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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1080/00268976.2010.496742>

Molecular Physics, 108, 17, pp. 2195-2205, 2010-09-10

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INVITED ARTICLE

High-resolution infrared spectroscopy of carbon dioxide dimers, trimers, and larger clusters

M. Dehghany^a, A.R.W. McKellar^{b*}, Mahin Afshari^a and N. Moazzen-Ahmadi^{a*}

^aDepartment of Physics and Astronomy, University of Calgary, 2500 University Drive North West, Calgary, Alberta T2N 1N4, Canada; ^bSteacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

(Received 13 April 2010; final version received 19 May 2010)

From 1984 to 1996 there was rapid progress in the spectroscopy of CO₂ dimers and trimers, but since then little work has appeared. Here we report a number of new high-resolution infrared results. For the dimer, a combination band provides the first experimental intermolecular vibrational frequency, and ¹³C isotopic spectra clarify the role of resonant and non-resonant vibrational shifts. For the cyclic trimer, a new parallel combination band involving an out-of-plane intermolecular mode is observed, and various ¹³C isotope results are analysed. In addition to these dimer and trimer results, the spectra also contain features which must be due to larger (CO₂)_N clusters in the range $N \approx 5$ –15.

Keywords: carbon dioxide; dimer; trimer; cluster; spectroscopy

1. Introduction

The aggregation of individual carbon dioxide molecules into dimers, trimers, clusters, larger aerosol particles, and ultimately into the bulk condensed phases is of considerable interest in terms of its basic aspects (intermolecular forces, nucleation, condensation) as well as applications (atmospheric sciences, supercritical solvation). The carbon dioxide dimer was one of the first weakly bound van der Waals complexes to be studied by high-resolution infrared spectroscopy. In 1984, Miller and Watts [1] observed sharp lines corresponding to the resolved (CO₂)₂ rotational structure in the 3700 cm⁻¹ region of the $\nu_1 + \nu_3/2\nu_2 + \nu_3$ combination bands of CO₂. Three years later, the analysis of this [2–4] and a corresponding spectrum [5] in the ν_3 fundamental band region (~ 2350 cm⁻¹) showed that the dimer has a planar slipped-parallel structure with centrosymmetric C_{2h} symmetry. Around the same time, an interesting symmetric-top spectrum of the CO₂ trimer in the 3700 cm⁻¹ region was studied by Fraser *et al.* [6], who derived a planar cyclic structure with C_{3h} symmetry. Later, this same cyclic form of (CO₂)₃ was observed in the 2350 cm⁻¹ region by Weida *et al.* [7], who proceeded to discover a distinct non-planar isomer of the trimer having a sort of twisted barrel shape with C₂ symmetry and an asymmetric rotor spectrum [8].

In the intervening 15 years, new experimental results on high-resolution spectroscopy of CO₂

clusters have been rare. There were only two publications, both involving the ν_3 fundamental region: Konno and Ozaki [9] observed the ¹⁸O-substituted dimer, (¹²C¹⁸O₂)₂, and Dehghany *et al.* [10] studied a combination band of the cyclic trimer involving an out-of-plane vibrational mode. In the present paper, we offer additional spectroscopic data on CO₂ clusters as observed in the monomer ν_3 fundamental region. For the dimer, a weak combination band is analysed, and the fundamental bands of fully and partially ¹³C-substituted isotopomers are studied in detail. For the cyclic trimer, a second combination band involving out-of-plane vibration is discovered, and ¹³C-substituted isotopomers are observed. We also describe a few new bands involving larger (CO₂)_N clusters with $N \approx 5$ –15.

In addition to the high-resolution studies already mentioned, there has of course been other spectroscopic work where rotational structure was not resolved. Much attention has centred on the CO₂ $\nu_1/2\nu_2$ Fermi-doublet bands around 1300 cm⁻¹ where absorption by isolated monomers is forbidden (except for asymmetrically substituted forms like ¹⁶O¹²C¹⁸O), enabling features due to dimers to be observed using relatively high sample pressures. Dimer spectra were reported in 1971 by Mannik *et al.* [11], who ascribed the observed band contours to T-shaped (CO₂)₂, and much further interest has been shown in these 7 μ m dimer bands [12–15]. Is it necessary to invoke T-shaped

*Corresponding authors. Emails: robert.mckellar@nrc-cnrc.gc.ca; ahmadi@phas.ucalgary.ca

(or other) geometries which differ from the ‘known’ C_{2h} structure in order to explain these bands? Ultimately it seems that they can successfully be modelled in terms of the known structure [16]. Dimers in the $\nu_1/2\nu_2$ spectral region have also been studied by Raman spectroscopy in a supersonic jet [17–19]. Larger clusters have been observed in jets [20–22] and cryogenic cells [23–25] by means of infrared spectroscopy and other techniques [26].

Theoretical descriptions of the intermolecular potential function describing the forces between two CO_2 molecules have a long history because of the fundamental nature and practical importance of this system. Noteworthy among more recent *ab initio* results are a comprehensive study by Bukowski *et al.* [27] using SAPT (symmetry adapted perturbation theory), a high-level CCSD(T) study of dimer and trimer geometries by Tsuzuki *et al.* [28], and a large MP2 study by Bock *et al.* [29]. Simpler empirical potential energy models are often used to simulate the properties of large CO_2 clusters as well as the bulk liquid and solid phases, and that of Murthy *et al.* [30,31] has been especially popular. This is a large and active area of research; for a recent discussion, see Ref. [32].

The experimental results described in the present paper were obtained using a pulsed supersonic slit-jet expansion of dilute mixtures of carbon dioxide ($\sim 0.2\%$) in helium carrier gas. All the spectra were recorded by direct absorption using a rapid-scan tuneable diode laser spectrometer at The University of Calgary, as described previously [33–36]. Wavenumber calibration was ensured by simultaneously recording signals from a fixed etalon and a room temperature reference gas cell, which was usually filled with CO_2 or N_2O . Spectra were assigned, simulated, and fitted using Colin Western’s computer program PGOPHER [37]. Table 1 lists the wavenumber ranges that were surveyed for the present work. Although the coverage is fairly good, it is of course still restricted by the tuning ranges of our available diode laser sources and the limited supply of isotopically substituted gas.

2. New results for the CO_2 dimer

2.1. $(^{12}C^{16}O_2)_2$

The spectrum of the normal isotope of $(CO_2)_2$ in the ν_3 fundamental band region has already been well studied in the pioneering work of Walsh *et al.* [5]. Here we report our own analysis of this spectrum, not so much because of improvements (which are slight), but rather for consistency with the ^{13}C results described below.

Table 1. Wavenumber ranges surveyed in the present work.

Gas	Range (cm^{-1})
$^{12}C^{16}O_2$	2346.2–2356.7
	2360.6–2372.5
	2377.2–2379.1
$^{13}C^{16}O_2$	2380.3–2383.1
	2283.3–2288.0
	2297.5–2299.2
$^{12}C^{16}O_2 + ^{13}C^{16}O_2$	2281.4–2287.9
	2297.8–2298.8

Compared with Ref. [5] the main improvement here is a narrower line width (~ 0.0017 vs. 0.004 cm^{-1}) resulting from a jet source with a slit (rather than pinhole) nozzle. This is illustrated in the top panel of Figure 1, which covers the same region as shown in Ref. [5]. In our analysis, we assigned a total of 144 observed lines to 149 transitions. These were fitted [37] to a conventional A -reduced asymmetric rotor Hamiltonian in the I' representation [38], varying the band origin, rotational constants, and all quartic centrifugal distortion parameters, with results as given in Table 2. As in Ref. [5], we noticed no perturbations in the spectrum. The root mean square (rms) deviation of the fit was less than 0.00013 cm^{-1} . The simulation shown in Figure 1 is based on the parameters of Table 2, and assumes a value of 1.16 for the ratio of the b-type to a-type dipole transition moments.

The parameters in Table 2 agree well with previous studies. Our band origin is 0.0008 cm^{-1} lower than that of Ref. [5], which is much larger than the rms deviation but not excessive in terms of the systematic uncertainties in absolute wavenumber calibration of diode laser spectra, both here and in Ref. [5]. The rotational constants also differ somewhat, but this is mainly due to the fact that the centrifugal distortion parameters were varied here but not in Ref. [5]. Our ground state parameters, including the distortion terms, also agree remarkably well with those of Ref. [3] (see Table 2), which were based on dimer spectra in the $\nu_1 + \nu_3/2\nu_2 + \nu_3$ region.

2.2. $(^{13}C^{16}O_2)_2$

We recorded and analysed the spectrum of the fully ^{13}C -substituted CO_2 dimer for its own sake, and also because we wanted to study spectra involving mixtures of $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$ (see below). This band occurs in the region from about 2283 to 2288 cm^{-1} , and the middle panel of Figure 1 shows part of this range

Figure 1. Part of the fundamental band of the CO₂ dimer for (¹²C¹⁶O₂)₂, (¹³C¹⁶O₂)₂, and ¹²C¹⁶O₂–¹³C¹⁶O₂. An analogous range is covered for each isotopomer, but this is not so obvious since the nuclear spin statistics are different. The asterisks mark lines that are partly or entirely due to the He–CO₂ complex. The simulations use parameters from Table 2, an effective rotational temperature of 3 K, and an assumed Gaussian linewidth of 0.0017 cm^{−1}.

which corresponds to that for (¹²C¹⁶O₂)₂ in the top panel. The observed line density is higher for (¹³C¹⁶O₂)₂ because half the rotational levels are missing for (¹²C¹⁶O₂)₂ (those with $K_c = \text{odd}$) due to nuclear spin statistics, whereas all levels are allowed for (¹³C¹⁶O₂)₂ (with a weight of 1:3 for $K_c = \text{even:odd}$). Analysis of the (¹³C¹⁶O₂)₂ band was straightforward, and we assigned a total of 111 observed lines in terms of 129 transitions. Results of the fit are given in Table 2. Since the data were less extensive than for the normal isotopomer, we fixed the off-diagonal

distortion parameters δ_K and δ_J at their (¹²C¹⁶O₂)₂ values in the fit. The rms deviation (about 0.00028 cm^{−1}) was larger than for (¹²C¹⁶O₂)₂, most likely because the greater line density results in weaker lines and more blended transitions.

2.3. ¹²C¹⁶O₂–¹³C¹⁶O₂

We expected the mixed dimer, ¹²C¹⁶O₂–¹³C¹⁶O₂, to have two fundamental bands corresponding to the CO₂ ν_3 vibration, one in the ¹³C¹⁶O₂ region (~ 2283 cm^{−1}) and the other in the ¹²C¹⁶O₂ region (~ 2349 cm^{−1}). In order to observe the spectrum while minimizing interference due to (¹³C¹⁶O₂)₂, we looked in the ¹³C¹⁶O₂ region using a 1:2 mixture of ¹³C¹⁶O₂ and ¹²C¹⁶O₂. A remarkably clean spectrum was observed between about 2282 and 2284 cm^{−1}, part of which is shown in the bottom panel of Figure 1. Since the two monomers in the dimer are not equivalent (it has C_s symmetry), the line density is similar to that of (¹³C¹⁶O₂)₂ but with all rotational levels having equal weight. The analysis was again quite easy, and a total of 176 observed lines were assigned in terms of 200 transitions. An rms deviation of 0.00022 cm^{−1} was achieved and the results of the least-squares fit are given in Table 2. No obvious perturbations were noted here, nor in the (¹²C¹⁶O₂)₂ and (¹³C¹⁶O₂)₂ spectra. Compared with (¹³C¹⁶O₂)₂, it was possible to assign more lines and obtain a better fit because there was less overlapping from spectra of trimers and larger clusters, especially in the R-branch region.

Not surprisingly, the rotational parameters for the mixed dimer are intermediate between those of (¹²C¹⁶O₂)₂ and (¹³C¹⁶O₂)₂ (except for A'). But it is the band origin that contains new information, since the nature of the vibration is fundamentally different in the mixed dimer. In the homodimers, each monomer stretching mode results in two dimer vibrations, corresponding to in-phase or out-of-phase monomer vibrations. Transitions involving the in-phase (A_g symmetry) combinations are infrared-forbidden because the two oscillating dipoles exactly cancel. Only the out-of-phase (B_u symmetry) combinations are infrared-allowed, and these are the bands which have been observed here and in Refs. [1–5,9] for (¹²C¹⁶O₂)₂, (¹³C¹⁶O₂)₂, and (¹²C¹⁸O₂)₂. But in a heterodimer like ¹²C¹⁶O₂–¹³C¹⁶O₂, the two possible dimer vibrations accompanying each monomer mode are predominantly localized on one or the other monomer, and both are allowed.

Weida *et al.* [7] discussed vibrational effects for the dimer in the CO₂ ν_3 region, and concluded that most of the observed 1.63 cm^{−1} blue shift for (¹²C¹⁶O₂)₂ is due

Table 2. Molecular parameters for the CO₂ dimer (in cm⁻¹).^a

	(¹² C ¹⁶ O ₂) ₂	(¹² C ¹⁶ O ₂) ₂	(¹³ C ¹⁶ O ₂) ₂	¹² C ¹⁶ O ₂ – ¹³ C ¹⁶ O ₂
	[3]	Present work	Present work	Present work
ν_0		2350.7713(1)	2285.0787(1)	2283.0619(1)
A'		0.300532(13)	0.299743(30)	0.298421(20)
B'		0.0533191(45)	0.0522859(71)	0.0530885(40)
C'		0.0451288(38)	0.0443694(71)	0.0449208(39)
$10^5 \times \Delta'_K$		1.257(74)	0.949(148)	1.309(109)
$10^6 \times \Delta'_{JK}$		–2.46(19)	–2.73(41)	–2.45(37)
$10^7 \times \Delta'_J$		2.49(21)	3.00(58)	2.34(25)
$10^6 \times \delta'_K$		2.92(110)	2.92 ^b	2.92 ^b
$10^8 \times \delta'_J$		5.79(97)	5.79 ^b	5.79 ^b
A''	0.3002815(39)	0.300260(10)	0.299527(39)	0.299920(19)
B''	0.0536041(13)	0.0535962(37)	0.0525612(64)	0.0530685(40)
C''	0.0453370(13)	0.0453295(32)	0.0445745(67)	0.0449208(39)
$10^5 \times \Delta''_K$	1.343(33)	1.245(37)	0.78(35)	1.31(10)
$10^6 \times \Delta''_{JK}$	–2.393(61)	–2.32(13)	–2.34(52)	–2.30(30)
$10^7 \times \Delta''_J$	2.831(55)	2.43(16)	3.87(50)	2.11(22)
$10^6 \times \delta''_K$	1.40(46)	1.41(76)	1.41 ^b	1.41 ^b
$10^8 \times \delta''_J$	5.79(32)	5.34(73)	5.34 ^b	5.34 ^b

Notes:^aUncertainties in parentheses are 1 σ from the least-squares fits in units of the last quoted digit.

^bThese parameters were fixed.

to a resonant dipole–dipole interaction, with any remaining non-resonant shifts being of the order of 0.1 cm⁻¹. The implication is that this blue shift is balanced by an approximately equal red shift for the forbidden A_g mode, which must then be located at about 2347.5 cm⁻¹.

These ideas can now be tested using our new mixed dimer results. We assume that the dimer vibrational shifts are the sums of a ‘non-resonant’ diagonal term which is the same for the A_g and B_u modes, and a ‘resonant’ off-diagonal term which couples them, a situation similar to that described for the NO dimer [39]. The off-diagonal term is likely due mostly to the resonant dipole–dipole interaction, but could have other contributions. We further assume that the non-resonant and resonant terms are isotopically independent except for a simple scaling factor proportional to the CO₂ monomer ν_3 frequency (this scaling actually has little effect on the result). Solving for the vibrational shifts, we obtain a non-resonant term of –0.37 cm⁻¹ and a resonant term of 2.0 cm⁻¹. The predicted positions of the forbidden A_g mode are then 2346.76 and 2281.17 cm⁻¹ for (¹²C¹⁶O₂)₂ and (¹³C¹⁶O₂)₂, respectively. The predicted position of the ¹²C¹⁶O₂–¹³C¹⁶O₂ vibration in the ¹²C¹⁶O₂ region is 2348.83 cm⁻¹.

These results indicate that Weida *et al.* [7] were essentially correct: the non-resonant CO₂ dimer

vibrational shift is indeed small, though not quite as small as 0.1 cm⁻¹. The observed shifts are mostly due to a resonant effect, that is a perturbation term that pushes the A_g and B_u modes apart. Qualitatively, this conclusion was already evident from the fact that our mixed dimer (¹²C¹⁶O₂–¹³C¹⁶O₂) band origin (2283.06 cm⁻¹) was located close to the monomer origin (2283.49 cm⁻¹).

2.4. Dimer combination band at 2382.28 cm⁻¹

In spite of considerable searching (Table 1), we have so far been able to detect only one CO₂ dimer combination band. It is centred at 2382.28 cm⁻¹, and gives quite a clear and unambiguous spectrum. Part of the observed band is illustrated in Figure 2(a) together with our simulation. We assigned 94 observed lines in terms of 96 b-type transitions with values of J' and K'_a up to 11 and 4. These were fitted by varying the upper state parameters indicated in Table 3, while keeping the lower state parameters fixed at the values determined from the fundamental band (Table 2). The rms deviation of the fit was 0.00017 cm⁻¹.

Since this band has b-type selection rules, its upper state must have B_u symmetry. This can arise in two different ways, either as the sum of the allowed B_u intramolecular mode (2350.77 cm⁻¹) plus an A_g intermolecular mode, or as the sum of the forbidden

Figure 2. Portions of the observed and simulated combination bands of (a) the CO₂ dimer and (b) the CO₂ trimer. Parameters used for the simulations are from Tables 3 and 4.

Table 3. Molecular parameters for a ¹²C¹⁶O₂ dimer combination band (in cm⁻¹).^a

	(¹² C ¹⁶ O ₂) ₂
	Combination band
ν_0	2382.2804(1)
A'	0.308080(14)
B'	0.0496955(43)
C'	0.0428974(32)
$10^5 \times \Delta'_K$	4.15(11)
$10^6 \times \Delta'_{JK}$	0.470(18)
$10^7 \times \Delta'_J$	1.05(17)

Note:^aUncertainties in parentheses are 1σ from the least-squares fits in units of the last quoted digit. The remaining centrifugal distortion parameters were fixed at the ground state values from the present work (Table 2).

A_g intramolecular mode plus a B_u intermolecular mode. In the former case, the intermolecular frequency is exactly 31.509 cm⁻¹. In the latter case it is approximately 35.5 cm⁻¹ (using 2346.76 cm⁻¹ for the A_g intramolecular mode from the previous section).

There are four intermolecular modes: van der Waals stretch (A_g), symmetric in-plane bend (A_g), antisymmetric in-plane bend (B_u), and out-of plane torsion (A_u). Thus the combination band could be the stretch or symmetric bend at 31.5 cm⁻¹ or the antisymmetric bend at 35.5 cm⁻¹, assuming that the intermolecular mode is a fundamental one.

But this assumption is not necessarily valid. Chen and Light [40] made detailed calculations of CO₂ dimer intermolecular vibrations based on a high-quality potential energy surface [27], and the energies, symmetries, and most likely assignments of their first six excited states are as follows:

- (1) 19.69 cm⁻¹, B_u antisymmetric bend fundamental.
- (2) 22.62 cm⁻¹, A_u out-of-plane torsion fundamental.
- (3) 29.45 cm⁻¹, A_g antisymmetric bend overtone.
- (4) 39.30 cm⁻¹, B_u antisymmetric bend second overtone.
- (5) 40.84 cm⁻¹, A_g van der Waals stretch fundamental.
- (6) 41.01 cm⁻¹, B_g antisymmetric bend plus torsion combination.
- (7) 44.35 cm⁻¹, A_g out-of-plane torsion overtone.

The best possibilities for agreement with our observed combination band seem to be the A_g states at 29.45 or 40.84 cm⁻¹ (compared with our 31.509 cm⁻¹ value) or the B_u state at 39.30 cm⁻¹ (compared with our 35.5 cm⁻¹ value). The two closer possibilities would mean that the intermolecular mode is not a fundamental, and the observed band is a ternary combination. This would be unlikely in a normal molecule, but in a weakly bound complex there can be extensive mixing of intermolecular modes (as shown in Ref. [40]) and so the observation of a ternary combination band is not out of the question. Note of course that the calculations [40] are for the ground intramolecular state of the CO₂ dimer, whereas our observations refer to the excited ν_3 monomer state. But changes in intermolecular vibrations as a function of intramolecular excitation are usually considered to be small for weakly bound complexes [41].

The centrifugal distortion parameters obtained for the upper state of the combination band in Table 3 are somewhat different from those of the ground state or the fundamental band (Table 2). This may indicate the presence of perturbations from other intermolecular modes. There are also rather large changes of the A , B , and C rotational constants in the combination band. Using them we obtain an effective upper state structure of $R = 3.73$ Å, $\theta = 56.7^\circ$. Compared with the ground state values (3.60 Å, 58.0°), this corresponds to a rather

large increase in the intermolecular centre-of-mass separation and a small change in the angle between the intermolecular and monomer axes. This seems consistent with excitation of the van der Waals stretch, but the complicated mixing of intermolecular modes [40] makes it dangerous to jump to conclusions. Also, there is the possibility that one or more upper state constants is affected by Coriolis interactions with other intermolecular modes [42]. A further clue about the combination band comes from its predominantly b-type character. We estimate that the ratio of a-type to b-type dipole moment components is no greater than about 0.25, as compared with the fundamental band where this ratio is about 0.86. But it is difficult to draw simple geometrical conclusions from this for a combination band since the direction of the transition dipole depends on anharmonic electrical and mechanical interactions between the two (or more) modes involved in the combination.

3. New results for the CO₂ trimer

3.1. Trimer combination band at 2370.49 cm⁻¹

Two isomers are known for the CO₂ trimer: a planar cyclic symmetric top with C_{3h} symmetry in which all three CO₂ monomers are equivalent [6,7], and a barrel-shaped asymmetric top with C₂ symmetry and two equivalent monomers [8]. The fundamental bands of the cyclic trimer in the CO₂ ν₃ region consist of an infrared-inactive mode with A' symmetry corresponding to the in-phase combination of the three ν₃ monomer vibrations, and a degenerate out-of-phase mode with E' symmetry which gives rise to the observed [7] perpendicular (Δ*K* = ±1) band at 2351.72 cm⁻¹. Recently, we analysed a parallel (Δ*K* = 0) combination band of the cyclic trimer at 2364.02 cm⁻¹ involving an out-of-plane vibration [10]. It has a rather simple and beautiful structure, in part because only rotational levels with *K* = 3*n* are populated due to the zero nuclear spins of ¹²C¹⁶O₂ and the C_{3h} symmetry of the trimer. It establishes a value of 12 to 13 cm⁻¹ for an out-of-plane intermolecular bending frequency. There are two ways to obtain the observed A'' upper state, which can either be the combination of the forbidden A' intramolecular fundamental plus the symmetric A'' intermolecular out-of-plane bend, or the combination of the allowed E' intramolecular fundamental plus the degenerate E'' intermolecular out-of-plane bend. The latter combination gives rise to two A'' vibrations, so there should actually be three possible binary combination bands involving out-of-plane vibrations. We favoured [10] the former assignment (A' + A'') for the 2364.02 cm⁻¹ band, but in any case it

was clear that more such parallel bands might be observable.

We have now found a second (CO₂)₃ parallel combination band located about 6.47 cm⁻¹ above the original one. The new one ('band II') is weaker than the original ('band I'), but it is difficult to be quantitative about this because of changes in laser power and other experimental parameters. Band II is also more obscured by unrelated (and unassigned) transitions, but otherwise its appearance is similar to band I. Neither band shows any obvious effects of perturbations. The P-branch is most affected by the obscuration, so in Figure 2(b) we illustrate the Q- and R-branch regions. Analysis of this trimer combination band yields the band II parameters given in Table 4, where those of the ground state [7] and band I [10] are also listed for comparison. In both combination bands, the upper state *C* parameter increases, but for band II this change is smaller. For this reason, the *K*-structure of the Q-branch is more compact and the *K* = 3 and 6 components are no longer resolved from each other.

So now we have two intermolecular bending frequencies for the cyclic CO₂ trimer: 12–13 cm⁻¹ for band I, and 18.5–19.5 cm⁻¹ for band II. But there is still the question of their assignment in terms of the possible (A' + A'') and (E' + E'') combinations. At the moment, we cannot think of any clear criteria for this assignment, except perhaps that the relatively large separation (6.47 cm⁻¹) of the two bands suggests that they are not the (E' + E'') pair, since this pair, though not itself degenerate, does arise from a single degenerate E'' intermolecular mode. Ultimately we should keep in mind that the three possible upper states may be mixed and inherently difficult to distinguish from each other since they all have the same A'' symmetry.

3.2. (¹³C¹⁶O₂)₃

We observed the fundamental perpendicular band of cyclic (¹³C¹⁶O₂)₃ in the 2285–2287 cm⁻¹ region. All rotational levels are populated for this isotopomer with equal nuclear spin weights for ground state levels of A and E symmetry, whereas only A levels (those with *K* = 3*n*) are possible for the normal species. So the (¹³C¹⁶O₂)₃ band has many more transitions, as does the (¹³C¹⁶O₂)₂ spectrum which partially overlaps. This added congestion, combined with the fact that our spectral resolution is not quite as good as in Ref. [7], means that an equally detailed analysis was not possible. Key to the assignment was a fortuitous piling-up of transitions in the 'Q₀ branch [7] due to *l*-type doubling. For (¹³C¹⁶O₂)₃, this gives a strong, sharp feature at 2285.932 cm⁻¹. In our analysis, we

Table 4. Molecular parameters for parallel combination bands of the planar cyclic trimer ($^{12}\text{C}^{16}\text{O}_2$)₃ involving out-of-plane intermolecular modes (in cm^{-1}).^a

	Combination band II	Combination band I	Ground state
	Present work	[10]	[7]
ν_0	2370.4886(1)	2364.0195(1)	
B	0.0397929(44)	0.0398332(13)	0.0398104
C	0.0200013(23)	0.0200528(15)	0.0199052
D_K	$0.158(27) \times 10^{-6}$	$0.105(11) \times 10^{-6}$	0.084×10^{-6}
D_{JK}	$-0.261(46) \times 10^{-6}$	$-0.184(14) \times 10^{-6}$	-0.140×10^{-6}
D_J	$0.088(25) \times 10^{-6}$	$0.085(6) \times 10^{-6}$	0.0551×10^{-6}

Note:^aUncertainties in parentheses correspond to 1σ from the least-squares fit in units of the last quoted digit. In the combination band fits, the ground state parameters were fixed at the indicated values.

fixed the centrifugal distortion parameters and l -type doubling parameters at their ($^{12}\text{C}^{16}\text{O}_2$)₃ values [7] and obtained the results listed in Table 5. We also observed the cyclic ($^{13}\text{C}^{16}\text{O}_2$)₃ parallel combination band analogous to band I of ($^{12}\text{C}^{16}\text{O}_2$)₃, with results that are also given in Table 5.

The cyclic ($^{13}\text{C}^{16}\text{O}_2$)₃ fundamental band origin determined here represents a shift of $+2.464\text{cm}^{-1}$ with respect to the monomer, which is slightly less than the value of $+2.503\text{cm}^{-1}$ obtained by simple scaling of the ($^{12}\text{C}^{16}\text{O}_2$)₃ shift. The parallel band origin is shifted by 12.303cm^{-1} with respect to the trimer fundamental, as compared with 12.301cm^{-1} for combination band I of ($^{12}\text{C}^{16}\text{O}_2$)₃. This close agreement is presumably a reflection of the fact that there is little or no motion of the C atoms during the out-of-plane intermolecular vibrations.

Turning to the non-cyclic trimer ($^{13}\text{C}^{16}\text{O}_2$)₃, we observed the Q-branch of ‘band III’ as observed for the normal isotopomer in Ref. [8], which occurs about 1.0cm^{-1} above the origin of the cyclic trimer fundamental, but did not scan the region of non-cyclic trimer ‘band I’. Due to spectral congestion and the relative weakness of the band, we were not able to analyse band III in detail, but our simulation did yield a band origin of $2286.977(2)\text{cm}^{-1}$. This represents a shift of $+3.490\text{cm}^{-1}$ with respect to the monomer, as compared with $+3.578\text{cm}^{-1}$ for non-cyclic ($^{12}\text{C}^{16}\text{O}_2$)₃.

3.3. ($^{13}\text{C}^{16}\text{O}_2$)-($^{12}\text{C}^{16}\text{O}_2$)₂ and ($^{13}\text{C}^{16}\text{O}_2$)₂- ($^{12}\text{C}^{16}\text{O}_2$)

Using a 1:2 mixture of $^{13}\text{C}^{16}\text{O}_2$ and $^{12}\text{C}^{16}\text{O}_2$ in He carrier gas as described above, we surveyed the

Table 5. Molecular parameters for the planar cyclic trimer ($^{13}\text{C}^{16}\text{O}_2$)₃ (in cm^{-1}).^a

	Fundamental band ^b	Parallel combination band I	Ground state
ν_0	2285.9512(1)	2298.2540(1)	
B	0.0389917(39)	0.0390806(43)	0.0390472(49)
C	0.0196080(38)	0.0197781(46)	0.0196345(41)

Notes:^aUncertainties in parentheses correspond to 1σ from the least-squares fit in units of the last quoted digit. Centrifugal distortion parameters were fixed at their ($^{12}\text{C}^{16}\text{O}_2$)₃ values (see Ref. [7] and Table 4).

^b q was fixed at its ($^{12}\text{C}^{16}\text{O}_2$)₃ value and ζ^c was fixed to zero [7].

$2285\text{--}2287\text{cm}^{-1}$ region for evidence of partially ^{13}C -substituted cyclic CO_2 trimers. The good news was that two new series of features were observed which were clearly due to these trimers, but the bad news was that definitive assignment was difficult. When the cyclic trimer is partially substituted, it becomes a very-near-oblate asymmetric rotor ($A \approx B \approx 2C$) with no symmetry except for planarity. The perpendicular bands of such a molecule are made up of a series spaced by about $2C$ whose centre is not easily located. One of these two new mixed trimer bands was about twice as strong as the other, and we suspect that it is due to the singly substituted species ($^{13}\text{C}^{16}\text{O}_2$)-($^{12}\text{C}^{16}\text{O}_2$)₂ while the weaker band is due to the doubly substituted one ($^{13}\text{C}^{16}\text{O}_2$)₂- ($^{12}\text{C}^{16}\text{O}_2$). We also made a fragmentary observation in the region of parallel combination band I, and observed two new mixed-isotope bands with a similar 2:1 intensity ratio. The separation of their Q-branches was also similar to the apparent (but less certain!) separation of the origins in the fundamental region.

Using these spectroscopic observations together with predicted rotational constants based on the known [7] trimer structure, a set of parameters based on our most likely assignment was derived. They are given in Table 6, but no statistical uncertainties are included because of the very empirical way in which this ‘fit’ was made. For example, the asymmetry parameters ($A-B$) were fixed at an estimated value since the observed spectra were not sensitive to this quantity. The chosen fundamental band origins were those that gave the best fit, but it is important to note that these can be moved up or down in steps of about 0.0395cm^{-1} without too much effect. The assignments of the bands to the two isotopomers, ($^{13}\text{C}^{16}\text{O}_2$)-($^{12}\text{C}^{16}\text{O}_2$)₂ and ($^{13}\text{C}^{16}\text{O}_2$)₂- ($^{12}\text{C}^{16}\text{O}_2$), were made on the basis of the observed intensities and rotational constants, but even this is not completely certain. It is

Table 6. Molecular parameters for partially ^{13}C -substituted cyclic CO_2 trimers (in cm^{-1}).^a

	$(^{13}\text{C}^{16}\text{O}_2)-(^{12}\text{C}^{16}\text{O}_2)_2$		$(^{13}\text{C}^{16}\text{O}_2)_2-(^{12}\text{C}^{16}\text{O}_2)$	
	Perpendicular fundamental band	Parallel combination band I	Perpendicular fundamental band	Parallel combination band I
ν^0	2285.7735	2298.0506	2286.0050	2298.3312
A'	0.03961	0.03970	0.03939	0.03948
B'	0.03921	0.03930	0.03899	0.03908
C'	0.019781	0.019947	0.019635	0.019784
A''		0.03965		0.03943
B''		0.03925		0.03903
C''		0.01980		0.01966

Note:^aCentrifugal distortion parameters were fixed at zero. Parameter uncertainties are not given because of the highly empirical nature of the fit (see text).

interesting that the shifts between the fundamental and combination bands (12.277 and 12.326 cm^{-1} , respectively) are almost identical to the values observed for $(^{12}\text{C}^{16}\text{O}_2)_3$ and $(^{13}\text{C}^{16}\text{O}_2)_3$ (12.301 and 12.303 cm^{-1}), but we caution that this was one of the criteria used in the assignment.

The species $(^{13}\text{C}^{16}\text{O}_2)-(^{12}\text{C}^{16}\text{O}_2)_2$ should have one fundamental band in the $^{13}\text{C}^{16}\text{O}_2$ region, and we believe this is the 2285.7 cm^{-1} band as indicated in Table 6. But $(^{13}\text{C}^{16}\text{O}_2)_2-(^{12}\text{C}^{16}\text{O}_2)$ should have two fundamentals in the $^{13}\text{C}^{16}\text{O}_2$ region, and we only observed one, the 2286.0 cm^{-1} band in Table 6. This remains a puzzle, for which one possible solution is that the two $(^{13}\text{C}^{16}\text{O}_2)_2-(^{12}\text{C}^{16}\text{O}_2)$ bands are almost coincident and remain unresolved in our spectrum. The fact that the mixed trimer fundamentals are only slightly shifted ($<0.2\text{ cm}^{-1}$) from that of $(^{13}\text{C}^{16}\text{O}_2)_3$ seems to contradict the (apparently successful) resonant dipole model [7] which would predict that they should lie closer to the monomer origin (2283.5 cm^{-1}). But this tends to support a later finding by Boychenko and Huber [43] that the resonant dipole interaction is not actually dominant for the cyclic trimer.

A new Q-branch feature appears in the mixed $^{13}\text{C}^{16}\text{O}_2$ and $^{12}\text{C}^{16}\text{O}_2$ spectrum at 2287.121 cm^{-1} which we tentatively assign to the non-cyclic trimer $(^{13}\text{C}^{16}\text{O}_2)-(^{12}\text{C}^{16}\text{O}_2)_2$ with the $^{13}\text{C}^{16}\text{O}_2$ monomer in the ‘top’ position [8], but it was not possible to assign any P- or R-branch transitions. This is just 0.144 cm^{-1} above the non-cyclic $(^{13}\text{C}^{16}\text{O}_2)_3$ band III origin mentioned in the previous section.

4. Larger CO_2 clusters

After accounting for all the known $(\text{CO}_2)_2$, $(\text{CO}_2)_3$, and $\text{CO}_2\text{-He}$ [44, 45] bands, our spectra still contain many other features. A few of these are described here, and

more complete details will be published later as their analysis proceeds.

In 1995, Weida *et al.* [7] observed two prominent Q-branch features of roughly equal intensity at 2352.60 and 2352.72 cm^{-1} , labelled Q_A and Q_B , respectively. Their dependence on jet backing pressure seemed to indicate that they were due to CO_2 trimers. Indeed, Q_B turned out to be band III of the non-cyclic CO_2 trimer, but Q_A remained unassigned and they concluded that it “is probably due to a $(\text{CO}_2)_N$ cluster where $N \geq 4$ ” [8]. In our spectra, Q_A is more than twice as strong as Q_B , but as in Ref. [8] we are unable to assign any patterns in the accompanying P- and R-branch regions, where there is a lot of interference from CO_2 dimers, from both CO_2 trimers, and from other unassigned bands. The analogous Q_A feature in the $^{13}\text{C}^{16}\text{O}_2$ region occurs at 2286.83 cm^{-1} . The fact that P- and R-branch patterns are not apparent suggests that the species responsible is an asymmetric rotor, since increasing asymmetry has the effect of spreading out the intensity into a more or less continuous series of transitions. Perhaps the most likely candidate, based on the pressure dependence seen by Weida *et al.* [7], is the CO_2 tetramer. There appear to be no high-level *ab initio* calculations for $(\text{CO}_2)_4$, but recent simulations [46,47] obtain trigonal bipyramid shapes giving an asymmetric rotor with $(A, B, C) \approx (0.026, 0.022, 0.018\text{ cm}^{-1})$. Our simulated spectra indicate that this sort of cluster could possibly be responsible for the Q_A feature, particularly if the transition dipole involves two or three of the possible a-, b-, and c-type transitions since this helps to spread out the P- and R-branch intensities even more.

Figure 3 shows three newly observed features which resemble the parallel bands of symmetric (or near-symmetric) rotor molecules. The top panel shows a regular line series around $2354.5\text{--}2355.1\text{ cm}^{-1}$ which seems to be an R-branch with its Q-branch at

2354.49 cm^{-1} . The accompanying P-branch is heavily obscured and seems to be weaker than expected, but can still be identified. A fit to this band (shown by the simulation) gives $\nu_0 = 2354.489$, $B'' = 0.01171\text{ cm}^{-1}$. The A (or C) constant is not well determined, but a value of $\approx 0.014\text{ cm}^{-1}$ gives a reasonable simulation of the relative Q- and R-branch intensities. The middle panel shows a rather similar feature centred near 2378.17 cm^{-1} , for which a fit gives $\nu_0 = 2378.172$, $B'' = 0.01201$, and $C'' \approx 0.010\text{ cm}^{-1}$. These two bands have rather similar (but not equal) B -values, which correspond roughly to those expected [47] for $(\text{CO}_2)_N$ clusters in the range $N \approx 5$ –7. The lower panel of Figure 3 shows another parallel-type band with more closely spaced lines. A fit to this feature gives $\nu_0 = 2361.149$, $B'' = 0.0049649$, and $C'' \approx 0.003\text{ cm}^{-1}$. This corresponds to the sort of B -value expected for a cluster with $N \approx 10$ [47].

The bands mentioned in the previous paragraph are only three out of many unexplained features noted in our spectra which must be due to CO_2 clusters. Relatively narrow single Q-branch-like features without obvious P- and R-branches are frequent. Some of these are visible, for example at 2370.804 and 2370.926 cm^{-1} in Figure 2 and at 2354.936 , 2378.133 , and 2378.423 cm^{-1} in Figure 3.

Finally, there is a region from about 2368.5 to 2370.5 cm^{-1} (not shown here) where we observe an extensive and irregular pattern of transitions, most strongly around 2369.2 cm^{-1} . Judging by the line density, these arise from a fairly small cluster or clusters ($N \approx 2$ –5), and judging from their position, they involve a combination band. But so far we have been unable to find any meaningful patterns or regularity.

5. Conclusions

The three unidentified bands mentioned in the previous section appear to be due to symmetric tops, whereas according to Ref. [47] only two of the calculated $(\text{CO}_2)_N$ minimum energy structures for $N = 4$ –15 are symmetric tops, those for $N = 6$ and 13. Of course, there may be other isomers present in the jet expansion in addition to these most stable forms. But there is also a selection effect which makes it more likely to observe and recognize symmetric clusters. Symmetry gives a simpler rotational structure which is more easily recognized, and tends to cause transitions to pile up on top of each other, leading to stronger features which are more easily detected. This is particularly true when rotational structure is only partially resolved, as is more likely with larger clusters. In addition, symmetry

Figure 3. Three CO_2 cluster absorption features that can be assigned as parallel bands of symmetric or nearly symmetric tops. The bands in the upper two panels have similar, but not identical, rotational constants which are appropriate for $(\text{CO}_2)_N$ with $N \approx 5$ –7. The band in the lower panel corresponds to $N \approx 10$.

also leads to degenerate vibrations and some forbidden modes, thus concentrating the total vibrational transition moment of a given cluster into fewer, stronger bands.

In the future, it should be possible to extend the present assignments of CO_2 dimer and trimer vibration–rotation bands to larger clusters. For this purpose, improved and more comprehensive theoretical calculations on CO_2 clusters in the size range $N \approx 4$ –20 would be very valuable. To date, most such work has tended to concentrate on methodology and/or thermodynamics rather than on accurate cluster structures, symmetry properties, and spectroscopic parameters. In this connection the recent work of Takeuchi [47] with its extensive Supporting Information is very useful, but even more such data is needed. For example, the more

likely low-energy isomer structures should be probed for each cluster size, and the effect of alternative potential functions should be investigated. The present results suggest that rotational resolution is at least partially possible for $(\text{CO}_2)_N$ clusters with $N \approx 10$ and even higher. We hope that our glimpse into this important and relatively unexplored intermediate size range will stimulate renewed interest in the high-resolution spectroscopy of CO_2 clusters.

Acknowledgements

We thank L. Murdock for technical assistance, J. Norooz Oliiae and F. Mivehvar for some of the measurements, and S.R. Gadre for some unpublished results. Many of our results were greatly facilitated by use of PGOPHER, and we are pleased to acknowledge C.M. Western for helpful advice and program updates. We gratefully acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada.

Note

All figures can be viewed in colour online.

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