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Theoretical treatment of predissociation of the CO (3sσ) B and (3pσ) $C^1\Sigma^+$ Rydberg states based on a rigorous adiabatic representation*

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Abstract. Ab initio multireference configuration interaction calculations for adiabatic potential curves, nonadiabatic couplings $\langle\phi_i(R,r)|\mathrm{d}/\mathrm{d}R|\phi_j(R,r)\rangle$ and $\langle\phi_i(R,r)|\mathrm{d}^2/\mathrm{d}R^2|\phi_j(R,r)\rangle$, and nuclear kinetic energy corrections $\langle \mathrm{d}\phi_i(R,r)/\mathrm{d}R|\mathrm{d}\phi_i(R,r)/\mathrm{d}R\rangle$ for the $(3s\sigma)$ B and $(3p\sigma)$ $C^1\Sigma^+$ Rydberg states of the CO molecule have been carried out. The energy positions and predissociation linewidths for the observed vibrational levels of these two states have been determined in a rigorous adiabatic representation by the complex scaling method employing a basis of complex scaled harmonic vibrational functions in conjunction with the Gauss-Hermite quadrature method to evaluate the complex Hamiltonian matrix elements. The present treatment correctly reproduces the observed trends in energies and line broadening for vibrational levels of the $B^1\Sigma^+$ state and represents an improvement over the previous treatment in literature. The errors in the determined spacings of the $v = 0$–4 vibrational levels of the $C^1\Sigma^+$ state are less than 2% compared with measured data. The predissociation linewidths for the $v = 3, 4$ levels of the $C^1\Sigma^+$ state are found to be 4.9 and 8.9 cm^{-1}, respectively, in good agreement with the observed values.

Key words: Carbon monoxide – Predissociation – Rydberg states – Nonadiabatic coupling

1 Introduction

Carbon monoxide is the most abundant molecule after H_2 in interstellar clouds and circumstellar envelopes. In these media the abundance ratio of H_2/CO is determined largely on the basis of photodissociation processes of the CO molecule induced by stellar radiation. The photodissociation takes place predominantly through Rydberg states, which lie in an energy range higher than the CO dissociation limit [1–5].

Numerous spectroscopic studies of the CO molecule have been reported over a period of many years [6]. In recent times a large number of investigations have been devoted to understanding the nature of the CO Rydberg states [4, 5, 7, 8]. Because of their predissociation the $(3s\sigma)$ B and $(3p\sigma)$ $C^1\Sigma^+$ states have attracted special attention [4, 5, 7–20]. Lee and Guest [9] measured photoabsorption cross sections for the $(0 - 0)$ transition of the $B^1\Sigma^+$- and $C^1\Sigma^+$-$X^1\Sigma^+$ band systems. Klopotek and Vidal [10] observed predissociation of $v = 1$ rotational levels of the $B^1\Sigma^+$ state, while Amiot et al. [11] studied rotational predissociation of the $v = 0, 1$ vibrational levels of both the B and $C^1\Sigma^+$ states. Letzelter et al. [4] measured cross sections for photoabsorption and photodissociation of various other Rydberg states ($n = 3$–5) of the CO molecule, whereby the integrated photodissociation cross section above 91.2 nm was found to be notably larger than previously thought. Eidelsberg et al. [12] investigated the $B^1\Sigma^+$-$X^1\Sigma^+$ band system in both absorption and emission spectra. Molecular parameters for the $v = 0$–2 levels of the $B^1\Sigma^+$ state have been derived and predissociation of the $v = 2$ level has been observed. A model of a B-$D'^1\Sigma^+$ Rydberg-valence interaction has been proposed by these authors to explain the observed predissociation of the B and $C^1\Sigma^+$ states [12, 13]. Baker [14] reanalyzed the observed local perturbation in the $v = 2$ level of $B^1\Sigma^+$ and identified the perturbing state to be the $k^3\Pi$. Viala et al. [5], Eidelsberg et al. [7], and Ubachs et al. [8] have reported extensive spectroscopic data for absorption and photodissociation of various Rydberg states ($n = 3$–6) of the CO molecule and its isotopic species. Very recently, Baker et al. [15] have also observed the $v = 3$ level of the $B^1\Sigma^+$ state and found it to have a very broad appearance.

On the theoretical side, O'Neil and Schaefer [21] have reported ab initio calculations for 72 states of the CO molecule which dissociate to various states of the neutral carbon and oxygen atoms. Cooper and Langhoff [22], Cooper and Kirby [23], and Chantranupong et al. [24] have also carried out calculations for the $^1\Sigma^+$ and $^1\Pi$ Rydberg states ($n = 3$) of the CO molecule. The com-

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* Dedicated to Prof. Dr. Wilfried Meyer on the occasion of his 60th birthday

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puted spectroscopic constants and oscillator strengths for the vibrational levels considered are found to be in good agreement with observed data. Cooper and Kirby [23] found that the potential curve of the second $^1\Sigma^+$ state has a double minimum, whereby the outer well corresponds to the $\mathrm{D}'\,^1\Sigma^+$ state observed by Wolk and Rich [13]. The observed predissociation of the $\mathrm{B}^1\Sigma^+$ state was also addressed by these authors [23]. The linewidth of the $v = 2$ level was calculated to be $4 \times 10^{-5}\,\mathrm{cm}^{-1}$, however, far less than the observed value of $0.5\,\mathrm{cm}^{-1}$ [25]. Tchang-Brillet et al. [25] have carried out calculations employing the close-coupling approach based on empirically adjustable potentials which model the B-$\mathrm{D}'\,^1\Sigma^+$ Rydberg-valence interaction. Their results reproduce fairly well the observed spacing and linewidths for $v = 0$–2 vibrational levels of the $\mathrm{B}^1\Sigma^+$ state.

As contrasted with the many experimental studies mentioned above, up to the present there has been no theoretical treatment of the observed predissociation of the $\mathrm{C}^1\Sigma^+$ state, however. In the present work we present ab initio calculations based on adiabatic potential curves and nonadiabatic couplings as well as nuclear kinetic energy corrections for the B and $\mathrm{C}^1\Sigma^+$ states. These data are obtained with highly correlated multireference configuration interaction (MRD-CI) wavefunctions [26–31] and are subsequently employed to determine the energies and linewidths of the rovibrational levels of the B and $\mathrm{C}^1\Sigma^+$ states by using a recently developed procedure for applying the complex scaling technique [32]. A brief description of the method for solving the corresponding coupled equations is given in Sect. 2 along with computational details of the ab initio and CI calculations themselves. In Sect. 3 a discussion of the calculated results is presented, and concluding remarks are given in Sect. 4.

2 Theoretical formulation and computational details

The nonadiabatic wavefunctions $\Phi(R,r)$ can be expanded in terms of products of appropriate basis functions $\phi_i(R,r)$ and $f_i(R)$ which describe the electronic and nuclear motions, respectively:

$$\Phi(R,r) = \sum_i f_i(R)\phi_i(R,r) = \mathbf{f}(R) \cdot \phi(R,r) \tag{1}$$

The vector $\mathbf{f}(R)$ satisfies the coupled equations [33]

$$\begin{aligned}\big\{&-(2\mu)^{-1}[(\mathrm{d}^2/\mathrm{d}R^2 - J(J+1)/R^2)\mathbf{I} + 2\mathbf{A}(R)\mathrm{d}/\mathrm{d}R \\ &+ \mathbf{B}(R)] + \mathbf{U}(R) - E\mathbf{I}\big\}\mathbf{f}(R) = 0\end{aligned} \tag{2}$$

where $\mathbf{I}$ is the unit matrix, μ is the reduced mass, and J is the rotational quantum number of the diatomic molecule, and

$$\begin{aligned}U_{ij}(R) &= \langle\phi_i(R,r)|H_{\mathrm{el}}(R,r)|\phi_j(R,r)\rangle \\ A_{ij}(R) &= \langle\phi_i(R,r)|\mathrm{d}/\mathrm{d}R|\phi_j(R,r)\rangle \\ B_{ij}(R) &= \langle\phi_i(R,r)|\mathrm{d}^2/\mathrm{d}R^2|\phi_j(R,r)\rangle\end{aligned} \tag{3}$$

where $H_{\mathrm{el}}(R,r)$ is the electronic Hamiltonian. If the $\phi_i(R,r)$ are eigenvectors of the electronic Hamiltonian $H_{\mathrm{el}}(R,r)$, then $U_{ij}(R) = 0$ for $i \neq j$, which is referred to as the adiabatic representation, while by definition in the diabatic representation [33] $A_{ij}(R) = 0$, but $U_{ij}(R) \neq 0$.

Since it is not convenient computationally to solve the coupled equations based on the adiabatic representation, rigorous [34] or approximate [35–37] procedures for transforming from the adiabatic to the diabatic representation have been developed. In treating a molecular predissociation process arising from the avoided crossing of two potential curves the conventional procedure employed in the complex scaling method involves an analytical fit of the potential curves and generally works very efficiently in the diabatic representation [35–37]. It often fails, however, when the adiabatic representation is adopted because the corresponding potential curves are very difficult to fit to an analytic function. Recently a new numerical procedure has been implemented in our laboratory for the complex scaling method which employs a basis of complex scaled harmonic vibrational functions in conjunction with use of the Gauss-Hermite quadrature method to evaluate the complex Hamiltonian matrix elements [32]. In dealing with molecular predissociation, this new procedure allows one to start directly from the adiabatic potential curves and nonadiabatic couplings which are provided pointwise by ab initio calculations, thus avoiding the diabatization and fit steps. Test calculations for model potentials have demonstrated that the energy positions and linewidths of resonances determined by using the new procedure in the diabatic and adiabatic representations are equal to each other to a high degree of accuracy [32]. The present study reports the first practical application of this numerical complex scaling procedure to the treatment of the multistate problem of molecular predissociation based on a rigorous adiabatic representation.

The first derivative terms $A_{ij}(R)$ can be calculated analytically by computing the operator's expectation values over the adiabatic electronic wavefunctions [38], but in the present study they are evaluated by the numerical differentiation method [39]. It has been demonstrated elsewhere [40] that there is essentially no difference between the calculated results obtained by using either analytic or numerical methods. The second-derivative terms $B_{ij}(R)$ are obtained by computing the integrals

$$M_{ij}(R) = \langle\mathrm{d}\phi_i(R,r)/\mathrm{d}R|\mathrm{d}\phi_j(R,r)/\mathrm{d}R\rangle \tag{4}$$

and utilizing the relationship

$$B_{ij}(R) = \mathrm{d}A_{ij}(R)/\mathrm{d}R \; - M_{ij}(R) \tag{5}$$

The nuclear kinetic energy corrections $M_{ii}(R) = \langle\mathrm{d}\phi_i(R,r)/\mathrm{d}R|\mathrm{d}\phi_i(R,r)/\mathrm{d}R\rangle$, which play no direct role in predissociation but can result in a relative shift of the adiabatic potential curves, are also evaluated in the present study. It should be noted that the first derivative terms $A_{ij}(R)$ are anti-Hermitian, while the second-derivative terms $B_{ij}(R)$ are non-Hermitian, but that the global Hamiltonian matrix resulting from integrations over both electronic and vibrational wavefunctions is nonetheless Hermitian.

The ab initio configuration interaction calculations of the potential curves and wavefunctions for the $(3s\sigma)$ B and $(3p\sigma)$ $\mathrm{C}^1\Sigma^+$ Rydberg states of CO are carried out with the aid of an effective core potential (ECP). The ECP of Pacios and Christiansen [41] is employed to describe the carbon and oxygen atoms, whereby only 2*s* and 2*p* electrons need to be considered explicitly in the SCF and CI calculations. Their (4*s*4*p*) basis set is employed without contraction, augmented by two sets of *d*-type polarization functions and two *s*- and one set of *p*-type Rydberg functions. The exponents of polarization functions are determined by energy minimization and those of the Rydberg functions are taken from Dunning [42].

It was observed that the MOs resulting from SCF calculations of the $X^1\Sigma^+$ ground state are suitable for configuration interaction calculations of valence and Rydberg excited states in the bonding region, but that they fail to describe the proper dissociation limits at large R. Thus MOs from SCF calculations for the $^5\Sigma^-$ excited state of CO are taken to form the one-electron basis for the MRD-CI treatment [26–31] of the B and $C^1\Sigma^+$ states. The number of reference configurations employed is 134. Configuration selection [26] is done for the lowest four roots, including three $^1\Sigma^+$ and one $^1\Delta$ states, which are in the same representation in the D_{2h} subgroup. Employing a selection threshold of 0.13 μE_h leads to secular equations of order 200 000 on the average. The construction of the Hamiltonian matrix is made with the aid of the Table CI algorithm [29, 30] and a Direct CI procedure [31] is employed to compute the desired eigenvalues and eigenvectors.

The energy positions and linewidths of the vibrational levels of the B and $C^1\Sigma^+$ states are determined by employing the complex scaling method [32] based on the computed adiabatic potential curves and nonadiabatic couplings. For this purpose a basis of 120 complex scaled harmonic vibrational functions is employed and the Gauss-Hermite quadrature technique is applied with 200 integration points to evaluate the complex Hamiltonian matrix elements. A series of rotation angles in the range of 3°–8° is considered in order to search for the desired stabilized complex eigenvalues of the resonance solutions.

3 Discussion of results

The calculated adiabatic potential curves for the second and third $^1\Sigma^+$ states of the CO molecule are shown in Fig. 1 together with the corresponding schematic diabatic curves. The various computed nonadiabatic couplings as well as the nuclear kinetic energy corrections are presented in Fig. 2. As can be seen in Fig. 1, near the avoided crossing point, which is located at an internuclear distance of about $2.43a_0$, the second adiabatic $^1\Sigma^+$ state is composed of ($3s\sigma$) Rydberg B and valence $D'\,^1\Sigma^+$ character; the MO configuration of the latter is $\pi^3\pi^*$. The $C^1\Sigma^+$ state arises from mixing of ($3s\sigma$), ($3p\sigma$) Rydberg and D′ valence $^1\Sigma^+$ character. The $C'\,^1\Sigma^+$ state, which is not important in the present study, arises from the MO configuration $\pi^2\pi^{*2}$. From the adiabatic point of view it is clear that the predissociation of the $B^1\Sigma^+$ state occurs mainly via tunneling through the energy barrier centered at the avoided crossing point, whereas the $C^1\Sigma^+$ state is predissociated because of an interaction with the $D'\,^1\Sigma^+$ valence state, i.e. a nonadiabatic effect.

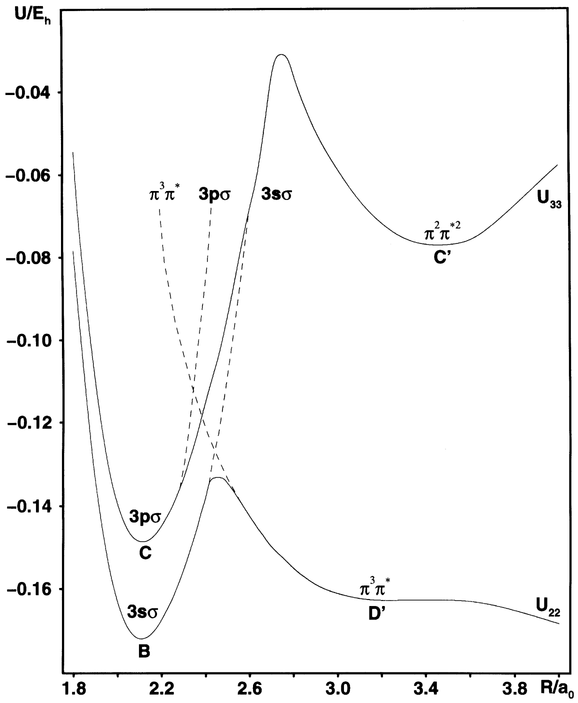

Fig. 1. Calculated adiabatic potential curves U_{22} and U_{33} for the second and third $^1\Sigma^+$ states of the CO molecule. The estimated diabatic curves are indicated by *dashed lines*

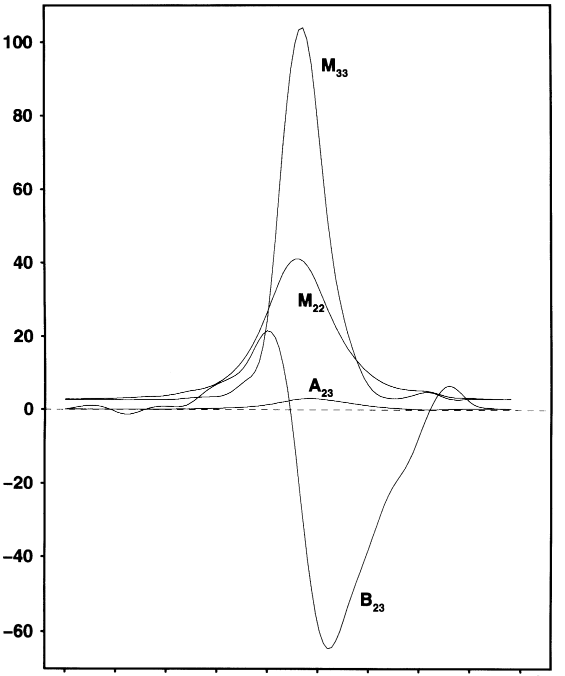

Fig. 2. Calculated nonadiabatic couplings A_{23} (in a_0^{-1}) and B_{23} (in a_0^{-2}) between the second and third $^1\Sigma^+$ states of the CO molecule as functions of the bond distance R together with the nuclear kinetic energy correction terms M_{22} and M_{33} (in a_0^{-2})

Table 1. Comparison between calculated and measured vibrational energy spacings ΔG_v, predissociation linewidths Γ_v, and lifetimes τ_v for the B and $C^1\Sigma^+$ states of the CO molecule

State	v	ΔG_v (cm^{-1})		Γ_v (cm^{-1})			τ_v (s)	
		This work	Exptl.	This work[a]	Calc.	Exptl.	This work[b]	Exptl.
$B^1\Sigma^+$								
	0			0				2×10^{-8} [g]
		2128	2082[c]					
	1			0				3×10^{-8} [g]
		2081	1990[c]					
	2			0.1	4×10^{-5} [e]	> 0.5[f]		
		2045	~1900[d]					
	3			23	5×10^{-1} [e]	very diffuse[d]		
$C^1\Sigma^+$								
	0			$< 10^{-4}$			5×10^{-8}	10^{-9} [c], 5×10^{-10} [g]
		2100	2146[c]					
	1			0.05			10^{-10}	10^{-9} [c]
		2086	2111[c]					
	2			1.1			5×10^{-12}	10^{-10} [c], 10^{-11} [h]
		2104	2068[c]					
	3			4.9		~2.3[f]		
		2105	2147[c]					
	4			8.9		< 5[f]		

[a] For comparison with the experimental data the calculated linewidth values are given for the rotational quantum number $J = 15$
[b] $\tau(\mathrm{s}) = 2.419 \times 10^{-17} \times [\Gamma(E_\mathrm{h})]^{-1}$
[c] [7] [d] [15] [e] [23] [f] [25] [g] [8] [h] [5]

It is interesting to compare the behavior of the nonadiabatic couplings and the nuclear kinetic energy corrections shown in Fig. 2. Both energy correction terms $M_{22}(R)$ and $M_{33}(R)$ have maxima at the avoided crossing point and become constant far beyond the crossing point, but the coupling terms decrease quickly to zero at some distance not far from the crossing point. The first-derivative term $A_{23}(R)$ has a symmetric appearance, but the second derivative is more asymmetric. In addition, the peak of the absolute value of the $B_{23}(R)$ term is much larger than that of $A_{23}(R)$. As has been pointed out [32], the second-derivative term plays the dominant role in the predissociation process.

The determined energy spacing and predissociation linewidths for various vibrational levels of the B and $C^1\Sigma^+$ states of the CO molecule are given in Table 1 together with experimental values where available. Wolk and Rich [13] have observed an outer energy well in the potential curve of the second $^1\Sigma^+$ state that supports three vibrational levels. The present calculations fail to reproduce the outer energy well, and we ascribe this to a deficiency in the atomic basis employed in the present treatment. It has been found [25], however, that the outer energy barrier of the second $^1\Sigma^+$ state has no effect on the predissociation of rovibrational levels of the $B^1\Sigma^+$ state for low rotational quantum numbers (for example, for $J \leq 15$), so the deficiency in the long-range portion of the calculated potential curve of the second $^1\Sigma^+$ state is of little quantitative importance in the present study.

The T_0 (0–0) value for the $B^1\Sigma^+$-$X^1\Sigma^+$ transition is calculated to be 87 706 cm^{-1}, which represents a difference of 790 cm^{-1} from the measured value. The energy gap between the $v = 0$ levels of the B and $C^1\Sigma^+$ states, which is quite important in the present study, is found to be 5030 cm^{-1}, in quite good agreement with the measured value of 5003 cm^{-1}.

The present calculations predict that there are four vibrational levels supported by the $B^1\Sigma^+$ state, and that the $v = 3$ level has the broadest linewidth (see Table 1). This is in agreement with the observed trends for the line broadening of the vibrational levels of the $B^1\Sigma^+$ state and represents an improvement over the previous theoretical treatment in the literature [23]. However, the calculated vibrational spacings are too high by 2–5% and the linewidth determined for the $v = 2$ level is too narrow by a factor of 5. Obviously, the errors come from a deficiency in the calculated potential curve of the second $^1\Sigma^+$ state, whose energy barrier is both too high and too wide (see Fig. 1). It can be noted that the MOs that have been adopted to form the common one-electronic basis for the present CI calculations do not lead to a compact description of the second $^1\Sigma^+$ state, which suggests that a larger-scale CI treatment employing polarization functions of higher angular momenta and a smaller selection threshold is necessary to compute the potential curve of the second $^1\Sigma^+$ state with high enough accuracy to significantly reduce the above error.

The calculated results for the $C^1\Sigma^+$ state are quantitatively in good agreement with measured data (see Table 1). The errors in the determined vibrational spacings are less than 2% compared with experimental data. The observed trend in line broadening of the $v = 0$–4 levels of the $C^1\Sigma^+$ state has been reproduced correctly in the present treatment. For the $v = 3, 4$ levels, for which experimental values are available, the predissociation linewidths are found to be 4.9 and 8.9 cm^{-1}, respectively, differing from the measured values by a factor of two, and this indicates that the various calculated nonadiabatic coupling terms are reliable. For further improvement of the agreement between calculations and measurements of the line broadening for the $C^1\Sigma^+$ state, in addition to checking the convergence of the calculated nonadiabatic couplings thoroughly, uncertainties in the corresponding measured data also need to be eliminated.

4 Conclusion

Ab initio MRD-CI calculations for the potential curves of the ($3s\sigma$) B and ($3p\sigma$) $C^1\Sigma^+$ Rydberg states of the CO molecule and the nonadiabatic couplings of first- and second-derivative type as well as nuclear kinetic energy corrections for these two states have been carried out in order to investigate the observed predissociation of the two states. The energy locations and predissociation linewidths of their vibrational levels have been determined by using a recently developed numerical procedure for applying the complex scaling method in a rigorous adiabatic representation.

The present treatment correctly reproduces the observed trends in energy positions and line broadening of vibrational levels of the $B^1\Sigma^+$ state and represents an improvement over the previous theoretical treatment in the literature. The calculated results for energy spacings and predissociation linewidths of vibrational levels of the $C^1\Sigma^+$ state are in good agreement with observed data. The errors in the determined vibrational spacing of the $v = 0$–4 levels of the $C^1\Sigma^+$ state are less than 2% , whereas the linewidths of the $v = 3, 4$ levels of the $C^1\Sigma^+$ state are found to be 4.9 and 8.9 cm^{-1}, respectively, differing from the measured values by a factor of two.

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