

TABLE I.

Temp. °C	Densities: g per cc			
	$\rho_L$ obs	$\rho_L$ calc	$\rho_V$ obs	$\rho_V$ calc
155.8	0.70520	0.7052	0.0079	0.00903
173.3	0.67059	0.6705	0.012494	0.01241
123.6	0.62478	0.6500	0.01587	0.01530
198.9	0.61920	0.6192	0.02106	0.02120
212.0	0.59305	0.5935	0.02775	0.02745
232.4			0.04280	0.04255
237.3	0.5359	0.5350		
244.6	0.51993	0.5202	0.05516	0.05400
260.6	0.48589	0.4835	0.07733	0.07750
268.9	0.45740	0.4570	0.09480	0.09520
272.25	0.43200	0.4460	0.1023	0.1024
276.45	0.42370	0.4205	0.1300	0.1270
283.94	0.3620	0.3580	0.1681	0.1662
285.72	0.3620	0.3220	0.2402	0.2220

calibrated glass capillary containing the samples and enclosed in a constant temperature apparatus. Pressures were measured by a Barrett dead weight test gauge with calibrated piston diameters and weights. Temperatures were maintained by an atmosphere of pure organic vapors distilling at constant temperature, and were measured by copper-constantan thermocouples calibrated against a platinum resistance thermometer with an NBS certificate. For a series of specific temperatures, the pressures and volumes were read, the latter by using a cathetometer calibrated against a standard meter stick. Corrections for menisci, interphase levels, and ambient conditions were made. Corrections for expansion of the glass capillary due to pressure and temperature changes were made using the Bridgman equation<sup>2</sup>  $\Delta V = V_0(30.27 \times 10^{-7} p + 9.9 \times 10^{-12} p^2)$  where  $p$  = pressure in Kgm/cm<sup>2</sup>, and a coefficient of cubical expansion of  $9.9 \times 10^{-6}$ .<sup>3</sup>

The *n*-butanol (C.P. grade) was distilled at high reflux successively from calcium oxide, fresh magnesium, and activated alumina. Middle cuts were collected, and the final product gave a refractive index of 1.3973 at 25°C and a boiling point of 117.5°C at 760 mm.

Densities for the saturated vapor and liquid are given in Table I. Equations for the saturated vapor and for the liquid densities have been determined as

$$\rho_V = 0.1424 + 0.44 \times 10^{-2} n + 5.93125 \times 10^{-4} n^2 + 1.8408 \times 10^{-4} n^3 + 1.6317 \times 10^{-5} n^4,$$

and

$$\rho_L = 0.39718 - 0.005899n - 2.1212 \times 10^{-4} n^2 - 1.48145 \times 10^{-4} n^3 - 2.3350 \times 10^{-5} n^4,$$

where  $n = t^\circ\text{C} - 280.5^\circ\text{C}$ .

In Table I observed values are experimentally determined, and calculated values were those obtained by the above equations and show a mean deviation of 0.15 percent for the liquid densities and 0.6 percent for the vapor densities. The critical density has been determined by the "law of rectilinear diameters,"<sup>4,5</sup> and the equation for rectilinear diameters determined as

$$d = 0.28637 - 0.6165 \times 10^{-3} m + 5.7986 \times 10^{-7} m^2 + 5.324 \times 10^{-8} m^3 + 1.35732 \times 10^{-9} m^4,$$

where  $m = t^\circ\text{C} - 250.0^\circ\text{C}$ . The critical constants were determined both analytically and graphically with excellent agreement, and

TABLE II.

Date	$t_c$ °C	$p_c$ atmos	$\rho_c$ g/cc	Investigators
1883	287.1			Pawlewski <sup>a</sup>
1884	270.5			de Heen <sup>b</sup>
1923	287.0	48.4		Herz and Neukirch <sup>c</sup>
1943	288.0			Fischer and Reichel <sup>d</sup>
1955	286.95	48.60	0.2700	This investigation

<sup>a</sup> B. Pawlewski, Ber. deut. chem. Ges. 15, 2143, 2460 (1882).

<sup>b</sup> de Heen, Landolt, and Bornstein (Verlag Julius Springer, Berlin, 1923), Vol. 1, p. 256.

<sup>c</sup> W. Herz and E. Neukirch, Z. Physik 104, 433 (1923).

<sup>d</sup> R. Fischer and T. Reichel, Mikrochimie 31, 192 (1943).

the results are shown, in comparison to other investigations, in Table II. It is considered that the critical temperature is accurate to  $\pm 0.05^\circ\text{C}$ , the pressure to  $\pm 0.05$  atmos and the density to  $\pm 0.0002$  g per cc. A more extensive report on the P-V-T relationships for *n*-butanol will be submitted for publication shortly.

*Acknowledgments.*—The assistance of R. W. Esplen and D. Clegg in making measurements, of W. Pye in glassblowing, and of the National Research Council of Canada in making a grant-in-aid is gratefully acknowledged.

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<sup>1</sup> W. B. Kay, Ind. Eng. Chem. 24, 291 (1932).

<sup>2</sup> P. W. Bridgman, Am. Sci. J. 7, 81 (1929).

<sup>3</sup> Catalog No. L. P. 34 (1954), Corning Glass Works, Corning, New York.

<sup>4</sup> L. Callette and E. Mathies, Compt. rend. 102, 1202 (1886).

<sup>5</sup> S. Young, Sci. Proc. Roy. Dublin Soc. 12, 374 (1909-10).

## Frequency Shift of the CO Stretching Band in Polypeptides and Proteins

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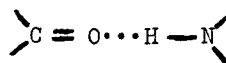
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(Received April 28, 1955)

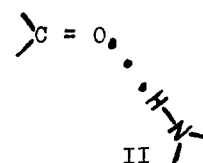
IT has been observed<sup>1,2</sup> that the frequency of the CO stretching mode in synthetic polypeptides and natural proteins depends upon the configuration of the polypeptide chain: in the  $\alpha$ , or folded, form this frequency is close to  $1660\text{ cm}^{-1}$ , whereas in the  $\beta$ , or extended, form this frequency is close to  $1630\text{ cm}^{-1}$ . Although used as a means of distinguishing between  $\alpha$  and  $\beta$  forms of polypeptides and proteins,<sup>3</sup> it does not appear that any explanation has been offered for the frequency shift. It is the purpose of this note to suggest a possible reason, one which seems to be supported by the presently available experimental evidence.

Although heretofore correlated with the  $\alpha$  and  $\beta$  configurations of the polypeptide chain, it is clear that the shift is more a reflection of the local environment of the CO group than it is of the over-all chain configuration. Such a change in environment would most naturally be related to the hydrogen bonding in which the CO group participates. Frequency shifts involving hydrogen bonding have been correlated with the distance between the atoms partaking in the hydrogen bond.<sup>4,5</sup> This cannot, however, be the entire explanation in the present case, because the significant fact is that the NH stretching frequency does not shift by any appreciable amount from  $\alpha$  to  $\beta$  polypeptides,<sup>1</sup> which it would be expected to do if the only result of the configurational change was a change in the O...N distance.

It is suggested that the frequency shift results from a configurational change in the CO...NH angle of the type schematically illustrated in I and II below. Assuming that the O...H force



I



II

constant is essentially the same in I and II, it is clear that we would expect a relatively larger change in the CO frequency from I to II than in the NH frequency, since the CO force constant is more strongly affected. We would further expect that the CO frequency in I would be lower than in II. If the H atom were not along the O...N line, the result would be essentially the same, although the NH stretching frequency might undergo a small shift.

This explanation for the frequency shift seems to be consistent with the known structural features of present protein models and

TABLE I. Correlation between CO stretching frequency and CO...NH angle.

Substance	CO...HN angle	CO stretching frequency, cm <sup>-1</sup>	References
Silk	~180°	1640	b; see footnote 3
Nylon	~160°	1650	c; d
Acetanilide	145°	1660	e; f
Urea	180° <sup>a</sup>	1680	g; h
Diketopiperazine	~120°	1705	i; j

- <sup>a</sup> But not colinear (see text).  
<sup>b</sup> Marsh, Corey, and Pauling, *Biochim. et Biophys. Acta* **16**, 1 (1955).  
<sup>c</sup> Ambrose, Elliott, and Temple, *Proc. Roy. Soc. (London)* **A199**, 183 (1949).  
<sup>d</sup> Elliott, Ambrose, and Temple, *J. Chem. Phys.* **16**, 877 (1948).  
<sup>e</sup> C. J. Brown and D. E. C. Corbridge, *Acta Cryst.* **7**, 711 (1954).  
<sup>f</sup> J. Mann and H. W. Thompson, *Proc. Roy. Soc. (London)* **A211**, 168 (1952).  
<sup>g</sup> P. A. Vaughan and J. Donohue, *Acta Cryst.* **5**, 530 (1952).  
<sup>h</sup> W. E. Keller, *J. Chem. Phys.* **16**, 1003 (1948).  
<sup>i</sup> R. B. Corey, *J. Am. Chem. Soc.* **60**, 1598 (1938).  
<sup>j</sup> Ambrose, Elliott, and Temple, *Proc. Roy. Soc. (London)* **A206**, 192 (1951).

of simple compounds. In Table I we present some results which correlate the CO...HN angle with the CO stretching frequency. It is seen that the relationship discussed above is well obeyed. The case of urea corresponds to structure II in which the H is not on the O...N line (but CO and HN bonds are parallel), and is seen to fit in well with the present explanation. The frequencies do not correlate as well with the hydrogen bond distances; e.g., 2.76 Å in silk, 2.85 Å in diketopiperazine, 2.97 Å in acetanilide. In all cases the NH stretching frequency is close to 3300 cm<sup>-1</sup>, the value expected when hydrogen bonding occurs. Data on simple amides in solution and in the solid state<sup>6,7</sup> are also in agreement with the above explanation: the more nearly colinear the CO...HN hydrogen bond, the lower the CO stretching frequency. An accompanying shift in the 1530 cm<sup>-1</sup> band<sup>1</sup> from  $\alpha$  to  $\beta$  polypeptides is perhaps a result of the interaction between the CO frequency and the other modes of the peptide group.<sup>8</sup>

To the extent that the CO frequency is a measure of the CO...HN bonding angle, variations in this frequency would be indicative only of variations in the configuration of this hydrogen bond. It may not always be justifiable, therefore, to extrapolate from the value of this frequency to a particular polypeptide chain configuration.

- <sup>1</sup> E. J. Ambrose and A. Elliott, *Proc. Roy. Soc. (London)* **A205**, 47 (1951).  
<sup>2</sup> A. Elliott, *Proc. Roy. Soc. (London)* **A221**, 104 (1953).  
<sup>3</sup> E. J. Ambrose and A. Elliott, *Proc. Roy. Soc. (London)* **A206**, 206 (1951).  
<sup>4</sup> R. E. Rundle and M. Parasol, *J. Chem. Phys.* **20**, 1487 (1952).  
<sup>5</sup> R. C. Lord and R. E. Merrifield, *J. Chem. Phys.* **21**, 166 (1953).  
<sup>6</sup> S. Mizushima *et al.*, *J. Am. Chem. Soc.* **72**, 3490 (1950).  
<sup>7</sup> S. Mizushima *et al.*, *J. Am. Chem. Soc.* **75**, 1863 (1953).  
<sup>8</sup> R. D. B. Fraser and W. C. Price, *Nature* **170**, 490 (1952).

### Absorption Coefficients of Nitric Oxide in the Vacuum Ultraviolet\*

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(Received April 25, 1955)

PRELIMINARY results of the absolute absorption of light in NO have been obtained between 374 Å and 1300 Å from photometric measurements of 60 light source emission lines (Fig. 1 and Table I). The coefficients  $\mu$ , in units of cm<sup>-1</sup> at NTP, are defined by the relation  $I = I_0 \exp(-\mu x)$ , and the techniques used were essentially those described in earlier papers<sup>1</sup> for a grazing incidence vacuum spectrograph. The impurities of NO were stated by the manufacturer (Matheson Company) to be nitrogen and its higher oxides, and it was attempted to freeze out the latter by passing the continuously flowing gas through alcohol cold traps (-110°C). Because of the fact that the absorption

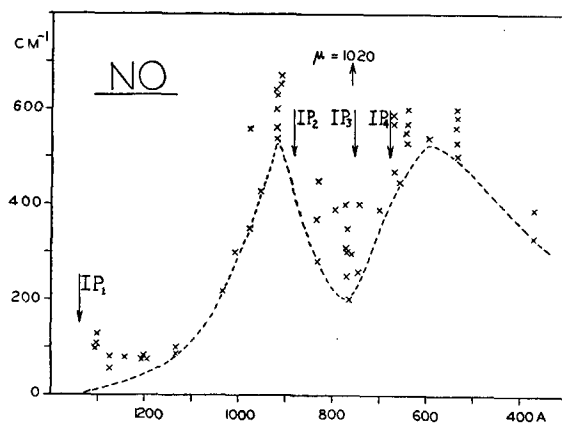


FIG. 1. Absorption coefficients in NO.

coefficients of most gases in their ionization continua are of about the same order of magnitude, it was assumed that the observed absorption in the NO continuum was probably not seriously falsified by any remaining impurities. This received further support from the fact that Zelikoff *et al.*<sup>2</sup> reported a broad absorption region (half-width about 55 Å) in N<sub>2</sub>O with a peak of 2465 cm<sup>-1</sup> at 1285 Å, whereas the measurements for NO at 1276 Å and 1302 Å yielded values of  $\mu = 81$  cm<sup>-1</sup> and 130 cm<sup>-1</sup>, respectively.

Previous NO results obtained by Marmo<sup>3</sup> and Watanabe<sup>4</sup> between 1100 Å and 2300 Å agree reasonably well with those presented here in the region where overlapping occurred. It should be kept in mind, however, that all those coefficients which fall into resonance bands with well-delineated structure can only give an indication of the magnitude of the absorption there, except for those values which lie within a diffuse band or within dissociation and ionization continua and can therefore be expected to be more accurate. The region from 680 Å towards longer wavelengths is well populated with bands which have been classified by Tanaka<sup>5</sup> and others into Rydberg and non-Rydberg progressions, and his series limits are indicated by arrows in Fig. 1. This band structure is also apparent in the figure, where adjacent coefficients show widely different values such as  $\mu = 1020$  cm<sup>-1</sup> at 764.357 Å and  $\mu = 200$  cm<sup>-1</sup> at 765.140 Å.

The value of the continuum below 1300 Å may be estimated by connecting together with a line the lowest coefficients, and the

TABLE I. Absorption coefficients ( $\mu$ ) of NO.

$\lambda$ (Å)	$\mu$ (cm <sup>-1</sup> )	$\lambda$ (Å)	$\mu$ (cm <sup>-1</sup> )		
1306.038	O I	100	796.661	O II	390
1304.864	O I	110	775.957	O II	400
1302.192	O I	130	772.975	N III	310
1276.18	N II	81	772.385	N III	300
1276.06	N II	56	771.901	N III	250
1243.297	N II	82	771.544	N III	350
1200.706	N I	74	765.140	N IV	200
1200.22	N I	82	764.357	N III	1020
1199.527	N I	74	763.340	N III	300
1134.98	N I	84	746.976	N II	260
1134.419	N I	100	745.836	N II	400
1037.332	C II	220	703.805	O III	390
1037.020	C II	220	702.890	O III	390
1006.051	N II	300	702.332	O III	390
979.919	N III	350	673.768	O II	590
977.020	C III	560	672.948	O II	570
955.335	N IV	430	671.397	N II	470
924.274	N IV	640	660.280	N II	450
923.669	N IV	630	645.167	N II	550
923.211	N IV	600	644.825	N II	570
923.045	N IV	560	644.621	N II	600
922.507	N IV	540	644.148	O II	530
916.708	N II	670	599.589	O III	540
916.01	N II	650	539.853	O II	560
915.96	N II	670	539.547	O II	530
835.293	O III	370	539.086	O II	600
834.467	O III	370	538.318	O II	500
833.749	O III	280	537.830	O II	580
833.332	O II	450	374.330	O III	390
832.930	O III	280	374.075	O III	340