Observation of an exciton luminescence of nitrogen crystals in the region of the vacuum ultraviolet

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Two systems of bands, corresponding to the forbidden molecular transitions $a\,^1\Pi_g \rightarrow X\,^1\Sigma_g{}^+$ and $a'\,^1\Sigma_e{}^- \rightarrow X\,^1\Sigma^+{}_g$ were observed in the emission spectrum of crystalline nitrogen in the vacuum ultraviolet region. A splitting of the vibronic bands was observed. Proof is presented of exciton character of the luminescence.

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It is known that the luminescence visible band induced by an electron beam in solid nitrogen is due to formation of an active N radical in the lattice.[1] So far, however, no study was made of the intrinsic luminescence of the excited molecules of pure nitrogen crystals. All that are known are the earlier works of Vegard,[2] which describe the emission of the forbidden series of solid molecular nitrogen $A^3\Sigma_e^+ \rightarrow X^1\Sigma_g^+$ in the ultraviolet region. We have investigated the luminescence in a broad spectral band, from 6000 to 500 Å. A surprising feature of the nitrogen crystals was the simultaneous emission from four excited molecular states. Besides the known Vegard spectrum, we registered

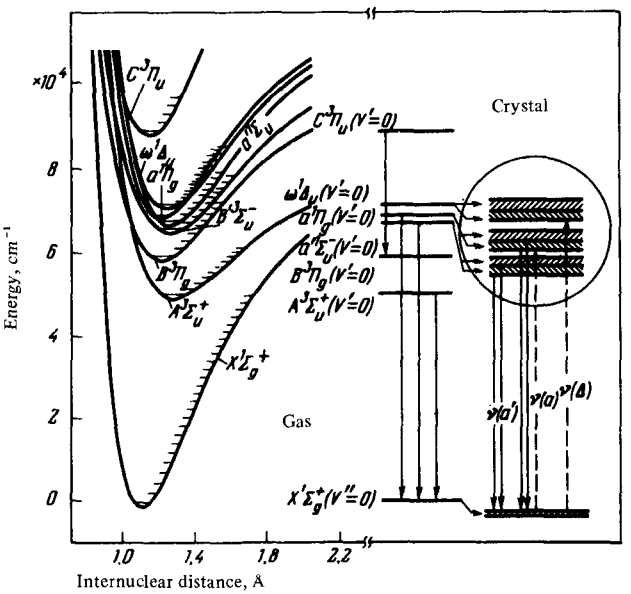

FIG. 1. Potential curves of diatomic molecule N_2 and scheme of singlet exciton states of nitrogen crystal.

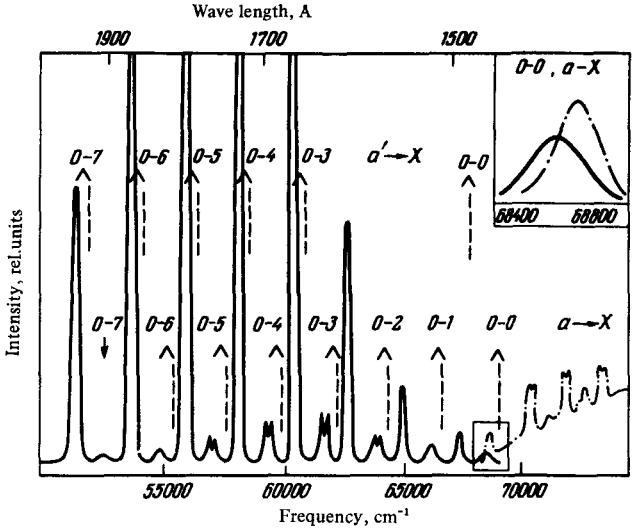

FIG. 2. Luminescence spectrum of solid nitrogen at 20 °K (solid curve). Dash-dot curve—absorption spectra of solid nitrogen[4] ($a\,^1\Pi_g \rightarrow X^1\Sigma_g^+$). The dashed lines mark the position of the emission band in the spectrum of nitrogen gas. The numbering of the ($v'-v''$) bands is indicated separately for the systems $a-X$ and $a'-X$. In the upper corner is shown the overlap of the 0—0 luminescence band (solid) and absorption band (dash-dot) of the $a-X$ system.

for the first time the vibronic series $C^3\Pi_u \rightarrow B^3\Pi_g$ in the near-ultraviolet region, and two singlet transitions $a^1\Pi_g \rightarrow X^1\Sigma_g^+$ and $a'^1\Sigma_u^- \rightarrow X^1\Sigma_g^+$ in the vacuum-ultraviolet region. The observed transitions are marked on the molecular-term scheme (Fig. 1). In this paper we report on the singularities of singlet molecular transitions and present arguments that they are of exciton origin.

The nitrogen crystals were excited by bombarding them with a beam of slow (300—500 eV) electrons. The radiation was registered with a VMR-2 vacuum

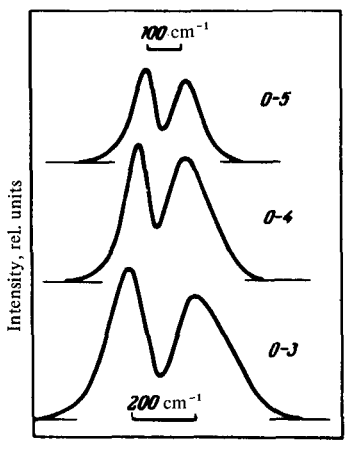

FIG. 3. Change in the value of the splitting for different vibronic emission bands of the $a-X$ system.

monochromator in the single-photon-counting mode. The samples were grown by condensation on a cooled substrate in a helium cryostat.[3] The experiments were performed at temperatures from 8 to 20 °K. In this temperature interval, the nitrogen crystallizes into an α modification with an FCC lattice in which there are four translationally-nonequivalent molecules per unit cell.

Figure 2 shows the nitrogen emission observed in the 2000—1400 Å region. The spectrum consists of two vibronic systems that differ greatly in band shape and intensity. The distances between the bands in each individual system correspond to the vibrational series of the ground state of nitrogen with frequency $\omega_0 = 2360$ cm^{-1}. The luminescence becomes stronger with increasing temperature. The brightest spectra are observed for samples with perfect structure, obtained by condensation on a "hot" substrate, followed by annealing. The short-wave emission band of the weaker system, at $\nu = 68600$ cm^{-1}, is practically at exact resonance with the 0—0 band of the $a\,^1\Pi_g - X^1\Sigma_g^+$ transition in the exciton-absorption spectrum of the nitrogen crystals (Fig. 2). The shift of the luminescence band relative to the absorption maximum is 80 cm^{-1} at a bandwidth ~ 300 cm^{-1}. Comparison with the spectrum of the gas[5,6] confirms the identification of the weak system as being the transition $a\,^1\Pi_g \rightarrow X^1\Sigma_g^+ (a - X)$. The system in the solid nitrogen is shifted relative to the gas by 370 cm^{-1} towards the red side. In the gas, the $a - X$ transition is parity-forbidden; the forbiddenness is weakened in the crystal.[4]

The second more intense system of emission bands was identified as the vibronic series $a'\,^1\Sigma_u^- \rightarrow X^1\Sigma_g^+ (a' - X)$. With respect to the gas, all the bands of the $a' - X$ system are likewise shifted towards the red side by 440 cm^{-1}. In the absorption spectrum of solid nitrogen, and all the more in the gas, the $a' - X$ system is not observed, since the transitions between Σ states of different symmetry are strongly forbidden. The lifetime of the states $a\,^1\Pi_g$ and $a'\,^1\Sigma_u^-$ in the gas phase amounts to 10^{-4} and 10^{-2} sec, respectively.[5]

A distinguishing feature of emission on forbidden transitions of solid nitrogen is the existence of doublet splitting of vibronic bands. The fine structure of the $a - X$ system is shown in Fig. 3. The magnitude of the splitting differs for bands with different vibrational numbers and turns out to be proportional to their total intensity. The most intense vibronic band 0—3 has a maximum splitting $\Delta E_{0-3} = 210$ cm^{-1}. It turned out to be difficult to measure the much weaker 0—0 and 0—6 bands in the experiments. Extrapolation of the splitting energy by using the dependence on the intensity yields for the 0—0 band a value $\Delta E_{0-0} \approx 40$—50 cm^{-1}. This energy agrees with the splitting of the 0—0 band in the exciton absorption spectrum of the $a - X$ system.[4] The splitting of the vibronic bands in the absorption spectrum[4] is interpreted as Davydov splitting. The magnitude of the splitting is written in the form

$$\Delta E_{v'-v''} = A f q_{v'-v''}, \tag{1}$$

where A is a constant, f is the oscillator strength of the given transition, and $q_{v'-v''}$ are the Franck-Condon overlap factors. The splitting of the vibronic luminescence bands observed by us is also well accounted for by a formula such as (1).

The emission bands of the $a' - X$ system have smaller splittings. In the most intense vibronic band (0—5), the doublet splitting amounts to 80 cm^{-1}. Extrapolation for the 0—0 transition of the $a' - X$ series yields a value $E_{0-0} = 3$—4

cm^{-1}. The splitting of the bands of the $a'-X$ transition also agrees with a formula similar to (1). Their values turn out to be much less than for the $a-X$ transition, inasmuch as the oscillator strength of the $a'-X$ system is smaller. The aggregate of all the data indicates that the splitting of the bands in the luminescence spectrum is connected with the collective character of the emission and cannot be attributed to defect or impurity emission centers. An additional confirmation of this interpretation is the absence of a doublet structure of the impurity luminescence of nitrogen in inert-gas crystals.

Since the question of the nature of the luminescence of crystalline nitrogen is a new one, and the singularities of the spectrum are themselves unusual, let us summarize the main experimental data, which confirm the exciton origin of the emission. 1. The position of the 0—0 bands of $a-X$ in the emission spectra and in the exciton absorption spectra coincide. 2. The luminescence is observed only in samples with good crystal structure. 3. Introduction of small inert-element impurities into the crystal (10^{-3} mol.% Xe or Ar) quenches strongly the intrinsic luminescence of the nitrogen. 4. The position of the bands and their relative intensity are constant for the different samples.

Simultaneous emission from several excitonic states should apparently be interpreted in connection with the weak exciton-phonon interaction for these excitations and the singularities of forbidden transitions. The presence of luminescence from $a'^1\Sigma_u^-$ suggests an intensive population of this state and a partial listing of the strict forbiddenness of the transition in the emission. Population of the level $a'^1\Sigma_u^-$ is facilitated by the closeness of the three singlet terms and by the intersection of the potential curves $a'^1\Pi_g$ and $a'^1\Sigma_u$ (Fig. 1). The partial lifting of the hindrance on the emission can be due to collective interactions at high population densities of the metastable states.

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