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An optical-optical double resonance study of the $d3s\sigma g(1\Pi_g)$ Rydberg state of O_2 using $b(1\Sigma_g^+)$ as the resonant intermediate state

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An optical-optical double resonance study of the $d3s\sigma_g(^1\Pi_g)$ Rydberg state of O_2 using $b(^1\Sigma_g^+)$ as the resonant intermediate state

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Several $(2+1)$ resonance enhanced multiphoton ionization (REMPI) studies of the first four vibrational levels of the $d3s\sigma_g(^1\Pi_g)$ state of O_2 from both the $X(^3\Sigma_g^-)$ ground state and the $a(^1\Delta_g)$ and $b(^1\Sigma_g^+)$ states, generated by a microwave discharge, have been reported.¹ The $b(^1\Sigma_g^+)$ state, like the $a(^1\Delta_g)$, is a relatively pure singlet state, and a predominantly singlet manifold of states is accessed from it. Bloemink, Copeland, and Slinger² prepared the b state in single rotational levels of $v=1$ and 2 by optical pumping from the ground state in a gas cell. They then monitored its population in a REMPI experiment using the $d(v=3)\leftarrow b(v=1)$ transition in a one-color resonant step, in an optical-optical double resonance (OODR)/REMPI, $1+[(2')+1']$ experiment. In a previous study,³ we also accessed the $v=3$ level of the d state by the same route via the b state but in a jet in order to characterize the strong J -dependent homogeneous perturbation of this upper state. The limited number of J' levels accessed from each $b(v=0, J_b)$ level permitted their absolute assignment and simultaneous calibration of the probe laser wavelength gave accurate transition energies. We have now extended this technique to the spectroscopy of the lowest vibrational level of the d state, for which improved data are required.

O_2 has a relatively high ionization potential of 98 000 cm^{-1} . If ionization from the ground state is to be achieved with four photons from the ground state, and the pump photon is restricted to ~ 760 nm ($13\,000\text{ cm}^{-1}$) in order to excite the $b\leftarrow X$ transition, the two probe photons required for the $d(v)\leftarrow b(v=0)$ step must have a combined energy of $\sim 56\,000\text{ cm}^{-1}$. This is just at the threshold energy required to ionize the d state with another probe photon in a $1+[(2')+1']$ OODR/REMPI scheme. More precisely, $v=0$ and 1 of the d state cannot be ionized by this route, which only becomes available for $v\geq 2$. For this reason we use a two-color coherent two-photon step for the $d(v=0)\leftarrow b(v=0)$ transition, $(1+1')$, in which the more energetic probe photon can cause efficient ionization in an overall $1+[(1+1')+1']$ scheme from $X(v''=0)$. We have also used the same route to access $v=1$ of the d state.

This technique results in relatively sparse spectra through the selection of a single J_b level selected at the $b(J_b)\leftarrow X(J'')$ pump stage. Intruding lines from accidental resonances, perhaps arising from $1+[(1+1')+1']$, are thus readily identified and rarely overlap lines of interest. If they do overlap, there is a characteristic structuring of the line profile, which becomes asymmetric. Another advantage of

the preliminary J -state selection is that the beam can be run under conditions of weak rotational cooling, leaving a range of J'' states from which to select the intermediate J_b states.

The laser system consists of two independently tunable dye lasers (a Lambda Physik FL3002 and a Lambda Physik FL2002) pumped by a XeCl excimer laser (Lambda Physik EMG201MSC). The output of R700 (≤ 5 mJ per pulse) was used to pump the $(0,0)$ band of the $b\leftarrow X$ transition in O_2 around 760 nm). The probe photons were generated by frequency-doubled C307. The wavelength of the probe laser was calibrated by simultaneously recording the neon optogalvanic spectra to give an estimated accuracy in the two-photon energy of $\pm 0.5\text{ cm}^{-1}$. The wavelength of the pump laser was calibrated from the accurately known $b(0, J)\leftarrow X(0,0)$ rotational transitions.⁴ The counterpropagating plane-polarized pump and probe laser beams, with the planes of polarization mutually orthogonal to increase the Hönl-London factor for a two-photon $\Delta\Omega=1$ transition, were focused to an overlapping point in a differentially pumped ionization chamber using lenses of focal length 6 cm and intersected at 90° by the pulsed molecular beam generated using a backing pressure of 800 torr of O_2 . The resulting ion signal was detected as described previously.³

Using the OODR/REMPI scheme $1+[(1+1')+1']$ and detecting O_2^+ , $J=1-18$ of the $d3s\sigma_g(^1\Pi_g; v=0)$ state were observed [Figs. 1(a) and 1(b)]. The line positions in Table I were fitted to $\pm 1.5\text{ cm}^{-1}$ with $B'=1.684\text{ cm}^{-1}$ and $\nu_0=66\,357.7\text{ cm}^{-1}$, which is in reasonable agreement with those calculated by Lewis *et al.*⁵ from the less precise experiments of Ogorzalek-Loo *et al.*⁶ Some lines arising from a $1+[(2')+1']$ REMPI process are also visible. These are the Q branch of the transition to $5d\pi(^1\Sigma_0^+; v=0)$ and the O , P , R , and S branches of $5s\sigma(^3\Pi_1; v=2)$.

The S branch from $J_b=0$ has an anomalous profile and width, which only appears when the pump power is increased. The same final state, $J'=2$, accessed via the O branch from $J''=4$ has a normal line profile. The pump and probe wavelengths required for the two routes are different and the extra pump photon in the former route apparently excites a further resonant transition via an ungerade state, thereby enhancing the ionization cross section. Line positions in the $d(J')\leftarrow b(J_b)\leftarrow X(J'')$, $1+[(1+1')+1']$ spectrum can also be shifted by increasing the pump power. Shifts of up to 2 cm^{-1} to the blue were induced in the $J=2\leftarrow 0$ line, for instance, which are also caused by further pump-induced transitions leading to line broadening.

FIG. 1. The $1 + [(1 + 1') + 1']$ REMPI spectrum of $v=0$ of the $d3s\sigma_g(^1\Pi_g)$ state of O_2 via various rotational levels of the b state under tightly focused conditions: (a) $J_b=0-8$ and (b) $J_b=10-16$. The energy scale is relative to $X(v=0)$. Asterisk and plus signs refer to $1 + (2') + 1'$ REMPI signals from $v=0$ of the $5d\pi_g(^1\Sigma_0^+)$ state and $v=2$ of the $5s\sigma_g(^3\Pi_1)$ state, respectively.

Linewidths of low J levels of $v=0-2$ of the $3d(^1\Sigma_g^+)$ Rydberg state have been reported⁷ to be $\leq 0.05\text{ cm}^{-1}$. We accessed these levels in a $1 + (2')$ scheme via the b state and with various probe powers and found a minimum linewidth

TABLE I. Rotational term values for the $d(v=0)$ state of O_2 .

J'	$\bar{E}\text{ cm}^{-1}$	J'	$\bar{E}\text{ cm}^{-1}$
1	66361.4	10	66543.7
2	66367.7	11	66580.1
3	66377.9	12	66621.3
4	66391.4	13	66663.6
5	66408.2	14	66711.5
6	66428.5	15	66762.4
7	66451.7	16	66816.0
8	66478.9	17	66874.9
9	66509.2	18	66932.3

of 0.4 cm^{-1} , consistent with the expected laser fundamental linewidth for a two-photon process. The same line with a more powerful probe beam can be broadened to 2 cm^{-1} , and further broadened by increasing the power of the pump laser. The minimum observable linewidth of $J'=2$, pumped via $J_b=0$, was measured with various pump and probe laser powers was 1.5 cm^{-1} , which is thus an upper limit to the true linewidth. The observed linewidths of the other rotational lines of $v=0$ of the d state increase with J , probably the result of increasing the pump and/or laser powers to maintain the signal-to-noise ratio, but the minimum linewidth observed remains an order of magnitude less than the value of $\sim 30\text{ cm}^{-1}$ for $v=0$ of the $C^3\Pi_g$ state.¹ The latter is homogeneously broadened by a repulsive $^3\Pi_g$ state that passes through the C state near its potential minimum. Since the minima of the C and d states are only 800 cm^{-1} apart and their R_e values are very similar, the same repulsive triplet state will pass close to the minimum of the d state. The very much reduced width of the $d(v=0, J') \leftarrow b(v=0, J_b)$ lines compared with the corresponding $C \leftarrow X$ transition thus underlines the nearly pure singlet character of the d state.

In summary, the $b(^1\Sigma_g^+)$ state of O_2 can be efficiently pumped from the ground state and used as the first resonant intermediate in a two-color double resonance MPI study of both gerade and ungerade Rydberg states, beginning with $v=0$ of the $d3s\sigma_g(^1\Pi_g)$ state reported here. To obtain linewidths and positions to $<1\text{ cm}^{-1}$ for new states, a careful survey of the effect of the pump power must be made if the pump photon energy is not sufficient to ionize the final state. The b state becomes an increasingly attractive intermediate for more easily ionized higher electronic states for which a $1 + [(2') + 1']$ OODR/REMPI scheme is viable.

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¹ J. S. Morrill, M. L. Ginter, B. R. Lewis, and S. T. Gibson, J. Chem. Phys. **111**, 173 (1999).

² H. Bloemink, R. A. Copeland, and T. G. Slanger, J. Chem. Phys. **109**, 4237 (1998).

³ P. O'Keeffe, T. Ridley, S. Wang, K. P. Lawley, R. J. Donovan, H. H. Telle, D. C. S. Beddows, and A. G. Urena, J. Chem. Phys. **113**, 1 (2000).

⁴ L. C. O'Brien, H. Cao and J. J. O'Brien, J. Mol. Spectrosc. **99**, 207 (2001).

⁵ B. R. Lewis, S. T. Gibson, J. S. Morrill, and M. L. Ginter, J. Chem. Phys. **111**, 186 (1999).

⁶ R. R. Ogorzalek-Loo, W. J. Marinelli, P. L. Houston, S. Arepalli, J. R. Weisenfeld, and R. W. Field, J. Chem. Phys. **91**, 5185 (1989).

⁷ H. Park, L. Li, and W. A. Chupka, Chem. Phys. Lett. **162**, 317 (1989).