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Key Points:

- To parameterize O₂ absorption, we generated a correlated-k table based on detailed line-by-line calculations at 150, 200, 250, and 300 K
- The new parameterization matches laboratory measurements and is well suited to include scattering at lower O₂ levels
- Early earth photochemical models based on the old exponential sum fits should consider the new correlated-k to achieve more accurate results

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A Correlated-K Parameterization for O₂ Photolysis in the Schumann-Runge Bands

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Abstract A recent study comparing ozone column depths and methane lifetimes at varied atmospheric O_2 (pO_2) levels calculated in the Kasting-group 1-D photochemical model and the Whole Atmosphere Community Climate Model version 6 (WACCM6) 3-D model (Ji, Kasting, et al., 2023; https://doi.org/10.1098/rsos.230056) has exposed weaknesses in both models in parameterizing photolysis in the O_2 Schumann-Runge bands, 175–205 nm. WACCM6 does a good job for Earth's present atmosphere but neglects scattering, which becomes important at low pO_2 . The 1-D model includes scattering but is based on an out-of-date band model, and it neglects the temperature dependence of photolysis at low pO_2 . We have revised and improved the 1-D photochemical model by replacing the old O_2 photolysis algorithm with a new correlated-k parameterization, which improves accuracy for all O_2 levels and all temperature profiles. The WACCM6 photolysis algorithms agree well for both the present atmosphere and for an atmosphere containing 10^{-3} times the present O_2 level, but only if multiple scattering is included at low pO_2 . The correlated-k parameterization will be made available to photochemical modeling groups who might choose to adopt it.

Plain Language Summary In today's atmosphere, the absorption of incoming ultraviolet radiation by O_2 plays a decisive role in creating O atoms that can react to form ozone (O_3), as well as shielding other gases from photolysis. However, this absorption is difficult to parameterize in atmospheric models due to its complex structure at wavelengths of 175–205 nm, which we call the Schumann-Runge bands. Good models for SR absorption in today's atmosphere already exist, but not all of them may be suitable for use in low- O_2 atmospheres in which multiple scattering is important. Here, we develop a new parameterization for SR absorption by employing a "correlated-k" approach that has been widely used in climate models at both visible and infrared wavelengths. This approach accounts for the strong temperature dependence of the absorption and agrees well with existing models of O_2 absorption in the present atmosphere. It should also be useful in simulations of low- O_2 atmospheres on early Earth, for which scattering must be included, as well as for atmospheres of putative Earth-like exoplanets that astronomers hope to identify over the next several decades.

1. Introduction

The Schumann-Runge (SR) bands of O_2 (175–205 nm) play an important role in Earth's atmospheric photochemistry for two reasons: First, photodissociation of O_2 in this wavelength region dominates the production of odd oxygen in the mesosphere and upper stratosphere and therefore plays a substantial role in creating the ozone layer. The dominant reaction that occurs within this wavelength region is

$$O_2 + h\nu \to O_2^* \to O + O \tag{R1}$$

Here, O is a ground-state O atom, technically O (3 P), and O₂^{*} is a bound excited state that can come apart to form two O atoms by interacting with other high-energy states in a process called predissociation (Flory, 1936). The



Writing – original draft: Aoshuang Ji, James F. Kasting Writing – review & editing: Aoshuang Ji, Orlando G. Tomazzeli, Gustavo G. Palancar, Guillaume Chaverot, Mackenzie Barker, Rafael P. Fernández, Kenneth Minschwaner, James F. Kasting fact that it first goes to a bound upper state means that a rotation-vibration spectrum is superimposed on the electronic transition, giving it the complex band structure shown in Figure 1.

Second, absorption by O_2 within the SR bands helps control how deeply solar ultraviolet (UV) radiation can penetrate into the atmosphere. This influences the photolysis rates of other species in the stratosphere, notably H₂O and N₂O (Trentmann et al., 2003), and that, in turn, also influences ozone photochemistry. Various parameterizations (Allen & Frederick, 1982; Blake, 1979; Hudson & Mahle, 1972; Koppers & Murtagh, 1996) have therefore been created to calculate O_2 SR band absorption over the last 50 years. However, this is not an easy job, and deriving these parameterizations requires extreme care. One reason is the complex structure created by thousands of O₂ absorption lines. Another reason is that the absorption of UV radiation within these lines depends strongly on temperature; consequently, solar transmittance is highly sensitive to changes in this parameter along the optical path. To further complicate matters, most of the existing parameterizations were developed for the modern O₂-rich atmosphere, in which SR absorption occurs at high altitudes where the air is thin and multiple scattering can be neglected. At low pO_2 , however, SR radiation penetrates into the troposphere, where scattering is important at these wavelengths. To deal with this problem successfully requires an absorption parameterization that includes temperature dependence and that remains valid when multiple scattering is included. Computational speed is also a factor, especially when the parameterization is implemented in 3-D models. An improved treatment of O₂ photolysis in the SR bands will enable more accurate simulations of paleoclimate on the early Earth and on putative exoplanets with low-O2 atmospheres (Chen et al., 2019; Cooke et al., 2023).

2. Brief Description of Existing SR Absorption Parameterizations

The current paper was motivated by studies by Cooke et al. (2022) and Ji, Kasting, et al. (2023), in which the authors compared calculations of ozone column depth vs. atmospheric pO_2 using several different photochemical models. Two of these models received special attention: (a) the Kasting-group 1-D photochemical model (see, e.g., Kasting, 1979; Kasting et al., 1985; Segura et al., 2003), and (b) the (3-D) Whole Atmosphere Community Climate Model version 6, WACCM6, developed at the National Center for Atmospheric Research (Cooke et al., 2022; Gettelman et al., 2019). Earlier versions of WACCM used by other groups (Chen et al., 2019; Marsh et al., 2013; Proedrou et al., 2016) share the same O_2 photolysis routine, so here we treat the WACCM parameterization for Schumann-Runge Bands (SRB) as a single model and henceforth refer to it as WACCM. Similarly, the Kasting-group 1-D model served as the starting point for several related models, including ATMOS (Arney et al., 2016), EXO-PRIME 2 (Payne and Kaltenegger, 2024), Photochem (Wogan et al., 2023, 2024; https://github.com/Nicholaswogan/photochem), as well as a version used by German researchers (e.g., Grenfell et al., 2007, 2011). It is useful for users of those models to understand how they compare with the new, correlated-k approach presented here.

2.1. Kasting Group 1-D Model

The 1-D model parameterization is adapted from Allen and Frederick (1982), henceforth AF82. They published a band model that was based on quantum mechanical calculations by Frederick and Hudson (1980a, 1980b). Those calculations, in turn, took advantage of low-pressure, high-resolution laboratory measurements of O_2 absorption by Hudson and Carter (1968). The emphasis in all these studies was on the present atmosphere, for which predissociation of O_2 in the SR bands is a major source of atomic oxygen at altitudes above 60 km. The AF82 parameterization is also employed in the widely used 1-D photochemical model, KINETICS, developed by (the late) Mark Allen at JPL and Yuk Yung at Caltech (see, e.g., Allen et al., 1984). This is not surprising, as Mark Allen was the first author of AF82.

In AF82, the wavelength region containing the SR bands was divided into 17 intervals, ranging from 48,600 to $57,000 \text{ cm}^{-1}$ (see AF82 Table 1). Numbering started at the low-wavenumber (long-wavelength) end of this range. All the intervals except for interval L1 were 500 cm^{-1} in width; interval L1 was only 400 cm^{-1} wide. The 1-D and 3-D models discussed here use essentially this same wavelength grid, except that numbering starts at the shortwavelength end, and the old interval L1 (now interval L17) is 500 cm^{-1} wide, like all the others. Table 1 lists the SR wavelength intervals used in both our 1-D model and in WACCM. For reference, the complete wavelength range over which photolysis rates are calculated in the 1-D model extends from 121.6 (Lyman alpha line) to 855 nm. O₂ photolyzes only below 240 nm. Wavelength intervals below 175 nm are numbered independently from those shown in Table 1.





Figure 1. Absorption cross sections of O_2 , H_2O , CO_2 , and O_3 . O_2 can be photolyzed within the Schumann-Runge continuum (SRC, 137–180 nm), the SR band system (Schumann-Runge Bands, 175–205 nm), and the Herzberg continuum (HZC, 194–240 nm). Photolysis of O_2 at wavelengths <175 nm generally produces one excited O (¹D) radical, along with one ground-state O (³P) atom; photolysis at longer wavelengths yields two ground-state O atoms. At some wavelengths (175–180 nm, see Table 2), both processes can occur. Data were obtained from https://lweb.cfa.harvard.edu/amp/ampdata/cfamols.html and references listed in the figure (Campbell, 1986; Lu et al., 2010; Molina & Molina, 1986; Parkinson & Yoshino, 2003; Parkinson et al., 2003; Ranjan et al., 2020; Yoshino et al., 1988, 1996, 1997).

The AF82 parameterization was designed for Earth's present atmosphere, within which radiation at SR wavelengths is absorbed in the upper stratosphere and mesosphere where the air is thin. But in low- pO_2 atmospheres, SR predissociation occurs lower in the atmosphere where the density is higher and multiple (Rayleigh) scattering is important (for each factor of 10 decrease in pO_2 , peak SR absorption moves downward by one decadal scale height, or ~ 16 km). This problem was recognized by Kasting (1982) and discussed in more detail by Kasting et al. (1985). At that time, the Kasting photochemical model was still using the Hudson and Mahle (1972) parameterization for SR absorption. Kasting et al. were concerned that it was not really compatible with radiative transfer techniques involving multiple scattering, which at that time they were treated using the method of Yung (1976). Some time later, Kasting replaced the Hudson and Mahle SR parameterization with the AF82 band model and the multiple scattering routine with the 2-stream model of Toon et al. (1989). To attempt to meld the band model and the scattering model together self-consistently, Kasting derived 4-term exponential sum fits to the AF82 band model. These fits were not published at that time—they were part of a long paper that never found its way into print—but they were described recently by Ji, Kasting, et al. (2023) (see Table S5 in their Supporting Information). These fits reproduced the correct behavior of the AF82 band model in the present atmosphere but did not include explicit temperature dependence. Because pressure and temperature are related differently along incoming ray paths at low pO_2 compared to present-day atmospheres, the exponential sum model may not be accurate in the former regime. In Section 5 below, we compare the behavior of this old exponential sum model with the newer models discussed here and with SR transmission functions based on high-resolution laboratory data. Comparisons between the exponential sum model and WACCM for different pO_2 conditions are also shown in Figures 5-7 of Ji, Kasting, et al. (2023).

2.2. WACCM 3-D Model

The O_2 photolysis routine implemented in the 3-D WACCM model is based on the Koppers and Murtagh (1996) (K&M hereafter) method. It uses Chebyshev polynomials to compute an effective O_2 cross section at each layer as a function of O_2 pathlength and local temperature. The coefficients used in WACCM are part of the MOZART-3 chemistry package (Kinnison et al., 2007) and have been widely implemented in other radiative transfer models like Tropospheric Ultraviolet Visible (TUV) model (Madronich, 1993). Notably, the absorption coefficients in WACCM have been re-derived and are different from those in the original K&M model, for reasons that remain unclear, as we have been unable to find the documentation for this change either in the code or in recent WACCM



Table 1

Wavelength Intervals in the 1-D Model and Corresponding O_2 Absorption Cross Sections in the Overlapping Herzberg Continuum (Herzberg Continuum [HZC])

Interval L	Wavenumber range (cm ⁻¹)	Mid-interval wavelength (nm)	New HZC O ₂ absorption cross sections (cm ²
1	56,500-57,000	176.2	0
2	56,000-56,500	177.8	0
3	55,500-56,000	179.4	0
4	55,000-55,500	181.0	0
5	54,500-55,000	182.6	0
6	54,000-54,500	184.3	0
7	53,500-54,000	186.0	0
8	53,000-53,500	187.8	0
9	52,500-53,000	189.6	0
10	52,000-52,500	191.4	0
11	51,500-52,000	193.2	0
12	51,000-51,500	195.1	6.124×10^{-24}
13	50,500-51,000	197.0	6.439×10^{-24}
14	50,000-50,500	199.0	6.682×10^{-24}
15	49,500-50,000	201.0	6.841×10^{-24}
16	49,000–49,500	203.0	6.907×10^{-24}
17	48,500-49,000	205.1	6.875×10^{-24}
SR bands	end here at interval L17		
18	48,000-48,500	207.3	6.742×10^{-24}
19	47,500-48,000	209.4	6.511×10^{-24}
20	47,000-47,500	211.6	6.190×10^{-24}
21	46,500-47,000	213.9	5.790×10^{-24}
22	46,000-46,500	216.2	5.326×10^{-24}
23	45,500-46,000	218.8	4.763×10^{-24}
24	45,000-45,500	221.2	4.222×10^{-24}
25	44,500-45,000	223.5	3.729×10^{-24}
26	44,000–44,500	226.0	3.189×10^{-24}
27	43,500-44,000	228.6	2.675×10^{-24}
28	43,000–43,500	231.2	2.198×10^{-24}
29	42,500-43,000	233.9	1.769×10^{-24}
30	42,000-42,500	236.7	1.393×10^{-24}
31	41,500-42,000	239.5	1.073×10^{-24}
32	41,000-41,500	242.4	0
33	40,500-41,000	245.4	0
34	40,000-40,500	248.4	0
35	39,500-40,000	251.6	0

model development references (e.g., refs. 13–16 in Ji, Kasting, et al., 2023). This can be seen by comparing the coefficients in Table 2 of K&M with those in the corresponding table, also called Table 2, downloaded from the WACCM model. The WACCM O_2 photolysis scheme does a good job of matching a transmission function based on high-resolution laboratory data by Yoshino et al. (1992), whereas the original K&M scheme does not. A comparison of transmission functions calculated using these three methods (WACCM, K&M, and Yoshino et al.) in SR interval L10 is shown in Figure 2. The data of Yoshino et al. are spaced approximately every 0.05 cm⁻¹, so

each of the 17 SR intervals contains ~10,000 data points. Beer's law was used to compute the transmission at each wavelength point and O_2 pathlength, and the results were averaged over the entire interval to compute the broadband transmission. Note that Yoshino's wavelength intervals are different from ours, so one needs to combine data from different files to compute transmission on our wavelength grid. Chebyshev polynomial coefficients from WACCM were downloaded from their website. The K&M coefficients were entered manually, copying from Table 2 of Koppers and Murtagh (1996). The WACCM parameterization agrees well with the transmission function calculated from the data of Yoshino et al. (1992), whereas the original K&M parameterization does not. The K&M study was published well after these laboratory results became available, so why they fail to fit observations remains a mystery. This comparison has only been made for wavelength interval L10, but one expects differences in the other SR wavelength intervals, as well, as the Chebyshev polynomial coefficients between WACCM and K&M are different in every interval.

The WACCM O_2 photolysis routine does not include scattering at SR band wavelengths. The original formulation, as employed by Cooke et al. (2022), also did not include H_2O or CO_2 as major absorbers in this wavelength region, and that led to an overestimate of H_2O photolysis rates at low pO_2 and a corresponding overestimate of tropospheric OH densities. Adding these two species as major absorbers (i.e., accounting for their effect in diminishing the downward solar UV flux) brings calculated OH densities closer to those predicted by the 1-D model (Ji, Kasting, et al., 2023, Figures 10 and 11); however, this still fails to account for backscattering of incident UV photons within the dense lower atmosphere.

3. Line-By-Line Calculations and Related Improvements in Representing O_2 Absorption

To more accurately include scattering in the O₂ SR bands, we created a correlated-k table for O₂ absorption cross sections from detailed line-by-line (LBL) calculations. The correlated-k technique, which is described in more detail in Section 4, has been widely used in the near- and thermal-infrared to compute absorption of incoming solar and outgoing thermal radiation in climate models (Kato et al., 1999; Mlawer et al., 1997). In this method, the absorption over broadband spectral intervals is parameterized as being equal to a weighted sum of exponentials with absorption coefficients, k_i . The k_i 's are computed from sampling the distribution created from the LBL calculations. The coefficients vary along the path, but it is assumed that the low and high k_i 's at each point are sampling the same regions of wavelength space (hence the adjective "correlated"). By contrast, in a band model, the broadband absorption coefficients also vary along the path, but any detailed information about photon behavior at discrete wavelengths is lost. Or, to say this in another way, the single scattering albedo, $\omega_0 = \sigma_s/(\sigma_s + \sigma_a)$, is better defined in the correlated-k model. Here, σ_s and σ_a are the scattering and absorption coefficients, so σ_a is the same as k_i in the terminology used here. Hence, the correlated-k method is considered to be more accurate than band models when scattering is included.

As an aside, a technique similar to the correlated-k method was applied to SR band absorption by Minschwaner et al. (1993). Instead of calling their absorption coefficients "correlated-k's", however, they called them "opacity distribution functions" (ODF's). Their ODF's were computed using a different LBL model than the one employed here, and they were calculated over a different set of SR band spectral intervals, making them difficult to employ in photochemical models as those discussed here (one could use them, but then the photolysis grid in most 1-D and 3-D models would need to be redesigned). We mention this mainly to show that the use of correlated-k's at UV wavelengths is not really a new idea. The LBL model used here, which is originally from Fernández et al. (2007), is in excellent agreement with the model developed by Minschwaner et al. (1992, 1993).

3.1. LBL Calculations Over the SR Continuum and SR Band System

The oxygen absorption cross section considered in this work includes the Schumann-Runge continuum (SRC, 137–180 nm), the Schumann-Runge Bands (SRB, 175–205 nm) and the Herzberg continuum (HZC, 194–240 nm) (see Figure 1). The SRC and the SRB are generated by $X^3\Sigma_g^- \rightarrow B^3\Sigma_u^-$ transitions (Brasseur & Solomon, 2005). If the transition is produced with a wavelength lower than 175 nm, the energy is enough to produce a direct dissociation, yielding a ground state oxygen atom, O (³P), and an excited oxygen atom, O (¹D). However, if the wavelength is longer than 175 nm, the energy is usually not enough to break the molecule in a single step, and a predissociation occurs. This process is promoted by the crossing of the repulsive anti-bonding state ³ Π_u (and others like ${}^{1}\Pi_u$, ${}^{5}\Pi_u$, and ${}^{3}\Sigma_u^+$, Cheung et al., 1990) with the excited electronic state $B^3\Sigma_u^-$ to yield two ground-



state oxygen atoms. As these predissociative transitions with wavelengths longer than 175 nm occur between the rovibrational levels of two electronic bound states, the cross section shows a complex structure within the SRB (Frederick & Hudson, 1980b), which, in turn, presents a pronounced temperature dependence. Here, it is worth noting that direct O_2 photolysis and indirect predissociation can both occur for wavelengths between 175 and 180 nm, with variable and temperature dependent quantum yields as shown in Table 2 (see Section 3.2). (The SR continuum energy threshold can be exceeded if the original O_2 molecule is in an excited ro-vibrational state.) Finally, the HZC involves the transition from the electronic ground state to the $A^3\Sigma_u^+$ state to produce two O (³P) atoms, being the transition of lower energy.

The computation of correlated-k coefficients requires a highly resolved O_2 absorption cross section. In our case, this was achieved by using a LBL model run over the appropriate wavelength range and over a range of different temperatures relevant to Earth's atmosphere. Our LBL calculations are based on the work of Fernández et al. (2007) but in this work a set of important improvements has been incorporated. First, the HIgh-resolution TRANsmission molecular absorption (HITRAN) database has been updated to the 2020 edition (Gordon et al., 2022). Unlike the original HITRAN 2000 format, in which the predissociation linewidths of the SRB were listed as FWHM (full width at half maximum), the newest 2020 database tabulates SRB linewidths using HWHM (half width at half maximum), which is the standard HITRAN format provided for computing the self- and airdependent pressure-broadening at longer wavelengths (FWHM = $2 \times$ HWHM). However, in order to reproduce the results of Fernández et al. (2007) and to match up with the Yoshino et al. (1992) experimental measurements at 79 and 300 K, the 2020 linewidths had to be multiplied by a factor of 4 (instead of 2) due to a formatting-change error when updating different HITRAN versions since 2000 (Iouli Gordon, personal communication). We note that based on the updated LBL computations performed here, the handling of predissociation widths in the coming 2024 version will be fixed, following the HAPI application interface used in previous HITRAN updates (Gomez et al., 2024). Secondly, the SR continuum was explicitly incorporated, allowing us to accurately consider not only its contribution in the wavelength range where SRC and SRB overlaps (i.e., between 175 and 180 nm), but also to consider the pronounced temperature variability of the SRC. The SRC transitions exhibit a strong temperature dependence as they rely on the populations of the vibrational and rotational states in the electronic ground-state, as well as the number of levels available in the excited state. The inclusion of the SRC in our LBL computations has been done following the work of Minschwaner et al. (1992), which in turn is based on the works of Lewis et al. (1985a, 1985b).

The transitions considered in our LBL calculations are listed in Table 7 of Rothman et al. (1998). Briefly, each transition in the SRB ($48,500-57,000 \text{ cm}^{-1}$) was calculated on a wavelength grid with a resolution of 0.5 cm⁻¹, using a Voigt profile, and accounting for all the contributions (from the wings of other transitions) within a distance of 500 cm^{-1} , and at four temperatures (150, 200, 250, and 300 K). The SR bands are also overlapped at longer wavelengths by the Herzberg continuum. This continuum is not included in the new LBL calculations because it is slowly varying with wavelength and independent of temperature, allowing it to be easily incorporated into the transmission computation at a later stage. Any future adjustments to the Herzberg continuum can therefore be implemented without having to redo the correlated-k parameterization of the SR band system. A detailed description of the LBL updates with respect to Fernández et al. (2007), including the independent contributions from the SRC, SRB, and HZC transitions, as well as a detailed temperature and resolution sensitivity analysis, is currently under preparation and will be published and made available online.

3.2. Improvements Made to SR Continuum Absorption

As the underlying contribution of the SRC has been included in the new LBL calculation of the SRB, and thus in the 1-D calculation, we need to compute the branching ratio for O₂ photolysis rates at SR wavelengths intervals where both SRC and SRB contribute (first three intervals L = 1–3 in Table 1) and in the far-UV loop of the 1-D photochemical model (Lyman alpha, 130–135 and 135–139 nm). In our previous versions of the 1-D model, we only considered the reaction: $O_2 + h\nu \rightarrow O + O$ at wavelengths >175 nm (intervals L = 1–35), where both oxygen atoms produced here are in the ground state. That was poorly parameterized, however, because the first three intervals in the SR band region (175.4–180 nm) are overlain by the SRC. As mentioned previously, photolysis within the SRC leads to one ground state and one excited state oxygen atom. Therefore, both the SRC and the SRB system have been included in the LBL calculations for intervals L1–3. The relative contribution of each process to O₂ photolysis within each interval is described by a branching ratio of the O₂ absorption cross-section computed as SRC/(SRB + SRC) (see Table 2).



During this reevaluation, O_2 photolysis in the far-UV loop of our 1-D model has also been treated more accurately. As pointed out by Lee et al. (1977), photolysis at wavelengths <139 nm can yield either O (³P) + O (¹D) or two O (³P) atoms. Lee et al. list O (³P) + O (¹D) quantum yields for the O_2 photolysis reaction, which affect only the last three (shortest wavelength) intervals of the far-UV loop. The last one is really just the Lyman alpha line at 121.6 nm. The quantum yield into O (³P) + O (¹D) is 0.44; production of O (³P) + O (³P) makes up the difference (1–0.44 = 0.56). The QYs for the other two intervals are digitalized from Lee et al. Figure 2 and are shown in Table 2. Between 139 and 175.4 nm, the SRC always yields O (³P) + O (¹D).

3.3. Improvements Made to the Herzberg Continuum (HZC) Absorption

Another improvement in the 1-D model is the replacement of the old O_2 HZC absorption cross section in the wavelength region (194–240 nm). Between 205 and 240 nm, accurate values of the HZC cross section are available in Yoshino et al. (1988) and Cheung et al. (1986). Below 205 nm, however, the contribution of the SRB is increasingly higher and it is no longer possible to subtract its contribution or measure the contribution of the HZC separately. Unfortunately, the different approaches to consider both contributions lead to contrasting results, as shown by Yoshino et al. (1992). In this work, we calculate the contribution of the HZC, $\sigma_H(\lambda)$, in the 194–240 nm range using Equation 3 of Yoshino et al. (1988):

$$\sigma_{\rm H}(\lambda) = A\left(\frac{\lambda_{\rm H}}{\lambda}\right) \times \exp\left[-B \times \left(\ln\frac{\lambda_{\rm H}}{\lambda}\right)^2\right] \tag{1}$$

In this expression, $A = 6.88410^{-24}$ cm², B = 69.7374, and H = 204.87 nm. These values arise from fitting calculations and experimental measurements in the range 194–240 nm (Yoshino et al., 1988) to an equation of the form given by Johnston et al. (1984). The same expression is used by other authors, although with slightly different values for *A*, *B*, and *H* (Johnston et al., 1984; Nicolet & Kennes, 1986).

4. Correlated-K Fits

Even though LBL calculations can provide the best estimate of the direct solar radiation transmitted by gases in the atmosphere, these calculations are computationally expensive, particularly when considering scattering. It is not realistic to compute LBL spectra in-line in photochemical models in acceptable timescales.

To circumvent this issue we use a technique called the correlated-k method (Lacis & Oinas, 1991; Liou, 1980), which has been used routinely in radiative transfer calculations at infrared wavelengths (Kato et al., 1999; Mlawer et al., 1997). The idea is to pre-compute a set of high-resolution spectra for different pressure and temperature conditions. These spectra are then sampled into several wavelength bands in which the cumulative absorption probability is computed. This means that the key information is the distribution of the absorption per band (i.e., its mean intensity), but not the wavelength position of the absorption within the band. From high-resolution spectra, we derived a correlated-k table using the Exo_k model (Leconte, 2021) for four different temperatures (150, 200, 250, and 300 K), spanning the range of temperatures observed in Earth's present lower atmosphere. As the SR bands are not pressure-dependent, we do not define any pressure grid. The cumulative probability of absorption is computed following a Gauss-Legendre distribution, assuming 4, 8 or 12 G points for each band. The wavelength bands used for the correlated-k methods are the same as intervals L1–17 in Table 1.

The results of the 4–12-point integrations were so similar that the 8-point fits are not further discussed. O_2 transmission functions and photolysis rates for the 4–12-term sums are shown in Section 5.

5. Evaluation of the Correlated-K Method in the 1-D Photochemical Model

5.1. Comparisons of Transmission in Specific SRB Wavelength Intervals

In this section, we show comparisons of O_2 transmission calculated using different methods in several different spectral intervals within the SR band system. The correlated-k method was described in Section 4. We use 12-term correlated-k coefficients for the comparisons shown here. WACCM transmission functions were calculated using the code downloaded from the WACCM6 model stored at the NCAR in Boulder, Colorado. Transmission functions derived from the LBL model and from the observational data of Yoshino et al. (1992) were calculated using Beer's law at each wavelength point and then averaging over each individual spectral interval.





Figure 2. Comparison of the transmission in Schumann-Runge wavelength interval L10 (52,000–52,500 cm⁻¹) along an O₂ path at 300 K in WACCM, K&M, and using a transmission function based on laboratory measurements by Yoshino et al. (1992). Yoshino's data can be found at https://lweb.cfa. harvard.edu/amp/ampdata/o2pub92/S-R.html.

In Figure 3a/b, the comparison at 300 K is shown for two short-wavelength SRB intervals: L1 and L4. Both the correlated-k fits and the WACCM model agree quite closely with the LBL model in interval L1. Yoshino's data do not extend to wavelengths as short as this. The old exponential sum model agrees with the other two models to better than 5% at all O_2 pathlengths. The agreement in interval L1 is probably due to the importance of the overlapping SR continuum, which is calculated in much the same way in all three models.

In interval L4 (Figure 3b), the LBL model, WACCM model, and correlated-k model all lie close to the transmission curve calculated from the Yoshino et al. (1992) data, indicating that all three models are doing a good job. The old exponential sum model is an outlier, being as much as 1.5 times less transparent at an O₂ pathlength of 3×10^{20} cm⁻². This behavior is different from that seen at longer SR wavelengths for intervals L15 and L17, where the exponential sum model is too opaque (Figures 3c and 3d). (The HZC is included in all these calculations, but it was calculated differently in the old exponential sum model, following Ditchburn and Young (1962). We used Equation 1 from the previous section.) Both WACCM and the correlated-k method agree well with the LBL method at the longer wavelengths, indicating that both methods should be considered reliable. The longer wavelength intervals are also not covered by the data from Yoshino et al. (1992).

To further test the performance of the correlated-k coefficients in our 1-D model, we calculated O_2 transmission at four different temperatures (150,

200, 250, and 300 K) within interval L10 (52,500–52,000 cm⁻¹). The rationale for selecting band L10 is that this interval includes only absorption from the SRB system, without any underlying contribution from either the SRC (which affects the short-wavelength bands) nor the HZC (affecting the long-wavelength bands). Interval L10 is also the only interval for which K&M plotted the A and B coefficients of their Chebyshev polynomial expansion (see their Figure 5). Results are shown in Figure 4. At high temperatures, especially 300 K, all methods agree well with each other, whereas at low temperatures, the old exponential sum in the model, which lacks temperature dependence, results in too much absorption compared to the others. For example, at 150 K and a pathlength of 10^{22} cm⁻², the computed transmission with the exponential sum method is only about half that of the other methods (~0.3 instead of 0.6). This comparison further demonstrates not only the reliability of the correlated-k parameterization in the 1-D model, but also that it is more transparent than the old exponential sum formulation at most SR wavelengths. Thus, the correlated-k model allows more photons to penetrate into the lower atmosphere and increase the photolysis of species like H₂O, N₂O, and CH₃Cl. Consequently, it can lead to differences in ozone column depths compared to those calculated using the old 1-D model.

5.2. Effect of New Correlated-K Parameterizations on Photolysis Rates of O₂ and Other Species in the 1-D Photochemical Model

(Here, we compare 4-term and 12-term correlated-k coefficients in the 1-D model with the old exponential sum formulation for O_2 SR photolysis. A comparison between correlated-k coefficients, the exponential sum method, and the two different band models is made in the next subsection).

Having verified that the new correlated-k method produces reliable transmittance results within multiple SR spectral intervals, we then tested it in the 1-D photochemical model developed in the Kasting group. We substituted the old exponential sum fits for O_2 photolysis with the new correlated-k parameterization and conducted a series of simulations for the present O_2 level and for a lower pO_2 (10^{-3} PAL or present atmospheric level) atmosphere. Doing this required developing an interpolation scheme to account for the variation in temperature with altitude. These simulations compared the correlated-k and original exponential sum formula by calculating the photolysis frequencies (s⁻¹) as a function of altitude for several species, including O_2 , H_2O , N_2O , and CH_3Cl because those species can affect ozone chemistry by either producing odd oxygen (in O_2 photolysis) or by destroying odd oxygen by way of catalytic cycles. Photolysis frequencies for those four species as a function of altitude are shown in Figures 5 and 6.





Figure 3. O_2 transmission for (a) interval L1, (b) interval L4, (c) interval L15, and (d) interval L17 with different methods at 300 K.

Figure 4. O_2 transmission in interval L10 (52,500–52,000 cm⁻¹) with different methods at (a) 150 K, (b) 200 K, (c) 250 K, and (d) 300 K.

Figure 5. Photolysis frequencies with different parameterizations of O_2 absorption cross-sections at the 175–205 nm in the 1-D photochemical model at 1 PAL from 5 to 60 km. Green curves show the old exponential sum fits, dashed red curves show 4-term correlated-k parameterization and dashed purple curves show 12-term correlated-k.

All vertical profiles were computed for the same atmospheric composition with a single solar zenith angle (48.2°) and a diurnal averaging factor equal to 0.375. This is the insolation-weighted daytime solar zenith angle calculated by Cronin (2014). Results at 1 PAL O_2 are shown in Figure 5. The O_2 photolysis frequencies plotted here are for the reaction: $O_2 + hv \rightarrow O + O$ ($\lambda < 240$ nm), where O is the ground-state atom. We used both the 4-term and 12-term correlated-k's described in Section 4 to compare with the old exponential sum fits and determined that it should be sufficient to employ 4-term k's, given the tradeoff between computational speed and

Figure 6. Photolysis frequencies with different parameterization of O_2 absorption cross sections at the 175–205 nm in the 1-D photochemical model at 10^{-3} PAL. Green curves show the old exponential sum fits, dashed red curves show the 4-term correlated-k's, and dashed purple curves show the 12-term correlated-k parameterization.

Relative difference (%) between 4-term and 12-term in photolysis frequencies

accuracy. As mentioned previously, faster computation times (corresponding to smaller number of terms) are preferred, especially if the correlated-k method is implemented in 3-D model calculations.

The first point to note about these calculations is that the O_2 photolysis frequencies for the new correlated-k model and the old exponential sum model appear to be reasonably close at 1 PAL O_2 (Figure 5a). The agreement is largely illusory, however, because the differences are minimized by the multi-log scale used in the plot. Looking more carefully at Figure 5a shows that the O_2 photolysis frequencies in the correlated-k model are generally lower above 30 km and higher below 30 km than in the old exponential sum model. That is consistent with the greater transparency of O_2 in the new model seen in the individual interval transmission plots shown in the previous section. The O_2 photolysis frequency is higher below 30 km in the correlated-k model because more UV photons are available. The biggest differences between the new and old models are in the photolysis frequencies of H_2O , N_2O , and CH_3Cl , which are higher in the correlated-k model than in the old exponential sum model (see Figures 5b–5d). The greater transparency of O_2 means that more UV photons are getting through to photolyze H_2O , N_2O , and CH_3Cl . Note that if the new calculations are correct, the errors in the old photolysis frequencies are

Table 2

Quantum Yield Into $O({}^{3}P) + O({}^{1}D)$ in the Far-UV Loop and the Branching
Ratio for Schumann-Runge Continuum (SRC)

Wavelength range (nm)	Approximate QY			
far-UV				
121.6	0.44			
130.0–135.0	0.39			
135.0–139	0.78			
Branching ratio for SRC				
	150 K	200 K	250 K	300 K
175.4–177.7	0.074	0.130	0.189	0.247
177.7–178.6	0.005	0.008	0.015	0.029
178.6–180.2	0.003	0.003	0.004	0.007

quite large. For example, at 20 km, the H_2O photolysis frequency (Figure 5b) is a factor of 60–100 times higher than that found using our old exponential sum coefficients. The N_2O photolysis frequency in the new model is also considerably higher in the lower stratosphere, and this has a profound effect on ozone photochemistry, as demonstrated in subsection 5.4 below.

We also compared photolysis frequencies for the same four species at 10^{-3} PAL O₂ (Figure 6). O₂ photolysis frequencies are substantially higher in the upper atmosphere and slightly lower in the lower stratosphere in the new model, but photolysis frequencies of H₂O, N₂O, and CH₃Cl are almost identical between two methods, presumably because O₂ is blocking out far fewer photons (At this low O₂ level, most of the UV photons are absorbed by CO₂ and H₂O.) The new correlated-k method does predict a higher photolysis frequency of O₂ at the top of the atmosphere (80–100 km) by a factor of 50. This difference is likely caused by the fact that O₂ photolysis at Lyman α line (121.6 nm) in the new model produces two ground-state O atoms with 44% efficiency, whereas in the old model it was assumed that all this far-UV

photolysis produced $O + O(^{1}D)$, as mentioned in Section 3.2. Figure 6a shows only the photolysis branch leading to the two ground-state O atoms.

The performances of 4-term and 12-term correlated-k in calculating the photolysis frequencies of O_2 and H_2O are shown in Figure 7 to further illustrate the small difference between the two parameterizations. In general, the difference is much smaller at the lower pO_2 level (10^{-3} PAL), within 5% for O_2 and 0.6% for H_2O . Even though the difference is about 25% around 9 km in Figure 7a, the absolute value of the photolysis frequency at this altitude ($\sim 2 \times 10^{-20}$ s⁻¹) is too low to matter. Thus, it is probably safe to simply use the 4-term correlated-k coefficients in both 1-D and 3-D photochemical models unless extremely high accuracy is desired.

5.3. Comparison of Correlated-K, Exponential Sum, and Band Model Formulations of O_2 Photolysis, With and Without Scattering

For those researchers who have been using various parameterizations of O_2 SR cross sections to perform photochemical calculations, it may be useful to see how their parameterizations compare with those described in this paper. To accomplish this, we tested each parameterization (AF82/exponential sum fits, WACCM, and correlated-k) with and without scattering at two different O_2 levels (1 PAL and 10^{-3} PAL). The implementation of the AF82 approach in our 1-D photochemical model does not include scattering; however, the old exponential sum fits can be regarded as the AF82 method with scattering (but without temperature dependence). It should be noted that in previous 1-D calculations with our photochemical model, the AF82 band model was used only for the present atmosphere; for low- O_2 atmospheres, exponential sum fits were used instead (e.g., Segura et al., 2003).

As pointed out by Koppers and Murtagh (1996), it is important to limit band models to the range of O_2 column depths, $N(O_2)$, for which they have been developed. For the K&M and WACCM models, that range is: $38 \le \ln [N(O_2)] \le 56$. The AF band model was developed for altitudes of 20–120 km in the present atmosphere, which corresponds to vertical O_2 column depths of approximately: $38 \le \ln [N(O_2)] \le 54$. They fit slant column depths, however, so the useful upper limit on $\ln [N(O_2)]$ may be higher than estimated here. We further note that the AF band model linked the O_2 column depth linearly to the pressure at that level. This relationship is obviously different at low O_2 levels. In our original 1-D model, that variation was not accounted for. The best way to fix this problem is to add the common logarithm of the O_2 level (in PAL) to the logarithm of pressure at a certain height. Equivalently, one may add this value to the quantity X_i in Equation 3 of AF82, which is called "BIGX(I)" in the model. For example, $\log (10^{-3}) = -3$; thus, at 10^{-3} PAL, the corresponding pressure term should be $\log [P(z)]$ —3, where *z* is the height (It may be safer to modify X_i in the code because $\log [P(z)]$ is also used in calculating the effective cross section of NO).

Figure 8 shows the photolysis frequencies and O_x production rates for the various models, both with scattering (solid curves) and without (dashed curves). Differences are relatively small at 1 PAL O_2 (Figure 8a), except in the middle stratosphere, where both the AF82 and exponential sum models exhibit too much absorption, resulting in higher O_x production rates (Figure 8c). This turns out to be important for the formation of the ozone layer, as pointed out in the previous subsection. As expected, scattering does not have much effect on O_2 photolysis rates in the present atmosphere.

The differences between the various models are much larger at 10^{-3} PAL at both high (>60 km) and low (<25 km) altitudes (Figures 8b and 8d). In between, that is, throughout most of what is today called the stratosphere, all the models agree with each other. That is because most of the absorption is being caused by H₂O and CO₂, as pointed out earlier. The differences at high altitudes are mostly caused by the different assumptions about O₂ branching ratios at Ly α , as discussed in Section 3.2. The new model has a higher O₂ photolysis frequency in this region because some of the Ly α photons are creating two O (³P) atoms and because we are only showing that branch. At low altitudes, the differences are mostly caused by the inclusion, or exclusion, of scattering. Neglecting scattering causes O₂ photolysis frequencies near the surface to be around 3 times higher than when scattering is included. This impact is more visible when comparing O_x production at 10^{-3} PAL in Figure 8d. Scattering leads to less O_x production (about 6 times lower) near the surface (see solid curves in Figure 8d). At the same time, O₂ photolysis frequencies in the upper atmosphere increase by a much smaller amount, less than 5%. The likely reason for this behavior is a process called diffuse reflection. When short-wavelength UV photons enter the dense lower atmosphere, they undergo multiple Rayleigh scattering interactions, causing some of them to be reflected back to the upper atmosphere or to space. These results are similar to those shown in previous studies (Ji, Kasting,

Figure 8. Comparisons of different parameterizations with/without scattering on photolysis frequencies of O_2 (s⁻¹) as a function of altitude (km) at (a) 1 PAL and (b) 10⁻³ PAL, as well as on production rate of O_x (10⁵ cm⁻³ s⁻¹) at (c) 1 PAL and (d) 10⁻³ PAL. Dashed curves represent cases without scattering (No S); solid curves include scattering in parameterizations. The AF82 band model, as implemented in our model, does not include scattering. In panels (a) and (b), the dashed red and dashed purple curves overlap with each other, making them hard to distinguish, especially near the surface.

et al., 2023). Note that the WACCM and correlated-k models agree well everywhere below 60 km. Surprisingly, the agreement is even better when scattering is included (see Figure 8d). So, the WACCM 3D model itself can probably be safely used for low- O_2 atmospheres, provided that scattering and absorption by H_2O and CO_2 are accounted for at SR wavelengths.

5.4. Effect of Different Parameterizations on Calculated Ozone Column Depths in the 1-D Model

The final task of including the new O_2 cross sections parameterization in the 1-D photochemical model was to integrate the 1-D model to convergence and to study the effects on important model outputs, notably, ozone column depth and the methane lifetime. We performed such calculations at two different O_2 levels, 1 PAL and 10^{-3} PAL. The results, which were somewhat unexpected, are shown in Table 3 (Note: These results are not directly comparable to those shown in Ji, Kasting, et al. (2023), because the Ji et al. standard model did not include chlorine chemistry and because Ji et al. used an 8-pt. Gaussian integration of solar zenith angle, rather than the single 48.2° zenith angle assumed here).

At 1 PAL O₂, the ozone column depth, listed in Dobson units (DU), increases by approximately 18% in the new correlated-k model compared to the old exponential sum model. Although causality is difficult to establish in a complex model of this sort, this large change appears to be caused by the greater transparency of O₂, which leads to a higher photolysis rate of N₂O: N₂O + $h\nu \rightarrow$ N₂ + O. This reaction essentially deactivates N₂O, as it returns the two N atoms back to N₂. The other way that N₂O is destroyed in the atmosphere is by the reaction:

Table 3

Comparisons of Ozone Column Depth and Methane Lifetime in the 1-D Model								
pO ₂	1 PAL		10^{-3} PAL					
Method	Old exponential sum model	Correlated-k model	Old exponential sum model	Correlated-k model				
Ozone column depth (DU)	280	330 ^a	24	18				
Methane lifetime (yr)	7.7	8.6	1.4	0.9				

^aThis result is the same for both the 4-term and 12-term correlated-k parameterizations.

 $N_2O + O(^1D) \rightarrow 2NO$. Nitric oxide, NO, is part of the odd nitrogen family: $NO_x \equiv NO + NO_2$. NO_x can destroy ozone via the catalytic cycle:

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + O \rightarrow NO + O_2$$
$$Net : O_2 + O \rightarrow 2 O_2$$

When N₂O is photolyzed faster, as it is in the correlated-k model, less of it is available to react with O (¹D); hence, less NO_x is formed, and less ozone is destroyed by the NO_x catalytic cycle. This hypothesis about what is happening in the model is supported by looking at the column-integrated rate of the slower of the two steps in the NO_x catalytic cycle (the NO₂ + O reaction), which is about 25% slower in the new model.

Somewhat surprisingly, the two different parameterizations behave in the opposite way at lower pO_2 levels. At 10^{-3} PAL, the ozone column depth actually drops by about 25% using the correlated-k method. This is probably because the greater transparency of O_2 leads to higher H_2O photolysis rates in the troposphere, where water vapor is much more abundant than in the stratosphere: $H_2O + h\nu \rightarrow H + OH$. The hydroxyl radical, OH, is part of the odd hydrogen family: $HO_x \equiv H + OH + HO_2$, which can also cause catalytic destruction of ozone. This same change in the H_2O photolysis rate may explain why the methane lifetime is significantly shorter in the new model at low pO_2 (see Table 3). OH is the main sink for methane via the reaction: $CH_4 + OH \rightarrow CH_3 + H_2O$. Higher rates of H_2O photolysis lead to higher OH densities, and hence a shorter lifetime for methane.

In summary, the changes made in the parameterization of O_2 cross sections have major effects on the ozone chemistry in our 1-D photochemical model. The photochemical model had previously been "tuned" to produce an ozone column depth near the observed mean global value of 292 DU (Braesicke et al., 2019). With the new parameterization, the predicted ozone column depth at 1 PAL O_2 is much too high. Future work should focus on how the 1-D model could be adjusted so as to reproduce an ozone column depth closer to the observed value. But this project also demonstrates that it is difficult for a 1-D model to accurately simulate an Earth with a decidedly 3-D atmosphere.

6. Conclusions

In this study, we employed a correlated-k parameterization obtained from LBL calculations, including temperature and wavelength dependence, to compute O_2 absorption cross sections in the SR bands, and we tested the reliability of the new approach by comparing with transmission functions calculated from other parameterizations and from observed data. The overlapping SR continuum is included in this parameterization but the Herzberg continuum is not. We further demonstrated the necessity of considering scattering in photochemical models when simulating low-O₂ atmospheres. The new correlated-k method, as implemented in the Kasting-group 1D model, agrees well with other up-to-date methods like the one used in WACCM and with transmission functions calculated from observed data. The new correlated-k parameterization allows more UV photons to penetrate into the lower stratosphere in today's atmosphere compared to our old model, leading to faster photolysis rates of H_2O , N₂O, and CH₃Cl. Consequently, calculated ozone column depths are higher than those in the old 1-D model, at least for the modern atmospheric O₂ level (1 PAL). We attribute this to a higher photolysis rate for N₂O, leading to less NO_x, and consequently less destruction of ozone by the NO_x catalytic cycle. Conversely, at low pO_2 (10⁻³ PAL), the new correlated-k parameterization leads to lower ozone column depths, presumably because of the greater rate of photolysis of H₂O and correspondingly higher destruction of ozone by HO₂ catalytic cycles. Users of photochemical models employing our old exponential sums parameterization or the Allen and Frederick band model may be able to improve the accuracy of their calculations by switching to either our new correlated-k parameterization or the band model used in WACCM.

Data Availability Statement

The source code for the 1-D photochemical model is archived at the Zenodo repository via https://doi.org/10. 5281/zenodo.10384004 (Ji & Kasting, 2023a). This version is updated based on previous one used in Ji, Tom-azzeli, et al. (2023), which can also be found via https://doi.org/10.5281/zenodo.7818127 (Ji & Kasting, 2023b).

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Data used for comparing in this study are available at the Zenodo repository via https://doi.org/10.5281/zenodo. 10380089 (Ji, Tomazzeli, et al., 2023).

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