysical discontinuities in the PES resulting from the sudden switching of electronic configurations as the geometry is changed. Except for the change in the level of theory employed, the PES is calculated as above; namely, an Al atom is moved around a CO_2 molecule, and the Al-C-O angle is the only frozen degree of freedom. Here again, we see two minima: a linear isomer bound by 192 cm^{-1} and a T-shaped isomer bound by 139 cm^{-1} . Harmonic frequency calculations of the two fully geometry-optimized structures predict the linear isomer to be only slightly blue-shifted from $^{13}\text{CO}_2$ monomer by 0.02 cm^{-1} and the T-shaped isomer to be red-shifted from $^{13}\text{CO}_2$ monomer by 11 cm^{-1} . The calculated rotational constants are provided in Table I.

Figure 10 shows the spectrum obtained when the Al oven is heated to $\sim 785^\circ\text{C}$. At this temperature, the spectral impurity seen in the $\text{Mg-}^{13}\text{CO}_2$ spectrum (Figure 3) was already burned away from the crucible prior to evaporation of Al atoms. Upon warming of the oven to $\sim 785^\circ\text{C}$, two new broad

FIG. 10. IR spectrum of $\text{Al-}^{13}\text{CO}_2$ complexes assembled in helium droplets. Two broad features at $\sim 2277\text{ cm}^{-1}$ (red) and at $\sim 2284\text{ cm}^{-1}$ (blue) appear concurrently when the Al oven is warmed. The features were fit with single Lorentzian peaks with FWHM line widths of 2 cm^{-1} and 3 cm^{-1} , respectively. A zoomed-in view is shown in the inset.

FIG. 11. $^{13}\text{CO}_2$ pickup cell pressure dependence curves for $^{13}\text{CO}_2$ monomer, dimer, and the bands centered at $\sim 2277\text{ cm}^{-1}$ and at $\sim 2284\text{ cm}^{-1}$. The curves for the new bands match the $^{13}\text{CO}_2$ monomer curve.

features emerge at $\sim 2277\text{ cm}^{-1}$ and $\sim 2284\text{ cm}^{-1}$. Unfortunately, OSMS spectra for these two features could not be obtained with acceptable signal-to-noise due to the low peak intensity. We were, however, able to determine the pickup cell dependence (Figure 11) and the Al oven temperature dependence (Figure 12) for the two features. Both $^{13}\text{CO}_2$ pickup cell pressure dependences match that of the $^{13}\text{CO}_2$ monomer $R(0)$ line, indicating that both result from a complex containing a single $^{13}\text{CO}_2$ molecule. Additionally, the Al oven temperature dependences of both features are identical to one another. Since these are the first signals to appear as the oven is warmed, it suggests that both are due to structures containing a single Al atom as well.

The observation of two new features is consistent with the theoretical results shown in Figure 9. Here again, we might expect to assemble both isomers, and since $kT \approx 0.25\text{ cm}^{-1}$ at the droplet temperature, we would not expect the rearrangement barrier to be surmountable in either directions once assembly and cooling of the complexes are complete. Based upon the observed vibrational shifts, which are in reasonable

FIG. 12. Al oven temperature dependence curves for features at $\sim 2277\text{ cm}^{-1}$ and at $\sim 2284\text{ cm}^{-1}$ in the $\text{Al-}^{13}\text{CO}_2$ IR spectrum.

agreement with the calculated shifts for the two isomers, we tentatively assign the band at $\sim 2277\text{ cm}^{-1}$ to the T-shaped isomer and the band at $\sim 2284\text{ cm}^{-1}$ to the linear isomer. The $\text{Al-}^{13}\text{CO}_2$ bands are both quite broad, so broad that neither the individual rotational lines nor the band contours can be clearly discerned. In fact, the two bands are well-described by single Lorentzian peaks of width 3 cm^{-1} (for the linear isomer) and 2 cm^{-1} (for the T-shaped isomer). This level of homogeneous broadening would correspond to upper state lifetimes of 1.8 ps for the linear isomer and 2.7 ps for the T-shaped isomer. Given that the broadening obscures all rotational structure in the bands and lowers the peak intensity sufficiently to preclude OSMS, confident assignments of the identities of the absorbing species cannot be made. However, taking these results at face value allows us to consider the assignments and the broadening in more detail via additional theoretical, experimental, and the literature results, discussed below.

In general, there are several possible explanations for a short lifetime for the upper vibrational state of a dimer. One possibility is rapid energy transfer between moieties in the complex. This idea would not seem to be applicable in this instance since we are exciting the CO_2 antisymmetric stretch and the metal atom lacks any vibrational degrees of freedom. A related possibility is that a fast intramolecular vibrational redistribution (IVR) occurs between modes in the complex. This notion also seems unlikely since no such broadening was observed for either of the $\text{Mg-}^{13}\text{CO}_2$ complexes. We would also expect an IVR process to be sensitive to the structure of the complex, yet the bands from both of the $\text{Al-}^{13}\text{CO}_2$ structural isomers are quite broad. Another possibility is that a rapid dissociation occurs upon photon absorption, presumably due to good momentum matching between the antisymmetric stretch of the $^{13}\text{CO}_2$ molecule and the metal atom. This suggestion also seems unlikely since the calculated reduced mass of the antisymmetric stretch is 12.9 amu , compared with the atomic mass of 27.0 amu for an Al atom or 24.3 amu for a Mg atom. Not only are these dissimilar to the reduced mass of the $^{13}\text{CO}_2$ antisymmetric stretch but we would also expect better matching and thus more broadening with the Mg atoms, which instead exhibit less broadening. A final possibility is that the broadening results from prompt chemical reaction following photon absorption. This seems the most likely explanation given the greater reactivity of Al atoms compared to Mg atoms. As discussed above, Al atoms have been shown to spontaneously react with HF and HCN,^{30,32,33} even at the droplet temperature; also, photo-induced reaction has been observed for Al-(CO)_n complexes.³⁴

To further explore the possibility of a photo-induced chemical reaction, we calculated the radial PES for both the $\text{Mg-}^{13}\text{CO}_2$ and $\text{Al-}^{13}\text{CO}_2$ systems, as shown in Figure 13. These were calculated using the same levels of theory and basis sets noted above for the corresponding angular potential energy surfaces. In both cases, the metal atom-C distance is the only degree of freedom frozen in this calculation. For $\text{Mg-}^{13}\text{CO}_2$, only vdW interactions are found; reduction of the distance between the Mg atom and the CO_2 molecule only results in steadily increasing repulsion. We note, however, that a previous theoretical study predicted the existence of a reacted

FIG. 13. Radial cut through the potential energy surfaces for Mg-CO_2 and Al-CO_2 .

structure at energies higher than those considered here.²⁸ In the case of the $\text{Al-}^{13}\text{CO}_2$ system, two energy minima are observed on the PES: a vdW minimum at longer Al-C distance and a reacted minimum bound by $\sim 2000\text{ cm}^{-1}$ at shorter Al-C distance. The two minima are separated by a barrier of $\sim 900\text{ cm}^{-1}$. This surface is in reasonable agreement with an experimental investigation which suggested that an AlCO_2 adduct is an important intermediate in the $\text{Al} + \text{CO}_2 \rightarrow \text{AlO} + \text{CO}$ reaction and estimated the reaction barrier as $>350\text{ cm}^{-1}$, and the reaction energy associated with formation of the adduct as several thousand wavenumbers.³⁵

Given that the photon energy associated with excitation of the $^{13}\text{CO}_2$ antisymmetric stretch for the isomers of $\text{Al-}^{13}\text{CO}_2$ is in excess of the calculated reaction barrier, a photo-induced chemical reaction in this system seems plausible. We also note that the photon energy is in excess of the rearrangement barrier (in either directions), as evident in Figure 9. Thus, both isomers are calculated to have at least one energetically accessible pathway to the reacted structure once photo-excited. These theoretical results are consistent with our experimental observations that the bands assigned to both $\text{Al-}^{13}\text{CO}_2$ isomers are significantly lifetime-broadened. In contrast, no reactive pathways are calculated to be available (at this photon energy) for $\text{Mg-}^{13}\text{CO}_2$, and neither band exhibits this broadening.

While still somewhat speculative, this hypothesis could explain not only the broadening observed in the present study but also the absence of signals from unreacted Al-CO_2 complexes in matrix isolation experiments.³⁷ Namely, co-deposition of Al and CO_2 in those experiments could have produced unreacted complexes, but the first exposure to the incident broadband IR light used to probe the matrix via Fourier Transform IR (FTIR) detection would have promptly converted them to the reacted adduct. The spectrum corresponding to the adducts only would then have been recorded for the duration of the spectrum integration time of the FTIR experiment.

One final piece of evidence for this hypothesis for the interesting broadening observed in the Al-CO_2 system is found in the experimental intensities of the IR bands. The calculated

IR intensities for the CO₂ monomer, Mg-¹³CO₂ isomers, and Al-¹³CO₂ isomers are all quite similar. Relative to the ¹³CO₂ monomer they are 1.24 for the Mg-¹³CO₂ linear isomer, 0.79 for the Mg-¹³CO₂ T-shaped isomer, 1.25 for the Al-¹³CO₂ linear isomer, and 0.96 for the Al-¹³CO₂ T-shaped isomer. The integrated intensities of both the Mg-¹³CO₂ linear isomer band and the Mg-¹³CO₂ T-shaped isomer band in Figure 3, relative to the ¹³CO₂ monomer band in Figure 2, are 0.5 and 0.4, respectively. Thus, the sum of the integrated intensities of the two Mg-¹³CO₂ bands is similar to that obtained for the ¹³CO₂ monomer. However, the integrated intensities of the bands assigned to the Al-¹³CO₂ linear isomer and the Al-¹³CO₂ T-shaped isomer are 2.1 and 0.8, respectively. The fact that the signals obtained for the two Al-¹³CO₂ isomers are approximately three times that of the ¹³CO₂ monomer is difficult to explain in the absence of a chemical reaction. This would make sense, however, if the photo-induced reaction hypothesis is correct. In that case, in addition to the photon energy being relaxed to the droplet, the reaction energy will also have to be dissipated. The calculated reaction energy in Figure 13 is as large as the photon energy used to excite the CO₂ molecule. Experimental estimates of the reaction energy are even larger.³⁵ This extra energy contribution would ultimately manifest in the evaporation of additional helium atoms from the droplets and increase depletion of the droplet beam, i.e., a higher signal in the depletion spectrum, which is precisely what is observed.

Taken together, the available experimental and computational results seem to point to a prompt photo-induced chemical reaction in the case of both the linear and the T-shaped isomers of the Al-CO₂ system. We wish to note that although this hypothesis is consistent with the available experimental and theoretical data and would reconcile the two seemingly contradictory previous literature reports (one³⁵ that indicated a reaction barrier >350 cm⁻¹ for Al + CO₂ and another that observed only reaction products from co-deposition in a cryogenic matrix³⁷), this explanation is still somewhat speculative because the severe broadening in the IR bands prevents definitive assignments of the identities of the absorbing species. In the future, we hope to investigate this further by performing IR-IR double resonance experiments via attachment of an additional CO₂ molecule to the (presumably) photochemically induced Al-¹³CO₂ reaction product and vibrationally exciting the antisymmetric stretch of the second ¹³CO₂ molecule.

SUMMARY

In summary, we have used high resolution IR spectroscopy to investigate Mg-¹³CO₂ and Al-¹³CO₂ vdW complexes assembled in helium droplets and compared the experimental results with theoretical predictions. In both systems, two IR bands are obtained: one assigned to a linear isomer and the other to a T-shaped isomer. In the case of the Mg-¹³CO₂ complexes, the vibrational frequencies and rotational constants associated with the two isomers are in good agreement with theoretical values. In the case of the Al-¹³CO₂ complexes, the vibrational frequencies agree with theoretical predictions, but both IR bands exhibit significant homogeneous broadening sufficient to completely obscure the rotational structure

of the bands. The broadening observed would be consistent with an upper state lifetime of the complex of 2.7 ps for the linear isomer and 1.8 ps for the T-shaped isomer. The short lifetimes are tentatively attributed to a prompt photo-induced chemical reaction between the ¹³CO₂ molecule and the Al atom comprising the complex. Additional theoretical calculations support this hypothesis and predict a bent reaction product is formed.

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