

## Absolute Intensities for the Ultraviolet $\gamma$ Bands of NO\*

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Absolute intensities have been measured for three of the ultraviolet  $\gamma$  bands of NO. The corresponding electronic absorption oscillator strength is estimated to be  $0.0024 \pm 0.0004$ .

**A**BSOLUTE intensities and total electronic  $f$  values for three of the  $\gamma$  bands of NO have been determined from measurements utilizing self-broadening in order to eliminate rotational fine structure.<sup>1</sup> A Cary Model 11M spectrophotometer was used in the present studies.

Commercial grade NO (Matheson and Company, 98% pure) was carefully purified.<sup>2</sup> The gas used in the present investigations contained impurities of NO<sub>2</sub> and N<sub>2</sub>O<sub>3</sub> in concentrations below 1 part in 3000. Results obtained for the integral of the logarithm of the reciprocal fractional transmission  $A$  (in cm<sup>-1</sup>) as a function of optical density  $pL$  (in cm atmos) are plotted in Figs. 1 to 3, respectively, for the  $\gamma(0,0)$ ,  $\gamma(1,0)$ , and  $\gamma(2,0)$ † ultraviolet bands of NO ( $A^2\Sigma^+$  to  $X^2\Pi$  transition). Also shown in Figs. 1 and 3 are measurements for

NO in a large (1.33 cm long) cell utilizing helium at a total pressure of 500 psia. The cell lengths used in self-broadening experiments were 0.005, 0.00178, and 0.000635 cm at total pressures between 60 and 400 psia.

The integrated intensities  $S$  (in cm<sup>-2</sup>-atmos<sup>-1</sup>) may be obtained from the data plotted in Figs. 1 to 3 by use of the relation

$$S = 2.303d(A)/d(pL). \quad (1)$$

Reference to Figs. 1 to 3 shows that the measured values of  $A$  increase linearly with  $pL$ , as would be expected if valid absorption measurements had been made at all of the total pressures used. The fact that adequate pressures had been obtained to eliminate instrumental errors associated with lack of resolving power was verified independently by studying the change in rotational fine structure with pressure. The observed values of  $S$ , as well as the corresponding total absorption oscillator strengths  $f_{ul}$ , are listed in Table I. The  $f_{ul}$  values were

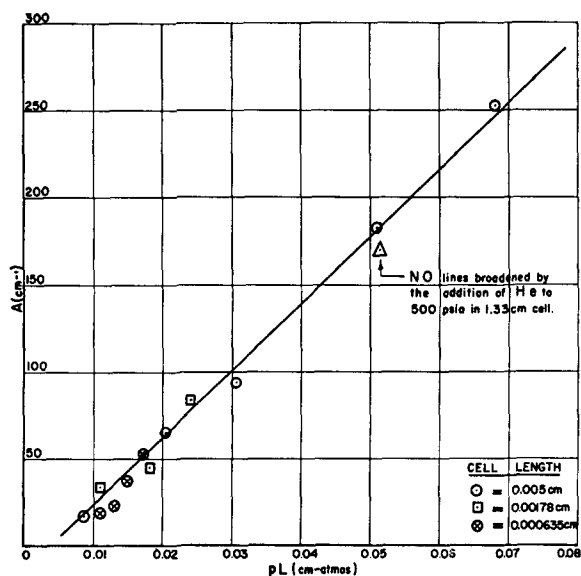


FIG. 1. Observed integrals of the logarithm of the reciprocal fractional transmission  $A$  (in cm<sup>-1</sup>) as a function of  $pL$  (in cm atmos) for the  $\gamma(0,0)$  band.

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<sup>1</sup> This procedure was used some years ago for absolute infrared intensity measurements. [See S. S. Penner and D. Weber, *J. Chem. Phys.* **19**, 807, 817, 974 (1951).]

<sup>2</sup> H. L. Johnston and W. F. Giauque, *J. Am. Chem. Soc.* **51**, 3194 (1929).

† The listed data for the  $\gamma(2,0)$  band include weak contributions from the  $\beta(3,0)$  and  $\beta(4,0)$  bands, which we shall assume to be negligibly small in the following calculations.

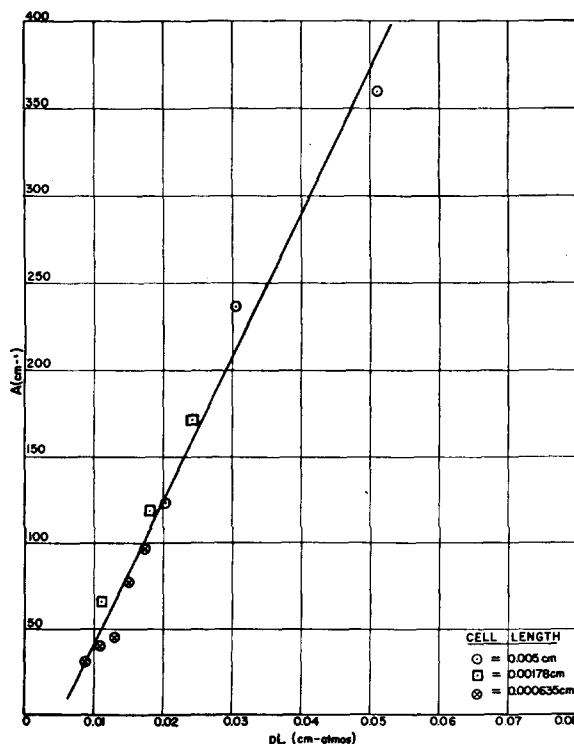


FIG. 2. Observed values of  $A$  (in cm<sup>-1</sup>) as a function of  $pL$  (in cm atmos) for the  $\gamma(1,0)$  band.

computed from the approximate relation<sup>3</sup>

$$f_{ul} = \frac{S}{2.3789 \times 10^7 (273.1/T) N_l} \frac{N_T}{N_l} \times [1 - \exp(-hc\bar{\omega}/kT)]^{-1}. \quad (2)$$

Here  $T$  is the absolute temperature,  $N_l/N_T$  is the fractional number of molecules in the lower energy level for the transition under study,  $h$  is Planck's constant,  $c$  is the velocity of light,  $\bar{\omega}$  equals an average wave number corresponding to the center of the particular  $\gamma$  band under study, and  $k$  is the Boltzmann constant.

The total emission oscillator strengths  $|f_{lu}|$  for the  $\gamma$  bands may be shown<sup>3</sup> to be given by the relation

$$|f_{lu}| = \frac{g_l}{g_u} f_{ul} = \frac{8\pi^2 mc}{3h} \frac{1}{g_u} \sum_{l',u'} |r_{l'u'}|^2 \quad (3)$$

where  $g_l$  and  $g_u$  represent, respectively, the statistical weights for the lower and upper energy levels,  $m$  is the electronic mass, and  $r_{l'u'}$  is the matrix element for a

TABLE I. Experimental results obtained for three  $\gamma$  bands of NO.

Band	$S$ (cm <sup>-2</sup> ·atmos <sup>-1</sup> )	$f_{ul}$	$(f_{ul})_{el}$
$\gamma(0,0)$	8830	0.00041	0.0025
$\gamma(1,0)$	19 100	0.00088	0.0025
$\gamma(2,0)^a$	14 700	0.00067	0.0021

<sup>a</sup> Includes weak contributions from the  $\beta(3,0)$  and  $\beta(4,0)$  bands, which were neglected in the present calculations.

transition between one of the  $g_u$  fold degenerate upper energy levels  $u'$  and the corresponding lower energy level  $l'$ . It is known that the total wave function may be written, in good approximation, as the product of electronic and vibrational wave functions; furthermore, the electronic transition integral may often be assumed to be constant for a given band system. We may then obtain the value

$$(f_{ul})_{el} = \frac{(f_{ul}) \bar{\omega}_{\gamma(0,0)}}{(v_l v_u)^2 \bar{\omega}_{lu}}, \quad (4)$$

by utilizing the results<sup>4</sup> of approximate theoretical calculations for the square of the vibrational overlap

<sup>3</sup> See, for example, A. Unsöld, *Physik der Sternatmosphären*, (Julius Springer, Berlin, 1938), pp. 170-186. Equation (2) may be derived by using the appropriate relations given by Unsöld.

<sup>4</sup> Jarman, Fraser, and Nicholls, *Astrophys. J.* **118**, 228 (1953). Our  $(v_l v_u)^2$  corresponds to  $(v', v'')^2$  in the paper by Nicholls *et al.*

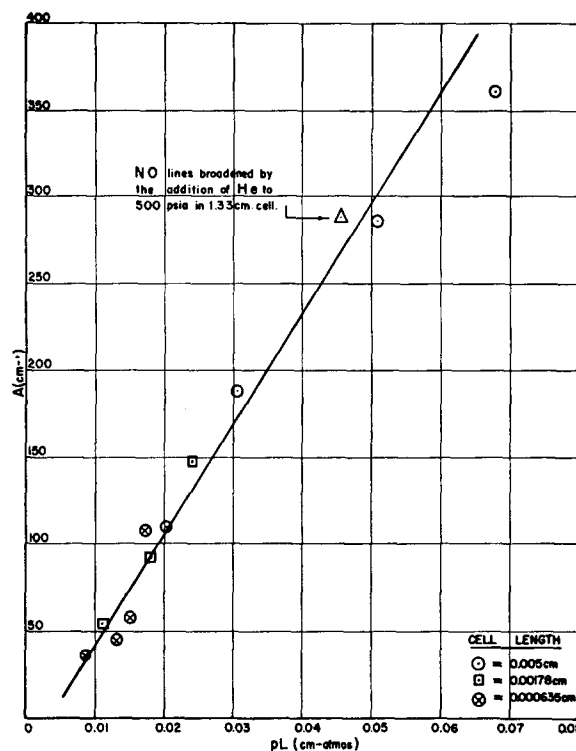


FIG. 3. Observed values of  $A$  (in cm<sup>-1</sup>) as a function of  $pL$  (in cm atmos) for the  $\gamma(2,0)$  band, including weak contributions from the  $\beta(3,0)$  and  $\beta(4,0)$  bands.

integral  $(v_l v_u)^2$ . In Eq. (4) the subscripts  $\gamma(0,0)$  and  $lu$  identify, respectively, appropriate values for the  $\gamma(0,0)$  band and for a particular transition between the lower state  $l$  and upper state  $u$ . The values of the electronic absorption oscillator strengths  $(f_{ul})_{el}$  obtained from Eq. (4) are also listed in Table I. Since  $(f_{ul})_{el}$  for the three gamma bands is fairly constant, we conclude that the corresponding calculated squares of the vibrational overlap integrals represent relative vibrational intensities in fair approximation.

The principal source of error in the present investigations is associated with inaccuracies in estimating the small cell lengths. For higher pressures (corresponding to larger values of  $pL$  for a given cell length) the apparent values of  $A$  seem to increase slightly more rapidly with  $pL$  than linearly, presumably because the effective cell lengths increased slightly with pressure. We estimate the probable limits of accuracy for our cell lengths at  $\pm 10\%$  of the listed values; the corresponding results for the integrated absorption should be reliable to  $\pm 20\%$ .