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Citation for published version:
Lefebvre-Brion, H & Ridley, T 2005, 'The ns and nd Rydberg states of O-2 described by Hund's case (e)'
The Journal of Chemical Physics, vol. 123, no. 14, 144306. DOI: 10.1063/1.2047571

Digital Object Identifier (DOI):
10.1063/1.2047571

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Publisher's PDF, also known as Version of record

Published In:
The Journal of Chemical Physics

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The ns and nd Rydberg states of O₂ described by Hund’s case (e)

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(Received 27 June 2005; accepted 9 August 2005; published online 10 October 2005)

Using Hund’s case (e) representation, we have obtained a simulation of the 5s Rydberg states of O₂ 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 3d Rydberg state, J=2, we have been able to suggest for the first time an assignment for both the 3Δσ 1^1Πg and the 3dδ 1^1Πg states. © 2005 American Institute of Physics. [DOI: 10.1063/1.2047571]

I. INTRODUCTION

The Rydberg states of O₂ have been studied by many authors. In this paper, we are concerned with the optical-optical double-resonance study of the Rydberg states of O₂ by Sheard et al.1 More precisely, these authors have studied the s and d Rydberg series converging to the ground state of O₂⁺ by two-photon transitions from a given rotational level of the b 1^1Σ⁺ 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 O₂ with an ns Rydberg orbital in the X 2^1Πg ion core are only of two types: 1^1Πg and 3^1Πg. Because the s series converges to a 3^1Π 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, Jₕ, 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 3^1Π ion state.8 Here the X 2^1Πg of O₂⁺ is regular and consequently the order of the levels of Table I 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 1^1Σ⁺ for n=5 and n=9 with B₀=1.69 cm⁻¹. The ionization potential for X 2^1Π₁/₂ is taken to be 97 348.0 cm⁻¹ and that for X 2^1Π₃/₂ to be 97 548.0 cm⁻¹. The solutions can be written in terms of Hund’s case (a).

The results for 5s, ν’=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:

\begin{align*}
\text{3}^1\Pi_1' &= 0.20 \text{3}^1\Pi_2 - 0.73 \text{1}^1\Pi_1 + 0.66 \text{3}^3\Pi_1, \\
\text{3}^1\Pi_2' &= 0.98 \text{3}^1\Pi_2 + 0.15 \text{1}^1\Pi_1 - 0.14 \text{3}^3\Pi_1, \\
\text{3}^1\Pi_1 &= 0.62 \text{1}^1\Pi_1 + 0.68 \text{3}^1\Pi - 0.39 \text{3}^3\Pi_0, \\
\text{3}^1\Pi_0' &= 0.26 \text{1}^1\Pi_1 + 0.29 \text{3}^3\Pi_1 + 0.92 \text{3}^3\Pi_0.
\end{align*}

The mixing of 3^1Π₁ and 3^1Π are already nearly complete and the position of the states are near to the situation for n=∞, i.e., Hund’s case (e). This means that the 1^1=1/(1-Θ)(3^1Π₁+3^1Π) and 3^1Π₀ states are converging to 2^1Π₁/₂ and, on the other hand, the 1^1=1/(1-Θ)(3^1Π₁-3^1Π) and 3^1Π₂ states are converging to 2^1Π₃/₂ (see Fig. 5.1 of Ref. 8 or Fig. 3.13 of Ref. 7). Already the effect of the S uncoupling

<table>
<thead>
<tr>
<th>ns</th>
<th>nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1^1Π₁</td>
<td>(1.2025)</td>
</tr>
<tr>
<td>3^1Π₁</td>
<td>(1.2075)</td>
</tr>
</tbody>
</table>

Electronic mail: helene.lefebvre-brion@ppm.u-psud.fr
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 $S(0) - ^3\Pi_1'$.

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

$$1^- = ^3\Pi_1' = 0.40 ~ ^3\Pi_2 - 0.65 ~ ^1\Pi_1 + 0.64 ~ ^3\Pi_1,$$

$$3\Pi_2' = 0.92 ~ ^3\Pi_2 + 0.29 ~ ^1\Pi_1 - 0.28 ~ ^3\Pi_1,$$

$$3\Pi_0' = 0.48 ~ ^1\Pi_1 + 0.49 ~ ^3\Pi_1 - 0.73 ~ ^3\Pi_0,$$

$$1^+ = ^3\Pi_1' = 0.51 ~ ^1\Pi_1 + 0.52 ~ ^3\Pi_1 + 0.68 ~ ^3\Pi_0$$

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

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 ($^3\Pi$)nd configuration is equal to $4$ for $J=0$ and $16$ for $J=2$ since $\Omega \approx J$. 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>
<thead>
<tr>
<th>State</th>
<th>Quantum defect</th>
<th>$T_1$</th>
<th>$T_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\Sigma_g^+\pi$</td>
<td>-0.052</td>
<td>10.0</td>
<td>4.0</td>
</tr>
<tr>
<td>$^3\Sigma_g^+\pi$</td>
<td>-0.0007</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$^3\Pi_g^+\sigma$</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$^3\Pi_g^+\delta$</td>
<td>0.04</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$^3\Sigma_g^+\delta$</td>
<td>-0.0007</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$^3\Sigma_g^+\sigma$</td>
<td>-0.005</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$^3\Pi_g^+\sigma$</td>
<td>-0.015</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>$^3\Pi_g^+\delta$</td>
<td>0.00</td>
<td>0</td>
<td>0</td>
</tr>
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<td>$\Delta_g^+\pi$</td>
<td>0.01</td>
<td>0</td>
<td>0</td>
</tr>
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<td>$\Pi_g^+\sigma$</td>
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<td>0</td>
<td>0.5</td>
</tr>
<tr>
<td>$\Pi_g^+\delta$</td>
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<td>0</td>
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<td>0</td>
<td>5.0</td>
</tr>
<tr>
<td>$\Delta_g^+\sigma$</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Phi_g\delta$</td>
<td>0.06</td>
<td>0</td>
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</tr>
</tbody>
</table>

B. Results and discussion

For $3d$, $\nu=1$, we have added $\Delta G=1866$ 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 $^1\Sigma_g^+$ are calculated to be distant of about $12$ cm$^{-1}$ (experiment: $11$ cm$^{-1}$). The corresponding lines for $^3\Sigma_g^+$ which borrow their intensity by spin-orbit interaction to $^1\Sigma_g^+$ 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 $\Sigma$ 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
assigned in the previous paper. The weak peak at 87.314.6 cm$^{-1}$ is assigned here to the 3d/H9268/1 state, as had been previously suggested. This is the first observation of this state. The corresponding 3d/H9268/3 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/H9254/1 state. This would also be the first observation of this state. The corresponding 3d/H9254/3 state would appear at about 86.736 cm$^{-1}$ under the 3d/H9254/3 states as suggested in Fig. 20 of Ref. 5. The third peak at 87.256 cm$^{-1}$ could be the 3Sigma^+ $n=1$ observed by Yokelson et al. in their Table 1. If a similar calculation is performed for the f states, with a quantum defect of 0.027 for the 1Sigma^+ state, a good agreement of 1–3 cm$^{-1}$ with experiment is obtained for the Q line of both the 1Sigma^+ and 3Sigma^+ states.$n=1$.

Unfortunately for $n>3$, the intensities of the nd-sigma and nd-delta 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 2Sigma^+ ion state, we have been able to suggest an assignment for both the 3d-sigma and the 3d-delta states. New experiments using, for example, 18O$_2$ could be useful to assign the successive terms of these two Rydberg series.

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