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A Coupled Schrodinger Equation Approach to Modeling Predissociation in Sulfur Monoxide and Carbon Monoxide

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A Coupled Schrödinger Equation Approach to Modeling Predissociation in Sulfur Monoxide and Carbon Monoxide

Kathryn Ledbetter

Submitted in Partial Fulfillment of the Prerequisite for Honors in Chemical Physics

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Chapter 1

Introduction

Understanding the chemical behaviors of atmospheres and astronomical gas clouds relies on knowledge of the photochemistry of each molecule present. Each molecule absorbs specific wavelengths of light as a consequence of the quantum mechanical energy levels of the molecule. When a molecule absorbs a photon, it becomes excited, and in some cases the energy absorbed from the photon causes the molecule to dissociate. If the probability of dissociation depends on the isotopic composition of the molecule, some isotopologues will be disproportionately dissociated, leading to anomalous isotope ratios in the dissociation products, which are important markers of the history of both extraterrestrial objects and our own planet.

Photodissociation occurs when a molecule absorbs a photon with enough energy to overcome the attraction between the atoms, breaking the bond between them. Because the free atoms themselves can have a variety of energy states, there are multiple dissociation limits for each molecule, corresponding to different energy levels of the free atoms after dissociation. For example, Figure 1.1 shows two electronic potential curves for sulfur monoxide which approach different energies (dissociation limits) as the separation between the atoms becomes large.

Most photodissociation is caused by a continuum of light energies: any photon
with enough energy to excite the molecule above the dissociation limit can cause disso-
ciation. For example, if a molecule was in the state defined by the potential curve B in
Figure 1.1 it would be expected it to dissociate only if it gained enough energy to surpass
the dissociation limit of the B state, which happens to be the second dissociation limit of the
molecule. However, in complex systems such as diatomic molecules, single basis states such
as this one do not completely describe the state of the system. Because the Schrödinger
equation, which describes energy states of a quantum mechanical system, is analytically un-
solvable for all but the simplest of systems, more complex systems require an approximate
approach. The true wavefunctions of the molecule must be constructed from a basis set
of functions. That is, some combination of basis states, such as the states defined by the
potential curves in Figure 1.1 represents the true state of the molecule, and the constituent
basis states are said to “interact.”

![Figure 1.1: Potential curves for B (red) and C (green) states of sulfur monoxide.](image)

One consequence of interaction, which can be thought of as a “mixing of charac-
ter” between multiple states, is predissociation. When a state with a higher dissociation
limit, such as the B state shown in Figure 1.1 interacts with one of a lower dissociation
limit, such as the C′ state, the dissociating character of the lower state allows the molecule
to dissociate when it is excited to nominally bound energy levels of the upper state. In
contrast to ordinary dissociation, which is a continuum process, predissociation only occurs
at discrete ranges of wavelength, defined by the discrete rotational and vibrational levels of the interacting states. Importantly, different isotopologues of the same molecule will be predissociated by different wavelengths of light. This leads to isotope fractionation, a phenomenon where the ratio of isotopes of a certain element present in one environment differs from the overall ratio of isotopes observed for that element.

In order to take predissociation into account in photochemical models, a computational model is needed which calculates the true wavefunctions of the molecule from a combination of basis states, allowing predissociation effects to be calculated for a range of conditions. There are multiple methods for calculating these combinations, which will be discussed in Chapter 2, including perturbation theory and the Coupled Schrödinger Equation (CSE) method. The best method for addressing large interactions is the CSE approach, which is used in this thesis. The CSE approach is a method of solving the Schrödinger equation for a molecule which simplifies the problem by abstracting an unknown combination of vibrational wavefunctions into a single function. This allows wavefunctions and energies to be calculated by taking into account interactions with all vibrational levels, instead of only a few (as is the case with perturbation theory). Hence, the CSE method is useful in the case of strong interactions, when perturbations among many vibrational levels are important.

This thesis focuses on two examples of astrophysically important molecules in vastly different stages of their study. The sulfur monoxide radical (SO) is challenging to study experimentally, and the interactions between its electronic states are not well known. Carbon monoxide (CO), on the other hand, is a common and widely studied gas for which models already exist. The first half of the thesis is focused on creating a basic framework for a model for transitions between two electronic states of SO, the B state and the X (ground) state, and determining what interactions with the B state are important to be included in a useful model. The second half consists of refining an existing model for the B-X system of CO (no relation), using recent data collected at the SOLEIL synchrotron.
1.1 The $B^3\Sigma^- - X^3\Sigma^-$ System of Sulfur Monoxide

The SO radical is a highly reactive species which exists only for a short time under standard conditions. The fact that it so readily reacts to form larger molecules means that SO has a short lifetime in all but very low-density environments, such as those in space. Indeed, it has been found in multiple extraterrestrial environments, including interstellar gas clouds \[1\] and atmospheres such as those of Venus and some moons of Jupiter \[2\]. SO also exists as a short-lived intermediate in chemical reactions. For example, it is the first dissociation product of SO$_2$. Because both SO$_2$ and SO can be photodissociated by ultraviolet light, a series of reactions can take place:

\[
\begin{align*}
\text{SO}_2 + h\nu & \rightarrow \text{SO} + \text{O} \\
\text{SO} + h\nu & \rightarrow \text{S} + \text{O}
\end{align*}
\]

These two reactions were prevalent in the early atmosphere of Earth. Prior to 2.5 billion years ago, in the Archean eon of Earth’s history, the atmosphere was very different from what we see today: the amount of oxygen in the atmosphere was less than $10^{-5}$ times its current level \[3\]. Because O$_2$, as well as O$_3$, are strong absorbers of ultraviolet light, most UV light today is absorbed in the upper reaches of the atmosphere. In contrast, the Archean atmosphere was permeated by ultraviolet light, and UV photochemistry played a large role in the chemistry of the atmosphere.

The photodissociation of SO$_2$, and subsequently of SO, by UV light leads to the formation of elemental sulfur. This sulfur, if it does not react with another species (such as oxygen), can be deposited into rocks, forming a record of the atmospheric chemistry which can be read today. The relative abundances of different sulfur isotopes, $^{33}$S, $^{34}$S, and $^{36}$S, in comparison to the most common isotope $^{32}$S, in sulfur-bearing minerals from the Archean time period are different from what is seen today \[4\]. In general, the relative enrichment of each isotope in a sample scales with the mass of the isotope. When the isotope ratios do not scale with mass as expected, the sample is said to display anomalous isotope
fractionation. The anomalous fractionation seen in sulfur deposits from the Archean period could be attributed to photodissociation of \(\text{SO}_2\), and the isotope distribution of sulfur over time can be used to track the rise of \(\text{O}_2\) in the atmosphere \[4\]. However, an understanding of the UV photodissociation of both \(\text{SO}_2\) and \(\text{SO}\) is required to test this theory.

In order to understand the photodissociation of \(\text{SO}\), we need to model for its predissociation by UV light, specifically by modeling its absorption spectrum in the UV. Because sulfur and oxygen reside in the same column of the periodic table, parallels can be drawn between \(\text{O}_2\) and \(\text{SO}\). The Schumann-Runge bands of molecular oxygen, the name given to the set of transitions between the \(\text{B}^3\Sigma^-\) and \(\text{X}^3\Sigma^-\) electronic states, are some of the strongest absorption features of \(\text{O}_2\) and their predissociation has been studied in detail. The analogous \(\text{B}^3\Sigma^-\text{-X}^3\Sigma^-\) system in \(\text{SO}\) also displays predissociation, but there is currently no working model of this predissociation due to the dearth of experimental data on \(\text{SO}\).

However, enough data exist (e.g. \[5\]) to see patterns in predissociation within the vibrational levels of the \(\text{B}\) state. The goal of this project was to determine which electronic states are the most likely candidates for causing predissociation in the \(\text{B}\) state, by utilizing the CSE method to attempt to reproduce patterns in experimental linewidths. Five electronic states were considered, and three were found to be likely candidates for causing the observed predissociation. Once more experimental data become available, this preliminary model could be refined to more accurately reproduce predissociation observations.

1.2 The \(\text{B}^1\Sigma^+\text{-X}^1\Sigma^+\) System of Carbon Monoxide

Carbon monoxide, unlike sulfur monoxide, is a stable molecule, and is in fact the second most abundant molecule in the universe \[6\]. It is an important ingredient in interstellar clouds and circumstellar disks, and, billions of years ago, was a component of the solar nebula that would form our own Solar System. Today, we rely on remnants from the solar nebula to piece together what the environment was like at the birth of the Solar System. One piece
of evidence that exists for the chemical makeup of the solar nebula lies in deposits found in meteorites, known as calcium-aluminum-rich inclusions (CAIs), which preserve isotopic ratios from the earliest days of the solar system. In these meteorites, the ratios between $^{16}\text{O}$, $^{17}\text{O}$, and $^{18}\text{O}$ differ from ratios seen today. For most processes that cause isotope fractionation, it is the mass of the isotope that determines the amount of enrichment, so that the enrichment of $^{18}\text{O}$ would be expected to be twice that of $^{17}\text{O}$. In meteorite CAIs, however, the fractionations of $^{17}\text{O}$ and $^{18}\text{O}$ are nearly equal. This indicates that some mechanism affected the isotope ratios in a way that did not scale linearly with the mass of the isotope [7]. One explanation for the observed ratios is that different isotopologues of CO absorb UV at slightly different wavelengths; consequently, a phenomenon known as self-shielding could be responsible for the anomalous isotope ratios [8].

Self-shielding is a phenomenon that occurs when a gas absorbs light strongly enough to absorb all incident light at a certain wavelength in the outer layers of a sample, so that no light of the absorbed wavelength reaches the inner region of the sample. When different isotopologues of a molecule are present, and they absorb slightly different wavelengths of light, self-shielding can affect the amount of each isotopologue that is exposed to its particular predissociating wavelengths. In this case, molecules containing the most common oxygen isotope, $^{16}\text{O}$, are much more abundant than those containing $^{17}\text{O}$- and $^{18}\text{O}$. Therefore, when the gas is dense enough, the particular wavelengths that dissociate C$^{16}$O will become saturated in the outer layers of the sample, and C$^{16}$O molecules in the inner region are not dissociated. The less common isotopologues, on the other hand, are not present in high enough density to saturate their dissociating wavelengths, and those wavelengths are able to penetrate the whole sample, so that virtually all of the $^{17}\text{O}$ and $^{18}\text{O}$-containing CO molecules are dissociated. This leads to isotope fractionation, because the rarer isotopes are dissociated disproportionately to the most common isotope. This mechanism could explain the fractionation of oxygen isotopes in CAIs and, in doing so, could provide clues about the type of stars (and therefore the type of UV light) in the solar system birth cluster [9].
In order to test the self-shielding hypothesis, accurate models are needed for predissociation of CO due to ultraviolet light. Carbon monoxide experiences significant predissociation from ultraviolet light between 91.2-111.8 nm (higher in energy than the first dissociation limit of CO and lower than the ionization energy of atomic hydrogen, which blocks most ultraviolet light above this energy). This energy regime includes the lowest electronic transitions of the molecule, the first of which are the $B^1\Sigma^+-X^1\Sigma^+$ transitions. The predissociation of the lowest vibrational levels of this state has been attributed to an interaction with the $D'^1\Sigma^+$ state, which crosses both the B state and several higher states. Tchang-Brillet et al. constructed a model for the interaction between the B and D$'\Sigma^+$ states in 1992 [10]. This model was recreated as part of Lucy Archer’s thesis in 2012; however, in its current form it was unable to predict isotope-dependent predissociation patterns and rotationally dependent effects [11]. In an attempt to improve the two-state model, this work presents a new model of the B-D$'$ interaction.
Chapter 2

Theory and Modeling Approach

2.1 The Hamiltonian

A quantum mechanical system, for example a diatomic molecule, can be described by its Hamiltonian, an operator which corresponds to the sum of the kinetic and potential energies of the system. Both the nuclei and the electrons have kinetic and potential energy, and the Hamiltonian ($H$) for a diatomic molecule can be written as the sum of the nuclear kinetic energy, the electrons' kinetic energy, and three Coulombic potential energies: nucleus-nucleus repulsion, electron-electron repulsion, and electron-nucleus attraction:

$$
H = -\frac{\hbar^2}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla^2 r_{\alpha} - \frac{\hbar^2}{2m_e} \sum_i \nabla^2 r_i + \frac{Z_{\alpha}Z_{\beta}e^2}{4\pi\epsilon_0 r_{\alpha\beta}} + \sum_i \sum_{j>i} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_{\alpha} \sum_i \frac{Z_{\alpha}e^2}{4\pi\epsilon_0 r_{\alpha i}} \tag{2.1}
$$

In this equation, $\alpha$ and $\beta$ refer to the two nuclei, and $i$ and $j$ to the electrons. The coordinate system defines $r_{\alpha}$ and $r_i$ as the positions of the nuclei and electrons respectively, while an $r$ with two subscripts refers to the distance between two particles. The distance between the nuclei, $r_{\alpha\beta}$, will henceforth be known as $R$, also called the internuclear separation. $Z_{\alpha}$ and $Z_{\beta}$ are the charges of the nuclei.
This Hamiltonian neglects the effects of the spin of the electrons and nuclei; in fact, there are three more terms $H^{SO}$, $H^{SS}$, $H^{SR}$ which describe the spin-orbit, spin-spin, and spin-rotation energies. These terms arise from the fact that each electron and nucleus has an intrinsic dipole moment, which can interact with the dipole moments associated with the orbital motions of these charged particles. These three terms are initially neglected when using the non-relativistic Hamiltonian, as we will do here.

Unfortunately, even the non-relativistic molecular Hamiltonian is analytically unsolvable. Additionally, it is useful to be able to separate energies not by the labels “kinetic” and “potential”, but by the degrees of freedom of the molecule. A molecule has four types of energy: electronic, vibrational, rotational, and translational. Translational energy is generally irrelevant to spectroscopy; although translational energy appears in spectra as Doppler broadening, it provides no information about the structure of the molecule. The three remaining types of energy are what appear in molecular spectra: electronic bands contain many vibrational bands, which contain many rotational transitions. We would like to be able to solve the Hamiltonian in such a way as to separate these types of energies. This task requires approximations.

2.2 Matrix Mechanics

Because the Hamiltonian is analytically unsolvable, the wave functions which are its eigenfunctions will not have analytical forms. Therefore, it is useful to transition from using an operator $\hat{H}$, and its eigenfunctions, to using a matrix $H$ and its eigenvectors. Theoretically, this matrix and its eigenvectors are infinite-dimensional. Practically, however, it is difficult to work with infinite-dimensional matrices; approximate methods have different ways of dealing with this issue.

The Schrödinger equation thus becomes an eigenvalue problem expressed in matrices:

$$H\Psi = E\Psi \quad (2.2)$$
where $\mathbf{H}$ is a square matrix and $\Psi$ is a column vector:

$$
\begin{pmatrix}
H_{11} & H_{12} & \ldots \\
H_{21} & H_{22} & \ldots \\
\vdots & \vdots & \ddots
\end{pmatrix}
\begin{pmatrix}
c_1 \\
c_2 \\
\vdots
\end{pmatrix}
= E
\begin{pmatrix}
c_1 \\
c_2 \\
\vdots
\end{pmatrix}
$$

(2.3)

The basis of these vectors is arbitrary; in practice, the basis is chosen to be a set of eigenvectors to a solvable, zero-order Hamiltonian $H^0$. Theoretically, the energies and wavefunctions of the complete Hamiltonian $H$ could be found exactly, without any approximation, by diagonalizing the matrix $H$ and describing its eigenvectors as a linear combination of the basis vectors defined by $H^0$. However, this is impossible in practice because the matrices and vectors involved are infinite-dimensional. Therefore, we choose as a basis set the eigenvectors of a Hamiltonian $H^0$ that is as close as possible to the Hamiltonian of interest $H$, and then resort to approximate methods such as perturbation theory. A useful basis set can be obtained by employing the Born-Oppenheimer Approximation, described in section 2.3.1.

In this basis, $H^0$ is diagonal, while $H$ contains off-diagonal elements. These off-diagonal elements determine how much “mixing” occurs between basis states; that is, how much of each basis state appears in the linear combinations that make up the eigenvectors of $H$. Two approaches to finding these combinations are the subject of sections 2.3.3 and 2.3.4.

### 2.3 Approximations and Methods

#### 2.3.1 Born-Oppenheimer Approximation

We would like to be able to separate the energy of the molecule (and therefore its Hamiltonian) into electronic, vibrational, and rotational energies, so that the total energy can be
expressed as:

\[ E^T = E^{el} + G(v) + F(J) \]  \hspace{1cm} (2.4)

Notationally, \( E^{el} \) is the electronic energy, \( G(v) \) is the vibrational energy (a function of the vibrational quantum number \( v = 0, 1, 2, \ldots \)), and \( F(J) \) is the rotational energy (a function of the rotational quantum number \( J = 0, 1, 2, \ldots \)). This is a useful separation because in spectroscopy, what is observed are electronic transitions containing vibrational bands, which have rotational structure. Vibrational and rotational energies can be described empirically as power series, with experimentally determined coefficients:

\[
G(v) = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2 + \ldots \]  \hspace{1cm} (2.5a)

\[
F(J) = B_v J(J + 1) - D_v [J(J + 1)]^2 + \ldots \]  \hspace{1cm} (2.5b)

The additive separation of electronic, vibrational, and rotational energies implies a separable Hamiltonian with solutions that are products of the solutions of the parts. The true Hamiltonian is not thus separable, so we make what is known as the Born-Oppenheimer approximation, which removes terms from the Hamiltonian, including those that couple nuclear and electronic motions. Using the Born-Oppenheimer approximation, an approximate wavefunction can be written as a product of electronic \( \phi^{el} \) and rotational-vibrational \( \chi \) wavefunctions:

\[
\phi^{BO} = \phi^{el}(r; R) \chi(R, \theta, \phi) \]  \hspace{1cm} (2.6)

Here, \( \chi \) is a function of \( R, \theta, \) and \( \phi \); since it is not a function of \( r \), it is independent of the position of the electrons. The notation \( \phi^{el}(r; R) \) indicates that \( \phi^{el} \) is a function of \( r \), the position of the electrons, and depends parametrically on \( R \), the internuclear distance. This means that \( \phi^{el} \) is not a function of \( R \), but it has a different form for each value of \( R \).
These Born-Oppenheimer product solutions form a basis set from which true energies and wave functions of the molecule can be constructed. Every observed transition in a real molecule is evidence of quantum mechanical states which can be described as a linear combination of these basis functions. Unfortunately, the true states of molecules are referred to by the same names as members of the basis set. For example, spectroscopy of the CO molecule finds a set of rovibrational bands beginning at 86916 cm\(^{-1}\), they are attributed to a bound state of \(1\Sigma^+\) symmetry which was named the B state. Ab initio calculations also find a bound state near that energy, and this state in the basis set is also called the B state. However, these are two separate entities. The experimentally observed B state is a linear combination of basis states, the dominant one being the B basis state. The B basis state is said to “interact” with other basis states to form what we experimentally see as the B state. These interactions or “couplings” between states are a result of off-diagonal elements in the true Hamiltonian.

In practice, there are two formulations of the Born-Oppenheimer approximation which allow the separation of the wavefunction to be made. Each formulation removes different terms from the Hamiltonian. The first is the adiabatic representation, for which the nuclear motion is removed from the Hamiltonian; the second is the diabatic representation, which neglects interelectronic repulsion but includes the nuclear kinetic energy.

The adiabatic Born-Oppenheimer approximation relies on the fact that because electrons are a thousand times less massive than protons and neutrons, in even the lightest of atoms the nuclei are significantly heavier than the electrons. Consequently, the motions of the nuclei are very slow compared to that of the electrons—in the same potential, the electrons will accelerate about a thousand times more quickly. Therefore, it is reasonable to assume that the electrons have a set of states for each fixed configuration of the nuclei, and as the nuclei move the electrons “instantaneously” adjust to the new nuclear configuration. This is the heart of the Born-Oppenheimer approximation, which simplifies the total Hamiltonian by assuming the nuclei are fixed. In the coordinates of a diatomic molecule, this means that \(R\), the internuclear separation, is constant. The energy can then be calculated
for each value of $R$, which produces what is known as a potential energy curve—a plot of energy versus internuclear separation for a given electronic state.

Fixing the nuclei in space eliminates the nuclear kinetic energy term from the total Hamiltonian (Equation 2.1). It also turns the internuclear repulsion term into a constant, since $R$ is constant. Removing these two terms, the Hamiltonian now refers only to the motions and potentials of the electrons. This is known as the electronic Hamiltonian:

$$H^{el} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_{r_i}^2 + \sum_i \sum_{j>i} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_{\alpha} \sum_i \frac{Z_{\alpha}e^2}{4\pi\epsilon_0 r_{\alpha i}}$$

(2.7)

The electronic Hamiltonian is numerically solvable, and its eigenfunctions form the basis set of electronic wave functions $\phi^{el}$. The energies of the electronic Hamiltonian are then calculated at each value of $R$, and added to the internuclear repulsion, to form potential energy curves. The nuclei can be thought of as moving subject to these potential energy curves, which for bound states often follow the general shape exemplified by the B state shown in Figure 1.1. At the bottom of the potential well, the potential resembles that of a harmonic oscillator, which is what gives rise to the harmonic-oscillator-like form of Equation 2.5a.

Considering the potential energy curve $U(R)$, calculated from the energies of the electronic Hamiltonian, as a potential in which the nuclei move, we can form the nuclear Hamiltonian from the sum of the kinetic and potential energies of the nuclei:

$$H^N = -\frac{\hbar^2}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \nabla_{r_{\alpha}}^2 + U(R)$$

(2.8)

In order to make this Hamiltonian solvable, one more approximation must be made. In describing the position of the nuclei by a single variable, $R$, we ignore angular motion of the nuclei. Therefore, the Laplacian $\nabla_{r_{\alpha}}^2$ becomes a second derivative with respect to nuclear position $r_{\alpha}$, because changes in $\theta$ and $\phi$ are ignored. This, like the electronic Hamiltonian, is solvable, with a set of eigenvectors $\psi^N$. The total basis function we were
looking for is therefore
\[
\Psi^{BO}(r, R) = \psi^{el}(r; R)\psi^{N}(R). \tag{2.9}
\]

But, since we have ignored rotations, \(\psi^{N}(R)\) can only describe vibrational movements of the nuclei; therefore, \(\psi^{N}(R)\) is in fact a vibrational wavefunction \(\chi_v\). In this way, the Born-Oppenheimer approximation separates the electronic and vibrational energies of a molecule. The rotational energies are added as a perturbation.

It is a feature of the adiabatic approach that potential energy curves of the same symmetry do not cross. This leads to potential curves with complex shapes, such as multiple wells or maxima, as seen in Figure 2.1.

The diabatic formulation of the Born-Oppenheimer approximation does not as strictly separate nuclear and electronic motions. Instead of neglecting the nuclear kinetic energy \(T^N\) when calculating the potential curve, the electron-electron repulsion is ignored. This is also known as a crossing representation, because curves are allowed to cross.

Both the adiabatic and diabatic formulations result in a complete and valid basis set; consequently, the adiabatic and diabatic wave functions are necessarily linear combinations of one another. One manifestation of this relationship is the phenomenon of an “avoided crossing” in the adiabatic basis, as shown in Figure 2.1. The coupling between the two states in the diabatic basis is given by the distance between the curves at their closest approach in the adiabatic basis (labeled \(H^e\) in Figure 2.1).

2.3.2 Rydberg-Klein-Rees (RKR) method

Potential energy curves can be calculated ab initio from the molecular Hamiltonian; however, it is not operators which we observe but their eigenvalues. That is, experiments provide us with values for the energies of transitions and therefore the relative energies of states, and it is often necessary to construct potential energy curves from the observed transition energies rather than calculating transition energies from potential curves. The
Figure 2.1: Diabatic (solid) and adiabatic (dotted) potential curves. The coupling between the two states (H°) in the diabatic basis is one-half the separation of the curves in the adiabatic basis. Figure from Lefevbre-Brion and Field, p 164 [12].

Figure 2.2: RKR curve generated from the first 25 vibrational energies and rotational constants of the X 1 Σ + state of CO. Green points show calculated turning points; the curve is a spline fit between these points. The inner and outer limbs beyond the turning points are Morse potential extensions.

Rydberg-Klein-Rees (RKR) method is one method for calculating potential curves from spectroscopic data; a detailed description of the method is given in Yomay Shyur’s thesis [13]. Given the vibrational energy levels G(v) and rotational constants B(v), the RKR method calculates classical turning points R± for a particle with the reduced mass of the
molecule. These turning points are then connected to form a smooth curve, which is the potential energy curve of the state. However, this only produces a curve up to the highest energy vibrational state that is provided. In order to make a complete potential curve, the inner and outer limbs must be extrapolated from the RKR data. The simplest model for a potential curve is a Morse potential, which has the form:

\[ V(R) = D_e (1 - e^{-\alpha(R/R_e)})^2. \]  

(2.10)

In this equation, \( D_e \) represents the dissociation limit of the molecule, which the function asymptotically approaches at large \( R \). \( R_e \) is the equilibrium internuclear distance, that is, the \( R \) value corresponding to the lowest point in the well. \( \alpha \) is a free parameter that controls the width of the well. By fitting two Morse potentials, one to the inner edge and one to the outer edge of the RKR data, a complete potential function can be constructed (Figure 2.2).

In this thesis, I used an RKR program developed by Dr. Steve Gibson of the Australian National University.

### 2.3.3 Perturbation Theory

Once the potential curves are known, they can be used to form a basis set of vibronic (electronic and vibrational) wavefunctions, combinations of which will describe the true wavefunction. It may seem like a simple task to go from a known electrostatic coupling (for example, the coupling constant labeled \( H^e \) in Figure 2.1) to the energy levels for two coupled electronic states. The challenge is that each electronic state contains an infinite number of vibrational states, all coupled together to varying degrees.

The most common method for calculating the energies of two interacting states is perturbation theory. Perturbation theory begins with a definition of the Hamiltonian as the sum of an unperturbed Hamiltonian \( H^0 \) and a perturbation, \( W \). The problem is done in the basis of the eigenvectors of \( H^0 \), so that the matrix \( H^0 \) is diagonal; all off-diagonal elements of the total Hamiltonian are collected in \( W \).
The heart of perturbation theory is the expansion of the true energies and wavefunctions as power series in a parameter $\lambda$, which is introduced as an arbitrary small number scaling the perturbation matrix $W$:

$$H = H^0 + \lambda W$$  \hspace{1cm} (2.11)

When $\lambda = 1$, this represents the true Hamiltonian. The wavefunctions $\psi_n$ and energies $E_n$ are then expanded as power series in $\lambda$:

$$\psi_n = \psi_n^0 + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \ldots$$ \hspace{1cm} (2.12a)

$$E_n = E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots$$ \hspace{1cm} (2.12b)

The Schrödinger equation can then be rewritten in terms of these energies and wavefunctions. This equation contains many terms, each of which contains some power of $\lambda$. For this equation to be true for all values of $\lambda$, the terms in each power on each side of the equation must equal one another. First-order perturbation theory solves the equation for terms in $\lambda^1$, second-order for terms in $\lambda^2$, and so on, each one producing an expression for an energy correction. Detailed derivations for the energy corrections can be found in many textbooks, for example [14].

Since $H^0$ is usually chosen to include all the diagonal elements, the first-order correction $E_n^{(1)} = \langle \psi_n^0 | W | \psi_n^0 \rangle$, which is simply the $(n,n)$ diagonal element of $W$, is zero. The second-order energy correction is the significant one:

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \psi_m^0 | W | \psi_n^0 \rangle|^2}{E_n^0 - E_m^0} = \sum_{m \neq n} \frac{|W_{m,n}|^2}{E_n^0 - E_m^0}$$  \hspace{1cm} (2.13)

The $(m,n)$ element of the matrix $W$ is given by the bracket of the $m$ and $n$ states with the coupling term $c(r,R)$. We can express the interacting states as products of
electronic and vibrational wavefunctions, so that the matrix element $W_{m,n}$ is:

$$W_{m,n} = \langle \psi_m^0 \chi_{m,v_m}^0 | c(r,R) | \psi_n^0 \chi_{n,v_n}^0 \rangle \quad (2.14)$$

Because the vibrational wavefunctions $\chi_{n,v_n}^0$ do not depend on $r$, the integral can be split into two terms:

$$W_{m,n} = \langle \psi_m^0 | c | \psi_n^0 \rangle \langle \chi_{m,v_m}^0 | \chi_{n,v_B}^0 \rangle \quad (2.15)$$

In general, $c$ can be a function of $r$ and $R$; for simplicity, we will assume that it does not depend on $R$. When examining the interaction between the two electronic states $A$ and $B$, we can calculate the integral $\langle \psi_A^0 | c | \psi_B^0 \rangle$, which gives us a constant coupling $C$ between all the vibrational levels of the two states.\footnote{The fact that $C$ is a constant is an approximation arising from treating $c$ as independent of $R$; however, because the overlap integral is usually only nonzero over a small range of $R$, it is common to use this approximation.} Hence, the matrix elements are given by a constant $C$ multiplied by the overlap integral of the two vibrational wavefunctions:

$$W_{m,n} = C \langle \chi_{m,v_A}^0 | \chi_{n,v_B}^0 \rangle \quad (2.16)$$

In theory, this matrix, and the unperturbed Hamiltonian $H^0$, should contain infinitely many vibrational levels for each of the two states. As an example, we will consider two electronic states with two vibrational levels each. The total Hamiltonian is:

$$H = H^0 + W = \begin{pmatrix}
E_{0,A}^0 & 0 & W_{00} & W_{01} \\
0 & E_{1,A}^0 & W_{10} & W_{11} \\
W_{00} & W_{01} & E_{0,B}^0 & 0 \\
W_{10} & W_{11} & 0 & E_{1,B}^0
\end{pmatrix} \quad (2.17)$$

Notice that the off-diagonal elements between vibrational states of the same electronic state are 0; this is because for the same electronic state, the vibrational wavefunctions are orthogonal and their overlap integral is zero.
The second-order energy correction depends on the off-diagonal elements as well as the energy difference between the interacting states. Perturbation theory works well in cases where the coupling $W_{mn}$ is significantly smaller than the energy difference between the two states. This condition ensures that each vibrational interaction only contributes a small change in energy, and that the effect decreases quickly for more distant vibrational levels. However, if the coupling is large compared to the energy spacing, second-order perturbation theory will not satisfactorily calculate the energy correction. Because perturbation theory approximates the energies as a power series, a higher-order approach would be needed to correct the second-order answer. Additionally, when the coupling is large, more vibrational levels need to be taken into account, requiring calculations to be performed on larger and larger matrices. In cases where the coupling is relatively large, it is best to use a “close coupling” method instead of perturbation theory.

2.3.4 The Coupled Schrödinger Equation Method (CSE)

When the coupling between states is larger than their energy separation, a new approach is needed. The Coupled Schrödinger Equation Method, also known as the close coupling method, overcomes the problem of infinite vibrational levels by packaging them into a single function. In this way, all the vibrational levels are taken into account at once. This is an important step when the coupling constant is large, because even relatively distant vibrational levels can have significant effects on one another.

The CSE method relies on the Born-Oppenheimer approximation to separate the electronic and nuclear energies of the molecule. Thus, the Hamiltonian is separated into an electronic and nuclear part, and the solution wavefunctions are products of the electronic and nuclear (vibrational) wavefunctions. The electronic wavefunctions can be expressed in the diabatic or adiabatic basis; here we will use the diabatic basis, with electronic wavefunctions $\phi^d_i$. The diabatic basis is developed by including the nuclear kinetic energy $T^N$, while neglecting the electron-electron repulsion term in $H^{el}$. Consequently, $T^N$ is diagonal in the diabatic basis while $H^{el}$ is not; the off-diagonal terms in $H^{el}$ are referred to as ele-
trostatic couplings. The elements of $H^{el}$ are calculated just as the perturbation matrix $W$ was calculated in Equation 2.16 by the electrostatic coupling constant multiplied by the overlap integral of the two interacting states.

$$H = H^{el} + T^N$$

$$\psi_{i,v}^0 = \phi_i^d(r, R)\chi_{i,v}(R)$$

In this separation, rotations are considered perturbations of the electronic potential energy. Hence, the rotational component is subsumed within the electronic wavefunction $\phi_i$ and implicitly added to the electronic energy. Practically, this means that the CSE method must be run separately for each value of $J$, since changing $J$ will alter the original potential curve.

The true wavefunctions of the molecule are expressed as a linear combination of these basis functions:

$$\Psi_n(r, R) = \sum_{i=1}^{N} \sum_{v=0}^{\infty} c_{n,i,v} \phi_i^d(r, R)\chi_{i,v}(R)$$

where we are only considering $N$ different electronic states, but keeping all $\infty$ vibrational states. Here, $n$ indexes the full wavefunctions, $i$ indexes electronic basis states, and $v$ indexes the vibrational level. Since it is impossible to explicitly handle each of the infinite vibrational states, we package the vibrational functions and their weights $c_{n,i,v}$ into a function $f_{n,i}$:

$$f_{n,i} = \sum_{v=0}^{\infty} c_{n,i,v}\chi_{i,v}(R)$$

Now our expression for the total wave function contains only a finite sum over $N$ electronic states.

$$\Psi_n(r, R) = \sum_{i=1}^{N} \phi_i^d(r, R)f_{n,i}(R)$$
We can then substitute our total wavefunction and separated Hamiltonian into the Schrödinger equation:

\[
(H_{el} + T^N) \sum_{i=1}^{N} \phi^d_i(r, R)f_{n,i}(R) = E_n \sum_{i=1}^{N} \phi^d_i(r, R)f_{n,i}(R)
\] (2.22)

Taking the inner product of both sides of the equation with the basis electronic wavefunction \(\phi^d_j\), the equation becomes:

\[
\sum_{i=1}^{N} \langle \phi^d_j | H_{el} | \phi^d_i \rangle f_{n,i} + \sum_{i=1}^{N} \langle \phi^d_j | T^N | \phi^d_i \rangle f_{n,i} = E_n \sum_{i=1}^{N} \langle \phi^d_j | \phi^d_i \rangle f_{n,i}
\] (2.23)

Now we are able to exploit the orthogonality of the wavefunctions, as well as the fact that the nuclear kinetic energy is independent of the electronic configuration. Because \(\phi^d_n\) describes the electronic configuration, and \(T^N\) is only concerned with the nuclear configuration, we can rearrange the \(T^N\) term, and use the fact that \(\phi^d_i\) and \(\phi^d_j\) are orthogonal to find that:

\[
\langle \phi^d_j | T^N | \phi^d_i \rangle = T^N \langle \phi^d_j | \phi^d_i \rangle = \begin{cases} 0, & \text{if } i \neq j, \\ T^N, & \text{if } i = j. \end{cases}
\] (2.24)

We can also separate the \(H_{el}\) term into two cases. When \(i = j\), this term is the unperturbed energy of the electronic state, that is, the diabatic potential energy curve \(U^d_j(R)\). Otherwise, this term is the off-diagonal perturbation from \(H_{el}\).

\[
\langle \phi^d_j | H_{el} | \phi^d_i \rangle = \begin{cases} H^e_{ij}, & \text{if } i \neq j, \\ U^d_j(R), & \text{if } i = j. \end{cases}
\] (2.25)

Taking into account these simplifications, and plugging in the nuclear kinetic energy oper-
ator for $T^N$, the Schrödinger equation is now:

$$-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} f_{n,j}(R) + U^d_j(R) f_{n,j}(R) + \sum_{i\neq j} H^{el}_{ij} f_{n,j}(R) = E_n f_{n,j}(R) \quad (2.26)$$

Since $j$ ranges from 1 to $N$, this equation actually represents $N$ coupled differential equations. It is the term involving $H^{el}$ that couples the equations, since it involves off-diagonal matrix elements. In the absence of this term, we have simply rewritten the Schrödinger equation for a potential $U^d_j$.

Equation 2.26 can be recast in matrix form. Moving the term $E_n f_{n,j}(R)$ to the left of the equation, each term can be written as a matrix multiplying the column vector $f_n$, which has dimension $N$. For $N=2$, the equations would be written as:

$$\begin{bmatrix} -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} & 1 & 0 \\ 0 & 1 & 0 \end{bmatrix} + \begin{bmatrix} U^d_1(R) & H^{el}_{1,2}(R) \\ H^{el}_{2,1}(R) & U^d_2(R) \end{bmatrix} - E_n \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} f_{n,1} \\ f_{n,2} \end{bmatrix} = 0 \quad (2.27)$$

We have combined the potential $U^d_j$ and $H^{el}_{ij}$ into a single matrix. Note that $H^{el}_{ij}$, like $U$, can be a function of $R$, though this is not always taken into account. We can then write this equation in general form for any $N$, where $I$ represents the identity matrix.

$$\left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} I + V - E_n I \right) f_n = 0 \quad (2.28)$$

This matrix equation represents a set of $N$ coupled differential equations. $V$ is known from the potential curves and coupling constants, making these equations numerically solvable for $E_n$ and $f_n$. Each energy level has its own set of equations, so CSE must be used level-by-level, for a given electronic, vibrational, and rotational number.

For large couplings, the CSE model is significantly more accurate than perturbation theory. Lucy Archer performed a comparison between CSE, second-order perturbation...
theory, and exact results through diagonalization for a test system with two electronic states of three vibrational levels each, with various coupling constants [11]. The results of her analysis are shown in Figure 2.3. CSE closely matches the exact result even for larger couplings, where perturbation theory diverges from the exact result. However, the advantages of CSE are not without drawbacks. Because all of the vibrational wavefunctions were packaged into a single function, it is impossible to know what superposition of vibrational wavefunctions was used to produce $f_n$.

![Figure 2.3: Comparison of CSE to perturbation theory on a test system, for which exact solutions (diagonalized energies) are available. CSE reproduces the exact values for the whole range of couplings, while perturbation theory diverges from the exact result for coupling terms higher than 7 cm$^{-1}$. Figure from Archer [11].](image)

### 2.4 Predissociation

Predissociation occurs when two states which dissociate to different limits couple strongly enough to allow dissociation of the molecule when it is excited to a nominally bound level. It can be observed experimentally in one of two ways: through emission spectra or absorption spectra. In emission, predissociation appears as a weakening or disappearance of emission lines; that is, when a molecule is excited into a predissociated state, it may fall apart instead of radiating a photon and relaxing back to a lower state. In absorption, predissociation appears as a broadening of absorption lines. I will focus on the absorption picture of predissociation, as it is absorption spectra taken at the SOLEIL synchrotron which provide experimental data to build the CSE model.
2.4.1 Absorption Spectra and Cross Sections

Absorption spectra measure light absorbed by a sample as a function of frequency or wavelength. Generally, the energy of the light is measured in wavenumbers, cm$^{-1}$, a measure of the spatial frequency of the light which increases with increasing energy. An example absorption spectrum of CO is shown in Figure 2.4. Absorption spectra provide information about the quantum mechanical structure of a molecule by measuring the position and characteristics of light-induced transitions between energy levels. The position of a feature represents the energy difference between the lower and upper levels of the transition, while the shape of the peak is determined by several factors. The “natural” or “intrinsic” width of a peak is determined by the time-energy uncertainty principle,

\[ \Delta E \Delta t \approx \hbar \]

where $\Delta t$ refers to the lifetime of the state. Therefore, states with long lifetimes have very narrow energy resonances, while those with short lifetimes are broader. The observed width of a peak also depends on other factors, such as the speed of the molecules (Doppler broadening) and the probability of collisions between them (pressure broadening). Experimentally, these factors can be measured and their effects separated from the intrinsic linewidth.

Another measure of absorption is the absorption cross section, $\sigma$. The absorption cross section measures the probability that light of a certain energy will be absorbed by a molecule. However, instead of being measured as a unitless probability, the cross section is measured in cm$^2$; that is, units of area. This area represents the effective area that a molecule presents to an incoming photon, where a successful absorption is modeled as a “collision”. For example, if the molecule is very unlikely to absorb light of a certain energy, the cross section can be much smaller than the physical dimension of the molecule.

The absorption spectrum is related to the absorption cross section by the length
and number density of the sample via the equation

\[ I(\lambda) = I_0 e^{-nL\sigma(\lambda)} \]  

(2.30)

In this equation, \( I(\lambda) \) represents the intensity of transmitted light at a certain wavelength. \( I_0 \) is the original intensity of the light. The intensity is exponentially reduced by the number density \( n \) of the sample, the path length \( L \) of the light through the sample, and \( \sigma(\lambda) \), the cross section of the species in question at that particular wavelength.

Figure 2.4: Experimental absorption spectrum of the B\((v=2)\)-X\((v=0)\) band of CO. A single vibrational band contains many rotational lines; broadening from predissociation is causing the higher-energy rotational lines to overlap (above \( \sim 90990 \text{ cm}^{-1} \)).

The CSE modeling program produces calculated absorption cross sections from the numerical wavefunctions that it generates for the coupled states. The probability of a transition depends on the overlap integral of the lower and upper state wavefunctions (here, the lower state is the \( v=0 \) level of the ground state), as well as on the electric-dipole transition moment, which is another parameter of the model. Because CSE can only calculate single rotational levels at a time, these cross sections do not reproduce the rotational structure of full bands; however, the linewidths of the individually calculated transitions can be fruitfully compared to experimental data.
2.4.2 Dissociation and Predissociation

It is the well of a bound potential curve that leads to discrete energy levels; purely dissociative or “repulsive” potentials (and bound potentials above their dissociation limit) contain a continuum instead of a set of discrete levels. If a molecule is excited into this continuum by a photon of light, it dissociates, in what is known as direct dissociation, because the molecule now has more energy than its constituent free atoms and the atoms are no longer energetically more stable together than apart.

Predissociation occurs when an energy level has a mixture of bound and dissociating character, resulting from a coupling between discrete and continuum basis states (Figure 2.5). When a molecule is excited to such a “quasi-bound” state, it can follow one of two paths. The first is radiative decay, which would be expected for the bound state; the second is dissociation, which would be expected for the continuum state. Each of these processes has a characteristic rate, $A$, so that the number of excited molecules relaxing through a certain pathway, as a function of time, is given by:

$$N = N_0 e^{-At}$$

(2.31)

where $N_0$ is the initial population of excited molecules. For the radiative process, relaxing back to the ground state via the release of a photon, $A$ is generally $\sim 10^8 \text{ s}^{-1}$ [12]. The rate $A$ can also be converted to a characteristic “lifetime” $\tau = A^{-1}$, which has units of time and represents the amount of time it takes for a fraction of 1/e molecules to remain in the excited state. If there are competing processes, in this case radiation ($A_{rad}$) and predissociation ($A_{pd}$), the overall lifetime of the state is the reciprocal of the sum of the two rates:

$$\tau_{tot} = \frac{1}{A_{rad} + A_{pd}}$$

(2.32)

The total lifetime determines the intrinsic linewidth of the transition via the time-energy uncertainty principle, as discussed above. The experimentally measured full width at half-
maximum (FWHM) of an absorption peak, denoted as $\Gamma$, is related to the total lifetime:

$$\Gamma(cm^{-1}) = (2\pi c \tau)^{-1} = 5.3 \times 10^{-12} A(s^{-1})$$ (2.33)

Therefore, when the only available pathway is radiation with a typical rate of $10^8 s^{-1}$, the linewidth $\Gamma$ for a transition is on the order of $10^{-4} cm^{-1}$. When the competing dissociation process has a higher rate than the radiative process, the energy level is said to be predissociated. In this case, the overall lifetime of the state is shortened and the linewidth of the corresponding transition broadens according to Equation 2.33. In general, predissociation becomes experimentally noticeable when linewidths are on the order of $10^{-2} cm^{-1}$ or more, which corresponds to a predissociation rate $A_{PD} \sim 10^9$ ([12], Table 7.2).

Figure 2.5: Predissociation between two generic potential curves. The bound state $v_1$ and the continuum state $v_e$ are “mixed,” leading to the molecule in the $v_1$ state dissociating to the ground state of separate atoms $A + B$. Figure from Lefevbre-Brion and Field, p 494 [12].

Although the true combination of coupled states comprising a predissociated state do not form an adiabatic state, it can be useful to use the adiabatic potential curves, which are linear combinations of crossing diabatic curves, to visualize the effect of coupling between
levels with different dissociation limits. It is said that when a dissociating state crosses a bound state, it “pushes” the vibrational levels downward as well as broadening their cross section. In the picture of coupled curves, this can be understood by the fact that the combined curve (exemplified by curve II in Figure 2.6) has a broader well than the original bound state; a broader well corresponds to more closely spaced energy levels, leading to the bound vibrational states being “pushed down.” The possibility of dissociation is also visually explained by the fact that the outer limb of the potential is now a barrier which falls to the lower dissociation limit, and the molecule can dissociate by tunneling through that barrier. Hence, levels closer to the crossing point show more predissociation than those far below the crossing, where the barrier is larger.

![Figure 2.6: Diabatic curves A and B combine to form adiabatic curves I and II. Figure from Alan Heays' thesis [15].](image)

It is also important to remember that the matrix element $H_{ij}^{el}$, which determines the magnitude of the interaction, depends both on the coupling coefficient (which is usually considered constant for two interacting electronic states) and on the overlap integral between the two vibrational wavefunctions. Therefore, even if two electronic states have a very large coupling constant, the effect on the energies will be small if the wavefunctions do not significantly overlap in space.
2.5 Implementation of CSE

The CSE implementation used in this thesis was written by Dr. Stephen Gibson of the Australian National University. Given a set of potential curves, transition moments and coupling constants, the program uses the renormalized Numerov method to solve the coupled differential equations numerically, producing a set of energies and wavefunctions for the combined states.

2.5.1 Optimization

To connect the computational CSE implementation to experimental data, Dr. Alan Heays developed an optimization routine which attempts to alter a given model to more closely match experimental data. A detailed description of this method can be found in his thesis [15]. The program works by running the CSE program for an initial set of inputs and generating the absorption cross section. From this cross section, the line positions and/or linewidths and oscillator strengths are calculated for a set of transitions. These values are then compared to experimental values by calculating residuals, i.e. the difference between the experimental and calculated values.

\[ d = x_{\text{exp}} - x_{\text{calc}} \] (2.34)

Then, the model parameters are altered and the calculation repeated. The Levenberg-Marquardt algorithm is used to iteratively reduce the least-squares measure of fit (the sum of the squares of the residuals, each multiplied by an optional weighting coefficient). When the fit has converged, the program returns an improved set of model parameters. These parameters can include the coupling constant and parameters altering the potential curves, including their position and shape. Because the only experimentally derived potential curves already include perturbations, basis curves cannot be experimentally generated; optimizing the parameters that characterize potential curves ideally leads to a set of basis curves and couplings that reproduce experimental data. Since there is no single “true” basis set, it
is only necessary to find a combination which satisfactorily reproduces experimental data: “The selection of included electronic states and state couplings which may lead to a satisfactory reproduction of the constraining observations is not necessarily unique, and neither is their precise formulation in terms of numerical parameters. . . the diabatic representation of electronic states is also inherently nonunique and alternative model formulations are equally valid as long as their constituent states and interactions are treated together and not quoted in isolation” [15].

2.5.2 Parameter Sweeps

Because the optimization routine follows the gradient of the residuals, it can become “stuck” in local minima where changing any parameter results in a worse fit, but this point does not necessarily represent the best fit in all of parameter space. Also, the size of the initial steps in each parameter can affect how far the model wanders from its initial state in the process of the optimization. Therefore, it is necessary to understand the sensitivity of the model to each parameter, and to find the neighborhood of the best combination of parameters. In order to do this, I wrote a Python script that runs the optimization routine without actually optimizing parameters. Instead, residuals are calculated for a range of values for each parameter. Looking at how the model changes in response to each parameter informed the step size and initial conditions of the optimization.
Chapter 3

Predissociation in the $B^3 \Sigma^--X^3 \Sigma^-$ System of Sulfur Monoxide

The absorption spectrum of sulfur monoxide is dominated by the $B^3 \Sigma^--X^3 \Sigma^-$ system in the 41000-52000 cm$^{-1}$ region of the ultraviolet, comprised of very strong absorption bands displaying predissociation in the $v=4$ bands and higher. Predissociation in the B-X system is an important mechanism for SO photodissociation, which is especially relevant to understanding the chemical pathways following from the photodissociation of SO$_2$ in the early Earth atmosphere.

Some parallels can be drawn between SO, which is a radical species and difficult to work with experimentally, and O$_2$, which has been studied much more extensively. Because sulfur and oxygen reside in the same column of the periodic table, SO and O$_2$ are isovalent, meaning they share the same number of valence electrons. The two molecules have similar molecular orbitals and therefore similar electronic states, although the states differ due to the higher energy of the sulfur orbitals and the fact that O$_2$ has a center of inversion while SO does not. The $B^3 \Sigma^-$ state of SO is analogous to the $B^3 \Sigma_u^-$ state of O$_2$, which has the same electron configuration. The analogous states are shown in Figure 3.1 along with nearby states that can interact with the B state. Many more states can interact with the
B state of SO due to the fact that SO does not have an inversion center, while in O$_2$ the B state, which is an *ungerade* state (antisymmetric with respect to inversion), can only interact with other *ungerade* states. Another relevant difference is that the dissociation limit of SO is within the bound region of the SO B state, while the dissociation limit of O$_2$ is below the O$_2$ B state. Therefore, predissociation in SO starts above the $v=3$ level, while all the B-X levels of O$_2$ are potentially predissociated. However, despite these differences, the parallel with oxygen can offer some clues to the origin of predissociation in SO, since O$_2$ has been much more extensively studied.

In SO, predissociation in the B-X system was first observed in 1932 by Martin [18], who assumed that the predissociation was due to an interaction with a $^3\Pi$ state, and that this state’s potential curve would have a shallow minimum. Since that time, many states have been suggested as possible causes for the observed predissociation. Clerbaux and Colin produced a more accurate value for the dissociation limit through emission spectroscopy [19]. More recently, Liu et al. used degenerate four wave mixing, a form of laser absorption spectroscopy, to determine approximate linewidths for transitions to the first 16 vibrational
Using the linewidths reported by Liu et al. as a guide, I explored five possible states which could cause predissociation by interacting with the B state. By constructing potential curves and observing the effect of interactions on linewidths simulated by the CSE program, I identified two states which may be important in causing predissociation in this region.

3.1 Relevant Electronic States

Five states were tested as candidates for predissociating interactions with the B state. Three $^3\Pi$ states (C, C$'$ and A), the d$^1\Pi$ state, and the (1)$^5\Pi$ state were considered.

Figure 3.2: Potential curves for the B$^3\Sigma^-$ state of SO and five possible candidates for predissociation interactions.
3.1.1 \( \text{B}^3\Sigma^- \) State

The \( \text{B}^3\Sigma^- \) state of SO is analogous to the \( \text{B}^3\Sigma_u^- \) state in \( \text{O}_2 \), and transitions to this state form a strong absorption band system. Experiments reveal that this state is strongly perturbed; that is, it must be interacting strongly with other states because its vibrational and rotational levels do not follow the expected pattern for an unperturbed bound state [5]. For instance, the rotational constant \( B \) is expected to decrease linearly with vibration number for a smooth anharmonic potential. However, in the B state, the experimentally determined rotational constant deviates from the expected linear trend for some values of \( v \), as shown in Figure 3.3.

![Figure 3.3](image.png)

Figure 3.3: The rotational constant of the \( \text{B}^3\Sigma^- \) state of SO as a function of vibrational number. Data from Liu et al. [5].

In order to construct a CSE model, it was necessary to have a potential curve for the B state that is as close as possible to the unperturbed basis state, rather than the true state represented by the experimental data. To that end, the most strongly perturbed levels (\( v=2, 3, 11, 12, \) and 13) were omitted when constructing a potential curve using the RKR method.
3.1.2 $^3\Pi$ States

Martin’s initial assessment in 1932 was that the predissociation he observed was caused by a $^3\Pi$ state. Since then, multiple $^3\Pi$ states have been identified which may cause predissociation. Colin [20] in 1969 called this perturbing state the C state, concluding that it had a shallow potential well and that it approached the same dissociation limit as the ground state. Ab initio calculations such as those of Yu [17] and Danielache [3] suggest that what Colin called the C state is a $^3\Pi$ state, but that it actually approaches the same dissociation limit as the $B^3\Sigma^-$ state itself; transitions have also been experimentally observed to this C state using multiphoton ionization spectroscopy [21]. However, another $^3\Pi$ state, which is purely dissociating and is labeled C’, crosses the C state before approaching a lower dissociation limit. In the adiabatic basis, the C and C’ curves exhibit an avoided crossing (such as the one shown in Figure 2.1), implying that their diabatic counterparts are coupled, in this case by about 300 cm$^{-1}$. Because of this coupling, the dissociating character of the C’ state could affect the B state, if the B state is coupled to the C state. When predissociation occurs through a “chain” of interactions, such as B-C-C’, it is known as an indirect predissociation. I obtained potential curves for the C and C’ states from the ab initio work of Danielache et al. [3], which were calculated in the adiabatic basis. In
order to obtain diabatic representations of these curves, points in the crossing region were
interpolated to cross the curves, resulting in one curve with a potential well approaching
the upper dissociation limit and a purely repulsive curve approaching the lower limit. These
curves are shown in Figure 3.4.

![Figure 3.4: Potential curves for the A3Π state of SO.](image)

Another 3Π state lies below the B state, and approaches the lower dissociation
limit. Called the A state, it is a bound state to which transitions have been experimentally
measured. Liu et al. identify the A state as a potential cause of predissociation, since it
has the same spin multiplicity as the B state and approaches a lower dissociation limit.
A potential curve for the A state, obtained via RKR using experimental data from Elks
(1999), is shown in Figure 3.5 [22].

3.1.3 d1Π State

In the previous section, only states which share the same spin were considered to interact
with the B state. These states can have electrostatic interactions, which are generally
stronger (can have larger coupling constants) than other interactions. However, it is possible
for states of different spin to interact via spin-orbit coupling. The d1Π state is therefore
another candidate for causing predissociation, as it overlaps the B state and approaches
the lower dissociation limit. Liu identified this state as perturbing the $v=5$ level of the B state. The shape of the d potential curve has a maximum near $R = 2.3$ Å. This is evidence that the d state is actually a combination of two states, similar to the C-C' combination discussed above, and predissociation due to this state is actually an indirect dissociation. A potential curve for the d state, shown in Figure 3.6, was obtained from the ab initio calculations of Yu et al. [17].

3.1.4 (1)$^5\Pi$ State

Another state of different spin which may cause predissociation in the B state is the (1)$^5\Pi$ state. Yu et al. identify spin-orbit coupling to this state as a “weak predissociation pathway” for the B state, because of its crossing with the B state. A potential curve for the (1) state, shown in Figure 3.7, was obtained from their ab initio calculations [17].

3.2 Interaction Models

A CSE model of each of these states interacting with the B state was performed to generate a calculated absorption cross section. A MATLAB script was then used to measure the full
width at half maximum (FWHM) of the sixteen absorption peaks corresponding to the first sixteen vibrational levels of the B state. The results of each model are shown in Table 3.1.

**Table 3.1:** Calculated linewidths resulting from five interactions, compared to experimental data given by Liu et al. [5]. Coupling constants are given in cm\(^{-1}\). 0 indicates a width smaller than 1\(\times10^{-4}\) cm\(^{-1}\).
3.2.1 $B^3\Sigma^−-C^3\Pi-C′^3\Pi$ Interactions

The coupling between the C and C′ states was assumed to be half of the separation between the adiabatic version of these curves, i.e. $300 \text{ cm}^{-1}$. From ab initio calculations, the B-C coupling is on average $30 \text{ cm}^{-1}$ \[17\]. When this interaction was modeled using CSE, the widths of the resulting peaks were still at least ten times smaller than the experimental widths. However, the relative broadening of $v=9–12$ follows the general pattern of broadening seen in experiment \[5\].

The predissociation due to interaction with C′ may not be purely indirect, so another scenario was explored where there is some direct coupling (also $30 \text{ cm}^{-1}$) between the B and C′ states. In this case, the predissociation was much stronger between $v=9$ and $v=12$. However, this model did not reproduce the broadenings seen in $v=4–7$ and above 12. The linewidths are also very small compared to experiment, by a factor of 10 or more.

3.2.2 $B^3\Sigma^−-A^3\Pi$ Interaction

Yu suggests a coupling constant of $20 \text{ cm}^{-1}$ between the A and B states from ab initio calculations. For this coupling, there was no appreciable broadening; the peak widths were too small to measure for a grid spacing of $0.01 \text{ cm}^{-1}$. Even with a coupling constant of $100 \text{ cm}^{-1}$ (improbably high based on the ab initio coupling of only $20 \text{ cm}^{-1}$), none of the peaks were broadened beyond $0.03 \text{ cm}^{-1}$. Realistically, the coupling would be smaller and the A state would not significantly contribute to predissociating the B state. This result can be interpreted by considering that the interaction between the two states would very small, due to small wavefunction overlap. Wavefunctions of continuum states are oscillatory, and the frequency of the oscillation depends on the difference between the energy of the state and the potential. Therefore, states in the continuum of the A, with energies near those of the bound states of B, oscillate at a high frequency. The strength of the interaction depends

\[1\] This and other coupling constants are approximated as being constant. In reality, they are functions of \(R\); because the effect of the coupling is only large where there is large wavefunction overlap (i.e. in a small region of \(R\)), this can be a reasonable approximation.
on the overlap integral between vibrational wavefunctions (Equation 2.16), and the overlap of a bound wavefunction of B with the small-wavelength oscillatory wavefunction of the continuum state is very small.

### 3.2.3 $B^3Σ^−-d^1Π$ Interaction

For the B-d interaction, Yu calculates a coupling constant of 30 cm$^{-1}$. This interaction only appreciably broadened the $v=8$ level, and the broadening was only 0.3 cm$^{-1}$. Interestingly, this width does match up with experimental data; however, the $v=8$ level is much narrower than its neighbors. Therefore, the B-d interaction is unlikely to be a major cause of predissociation.

### 3.2.4 $B^3Σ^−-(1)^5Π$ Interaction

With a coupling of 30 cm$^{-1}$ as suggested by Yu, the B-(1) interaction is does not broaden any lines more than 0.5 cm$^{-1}$. However, this interaction does produce broadening in $v=4-7$, which was not explained by the B-C-C$'$ interaction, although the widths are not on the scale of the observed widths.

### 3.3 Discussion

None of the models produced widths as large as the ones seen in experiment. In fact, where broadening did happen, the widths were usually only about a tenth of the experimental value. It can be concluded that there is either another cause for the predissociation, or the coupling between the states is larger than expected. Also, none of the models showed much predissociation above $v=12$, where the experimental data shows widths of up to 40 cm$^{-1}$, so there must be another state responsible for this effect. Indeed, there are several dissociating states which cross the B state near its higher vibrational levels. However, in levels $v=12$ and below, the general pattern of predissociation lines up with model results from two different
interactions, as shown in Figure 3.8. The B-(1) model shows the same general shape as the experimental data from $v=4–7$, while the B-C-C' model follows the shape of the data from $v=9–12$. The plot shows the model with direct coupling between B and C'; the purely indirect predissociation model does not reproduce the broadening in $v=10$. Overall, we can conclude that that the C and C' states, along with the (1) state, could be responsible for the observed predissociation below $v=13$. Above this level, another dissociating state, with a crossing in that region, must be causing the observed broadening. On the other hand, the A and d states were found to have no significant effect.

Because the models have such a significant disparity in magnitude from the experimental data, the next step is to explore the sensitivity of the model to small changes in coupling and potential curves. Initial tests show that doubling the B-C and B-C' coupling to 60 cm$^{-1}$ has little effect on the width of the broadened lines. However, small changes in the potential curves might have a large effect on the line broadenings. In the future, the SO
molecule could be added to the CSE optimizing program described in Section 2.5.1 which would greatly expedite testing a range of couplings and modified potential curves.
Chapter 4

Predissociation in the $B^1\Sigma^+ - X^1\Sigma^+$ System of Carbon Monoxide

4.1 Predissociation in Rydberg States of CO

The interaction of ultraviolet light in the wavelength range 91.2-111.8 nm (89,450-109,600 cm$^{-1}$) with carbon monoxide is of particular astrophysical interest, as discussed in the Introduction. This region of the CO absorption spectrum becomes increasingly congested and complex at higher energies; however, the low-energy end of the spectrum is less complex. The low-energy region contains a series of transitions to the lowest Rydberg states of the molecule. Rydberg states are states in which one electron is excited into a higher energy level while the remaining electrons occupy low energy states close to the nuclei. The excited electron is far from the “core” of the molecule, which is made up of the remaining electrons and the nuclei. In the limit of the one excited electron being very far from the core of the molecule, these Rydberg states approach the ground state of the CO$^+$ ion. The lowest two Rydberg states, $B^1\Sigma^+$ and $C^1\Sigma^+$, are shown in Figure 4.1. These states can be labeled by their electron configuration, for which the core is the CO$^+$ X state and the excited electron is in some higher level. The B state has the electron configuration $[\text{CO}^+ \text{ X}]3s\sigma$, meaning...
that the excited electron is in the $3s$ state and the projection of its angular momentum on the internuclear axis is zero ($\sigma$). The C state has electron configuration $[\text{CO}^+ \ X]3p\sigma$. These states represent the first in two series of Rydberg states, the $n\sigma\sigma$ and $np\sigma$ series.

Both the B and C states display predissociation, which has been identified as being caused by interactions with valence states of the same symmetry, $D'^1\Sigma^+$ and $C'^1\Sigma^+$. The B state is the lowest energy state displaying predissociation, which begins to appear in the $v=2$ level, as the $v=0$ and $1$ levels fall below the dissociation limit. Understanding the interactions which lead to this predissociation is the first step in developing a model for predissociation in the whole $n\sigma\sigma$ series. The B state predissociation, to date attributed to electrostatic interaction with the $D'$ state, has been modeled by Tchang-Brillet et al. [10]. This project examined the Tchang-Brillet model and attempted to improve upon its results in the light of new data for the linewidths of B(2)-X(0) transitions.

![Figure 4.1: Potential energy curves for the lowest Rydberg (B$^1\Sigma^+$ and C$^1\Sigma^+$) and valence (D$'^1\Sigma^+$ and C$'^1\Sigma^+$) states of CO. Figure from Lefevbre-Brion [23].](image-url)
4.2 The Two-State B$^1\Sigma^+$-D$'^1\Sigma^+$ Model

Predissociation in the B state, particularly the $v$=2 band, was attributed to the repulsive part of the D$'^1\Sigma^+$ state \[24\]. The D$'$ state is a valence state, meaning that the electrons all reside in molecular orbitals constructed from atomic orbitals of low principal quantum number $n$, in contrast to Rydberg states, in which one electron is in an orbital corresponding to high $n$. In particular, in the D$'$ state, the excited electrons fill antibonding molecular orbitals, which weakens the C-O bond and causes the equilibrium $R$ to be larger than that of the ground state. Because the potential well of the D$'$ state is shallow and lies at a higher $R$ than that of the ground state, transitions to the D$'$ state are difficult to observe. Transitions were first observed by Wolk and Rich in 1983, using laser-induced fluorescence \[25\]. Three vibrational levels were observed, and these data can be used to construct an RKR representation of the potential well, from which the limbs of the potential can be extrapolated.

Tchang-Brillet et al. constructed a close coupling model of the B-D$'$ interaction in 1992 \[10\], which was able to closely reproduce the positions of absorption lines for the B state while using a simple model. The B state was constructed from four parameters: $\omega_c$ and $\omega_c x_c$, which describe the spacing and anharmonicity of the vibrational levels according to Equation 2.5a, and $B_e$ and $\alpha_e$, which are used to calculate the rotational constant $B_v$ for each vibrational level. The rotational constant is calculated via a power series expansion:

$$B_v = B_e - \alpha_e \left( v + \frac{1}{2} \right) + \ldots$$  \hspace{1cm} (4.1)

This rotational constant in turn determines the rotational energy according to Equation 2.5b.

All four parameters ($\omega_c$, $\omega_c x_c$, $B_e$, and $\alpha_e$) were allowed to vary. Because $\alpha_e$ was included as a free parameter, the potential could not be modeled by a simple Morse potential (Equation 2.10); therefore, the RKR method was used to generate the potential curves. The four parameters were allowed to vary in an iterative process to remove the effects of perturbations in the experimentally observed values, resulting in a final "deperturbed"
B state potential curve.

The D primed state was modeled as a decaying exponential:

\[ V(R) = Ae^{-bR} + C \] (4.2)

The exponential was fit to the inner limb of a curve extrapolated from experimental data for the D primed state. Because the D primed state has a potential well, following the inner limb of the extrapolated curve results in the exponential falling below the dissociation limit, as shown in Figure 4.2. However, it very closely matches the extrapolated curve where it crosses the B state, which is where the wavefunction overlap is largest and where the interaction effect is strongest. Tchang-Brillet concluded that the “calculated level shifts are insensitive to the shape of the D primed potential beyond the short-range repulsive part.” One drawback of this approach lies in the fact that the position of the long-range part of the potential does affect predissociation, so calculated widths below the barrier maximum of the true D primed state are not meaningful in this model. However, the \( v=2 \) levels of the B state, which display predissociation, all lie above the barrier maximum.

### 4.2.1 Isotope Effects and Rotational Dependence of Linewidths

The Tchang-Brillet model was constructed to reproduce experimental data from \( ^{12}\text{C}^{16}\text{O} \). For this isotopologue, the model reproduces the \( J=0 \) rotational energy levels of \( v=0 \) and 1 to within 1 cm\(^{-1} \), and \( v=2 \) to within 7 cm\(^{-1} \). It also reasonably well reproduces linewidths from experimental data available at the time. Lucy Archer reproduced the Tchang-Brillet model as part of her thesis, comparing its linewidth results to new experimental data recorded at the SOLEIL synchrotron and extending the analysis to the \( ^{13}\text{C}^{16}\text{O} \) and \( ^{12}\text{C}^{18}\text{O} \) isotopologues. Her comparison of experimental and model linewidths is shown in Figure 4.3.

The measured linewidths increase with \( J \) much more quickly than the model predicts, and the model also overestimates low-\( J \) linewidths for heavier isotopologues. Because the Tchang-Brillet model was designed to reproduce \( ^{12}\text{C}^{16}\text{O} \) data, and more accurate data
have become available, the goal of this project was to create a new two-state model on the basis of the new data.

### 4.3 Development of a New $B^1\Sigma^+-D^1\Sigma^+$ Model

The challenge of developing a CSE model to recreate experimental data is that a single set of observable transitions arises from a combination of unknown basis states. Even in the simplest case, a two-state model, one must essentially find two potential curves from one set of transitions. The potential curves for both interacting states are unknown, as is the coupling between them. The general shape of the basis potential curves can be inferred from observations, but their exact form is necessarily slightly different from the form of the real, perturbed curves. The number of parameters can expand quickly, as each potential curve can be varied in many ways (shifting and stretching in horizontal and vertical directions to name a few). Therefore, it is extremely important that the starting point be as close as
possible to the basis functions, and that the number of free parameters is kept to a reasonable number. In developing this model, the B state was constructed from the ground state of the CO$^+$ ion, the D$'$ state fitted to the potential curve extrapolated from the experimental data of Wolk and Rich [25], and four independent and impactful parameters were identified. The effects of these four parameters were studied to identify the neighborhood of the best fit, which was then refined with the optimization routine (Section 2.5.1). Data for term values of the $J=0$ and $J=10$ levels of the $v=0$, 1, and 2 bands were used as targets for the initial fit. The $J=10$ levels were chosen as an arbitrary higher-$J$ level to give the model a target for rotationally-dependent effects, without having to consider many rotational levels. After a close fit to the line positions was achieved, the linewidths of the $J=0$ and $J=10$ levels of the $v=2$ band were also added to the fit.

4.3.1 The B$^1\Sigma^+$ State

The B$^1\Sigma^+$ state, as a Rydberg state, has a core of electrons in the [CO$^+$ X] configuration, so the B state should have a potential curve similar to that of the ground state of the CO$^+$ ion. The single excited (but still bound) electron contributes an overall downward energy shift.

Figure 4.3: Linewidths vs rotational number $J$ for two isotopologues. Points represent experimental data; solid line represents linewidths calculated by the Tchang-Brillet model. Figures from Archer [11].
relative to the ion curve, but does not significantly affect the shape of the curve. Therefore, the ground state of the CO\(^+\) ion was used as a starting point for the B state potential in the new model.

Multiple choices are available for constructing a potential curve; an RKR curve effectively reproduces the energy levels used to create it, while a Morse potential (Equation 2.10) is more flexible in optimization because it is an analytical function whose parameters are easily changed. An RKR curve for CO\(^+\) was generated from G values from [26] and B values from [27]. This curve was placed so that its potential minimum was positioned at 86929.1 cm\(^{-1}\), to align with the minimum of an RKR curve generated from B state data. It was then adjusted vertically by \(-33.9\) cm\(^{-1}\) as suggested by Tchang-Brillet (Table III), who had carefully compared experimental data for the B state to the ion state. This placement produced good agreement between the lowest vibrational level of the B state, as measured experimentally, and the lowest vibrational level of the ion-derived B state.

A Morse potential was also generated from the constants of the ion ground state. However, the Morse potential, because it only depends on three parameters, is not able to closely approximate all potential wells. In this case, the Morse potential well was significantly wider than that of the RKR curve, so the flexibility of an analytical function was sacrificed for the accuracy of RKR, and the RKR potential was used in the final model.

4.3.2 The D\(^{1}\Sigma^+\) State

Because the D\(^{1}\) state has a shallow potential well, it supports a few bound levels, which have been observed experimentally. The existence of an experimentally derived form for the D\(^{1}\) state is extremely useful; however, its complicated shape (the presence of an intermediate maximum after the potential well) makes this an undesirable form for an optimizable model. Even an RKR curve cannot capture this form, since RKR works by calculating the bottom of the well and extrapolating the limbs as Morse potentials. The experimentally derived form of the curve shown in Figures 4.2 and 4.5 is in fact only an RKR curve at the bottom
of the well, which is connected to a Morse potential until the barrier maximum, from which point the outer limb is extrapolated as a Gaussian function returning to the dissociation limit. Clearly, if a simpler form captures the behavior of this curve, that form is preferable in an optimizable model.

The Tchang-Brillet model uses a simple decaying exponential to model the D\textsuperscript{′} state. In her analysis, she assumed that the most important feature of the experimental curve to match is the slope at the point where the D\textsuperscript{′} state crosses the B state. In order to achieve this with a decaying exponential, the dissociation limit was changed. The new model was developed with both the slope and dissociation limit in mind.

Figure 4.4: A decaying exponential curve fit to two points on the extrapolated experimental curve. Because the function is constrained to approach a dissociation limit only \(~6000\ \text{cm}^{-1}\) below the crossing point, in order to reproduce the steep curvature at the crossing, the inner limb quickly deviates from the extrapolated curve and approaches an unphysically high value.

Many functional forms were tested to approximate the D\textsuperscript{′} state. First, a decaying exponential shifted to approach the dissociation limit was tested. However, the D\textsuperscript{′} state is
very steep at the crossing point, and a decaying exponential cannot reproduce such a steep
slope at a point so close, vertically, to its asymptote, without being very sharply curved
and approaching unphysically high energy values at small $R$ (Figure 4.4). For example, the
Morse inner limb of RKR curves generally reach thousands of eV for small ($\sim 0.01 \text{ Å}$) $R$. A
decaying exponential fitted to the slope of the RKR curve and constrained to the dissocia-
tion limit reaches energy values of $10^{30}$ eV at $R=0.01 \text{ Å}$. Tchang-Brillet circumvented this
problem by lowering the asymptote; to keep the asymptote at the dissociation limit another
functional form is needed.

Several functional forms were tested to mimic the experimentally derived curve’s
slope at the point where it crosses the B state, and the functions were constrained to pass
through the crossing point. Two of the most common functions for constructing potential
curves, the Morse potential (Equation 2.10) and the Lennard-Jones potential (below) were
initially tested.

$$V_{LJ}(R) = \epsilon \left[ \left( \frac{r_e}{R} \right)^{12} - 2 \left( \frac{r_e}{R} \right)^{6} \right]$$

In this equation, $\epsilon$ represents the well depth and $r_e$ the equilibrium internuclear distance.
Using appropriate constants from the experimental data for the $D'$ state, neither the Morse
nor the Lennard-Jones potential could satisfactorily reproduce the extrapolated curve. Both
the Morse potential and the Lennard-Jones potential assume that the width-to-depth ratio
and the asymmetry of the potential well are somewhat typical. The $D'$ state has a potential
barrier because it is actually a combination of two states (much like the C and $C'$ states
of SO), and so its shape is not typical. Therefore, both of these functions were unable to
simultaneously match the depth of the well and the position of the crossing point. Figure 4.5
shows a Morse potential constrained to the well depth, which is far from the crossing point,
and a Lennard-Jones potential constrained to the crossing point, which is far from the well
minimum.

Because the most common potential well functions were unable to reasonably
reproduce the $D'$ curve, I returned to a simpler, purely repulsive representation, which
ignores the presence of the potential well. To allow the function to be steeper at larger
Figure 4.5: Several functional forms to approximate the D' state, in comparison to RKR curve (blue). A pure decaying exponential (cyan), such as the one used by Tchang-Brillet, cannot approach the correct dissociation limit and simultaneously reproduce the slope of the RKR curve, without becoming unphysically large at small $R$. Morse and Lennard-Jones potential functions (red, green) cannot match both the depth of the well and the crossing point simultaneously. An exponential multiplied by a polynomial, of the form $V_{pe}(R) = (AR + B)e^{-CR} + De$ (magenta), can match the slope and dissociation limit while staying reasonably small at small $R$.

$R$ without becoming unphysically large at small $R$, a polynomial multiplied by a decaying exponential was used:

$$V_{pe}(R) = (AR + B)e^{-CR} + De$$  \hspace{1cm} (4.4)

A rearrangement of this equation yields a form constraining the function to pass through a specific point. Here, that point is $(C_x, C_y)$, the point at which the D' potential curve crosses the B curve.

$$V_{pe}(R) = (A(R - C_x) + (C_y - De))e^{-B(R - C_x)} + De$$  \hspace{1cm} (4.5)
Constraining the function to the crossing point allows for flexibility in the parameters without the curve quickly diverging from from the crossing point. This form for the D’ state was used in the final model. In the initial formulation of the curve, \((C_x, C_y)\) was the point where the D’ extrapolated curve crosses the ion B curve. \(A\) and \(B\) were calculated to fit the curve to another point higher on the inner limb of the D’ curve. Because high values of \(A\) can cause the inner limb of the potential to turn over and decrease as it approaches zero, \(A\) had to be adjusted until the potential had a negative slope everywhere. Although the inner limb still goes to \(10^6\) eV at small \(R\), this is a major improvement over the pure decaying exponential.

4.3.3 Parameters

The potential curves described above were used as a starting point for the model. The initial value for the coupling, \(2900\) cm\(^{-1}\), was taken from the Tchang-Brillet model; the exact value arose from the fit of the model, but it is within the range expected from the extent of the avoided crossing in ab initio calculations, e.g. \([28]\). A CSE solution for the initial form of the curves, coupled by \(2900\) cm\(^{-1}\), yielded term values differing from the targets by \(100\) or more cm\(^{-1}\) for the \(v=0, 1, \) and \(2\) levels of the B state. From this starting point, there were many parameters that could be adjusted. The D’ curve function has four parameters \(A\), \(B\), \(C_x\), and \(C_y\). The B curve, as an RKR curve, is less flexible, but can be adjusted by shifting or stretching in the \(x\) and \(y\) directions. The coupling between the two curves is also a free parameter.

In narrowing down the number of parameters, some pairs of parameters can be identified which have similar effects on the system. In this case, only one of the pair need be varied. For example, varying the \(C_x\) or \(C_y\) parameters of the D’ potential would have similar effects for small variations, since either one essentially just changes the position of the crossing along the B curve. Shifting the B curve in the \(x\) direction would have a similar effect. Therefore, only one of these three is necessary as a free parameter; I chose \(C_x\) as the parameter to control the position of the crossing point. The B curve can also be
shifted vertically, which directly affects the position of the vibrational levels. This $y$-shift was included as a second free parameter. Stretches and other distortions of the B state are also possible, but they were found to be unnecessary.

In the model of the $D'$ curve, there are two more parameters, $A$ and $B$. Both affect the curvature; $B$ was found to have the most pronounced effect on the steepness of the curve at the crossing point. Therefore, $B$ was chosen as a third free parameter. The fourth free parameter was the coupling between the two curves. The initial values for all parameters in the model are shown in Table 4.1.

<table>
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<tr>
<th>Parameter</th>
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<th>Varied?</th>
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<tr>
<td>$B$</td>
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</tr>
<tr>
<td>Coupling</td>
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</tr>
</tbody>
</table>

Table 4.1: Initial values for model parameters. The B potential curve is the RKR curve described in 4.3.1.

To create a “map” of the parameter space near these initial values, each parameter was individually varied along a range of values, while keeping the other three constant at their initial values. The results of these parameter sweeps are shown in Figure 4.6. These plots show the residuals, that is, the difference between the model value and the target data, as each parameter is varied. The red lines represent residuals in the position of the $J=0$ levels of the three vibrational levels $v=0$, 1, and 2. The blue lines represent residuals in the spacing between them.

As seen in the plots, for almost all configurations of parameters within the sampled space, the spacings between the three levels are too large. This indicates that the initial model does not provide enough interaction. More interaction would “push down” the vibrational levels as described in Section 2.4.2 by “widening” the combined-state potential well. This effect is most pronounced in the levels closer to the crossing point, so the
Figure 4.6: Residuals (experimental value − model value, as in Equation 2.34) for the position of the $J=0$ levels of the first three vibrational levels (red), as well as the spacing between them (blue). The black line marks zero: wherever a line crosses zero, the model perfectly reproduces that data point. The “bump” in graph (b) seems to be an artifact of the width-calculation routine and has no significance.
energy of \( v=2 \) would be decreased more than \( v=1 \), and \( v=0 \) would be the least affected. Therefore, the \( v=2 \) to \( v=1 \) spacing would be decreased more than the \( v=1 \) to \( v=0 \) spacing. The need for more interaction is also indicated in the graphs by the fact that increasing the coupling constant, or moving the D' curve to the left (decreasing \( C_x \)), brings the error in the spacings closer to zero. In fact, there is a point in the coupling graph (Figure 4.6a) where the spacing curves cross near zero. This is extremely important, because it means that for these two initial curves, there is a coupling for which the vibrational levels are almost ideally spaced relative to one another. In contrast, in the \( C_x \) plot (Figure 4.6b), the spacing curves cross below zero. This indicates that although the error in spacing decreases with decreasing \( C_x \), there is no point at which both errors are simultaneously close to zero.

However, adjusting the coupling to 4378 cm\(^{-1}\), which is the value at which the residuals in both spacings are almost zero, would result in an error in the absolute value of the vibrational level positions (red lines) in the hundreds. Fortunately, there is a parameter which reliably controls the absolute shift in the vibrational levels: the \( y \)-shift parameter of the B curve. As shown in Figure 4.6d, the model’s response to varying the \( y \)-shift is nearly linear; the small deviation from linearity is attributed to the fact that moving the B curve up and down does slightly vary the position of the crossing. However, over the course of a 390 cm\(^{-1}\) sweep, the absolute position of the levels changed by 388.5 cm\(^{-1}\), while the spacing changed by only 1.7 cm\(^{-1}\). Therefore, the \( y \)-shift parameter can be used to adjust the absolute position of the levels by large amounts without significantly affecting their relative positions.

From these two pieces of information—the “ideal” coupling which reproduces the spacing between the levels, and the nearly linear response of the model to the \( y \)-shift—we can find the neighborhood of a good fit. Setting the coupling to 4378 cm\(^{-1}\) (where the residuals in the spacings are nearly zero\(^1\)) and the \( y \)-shift to 314 cm\(^{-1}\) (the error in the absolute position when the coupling is 4378 cm\(^{-1}\)), the model reproduces the position of

\(^1\)This coupling seems surprisingly high compared to Tchang-Brillet’s value of 2900 cm\(^{-1}\). However, other sources do suggest much higher values, for example, the ab initio calculations of Vazquez [28] give the coupling a value of 3481 cm\(^{-1}\).
the lines within ~60 cm\(^{-1}\). Optimizing those two parameters, while leaving the D’ state in its intuitively constructed, somewhat arbitrary form, produced a model with residuals of less than 1.5 cm\(^{-1}\) for all six target values: a level of accuracy comparable to that of Tchang-Brillet (Table 4.2).

<table>
<thead>
<tr>
<th>v</th>
<th>J</th>
<th>Line position residual (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.9 1.13</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0.1 0.78</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>6.7 0.77</td>
</tr>
</tbody>
</table>

Table 4.2: Residuals in the \(J=0\) line positions of the \(v=0\), 1, and 2 levels in the Tchang-Brillet model and the initial model, optimized in coupling and \(y\)-shift, described above.

While the choice of the function for the D’ curve is arbitrary, an extremely good fit was achieved by varying the two parameters from which the shape of the D’ state is independent, although the shape of the D’ state was the biggest approximation made in the model. The success of this approach raised the question, is there such an “ideal” coupling for any exponential D’ state? If so, the model is underconstrained and cannot have much practical application. The validity of the model was tested by varying the \(B\) and \(C_x\) parameters and rerunning the coupling sweep. In every other tested case, there was no value for the coupling for which the residuals in both spacings are almost zero, i.e. these forms of the D’ curve could not yield a good fit by changing the coupling.

Therefore, the success of the model did undoubtedly depend on the choice of the D’ curve.

### 4.4 The “Best-Fit” Model

From the starting point described above, after optimizing the coupling and \(y\)-shift parameters, all four free parameters were allowed to optimize, fitting to the original six target points for the \(^{12}\text{C}^{16}\text{O}\) isotopologue. The resulting model parameters are given in Table 4.4. The offset from the target values (residuals) for these six points are shown in the upper half
of Table 4.3, the residuals in position are all \( \leq 0.65 \text{ cm}^{-1} \). This model was then used for a second isotopologue, \(^{13}\text{C}^{16}\text{O}\), without changing any parameters, and the residuals were still below 2 \( \text{ cm}^{-1} \), as shown in the lower half of Table 4.3. This is a positive indicator of the model’s predictive ability and flexibility. Since the data are available, the model can be made better by optimizing also to the \(^{13}\text{C}^{16}\text{O}\) data.

<table>
<thead>
<tr>
<th>Isotopologue</th>
<th>( v )</th>
<th>( J )</th>
<th>( \Gamma ) (cm(^{-1}))</th>
<th>Residual (cm(^{-1}))</th>
<th>( \Gamma ) (cm(^{-1}))</th>
<th>Residual (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{12}\text{C}^{16}\text{O})</td>
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<td>0</td>
<td>86915.69</td>
<td>0.65</td>
<td>0.812</td>
<td>0.008</td>
</tr>
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<td></td>
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<td>0</td>
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<td></td>
</tr>
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<td>88998.42</td>
<td>-0.18</td>
<td>89210.18</td>
<td>-0.63</td>
</tr>
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<td></td>
<td>10</td>
<td>0</td>
<td>90987.57</td>
<td>0.58</td>
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<td>-0.26</td>
</tr>
<tr>
<td></td>
<td>2</td>
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<td>91194.84</td>
<td>0.58</td>
<td>0.812</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
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<td>90904.91</td>
<td>1.58</td>
<td>91103.41</td>
<td>0.48</td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
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<td>89156.55</td>
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</tr>
<tr>
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<td>0</td>
<td>90904.91</td>
<td>1.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0</td>
<td>91103.41</td>
<td>0.48</td>
<td>0.812</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0</td>
<td>91103.41</td>
<td>0.48</td>
<td>0.812</td>
<td>0.008</td>
</tr>
</tbody>
</table>

Table 4.3: Generated term values and widths for the best-fit model optimized to \(^{12}\text{C}^{16}\text{O}\) data, with residuals for each value.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( B )</td>
<td>12.1453</td>
</tr>
<tr>
<td>( C_x )</td>
<td>1.2999 A</td>
</tr>
<tr>
<td>( y )-shift</td>
<td>372 cm(^{-1})</td>
</tr>
<tr>
<td>Coupling</td>
<td>4272 cm(^{-1})</td>
</tr>
</tbody>
</table>

Table 4.4: Final parameters for the best-fit model of \(^{12}\text{C}^{16}\text{O}\).

### 4.4.1 Extension to \(^{13}\text{C}^{16}\text{O}\)

The model was then allowed to optimize to twice as many targets, by adding the \( J=0 \) and \( J=10 \) levels of the \( v=0, 1, \) and 2 levels of \(^{13}\text{C}^{16}\text{O}\) to the targets. The optimization was able to reduce the residuals for a better fit to \(^{13}\text{C}^{16}\text{O}\), with a small sacrifice in accuracy to the \(^{12}\text{C}^{16}\text{O}\) data, as seen in Table 4.5. Interestingly, the \( v=2, J=0 \) level of \(^{13}\text{C}^{16}\text{O}\), which the \(^{12}\text{C}^{16}\text{O}\)-optimized model was farthest from reproducing, still has a much larger residual than any of the other levels.


<table>
<thead>
<tr>
<th>Isotopologue</th>
<th>v</th>
<th>J</th>
<th>(T) (cm(^{-1}))</th>
<th>Residual (cm(^{-1}))</th>
<th>(\Gamma) (cm(^{-1}))</th>
<th>Residual (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
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<td>0</td>
<td>86915.95</td>
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<tr>
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<tr>
<td></td>
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<td>0</td>
<td>90988.13</td>
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<tr>
<td></td>
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<td></td>
</tr>
<tr>
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<td>91195.47</td>
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<td>0.981</td>
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<tr>
<td>(^{13}\text{C}^{16}\text{O})</td>
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<td>91103.93</td>
<td>-0.04</td>
<td>0.698</td>
<td>0.143</td>
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</table>

Table 4.5: Generated term values and widths for the best-fit model optimized to \(^{12}\text{C}^{16}\text{O}\) and \(^{13}\text{C}^{16}\text{O}\) data, with residuals for each value.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D') curve</td>
<td></td>
</tr>
<tr>
<td>(B)</td>
<td>11.6171</td>
</tr>
<tr>
<td>(C_x)</td>
<td>1.3061 A</td>
</tr>
<tr>
<td>B curve</td>
<td></td>
</tr>
<tr>
<td>(y)-shift</td>
<td>336 cm(^{-1})</td>
</tr>
<tr>
<td>Coupling</td>
<td>4272 cm(^{-1})</td>
</tr>
</tbody>
</table>

Table 4.6: Final parameters for the best-fit model of \(^{12}\text{C}^{16}\text{O}\) and \(^{13}\text{C}^{16}\text{O}\).

Although this model reproduces line positions very well (within \(\sim 1\) cm\(^{-1}\)), it performs less accurately with linewidths. Only the \(v=2\) levels have appreciable linewidths in experiment, so four data points were used for width. In each isotopologue, the \(J=0\) linewidth is too large, while the \(J=10\) is too small. This is a sign that the optimization routine was unable to find a good fit, and settled in the middle since “the minimisation ... will tend to evenly distribute the residual error” (Section 6.2). A similar effect is seen in the pattern of residuals for the line positions: every \(J=0\) level is too low and every \(J=10\) level is too high. These results are examined in more detail in the next section.

Parameters for this two-isotopologue-optimized model are found in Table 4.6. Interestingly, the parameters vary somewhat significantly from those of the \(^{12}\text{C}^{16}\text{O}\)-optimized model. This is a sign that there is considerable “wiggle room” in the parameters; that is, the effects of each parameter are not independent of one another and they can change to compensate for one another’s effects. Because “good” model formulations are not necessar-
ily unique (see Section 2.5.1), the goal is to find a formulation that reproduces experimental data and has some predictive ability.

Figure 4.7: Comparison of potential curves for best-fit model (red) and Tchang-Brillet model (black); the dissociation limit is shown by the dashed line. There are major differences in almost every part of the potential curves; notably the vertical position of the crossing point differs by 1469 cm\(^{-1}\) and the bottom of the B state well differs by 335 cm\(^{-1}\).

4.4.2 Rotational Dependence of Linewidths

The major improvement that was hoped for in the new model was to reproduce the \(J\)-dependence of the linewidths. The new model, although it is significantly different from the Tchang-Brillet model in both potential curves (Figure 4.7)\(^2\) and coupling, produces a strikingly similar trend in calculated widths. A comparison between the Tchang-Brillet model, this model, and experimental data is shown in Figure 4.8. The new model shows widths that increase at roughly the same rate as the Tchang-Brillet model, but with a vertical shift due to the fact that the new model was fitted to the new data, which have larger average linewidths than the data Tchang-Brillet fitted to \([29]\).

\(^2\)This reproduction of the Tchang-Brillet model, from values given in the paper, has an offset of 165 cm\(^{-1}\) from the reported results, but even a shift of this magnitude does not cancel out the large differences between the new model and Tchang-Brillet. A discussion of the shift can be found in Lucy Archer’s thesis \([11]\).
Table 4.7: Target values for model fit. Term values $T$ from [24]; widths from unpublished data [29].

However, since models are not necessarily unique, it was necessary to check whether any combination of parameters might produce widths that increase more quickly with $J$. To achieve this, a rough four-dimensional walk through the parameter space was used. A “walk” in parameter space involves the same kind of parameter sweeps used in Section 4.3.3, but repeated to cover an entire section of parameter space. The sweeps are done in a nested fashion, so that the model is run for every combination of parameters within the boundaries of the walk. The boundaries of the area sampled were 3500-4500 cm$^{-1}$ for coupling, 200-500 cm$^{-1}$ for the $y$-shift, 1.23-1.36 Å for $C_x$, and 10-15 for $B$. The quality of fit to the linewidths was determined by the sum of the absolute value of the residuals for the $^{12}$C$^{16}$O $v=2$, $J=0$ and $v=2$, $J=10$ data points. Among all the 7800 parameter combinations sampled, no combination gave a combined residual of less than 0.8 cm$^{-1}$; additionally, for combinations with the smallest residuals, the linewidth for $J=0$ is too large and $J=10$ too small. That is, there was never a large enough difference between the linewidths of the two rotational levels to match the experimental data.
4.5 Next Steps

The fact that two very different models of the B-D′ interaction, the Tchang-Brillet model and the model in this work, produce such similar trends in linewidth vs. \( J \), as well as the fact that none of the tested combinations of parameters produces any significantly steeper \( J \)-dependence, indicates that a simple two-state model with a purely repulsive D′ state cannot explain the steep increase in widths. It is known that the D′ state actually has a much more complicated shape, so the \( J \)-dependent effect could potentially be due to the D′ state and the error is in the approximation of D′ as a purely repulsive potential.

4.5.1 The D′ Potential Barrier

Tchang-Brillet assumed that the presence of the potential barrier at 1.98 Å did not affect widths above the top of the barrier. To test this assumption, a Gaussian function of height 1048 cm\(^{-1}\) was added to the outer limb of the D′ state, as seen in Figure 4.9. No other parameters were altered from the best-fit model. When this model was used, the \( v=2, J=0 \) level of \( ^{12}\text{C}\text{^{16}O} \), as well as both \( v=2 \) levels of \( ^{13}\text{C}\text{^{16}O} \), were broadened (Table 4.8) relative to the best-fit model. That is, the lower-lying levels were affected by the presence of the
barrier. This is a discouraging result—we need to explain a broadening in the higher levels, and the presence of the barrier produces the opposite effect. More testing is necessary to determine whether the presence of the potential well also affects the linewidths.

Figure 4.9: The $D'$ polynomial-exponential potential curve, with an added Gaussian barrier at 1.98 Å with a height of 1048 cm$^{-1}$, as suggested by Tchang-Brillet.

<table>
<thead>
<tr>
<th>Isotopologue</th>
<th>$v$</th>
<th>$J$</th>
<th>Linewidth (cm$^{-1}$)</th>
<th>Best-fit model</th>
<th>$D'$ barrier model</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{12}$C$^{16}$O</td>
<td>2</td>
<td>0</td>
<td>0.998</td>
<td>1.300</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>1.220</td>
<td>1.220</td>
<td></td>
</tr>
<tr>
<td>$^{13}$C$^{16}$O</td>
<td>2</td>
<td>0</td>
<td>0.571</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
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<td>0.801</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.8: Calculated linewidths from $D'$ barrier model, compared to the best-fit model. The barrier affected the widths of lower-lying lines.

4.5.2 Other Interactions?

Unless the exact shape of the $D'$ state is responsible for the rotational dependence of the predissociation, other interactions will need to be explored to explain this effect. One candidate is a heterogeneous perturbation. The B and $D'$ states are both $^1\Sigma^+$ states, so in the diabatic basis interactions between them are homogeneous electrostatic interactions. Homogeneous interactions, since they arise from the electronic Hamiltonian and do not
depend on rotations, have the same coupling term for all values of $J$. On the other hand, interactions arising from the rotational part of the Hamiltonian can be heterogeneous, and increase as a function of $J$. Heterogeneous interactions occur between two states that differ in the quantum number $\Omega$, the total angular momentum along the internuclear axis. One candidate for such an interaction is the $A^1\Pi$ state, which lies below the $B$ state. This state has been identified as a candidate for causing predissociation in a higher-energy state, the $E^1\Pi$ state \[30\], and may also affect the $B$ state.

### 4.6 Conclusions

A new two-state model for the $B-D'$ interaction in CO was constructed that reproduces line positions in the $v=0$, 1, and 2 levels of the $B$ state of $^{12}\text{C}^{16}\text{O}$ and $^{13}\text{C}^{16}\text{O}$ to within 1.2 cm$^{-1}$, an improvement over the published model of Tchang-Brillet et al. \[10\], and comparably reproduces line width trends. The validity of the model and the choice of functional form for the $D'$ state was verified by varying the form of the $D'$ state; the model also reproduces the experimentally observed dissociation limit.

Several conclusions can be drawn from the new $B-D'$ model. Most importantly, it shows that although the line positions observed in the $B$ state can be explained by interaction with a simplified $D'$ state, the observed widths cannot. In addition, future models must take into account the shape of the $D'$ state beyond $R=1.3$ Å to make meaningful predictions about the $B$ state linewidths, even for states above the $D'$ potential barrier. A purely repulsive $D'$ state cannot explain the swift $J$-dependent broadening of the $B(v=2)$ lines, and future models should consider other states that might cause this effect.


