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Note: Calculation of the branching ratios for the predissociation of the Rydberg CO $W^1\Pi(v=1)$ level

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In our previous paper,[1] we have succeeded in reproducing the experimental predissociation width of the $v = 1$ level of the $W^1\Pi$ CO state, a Rydberg state that converges to $A^2\Pi$ of the CO^+ cationic system and observed by Heays *et al.*[2] This has been accomplished by solving a system of seven coupled equations. The only problem to be solved was the calculation of the predissociation branching ratios observed by Gao *et al.*[3]

In order to evaluate the partial widths, Γ_j, of the jth dissociation channel, we have employed the method due to Humblet and Rosenfeld.[4] We apply their formalism to the adiabatic nuclear wave functions ξ_j which are written as

$$\xi_j(R) = \sum_n c_{nj}(R)\chi_n^d(R), \tag{1}$$

where the c_{nj} are the components of the eigenvectors of the potential matrix and χ_n^d the diabatic nuclear functions. Provided that the non-adiabatic couplings are vanishingly small in the asymptotic region, the total width is given by

$$\Gamma = \sum_j \Gamma_j, \tag{2}$$

where

$$\Gamma_j = (\mu^{-1})\frac{Im(\xi_j(R)^*\xi_j'(R))}{\sum_i \int_0^R dR'|\xi_i(R')|^2} \tag{3}$$

and μ is the reduced nuclear mass.

Although both numerator and denominator are R-dependent, their ratio is R-independent; see Refs. 4 and 5.

The seven potentials of the coupled equations are as follows: the potential curves of the two $^1\Pi$ Rydberg E and W states are the empirical curves of Ref. 6 fitted to reproduce correctly the experimental vibrational energies. That of the $w^3\Pi$ Rydberg state, which has the same dominant configuration as the $W^1\Pi$ state, has been taken parallel to the empirical $W^1\Pi$ state and lowered by 441 cm^{-1}, a value taken from the energy difference of the two *ab initio* $W^1\Pi$ and $w^3\Pi$ potential curves. The $k^3\Pi$ valence state has been empirically adjusted in order to agree with experiment; see Ref. 7. The potentials of the $4^3\Pi$, the R, and $E'^1\Pi$ valence states are taken from the *ab initio* calculations of Ref. 1.

Usually (see, e.g., Table 5.4 of Ref. 8), the electrostatic couplings are evaluated at the position of the avoided crossing between the Rydberg and valence adiabatic potential curves (see Table I for numerical values of the R distance). The invariance with R has been checked in the study of the predissociation of the $^3\Pi_u$ states of N_2 (Ref. 9) where it has not been possible to determine significant R-dependence during the fitting procedure.

The R-dependence of the diagonal spin-orbit of the $k^3\Pi$ state is found to be relatively weak.[7] Its value is that of the equilibrium value R_e of the k state. The calculated spin-orbit interaction between $4^3\Pi$ and $E'^1\Pi$ is approximated by this diagonal spin-orbit term.

From Fig. 3 of our previous paper,[1] after adiabatization of the potential curves (see also Figs. 1 and 2), it can be seen that the $k^3\Pi$ and $R^1\Pi$ states correlate to the $C(^3P) + O(^3P)$ channel whereas the $4^3\Pi$ state dissociates to the $C(^1D) + O(^3P)$ asymptote. The other triplet states are not considered in the calculation since they do not interact with the $W^1\Pi$ state. With the parameters given in our previous study,[1] only 2% of the predissociation width appears in the $C(^1D) + O(^3P)$ channel.

In conformity with the suggestion by Gao *et al.*,[3] we have thought that the electrostatic coupling between the k and $4^3\Pi$ triplet states could play a fundamental role. It appears that the minimum interval between these two adiabatic curves was very different in the calculation of Vázquez *et al.*[10] (650 cm^{-1}) and the more recent ones; see our latest paper[1] and the one by Guberman.[11] Consequently after a long trial and error study, we have ended up with the value of 941 cm^{-1} which is also compatible with the new *ab initio* potential curves. Two other interaction terms have been modified with their numerical values given in Table I. The parameter $\langle W^1\Pi|H_{so}|w^3\Pi\rangle$ has been slightly modified from the value of 40 cm^{-1} to the value of 30 cm^{-1} (there is a misprint in Table I of Ref. 1: the value was 40 cm^{-1} and not 60 cm^{-1}). The value of the parameter $\langle w^3\Pi|H_{el.}|4^3\Pi\rangle$ has been drastically changed from 1185 to 685 cm^{-1} but this modification resulted in a very weak change of only 3% on the branching ratios. With this new set of parameters, we have obtained the same results with regard to the predissociation width of the $v = 1$ level and its variation with the rotational number J, but the branching ratios are now

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TABLE I. Electrostatic and spin-orbit interactions between the Π states of CO.

Interaction	R (a.u.)	Value (cm^{-1})	Reference
$\langle E^1\Pi \vert H_{el.} \vert E'^1\Pi\rangle$	2.47	600	1
$\langle w^3\Pi \vert H_{el.} \vert 4^3\Pi\rangle$	2.13	685	This work
$\langle W^1\Pi \vert H_{el.} \vert E'^1\Pi\rangle$	2.37	100	1
$\langle W^1\Pi \vert H_{so} \vert w^3\Pi\rangle$	2.38	30	This work
$\langle E'^1\Pi \vert H_{el.} \vert R^1\Pi\rangle$	3.29	300	1
$\langle k^3\Pi \vert H_{so} \vert E'^1\Pi\rangle$	2.6	28.21	1
$\langle k^3\Pi \vert H_{el.} \vert 4^3\Pi\rangle$	3.49	941	This work
$\langle 4^3\Pi \vert H_{so} \vert E'^1\Pi\rangle$	2.55	52	1

TABLE II. Experimental and calculated branching ratios for the predissociation of the v=1 level of the $W^1\Pi$ state of $^{12}C^{16}O$ (cm^{-1}).

	T_1	Γ	$C(^3P) + O(^3P)$	$C(^1D) + O(^3P)$
Expt.[2]	104 578.37	1.97	75%[3]	25%[3]
Calc.	104 577.12	1.93	80%	20%

found in excellent agreement with the experimental values (see Table II).

It must be noted that there exist relatively very few *ab initio* studies of the branching ratios for the predissociation of diatomic molecules that are in agreement with experiment. This is the case for the OH predissociation studied by Parlant and Yarkony[12] which agrees remarkably well with the recent experimental results of Zhou *et al.*[13] The present study could be regarded as a nice addition to the existing ones.

Another emerging problem is the reproduction of the fine structure distribution of the $C(^3P_{2,1,0})$ product in the predissociation as observed in Ref. 14.

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