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The *ns* and *nd* Rydberg states of O_2 described by Hund's case (e)

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Using Hund's case (e) representation, we have obtained a simulation of the 5*s* Rydberg states of O_2 for $J=2$ by fitting the experimental data obtained recently by Sheard *et al.* [J. Chem. Phys. **118**, 8781 (2003)]. Our analysis permits us to include evidence of not only the mixing of Hund's case (a) states by spin-orbit interaction, but also by *L* and *S* uncouplings. This mixing is even more important for the *nd* Rydberg states. For the 3*d* Rydberg state, $J=2$, we have been able to suggest for the first time an assignment for both the $3d\sigma\ ^1\Pi_g$ and the $3d\delta\ ^1\Pi_g$ states. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2047571]

I. INTRODUCTION

The Rydberg states of O_2 have been studied by many authors. In this paper, we are concerned with the optical-optical double-resonance study of the Rydberg states of O_2 by Sheard *et al.*[1] More precisely, these authors have studied the *s* and *d* Rydberg series converging to the ground state of O_2^+ by two-photon transitions from a given rotational level of the $b\ ^1\Sigma_g^+$ state. By this original method, they have been able to observe only one (or two) rotational levels of each high *ns* and *nd* Rydberg state.

We have performed a simulation of some of these spectra starting from Hund's case (e) representation. This has made possible the understanding of the role of the *L* and *S* uncouplings in these spectra which had not been considered by the previous authors.[2–5]

II. THE *ns* RYDBERG STATES

A. Method of calculation

The Rydberg states of O_2 with an *ns* Rydberg orbital in the $X\ ^2\Pi_g$ ion core are only of two types: $^1\Pi_g$ and $^3\Pi_g$. Because the *s* series converges to a $^2\Pi$ state, for large *n*, the good angular coupling scheme is Hund's case (e).[6] For an intermediate value of *n*, the levels can be described by a coupling intermediate between Hund's case (a) (good quantum numbers: *J*, *S*, Λ, Σ, Ω, and *l*) and Hund's case (e) (good quantum numbers: *J*, J^+, Ω^+, *l*, and *j*) (see p. 103 of Ref. 7). Pratt *et al.*[4] have been the first to point out the necessity to use Hund's case (e).

We start from Hund's case (e) basis set to write the matrix elements of the Hamiltonian [Eq. (16) of Ref. 8]. The basis set has been given previously for the *s* series converging to an inverted $^2\Pi$ ion state.[6] Here the $X\ ^2\Pi_g$ of O_2^+ is regular and consequently the order of the levels of Table 1 of Ref. 6 must be inverted.

B. Results and discussion

Using the quantum defects given in Table I, we have calculated the two-photon transitions from the $b\ ^1\Sigma_g^+$ for $n=5$ and $n=9$ with $B_0=1.69\ \mathrm{cm}^{-1}$. The ionization potential for $X\ ^2\Pi_{1/2}$ is taken to be $97\ 348.0\ \mathrm{cm}^{-1}$ and that for $X\ ^2\Pi_{3/2}$ to be $97\ 548.0\ \mathrm{cm}^{-1}$. The solutions can be written in terms of Hund's case (a).

The results for $5s$, $v'=0$, are in good agreement with the experimental results of Ref. 1 (see Fig. 1). The expressions of the solutions for $J'=2$ in terms of Hund's case (a) are given, in order of reverse energy, and we note each eigenstate by its *nominal* character (p. 235 of Ref. 7), put in single quotation marks, that corresponds to the largest coefficient in the linear combination of the basis functions:

$$'^1\Pi_1' = 0.20\ ^3\Pi_2 - 0.73\ ^1\Pi_1 + 0.66\ ^3\Pi_1,$$

$$'^3\Pi_2' = 0.98\ ^3\Pi_2 + 0.15\ ^1\Pi_1 - 0.14\ ^3\Pi_1,$$

$$'^3\Pi_1' = 0.62\ ^1\Pi_1 + 0.68\ ^3\Pi_1 - 0.39\ ^3\Pi_0,$$

$$'^3\Pi_0' = 0.26\ ^1\Pi_1 + 0.29\ ^3\Pi_1 + 0.92\ ^3\Pi_0.$$

The mixing of $^1\Pi_1$ and $^3\Pi_1$ is already nearly complete and the position of the states are near to the situation for $n=\infty$, i.e., Hund's case (e). This means that the $1^+=(1/\sqrt{2})(^1\Pi_1+{}^3\Pi_1)$ and $^3\Pi_0$ states are converging to $^2\Pi_{1/2}$ and, on the other hand, the $1^-=(1/\sqrt{2})(^1\Pi_1-{}^3\Pi_1)$ and $^3\Pi_2$ states are converging to $^2\Pi_{3/2}$ (see Fig. 5.1 of Ref. 8 or Fig. 3.13 of Ref. 7). Already the effect of the *S* uncoupling

TABLE I. Quantum defects for $s\sigma$ Rydberg orbital.

$^1\Pi$	$^3\Pi$
1.2025	1.2075

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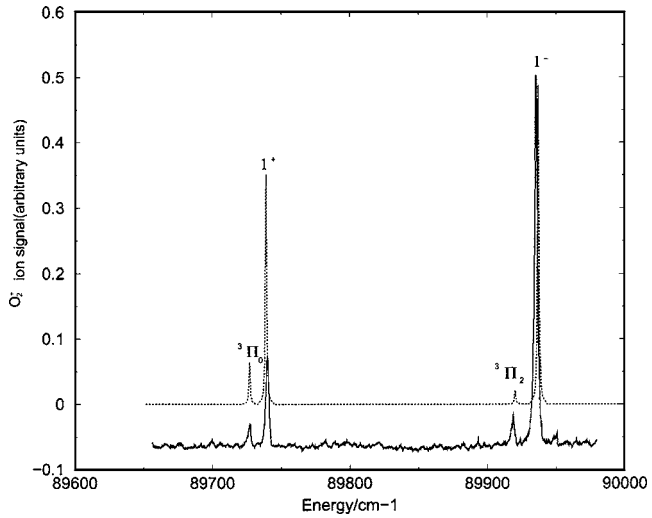

FIG. 1. (1+[(2′)+1′]) optical-optical double-resonance (OODR)/REMPI spectrum of $5s$ $v'=0$ Rydberg states of O_2 recorded via $v=0$, $J=0$ of the $b\,^1\Sigma_{0g}^+$ state. Experiment: full lines, calculated: dotted lines.

due to the mixing of $^3\Pi_0$ and $^3\Pi_1(\Delta\Omega=1)$ can be seen since the calculated intensity of $S(0)$ '$^3\Pi_0$' is larger than that of $S(0)$ '$^3\Pi_2$'.

This is more evident for $9s$, $v'=0$, $J'=2$, where the mixing of the 1^+ and $^3\Pi_0$ states is nearly total:

$$1^- = {}^{`1}\Pi_1{}' = 0.40\,{}^3\Pi_2 - 0.65\,{}^1\Pi_1 + 0.64\,{}^3\Pi_1.$$

$${}^{`3}\Pi_2{}' = 0.92\,{}^3\Pi_2 + 0.29\,{}^1\Pi_1 - 0.28\,{}^3\Pi_1$$

$${}^{`3}\Pi_0{}' = 0.48\,{}^1\Pi_1 + 0.49\,{}^3\Pi_1 - 0.73\,{}^3\Pi_0$$

$$1^+ = {}^{`3}\Pi_1{}' = 0.51\,{}^1\Pi_1 + 0.52\,{}^3\Pi_1 + 0.68\,{}^3\Pi_0$$

Figure 2 shows the calculated spectrum for $9s$, $v'=0$.

Unfortunately, the comparison with the experimental spectrum is difficult because the observed intensity in this type of experiment results from a competition between ionization and predissociation, phenomena which are not introduced in the calculations.

III. THE *nd* RYDBERG STATES

A. Method of calculation

The number of states in case (a) coming from the $(^2\Pi)nd$ configuration is equal to 4 for $J=0$ and 16 for $J=2$ since $\Omega \leqslant J$. They are given in Table II both with the quantum defects for $n=3$ (e levels) used in this paper. These quantum defects correspond to the case (a) states, i.e., to those which can be obtained by *ab initio* calculations without including the spin-orbit interactions and which can be compared, for example, to those of column I of Fig. 1 of Ref. 3. The starting values have been taken by comparing column I and column III of the same figure and they have been adjusted to obtain the best agreement with the experimental results of Fig. 1 of Ref. 1 and with those of Ref. 5 for the states which are not seen in the present excitation.

TABLE II. Quantum defects and intensities of case (a) *nd* Rydberg states (see text).

State	Quantum defect	T_1	T_2
$^1\Sigma_0^+ d\pi$	−0.052	10.0	4.0
$^3\Sigma_0^- d\pi$	−0.0007	0	0
$^3\Pi_0 d\sigma$	0.0	0	0
$^3\Pi_0 d\delta$	0.04	0	0
$^3\Sigma_1^- d\pi$	−0.0007	0	0
$^3\Sigma_1^+ d\pi$	−0.005	0	0
$^1\Pi_1 d\sigma$	−0.015	0	1.0
$^3\Pi_1 d\sigma$	0.0	0	0
$^3\Delta_1 d\pi$	0.01	0	0
$^1\Pi_1 d\delta$	0.0292	0	0.5
$^3\Pi_1 d\delta$	0.04	0	0
$^3\Pi_2 d\delta$	0.04	0	0
$^3\Pi_2 d\sigma$	0.0	0	0
$^1\Delta_2 d\pi$	−0.0285	0	5.0
$^3\Delta_2 d\pi$	0.01	0	0
$^3\Phi_2 d\delta$	0.06	0	0

B. Results and discussion

For $3d$, $v=1$, we have added $\Delta G=1866\ \mathrm{cm}^{-1}$. The results can be well compared with the experiment (see Fig. 3). T_1 and T_2 are, respectively, the zero-rank and the second-rank components of the two-photon transition tensor in case of linear polarized light (see, for example, Ashfold[9]). Their values have been taken to obtain the best agreement with experiment. The Q line and the S line of $^1\Sigma_0^+$ are calculated to be distant of about 12 cm^{-1} (experiment: 11 cm^{-1}). The corresponding lines for $^3\Sigma_0^-$ which borrow their intensity by spin-orbit interaction to $^1\Sigma_0^+$, are separated by 17 cm^{-1}. The experimental S line of the latter is very weak and is probably hidden in the background.

These Q and S separations are related to the different mixings of the Σ states by L and S uncouplings, for $J=0$ and $J=2$, respectively, with the other states which have different quantum defects.

Three weak experimental peaks were not conclusively

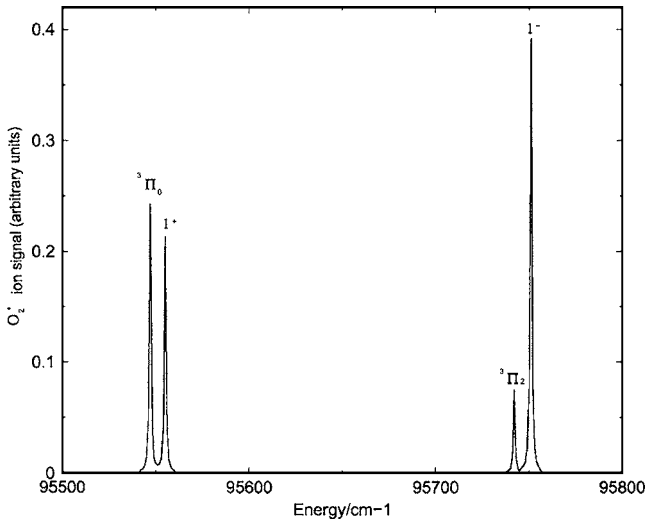

FIG. 2. Calculated (1+[(2′)+1′]) OODR/REMPI spectrum of $9s$ $v'=0$ Rydberg states of O_2 recorded via $v=0$, $J=0$ of the $b\,^1\Sigma_{0g}^+$ state.

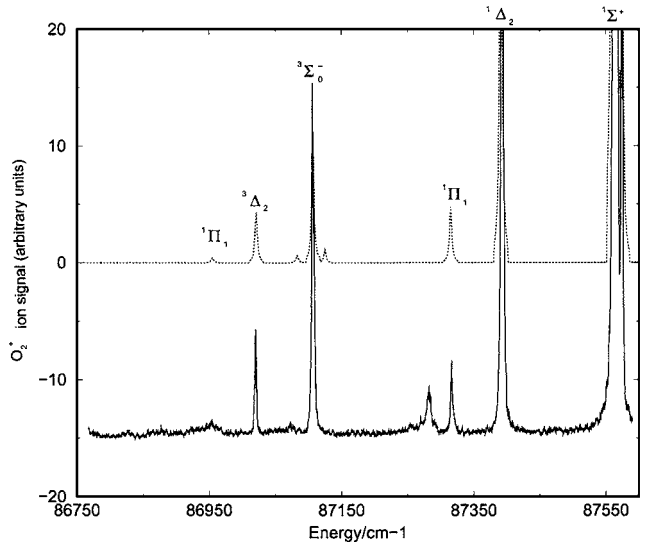

FIG. 3. $(1+[(2')+1'])$ OODR/REMPI spectrum of $3d\ v'=1$ Rydberg states of O_2 recorded via $v=0$, $J=0$ of the $b\,^1\Sigma_{0g}^+$ state. Experiment: full lines, calculated with a width of 4 cm^{-1}: dotted lines.

assigned in the previous paper.[1] The weak peak at 87 314.6 cm^{-1} is assigned here to the $3d\sigma\,^1\Pi_1$ state, as had been previously suggested.[1] This is the first observation of this state. This state in terms of Hund's case (a) states is expressed by $0.86\,^1\Pi_1-0.49\,^3\Pi_1-0.10\,^1\Delta_2$. The corresponding $3d\sigma\,^3\Pi_1$ state, calculated at 87 082 cm^{-1}, probably corresponds to the very weak peak at 87 075 cm^{-1}. The peak at 86 954.1 cm^{-1} can be assigned to the $3d\delta\,^1\Pi_1$ state. This would also be the first observation of this state. The corresponding $3d\delta\,^3\Pi_1$ state would appear at about 86 736 cm^{-1} under the $3d\delta\,^3\Phi_g$ states as suggested in Fig. 20 of Ref. 5. The third peak at 87 256 cm^{-1} could be the $^3\Sigma_1^+$ $v=1$ observed by Yokelson *et al.*[5] at 87 251.8 cm^{-1} for $J=1$, although the calculated intensity is very small.

The values used here for the quantum defects are justified by the good agreement between the calculated peaks and the other states listed by Yokelson *et al.*[5] in their Table 1. If a similar calculation is performed for the f levels, with a quantum defect of 0.027 for the $^1\Sigma_0^-$ state, a good agreement of 1–3 cm^{-1} with experiment is obtained for the Q line of both the $^1\Sigma_0^-$ and $^3\Sigma_0^+$ states $v=1$.

Unfortunately for $n>3$, the intensities of the $nd\sigma$ and $nd\delta\,^1\Pi_g$ states decrease, the peaks are closer together and overlap with other vibrational bands. This causes a great difficulty in assigning these peaks.

IV. CONCLUSION

Thanks to our calculation method of Rydberg states converging to a $^2\Pi$ ion state, we have been able to suggest an assignment for both the $3d\sigma$ and the $3d\delta\,^1\Pi_g$ Rydberg states. New experiments using, for example, $^{18}O_2$ could be useful to assign the successive terms of these two Rydberg series.

The calculations were performed at the French National Computer Center (CINES).

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