New infrared spectra of CO$_2$–Xe: modelling Xe isotope effects, intermolecular bend and stretch, and symmetry breaking of the CO$_2$ bend

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ABSTRACT

The infrared spectrum of the weakly bound CO$_2$–Xe complex is studied in the region of the carbon dioxide $\nu_3$ fundamental vibration ($\approx 2350$ cm$^{-1}$), using a tunable OPO laser source to probe a pulsed supersonic slit jet expansion. The Xe isotope dependence of the spectrum is modelled by scaling the vibrational and rotational parameters, with the help of previous microwave data. The scaling model provides a good simulation of the observed broadening and (partial) splitting of transitions in the fundamental band, and it is essential for understanding the intermolecular bending combination band where some transitions are completely split by isotope effects. The combination band is influenced by a significant bend–stretch Coriolis interaction and by the relatively large Xe isotope dependence of the intermolecular stretch frequency. The weak CO$_2$–Xe spectrum corresponding to the (0111) $\leftarrow$ (0110) hot band of CO$_2$ is also detected and analysed, providing a measurement of the symmetry breaking of the CO$_2$ bending mode induced by the nearby Xe atom. This in-plane/out-of-plane splitting is determined to be 2.14 cm$^{-1}$.

1. Introduction

Rotationally resolved spectroscopy of weakly bound van der Waals complexes provides direct and specific information on intermolecular forces and dynamics. Dimers containing CO$_2$ and a rare gas (Rg) atom have been of notable experimental and theoretical interest, starting with the original observation of a microwave spectrum of CO$_2$–Ar by Steed et al. in 1979 [1]. Since then the majority of CO$_2$–Rg publications have continued to deal with CO$_2$–Ar, and for the particular case of CO$_2$–Xe there have been only three relevant experimental studies. First, in 1988 Randall et al. [2] measured the rotationally resolved infrared spectrum of CO$_2$–Xe in the region of the CO$_2$ $\nu_3$ fundamental band ($\approx 2350$ cm$^{-1}$). Next, in 1993, Iida et al. [3] measured pure rotational microwave spectra of CO$_2$–Xe, and finally in 2006, Konno et al. [4] measured the $\nu_3$ region infrared spectrum of the $^{18}$O isotopologue of CO$_2$–Xe ($\approx 2314$ cm$^{-1}$). There are six isotopes of xenon with significant natural abundances, as listed in Table 1. In their microwave spectra, Iida et al. [3] measured transitions involving the four most abundant of these ($^{129}$Xe, $^{131}$Xe, $^{132}$Xe, and $^{134}$Xe), but in the infrared spectra any isotopic splitting remained unresolved.

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In the present paper, we revisit the spectrum of CO$_2$–Xe in the CO$_2$ $v_3$ region. Coverage of the $v_3$ fundamental band is expanded and the influence of the range of Xe isotopes is explored. The intermolecular bend and stretch modes are observed by means of their combination bands with the intramolecular CO$_2$ $v_3$ stretch, and here the Xe isotope effects turn out to be much larger than in the fundamental. Finally, CO$_2$–Xe is detected in the region of the CO$_2$ (0111)$\rightarrow$(0110) hot band near 2337 cm$^{-1}$, enabling observation of the splitting of the degenerate CO$_2$ bending vibration into two modes (in-plane and out-of-plane) due to the presence of the nearby Xe atom.

The minimum energy structure of CO$_2$–Xe (and the other CO$_2$–Rg dimers) is T-shaped, such that the Xe atom is located ‘beside’ the linear CO$_2$ molecule with an effective C to Xe distance of about 3.8 Å [2]. The $a$-inertial axis of the dimer connects C and Xe, and the $A$ rotational constant of CO$_2$–Xe is similar to the $B$ constant of CO$_2$ ($\approx 0.39$ cm$^{-1}$). The $b$-axis is parallel to the O–C–O axis, and the $c$-axis is perpendicular to the CO$_2$–Xe plane. CO$_2$–Xe has six normal modes of vibration. Four of these correspond to intramolecular (CO$_2$) vibrations: the symmetric stretch ($v_1 \approx 1388$ cm$^{-1}$), the doubly-degenerate bend ($v_2 \approx 667$ cm$^{-1}$), and the asymmetric stretch ($v_3 \approx 2350$ cm$^{-1}$). The two remaining normal modes are intermolecular vibrations: the van der Waals stretch, and the bend. Note the distinction between the two bending modes, both important in this work: the intramolecular CO$_2$ $v_2$ bend at 667 cm$^{-1}$, and the intermolecular bend at 31 cm$^{-1}$ (as shown below). The T-shaped equilibrium structure corresponds to the C$_2g$ point group, for which fundamental vibrations can have $A_1$ symmetry ($v_1$ CO$_2$ stretch, in-plane component of the $v_2$ CO$_2$ bend, and van der Waals stretch), $B_2$ symmetry ($v_3$ CO$_2$ stretch, intermolecular bond), or $B_1$ symmetry (out-of-plane component of the CO$_2$ $v_2$ bend). $A_2$ symmetry modes can only occur for states which are combinations involving $B_1 \times B_2$ modes. Note that the degeneracy of $v_2$ for the CO$_2$ monomer is lifted in CO$_2$–Xe, giving two distinct modes, with $A_1$ and $B_1$ symmetry. Nuclear spin statistics allow only even values of $K_a$ in $A$ symmetry modes (including the ground state) of dimers containing C$^{16}$O$_2$, and only odd values in $B$ symmetry modes. Two more recent theoretical publications have reported detailed potential energy surfaces for the CO$_2$–Xe interaction, using ab initio methods at the CCSD(T) level. The results were similar, with Chen and Zhu [5] obtaining a global minimum energy of $-261.4$ cm$^{-1}$ at an intermolecular distance of 3.81 Å, while Wang et al. [6] reported $-258.8$ cm$^{-1}$ at 3.78 Å. Notably, the former authors also included the dependence of the potential on the CO$_2$ $v_3$ vibration, allowing for more detailed comparisons with infrared spectra.

## 2. Results

### 2.1. Description of the spectra

Spectra were recorded using a pulsed supersonic slit jet expansion probed by a rapid-scan optical parametric oscillator source [7–9]. The gas expansion mixture contained about 0.03% carbon dioxide plus 0.3% xenon in helium carrier gas, and the backing pressure was about 12 atmospheres. Wavenumber calibration was made by simultaneous recording of signals from a fixed etalon and a reference gas cell containing room temperature CO$_2$. Spectral simulation and fitting were made using the PGOPHER software [10].

The observed spectra are shown in Figures 1–4. The $v_3$ fundamental band in Figure 1, which has been studied previously [2], and the CO$_2$ (0111)$\rightarrow$(0110) hot band in Figure 4 have $b$-type rotational selection rules ($\Delta K_a = \pm 1$). These bands show relatively little effect of Xe isotope splitting (except at high $J$-values) because the intramolecular vibrational frequencies have almost no dependence on xenon atomic mass. The bending combination band in Figures 2 and 3 has $a$-type selection rules ($\Delta K_a = 0$). It does show significant isotope splitting, especially in the $Q$- and $R$-branches (Figure 3). The splitting arises mostly because there is a strong Coriolis interaction between the intermolecular bend and the nearby intermolecular (van der Waals) stretch, whose frequency does have a significant dependence on xenon mass. In the following section, we first describe the approach we used to analyse the isotopic dependence of the spectrum. This approach was especially required for the combination band, but it also proved useful for the fundamental band.

### 2.2. Xenon isotope effects

The isotopes are far from being fully resolved in our infrared spectra, so we could not individually determine all the vibrational and rotational parameters for all six isotopes. Instead, we wanted to model the isotopic

### Table 1. Xenon isotope atomic mass, abundance, and rigid model scaling factors.

| Atomic mass number $N$ | Atomic mass (Dalton) | Abundance | $F_R$  | $F_C$  |
|------------------------|----------------------|-----------|--------|--------|
| 129                    | 128.905              | 0.264     | 1.003902 | 1.003576 |
| 130                    | 129.904              | 0.041     | 1.001938 | 1.001776 |
| 131                    | 130.905              | 0.212     | 1.000000 | 1.000000 |
| 132                    | 131.904              | 0.269     | 0.998095 | 0.998253 |
| 133                    | 133.905              | 0.104     | 0.994365 | 0.994834 |
| 136                    | 135.907              | 0.089     | 0.990743 | 0.991507 |
dependence using only a few free parameters. As a starting point, we determined the Xe isotopic dependence of the B and C rotational constants for a rigid T-shaped model of CO$_2$–Xe (the A constant has no dependence in this model). Not surprisingly, B simply varies as the ratio of the reduced mass of the CO$_2$ and Xe pair. C has a somewhat different dependence, since the CO$_2$ monomer is not parallel to the c-axis.

Using these scaling factors, we tried fitting the 27 observed microwave transitions [3] of CO$_2$–$^{129}$Xe, $^{131}$Xe, $^{132}$Xe, and $^{134}$Xe (with hyperfine splitting removed for $^{131}$Xe) in a unified fashion using a single value for B and C, with scaling, rather than individual values for each isotope. This gave good results, but there was still some remaining systematic dependence on xenon mass. This dependence was minimised by introducing new empirical parameters $B_{adj}$ and $C_{adj}$ which act as slight corrections to the rigid model scaling factors. The B and C rotational parameters are then given by

$$B(N) = B(N_0) \times \left[ F_B(N) + B_{adj} \times (N - N_0) \right]$$

$$C(N) = C(N_0) \times \left[ F_C(N) + C_{adj} \times (N - N_0) \right]$$

where $N$ is the xenon atomic mass number (129, 130, etc.), $N_0$ is a ‘standard’ atomic mass number (taken to be 131, closest to the weighted average atomic mass), and $F_B$ and $F_C$ are the rigid model scaling factors relative to $^{131}$Xe, as listed in Table 1. For simplicity, we use atomic mass number here rather than the actual atomic masses, but the difference is negligible in the present context.

The microwave test fits also included the centrifugal distortion parameters $\Delta_{JK}$ and $\Delta_J$, which were scaled by the factors $F_B$ and $F_B^2$, respectively (without $B_{adj}$ or $C_{adj}$). In the original fit by Iida et al. [3], 27 microwave transitions (not counting hyperfine splitting) had been fitted using 12 adjustable parameters to obtain an rms deviation of 2 kHz. Our unified fit using 4 parameters (B, C,
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Figure 2. Observed and simulated spectra of CO$_2$–Xe in the region of the intermolecular bend combination band. Gaps in the observed spectrum correspond to regions of CO$_2$ monomer absorption. Simulated contributions of the various Xe isotopes are colour-coded, with their sum shown in red.

$\Delta_{JK}, \Delta_J$ gave a deviation of 200 kHz. By including the empirical parameters $B_{adj}$ and $C_{adj}$ this was reduced to 9 kHz, which we considered to be adequate for our infrared analysis. The advantage of the unified approach is that all the isotopes can be represented, including $^{130}$Xe and $^{136}$Xe for which microwave data are not available. Even better, the same rotational scaling factors can be used for excited state parameters in the infrared analysis, having been ‘verified’ with the accurate ground state microwave data.

To allow for isotopic variation of vibrational band origins, another empirical parameter called Offset was introduced, assuming a simple linear shift with isotope mass number, so that

$$v_0(N) = v_0(N_0) + \text{Offset} \times (N - N_0). \quad (3)$$

The parameter Offset describes the band origin shift for each change of one in the Xe atomic mass number. Of course, we know that a harmonic stretching frequency actually scales as the square root of the appropriate reduced mass, and this is not quite linear in N. But in the present case the difference is essentially negligible.

### 2.3. The $\nu_3$ fundamental band

The value of the $A$ rotational constant has only a very small effect on the microwave spectrum (where all transitions have $\Delta K_a = 0$) and must be determined using the infrared $\nu_3$ fundamental band (where $\Delta K_a = \pm 1$). So our microwave and fundamental band fit was a combined one, in which microwave measurements were weighted by a factor of 2000 to reflect their higher precision. In this fit, the excited state distortion parameters $\Delta_{JK}$ and $\Delta_J$ were constrained to equal their ground state values, as in much previous work on CO$_2$–Rg dimers [2]. Similarly, the parameters $B_{adj}$ and $C_{adj}$ were common to both states, as mentioned above. Input data for the fit consisted of the 27 microwave transitions, plus 89 infrared transitions, most of which were blends of two or more isotopes. Each blend was fitted to an intensity weighted average of its components using the Mergeblends option of PGOPHER [10].

The parameters resulting from the fit are listed in Table 2. As noted, these parameters apply specifically to CO$_2$–$^{131}$Xe, and they can also be considered as isotopic averages since $^{131}$Xe (atomic mass 130.905) is close to the weighted average mass (131.293). The scaled
Figure 3. Expanded view of the $Q$- and $R$-branch regions of the CO$_2$–Xe intermolecular bend combination band. Note the large isotopic splitting of some transitions and the good match between the observed spectrum (black) and the summed simulation (red) traces.

parameter values for the other isotopes, and the observed infrared transitions, are given as Supplementary Information. Average rms deviations in the fit were 9 kHz for the microwave measurements and 0.00020 cm$^{-1}$ for the infrared measurements. The latter is essentially equal to the experimental precision, while the experimental line width is about ten times greater. The simulated spectrum in Figure 1 is based on the parameters in Table 2.

The empirical shift parameters $B_{\text{adj}}$ and $C_{\text{adj}}$ are based almost entirely on the isotopic microwave data, and are reasonably well determined. In contrast, the Offset parameter giving the isotopic dependence of the $\nu_3$ fundamental band origin is only marginally significant. Its magnitude implies a total difference of only about 0.0004 cm$^{-1}$ between CO$_2$–$^{136}$Xe and CO$_2$–$^{129}$Xe, and its negative sign means that the band origin shifts down slightly as the xenon atomic weight increases. This direction can be understood as an anharmonic effect due to the (slight) decrease in zero point intermolecular distance with increased mass. In other words, a heavier Xe atom is closer on average to CO$_2$ and the vibrational red shift increases. The actual value of this shift is $-1.472$ cm$^{-1}$ (for $^{131}$Xe) relative to the free CO$_2$ molecule, in good agreement with the value of $-1.471$ cm$^{-1}$ reported by Randall et al. [2]. The other parameters in Table 2 also agree well with Randall et al., but should be more reliable since we have a wider range of infrared data plus the advantage of including ground state microwave results [3].

The expanded view in the top panel in Figure 2 shows how the Xe isotopic scaling in the combined fit gives a good representation of the broadening and (partially resolved) splitting of higher $J$-value transitions in the fundamental infrared spectrum. This is satisfying, but the real motivation for the scaling is to understand the combination bands where splittings are much larger as described in the following section.

2.4. The bend and stretch combination bands

As we have just seen, the $\nu_3$ fundamental band origin has very little Xe isotope dependence, and isotope splitting is only partially evident for transitions with higher $J$-values where the isotopic dependence of the rotational constants becomes important. In contrast, it is clear by inspection that many transitions in the bending combination band (Figures 2 and 3) show significant Xe isotopic splitting.
The point here is that the CO$_2$–Xe intermolecular bending frequency is likely to be isotope dependent due to changes in the effectively reduced mass for bending. But there is a more important factor, namely the proximity of the van der Waals stretch vibration, which is predicted [5,6] to lie within about 2 cm$^{-1}$ of the bend.

It turns out that the stretch lies 1.24 cm$^{-1}$ above the bend, and the Coriolis interaction between bend and stretch has a large effect on the bending combination band, even though it appears that the stretch combination band has little or no strength on its own. The c-type Coriolis interaction is characterised by the matrix element...
Figure 5. Energy level diagram illustrating the Xe isotope dependence of the Coriolis interaction between the intermolecular bend and stretch states of CO$_2$–Xe for $J = 2$. The actual (perturbed) energies of the $J_{K\alpha\epsilon\kappa} = 2_{20}, 2_{21}, 2_{11},$ and $2_{12}$ rotational levels are shown by red and blue circles. Their deperturbed energies (Coriolis interaction removed) are shown as small black circles connected by lines (the asymmetry splitting between $2_{20}$ and $2_{21}$ is too small to see here). For CO$_2$–$^{129}$Xe, the $K_a = 1$ levels of the stretch lies well above $K_a = 2$ of the bend. But the stretching frequency decreases with increasing Xe atomic mass, so that the deperturbed bend and stretch levels are almost coincident for CO$_2$–$^{134}$Xe, and the stretch lies below the bend for CO$_2$–$^{136}$Xe.

Our fit of the bend combination band involved a total of 125 observed lines which were fitted with an rms average error of 0.00034 cm$^{-1}$. As can be seen from the simulated spectra in Figure 3, many of these lines show partial or complete isotopic resolution, while many others are blends. A significant number of the lines were actually assigned to the stretch combination band, where transitions to excited state $K_a = 1$ levels borrow intensity due to their mixing with $K_a = 2$ of the bend. In the fit, ground state parameters were fixed at the values already determined, and upper state rotational parameters and band origins were isotopically scaled as described previously. The $c$-type Coriolis parameter was scaled the same as the $C$ constant. There were 12 adjustable parameters, whose fitted values are shown in the right-hand columns of Table 2. For the bending state these parameters were $\nu_0, A, B, C, \Delta_{JK}$, and $\Delta_J$. For the stretching state they were $\nu_0, B$, and $C$, but $A$ could not be well determined. In addition, the Coriolis parameter $\xi_{\epsilon}$ was determined, as were the Offset parameters describing the Xe isotope scaling of the two band origins. The observed bend–stretch Coriolis interaction parameter, $\xi_{\epsilon} = 0.0299$ cm$^{-1}$, implies a

$\langle \text{bend, } J, k | H | \text{stretch, } J, k \pm 1 \rangle = 1/2 \xi_{\epsilon} \times [J(U + 1) - k(k \pm 1)]^{1/2}$, where $k$ is signed $K_a$, and $\xi_{\epsilon}$ is the Coriolis interaction parameter. The influence of the stretch is accentuated by the fact that the stretch frequency has a relatively large Xe isotopic dependence, and by the fact that the $K_a = 2$ levels of the bend happen to lie very close to the $K_a = 1$ levels of the stretch. As mentioned above, the bend combination band has $a$-type selection rules ($\Delta K_a = 0$), and its most prominent transitions are the $P$- and $R$-branches with $K_a = 0$, as labeled in Figure 2. Note how the $P$-branch lines remain relatively sharp even for higher $J$-values, while the $R$-branch lines show more isotopic splitting, reducing their peak height. The difference arises because vibrational and rotational isotopic shifts tend to cancel in the $P$-branch and to add in the $R$-branch. Isotope splitting is especially noticeable for $Q$-branch transitions with $K_a = 2$, shown in detail in the upper panel of Figure 3. Note that the $K_a = 0$ $Q$-branch is forbidden, and the $K_a = 4$ $Q$-branch (at about 2378.41 cm$^{-1}$) is very weak since there is little $K_a = 4$ population at the experimental temperature of $\approx 2$ K.
value of about 0.48 for the dimensionless Coriolis zeta parameter, $\zeta$.

By subtracting the $v_3$ fundamental band origin from the combination band origins in Table 2 we determine experimental intermolecular bend and stretch frequencies for CO$_2$–Xe (in the CO$_2$ $v_3$ state). These values are listed in Table 3, where they are compared with previous estimates from ab initio theory [5,6] and from an experimentally based empirical harmonic force field [3]. The agreement with our experimental results is quite satisfactory, particularly for the calculations of Chen and Zhu [5]. As mentioned, the $A$ rotational constant could not be determined for the stretching combination state, since only $K_a = 1$ levels were observed. As a result, the real uncertainty in the stretching combination band origin (Table 2) and the derived stretching frequency (Table 3) are perhaps around 0.01 cm$^{-1}$. In other words, even though $K_a = 1$ levels of the stretch state were precisely (0.002 cm$^{-1}$) determined, the (forbidden) $K_a = 0$ levels which define the origin still have an uncertainty of around 0.01 cm$^{-1}$.

The scaling parameters (called Offset) for the bending and stretching vibrations describe how much each band origin shifts for a change of one Dalton in the Xe atomic mass. Although Offset for the bend is ten times larger than that determined above for the $v_3$ fundamental band, it is still quite small, just $-0.0006$ cm$^{-1}$ per Dalton. But Offset for the stretch is $-0.025$ cm$^{-1}$ per Dalton, a further 40 times greater in magnitude. The negative signs show that the bend and stretch frequencies decrease with increasing Xe mass, as expected. Interestingly, the observed value of the stretch Offset parameter corresponds to that expected for a harmonic frequency of 26.2 cm$^{-1}$, while the actual stretch frequency (Table 3) is 31.78 cm$^{-1}$. Thus the Xe isotope dependence of the CO$_2$–Xe intermolecular stretch frequency is somewhat smaller than might be expected.

Figure 5 illustrates the interaction between $K_a = 2$ of the bend and $K_a = 1$ of the stretch, explaining why the isotopic shifts are so prominent for these levels. Here the actual (perturbed) energy levels for $J = 2$ are shown as red and blue circles, and the deperturbed levels (that is, with Coriolis interaction removed) are smaller black circles and lines. For CO$_2$–$^{129}$Xe, the stretch levels are above the bend levels by more than 0.1 cm$^{-1}$. But with increasing Xe atomic mass, the stretching frequency declines much faster than the bending frequency, so that for $^{134}$Xe the unperturbed levels are virtually coincident and then for $^{136}$Xe they cross so that the stretch is below the bend. Of course in reality the crossing is avoided due to the Coriolis interaction, so the real bend and stretch levels never become any closer than about 0.06 cm$^{-1}$ (twice the Coriolis matrix element).

### 2.5. The CO$_2$ (01$^1$1) – (01$^1$0) hot bands

In our supersonic expansion, there is a sufficient population of CO$_2$–Xe in the excited CO$_2$ $v_2$ intramolecular bending state [(v$_1$, v$_2^2/2$, v$_3$) = (01$^1$0) at $\approx$ 667 cm$^{-1}$] to enable observation of the (01$^1$1) $\leftrightarrow$ (01$^1$0) hot band near 2337 cm$^{-1}$ in the $v_3$ region. The situation is similar to that described for CO$_2$–Ar in a recent paper, to which the reader is referred for more details [11]. Analogous spectra have also been observed for C$_2$H$_2$–Ar [12] and CO$_2$–N$_2$ [13]. The nearby Xe atom splits the degenerate CO$_2$ bend into an in-plane (i-p) and an out-of-plane (o-p) mode. In the (01$^1$0) lower state, these modes have $A_1$ or $B_1$-symmetry, and hence allowed $K_a$ = even or odd levels, respectively. In the (01$^1$1) upper state, the symmetries become $B_2$ or $A_2$ with allowed $K_a$ = odd or even levels, respectively. The (01$^1$1) $\leftrightarrow$ (01$^1$0) hot band has $b$-type selection rules ($K_a = \pm 1$) just like the $v_3$ fundamental. The i-p component of the hot band has subbands with $K_a = odd \leftrightarrow even$, and the o-p component has $K_a = even \leftrightarrow odd$. There is $b$-type Coriolis mixing between the i-p and o-p modes, characterised by the matrix element $[i-p, J, k|H|o-p, J, k \pm 1] = 1/2 \xi_b \times [J(J+1) - k(k \pm 1)]^{1/2}$, where $k$ is signed $K_a$, and $\xi_b$ is the Coriolis parameter. As for the intermolecular Coriolis interaction in the previous section, the rotational constant and the dimensionless zeta parameter $\zeta$ are related by $\xi_b = 2B\zeta_b$. The Coriolis mixing is strong ($\zeta_b \approx 1$) because it is the direct consequence of the CO$_2$ $v_2$
vibrational angular momentum which is now quenched in the CO2–Xe complex.

By analogy with CO2–Ar [11], we expected the CO2–Xe rotational constants and hot band vibrational shift to be similar to those of the fundamental. So to assign the spectrum (Figure 4), the main unknown quantity was the splitting between the i-p and o-p modes, expected to be similar in the lower and upper states. After some trial and error, we found that this splitting had a value of about 2.1 cm⁻¹ (compared to 0.88 cm⁻¹ for CO2–Ar) and assigned a total of 74 hot band lines. The detailed assignments are given as Supplementary Information. There was little isotope splitting, so this was ignored in the fit, meaning that the result should approximate that for the weighted average atomic mass (131.29). The rms error in the fit was 0.00028 cm⁻¹ and the parameters resulting from the fit are listed in Table 4. We did not attempt to determine centrifugal distortion parameters, but found that the fit was improved slightly by fixing ΔJK and ΔJ at their ground state values from Table 2.

By far the strongest feature in the spectrum is the narrow Q-branch of the Ka = 1 ← 0 subband of the i-p mode at 2335.500 cm⁻¹ (see Figure 4). Also labeled in Figure 4 are the Ka = 1 ← 2, 0 ← 1, and 2 ← 1 subbands. In addition, two very weak lines with Ka = 3 ← 2 were assigned (not shown in the figure). In the case of CO2–Ar, some cross transitions (i-p ← o-p and o-p ← i-p) were observed [11]. However, such ‘forbidden’ transitions could not be detected in the present case. They are much weaker for CO2–Xe because the wider spacing of the i-p and o-p modes reduces Coriolis mixing. It was not possible to reliably determine all of the parameters in Table 4 at the same time without some constraint. After trying various schemes, we decided on the following two constraints: (A′−A′′) = -0.0031 cm⁻¹ for the i-p state (similar to the ν3 fundamental band), and ξb′ = ξb′′ for the Coriolis parameter. Both constraints are reasonable based on the results for CO2–Ar, where more parameters could be varied thanks to more data [11].

The ξb parameter from Table 4 results in a value of about 0.990 for ξb, depending slightly on exactly what value is used for B. This can be compared to reported values of 1.01 for CO2–Ar and 1.003 for CO2–N2 [11,13]. These near unity values of ξb are a reflection of the fact that the CO2 bend is only slightly perturbed in these weakly bound complexes. An important aspect of the results is the splitting between i-p and o-p modes, determined to be 2.140(4) cm⁻¹ for CO2–Xe in the lower (01 10) state and 2.171(4) cm⁻¹ in the upper (01 11) state, with o-p higher than i-p. This is larger than the 0.877 cm⁻¹ splitting [11] observed in CO2–Ar and quite similar to the 2.307 cm⁻¹ splitting [13] in CO2–N2. Although the splittings are determined by our hot band spectrum, the actual CO2 bending frequency is not. The parameter X in Table 4 represents this bending frequency (for the i-p mode), and X is equal to 667.38 cm⁻¹ plus or minus an unknown (but relatively small) vibrational shift which is unlikely to be more than a few cm⁻¹.

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The strongest lines in the CO2–Xe (01 11) ← (01 00) hot band were about 0.02 times the strength of those in the (001) ← (000) fundamental band. This is similar to CO2–Ar, so we can repeat the conclusions made previously [11]. Very roughly, the observed hot band strength is about half of that expected if all the original room temperature population of CO2 in the (01 00) state survived the supersonic expansion without any relaxation. This relatively inefficient vibrational relaxation is probably related to the fact that the gas
mixture contained over 99% helium in both cases, and it means that the effective vibrational temperature for the CO$_2$ $\nu_2$ mode is (very roughly) 240 K even though the effective CO$_2$–Xe rotational temperature is about 2 K.

3. Conclusions

In this paper, we have shown how the Xe isotope dependence of the CO$_2$–Xe spectrum can be parameterised in order to allow fitting and simulation of infrared spectra, even though the isotopic splittings range from unresolved through partly resolved (e.g. for higher-$J$ lines of the $\nu_3$ fundamental band) to fully resolved (e.g. for $K_a = 2$ lines of the bending combination band). Implementation of this parameterised fitting depended on the availability of precise, though incomplete, microwave data [3], and was greatly facilitated by the various features of the PGOPHER software package [10] which allow parameters to be varied and/or constrained in a flexible and user-friendly fashion. The most significant new results obtained here are the determination of the intermolecular bend and intermolecular stretch frequencies for CO$_2$–Xe in the CO$_2$ $\nu_3$ state (and their Xe isotope dependence), and characterisation of the splitting of the degenerate CO$_2$ $\nu_2$ bending vibration into in-plane and out-of-plane modes.

In conclusion, new infrared spectra of the weakly bound CO$_2$–Xe complex are reported and their Xe isotope dependence is investigated in detail. The fundamental band (CO$_2$ $\nu_3$) is analysed together with previous microwave data in terms of a unified set of parameters including Xe isotope scaling. Infrared combination bands involving the intermolecular bend and (van der Waals) stretch are observed for the first time, yielding experimental frequencies of 30.57 and 31.78 cm$^{-1}$, respectively (in the excited CO$_2$ $\nu_3$ state). Isotope splitting in the combination bands is accentuated by the strong bend–stretch Coriolis interaction and the relatively large isotope dependence of the stretch frequency. CO$_2$–Xe spectra are also observed corresponding to the CO$_2$ (01$^1$1) $\leftarrow$ (01$^1$0) hot band, and their analysis results in a value of 2.14 cm$^{-1}$ for the splitting of the CO$_2$ $\nu_2$ bend into in-plane and out-of-plane modes, strongly linked by Coriolis interaction.

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Disclosure statement

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