Edinburgh Research Explorer

The ns and nd Rydberg states of O-2 described by Hund's case (e)

Citation for published version:

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

Publisher Rights Statement:
Copyright © 2005 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics.

General rights
Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.
The ns and nd Rydberg states of O₂ described by Hund’s case (e)

Hélène Lefebvre-Briona
Laboratoire de Photophysique Moléculaire, Bâtiment 213, Université Paris-Sud, 91405 Orsay Cedex, France
Trevor Ridley
School of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ Scotland, United Kingdom

(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 3dσ 4Π₈ and the 3dδ 3Π₈ 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. 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 1Σ⁺ 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.

II. THE ns RYDBERG STATES

A. Method of calculation

The Rydberg states of O₂ with an ns Rydberg orbital in the X 3Π₈⁺ ion core are only of two types: 1Π₈ and 3Π₈. Because the s series converges to a 3Π state, for large n, the good angular coupling scheme is Hund’s case (e). 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, L, 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. 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 3Π state. Here the X 3Π₈ 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 1Σ⁺ for n=5 and n=9 with Bₚ=1.69 cm⁻¹. The ionization potential for X 3Π₁/₂ is taken to be 97 348.0 cm⁻¹ and that for X 3Π₃/₂ 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:

\[ ^1\Pi_1 ' = 0.20 \ 3\Pi_2 - 0.73 \ 1\Pi_1 + 0.66 \ 3\Pi_1, \]
\[ ^3\Pi_2 ' = 0.98 \ 3\Pi_2 + 0.15 \ 1\Pi_1 - 0.14 \ 3\Pi_1, \]
\[ ^3\Pi_1 ' = 0.62 \ 1\Pi_1 + 0.68 \ 3\Pi_1 - 0.39 \ 3\Pi_0, \]
\[ ^3\Pi_0 ' = 0.26 \ 1\Pi_1 + 0.29 \ 3\Pi_1 + 0.92 \ 3\Pi_0. \]

The mixing of 1Π₁ and 3Π₁ is 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+=1/2(1Π₁+3Π₁) and 3Π₀ states are converging to 2Π₁/₂ and, on the other hand, the 1−=(1/√2)(1Π₁−3Π₁) and 3Π₂ states are converging to 2Π₃/₂ (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>Table I. Quantum defects for σ Rydberg orbital.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Π</td>
</tr>
<tr>
<td>1.2025</td>
</tr>
</tbody>
</table>

---

4 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 \( S(0) \) \( ^5\Sigma_0^+ \) is larger than that of \( S(0) \) \( ^3\Pi_0^+ \).

This is more evident for \( 9s \), \( \nu = 0 \), \( J' = 2 \), where the mixing of the \( 1^+ \) and \( 3\Pi_0 \) 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 \((^2\Pi)nd\) configuration is equal to 4 for \( J = 0 \) and 16 for \( J = 2 \) since \( \Omega \leq J \). 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.

B. Results and discussion

For \( 3d \), \( \nu = 1 \), we have added \( \Delta G = 1866 \text{ cm}^{-1} \). 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 \( ^1\Sigma_0^- \) 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 \( \Sigma \) 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 cm\(^{-1}\) is assigned here to the \(3d^1\Pi_1\) state, as had been previously suggested. This is the first observation of this state. This state in terms of Hund’s case (a) states is expressed by 0.86 \(3\Pi_1\) − 0.49 \(3\Pi_1\) − 0.10 \(3\Delta_2\). The corresponding \(3d\delta^3\Pi_1\) state, calculated at 87.082 cm\(^{-1}\), probably corresponds to the very weak peak at 87.075 cm\(^{-1}\). The peak at 86.954 cm\(^{-1}\) can be assigned to the \(3d^1\Pi_1\) 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 \(3d\delta\Pi_1\) and the \(3d\delta^1\Pi_g\) Rydberg states. New experiments using, for example, \(^18\text{O}_2\) could be useful to assign the successive terms of these two Rydberg series.

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