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Abstract

We propose a new numerically optimized discrete variable representation using eigenstates of diabatic Hamiltonians. This procedure provides an efficient method to solve non-adiabatic coupling problems since the generated basis sets take into account information on the diabatic potentials. The method is applied to the $B^1\Sigma^+ - D'^1\Sigma^+$ Rydberg-valence predissociation interaction in the CO molecule. Here we give an account of the discrete variable representation and present the procedure for the calculation of its optimized version, which we apply to obtain the total photodissociation cross sections of the CO molecule.

1. Introduction

The existence of non-adiabatic couplings between different electronic states is rather common in molecular systems. They play an important role in various molecular and chemical processes such as, for example, photodissociation, predissociation, charge transfer and spin-changing reactions (see Tully (1986), Baer (1985), Nakamura (1991), Yarkony (1996) and references therein). In such processes involving coupled electronic states, the Hamiltonian operator associated with the motion of the nuclei can be represented by a matrix in a diabatic representation, where the diagonal elements are the diabatic potentials and the off-diagonal elements are the coupling terms. In the particular case of two coupled final states, the diabatic potentials can have completely different characteristics, as in the case of the predissociation processes where an electronic state presents rovibrational bound states and the other is purely repulsive. In these conditions it is not easy to find basis functions simultaneously appropriate to

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expand the eigenfunctions of the coupled problem. The number of basis functions necessary to treat this problem tends to increase quickly and it implies a large computational effort, due to the dimensions of the matrix arising from the application of the variational method. This is particularly observed in problems involving polyatomic molecules and/or larger number of coupled (diabatic or adiabatic) electronic states. Therefore, it is important to look for procedures that reduce the number of basis functions used to expand the eigenfunctions of the problem and consequently decrease the computer time necessary to treat the coupled problem.

One technique that has been widely used with success to solve quantum problems in molecular physics and other fields is the discrete variable representation (DVR) method (Harris *et al* 1965, Dickinson and Certain 1968, Lill *et al* 1982, Light *et al* 1985, Muckerman 1990, Szalay 1996, Prudente *et al* 2001, Prudente *et al* 2005). In particular, the DVR method has been employed to study problems such as bound states (Wei and Carrington 1992, Choi and Light 1992, Tennyson 1993, Costa *et al* 1999, Bittencourt *et al* 2004), predissociation (Brems *et al* 1996, Prudente *et al* 1997), photodissociation (Heather and Light 1983, Quéré and Leforestier 1991, Seideman 1993a, Prudente *et al* 1997) and reactive scattering (Colbert and Miller 1992, Lill *et al* 1986, Manopoulos and Wyatt 1988, Baćić *et al* 1990, Seideman and Miller 1992a), because it provides a simple and efficient procedure to evaluate the potential and kinetic energy matrix elements. In such a method, the DVR basis functions are obtained by diagonalizing the matrices of coordinates from primitive basis sets. Many applications are discussed in detail in recent reviews (Baćić and Light 1989, Light and Carrington 2000). One of the most efficient and employed DVR procedures is the potential-optimized DVR (PO-DVR) (Echave and Clary 1992, Wei and Carrington 1992) where the quadrature points and the associated DVR functions are built according to features of the potential energy surface. These functions are generated using as primitive basis set the lowest eigenfunctions of a one-dimensional Hamiltonian with a convenient reference potential. Recently, some progress has been made to obtain multidimensional DVR basis functions that are not a direct product of one-dimensional DVRs (see Littlejohn *et al* (2002), Dawes and Carrington (2004), Yu (2005) and references therein). It is interesting to point out that other potential-optimized methods have been recently introduced and successfully employed in molecular physics to treat both bound and scattering problems as, for example, the mapped grid methods (Tiesinga *et al* 1998, Kokooouline *et al* 1999, Willner *et al* 2004, Grozdanov and McCarroll 2007), the phase-space-optimized DVR (Poirier and Light 1999, 2001, Bain and Poirier 2003) and the optimized mesh finite element method (Prudente and Soares Neto 1999).

In the present paper, we propose a procedure inspired in PO-DVR and in the numerical generation of DVR (Soares Neto and Costa 1998) to treat systems which have non-adiabatic couplings between two or more electronic states. This method, named diabatic potential-optimized DVR (DPO-DVR), consists of building DVR basis functions on a grid numerically generated that employs information on the diabatic potential energy surfaces involved in the problem. We have applied the DPO-DVR technique to study the photodissociation process where there is a transition into two final coupled electronic states. In the case treated here, the process is dominated by the existence of non-adiabatic coupling between an electronic state which contains bound states and one which contains only continuum states. This non-adiabatic coupling is responsible for the appearance of the predissociative resonances on the total photodissociation cross section (PCS).

The photodissociation process can be studied by using exact quantum mechanical formulations and approximate approaches (see Schinke (1993) and references therein). When the resonance effects are important, the time-independent approaches are appropriate because they determine more accurately the details of the resonant structure (Schinke 1998) (see Prudente *et al* (2003) for a time-dependent example). One of the time-independent formalisms

uses formal Green's functions (Roman 1964) which is very complicated to employ for the scattering problem. However, it is possible to obtain a well-behaved representation of Green's operator adding a non-physical negative imaginary (or complex) function to the physical potential in the dissociative region (Seideman 1993a). In such a case, the molecular Hamiltonian becomes non-Hermitian and the process to obtain Green's operator is, in principle, transformed into that of inverting a non-Hermitian matrix (see discussion in section 3). This procedure, named as the negative imaginary potential (NIP) or absorbing boundary conditions (ABC) methods, was originally proposed to study nuclear reactions (Feshbach *et al* 1954) and it has been utilized to treat molecular reactions (Neuhasuer and Baer 1989 Seideman and Miller 1992a, 1992b), metastable states (Jolicard and Humbert 1987, Jolicard *et al* 1988, Prudente *et al* 1997) and photodissociation processes (Seideman 1993a, 1993b, Mayrhofer and Bowman 1994, Grozdanov and McCarroll 1996, Prudente *et al* 1997, Prudente and Soares Neto 1998).

In order to test the DPO-DVR methodology, we have applied it, jointly with the NIP method, to calculate the total photodissociation cross section of the $B^1\Sigma^+ - D'^1\Sigma^+$ Rydberg-valence predissociation interaction of the CO molecule. Indeed, the strong non-adiabatic coupling between the bound $B^1\Sigma^+$ Rydberg state and dissociative $D'^1\Sigma^+$ valence state causes significant changes in the vibrational and rotational constants of the B state and in its predissociation of many rovibrational levels of B (Tchang-Brillet *et al* 1992, Baker *et al* 1995). This indicates that it is necessary to consider the two coupled states to describe the photodissociation process correctly. Moreover, the existence of both wide and narrow resonances in the photodissociation cross section makes this system a highly sensitive test of the novel theoretical methodologies (Andric *et al* 1999). Tchang-Brillet *et al* (1992) proposed a two-state diabatic coupling model of $B^1\Sigma^+ - D'^1\Sigma^+$ interaction optimized to best reproduce and explain the experimental data of the $B^1\Sigma^+(v = 0-2)$ states. This model has been widely employed to interpret the vibrational levels of the $B^1\Sigma^+$ Rydberg state from the experiment (Baker *et al* 1995, Baker 2005), and to determinate theoretically the photodissociation cross section (Andric *et al* 1999, Andric *et al* 2004, Grozdanov *et al* 2004) and metastable states (Monnerville and Robbe 1994, Li *et al* 1997, Monnerville and Robbe 1999, Karlsson 2000) of the $B^1\Sigma^+ - D'^1\Sigma^+$ Rydberg-valence predissociation interaction of the CO molecule. In particular, in the present paper we have used the DPO-DVR methodology with different numbers of basis functions to calculate the photodissociation cross sections. The calculations have been compared with results obtained here using the equally spaced discrete variable representation (ES-DVR) method.

The structure of the paper is as follows. Section 2 presents the basic theory of DVR basis and our optimization DVR basis: section 2.1 describes the general formalism, while the DPO-DVR method is presented in section 2.2. The theoretical framework and the main aspects of the total photodissociation cross-section calculation are presented in section 3. Section 4 presents a comparison between different numbers of DPO-DVR basis functions to calculate PCS and resonance states. The paper ends with some concluding remarks in section 5.

2. DVR methodology

2.1. General formalism

In the present subsection, we present a brief introduction to DVR and PO-DVR methods considering only one adiabatic electronic state. More details of the DVR methodology can be found in many other papers (e.g., see Baćić and Light (1989), Light and Carrington (2000), Prudente *et al* (2001), Littlejohn *et al* (2002) and references therein).

Consider the one-dimensional time-independent Schrödinger equation given by

$$\left(-\frac{1}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)\right)\psi(x) = \left(\hat{T} + V(x)\right)\psi(x) = E\psi(x). \tag{1}$$

The DVR method consists of (i) the construction of a set of orthonormalized basis functions $\{f_i(x)\}$, $i = 1, \ldots, k$ obeying the following condition:

$$f_i(x_j) = \frac{\delta_{ij}}{\sqrt{w_i}}, \qquad (i, j = 1, \ldots, k), \tag{2}$$

where $\{x_i\}$ and $\{w_i\}$, $i = 1, \ldots, k$, are the points and the weights of the Gaussian quadrature, (ii) the expansion of the eigenfunction $\psi(x)$ using the basis functions $\{f_i(x)\}$, and (iii) the solution of the associated eigenvalue-eigenvector problem. In this method, the matrix elements of the potential energy using the DVR basis (2) are given by

$$V_{ij} \approx V(x_i)\delta_{ij}, \tag{3}$$

while, in general, the kinetic energy matrix elements can be calculated analytically. The DVR basis functions $\{f_i(x)\}$ (equation (2)) are obtained by using the set of orthonormalized primitive functions $\{g_l(x)\}$, $(l = 1, 2, \ldots, k)$, which generate one given Gaussian quadrature as follows:

$$f_i(x) = \sum_{l=1}^{n} \sqrt{w_i} g_l^*(x_i)g_l(x), \qquad (i = 1, \ldots, k). \tag{4}$$

A usual Gaussian quadrature has an equally spaced grid,

$$x_i = a + \frac{(b-a)i}{n}, \qquad (i = 1, 2, \ldots, k), \tag{5}$$

with a grid spacing (or the weights) given by

$$w_i \equiv \Delta x = \left(\frac{b-a}{n}\right), \tag{6}$$

where $n = k + 1$. The primitive functions for this particular quadrature are eigenfunctions of a particle in a one-dimensional box of range $[a, b]$,

$$g_l(x) = \left(\frac{2}{b-a}\right)^{\frac{1}{2}} \sin\left[\frac{l\pi(x-a)}{b-a}\right], \qquad (l = 1, 2, \ldots, n-1), \tag{7}$$

and it generates the equally spaced DVR functions using equation (4). In such a case, the kinetic energy matrix elements are then given by (Colbert and Miller 1992)

$$[\mathbf{T}]_{ii} = \frac{1}{2\mu}\frac{\pi^2}{2(b-a)^2}\left[\frac{2n^2+1}{3} - \frac{1}{\sin^2\left[\frac{i\pi}{n}\right]}\right], \tag{8}$$

for diagonal elements, and

$$[\mathbf{T}]_{ij} = \frac{1}{2\mu}\frac{\pi^2(-1)^{i-j}}{2(b-a)^2}\left[\frac{1}{\sin^2\left[\frac{\pi(i-j)}{2n}\right]} - \frac{1}{\sin^2\left[\frac{\pi(i+j)}{2n}\right]}\right], \tag{9}$$

for off-diagonal elements ($i \neq j$). We can note that these expressions depend only on the grid points, so they are a general expression for all one-dimensional systems.

On the other hand, the PO-DVR method (Echave and Clary 1992) allows us to obtain DVR basis functions that already incorporate information on the potential energy surface of a specific system. In such a method, the purpose is to solve the Schrödinger equation for a multidimensional Hamiltonian given by

$$\hat{H} = \hat{H}_0 + \hat{V}(x, y, \ldots), \tag{10}$$

where $\hat{H}_0$ is written as $\hat{H}_0 = \hat{H}_{\mathrm{ref}}^x(x) + \hat{H}_{\mathrm{ref}}^y(y) + \cdots$, with the reference Hamiltonians $\hat{H}_{\mathrm{ref}}^x(x), \hat{H}_{\mathrm{ref}}^y(y), \ldots$ chosen according to the problem and containing the term of kinetic energy and a part of the potential energy, while $\hat{V}(x, y, \ldots)$ is the potential part not considered in $\hat{H}_0$.

This method consists of the construction of basis functions to treat the multidimensional problem as the direct product of the unidimensional PO-DVR basis functions for the dimensions $x, y, \ldots$, i.e.

$$f_{ij\ldots}(x, y, \ldots) = f_i^{\prime\mathrm{po}}(x) f_j^{\prime\mathrm{po}}(y)\ldots, \tag{11}$$

where each set of unidimensional PO-DVRs $\left(\left\{f_i^{\prime\mathrm{po}}(x)\right\}, \left\{f_j^{\prime\mathrm{po}}(y)\right\}, \ldots\right)$ is generated from primitive basis sets $\left(\left\{g_l^{\mathrm{po}}(x)\right\}, \left\{g_m^{\mathrm{po}}(y)\right\}, \ldots\right)$ following the steps described previously. The primitive functions for each coordinate, $\left\{g_l^{\mathrm{po}}(x), l = 1, \ldots, n_x^{\mathrm{po}}\right\}, \left\{g_m^{\prime\mathrm{po}}(y), m = 1, \ldots, n_y^{\mathrm{po}}\right\}, \ldots$, are the eigenfunctions of each unidimensional reference Hamiltonian $\left(\hat{H}_{\mathrm{ref}}^x(x), \hat{H}_{\mathrm{ref}}^y(y), \ldots\right)$ obtained by solving the respective one-dimensional Schrödinger equations employing an usual DVR method. These primitive functions define novel Gaussian quadratures which are optimized with respect to the reference potentials. The number of primitive functions for each space direction $\left(n_x^{\mathrm{po}}, n_x^{\mathrm{po}}, \ldots\right)$ depends on the potential features and on the problem to be solved.

2.2. DPO-DVR method

We are considering a one-dimensional system with non-adiabatic coupling between two diabatic electronic states, and therefore the Hamiltonian operator is a 2×2 matrix (for more details, see Köppel *et al* (1984) and references therein). The generalization of the algorithm is straightforward for more states and also to an adiabatic formulation. In an adiabatic representation, the Hamiltonian can be formulated in a way that is numerically Hermitian within a DVR and involve operators that can be evaluated analytically (Tuvi and Band 1997). The diabatic Hamiltonian matrix representation, with fixed total angular momentum J, in a DVR basis has a $2k \times 2k$ dimension, where k is the number of DVR basis functions, and is given by

$$\begin{aligned}
\mathbf{H}_J^d(R) &= \mathbf{T}_R + \mathbf{V}_J(R) \\
&= \begin{pmatrix} T_{ij} & 0 \\ 0 & T_{ij} \end{pmatrix} + \begin{pmatrix} \left[V_1 + \frac{J(J+1)\hbar^2}{2\mu R^2}\right]\delta_{ij} & [V_{12}]\delta_{ij} \\ [V_{12}]\delta_{ij} & \left[V_2 + \frac{J(J+1)\hbar^2}{2\mu R^2}\right]\delta_{ij} \end{pmatrix},
\end{aligned} \tag{12}$$

where R is the internuclear distance, T_R is the radial kinetic energy operator

$$T_R = -\frac{1}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}R^2} \tag{13}$$

and $\mathbf{V}_J$ is the effective potential energy, $\mathbf{V}_1$ and $\mathbf{V}_2$ are the diabatic potentials and $\mathbf{V}_{12}$ is the coupling term.

The present proposal to obtain DPO-DVR basis functions consists of the following.

(i) Generate a set of DVR basis functions $\{f_i(R), i = 1, 2, \ldots, k\}$, using a set of primitive functions $\{g_l(R), l = 1, 2, \ldots, k\}$, for example equally spaced quadrature with points $\{x_j\}$ and weights $\{w_j\}$, $j = 1, \ldots, k$.

(ii) Obtain the eigenfunctions and eigenvalues for each diabatic potential by solving

$$\begin{aligned}
\hat{H}_1^d g_l^1(R) &= E_l^1 g_l^1(R) & (l = 1, \ldots, k) \\
\hat{H}_2^d g_m^2(R) &= E_m^2 g_m^2(R) & (m = 1, \ldots, k),
\end{aligned} \tag{14}$$

where

$$g_l^1(R) = \sum_{i=1}^{k} c_{li}^1 f_i(R) \qquad \text{and} \qquad g_m^2(R) = \sum_{i=1}^{k} c_{mi}^2 f_i(R). \qquad (15)$$

A set of these eigenfunctions is then used to obtain a new set of primitive functions, typically establishing an upper limit for the energy. In particular, one can use n_1 eigenfunctions of V_1, and n_2 of V_2:

$$\{g_l^1(R), l = 1, \ldots, n_1\}$$
$$\{g_m^2(R), m = 1, \ldots, n_2\}, \qquad (16)$$

where the numbers n_1 and n_2 are arbitrary. Here we propose a criterion based on the energy eigenvalues where n_1 and n_2 are, respectively, the number of eigenvalues E_l^2 and E_m^2 (and of eigenfunctions) with smaller values than a certain cut energy E^{cut}. This choice will depend on the eigenvalues associated with the eigenfunctions for each diabatic potential. It is natural to expect that $n_1 + n_2 \leqslant k$ for the proposed set of functions.

(iii) Define a set $\{\tilde{\mathcal{G}}_i(R), i = 1, \ldots, n_1 + n_2\}$ as

$$\tilde{\mathcal{G}}_i(R) = g_i^1(R), \qquad (i = 1, \ldots, n_1)$$
$$\tilde{\mathcal{G}}_i(R) = g_{i-n_1}^2(R), \qquad (i = n_1 + 1, \ldots, n_1 + n_2). \qquad (17)$$

(iv) Construct a new set of primitive functions, orthonormalizing the set $\{\tilde{\mathcal{G}}_i(R)\}$, for example using the Gram–Schmidt algorithm (Press *et al* 1986)

$$\{\mathcal{G}_i(R), i = 1, \ldots, n_1 + n_2\}. \qquad (18)$$

Using equation (15), then

$$\mathcal{G}_j(R) = \sum_{i=1}^{k} b_{ji} f_i(R), \qquad (j = 1, \ldots, n_1 + n_2), \qquad (19)$$

where b_{ji} are obtained through the orthonormalization process.

(v) Solve the eigenvalue equation

$$\hat{R}\mathcal{F}_\alpha(R) = R_\alpha \mathcal{F}_\alpha(R), \qquad (\alpha = 1, \ldots, n_1 + n_2), \qquad (20)$$

where the eigenvalues R_α are the points of the optimized quadrature and the eigenfunctions are obtained by the expansion

$$\mathcal{F}_\alpha(R) = \sum_{j=1}^{n_1+n_2} d_{\alpha j} \mathcal{G}_j(R), \qquad (21)$$

where $d_{\alpha j}$ are the coefficients to be determined by solving equation (20). According to equation (19),

$$\mathcal{F}_\alpha(R) = \sum_{j=1}^{n_1+n_2} d_{\alpha j} \sum_{i=1}^{k} b_{ji} f_i(R), \qquad (\alpha = 1, \ldots, n_1 + n_2). \qquad (22)$$

Considering the points of the initial quadrature, denoted by $\{R_j\}$, $(j = 1, \ldots, k)$, it can be shown that

$$\mathcal{F}_\alpha(R_j) = \sum_{i=1}^{n_1+n_2} d_{\alpha i} \frac{b_{ij}}{\sqrt{w_j}}, \qquad (\alpha = 1, \ldots, n_1 + n_2). \qquad (23)$$

On the other hand, the weights of this optimized quadrature are given by

$$w_\alpha = \left[\sum_{\beta=1}^{n_1+n_2} \mathcal{G}_\beta^*(R_\alpha) \mathcal{G}_\beta(R_\alpha) \right]^{-1}. \qquad (24)$$

Alternatively, one could use a set of non-orthonormalized primitive functions and, in this case, the DPO-DVR basis functions will be obtained by a generalized eigenvalue problems. We have used the Gram–Schmidt algorithm because it works well in our case, when functions (eigenfunctions of the diabatic potentials) are in two different regions of the space.

The Hamiltonian matrix representation in a DPO-DVR basis $\{\mathcal{F}_\alpha(R)\}(\alpha = 1, \ldots, n_1 + n_2)$ has a $2(n_1 + n_2) \times 2(n_1 + n_2)$ dimension, so

$$\mathbf{H}^d(R) = \begin{pmatrix} T_{\alpha\beta} & 0 \\ 0 & T_{\alpha\beta} \end{pmatrix} + \begin{pmatrix} \left[V_1 + \frac{J(J+1)\hbar^2}{2\mu R^2}\right]_{\alpha\beta} & [V_{12}]_{\alpha\beta} \\ [V_{12}]_{\alpha\beta} & \left[V_2 + \frac{J(J+1)\hbar^2}{2\mu R^2}\right]_{\alpha\beta} \end{pmatrix}. \tag{25}$$

Since the DPO-DVR preserves the DVR basis properties, the potential energy matrix representation $\mathbf{V}(R)$ is block diagonal and its elements are the potentials calculated on the quadrature points. The kinetic energy matrix elements are

$$T_{\alpha\beta} = \sum_{j,j'=1}^{n_1+n_2} d_{\alpha j} d_{\beta j'} \sum_{i,i'=1}^{k} b_{ji} b_{j'i'} T_{ii'}, \tag{26}$$

where $T_{ii'}$ are the kinetic energy matrix elements shown in equations (8) and (9), and $\alpha, \beta = 1, \ldots, n_1 + n_2$.

The number of functions of the DPO-DVR basis necessary to solve problems with non-adiabatic couplings should be smaller than the equally spaced DVR, because these functions take into account information of the diabatic potential in the spirit of the PO-DVR procedure.

3. Photodissociation cross section

The total photodissociation cross section is presented in the Green operator formalism for the weak radiation field limit and in the electric dipole approximation. In the particular case of transitions from an initial electronic state to two coupled states with the integration over rotational degrees of freedom carried out (Seideman and Miller 1992b, Seideman 1993a), the total photodissociation cross section can be written as

$$\sigma_{i0}(\omega) = \frac{-4\pi\omega}{3c} \operatorname{Im}\langle\psi_{i,0}|\hat{\varepsilon} \cdot \boldsymbol{\mu} \left[\frac{J_0 + 1}{2J_0 + 1}\hat{G}^+(E, J_0 + 1) + \frac{J_0}{2J_0 + 1}\hat{G}^+(E, J_0 - 1)\right] \hat{\varepsilon} \cdot \boldsymbol{\mu}|\psi_{i,0}\rangle, \tag{27}$$

where $\omega = E - E_i$ is the radiation frequency, while E_i, J_0 and $|\psi_{i,0}\rangle$ are, respectively, the energy, the total angular momentum and the wavefunction of the molecule in the initial state, the $\hat{\varepsilon} \cdot \boldsymbol{\mu}$ term is the electric dipolar operator in the direction of the electromagnetic field and $\hat{G}^+(E)$ is the Green operator given by (Sakurai 1994)

$$\hat{G}^+(E, J) = \lim_{\eta \to 0} \frac{1}{E - \hat{H}_J + i\eta}. \tag{28}$$

In studying general behaviour of the photodissociation cross sections, the differences between $G^+(E, J_0 + 1)$, $G^+(E, J_0)$ and $G^+(E, J_0 - 1)$ can be disregarded (Seideman 1993a, Andric et al 1999) and equation (27) becomes

$$\sigma_{i0}(\omega) = \left(\frac{-4\pi\omega}{3c}\right) \operatorname{Im}\langle\psi_{i,0}|\hat{\varepsilon} \cdot \boldsymbol{\mu}\hat{G}^+(E, J_0)\hat{\varepsilon} \cdot \boldsymbol{\mu}|\psi_{i,0}\rangle. \tag{29}$$

We can assume that the initial molecular state, within the Born–Oppenheimer approximation, can be rewritten as

$$\psi_{i,0} = \xi_{i,0}(\mathbf{R})\zeta_0(\mathbf{r}; \mathbf{R}), \tag{30}$$

where $\xi_{i,0}(\mathbf{R})$ is the ith bound rovibrational state from the ground electronic state $\zeta_0(\mathbf{r}; \mathbf{R})$, and that the functions $\{\zeta_\gamma(\mathbf{r}; \mathbf{R})\}$ constitute a complete set of electronic states that satisfy the completeness relation

$$\sum_\gamma \zeta_\gamma(\mathbf{r}; \mathbf{R})\zeta_\gamma^*(\mathbf{r}'; \mathbf{R}) = \delta(\mathbf{r} - \mathbf{r}'). \tag{31}$$

In such a case, the total photodissociation cross section (equation (29)) for a diatomic system, after integration over the electronic coordinates, is given by

$$\sigma_{\mathrm i}(\omega) = \left(\frac{-4\pi\omega}{3c}\right) \mathrm{Im} \sum_{\gamma\gamma'} \int \mathrm{d}R \int \mathrm{d}R' \xi_{i,0}^*(R)\hat{\varepsilon} \cdot \boldsymbol{\mu}_{0\gamma}(R)$$
$$\times \hat{G}_{\gamma\gamma'}^+(R, R'; E, J_0)\hat{\varepsilon} \cdot \boldsymbol{\mu}_{\gamma'0}(R')\xi_{i,0}(R'), \tag{32}$$

where R is the radial nuclear coordinate, $\boldsymbol{\mu}_{\gamma,0}(R)$ is the dipole transition moment operator between the ground and excited electronic states, i.e.

$$\boldsymbol{\mu}_{0\gamma}(R) = \int \zeta_0^*(\mathbf{r}; R)\hat{\varepsilon} \cdot \mathbf{d}(\mathbf{r}, R)\zeta_\gamma(\mathbf{r}; R)\,\mathrm{d}^{3\mathcal{N}}\mathbf{r}\,\mathrm{d}^{3\mathcal{N}_A}R;$$

and $G_{\gamma\gamma'}^+(R, R'; E, J_0)$ is an element of the matrix representation of the Green operator in the electronic basis set, i.e.

$$G_{\gamma\gamma'}^+(R, R'; E, J_0) = \int \zeta_\gamma^*(\mathbf{r}''; R)\hat{G}^+(\mathbf{r}'', R, \mathbf{r}''', R'; E, J_0)\zeta_{\gamma'}(\mathbf{r}'''; R)\mathrm{d}^{3\mathcal{N}}\mathbf{r}''\mathrm{d}^{3\mathcal{N}}\mathbf{r}''', \tag{33}$$

with

$$\hat{G}^+(\mathbf{r}'', R, \mathbf{r}''', R'; E, J_0) = \langle \mathbf{r}'', R|\hat{G}^+(E, J_0)|\mathbf{r}''', R'\rangle. \tag{34}$$

Rewriting equation (32) in the Dirac notation and expanding it in a DVR basis set $\{|f_i\rangle\}$ which satisfies the relation

$$\mathbf{1} \approx \sum_k |f_k\rangle\langle f_k|, \tag{35}$$

the total photodissociation cross section becomes $\{|f_k\rangle\}$:

$$\sigma_{\mathrm i}(\omega) = \left(\frac{-4\pi\omega}{3c}\right) \mathrm{Im} \sum_{\gamma\gamma'} \sum_{kk'} \langle\xi_{i,0}|\hat{\varepsilon} \cdot \boldsymbol{\mu}_{0\gamma}|f_k\rangle\langle f_k|\hat{G}_{\gamma\gamma'}^+(E, J_0)|f_{k'}\rangle\langle f_{k'}|\hat{\varepsilon} \cdot \boldsymbol{\mu}_{\gamma'0}|\xi_{i,0}\rangle, \tag{36}$$

or

$$\sigma_{\mathrm i}(\omega) = \left(\frac{-4\pi\omega}{3c}\right) \mathrm{Im} \sum_{\gamma\gamma'} \sum_{kk'} (c_{i,0}^*)_k\hat{\varepsilon} \cdot \boldsymbol{\mu}_{0\gamma}(R_k)\hat{G}_{\gamma\gamma'kk'}^+(E, J_0)\hat{\varepsilon} \cdot \boldsymbol{\mu}_{\gamma'0}(R_{k'})(c_{i,0})_{k'}, \tag{37}$$

where it is assumed that

$$\langle f_k|\hat{\varepsilon} \cdot \boldsymbol{\mu}_{\gamma0}^r|\xi_{i,0}\rangle = \mu_{\gamma0}^r(R_k)(c_{i,0})_k, \tag{38}$$

with $(c_{i,0})_k$ being the kth coefficient of the expansion

$$\xi_{i,0}(R) = \sum_k (c_{i,0})_k f_k(R). \tag{39}$$

The matrix representation of the Green operator in the DVR basis, within the NIP method, is obtained by the introduction of the negative imaginary potential $-iU(R)$ in the Hamiltonian as follows:

$$\langle f_k|\hat{G}_{\gamma\gamma'}^+(E, J_0)|f_{k'}\rangle = \hat{G}_{\gamma\gamma'kk'}^+(E, J_0) = \left[\left(E + \mathrm{i}U - \hat{H}_{J_0}\right)\right]_{\gamma k,\gamma'k'}^{-1}. \tag{40}$$
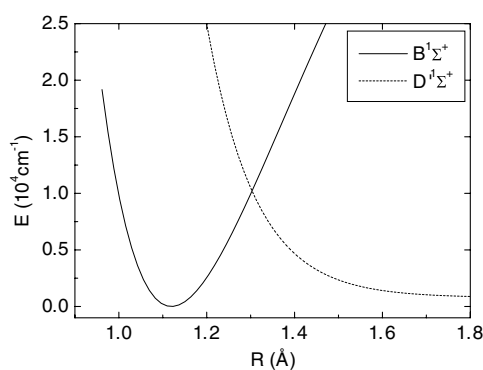
Figure 1. Diabatic potential energy curves corresponding to predissociation $B^1\Sigma^+ - D'^1\Sigma^+$ states of the CO molecule.

For the potential $U(R)$, we have used a power law (Rom *et al* 1991):

$$U(R) = \begin{cases} 0, & R \leqslant R_0 \\ g_o \left(\frac{R-R_0}{R_{\max}-R_0} \right)^2, & R_0 < R < R_{\max}, \end{cases} \tag{41}$$

where g_o, R_0 and $R_{\max}$ are the parameters which have to be chosen in order that we have the total absorption of the wavefunction in the dissociation interval. So, this function has to rise slowly in the asymptotic region and vanish inside the strong interaction region.

Equation (40) shows that the matrix representation of the Green operator ($\mathbf{G}^+(E, J_0)$) can be determined directly by inversion of the $\mathbf{A} = (E\mathbf{S} + i\mathbf{U} - \mathbf{H})$ matrix for each total energy E ($\mathbf{S}$ is an overlap matrix which is equal to the identity within DVR methods). However, there are various approaches that evaluate $\mathbf{G}^+(E, J_0)$ more efficiently as, for example, by means of its spectral decomposition from the eigenvectors and eigenvalues of the complex symmetric matrix $\mathbf{H} - i\mathbf{U}$ (Mayrhofer and Bowman 1994) or by using recursive methods based on damped Chebyshev polynomial expansions (Mandelshtam and Taylor 1995, Grozdanov and McCarroll 1996, Guo 1998) or the Lanczos algorithm (Moro and Freed 1981, Karlsson and Goscinski 1994, Xu *et al* 2002, Grozdanov *et al* 2004). Despite this, since the major goal of this paper is to present a novel methodology of expansion of the wavefunction with the objective to reduce the number of basis functions (and consequently, the dimension of the involved matrices), we have employed the process of inversion of the $\mathbf{A}$ matrix to determine $\mathbf{G}^+(E, J_0)$.

The application to the CO molecule involves two electronic states, and therefore the photodissociation cross section is calculated by equation (37) with $\gamma, \gamma' = 1, 2$.

4. Results

The DPO-DVR method is applied here for the calculation of the total photodissociation cross sections of the CO molecule corresponding to transitions from the ground $X^1\Sigma^+$ state into Rydberg-valence predissociation $B^1\Sigma^+ - D'^1\Sigma^+$ states.

We have used the model proposed by Tchang-Brillet *et al* (1992), Andric *et al* (1999) to represent the interaction states. In the previous notation, the diabatic potential $\hat{V}_1$ corresponds to $B^1\Sigma^+$ electronic state and it is a Rydberg–Klein–Rees (RKR) potential. In particular, we have used a cubic spline interpolation of RKR's points (Tchang-Brillet 2003). The diabatic potential $\hat{V}_2$ corresponds to $D^1\Sigma^+$ electronic state, and it is a purely repulsive potential. These diabatic potentials are presented in figure 1. The range of the nuclear configurations considered
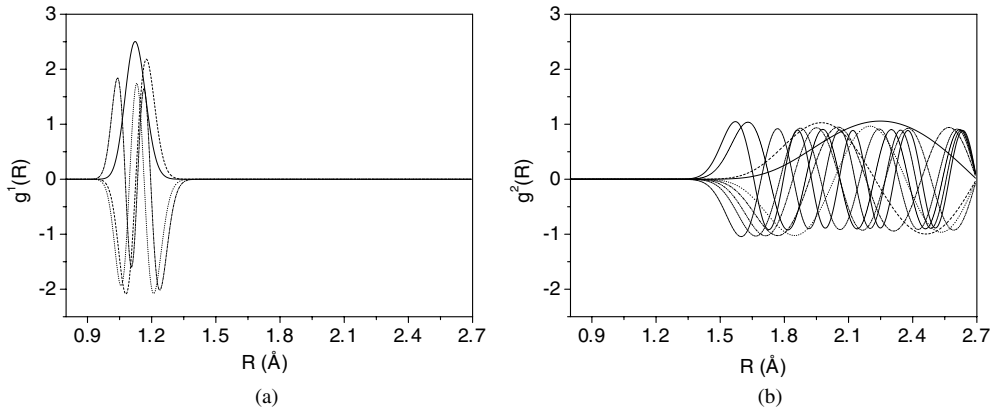
Figure 2. Eigenfunctions, respectively, for the diabatic potentials $\hat{V}_1(R)$ and $\hat{V}_2(R)$ using equally spaced DVR: (a) the four lowest eigenfunctions $g_l^1(R)$ and (b) the nine lowest eigenfunctions $g_m^2(R)$.

in our calculation is from 0.8 Å to 2.7 Å. In such a model the coupling operator $\hat{V}_{12}$ is given by

$$V_{12}(R) = \begin{cases} 2900, & R \leqslant R_c \\ 2900 \exp\left[-\ln 2 \left(\frac{R-R_c}{\Delta R}\right)^2\right], & R > R_c, \end{cases} \tag{42}$$

where $R_c = 1.30711$ Å and $\Delta R = 0.20$ Å. For the potential energy of the electronic ground state $X^1\Sigma^+$, we have used a Morse potential (Murrell *et al* 1984), with $D_e = 83776.6874 \, \text{cm}^{-1}$, $R_e = 1.128323$ Å, $\alpha_e = 0.01750441 \, \text{cm}^{-1}$, $\omega_e = 2169.81358 \, \text{cm}^{-1}$, and $B_e = 1.93128087 \, \text{cm}^{-1}$. These parameters were determined experimentally by Floch (1991).

As discussed previously, the first step to calculate the photodissociation cross section is the determination of the DPO-DVR basis functions using the procedure described in subsection 2.2. For this, we have to solve the radial Schrödinger equation for each diabatic potential

$$\left[\hat{T} + \hat{V}_1(R) + \frac{J_0(J_0+1)}{2\mu R^2}\right] g_l^1(R) = E_l^1 g_l^1(R)$$

$$\left[\hat{T} + \hat{V}_2(R) + \frac{J_0(J_0+1)}{2\mu R^2}\right] g_m^2(R) = E_m^2 g_m^2(R), \tag{43}$$

where $\hat{T} = -\frac{1}{2\mu}\frac{d^2}{dR^2}$, μ is the reduced mass of the CO molecule, and $g_l^1(R)$ and $g_m^2(R)$ are the eigenfunctions with associated eigenvalues E_l^1 and E_m^2, respectively, for the diabatic potentials $\hat{V}_1(R)$ and $\hat{V}_2(R)$. In such a case, we have used equations (3), (8) and (9) with a set of 140 equally spaced (ES) points in the interval from 0.8Å up to 2.7Å. These parameters have been used in the literature (Andric *et al* 1999).

We emphasize that in the DPO-DVR procedure $g_l^1(R)$ and $g_m^2(R)$ do not have any physical significance. They are used to originate a new set of functions as in equation (17). The number of eigenfunctions considered in the present calculations is in agreement with the energy criterion discussed in section 2.2. In table 1, the considered values of E^{cut} are shown together with the number of eigenfunctions n_1 and n_2 associated with the V_1 and V_2 potentials. As an example, in figure 2 the four lowest eigenfunctions $g_l^1(R)$ and the nine lowest eigenfunctions
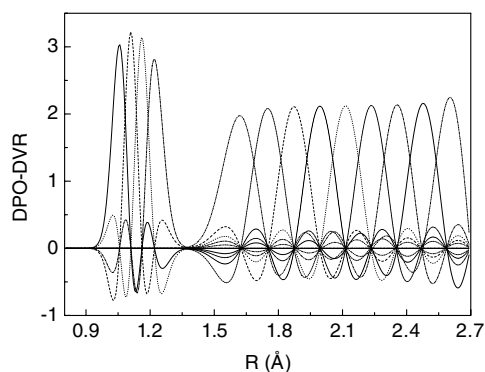
Figure 3. DPO-DVR basis functions calculated using four eigenfunctions $g_l^1(R)$ and nine eigenfunctions $g_m^2(R)$.

Table 1. Numbers of eigenfunctions n_1 and n_2 associated with the V_1 and V_2 diabatic potentials of the $B^1\Sigma^+$ and $D'^1\Sigma^+$ electronic states with the eigenvalues below E^{cut} (cm^{-1}); $n_1 + n_2$ represents the number of DPO-DVR basis functions.

E^{cut}(cm^{-1})	n_1	n_2	$n_1 + n_2$
21 000	12	40	52
22 000	13	42	55
23 000	13	43	56
25 000	15	45	60
26 000	16	46	62
30 000	23	50	73

$g_m^2(R)$ are displayed. Note that due to the small number of basis functions employed, only a small overlap between the eigenfunctions of $g_l^1(R)$ and $g_m^2(R)$ is shown.

Next we have employed the Gram–Schmidt orthonormalization algorithm to construct the set of primitive functions $\{\mathcal{G}_j(R); j = 1, \ldots, n_1 + n_2\}$, equation (19). The orthonormalization is performed only in this stage of the calculation and involves only the number $(n_1 + n_2)$ of functions that will be orthonormalized. Finally, these functions allow us to generate a diabatic potential-optimized quadrature and the DPO-DVR basis functions ($\{\mathcal{F}_\alpha(R); \alpha = 1, \ldots, n_1 + n_2\}$), following the procedure described in section 2.2. Figure 3 displays the set of 13 DPO-DVR functions $\mathcal{F}_\alpha(R)$ calculated using four $g_l^1(R)$ and nine $g_m^2(R)$ eigenfunctions shown in figure 2.

The total photodissociation cross section is then calculated using equation (37). The initial rovibrational state $\xi_{i,0}(R)$ is assumed to be the fundamental one (i = $(\nu_0, J_0) = (0, 0)$) and is obtained by diagonalization of the Hamiltonian matrix representation of the ground electronic state in the DPO-DVR basis set. As parameters of the negative imaginary potential ($U(R)$) given by equation (41), we have defined $R_0 = 1.8$ Å and $R_{\text{max}} = 2.7$ Å, because the segment $[R_0; R_{\text{max}}]$ represents the asymptotic region of the scattering coordinate, and $g_0 = 0.5$, as has been used in literature (Andric *et al* 1999).

Figures 4(a) and (b) present the total photodissociation cross sections using different DPO-DVR quadratures, in the energy intervals from 4000 cm^{-1} to 14 000 cm^{-1} and from 14 000 cm^{-1} to 22 000 cm^{-1}. In all cases, we have compared our DPO-DVR calculations with those performed using an ES-DVR with 300 basis functions.
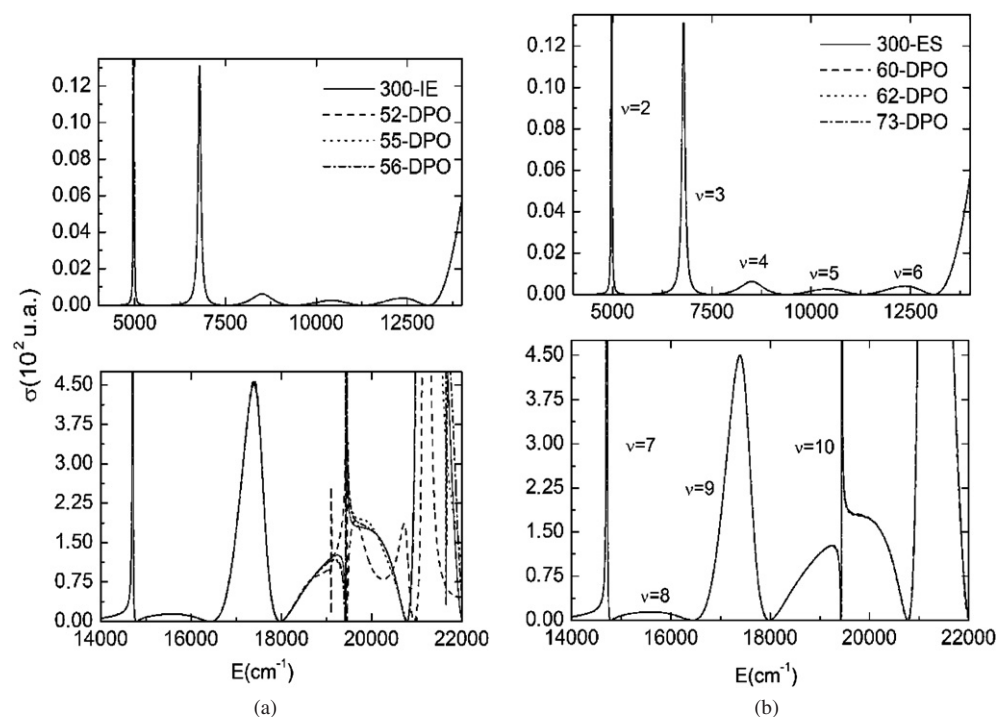
Figure 4. Total photodissociation cross sections to transitions $X^1\Sigma^+ \rightarrow B^1\Sigma^+ - D'^1\Sigma^+$ of the CO molecule using: (a) 52, 55 and 56 DPO points; and (b) 60, 62 and 73 DPO points, compared with a similar calculation using 300 ES points.

In figure 4(a), the photodissociation cross sections calculated with 52, 55 and 56 diabatic potential-optimized points are displayed, while in figure 4(b) we have employed 60, 62 and 73 DPO-DVR points according to the choice shown in table 1. From the obtained comparison, we can see a close relationship between the quality of the calculated cross section and the number of eigenfunction of each diabatic potential used to construct the DPO-DVR basis. The analysis of figures 4(a) and (b) allows us to conclude that the photodissociation cross section for each basis is satisfactory for energies below E^{cut} from table 1. Moreover, the calculated photodissociation cross section becomes more accurate as the number of basis functions increase when compared with the ES-DVR results; therefore, this illustrates the convergence properties of the method.

The features of the photodissociation cross sections presented here are in agreement with previous ones (Andric *et al* 1999, Grozdanov *et al* 2004, Andric *et al* 2004). We can observe structures revealing different behaviour for a given resonance state ν. The resonances for the bound region, $\nu = 2$ and 3, are quite narrow, while in the coupling region $\nu = 4, 5$ and 6 are weak and wide. In the energy interval from $14000\,\text{cm}^{-1}$ to $20\,000\,\text{cm}^{-1}$, where strong interference effects can be observed, the resonance $\nu = 7$ and specifically resonance $\nu = 10$ are very narrow, while resonances $\nu = 8$ and 9 are very wide.

We present in figures 5(a) and (b) a closeup of figures 4(a) and (b), respectively, to offer a more detailed analysis. In figure 5(a), we have used the following energy intervals: from $6700\,\text{cm}^{-1}$ to $6900\,\text{cm}^{-1}$ and from $17\,200\,\text{cm}^{-1}$ to $17\,600\,\text{cm}^{-1}$, which present details of resonances $\nu = 2$ and $\nu = 9$, respectively. In figure 5(b), we have used the following energy

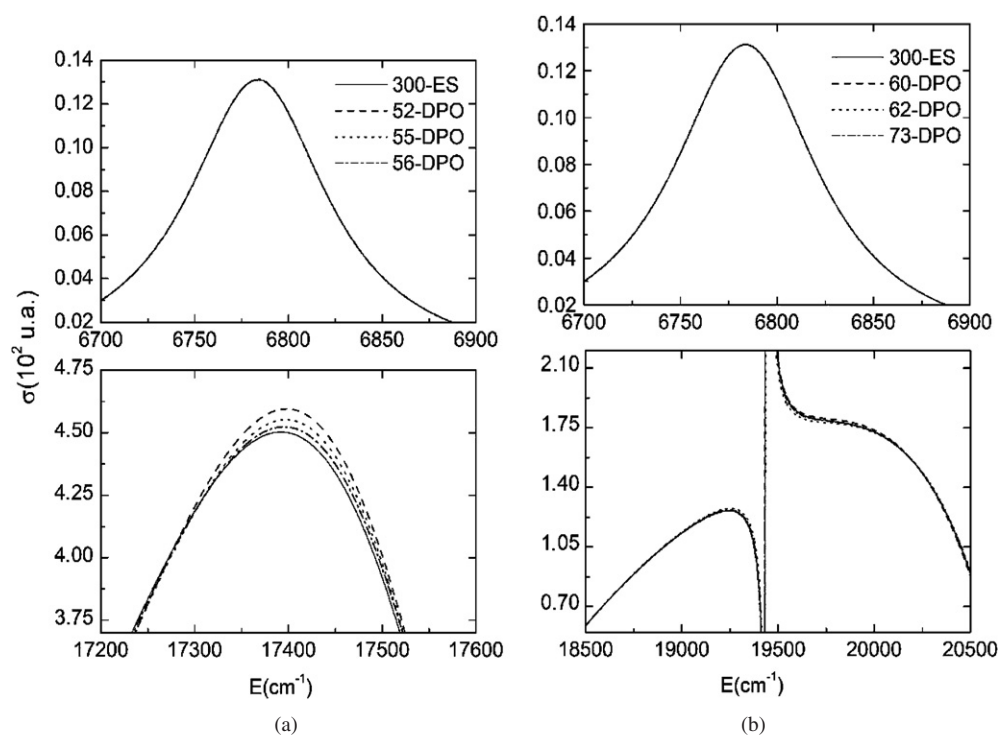**Figure 5.** Total photodissociation cross sections using the following energy intervals: (a) from $6700\,\mathrm{cm}^{-1}$ to $6900\,\mathrm{cm}^{-1}$ and from $17\,200\,\mathrm{cm}^{-1}$ to $17\,600\,\mathrm{cm}^{-1}$, using 52, 55 and 56 DPO points; and (b) from $6700\,\mathrm{cm}^{-1}$ to $6900\,\mathrm{cm}^{-1}$ and from $18\,500\,\mathrm{cm}^{-1}$ to $20\,500\,\mathrm{cm}^{-1}$, using 60, 62 an 73 DPO points. Comparison is made with a similar calculation using 300 ES points.

intervals: from $6700\,\mathrm{cm}^{-1}$ to $6900\,\mathrm{cm}^{-1}$ and $18\,500\,\mathrm{cm}^{-1}$ to $20\,500\,\mathrm{cm}^{-1}$ to show details of resonances $\nu = 2$ and $\nu = 10$, respectively. The comparison is made with the ES-DVR calculation using 300 basis functions.

In figure 5(a), in the energy interval from $17\,200\,\mathrm{cm}^{-1}$ to $17\,600\,\mathrm{cm}^{-1}$, the curves present prominent disagreement as the basis decreases. However, we note that until approximately $17\,300\,\mathrm{cm}^{-1}$ the calculation using 56 optimized points, with cut energy $E^{\mathrm{cut}} = 23\,000\,\mathrm{cm}^{-1}$, presents good agreement. In figure 5(b), in the energy interval from $18\,500\,\mathrm{cm}^{-1}$ to $20\,500\,\mathrm{cm}^{-1}$, until approximately $19\,000\,\mathrm{cm}^{-1}$ the calculation using 60 optimized points, with cut energy $E^{\mathrm{cut}} = 25\,000\,\mathrm{cm}^{-1}$, presents excellent agreement. We note that the curves using 62 and 73 points in the considered energy interval are similar to those from ES-DVR calculation with 300 points. Then we can conclude that the photodissociation cross section is accurately reproduced up to energies approximately $6000\,\mathrm{cm}^{-1}$ below E^{cut}. This value can be considered as an estimate of the limit to the accuracy of photodissociation cross-section calculations using the DPO-DVR procedure.

We have shown that it is possible to reduce the number of basis functions of the cross-section calculation in comparison with the usually chosen basis. Andric *et al* (1999) have presented a study for the title system using 140 equally spaced DVR points which leads to work with matrices with dimension 280×280. A similar number of ES-DVR functions have been employed in another recent work of same research group (Grozdanov *et al* 2004) to analyse the

use of Lanczos algorithm in the calculation of the photodissociation cross sections. However, our calculations have involved matrices of maximum dimension 146×146 that represent 73 DPO-DVR basis functions. Considering that the DPO-DVR basis set needs to be calculated only one time to a given problem and it is independent of NIP parameters, the decrease of the number of basis functions reduces the computation cost since the Green operator must be determined for each energy of the spectrum.

5. Concluding remarks

The present study confirms the efficiency of our proposed DPO-DRV method. We calculated the total photodissociation cross section for the $B^1\Sigma^+ - D'^1\Sigma^+$ Rydberg-valence predissociation interaction in the CO molecule, comparing the number of DPO-DVR basis functions with those giving similar results using equally spaced grids.

The total photodissociation cross sections were calculated with satisfactory agreement up to energy below about $6000 \, \text{cm}^{-1}$ under the E^{cut} considered in the definition of the basis sets. Therefore, it has demonstrated that our DPO-DVR method involves the reduction of the basis needed for the treatment of problems which include non-adiabatic couplings.

As a perspective, we will study the rovibrational predissociated states using the DPO-DVR method. The energies and widths (respectively the real and the imaginary parts of the resonance) of predissociated states of diatomic molecules are straightforwardly obtained by using the negative imaginary potential (or absorbing boundary condition) method (see (Jolicard and Austin 1985, Jolicard and Humbert 1987, Jolicard *et al* 1988, Monnerville and Robbe 1994, Prudente *et al* 1997, Monnerville and Robbe 1999) and references therein). We are interested to understand the convergence of these states with the DPO-DVR method. Moreover, a numerical comparison of the DPO-DVR with other types of mapped grids as the ones cited in the introduction can be instructive, and we plan to make it in the near future.

Acknowledgments

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