PHYSICAL REVIEW VOLUME 140, NUMBER 4A 15 NOVEMBER 1965

Observation of a $^1\Pi-{}^1\Sigma^-$ Transition in the N_2 Molecule

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(Received 14 June 1965)

A new emission system has been observed in the singlet spectrum of nitrogen. It occurs between the two lowest excited singlet levels of the molecule. The emission is in the range of 3.3 to 8.2 μ and arises from transitions between the $a\,{}^1\Pi_g$ and $a'\,{}^1\Sigma_u^-$ states. The measurements are in good agreement with vacuum-ultraviolet-absorption data for these states.

We report the observation of a new emission system in the singlet spectrum of nitrogen on what we believe to be the first confirmed $^1\Pi\rightarrow{}^1\Sigma^-$ transition for a homonuclear molecule.[1] The present work extends the long-wavelength limit of emission studies in N_2 from the previous value[2] of 2.6 μ to approximately 8.2 μ. By use of the technique of stimulated emission it has proved possible to observe a number of emission lines between 3.3 and 8.2 μ which arise from transitions between the $a\,{}^1\Pi_g$ and $a'\,{}^1\Sigma_u^-$ states of the nitrogen molecule. The measurements are in good agreement with recent high-resolution vacuum-ultraviolet-absorption studies of the $a\,{}^1\Pi_g\leftarrow X\,{}^1\Sigma_g^+$ system[3,4] and of the $a'\,{}^1\Sigma_u^-\leftarrow X\,{}^1\Sigma_g^+$ system.[5] The observations are consistent with the long radiative lifetime of the $a'\,{}^1\Sigma_u^-$ state reported in Ref. 5.

The experiment consisted of observing the emission from two high-current pulsed-discharge gas optical masers. The first employed a near-confocal resonator with opaque gold mirrors spaced 4.25 m apart at the ends of a 75-mm i.d. discharge tube. Output coupling was provided by a 2-mm aperture in the center of one mirror. In the second maser the concave mirrors were spaced 2.25 m apart and the discharge tube was 15 mm i.d. Coupling was by means of a 1-mm aperture. Tungsten pin electrodes[6] were used and the maser was excited by repetitively discharging through the gas column a 2-μF capacitor which had been charged to between 5 and 15 kV. Pulses lasted approximately 10 μsec and attained peak currents of several hundred A. The large maser was used for the 8-μ measurements with a gas mixture of 0.15-Torr N_2 and 0.5-Torr Ne. The 3-μ measurements were made in the small maser with 0.6 Torr of pure N_2. Pressures up to 2 Torr gave similar results.

Wavelength measurements were made using a Jarrell-Ash $\frac{1}{2}$-m Ebert spectrometer equipped with a 64 mm $\times$64 mm 105 1/mm Bausch and Lomb grating blazed at 8.6 μ in first order. The spectrometer was calibrated by operating the maser on ten argon transitions between 1.24 and 2.57 μ, the air wavelengths of which can be accurately computed from known term differences[7] and refractive index corrections.[8] The 8-μ measurements are believed accurate to $1:10^4$ and the 3-μ measurements to $5:10^5$.

The results are summarized in Table I. All of the observed wavelengths are Q-branch transitions which are favored by nearly a factor of 2 as determined from the Hönl-London formulas for a $^1\Pi\rightarrow{}^1\Sigma$ transition. For a specified vibrational transition the individual rotational lines have been fitted by the method of least squares to a curve of the form

$$\nu=\nu_0+(B_v'-B_v'')J(J+1)\,. \qquad (1)$$

The band-center frequencies ν_0 and rotational-constant differences derived from the present measurements are included in Table I.

TABLE I. Observed transitions of the $a\,{}^1\Pi_g\rightarrow a'\,{}^1\Sigma_u^-$ system.

Transition	Observed this work (cm^{-1})	NRL[a] obs-obs (cm^{-1})
2 → 1 $Q(4)$	3013.03	3012.63[b]
$Q(6)$	3015.54	3015.43[b]
$Q(8)$	3018.96	3018.86[b]
$Q(10)$	3023.38	3023.40
$Q(12)$	3028.78	3028.63
$Q(14)$	3035.25	3034.98
	$\nu_0=3010.61\ cm^{-1}$	
	$B_2'-B_1''=0.1169\ cm^{-1}$	
1 → 0 $Q(4)$	2880.79	···
$Q(6)$	2883.47	2882.99
$Q(8)$	2887.03	2886.68
$Q(10)$	2891.41	···
$Q(12)$	2896.77	···
	$\nu_0=2878.52\ cm^{-1}$	
	$B_1'-B_0''=0.1172\ cm^{-1}$	
0 → 0 $Q(6)$	1217.87	···
$Q(8)$	1221.92	···
	$\nu_0=1212.19\ cm^{-1}$	
	$B_0'-B_0''=0.1351\ cm^{-1}$	

[a] Difference in observed wave numbers given in Refs. 4 and 5.
[b] Blend.

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[1] G. Herzberg, *Molecular Spectra and Molecular Structure—I. Spectra of Diatomic Molecules* (D. Van Nostrand, Inc., New York, 1950), p. 256.

[2] G. Hepner and L. Herman, Ann. Geophys. **13**, 242 (1957).

[3] P. G. Wilkinson, Astrophys. J. **126**, 1 (1957).

[4] J. T. Vanderslice, S. G. Tilford, and P. G. Wilkinson, Astrophys. J. **141**, 395 (1965).

[5] S. G. Tilford, P. G. Wilkinson, and J. T. Vanderslice, Astrophys. J. **141**, 427 (1965).

[6] L. E. S. Mathias and J. T. Parker, Appl. Phys. Letters **3**, 16 (1963).

[7] C. E. Moore, *Atomic Energy Levels* (U. S. National Bureau of Standards, Washington, D. C., 1949), Vol. I.

[8] *Table of Wavenumbers* (U. S. National Bureau of Standards, Washington, D. C., 1960).

Extensive high-resolution vacuum-uv-absorption data have recently been reported on the $a\,^1\Pi_g \leftarrow X\,^1\Sigma_g^+$ and $a'\,^1\Sigma_u^- \leftarrow X\,^1\Sigma_g^+$ systems.[4,5] By subtraction of the observed wave numbers for the same Q-branch transition of the $a \leftarrow X$ and $a' \leftarrow X$ systems, it is possible to determine the positions of corresponding Q branch transitions in the present $a \rightarrow a'$ system. Where the data were available this difference has been computed and is shown in Table I.

The difference in band centers for the $1 \rightarrow 0$ and $0 \rightarrow 0$ transitions gives the vibrational energy of the $v=1$ level of $a\,^1\Pi_g$. The band centers determined from the present work indicate a value of 1666.33 cm^{-1}. The NRL data show 1666.31 cm^{-1}, and Wilkinson[3] observes 1666.37 cm^{-1}.

The present measurements combined with the $a\,^1\Pi_g$ data of Refs. 3 and 4 give a vibrational energy of the $v=1$ level of $a'\,^1\Sigma_u^-$ of 1506.50 cm^{-1}. The observed vibrational energy in Ref. 5 is 1506.25 cm^{-1}, while measurements on the fifth positive system by Lofthus[9] give a vibrational energy of 1506.6 cm^{-1}.

It was found that the maser oscillated only during the initial portion of the 10-μsec current pulse, the output lasting for approximately 1 μsec. An exact determination of output duration was not possible as the detector and electronics exhibited a rise time of this order and the output pulse duration may have been substantially less. The process of oscillation results in a rapid increase in the population of the $a'\,^1\Sigma_u^-$ state and the oscillation ceases when the population inversion has been destroyed. The radiative lifetime of the $a'\,^1\Sigma_u^-$ state has been estimated to be 0.7 sec.[5] This is consistent with the observation that the peak maser output increased as the pulse repetition rate was decreased.

The depopulation of the $a'\,^1\Sigma_u^-$ state appeared, however, rather more complex than a simple decay. Qualitatively it was observed that the peak output was reduced if the maser was refired before the disappearance of the Lewis-Rayleigh afterglow. A plot of peak maser output on the $Q(8)$ $1 \rightarrow 0$ transition (1.75-Torr N_2) as a function of interpulse period showed a rapid rise in output as the period was increased from 0.1 to 0.5 sec followed by a slower increase in power as the period was extended to several seconds. By use of a 7102 photomultiplier to monitor the sidelight from the discharge, a similar time dependence was observed in the *decay* of the Lewis-Rayleigh afterglow. Young and Clark[10] remark that the afterglow changes from the early hyperbolic form characterizing recombination of two active particles to the late exponential decay due to wall losses. The present observations suggest that the $a'\,^1\Sigma_u^-$ state is being populated continuously during the afterglow period by a process similar to that responsible for the afterglow itself. It is known from the observation of the Lyman-Birge-Hopfield bands in the afterglow[11] that the upper maser level (the $a\,^1\Pi_g$) is itself populated throughout the afterglow. We therefore conclude that atomic recombination leads to population of both maser levels but preferentially of the lower level probably as a result of its longer lifetime.

A second system of several dozen emission lines between 5.2 and 6.3 μ[12] has not yet been identified. Work is continuing to determine if these are associated with transitions between the $B\,^3\Pi_g$ state and a theoretically predicted but not yet experimentally confirmed $^3\Delta_u$ state.[13]

It is a pleasure to thank C. G. B. Garrett and J. A. Howe for profitable discussions during the course of this work and D. E. Thomas for the design of the measurement system used for observing the maser time dependence.

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[9] A. Lofthus, J. Chem. Phys. 25, 494 (1956).

[10] R. A. Young and K. G. Clark, J. Chem. Phys. 32, 604 (1960).

[11] Y. Tanaka, A. Jursa, and F. Leblanc, *The Threshold of Space* (Pergamon Press, Inc., New York, 1957), p. 89.

[12] R. A. McFarlane and W. L. Faust (to be published).

[13] R. S. Mulliken, *The Threshold of Space* (Pergamon Press, Inc., New York, 1957), p. 169.