

Use of Gauss-Hermite Quadrature to Approximate the Asymptotic Behavior of Vibronic Resonance Wave Functions

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Abstract

Wave functions obtained employing a standard complex Hamiltonian matrix diagonalization procedure are square-integrable and therefore cannot accurately describe the asymptotic character of resonance solutions of the Schrödinger equation. The nature of this approximation is investigated by means of explicit calculations which are based on diabatic RKR potentials for the $B^1\Sigma^+ - D^1\Sigma^+$ vibronic resonance states of the CO molecule. It is shown that expanding the basis of complex harmonic oscillator functions gradually improves the description of the exact

resonance wave functions out to ever larger internuclear distances on the real axis before they take on artificial bound-state characteristics due to the square-integrable character of the basis functions. In order to solve the diagonalization problems for as many as 500 such basis functions, it proves necessary to employ specialized numerical techniques such as Gauss-Hermite quadrature to evaluate the required Hamiltonian matrix elements.

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I. Introduction

Resonance wave functions differ from their bound-state counterparts in at least two essential ways: 1) they are not square-integrable and 2) they correspond to complex (non-real) eigenvalues of the Hamiltonian [1-3]. One of the most interesting applications in which such metastable states play a key role is in the field of vibrational spectroscopy. Such problems can generally be formulated in terms of the mixing of a bound vibrational state with an unbound exponential function with a complex exponent (Sievert function). In the Born-Oppenheimer approximation this situation arises in a straightforward manner when two or more diabatic potentials, at least one bound and one repulsive, undergo a crossing at some internuclear distance. One of the classic examples of this type that has been treated extensively with numerical calculations occurs for the $B^1\Sigma^+ - D'^1\Sigma^+$ vibronic resonance states of CO. Good agreement has been found for the complex energy eigenvalues of this system obtained using a variety of theoretical methods [4-6], and so there is good reason to believe that the corresponding wave functions are also obtained to high accuracy. When the latter are expanded in terms of exclusively square-integrable functions, as is the case in the complex matrix diagonalization procedure employed by Li et al. [6], it is nonetheless clear that the resulting asymptotic behavior at large CO bond distances must be seriously flawed.

It was therefore decided to carry out further calculations for the CO B-D' system to obtain a clearer picture of how accurately resonance wave functions can be represented without the benefit of non-square-integrable functions in the basis set of the theoretical treatment. One difficulty with such an undertaking is that the corresponding exact solutions with which one would like to compare the approximate functions are not known and appear to be unattainable in

the foreseeable future. The hope is that by gradually expanding the basis set in which such calculations are carried out, it might be possible to at least obtain some level of certainty about various aspects of the exact solutions without being able to actually generate them explicitly. In order to accomplish this goal to a satisfactory extent, it is necessary to go beyond the level of accuracy achieved in the original calculations of Li et al. [6], however, as will be discussed in the following section. For this purpose, a brief review of the matrix methods employed to obtain the approximate solutions will first be given.

II. Hamiltonian matrix representation

The computational procedure employed in ref. [6] is quite straightforward. It involves the use of a relatively large basis of one-dimensional complex harmonic oscillator functions $\chi_i(r)$ to form a matrix representation of the Hamiltonian for two electronic states of CO. The diabatic (RKR) potentials [7] shown in Fig. 1 have been used for this purpose. It is seen that one of the potentials (H_{11}) has a minimum at $r=2.10 a_0$ near the equilibrium bond distance of the CO ground state. The other (H_{22}) is completely repulsive and thus would have no bound states in an uncoupled treatment. The corresponding coupling term (H_{12}) is seen to have a nearly constant value of 0.013 Hartree for $r < 2.6 a_0$ before gradually decreasing until a null value is reached at $r=3.5 a_0$, continuing out to the asymptotic limit. The dimension of the resulting complex symmetric Hamiltonian matrix is $2n$, where n is the size of the harmonic oscillator basis. A vibronic solution $\Psi(R, r)$ for the associated Schrödinger equation consists of a sum of Born-Oppenheimer product functions of the form:

$$\Psi(R, r) = \psi_1(R, r) \Phi_1(r) + \psi_2(R, r) \Phi_2(r),$$

(1)

where $\psi_1 (R,r)$ and $\psi_2 (R,r)$ are the electronic wave functions associated with the H_{11} and H_{22} potentials (R for electronic coordinates and r for nuclear), respectively, and $\Phi_1 (r)$, $\Phi_2 (r)$ are the corresponding vibrational functions. The desired Hamiltonian matrix representation consists of subblocks of order $n \times n$ each, where n is the size of the harmonic oscillator basis in which the two vibrational functions are expanded as:

$$\Phi_j (r) = \sum (i) c_{ij} \chi_i (r).$$

(2)

The two diagonal subblocks employ the operator $T + H_{ii} (r)$ while the corresponding off-diagonal matrix elements use $H_{12} (r)$ without the kinetic energy $T = (2\mu)^{-1} d^2/dr^2$ because of the orthogonality of ψ_1 and ψ_2 . The dimension of the resulting complex symmetric Hamiltonian matrix is therefore $2n \times 2n$. The common exponent in the harmonic oscillator functions is of the form $\alpha e^{-i\theta}$, where θ is real and serves as a scaling parameter [8] for determining the required stationary solutions for the vibronic wave functions. More details of this computational procedure may be found in ref. [6]. The calculations are carried out formally with a complex-rotated Hamiltonian $H (re^{i\theta})$. The Hamiltonian matrix representation is independent of θ , however, because of the Cauchy-Coursat theorem [9]. As a result, the coefficient vector c_j in eq. (2) can be applied directly along the real axis to obtain the desired approximate vibronic wave functions. It is important to see that both the complex energy eigenvalues and the corresponding coefficient vectors are therefore completely independent of θ as long as both the Hamiltonian and the basis functions are rotated by the same angle in the present theoretical treatment.

As indicated in the Introduction, the goal of the present work was to employ larger

complex harmonic oscillator basis sets than in the original work [6]. It was therefore necessary to improve the accuracy by increasing the number of quadrature points in the integration procedure and also by carrying out the computations in quadruple precision. The number of Gauss-Hermite quadrature points was increased from 250 to 600 by employing 800 basis functions in the generation procedure [6] and eliminating the first and last 100 roots of the resulting polynomial. This allowed us to employ as many as 250 complex harmonic oscillator basis functions $\chi_i(r)$ in eq. (2) for each electronic state in eq. (1), i.e., the maximum dimension of the vibronic Hamiltonian matrix for which complex energy eigenvalues and eigenvector results were obtained in the present work was therefore 500x500.

III. Discussion of Results

The first calculations to be discussed have been carried out with a basis of $n = 80$ complex harmonic oscillator functions per electronic state. The real and imaginary parts of the $v=3$ vibronic function are shown together in Figs. 2a,b for $\Phi_1(r)$ and $\Phi_2(r)$, respectively [see eq. (1)], that is, for the bound and repulsive vibrational functions separately. The corresponding energy eigenvalue is $6784.09 - i 45.45 \text{ cm}^{-1}$, very nearly the same value as obtained in the original work [6] in which a basis of $n=120$ functions has been used. It is seen that at this level of approximation the real bound-state part (Fig. 2a) has the appearance expected for a $v=3$ vibrational function, with two clearly defined minima and maxima in the neighborhood of the H_{11} potential minimum (in this figure and the following, $r=0$ corresponds to the equilibrium bond distance for the bound electronic state in Fig. 1). There is only a small imaginary contribution for this function. The corresponding repulsive part (Fig. 2b) consists of real and imaginary components of very nearly equal magnitude, as one expects for a oscillatory function

of the general form: $\exp(ik_r r) = \cos(k_r r) + i \sin(k_r r)$. It is only non-zero in a fairly narrow range of bond distance, however, from roughly $r=0$ to $r = 2.2 a_0$.

The corresponding results for the treatment for $n=150$ are shown in Figs. 3a-b. There is very little change in the bound-state's vibrational function relative to that in Fig. 2a, with the possible exception of a small oscillatory feature that develops in the $r=2-3 a_0$ region. The functions (Φ_2) corresponding to the repulsive electronic state are easily distinguishable, however. The $n=150$ version (Fig. 3b) does not vanish beyond $r=2.0 a_0$ but rather begins to oscillate rapidly at that distance and to increase in amplitude from one maximum to the next. It becomes rather difficult to distinguish the real and imaginary parts in this region as well. A maximum amplitude occurs near $r = 2.4 a_0$, before the function tails off rather quickly until a constant null value is reached beyond $r= 3.2 a_0$. It should be noted that the complex energy eigenvalue is all but unaffected by this change in the wave function.

Calculations have also been carried out for $n=200$ and 250 basis functions. The $v=3$ results for the larger of these treatments are given in Figs. 4a,b. Comparison with the results of Fig. 3a shows that the bound-state's vibrational function (Φ_1) has changed in several ways as a result of the increased size of basis. Strongly oscillatory features are found to both sides of the normal vibrational function near $r=0$. The relation between the various maxima and minima in the latter portion of the wave function has also changed somewhat. The various maxima of the oscillatory feature in the $r=2.0-4.0 a_0$ region are notably larger than those found from $r=-3.0$ to $-1.0 a_0$. The largest changes occur for Φ_2 , however. The oscillatory portion of this function is much more prominent in the $n=250$ version. A clearly defined exponential envelope forms in Fig. 4b starting at $r=2.0 a_0$, and it continues rising until $r=3.0 a_0$, going briefly off-scale in the diagram. At that point the envelope starts to decrease just as quickly as it increased at smaller bond distances, reaching a constant null value near $r=4.0 a_0$. Similar behavior is observed

in the $n=200$ calculations to be discussed subsequently, although the absolute maximum in the corresponding function is not as pronounced as for the larger basis. Both of the latter results for Φ_2 can be characterized as a Siegert-type complex exponential function [1] ($k=k_r + ik_i$):

$$\exp(ikr) = \exp(ik_r r) \exp(-k_i r), \quad (3)$$

with $k_i < 0$. The corresponding behavior for $n=150$ in Fig. 3b is less apparent but nevertheless easily recognized, whereas there is no real hint of such an exponential envelope when only 80 harmonic oscillator functions are used (Fig. 2b). Increasing the size of the basis has the effect of pushing the maximum of the envelope to a higher value as well as moving its location out to a larger CO distance. Despite the strong dependence of Φ_2 on the size of basis, however, virtually no significant change in the complex energy eigenvalue is observed as a result. There is clearly almost total compensation at large r in this regard for such protracted changes in the wave function in the exponentially increasing region. Since there is coupling between the two electronic functions χ_1 and χ_2 , some admixture of imaginary character to Φ_1 is unavoidable, but the oscillatory behavior that develops for it as n is increased seems far less important for the vibronic function as a whole.

The vibronic functions are also sensitive to the choice of the scaling parameter Θ employed to determine stationary solutions for the complex Hamiltonian diagonalizations. In each of the calculations discussed thus far the optimum value of $\Theta = 4.0$ deg has been used in the scaling of the common exponent ($\alpha e^{-i\Theta}$) in the complex harmonic oscillator basis functions $\chi_i(r)$ in eq. (2). The $v=3$ wave function is given for three different values of Θ in the $n=200$ calculations in Figs. 5a-c, where again a value of 4.0 deg has been found to be optimal. In these diagrams the sum of the two vibrational

functions ($\Phi_1 + \Phi_2$) is shown rather than giving separate plots for each. As might be expected, the bound part in the neighborhood of $r=0$ is almost completely independent of Θ . The envelope for the strongly oscillating part of the wave function changes significantly with variation of this parameter, however. For $\Theta = 3.5$ deg (Fig. 5a) this feature starts to develop near $r=2.0 a_0$, reaching a maximum value of 5.0 at $r=2.8 a_0$. The corresponding results for the $\Theta = 4.0$ deg in Fig. 5b show an earlier onset ($r=1.5 a_0$) of the exponential character with a notably greater slope, so that the maximum value is well above the 5.0 limiting value in the diagram. This trend is continued in the results for $\Theta = 4.5$ deg (Fig. 5c), with a still earlier onset location as well as a greater slope compared to the previous case. As before with the variations in basis-set size n , it is found that the complex energy eigenvalue itself does not depend significantly on the value of the scaling parameter, at least not in the narrow range relevant for the optimization. This behavior is expected because of the large basis that has been employed in these calculations.

The exponential character found for the $v=3$ wave function is mirrored in the results for the other CO B-D' vibronic resonances. Corresponding plots for $v= 0$ and 4 are shown in Figs. 6a,b, respectively, also at the $n=200$ level of treatment ($\Theta=4.0$ deg). The real part of the $v=0$ function has a single maximum around the equilibrium bond distance characteristic of a bound vibrational ground state (Fig. 6a). It nonetheless does possess an exponentially increasing envelope for a strongly oscillating feature in the $r=1.5-2.5 a_0$ range. This exponential character is clearly less developed than for $v=3$, but this is to be expected because of the considerably smaller linewidth for $v=0$ ($\Gamma < 0.01 \text{ cm}^{-1}$ as opposed to the value of 90.9 cm^{-1} for $v=3$; see Table II of ref. [6]). The corresponding feature for the $v=4$ wave function (Fig. 6b) is even more pronounced than for $v=3$

(note the larger scale used in this figure than for $v=3$ in Fig. 5b). This result is expected because of its considerably larger linewidth ($\Gamma=801.8 \text{ cm}^{-1}$). The $v=4$ bound-state character in the $r=0$ region joins on smoothly with the $\exp(ik_r r)$ sinusoidal part of the function starting near $r=0.8 a_0$. As before with $v=3$, the bond-distance region in which the exponential character appears as well as the maximum value of the wave function attained therein is found to increase sharply with the number of basis functions employed. As a result, there seems to be little room for doubt that further improvements in the basis would simply give additional support to the conclusion that this exponential behavior extends to the asymptotic limit for the corresponding exact vibronic solutions.

IV. Analysis of the asymptotic character of the computed wave functions

The coupled vibronic Schrödinger equation considered above cannot be solved exactly, but it is nonetheless relatively easy to determine the behavior of its solutions in the asymptotic limit of infinite CO bond distance. First of all, it is seen in Fig. 1 that the diabatic coupling term $H_{12}(r)$ vanishes at this limit, so it becomes possible to treat each electronic state separately. The corresponding equations are of the same simple form:

$$[-(2\mu)^{-1} d^2/dr^2 + (A_j - E)] \Phi_j = 0, \quad (4)$$

where A_j is the constant value of the corresponding potential energy for infinite CO separation. These equations have the same general solution, namely that already given in eq. (3). The corresponding energy eigenvalue is:

$$E = E_r + iE_i = (2\mu)^{-1} k^2 + A_j. \quad (5)$$

The solution of eq. (4) for the bound electronic state $\psi_1(R, r)$ must vanish at infinity, so the imaginary component of k (k_i) is either positive or zero in this case. This part of a given vibronic

solution of eq. (1) therefore makes no contribution to the expectation value of the vibronic Hamiltonian *when integration is restricted to a narrow region of (large) CO distance* near the asymptotic limit. For the exact solution, the latter expectation value is equal to the energy eigenvalue E in eq. (4) and is therefore complex, i.e., has a non-zero imaginary component. This means that the corresponding contribution from Φ_2 to this expectation value must also be complex. Since the asymptotic Hamiltonian is Hermitean, this can only occur if the solution in eq. (3) is not square-integrable, i.e., $k_1 < 0$.

The calculations for the CO B-D' vibronic resonances in the present work indicate that exponentially damped oscillations typically begin to be apparent starting at $r=2.0 a_0$ or somewhat smaller bond distance. Their representation by means of the square-integrable functions of eq. (2) simply improves as the size of the basis is systematically increased, with the exponential character continuing out to increasingly larger bond distances. In short, this behavior is consistent with the above analysis of the expected asymptotic behavior of the vibronic solutions for the diabatic potentials in Fig. 1. The indication is that the wave functions in the region of relatively small CO distance will be stable to further increases in the size of basis employed and thus to provide an accurate description of the corresponding exact solutions up to the point where the damping envelope begins to turn downward in a given level of treatment. In other words, it would appear that one can obtain a good approximation to the exact solutions at still larger r by simply extending the exponential damping of the oscillations beyond the latter point. One must only be careful thereby to ensure that the complex energy eigenvalue is not significantly affected by such an extrapolation procedure, since this quantity already appears to have reached a satisfactory degree of convergence in the present calculations.

It is interesting to compare the above results with those carried out earlier for a non-Hermitian Hamiltonian by Csóto et al. [10]. The exact solution was obtained for the complex-

rotated Hamiltonian and then approximate calculations were carried out to obtain the corresponding (back-rotated) function along the real axis. Both the real and imaginary parts of this function contain a rapidly oscillating feature over a significant range of bond distance (see their Figs. 3c-d) when harmonic oscillator basis functions are employed. There is also an exponential-type envelope for the oscillations up to the point where a maximum is reached in each case. These oscillations are not present when a Gaussian basis is used instead, however. It is important to note that the asymptotic form of their Hamiltonian {see eq. (3) of ref. [10]} is identical to that in eq. (4) for the present vibronic calculations, so the above analysis should also apply in this case. Only $n=20$ basis functions were employed in ref. [10], so that one would expect that the asymptotic behavior would be somewhat less accurately represented in this treatment than for any of the basis sets considered above for the CO vibronic calculations. The indication from the present work is that the harmonic oscillator basis results of ref. [10] are considerably more accurate than those obtained with the Gaussian basis of the same size and that the exponential damping of the oscillations in the former case would be further enhanced if larger basis sets were used.

The value of k for the Siegert function of eq. (3) can be obtained in two different ways from the matrix diagonalization procedure employed in the present work. One possibility is to fit the vibronic wave functions in the asymptotic region. The computed results in Figs. 2-4 demonstrate that such an approach is fraught with numerical difficulties, however. A rather large basis set is required, for example, before the exponential envelope is formed to a reasonable degree. If we define the difference in r for successive real and imaginary parts of the oscillating function in the asymptotic region as Δ , we can obtain an estimate for k_r as $\pi/2\Delta$ on this basis. The shape of the envelope has been found to be relatively sensitive to the basis size n , however, so that

there is a great deal of uncertainty in a given treatment as to what the optimum value of k_i is for the fitting of the real exponential factor of the Siegert function.

Fortunately, there is a simpler computational method to obtain the value of k to relatively high accuracy. This is because the complex energy value $E = E_r + iE_i$ reaches satisfactory convergence in this type of calculation when relatively small basis sets are employed. The relationship between the exact value of E and the argument k of the asymptotic Siegert function of eq. (3) has already been given in eq. (5). Solving the latter equation for the real and imaginary parts of k gives:

$$k_r = -\mu^{0.5} E_i [(F^2 + E_i^2)^{0.5} - F]^{-0.5} \quad (6)$$

$$k_i = -\mu^{0.5} [(F^2 + E_i^2)^{0.5} - F]^{0.5},$$

where $F = E_r - A_2$ and A_2 is the asymptotic energy of the repulsive state [$H_{22}(\infty)$ in Fig. 1; $E_r > A_2$]. Note that $k_i < 0$ (exponentially increasing envelope) for a resonant state and $k_r > 0$ ($E_i < 0$, exponential decay). The value of $-k_i$ increases with the amount of instability (magnitude of the imaginary component of the energy, E_i), consistent with the trends observed for the $v=0, 3$ and 4 vibronic functions in Figs. 5-6.

IV. Conclusion

The present calculations have investigated how the description of CO B-D' vibronic resonance wave functions varies with the size of the complex harmonic oscillator basis employed in the theoretical treatment. The main finding is that the asymptotic behavior of these wave functions is quite sensitive to the number of such basis functions, while the corresponding complex energy eigenvalues and the short-range part of the wave functions are not. The unbound asymptotic character of the resonances along the real axis becomes increasingly better developed as more basis functions are added. The envelope for the rapid oscillations in the intermediate

region of bond distance takes on the expected exponential character for the Siegert function of eq. (3) and simply extends out to a larger distance as the size of the basis is increased.

The computational procedure employed in these calculations is quite standard for bound-state calculations. A matrix representation of the two-state vibronic Hamiltonian is formed in a basis of square-integrable functions and the desired energy eigenvalues and approximate wave functions are obtained from diagonalization of the resulting matrix. It would therefore appear that the conventional arguments regarding the basis-set limit for bound states also apply for resonances. One assumes that the exact solutions of the corresponding Schrödinger equation can be obtained from such a matrix procedure by going to the limit of a complete set of basis functions.

The present calculations have been carried out exclusively for a Hamiltonian defined on the real axis. In order to obtain complex energy eigenvalues, it is simply necessary to employ complex harmonic oscillator basis functions whose common exponent is scaled by $\exp(-i\Theta)$. The scaling parameter Θ is then chosen so as to satisfy a stationary condition for the resonance solutions. The Cauchy-Coursat theorem ensures that the matrix representation is unchanged when the coordinates of the Hamiltonian are rotated into the complex plane as long as an equivalent rotation of the basis functions is also made. As a result, once the optimum value for the basis-function scaling parameter Θ has been determined on the real axis, there is no point in carrying out additional calculations for a rotated Hamiltonian. The same complex energy eigenvalues and corresponding coefficient vectors will be obtained independent of the angle of rotation as long as the basis functions are rotated by the same amount. The argument that such a rotation of the coordinates of the Hamiltonian converts an unbound solution into one that is bound on the real axis loses its importance under the circumstances. Indeed, whether the rotated function is bound

or not depends on whether it is evaluated along the real axis, as is normally the case in discussions of this subject, or along an axis that is also rotated into the complex plane by the same angle as the Hamiltonian. In the latter case, it is unchanged relative to the original unrotated wave function and thus remains an unbound function. The Cauchy-Coursat theorem does not distinguish between these two possibilities since it employs integration limits of $\pm \infty$ [9].

Finally, it is not necessary in practice to use such large basis sets as those of the present study to determine the asymptotic behavior of the computed resonance wave functions. The value of k in the Siegert function can be obtained to high accuracy from eq. (6) once the complex energy eigenvalue has been computed to suitably high accuracy by employing relatively modest numbers of square-integrable basis functions.

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Figure captions

Figure 1. Diabatic RKR potential curves for the $B\ ^1\Sigma^+ - D'\ ^1\Sigma^+$ states of CO employed in the complex vibronic calculations.

Figure 2. Real and imaginary components of the wave function for the $v=3$ resonance state in the

B $^1\Sigma^+$ - D' $^1\Sigma^+$ band system of the CO molecule obtained by employing a basis set of 80 complex-rotated ($\Theta= 4.0$ deg) harmonic oscillator solutions for each of the vibrational functions $\Phi_i(r)$ in eq. (1) multiplying a) the bound electronic state $\psi_1(R, r)$ and b) the repulsive electronic state $\psi_2(R, r)$. Note that $r=0$ corresponds to the equilibrium bond distance of the bound potential H_{11} in Fig. 1.

Figure 3. Real and imaginary components of the wave function for the $v=3$ resonance state in the B $^1\Sigma^+$ - D' $^1\Sigma^+$ band system of the CO molecule obtained by employing a basis set of 150 complex-rotated ($\Theta= 4.0$ deg) harmonic oscillator solutions for each of the vibrational functions $\Phi_i(r)$ in eq. (1) multiplying a) the bound electronic state $\psi_1(R, r)$ and b) the repulsive electronic state $\psi_2(R, r)$. Note that $r=0$ corresponds to the equilibrium bond distance of the bound potential H_{11} in Fig. 1.

Figure 4. Real and imaginary components of the wave function for the $v=3$ resonance state in the B $^1\Sigma^+$ - D' $^1\Sigma^+$ band system of the CO molecule obtained by employing a basis set of 250 complex-rotated ($\Theta= 4.0$ deg) harmonic oscillator solutions for each of the vibrational functions $\Phi_i(r)$ in eq. (1) multiplying a) the bound electronic state $\psi_1(R, r)$ and b) the repulsive electronic state $\psi_2(R, r)$. Note that $r=0$ corresponds to the equilibrium bond distance of the bound potential H_{11} in Fig. 1.

Figure 5. Real and imaginary components of the wave function for the $v=3$ resonance state in the B $^1\Sigma^+$ - D' $^1\Sigma^+$ band system of the CO molecule obtained by employing a basis set of 200 complex-rotated harmonic oscillator solutions for the vibrational function multiplying each electronic state [see eq. (1) for definitions] for different values of the scaling parameter: a) $\Theta= 3.5$ deg, b) $\Theta= 4.0$ deg and c) $\Theta= 4.5$ deg.

Figure 6. Real and imaginary components of the wave functions for the a) $v=0$ and b) $v=4$ resonance states in the B $^1\Sigma^+$ - D' $^1\Sigma^+$ band system of the CO molecule obtained by

employing a basis set of 200 complex-rotated ($\Theta = 4.0$ deg) harmonic oscillator solutions for the vibrational function multiplying each electronic state [see eq. (1) for definitions].

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