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Abstract of the doctoral thesis

High-resolution Fourier-transform spectroscopy of the less-abundant carbon monoxide $^{12}C^{18}O$ isotopologue and deperturbation analysis of the $A^1\Pi$ (v = 1–3) state

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In this dissertation, the rotational structure of the v = 1–3 vibrational levels of the $A^1\Pi$ electronic state in the rare $^{12}C^{18}O$ isotopologue was investigated with high precision. The analysis was based on an extensive set of high-accuracy experimental data obtained using two complementary Fourier-transform spectroscopic techniques. The high-resolution spectra of the $B^1\Sigma^+ \rightarrow A^1\Pi$(0, 1), (1, 1), (0, 2), (0, 3) and $C^1\Sigma^+ \rightarrow A^1\Pi$(0, 1), (0, 2), (0, 3) emission bands were recorded in the visible (Vis) range using a Bruker IFS 125-HR Fourier-transform spectrometer installed at the Department of Materials and Spectroscopic Research of the Institute of Physics, University of Rzeszów. The spectra were produced using an air-cooled, graphite hollow-cathode lamp, filled with a static gas mixture of $^{18}O_2$ and $^{16}O_2$ molecules. Spectral line positions were measured with an absolute accuracy of approximately 0,005 cm^{-1}. The high-resolution spectra of the $A^1\Pi(v = 1, 2, 3) \leftarrow X^1\Sigma^+(v = 0)$, $B^1\Sigma^+(v = 0, 1) \leftarrow X^1\Sigma^+(v = 0)$ and $C^1\Sigma^+(v = 0) \leftarrow X^1\Sigma^+(v = 0)$ absorption bands were recorded using a vacuum ultraviolet (VUV) FT spectrometer at the SOLEIL synchrotron (St. Aubin, France) with an accuracy of about 0,03 cm^{-1}. The spectra were produced from isotopically enriched $^{12}C^{18}O$ gas introduced into an open (windowless), high-temperature absorption cell, typically 40 cm long (also 20 cm) or into a 9 cm MgF_2 absorption cell placed in the synchrotron beam path. A higher population of rotational levels was achieved (J_{max} = 54) than in previously reported studies in the literature (J_{max} = 37) [1–11]. In the studied bands associated with the $A^1\Pi(v = 1–3)$ levels, as many as 75 extralines originating from the perturbers of the $A^1\Pi$ state were found and identified.

The experimental dataset included in the analysis comprised 1738 high-resolution transitions originating from 13 bands. For each of the $A^1\Pi(v = 1, 2, 3)$ vibrational levels a complete deperturbation analysis was performed based on an effective Hamiltonian and the method of simultaneous fitting of term values and molecular constants. The analysis enabled verification of 119 cases of intramolecular interactions potentially occurring in the $A^1\Pi(v = 1–3)$ state, whereas previous authors had considered only 20 interactions in total. Among the interactions examined, 38 proved to be significant and had a substantial impact on the model. 16 perturbation parameters (including 12 new ones) were determined:

i) spin-orbit interaction:

- $A^1\Pi(v = 1) \sim [a'^3\Sigma^+(v = 10), e^3\Sigma^-(v = 3), d^3\Delta(v = 5)]$,
- $A^1\Pi(v = 2) \sim [e^3\Sigma^-(v = 4), d^3\Delta(v = 7), a'^3\Sigma^+(v = 12)]$,
- $A^1\Pi(v = 3) \sim [e^3\Sigma^-(v = 6), a'^3\Sigma^+(v = 13)]$

and

ii) rotation-electronic ($\hat{\boldsymbol{L}}$-uncoupling type) interaction:

- $A^1\Pi(v = 1) \sim [D^1\Delta(v = 1), I^1\Sigma^-(v = 1, 2)]$,
- $A^1\Pi(v = 2) \sim [D^1\Delta(v = 3), I^1\Sigma^-(v = 3, 4)]$,
- $A^1\Pi(v = 3) \sim [D^1\Delta(v = 4), I^1\Sigma^-(v = 5)]$.

Moreover, the high measurement precision, the verification of all perturbers capable of affecting the $A^1\Pi(v = 2)$ level within the observed spectral range, and the enriched description of the intramolecular interactions through quantifying the fractional $^1\Pi$ character in the investigated rovibronic levels, enabled – for the first time – the identification and full characterization of indirect interactions between the $a^3\Pi$ and $A^1\Pi$ states in the $^{12}C^{18}O$ isotopologue. The intermediate perturbers in this case were the $e^3\Sigma^-(v = 4)$, $d^3\Delta(v = 7)$, $a'^3\Sigma^+(v = 12)$, $D^1\Delta(v = 3)$ and $I^1\Sigma^-(v = 3)$ levels. In turn, the deperturbation analysis of the $A^1\Pi(v = 3)$ level revealed two additional significant indirect interactions: (*i*) spin-orbit/spin-electronic/rotation-electronic $a^3\Pi(v = 14) \sim e^3\Sigma^-(v = 6) \sim A^1\Pi(v = 3)$ mediated by the $e^3\Sigma^-(v = 6)$ level; (*ii*) a spin-orbit interaction $a'^3\Sigma^+(v = 14) \sim A^1\Pi(v = 3) \sim e^3\Sigma^-(v = 6)$ mediated by the $A^1\Pi(v = 3)$ level.

As a result of the analysis, 29 precise molecular constants (including 19 determined for the first time) were obtained for the $A^1\Pi(v = 1–3)$ levels and their perturbers: $a'^3\Sigma^+(v = 10, 12, 13)$, $e^3\Sigma^-(v = 4)$, $d^3\Delta(v = 7)$, $D^1\Delta(v = 1, 4)$ and $I^1\Sigma^-(v = 2, 3, 5)$. In addition, 308 rotational term values of the $A^1\Pi(v = 1–3)$ levels and their perturbers were determined, as well as 142 terms of $B^1\Sigma^+(v = 0, 1)$ and $C^1\Sigma^+(v = 0)$ levels, with an accuracy ten times higher than the best values

previously reported in the literature [4]. Finally, the electronic isotope invariants of the investigated interactions were calculated.

Carrying out a complete deperturbation analysis of the $v = 1–3$ levels of the $A^1\Pi$ electronic state enabled a much more comprehensive – than previously available [4,12] – quantum-mechanical description of the extensively and multistate-perturbed $A^1\Pi$ electronic state in the $^{12}C^{18}O$ isotopologue.

The general part of this dissertation presents the theoretical background required to achieve the stated research objectives. The detailed part describes the experimental methodology used to produce, record, and analyse the spectra, as well as the deperturbation analysis, and presents the results obtained in this study.

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