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Optical potential discrete variable representation method in the adiabatic representation

Application to the CO($B^1\Sigma^+$–$D'^1\Sigma^+, J = 0$) predissociation process

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Abstract. The optical potential discrete variable representation method (OP-DVR) has been applied recently to calculate resonances in the framework of the diabatic representation [J. Chem. Phys. **101**, 7580 (1994)]. This method is based on the conjoint use of the discrete variable representation (DVR) method and the properties of a complex absorbing potential (CAP). The OP-DVR method is the DVR version of the CAP stabilization method initially proposed by Jolicard and Austin [Chem. Phys. Lett. **121**, 106 (1985)]. In the present study, we show that this efficient and accurate method can also be applied within the adiabatic representation since it allows one to overcome in a simple way, numerical difficulties associated with the first derivative operator which appears in the expression of non adiabatic couplings. Within the OP-DVR method, the choice of the representation (diabatic or adiabatic) is governed by physical arguments and by the fact that the potentials and the couplings are known in one or the other of these two representations. In the case where the potentials and the couplings are obtained in the adiabatic representation, we show in this paper that the transformation into the diabatic framework is not necessary. We demonstrate that the discrete variable representation can be a simple and an efficient way to deal with the adiabatic representation.

PACS. 33.80.Gj Diffuse spectra; predissociation, photodissociation – 03.65.Ge Solutions of wave equations: bound states – 02.70.Jn Collocation methods

1 Introduction

Ab initio calculations done in the Born-Oppenheimer [1,2] (BO) approximation give adiabatic [3,4] potential energy surfaces (PES) but, in quantum dynamical calculations involving generally more than one PES, the diabatic representation [4–10] is often preferred for the following two reasons:

1. first, the numerical cost required to determine the derivative couplings in the adiabatic representation was, some years ago, expensive. This point can at present time, be removed using analytic gradient techniques [11];
2. second, in the adiabatic representation, the non adiabatic transitions between states are caused by the nuclear kinetic energy which produces derivative couplings. These couplings can lead to difficulties in the nuclear dynamics calculations when a sharply avoided crossing is encountered or for calculations at high collision energy [10]. These difficulties vanish in the diabatic representation where couplings between states are transferred into the Hamiltonian potential operator. Another difficulty is the complexity of solving the time-independent Schrödinger equation when the first derivative operator contained in non adiabatic couplings appears.

To solve this numerical difficulty in the time-independent approach we propose to use the efficient discrete variable representation method initially proposed by Light and coworker [12,13]. A different way to solve this problem was proposed by Parlant and Yarkony [14] with the time-dependent wave packet method using the properties of Fourier transform to compute the action of the first derivative operator. We showed in a recent paper [15] that the conjoint use of the DVR and the absorbing properties of an optical potential (negative imaginary potential) is an efficient and accurate way to obtain resonance states. We applied this method to the calculation of the quasi-bound vibrational levels resulting from the predissociating interaction of the Rydberg $B^1\Sigma^+$ and the valence $D'^1\Sigma^+$ states of the CO molecule in the diabatic representation. Recently, Baker *et al.* [16] have published a paper devoted to the experimental observation of a broad diffuse band

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assigned to the $B{-}X(3{-}0)$ transition. It confirms that the $\nu = 3$ level is quite predissociated and that it is located at about 92 800 cm^{-1} almost exactly where we predicted it [15].

In the present study, we show that the OP-DVR method is quite general and can also be applied without any difficulties in the framework of the adiabatic representation. To do that, we compute the first 11 resonances of the CO molecule in the adiabatic representation and compared them to those obtained previously [15] within the diabatic representation. The outline of the paper is as follows. In Section 2.1 we first summarize theoretical aspects of the diabatic and the adiabatic representations for diatomic molecules. In Section 2.2 we present some elements of the optical potential discrete variable representation method. In Section 3 we present results about resonances induced in the CO molecule using both diabatic and adiabatic representations. Finally, in Section 4 we draw some conclusions about the method.

2 Theoretical method

2.1 Diabatic and adiabatic representation

For a diatomic molecule and restricting the study to a two states problem, the Hamiltonian H^{dia} in the diabatic representation and H^{adia} in the adiabatic representation are both written as a 2×2 matrix operator. To a better understanding of the next developments, we reproduce here the well-known expressions [3,14] of these Hamiltonians

$$H^{dia} = \begin{pmatrix} D^d(R) & 0 \\ 0 & D^d(R) \end{pmatrix} + \begin{pmatrix} V_1^d(R) & V_{12}^d(R) \\ V_{12}^d(R) & V_2^d(R) \end{pmatrix}, \quad (1)$$

with:

$$D^d(R) = -\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dR^2} - \frac{J(J+1)}{R^2}\right), \quad (2)$$

where μ is the reduced mass of the molecule, J is the rotational angular momentum which is set here equal for the two electronic states and R is the internuclear distance. $V_i^d(R)$, $(i = 1, 2)$ represent diabatic electronic potentials associated with diabatic electronic states, $|\psi_i^d\rangle$, $(i = 1, 2)$, and $V_{12}^d(R)$ is the diabatic electronic coupling between the diabatic electronic states $|\psi_1^d\rangle$, and $|\psi_2^d\rangle$.

According to Smith's definition [6] of the strictly diabatic and adiabatic representations, the adiabatic representation is perfectly equivalent to the strictly diabatic one, and H^{adia} is given by:

$$H^{adia} = \begin{pmatrix} D_1^a(R) & K_{12}(R) \\ K_{21}(R) & D_2^a(R) \end{pmatrix} + \begin{pmatrix} V_1^a(R) & 0 \\ 0 & V_2^a(R) \end{pmatrix}, \quad (3)$$

with:

$$D_i^a(R) = -\frac{\hbar^2}{2\mu}\left(\frac{d^2}{dR^2} - \frac{J(J+1)}{R^2} + h_{ii}^a(R)\right), \quad i = 1, 2, \quad (4)$$

$$K_{ij}(R) = -\frac{\hbar^2}{2\mu}\left(h_{ij}^a(R) + 2f_{ij}^a(R)\frac{d}{dR}\right), \quad i \neq j = 1, 2. \quad (5)$$

In these formula $V_i^a(R)$, $(i = 1, 2)$, represent adiabatic electronic potentials associated with adiabatic electronic states, $|\psi_1^a\rangle$ and $|\psi_2^a\rangle$. The component

$$f_{12}^a(R) = \langle\psi_1^a(\mathbf{r}, R)|\frac{d}{dR}\psi_2^a(\mathbf{r}, R)\rangle_{\mathbf{r}}, \quad (6)$$

is the extra diagonal matrix element of the first derivative operator in the adiabatic electronic basis $\{|\psi_1^a\rangle, |\psi_2^a\rangle\}$. Note that $\mathbf{f}^a$ is an antisymmetric operator if the adiabatic electronic states are real. The matrix elements $h_{11}^a(R)$, $h_{22}^a(R)$, $h_{12}^a(R)$, and $h_{21}^a(R)$ obey *(assuming the two states basis is complete)*:

$$h_{11}^a(R) = h_{22}^a(R) = -\left[f_{12}^a(R)\right]^2, \quad (7)$$

$$h_{12}^a(R) = -h_{21}^a(R) = \frac{d}{dR}f_{12}^a(R). \quad (8)$$

In the adiabatic representation, the potential operator is diagonal and transitions between adiabatic states $|\psi_1^a\rangle$, and $|\psi_2^a\rangle$ are due to the so-called non adiabatic couplings $K_{12}(R)$ and $K_{21}(R)$ contained in the kinetic operator. The term $-(\hbar^2/2\mu)h_{11}^a(R) = -(\hbar^2/2\mu)h_{22}^a(R)$, called the adiabatic correction, appears as a function of R and then, is local in the coordinate representation. It represents a correction to the adiabatic potentials. These two representations being connected through a unitary transformation, it is possible to obtain adiabatic potentials and non adiabatic couplings from diabatic ones, see equations (29, 30) of reference [14]. As our main goal is to show the efficiency of the OP-DVR method in solving predissociation problems within the adiabatic formulation, we build adiabatic potentials and associated non adiabatic couplings from previously defined diabatic potentials and couplings [15,17]. This is done to compare on the same system the OP-DVR in the adiabatic and in the diabatic representation. These diabatic potentials $V_1^d(R)$, and $V_2^d(R)$ are represented in Figure 1, and the deduced adiabatic potentials $V_1^a(R)$, and $V_2^a(R)$ are represented in Figure 2. Coupling operators such as $V_{12}^d(R)$, $-(\hbar^2/2\mu)h_{12}^a(R)$, and $-(\hbar^2/2\mu)f_{12}^a(R)$ are represented in Figure 3. The influence of the adiabatic correction on these latter potentials is shown in Figure 4, and Figure 5. From these figures it is clear that this correction modifies the potentials only in the region close to the diabatic crossing point R_c. Following this latter point, we can expect a great sensitivity to this adiabatic correction only for states located near the crossing point R_c.

2.2 The optical potential discrete variable representation method

The OP-DVR method is the DVR version of the CAP stabilization method initially proposed by Jolicard *et al.* [18–20] as it is based on a conjoint use of a CAP and

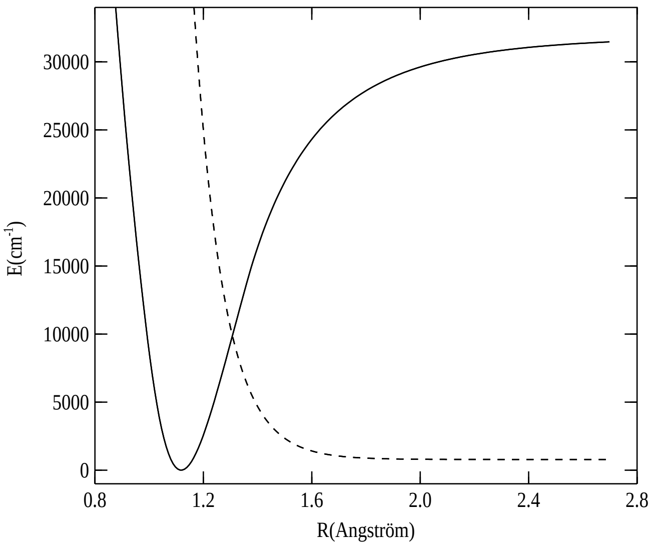

Fig. 1. Diabatic potentials $B^1\Sigma^+$, (solid line), $D'^1\Sigma^+$, (dashed line), as a function of the internuclear distance R.

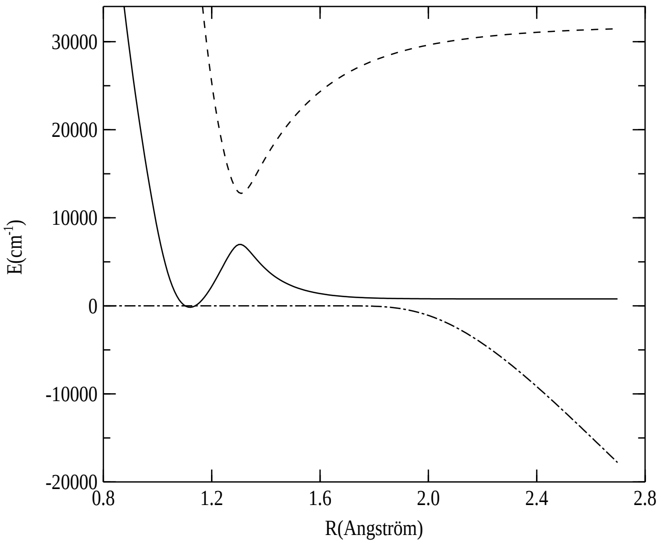

Fig. 2. Adiabatic potentials $V_1^a(R)$, (solid line), $V_2^a(R)$, (dashed line), and $-|V_{opt}(R)|$, (dashed dotted line), as a function of the internuclear distance R.

the DVR. In this method, a CAP is added to the Hermitian Hamiltonian to lead to an effective non-Hermitian Hamiltonian. Diagonalization of this effective Hamiltonian in the DVR gives rise to complex eigenvalues with the real part corresponding to the energy position of the resonances and the imaginary part being half the width of the resonances. Converged resonance energies and widths are obtained using their stability in the complex energy plane with respect to changes in the parameters of the CAP as well as in those of the DVR. In the study presented here, the lower potential $V_1^a(R)$, supports bound states as well as a continuum, and the upper potential $V_2^a(R)$, is bounded (Fig. 2). Two kinds of resonances are induced by these potentials: shape resonances, for states located in the well of $V_1^a(R)$, and coupled by tunneling effect with the continuum of $V_1^a(R)$, and Feshbach resonances, for states located in the $V_2^a(R)$ potential and coupled to the continuum of $V_1^a(R)$ by the non adiabatic couplings. As the continuum is supported by the lower potential $V_1^a(R)$, the optical potential $V_{opt}(R)$ will be placed at a distance R_{opt} on this lower curve. Adding this optical potential, the adiabatic potential $V_1^a(R)$ becomes now complex and is noted $V_1^{a'}(R)$ (see Eq. (22) in Ref. [15]).

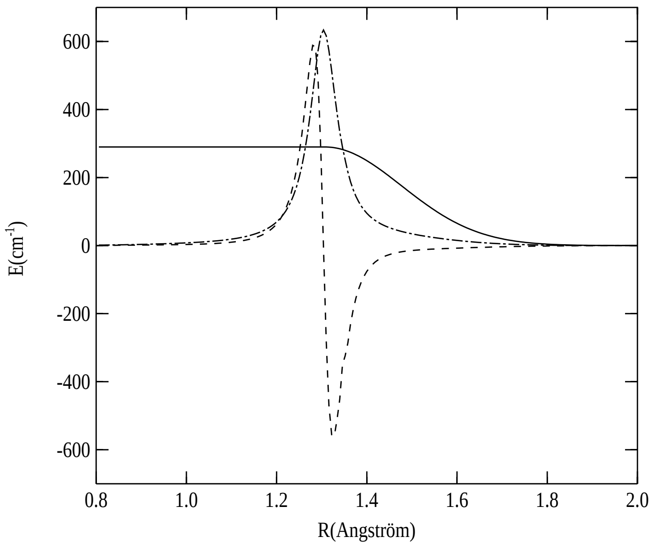

Fig. 3. Diabatic coupling $0.1\,V_{12}^d(R)$, (solid line), and components of the non adiabatic coupling, $-(\hbar^2/2\mu)h_{12}^a(R)$, (dashed line), and $-10(\hbar^2/2\mu)f_{12}^d(R)$, (dashed dotted line), as a function of the internuclear distance R.

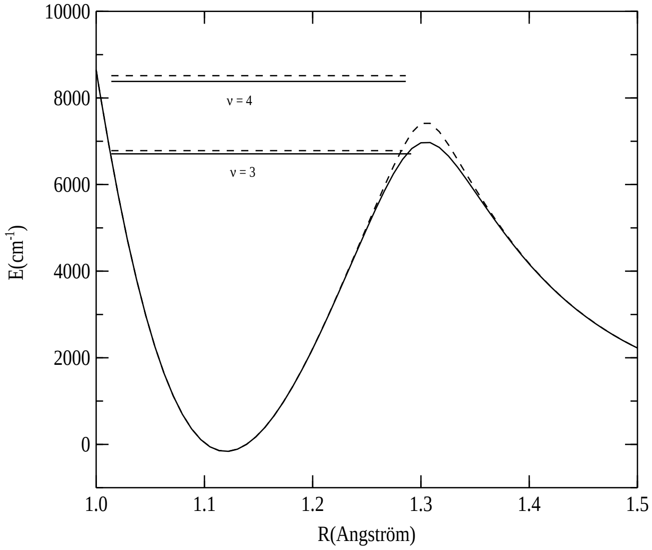

Fig. 4. Adiabatic potential $V_1^a(R)$ without the adiabatic correction, (solid line), and the same potential including this correction, (dashed line), as a function of the internuclear distance R. The states $\nu = 3$ and $\nu = 4$ are also represented for these two potentials, solid lines represent the states of $V_1^a(R)$ without the adiabatic correction.

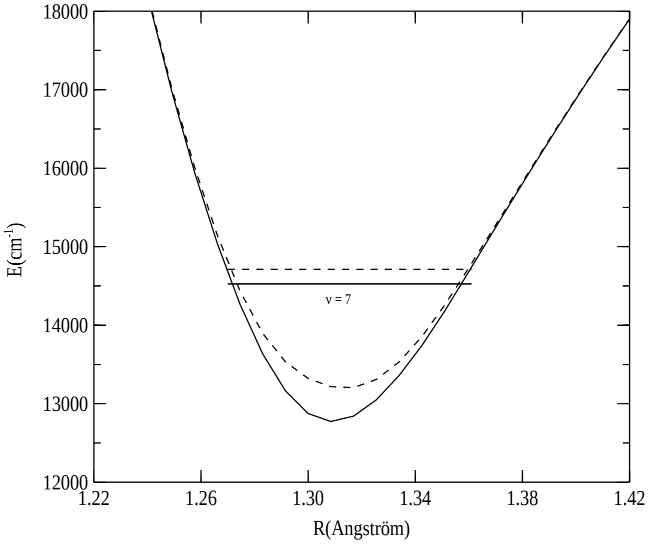

Fig. 5. Adiabatic potential $V_2^a(R)$ without the adiabatic correction, (solid line), and the same potential including this correction, (dashed line), as a function of the internuclear distance R. The state $\nu = 7$ is also represented for these two potentials, solid line represents the state of $V_2^a(R)$ without the adiabatic correction.

According to our previous study [15] concerning the influence of the shape of the optical potential on the resonance states, we retained the exponential optical potential proposed by Vibók and Balint-Kurti [22,23]. Its functional form is given by:

$$V_{opt}(R) = -iA(L_{opt})N\exp(-2L_{opt}/(R - R_{opt})). \quad (9)$$

where N is a normalization constant equal to 13.22 [22,23], L_{opt} is the "damping" length of the potential and $A(L_{opt})$ is a premultiplier used to minimize reflection plus transmission with respect to L_{opt}. A table containing dimensionless optimized parameters L_{opt}/λ, and $A(L_{opt})/E$, with $\lambda = h/\sqrt{2\mu E}$, is proposed in references [22,23]. To absorb a range of energies from E_{min} to E_{max}, Vibók and Balint-Kurti proposed to use the energy formula:

$$E = \log^{-1}\left[0.6242\log(E_{min}) + 0.3759\log(E_{max})\right]. \quad (10)$$

The DVR used here is the Fourier Grid Hamiltonian (FGH) method proposed by Marston and Balint-Kurti [24,25]. Using this DVR the Hamiltonian matrix expressed in the adiabatic representation becomes very simple due to available analytical formulas for matrix elements of differential operators such as d/dR and d^2/dR^2 [25,26]. In the DVR a uniform grid of N points is used, and the normalized matrix representation of the Hamiltonian in the adiabatic representation is given by:

$$\mathcal{H}^{adia} = \begin{pmatrix} \mathcal{H}_1 & \mathcal{K}_{12} \\ \mathcal{K}_{21} & \mathcal{H}_2 \end{pmatrix}, \quad (11)$$

where:

$$\mathcal{H}_i = \begin{pmatrix} (H_i)_{11} & \ldots & (H_i)_{1N} \\ \vdots & \ldots & \vdots \\ (H_i)_{N1} & \ldots & (H_i)_{NN} \end{pmatrix}, \quad i = 1, 2, \quad (12)$$

$$\mathcal{K}_{ij} = \begin{pmatrix} (K_{ij})_{11} & \ldots & (K_{ij})_{1N} \\ \vdots & \ldots & \vdots \\ (K_{ij})_{N1} & \ldots & (K_{ij})_{NN} \end{pmatrix}. \quad (13)$$

Matrix elements $(H_2)_{nm}$ are given by equation (18) of reference [15] and $(H_1)_{nm}$ are given by the same equation with the complex potential $V_1^{a'}(R)$. Matrix elements $(K_{ij})_{nm}$ of the coupling operator are given by:

$$[K_{ij}]_{nm} = \frac{-\hbar^2}{2\mu}\begin{cases} h_{ij}^a(R_n) + 2if_{ij}^a(R_n)\frac{\pi}{L} \\ \qquad \text{if } n = m. \\ (-1)^{n-m}f_{ij}^a(R_n)\frac{2\pi}{L}\left[i - \frac{1}{\tan(\pi(n-m)/N)}\right] \\ \qquad \text{if } n \neq m \end{cases} \quad (14)$$

The main difference between the Hamiltonian matrices $\mathcal{H}^{dia}$, and $\mathcal{H}^{adia}$ comes from the structure of the coupling matrices $\mathcal{V}_{12}$ in the diabatic representation [15] and $\mathcal{K}_{12}$ in the adiabatic representation. The matrix $\mathcal{K}_{12}$ is full due to the non local character of the first derivative operator in the coordinate representation $\{|R\rangle\}$ and consequently in the DVR while, the coupling operator $V_{12}^d(R)$ is local in the $\{|R\rangle\}$ representation so that, $\mathcal{V}_{12}$ is diagonal in the DVR, its elements being only the coupling function $V_{12}^d(R)$ taken at the N grid points R_n. The use of the finite basis representation (FBR) as primary representation is also possible since DVR and FBR are unitarily equivalent [12,13] from a formal point of view. Nevertheless, from a numerical point of view, and when a direct diagonalization is performed, the choice of DVR can be more advantageous. For a one-dimensional one state problem the Hamiltonian matrix is in the FBR:

$$H_{kk'}^{FBR} = T_{kk'}\delta_{kk'} + V_{kk'} \Rightarrow H^{FBR} = T^{FBR} + V^{FBR} \quad (15)$$

where, T^{FBR} is diagonal and its elements are calculated analytically, and V^{FBR} is full and its element must be determined numerically.

In the DVR we get:

$$H_{nm}^{DVR} = T_{nm} + V_{nm}\delta_{nm} \Rightarrow H^{DVR} = T^{DVR} + V^{DVR} \quad (16)$$

where, V^{DVR} is diagonal and its elements are determined numerically or analytically, and T^{DVR} is full and its elements can be calculated analytically due to analytical formulas for matrix elements of differential operators available in DVR [25–27]. According to that, using

Table 1. (A) Comparison of the energies of the first 11 predissociated states of CO($B^1\Sigma^+ - D'^1\Sigma^+, J = 0$), obtained with the OP-DVR: (a) within the diabatic representation, (b) within the adiabatic representation including the adiabatic correction, (c) within the adiabatic representation without the adiabatic correction. (d) Difference between column a and column b, (e) difference between column b and column c. For all this calculations, the density of points N/L is set constant and equal to 118.0 Å^{-1}. The physical space length L is equal to $R_{opt} + L_{opt} - R_{min}$. The position R_{opt} and the range L_{opt} of the optical potential are respectively set equal to 1.500 Å and 1.1982 Å $\Rightarrow$ $(L_{opt}/\lambda = 9.5)$. The transmission plus reflection is equal to about 3.8810^{-16}. $R_{min} = 0.8$ Å, $E_{min} = 2987$ cm^{-1} and $E_{max} = 20\,000$ cm^{-1}. (B) Same as (A), but for the widths. Energies, and widths are in cm^{-1}.

(A)

ν	$E^{(a)}$	$E^{(b)}$	$E^{(c)}$	$\Delta E^{(d)}$	$\Delta E^{(e)}$
0	905.3881	905.3881	904.2655	$< 1.0 \times 10^{-4}$	1.1226
1	2988.2944	2988.2944	2984.6269	$< 1.0 \times 10^{-4}$	3.6675
2	4971.5328	4971.5328	4955.4874	$< 1.0 \times 10^{-4}$	16.0454
3	6783.9228	6783.9223	6710.3195	0.0005	73.6028
4	8514.4756	8514.4707	8381.8659	0.0049	132.6048
5	10629.0234	10628.9996	10593.3976	0.0238	35.6020
6	13228.4403	13228.4324	13264.0808	0.0079	−35.6484
7	14713.0418	14713.0395	14525.8054	0.0023	187.2341
8	16922.2953	16922.2800	16875.1747	0.0153	47.1053
9	17533.8630	17533.8699	17483.3987	−0.0069	50.4712
10	19437.4275	19437.4274	19383.0363	0.0001	54.3911

(B)

ν	$\Gamma^{(a)}$	$\Gamma^{(b)}$	$\Gamma^{(c)}$	$\Delta\Gamma^{(d)}$	$\Delta\Gamma^{(e)}$
0	0.0000	0.0000	0.0000	$< 1.0 \times 10^{-4}$	$< 1.0 \times 10^{-4}$
1	0.0004	0.0004	0.0005	$< 1.0 \times 10^{-4}$	−0.0001
2	0.8949	0.8949	1.3313	$< 1.0 \times 10^{-4}$	−0.4364
3	90.8899	90.8898	137.5975	0.0001	−46.7077
4	801.7479	801.7464	1078.6223	0.0015	−276.8759
5	1854.3533	1854.3761	2262.2734	−0.0228	−407.8973
6	2149.2798	2149.3444	2011.1497	−0.0646	138.1947
7	9.3896	9.3865	53.6249	0.0031	−44.2384
8	1191.3336	1191.3158	968.4739	0.0178	222.8419
9	622.4359	622.4400	768.4728	−0.0041	−146.0328
10	0.2877	0.2878	0.0796	−0.0001	0.2082

DVR leads to simpler calculations as only potential values must be numerically evaluated. When dealing with one-dimensional two states processes in the adiabatic representation, the 2×2 kinetic matrix operator is full. Its diagonal elements d^2/dR^2 are local in the FBR while its extra diagonal elements $K_{ij}(R) = -\frac{\hbar^2}{2\mu}\left(h^a_{ij}(R) + 2f^a_{ij}(R)\frac{d}{dR}\right)$, are not due to the occurrence of R dependent functions $h^a_{ij}(R)$, and $f^a_{ij}(R)$. Determination of the kinetic matrix representation in the FBR requires numerical calculations of matrix elements of these latter functions. On the other hand, these functions are local in the DVR. Moreover, as matrix elements of the first and second derivative operators can be represented analytically, in the DVR, it is clear that this representation leads to simpler numerical implementations. According to the previous discussion, the DVR has been retained as primary representation in this study.

3 Results

Table 1 contains comparisons of energies and widths, for the first eleven predissociated states of CO($B^1\Sigma^+ - D'^1\Sigma^+, J = 0$), obtained with the OP-DVR method within diabatic and adiabatic representations. Column a presents results obtained within the diabatic representation, column b, those obtained within the adiabatic representation including the adiabatic correction, and column c, those obtained within the adiabatic representation without the adiabatic correction. Column d resumes differences between column a and b, and column e resumes differences between column b and c. All these calculations have been done using atomic units and have been converted to cm^{-1}. Characteristic parameters used are: $\mu = 6.85626$ amu, $J = 0$, $R_{min} = 0.8$ Å, $N = 224$, $L = 1.8983$ Å, $R_{opt} = 1.5001$ Å, $L_{opt} = 1.1982$ Å $\Rightarrow (L_{opt}/\lambda = 9.5)$, $E_{min} = 2987$ cm^{-1} and $E_{max} = 20\,000$ cm^{-1}. Dependence of energies and widths of resonance states with respect to the shape of the optical potential as well as to the parameters N, R_{opt}, and L_{opt}, has been already studied in our previous paper [15], and we assumed that those results remain valid also in the present study. The results given here in the diabatic case (column a) present small differences with those of reference [15] due to the use of a slightly erroneous value of the energy conversion's factor from atomic units to cm^{-1}. Deviations observed are very small, as they affect only the second or the third decimal of the energies or of the widths. This study show clearly that the OP-DVR method is able to give resonances in the diabatic representation as well as in the adiabatic representation with the same order of accuracy. Relating to the energies, the largest deviations between these two calculations are found for the levels $\nu = 4$, $\nu = 5$, $\nu = 6$, $\nu = 8$, $\nu = 7$, and $\nu = 9$, for which the differences are about 0.0049 cm^{-1}, 0.0238 cm^{-1}, 0.079 cm^{-1}, 0.0023 cm^{-1}, 0.0153 cm^{-1}, and -0.0069 cm^{-1}. For the other states, differences observed are smaller or equal to about 0.0005 cm^{-1}. Concerning widths, the largest deviations between these two calculations are observed for the same levels and are about equal to 0.0015 cm^{-1}, -0.0228 cm^{-1}, -0.0646 cm^{-1}, 0.0031 cm^{-1}, 0.0178 cm^{-1}, and -0.0041 cm^{-1}. For the other states, differences are smaller or equal to about 0.0001 cm^{-1}. These states for which a maximum but relatively small difference appears, correspond to broad resonances as their widths are greater than 600 cm^{-1} except for $\nu = 7$ for which the width is equal to 9.3896 cm^{-1}. Column e in Table 1, shows that the adiabatic correction plays an important role, as differences observed for energies as well as widths are significant. This operator being diagonal in the $\{|R\rangle\}$ coordinate representation it acts as a correction to the adiabatic potentials $V_1^a(R)$, and $V_2^a(R)$, illustrated in Figures 4 and 5. As a consequence, the energies of the $\nu = 4$ state located near the barrier of $V_1^a(R)$ and of the $\nu = 7$ state situated at the bottom of the well of $V_2^a(R)$ will be strongly affected by this correction. In fact, the largest deviations for energies are observed for these two particular states. The states $\nu = 5$, and $\nu = 6$ which are located now directly in the continuum of $V_1^a(R)$ and the states $\nu = 9$ and 10 which are located higher on $V_2^d(R)$, are less affected by this correction. Insight of column e (Tab. 1B), shows that widths do not present a specific behavior and as a general rule, are much more sensitive to slight modifications of the potentials.

4 Conclusion

The present study confirms the validity of the OP-DVR method in resonance calculations independently of the chosen representation. Calculations of Hamiltonian matrix elements and diagonalization require about the same numerical effort in the two representations diabatic or adiabatic and there is a very good convergence between the two sets of results. The choice of the representation is monitored only by physical arguments and also by the basis in which potentials and couplings have been calculated. If potentials and couplings are first available in the adiabatic representation, we show that it is not necessary to transform this initial adiabatic problem in a diabatic one. We demonstrate that the FGH and in general the DVR, can be a simple and an efficient way to overcome difficulties associated with the first derivative operator. Simple expressions obtained for the Hamiltonian matrix representation within the DVR is essentially due to available analytical formulas for matrix elements of differential operators in this representation. In this study the FGH method has been chosen but it is quite possible to extend this simple analytic formulation of the OP-DVR method to other DVR as analytical formulas for matrix elements of differential operators have been proposed recently [27] for orthogonal polynomials like Hermite, Laguerre, generalized Laguerre, Legendre and Jacobi. In this paper we focused our attention on analytic expressions of the kinetic energy matrix, but the OP-DVR method is not restricted to this particular case and is quite general. Standard procedures based on unitary transformations between DVR and FBR [12,13] can be used with our technique to compute the Hamiltonian matrix representation.

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