Spectroscopic parameters for $^{12}C^{16}O$ from PGOPHER analysis of HITRAN data

Jacob Tran, Hayden Netral, Dylan Troglen, Grace Browning, Cierra Moore, and Dr. Roderick Macrae

Department of Chemistry, College of Arts and Sciences, Marian University, Indianapolis

Abstract

Carbon monoxide (CO) is one of the six major air pollutants regulated by many nations across the world [1]. CO is a trace gas in the atmosphere, and plays a role in atmospheric chemistry by affecting the ability of the atmosphere to cleanse itself of other polluting gases [1]. Our objective is to determine spectroscopic parameters for CO for the observed rotational-vibrational transitions from the ground state using the program PGOPHER [2] together with high-resolution spectroscopy data from the HITRAN database.

The HITRAN Database

The HITRAN (HIgh Resolution TRANsmission) database is a spectral linelist containing position, intensity, and lineshape data for about 55 molecules significant for the modeling of radiative transfer in the atmospheres of the Earth and other planets. It is periodically updated, the most recent edition having appeared in 2016.10

All six nonradioactive isotopologues of CO are represented in the database, a total of 5381 lines including pure rotational transitions, allowed and forbidden transitions from the vibrational ground state, and hot bands.

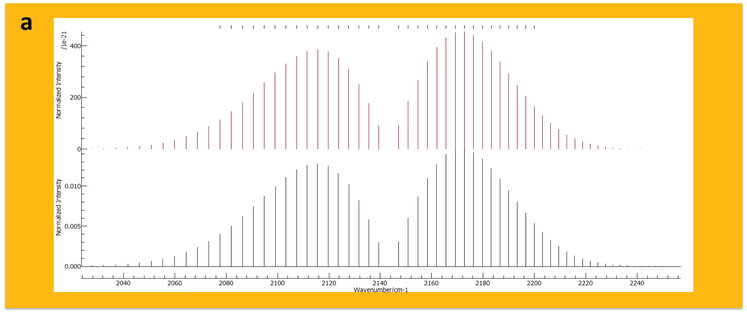
PGOPHER

PGOPHER is a program for simulating and fitting rotational, vibrational, and electric molecular spectra. This program can be used to determine the spectroscopic parameters for the rotational-vibrational transitions from the ground state of a molecule.

Our goal is to obtain an estimate of the bond dissociation energy using the Birge-Sponer method.

Transitions

We analyzed all rovibrational "cold bands" (originating from v=0) of $^{12}C^{16}O$ available in the HITRAN database, which range from the Δv=1 fundamental to forbidden transitions up to Δv=7.



Figures a-d. A visual representation of the CO rotational-vibrational spectrum (red) alongside the experimentally fit model (black) for Δv=1 (a), Δv=4 (b), Δv=5 (c), and Δv=7 (d).

Analysis

Data set	band origin	B"	B'	D" (x10^{-6})	D' (x10^{-6})
HITRAN $\Delta v = 1$ data (near 2150 cm^{-1})	2143.271	1.922529	1.905025	6.116	6.115
HITRAN $\Delta v = 2$ data (near 4250 cm^{-1})	4260.062	1.922529	1.887524	6.118	6.117
HITRAN $\Delta v = 3$ data (near 6350 cm^{-1})	6350.439	1.9225287	1.870023	6.116	6.116
HITRAN $\Delta v = 4$ data (near 8450 cm^{-1})	8419.469	1.922525	1.852522	6.112	6.112
HITRAN $\Delta v = 5$ data (near 10500 cm^{-1})	10452.222	1.92253	1.83503	6.123	6.123
HITRAN $\Delta v = 6$ data (near 12500 cm^{-1})	12463.77	1.922529	1.817534	6.12	6.124
HITRAN $\Delta v = 7$ data (near 14500 cm^{-1})	14449.18	1.922527	1.800039	6.115	6.119

Figure 4. *More data*

All bands show rotational fine structure in the form of P and R branches. In the higher forbidden bands, band heads are visible in the R branch, indicating that the rotational constants for the upper and lower states are quite different from one another.

Conclusions

The difference in the spectra produced in PGOPHER represents each vibrational transition with a unique pair of vibrational energy levels, each with its own rotational constant. As our delta V increases, anharmonic effects become more significant, causing shifts in the band origin, and changes in the spacing and convergence of rotational lines. These also modify the intensity pattern of the R and P branches. The changes and intensity in line spacing in our spectra are a result of vibrational coupling, and the increase of anharmonicity in higher delta V values,

Literature Cited

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[3] Gordon, I. E., Rothman, L. S., Hill, C., et al., The HITRAN2016 Molecular Spectroscopic Database, J Quant. Spectrosc. Radiat. Transf. 2017, 203, 3-69.