EXPERIMENTAL DETERMINATION OF THE MATRIX ELEMENT OF THE ELECTRONIC TRANSITION OF THE γ- AND β-SYSTEMS OF THE NO MOLECULE

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Abstract

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EXPERIMENTAL DETERMINATION OF THE MATRIX ELEMENT OF THE ELECTRONIC TRANSITION OF THE γ- AND β-SYSTEMS OF THE NO MOLECULE

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As is known (^{1}), the square of the matrix element $|R_e|^2$, characterizing the oscillator strength f_e of an electronic transition of a molecular band system, can be determined from the relation

$$\alpha \equiv \int_{v'v''} k_\nu d\nu = \frac{8\pi^3 \nu^3_{v'v''}}{3hc} \frac{N_0}{Z_{el} Z_{vib}} e^{-(E_{el}+E_{vib})/kT} |R_e|^2 q_{v'v''}. \tag{1}$$

Here the integral on the left-hand side is taken over the entire vibrational band corresponding to the transition (v', v''); $\nu_{v'v''}$ is the frequency of the band head; N_0 is the concentration of the absorbing molecules; Z_{el} and Z_{vib} are, respectively, the electronic and vibrational statistical sums; $q_{v'v''}$ is the so-called Franck–Condon factor; α is the integral absorption coefficient over the entire band. The remaining notation is standard. The quantity α, the experimentally measured parameter, was obtained by photometric processing of absorption spectra. In the case of the bands $\gamma(0,3)$ and $\beta(2,4)$, which undergo strong overlap with the band $\gamma(1,4)$, only the part of the band free from overlap was photometered, and a correction was introduced for the unaccounted portions of the bands.

The absorption spectra of the bands $\gamma(0,0)$, $\gamma(0,1)$, and $\gamma(0,2)$ were obtained with a KS-55 spectrograph. The radiation source was a gas-discharge lamp DKSh-1000, whose radiation was passed through a sealed quartz cell ($l = 400$ mm) filled with a mixture of NO + Ar. The working pressure of the mixture was $15 \div 20$ atm.; the temperature was $400 \div 600^\circ$ K; the relative NO concentrations x_{NO} were 0.25, 7, and 30%, respectively, for obtaining the bands $\gamma(0,0)$, $\gamma(0,1)$, and $\gamma(0,2)$. The cells were filled with gases by distillation with cooling to liquefaction.

Obtaining absorption in the bands (v', v'') for $v'' > 2$ by this method is difficult because of the thermal decomposition of NO and the formation of $\mathrm{N_2O_3}$ at high temperatures (^{2}), which are necessary for appreciable population of levels with $v'' > 0$.

The absorption spectra in the bands $\gamma(0,2)$, $\gamma(0,3)$, and $\beta(2,4)$ were obtained by means of a shock tube ($d = 90$ mm) (^{3}) and an EV-45 pulsed gas-discharge

Figure 1. Dependence $R_e(r)$ for the γ-system of NO. Experimental points: a—according to Bethke (^{11}); b—results of the present work; c—smoothed experimental data of Robinson and Nicholls (^{9}); g—data obtained in (^{9}) by extrapolation

Figure 1: Figure 1. Dependence $R_e(r)$ for the γ-system of NO. Experimental points: a—according to Bethke (^{11}); b—results of the present work; c—smoothed experimental data of Robinson and Nicholls (^{9}); g—data obtained in (^{9}) by extrapolation

source (^{4}). The spectrum was recorded with a 4-meter DFS-13 spectrograph.

The shock-tube method (^{5}) makes it possible to obtain, behind the reflected shock wave, samples of gas mixtures with predetermined thermophysical parameters. The experimental conditions were chosen so that, by the time the absorption spectrum was recorded, vibrational equilibrium had already been established, while dissociation was still insignificant. The gas temperature can be determined by calculation from the measured shock-wave velocity (^{5}). In our case, the shock-wave velocity was measured with piezoelectric barium titanate sensors (^{6}). In some of the experiments we measured the temperature by the method of reversal of spectral lines (^{7}).

In the latter case, a pulsed gas-discharge source (^{8}) was used as the radiation source for obtaining absorption spectra.

with a flash duration of $\sim$ 30 μsec. Measurement of the temperature by the generalized reversal method when the EV-45 source was used was limited by the fact that, in view of the comparatively long flash duration of the EV-45 ($\sim$ 200 μsec), only a very short time interval remained for the temperature measurement (the portion of the oscillogram between the moments of passage of the shock wave and the flash of the source). It was found that precisely this region of the oscillogram, close to the front, is subject to the influence of the teppler effect and cannot be used for reliable temperature measurement. For such experiments the temperature was calculated from the measured velocity (^{5}). It was established that the discrepancy between the calculated and measured temperatures did not exceed 10%.

The thermodynamic parameters of the $N_2 + NO$ mixture (conditions behind the reflected wave) in these experiments were: temperature $T = 2300 \div 2500^{\circ}K$; total pressure $p \simeq$ 60—70 atm.; x_{NO} from 0.6 to 4.0%. Owing to the short duration of the adiabatic compression of the mixture under study and the short flash duration of the pulsed lamp, nitric oxide does not have time to decompose appreciably during the experiment ($\sim 150 \div 300$ μsec).

Fig. 1. Dependence $R_e(r)$ for the γ-system of NO. Experimental points: a—according to Bethke (^{11}); b—results of the present work; c—smoothed experimental data of Robinson and Nicholls (^{9}); g—data obtained in (^{9}) by extrapolation.

This conclusion is confirmed both by consideration of literature data on the half-life times of NO (2) and by the absence in the working photographs of noticeable absorption in the bands of NO_2 and of the Schumann–Runge O_2 bands.

The results of the measurements are presented in Table 1. In the last column is given the approximate accuracy of our measurements in the shock tube. The data obtained with the tube furnace are somewhat more accurate.

It is seen that for the γ-system there is a noticeable increase in the quantity $|R_e|^2$ with v'' in the series of vibrational transitions $(0, v'')$. This fact is in qualitative agreement with the conclusions of Robinson and Nicholls (9) concerning the dependence of $|R_e|$ on $r_{v'v''}$ (the r-centroid).

In Fig. 1 are presented the experimental data of Bethke (11), our measurements, and also the values of R_e obtained by normalizing the relative data of Robinson and Nicholls with the aid of our numbers.

The straight line I in the graph is the dependence $R_e = C(1-0.899\,r)$, proposed by Robinson and Nicholls (when normalized with the aid of our values, $C = 4$ was obtained). It is seen that the dependence of Robinson and Nicholls, valid for $r < 1.07$ Å, diverges from the experimental data at $r > 1.07$ Å. At $r = 1.11$ Å, R_e becomes 0, whereas the experimental data give finite values of R_e.

It was found that the obtained experimental data can be approximated by means of a cubic parabola (curve II in Fig. 1)

$$R_e = 116.172 - 301.319r + 260.824r^2 - 75.263r^3. \tag{2}$$

The electronic-transition probability of a molecule is often characterized by the electronic oscillator strength of the system f_e, related to $|R_e|^2$.

Table 1 gives the values of the oscillator strength calculated by formula (3):

$$f_e = \frac{8\pi^2 mc\nu_{00}}{3he^2}\,|R_e|^2. \tag{3}$$

Here ν_{00} is the frequency of the center of gravity of the system, practically ν_{00} is the frequency of the head of the $\gamma(0,0)$ band.

Measurements of the oscillator strengths of the γ-system of NO had earlier been carried out mainly by absorption of radiation in a cold gas (10, 11) for the bands $(v', 0)$. Of such measurements, the data of Bethke (11), who carried out measurements at pressures of the broadening gas up to 140 atm, appear especially reliable. In that work, for the bands $\gamma(0,0)$, $\gamma(1,0)$, $\gamma(2,0)$, $f_e = 0.0022$ was obtained, which, within the errors of the experiment, agrees with our value for $\gamma(0,0)$.

Table 1

Band	$\lvert R_e\rvert^2$, arb. units	f_e	$\dfrac{\Delta f_e}{f_e} \cdot 100,\ \%$
$\gamma(0,0)$	0.018	0.0024	20
$\gamma(0,1)$	0.026	0.0034	30
$\gamma(0,2)$	0.034	0.0043	40
$\gamma(0,3)$	0.039	0.0047	45
$\beta(2,4)$	0.048	0.0059	50

Comparatively recently there appeared the work of Daiber and Williams (^{12}), who obtained $f_e = 0.0034$ for the bands $\gamma(0,1)$, $\gamma(0,2)$, and $\gamma(0,3)$ from absorption in a hot gas; this value is also very close to our data (see Table 1). The value $f_e = 0.001$, obtained from emission in a shock tube (^{13}), can be regarded only as an estimate.

The literature data on the β-system are less definite. Bethke gives the value 0.0015, Kek et al. (^{13}) obtained $f_e = 0.006$; Daiber and Williams (^{12}) give an estimate $f_e \lesssim 0.006$, and in Weber' s work (^{14}), unavailable to us, the value $f_e = 0.008$ was obtained. All these data, except Bethke' s data, may be considered (within the errors of the experiment) to agree with our value $f_e^{\beta} = 0.0059$. Such a comparison is quite conditional in the sense that different values in ($^{11-13}$) were obtained for different bands, and may be justified in part only by the consideration that, according to (^{9}), the dependence of R_e on r is not very strong.

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