Study of the perturbed $W^1\Pi(\nu = 1)$ state of CO in five isotopologues

A. N. Heays,¹ M. Eidelsberg² G. Stark³ S. R. Federman⁴
L. Lemaire² J. R. Lyons⁵ B. R. Lewis⁶ L. Gavilan²,⁷
N. de Oliveira⁸ D. Joyeux⁸

¹ Leiden Observatory, The Netherlands
² Observatoire de Paris, Meudon, France
³ Department of Physics, Wellesley College, USA
⁴ Department of Physics and Astronomy, University of Toledo, USA
⁵ School of Earth and Space Exploration, Arizona State University, USA
⁶ Research School of Physics and Engineering, The Australian National University
⁷ Current address: Institut d’ Astrophysique Spatiale, Orsay, France
⁸ Synchrotron SOLEIL, Gif sur Yvette Cedex, France
Motivation

- CO and vacuum-ultraviolet radiation are throughout the Universe
- The liberation of C and O by photodissociation promotes chemistry
- Line spectrum and isotopic shifts → self-shielding
- Spectroscopic puzzle
The SOLEIL/DESIRS experiment

- Interferometric spectrometer
- Maximum path difference: 10 cm
- Maximum resolution: \( \sim 0.07 \text{ cm}^{-1} / 10^{-4} \text{ nm} \)
- Beam bandwidth: 5 nm

Krypton absorption spectrum

$W^1 \Pi \leftarrow X^1 \Sigma^+$ bands in absorption

$^{12}C^{16}O$

Absorption spectra $W(\nu' = 1) \leftarrow X(\nu'' = 0)$
$W^1\Pi (v' = 1) \leftarrow X^1\Sigma^+ (v'' = 0)$

$^{12}\text{C}^{18}\text{O}$

SOLEIL spectra  Fitted lines  Residual of fit

- $P(9)$, $Q(8)$, $R(7)$ lines key to assignment
- These lines are also shifted
- Weak extra lines labelled $E''(0) \leftarrow X(0)$
$W^1 \Pi (v' = 1) \leftarrow X^1 \Sigma^+ (v'' = 0)$

$^{12}\text{C}^{16}\text{O}, \quad ^{12}\text{C}^{17}\text{O}, \quad ^{13}\text{C}^{16}\text{O}, \quad ^{12}\text{C}^{18}\text{O}$
Deperturbation - level energies

Model the local interaction by matrix diagonalisation:

\[
\begin{bmatrix}
T_W(J) & H_{WE''} \\
H_{WE''} & T_{E''}(J)
\end{bmatrix}
\]

Results:

\[T_{vW} = 105627 \text{--} 105657 \text{~cm}^{-1}\]
\[B_W = 1.41 \text{--} 1.58 \text{~cm}^{-1}\]
\[T_{vE''} = 105678 \text{--} 105688 \text{~cm}^{-1}\]
\[B_{E''} = 0.62 \text{--} 0.77 \text{~cm}^{-1}\]
\[H_{WE''} = 4.2 \text{--} 6.4 \text{~cm}^{-1}\]

- \(W(1) \times \text{perturber } E''(0)\)
1 Π potential-energy curves

Ab initio valence curves
Stephen V. O’Neil and Henry F. Schaefer III

Ab initio Rydberg-valence curves

Experimental Morse potential
H. Lefebvre-Brion and M. Eidelsberg

Experiment: $B_{E''} = 0.7 \text{ cm}^{-1} \rightarrow R_e = 3.5 \text{ au}/1.9 \text{ Å}$
Deperturbation – predissociation linewidths

\[ W(1) \quad \text{perturber} \quad \bullet/\square \text{ experiment} \quad \rightarrow \text{ model} \]
Conclusions

- $W(1)$ has perturbed energy-levels and predissociation linewidths

- The perturber is a newly-observed $^1\Pi$ state, “$E''$”

- Probably we have observed the $E''(v = 0)$ level

- These results are a step towards a quantitative model of CO excited states and photodissociation