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# Interpretation of the predissociation of the CO Rydberg W $^1\Pi$ ( $v = 1$ ) level

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With the goal to interpret the experimental results obtained quite recently by Heays *et al.* [J. Chem. Phys. **141**, 144311 (2014)] on the predissociation of the Rydberg W  $^1\Pi$  ( $v = 1$ ) vibrational level of the CO molecule, we report herein *ab initio* potential energy curves of some of its valence and Rydberg states of both  $^1\Pi$  and  $^3\Pi$  symmetry. Our results confirm that the above vibrational level is perturbed by a new electronic  $^1\Pi$  state not observed until now. They correctly reproduce the linewidths of predissociation of the two interacting levels. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4945117>]

## I. INTRODUCTION

Numerous studies have been performed on the predissociation of several CO states since 2008.<sup>1</sup> It suffices to mention the paper by Visser *et al.*<sup>2</sup> who showed the importance of the predissociation mechanism for the calculation of the self-shielding and the isotope effects of its VUV spectrum. These studies have encouraged high resolution experiments on the predissociation rates of some of its high Rydberg states.<sup>3–5</sup> We have already tried to explain the accidental predissociation of the  $E^1\Pi$  CO state.<sup>6,7</sup>

The W $^1\Pi$  state is a  $3s\sigma$  Rydberg state with an  $A^2\Pi$  CO<sup>+</sup> excited core. The predissociation of its  $v = 0-3$  levels has been recently studied at high resolution using the vacuum ultraviolet Fourier transform spectrometer installed on the DESIRS beamline at the SOLEIL synchrotron. This has been made successively for  $^{12}\text{C}^{16}\text{O}^3$  and for the isotopologues  $^{13}\text{C}^{16}\text{O}$  and  $^{12}\text{C}^{18}\text{O}^4$ . The  $v = 1$  vibrational level is strongly perturbed by a level that is assumed to be the  $v = 0$  level of the  $E'^1\Pi$  adiabatic state.<sup>5</sup> This is the reason we have performed new *ab-initio* calculations of the  $^1\Pi$  states of CO, in order to be able to treat theoretically this predissociation. Also, the indirect role of the triplet states has been questioned in Ref. 5. For this reason, we have also calculated the valence and Rydberg  $^3\Pi$  states.

In Section II we report our computational details along with a discussion on previous theoretical work. The calculated potential energy curves are displayed in Figures 1 and 2. Previous work either did not include any of the Rydberg states<sup>8,9</sup> or did not correctly reproduce their shape.<sup>10</sup> Two valence  $^1\Pi$  states are particularly important for the predissociation mechanism of the Rydberg states, namely, the  $E'$  and  $E''$ ; see Fig. 1. In Section IV, we diabaticize these states and obtain a new curve,  $E'$ , with two minima and a repulsive one,  $R$ . Then after a slight modification of their  $T_e$  for a

better agreement with the experimental results we calculate the predissociation widths of the W  $^1\Pi$  ( $v = 1$ ) level through the coupled channel method.

## II. AB-INITIO CALCULATIONS OF THE POTENTIAL ENERGY CURVES

For both the C and O atoms we have employed the Dunning augmented correlation consistent polarized valence quintuple zeta (aug-cc-pV5Z) basis set (15s9p5d4f3g2h)<sup>11</sup> generally contracted to [7s6p5d4f3g2h] comprising a total of 254 spherical Gaussian functions. Our zeroth order wavefunction is of the complete active space self-consistent field (CASSCF) type and results from the distribution of 8 electrons in the active space of 11 [(2s + 2p + 3s + 3p)<sub>C</sub> + (2p)<sub>O</sub>] orbitals. For the construction of the potential curves that capture both the valence and some of the Rydberg states we have optimized the reference wavefunction within the state average (SA) CASSCF ansatz. Valence correlation (10 electrons) was extracted through single and double excitations out of all configuration functions of the reference space within the internally contracted MRCI scheme as implemented in the MOLPRO 2012.1 program.<sup>12</sup>

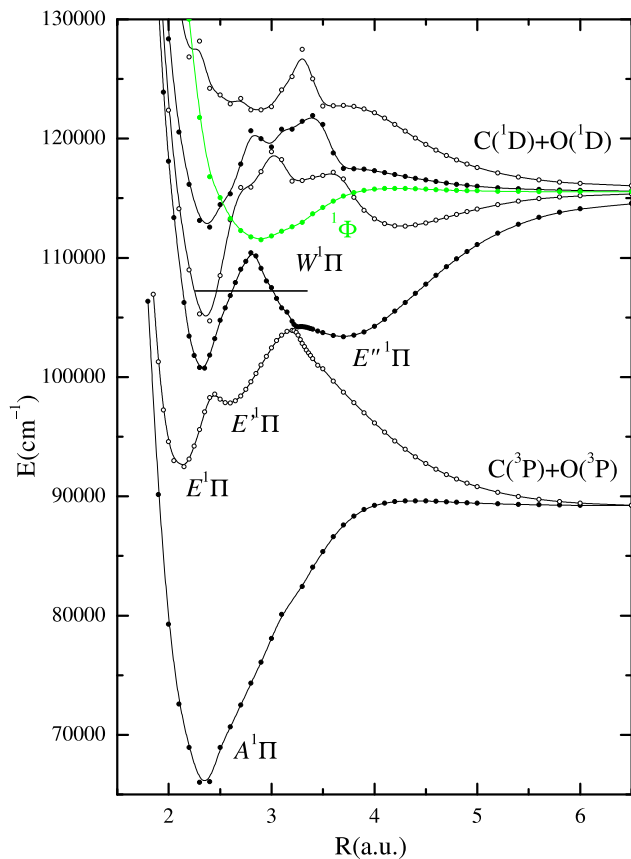
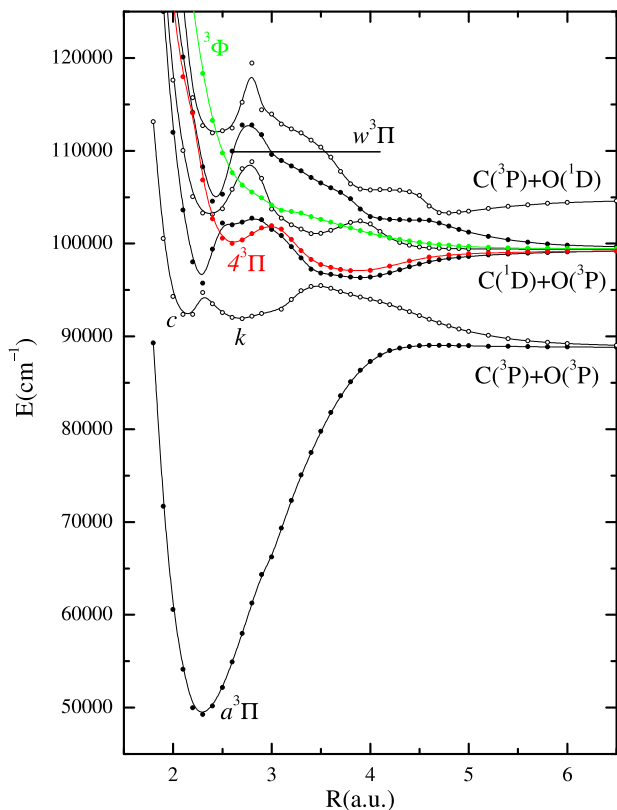
We have calculated the potential energy curves of states of  $^1\Pi$  and  $^3\Pi$  symmetry of both valence and valence/Rydberg character. In particular we have calculated all  $^1\Pi$  states dissociating adiabatically to  $\text{C}(^3P) + \text{O}(^3P)$  and to  $\text{C}(^1D) + \text{O}(^1D)$  (see Fig. 1) and all  $^3\Pi$  states correlating adiabatically to  $\text{C}(^3P) + \text{O}(^3P)$  and to  $\text{C}(^1D) + \text{O}(^3P)$ , and one state arising from  $\text{C}(^3P) + \text{O}(^1D)$  (see Fig. 2).

The second  $^1\Pi$  state dissociating to the ground state fragments displays a double minimum character, the  $E$ (Rydberg) and  $E'$ (valence); see Fig. 1. The lowest  $^1\Pi$  state correlating to  $\text{C}(^1D) + \text{O}(^1D)$  displays a minimum, named  $E''$ , that severely interacts with the  $E/E'$  potential curve.

A similar pattern is shown in Fig. 2 for the triplet states. The second  $^3\Pi$  state dissociating to two ground state fragments displays two minima, the  $c$ (Rydberg) and  $k$ (valence) while a

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FIG. 1. MRCI/aug-cc-pV5Z potential energy curves of  $^1\Pi$  symmetry.FIG. 2. MRCI/aug-cc-pV5Z potential energy curves of  $^3\Pi$  symmetry.TABLE I. Spectroscopic constants of the most relevant  $^{12}\text{C}^{16}\text{O}$  states. For the more perturbed ones,  $T_0$ ,  $R_0$ , and  $\Delta G_0$  are given in square brackets instead of  $T_e$ ,  $R_e$ ,  $\omega_e$ , and  $\omega_e x_e$ .

| State         | $T_e$ (cm $^{-1}$ )    | $\omega_e$ (cm $^{-1}$ ) | $\omega_e x_e$ (cm $^{-1}$ ) | $R_e$ (a.u.) | Reference              |
|---------------|------------------------|--------------------------|------------------------------|--------------|------------------------|
| $X^1\Sigma^+$ | 0.0                    | 2169.8                   | 13.29                        | 2.1322       | Expt. <sup>13</sup>    |
|               | 0.0                    | 2131.0                   | 9.6                          | 2.1399       | This work              |
| $a^3\Pi$      | 48 686.7               | 1738.3                   | 14.25                        | 2.2785       | Expt. <sup>13,14</sup> |
|               | 47 978.0               | 1736.0                   |                              | 2.279        | This work              |
| $A^1\Pi$      | 65 075.8               | 1518.2                   | 19.4                         | 2.3344       | Expt. <sup>13</sup>    |
|               | 64 415.0               | 1489.0                   | 12.1                         | 2.3409       | This work              |
| $k^3\Pi$      | 91 012.2               | 805.1                    | -2.85                        | 2.606        | Expt. <sup>15</sup>    |
|               | 90 010.0               | 858.0                    |                              | 2.680        | This work              |
| $c^3\Pi$      | [92 076.9]             | [2190.0]                 |                              | [2.1171]     | Expt. <sup>16</sup>    |
|               | 90 687.0               |                          |                              | 2.15         | This work              |
| $E^1\Pi$      | [92 929.9]             | [2152.9]                 |                              | [2.1205]     | Expt. <sup>17</sup>    |
|               | 93 290.0               | 2154.6                   | 18.9                         | 2.1179       | This work              |
| $E'^1\Pi$     | 98 487.7               | [750.0]                  | ...                          | 2.48         | 10                     |
|               | 100 255.0              | 1116.0                   | 16.99                        | 2.5347       | 9                      |
|               | 101 134.0              | 1049.0                   |                              | 2.558        | This work              |
| $E''^1\Pi$    | 104 640.0 <sup>a</sup> |                          | ...                          | 3.65         | 10                     |
|               | 105 094.0              | 492.0                    | -30.19                       | 3.5965       | 9                      |
|               | 104 694.0              | 685.0                    |                              | 3.67         | This work              |
| $4^3\Pi$      | 100 013.0              | 1259.0                   | 59.97                        | 2.6041       | 9                      |
|               | 100 132.0              | 1258.0                   | 71.2                         | 2.60         | This work              |
| $w^3\Pi$      | 102 999.0              | 2943.0                   | 78.3                         | 2.4          | This work              |
| $W^1\Pi$      | [102 806.7]            | [1770.0]                 |                              | [2.3694]     | Expt. <sup>18,19</sup> |
|               | 103 175.0              | 2235.0                   |                              | 2.366        | This work              |

<sup>a</sup>Deduced from the potential curve.

$4^3\Pi$  state (in red in Fig. 2) of valence character, although it belongs to the lowest  $^3\Pi$  state correlating to  $C(^1D) + O(^3P)$ , is calculated separately than the rest of the states due to technical problems related to the instability of the MCSCF equations, or in other words to the existence of several solutions in the MCSCF variational space. A rather common solution is provided by changing the initial guess of the SCF procedure. Also the  $w^3\Pi$  state (Fig. 2) having the same configuration as the Rydberg  $W^1\Pi$  (Fig. 1) has been considered.

The spectroscopic constants of these calculated states are given in Table I and compared to both the experimental and previous theoretical results.

### III. CALCULATION OF THE PREDISSOCIATION WIDTHS

We have employed the coupled equations method to calculate the predissociation widths. The  $i$ th solution, with energy  $\varepsilon_i$ , is written as

$$\Psi_i(q, R) = \sum_{n=1}^7 \Phi_n^d(q, R) \chi_{n,i}^d(R), \quad (1)$$

where  $q$  stands for the set of electronic coordinates and  $R$  for the internuclear distance.

The diabatic nuclear functions  $\chi_{n,i}^d(R)$  of the seven states presently considered with interactions between the diabatic electronic states denoted  $H_{m,n}^d$  are solutions of the coupled equations,

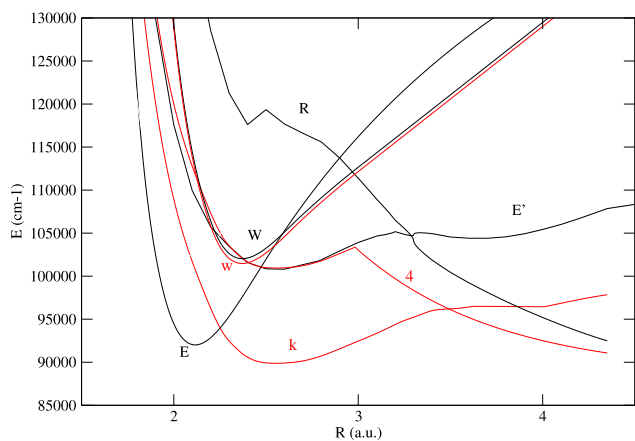


FIG. 3. Semi-empirical curves of  $^1\Pi$  (black line) and  $^3\Pi$  (red line) symmetry used in the coupled equations.

$$\begin{aligned} &[-(\hbar^2/2\mu)\frac{d^2}{dR^2} + V_n^d(R)]\chi_{n,i}^d(R) + \sum_{m \neq n} H_{m,n}^d(R)\chi_{m,i}^d(R) \\ &= \varepsilon_i \chi_{n,i}^d(R) \quad n = 1, \dots, 7 \end{aligned} \quad (2)$$

$\mu$  being the reduced nuclear mass.

The potential curves of the two  $^1\Pi$  Rydberg states,  $E$  and  $W$ , have been taken from Ref. 20 while that of the  $k^3\Pi$  state from Ref. 6. The potential curve of the triplet  $w^3\Pi$  Rydberg state was considered from Ref. 20 with its  $T_e$  lowered by  $441 \text{ cm}^{-1}$ . The  $\text{III}^3\Pi$  repulsive potential curve of Refs. 6 and 7 has been replaced by the  $4^3\Pi$  potential calculated in this work. The two adiabatic curves  $E'$  and  $E''$ , presently computed, have been transformed to two diabatic curves; a new curve ( $E'$ ) with two minima and a repulsive curve ( $R$ ) (see Fig. 3). To obtain a good agreement with the experimental values, we had to slightly modify the *ab initio* potential curves to agree with the observed  $T_v$  values. Especially, the  $E'$  diabatic curve, featuring two minima, which plays an essential role in the predissociation mechanism, has been modified, the first minimum being at  $100\,695 \text{ cm}^{-1}$  for  $R_e = 2.6 \text{ a.u.}$  and the second minimum at  $104\,345 \text{ cm}^{-1}$  for  $R_e = 3.7 \text{ a.u.}$  This value of the first minimum is close to the value suggested by the experiments of Couto *et al.*<sup>21</sup>

The electrostatic interaction determined in Ref. 20, namely, the  $\langle E^1\Pi | H_{el} | E'^1\Pi \rangle = 600 \text{ cm}^{-1}$  has been considered. The spin-orbit interaction between the  $E'^1\Pi$  and the  $k^3\Pi$  states is  $28.21 \text{ cm}^{-1}$ .<sup>6</sup> The coupling between the  $k^3\Pi$  state

TABLE II. Electrostatic and spin-orbit interactions between different CO states.

| Interaction                                 | Value ( $\text{cm}^{-1}$ ) | Reference |
|---|----------------------------|-----------|
| $\langle E^1\Pi   H_{el}   E'^1\Pi \rangle$ | 600                        | 20        |
| $\langle w^3\Pi   H_{el}   4^3\Pi \rangle$  | 1185                       | This work |
| $\langle W^1\Pi   H_{el}   E'^1\Pi \rangle$ | 100                        | This work |
| $\langle W^1\Pi   H_{so}   w^3\Pi \rangle$  | 60                         | This work |
| $\langle E'^1\Pi   H_{el}   R^1\Pi \rangle$ | 300                        | This work |
| $\langle k^3\Pi   H_{so}   E'^1\Pi \rangle$ | 28.21                      | 6         |
| $\langle k^3\Pi   H_{el}   4^3\Pi \rangle$  | 241                        | 6         |
| $\langle 4^3\Pi   H_{so}   E'^1\Pi \rangle$ | 52                         | This work |

TABLE III. Experimental and calculated results for the  $W^1\Pi$  ( $v=1$ ) level and the one of  $E'$  corresponding to the  $E''^1\Pi$  ( $v=0$ ) level of the adiabatic state of  $^{12}\text{C}^{16}\text{O}$  ( $\text{cm}^{-1}$ ).

|                    | $v$     | $T_v$      | $B_v$ | $\Gamma_v^f$   |
|--------------------|---------|------------|-------|----------------|
| Expt. <sup>5</sup> | $E''^0$ | 104 607.1  | 0.69  | 2.46 ( $J=2$ ) |
| Calc.              | $E''^0$ | 104 602.29 | 0.75  | 2.66           |
| Expt. <sup>5</sup> | $W^1$   | 104 578.37 | 1.575 | 1.97           |
| Calc.              | $W^1$   | 104 575.26 | 1.459 | 1.92           |

and the new repulsive  $4^3\Pi$  was considered to be equal to the interaction between  $k$  and the old  $\text{III}^3\Pi$  used in Ref. 6. The spin-orbit coupling between the  $E'^1\Pi/4^3\Pi$  and the  $W/w$  states has been calculated in this work along with the electrostatic interaction between the  $w$  and the  $4^3\Pi$  states. The interaction  $\langle W^1\Pi | H_{el} | E'^1\Pi \rangle = 400 \text{ cm}^{-1}$  calculated in Ref. 20 has been lowered up to  $100 \text{ cm}^{-1}$  in order to obtain the best agreement with the experimental widths. Therefore, the lowering of this interaction improves the results obtained in Ref. 20: the calculated value for  $Wv=1$ , before adjustment, was  $104\,572 \text{ cm}^{-1}$  against  $104\,600 \text{ cm}^{-1}$  in Ref. 20 while the experimental value was  $104\,578 \text{ cm}^{-1}$ . We have added  $\langle R^1\Pi | H_{el} | E'^1\Pi \rangle = 300 \text{ cm}^{-1}$  obtained by diabatization of the  $E'$  and  $E''$  adiabatic curves. All these interactions denoted  $H^d$  in Equation (2) are given in Table II.

In conclusion, it is only the  $E'$  diabatic curve, a part of the  $4^3\Pi$  potential, the energy distance between  $W$  and  $w$  and five of the interactions that have been considered from the current *ab-initio* calculations. Only the interaction between  $W$  and  $E'$  has been slightly varied to obtain the best agreement with the quantitative value of the observed width.

To solve Eq. (2), we apply the Fox-Goodwin propagation scheme<sup>22</sup> with matching of the propagated outward and inward matrices of solutions.<sup>23</sup> The number of integration points has been taken equal to 8001, with a grid extending from  $R_{\min} = 1.65 \text{ a.u.}$  to  $R_{\max} = 7.05 \text{ a.u.}$

An external complex scaling<sup>24</sup> of the coordinates of all potentials and interactions in the asymptotic region allows the use of the same boundary conditions for resonance and bound

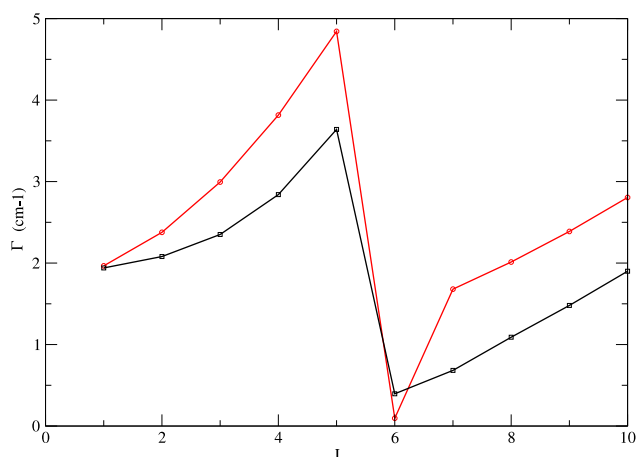


FIG. 4. Variation of the width of  $W(v=1)$  with  $J$ , red line: expt.,<sup>5</sup> black line: calc., this work.

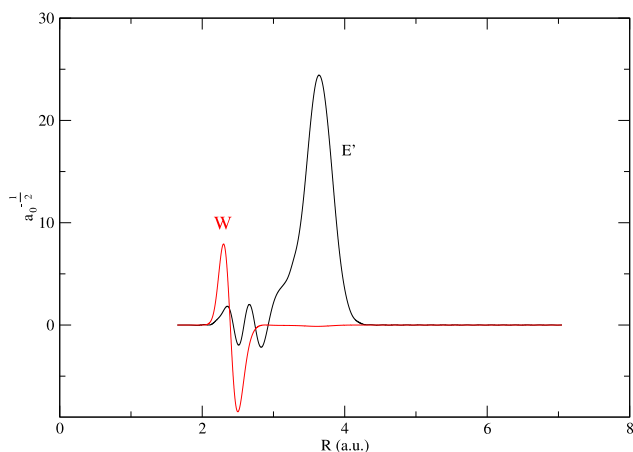


FIG. 5. Vibrational components of the  $W(v=1)$  (red line) and  $E'$  channels (black line) for  $J=1$ ; the latter being similar to the  $E''(v=0)$  level ( $T_v = 104\,602\text{ cm}^{-1}$ ).

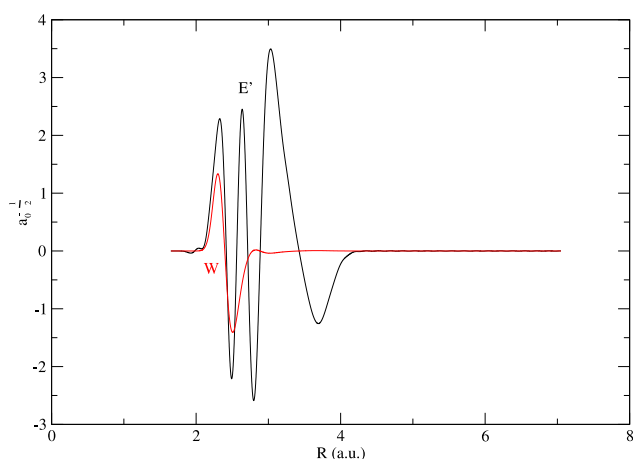


FIG. 6. Vibrational components of the  $W(v=1)$  (red line) and  $E'$  channels for the diabatic level  $E'(v=5, J=1)$  ( $T_v = 104\,693\text{ cm}^{-1}$ ).

states.<sup>25</sup> The resonance widths  $\Gamma$  are given by  $-2I_m(\varepsilon_{i,n})$ . The results are given in Table III.

#### IV. RESULTS

We have been able to reproduce the width variation of the  $v=1$  level of the  $W^1\Pi$  state (Fig. 4) by just making an adjustment of the vertical  $T_e$  values in order to reproduce the best experimental energy distance and energy values between  $W$  and  $E'$ . Then by a slight variation of the electrostatic interaction between  $W$  and  $E'$ , we have obtained the best value for the width of the  $W(v=1)$  level. This width is due to the interaction with all the levels of the  $E'$  diabatic curve featuring two minima. The largest mixing of the  $W(v=1)$  (20%) is with a level of  $E'$  corresponding mainly to the level  $v=0$  of the adiabatic curve  $E''$ ; see Fig. 5. It is this level that cuts experimentally the  $W(v=1)$  level. There is another level of the  $E'$  diabatic state weakly interacting with  $W(v=1)$  and it is mainly represented by its  $v=5$  level (see Fig. 6). Situated at  $104\,693.5\text{ cm}^{-1}$  and with a width of  $11\text{ cm}^{-1}$ , it

could correspond to the level observed by Heays *et al.*<sup>5</sup> at  $104\,545\text{ cm}^{-1}$  with a width of  $8\text{ cm}^{-1}$  for the  $^{13}\text{C}^{18}\text{O}$  isotope and attributed by them to a level of their  $E'$  adiabatic curve.

#### V. CONCLUSIONS

We think that we have successfully accounted for the predissociation of  $W(v=1)$  level observed experimentally by Heays *et al.*<sup>5</sup> by our theoretical calculations. We plan to apply our method to calculate the predissociation widths of other vibrational levels of both the  $W$  and  $L^1\Pi$  states. This will permit us to interpret the results of the branching ratios observed recently by Gao *et al.*<sup>26–28</sup>

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