

# Absorption spectrum of the NO molecule

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Objektyp: **Article**

Zeitschrift: **Helvetica Physica Acta**

Band (Jahr): **36 (1963)**

Heft III

PDF erstellt am: **25.09.2024**

Persistenter Link: <https://doi.org/10.5169/seals-113371>

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## Absorption spectrum of the NO molecule

III The heterogeneous perturbation  $H^2\Sigma^+ - H'^2\Pi$

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(1. X. 62)

*Abstract.* A rotational analysis is presented for 2 complex bands  $H, H' - X$  observed in the NO absorption spectrum. (0,0) band at 1595 Å; (1,0) band at 1538 Å. The upper states are  $H^2\Sigma^+$  and  $H'^2\Pi$ , two nearly coinciding Rydberg-states interacting with each other in a hitherto unobserved mode. A deperturbation is carried out, and for the first time a consistent interpretation can be given of all known Rydberg-states belonging to the first ionization limit of the NO molecule.

### 1. Introduction

In the system of the excited states of the NO molecule "Rydberg-states" have to be found belonging to the first ionization potential of the molecule. Rotational and vibrational constants of these states very closely agree with the constants of the  $^1\Sigma^+$  ground state of the  $\text{NO}^+$  ion. The Rydberg-states  $A^2\Sigma^+$ ,  $C^2\Pi$ ,  $D^2\Sigma^+$  and  $E^2\Sigma^+$  are, for a long time, well known, and recently LAGERQVIST and MIESCHER<sup>1)2)</sup> have published provisional data for a number of further such states resulting from new finestructure analyses in the NO absorption spectrum. In the present paper more detailed information will be given for the Rydberg-states designated  $H$  and  $H'$ . Complete rotational analyses of the (0,0) and the (1,0) bands of the  $H, H' - X^2\Pi$  system have now been made. It turned out that in this system a new case of interaction occurs between a  $\Sigma$  and a very close lying  $\Pi$  state. A consistent interpretation, hitherto lacking, of all known low lying Rydberg-states of the molecule can now be given. In addition the states  $H$  and  $H'$  deserve special interest, because they are the upper states of bands, so far not understood, but often observed, in the visible and near infrared emission spectrum of a discharge in NO gas. Partial analyses of these emission bands have been published<sup>10)</sup>.

The photographic plates of the NO absorption spectrum ( $\text{N}^{14}\text{O}$  and  $\text{N}^{15}\text{O}$ ), which form the basis of the present investigation, were taken at Ottawa with the 10 meter vacuum spectrograph built by Dr. A. E. DOUGLAS and Dr. G. HERZBERG at the National Research Council of Canada (reciprocal dispersion 0.2 Å/mm). Particularly useful was a plate obtained with the NO gas in the absorption tube cooled to the temperature of liquid oxygen. On the reproduction of the NO absorption spectrum (earlier plate from the 3 meter instrument) given by LAGERQVIST and MIESCHER<sup>3)</sup> the  $H, H' - X$  bands are clearly visible: (0,0) band at 1595 Å, to the left of  $\beta$  (19,0); (1,0) band at 1538 Å, to the left of  $\beta$  (22,0).

### 2. Results of the rotational analyses

The very complex structures of the (0,0) and (1,0) bands match each other perfectly. For  $\text{N}^{14}\text{O}$  the (0,0) band is slightly overlapped at the long wavelength side by

the (19,0) band of the  $\beta$ -system ( $B \ ^2\Pi - X \ ^2\Pi$ ). As was already stated in<sup>1)</sup> each band can be divided into two mutually overlapping bands designated  $H - X$  and  $H' - X$  respectively\*). The band at the shorter wavelength  $H' - X$  is a little stronger than  $H - X$ . Using the well known second term differences  $\Delta_2 F''$  of the  $X \ ^2\Pi$  ground state of the NO molecule the total of 24 branches of Table 1 was isolated and numbered. Wavenumbers are given for the conspicuous bandheads formed by a few P-branches. In Table 2 are listed the wavenumbers of all measured lines of the  $N^{14}O$  bands. Q-branches are not observed.

Table 1

$H \ ^2\Sigma^+ - X \ ^2\Pi$			$H' \ ^2\Pi_c - X \ ^2\Pi$			$H' \ ^2\Pi_d - X \ ^2\Pi$			
$R_{21}$	$P_{21}$	{ 62673 65011	$R_{21}$	$cd$	$P_{21}$	{ 62716 65055	$R_{21}$	$dc$	$P_{21}$
$R_{22}$	$P_{22}$		$R_{22}$	$cc$	$P_{22}$		$R_{22}$	$dd$	$P_{22}$
$R_{11}$	$P_{11}$		$R_{11}$	$cc$	$P_{11}$	{ 62696 65034	$R_{11}$	$dd$	$P_{11}$
$R_{12}$	$P_{12}$		$R_{12}$	$cd$	$P_{12}$		$R_{12}$	$dc$	$P_{12}$

Table 2

$H' \ ^2\Pi - X \ ^2\Pi \ (0,0)$												
$J - 1/2$	$cd$	$R_{21}$	$dc$	$cd$	$P_{21}$	$dc$	$cc$	$R_{22}$	$dd$	$cc$	$P_{22}$	$dd$
0	62729.1		62738.3									
1	36.3		50.6	62715.6		62720.5	62616.5		62630.7			
2	44.1		63.6	15.6		25.0	24.0		43.4			
3			77.1	16.4		30.5	32.2		56.8	62595.8		62610.0
4	62.1		91.4	17.4		36.9	41.2		70.6	96.6		15.9
5	70.3		806.3	19.2		43.6	49.1		85.3	97.8		22.3
6	80.9		22.0	21.7		51.3	58.9		700.1	99.9		29.3
7	92.0		38.3	23.5		59.5	69.3		15.6	600.7		36.9
8	803.8		55.3	27.4		68.5	80.2		31.9	04.0		45.0
9	16.2		72.9	31.9		78.1	91.8		48.6	07.4		53.8
10	29.2		91.1	36.9		88.3	703.9		65.7	11.5		63.1
11	42.9		909.9	42.7		99.3			83.7	16.2		73.0
12	57.3		29.5	49.0		810.8				21.5		83.5
13	72.3		49.7	56.1		23.0						94.4
14	88.0		70.5	63.6		36.0						705.9
15	904.2			72.1		49.3						18.0
16	21.3			80.9		63.4						
17	38.9			90.6		78.1						
18	56.9			800.9		93.7						
19				11.8								
20				23.2								

\*) The designation  $H$  and  $H'$  has been inverted compared to <sup>1)</sup>.

Table 2 continued

<u><math>H' \ ^2\Pi - X \ ^2\Pi \ (0,0)</math></u>												
$J-1/2$	<i>cc</i>	$R_{11}$	<i>dd</i>	<i>cc</i>	$P_{11}$	<i>dd</i>	<i>cd</i>	$R_{12}$	<i>dc</i>	<i>cd</i>	$P_{12}$	<i>dc</i>
0	62721.7		62724.7									
1	24.5		32.3				62604.6					
2	28.0		40.9	62708.2		62711.3	07.9			62588.2		
3	32.3		50.4	04.4		12.3	11.9	62630.0		83.9		
4	37.3		60.1	01.4		14.2	16.5	39.5		80.5		
5	43.1		72.3	698.8		16.9	21.5	51.1		77.6		
6	49.3		83.7	97.2		20.0	27.3	61.9		75.2		
7	56.3		96.0	96.3			33.6			73.4	62603.0	
8	63.9		809.0	95.8		30.5	40.6			72.4	06.9	
9	72.3		22.5	96.1		35.8	48.0			71.8	11.5	
10	81.2		36.7	97.2		42.2	56.1			71.8		
11	90.9		51.7	98.8		49.0	64.6			72.4		
12	801.2		67.2	701.1		56.5	73.6			73.4		
13	12.2		83.3	04.1		64.7	83.5			75.2		
14	23.8		900.2	07.7		73.6	93.7			77.6		
15	36.0		17.6	12.0		83.1				80.5		
16	49.0		35.7	16.9		93.1				83.9		
17	62.7		54.4	22.5		803.8						
18	76.9		73.8	28.7		15.3						
19	91.8			35.8		27.4						
20	907.2			43.2		40.0						

<u><math>H \ ^2\Sigma^+ - X \ ^2\Pi \ (0,0)</math></u>								
$J-1/2$	$R_{21}$	$P_{21}$	$R_{22}$	$P_{22}$	$R_{11}$	$P_{11}$	$R_{12}$	$P_{12}$
0	62707.8							
1	09.7	62699.6			62704.2			overlapped by $\beta$ (19,0)
2	12.0	94.4			02.7	62692.7		
3	15.1	89.6			01.7	84.2		
4	18.7	85.3	62597.8	62564.4	01.4	76.1		
5	22.9	81.7	601.5	60.2	01.7	68.4		
6	28.0	78.6	05.8	56.4	02.7	61.4		
7	33.3	76.1	10.6	53.3	04.2	54.9		
8	39.5	74.2		50.7	06.4	49.1		
9	46.3	73.2		48.7	09.3	44.0		
10		72.6		47.2	12.8	39.5		
11		72.8		46.3		35.8		
12						32.5		

Table 2 continued

<u><math>H' \ ^2\Pi - X \ ^2\Pi \ (1,0)</math></u>										
$J-1/2$	$R_{21}$		$P_{21}$		$R_{22}$		$P_{22}$			
	$cd$	$dc$	$cd$	$dc$	$cc$	$dd$	$cc$	$dd$	$cc$	$dd$
0	65068.1	65077.4								
1	75.3	89.4		65059.6	64955.4					
2	82.9	102.1	65054.7	63.9	62.8	64982.2	64934.8			
3	91.2	15.5	55.3	69.3	70.8	95.1	34.8			
4	100.2	29.5	56.2	75.3	79.6	5008.7	35.2			
5	08.3	44.2	57.7	82.0		22.9	36.4	64960.8		
6	18.7	59.5		89.4		37.7	38.3	67.4		
7	29.5	75.4	61.6	97.3			38.9			
8	40.8	91.8	65.1	105.9						
9	52.8		69.3							
10	65.2		73.9							
11	78.4		79.2							

$J-1/2$	$R_{11}$		$P_{11}$		$R_{12}$		$P_{12}$			
	$cc$	$dd$	$cc$	$dd$	$cd$	$dc$	$cd$	$dc$	$cc$	$dd$
0	65060.8	65063.9								
1	63.4	71.2								
2	67.0	79.7	65047.3	65050.4	64946.9		64927.3			
3	71.2	88.8	43.5	51.2	50.8		23.0			
4	75.9	98.4	40.2	52.9	55.2		19.4			
5	81.3		37.7	55.3	60.0	64989.3	16.3			
6	87.3	121.8	35.8	58.3		99.6	13.8			
7	94.0	33.5	34.5	63.9			11.8	64941.3		
8	101.3	46.1	33.9	68.1			10.4	44.6		
9	09.1		33.9	73.5				48.8		
10	17.8		34.5	79.2						
11	27.0									

<u><math>H \ ^2\Sigma^+ - X \ ^2\Pi \ (1,0)</math></u>				
$J-1/2$	$R_{21}$	$P_{21}$	$R_{11}$	$P_{11}$
	0	65047.3		
1	49.1	65039.1		
2	51.2	33.9	65042.2	65032.3
3	54.2	29.0	41.2	23.7
4	57.7	24.6	40.7	15.5
5	61.6	20.8	40.7	07.8
6	66.3	17.5	41.4	00.6
7	71.6	14.9	42.8	4994.0
8	77.4	12.9	44.7	88.0
9		11.4	47.3	82.6
10		10.6		77.8
11		10.6		73.7

Corresponding to the number of identified branches, six term curves as functions of  $J$  can be drawn. Each two adjoining curves are the two components  $F_1$  and  $F_2$  of three doublet states following HUND's coupling case  $b$ . Case  $b$  is to be expected for the Rydberg-states of the NO molecule, and is in fact so nearly realized that the spin can be disregarded in what follows. Therefore, the quantum number  $N$  (total angular momentum  $J$  minus electron spin) will be used instead of  $J$ . Figure 1 shows for  $v = 0$

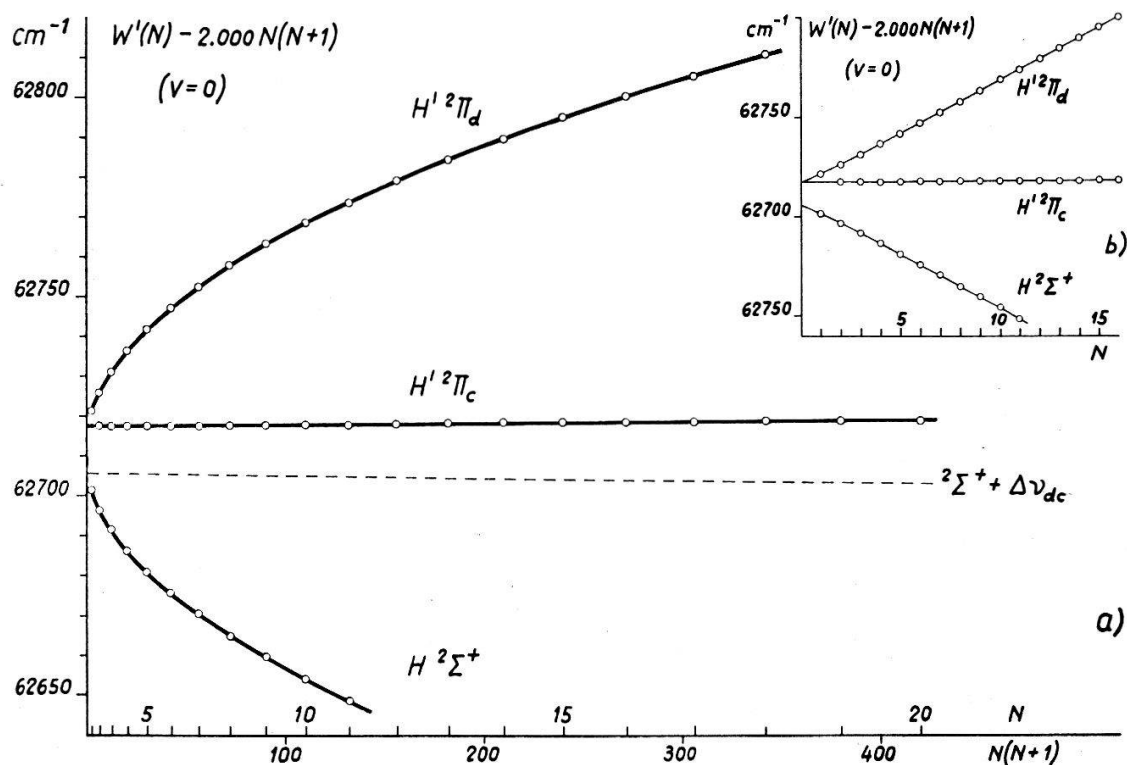


Figure 1

Energies of  $H^2\Sigma^+$ ,  $H'^2\Pi_c$  and  $H'^2\Pi_d$  as functions of  $N(N+1)$  and (inserted Figure 1b) as functions of  $N$ .  $B N(N+1)$  is subtracted.

( $N^{14}\text{O}$ ) the course of the observed energies  $W'$  of the three doublet states as functions of  $N(N+1)$ . The mean of the very small doublet splitting (s. Figure 3a) is plotted, and  $B N(N+1)$  is subtracted from the total energy  $W'$  [ $B = 2.000 \text{ cm}^{-1}$ ]. While the central curve  $H'^2\Pi_c$  follows a perfectly regular pattern, the two outermost curves repel each other more and more with increasing  $N$ . This behaviour is to be interpreted as a heterogeneous perturbation between a  $\Sigma$  and a  $\Pi$  state, and it will be evaluated quantitatively in chapter 3. For reasons of symmetry the  $\Sigma$  state can interact with only one of the two  $A$ -components of the  $\Pi$  state – according to MULLIKEN's<sup>4</sup>) definition it is the  $\Pi_d$  component – while the  $\Pi_c$  component is not affected by this interaction. When the amount of the  $A$ -splitting is added to the perturbed  $\Sigma$  state, the dashed straight line of Figure 1 for the “deperturbed”  $\Sigma$  state is obtained. The energy difference between the rotationless  $\Sigma$  and  $\Pi$  states amounts to only  $12 \text{ cm}^{-1}$ . The rotational constants  $B$  of both states are very nearly equal. The same result is obtained when the curves of the differentiated rotational energy are considered in Figure 2. The straight line for the  $\Pi_c$  component crosses the ordinate axis at  $B = 2.006 \text{ cm}^{-1}$ , which

is the  $B$ -value of the  $H' \ ^2\Pi$  state. Another straight line is obtained by plotting the mean of the mutually perturbed  $\Pi_d$  and  $\Sigma$  curves. This line crosses the axis at  $2.000 \text{ cm}^{-1}$ .

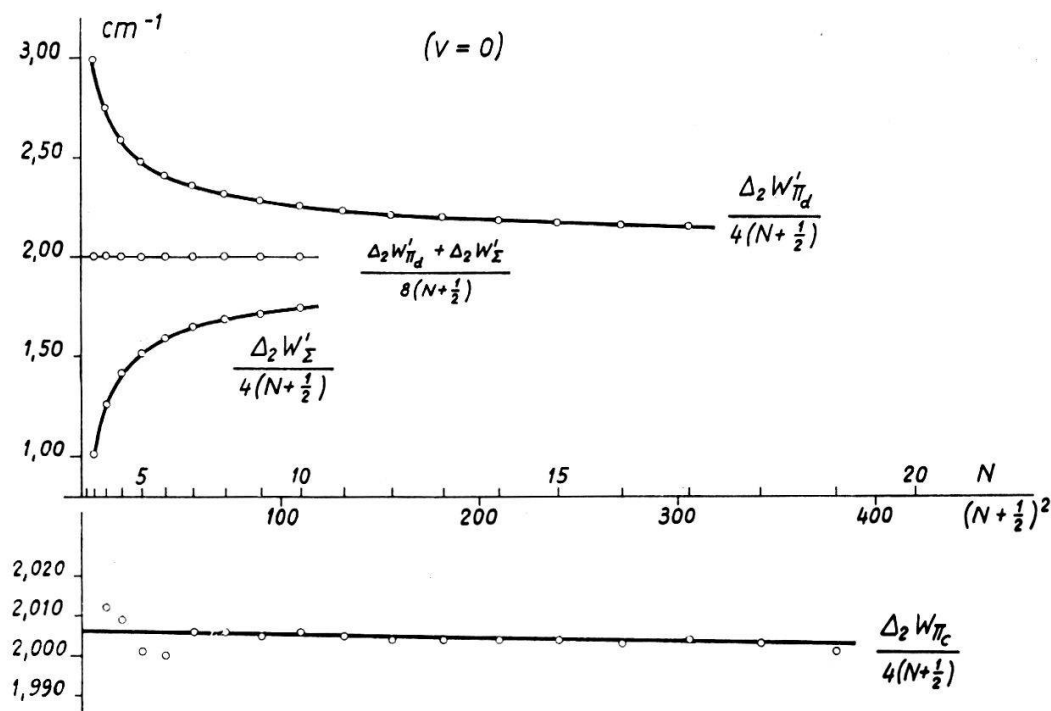


Figure 2

Differentiated rotational energies of  $H \ ^2\Sigma^+$ ,  $H' \ ^2\Pi_c$  and  $H' \ ^2\Pi_d$ .

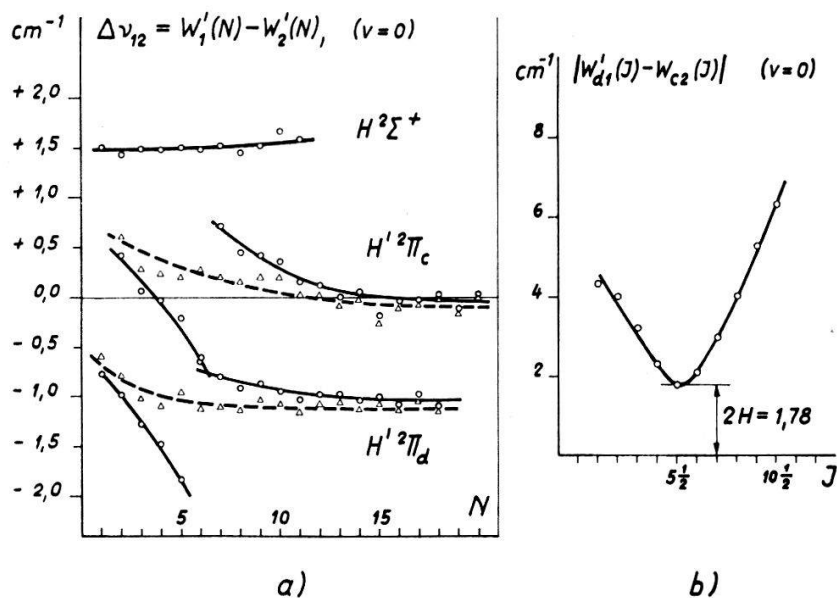


Figure 3

Doublet splitting and perturbation between  $H' \ ^2\Pi_{d1}$  and  $H' \ ^2\Pi_{c2}$

A much weaker local perturbation of the homogeneous type is observed at the point where  $W_{c2}(J)$  of  $H' \ ^2\Pi_c$  and  $W'_{d1}$  of  $H' \ ^2\Pi_d$  have the same energy for equal  $J$ . This perturbation manifests itself plainly in the curves (Figure 3a) of the doublet splitting

$\Delta\nu_{12}$  of both  $\Lambda$ -components. From the minimum value of the difference  $|W'_{d1}(J) - W'_{c2}(J)|$  of the two perturbed doublet components (s. Figure 3b) the interaction parameter is calculated to  $0.89 \text{ cm}^{-1}$ . For  $v = 1$  the same constant is  $0.97 \text{ cm}^{-1}$ . This small homogeneous perturbation is eliminated in what follows by taking the deperturbed values of  $\Delta\nu_{12}$  indicated by small triangles and dashed curves in Figure 3a.

### 3. The heterogeneous perturbation $H^2\Sigma^+ - H'^2\Pi$

Since both states involved in the heterogeneous perturbation are observed over an extended  $N$ -region, it is possible to undertake a deperturbation and to calculate meaningful constants for the deperturbed states. The following equation can easily be verified from Figure 4:

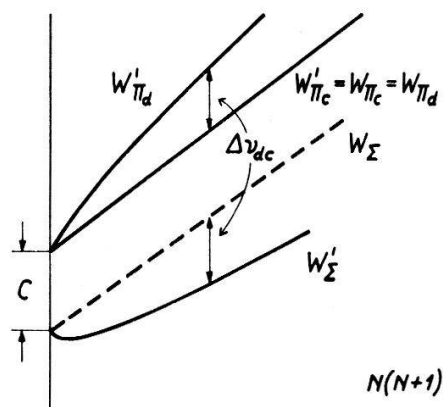


Figure 4

Heterogeneous perturbation  $\Sigma - \Pi$ .

$$\frac{W'_{\Pi d} - W'_{\Sigma}}{2} - \Delta\nu_{dc} = \frac{B_{\Pi} - B_{\Sigma}}{2} N(N+1) + \frac{C}{2}, \quad (1)$$

$$\Delta\nu_{dc} = W'_{\Pi d} - W_{\Pi c} = \Lambda\text{-splitting of the } \Pi \text{ state,}$$

$$W'_{\Pi d}, W'_{\Sigma} = \text{observed perturbed states,}$$

$$B_{\Pi}, B_{\Sigma} = \text{rotational constants,}$$

$$C = W_{\Pi} - W_{\Sigma} \quad \text{for } J = 0.$$

The left side of equation (1) contains observed quantities only and is a linear function of  $N(N+1)$ . The slope of the corresponding straight line is equal to half the difference of the  $B$ -values of the two states. Since  $B_{\Pi}$  is equal to the already known  $B$ -value of the unperturbed  $\Pi_c$  component,  $B_{\Sigma}$  too can immediately be calculated.



Figure 5 shows for  $v = 0$  the straight line according to equation (1). Its slope  $(B_{II} - B_{\Sigma})/2$  is  $0.006 \text{ cm}^{-1}$ , and it crosses the ordinate axis at  $C/2 = 5.9 \text{ cm}^{-1}$ . The calculated constants for the two states  $H^2\Sigma^+$  and  $H'^2\Pi$  are included in Tables 3 and 4.

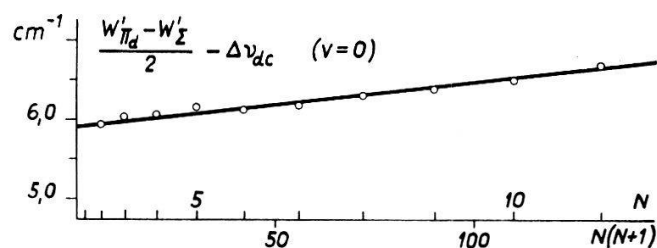


Figure 5

Straight line according to equation (1).

Table 3

$H^2\Sigma^+$ $v$	$H'^2\Pi$ $v$	$C$ ( $\text{cm}^{-1}$ )	$B_{II} - B_{\Sigma}$ ( $\text{cm}^{-1}$ )	$\alpha$ ( $\text{cm}^{-1}$ )
0	0	11.8	0.012	5.43
1	1	11.5	0.009	5.36

Table 4

	$v$	$T_0$ ( $\text{cm}^{-1}$ )	$\Delta G_{1/2}$ ( $\text{cm}^{-1}$ )	$B_v$ ( $\text{cm}^{-1}$ )	
$H^2\Sigma^+$	0	62705.5	2339.4	1.994	$B_e = 2.003 \text{ cm}^{-1}$ $\alpha_e = 0.018 \text{ cm}^{-1}$ $r_e = 1.062 \text{ \AA}$
	1	65044.9		1.976	
$H'^2\Pi$	0	62717.3	2339.1	2.006	
	1	65056.4		1.985	$B_e = 2.017 \text{ cm}^{-1}$ $\alpha_e = 0.021 \text{ cm}^{-1}$ $r_e = 1.058 \text{ \AA}$

$T_0 =$  energy above  $X^2\Pi_{1/2} (J = 1/2)$

The following relation between the perturbed energies  $W'$  and the unperturbed  $W$  is given by the theory of the heterogeneous perturbation ( $\alpha =$  parameter of interaction)

$$W_{IIa} - W_{\Sigma} = (B_{II} - B_{\Sigma}) N(N+1) + C = \sqrt{(W'_{IIa} - W'_{\Sigma})^2 - 4\alpha^2 N(N+1)}. \quad (2)$$

In the present case  $B_{II} - B_{\Sigma}$  is so small that (2) simplifies for all observed  $N$  to

$$(W'_{IIa} - W'_{\Sigma})^2 = 4\alpha^2 N(N+1) + C^2. \quad (3)$$

This can clearly be seen in Figure 6 where  $(W'_{II_a} - W'_{\Sigma})^2$  is plotted against  $N(N+1)$ . From the slope of the straight line the interaction parameter  $\alpha$  can be obtained. The values  $\alpha$  for  $v = 0$  and  $v = 1$  are also included in Table 3. They very nearly coincide.

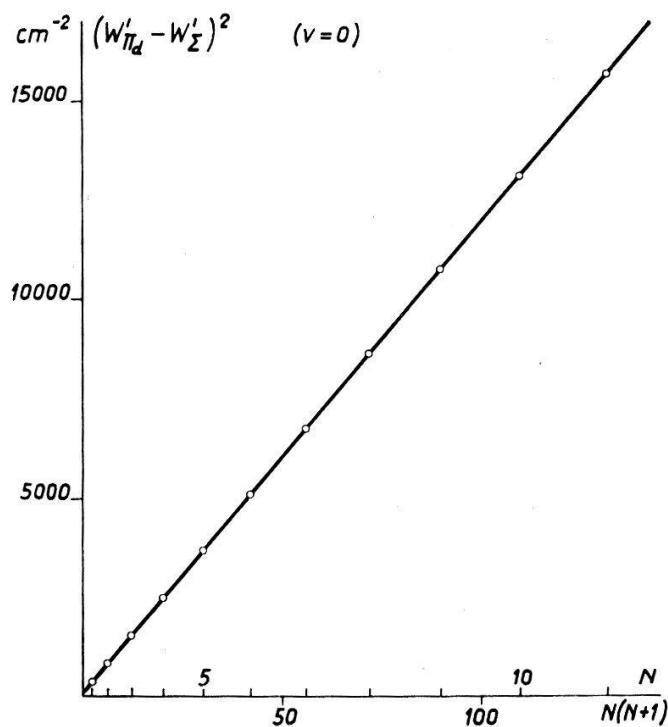


Figure 6

Straight line according to equation (3).

#### 4. Discussion

The matrix element  $S_{12}$  of the perturbation function  $S$ , which in respect of  $A$  is nondiagonal, was calculated by VAN VLECK<sup>5)</sup>

$$S_{12} = (A | S | A \pm 1) = \alpha \sqrt{(J + 1/2 - \bar{A})(J + 1/2 + \bar{A})}, \quad \bar{A} = A \pm 1/2. \quad (4)$$

For the  $\Sigma - II$  interaction ( $A = 0, 1; \bar{A} = 1/2$ ) and for coupling case  $b$  this means

$$S_{12} = \alpha \sqrt{N(N+1)}$$

as it was used in equation (2). The part  $\alpha$  which is independent of the rotational quantum number  $N$  was evaluated by DIEKE<sup>6)</sup> under the assumptions of weak coupling between electron angular momentum  $L$  and molecular axis, and independence of the internuclear distance from the angle formed by  $L$  with this axis. Both assumptions hold for the Rydberg-states under consideration. The  $B$ -values are the same for both states ( $A = 0$  and  $1$ ). In the NO molecule fourteen electrons form the  ${}^1\Sigma^+$  core and only one electron, the fifteenth, is excited.  $l$  and  $\lambda$  of this one electron can be substituted for  $L$  and  $A$  respectively. Therefore, DIEKE's result can be written

$$\alpha_l = (l, \lambda | \alpha | l, \lambda \pm 1) = B \sqrt{l(l+1) - \lambda(\lambda \pm 1)}. \quad (5)$$

In the present case of a  $\Sigma - \Pi$  interaction  $\lambda (\lambda \pm 1)$  in this equation is zero. With  $B = 2.00 \text{ cm}^{-1}$  it follows from (5)

$$l = 1 \quad \alpha_1 = 2.83 \text{ cm}^{-1}, \quad l = 2 \quad \alpha_2 = 4.90 \text{ cm}^{-1}, \quad l = 3 \quad \alpha_3 = 6.93 \text{ cm}^{-1}.$$

The potential energy curves for  $H \ ^2\Sigma^+$  and  $H' \ ^2\Pi$  nearly coincide; hence the Franck-Condon factor is unity, and a straightforward comparison is possible of the  $\alpha_l$ -values obtained from (5) with the observed value  $\alpha = 5.4 \text{ cm}^{-1}$  from Table 3. For  $l = 2$  correspondence is found within 10%. This points to the Rydberg-electron being a  $d$ -electron.

In a conference report<sup>2)</sup> given before the analysis of the  $H, H' - X$  system had fully succeeded, an attempt was made to connect the rotational structures of the  $H, H'$  state with HUND's case  $d$  ( $l$ -uncoupling). Although it since turned out that this is not appropriate, short notice will be given in this relation. Theoretically case  $d$  can be expected for a high-excited state;  $\Delta$ -doubling is already a sign of  $l$ -uncoupling. DIEKE<sup>7)</sup> has synoptically outlined the principles for the rotational levels in the case of transition from normal coupling ("Fall I") to pure case  $d$  ("Fall II"). His Figure 3 for the  $d$ -complex can be compared with Figure 1b of the present paper. DIEKE's formulas (10) indicate for large  $N$  a linear increase of the  $\Delta$ -doubling  $\Delta\nu_{dc} = \Pi_d - \Pi_c$  ( $\delta_0 - \delta_1$  in DIEKE's paper) with  $N$ , as this is actually found in the  $H' \ ^2\Pi$  state (s. Fig. 1b). However, while according to DIEKE's formulas  $\Delta\nu_{dc} = 2 B N$  should be valid in the  $p$ - as well as in the  $d$ -complex, the slope of the curve in Figure 1b for the  $H' \ ^2\Pi_d$  state is  $5.2 \text{ cm}^{-1}$  instead of  $2 B = 4.00 \text{ cm}^{-1}$ . But, as DIEKE's Figure 3 shows, the limit value  $2 B$  can be exceeded for medium  $N$  values. In this positive deviation the influence of the  $\Delta$ -components appears whereas, as DIEKE's Figure 1 shows, for the  $p$ -complex ( $\Pi_d$  and  $\Pi_c$  correspond to  $q = -1$  and  $q = 0$  respectively in DIEKE's Figure) the slope remains always below the limit  $2 B$ . This fact can be considered as an indication that the Rydberg-electron in our case is a  $d$ -electron. It should be mentioned, however, that in our  $d$ -complex, since the pertinent  $\Delta$  state ( $F \ ^2\Delta$ ) is relatively far removed, the  $H, H'$  term curves in their general appearance resemble the curves given in DIEKE's Figure 1 more than in his Figure 3. In the present case the coupling of the electron angular momentum  $l = 2$  to the molecular axis is not normal. The reason for this is the promotion, discussed below, of the  $\Sigma$  and the  $\Pi$  state. Therefore, the formulas for case  $d$  are not appropriate for the present example; the treatment as a heterogeneous perturbation, as shown above, is better adapted to the problem; it also could be called "accidental  $l$ -uncoupling".

In Figure 7 we propose an interpretation of all hitherto known Rydberg-states of the NO molecule belonging to the first ionization limit  $T_\infty = 74750 \text{ cm}^{-1}$  (9.267 eV). The  $1\Sigma^+$  ground state of the ion must dissociate into  $\text{N}(^4\text{S})$  and  $\text{O}(^4\text{S})$ ; therefore, the excited molecular states correspond in the limit of dissociation to excited states of the oxygen atom, as was discussed recently by HUBER<sup>8)</sup>. The molecular states can either be designated with the symbol  $\lambda n l$  corresponding to "separated nuclei" or with  $n l \lambda$  corresponding to "united nuclei". In the transition from the first to the second model, in certain well known cases,  $l$  and  $n$  will increase. The first designation is used in Figure 7, but in all cases of promoting states the second is added in brackets.

We first discuss the states  $H \ ^2\Sigma^+$  and  $H' \ ^2\Pi$  described in this paper. According to chapter 3 they are with each other in the relation of "pure precession", that is of a

*d*-electron ( $l = 2$ ). Their position (s. Figure 7) is slightly (quantum defect  $a = -0.02$ ) above  $T = T_\infty - R/3^2$  ( $R =$  Rydberg-constant) at an energy where for the first time a *d*-electron is expected.  $H \ ^2\Sigma^+$  is the  $\sigma \ 3d$  and  $H' \ ^2\Pi$  the  $\pi \ 3d$  state of this electron. Separated by  $600 \text{ cm}^{-1}$  only, the lowest  $^2\Delta$  Rydberg-state is found,  $F \ ^2\Delta$ , which scarcely can be anything other than the appertaining  $\delta \ 3d$  state. Its quantum defect is  $+0.06$ . That the position of  $\sigma \ 3d$  and  $\pi \ 3d$  is higher than that of  $\delta \ 3d$  has to be accounted as weakly starting promotion, because only those two electrons and not  $\delta \ 3d$  are being promoted. The promotion slightly outweighs the Stark effect exerted by the molecular core on the Rydberg-electron, to a greater extent in  $\sigma \ 3d$  than in  $\pi \ 3d$ , because the promotion for  $\sigma \ 3d \rightarrow 5g\sigma$  is twofold whereas single for  $\pi \ 3d \rightarrow 4f\pi$ . These relations also must be the reason for the near chance-coincidence of the two states  $H \ ^2\Sigma^+$  and  $H' \ ^2\Pi$ , with the result of showing the type of interaction, described in chapter 3, never observed before.

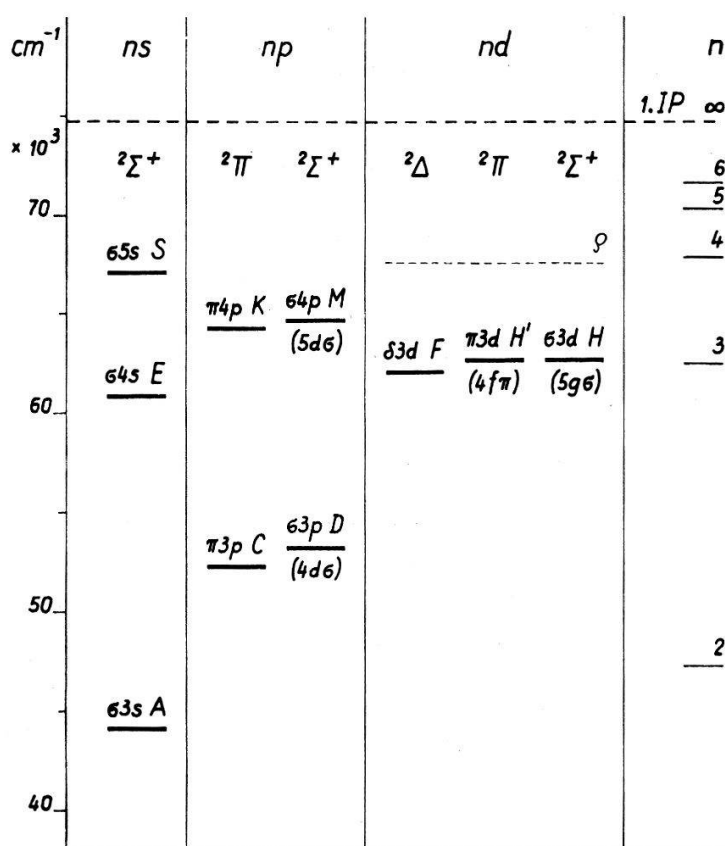


Figure 7

Rydberg-states of the NO molecule.

Furthermore, in Figure 7 two pairs of states will be noted, namely  $D \ ^2\Sigma^+$ ,  $C \ ^2\Pi$  and  $M \ ^2\Sigma^+$ ,  $K \ ^2\Pi$ . They form the two first members of the series in which the Rydberg-electron is a *p*-electron. The quantum defect is  $+0.7$  for the  $^2\Sigma^+$  and  $+0.8$  for the  $^2\Pi$  states. Starting promotion of the  $\Sigma$  states may well be the reason for the  $\Sigma$  states being found slightly above the  $\Pi$  states. The size of the  $A$ -splitting in the  $C \ ^2\Pi$  state shows, as was mentioned earlier<sup>3)</sup>, that this state with  $D \ ^2\Sigma^+$  is in the relation of "pure precession", with  $l = 1$ . The same is true for the pair  $K \ ^2\Pi$  and  $M \ ^2\Sigma^+$ , and will be presented in a forthcoming paper<sup>9)</sup>. In the spectrum all 4 band systems  $C - X$  ( $\delta$ -bands),

$D - X$  ( $\epsilon$ -bands),  $K - X$  and  $M - X$  are prominent by their absorption strength. The  $K \ ^2\Pi$  state, moreover, was predicted by HUBER<sup>8)</sup> in the now observed position.

Finally the  $^2\Sigma^+$  states  $A$ ,  $E$  and  $S$  of Figure 7 are the first three members of the series with the Rydberg-electron in the  $s$  state. As expected, the quantum defect + 1.1 is largest in this series.

It is noteworthy that both  $^2\Pi$  states of the  $p$ -Rydberg series ( $C \ ^2\Pi$  and  $K \ ^2\Pi$ ) interact strongly with higher vibrational levels of the  $B \ ^2\Pi$  non-Rydberg-state. This highly interesting interaction has been described in detail earlier<sup>3)</sup> for  $C \ ^2\Pi - B \ ^2\Pi$ , and provisionally<sup>1)2)</sup> for  $K \ ^2\Pi - B \ ^2\Pi$ . A fuller description for the latter case will follow<sup>9)</sup>. On the contrary a comparable homogeneous perturbation of the  $H' \ ^2\Pi$  state of the  $d$ -Rydberg series by  $B \ ^2\Pi$  vibrational levels is not observed, neither in  $v = 0$  nor in  $v = 1$  which in energy come close to the levels  $v = 19$  and  $v = 22$  of  $B \ ^2\Pi$  respectively. For  $N^{15}O$  the rotational levels of  $H' \ ^2\Pi$  ( $v = 1$ ) and  $B \ ^2\Pi$  ( $v = 23$ ) actually cross at  $J = 10^{1/2}$  where only a very small perturbation occurs. Vibrational and rotational isotope shifts for  $v = 0$  and 1 of the  $H$  and  $H'$  states are entirely normal.

Beyond the spectral region which contains the bands  $H$ ,  $H' - X$ , discussed in this paper, i.e. below 1535 Å many more bands, most with well defined structure, are visible on the plates. However, without further analyses which are in progress, it is not possible to continue to higher members the short beginnings of the Rydberg series of the  $ns$ -,  $np$ - and  $nd$ -electrons. The bands accumulate to a greater extent and overlap each other; more and more new states coincide with the increasing number of vibrational levels of the lower states. The " $\rho$ -band"<sup>2)</sup> at 67700  $\text{cm}^{-1}$  could well represent the  $4d$ -state (s. Figure 7), as is indicated by the high  $B$ -value (2.00  $\text{cm}^{-1}$ ). The corresponding  $N^{15}O$  band, however, does not show the expected behaviour.

The present investigations would not have been possible without the very kind collaboration of Dr. G. HERZBERG and Dr. A. E. DOUGLAS who for this purpose supplied the plates taken with the powerful vacuum grating instruments of the National Research Council of Canada. First and foremost our thanks are therefore due to them and to their skilful helpers J. SHOOSMITH and F. ALBERTI. Prof. A. LAGERQVIST (Stockholm), during his stay in Basel, participated in the early stages of the analyses. Prof. CLUSIUS (Zürich) kindly prepared the  $N^{15}O$  sample. This research was supported in part by the Swiss National Fund, and was sponsored in part by the Cambridge Research Laboratories OAR through the European Office of Aerospace Research under grant No. AF-EOARDC 61-19.

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