State-Selective Spectroscopy in a Molecular Nitrogen Discharge by Use of Optogalvanic Double-Resonance Spectroscopy

K. Miyazaki,[a] H. Scheingraber, and C. R. Vidal
Max-Planck-Institut für Extraterrestrische Physik, D-8046 Garching bei München, Federal Republic of Germany
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Transitions between excited states of molecular nitrogen, which are generated in a hollow-cathode discharge, have been studied by use of optogalvanic double-resonance spectroscopy as a state-selective method. By pumping of the known (0, 0) band of the $c_4{}^1\Pi_u$-$a''\,{}^1\Sigma_g{}^+$ system in N_2 the (16, 0) and (17, 0) bands of the $b'\,{}^1\Sigma_u{}^+$-$a''\,{}^1\Sigma_g{}^+$ system have been identified for the first time, and the recent assignment for the (0, 0) band of the $c_5'\,{}^1\Sigma_u{}^+$-$a''\,{}^1\Sigma_g{}^+$ system has been verified.

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A valuable aspect of laser spectroscopy in the analysis of dense atomic or molecular spectra is the possibility of performing state-selective spectroscopy which greatly simplifies the assignment of unidentified spectra. Several state-selective techniques have been reported such as laser-induced fluorescence, saturation spectroscopy, and polarization labeling[1] which are extremely useful for nonradiating samples.

In this paper a new technique of state-selective spectroscopy is reported which is based on optogalvanic double-resonance (OGDR) spectroscopy.[2] The method can be applied to dense spectra originating from transitions between excited atomic and/or molecular states in radiating plasmas where the existing methods have only a limited sensitivity because of the perturbing spontaneous emission.

In a recent paper,[3] we have studied theoretically as well as experimentally the amplitude and polarity of the OGDR signals in a neon discharge using the well-known atomic transitions. Different situations have been investigated where two cw lasers pump transitions which have no state (N type), the upper state (Λ type), the lower state (V type), or both states (P type) in common. The results have suggested that in a weakly ionized molecular discharge the OGDR signals can be restricted to those for the V- and P-type double resonances which have identical signal polarities. The actual power of the new state-selective method is demonstrated in a study of the transitions involving the metastable $a''\,{}^1\Sigma_g{}^+$ state of the N_2 molecule. By pumping of the (0, 0) band of the $c_4{}^1\Pi_u$-$a''\,{}^1\Sigma_g{}^+$ system, first identified by Ledbetter,[4] new visible bands of the $b'\,{}^1\Sigma_u{}^+$-$a''\,{}^1\Sigma_g{}^+$ system (Fig. 1) have been assigned for the first time. In addition, we have verified the (0, 0) band of the $c_5'\,{}^1\Sigma_u{}^+$-$a''\,{}^1\Sigma_g{}^+$ system which was recently identified by Suzuki and Kakimoto[5] using a Doppler-free optogalvanic technique.

The experimental setup employed was nearly the same as that in our previous study of neon.[3] Briefly, two beams from a cw ring dye laser (laser I) and from a cw linear dye laser (laser II), which were both operated with rhodamine 6G, were modulated by a mechanical chopper at the frequencies $f_1 = 550$ Hz and $f_2 = 825$ Hz, respectively. The modulated beams were sent in opposite directions through a home-made hollow-cathode discharge running in nitrogen. The dis-

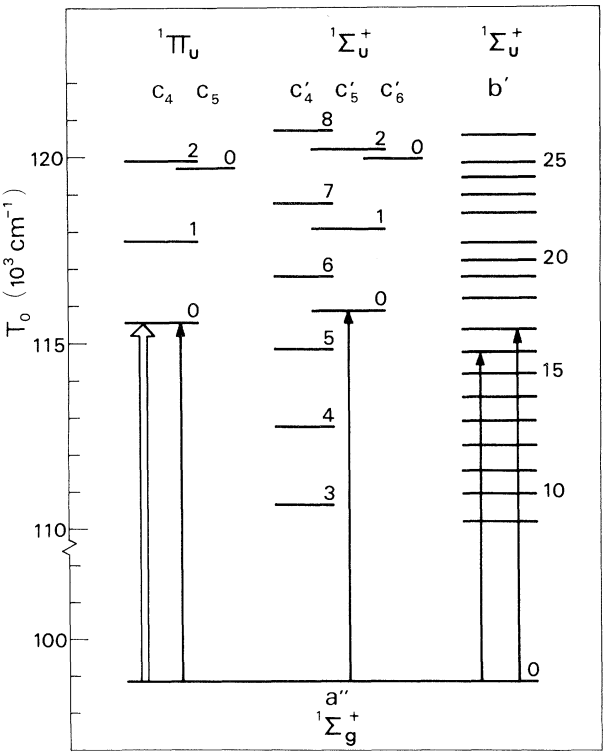

FIG. 1. Energy-level diagram for some of the excited states of N_2 taken from Ref. 6. The big and small arrows indicate the pump transition and the transitions observed in the OGDR experiments, respectively.

charge was operated at a nitrogen pressure of 0.05 Torr and a discharge current of 2 mA. The discharge conditions were optimized with respect to the Ledbetter system around 598 nm. The low-pressure discharge was crucial in order to enhance transitions to the $a''\,^1\Sigma_g^+$ state of interest. At N_2 pressures higher than about 0.5 Torr, the first positive bands dominated the OG spectrum within the spectral range (565–640 nm) of the dye lasers.

For studying transitions from the $a''\,^1\Sigma_g^+$ state, laser I (typical spectral width 3 GHz) was tuned to one of the lines of the Ledbetter system, while laser II (typical spectral width 30 GHz) was scanned over its entire spectral range. The resulting laser-induced impedance changes of the discharge, i.e., OGDR signals, were detected with a lock-in amplifier at the sum of the modulation frequencies, $f_D = 1375$ Hz. The signal at the sum frequency is proportional to the product of the intensities of lasers I and II. With laser I kept fixed on a particular molecular transition laser II scans a state selective spectrum where both lasers have the lower state in common (V type). The OG signals were also observed at f_2 by use of a second lock-in amplifier, providing a single-resonance spectrum due to laser II. The OGDR and OG single-resonance spectra were recorded simultaneously on a strip chart recorder. The OGDR signals were then easily correlated with the corresponding single-resonance lines. The wavelength calibration was carried out by an additional OG signal resonance experiment using a commercial neon hollow-cathode discharge.

The analysis of the N_2 spectrum was started with the most prominent feature in the spectral region of interest. Figure 2 shows the OG single-resonance spectrum (lower spectrum) and three different OGDR spectra (upper spectra) of the (0, 0) band of the $c_4\,^1\Pi_u$-$a''\,^1\Sigma_g^+$ system (Ledbetter system) which are obtained by pumping the corresponding $R(J)$ lines. These $R(J)$ lines of the Ledbetter system have been used in all the subsequent OGDR experiments. For a $^1\Pi$-$^1\Sigma$ transition, the OGDR spectrum consists of a $P(J)$, a $Q(J)$, and an $R(J)$ line having a common lower state $|v'', J''\rangle$. It is interesting to note that the $Q(J)$ lines have not been resolved in the OG single-resonance spectrum, whereas they can easily be separated in the OGDR spectra. To resolve all the $Q(J)$ lines in the single-resonance spectrum, a Doppler-free technique is required as done by Suzuki and Kakimoto.[5]

By pumping again the $R(J)$ lines of the Ledbetter

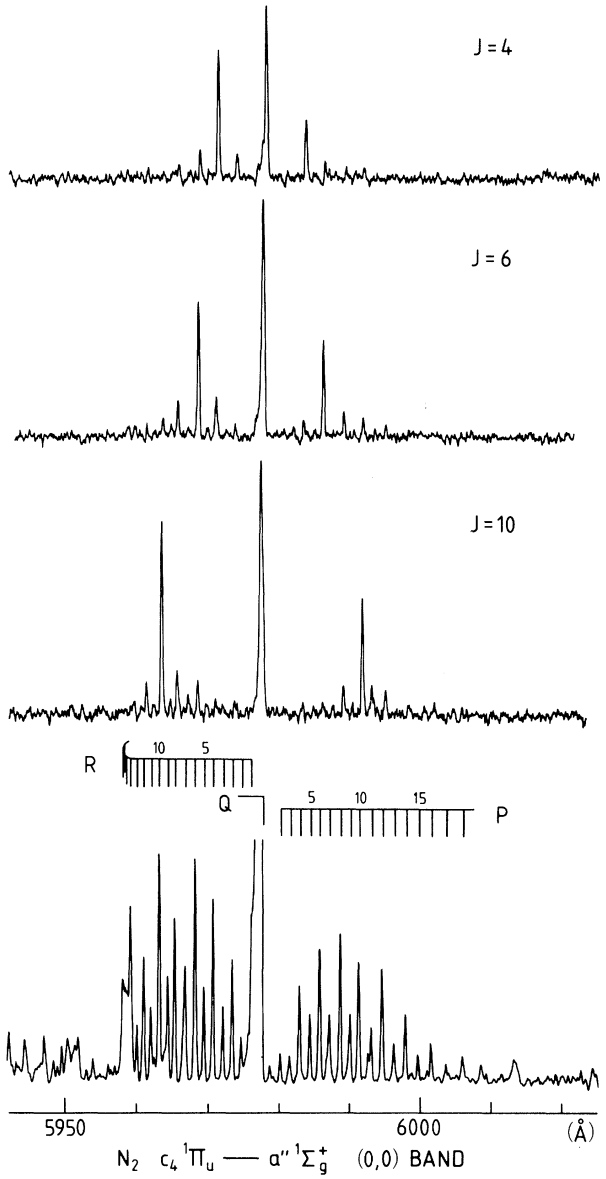

FIG. 2. OG single-resonance spectrum (lowest spectrum) and examples of the OGDR spectra (upper three spectra) for the (0, 0) band of the $c_4\,^1\Pi_u - a''\,^1\Sigma_g^+$ system of N_2. The signal polarities of the OGDR spectra are reversed.

band, we have verified the recent assignment[5] for the (0, 0) band of the $c_5'\,^1\Sigma_u^+$-$a''\,^1\Sigma_g^+$ system. The assignment was supported by the OGDR spectra revealing the common lower $a''\,^1\Sigma_g^+$ state. For a $^1\Sigma$-$^1\Sigma$ transition, the OGDR spectra consist only of an $R(J)$ and a $P(J)$ line, and all the lines with $J'' \leq 14$ have been definitely identified.

Pumping the same $R(J)$ lines and scanning through the remaining spectral range of laser II, we detected two more bands which have not been previously assigned. The OGDR spectra for both

bands consist only of two lines, a P and R line. One of the new bands is shown in Fig. 3.

The OGDR spectra immediately identify the common lower $a''\,^1\Sigma_g^+$ state. Because of the selection rules for a homonuclear diatomic molecule the upper state of the new bands has to be in both cases a $^1\Sigma_u^+$ state. Figure 3 clearly demonstrates the power of the OGDR spectrum especially since the OG-signal resonance spectrum is heavily overlapped by the first positive system. Two band heads of the first positive system can be clearly recognized. The reversal of the signal polarity indicates a change of the phase in the phase-sensitive detection.

It should be noted that all the OGDR spectra observed show weak satellite lines which originate from collision-induced transitions. The satellites in the OGDR spectra were already expected by Vidal[2] and are similar to those frequently observed in laser-induced fluorescence.[1] In a plasma the collisional cross sections are expected to be very large because of the Coulomb-type interaction potentials giving rise to large collisional depopulation rates even at very low particle densities. In order to maintain the value of the OGDR spectra one should always try to minimize the collisional rates and hence the number of satellite lines. In Figs. 2 and 3 the satellites coincide with the OGDR lines pumping different J''.

In assigning the upper-state vibrational quantum numbers v' of the unknown bands, we tested whether the excited state had already been seen by transitions in other parts of the spectrum. The N_2 spectrum has recently been reviewed by Lofthus and Krupenie,[6] and Fig. 1 reproduces the relevant part of the energy levels taken from their review.

The measured line positions are summarized

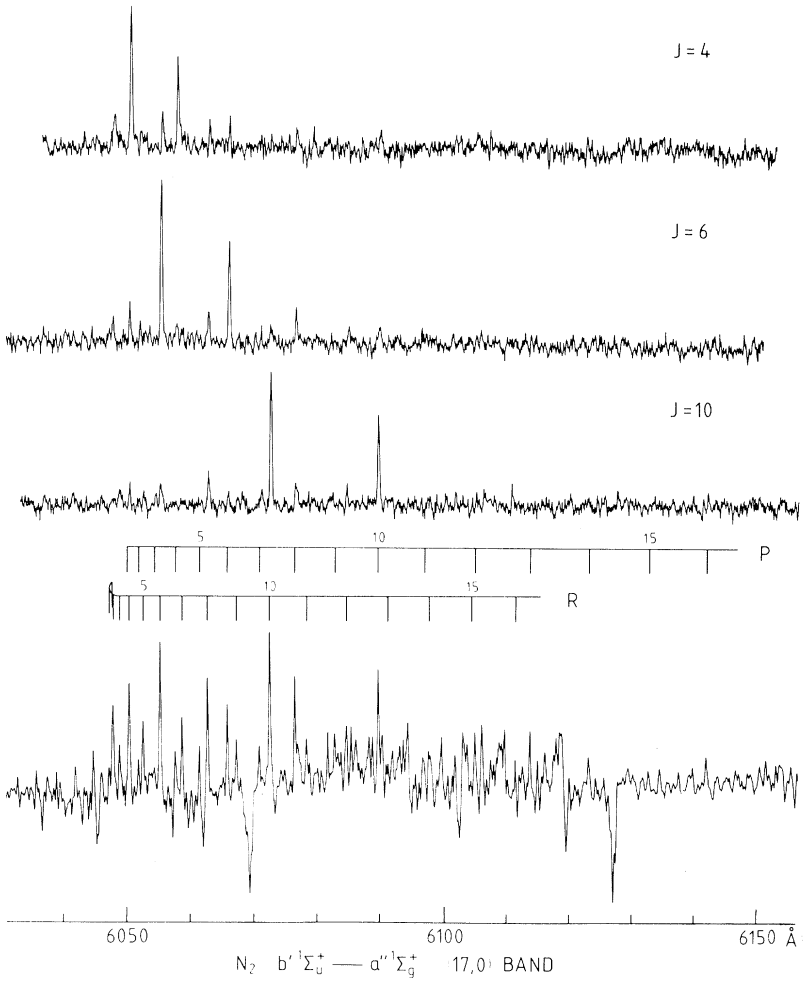

FIG. 3. OG single-resonance spectrum (lowest spectrum) and examples of the OGDR spectra (upper three spectra) for the (17, 0) band of the $b'\,^1\Sigma_u^+ - a''\,^1\Sigma_g^+$ system of N_2. The signal polarities of the OGDR spectra are reversed.

TABLE I. Measured line positions (cm^{-1}) of the (16, 0) and (17, 0) bands of the N_2 $b'\,^1\Sigma_u^+ - a''\,^1\Sigma_g^+$ system. The standard error is 0.06 cm^{-1}.

	(16, 0)		(17, 0)	
J	$R(J)$	$P(J)$	$R(J)$	$P(J)$
0	15916.06			
1	917.86	15909.59	16531.84	16524.58
2	918.06	904.55	530.59	519.56
3	917.02	898.55	527.71	512.51
4	914.32	891.30	523.52	503.63
5	909.99	882.57	517.57	493.37
6	903.97	872.26	510.16	481.43
7	895.92		500.87	467.81
8	886.03	846.46	490.05	452.75
9	874.30	830.95	477.65	435.82
10	860.39	813.33	463.54	417.01
11	844.68	794.12	447.72	397.25
12	827.09	772.68	430.58	375.55
13	807.56	749.23	412.64	352.24
14	785.87	724.08	395.35	327.48
15				301.69
16			358.25	277.31

in Table I. A least-squares fit of the lines immediately showed that the bands are perturbed preventing a meaningful analysis in terms of Dunham-type coefficients. By restricting the least-squares fit to the lines with $J'' \leq 8$, we obtained a rotational constant $B_v' = 1.397 \pm 0.004$ cm^{-1} and a band origin $\nu_\infty = 15913.3 \pm 0.05$ cm^{-1} for one of the new bands. For the other unknown band shown in Fig. 3, we obtained $B_v' = 1.085 \pm 0.003$ cm^{-1} and $\nu_\infty = 16528.9 \pm 0.05$ cm^{-1}. With the value $\nu_\infty = 98840.30 \pm 0.07$ cm^{-1} for the spacing between the $a''\,^1\Sigma_g^+$ state and the $X\,^1\Sigma_g^+$ ground state, which was given by Ledbetter,[4] the band origins of the new bands are in good agreement with those given for the $b'\,^1\Sigma_u^+$ state with $v' = 16$ and 17 by Carroll, Collins, and Yoshino.[7] This state has also the proper symmetry predicted above by the OGDR spectra. The data of Carroll, Collins, and Yoshino have been evaluated from vacuum uv spectra around 87 nm originating from transitions to the ground state. They obtain $B_v' = 1.30$ cm^{-1} and $\nu_\infty = 114754.5$ cm^{-1} for the (16, 0) band of the $b'\,^1\Sigma_u^+ - X\,^1\Sigma_g^+$ system, and $B_v' = 1.104$ cm^{-1} and $\nu_\infty = 115369.6$ cm^{-1} for the (17, 0) band of the same system. In view of the perturbations, which can be seen already from the anomalous vibrational spacing in Fig. 1, the agreement of the B_v' values is satisfactory and depends, of course, to some extent on the maximum value of J'' used in the least-squares fit. For the two new bands of the $b'\,^1\Sigma_u^+ - a''\,^1\Sigma_g^+$ system observed, the values of ν_∞ calculated from the data of Carroll, Collins, and Yoshino[7] and Ledbetter[4] exceed our values of ν_∞ by 0.9 and 0.4 cm^{-1}, respectively. This is very good in view of the calibrational difficulties generally encountered in the vacuum uv.

From Fig. 1 it is clear that further unknown bands can be expected beyond the spectral region of the rhodamine 6G dye laser. The present results clearly demonstrate the ability of the OGDR technique for assigning transitions between excited states which are otherwise difficult to identify especially if the bands are heavily perturbed. Similar experiments in molecular hydrogen have also been carried out providing very clear OGDR signals.

[a]On leave from the Electrotechnical Laboratory, Ibaraki 305, Japan.

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