VIS and VUV spectroscopy of $^{12}\text{C}^{17}\text{O}$ and deperturbation analysis of the $A^{1}\Pi$, $\nu = 1–5$ levels

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High-accuracy dispersive optical spectroscopy measurements in the visible (VIS) region have been performed on the less-abundant $^{12}\text{C}^{17}\text{O}$ isotopologue, observing high-resolution emission bands of the $B^{2}\Sigma^+ (\nu = 0) \rightarrow A^{1}\Pi (\nu = 3, 4, 5)$ Angstrom system. These are combined with high-resolution photoabsorption measurements of the $^{12}\text{C}^{17}\text{O} B^{2}\Sigma^+ (\nu = 0) \leftrightarrow X^{2}\Sigma^+ (\nu = 0)$ and $C^{2}\Sigma^+ (\nu = 0) \leftrightarrow X^{2}\Sigma^+ (\nu = 0)$ Hopfield–Birge bands recorded with the vacuum-ultraviolet (VUV) Fourier transform spectrometer, installed on the DESIRS beamline at the SOLEIL synchrotron. The frequencies of 429 observed transitions have been determined in the $15\,100–18\,400$ cm$^{-1}$ and $86\,900–92\,100$ cm$^{-1}$ regions with an absolute accuracy of up to 0.003 cm$^{-1}$ and 0.005 cm$^{-1}$ for the B–A, and B–X, C–X systems, respectively. These new experimental data were combined with data from the previously analysed C $\rightarrow$ A and B $\rightarrow$ A systems. The comprehensive data set, 982 spectral lines belonging to 12 bands, was included in a deperturbation analysis of the $A^{1}\Pi$, $\nu = 1–5$ levels of $^{12}\text{C}^{17}\text{O}$, taking into account interactions with levels in the $d^{3}\Delta$, $e^{3}\Sigma^-$, $a^{3}\Sigma^-$, $1^{1}\Sigma^-$ and $D^{1}\Delta$ states. The $A^{1}\Pi$ and perturber states were described in terms of a set of deperturbed molecular constants, spin–orbit and L–uncoupling interaction parameters, equilibrium constants, 309 term values, as well as isotopologue-independent spin–orbit and rotation–electronic perturbation parameters.

1. Introduction

Carbon monoxide (CO) is one of the most thoroughly studied molecules, bearing significance to astronomy and cosmology. After H$_2$, it is the second most abundant molecule in the interstellar medium (ISM), where it is investigated as a tracer of gas properties, structure and kinematics.$^1$ In such astrophysical environments CO controls much of the gas-phase chemistry, and is a precursor to complex molecules. The CO spectrum has been observed in comets, cool dwarfs, quasars, supernova remnants, and interstellar molecular clouds as well as in atmospheres of planets and transiting exoplanets. Emissions originating from the $B^{2}\Sigma^+ (\nu = 0)$, $B^{2}\Sigma^+ (\nu = 1)$, and $C^{2}\Sigma^+ (\nu = 0)$ vibrational levels were recorded from the Martian and Venusian atmospheres by the Hopkins Ultra-violet Telescope,$^7$ the FUSE satellite,$^8$ and the Cassini UVIS instrument.$^{10}$ Large CO abundances produce detectable signals even for the rare isotopologues, including $^{12}\text{C}^{17}\text{O}$. Investigations of minor isotopologues are applied to unravel ‘depth effects’ in the interstellar absorptions$^{14}$ and for precise determination of the $[^{12}\text{C}]/[^{13}\text{C}]$ and $[^{16}\text{O}]^{17}\text{O}/[^{18}\text{O}]$ ratios in the ISM.$^{13,15}$ The CO vacuum ultraviolet absorption spectrum is of astrophysical relevance due to the photodissociation of VUV-excited states, e.g. the $C^{2}\Sigma^+$, $B^{2}\Sigma^+$ and $E^{1}\Pi$ states.$^{15}$ Isotopod dependent photodissociation effects, due to self-shielding in high-column density environments,$^{15,17}$ lead to isotopic fractionation of CO.$^{15,18}$

The less-abundant $^{12}\text{C}^{17}\text{O}$ isotopologue was detected in the ISM for the first time in 1973 in the Orion Nebula$^{19}$ and has been studied in the laboratory in a number of investigations.$^{20–25}$
Table 1 Transition frequencies (in cm⁻¹) of the ¹²C¹⁷O B²Σ⁺ → A²Π emission bands from the high-accuracy dispersive optical spectroscopy measurements

| J' | B²Σ⁺ → A²Π (0, 3) |  |  |
|---|---|---|---|
| f' | P₁₁₀(f') | Q₁₁₀(f') | R₁₁₀(f') |
| 1 | 17873.5145w | 17877.3487 | 17884.9340w |
| 2 | 17879.5600w | 17890.3448w | 17890.9538w |
| 3 | 17890.7578 | 17895.3730 | 17896.5332 |
| 4 | 17891.6971b | 17895.4024 | 17896.5332 |
| 5 | 17892.3988b | 17894.5914 | 17905.5738 |
| 6 | 17896.6234b | 17888.6168 | 17911.3897 |
| 7 | 17870.6627b | 17893.4497 | 17920.0175 |
| 8 | 17872.5000 | 17899.0872b | 17924.4948b |
| 9 | 17875.1945 | 17905.5280 | 17939.6817 |
| 10 | 17878.6007 | 17912.7727 | 17950.7216 |
| 11 | 17882.8628 | 17920.8230 | 17962.5630 |
| 12 | 17887.9333b | 17929.6776 | 17975.2018 |
| 13 | 17893.8041b | 17939.3308 | 17988.6474 |
| 14 | 17900.4819 | 17949.0852 | 18002.9017 |
| 15 | 17907.9701 | 17961.0768 | 18017.9529 |
| 16 | 17916.2703 | 17976.1496 | 18033.7998 |
| 17 | 17923.3745 | 17986.0335 | 18050.4689 |
| 18 | 17935.2870b | 17999.7350b | 18076.9402b |
| 19 | 17946.0199 | 18014.2502 | 18086.9402b |
| 20 | 17957.6189b | 18029.6005b | 18035.3022b |
| 21 | 17969.9100 | 18045.6680 | 18075.1280 |
| 22 | 17978.0826b | 18062.6124 | 18086.9402b |
| 23 | 17997.0643 | 18080.4029 | 18107.3898 |
| 24 | 18011.8926 | 18099.0791 | 18118.7235 |
| 25 | 18027.3585 | 18119.3843 | 18127.8378 |
| 26 | 18044.1309 | 18137.7277b | 18136.9469 |
| 27 | 18061.8968 | 18159.0512b | 18162.2549b |
| 28 | 18076.9080 | 18180.9483b | 18184.7404b |
| 29 | 18097.1576 | 18203.6581b | 18213.4882b |
| 30 | 18117.0973b | 18227.4324 | 18339.8457b |
| 31 | 18137.6823b | 18250.1705b | 18367.8876b |
| 32 | 18159.0776b | 18275.8613b | 18396.7270b |
| 33 | 18181.1794b | 18301.8278w | 18431.5674w |
| 34 | 18204.5622w | 18328.9618wb | 18682.2995w |
| 35 | 18227.8885w | 18356.0240w | 18691.7250w |
| 36 | 18252.4900w | 18384.3289w | 18413.4754w |

| J' | B²Σ⁺ → A²Π (0, 4) |  |  |
|---|---|---|---|
| f' | P₁₁₀(f') | Q₁₁₀(f') | R₁₁₀(f') |

| J' | B²Σ⁺ → A²Π (0, 5) |  |  |
|---|---|---|---|
| f' | P₁₁₀(f') | Q₁₁₀(f') | R₁₁₀(f') |

Notes:
- The estimated absolute calibration 1σ uncertainty was 0.002 cm⁻¹. Lines marked with ‘w’ were weak and with ‘b’ were blended in the spectra.
- Absolute accuracy of the line frequency measurements varies between 0.003 and 0.07 cm⁻¹ for the strongest and weakest lines, respectively.
- The P(10) line of the B(A0, 5) band was overlapped by the deuterium atomic line at 15197.891 cm⁻¹ of significantly higher intensity and half-width. The identification after NIST ASD.26,27b The P(15) line of the B(A0, 5) band was overlapped by the deuterium atomic line at 15237.272 cm⁻¹ of significantly higher intensity and half-width. The identification after NIST ASD.26,27b The R(6) line of the B(A0, 5) band was overlapped by the hydrogen atomic line at 15233.157 cm⁻¹ (Hg of the Balmer series) of significantly higher intensity and half-width. The identification after NIST ASD.26,27b The Q(27) line of the B(A0, 5) band is significantly weakened by multistate, strong perturbations derived from interactions with the dΔₗ (v = 11) and aΣ⁺ (v = 16) states, by which it was not possible to distinguish this line from the noise. The additionally assigned lines based on better, than in the previous works understanding of the spectrum of the ¹²C¹⁷O. The (1, 5) lines originate from above the first predissociation limit of CO located at 90679.1 cm⁻¹.26,27b
Hakalla and co-workers have investigated the visible spectrum of $^{12}\text{C}^{17}\text{O}$, comprising the $B^1\Sigma^+ - A^1\Pi$ Ångström system,\cite{26,27} as well as the $C^1\Sigma^+ - A^1\Pi$ Herzberg system.\cite{28} The VUV spectrum of the $C^1\Sigma^+ - X^1\Sigma^+$ system was investigated by laser excitation\cite{22,29} and the $B^1\Sigma^+ - X^1\Sigma^+$ system by absorption of synchrotron radiation.\cite{25}

The $A^1\Pi$ state is subject to some of the most extensive and complex perturbations among all the states that are known in the carbon monoxide molecule.\cite{30–38} The $d^3\Delta$, $e^3\Sigma^+$, $a^3\Sigma^+$, $i^3\Sigma^+$, and $D^1\Delta$ electronic states are responsible for all of the existing irregularities. A systematic classification of the perturbations of

Fig. 1 High resolution emission spectra, recorded with the high-accuracy dispersive optical spectroscopy setup\cite{66} at an instrumental resolution of 0.15 cm$^{-1}$, of the $^{12}\text{C}^{17}\text{O} B^1\Sigma^+ \rightarrow A^1\Pi (0, 3)$ band, with the perturber lines associated with the $B^1\Sigma^+ \rightarrow D^1\Delta (0, 4)$, and $B^1\Sigma^+ \rightarrow a^3\Sigma^+ (0, 13)$ transitions (upper trace) together with the final branch assignments, calibrating Th atomic lines (going beyond the scale), as well as simulated spectra\cite{67} (lower trace). The ratio of the gas compositions used to obtain the molecular spectra was $^{12}\text{C}^{17}\text{O} : ^{12}\text{C}^{16}\text{O} = 1 : 0.35$.

Fig. 2 High resolution emission spectra, recorded with the high-accuracy dispersive optical spectroscopy setup\cite{66} at an instrumental resolution of 0.15 cm$^{-1}$, of the $^{12}\text{C}^{17}\text{O} B^1\Sigma^+ \rightarrow A^1\Pi (0, 4)$ band, with the perturber lines associated with the $B^1\Sigma^+ \rightarrow e^3\Sigma^+ (0, 7)$, $B^1\Sigma^+ \rightarrow i^1\Sigma^-$ (0, 6), and $B^1\Sigma^+ \rightarrow a^3\Sigma^+ (0, 14)$ transitions (upper trace) together with the final branch assignments, calibrating Th atomic lines (going beyond the scale), as well as simulated spectra\cite{67} (lower trace). The ratio of the gas compositions used to obtain the molecular spectra was $^{12}\text{C}^{17}\text{O} : ^{12}\text{C}^{16}\text{O} = 1 : 0.35$.

Fig. 3 High resolution emission spectra, recorded with the high-accuracy dispersive optical spectroscopy setup\cite{66} at an instrumental resolution of 0.15 cm$^{-1}$, of the $^{12}\text{C}^{17}\text{O} B^1\Sigma^+ \rightarrow A^1\Pi (0, 5)$ band with the perturber lines associated with the $B^1\Sigma^+ \rightarrow d^3\Delta (0, 11)$ transition. The ratio of the gas compositions used to obtain the molecular spectra was $^{12}\text{C}^{17}\text{O} : ^{12}\text{C}^{16}\text{O} = 1 : 0.35$. (Panel (a)) An overview of the observed $B^1\Sigma^+ \rightarrow A^1\Pi (0, 5)$ and $B^1\Sigma^+ \rightarrow d^3\Delta (0, 11)$ spectra (upper trace) together with the final branch assignments, calibrating Th atomic lines (going beyond the scale), as well as simulated spectra\cite{67} (lower trace). The empty circles indicate spectral lines of undetermined location due to overlap with much more intense atomic lines of carbon, hydrogen, and deuterium. (Panel (b)) Expanded view of the $B \rightarrow A (0, 5)$ band head region in $^{12}\text{C}^{17}\text{O}$ at an enlarged scale.
the A'\Pi state in the main 12C16O molecule was carried out by Krupenie. Simmons et al. made a critical analysis of this study as well as completed it. A conclusive analysis and perturbation calculations were carried out by Field et al. Next, Le Floch et al. conducted a comprehensive study of perturbations in the A'\Pi, v = 0 vibrational level. In his next works he analysed perturbations occurring in the A'\Pi, v = 0–4 levels, and calculated very precise term values for the A'\Pi, v = 0–8 states, respectively. Recently, the A'\Pi state of the main 13C16O isotopologue has been studied in the A-X transition by the Amsterdam group by means of highly accurate two-photon Doppler-free excitation using narrow band lasers with relative accuracy up to $\Delta \lambda/\lambda = 2 \times 10^{-8}$, as well as by vacuum ultraviolet Fourier-transform spectroscopy (VUV-FTS) at the SOLEIL synchrotron. An improved perturbation analysis of A'\Pi in ordinary CO has recently been performed by Niu et al. Far fewer perturbation analyses of the A'\Pi state have been performed in other isotopologues of CO (12C18O and 13C17O). A considerable contribution to the identification and classification of the A'\Pi state perturbations has been made by Kepe and Rytel in a number of investigations over the years.

Here, the focus is on the deperturbation analysis of the A'\Pi state ($v = 1, 2, 3, 4$, and 5) levels in the $^{12}$C$^{17}$O isotopologue. The deperturbation is based on new observations of the $^{12}$C$^{17}$OB $\rightarrow$ A (0, 3), (0, 4), (0, 5) bands recorded in visible emission at high resolution and previously published studies of the Ångström and Herzberg bands. The deperturbation analysis prompted some reassignment of lines in the B-A and C-A systems. New, highly accurate measurements of the $^{13}$C$^{17}$OB $\rightarrow$ X (0, 0) and C $\rightarrow$ X (0, 0) transitions with VUV-FTS were performed and included in the study in order to (i) establish and verify that B (v = 0) and C (v = 0) levels are unperturbed, and that our perturbation analysis of A-state is not affected by shifts in the upper states, (ii) include an independent set of improved constants, therewith level energies, of B (v = 0) and C (v = 0), as well as (iii) determine level energies of A-state with respect to ground state of CO. The comprehensive fit on B-A, C-A, B-X, and C-X systems allowed us to perform the most accurate deperturbed rotational constants of the states under consideration.

2. Experimental details

2.1. Emission spectra of the B$^1\Sigma^+ \rightarrow$ A$^1\Pi$ system

In this study, a water-cooled, hollow-cathode lamp with two anodes and a high-accuracy dispersive optical spectroscopy method were used for a high-resolution spectroscopic investigation of the $^{13}$C$^{17}$OB B$^1\Sigma^+$ ($v = 0 \rightarrow$ A'\Pi ($v = 3, 4$, and 5) bands in the visible region. The lamp was initially filled with a mixture of helium and acetylene $^{13}$C$_2$D$_2$ (Cambridge Isotopes, $^{13}$C 99.99%) under the pressure of approximately 6 Torr. An electric current was passed through the mixture for about 200 h, after which a small quantity of $^{12}$C carbon became deposited on the electrodes. Subsequently, the lamp was evacuated and cooled to a temperature of about 400 K.

### Table 2: Transition frequencies of the (B$^1\Sigma^+$, C$^1\Sigma^+ ) \rightarrow (d^3\Delta, e^5\Sigma^+, a^5\Sigma^+, l^1\Sigma^+,$ and D$^3\Delta$) extra-line bands in $^{12}$C$^{17}$O$^{ab}$

| System | Band | Branch | $J'$ | Frequency (cm$^{-1}$) | B-A or C-A band of occurrence |
|--------|------|--------|------|-----------------------|-----------------------------|
| B$^1\Sigma^+$ $\rightarrow$ d$^3\Delta$ | (0, 7) | $^gP_{12ee}$ | 35 | 19632.935 | B$^1\Sigma^-$A$^1\Pi$ (0, 2) |
| | (0, 11) | $^gP_{11ee}$ | 32 | 15487.171$^x$ | B$^1\Sigma^-$A$^1\Pi$ (0, 5) |
| | (0, 12) | $^P_{12ee}$ | 27 | 15552.369 | |
| B$^1\Sigma^+$ $\rightarrow$ e$^5\Sigma^-$ | (0, 4) | $^gQ_{12eff}$ | 26 | 19460.541$^x$ | B$^1\Sigma^-$A$^1\Pi$ (0, 2) |
| | (0, 7) | $^gP_{11ee}$ | 35 | 17002.628$^x$ | B$^1\Sigma^-$A$^1\Pi$ (0, 4) |
| | (0, 10) | $^P_{12ee}$ | 20 | 20761.828$^x$ | B$^1\Sigma^-$A$^1\Pi$ (0, 1) |
| | (0, 13) | $^P_{12ee}$ | 22 | 20820.661 | |
| | (0, 14) | $^P_{12ee}$ | 24 | 18005.897$^x$ | B$^1\Sigma^-$A$^1\Pi$ (0, 3) |
| | (0, 15) | $^P_{12ee}$ | 30 | 18260.250$^x$ | |
| | (0, 16) | $^P_{12ee}$ | 31 | 18307.498$^x$ | |
| | (0, 19) | $^P_{12ee}$ | 29 | 18342.563 | |
| | (0, 20) | $^P_{12ee}$ | 29 | 18392.832 | |
| | (0, 21) | $^P_{12ee}$ | 25 | 16658.293$^x$ | B$^1\Sigma^-$A$^1\Pi$ (0, 4) |
| | (0, 22) | $^P_{12ee}$ | 24 | 16783.703$^x$ | B$^1\Sigma^-$A$^1\Pi$ (0, 4) |
| B$^1\Sigma^+$ $\rightarrow$ l$^1\Sigma^+$ | (0, 1) | $^P_{12ee}$ | 7 | 19291.955 | B$^1\Sigma^-$A$^1\Pi$ (0, 2) |
| | (0, 4) | $^P_{12ee}$ | 27 | 20986.818$^x$ | B$^1\Sigma^-$A$^1\Pi$ (0, 1) |
| | (0, 5) | $^Q_{12eff}$ | 33 | 18327.789$^y$ | B$^1\Sigma^-$A$^1\Pi$ (0, 3) |
| C$^1\Sigma^+$ $\rightarrow$ e$^5\Sigma^-$ | (0, 4) | $^gP_{12ee}$ | 25 | 24430.966$^yb$ | C$^1\Sigma^-$A$^1\Pi$ (0, 2) |
| | (0, 10) | $^P_{12ee}$ | 29 | 24578.958$^y$ | |
| | (0, 13) | $^P_{12ee}$ | 24 | 25952.917$^yb$ | C$^1\Sigma^-$A$^1\Pi$ (0, 1) |
| | (0, 14) | $^P_{12ee}$ | 28 | 23111.431 | C$^1\Sigma^-$A$^1\Pi$ (0, 3) |
| | (0, 15) | $^P_{12ee}$ | 26 | 25849.807$^y$ | C$^1\Sigma^-$A$^1\Pi$ (0, 1) |

$^a$ The estimated calibration uncertainty was 0.002 cm$^{-1}$. The absolute accuracy of the significant majority of extra-lines should be assumed as not better than approximately 0.01 cm$^{-1}$ due to their weakness. $^b$ Lines marked with $'$ were weak and with $b$ were blended in the spectra. The superscript $o$, p, r, s, or q preceding the main notation P, Q, R of the branch indicates the change in total angular momentum excluding spin for transition to the perturber state.
Table 3 Extended and corrected assignment\textsuperscript{a} of some of heavily perturbed or extremely weak lines located mostly in the region of strong and multistate interactions\textsuperscript{b,c}.

| System | \( J' \) | Branch | Frequency (cm\(^{-1}\)) |
|--------|---------|--------|-------------------------|
| B\(^{1}\Sigma^{-}\text{A}^{1}\Pi\) (0, 1) | 1 | Q\(_{1}\text{tof}\) | 20701.471\textsuperscript{w} |
| | 2 | Q\(_{1}\text{tof}\) | 20702.936\textsuperscript{w} |
| | 5 | Q\(_{1}\text{tof}\) | 20711.661\textsuperscript{w} |
| | 26 | P\(_{1}\text{tee}\) | 20855.286\textsuperscript{w} |
| | 26 | R\(_{1}\text{tee}\) | 21055.609\textsuperscript{w} |
| | 34 | Q\(_{1}\text{tof}\) | 21128.729\textsuperscript{w} |
| B\(^{1}\Sigma^{-}\text{A}^{1}\Pi\) (0, 2) | 26 | R\(_{1}\text{tee}\) | 19640.375 |
| | 28 | Q\(_{1}\text{tof}\) | 19587.541 |
| | 29 | Q\(_{1}\text{tof}\) | 19600.539 |
| | 30 | Q\(_{1}\text{tof}\) | 19624.714 |
| | 31 | Q\(_{1}\text{tof}\) | 19648.885\textsuperscript{w} |
| | 31 | P\(_{1}\text{tee}\) | 19534.375\textsuperscript{w} |
| | 32 | Q\(_{1}\text{tof}\) | 19673.557\textsuperscript{w} |
| | 32 | P\(_{1}\text{tee}\) | 19550.099\textsuperscript{w} |
| | 33 | Q\(_{1}\text{tof}\) | 19698.930\textsuperscript{w} |
| | 33 | P\(_{1}\text{tee}\) | 19573.885\textsuperscript{w} |
| B\(^{1}\Sigma^{-}\text{A}^{1}\Pi\) (1, 1) | 1 | P\(_{1}\text{tof}\) | 22754.143\textsuperscript{w} |
| | 1 | R\(_{1}\text{tof}\) | 22765.387\textsuperscript{w} |
| B\(^{1}\Sigma^{-}\text{A}^{1}\Pi\) (1, 5) | 2 | R\(_{1}\text{tof}\) | 17257.095\textsuperscript{w} |
| C\(^{1}\Sigma^{-}\text{A}^{1}\Pi\) (0, 1) | 26 | P\(_{1}\text{tof}\) | 25855.228\textsuperscript{w} |
| | 26 | Q\(_{1}\text{tof}\) | 25953.327 |
| | 26 | R\(_{1}\text{tof}\) | 26055.176\textsuperscript{w} |
| C\(^{1}\Sigma^{-}\text{A}^{1}\Pi\) (0, 2) | 27 | Q\(_{1}\text{tof}\) | 24561.747\textsuperscript{w} |
| | 28 | Q\(_{1}\text{tof}\) | 24586.932\textsuperscript{w} |
| | 29 | Q\(_{1}\text{tof}\) | 24599.645\textsuperscript{w} |
| | 30 | Q\(_{1}\text{tof}\) | 24623.687\textsuperscript{w} |
| C\(^{1}\Sigma^{-}\text{A}^{1}\Pi\) (0, 3) | 11 | P\(_{1}\text{tof}\) | 22889.944 \textsuperscript{w} |
| | 15 | R\(_{1}\text{tof}\) | 23035.165 |
| | 16 | P\(_{1}\text{tof}\) | 22992.713 \textsuperscript{w} |
| | 20 | P\(_{1}\text{tof}\) | 22970.859 |
| | 25 | R\(_{1}\text{tof}\) | 23236.712 \textsuperscript{w} |

\textsuperscript{a} Extended and corrected assignment of the lines already published in previous publication (ref. 26–28).

\textsuperscript{b} The estimated calibration 1\(\sigma\) uncertainty was 0.002 cm\(^{-1}\). The absolute accuracy of the significant majority of the lines should be assumed as not better than approximately 0.01 cm\(^{-1}\).

\textsuperscript{c} Lines marked with 'w' were weak and with 'b' were blended in the spectra.

Spectroscopic measurements were made by means of a 2 m Ebert plane-grating spectrograph equipped with a 651.5 grooves per mm grating with a total of 45 600 grooves, blazed at 1.0 \(\mu\)m in 3\(^{rd}\) and 4\(^{th}\) order, giving reciprocal dispersion and resolving power in the ranges 0.11–0.19 nm mm\(^{-1}\) and 182 400–136 800, respectively. Discharge emission signals were recorded by means of a photon multiplier tube (HAMAMATSU R943-02) mounted on a linear stage (HIWIN KK5002) along the focal curve of the spectrograph. The input and exit slits were 35 \(\mu\)m in width. The intensities of the lines were measured by means of photon counting (HAMAMATSU C3866 photon counting unit and M8784 photon counting board) with a counter gate time of 200–500 ms (no dead time between the gates). The position of the exit slit was measured by means of a He–Ne laser interferometer (LASERTEX) synchronized with the photon counting board. During one exposure of the counter gate, the position was measured 64 times. Simultaneously recorded thorium atomic lines, \textsuperscript{69} obtained from an auxiliary water-cooled, hollow-cathode tube filled with Th foil, were used for absolute CO wavenumber calibration.

The peak positions of spectral lines were derived by means of a least-squares procedure assuming a Gaussian line-shape for each spectral contour (30 points per line), with a fitting uncertainty of the 17O2 isotope (Sigma-Aldrich, 17O2 60%) was admitted at a static gas pressure of 2 Torr. The anodes were operated at 2 × 650 V and 2 × 50 mA dc. During the discharge process the 17O2 molecules decay into atomic oxygen, which then combine with 12C-carbon atoms, ejected from the outer layer of the cathode, thus forming the 12C\(^{17}\)O molecules in the gas phase. The temperature of the plasma formed at the centre of the cathode was about 600–700 K. These conditions were found to be optimal for the production of CO molecular spectra under control of isotopic composition. The experimental equipment of the Rzeszow laboratory, where these measurements were conducted, has been described in detail by Hakalla et al.\textsuperscript{66}

Fig. 4 High resolution absorption spectrum of the B\(^{1}\Sigma^{-}\) → X\(^{1}\Sigma^{+}\) (0, 0) Hopfield–Birge band system in the less-abundant 12C\(^{17}\)O isotopologue recorded with the VUV-FTS setup at the SOLEIL synchrotron at an instrumental resolution of 0.20 cm\(^{-1}\). The estimated absolute calibration 1\(\sigma\) uncertainty was 0.005 cm\(^{-1}\). The 1\(\sigma\) uncertainty due to fitting errors of measured wavenumbers (exclusive of calibration uncertainty) was estimated from the least-squares optimisation algorithm and varies between 0.002 and 0.1 cm\(^{-1}\) for the strongest and weakest lines, respectively. The ratio of the gases used in the experiment was 12C\(^{17}\)O : 12C\(^{16}\)O : 12C\(^{18}\)O = 1 : 0.85 : 0.20.
uncertainty of the peak position for a single unblended line in the range 0.1–0.2 μm, that is 2.5–8 × 10⁻⁴ cm⁻¹ in the observed region. To determine the ¹²C¹⁷O B’Σ⁺ → A’Π wavenumbers, 5th- and 6th-order interpolation polynomials were used for the (0, 3), (0, 4), and (0, 5) bands. The absolute wavenumber calibration at 1σ uncertainty is 0.002 cm⁻¹. The strong and unblended lines exhibit a full-width-half-maximum (FWHM) of 0.15 cm⁻¹, maximum signal-to-noise ratio of about 100 : 1 as well as count rates of up to about 16 000–60 000 photons per s for the ¹²C¹⁷O B’Σ⁺, (v = 0) → A’Π, (v = 3, 4, and 5) bands. The absolute accuracy of the frequency measurements was 0.003 cm⁻¹, corresponding to a relative accuracy of Δλ/λ = 2 × 10⁻⁷, for the 15 180–18 400 cm⁻¹ spectral region. However, weaker or blended lines have lower accuracy, at worst 0.07 cm⁻¹ or Δλ/λ = 4 × 10⁻⁶.

Preliminary identification of the B’Σ⁺, (v = 0) → A’Π, (v = 3, 4, and 5) bands was carried out by means of the information provided in our recent works on the ¹²C¹⁷O molecule.⁴⁻²⁷ For the frequency measurements of the lines investigated, blending effects of the ¹²C¹⁶O Ångström system were taken into account. They occur as a result of using oxygen¹⁷O₂ with spectral purity of only 60%. In total, 283 emission lines belonging to the B’Σ⁺ → A’Π band system in ¹²C¹⁷O were identified and rotationally assigned. The transition frequencies are provided in Table 1. The observed ¹²C¹⁷O B’Σ⁺, (v = 0) → A’Π, (v = 3, 4, and 5) spectra, together with extra-lines, assignments, calibrating Th atomic lines, and final simulated spectra are shown in Fig. 1–3. By “extra-lines”, we refer to the spectral emission lines terminating on perturber states and gaining intensity from mixing with the A’Π state. An additional impediment was the appearance of four atomic lines overlapping the region of the ¹²C¹⁷O B → A, (0, 5) band with significantly higher intensities and broader FWHMs. They were identified by means of the Atomic Spectra Database (ASD) of NIST⁴⁷⁻⁴⁸ as the C lines at 15186.739 cm⁻¹ and 15197.891 cm⁻¹, as well as the H Balmer-alpha line at 15233.157 cm⁻¹ and deuterium D line at 15237.272 cm⁻¹. As a result, it was not possible to measure the positions of the P(11), P(15), and R(6) B → A, (0, 5) lines (marked with empty circles in Fig. 3a).

Our deperturbation analysis allowed us to assign 24 rotational lines from 14 bands of the B’Σ⁺ → d¹Δ, B’Σ⁺ → e¹Σ⁺, B’Σ⁺ → a¹Δ⁺, B’Σ⁺ → I¹Σ⁺, B’Σ⁺ → D¹Δ, C’Σ⁺ → e¹Σ⁺, C’Σ⁺ → a¹Δ⁺, and C’Σ⁺ → D¹Δ systems in ¹²C¹⁷O. The transition frequencies and assignments are presented in Table 2. Since most of them are weak their accuracy is not better than 0.01 cm⁻¹. The deperturbation included some lines from the ¹²C¹²O B’Σ⁺ → A’Π, (0, 1) and (1, 5) bands which we have measured with an improved accuracy²⁶⁻²⁸ and reassigned. Lines in the B → A, (1, 5) band originate from above the first dissociation limit of CO located at 90679.1 cm⁻¹,⁶⁴ and have low intensities due to the competition of emission with predissociation.²⁸ The wavelengths for these lines are collected in Table 1. All high-J lines located in the perturbation regions, previously analysed²⁶⁻²⁸ in ¹²C¹²O, were checked carefully with regard to their quality, because these lines are usually weak. Those lines that were too weak and/or blended were removed from the deperturbation analysis. Also, we extended and corrected the assignment of some heavily perturbed or extremely weak lines located in the region of strong and multistate interactions. They are collected in Table 3.

2.2. VUV-FTS of the B’Σ⁺ ← X’Σ⁺ and C’Σ⁺ ← X’Σ⁺ systems

We have measured photoabsorption spectra for two bands of ¹²C¹⁷O: B’Σ⁺ ← X’Σ⁺, (0, 0) and C’Σ⁺ ← X’Σ⁺, (0, 0). Their spectra, shown in Fig. 4 and 5, respectively, were recorded at the SOLEIL synchrotron utilising the tunable-undulator radiation source of the DESIRS beamline and its permanently-installed vacuum-ultraviolet Fourier-transform spectrometer. The
### Table 4: Transition frequencies (in cm⁻¹) of the $^{12}$C$^{17}$O $B^1\Sigma^+ \rightarrow X^1\Sigma^+$ and $C^3\Sigma^+ \rightarrow X^1\Sigma^+$ absorption bands from the VUV-FTS measurements

| $J''$ | $P(J'')$ | $R(J'')$ | $J''$ | $P(J'')$ | $R(J'')$ |
|-------|----------|----------|-------|----------|----------|
| 0     | 86920.218                      | 91922.750                      |
| 1     | 86912.686bw                    | 91915.194bw                    |
| 2     | 86908.974bw                    | 91911.507bw                    |
| 3     | 86905.328bw                    | 91907.829bw                    |
| 4     | 86901.729bw                    | 91904.201bw                    |
| 5     | 86898.177bw                    | 91900.614bw                    |
| 6     | 86894.685bw                    | 91897.078bw                    |
| 7     | 86891.238                      | 91893.580                      |
| 8     | 86887.842                      | 91890.124                      |
| 9     | 86884.500                      | 91886.709                      |
| 10    | 86881.206                      | 91883.337                      |
| 11    | 86777.962                      | 91880.012                      |
| 12    | 86747.775                      | 91876.725                      |
| 13    | 86716.626                      | 91873.481                      |
| 14    | 86686.537                      | 91870.286                      |
| 15    | 86654.979                      | 91867.128                      |
| 16    | 86625.507                      | 91864.012                      |
| 17    | 86595.563                      | 91860.940                      |
| 18    | 86566.674                      | 91857.913                      |
| 19    | 86533.842                      | 91854.931                      |
| 20    | 86510.065                      | 91851.197                      |
| 21    | 86484.308                      | 91849.087                      |
| 22    | 86456.611                      | 91846.230                      |
| 23    | 86434.001                      | 91843.421                      |
| 24    | 86409.395bw                    | 91840.656                      |
| 25    | 8637.900bw                     | 91837.939                      |
| 26    | 86313.356bw                    | 91835.262                      |
| 27    | 8632.887bw                     | 91832.639                      |
| 28    | 8630.458bw                     | 91830.039                      |
| 29    | 8627.507bw                     | 91827.598                      |
| 30    | 8625.005                       | 91825.043                      |
| 31    | 8622.556bw                     | 91822.750                      |
| 32    | 8620.138bw                     | 91819.749                      |
| 33    | 8617.774                      | 91819.749                      |
| 34    | 8615.466bw                     | 91815.466                      |

The estimated absolute calibration 1σ uncertainty was 0.005 cm⁻¹. Lines marked with ‘w’ were weak, and with ‘b’ were blended in the spectra. Absolute accuracy of the line frequency measurements varies between 0.002 and 0.1 cm⁻¹ for the strongest and weakest lines, respectively.

The characteristics of the beamline and spectrometer are described by Nahon et al. and de Oliveira et al. Two room-temperature spectra were recorded with approximate column densities of $2 \times 10^{15}$ and $6 \times 10^{13}$ cm⁻², and have spectral resolutions of 0.32 and 0.21 cm⁻¹ FWHM, respectively. The lower column density measurement was necessary to avoid saturation of the strongest rotational transitions of $C^3\Sigma^+ \rightarrow X^1\Sigma^+ (0, 0)$ (as indicated in Fig. 5), and was also used by Stark et al. to determine the oscillator strength of this band.

There is significant admixture of the $^{12}$C$^{16}$O and $^{12}$C$^{18}$O isotopologues in our gas sample and lines from these isotopologues frequently overlap the transitions of $^{12}$C$^{17}$O. Despite this, we were able to fit wavenumbers with an accuracy better than 0.01 cm⁻¹ for many $^{12}$C$^{17}$O transitions by modelling the sinc-function line broadening inherent to Fourier-transform spectrometry, as previously implemented and shown with multiple independent codes. A brief summary of the steps involved in our spectral modelling is as follows:

- An initial wavenumber and integrated cross section was assigned to every observed rotational transition in a recorded B ← X or C ← X band, and assuming a column density for each isotopologue component of our spectrum.
- A Gaussian wavelength-dependent cross section for each simulated line was calculated from these values, assuming a Doppler width characteristic of the known experimental temperature (FWHM of 0.20 cm⁻¹ for the case of $^{12}$C$^{17}$O and 295 K). The summation of all lines provided a total cross section.
- The total cross section was converted into a transmission spectrum by the Beer–Lambert law, then convolved with a sinc function to represent the known instrumental broadening of the FTS, and multiplied by the slightly wavelength dependent synchrotron beam intensity, giving a completely simulated absorption spectrum.
- The simulated spectrum was compared with the raw experimental data and model line wavenumbers and cross sections, and isotopologue column densities, were adjusted to minimise the model-to-experiment difference in a pointwise least-squares sense.

The wavenumbers of $^{12}$C$^{16}$O and $^{12}$C$^{18}$O B ← X (0, 0) and C ← X (0, 0) transitions were determined by the analysis of separate spectra recorded with pure samples of those gases. Additionally, the oscillator strengths of the two bands were shown to be independent of isotopic composition and have the rotational dependence of unperturbed $^1\Sigma^+ \rightarrow ^1\Sigma^+$ transitions. Thus, we could fix all details of the individual $^{12}$C$^{16}$O and $^{12}$C$^{18}$O lines in our mixed-gas spectrum while fitting the $^{12}$C$^{17}$O lines. The final assessment of column densities allowed us to estimate the admixture of isotopologues in our mixed sample to be $^{12}$C$^{17}$O : $^{12}$C$^{16}$O : $^{12}$C$^{18}$O = 1 : 0.85 : 0.20. The residual error, after optimally fitting B ← X (0, 0), is nearly consistent with the statistical noise.

Absolute wavenumber calibrations of our spectra were made by comparing lines appearing from contaminant species with their literature wavenumbers: H₂ (ref. 74), Xe (ref. 75 and 76), H (ref. 77), and O (ref. 77). The estimated absolute calibration 1σ uncertainty was 0.005 cm⁻¹. The 1σ uncertainty due to fitting errors of measured wavenumbers (exclusive of calibration uncertainty) was estimated from the least-squares optimisation algorithm and varies between 0.002 and 0.1 cm⁻¹ for the strongest and weakest lines, respectively. A listing of 122 measured transition wavenumbers is given in Table 4.

### 3. Results

#### 3.1. Level energies

Rovibronic term values of the $B^1\Sigma^+$ ($v = 0$) and $C^3\Sigma^+$ ($v = 0$) Rydberg states, with regard to the lowest $X^1\Sigma^+$ ($v = 0$) rovibrational level of the $^{12}$C$^{17}$O ground state, were calculated by using the B ← X (0, 0) and C ← X (0, 0) transition frequencies obtained from a VUV-FTS experiment and using the ground state molecular parameters by Coxon et al., given for the $^{12}$C$^{17}$O
| \(e\) | \(\beta_1\) | \(\beta_2\) | \(\beta_3\) | \(\alpha_{\mathrm{A}}\) | \(\alpha_{\mathrm{B}}\) |
|-----|-----|-----|-----|-----|-----|
| 0   | 91934.842 | 68904.451 | 88681.823 | 66218.768 | 66218.768 |
| 1   | 91934.842 | 68904.451 | 88681.823 | 66218.768 | 66218.768 |
| 2   | 91941.035 | 68921.818 | 88692.286 | 66224.129 | 66224.129 |
| 3   | 91941.035 | 68921.818 | 88692.286 | 66224.129 | 66224.129 |
| 4   | 91947.228 | 68939.206 | 88703.654 | 66239.565 | 66239.565 |
| 5   | 91947.228 | 68939.206 | 88703.654 | 66239.565 | 66239.565 |
| 6   | 91953.421 | 68957.604 | 88715.101 | 66254.905 | 66254.905 |
| 7   | 91953.421 | 68957.604 | 88715.101 | 66254.905 | 66254.905 |
| 8   | 91959.614 | 68975.993 | 88726.548 | 66270.345 | 66270.345 |
| 9   | 91959.614 | 68975.993 | 88726.548 | 66270.345 | 66270.345 |
| 10  | 92017.807 | 68994.391 | 88738.094 | 66285.785 | 66285.785 |
| 11  | 92017.807 | 68994.391 | 88738.094 | 66285.785 | 66285.785 |
| 12  | 92034.000 | 69012.839 | 88750.636 | 66301.226 | 66301.226 |
| 13  | 92034.000 | 69012.839 | 88750.636 | 66301.226 | 66301.226 |
| 14  | 92051.203 | 69031.287 | 88763.178 | 66316.666 | 66316.666 |
| 15  | 92051.203 | 69031.287 | 88763.178 | 66316.666 | 66316.666 |
| 16  | 92068.406 | 69049.735 | 88775.719 | 66332.106 | 66332.106 |
| 17  | 92068.406 | 69049.735 | 88775.719 | 66332.106 | 66332.106 |
| 18  | 92085.609 | 69068.183 | 88788.260 | 66348.546 | 66348.546 |
| 19  | 92085.609 | 69068.183 | 88788.260 | 66348.546 | 66348.546 |
| 20  | 92102.812 | 69086.631 | 88800.801 | 66364.986 | 66364.986 |
| 21  | 92102.812 | 69086.631 | 88800.801 | 66364.986 | 66364.986 |
| 22  | 92120.015 | 69105.079 | 88813.342 | 66381.426 | 66381.426 |
| 23  | 92120.015 | 69105.079 | 88813.342 | 66381.426 | 66381.426 |
| 24  | 92137.218 | 69123.527 | 88825.883 | 66396.866 | 66396.866 |
| 25  | 92137.218 | 69123.527 | 88825.883 | 66396.866 | 66396.866 |
| 26  | 92154.421 | 69141.975 | 88838.423 | 66414.306 | 66414.306 |
| 27  | 92154.421 | 69141.975 | 88838.423 | 66414.306 | 66414.306 |
| 28  | 92171.624 | 69160.423 | 88850.964 | 66430.746 | 66430.746 |
| 29  | 92171.624 | 69160.423 | 88850.964 | 66430.746 | 66430.746 |
| 30  | 92188.827 | 69178.872 | 88863.505 | 66447.186 | 66447.186 |
| 31  | 92188.827 | 69178.872 | 88863.505 | 66447.186 | 66447.186 |
| 32  | 92206.030 | 69197.320 | 88876.046 | 66463.626 | 66463.626 |
| 33  | 92206.030 | 69197.320 | 88876.046 | 66463.626 | 66463.626 |
| 34  | 92223.233 | 69215.769 | 88888.586 | 66480.066 | 66480.066 |
| 35  | 92223.233 | 69215.769 | 88888.586 | 66480.066 | 66480.066 |
isotopologue. These data were combined with the B → A (this work, and ref. 26 and 27) as well as C → A transitions to give term values of the A′Π (v = 1, 2, 3, 4, and 5) levels as high as Jmax = 27–30. They were calculated as differences of energies of the B′Σ+ (v = 0), C′Σ+ (v = 0) terms and B → A (0 − ν′), C → A (0 − ν′) transition frequencies. A similar procedure was adopted to determine terms of the D, I, e, a′, and d perturbers in 12C17O using the B1 state with the hypothetical unperturbed and crossing perturber levels, where BA and DA refer to perturbed rotational constants of the corresponding A′Π level. The reduced term values were calculated in relation to the lowest ν = 0 vibrational level of the 12C17O X′Σ+ ground state by means of the term values given in Tables 5 and 6. Those among the reduced terms which we were not able to determine from the experimental data, were calculated on the basis of isotopically recalculated equilibrium molecular constants by Field94 for d3Δi, e3Σ+, a′3Σ+, and I′Σ− states and by Kittrell et al.95 for D′Δ state. The Tν values were taken from ref. 81–83, and the G(v = 0) value for the X′Σ+ state in 12C17O, 1068.0310 cm−1, from Coxon et al.96 The results are presented in Fig. 6. Identification of perturbers for both e and f A-doubling components of the A′Π (v = 3, 4, and 5) levels are summarized in Table 7.

3.2. Deperturbation analysis of the A′Π state in 12C17O

In total, 982 transitions from 12 B–A, C–A, B–X, and C–X bands and their extra-lines of 12C17O were used in the global fitting procedure. This results in 72 molecular parameters fitted for this minor CO species. This analysis is performed, in analogy to deperturbation analyses of the main 13C16O isotopologue,4,8,9 by the Pgopher software.87 Applying this program we simulated each member of the B(v′ = 0, 1) − A(v′) and C(v′ = 0) − A(v′) progressions independently with a parameterised model of the A(v) levels, perturber levels, and their interactions. The computed level positions, line frequencies, and intensities are the result of a matrix diagonalization including all interacting levels. The assignment of perturber levels, the selection of which parameters and interactions could be discriminated from our spectra, and the values of these parameters were iteratively optimised. The Pgopher program uses the effective Hamiltonian with matrix elements similar to Field,84 Bergeman et al.,45 and Le Floch et al.41 The model is presented in Table 8. The non-diagonal elements describe the interaction of the A′Π state with its perturbers, that is the d3Δi, e3Σ+, a′3Σ+, I′Σ−, and D′Δ states. Interactions between the perturbing states were neglected. For the A′Π diagonal element the ‘+’ and ‘−’ signs relating to A-doubling refer to the e- and f-symmetry states, respectively. Tν denotes the rotation-less energies calculated relative to the lowest vibrational level of the X′Σ+ ground state, ηi is the spin–orbit interaction parameter, 4i is the L-coupling interaction parameter.

The D′Δ and d′Δ states have nearly degenerate e and f A-doubled components. The e3Σ− state has two fine structure levels of e type and one f type, while the a′3Σ− state has two fine structure levels of f type and one e type. By contrast, the I′Σ− state has only f levels. The interactions between the A′Π state and the e3Σ−, a′3Σ+, and d′Δ triplet states are caused by spin–orbit coupling, represented by J-dependent matrix elements. Interactions of A′Π with the I′Σ− and D′Δ singlet states result from L-uncoupling and, therefore, produce heterogeneous interactions with J-dependent matrix elements.82

It was necessary to adopt some isotopically recalculated molecular constants, using Dunham’s relationship within the Born–Oppenheimer approximation,85 of 12C17O d3Δi, e3Σ+, a′3Σ+, I′Σ−, and D′Δ states from ref. 30 and 81, because there are insufficient term-value data for these levels in 12C17O to determine these independently. These values were held fixed during the calculations. We only fitted molecular constants to those perturber states for which a sufficient number of transitions were observed in the present experiments. All possible vibrational levels of the perturbers which have a non-negligible influence on the A′Π, v = 1, 2, 3, 4, and 5 levels were included in the calculation. Some of them do not have crossings with the A′Π state but still result in recognisable A-state energy level shifts.

The frequencies of strong and isolated lines were assigned relative weights of 1.0 during the fitting. However, the

Table 6 Rovibronic term values of the d3Δi (ν = 11), e3Σ− (ν = 4), a′3Σ+ (ν = 10, 13), I′Σ− (ν = 3, 6), and D′Δ (ν = 1) levels in 12C17O

| State   | ν | J   | Energy (cm⁻¹) | Triplet component | Electronic symmetry |
|---------|---|-----|---------------|-------------------|---------------------|
| e3Σ−    | 4  | 25  | 68622.59 F₁   | e                 |                     |
|         | 4  | 26  | 68684.69 F₁   | e                 |                     |
|         | 4  | 25  | 68687.47 F₁   | f                 |                     |
| a′3Σ+   | 10 | 20  | 66875.28 F₁   | e                 |                     |
|         | 10 | 22  | 66923.16 F₁   | e                 |                     |
|         | 10 | 22  | 66971.69 F₂   | e                 |                     |
|         | 13 | 24  | 69942.13 F₁   | f                 |                     |
|         | 13 | 24  | 70047.62 F₁   | f                 |                     |
|         | 14 | 3   | 70296.10 F₂   | e                 |                     |
| I′Σ−    | 3  | 7   | 67730.78 F₁   | f                 |                     |
|         | 6  | 24  | 71269.82 F₁   | f                 |                     |
| D′Δ     | 1  | 26  | 67298.11 F₁   | f                 |                     |
|         | 1  | 27  | 67361.47 F₁   | f                 |                     |

All values in cm⁻¹. Level energies were calculated relative to the lowest ν = 0 vibrational level of the X′Σ+ ground state of 12C17O from the combined data sets of two experiments: the VUV-FTS study for the C′Σ− (v = 0) and B′Σ+ (v = 0) levels, as well as VIS high-accuracy dispersive optical spectroscopy measurements for the e3Σ− (v = 4), a′3Σ+ (v = 10, 13), I′Σ− (v = 3, 6), and D′Δ (ν = 1) levels. The final values of the terms were obtained using the weighted average method.
frequencies of weak and/or blended lines have lower accuracy, so they were individually weighted between 0.5 and 0.1, according to the degree of their weakening and/or overlap. Initial fits were made by varying the $B$, $D$, $H$ rotational constants and the $q$ A-doubling constant of the $A^1\Pi$ ($v = 1–5$) levels. This means that all parity-dependent interactions were included explicitly in the interactions contained in our deperturbation. Any additional $L$-doubling from remote perturbers was aliased by the interactions included in our perturbation. During the deperturbation, the rotational $B$ and $D$ parameters of the $X^1\Sigma^+$ ground state were fixed to the values given by Coxon et al. for $^{12}\text{C}^{17}\text{O}$.

The unweighted obs-calc residuals of the fitting method are dominated by the uncertainties of the very weak and heavily perturbed lines that belong to the weakest $B$–$A$ $(1, 1)$ and $(1, 5)$ bands. The weighted contribution to the root-mean-square (rms) residual value of high-accuracy dispersive optical spectroscopy and VUV-FTS data is 0.006 cm$^{-1}$. This shows that the fitting model acceptably reproduces such a comprehensive experimental data set.

In a few cases, fitting of the interaction parameters was statistically unjustified because there was an insufficient quantity of experimental transitions in the vicinity of the avoided crossings of the perturbing states or because of the interaction of energetically remote states (for $J < 0$ or $J > J_{\text{max}}$) without any observed crossing points with the $A^1\Pi$ state in $^{12}\text{C}^{17}\text{O}$. In such cases we estimated the semi-empirical interaction parameters making use of the quality suggested in ref. 31, 41.

Fig. 6  The reduced $T(J) - B_J(J+1) + D_{\text{eff}}(J+1)^2 + 1\Sigma^+$ term values for the $^{12}\text{C}^{17}\text{O} A^1\Pi$ ($v = 1–5$) levels and for the hypothetical unperturbed crossing rovibronic levels of the perturbers. Filled and open circles indicate $e$ and $f$ electronic symmetry of the $A^1\Pi$ state, respectively. The reduced level energies (in cm$^{-1}$) were calculated in relation to the lowest $v = 0$ rovibrational level of the $X^1\Sigma^+$ ground state by means of terms calculated in this work (see Tables 5 and 6). Some reduced terms were calculated on the basis of isotopically recalculated equilibrium molecular constants given by Field et al. for $^\text{d3}\Delta$, $^\alpha\Sigma_x^+$, $^\beta\Sigma_x^+$, and $^\gamma\Sigma_x^+$ states and by Kittrell et al. for $^\text{D}\Delta$ state. The $T_e$ values were taken from ref. 81–83, and the $G(v = 0)$ value for the $X^1\Sigma^+$ state in $^{12}\text{C}^{17}\text{O}$, 1068.0310 cm$^{-1}$, from Coxon et al. $B_x$ and $D_x$ symbols refer to deperturbed rotational constants of the respective $A^1\Pi$ rovibronic level, determined in this work (see Table 10). Note that different reduced-energy scales in cm$^{-1}$ are used for different vibrational levels of $A^1\Pi$. 

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Table 7 Observed and predicted perturbations in the AII, \( v = 3, 4, \) and 5 rovibrational levels of the \( ^{12}\text{C}^{17}\text{O} \) isotopologue

| Perturbed state | Vibrational level | Triplet component | \( f \) value for the maximum of perturbation in A-doubling components |
|-----------------|------------------|-------------------|--------------------------------------------------|
| AII (\( v = 3 \)) | \( e^3\Sigma^- (v = 5) \) | F(1) | \( b \) | \( <1 \) | \( b \) | \( <1 \) |
| | | F(2) | \( \) | \( \) | \( \) | \( \) |
| | | F(3) | \( \) | \( \) | \( \) | \( \) |
| | \( d^3\Delta_0 (v = 8) \) | F(3) | \( \) | \( \) | \( \) | \( \) |
| | | F(2) | \( \) | \( \) | \( \) | \( \) |
| | | F(1) | \( \) | \( \) | \( \) | \( \) |
| AII (\( v = 4 \)) | \( a^3\Sigma^- (v = 13) \) | F(1) | 24–25 | 24–25 | 26–27 | 26–27 |
| | | F(2) | \( \) | \( \) | \( \) | \( \) |
| | | F(3) | \( \) | \( \) | \( \) | \( \) |
| | \( \) | \( \) | \( \) | \( \) | \( \) | \( \) |
| | \( D^3\Delta (v = 4) \) | F(1) | \( b \) | \( 33 \) | \( 33 \) | \( 33 \) |
| | | F(2) | \( \) | \( \) | \( \) | \( \) |
| | | F(3) | \( \) | \( \) | \( \) | \( \) |
| AII (\( v = 5 \)) | \( e^3\Sigma^- (v = 7) \) | F(1) | 23–24 | 23 | 33–34 | 34 |
| | | F(2) | \( \) | \( \) | \( \) | \( \) |
| | | F(3) | \( \) | \( \) | \( \) | \( \) |

The values in bold correspond to perturbations observed for the first time in \( ^{12}\text{C}^{17}\text{O} \). Theoretically predicted interaction of energetically remote states (for \( f < 0 \) or \( f > f_{\text{max}} \)) without any observed crossing points with the AII state but the deperturbation fit shows that they have a noticeable influence on the AII (\( v = 3, 4, \) or 5) levels (see Table 10). Perturbation difficult to identify on the basis of observations only (e.g. Fig. 6) due to stronger interaction that exists in this region deriving from the \( a^3\Sigma^- (v = 13) \) state. Its significance can be evaluated only on the basis of results of deperturbation fit provided in Table 10. Perturbation difficult to identify on the basis of observations only (e.g. Fig. 6) due to stronger interaction that exists in this region deriving from the F1 term of the \( a^3\Sigma^- (v = 16) \) state. Its significance can be evaluated only on the basis of results of deperturbation fit provided in Table 10. Perturbation difficult to identify on the basis of observations only (e.g. Fig. 6) because of uncharacteristic behaviour of the rovibrational e-parity terms at \( f = 20–28 \) due to overlapping interaction with distant substantially interaction with the F2 term of the \( a^3\Sigma^- (v = 16) \) state.

and 88, which shows that for perturbation between vibronic levels of a given pair of electronic states, the perturbation matrix element \( \alpha, \beta \) is the product of a vibrational factor and a constant electronic perturbation parameter \( \alpha, \beta \). The effective perturbation parameters \( \alpha, \beta \) in the e/f basis set, are defined as follows:

\[
\alpha_{A-d} = \langle A^I \Pi, v_A \mid H_{\text{SO}}^e \mid d^3\Delta, v_d \rangle = -\left(\frac{\sqrt{2}}{4}\right) a_{A-d} \langle v_A \mid v_d \rangle, \tag{1}
\]

\[
\alpha_{A-e} = \langle A^I \Pi, v_A \mid H_{\text{SO}}^e \mid e^3\Sigma^-, v_e \rangle = -\left(\frac{1}{4}\right) a_{A-e} \langle v_A \mid v_e \rangle, \tag{2}
\]

\[
\alpha_{A-a} = \langle A^I \Pi, v_A \mid H_{\text{RE}}^e \mid a^3\Sigma^+, v_a \rangle = \left(\frac{1}{4}\right) a_{A-a} \langle v_A \mid v_a \rangle, \tag{3}
\]

\[
2\beta_{A-11} \sqrt{J(J+1)} = \langle A^I \Pi, v_A \mid H_{\text{RE}}^e \mid 1^1\Sigma^+, v_1 \rangle = -\sqrt{J(J+1)} b_{A-11} \langle v_A \mid B(R) \rangle \langle v_1 \rangle, \tag{4}
\]

\[
\beta_{A-D} \sqrt{J(J+1) - 2} = \langle A^I \Pi, v_A \mid H_{\text{RE}}^e \mid D^3\Delta, v_D \rangle = \sqrt{J(J+1) - 2} b_{A-D} \langle v_A \mid B(R) \rangle \langle v_D \rangle, \tag{5}
\]

where \( H_{\text{SO}} \) and \( H_{\text{RE}} \) are the spin–orbit and rotation-electronic operators, respectively, and \( a = (2\pi|a'|2\sigma), \) \( b = (2\pi|b'|2\sigma). \) It
Table 8  Effective Hamiltonian and matrix elements for perturbation analyses of the A′IΠ ($\nu = 1, 2, 3, 4$, and 5) rovibronic levels and their perturbers in $^{12}$C$^{17}$O$^{6,9,5}$

|     | A′IΠ   | 1′Σ⁻ | D′Δ   | e′Σ⁻ | a′″Σ⁺ | d′Δ₁ |
|-----|--------|------|-------|------|-------|------|
| A′IΠ | $T_o + \left( B \pm \frac{d}{2} \right) N^2$ | $\xi(D_o) \times (N.L + N.L)$ | $\xi(D_o) \times (N.L + N.L)$ | $\eta(e_o) \cdot L \cdot S$ | $\eta(a_o) \cdot L \cdot S$ | $\eta(d_o) \cdot L \cdot S$ |
| 1′Σ⁻ | $T_o + BN^2$ | $0$ | $0$ | $0$ | $0$ | $0$ |
| D′Δ | $T_o + BN^2$ | $0$ | $0$ | $0$ | $0$ |
| e′Σ⁻ | $T_o + BN^2 - DN^4 + HN^6$ | $0$ | $0$ | $0$ |
| a′″Σ⁺ | $T_o + BN^2 - DN^4 + HN^6 + \frac{2}{3} \lambda (3S^2_z - S^2)$ | | | |
| d′Δ₁ | $T_o + BN^2 - DN^4 + HN^6 + \frac{2}{3} \lambda (3S^2_z - S^2) + \gamma (N \cdot S)$ | | | |

The model is consistent with that of Pgopher software. The matrix is symmetric, therefore, the lower left non-diagonal elements, which are not shown in the Hamiltonian, are equivalent to those of the corresponding upper right elements. The matrix elements set to zero are results of an approximation consisting in neglecting the mutual interaction between the perturbing states. For the A′IΠ diagonal element the ‘+’ and ‘−’ signs relating to Λ-doubling refer to the e- and f-symmetry states, respectively. $T_o$ denotes the rotation-less energies calculated relative to the lowest rovibrational level of the X′1Σ⁻ ground state, $\eta_i$ - spin–orbit interaction parameter, $\xi_i$ - L-uncoupling interaction parameter. The rest of the parameters used are defined in the open literature.68,86,87

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The spin–orbit and rotation-electronic parameters obtained from the $^{12}\text{C}^{17}\text{O}$ $A'\Pi$ ($v = 1$–$5$) deperturbation analysis are collected in Table 11. The isotopologue independent, electronic perturbation parameters $a$ and $b$ for the $A'\Pi$–($d^3\Delta$, $e^3\Sigma^-$, $a^3\Sigma^+$, $i^3\Sigma^-$, and $D^3\Delta$) interactions are in very good agreement with the values given by Le Floch$^{31}$ (see Table 9) Field$^{30}$ and Field et al.$^{32,87}$ While performing the deperturbation calculations, we also obtained the rovibrational constants for the $B^3\Sigma^+$ ($v = 0$ and 1) and $C^3\Sigma^+$ ($v = 0$) Rydberg states in $^{12}\text{C}^{17}\text{O}$. The results are given in Table 12. The constants for the $B^3\Sigma^+$ and $C^3\Sigma^+$ states are compared with analogous values derived in previous studies.$^{26–28}$

### 3.3. Equilibrium constants and transition probabilities in $^{12}\text{C}^{17}\text{O}$

Equilibrium constants of the $A'\Pi$ state in $^{12}\text{C}^{17}\text{O}$ were determined on the basis of the $A'\Pi$ ($v = 1$–$5$) deperturbed constants summarised in Table 10, using a weighted least-squares method. The results are collected in Table 13 and expressed as Dunham coefficients. Despite the fact that Dunham parameters do not include the parameters that describe perturbations between the zero-order states and they are not expected to fit the data to measurement accuracy, they are the most appropriate input to RKR and Franck–Condon Factors (FCF) calculations. It allowed for obtaining the FCF for the Ångström ($B^3\Sigma^+–A'\Pi$), Herzberg ($C^3\Sigma^+–A'\Pi$) and Fourth positive ($A'\Pi–X^3\Sigma^+$) systems using the deperturbed RKR potential energy curve parameters of the $^{12}\text{C}^{17}\text{O}$ $A'\Pi$ (this work), $B^3\Sigma^+$ (ref. 27), $C^3\Sigma^+$ (ref. 28), and $X^3\Sigma^+$ (ref. 80) states. The FCFs in $^{12}\text{C}^{17}\text{O}$ are provided in Table 14.

### 4. Discussion

Fig. 6a–e show plots of the $^{12}\text{C}^{17}\text{O}$ $A'\Pi$, $v = 1$–$5$ reduced term values together with a diabatic representation of the perturbers. The strongest perturbations occur because of the spin–orbit interactions with the $d^3\Delta$, $a^3\Sigma^+$, and $e^3\Sigma$ triplet states. They lead to clearly visible splitting of the $\Lambda$-doublet components in regions of avoiding crossings. This phenomenon is most visible for $A'\Pi$ ($v = 1$) at $J = 18–24$ caused by $a^3\Sigma^+$ ($v = 10$) with term shifts of $\sim 2.5$ cm$^{-1}$, $A'\Pi$ ($v = 2$) at $J = 25–32$ caused by $e^3\Sigma^+$ ($v = 4$) with maximum term shifts of $\sim 4$ cm$^{-1}$, $A'\Pi$ ($v = 3$) at $J = 24–30$ caused by $a^3\Sigma^+$ ($v = 13$) with maximum term shifts of $\sim 3$ cm$^{-1}$, and for $A'\Pi$ ($v = 5$) where we observe a complex perturbation pattern occurring at $J = 28–32$ resulting from the interactions with the three spin components of $d^3\Delta$ ($v = 11$) and $a^3\Sigma^+$ ($v = 16$) with maximum term shifts of about 2.5 cm$^{-1}$. In
| Constant/level | $A'\Pi (v = 1)$ | $A'\Pi (v = 2)$ | $A'\Pi (v = 3)$ | $A'\Pi (v = 4)$ | $A'\Pi (v = 5)$ |
|----------------|----------------|----------------|----------------|----------------|----------------|
| $T_c$          | 66214.2529 (87)| 67643.9829 (31)| 69039.7043 (16)| 70401.6687 (63)| 71729.6882 (17)|
| $B_c$          | 1.541 758 (21) | 1.519 578 (11) | 1.497 130 4 (92)| 1.474 504 (15) | 1.451 844 (11) |
| $D_c \times 10^6$ | 7.275 (16)    | 7.361 (11)     | 7.383 (10)     | 7.447 (13)     | 7.754 (15)     |
| $H_c \times 10^{11}$ | $-1.26^b$  | $-1.26^b$     | $-1.26^b$     | $-1.26^b$     | $-1.26^b$     |

| Constant/level | $d^3\Delta_l (v = 5)$ | $d^3\Delta_l (v = 7)$ | $d^3\Delta_l (v = 8)$ | $d^3\Delta_l (v = 10)$ | $d^3\Delta_l (v = 11)$ |
|----------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| $T_c$          | 66117.62$^d$           | 68178.22$^d$           | 69180.76$^d$           | 71131.06$^d$           | 72079.01$^d$           |
| $B_c$          | 1.186 79$^d$           | 1.154 46$^d$           | 1.138 55$^d$           | 1.107 25$^d$           | 1.091 82$^d$           |
| $A_e$          | $-16.523^d$            | $-16.630^d$            | $-16.984^d$            | $-17.291^d$            | $-17.444^d$            |
| $\lambda_e$   | 0.898$^d$              | 1.094$^d$              | 1.191$^d$              | 1.387$^d$              | 1.485$^d$              |
| $\gamma_e \times 10^3$ | $-8.13^d$  | $-8.13^d$          | $-8.13^d$             | $-8.13^d$             | $-8.13^d$             |
| $D_e \times 10^6$ | 6.13$^d$              | 6.10$^d$              | 6.09$^d$              | 6.08$^d$              | 6.08$^d$              |
| $H_e \times 10^{11}$ | $-7.41^d$            | $-7.41^d$            | $-7.41^d$             | $-7.41^d$             | $-7.41^d$             |
| $\alpha_{D_e} \times 10^5$ | $-4.94^d$           | $-4.94^d$           | $-4.94^d$             | $-4.94^d$             | $-4.94^d$             |
| $\eta$         | $-16.455$ (54)         | 10.21 (19)            | 0.15$^b$              | 1.72$^b$              | 7.915 (44)            |

| Constant/level | $a'^3\Sigma^+ (v = 10)$ | $a'^3\Sigma^+ (v = 11)$ | $a'^3\Sigma^+ (v = 12)$ | $a'^3\Sigma^+ (v = 13)$ | $a'^3\Sigma^+ (v = 14)$ | $a'^3\Sigma^+ (v = 15)$ |
|----------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| $T_c$          | 66900.71$^d$           | 67924.973 (35)         | 68930.84$^d$           | 70886.156 (13)         | 71836.97$^d$           | 72118.33$^d$           |
| $B_c$          | 1.191 69$^d$           | 1.175 145 (46)         | 1.158 79$^d$           | 1.126 417$^d$          | 1.110 34$^d$           | 1.045 32$^d$           |
| $\lambda_e$   | 0.542$^d$              | 0.557 (11)             | 0.576$^d$              | 0.611$^d$              | 0.628$^d$              | 0.628$^d$              |
| $\gamma_e \times 10^3$ | $-1.131$ (86) | $-1.126$             | $-1.114 1$ (75)       | $-1.106$              | $-1.092$              | $-1.092$              |
| $D_e \times 10^6$ | $-5.85$ (34)          | $-6.27$              | $-6.19$ (24)           | $-6.27$              | $-6.27$              | $-6.27$              |
| $H_e \times 10^{11}$ | 5.95$^d$              | 5.94$^d$              | 5.93$^d$              | 5.93$^d$              | 5.92$^d$              | 5.92$^d$              |
| $\alpha_{D_e} \times 10^5$ | $-3.75$         | $-3.75$              | $-3.75$              | $-3.75$              | $-3.75$              | $-3.75$              |
| $\eta$         | $-4.918$ (73)          | $-6.99$              | 7.091 (11)             | 7.63 (15)             | $-6.803$ (31)          |                        |

| Constant/level | $b'^3\Sigma^+ (v = 12)$ | $b'^3\Sigma^+ (v = 15)$ |
|----------------|------------------------|------------------------|
| $T_c$          | 68377.68$^d$           | 71210.21$^d$           |
| $B_c$          | 1.106 87$^d$           | 1.060 72$^d$           |
| $\lambda_e$   | $-1.119$               | $-1.099$              |
| $\gamma_e \times 10^3$ | $-6.27$            | $-6.27$              |
| $D_e \times 10^6$ | 5.94$^d$              | 5.92$^d$              |
| $H_e \times 10^{11}$ | $-3.75$         | $-3.75$              |
| $\eta$         | 5.65$^b$               | $-6.97$              |

| Constant/level | $I'^3\Sigma^- (v = 2)$ | $I'^3\Sigma^- (v = 3)$ | $I'^3\Sigma^- (v = 5)$ | $I'^3\Sigma^- (v = 6)$ | $I'^3\Sigma^- (v = 8)$ |
|----------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| $T_c$          | 66647.75$^d$           | 67664.68$^d$           | 69639.21$^d$           | 70596.1599 (73)        | 72454.96$^d$           |
| $B_c$          | 1.195 01$^d$           | 1.177 87$^d$           | 1.143 67$^d$           | 1.126 67$^d$           | 1.092 91$^d$           |
| $D_e \times 10^6$ | 6.54$^d$              | 6.56$^d$              | 6.60$^d$              | 6.62$^d$              | 6.66$^d$              |
| $H_e \times 10^{11}$ | 2.78$^d$            | 2.78$^d$              | 2.78$^d$              | 2.78$^d$              | 2.78$^d$              |
| $\xi \times 10^8$ | $-7.420$ (15)         | $-5.75$ (10)          | 3.25$^d$              | $-1.76$ (11)          | 1.98$^b$              |

| Constant/level | $D^3\Delta (v = 1)$ | $D^3\Delta (v = 2)$ | $D^3\Delta (v = 4)$ | $D^3\Delta (v = 5)$ | $D^3\Delta (v = 7)$ |
|----------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| $T_c$          | 66458.5762 (48)     | 67468.27$^d$         | 69429.99$^d$         | 70382.01$^d$         | 72228.37$^d$         |
| $B_c$          | 1.199 71$^d$         | 1.182 76$^d$         | 1.148 86$^d$         | 1.131 91$^d$         | 1.098 01$^d$         |
The parameters without indicating uncertainties are taken from the literature and held fixed during the fitting. $T_\text{c}$ denotes the energy level separations between the ground state $X\Sigma^+$ ($v = 0$, $J = 0$) and excited state ($v = 0$, $J = 0$) of $^{12}$C$^{17}$O. $\eta$ – spin-orbit interaction parameter, and $\xi$ – $L$-uncoupling interaction parameter. 4 Isotopically recalculated from Le Floch$^{32,41}$ and Le Floch et al.$^{31}$ as well as $\langle|\Delta E|\rangle_l$ and $\langle|\Delta E|\rangle_{l=0}$ in $^{12}$C$^{17}$O from Table 9, according to the eqn (1)-(8). See Section 3.2 for details. 5 Calculated on the basis of isotopically recalculated vibrational equilibrium constants of $\Delta^2\Pi$ by Field$^{30,31}$, $\Sigma^\text{X}$ by Le Floch$^{32}$ and $T_\text{c}$ of $\Delta^2\Delta$ from Herberg$^{et al.}\text{ et al.}^{30,31}$ Isotopically recalculated from Kittrell et al.$^{et al.}\text{ et al.}^{30,31}$ Isotopically recalculated from spin–spin $C$ constants of Field$^{30}$ taking into account the equation $\lambda = \left(-\frac{3}{5}\right)C$ (see Table 3.4 in ref. 87). 6 Isotopically recalculated from $^{12}$C$^{17}$O. 1. Uncertainties in parentheses represent one standard deviation. 2. The vibrational integrals were calculated on the basis of $^{12}$C$^{17}$O RKR's of $A$, $D$, $e$, $a^1$, and $D$ states obtained from isotopically recalculated equilibrium constants of Field$^{30}$, Field et al.$^{30,31}$ Le Floch et al.$^{32}$ and Kittrell et al.$^{31,32}$ and using the computer programs 'LEVEL' of Le Roy$^{33}$ as well as 'FRACON' of Jung$^{34}$ (later modified by Jakubeck$^{35}$). The spin–orbit and rotation-electronic perturbation parameters $a$ and $b$ were calculated on the basis of eqn (1)-(8). 3. The weighted average values of the electronic perturbation parameters obtained in this work.

### Table 10

| Constant/level | $D\Delta$ ($v = 1$) | $D\Delta$ ($v = 2$) | $D\Delta$ ($v = 4$) | $D\Delta$ ($v = 5$) | $D\Delta$ ($v = 7$) |
|---------------|----------------|----------------|----------------|----------------|----------------|
| $D_h \times 10^6$ | $6.69^{e}$ | $6.65^{e}$ | $6.62^{e}$ | $6.60^{e}$ | $6.56^{e}$ |
| $H_e \times 10^{11}$ | $-2.78^{e}$ | $-2.78^{e}$ | $-2.78^{e}$ | $-2.78^{e}$ | $-2.78^{e}$ |
| $\xi \times 10^2$ | $-6.64^{(23)}$ | $0.42^{b}$ | $-1.68^{(23)}$ | $-3.88^{(23)}$ | $3.52^{b}$ |

### Table 11

| Interaction | $\langle|\Delta E|\rangle_{l=0}$ ($\text{cm}^{-1}$) | $\eta$ ($\text{cm}^{-1}$) | $\eta/\langle|\Delta E|\rangle_{l=0}$ ($\text{cm}^{-1}$) | $\alpha'$ ($\text{cm}^{-1}$) | $\alpha''$ ($\text{cm}^{-1}$) |
|-------------|---------------------------------|----------------|---------------------------------|----------------|----------------|
| $A\Pi$ ($v = 1$)–$A\Pi$ ($v = 5$) | 0.2803 | $-16.455^{(54)}$ | $-58.71^{(19)}$ | 95.87 | 95.59 |
| $A\Pi$ ($v = 2$)–$A\Pi$ ($v = 7$) | $-0.1763$ | 10.21 | 11 | 94.6 | 18 |
| $A\Pi$ ($v = 5$)–$A\Pi$ ($v = 11$) | $-0.1362$ | 7.915 | 44 | 94.90 | 53 |
| $A\Pi$ ($v = 2$)–$e^1\Sigma$ ($v = 4$) | $-0.2967$ | 12.981 | 79 | $-43.76$ | 27 | 101.05 | 61 | 98.90 | 33 |
| $A\Pi$ ($v = 4$)–$e^1\Sigma$ ($v = 7$) | 0.1600 | $-6.792^{(27)}$ | $-42.46^{(17)}$ | 98.05 | 39 |
| $A\Pi$ ($v = 1$)–$A\Pi$ ($v = 10$) | $-0.1371$ | $-4.918^{(73)}$ | 35.87 | 53 | 82.9 | 12 | 83.6 | 12 |
| $A\Pi$ ($v = 3$)–$A\Pi$ ($v = 13$) | 0.1937 | 7.091 | 11 | 36.226 | 56 | 83.66 | 13 |
| $A\Pi$ ($v = 4$)–$A^3\Sigma^+$ ($v = 14$) | 0.2098 | 7.63 | 15 | 36.3 | 36 | 84.0 | 17 |
| $A\Pi$ ($v = 5$)–$a^1\Sigma^+$ ($v = 16$) | $-0.1883$ | $-6.803^{(31)}$ | 36.12 | 16 | 83.42 | 38 |

### Table 12

| Level/constant | $B^3\Sigma^+$ ($v = 0$) | $B^3\Sigma^+$ ($v = 1$) | $C^1\Sigma^+$ ($v = 0$) |
|---------------|----------------|----------------|----------------|
| $T_c$ | 86916.4256 ($12$) | 88972.9215 ($22$) | 91918.9337 ($14$) |
| $B_h$ | 1.889 934 5 ($75$) | 1.873 949 ($21$) | 1.894 573 ($176$) |
| $D_h \times 10^6$ | 6.472 1 ($88$) | 7.395 ($42$) | 5.877 ($47$) |

All values in cm$^{-1}$. Uncertainties in parentheses represent one standard deviation in units of the last quoted digit. $T_c$ denotes the energy level separations between a given excited state and the $X^2\Sigma^+$ ($v = 0$, $J = 0$) ground state in $^{12}$C$^{17}$O. After Ubachs et al.$^{17}$ $d$ After Hakalla et al.$^{16}$ $e$ After Hakalla et al.$^{16}$ $/f$ After Hakalla.$^{14}$

The weighted average values of the electronic perturbation parameters obtained in this work.

contrast, for $A\Pi$ ($v = 1$) we observe distinct upward shifts of only the lowest rovibrational levels, with no significant effects on the $\Delta$-doublings, despite the fact that the interaction is of a spin–orbit type. The reason is that this perturbation is caused by the lower lying $d^2\Delta$ ($v = 5$) state, which rapidly diverges with increasing rotation from the $1^\Pi$ partner. We deal with a similar situation for $A\Pi$ ($v = 4$), where the perturbation is caused by the $D^2\Delta$ ($v = 5$) level, but this is far less noticeable in the presented scale of the plot. It is worth considering the effect of $\Delta$-doubling caused by a state of $\Sigma$ symmetry. However, interactions with the $D^2\Delta$ and $d^2\Delta$ states induce perturbations of both $e$ and $f$ – parity levels, so do not result in $\Delta$-doubling. We should also notice the cases of spin–orbit interactions between $A\Pi$ and its $e^3\Sigma^+$, $a^3\Sigma^+$, $d^3\Delta$, triplet perturbers, for which negligible $\Delta$-doubling effects are observed, in spite of the
Table 13. Deperturbed equilibrium molecular constants of the A1IΠ state in 12C17O.

| Constant/state | A1IΠ       |
|----------------|------------|
| Y_00           | -0.57      |
| Y_10           | 1497.61    |
|                | 1497.94d   |
|                | 1497.76f   |
|                | 1501.18f   |
|                | 17.15      |
|                | 17.23d     |
|                | 17.43f     |
|                | 19.54f     |
| Y_20           | 6.69       |
| Y_50 × 10^3    | [-8.82]    |
|                | [4.37]     |
| Y_50 × 10^5    | 1.574 11   |
|                | 1.574 41d  |
|                | 1.574 59f  |
|                | 1.574 33f  |
| Y_11 × 10^5    | 2.059      |
|                | 2.172d     |
|                | 2.175f     |
|                | 2.067f     |
| Y_21 × 10^4    | -0.961     |
|                | -0.953f    |
|                | -0.11f     |
|                | -0.10f     |
| Y_31 × 10^4    | [2.862]    |
|                | [-5.085]   |
|                | [5.1251f]  |
|                | [-2.930f]  |
|                | [8.846f]   |
|                | [-1.106f]  |
| Y_41 × 10^4    | 7.03       |
|                | 6.97f      |
|                | 6.91f      |
| Y_41 × 10^6    | 1.33       |
|                | 1.19       |
|                | 1.22       |
| Y_12 × 10^7    | 1.233 87 (19) |
|                | 1.233 781 (25)f |
|                | 1.233 753 (86) |

* All values in cm^{-1} except r_e [Å]. Uncertainties of the Dunham parameters have not been included, because these are not the fitted parameters and they do not reflect inter-parameter correlations. Values given in square brackets were held fixed during the calculation. Values calculated within this work are given in bold. Isotopically recalculated from the 12C16O parameters given by Beaty et al. Isotopically recalculated from the 12C16O parameters given by Le Floch. Isotopically recalculated from the 12C16O parameters given by Field. Calculated by Field for the 12C16O molecule. Calculated by Beaty et al. for the 12C16O isotopologue.

The fact that the crossings occur within the observed 0 < J < 35 region. We deal with such a case for the A1IΠ, v = 3 and 5 levels where the perturbers are d3Δ_i (v = 8), and e3Σ^- (v = 8), respectively. The reduced effects are in this case caused by the very small values of the vibrational integrals for the interacting levels in 12C17O (see Table 9). In turn, the L-uncoupling interactions between the A1IΠ state and I1Σ^- , D1Δ singlet states are usually much weaker. We can notice these interactions distinctly in Fig. 6b-d, where there are interactions of A1IΠ (v = 2) with I1Σ^- (v = 3), and A1IΠ (v = 3) with D1Δ (v = 4) as well as A1IΠ (v = 4) with I1Σ^- (v = 6). In all these cases the largest term shifts do not exceed 0.5 cm^{-1}, which can be classified as weak interactions.

In Table 12, with the high accuracy of the results obtained, we notice a slight inconsistency of rotational constants B_i and D_i of B3Σ^- (v = 0 and 1) and C3Σ^+ (v = 0) in relation to those that were calculated in our previous works. This could be caused by the fact that the linear least-squares method in the version given by Curl and Dane and Watson takes no account of the impact of the Q(J) branches in the singlet-singlet fits. Improvement in the assignment of some of the heavily overlapped and/or extremely weak lines located in the region of strong and multistate perturbations, which was described in Section 2.1, could also be a reason for this inconsistency. It is worth noticing here that the deperturbation analysis conducted in this work was based on a global, three times more extensive experimental data set than was used in other works concerning the less-abundant 13C17O isotopologue.

The present work also allowed for verification and improvement in the observed perturbations of the A1IΠ, v = 1, and 2 rovibrational levels in 12C17O presented in ref. 26. For the A1IΠ, v = 1 state, the A1IΠ (v = 1)–D1Δ (v = 0) avoiding crossing occurs at J = 26–27, both for the e- and f-symmetry levels (see Fig. 6a). However, in the case of the A1IΠ, v = 2 level, it turns out that in the perturbation analysis we must take into account small, but not negligible, impacts of the a3Σ^- (v = 11) and D1Δ (v = 2) states on its band origin and the fact that the maximum of the A1IΠ (v = 1)–e3Σ^- (v = 4; F_3) interaction for the e-symmetry levels falls at J = 31–32, and not at J = 30–31 as had been thought (see Fig. 6b).

It can be seen in Table 10 that the energy levels, T_v, for A1IΠ (v = 1) and A1IΠ (v = 4) have larger uncertainties than the remaining rovibrational levels of this state. This could be due to uncertainties derived from interactions with the d3Δ_i (v = 5) and D1Δ (v = 5) states, respectively. It is important to note that the rotational progressions of these states do not cross the A1IΠ (v = 1) and A1IΠ (v = 4) states. The effects of such interactions result in global energy shifts of the A1IΠ (v = 1, and 4) states, just as in the case of vibrational perturbations. Thus, these interactions translate directly into uncertainties in T_v.

There is a very good agreement between the present and Le Floch’s, Field’s, and Field’s et al. values of the isotopologue independent electronic perturbation parameters a and b for the A1IΠ–(d3Δ_i, e3Σ^- , a3Σ^+, I1Σ^-, and D1Δ) interactions, highlighted in Tables 9 and 11. The obtained electronic perturbation parameters can be used to predict perturbations in other A1IΠ levels of all CO isotopologues. These parameters may be helpful in interpreting laboratory and astrophysical spectra of higher levels of the A1IΠ state.

5. Conclusion

Two different experimental methods, high-accuracy dispersive optical spectroscopy in the visible region and Fourier-transform spectroscopy in the vacuum ultraviolet region, were used to obtain high-resolution spectra of the B3Σ^- → A1IΠ, B3Σ^- ↔ X1Σ^+, and C3Σ^+ ↔ X1Σ^+ systems in the less-abundant 13C17O isotopologue; a total of 429 high-accuracy transition
perform deperturbation analysis of the \( A^1\Sigma^+ - C^2\Pi \) and \( A^2\Pi - X^1\Sigma^+ \) band systems in the \( ^{12}\text{C}^{17}\text{O} \) isotopologue.

| \( A^2\Pi \) (\( \nu' \)) | \( \nu' = 0 \) | \( \nu' = 1 \) | \( \nu' = 2^a \) |
|-----------------|-------------|-------------|-------------|
| 0               | 9.0101 \times 10^{-2} | 0.2537 | 0.3176 |
| 1               | 0.1849 | 0.1736 | 7.3587 \times 10^{-3} |
| 2               | 0.2135 | 2.7840 \times 10^{-2} | 7.1057 \times 10^{-2} |
| 3               | 0.1840 | 5.5201 \times 10^{-3} | 0.1122 |
| 4               | 0.1323 | 5.6103 \times 10^{-2} | 4.6893 \times 10^{-2} |
| 5               | 8.3982 \times 10^{-2} | 9.9048 \times 10^{-2} | 1.5129 \times 10^{-3} |
| 6               | 4.8926 \times 10^{-2} | 0.1082 | 1.3889 \times 10^{-3} |

| \( C^2\Sigma^+ \) (\( \nu' \)) | \( \nu' = 0 \) | \( \nu' = 1 \) | \( \nu' = 2^a \) |
|-----------------|-------------|-------------|-------------|
| 0               | 9.0795 \times 10^{-2} | 0.2373 | 0.2914 |
| 1               | 0.1901 | 0.1741 | 1.3703 \times 10^{-2} |
| 2               | 0.2195 | 2.8173 \times 10^{-2} | 6.2281 \times 10^{-2} |
| 3               | 0.1866 | 6.6188 \times 10^{-3} | 0.1167 |
| 4               | 0.1311 | 6.2383 \times 10^{-2} | 5.2013 \times 10^{-2} |
| 5               | 8.0901 \times 10^{-2} | 0.1075 | 1.7531 \times 10^{-3} |
| 6               | 4.5654 \times 10^{-2} | 0.1145 | 1.5607 \times 10^{-2} |

\(^a\) The vibrational levels, which have not been experimentally observed so far in \( ^{12}\text{C}^{17}\text{O} \).

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Notes and references

1. N. Neininger, M. Guelin, H. Ungerechts, R. Lucas and R. Wielebinski, *Nature*, 1998, 395, 871–873.
2. J. Bally, A. A. Stark, R. W. Wilson and W. D. Langer, *Astrophys. J., Lett.*, 1987, 312, L45–L49.
3. J. R. Lyons and E. D. Young, *Nature*, 2005, 435, 317–320.
4. R. T. Garrod, S. L. Widicus Weaver and E. Herbst, *Astrophys. J.*, 2008, 682, 283–302.
5. H. A. Weaver, P. D. Feldman, M. F. A’Hearn, N. Dello Russo and S. A. Stern, *Astrophys. J.*, 2011, 734, L5–L9.
6. Q. M. Konopacky, T. S. Barman, B. A. Macintosh and C. Marois, *Science*, 2013, 339, 1398–1401.
7. P. D. Feldman, E. B. Burgh, S. T. Durrance and A. F. Davidsen, *Astrophys. J.*, 2000, 538, 395–400.
8. V. A. Krasnopolsky and P. D. Feldman, *Icarus*, 2002, 160, 86–94.
9. P. D. Feldman, H. A. Weaver and E. B. Burgh, *Astrophys. J.*, 2002, 576, L191–L194.
10. J.-C. Gérard, B. Hubert, J. Gustin, V. I. Shematovich, D. Bisikalo, G. R. Gladstone and L. W. Esposito, *Icarus*, 2011, 211, 70–80.
11. E. F. Ladd, *Astrophys. J.*, 2004, 610, 320–328.
12 J. G. A. Wouterloot, J. Brand and C. Henkel, Astron. Astrophys., 2005, 430, 549–560.
13 Y. Sheffer, D. L. Lambert and S. R. Federman, Astrophys. J., 2002, 574, L171–L174.
14 F. Bensch, I. Pak, J. G. A. Wouterloot, G. Klapper and G. Winnewisser, Astrophys. J., Lett., 2001, 562, L185–L188.
15 R. L. Smith, K. M. Pontoppidan, E. D. Young, M. R. Morris and E. F. Van Dishoeck, Astrophys. J., 2009, 701, 163–175.
16 R. Visser, E. F. van Dishoeck and J. H. Black, Astron. Astrophys., 2009, 503, 323–343.
17 S. R. Federman, D. L. Lambert, Y. Sheffer, J. A. Cardelli, B.-G. Andersson, E. F. Van Dishoeck and J. Zsargó, Astron. Astrophys., 2003, 391, 986–999.
18 P. Sonnentrucker, D. E. Welty, J. A. Thorburn and D. G. York, Astron. Astrophys., Suppl. Ser., 2007, 168, 58–99.
19 P. J. Encerenaz, P. G. Wannier, K. B. Jefferits, A. A. Penzias and R. W. Wilson, Astrophys. J., 1973, 186, L77–L80.
20 G. Guelachvili, J. Mol. Spectrosc., 1979, 75, 251–269.
21 P. Cacciani, W. Hogervorst and W. Ubachs, J. Chem. Phys., 1995, 102, 8308–8320.
22 W. Ubachs, P. C. Hinnen, P. Hansen, S. Stolte, W. Hogervorst and P. Cacciani, J. Mol. Spectrosc., 1995, 174, 388–396.
23 W. Ubachs, I. Velchev and P. Cacciani, J. Chem. Phys., 2000, 113, 547–560.
24 A. Du Plessis, E. G. Rohwer and C. M. Steenkamp, J. Mol. Spectrosc., 2007, 243, 124–133.
25 G. Stark, A. N. Heays, J. R. Lyons, P. L. Smith, M. Eidselberg, S. R. Federman, J. L. Lemaire, L. Gavilan, N. de Oliveira, D. Joyce and L. Nahon, Astrophys. J., 2014, 788, 67–80.
26 R. Hakalla, W. Szajna and M. Zachwieja, J. Phys. B: At., Mol. Opt. Phys., 2012, 45, 215102.
27 R. Hakalla, M. Zachwieja and W. Szajna, J. Quant. Spectrosc. Radiat. Transfer, 2014, 140, 7–17.
28 R. Hakalla, J. Quant. Spectrosc. Radiat. Transfer, 2015, 164, 231–247.
29 P. Cacciani, F. Brandi, I. Velchev, C. Lyngå, C.-G. Wahlström and W. Ubachs, Eur. Phys. J. D, 2001, 15, 47–56.
30 R. W. Field, Ph.D. thesis, Harvard University, 1971.
31 A. C. Le Floch, F. Launay, J. Rostas, R. W. Field, C. M. Brown and K. Yoshino, J. Mol. Spectrosc., 1987, 121, 337–379.
32 R. W. Field, B. G. Wicke, J. D. Simmons and S. G. Tilford, J. Mol. Spectrosc., 1972, 44, 383–399.
33 C. Haridas, S. P. Reddy and A. C. Le Floch, J. Mol. Spectrosc., 1994, 167, 334–352.
34 B. A. Garetz, C. Kittrell and A. C. Le Floch, J. Chem. Phys., 1991, 94, 843–853.
35 R. Hakalla, W. Szajna, M. Zachwieja and R. Kępa, Acta Phys. Pol., A, 2012, 122, 674–682.
36 R. Hakalla, M. Zachwieja and W. Szajna, J. Phys. Chem. A, 2013, 117, 12299–12312.
37 R. Hakalla, RSC Adv., 2014, 4, 44394–44407.
38 M. Ostrowska-Kopeć, I. Piotrowska, R. Kępa, P. Kowalczyk, M. Zachwieja and R. Hakalla, J. Mol. Spectrosc., 2015, 314, 63–72.
39 P. H. Krupenie, The Band Spectrum of Carbon Monoxide, National Bureau of Standards, Washington, DC, 1966.
40 J. D. Simmons, A. M. Bass and S. G. Tilford, Astrophys. J., 1969, 155, 345–358.
41 R. W. Field, S. G. Tilford, R. A. Howard and J. D. Simmons, J. Mol. Spectrosc., 1972, 44, 347–382.
42 A. C. Le Floch, Ph.D. thesis, University Paris-Sud, 1989.
43 A. Le Floch, J. Mol. Spectrosc., 1992, 155, 177–183.
44 M. L. Niu, E. J. Salumbides, D. Zhao, N. de Oliveira, D. Joyce, L. Nahon, R. W. Field and W. Ubachs, Mol. Phys., 2013, 111, 2163–2174.
45 E. J. Salumbides, M. L. Niu, J. Bagdonaite, N. de Oliveira, D. Joyce, L. Nahon and W. Ubachs, Phys. Rev. A, 2012, 86, 022510.
46 M. L. Niu, F. Ramirez, E. J. Salumbides and W. Ubachs, J. Chem. Phys., 2015, 142, 044302.
47 W. Ubachs, K. S. E. Eikema, W. Hogervorst and P. C. Cacciani, J. Opt. Soc. Am. B, 1997, 14, 2469–2476.
48 N. de Oliveira, M. Roudjane, D. Joyce, D. Phalippou, J.-C. Rodier and L. Nahon, Nat. Photonics, 2011, 5, 149–153.
49 N. de Oliveira, D. Joyce, D. Phalippou, J. C. Rodier, F. Polack, M. Vervloet and L. Nahon, Rev. Sci. Instrum., 2009, 80, 043101.
50 L. Nahon, N. De Oliveira, G. A. Garcia, J.-F. Gil, B. Pilette, O. Marcouillé, B. Lagarde and F. Polack, J. Synchrotron Radiat., 2012, 19, 508–520.
51 M. L. Niu, E. J. Salumbides, A. N. Heays, N. de Oliveira, R. W. Field and W. Ubachs, Mol. Phys., 2016, 114, 627–636.
52 L. M. Beaty, V. D. Braun, K. P. Huber and A. C. Le Floch, Astrophys. J., Suppl. Ser., 1997, 109, 269–277.
53 C. Haridas, S. P. Reddy and A. C. Le Floch, J. Mol. Spectrosc., 1994, 168, 429–441.
54 R. Kępa and M. Rytel, J. Phys. B: At., Mol. Opt. Phys., 1993, 26, 3355–3362.
55 R. Kępa, J. Mol. Spectrosc., 1989, 135, 119–130.
56 R. Kępa, Can. J. Phys., 1988, 66, 1012–1024.
57 R. Kępa, U. Domin and K. Porada, Acta Phys. Pol., A, 2003, 103, 441–451.
58 R. Kępa, M. Ostrowska-Kopeć and I. Piotrowska, J. Mol. Spectrosc., 2011, 266, 104–112.
59 C. E. Moore and NIST ASD Team, NIST At. Spectra Database, National Institute of Standards and Technology, Gaithersburg, MD, 2014, http://physics.nist.gov/asd.
60 G. Tachiev and C. F. Fischer, J. Phys. B: At., Mol. Opt. Phys., 2000, 33, 2419–2435.
61 J. Baker and NIST ASD Team, NIST At. Spectra Database, National Institute of Standards and Technology, Gaithersburg, MD, 2014, http://physics.nist.gov/asd.
62 P. Zhao, W. Lichten, H. Layer, J. C. Bergquist and NIST ASD Team, NIST At. Spectra Database, National Institute of Standards and Technology, Gaithersburg, MD, 2014, http://physics.nist.gov/asd.
63 S. A. Mitchell and NIST ASD Team, NIST At. Spectra Database, National Institute of Standards and Technology, Gaithersburg, MD, 2014, http://physics.nist.gov/asd.
64 R. Kępa, M. Ostrowska-Kopeć, I. Piotrowska, M. Zachwieja, R. Hakalla, W. Szajna and P. Kolek, J. Phys. B: At., Mol. Opt. Phys., 2014, 47, 045101.
65 R. Bacis, J. Phys. E: Sci. Instrum., 1976, 9, 1081–1086.
66 R. Hakalla and M. Zachwieja, *J. Mol. Spectrosc.*, 2012, 272, 11–18.
67 C. M. Western, *PGOPHER, a Program for Simulating Rotational, Vibrational and Electronic Structure*, University of Bristol, 2015, http://pgopher.chm.bris.ac.uk.
68 D. C. Morton and L. Noreau, *Astrophys. J.*, Suppl. Ser., 1994, 95, 301–344.
69 B. A. Palmer and R. Engleman, *Atlas of the Thorium Spectrum*, Los Alamos Report LA-9615, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, 1983.
70 W.-Ü. L. Tchang-Brillet, P. S. Julienne, J.-M. Robbe, C. Letzelter and F. Rostas, *J. Chem. Phys.*, 1992, 96, 6735–6745.
71 A. N. Heays, G. D. Dickenson, E. J. Salumbides, N. De Oliveira, D. Joyeux, L. Nahon, B. R. Lewis and W. Ubachs, *J. Chem. Phys.*, 2011, 135, 244301.
72 M. Eidelsberg, J. L. Lemaire, S. R. Federman, G. Stark, A. N. Heays, Y. Sheffer, L. Gavilan, J.-H. Fillion, F. Rostas, J. R. Lyons, P. L. Smith, N. de Oliveira, D. Joyeux, M. Roudjane and L. Nahon, *Astron. Astrophys.*, 2012, 543, A69.
73 L. Gavilan, J. L. Lemaire, M. Eidelsberg, S. R. Federman, G. Stark, A. N. Heays, J.-H. Fillion, J. R. Lyons and N. de Oliveira, *J. Phys. Chem. A*, 2013, 117, 9644–9652.
74 D. Bailly, E. J. Salumbides, M. Vervloet and W. Ubachs, *Mol. Phys.*, 2010, 108, 827–846.
75 K. Yoshino and D. E. Freeman, *J. Opt. Soc. Am. B*, 1985, 2, 1268–1274.
76 F. Brandi, I. Velchev, W. Hogervorst and W. Ubachs, *Phys. Rev. A*, 2001, 64, 032505.
77 NIST ASD Team, *NIST At. Spectra Database*, National Institute of Standards and Technology, Gaithersburg, MD, 2014, http://physics.nist.gov/asd.
78 R. F. Curl and C. B. Dane, *J. Mol. Spectrosc.*, 1988, 128, 406–412.
79 J. K. G. Watson, *J. Mol. Spectrosc.*, 1989, 138, 302–308.
80 J. A. Coxon and P. G. Hajigeorgiou, *J. Chem. Phys.*, 2004, 121, 2992–3008.
81 C. Kittrell and B. A. Garetz, *Spectrochim. Acta*, 1989, 45, 31–40.
82 S. G. Tilford and J. D. Simmons, *J. Phys. Chem. Ref. Data*, 1972, 1, 147–188.
83 K. P. Huber and G. Herzberg, *Constants of diatomic molecules*, Van Nostrand Reinhold, New York, 1979.
84 T. Bergeman and D. Cossart, *J. Mol. Spectrosc.*, 1981, 87, 119–195.
85 J. L. Dunham, *Phys. Rev.*, 1932, 41, 721–731.
86 G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules*, reprinted 1989 by Krieger, Van Nostrand-Reinhold, Princeton, New Jersey, Malabar, 1950.
87 H. Lefebvre-Brion and R. W. Field, *The Spectra and Dynamics of Diatomic Molecules*, Elsevier Academic Press, Amsterdam, The Netherlands, 2004.
88 H. Lefebvre-Brion, *Can. J. Phys.*, 1969, 47, 541–545.
89 R. J. Le Roy, *LEVEL 8.2: A Computer Program for Solving the Radial Schrödinger Equation for Bound and Quasibound Levels*, University of Waterloo Chemical Physics Research Report CP-663, 2014, http://leroy.uwaterloo.ca/programs/.
90 C. Jung, *FRACON-Programmdokumentation Quantenchemie*, Akademie der Wissenschaften der DDR, Berlin, 1979.
91 C. Jung and Z. Jakubek, *FRACON-B-Programmdokumentation Quantenchemie FRACON (ver. B)*, Akademie der Wissenschaften der DDR and Pedagogical University of Rzeszów, Berlin – Rzeszów, 1988.
92 A. Le Floch, *Mol. Phys.*, 1991, 72, 133–144.
93 G. Herzberg, J. D. Simmons, A. M. Bass and S. G. Tilford, *Can. J. Phys.*, 1966, 44, 3039–3045.
94 K. F. Freed, *J. Chem. Phys.*, 1966, 45, 4214–4241.
95 B. G. Wicke, R. W. Field and W. Klemperer, *J. Chem. Phys.*, 1972, 56, 5758–5770.