Neon matrix isolation spectroscopy of CO₂ isotopologues

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The solid neon matrix isolated spectrum of CO₂ are recorded in the 2–5 μm region. Natural and 13C or 18O enriched CO₂ samples were used and the nν₁ + ν₃ (n = 0, 1, 2) series bands of different CO₂ isotopologues have been observed. The solid neon matrix shift due to Fermi-resonance of bands within the same vibrational polyad is analyzed.

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The spectrum of carbon dioxide have been extensively studied. The matrix isolation spectroscopy of CO₂ have been reported in solid N₂[1,2], O₂[3], Ar[1,2,4], Kr[5], p-H₂[6] and in helium droplet[7].

The matrix shift and matrix splitting provide a measure of the intermolecular interactions between host matrices and guest molecules. The strong fundamental anti-symmetric stretching band ν₃ of CO₂ has been most extensively studied, but the overtones are less considered because such bands are much weaker and often hard to be identified from the bands of other contaminations in the sample. Moreover, complicated spectroscopic structure can often be found for a single vibrational band of the dopant. The structure arises from matrix crystal field, dopant aggregations, different substitutional sites in matrices, vibrational band interactions and rotational structures, or from the isotopic effect. These effects also make it difficult to assign the overtone bands. By comparing the spectra from different isotope-enriched samples, we have successfully studied the overtones of N₂O in solid neon and p-H₂ matrices [8,9]. The relatively small matrix effect of solid neon resulted in resonant splitting of bands within the same vibrational polyad [8]. The small peaks are less considered because such bands are much weaker and often hard to be identified from the bands of other contaminations in the sample.

Natural and isotope concentrated CO₂ samples were used in the present study. The natural sample was bought from Nanjing Special Gas Co. The 13C enriched and 18O enriched samples were purchased from Icon Services Inc. The isotopic abundance of each sample was determined by the infrared spectroscopy and also the photo-ionization mass spectroscopy (PIMS) measurements. The PIMS measurement was carried out in the photochemistry end-station of National Synchrotron Radiation Laboratory (Hefei, China). All these sample was further purified with "thaw–frozen–thaw" procedure before using. Totally 10 different CO₂ isotopologues were studied: 12C¹⁶O₂, 16O¹²C¹⁷O, 16O¹²C¹₈O, 1⁷O¹²C¹₈O, 1₂C¹⁸O₂, 1₃C¹₆O₂, 1₆O¹₃C¹₇O, 1₆O¹₃C¹₈O, 1⁷O¹₃C¹₈O, and 1₃C¹₈O₂. These isotopologues will be noted as CO₂-626, 627, 628, and so on, respectively.

The sample gas was deposited on a BaF₂ substrate through a 0.1 mm diameter pinhole. The distance between the pinhole and the BaF₂ substrate was about 3 cm. The flow rate was controlled at about 27 mmol/h by a mass-flow controller (MK6 1479A). The BaF₂ substrate was attached to the cold head of a closed-cycle cryostat (Jain SHI-4-5). A LakeShore 331S controller was used to control the heating current in a wire attached to the cold head. In this way, the temperature can be adjusted in the range of 4–300 K with 0.2 K accuracy. Typically, the deposition temperature is 4.3 K and the annealing temperature is 10 K. After annealing, the temperature will be again lowered to 4.3 K. The infrared absorption spectra were recorded by a Bruker IFS120HR Fourier-transform spectrometer. The entire optical path was evacuated to avoid the atmospheric absorption. The spectra covering the 700–6000 cm⁻¹ region were recorded with proper selection of the light sources (glowbar or tungsten lamp), beam splitters (KBr or CaF₂) and detectors (ln₂ cooled MCT or InSb). The adopted spectral resolution was 0.02 cm⁻¹.

The band assignments can be readily made by the comparison with the gas phase band centers of respective isotopologues [10,11]. We have been able to assign the ν₁ + ν₃ (n = 0, 1, 2) bands in the region 2–5 μm. Parts of the observed spectrum, showing the ν₃, ν₁ + ν₃ and 2ν₁ + ν₃ band/polyads of the main isotopologue 1₂C¹⁶O₂ are given in Fig. 1. Fig. 2 shows the strongest band in the 2ν₁ + ν₃/ν₁ + 2ν₂ + ν₃/4ν₂ + ν₃ polyad of 1₂C¹⁶O₂. The small peaks

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appear in the spectrum with high CO2 concentration are attributed to the CO2 dimer. The assignments and the matrix shifts of different isotopologues of CO2. The neon matrix shift of the tum quantum number. The strongest band in the 2 \( \nu_3 \) polyad of \( ^{12}C^{16}O_2 \) in solid neon is presented in Table 1. As comparison, the vibrational term \( G_v \) values of gas phase CO2 are also given in the table. The vibrational notations follow Ref. [10] and the HITRAN database [12], where a vibrational state is denoted with quantum numbers \( v_1, v_2, v_3 \). The numbers \( v_1, v_2, v_3 \) are the quanta of the symmetric stretching, bending and anti-symmetric stretching vibration modes, respectively. \( \gamma \) is the vibrational angular momentum quantum number. \( \gamma \) is the index of the vibrational state within a Fermi-resonance polyad.

For the strong \( \nu_3 \) band, the transitions have been assigned for 10 isotopologues of CO2. The neon matrix shift of the \( \nu_3 \) band is very close for different isotopologues, which ranges from 1.28 to 1.35 cm\(^{-1}\). However, for the \( \nu_1 + \nu_3 \) and \( 2\nu_1 + \nu_3 \) polyads, the matrix shifts change a lot between different isotopologues. The reason can be that the interactions among the vibrational states in the polyad cause mixing of the wavefunctions. The change of the potential energy surface due to the matrix environment will lead the change of wavefunction mixing. As a result, the relative band intensities in a polyad changes in the neon matrices from the gas phase. The relative band intensities as the parts of the whole interacting polyad are also given in Table 1. The values change much from the gas phase ones [10,11]. In the last column of the table, we give the averaged matrix shifts weighted with the relative band intensities.

### Table 1

<table>
<thead>
<tr>
<th>Iso.</th>
<th>Vib.</th>
<th>( G_v )</th>
<th>( \nu_3 )</th>
<th>( \delta_{\nu_3} )</th>
<th>Int. %</th>
<th>( \Delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>838</td>
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<td>2247.291</td>
<td>2246.010</td>
<td>-1.281</td>
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<td></td>
</tr>
<tr>
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<td>00'11</td>
<td>2255.954</td>
<td>2254.656</td>
<td>-1.298</td>
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<td></td>
</tr>
<tr>
<td>638</td>
<td>00'11</td>
<td>2265.971</td>
<td>2264.671</td>
<td>-1.301</td>
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<tr>
<td>637</td>
<td>00'11</td>
<td>2274.087</td>
<td>2272.767</td>
<td>-1.320</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>00'11</td>
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<td>2282.174</td>
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<td></td>
</tr>
<tr>
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<td>00'11</td>
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<tr>
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<td>2321.114</td>
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</tr>
<tr>
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<td>00'11</td>
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<td>2329.462</td>
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<tr>
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<td>2347.798</td>
<td>2346.476</td>
<td>-1.340</td>
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<td></td>
</tr>
</tbody>
</table>

- Notation for the CO2 isotopologues, i.e. 638 for \(^{16}O^{13}C^{18}O\).
- Upper state, \( \nu_1, \nu_2, \nu_3 \); consistent with the HITRAN [12] notations.
- Gas phase values, from Refs. [10,11].
- Solid neon matrix shift, \( \Delta \) = \( \delta_{\nu_3} - G_v \).
- Observed relative band intensity in the vibrational polyad.
- Weighted matrix shift of the vibrational polyad.

![Fig. 1](https://example.com/fig1.png)

**Fig. 1.** The \( \nu_2 \), \( \nu_1 + \nu_3 \) and \( 2\nu_1 + \nu_3 \) bands of \(^{12}C^{16}O_2\) in solid neon. Spectrum were recorded after 0.5 mm CO2/Ne sample had been deposited at 4.3 K.

![Fig. 2](https://example.com/fig2.png)

**Fig. 2.** The strongest band in the \( 2\nu_1 + \nu_3 \) polyad of \(^{13}C^{16}O_2\) in solid neon. Spectrum were recorded after 0.5 mm CO2/Ne sample had been deposited at 4.3 K.

![Fig. 3](https://example.com/fig3.png)

**Fig. 3.** The \( \nu_1 + \nu_3 \) band shifts of several CO2 isotopologues in solid neon (CO2 isotopologue notation: 626 for \(^{16}O^{12}C^{16}O\), 638 for \(^{16}O^{13}C^{18}O\), etc.).
within a polyad. Fig. 3 shows the “weighted matrix shifts” of different isotopologues. We can see that the value changes little from one isotopologue to another. It is clear that the matrix shift values change almost linearly with \( n \) for the \( n v_1 + v_3 \) \( (n = 0, 1, 2) \) bands. This “regular” behavior can be an advantage to predict the matrix shifts of molecules in solid neon.

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