

# Theoretical study of homogeneous perturbations. II. Least-squares fitting method to obtain "deperturbed" crossing Morse curves. Application to the perturbed ${}^1\Sigma_u^+$ states of $N_2$

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A method to obtain a "deperturbation" of perturbed vibrational levels is developed. The vibrational functions associated with two (or three) crossing Morse curves are used to set up an interaction matrix. The eigenvalues of this matrix are compared with the observed levels and the "deperturbed" Morse curves are obtained by a least-squares fitting. This method applied to the  ${}^1\Sigma_u^+$  states of  $N_2$  confirms the interpretation given by Dressler (following paper).

On développe une méthode pour "deperturber" des niveaux vibrationnellement perturbés. En diagonalisant une matrice construite sur les fonctions vibroniques de deux (ou trois) courbes de Morse qui se croisent, on obtient des solutions qui sont comparées aux niveaux observés et par ajustement, on détermine des paramètres pour ces courbes de Morse deperturbées. La méthode, appliquée aux états  ${}^1\Sigma_u^+$  de  $N_2$  fournit une justification de l'interprétation donnée par Dressler.

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## I. Introduction

The homogeneous perturbations between two states can be interpreted as a result of the crossing of two curves of the same symmetry. If the rotational analysis can be made, it is possible, using a method due to Lagerqvist and Miescher (1958), to obtain the value of the interaction parameter, the position of the levels before interaction, and finally the "deperturbed" curves. This method has been applied with success by these authors to the interaction between valence and Rydberg  ${}^2\Pi$  states of the NO molecule and extended by Jungen (1966) to the  ${}^2\Delta$  states of the same molecule. This interpretation is supported by the following observation: in the spectrum of NO trapped in a matrix, the Rydberg states are washed out and the valence states  $B {}^2\Pi$  and  $B' {}^2\Delta$  are freed from the perturbations. Except for a constant shift, the observed vibrational levels agree well with the "deperturbed" levels (Roncin, Damany, and Romand 1967).

When the interaction parameter has not been obtained, it is nevertheless possible to make some reasonable assumptions to reach tentative deperturbed curves. Such a method has been used by Dressler (1967, 1969) to demonstrate that, in the spectrum of molecular nitrogen, the  ${}^1\Sigma_u^+$  levels in the energy range of  $100 - 115\,000\text{ cm}^{-1}$  can all be assigned to only two perturbed states.

We shall use, in this paper, the expression for the interaction parameter  $H$  given in Part I of

this series (Felenbok and Lefebvre-Brion 1966). Starting from values of observed vibrational levels only, we shall develop a systematic method to obtain, without an experimental rotational analysis, "experimental" parameters  $H$  and spectroscopic constants for Morse curves which describe deperturbed levels.

## II. Least-Squares Fitting Method

The method of Lagerqvist and Miescher (1958) treats the perturbations to a first approximation as the interaction between pairs of nearly degenerate vibrational levels belonging to different curves. The variation of the energy with the rotational quantum number gives information about the interaction parameter  $H$  and the position of deperturbed levels. The effect of the other levels is then introduced through second order perturbation theory and the final deperturbed levels are found to follow curves that almost coincide with Morse curves. When the interaction is strong, second order perturbation theory is not appropriate. It is necessary to consider simultaneously more than two levels and the deperturbation is made more delicate.

Our procedure is the inverse of this deperturbation process. Assuming that the "deperturbed" curves of interacting states are Morse curves we obtain, by diagonalizing a matrix, the perturbed levels which must coincide with the observed levels. The diagonal elements of the original

TABLE I  
 ${}^2\Delta$  states of the NO molecule. Comparison between calculated and observed perturbed levels

$\nu$	${}^{14}\text{N}{}^{16}\text{O}$				${}^{15}\text{N}{}^{16}\text{O}$		${}^{14}\text{N}{}^{18}\text{O}$	
	$T_\nu$ (calc.)	$T_\nu$ (obs.) <sup>a</sup>	$B_\nu$ (calc.) <sup>b</sup>	$B_\nu$ (obs.) <sup>c</sup>	$\Delta' \nu$ (calc.)	$\Delta' \nu$ (obs.) <sup>a</sup>	$\Delta' \nu$ (calc.)	$\Delta' \nu$ (obs.) <sup>a</sup>
<b><math>B' {}^2\Delta</math></b>								
0	60020.7	60018.6	1.321	1.321	-6.0	-8.1	-9.2	
1	61209.3	61203.4	1.300	1.302	14.4		21.1	
2	62363.6	62357.1	1.280	1.282	33.7	33.3	49.7	
3	63480.9	63475.6	1.261	1.257	51.7		76.2	
4	64589.4	64591.3	1.302	1.32	68.7	69.9	100.6	
5	65622.5	65626.6	1.228	1.225	85.4	86.6	125.5	127.2
6	66576.1	66572.7	1.470	1.45	95.8	94.6	140.8	140.7
7	67684.2	67689.5	1.400	1.445	166.8	163.2	211.4	206.7
8	68605.5	68609.3	1.162	1.147	125.8	125.2	184.8	184.3
9	69512.6	69504.3	1.169	1.152	134.6	131.4	198.0	195.0
10	70438.2		1.145		143.0		209.0	
<b><math>F {}^2\Delta</math></b>								
0	62041.4	62040.0	1.978	1.967	3.8	4.0	5.8	
1	64353.4	64355.7	1.887	1.852	46.0	44.2	68.3	
2	66794.9	66805.3	1.644	1.678	92.8	91.3	136.0	136.6
3	69003.4	69000.4	1.911	1.899	123.2	123.5	181.7	180.0
<b><math>N {}^2\Delta</math></b>								
0	67576.4	67580.5	1.760	1.69	-48.5	-44.0	-37.5	-32.8
1	69968.5	69967.0	1.887	1.863	54.7	54.0	80.9	80.0
2	72271.9	72278.3	1.935	1.907	85.2	85.0	125.4	124.3

<sup>a</sup>The observed values have been communicated by Dr. Jungen and correspond to extrapolated observed values of  $\frac{1}{2}[F_1(J) + F_3(J)]$  at  $J = 0$ .  
<sup>b</sup> $r_e = 1.302 \text{ \AA}$ ,  $\alpha_e = 0.021 \text{ cm}^{-1}$  for  $B' {}^2\Delta$  state,  $r_e = 1.065 \text{ \AA}$ ,  $\alpha_e = 0.021 \text{ cm}^{-1}$  for Rydberg states.  
<sup>c</sup>Values for  $J = 5\frac{1}{2}$ .

matrix are the "deperturbed" vibrational levels of the two states. If we assume that deperturbed curves are Morse curves, the diagonal elements depend linearly on six parameters ( $T_e$ ,  $\omega_e$ , and  $\omega_e x_e$  for each curve). The off-diagonal element between the vibrational level  $\nu_i$  of the state  $A$  and the level  $\nu_j$  of the state  $B$  is the interaction parameter  $H^{AB}_{ij}$ .

In Part I, we have interpreted this interaction parameter as an electrostatic interaction between the two electronic states  $A$  and  $B$  multiplied by the overlap  $S_{\nu_i \nu_j}$  between the vibrational functions:

$$[1] \quad H^{AB}_{ij} = H_e^{AB} \cdot S^{AB}_{\nu_i \nu_j}$$

This element depends linearly on the electrostatic parameter  $H_e$ . It also depends nonlinearly on the spectroscopic constants and the  $r_e$  values of the Morse curves through the overlap integral, but if we neglect this dependence, it is possible to fit the eigenvalues of the matrix by a least-squares method (for an account of such a method see for example Chedin and Cihla (1967)). For fixed values of  $r_e$ 's, we have a total of seven parameters.

A program has been written on CDC 3600. It calculates successive corrections to starting parameters by adjusting the calculated levels to fit the observed ones. The  $S_{\nu_i \nu_j}$ 's are recalculated at each iteration using Felenbok's program (Felenbok 1963). From the parameters which give the best agreement with experiment, we can calculate, assuming values for the  $\alpha_e$ 's, perturbed  $B_{\nu_j}$ 's and compare them with observed  $B_{\nu_j}$ 's; If there is disagreement, the procedure can, in principle, be repeated for other values of  $r_e$ 's.

### III. Results

#### A. The ${}^2\Delta$ States of the NO Molecule

The  ${}^2\Delta$  states of the NO molecule have been chosen as a test for the method. The deperturbation has been previously made by Jungen (1966) using the observed values of  $H_{ij}$  for the  $2 \times 2$  interaction matrix. From calculated values of  $S_{\nu_i \nu_j}$ , it is then possible to obtain values for  $H_e$ . For the second order effects the  $H_{ij}$  were obtained from these  $H_e$  values and calculated values of  $S_{\nu_i \nu_j}$ . The results have shown that the vibrational perturbations result from the interaction be-

tween the  $B' \ ^2\Delta$  valence state and the two  $F \ ^2\Delta$  and  $N \ ^2\Delta$  Rydberg states. The constants used for the "deperturbed" Rydberg states are assumed to be those of the ground state of the  $\text{NO}^+$  ion.

TABLE II  
Constants for deperturbed curves of  $^2\Delta$  states  
of  $^{14}\text{N}^{16}\text{O}$  ( $\text{cm}^{-1}$ )

	$T_0$	$\omega_e$	$\omega_e x_e$	$H_e$
$B' \ ^2\Delta$				
Jungen	60020.5	1217.4	15.61	
This work	60021.0	1223.1	16.70	
$F \ ^2\Delta$				
Jungen	62056.8	2370.0	15.0	450.0
This work	62045.5	2372.1	14.3	450.3
$N \ ^2\Delta$				
Jungen	67613.8	2370.0	15.0	400.0
This work	67609.3	2377.3	17.3	399.6

Using our method, good agreement between observed and calculated values is found with the constants given in Table II. These constants differ slightly from those of Jungen. We have represented the deperturbed potentials with Morse curves (which is certainly not very accurate for the  $B' \ ^2\Delta$  state) and the constants of the Rydberg states are varied. The agreement can be improved if the unobserved vibrational level  $v = 10$  is added. Table I shows that the difference between calculated and observed values does not exceed  $10 \text{ cm}^{-1}$  for all observed levels. The perturbed  $B_v$  values can be calculated for any value of  $J$ . The results are shown in Table I for one value of  $J$ . The values of  $\Delta^i = T(v) - T^i(v)$  have been calculated using the isotopic relations for the deperturbed curves, and compared with experimental values, which exhibit some anomalies, particularly when the order of the perturbing levels is changed by the isotopic effect (Table I). The results are very similar to those obtained by Jungen and this constitutes a good confirmation of the method.

### B. The $^1\Sigma_u^+$ States of the $\text{N}_2$ molecule

For a long time, the number of  $^1\Sigma_u^+$  observed states in the spectrum of the  $\text{N}_2$  molecule was estimated to be very large. In fact the study of isotopic effects (Mahon-Smith and Carroll 1964; Ogawa, Tanaka, and Jursa 1964) has shown that a large number of these "states" are certainly excited vibrational levels. Wave mechanical calculations of energy levels have indicated that it is only possible to find two  $^1\Sigma_u^+$  states in the region

$100 - 11\ 5000 \text{ cm}^{-1}$ . The observed  $^1\Sigma_u^+$  states have anomalous  $\Delta G$  curves which can probably be explained by strong perturbations (Lefebvre-Brion and Moser 1965). Recently Dressler (1967, 1969) and Carroll and Yashino (1967) have independently developed these ideas. Starting from the idea of a crossing between the curves of the  $b' \ ^1\Sigma_u^+$  (valence) state and the  $c' \ ^1\Sigma_u^+$  (Rydberg) state, Dressler has obtained deperturbed curves for these states. His deperturbation is based on the following hypothesis: (a) The Rydberg state is given the same vibrational constant as the ground state of  $\text{N}_2^+$ . (b) Since the observed values result from a diagonalization of the matrix, the sum of the shifts of the vibrational levels up to the  $n$ th level must be negative or zero.

It is interesting to see if such a deperturbation can be obtained by our method which takes into account the variation of  $H_{ij}$  with the  $S_{v_i v_j}$  overlap integrals.

The constants are obtained by fitting the constants  $v_{00}$  of 20 levels. The residual error is somewhat larger than for the  $^2\Delta$  states of  $\text{NO}$ , being of the order of  $20 \text{ cm}^{-1}$  for several levels (Table III). The anomalies in the  $\Delta G$  curve are well described by this fit (cf. Fig. 1). The calculated constants are very close to those obtained by Dressler (Table IV) and this supports the interpretation in terms of two states, one valence state and one Rydberg state. From the values obtained for the electrostatic parameter ( $H_e = 890 \text{ cm}^{-1}$ ) and for the overlap integrals (cf. Table V), we calculate  $H_2^{c' \ ^1\Sigma_u^+} = 235 \text{ cm}^{-1}$ . This can be compared with the experimental value of the smallest separation  $\Delta W'_{\min}$  between the rotational levels  $k$  ( $c'v = 2$ )

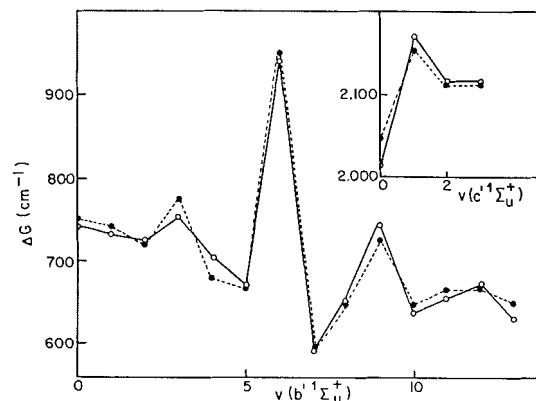


FIG. 1. Comparison of the observed (full lines) and calculated (dashed lines)  $\Delta G$  values of the  $b' \ ^1\Sigma_u^+$  state of the  $^{14}\text{N}_2$  molecule.

TABLE III  
 ${}^1\Sigma_u^+$  states of the  $N_2$  molecule. Comparison between calculated and observed perturbed levels ( $\text{cm}^{-1}$ )

$\nu$	${}^{14}N_2$					${}^{15}N_2$	
	$T_\nu$ (calc.)	$\nu_{00}$ (obs.) <sup>a</sup>	$T_\nu$ (calc.) $-T_\nu$ (obs.)	$B_\nu$ (calc.) <sup>b</sup>	$B_\nu$ (obs.) <sup>a</sup>	$\Delta^i\nu$ (calc.)	$\Delta^i\nu$ (obs.) <sup>a</sup>
$b' {}^1\Sigma_u^+$							
0	103 669.0	103 679.0	-10.0	1.149	1.151	-27.0	
1	104 421.0	104 421.0	0.0	1.143	1.146	-2.0	-0.3
2	105 160.0	105 154.0	6.0	1.135	1.152	21.0	
3	105 878.0	105 876.0	2.0	1.142	1.137	43.0	
4	106 652.0	106 633.0	19.0	1.251	1.18	77.0	80.0
5	107 331.0	107 338.0	-7.0	1.153	1.16	98.0	100.0
6	108 003.0	108 013.0	-10.0	1.201	1.187	122.0	129.0
7	108 958.0	108 953.0	5.0	1.334	1.356	151.0	
8	109 555.0	109 545.0	10.0	1.137	1.183	161.0	
9	110 206.0	110 199.0	7.0	1.097	{1.124 1.084}	173.0	175.0
10	110 928.0	110 945.0	-17.0	1.224		222.0	224.0
11	111 574.0	111 583.0	-9.0	1.097		232.0	232.0
12	112 239.0	112 240.0	-1.0	1.071	1.072	251.0	252.0
13	112 905.0	112 911.0	-6.0	1.109		269.0	285.0
14	113 556.0	113 543.0	13.0	1.057	1.057	285.0	287.0
$c' {}^1\Sigma_u^+$							
0	104 318.0	104 322.0	-4.0	1.897	1.929	-8.0	3.0
1	106 374.0	106 368.0	6.0	1.703	1.711	60.0	62.0
2	108 541.0	108 545.0	-4.0	1.465	1.435	148.0	149.0
3	110 654.0	110 657.0	-3.0	1.640	1.595	172.0	182.0
4	112 772.0	112 768.0	4.0	1.725	1.655	232.0	235.0

<sup>a</sup>Values tabulated by Dressler (1969).

<sup>b</sup>Values for  $J = 2$  using  $r_e = 1.445 \text{ \AA}$ ,  $\alpha_e = 0.008 \text{ cm}^{-1}$  for the  $b' {}^1\Sigma_u^+$  state and  $r_e = 1.12 \text{ \AA}$ ,  $\alpha_e = 0.02 \text{ cm}^{-1}$  for the  $c' {}^1\Sigma_u^+$  state.

TABLE IV  
 Constants for deperturbed curves of  ${}^1\Sigma_u^+$  states of  ${}^{14}N_2$  ( $\text{cm}^{-1}$ )

	$T_0$	$\omega_e$	$\omega_e x_e$	$H_e$
$b' {}^1\Sigma_u^+$				
Dressler	103673.8	745.5	2.25	
This work	103669.7	762.9	3.95	
$c' {}^1\Sigma_u^+$				
Dressler	104322.0	2208.0	18.0	
This work	104384.1	2193.1	22.07	890.0

and  $g$  ( $b'\nu = 7$ ). If the second order perturbation theory is valid for the effect of the other levels, we have  $\Delta W'_{\min} = 2H$ . Hence  $H = 202 \text{ cm}^{-1}$ .

Wave mechanical calculation of  $H_e$  is rather difficult. In this case it depends on the detailed form of the wave functions. For  $\bar{r} = 1.22 \text{ \AA}$ , the electronic wave function for the  $b' {}^1\Sigma_u^+$  valence state has been found to be a mixing of 65% of the singly excited configuration  $1\pi_u \rightarrow 1\pi_g$  and 35% of the singly excited configuration  $3\sigma_g \rightarrow 3\sigma_u$ . The electronic wave function for the  $c' {}^1\Sigma_u^+$

Rydberg state has been previously determined (Lefebvre-Brion and Moser 1965). Then, an estimated value is  $H_e = 1200 \text{ cm}^{-1}$ .

#### IV. Discussion

The calculated parameters depend on the number of vibrational levels fitted. We have included only up to 20 levels. We know that, for large vibrational numbers, Morse curves for excited states are inadequate. It would be possible to introduce new parameters (for example  $\omega_e y_e$ ) and to calculate vibrational overlap integrals using Zare's program (Zare 1963). However, our purpose has not been to determine very accurate parameters for "deperturbed" curves but to explain anomalous  $\Delta G$  curves and to give a theoretical background for deperturbation calculations.

The method described above might prove useful in the study of other anomalous  $\Delta G$  curves that have not yet received an adequate explanation.

TABLE V  
Vibrational overlap integrals for the  ${}^1\Sigma_u^+$  states of  ${}^{14}\text{N}_2$

$\nu$	$c' {}^1\Sigma_u^+$				
	$\nu = 0$	$\nu = 1$	$\nu = 2$	$\nu = 3$	$\nu = 4$
$b' {}^1\Sigma_u^+$					
0	0.001	-0.006	0.015	-0.033	0.063
1	0.005	-0.018	0.044	-0.086	0.144
2	0.013	-0.040	0.088	-0.154	0.227
3	0.026	-0.073	0.144	-0.222	0.277
4	0.045	-0.115	0.201	-0.267	0.270
5	0.071	-0.163	0.248	-0.273	0.200
6	0.104	-0.210	0.272	-0.232	0.085
7	0.141	-0.248	0.264	-0.150	-0.042
8	0.181	-0.272	0.223	-0.044	-0.145
9	0.220	-0.275	0.154	0.062	-0.198
10	0.255	-0.256	0.066	0.147	-0.191
11	0.284	-0.216	-0.025	0.195	-0.131
12	0.305	-0.157	-0.108	0.198	-0.040
13	0.316	-0.086	-0.169	0.159	0.056
14	0.317	-0.010	-0.202	0.091	0.132

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