

Thermoactivation spectroscopy of solid Ar doped with N₂.

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Introduction.

Studies of luminescence from rare gas solids subjected to high energy irradiation extends back more than eighty years to the work of Vegard, who hoped to gain this way understanding of auroral glow and its spectrum. Interestingly, the most prominent spectral features observed from solid argon were due to minor impurities, the so called “auroral” line at 557.7 nm due to the forbidden ¹S-¹D transition of O atoms, as well as lines due to atomic and molecular nitrogen [1]. In particular, a prominent system of strong lines in the UV range, today called Vegard-Kaplan bands, was later identified as the $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ phosphorescence of molecular N₂. The pioneering studies of Vegard led to the realization, that low temperature solids, and in particular rare gases provide an excellent medium for studies of free radicals and ionic species, and motivated the development of matrix isolation spectroscopy as a useful spectroscopic technique[2], which was discussed in a number of review articles [3,4].

The energetic radiation impinging on the solid results in excitation, break up, or ionization of the species present as already shown by Vegard, and a part of its energy thus remains stored in the solid in the form of defects, vacancies and interstitial atoms, as well as impurity atoms, radicals or ions. In 1962, Brocklehurst and Pimentel [5] investigated emission of such an irradiated solid during its subsequent warm up, a study which can be viewed as an early example of the so called “activation spectroscopy”, a method which is becoming a useful tool in studies of radiation “damage” in a variety of materials. As the temperature of the pre-irradiated sample is gradually raised, a number of processes is triggered or “activated”: electrons can be promoted to the conduction band and become mobile, they can recombine with any positive ions present, or exit the solid, and also atoms can be ejected from the sample surface. At higher temperatures also atoms and small radicals may start to diffuse through the solid, and these microscopic processes can then result in a number of observable, macroscopic effects: recombination and neutralization of the fragments may result in emission which can be spectrally- and time-resolved and studied as a so called TSL, thermally stimulated luminescence, electrons leaving the solid can be detected as an “exoelectron” current, TSEE, and atoms ejected from its surface result in a rise in pressure.

Conversely, observation of these macroscopic effects can provide a detailed insight into the microscopic processes in the solid, and a number of such studies have been reported.

While most previous studies have concentrated on just one of these “activation spectroscopy methods”, obviously a most detailed information can be gained by examining all the observable effects concurrently, on the same sample. For this purpose we have recently designed and constructed an apparatus which can, under computer control, arbitrarily choose the heating regime, and simultaneously record the spectrally resolved TSL and TSEE during the warm-up, while also recording the pressure and sample temperature. In the present study, we apply this apparatus to studies of pre-irradiated solid argon samples doped with molecular nitrogen.

Experimental

A schematic of our new experimental setup is shown in the Fig.1. The work is carried out in a fairly conventional matrix isolation cryostat, cooled by a closed cycle Leybold RGD 580 cryostat. The bottom temperature is about 6 K, the base pressure in the vacuum shroud around 10^{-8} mbar. In the present experiment, sample of argon doped with 1% of nitrogen is deposited on a copper substrate coated with thin layers of Au and MgF_2 . The gas flow rate during deposition controlled by means of a Brokhorst Gas Flow Controller was 2ml/min, the sample thickness, typically 100 μm , could also be independently determined by observing pressure drop in the gas handling system of a known volume. Concurrent with the deposition, the sample was irradiated by a 600 eV electron beam with a current density of about $30\mu\text{A}/\text{cm}^2$ (see Fig.2). The source of electrons was a heated 2.2V tungsten filament with the beam being focused on the sample by a special electromagnetic lens. After the completed deposition, the substrate was turned to the position for spectral measurements (see Fig.3), and the heating of the sample was carried out using a digital programmable controller Leybold LTC 60, with the temperature being monitored by means of silicon diodes located on the back side of the substrate.

The Thermally Stimulated Exoelectron Emission (TSEE) signal was detected by a Faraday plate kept at +9V, and amplified by a FEMTO DLPCA 200 current amplifier. A hole in the middle of the Faraday plate permitted detecting and recording the TSL luminescence. The optical signal could, when desired, be spectrally resolved, and recorded in the range from 200nm to 1100nm by an Ocean Optics S2000 spectrometer. In order to carry out the measurements of all the effects and parameters simultaneously and in real time, we had to develop a special software to control the entire apparatus. The program also allowed us to enter the parameters of the desired heating regime into the temperature controller, which in turn was connected to a computer via a GPIB interface. All the signals were digitized and recorded using a 16 channel BNC2110 analog/digital converter.

Results and Discussion

Spectrum of nitrogen in solid rare gases represents a convenient model system which, following the early studies by Vegard in the 1920's, was reexamined by a number of investigators. In a 1968 study by Tinti and Robinson [6] some 70 spectral bands were observed and identified, and a number of subsequent detailed investigations made N_2 one of the molecules, whose matrix spectra are best known and understood. Also the TSL "glow curves" of irradiated N_2 in rare gases were previously reported, but studied alone and without spectral resolution they yield little insight into the microscopic processes occurring in the solid. We have therefore applied our new apparatus to reexamine this system.

As we have previously shown, besides luminescence, the sample warm-up often also results in electrons being emitted, and we show in the Fig.4 a typical TSEE curve. In this case a layer of solid argon doped with about 1% of molecular N_2 was deposited at 6K, with a concurrent 500 eV electrons irradiation. After rotating the sample to the position for spectral acquisition, its temperature was then linearly raised at about 3.2 K/minute, while monitoring the current of electrons exiting the sample. The curve shows that the electron current starts to rise sharply around 8K, and exhibits several distinct maxima. The strongest one at 11K has a shoulder around 13K, the current then decreases sharply, with a second strong maximum appearing near 37K. Above about 43 K the sample is lost, and the signal disappears. The curve is similar to previously reported TSL "glow curves" which result when the intensity of the total sample luminescence as a function of temperature is monitored.

As noted above, a much more detailed insight is obtained in a spectrally resolved TSL experiment, where the entire thermo-luminescence spectra, and their changes, are repetitively recorded and stored as the temperature rises. The spectrum between 15000-50000 cm^{-1} recorded with the sample at 11K shown in the Fig. 5a exhibits as its most prominent feature the doubly forbidden $^2D \rightarrow ^4S$ transition of atomic nitrogen at 19119 cm^{-1} . Several progressions of rather intense bands are clearly due to the molecular N_2 , the Vegard-Kaplan $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ phosphorescence. Additional, weaker series of bands can be identified with the molecular NO $a^4\Pi \rightarrow X^2\Pi$ transition [7]. These are undoubtedly due to a small oxygen impurity, which is invariably present in the samples. Most of the spectral features observed in our TSL study were observed and assigned previously, and a list of the lines seen in our experiment and their respective assignments are presented in Table 1.

Interestingly, and consistent with the previous studies, also during the warm-up of pre-irradiated sample appear not only vibrationally relaxed lines originating from the $v'=0$ level, but also "hot bands" originating from vibrationally excited upper state levels. In the case of the Vegard-Kaplan transition, lines up to $v'=6$ are clearly identified, indicating that vibrational relaxation in the upper state is slow, even when compared with the very long, many second radiative lifetime of the

$A^3\Sigma_u^+$ excited state. Fig. 5b then shows a spectrum obtained similarly but at a higher, 25 K temperature, and it is clear that the spectral distribution has changed appreciably. The spectrum is significantly simplified, with the molecular N_2 emission now being more intense than the atomic $^2D \rightarrow ^4S$ line, and also the relative intensities of the NO impurity bands is greatly reduced. The most apparent change is, however, that now essentially only the $v'=0$ $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ are present, with the vibrationally unrelaxed $v'>0$ hot bands being almost absent.

The new software written specifically for our new experimental setup makes it possible to display the entire thermoluminescence data in the form of as a three-dimensional wavenumber-temperature-intensity array, as exemplified in the Fig.6. The spectra presented in the Figs. 5a and 5b are simply two-dimensional cuts through the 3-dimensional spectrum of the Fig.6 at selected temperatures. Obviously, instead of taking 2-D cuts through the 3-D data presented in the Fig.6 perpendicular to the temperature axis, that is at a given temperature as shown in the Fig. 5, one can similarly make 2-D cuts perpendicular to the wavenumber axis, showing then the temperature dependent intensity at a given wavenumber, that is of a selected spectral line.

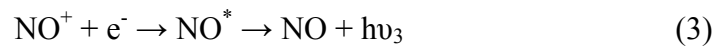
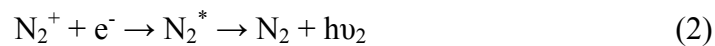
Several examples of such time dependent intensity profiles are presented in the Fig. 7, and the results are quite informative. In the figure, the top panels, 7a and 7c, represent the intensities of the metastable N-atom line at 19199 cm^{-1} , and of one NO $a^4\Pi \rightarrow X^2\Pi$ impurity emission bands. The comparison reveals significant differences, with the atomic emission exhibiting a secondary maximum near 25 K, absent in the NO emission profile. To obtain the bottom two panels, 7b and 7d, the intensities of one of the $v'=0$ $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ Vegard-Kaplan N_2 bands, and one of the corresponding vibrationally unrelaxed $v'>0$ bands, respectively, were monitored. Obviously, the time profiles in 7b are independent of which of the vibrationally relaxed bands was selected, and similarly the “hot band”, $v'>0$ emission time profile in 7d is independent of the specific v' value. The intensity profiles of the unrelaxed $v'>0$ bands $A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ are also essentially independent of the specific v' value.

With the detailed above data, one can try to get a consistent interpretation, and get some insights into the microscopic processes taking place in the solid. The TSEE curve in the Fig.4 reveals a prominent maximum in exo-electron current near 11-13 K, indicating that around this temperatures the electrons produced during the sample irradiation are promoted from shallow traps into the conduction band, become mobile, and if close to the surface, can be ejected from the sample. Examination of the four curves in the Fig.7 reveals that each of them exhibits a maximum – or at least a local maximum – at about the same temperature. This suggests strongly that the emission of all these species near this temperature is associated with the mobilization and reactions of the trapped electrons.

Our previously studies have shown that the major effect of electron irradiation of rare gas solids is the ionization of rare gas atoms, followed by a rapid formation of rare gas dimer ions, Ar_2^+ in the case of solid argon. These are then effectively indefinitely stable, “self trapped”, as long as

the matrix is maintained cold. When the temperature is raised, the electrons can be mobilized, and can recombine with these self-trapped holes, populating highly excited electronic states of neutral Ar₂. These then proceed through a complex cascade of nonradiative relaxation, and eventually relax radiatively to the ground state. This is then evidenced by a very intense VUV emission, as well as by anomalous surface atom desorption evidenced macroscopically by an anomalous pressure rise. The VUV emission is way outside the spectral range studied, but the results show that also the near UV and visible emission of N atoms and N₂ and NO molecules in this temperature range must be due to similar processes.

The ionization potentials of gas phase Ar atoms, N atoms and N₂ molecules are 15.755, 14.54 and 15.576 eV [Handbook of Chemistry and Physics]. The band gap energy of solid argon is 14.16 eV, and it is also known that also ionization energies of matrix isolated molecules are similarly lowered by about 1.5-2 eV. It therefore appears very likely, that under the electron irradiation, besides the self-trapped Ar₂⁺ “holes” also N⁺ as well as molecular ionic N₂⁺ and NO⁺ centers are formed. When, around 11-13 K, the electrons become mobile, obviously they can recombine not only with the intrinsic Ar₂⁺ centers, but also with any other cations present in the solid, in general producing the corresponding neutrals in highly excited electronic states and with a large excess of energy. These can then relax radiatively, resulting in photon emissions:



The neutralization of an ion by an electron will initially populate very high “Rydberg” states, which will then rapidly relax. Extensive studies of relaxation processes in the matrix have shown that such a relaxation proceeds efficiently by inter-electronic cascades, often involving several electronic states. This cascade can then eventually populate the lower excited valence states, such as in the present case N₂ A³Σ_u⁺ or NO a⁴Π, and if the vibrational relaxation in these states is also slow [8] vibrationally excited levels can be populated and “hot” bands will appear in the spectrum, as observed.

While the “glow curves” in the panels a, b, and d are rather similar, each exhibiting a strong maximum coincident with the prominent 11-13 K peak in the exoelectron spectrum, the curve 7c, representing the vibrationally relaxed, v'=0 A³Σ_u⁺ N₂ emission is clearly different. While also showing a local maximum at 11-13 K, it then starts to rise again above 15 K, reaching a prominent peak near 25 K, near the range where the TSEE curve actually exhibits a deep minimum. This suggests clearly that this second maximum is not connected with the electron-ion neutralization process. It appears, however, close to the temperature where atomic diffusion may start to take

place. It seems therefore likely to propose, that the process involved here is the recombination of nitrogen atoms:



Obviously, the energy available in such a recombination process is essentially the dissociation energy of N_2 , and is more than enough to populate the excited $\text{A}^3\Sigma_u^+$ electronic state. The excess energy is, however, significantly smaller than in the case of ion-electron neutralization, and this may explain why here only – or at least preferentially – the vibrationally relaxed $v'=0$ level is populated. Obviously, and alternative, but probably less likely interpretation of the absence of $v'>0$ bands, are the increased rates of vibrational relaxation in the $\text{A}^3\Sigma_u^+$ state of N_2 at higher temperatures.

Interestingly, also the atomic N emission line in the Fig.7a exhibits a secondary peak near the 25 K temperature, which should suggest that the recombination of nitrogen atoms and formation of N_2 also results in the production of electronically excited ^2D N atoms. Possible interpretations include reabsorption of the photons emitted by reaction (4) by ground state N atoms, or more likely by a nonradiative, Forster type transfer between the electronically excited N_2 and nearby N atoms. Clarification of this process would require further studies.

Summary

We have designed and constructed a new apparatus for “activation spectroscopy” studies, which concurrently records spectrally resolved temperature stimulated luminescence (TSL) as well as exoelectron emission (TSEE) current curves, and we apply it here to a detailed investigation of pre-irradiated solid Ar solids doped with molecular nitrogen. The samples are prepared by depositing N_2 doped argon from the gas phase on a 6 K substrate, with a simultaneous irradiation by 600 eV electrons. Lines of atomic N and molecular N_2 , as well as NO impurity bands are identified in the TSL spectrum which appears when the temperature of the sample is gradually raised. Time correlated recording of both temperature dependent TSEE current and of the TSL “glow” curves at specific wavelengths provides a better insight into the microscopic processes occurring in the solid, then studies using each of the activation techniques individually. At lower temperatures the observed TSL is shown to be mainly due to neutralization of ions produced during the pre-irradiation by detrapped electrons, while above about 20 K the neutral atom diffusion and recombination becomes important. The study provides a better, consistent understanding of the mechanisms of the release and relaxation of the energy stored in the sample during the electron beam irradiation process.

Literature.

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Nitrogen emission										NO	
Molecular									Atomic		
$A^3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$									$^2D \rightarrow ^4S$	$a^4\Pi \rightarrow X^2\Pi$	
v'	v''	$v(\text{cm}^{-1})$	v'	v''	$v(\text{cm}^{-1})$	v'	v''	$v(\text{cm}^{-1})$	$v(\text{cm}^{-1})$	v'	$v(\text{cm}^{-1})$
0	2	44982	2	2	47717	4	8	37355	19119	4	30629
0	3	42688	2	3	45519	4	11	31151(?)		5	28860
0	4	40438	2	4	43309	4	14	25191		6	27131
0	5	38256	2	6	38918	4	15	23309		7	25444
0	6	36061	2	7	36746	4	16	21398		8	23761
0	7	33941	2	8	34589	4	17	19535		9	22090
0	8	31803	2	10	30492(?)	4	18	17699		10	20474
0	9	29701	2	11	28443					11	18887
0	10	27618	2	12	26431	5	11	32445		12	17321
			2	13	24465	5	12	30492(?)			
1	2	46309	2	14	22493	5	16	22727			
1	3	44094				5	17	20846			
1	4	41888	3	11	27813						
1	5	39604	3	12	25844	6	14	27813			
1	7	35354	3	13	23882	6	16	24004			
1	8	33236	3	14	21913	6	18	20279			
1	9	31151(?)	3	15	20058						
1	10	29073	3	16	18189						

Table 1. List of spectral lines observed in our TSL, with their positions determined by derivatives the derivative method.

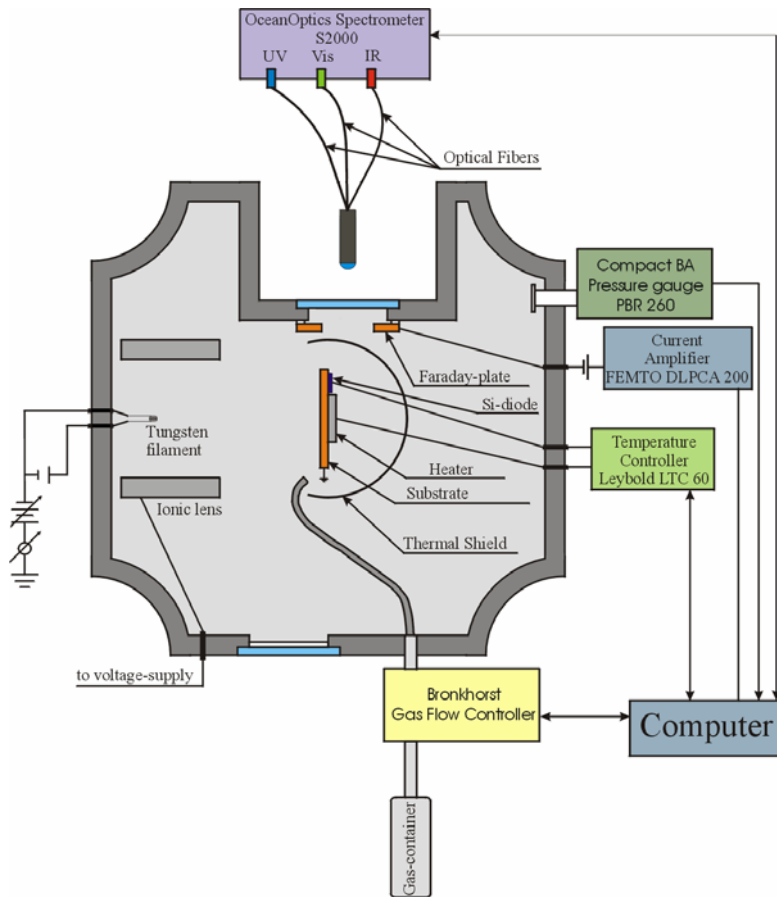


Fig.1. Schematic of the experimental setup used for time-correlated simultaneous measurements of TSEE and of spectrally resolved TSL.

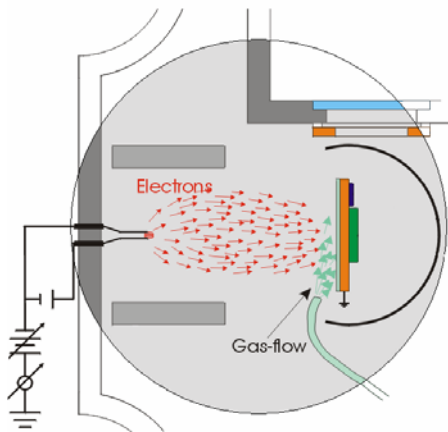


Fig.2. Substrate in position for sample deposition.

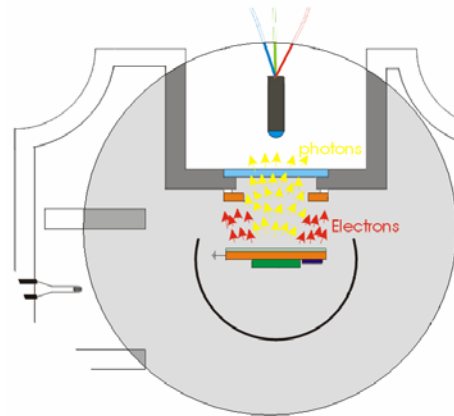


Fig.3. Substrate rotated for TSEE and TSL measurements.

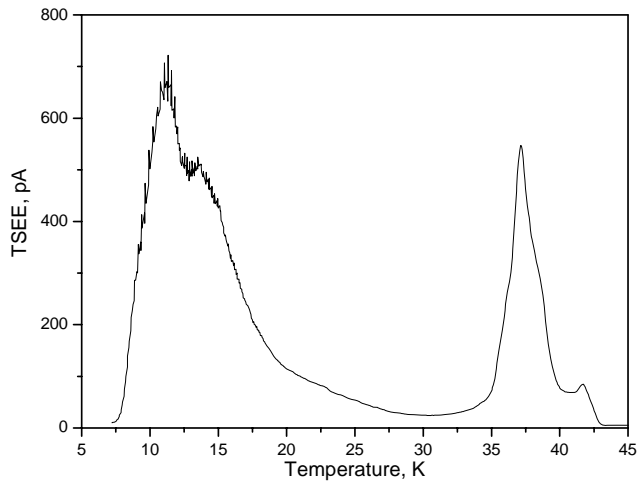


Fig.4. TSEE curve of solid Ar doped with 1% of N_2 .

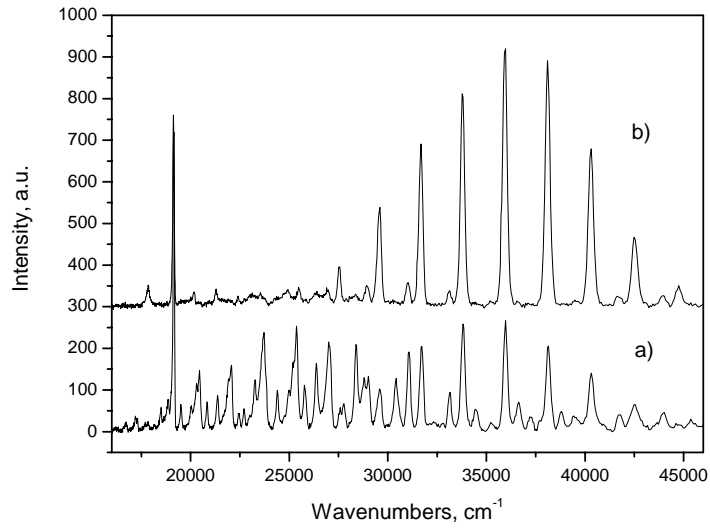


Fig.5. TSL spectrum taken at 11K (trace a) and 25K (trace b).

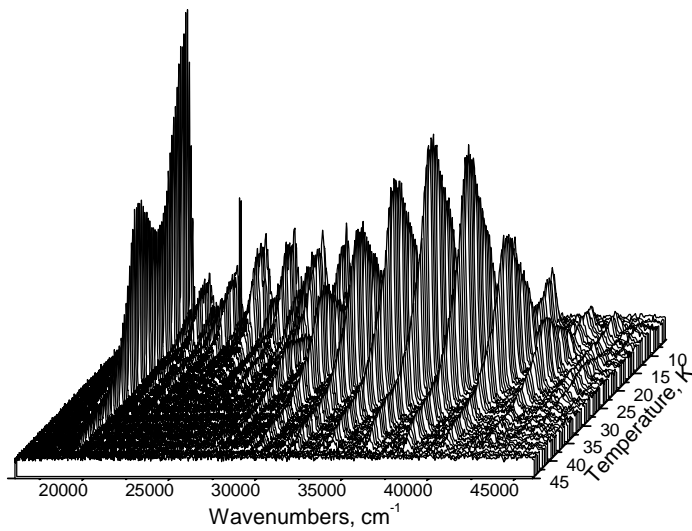


Fig.6. 3D TSL spectrum of solid Ar doped with 1% of N_2 .

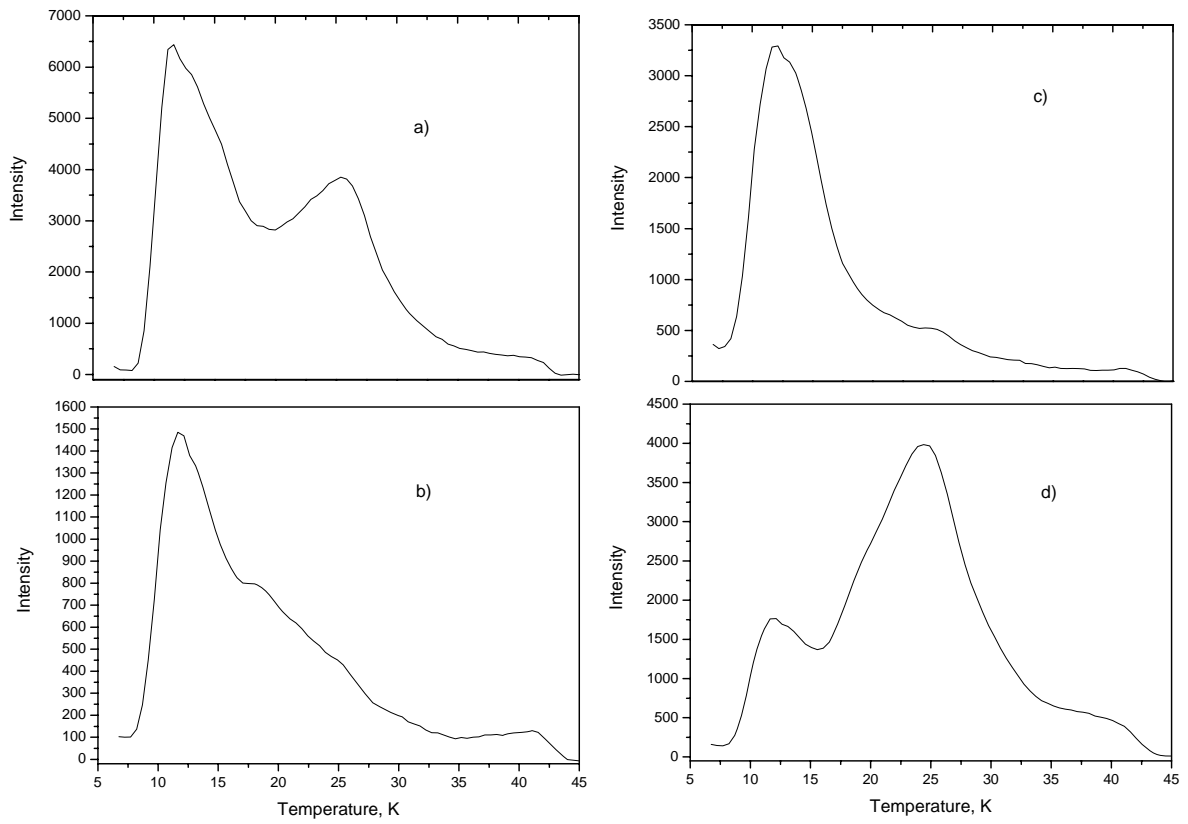


Fig. 7. The temperature dependence of the intensity of atomic nitrogen line (19119cm^{-1}) – trace a; “hot” molecular nitrogen line (31151 cm^{-1}) – trace b; “cold” molecular nitrogen line (36061 cm^{-1}) – trace d; and NO line (22075cm^{-1}) – trace c.