Accurate rest frequencies for the submillimetre-wave lines of C$_3$O in ground and vibrationally excited states below 400 cm$^{-1}$

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1. Introduction

Tricarbon monoxide (C$_3$O) is the longest oxygen-containing carbon chain observed in the interstellar medium (ISM). It was first identified by Matthews et al. (1984) through its $J = 2$–1 rotational line in the molecular cloud TMC-1 toward the cyanoopolyne peak, shortly after its first laboratory study (Brown et al. 1983). Recently, C$_3$O has been detected towards the carbon star IRC+10216 (Tenenbaum et al. 2006) together with other O-bearing species, such as H$_2$O (Melnick et al. 2001; Hasegawa et al. 2006), OH (Ford et al. 2003) and H$_2$CO (Ford et al. 2004). This object is an evolved low-mass AGB star whose mass loss produces a dusty, molecular-rich, extended envelope. The dredge-up process has altered the elemental C/O ratio of the star surface (which is C/O < 1 during the main sequence phase), resulting in a strong carbon enrichment which ultimately determines the kind of chemistry taking place in the inner envelope (Tsuji 1973): in these conditions, the bulk of oxygen in IRC+10216 is expected to be locked into the highly stable CO molecule.

The existence of other O-bearing species in IRC+10216 has been interpreted as the results of water ice evaporation from orbiting Kuiper belt-type objects (Melnick et al. 2001), or alternatively it has been supposed that gas-phase oxygen-rich chemistry, involving neutral-neutral reactions, occurs in the outer shell of the star (Tenenbaum et al. 2006; Agúndez & Cernicharo 2006). Also, in a very recent study, Palumbo et al. (2008) have suggested that in dense molecular clouds, where high CO depletion occurs, significant amounts of carbon chain oxides, C$_3$O, might be formed in the solid phase after cosmic ion irradiation of CO-rich dust grains, and then released to the gas phase when desorption of icy mantles takes place. This remains however an open question due to the paucity of observational data on carbon chain oxides.

In the laboratory, C$_3$O has been the subject of various spectroscopic investigations: after the first identification of its centimetre-wave (cm-wave) spectrum (Brown et al. 1983), the same authors performed a detailed microwave study on isotopic species, leading to a structure determination (Brown et al. 1985). Later, its ground-state millimetre-wave (mm-wave) spectrum was also recorded (Tang et al. 1985; Klebsch et al. 1985), and a high-resolution infrared study of the $v_1$ and some associated hot bands has been performed using Fourier transform infrared spectroscopy (FTIR) (McNaughton et al. 1991).

Presently, the best set of rotational and centrifugal distortion constants are those provided by the mm-wave study of Klebsch et al. (1985), which indeed allow the calculation of reliable rest-frequencies for the ground state lines of C$_3$O at millimetre wavelengths. However, it should be noted that C$_3$O is a molecule with a certain degree of floppiness (Botschwina 2005), which results in relatively large centrifugal distortion effects. Hence, the extrapolation of the high-$J$ submillimetre-wave (submm-wave) line positions from lower frequency laboratory measurements may be inaccurate, and the corresponding predicted uncertainties are likely to be misleadingly underestimated.

As regards the vibrationally excited states, the spectroscopic information is much more scarce. Few low-$J$ rotational lines of the $v_5 = 1$ bending state were recorded by Brown et al. (1985), while for the $v_5 = 2$ and $v_5 = 3$ overtone states the only available spectroscopic data are those derived from the rovibrational band-by-band analysis of the $v_1$ hot band system (McNaughton et al. 1991). The $v_5$ bending mode of C$_3$O has an energy of 114 cm$^{-1}$ (Hochlaf 2001), thus the first members of its vibrational ladder might be populated by the radiative pumping mechanism occurring in IRC+10216, which is one of the brightest objects of

* Tables 5 to 8 are only available in electronic form at the CDS via anonymous ftp to cdsarc.u-strasbg.fr (136.79.128.5) or via http://cdsweb.u-strasbg.fr/cgi-bin/qcat?J/A+A/492/875

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the infrared sky. In this object, several molecules in vibrationally excited states have already been detected, including the carbon chains C₂H, C₃H, and HC₃N (Cernicharo et al. 2000). The detection of vibrationally excited C₃O may provide additional clues to understanding oxygen chemistry in C-rich circumstellar envelopes, and for this the availability of reliable rest frequencies is a prime prerequisite.

The accuracy of the spectral data on astrophysically important molecules will become even more critical in the near future, when the ongoing HERSCHEL and ALMA projects will reach their full operating status. New perspectives in astrophysical spectroscopy will be provided by the extended spectral coverage of the HIFI spectrometer (onboard HERSCHEL) and by the unprecedented sensitivity and angular resolution of ALMA, whose very small beam sizes can be exploited to selectively study the densest and most excited regions. In this context, the availability of very accurate rest frequencies, ideally obtained by direct laboratory measurements, is highly desirable both for the unambiguous identification of the molecular signals and also for modelling purposes.

The aim of the present investigation is to provide improved rotational spectral data to assist the the mm-wave and submm-wave radioastronomical searches of C₃O in its ground and lowest vibrationally excited states. New laboratory measurements of the ground state C₃O spectrum have been carried out reaching a frequency as high as 739 GHz: thirty-seven new rotational transitions from \( J = 32 \rightarrow 31 \) to \( J = 77 \rightarrow 76 \) have been recorded and analysed, yielding much improved values of the rotational constant \( B \) and of the quartic and sextic centrifugal distortion constants \( D \) and \( H \). Moreover, the octic \( L \) constant, of the order of \( J^6 \), had to be included in the analysis in order to take into account the large centrifugal distortion effects exhibited by the C₃O molecule. New mm-wave and submm-wave rotational lines spanning the \( J \) range 7–59 (frequency interval 77–580 GHz) have also been recorded for the lowest fundamental \( v_5 \) = 1, and for its overtones \( v_5 = 2 \) and \( v_5 = 3 \). These transition frequencies have been analysed employing a model Hamiltonian that takes into account the \( I \)-type resonance effects arising between different sublevels of a given bending state as well as their centrifugal corrections. The resulting set of spectroscopic constants allows for the prediction of the rotational line positions of C₃O, with an uncertainty of few thousandths of km s⁻¹ up to 1 THz for the ground state lines and up to 600 GHz for the bending excited state spectra.

2. Experiment

In previous laboratory investigations the C₃O molecule was produced either by glow discharge of carbon suboxide, C₃O₂, (Tang et al. 1985) or by pyrolytic processes, employing various stable precursors (Brown et al. 1983; Klebsch et al. 1985; Brown et al. 1985; McNaughton et al. 1991). In the present investigation we found it convenient to produce C₃O by flow-pyrolysis of fumaryl chloride (Aldrich), using the same apparatus already employed to generate HCSN (Yamada et al. 2004) and HC₇N (Bizzocchi & Degli Esposti 2004). Briefly, vapours of the precursor were flowed through a quartz tube, 50 cm long and 1 cm in diameter, whose central part was heated at 900 °C by a 30 cm long cylindrical furnace. The high-temperature reactor was connected to the absorption cell of the spectrometer and the C₃O spectra were recorded while continuously pumping the pyrolysis products through the system. The pyrolysis reaction scheme is:

\[
\text{Cl}_2\text{C}≡\text{C}\text{Cl} \xrightarrow{900 \degree C} \text{C}≡\text{C}≡\text{C}\text{Cl}
\]

In our experimental conditions, C₃O has proven to be a quite unstable species with a lifetime of the order of 1 s, thus a high flow rate in the pyrolysis system and in the absorption cell was critical to achieve sufficiently strong spectral features. During the measurements we noticed that the addition of 50% methyl acetylene (CH₃CCH) to the precursor vapours produced a significant enhancement of the C₃O absorption signals, as well as a substantial reduction of the intensity of the interfering lines. This beneficial effect is well illustrated in Fig. 1 which shows recordings of the ground state \( J = 13 \rightarrow 12 \) transition of C₃O produced pyrolysing pure fumaryl chloride (lower trace) and a 2:1 mixture of fumaryl chloride and methyl acetylene. The reaction temperature was 900 °C.

![Fig. 1. Recordings of the J = 13–12 rotational transition of C₃O in its ground vibrational state obtained by a) pyrolysis of pure fumaryl chloride vapours and b) copyrolysis of a 2:1 mixture of fumaryl chloride and methyl acetylene. The reaction temperature was 900 °C.](image)
cell, the signals of C₃O quickly disappear while the intensity of the interfering lines remains nearly unchanged. The “trapping” can be easily achieved by first choking the valve of the pumping system, and then closing the precursors metering valves. A slow pumping through the choked valve is allowed until the pressure of the absorption cell has redescended to the typical flow value (≈2 Pa), and at this point the output valve is definitively closed leaving a static sample of pyrolysis products inside the cell. By taking the difference between the spectrum recorded under flowing conditions and that recorded with the static sample, it is possible to attain a nearly complete cancellation of the lines due to stable molecules, thus obtaining a much cleaner spectrum of C₃O. An example of this method is presented in Fig. 2, which shows the recording of the ground state J = 32–31 transition: the three interfering features existing in the flowing sample (trace a) completely vanish in the difference spectrum (trace c), resulting in a flat baseline and in a cleaner absorption profile of the relevant line.

Measurements were performed in the frequency range 75–740 GHz employing phase-locked Gunn oscillators (Carlstrom and RPG) as primary radiation sources working in the frequency range 75–115 GHz; power at submillimetre wavelengths was obtained using harmonic multiplication. Source frequency modulation at 16.7 kHz was applied and the signal was demodulated at 2f by a lock-in amplifier, thus obtaining the second derivative of the actual spectrum profile. A Schottky-barrier diode (Millitech) and a liquid-He-cooled InSb detector (QMC) were used to record the spectra below and above 190 GHz respectively. Measurement accuracy of the line positions lies in the range 10–20 kHz, depending on the signal-to-noise ratio.

3. Observed spectra and analysis

The spectra were recorded at 2b): constant frequency modulation at 16.7 kHz was applied and signal was demodulated at 2f. The resulting line was then corrected using a flat baseline and in a cleaner absorption profile of the relevant line.

Fig. 2. Recordings of the rotational spectrum of C₃O in the region of the J = 32–31 transition of the ground vibrational state. Trace a): flow pyrolysis of fumaryl chloride and methyl acetylene 2:1 mixture at 900 °C, cell pressure 12 mTorr (1.6 Pa). Trace b): static sample of the pyrolysis products, cell pressure 12 mTorr (1.6 Pa). Trace c): difference.

whereas off-diagonal (Δl₅ = ±2), l-type resonance terms are given by:

\[
\langle v₅, i₅ ± 2, J \mid \hat{H} \mid v₅, i₅, J \rangle = \frac{1}{4} [q₅ + qₛ₅(J + 1) + qₛl₅J(J + 1)]² \times \sqrt{(v₅ + i₅)(v₅ + i₅ + 2)} \times \sqrt{(J(J + 1) - l₅)(l₅ ± 2)\{J(J + 1) - (l₅ ± 1)(l₅ ± 2)\}}.
\] (2)

The resulting energy matrix has been then factorised in symmetric and antisymmetric blocks adopting Wang-type linear combinations of wavefunctions (Yamada et al. 1985). Any sublevel belonging to a given vibrational state can therefore be labelled through its l₅ value and by the “+” or “−” superscripts which designate which kind of symmetrised linear combination of wavefunctions has been chosen. Over 180 new transition frequencies have been measured, and some details dealing with the analyses performed for the various vibrational states investigated are given in the following subsections.

3.1. The ground state

The measurements performed for the various vibrational states investigated are given in the following subsections.

The previous investigations of the ground-state rotational spectra of C₃O cover the frequency interval almost continuously between 9 and 206 GHz, plus two isolated recordings at 300 and 375 GHz. We measured 37 new rotational transitions in the frequency range 307–740 GHz spanning J values from 31 to 76.
Table 1. Analysed transition frequencies and least-squares residuals (MHz) for C₃O in the vibrational ground state.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed</th>
<th>Obs. – Calc.</th>
<th>Transition</th>
<th>Observed</th>
<th>Obs. – Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–0</td>
<td>96217.762a</td>
<td>-0.008</td>
<td>38–37</td>
<td>375065.845a</td>
<td>0.007</td>
</tr>
<tr>
<td>2–1</td>
<td>19243.531a</td>
<td>0.010</td>
<td>40–39</td>
<td>384673.215</td>
<td>-0.006</td>
</tr>
<tr>
<td>3–2</td>
<td>28865.227a</td>
<td>-0.007</td>
<td>41–40</td>
<td>394279.878</td>
<td>0.002</td>
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<tr>
<td>4–3</td>
<td>38486.862a</td>
<td>-0.030</td>
<td>42–41</td>
<td>403885.778</td>
<td>-0.008</td>
</tr>
<tr>
<td>5–4</td>
<td>48108.504a</td>
<td>0.029</td>
<td>43–42</td>
<td>413490.938</td>
<td>0.005</td>
</tr>
<tr>
<td>6–5</td>
<td>57729.962a</td>
<td>-0.003</td>
<td>44–43</td>
<td>423095.307</td>
<td>0.006</td>
</tr>
<tr>
<td>7–6</td>
<td>67351.345b</td>
<td>0.003</td>
<td>50–49</td>
<td>480704.196</td>
<td>0.019</td>
</tr>
<tr>
<td>8–7</td>
<td>76792.582b</td>
<td>-0.007</td>
<td>51–50</td>
<td>490302.613</td>
<td>0.002</td>
</tr>
<tr>
<td>9–8</td>
<td>86593.678b</td>
<td>-0.009</td>
<td>52–51</td>
<td>499900.133</td>
<td>0.002</td>
</tr>
<tr>
<td>10–9</td>
<td>96214.619b</td>
<td>0.003</td>
<td>53–52</td>
<td>509496.724</td>
<td>0.005</td>
</tr>
<tr>
<td>11–10</td>
<td>105835.363b</td>
<td>0.003</td>
<td>54–53</td>
<td>519092.368</td>
<td>0.008</td>
</tr>
<tr>
<td>12–11</td>
<td>115455.899b</td>
<td>0.001</td>
<td>55–54</td>
<td>528687.035</td>
<td>-0.003</td>
</tr>
<tr>
<td>13–12</td>
<td>125076.212b</td>
<td>0.000</td>
<td>56–55</td>
<td>538280.736</td>
<td>0.002</td>
</tr>
<tr>
<td>14–13</td>
<td>134696.282b</td>
<td>-0.003</td>
<td>57–56</td>
<td>547873.422</td>
<td>-0.013</td>
</tr>
<tr>
<td>15–14</td>
<td>144316.098b</td>
<td>0.001</td>
<td>58–57</td>
<td>557465.113</td>
<td>-0.009</td>
</tr>
<tr>
<td>16–15</td>
<td>153935.639b</td>
<td>0.010</td>
<td>59–58</td>
<td>567055.754</td>
<td>-0.027</td>
</tr>
<tr>
<td>17–16</td>
<td>163554.868b</td>
<td>0.004</td>
<td>60–59</td>
<td>576645.383</td>
<td>-0.012</td>
</tr>
<tr>
<td>18–17</td>
<td>173173.799b</td>
<td>0.016</td>
<td>61–60</td>
<td>586233.922</td>
<td>-0.027</td>
</tr>
<tr>
<td>19–18</td>
<td>182792.354b</td>
<td>-0.014</td>
<td>62–61</td>
<td>595821.435</td>
<td>0.010</td>
</tr>
<tr>
<td>22–21</td>
<td>211645.924b</td>
<td>-0.007</td>
<td>63–62</td>
<td>605407.835</td>
<td>0.026</td>
</tr>
<tr>
<td>23–22</td>
<td>221262.992b</td>
<td>-0.002</td>
<td>64–63</td>
<td>614993.098</td>
<td>0.013</td>
</tr>
<tr>
<td>24–23</td>
<td>230879.625b</td>
<td>-0.007</td>
<td>65–64</td>
<td>624577.239</td>
<td>0.002</td>
</tr>
<tr>
<td>27–26</td>
<td>259726.819b</td>
<td>0.011</td>
<td>66–65</td>
<td>634160.259</td>
<td>0.010</td>
</tr>
<tr>
<td>31–30</td>
<td>298182.646b</td>
<td>-0.003</td>
<td>67–66</td>
<td>643742.117</td>
<td>0.011</td>
</tr>
<tr>
<td>32–31</td>
<td>307795.228</td>
<td>0.000</td>
<td>68–67</td>
<td>653322.803</td>
<td>0.011</td>
</tr>
<tr>
<td>33–32</td>
<td>317407.217</td>
<td>-0.003</td>
<td>69–68</td>
<td>662902.291</td>
<td>-0.002</td>
</tr>
<tr>
<td>34–33</td>
<td>327018.606</td>
<td>-0.001</td>
<td>70–69</td>
<td>672480.574</td>
<td>-0.018</td>
</tr>
<tr>
<td>35–34</td>
<td>336629.366</td>
<td>-0.004</td>
<td>71–70</td>
<td>682057.668</td>
<td>-0.006</td>
</tr>
<tr>
<td>36–35</td>
<td>346239.489</td>
<td>-0.003</td>
<td>75–74</td>
<td>720353.535</td>
<td>0.001</td>
</tr>
<tr>
<td>37–36</td>
<td>355848.955</td>
<td>-0.001</td>
<td>76–75</td>
<td>729924.299</td>
<td>-0.007</td>
</tr>
<tr>
<td>39–38</td>
<td>365457.744</td>
<td>0.001</td>
<td>77–76</td>
<td>739493.777</td>
<td>0.006</td>
</tr>
</tbody>
</table>

Notes – Assumed uncertainties are 20 kHz for all the transitions. a From Brown et al. (1983); b from Brown et al. (1985); c from Klebsch et al. (1985); d mean value of the measurement of Klebsch et al. (1985) and the present work.

Figure 3 presents the recording of the J = 71–70 rotational transition of C₃O in its ground vibrational state. Twenty-four scans with a time constant of 30 ms have been coadded (total integration time 58 s).

3.2. The bending excited states v₅ = 1, v₅ = 2 and v₅ = 3

A few cm-wave lines for the v₅ = 1 excited state were measured by Brown et al. (1985), while no previous information was available for the pure rotational spectra of the v₅ = 2 and v₅ = 3 bending overtones. Owing to the l-type resonance effects, each J + 1 ← J transition of v₅ = 1 is split into a doublet (l-type doubling), whereas the v₅ = 2 and v₅ = 3 lines are split into a triplet and a quadruplet of components, respectively. From ab initio calculations (Hochlaf 2001; Botschwina 2005) their vibrational energy can be estimated to be about 230 cm⁻¹ and 340 cm⁻¹, thus the 300 K peak intensity of their transitions is expected to be 1/3 and 1/5 of the corresponding ground state lines. At this level of intensity, the spectral congestion was very high and the method described in the Experiment section proved to be crucial for the identification and assignment of the line multiplets belonging to the v₅ = 2 and v₅ = 3 states.

Measurements were performed in the 77–581 GHz frequency range, reaching a J value as high as 59 for v₅ = 1, and 40
Table 2. Spectroscopic constants determined for the ground and \( v_5 = 1 \), \( v_5 = 2 \), and \( v_5 = 3 \) bending excited states of C\(_3\)O.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Observed</th>
<th>Obs. – Calc.</th>
<th>( \sigma^a )</th>
<th>Observed</th>
<th>Obs. – Calc.</th>
<th>( \sigma^a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2–1</td>
<td>19 367.345(^b)</td>
<td>0.038</td>
<td>0.100</td>
<td>19 421.465(^b)</td>
<td>-0.013</td>
<td>0.100</td>
</tr>
<tr>
<td>3–2</td>
<td>29 050.903(^b)</td>
<td>-0.002</td>
<td>0.100</td>
<td>29 132.134(^b)</td>
<td>-0.019</td>
<td>0.100</td>
</tr>
<tr>
<td>4–3</td>
<td>38 734.412(^b)</td>
<td>-0.024</td>
<td>0.100</td>
<td>38 842.747(^b)</td>
<td>-0.002</td>
<td>0.100</td>
</tr>
<tr>
<td>5–4</td>
<td>48 417.894(^b)</td>
<td>0.017</td>
<td>0.100</td>
<td>48 553.282(^b)</td>
<td>0.041</td>
<td>0.100</td>
</tr>
<tr>
<td>6–5</td>
<td>77 467.464</td>
<td>0.023</td>
<td>0.100</td>
<td>77 683.847</td>
<td>0.011</td>
<td>0.020</td>
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<td>7–6</td>
<td>87 150.299</td>
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<td>0.020</td>
<td>87 393.645</td>
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<td>8–7</td>
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<td>0.020</td>
<td>97 103.239</td>
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<td>0.020</td>
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<td>116 197.596</td>
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<td>0.020</td>
<td>116 521.624</td>
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<td>126 230.307</td>
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<td>0.020</td>
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<td>0.020</td>
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<td>17–16</td>
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<td>0.020</td>
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<tr>
<td>18–17</td>
<td>251 710.165</td>
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<td>0.020</td>
<td>252 403.962</td>
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<td>0.020</td>
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<td>19–18</td>
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<td>0.020</td>
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<td>20–19</td>
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<td>22–21</td>
<td>367 776.772</td>
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<td>368 773.902</td>
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<td>0.020</td>
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<td>23–22</td>
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<td>-0.001</td>
<td>0.020</td>
<td>378 465.787</td>
<td>-0.007</td>
<td>0.020</td>
</tr>
<tr>
<td>24–23</td>
<td>387 110.639</td>
<td>-0.000</td>
<td>0.020</td>
<td>388 156.714</td>
<td>0.005</td>
<td>0.020</td>
</tr>
<tr>
<td>25–24</td>
<td>396 776.279</td>
<td>0.002</td>
<td>0.020</td>
<td>397 846.615</td>
<td>-0.015</td>
<td>0.020</td>
</tr>
<tr>
<td>26–25</td>
<td>406 441.034</td>
<td>0.006</td>
<td>0.020</td>
<td>407 535.526</td>
<td>-0.008</td>
<td>0.020</td>
</tr>
<tr>
<td>27–26</td>
<td>416 104.882</td>
<td>0.009</td>
<td>0.020</td>
<td>417 223.400</td>
<td>0.001</td>
<td>0.020</td>
</tr>
<tr>
<td>28–27</td>
<td>425 767.799</td>
<td>0.007</td>
<td>0.020</td>
<td>426 910.220</td>
<td>0.017</td>
<td>0.020</td>
</tr>
<tr>
<td>29–28</td>
<td>503 035.432</td>
<td>0.005</td>
<td>0.020</td>
<td>504 363.848</td>
<td>0.035</td>
<td>0.020</td>
</tr>
<tr>
<td>30–29</td>
<td>512 689.126</td>
<td>0.002</td>
<td>0.020</td>
<td>514 040.103</td>
<td>0.010</td>
<td>0.020</td>
</tr>
<tr>
<td>31–30</td>
<td>522 341.719</td>
<td>0.017</td>
<td>0.020</td>
<td>523 715.116</td>
<td>0.016</td>
<td>0.020</td>
</tr>
<tr>
<td>32–31</td>
<td>589 875.793</td>
<td>0.002</td>
<td>0.020</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

Notes. – Standard errors in units of the last digit are given in parentheses for the fitted parameters. \(^a\) Fixed in the analysis.

Table 3. Analysed transition frequencies and least-squares residuals (MHz) for C\(_3\)O in the \( v_5 = 1 \) vibrationally excited state.

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Notes. – Standard errors in units of the last digit are given in parentheses for the fitted parameters. \(^a\) Fixed in the analysis.

for the overtone states. The spectra were analysed using Eqs. (1) and (2), and the previous cm-wave data for the \( v_5 = 1 \) state (Brown et al. 1985) were included in the corresponding data set with a reduced weighting factor (\( w = 1/\sigma^2 \)), in order to take into account their lower measurement precision. Assumed uncertainties \( \sigma = 20 \) kHz and \( \sigma = 100 \) kHz were adopted for the present measurements and for the data of Brown et al. (1985), respectively. The complete list of the transition frequencies analysed for the states \( v_5 = 1, v_5 = 2 \), and \( v_5 = 3 \), and of the corresponding least-squares residuals are reported in Tables 3 and 4.

The least-squares fits yielded accurate values of the rotational and centrifugal distortion constants, including the sextic constant \( H \), which was precisely determined for each state. Conversely, the octic centrifugal distortion constant \( L \) was kept fixed at the value determined for the ground state. The results of these least-squares fits are reported in Cols. 2–4 of Table 2.
Table 4. Analyzed transition frequencies and least-squares residuals (MHz) for C$_2$O in the $v_5 = 2$ and $v_5 = 3$ bending overtone states.

<table>
<thead>
<tr>
<th>Transition</th>
<th>$v_5 = 2, l_5 = 0$</th>
<th>$v_5 = 2, l_5 = 2$</th>
<th>$v_5 = 2, l_5 = 2^*$</th>
</tr>
</thead>
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<tr>
<td>9–8</td>
<td>87 943.091</td>
<td>0.011</td>
<td>87 944.878</td>
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<tr>
<td>10–9</td>
<td>97 711.921</td>
<td>−0.004</td>
<td>97 715.599</td>
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<tr>
<td>11–10</td>
<td>107 479.961</td>
<td>0.011</td>
<td>107 486.036</td>
</tr>
<tr>
<td>13–12</td>
<td>127 013.240</td>
<td>0.016</td>
<td>127 025.866</td>
</tr>
<tr>
<td>14–13</td>
<td>136 778.304</td>
<td>−0.013</td>
<td>136 795.255</td>
</tr>
<tr>
<td>34–33</td>
<td>331 759.467</td>
<td>−0.003</td>
<td>332 058.525</td>
</tr>
<tr>
<td>35–34</td>
<td>341 489.182</td>
<td>−0.010</td>
<td>341 813.337</td>
</tr>
<tr>
<td>36–35</td>
<td>351 216.968</td>
<td>0.002</td>
<td>351 567.133</td>
</tr>
<tr>
<td>37–36</td>
<td>360 942.793</td>
<td>−0.014</td>
<td>361 319.960</td>
</tr>
<tr>
<td>38–37</td>
<td>370 666.735</td>
<td>−0.001</td>
<td>371 071.664</td>
</tr>
<tr>
<td>39–38</td>
<td>380 388.782</td>
<td>0.004</td>
<td>380 822.326</td>
</tr>
<tr>
<td>40–39</td>
<td>390 108.966</td>
<td>0.004</td>
<td>390 571.894</td>
</tr>
<tr>
<td>41–40</td>
<td>399 827.329</td>
<td>0.011</td>
<td>400 320.340</td>
</tr>
</tbody>
</table>

Notes. – Assumed uncertainties are 20 kHz for all the transitions. * Unresolved $l$-doublet; $\beta$ deviation between the experimental frequency of a blend of unresolved lines and the mean value of the corresponding calculated frequencies.

4. Discussion

This paper extends to the submm-wave region the study of the rotational spectra of C$_2$O in its ground vibrational state and, additionally, reports new mm-wave and submm-wave measurements for three vibrationally excited states of the $v_5$ bending manifold lying below 400 cm$^{-1}$. The fairly high $J$-values reached in the present investigation made possible an accurate analysis of the centrifugal distortion effects, resulting in the determination of the sextic constant $H$ for all the vibrationally excited states and also of the octic constant $L$ for the ground state. The $l$-type resonance effects were taken into account in the analysis of the bending excited state spectra in order to obtain spectroscopic parameters with clear physical meaning. Indeed, the rotational and centrifugal distortion constants fitted for the overtone bending states $v_5 = 2$ and $v_5 = 3$ are in very good agreement with the values extrapolated from the singly excited bending state $v_5 = 1$.

In his theoretical work, Botschwina (2005) suggested that C$_2$O is a rather floppy molecule: on the basis of ab initio calculations he estimated a ratio between ground state and equilibrium centrifugal distortion constants $D_0/D_e$ of 1.46, and adopted this parameter as an indicator of molecular floppiness. Our experimental results provide a confirmation of this hypothesis as: (i) the value of the sextic centrifugal distortion constant $H$ is one order of magnitude higher than those of typical semirigid linear molecules containing four first-row atoms, such as HC$_3$N (Thorwirth et al. 2000) or HC$_3$H (Bizzocchi & Degli Esposti 2008); (ii) the octic centrifugal distortion constant $L$ gave non negligible contributions to the frequencies of transitions with $J > 40$ and had to be included in the analysis of the ground state spectra, which span the largest $J$ range; and (iii) both $D$ and $H$ centrifugal distortion constants exhibit a large vibrational dependence on the $v_5$ bending quantum number, undergoing changes of 30% and 90%, respectively, for a single excitation. This latter effect accounts for most of the unusually large $D_0/D_e$ ratio (Botschwina 2005).

The improved set of spectroscopic constants derived in the present investigation allows the calculation of a very reliable list of rest frequencies for the lowest vibrationally excited states of C$_2$O at millimetre and submillimetre wavelengths. The predicted $1\sigma$ uncertainties do not exceed 30 kHz up to 800 GHz (0.01 km s$^{-1}$) for ground state lines, whereas for the excited state spectra the uncertainties are less than 50 kHz up to 500 GHz (0.03 km s$^{-1}$).

Tables 5–8, available in electronic form at the CDS, collect a list of rest frequencies between 10 GHz and 800 GHz calculated from the spectroscopic data of Table 2, including also the estimated uncertainty at the $1\sigma$ level of each transition as determined statistically by the least-squares fits (Albritton et al. 1976). The corresponding Einstein $A$-coefficients for spontaneous emission from state $J'$ to $J$ can be calculated for each line using (Herzberg 1950)

$$A_{J'\rightarrow J} = \frac{16\pi^3}{5\epsilon_0 c^5} \frac{\nu_{J'J}^3}{2J' + 1} L(J', l)|\mu|^2,$$

where $\nu_{J'J}$ is the transition frequency, $\mu$ is the molecular dipole moment, whose experimental value is 2.391(5) D (Brown et al. 1983), and $L(J', l)$ is the Hönl-London factor for a $P$-branch $|\Delta l = 0$ transition (Herzberg 1950):

$$L(J', l) = (J' + l)(J' - l)/J'.$$
The detection of C$_3$O toward the extreme carbon star IRC+10216 stressed the similarity between the chemistry taking place in cold dense clouds and in the circumstellar envelopes of C-rich AGB stars (Agúndez et al. 2008), and it also put forth the need for a revised chemical model of these objects. Also, a recent study of IRC+10216 based on infrared observations (Fonfría et al. 2008) has shown that the IR pumping due to the MIR and FIR continuum coming from the dusty envelope is very effective in producing high non-LTE vibrational temperatures. Thus, the detection of vibrationally excited C$_3$O in IRC+10216 might provide useful information in understanding the mechanism of formation of O-bearing species in C-rich circumstellar envelopes.

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