RESONANCE SCATTERING OF LASER RADIATION BY NITROGEN AND NITROGEN OXIDE MOLECULES

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Resonance scattering of laser radiation by nitrogen and nitrogen oxide molecules is studied. It is shown that the concentration of N_2^+ *ions and NO molecules above 100 km can be measured with the help of the first positive system of* N_2^+ *ions and the* β *bands of NO.*

The first studies on the possibility of using resonance scattering (RS) of laser radiation to determine the composition of the atmosphere were published in the mid-1960s (see Refs. 1–3 and the references cited there). In studies performed in this country and abroad it has been suggested that metastable molecules and ions of nitrogen, nitrogen oxide, sodium, potassium, calcium, lithium, and other components be determined with the help of RS. In this connection there emerged a wide range of geophysical problems such as the study of the thermodynamic and wind regimes in the atmosphere, meteor matter entering the upper layers of the atmosphere, obtaining new information about the nature of sporadic E_s layers of the ionosphere and the downward ion fluxes from the F layer, and determining the parameters of internal gravity waves. In the last few years, however, experiments on determining the composition of the upper atmosphere have been confined to the measurements of the content metal, primarily, sodium atoms.

The choice of the atmospheric component whose concentration is to be measured by the RS method is made based on the following conditions.

1. The concentration of the reradiator and the RS cross-section must be high enough so that the resonance backscattering signal is stronger than the aerosol and molecular scattering.

2. The intensity of nighttime airglow (and during the day the airglow together with the background solar radiation) should not exceed the resonance backscattering signal at the sounding wavelength.

3. The lifetime of the upper excited state of the transition should be short. In this case the probability of quenching of the excitation is low, it is easier to interpret the data, and the RS cross section is significantly higher. The latter property is connected with the fact that the RS cross section is proportional to the oscillator strength and therefore the Einstein coefficient of spontaneous emission.

4. The absorption of the laser radiation at the chosen wavelength by other components of the atmosphere should be weak. This is especially important for sounding from the ground.

Assuming the conditions 1–4 are satisfied, we shall study the possibility of determining some nitrogen components in the upper atmosphere. These components are chosen primarily because they play a determining role in the formation of the lower ionosphere.

The nitrogen molecule undergoes six basic electronic transitions. Three of them (Birge-Hopfield I and II and Lyman-Birge-Hopfield) lie in the short-wavelength region of the spectrum ($\lambda < 260$ nm) and they cannot be employed for laser sounding because the radiation due to these transitions is strongly absorbed by oxygen and ozone. Transitions in the second positive system occur from the excited state $B^3\Pi_g$, whose population is low, and calculations show that the condition 1 is not satisfied. For this reason the Vegard-Kaplan electronic transitions ($A^3\Sigma_u^+ - (X^1\Sigma_g^+$, 230–506 nm) and transitions in the first positive system ($B^3\Pi_g - A^3\Sigma_u^+$, 470–4000 nm) can be used to determine the concentration of nitrogen molecules in the excited ($A^3\Sigma_u^+$) and ground ($X^1\Sigma_g^+$) states.

The Vegard-Kaplan transitions occurs from the metastable state $A^3\Sigma_u^+$ whose lifetime is about 2 s. Because its lifetime is long the probability of quenching of the excitation in the strato-mesosphere is high, since a free flight time of ~ 2 s corresponds to an altitude of 300 km.

Inaba[4] estimates that the concentration of $N_2\left(A\Sigma_u^{3+}\right)$ concentration at 100 km is equal to 10^8 cm^{-3}, and on this basis he believes that the concentration of metastable nitrogen molecules can be measured using the transitions in the first positive system.

The optical transitions from the ground state into the triplet state $A^3\Sigma_u^+$ are forbidden by an intercombination selection rule, and the main mechanism of excitation of daytime emissions in the first positive system (like also in the second positive system and the Vegard-Kaplan transitions) is excitation by photoelectrons

$$N_2(X^1\Sigma_g^+)+e\longrightarrow N_2(A^2\Sigma_u^+)+e. \qquad (1)$$

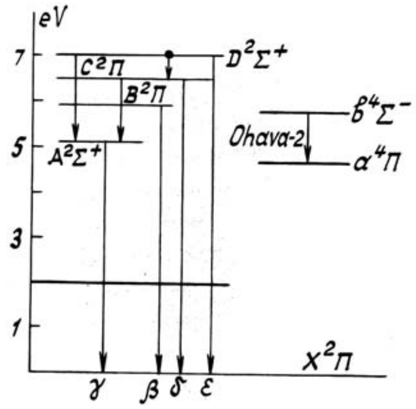

FIG. 1. The energy levels of the NO molecule.

The cross sections for inelastic collisions for the state $A^3\Sigma_u^+$ are maximum for electron energies in the range 7–20 eV. Radiative transitions from the $B^3\Pi_u$ and $C^3\Pi_u$ levels as well as the ion-molecular reaction

$$N_2^+ + NO \rightarrow N_2(A^3\Sigma_u^+) + NO^+ \qquad (2)$$

are additional processes which increase the concentration of $N_2(A^3\Sigma_u^+)$.

The rate of formation of these molecules is ~ $5 \cdot 10^9$ cm^{-2} s^{-1}, and atomic oxygen is the main component on which quenching occurs (the quenching rate constant is $5 \cdot 10^{-11}$ cm^{3}s^{-1}). Other reactions are also possible, for example, energetic coupling with excitation to a higher level.

Kiselev[5] calculated the distribution of $N_2(A^3\Sigma_u^+)$ molecules over vibrational levels as a function of the altitude. The maximum concentration at an altitude of about 140 km, about is $2 \cdot 10^3$ cm^{-3} (total concentration) and $3 \cdot 10^2$ cm^{-3} for the vibrational level with $v'' = 0$. The content of $N_2(A^3\Sigma_u^+)$ below 140 km is sharply lower.

Kiselev's calculation are in good agreement with the data obtained by other authors, and for daytime conditions they can be regarded as the most reliable data.

Since the flux of exciting photoelectrons is formed by the action of short-wavelength solar radiation the concentration of metastable nitrogen molecules can be expected to be sharply lower under nighttime conditions. This is indicated directly by data on the strong drop in nighttime emissions owing to transitions from the levels $C^3\Pi_u$, $B^3\Pi_g$, and $(A^3\Sigma_u^+)$.

Our calculations show that concentration levels $N_2(A^3\Sigma_u^+)$ are too low for performing lidar measurements using equipment with technically realistic parameters.

Among the transitions of the N_2^+ ion the transition of the first negative system with vibrational quantum numbers $v' = 0$, $v'' = 0$ is most preferable. Radiation with the wavelength of the transition 391.4 nm is weakly absorbed by atmospheric components and the transition is characterized by a short lifetime in the excited state (~ 10^{-7} s) and high oscillator strength, equal to $2.46 \cdot 10^{-2}$. For this reason the cross section for resonance backscattering is large and is equal to $1.7 \cdot 10^{-14}$ cm^2 sr^{-1} (for $T \simeq 200$ K). The observation of RS of laser radiation is not limited to atmospheric emission with $\lambda = 391.4$ nm. At night the intensity of the emission is less than 1R (1R = 10^6 photons $\cdot$ cm^{-2} $\cdot$ s^{-1}) (see Table I). This value is several orders of magnitude lower than the intensity of emission from a pulsed volume formed by excitation with laser radiation.

The minimum detectable concentrations of nitrogen ions – $(N_2^+)_{\text{lim}}$ – can be calculated with the help of the laser sounding equation, tables of the optical characterisitics of atmospheric aerosol,[6] and the standard atmosphere model. For such calculations we assume that the backscattering coefficient, determined by RS by N_2^+, should be an order of magnitude higher than the molecular and aerosol backscattering coefficients.

At an altitude of 100 |km this quantity is equal to $(N_2^+)_{\text{lim}} \simeq 2 \cdot 10^1$ cm^{-3}, and its value then drops in proportion to the decrease in the density of the atmosphere. Data from rocket experiments show that the ion concentration at the indicated altitudes is 10^2–10^3 cm^{-3}.

To determine the integration time (the time necessary for measuring the backscattering signal with a fixed accuracy δ, %) we shall employ the relation

$$T = \frac{\left[\frac{100}{\delta}\right]^2 2[N_s(H) + 2N_n(H)]}{N_s^2(H)\,t(\Delta H)\,f}, \qquad (3)$$

where N_s and N_n are the average number of signal and noise pulses, respectively, $t(\Delta H) = 2\Delta H/s$ is the gating time, and f is the pulse transmission frequency of the laser. In the case of sounding from the ground the integration time is 10^3 s with the following parameters: the laser radiation energy is 1 J, the diameter of the receiving optical antenna is 1 m; the transmission coefficient of the optical systems is 0.3, the quantum efficiency of the photodetector is 0.1, $\Delta H = 1$ km, the atmospheric transmission is 10^{-1}, the nitrogen ion concentration is 10^2 cm^{-3}, $N_n = 10^2$ s^{-1}, $f = 10$ Hz, $\delta = 5\%$, and $H = 100$ km. This means that the resonance backscattering signal can be measured over a period of tens of minutes with an accuracy of 5% with the help of a lidar on the ground with fully realistic values of the parameters indicated, while the N_2^+ ion concentration can be measured with an accuracy of ~ 20%. This uncertainty is determined primarily by the uncertainty in the coefficient of transmission of the atmosphere along the "lidar-scattering layer of the atmosphere-lidar" path and the uncertainty in the instrumental coefficient of the lidar and the resonance backscattering signal.

TABLE I.

The basic atmospheric emissions owing to resonance scattering.

Component	λ, nm	g, photon/s	daytime		evening		nighttime		Remark
			P	H, km	P	H, km	P	H, km	
$Mg^+(^2P_{1/2,\ 3/2})$	279.5; 280.2	$6.5\cdot10^{-2}$	360	108	—	—	—	—	
$OH(A^2\Sigma_u^+)$	306.4	$4.3\cdot10^{-4}$	10^3	50-100	—	—	—	—	laser sounding performed
$N_2^+(B^2\Sigma_u^+)$	391.4	$5\cdot10^{-2}$	$2\cdot10^3$	150	50-500	300	<1	—	first negative system (0, 0)
$Na(^2P)$	589.3	$8\cdot10^{-1}$	$3\cdot10^4$	92	$(1-5)\cdot10^3$	85-90	20-200*	92	laser sounding performed
$O_2(b^1\Sigma_g^+)$	761.9	$6.3\cdot10^{-9}$	$3\cdot10^5$	40-120	—	—	$6\cdot10^3$	80	Atmospheric system (0, 0)
$N_2^+(A^2\Pi_u)$	1103.6	$4.2\cdot10^{-2}$	$4\cdot10^3$	150	—	—	—	—	Meinel bands (1, 0)
$He(^3P)$	388.9	0.1	—	—	1	400	—	—	
$Ca^+(^2P)$	393.3; 396.8	0.3; 0.15	—	—	100	80-200	—	—	
$Li(^2P)$	670.8	16	—	—	$10-10^3$	90	—	—	laser sounding performed
$K(^2P)$	769.9	1.67	—	—	40	90	—	—	laser sounding performed
$He(^3P)$	1083.0	16.8	—	—	$3\cdot10^3$	500	—	—	
$O_2(A^3\Sigma_u^+)$	260-380	—	—	—	—	—	$6\cdot10^{2}$*	90	
$O_2(a^1\Delta_g)$	1270	$9.4\cdot10^{-11}$	$2\cdot10^7$	50	$5\cdot10^6$	80	$8\cdot10^{4}$**	90	IR atmospheric system (0, 1)
$OH(^2\Pi_1)$	380-450	—	$4.5\cdot10^6$	—	—	—	10^6	90	Meinel bands
Continuum	400-700	—	—	—	—	—	$1.5\cdot10^3$	—	On the average 5R/nm
Astronomical	400-700	—	—	—	—	—	$4.5\cdot10^3$	—	On the average 15R/nm

*Emissions owing to chemical reactions

**Emissions owing to photodissociation and collisions

We shall study the possibility of determining the content of nitrogen oxide in the upper atmosphere by the lidar method.

Inaba[4] belives that the Ogava-2 systems of bands for wavelengths in the range 864–874 nm (1, 0) and 768–794 nm (2, 0) can be employed in this case. The concentration so obtained is equal to the total content of NO in the first case and the concentration of NO is $\simeq 10^7$ cm^{-3} in the second case. This assertion is wrong, since the lower level of this transition $a^4\Pi$ corresponds to an excitation energy of $\simeq$ 5 eV and the population of such a high energy level is negligible (see Fig. 1). For this reason, as pointed out in the monograph of Ref. 7, the principal transitions for evening and daytime atmospheric NO emissions associated with the RS process are observed in the γ system of bands of nitrogen oxide.

Table II gives the wavelengths, the Frank-Condon factors ($q_{v'v''}$), the oscillator strengths, and the lifetime of the upper level according to the data from the monographs Refs. 8 and 9.

Let us examine the possibility of measuring the concentration of the nitrogen oxide at altitudes in the range 100–160 km, where the average concentration is $\simeq 10^7$ cm^{-3} (see Ref. 11). In the case of sounding from the ground the radiation with the shortest wavelength, which is not strongly absorbed by ozone and molecular oxygen, corresponds to the transition 0–10 of the β system of NO bands λ = 358.3 nm. The content of vibrationally excited NO molecules at these altitudes is not known. If local thermodynamic equilibrium is assumed, then according to the Boltzmann distribution the highest concentration of molecules in the level $v' = 10$ at $T \simeq 10^3$ K (150 km) is 10^3 cm^{-3}. The Franck-Condon factor, which determines the relative intensity of the transitions between the vibrational levels of two electronic states, exceeds for the transition 0–10 the analogous values for most other transitions. The maximum value of the resonance backscattering cross section, which we calculated under the assumption that the contour has a Doppler shape, is $3 \cdot 10^{-15}$ cm$^2 \cdot$ sr^{-1} ($T = 10^3$ K). The resonance backscattering coefficient, equal to $3 \cdot 10^{-12}$ cm$^{-1} \cdot$ sr^{-1} ([NO] = 10^3 cm^{-1}), is much greater than the molecular backscattering coefficient, which is $1.4 \cdot 10^{-16}$ cm$^{-1} \cdot$ sr^{-1} for $\lambda = 358$ nm and $H = 150$ km.

TABLE II.

The basic spectroscopic parameters of the γ and β bands of the nitrogen molecule

band system	$v'-v''$	$\lambda_{v'v''}$	$q_{v'v''}$	$f_{v'v''}$	$\tau_{v'}$, s
γ	0-4	284.9	0.092	—	$(1.75-2.16)\cdot10^{6}$; $v'=0$
	0-3	271.3	0.161	$(0.36-2.38)\cdot10^{-3}$	$(1.75-2.15)\cdot10^{-6}$; $v'=1$
	0-2	247.1	0.237	(0.0)	$(1.74-1.95)\cdot10^{-6}$; $v'=2$
	0-1	236.3	0.262	—	—
	0-0	226.9	0.162	—	—
	1-0	214.9	0.330	$2.4\cdot10^{-3*}$	—
	2-0	204.6	0.295	—	—
	3-0	195.6	0.151	—	—
β	14-0	170.8	6.897(-2)*	—	—
	11-0	175.6	5.482(-2)	$(2.7-5.8)\cdot10^{-3*}$	$4.5\cdot10^{-8**}$
	9-0	184.6	3.797(-2)	—	—
	6-0	144.8	1.342(-2)	—	—
	5-0	198.5	7.845(-3)	—	—
	4-0	202.4	4.018(-3)	—	—
	3-0	206.5	1.729(-3)	—	—
	2-0	210.8	5.877(-4)	—	—
	1-0	215.1	1.405(-4)	—	—
	0-0	219.9	1.761(-5)	—	—
	0-4	262.1	2.340(-2)	—	—
	0-10	358.3	1.385(-2)	—	—
	0-11	380.0	9.413(-1)	—	—
	0-12	388.0	5.325(-2)	—	—
	0-13	408.0	2.500(-2)	—	—
	0-14	430.0	9.691(-3)	—	—
	0-15	450.0	3.099(-3)	—	—

*The most probable value.
**According to the data of Ref. 10.

The integration time for the lidar parameters given above is about 3 h in the case of measurements of the NO concentration at an altitude of 150 km. Over this period of time the distribution of NO molecules can be determined at the indicated altitudes with a spatial resolution of 1 km, and the uncertainty in values obtained for the concentration is about 20%. The insignificant lifetime of the excited state (~ 10^{-8} s) makes it possible to employ the laser radar equation in its usual form, neglecting the specific features of the signal owing to reradiation from metastable states.

Calculations of the concentrations of different components measured by the lidar method require information about atmospheric emissions. The airglow in the chosen region of the spectrum for different times of day can limit the determination of the atmospheric components.

The airglow is excited by collisions with high-energy particles, solar radiation, chemical reactions, and excitation in thermal collisions. The action of the photons gives rise to RS, fluorescence, photodissociation, and photoionization while collisions with electrons can lead to excitation by photoelectrons.

Table I, which was constructed based on Refs. 7 and 11–15, summarizes these emissions. The intensity is expressed in Rayleighs and the radiation is assumed to be isotropic. For this reason for estimates of the background radiation owing to emissions which reaches the lidar receiver the indicated intensity will be approximately 4n times lower.

Table I also gives the value of g – the probability of RS of a photon of soldr radiation in the absence of collisional deactivation of the excited component:

$$g = \pi F \frac{\pi e^2}{m_e c^2} \lambda f, \qquad (4)$$

where πF is the intensity of solar radiation at the wavelength λ and f is the oscillator strength of the transition. The rest of the notation is standard.

According to rocket and lidar measurements the maximum concentrations of the components approximately correspond to the altitudes of the emissions. At night, which time is most suitable for lidar measurements, only part of the emissions owing to chemical processes is observed.

REFERENCES

1. V.M. Zakharov and O.K. Kostko, *Meteorological Lidar Sensing*, (Gidrometeoizdat, Leningrad, 1977).
2. O.K. Kostko, et al., *Use of Lidars for Determination of the Atmospheric Composition*, (Gidrometeoizdat, Leningrad, 1983).
3. V.M. Zakharov, O.K. Kostko, et al., *Lidar Sensing of the Atmosphere from Space,* (Gidrometeoizdat, Leningrad, 1988).
4. H. Inaba, *Laser Monitoring of the Atmosphere* [Russian translation], (Mir, Moscow, 1979).
5. V.A. Kiselev, Proceedings of the Institute of Applied Geodesy, Vyp. **32**, 82 (1977).
6. V.E. Zuev and G.M. Krekov, *Optical Models of the Atmosphere*, (Gidrometeoizdat, Leningrad, 1986).
7. M. Mclven and L. Phillips, *Chemistry of the Atmosphere*, [Russian translation], (Mir, Moscow, 1978).
8. Ya.B. Zeldovich and Yu.P. Raizer, *Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena,* (Fizmatgiz, Moscow, 1963).
9. L.A. Kuznetsova, et al., *Probabilities of Optical Transitions in Diatomic Molecules,* (Nauka, Moscow, 1980).
10. G. Brassie and S. Solomon, *Aeronomy of the Middle Atmosphere*, (Gidrometeoizdat, Leningrad, 1987).
11. A.D. Danilov and M.N. Vlasov, *Photochemistry of Ionized and Excited Particles in the Lower Ionosphere,* (Gidrometeoizdat, Leningrad, 1973).
12. A. Omholt, *Aurora Polaris*, [Russian translation], (Mir, Moscow, 1974).
13. R. Witten and I. Poppov, *Fundamentals of Aeronomy*, (Gidrometeoizdat, Leningrad, 1977).
14. J. Chaimberlen, *Physics of Aurora and Atmospheric Emissions*, [Russian translation], (Inostrannaya literatura, Moscow, 1963).
15. R. Bruce, *Airlow Thermospheric Circulation*, [Russian translation], (Mir, Moscow, 1975).