DeTERMINATION OF THE SQUARE OF THE MATRIX ELEMENT FOR THE DIPOLE MOMENT OF THE ELECTRONIC TRANSITION IN THE FIRST NEGATIVE SYSTEM OF N2^+

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It is of interest to determine |\textit{R}_{\textit{e}}|^{2} for the 1− system of N2^+ (transition B2\Sigma_u^+ → X2\Sigma_u^+), since these bands make a substantial contribution to the emission of air above 7000° K [1]. No reliable values of |\textit{R}_{\textit{e}}|^{2} were available when this work was started, although the quantity had been calculated [2, 3] and had been deduced from the lifetime in the state B2\Sigma_u [4] and from the emission of air [5] and nitrogen [6] in shock tubes. However, these |\textit{R}_{\textit{e}}|^{2} differed by more than a factor of five. We have determined this quantity from the emission of a reflected shock wave in a shock tube. While the work was in progress, papers [7–10] on the topic appeared; these are discussed below.

The 1− system of N2^+ consists of several sequences (Δv = 2, 1, 0 and −2) in the region 3000–5860 Å, the strongest bands being (0, 0) λ = 3914.4 Å, (0, 1) λ = 4278.1 Å, and (1, 2) λ = 4286 Å [11], which were clearly visible in our spectra, with the fine structure resolved. However, the (0, 1) and (1, 2) bands were overlapped by the spectra of impurities, which made it difficult to determine the intensities. There were no impurity lines between the head of the (0, 0) band at 3914.4 Å and the head of the (0, 0) band of the violet system of CN at 3883.4 Å, so this spectral region may be used to determine |\textit{R}_{\textit{e}}|^{2}.

The distance between levels with the same K in the 2\Sigma−→ 2\Sigma transition is small for the case of identical atoms [12], and the lines in the groups R1(K), R2(K), RQ2(K), P1(K), P2(K), and PQ1(K) are not resolved, so the spectrum corresponding to the 2\Sigma−→ 2\Sigma transition may be represented as consisting of the two branches R(ΔK = +1) and P(ΔK = −1). Each line in the R and P branches consists of three components; two of these, R1(K) and R2(K) or P1(K) and P2(K), for which ΔK = ΔJ, are roughly equal in intensity. The other components RQ2(K) and PQ1(K), which have ΔK ≠ ΔJ (satellite lines) are very weak, and so the lines appear as doublets at high resolution with alternating intensities, the lines with K odd being twice as strong as those with K even.* This effect is characteristic of molecules with identical atoms and a nuclear spin of one [12].

In the present case, |\textit{R}_{\textit{e}}|^{2} was calculated from the measured emission intensity of an optically thin layer of gas in thermodynamic equilibrium and heated in a shock tube by a reflected shock wave.

In the Born-Oppenheimer approximation [13] (in which we neglect interaction between the electron motion, the nuclear motion, and the rotation), the energy of a diatomic molecule may be represented as the sum of the electronic, vibrational, and rotational energies. The following expression then gives the line intensity:

\[
I_{\nu} d \nu = \frac{64 \hbar c}{3} N \frac{Q}{Q_{\text{nuc}}} \psi_{J_J'}^2 |\textit{R}_{\textit{e}}|^2 q_{\nu'\nu} i_{J_J'} e^{-\frac{E_{\nu'+E_{\nu}}-E_{J_J'}}{0.77}} p(J'),
\]

(1)

in which \(\nu (\text{cm}^{-1})\) is the wave number; N is the molecular concentration; Q is the sum over the electronic, vibrational, and rotational states (calculated from data of [14]); Q_{\text{nuc}} is the statistical weight of the nucleus (equal to 9); q_{\nu'\nu} is the Frank-Condon factor; \(i_{J_J'}\) is the intensity factor; p(J') is the nuclear statistical weight of a level (6 for K odd, 3 for K even); and \(E_{\nu'}\) and \(E_{\nu}\) are, respectively, the energies (\text{cm}^{-1}) of the upper electronic, vibrational, and rotational levels. The Frank-Condon factor is known [18–18].

The intensity factors for the 2\Sigma−→ 2\Sigma transition are known [19]. For lines of R-form (groups R1, R2, RQ2) and P-form (groups P1, P2, PQ1), respectively, they are

\[R_{ij} = 2K\quad \text{and} \quad P_{ij} = 2(K + 1).\]

It is usual to determine |\textit{R}_{\textit{e}}|^{2} from the measured intensity \(I_{\Delta \nu'}\), which equals the sum of the intensities of the rotational lines in a spectral region \(\Delta \nu\), i.e.,

\[\text{The numbering is with respect to } K' \text{ for the upper electron state.}\]
\[
I_{\Delta \nu} = \sum_{\Delta \nu} \int I_{\nu} d\nu = \frac{64 \pi^2 c}{3} \frac{N}{g_{\text{nucl}} Q} \left| R_{e}^{nm} \right|^2 q_{\nu' e'} e^{-\frac{E_{\nu'} + E_{e'}}{0.77 T}} \times 
\sum_{\Delta \nu} v_{\nu', \nu} p(J') i_{\nu', \nu} e^{-\frac{E_{\nu'}}{0.77 T}}.
\]

In terms of \( K \),

\[
I_{\Delta \nu} = \sum_{\Delta \nu} \int I_{\nu} d\nu = \frac{64 \pi^2 c}{3} \frac{N}{g_{\text{nucl}} Q} \left| R_{e}^{nm} \right|^2 q_{\nu' e'} e^{-\frac{E_{\nu'} + E_{e'}}{0.77 T}} \times 
\sum_{\text{over lines of R-form}} v_{K', K} p(K') 2K' e^{-\frac{E_{K'}}{0.77 T}} + \sum_{\text{over lines of P-form}} v_{K', K} p(K') 2(K' + 1) e^{-\frac{E_{K'}}{0.77 T}}.
\]

Formula (3) allows \( |R_{e}^{nm}|^2 \) to be deduced from the measured \( I_{\Delta \nu} \) if the gas pressure, composition, and temperature are known.

The \( N^+ \) concentration and the gas temperature behind the reflected shock wave were calculated from the initial gas pressure and the velocity of the incident shock wave at the end of the shock tube. Tables [20] were used to determine the parameters of the gas behind the incident wave, and then the equation of state was used to find the enthalpy behind the reflected shock wave, which was used to determine the temperature and pressure [20]. The calculation was performed with a step of 100 m/sec in velocity at the front of the incident wave. The results for the composition of nitrogen were calculated by Lazarev [21] with a temperature step of 200 °K in the range 6000-10 000 °K at pressures of 1, 2, 5, 10, 25, and 100 atmospheres. This gave the proportion of \( N^+ \) to \( \sim 1\% \).

To excite the \( 1- \) system of \( N^+ \) at thermodynamic equilibrium, it is necessary to heat the nitrogen above 6000 °K. Temperatures in this range are produced behind a reflected shock wave in a two-diaphragm tube, the driving gas being an oxygen-helium-hydrogen mixture with helium in the intermediate section. The nitrogen had an oxygen content less than 0.005%, the flow rate being such as to provide complete gas exchange in the low-pressure section (about 12 liters) in \( \sim 2 \) sec. This section included a U-tube manometer for measuring the pressure to \( \pm 1\% \). The pressure was set at 10 mm Hg.

The speed of the incident shock wave was measured to \( \pm 1.5\% \) with ionization or piezoelectric detectors. The emission 4 mm from the end was recorded with DN panchromatic film (sensitivity 380 units GOST) or photoelectrically with two grating spectrographs, DFS-4 (4.7 Å/mm) and SP-64 (13 Å/m). The photographic recording was accompanied by the standard spectrum of iron, while the photoelectric recording was performed with an FEU-17 photomultiplier viewing the exit slit of the spectrograph, the amplified signal passing to an OK-17M oscilloscope. The wavelength calibration was performed with mercury-cadmium and PRK-2 lamps, the wavelength setting accurate to \( \pm 1.2 \) Å for the SP-64 and \( \pm 0.15 \) Å for the DFS-4. The photoelectric recording system was calibrated for absolute sensitivity with an SI-8-200 standard tungsten lamp whose emission as a function of wavelength and temperature is known [22]. Linear operation of the OK-17M was provided by attenuating the incident flux with TS-7 and NS-8 filters, which have accurately known transmission curves.

The oscillograms for the \( (0, 0) \) band were used to calculate \( |R_{e}^{nm}|^2 \). (Figure 1 shows a typical oscillogram for part of the \( (0, 0) \) band.) The numbers of lines in the range \( \Delta \nu \) were deduced from the known wave numbers [23] of the lines.

![Fig. 1. Typical oscillogram from the SP-64: \( \lambda = 3907.9 \pm 6.5 \) Å, \( T = 8500^\circ \) K, \( p \approx 40 \) atm.](image-url)

The background was neglected, since preliminary experiments had shown that it was weak relative to the spectrum. Figure 2 gives the results from various experiments over the range 8000-9500 °K. The DFS-4 gave 0.40 atomic units, while the SP-64 gave 0.37; the difference of \( \sim 8\% \) is within the limits of error of the experiments.