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Infrared spectra reveal box-like structures for a pentamer and hexamer of mixed carbon dioxide-acetylene clusters

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Except for a few cases like water and carbon dioxide, identification and structural characterization of clusters with more than four monomers is rare. Here, we provide experimental and theoretical evidence for existence of box-like structures for a pentamer and a hexamer of mixed carbon dioxide-acetylene clusters. Two mid-infrared cluster absorption bands are observed in the CO₂ ν₃ band region using a tunable diode laser to probe a pulsed supersonic jet. Each requires the presence of both carbon dioxide and acetylene in the jet, and (from observed rotational spacings) involves clusters containing about 4 to 7 molecules. Structures are predicted for mixed CO₂ + C₂H₂ clusters using a distributed multipole model, and the bands are assigned to a specific pentamer, (CO₂)₃-(C₂H₂)₂, and hexamer, (CO₂)₄-(C₂H₂)₂. The hexamer has a box-like structure whose D_{2d} symmetry is supported by observed intensity alternation in the spectrum. The pentamer has a closely related structure which is obtained by removing one CO₂ molecule from the hexamer. These are among the largest mixed molecular clusters to be assigned by high-resolution spectroscopy.

Introduction

High-resolution spectroscopy of weakly-bound van der Waals complexes provides one of the most precise and direct experimental probes of intermolecular forces, free of the thermal averaging which is required to interpret other results such as molecular beam scattering or equation of state (PVT) measurements. Spectra of many molecular dimers and trimers have been studied in the gas-phase, but results for larger clusters are more limited.¹ Larger clusters are generally more difficult to produce in abundance, and their spectra are naturally more difficult to resolve, identify, and assign. Especially notable among such studies are remarkable results on water clusters.²⁻⁶

We have recently assigned infrared spectra of certain tetramers and larger clusters containing linear molecules, including (N₂O)₄,⁷ (OCS)₄,⁸ (CS₂)₄,⁹ (N₂O)₅,¹⁰ and (CO₂)_n clusters with *n* = 6 to 13.^{11,12} Here we report spectra of a pentamer and a hexamer containing carbon dioxide and acetylene molecules, namely (CO₂)₃-C₂H₂ and (CO₂)₄-(C₂H₂)₂. These assignments are aided by cluster calculations which use a distributed multipole model for the intermolecular forces. As illustrated in Fig. 1, the pentamer and hexamer have somewhat similar symmetric (C_{2v} and D_{2d} point groups) box-like structures. To our knowledge, these are the largest such *mixed* molecular clusters to be

characterized by rotationally-resolved spectroscopy.

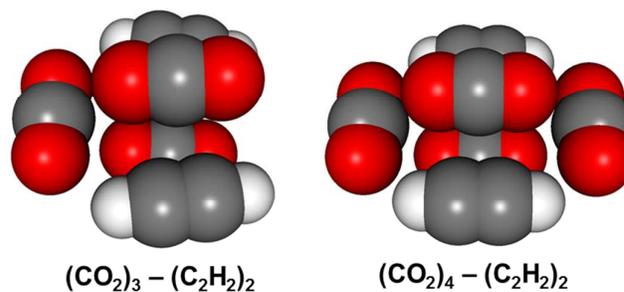


Fig. 1. Calculated structures of the most stable isomers of (CO₂)₃-(C₂H₂)₂ (C_{2v} symmetry) and (CO₂)₄-(C₂H₂)₂ (D_{2d} symmetry). In both cases, the C₂H₂ monomers and the “end” CO₂ monomer(s) are co-planar, and this plane is perpendicular to the plane containing the two middle CO₂ monomers. For (CO₂)₄-(C₂H₂)₂, the *a* inertial axis passes through the centers of mass of the equivalent end CO₂ monomers, the *b* axis through the centers of mass of the C₂H₂ monomers, and the *c* axis through the centers of mass of the middle CO₂ monomers. For (CO₂)₃-(C₂H₂)₂, the orientation of the axes is the same in this view.

Cluster Calculations

To estimate possible structures of mixed CO₂ / C₂H₂ clusters, we use a distributed multipole model for the intermolecular potentials¹³ which is relatively simple, computationally fast, and requires no additional parameters for the CO₂ – C₂H₂ interaction once the CO₂ – CO₂ and C₂H₂ – C₂H₂ parameters are known. As shown by Muenther,¹³ this model does a good job in describing the known structures of the dimers (CO₂)₂ and CO₂ – C₂H₂. For (C₂H₂)₂, the rotational parameters from the model are also good, but it does not quite yield the known T-shaped structure. This may not be too serious, since observation of acetylene dimer tunneling effects show that the potential is

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very flat in the region of the minimum. The model also does well for the two isomers of CO₂ trimer^{14,15} and for acetylene trimer,^{16,17} although apparently not for acetylene tetramer.¹⁸ Our cluster structure calculations for mixed CO₂ / C₂H₂ trimers, tetramers, pentamers, and hexamers use this potential energy model¹³ and a technique described previously.¹² They start with n CO₂ and m C₂H₂ molecules with random positions and orientations and adjust the multidimensional structure to find the nearest local energy minimum for (CO₂) _{n} – (C₂H₂) _{m} using the Powell method.¹⁹ The calculation is repeated hundreds of times for each cluster in order to find all low-lying isomers, including the global minimum. The number of local minima increases rapidly with cluster size, but we are still confident of finding all low-lying structures, even for hexamers. Key results of these calculations are listed in Table 1, where binding energy, rotational parameters, and symmetry are given for the two lowest energy isomers of each possible mixed tetramer, pentamer, and hexamer. The lowest energy calculated structures for $(n,m) = (3,2)$, and $(4,2)$ are illustrated in Fig. 1.

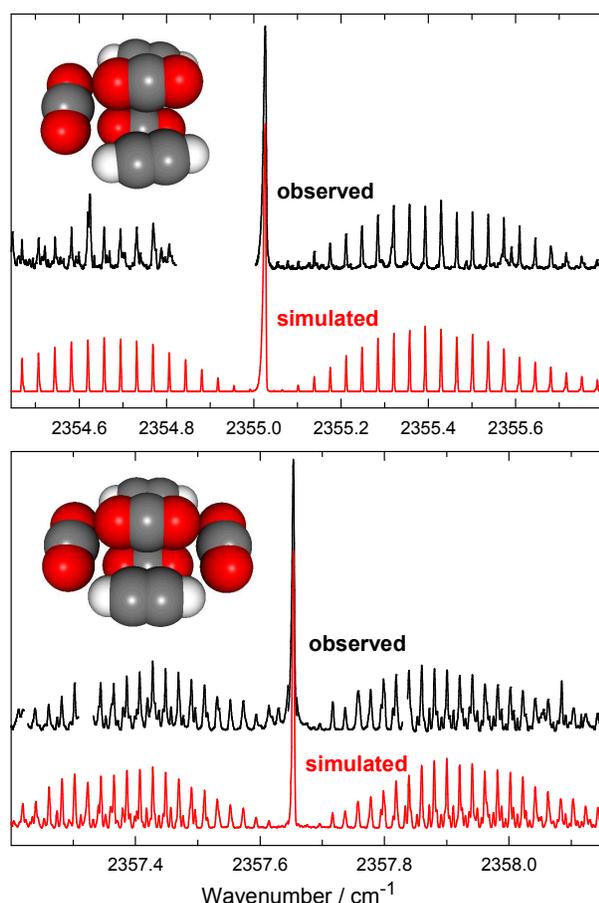


Fig. 2. Observed and simulated spectra of the pentamer (CO₂)₃-(C₂H₂)₂ (top panel) and hexamer (CO₂)₄-(C₂H₂)₂ (bottom panel). The gap around 2354.9 cm⁻¹ in the observed spectrum is due to incomplete laser coverage. The simulations assume a rotational temperature of 3.0 K and line broadening of 0.0025 cm⁻¹.

Table 1. Calculated energies, rotational parameters, and symmetries for the two most stable isomers of (CO₂) _{n} – (C₂H₂) _{m} clusters, based on a distributed multipole potential.¹³ E in cm⁻¹; A, B, C in MHz, letters (a, b, or c) following Sym (symmetry type) indicate the inertial axis coinciding with the symmetry axis (for C₂ and C_{2v}) or perpendicular to the symmetry plane (for C_s).

n	m	E	A	B	C	Sym	E	A	B	C	Sym
1	3	-2845	1365	898	759		-2829	1428	888	796	
2	2	-3173	1359	811	732		-3059	1284	917	706	D _{2h}
3	1	-3075	1149	705	653		-3061	1647	571	512	C _{2v-b}
1	4	-4034	1011	551	511	C _{s-c}	-3981	1032	573	478	
2	3	-4577	837	692	498	C _{s-a}	-4512	773	654	524	C _{2v-b}
3	2	-4659	689	563	554	C _{2v-a}	-4611	906	466	408	C _{s-a}
4	1	-4252	823	391	346		-4241	651	525	428	
1	5	-5322	580	555	389	C _{2v-b}	-5311	633	467	338	C _{s-c}
2	4	-5864	605	492	339	D _{2h}	-5813	652	418	332	
3	3	-6377	593	440	338	C _{2v-c}	-6160	646	381	344	C _{2v-a}
4	2	-6133	672	321	288	D _{2h}	-6054	472	451	347	C _{s-b}
5	1	-5581	462	351	340		-5556	478	369	287	

Observation and analysis

New vibration-rotation bands due to larger clusters appeared during our study²⁰ of the dimer CO₂ – C₂H₂ in the CO₂ ν₃ fundamental region (≈2350 cm⁻¹), using a pulsed supersonic expansion of a dilute CO₂ (0.16%) + C₂H₂ (0.32%) + He gas mixture from a slit jet source with a backing pressure of 8 atmospheres. The jet was probed by a tunable diode laser operating in a rapid-scan signal averaging mode. Wavenumber calibration utilized simultaneously recorded spectra from reference gas and etalon channels. Bands were assigned and analyzed with the aid of the PGOPHER computer program.²¹

The band shown at the top of Fig. 2 has a prominent Q-branch (2355.03 cm⁻¹), as well as clear R- and P-branch lines evenly spaced by 0.037 cm⁻¹. It resembles a parallel ($\Delta K = 0$) band of a symmetric rotor molecule with $B \approx 552$ MHz, but there are *no* calculated symmetric rotors in Table 1. However, the lowest energy isomer of the pentamer (CO₂)₃ – (C₂H₂)₂ is an asymmetric rotor with $(B + C)/2 \approx 558$ MHz which is close to the prolate symmetric limit. The calculated asymmetry of this cluster, which can be characterized by the parameter $(B - C) \approx 9.7$ MHz, is sufficiently small that its spectrum resembles that of a symmetric top. An *a*-type asymmetric rotor band with parameters close to the calculated ones matches the observed spectrum very well, as illustrated by the simulated trace in the upper panel of Fig. 2 which uses the parameters given in Table 2. These parameters agree well with the calculated ones (Table 1), but only $(B + C)/2$ is well-determined from the spectrum.

The band shown in the lower panel of Fig. 2 is similar to the previous band, but with a smaller effective *B*-value of about 310 MHz, implying a larger cluster. Unlike the 2355 cm⁻¹ band, there is resolved *K*-structure due to asymmetry splitting in the P- and R-branches. With persistence, we were able to fit this band with rotational constants: $A = 665$, $(B + C)/2 = 307$, $(B - C) = 32$ MHz. These parameters agree very well with those predicted for the lowest energy isomer of (CO₂)₄ – (C₂H₂)₂ (Table 1). The excellent agreement between observed and simulated spectra is also evident in Fig. 3. Support for the assignment is given by intensity effects due to nuclear spin

statistics. The calculated structure (Fig. 1) has D_{2h} symmetry, with three two-fold rotation axes, giving rise to spin weights of 7:3:3 for levels with $(K_a, K_c) = (e,e), (e,o), (o,e), (o,o)$, where e and o stand for even and odd. An intensity alternation caused by these weights is evident in the series of lines marked by asterisks in Fig. 3. This series involves transitions of the form $(J, K_a, K_c) = (J'' + 1, 0 \text{ and } 1, J'' + 1) \leftarrow (J'', 0 \text{ and } 1, J'')$. When J'' is even, the $K_a'' = 0$ component has extra (7/3) relative intensity, so the series itself has an intensity alternation of 10:6 for $J'' = \text{even:odd}$. This is visible in the simulation, which has built-in spin statistics, and is well-matched by the observed spectrum.

Table 2. Observed and calculated molecular parameters for $(\text{CO}_2)_3\text{-(C}_2\text{H}_2)_2$ and $(\text{CO}_2)_4\text{-(C}_2\text{H}_2)_2$ (ν_0 in cm^{-1} , other parameters in MHz).

	$(\text{CO}_2)_3\text{-(C}_2\text{H}_2)_2$		$(\text{CO}_2)_4\text{-(C}_2\text{H}_2)_2$	
	Obs	Calc	Obs	Calc
ν_0	2355.0285(1)		2357.6551(1)	
A'	687.961(107)		665.2(70)	
$\frac{1}{2}(B' + C')$	551.062(75)		306.918(41)	
$(B' - C')$	8.7 ^a		31.998(251)	
A''	689.0 ^a	688.8	665.5(70)	671.7
$\frac{1}{2}(B'' + C'')$	552.017(77)	558.5	307.180(42)	304.2
$(B'' - C'')$	8.7 ^a	9.7	32.440(255)	32.6

^a These fixed values were not directly determined in the analysis, but they are the parameters used in the simulation and are thus consistent with the observed spectrum.

Structures

The calculated structures of the clusters assigned as the carriers of the 2355 and 2358 cm^{-1} bands are shown in Fig. 1. The two geometries are closely related in the sense that the pentamer, $(\text{CO}_2)_3\text{-(C}_2\text{H}_2)_2$, is close to what would be obtained by removing one of the two equivalent "end" CO_2 monomers from the hexamer, $(\text{CO}_2)_4\text{-(C}_2\text{H}_2)_2$.

In general, 5N – 6 parameters are required to specify the structure of a cluster of N linear molecules, assuming that the internal structure of the monomers is fixed. But this number may be reduced by symmetry. For our hexamer, $(\text{CO}_2)_4\text{-(C}_2\text{H}_2)_2$, the D_{2h} symmetry reduces the number of structural parameters from twenty-four to only three. In our calculated structure, these may be specified as: separation of centers of mass of the "end" CO_2 monomers, 7.31 Å; separation of centers of mass of "middle" CO_2 monomers, 3.61 Å; and separation of centers of mass of C_2H_2 monomers, 5.40 Å. Since we have three well-determined rotational parameters, it is possible to determine an "experimental" structure for the hexamer, which is: 7.25, 3.65, and 5.41 Å, given in the same order. The good agreement between calculated and experimental structures reflects the good agreement already noted for the rotational parameters (Tables 1, 2). In the case of the pentamer, $(\text{CO}_2)_3\text{-(C}_2\text{H}_2)_2$, the C_{2v} symmetry reduces the number of structural parameters from nineteen to seven. But since only one rotational parameter, $\frac{1}{2}(B + C)$, is accurately determined, we cannot establish an experimental structure. The calculated pentamer structure is given as Supplementary

Information in the form of principal axis system atomic coordinates.

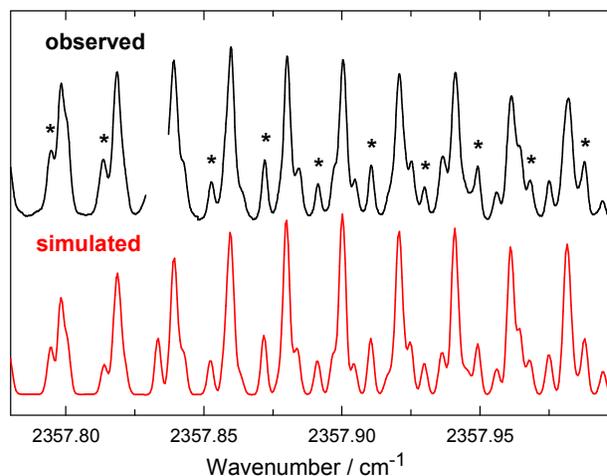


Fig. 3. Expanded view of the R-branch region of $(\text{CO}_2)_4\text{-(C}_2\text{H}_2)_2$. Asterisks indicate a series showing intensity alternation which helps confirm the assignment to the suggested D_{2h} structure. For reference, the transition at 2357.87 cm^{-1} is assigned as $(J, K_a, K_c) = (11, 0 \text{ and } 1, 11) \leftarrow (10, 0 \text{ and } 1, 10)$.

The good agreement between experiment and theory for the rotational constants (and for the detailed structure in the hexamer case) suggests to us that these clusters are relatively rigid by the standards of weakly-bound complexes. That is, they apparently do not possess large amplitude vibrational modes that could cause a large difference between the equilibrium and effective structures.

Resonant dipole model

Vibrational shifts and intensities in molecular clusters, aerosols, and crystals are often modeled in terms of resonant dipole-dipole interactions.²²⁻²⁴ Coupling of the transition dipoles within a cluster lifts the initial degeneracy of the vibrational transition, causing splitting and shifting into various components. If the geometrical structure and transition moment magnitude are known, then the shift, strength, and orientation (relative a -, b -, and c -type contribution) can be calculated for each vibrational mode using classical electrostatics. The model is imperfect because there are non-resonant effects and other intermolecular interactions beyond simple electrostatics.²⁵ But it is still qualitatively useful.¹⁻¹⁰⁻¹²

For the present clusters, only the CO_2 molecules need to be included in a resonant dipole calculation because we are interested in modes arising from the $\text{CO}_2 \nu_3$ vibration, and the active stretching fundamental of C_2H_2 is distant (3282 cm^{-1}) and relatively weak. The resonant dipole results shown in Table 3 assume the same $\text{CO}_2 \nu_3$ band strength value used previously^{12,14} and our calculated pentamer and hexamer structures. In both cases, a strong blue-shifted a -type mode is predicted, in qualitative agreement with our observed bands. The calculated shifts are +7.62, and +11.25 cm^{-1} for $(\text{CO}_2)_3\text{-(C}_2\text{H}_2)_2$ and $(\text{CO}_2)_4\text{-(C}_2\text{H}_2)_2$, respectively, in comparison with observed shifts of +5.89, and +8.51 cm^{-1} . For the pentamer,

this blue-shifted mode arises from in-phase vibration of the two equivalent CO₂ monomers, and for the hexamer it arises from the analogous “middle” CO₂ pair. The fact that these pentamer and hexamer bands lie close together is consistent with this assignment, in the sense that they are due to the “same” pair of CO₂ monomers. The out-of-phase vibrations of this same pair give rise to modes with equal but opposite red-shifts and little or no intensity. This intensity is strictly zero for (CO₂)₄-(C₂H₂)₂ by symmetry. But for (CO₂)₃-(C₂H₂)₂, the equivalent monomers are not quite parallel so they have a small projection on the *b*-axis giving a small residual intensity. The pentamer has another predicted mode with zero shift and *c*-type selection rules which arises from vibration of the “end” CO₂ monomer. In the hexamer, the two equivalent end monomers give rise to a forbidden mode at -1.36 cm⁻¹ and an allowed *b*-type partner at +1.36 cm⁻¹.

Table 3. Resonant dipole calculation for (CO₂)₃-(C₂H₂)₂ and (CO₂)₄-(C₂H₂)₂.

	Shift / cm ⁻¹	Intensity ^a		
		<i>a</i>	<i>b</i>	<i>c</i>
(CO ₂) ₃ -(C ₂ H ₂) ₂	-7.62	0.0	0.02	0.0
(CO ₂) ₃ -(C ₂ H ₂) ₂	0.0	0.0	0.0	1.0
(CO ₂) ₃ -(C ₂ H ₂) ₂	+7.62	1.98	0.0	0.0
(CO ₂) ₄ -(C ₂ H ₂) ₂	-11.25	0.0	0.0	0.0
(CO ₂) ₄ -(C ₂ H ₂) ₂	-1.36	0.0	0.0	0.0
(CO ₂) ₄ -(C ₂ H ₂) ₂	+1.36	0.0	2.0	0.0
(CO ₂) ₄ -(C ₂ H ₂) ₂	+11.25	2.0	0.0	0.0

^a Intensities for transition dipole components along the *a*-, *b*-, and *c*-inertial axes, in units of CO₂ monomer intensity. The total intensity for all bands of cluster (CO₂)_n-(C₂H₂)_m is equal to *n*.

For each cluster, the resonant dipole model predicts a second band with significant intensity in addition to those we have assigned. We have not been able to detect these bands, most likely because they are located closer to the CO₂ band origin where there is strong interference from other clusters, like (CO₂)₂, (CO₂)₃, CO₂-C₂H₂, etc.²⁰

Discussion and conclusions

We have analyzed two rotation-vibration bands, assigning one to (CO₂)₃-(C₂H₂)₂, and the other to (CO₂)₄-(C₂H₂)₂. In each case the spectrum agrees well with that expected for our lowest energy calculated structure (Table 1) in terms of rotational parameters, band type, and position. For the hexamer, there is additional support from nuclear spin intensity alternation. Therefore we are confident that the rather interesting clusters shown in Fig. 1 have been observed and characterized.

Why are the other clusters in Table 1 not observed? We note that an element of chance is involved in the observations. For one thing, tunable laser coverage may be incomplete. As well, even with a low effective rotational temperature (≈2.5 K), spectra are often densely crowded, with many assigned and unassigned lines. A new vibrational band is more likely to be recognized, and then analyzed, if it happens to lie in a clear

region, free from other bands. Clear regions are more likely as we move away from the monomer band origin of the chromophore of interest (in the present case: CO₂ ν₃, 2349.143 cm⁻¹). Bands arising from more symmetric clusters are more likely to be recognized. This is not only because higher symmetry results in distinctive patterns, but also because spectral features are stronger, since individual transitions tend to coincide (as in a symmetric rotor) and equivalent chromophores boost the vibrational transition moment. So the relatively high symmetry of the clusters reported here may have contributed to their detection. Although luck may always be a factor, we can hope to minimize its influence as experimental techniques and theoretical predictions improve.

The present results contribute further examples to a growing list¹² of “larger” weakly-bound molecular clusters that have been studied by high-resolution spectroscopy. In the case of our mixed CO₂-C₂H₂ clusters, a relatively simple distributed multipole potential energy model was successful in predicting not only the most stable isomers, but even their detailed structures. However this may be a favorable case, aided by the fact that the density of low-lying isomers is not too high. The OCS tetramer⁸ is perhaps a counter-example: for it the density of isomers is very high (at least 20 within 100 cm⁻¹ of the global minimum) and a highly accurate pair potential is thus required to safely distinguish the most stable structure.

There has been extensive study of carbon dioxide-acetylene mixed crystals and aerosols.²⁶⁻²⁸ Co-crystals with 1:1 stoichiometry have been observed spectroscopically, but it seems that this phase is metastable and so it has not yet been possible to characterize its structure by x-ray crystallography. Direct links between these results and the present ones are not obvious, but the underlying physics is the same and the rectangular (box-like) shape of our observed hexamer is certainly reminiscent of possible mixed crystal structures.²⁸ Pure rotational microwave observation of the present hexamer is not allowed by symmetry, but the pentamer should be detectable by means of *a*-type transitions, in which case more detailed structural determinations will be possible by means of isotopic substitution.

Acknowledgements

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