Rotational predissociation of strongly anisotropic van der Waals complexes: The He-CO example

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A very accurate method is applied, within the theoretical framework of the scattering close-coupling equations, to treat rotational predissociation processes in the He-CO van der Waals molecule. The method was already employed successfully to study vibrational predissociation of the He- I_2^* complexes and shows in the present case significant differences with several approximate methods used to estimate resonance positions. The physical implications of such differences are analyzed and discussed.

I. INTRODUCTION

The nature of the vibrationally and rotationally predissociating states of atom-diatom van der Waals (vdW) molecules has been the subject of a great deal of research in the last few years,¹ as the behavior of these systems carries great relevance in several apparently unrelated areas like the physics and chemistry of molecular interactions, the efficiency of collisional rotational, vibrational, and rovibrational translational energy transfers, and the kinetics of formation of stable dimers in interstellar clouds.

When one of the monomers in a vdW molecule is vibrationally or rotationally excited, the energy thus "stored" in that monomer is frequently larger than the dissociation energy of the vdW bond. The complex can therefore predissociate and the resultant reduction in the lifetime of the excited state leads to observable broadening of spectroscopic lines.² The predissociation phenomenon can thus be viewed as a simple unimolecular reaction along the vdW bond, with the vdW molecule representing an activated molecule that is capable of fragmenting to form products with several different possible internal states.

This aspect of the process obviously is directly related to the nature of the multidimensional potential-energy surface (PES) which is driving the motion of the relevant nuclei and which is added "locally" to the relative kinetic energies of the partners at each geometry.³ In other words, the individual probabilities for each of the final channels to be populated during the predissociative breakup are ultimately related to the couplings that act, while the particles are together, between the motion along the dissociation path (i.e., the vdW bond) and the internal motion of the "other" atoms which pertain to one of the monomers.⁴ The resonant nature of the predissociations discussed here, on the other hand, is also very reminiscent of what happens when a molecule (or atom) collides with another molecule (e.g., the simplest diatom) and translational energy can flow into the internal degrees of freedom of the target, thus defining the relative efficiency of rota-

tionally and/or vibrationally inelastic processes.^{5,6}

This all means, then, that a close examination of rotational and/or vibrational predissociation in a vdW molecule requires to put together our best knowledge of the anisotropic interaction between monomers and our most accurate methods that deal with rotational- and vibrational-translational collisional energy transfers. The latter processes, in fact, involve coupling between the same initial and final-state channels as in the former, but they differ from each other in that the inelastic processes must occur at energies above the appropriate internal motion excitation threshold and are observed in molecular beams experiments,⁵ while predissociation usually occurs at energies below this threshold and is observed spectroscopically. That information on one type of phenomenon can help to shed light on the nature of the other type which will be the subject of the present work.

The most intensively studied vdW molecules have involved H_2 as one partner and an inert gas as the other⁷⁻⁹ and have provided us with a very accurate knowledge of both the PES and the coupling mechanism that leads to predissociation. Hydrogen-halide-rare-gas complexes have also been analyzed rather in detail¹⁰⁻¹² since the anisotropy of their interactions, obviously quite different from that of the hydrogen molecule case, has been obtained accurately enough from the analysis of several experimental data.

In the last few years, however, an iterative analysis of several experimental observables has allowed us to obtain very realistic forms of the full PES for other more complicated molecules also interacting with rare gases,¹³⁻¹⁵ and therefore a different class of vdW molecules can be in principle analyzed by making use of their known anisotropies. Due to the many-electron nature of the diatomic monomers (N_2 , O_2 , and CO) their interaction with rare gases turns out to be much more anisotropic than for H_2 thus bringing in the effect of potential coupling in a very different way from that shown in, say, H_2 -Ar complexes.¹⁶ Moreover, the homonuclear (or nearly homonuclear) structure of these monomers, as opposed to the hydrogen

halides, causes the rotational torque within the excited vdW molecule to be different than in HF and HCl complexes, and therefore provides another interesting new element to be studied.

In Sec. II we present the different ways in which the simpler predissociation mechanism, i.e., the rotational one, can be studied in the present systems by stressing different aspects of the dynamical interaction. Section III carries out a discussion of our computational results and the conclusions that can be drawn from them.

II. THE DYNAMICAL MODELS

A. The Hamiltonian system

After separation of the center of mass of the whole system, the Hamiltonian for the nuclear motion of an $X-AB$ (rigid-rotor) triatomic molecule may be written as

$$H = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{I^2}{2\mu R^2} + B_e j^2 + V(R, \theta), \quad (1)$$

where R is the distance between the atom and the diatomic center of mass, μ is the atom-diatom reduced mass, and θ is the relative orientation between both subunits. Here j and I are angular momentum operators associated with the diatomic rotation (with rotational constant B_e) and the centrifugal rotation, respectively, while V describes the weak interaction and its full anisotropic features as a function of the vdW coordinate.

B. The scattering equations

In the space-fixed representation, the wave function may be expanded as

$$\Psi^{J(p)M}(\mathbf{R}, \hat{\mathbf{r}}; E) = \sum_{\alpha} \chi_{\alpha}^{J(p)}(R; E) \gamma_{\alpha}^{J(p)M}(\hat{\mathbf{R}}, \hat{\mathbf{r}}), \quad (2)$$

where $J(p)$ and M are quantum numbers associated with the total angular momentum $\mathbf{J} = \mathbf{j} + \mathbf{I}$ and its third component, respectively; $p = (-1)^{(J+j+l)}$ is the parity index; $\hat{\mathbf{r}}$ is the rotor orientation, E is the total energy, the χ are the radial channel wave functions, and the γ are a complete orthonormal set of angular basis functions, depending on $\hat{\mathbf{r}}$ and $\hat{\mathbf{R}}$, the atom-diatom orientation; $\alpha = (j, l)$ collects the quantum numbers j and l associated with the operators j and I , respectively. Representing the Hamiltonian (1) in the γ basis, the Schrödinger equation leads to the following system of coupled equations for the χ functions:¹⁷⁻¹⁹

$$\left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + V_{\alpha\alpha}^{J(p)}(R) - E \right] \chi_{\alpha}^{J(p)}(R; E) = - \sum_{\substack{\alpha, \alpha' \\ (\alpha' \neq \alpha)}} V_{\alpha\alpha'}^{J(p)}(R) \chi_{\alpha'}^{J(p)}(R; E), \quad (3)$$

where the $V_{\alpha\alpha'}^{J(p)}(R)$ functions are defined by

$$V_{\alpha\alpha'}^{J(p)}(R) = \left\langle \gamma_{\alpha}^{J(p)M} \left| \left[\frac{I^2}{2\mu R^2} + B_e j^2 + V(R, \theta) \right] \right| \gamma_{\alpha'}^{J(p)M} \right\rangle. \quad (4)$$

The usual boundary conditions for the χ functions allow one to get the relevant S matrix by solving the system of

equations (3) through some standard numerical procedure.^{19,20}

C. The scattering resonances

For isolated resonances,²⁰ the S matrix in the neighborhood of one of them may be expressed as²¹

$$\underline{S}(E) = \underline{S}_{bg}(E) \left[\underline{1} - \frac{i\underline{A}}{E - \bar{E} + i\Gamma/2} \right], \quad (5)$$

where $\underline{S}_{bg}$ is the background S matrix, i.e., that obtained in the absence of the resonance, $\bar{E}$ and Γ are the position and width of the resonance and may be considered as energy independent. The matrix $\underline{A}$ is a complex matrix that can be written as²⁰

$$\underline{A} = \mathbf{g} \cdot \mathbf{g}^{\dagger}, \quad (6)$$

where $\mathbf{g}$ is a complex vector that fulfills the condition

$$\sum_{i=1}^N |g_i|^2 = \Gamma \quad (7)$$

and has as many components as N , the number of open channels at the energy E considered.

We now define two energy-dependent real functions

$$\mathcal{R}(E) = \sum_{k=1}^N \text{Re}\{[\underline{S}_{bg}^{\dagger}(E)\underline{S}(E)]_{kk}\}, \quad (8a)$$

$$\mathcal{J}(E) = \sum_{k=1}^N \text{Im}\{[\underline{S}_{bg}^{\dagger}(E)\underline{S}(E)]_{kk}\}, \quad (8b)$$

where $\text{Re}\{z\}$ is the real part of the complex quantity z , with $\text{Im}\{z\}$ being its imaginary part; $\underline{S}_{bg}^{\dagger}$ is the adjoint matrix of $\underline{S}_{bg}$, i.e., its transposed and conjugate. Taking into account that $\underline{S}$ and $\underline{S}_{bg}$ are unitary matrices, the $\mathcal{R}$ and $\mathcal{J}$ functions assume the well-known Lorentzian expressions^{22,23}

$$\mathcal{R}(E) = N \frac{\Gamma^2/2}{(E - \bar{E})^2 + \Gamma^2/4}, \quad (9a)$$

$$\mathcal{J}(E) = - \frac{\Gamma(E - \bar{E})}{(E - \bar{E})^2 + \Gamma^2/4}, \quad (9b)$$

from which it becomes straightforward to calculate the relevant quantities E and Γ . For $E = \bar{E}$, we have, in fact, that

$$\mathcal{R}(\bar{E}) = N - 2 \quad \text{and} \quad \mathcal{J}(\bar{E}) = 0, \quad (10)$$

while for $E = \bar{E} \pm \Gamma/2$,

$$\mathcal{R}(\bar{E} \pm \Gamma/2) = N - 1, \quad (11)$$

and $\mathcal{J}(\bar{E} \pm \Gamma/2)$ is an extremum. Numerically, the S matrix corresponds to a convergent close-coupling calculation while the $\underline{S}_{bg}$ is obtained as the scattering matrix in an artificial calculation in which the closed channel that supports the resonance is neglected. Any departure from the predicted behavior of the $\mathcal{R}$ and $\mathcal{J}$ functions as given by Eqs. (9) must be attributed to a failure of the “isolated narrow resonances” approximation or of the assumption concerning the $\underline{S}_{bg}$ calculations. Since this method implies two scattering calculations at each sampled energy, it

becomes useful to devise realistic ways to know the approximate positions of the resonances.

D. The approximate resonance energies

The resonance energies in a molecular system correspond to eigenstates in the discrete subspace of the closed channels, but may be shifted from discrete levels due to discrete-continuum and continuum-continuum interactions.²⁴ Such couplings are often small and thus the eigenvalues of the Hamiltonian are close to the resonance energies. In order to get these eigenvalues we use a variational procedure where the eigenfunctions are expanded as linear combinations of chosen basis functions. The selection of the basis set is usually very important. In the following we describe four methods to generate discrete eigenvalues of the Hamiltonian (1) and the corresponding eigenfunctions that could be used as basis sets.

1. The diabatic rotational method

This method was proposed by Beswick *et al.*²⁴ and was numerically applied by us to various systems.^{12,25} It assumes that all nondiagonal $V_{\alpha\alpha'}$ elements in Eq. (3) are to be equal to zero and solves for each α channel the following equation:

$$\left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + V_{\alpha\alpha}^{J(p)}(R) \right] \chi_{\alpha}^{J(p)}(R; E_{\alpha k_{\alpha}}) = E_{\alpha k_{\alpha}} \chi_{\alpha}^{J(p)}(R; E_{\alpha k_{\alpha}}), \quad (12)$$

$$H_{\alpha k_{\alpha}; \alpha' k_{\alpha'}}^{J(p)M} = \langle \Psi_{\alpha k_{\alpha}}^{J(p)M} | H | \Psi_{\alpha' k_{\alpha'}}^{J(p)M} \rangle = E_{\alpha k_{\alpha}} \delta_{\alpha\alpha'} \delta_{k_{\alpha} k_{\alpha'}} + \langle \chi_{\alpha}^{J(p)}(R; E_{\alpha k_{\alpha}}) | V_{\alpha\alpha'}^{J(p)}(R) | \chi_{\alpha'}^{J(p)}(R; E_{\alpha' k_{\alpha'}}) \rangle (1 - \delta_{\alpha\alpha'}). \quad (15)$$

In the He-CO system, the double expansion (14) reduces to a few α values because the $V_{\alpha\alpha}$ potentials turn out to support discrete levels only for the lower-lying rotational excitations of the isolated diatom. Moreover, when they do have bound states only one level is found, i.e., $k_{\alpha} = 1$. Hence, the interaction of configurations becomes poor, and the corresponding results are expected to be close to those of the diabatic rotational method.

3. The full diabatic rotational plus configuration-interaction (FDCI) method

Assuming the discrete subspace to be the product of the radial subspace times the angular subspace, we can rewrite the wave function as follows:

$$\Phi_n^{J(p)M}(\mathbf{R}, \hat{\mathbf{r}}) = \sum_{\alpha, q} b_{\alpha q}^{(n)} \phi_q^{J(p)}(R) \gamma_{\alpha}^{J(p)M}(\hat{\mathbf{R}}, \hat{\mathbf{r}}), \quad (16)$$

where the summation extends over the previously discussed channel index α ; the new index q now represents the number of radial basis needed to achieve convergence

where k_{α} is the quantum number associated with stretching in the van der Waals bond. In this approximation the wave function is written as a simple product:

$$\Psi_{\alpha k_{\alpha}}^{J(p)M}(\mathbf{R}, \hat{\mathbf{r}}) = \chi_{\alpha}^{J(p)}(R; E_{\alpha k_{\alpha}}) \gamma_{\alpha}^{J(p)M}(\hat{\mathbf{R}}, \hat{\mathbf{r}}). \quad (13)$$

Since asymptotically the quantum number $|j\rangle$ becomes a good one, this method may provide accurate energies when the diatomic rotational spacing is large and the off-diagonal couplings $V_{\alpha\alpha'}$ are small compared to the diagonal elements $V_{\alpha\alpha}$. This is not the case for the He-CO system and therefore this method, as we shall see below, is not likely to yield accurate estimates of the resonance energies.

2. The diabatic rotational plus configuration-interaction method (DCI)

We can try to relax the above assumption by allowing the interaction among the eigenstates previously obtained to be switched on. In this way we write the wave functions as

$$\Psi_n^{J(p)M}(\mathbf{R}, \hat{\mathbf{r}}) = \sum_{\alpha, k_{\alpha}} \alpha_{\alpha k_{\alpha}}^{(n)} \chi_{\alpha}^{J(p)}(R; E_{\alpha k_{\alpha}}) \gamma_{\alpha}^{J(p)M}(\hat{\mathbf{R}}, \hat{\mathbf{r}}), \quad (14)$$

where the summation extends over all the bound states supported by each channel potential α given by the earlier Eq. (4). In principle the problem can now be solved by diagonalizing the matrix that represents the Hamiltonian (1) in the basis of the $\Psi_{\alpha k_{\alpha}}^{J(p)M}$ functions of Eq. (13), i.e.,

in the wave function expansion of Eq. (16), where now the radial basis $\{\phi_q\}$ is obtained after an orthonormalization of the previous functions χ , i.e.,

$$\phi_q^{J(p)}(R) = \sum_{\alpha', k'_{\alpha'}} \beta_{\alpha' k'_{\alpha'}}^{(q)} \chi_{\alpha'}^{J(p)}(R; E_{\alpha' k'_{\alpha'}}). \quad (17)$$

Here α goes from $\alpha = 1$ to $\alpha = \alpha_{\max}$, with $\alpha_{\max}$ being the highest body-fixed state supported by the potential. The k_{α} index labels the stretching bound states. The problem is reduced once more to diagonalizing the following matrix:

$$H_{\alpha q; \alpha' q'}^{J(p)M} = \left\langle \phi_q^{J(p)}(R) \left| -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} \right| \phi_{q'}^{J(p)}(R) \right\rangle \delta_{\alpha\alpha'} + \langle \phi_q^{J(p)}(R) | V_{\alpha\alpha'}^{J(p)}(R) | \phi_{q'}^{J(p)}(R) \rangle. \quad (18)$$

From Eqs. (17) and (12), the integral involving the kinetic energy may be evaluated as follows:

$$\left\langle \phi_q^{J(p)} \left| -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} \right| \phi_{q'}^{J(p)} \right\rangle = \sum_{\alpha, k_{\alpha}, \alpha', k'_{\alpha'}} \beta_{\alpha k_{\alpha}}^{(q)} \beta_{\alpha' k'_{\alpha'}}^{(q')} [E_{\alpha' k'_{\alpha'}} \langle \chi_{\alpha}^{J(p)}(R; E_{\alpha k_{\alpha}}) | \chi_{\alpha'}^{J(p)}(R; E_{\alpha' k'_{\alpha'}}) \rangle - \langle \chi_{\alpha}^{J(p)}(R; E_{\alpha k_{\alpha}}) | V_{\alpha\alpha'}^{J(p)} | \chi_{\alpha'}^{J(p)}(R; E_{\alpha' k'_{\alpha'}}) \rangle]. \quad (19)$$

This method may be expected to yield more accurate results than the previous ones, since bound states are here obtained from an improved coupling. On the other hand, its success strongly depends on the quality of the original χ functions employed to describe motion along the vdW vibrational coordinate.

4. The angular adapted FDCI (AAFDCI) method

The FDCI method starts with diabatic radial functions to get the orthonormal radial basis set. We can thus search for more suitable basis functions and then repeat the procedure as already described in Sec. II D 3. The He-CO system presents some features that may make more efficient the use of an adiabatic angular approximation. So, from potential surfaces available in the literature²⁶ we estimated, through the isotropic part, than an approximate stretching frequency of the van der Waals bond could be in the range of $14 \leq \omega_e \leq 25 \text{ cm}^{-1}$ while the rotational constants associated to the isolated diatomic rotation and to the centrifugal motion are 1.93 cm^{-1} and $\sim 0.30 \text{ cm}^{-1}$, respectively. Hence, by fixing the angle θ

in the range $[0, \pi]$ we could choose as radial functions the solutions of the following angle-dependent equation:

$$\left[\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + V(R, \theta_l) \right] \Psi_{k_l}(R; \theta_l) = E_{k_l}(\theta_l) \Psi_{k_l}(R; \theta_l), \quad (20)$$

where the index l spans the minimum number of angles which are needed to achieve a predecided level of convergence in Eq. (21)

The total wave function can be written as in Eq. (16) but now its ϕ_q radial functions are given by

$$\phi_q^{J(p)}(R) = \sum_{l, k_l} c_{l, k_l}^{(q)} \Psi_{k_l}(R; \theta_l), \quad (21)$$

the index l spans the angular values included and k_l the corresponding stretching quantum number to which that θ_l corresponds. The matrix to be diagonalized has therefore the same formal expression as that given by Eq. (18), but now the kinetic energy operator is given by the equation

$$\left\langle \phi_q^{J(p)} \left| -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} \right| \phi_q^{J(p)} \right\rangle = \sum_{l, k_l, l', k_{l'}} c_{l, k_l}^{(q)} c_{l', k_{l'}}^{(q')} [E_{k_{l'}}(\theta_{l'}) \langle \Psi_{k_l}(R; \theta_l) | \Psi_{k_{l'}}(R; \theta_{l'}) \rangle - \langle \Psi_{k_l}(R; \theta_l) | V(R; \theta_{l'}) | \Psi_{k_{l'}}(R; \theta_{l'}) \rangle], \quad (22)$$

where the meaning of symbols and indexes is the same as that discussed for Eqs. (20) and (21).

In order to examine the convergence of the angular expansion (21) with the basis size we have considered firstly three angles equally spaced in the range $[0, \pi]$, then five angles, then nine angles, and so on. In this way, each calculation includes the functions of the previous calculation. The number of angles which turned out to be necessary to achieve convergence for the present system was nine.

III. COMPUTATIONAL RESULTS AND DISCUSSION

We have employed in the present calculations the potential-energy surface called (IV) in the work of Thomas *et al.*²⁵ As usual, the potential was expanded in Legendre polynomials up to seven terms

$$V(R; \theta) = \sum_{\lambda=0}^6 V_{\lambda}(R) P_{\lambda}(\cos \theta). \quad (23)$$

Using spline interpolations and extensions of the C_6, C_8 coefficients, a total number of 1700 points in the range of distances $[3-87.95] \text{ a.u.}$ were considered to describe each V_{λ} term. An equilibrium distance for the CO bond $r_e = 1.128 \text{ \AA}$ was assumed, leading to a rotational constant $B_e = 1.931 \text{ cm}^{-1}$. This potential exhibits a great anisotropy that changes rapidly with the orientation θ and equilibrium configuration appears at about $\theta = \pi$, i.e., in the collinear geometry He-CO as it is to be expected from the anisotropic polarizability of CO. The isotropic part of the potential V_0 has a well depth $D_0 \approx 2.5 \text{ cm}^{-1}$ and an equilibrium distance $\bar{R}_0 \sim 7.5 \text{ a.u.}$ For the next anisotropic

ic coefficients of Eq. (23) the corresponding quantities are $D_1 \sim D_2 \sim 2.5 \text{ cm}^{-1}$ and $\bar{R}_1 \sim \bar{R}_2 \sim 8.5 \text{ a.u.}$, in such a way that at $\bar{R}_0$ the V_1 and V_2 terms are of the same order of magnitude as V_0 , but with opposite sign. This fact accounts for the anisotropy of this system, and a large dynamical coupling between rotations and van der Waals stretching motion may be expected. For $\lambda \geq 3$, the corresponding V_{λ} terms are increasingly less important.

This behavior is clearly demonstrated by the relative

FIG. 1. Diabatic potential curves for off-diagonal couplings between CO rotational states. The index j labels the molecular rotor states while Ω is the “tumbling” angular momentum quantum number.

TABLE I. Energy levels (cm^{-1}) of bound and metastable states in He-CO system for a total angular momentum $J=0$. The energy reference level is chosen to be that of the asymptotic rotor with $j=0$.

j	D	DCI	FDCI	AAFDCI	Exact
0	-2.268	-2.295	-3.331	-3.560	
1	2.212	2.226	1.410	1.094	0.939
2	10.830	10.843	10.208	9.079	9.037
3			22.817	23.149	22.440

strengths of the diabatic radial potentials of Eq. (12) which couple different diatomic rotor states via the lower multipolar coefficients of Eq. (23). Within the body-fixed (BF) representation of the coupled angular momenta,¹⁹ they indicate the off-diagonal elements that allow for the mixing of isolated rotor states due to the full anisotropic interaction with the third body.¹² For the present system they are shown in Fig. 1 for the $\Omega=0$ value and for the lowest three rotational states of the CO molecule. The helicity index Ω is defined as usual to be the eigenvalue of the corresponding operator $\Omega \equiv \hat{\mathbf{R}} \cdot \mathbf{J} = \hat{\mathbf{R}} \cdot \mathbf{j}$.

One easily sees that, around the well position, the couplings between $|0\rangle$ and $|1\rangle$ rotor states and between $|0\rangle$ and $|2\rangle$ rotor states are rather comparable. As they originate mostly from the direct terms $V_{\lambda=1}(R)$ and $V_{\lambda=2}(R)$ in the potential expansion (23), they confirm the qualitative findings obtained above by simple inspection of the relative behavior of the V_{λ} 's. They also tell us that in the full collision situation (free-free transitions) rotationally inelastic cross sections for the present system are likely to be relatively large, with $\Delta j=1$ and $\Delta j=2$ transitions being fairly comparable with each other. This was in fact the result of previous computations^{26,27} of collisional (R, T) energy transfers.

For the total angular momentum $J=0$, we present in Table I the energies obtained through the diabatic rota-

tional (D), DCI, FDCI, and AAFDCI methods, together with the exact resonance energies computed by the method described in Sec. II C. The reference energy level (chosen zero of energy) is the asymptotic rotor state with $j=0$. The negative energies correspond to true bound states of the triatomic system with respect to the same reference level. The far left column of the table reports the j value which accounts for the (dominant) diatomic rotational state within the complex at the energies considered here. In the diabatic picture, only one level is supported by the interaction with rotor states up to $j=2$. For higher rotational excitations bound levels do not appear any more. As compared with the exact energies, the diabatic values overestimate them by $\sim 1-2 \text{ cm}^{-1}$, and for $j=3$ no resonant level is found by the latter model. Because of the limited quality of the basis that can be used here, the DCI method does not provide significant changes with respect to the results of the simpler diabatic picture. However, a qualitative, and also quantitative improvement is found by the FDCI method, as the latter model leads to a lower ground energy and accounts for the $j=3$ level resonance. However, despite the $j=2$ level being lowered by an amount of $\sim 0.60 \text{ cm}^{-1}$, it is still overestimated by $\sim 1.2 \text{ cm}^{-1}$. Because the radial basis functions are here better suited to the physical characteristic of the system, the AAFDCI results agree much better

FIG. 2. Computed mixed S matrix (real part and imaginary part) in the region of the resonance below the $j=1$ rotational threshold. The two cases of $J=0$ and $J=1$ are shown.

FIG. 3. Same as Fig. 2 but for the collision energy region below the $j=2$ threshold. Two values 0 and 1 of total angular momentum are shown.

than the previous ones with the exact energies. The values shown correspond to a calculation including nine angles in the range $[0, \pi]$. For $j=0, 1$, and 2 , the energies showed a clear convergent behavior when going from three to five and then to nine angles. This was not the case for the $j=3$ level that behaved in oscillatory manner as the angle was changed. Therefore, it is not surprising that its accuracy turns out to be worse for this last resonance than that obtained by the FDCI method.

It is of interest to examine the behavior of the resonances shown by this system when the rigorous coupled equations of Sec. II C are employed to obtain them. Figure 2 reports in fact the shapes, as function of collision

energy, of the $\mathcal{R}$ function ("real part" in the figure) and the $\mathcal{I}$ function ("imaginary part" in the figure) for the total angular momentum values of $J=0$ and 1 . The energy range spans here the lowest resonance, where the dissociating partners leave CO in its $j=0$ rotational state. We can see that, for $J=0$, at the resonance position ($E_r=0.939 \text{ cm}^{-1}$) the $\mathcal{I}$ function goes to zero while the $\mathcal{R}$ function reaches the expected minimum value of -1 , i.e., the number of open channels ($N=1$) minus two, as shown by a previous equation (10). Moreover, the real function $\mathcal{R}$ reaches the value of $N-1$, i.e., of zero, at the same energies as the $\mathcal{I}$ function reaches its extremum and goes to $N=1$ as the energy goes beyond the resonant

FIG. 4. Same as in Figs. 2 and 3 but for the higher collision energy below the $j=3$ rotational state of the CO molecule. The notation is the same as in the previous figures.

value. In the same region, the function $\mathcal{J}$ goes to zero from the negative range, as expected from Eqs. (9a) and (9b). The expected behavior of the above functions is also shown by the case of $J=1(+)$ reported in the same figure.

Figures 3 and 4 exhibit the behavior of the correct functions that describes the resonances for the same total angular momentum values of Fig. 2, but for the dissociative situations with total energy below the $j=2$ state (Fig. 3) and $j=3$ state (Fig. 4) of CO. Because of the increased coupling with the lower-lying continua, one sees in Fig. 3 that the resonance width has increased for the nonrotating complex ($J=0$) and even more so for the rotating complex ($J=1$), where the increased number of coupled states is making the broadening process more effective.

Finally, the next predissociating process shown in Fig. 4 exhibits less markedly the increase in resonance widths shown in the previous case, as it begins to feel direct coupling from only the weaker $\lambda=3$ anisotropic coefficient and therefore predissociating mechanisms have to rely on the less effective indirect coupling with stronger V_1 and V_2 coefficients, as shown by the results of Fig. 1. This behavior is confirmed by the single resonance existing for the rotating complex ($J=1$ case of Fig. 4), where the increase in the number of states is partly offset by the decrease in strength of the coupling potential terms and by the presence of the close by $j=3$ threshold that makes the higher term disappear into the continuum.

Table II collects the calculated values of resonance positions and halfwidths for the $J(P)=0,1(+)$ states examined in the present work. As one goes from $J=0$ to 1, one observes a splitting of the resonances as discussed above and a corresponding increase of their halfwidths due to the increased coupling with other adjacent continua. This more efficient coupling between predissociating levels and the continua from lower-lying states is here an indicator of the more efficient energy transfer process that can occur during full collisions for the present system as mentioned earlier.^{26,27} This means that one might hope to observe experimentally the processes discussed here as their corresponding widths, contrary to what was observed for He-HF (Ref. 12), are now within the range of instrumental detection.²⁸ The "states" omitted in the calculations of the $\underline{S}_{bg}$ matrix elements are, from the top of the table, the values of $j=1,2$, and 3 for the asymptotic rotor states.

It is also worth stressing, however, that the simpler, approximate treatments discussed in Sec. II are useful models even for those cases where they are not expected to

TABLE II. Energies and full widths at half maximum (FWHM) for rotational predissociation in the He-CO system.

$J(p)$	E (cm ⁻¹)	$\Gamma/2$ (cm ⁻¹)	Missing state in
			the $\underline{S}_{bg}$ matrix of Eq. (5)
0(+)	0.939	0.283	1⟩
	9.037	0.690	2⟩
	22.440	0.585	3⟩
1(+)	0.301	0.040	1⟩
	1.818	0.205	1⟩
	8.512	0.580	2⟩
	10.756	0.428	2⟩
	21.059	0.962	3⟩

work, as they provide a simple physical picture which helps to better understand the results obtained from rigorous close-coupling calculations. The D method, for instance, is a reasonable model when off-diagonal coupling is expected to be small and therefore provides a good effective potential under which the vdW vibrational motion can be studied. It also gives a reasonable starting point for both DCI and FDCI approaches, where the full structure of the bound complexes is taken into account to generate radial eigenstates. The DCI model, as a matter of fact, should be a very useful method for systems where the number of diabatic levels supported by the interaction is large enough to ensure a better quality basis when configuration-interaction calculations are performed. Ar-N₂ and Ar-O₂ systems should be of this type and will be discussed elsewhere.²⁹ The FDCI model includes a more efficient representation to describe basis sets and should therefore improve on situations where the D method is already a good starting point. However, it is the AAFDCI that provides the most realistic of the models discussed in the present work. It is the one which yields results that are the closest to close-coupling calculations and it appears to be the best approach to use in complexes where a separation between show rotational motion of part of the system and fast vibrational motion along vdW coordinates may be applicable.

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