# Temperature dependence of the $O_2$ Schumann-Runge continuum photoabsorption cross section from a coupled-channel perspective

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## 1 Introduction

- This paper will demonstrate the utility of photodissociation cross section calculations that are based on the coupled-channel Schrödinger equation (CSE) technique.
- There is an increasing demand for a knowledge of the temperature dependence of the $O_2$ Schumann-Runge continuum (SRC) photoabsorption cross section, for use in planetary atmospheric models. However, there are only limited experimental measurements of the temperature variation of the $O_2$ SRC cross section,[1–5] reflecting the difficulties in undertaking such measurements covering a wide range of thermodynamic conditions.
- The CSE calculations provide a physical description of photodissociation at the quantum mechanical level, giving considerable insight into the nature of the temperature dependence of the $O_2$ Schumann-Runge continuum, defining limits for the possible temperature variation.

## 2 Coupled-channel Schrödinger Equation (CSE) model

$$\boxed{\mathbf{F}''(R)+\frac{2\mu}{\hbar^2}\left[E\mathbf{1}^\circ-\mathbf{W}(R)\right]\mathbf{F}(R)=\mathbf{0}^\circ}$$

*interaction matrix* *radial wavefunctions*

$$\begin{pmatrix} V_{00}(R) & V_{01} & V_{02} & \dots \\ & V_{11}(R) & V_{12} & \dots \\ & & \ddots & \\ & & & V_{NN}(R) \end{pmatrix} \begin{pmatrix} F_{00}(R) & F_{01}(R) & \dots & F_{0N_{\rm open}}(R) \\ F_{10}(R) & \dots & & \\ \vdots & & & \\ F_{N0}(R) & \dots & & F_{NN_{\rm open}}(R) \end{pmatrix}$$

B. R. Johnson, J. Chem. Phys. **69**, 4678 (1978).

**Normalization** F. H. Mies, Mol. Phys. **41** 953 (1980).

*scattering matrix*

$$\mathbf{F}^{\rm S}(R) \underset{R\to\infty}{\sim} ie^{-i\mathbf{k}R}-ie^{i\mathbf{k}R}\mathbf{S}$$

**Photoabsorption cross section**

$$\sigma_{v''J''vJ'}=\frac{2\pi^2\nu}{3\varepsilon_0}\left|\langle\mathbf{F}|\mathbf{M}|F_{\rm i}\rangle\right|^2$$

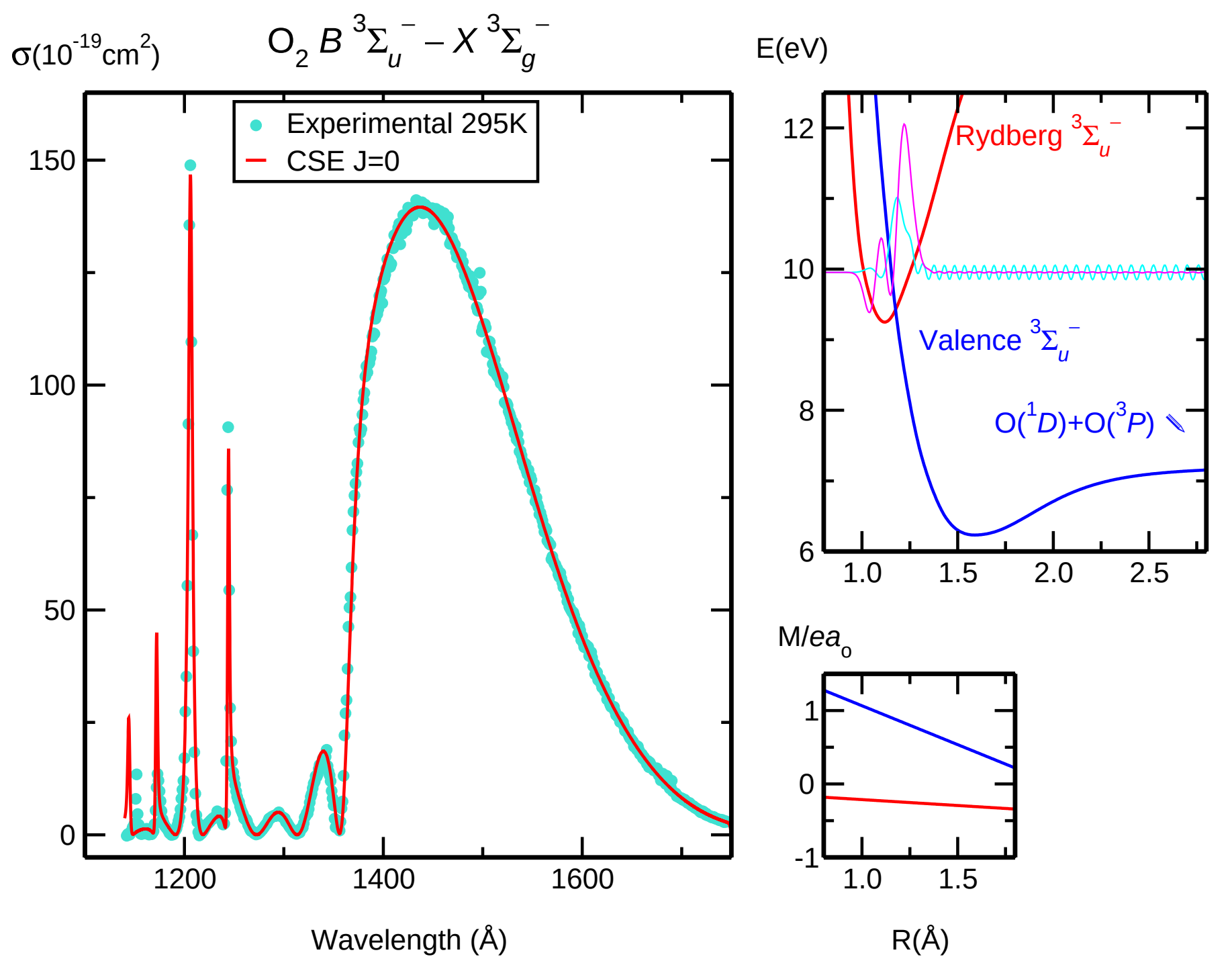
*electronic transition moment × rotational matrix element*

$$\underset{\text{open channel}}{\sigma_{\gamma v''J''vJ'}} \propto \left|\langle F_{0\gamma}|M_0|F_{\rm i}\rangle+\langle F_{1\gamma}|M_1|F_{\rm i}\rangle+\dots\right|^2$$

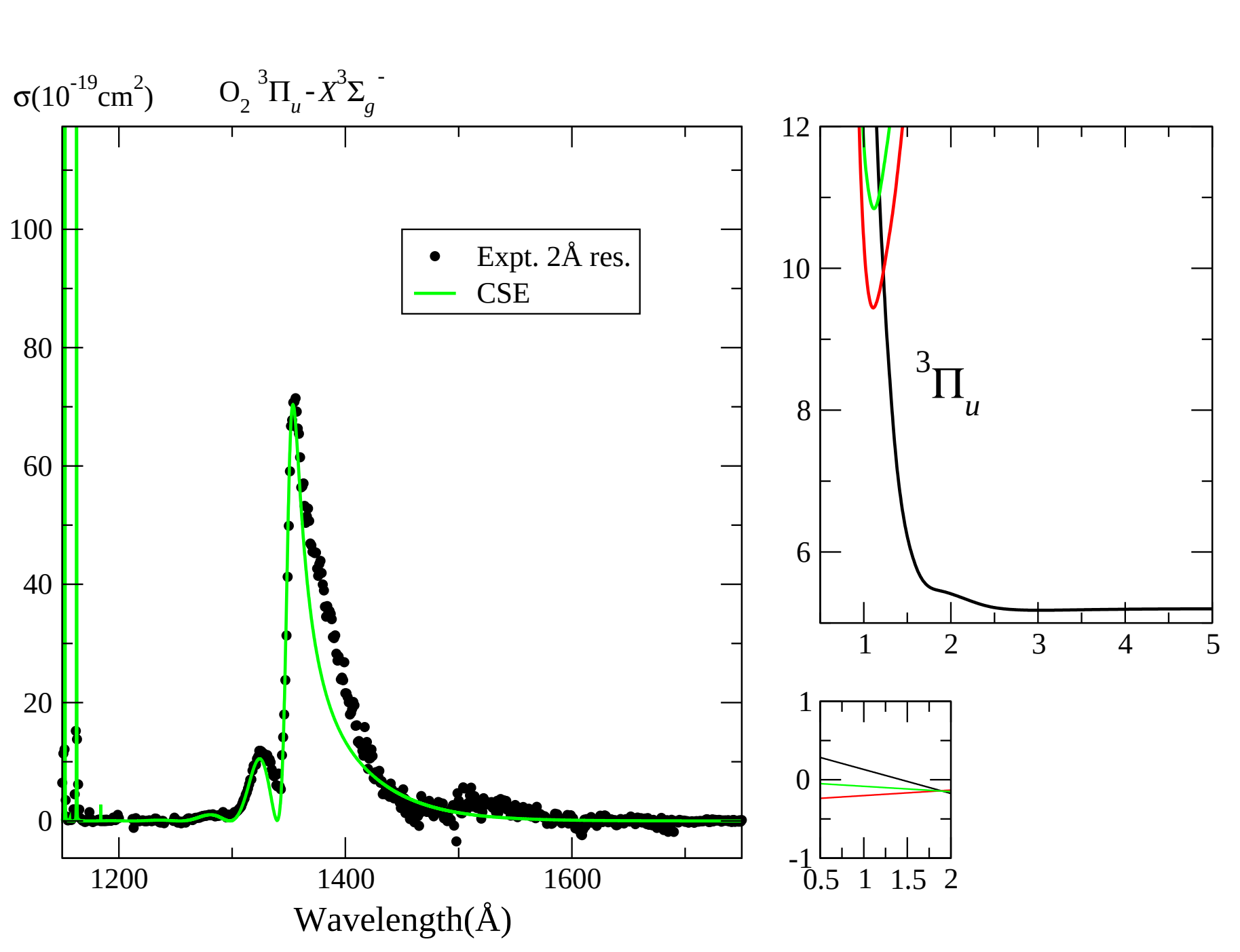
**Temperature dependance**

$$\sigma_\gamma(\lambda,T)=\frac{\sum_{v''J''}(2J''+1)\sigma_{\gamma v''J''\lambda J'}e^{-E_{v''J''}/kT}}{\sum_{v''J''}(2J''+1)e^{-E_{v''J''}/kT}}$$

## 3 $^3\Sigma_u^- - X^3\Sigma_g^-$ and $^3\Pi_u - X^3\Sigma_g^-$



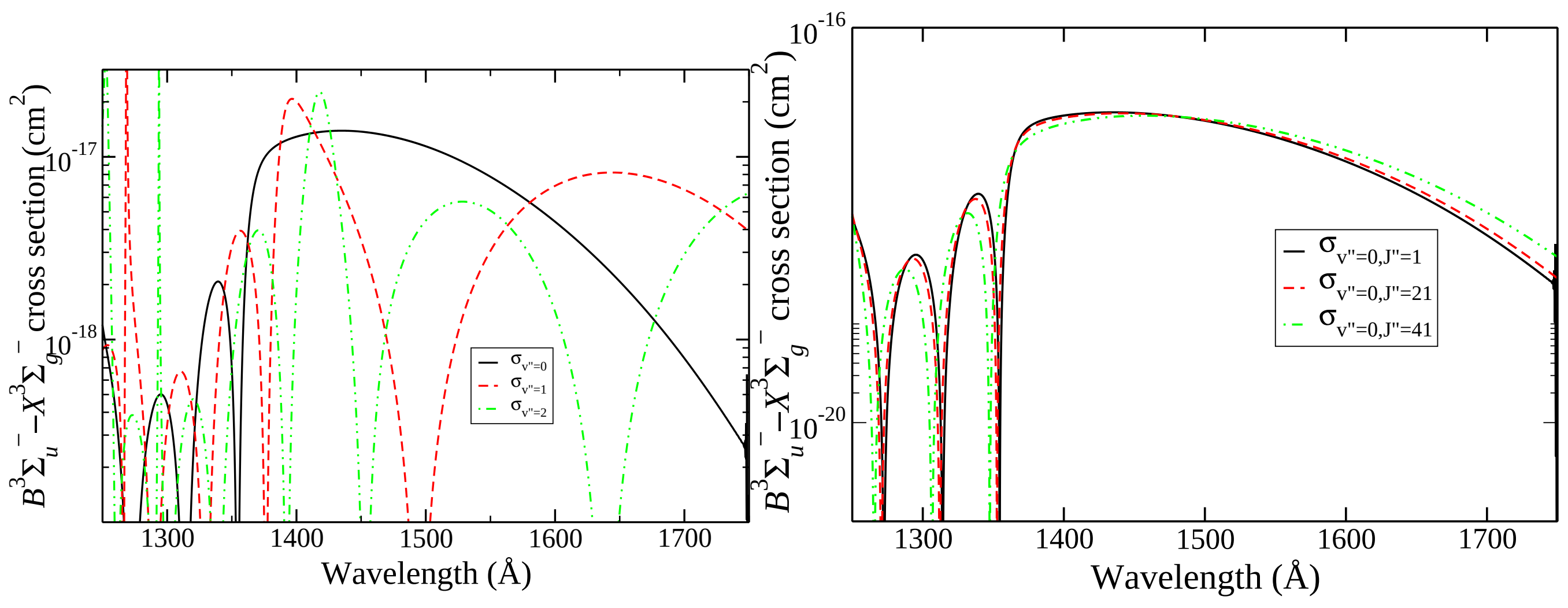
Minimal CSE model for the $^3\Sigma_u^- - {}^3\Sigma_g^-$ transition. The main features of the whole spectrum are reproduced using a model incorporating only one Rydberg and one valence state.[6] The Rydberg transition borrows intensity from the valence transition, which is demonstrated by the respective transition moment magnitudes.



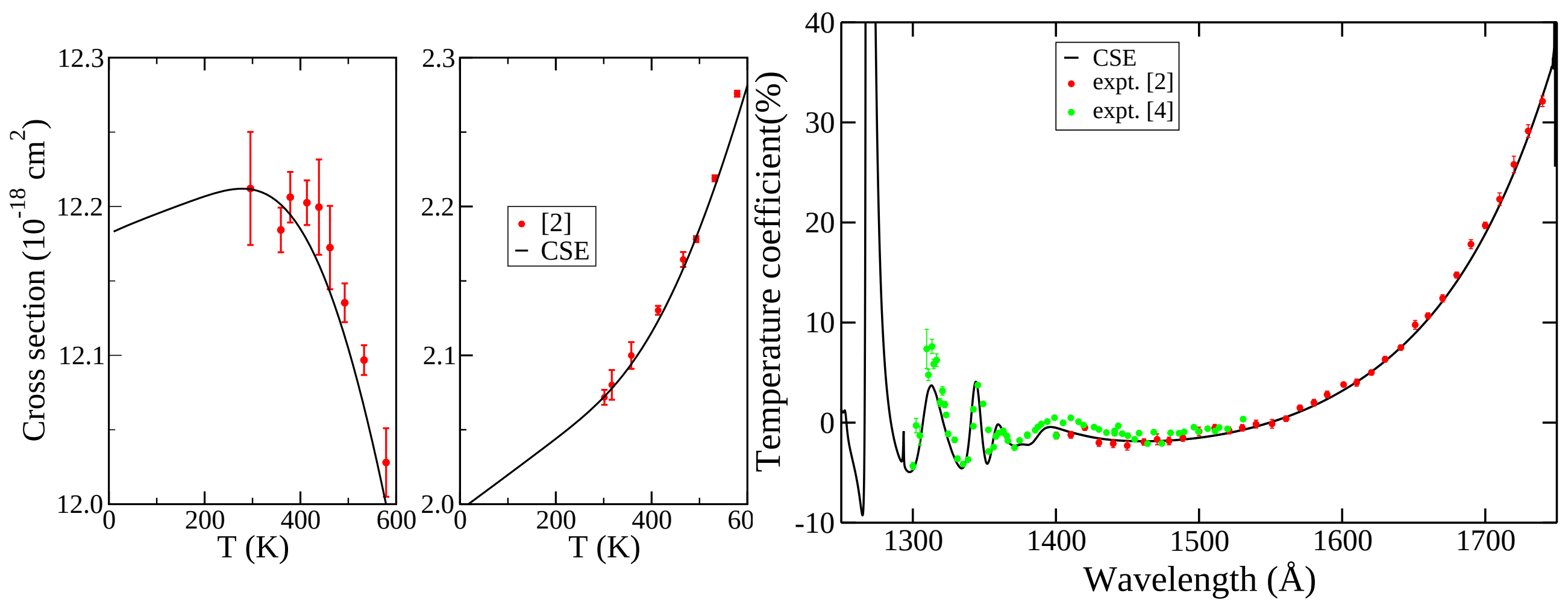
Minimal CSE model for the $^3\Pi_u - {}^3\Sigma_g^-$ transition. The main features of the spectrum are reproduced with two Rydberg and one valence state.[6] The valence transition borrows intensity from the Rydberg transition.
CSE model implicitly characterizes the interference between Rydberg (bound) levels and the valence (continuum).[6]

## 4 Temperature Dependence

- Calculated $^3\Sigma_u^- - X^3\Sigma_g^-$ cross section is effectively a reflection of the ground vibrational state, collapsing at short wavelengths, because of the Rydberg-valence interaction. The Rydberg transition, also adding resonance stucture in the short wavelength region. Within the SRC the node structure of hot vibrational levels yields a dramatic change in the rovibrational cross section.

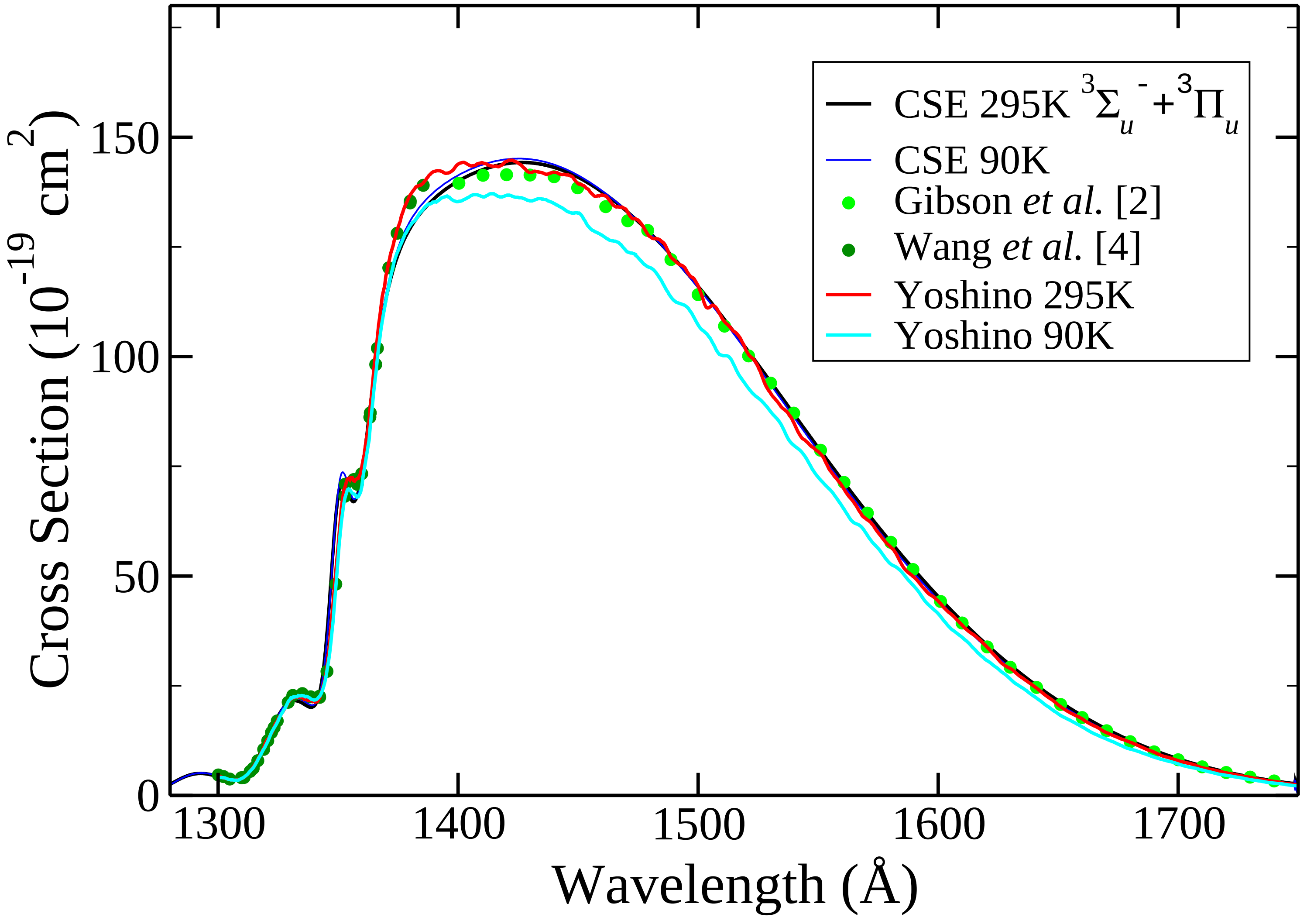


- Calculated cross section agrees favourably with the experimental data.



## 5 Total cross section 295 K and 90 K

**Total cross section** - add $^3\Sigma_u^-$ and $^3\Pi_u$ cross sections



The CSE calculation of the SRC cross section compared with experimental measurements. On this scale the CSE 90 K cross section virtually overlaps the 295 K values, in contrast to the experimental measurement. For the CSE model calculations, the more rounded collapse of the SRC is indicative of the constant coupling used for this model.

## 6 Discussion/Conclusions

- CSE calculations provide a physically-based quantum mechanical model of photoabsorption and photodissociation. For $O_2$ the CSE model accurately reproduces the SRC cross section, and in particular, accounts for the collapse of the continuum at short wavelengths, arsing from the Rydberg-valence interaction of $^3\Sigma_u^-$ electronic states.
- The temperature dependence of the $O_2$ Schumann-Runge continuum reflects the character of the dominantly weighted ground vibrational state.
  - Low temperature, below 300 K, variation arises from the displacement of the $v''=0$ “bell” to longer wavelength, as higher $J''$ becomes energetically accessible. For increasing temperature the cross section should increase for wavelengths above ∼1420 Å and decrease for the shorter wavelengths (top right figure of panel 4).
  - At higher temperatures, $v''$ transitions above $v''=0$ contribute. The wavefunction nodal structure may yield a decreasing cross section with increasing temperature, e.g. at 1488.7 Å(top left figure of panel 4).
- Complex temperature dependent behavour in the cross section occurs for wavelengths below 1350 Å as this region is influenced by transitions into $^3\Sigma_u^-$ and $^3\Pi_u$ Rydberg states. The correct description of the cross section in this region would require a full rotational manifold of transitions, corresponding to allowed branch transitions.

## References

[1] J. S. Evans and C. J. Schexnayder. An investigation of the effect of high temperature on the Schumann-Runge ultraviolt absorption continuum of oxygen. Technical report, NASA Technical Report, 1962.

[2] **S. T. Gibson**, H. P. F. Gies, A. J. Blake, D. G. McC oy, and P. J. Rogers. Temperature dependence in the Schumann-Runge photoabsorption continuum of oxygen. *J. Quant. Spectrosc. Rad. Transfer*, 30:385–393, 1983.

[3] G. Black, T. G. Slanger R. L. Sharpless, and M. R. Taherian. The 1150-1300 Å absorption spectrum of $O_2$ at 930 K. *Chem. Phys. Lett.*, 113:311–313, 1985.

[4] A. J. Blake J. Wang, D. G. McCoy and L. Torop. Effects of the close approach of potential curves in the photoabsorption by diatomic molecues-II. Temperature dependence of the $O_2$ cross section in the region 130-160 nm. *J. Quant. Spectrosc. Rad. Transfer*, 38:19–27, 1987.

[5] K.Yoshino, W. H. Parkinson, K. Ito, and T. Matsui. Absolute absorption cross section measurements of Schumann-Runge continuum of $O_2$ at 90 K and 295 K. *J. Mol. Spectrosc.*, 229:238–243, 2005.

[6] **S. T. Gibson** and B. R. Lewis. Understanding diatomic photodissociation with a coupled-channel Schrödinger equation model. *J. Electron Spectrosc. Relat. Phenom.*, 80:9–12, 1996.