On the $H\,{}^2\Sigma^+ - H'\,{}^2\Pi$ Perturbation of the NO-Molecule

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Abstract. By taking into account the spin-orbit interaction the unusual doublet splittings occuring in the $H\,{}^2\Sigma^+$ and $H'\,{}^2\Pi$ states of the NO molecule can be interpreted theoretically in a satisfactory way. In a higher approximation theory also leads to an understanding of the local perturbation observed at the energy where the two components ${}^2\Pi_{c2}$ and ${}^2\Pi_{d1}$ of the $H'\,{}^2\Pi$ state cross.

I. Introduction

A complete analysis of the $(0,0)$ and $(1,0)$ bands, lying at 1595 and 1538 Å respectively, of the $H, H' - X$ band system of the NO molecule has recently been published by HUBER and MIESCHER[1]). Detailed investigations have shown that the upper states essentially are ${}^2\Sigma^+$ and ${}^2\Pi$. They very nearly coincide and strongly perturb each other. The result of the interaction is a large Λ-splitting in the ${}^2\Pi$ state. The analysis showed that in the first approximation the interaction between rotation and electron spin in the $H\,{}^2\Sigma^+$ state can be neglected, whereas in the case of the $H'\,{}^2\Pi$ state the spin-orbit interaction is so small that this state almost completely belongs to Hund's case b. Therefore, HUBER and MIESCHER entirely omitted the electron spin from their theoretical interpretation of the $H\,{}^2\Sigma^+ - H'\,{}^2\Pi$ interaction. This proved to be successful. However, they didn't comment on the finer details, such as the nearly constant doublet splitting of about $1\cdot3$ cm^{-1} appearing in the ${}^2\Sigma^+$ state and in one Λ-component of the ${}^2\Pi$ state $({}^2\Pi_d)$, and, moreover, on the weak local perturbation occuring at small J values in two intersecting components of the ${}^2\Pi$ state. In the present paper a full theoretical interpretation of the experimental results will be given.

II. The $H\,{}^2\Sigma^+ - H'\,{}^2\Pi$ Interaction

Several cases of ${}^2\Sigma - {}^2\Pi$ perturbations have already been dealt with in detail by the present author in earlier papers[2])[3]). Thus it was shown that Π states lying in a proper distance from the Σ state change only the value of the constants occuring in the multiplet formulae of the Σ state, leaving the structure of the formula, i.e. its dependence on the rotational quantum number unchanged. For the experimental physicist this means that in such a case practically no perturbation is observed. If, however, the distance of two close lying interacting states changes rapidly with increasing rotational quantum number (i.e. when the difference of the rotational

constants B is large), the multiplet splitting will be different from what would be expected on the basis of the usual multiplet formulae. This has been proved by a number of experimental examples[3][4]).

In the present case of the NO molecule the two interacting states $H\,^2\Sigma^+$ and $H'\,^2\Pi$ almost coincide and have equal rotational constants B. According to HUBER and MIESCHER's investigations, these two states are parts of a d-complex. The appertaining $^2\Delta$ state – for some reason or other – is relatively far removed, and, consequently, its influence on the H and H' states may be disregarded to some extent. By taking into account the spin-orbit interaction as well the terms neglected at the separation of the wave equation, the perturbation calculation gives a determinant of sixth order for the energies of the six components $^2\Sigma_1^+$, $^2\Pi_{c1}$, $^2\Pi_{d1}$ ($N = J - 1/2$); $^2\Sigma_2^+$, $^2\Pi_{c2}$, $^2\Pi_{d2}$ ($N = J + 1/2$). This determinant, however, splits up into the following two determinants of third order only as a consequence of the symmetry properties of the wave functions:

$$
\begin{matrix} ^2\Pi_{c1} \\ ^2\Pi_{d2} \\ ^2\Sigma_2 \end{matrix}
\quad
\begin{vmatrix} W_1 - W' & H_{12} & H_{13} \\ H_{21} & W_2 - W' & H_{23} \\ H_{31} & H_{32} & W_3 - W' \end{vmatrix} = 0 ,
\tag{1a}
$$

$$
\begin{matrix} ^2\Pi_{c2} \\ ^2\Pi_{d1} \\ ^2\Sigma_1 \end{matrix}
\quad
\begin{vmatrix} W_4 - W' & H_{45} & H_{46} \\ H_{54} & W_5 - W' & H_{56} \\ H_{64} & H_{65} & W_6 - W' \end{vmatrix} = 0 .
\tag{1b}
$$

The unperturbed energies W_n ($n = 1, \ldots 6$) have been calculated by HILL and VANVLECK[5]) for any strength of spin-orbit coupling, but neglecting the coupling between rotation and spin. For Hund's case b one obtains:

$$
\left.\begin{aligned}
^2\Pi_1:\ & W_1 = W_5 = B\left[\left(J - \tfrac{1}{2}\right)\left(J + \tfrac{1}{2}\right) - 1\right] + \frac{A}{2\left(J + \tfrac{1}{2}\right)} + C , \\[2mm]
^2\Pi_2:\ & W_2 = W_4 = B\left[\left(J + \tfrac{1}{2}\right)\left(J + \tfrac{3}{2}\right) - 1\right] - \frac{A}{2\left(J + \tfrac{1}{2}\right)} + C , \\[2mm]
^2\Sigma_2:\ & W_3 = B\left(J + \tfrac{1}{2}\right)\left(J + \tfrac{3}{2}\right) , \\[2mm]
^2\Sigma_1:\ & W_6 = B\left(J - \tfrac{1}{2}\right)\left(J + \tfrac{1}{2}\right) .
\end{aligned}\right\}
\tag{2}
$$

($A = $ constant of spin-orbit interaction, $B = $ rotational constant, $C = W_\Pi - W_\Sigma$ for $J = 0$.)

The matrix elements H_{ik} are given by HILL and VANVLECK (formula 16):

$$
H_{12} = H_{45} = A\,\frac{\sqrt{\left(J - \tfrac{1}{2}\right)\left(J + \tfrac{3}{2}\right)}}{2\left(J + \tfrac{1}{2}\right)}
\tag{3a}
$$

and by Kovács[2]) (formula 29):

$$H_{13} = \sqrt{\frac{J - \frac{1}{2}}{2\left(J + \frac{1}{2}\right)}}\,\xi, \quad H_{23} = \sqrt{\frac{J + \frac{3}{2}}{2\left(J + \frac{1}{2}\right)}}\left[\xi + 4\eta\left(J + \frac{1}{2}\right)\right],$$

$$H_{46} = \sqrt{\frac{J + \frac{3}{2}}{2\left(J + \frac{1}{2}\right)}}\,\xi, \quad H_{56} = \sqrt{\frac{J - \frac{1}{2}}{2\left(J + \frac{1}{2}\right)}}\left[\xi - 4\eta\left(J + \frac{1}{2}\right)\right], \tag{3b}$$

$$H_{ik} = H_{ki}.$$

The constant ξ characterizes the spin-orbit interaction (for more detail see below), and η is the constant of the rotational perturbation originating from the terms omitted at the separation of the wave equation. If the form of the matrix elements (3a) and (3b) is kept unchanged, the exact solution of equation (1a) and (1b) would be very cumbersome, though these equations are most suitable for making numerical calculations. We arrive, however, at a good approximation of the actual situation, if we write

$$H_{12} = H_{45} = H_{13} = H_{46} \approx 0$$

thus leaving out of account all the interaction terms for which $\Delta J = 0$, but $\Delta N = \pm 1$ (N = rotational quantum number apart from spin). In this way the solution of (1a) and (1b) becomes easy, and using the number N, appropriate to Hund's case b, instead of J we get:

$$^2\Pi_{c1}: \quad W_1' = C + \frac{A}{2(N+1)} + B\left[N(N+1) - 1\right], \tag{4a}$$

$$\left.\begin{array}{l} ^2\Pi_{d2}: \quad W_2' \\[4pt] ^2\Sigma_2: \quad W_3' \end{array}\right\} = \frac{C-B}{2} - \frac{A}{4N} + B\,N(N+1)$$
$$\pm \sqrt{\left(\frac{C-B}{2} - \frac{A}{4N}\right)^2 + \left(\frac{\xi}{\sqrt{2}} + \eta\sqrt{8N(N+1)}\right)^2}, \tag{4b}$$

$$^2\Pi_{c2}: \quad W_4' = C - \frac{A}{2N} + B\left[N(N+1) - 1\right], \tag{4c}$$

$$\left.\begin{array}{l} ^2\Pi_{d1}: \quad W_5' \\[4pt] ^2\Sigma_1: \quad W_6' \end{array}\right\} = \frac{C-B}{2} + \frac{A}{4(N+1)} + B\,N(N+1)$$
$$\pm \sqrt{\left(\frac{C-B}{2} + \frac{A}{4(N+1)}\right)^2 + \left(\frac{\xi}{\sqrt{2}} - \eta\sqrt{8N(N+1)}\right)^2}. \tag{4d}$$

III. Comparison with experimental data

If the spin-orbit interaction is completely neglected, then $A = \xi = 0$ and the equations (4a)–(4d) reduce to

$$W'_{\Pi_c} = W'_1 = W'_4 = C - B + B N (N + 1) , \tag{5a}$$

$$W'_{\Pi_d} = W'_2 = W'_5 = \frac{C - B}{2} + B N (N + 1) + \sqrt{\left(\frac{C-B}{2}\right)^2 + 8\,\eta^2\,N\,(N+1)} , \tag{5b}$$

$$W'_{\Sigma} = W'_3 = W'_6 = \frac{C - B}{2} + B N (N + 1) - \sqrt{\left(\frac{C-B}{2}\right)^2 + 8\,\eta^2\,N\,(N+1)} . \tag{5c}$$

Thus the doublet splitting in the two Λ-components of the Π state as well as in the Σ state would vanish. This is the conception of HUBER and MIESCHER (see Figure 1 of [1])). If, however, our intention is to interpret theoretically these doublet splittings, the above exact formulae are just needed.

For small spin-orbit interaction one obtains from (4a–d):

$$\Delta\nu_{12}(\Pi_c) = W'_1 - W'_4 = \frac{A\left(N + \frac{1}{2}\right)}{N\,(N+1)} , \tag{6a}$$

$$\Delta\nu_{12}(\Pi_d) = W'_5 - W'_2 = \frac{A\left(N + \frac{1}{2} + \sigma\right)}{2\,N\,(N+1)} - \sqrt{2}\,\xi , \tag{6b}$$

$$\Delta\nu_{12}(\Sigma) = W'_6 - W'_3 = \frac{A\left(N + \frac{1}{2} - \sigma\right)}{2\,N\,(N+1)} + \sqrt{2}\,\xi . \tag{6c}$$

where

$$\sigma = \frac{\frac{C-B}{2}}{\eta\,\sqrt{8\,N\,(N+1)}}\left(N + \frac{1}{2}\right).$$

It follows from (6b) and (6c)

$$\Delta\nu_{12}(\Sigma) - \Delta\nu_{12}(\Pi_d) = A\,\frac{-\sigma}{N\,(N+1)} + 2\sqrt{2}\,\zeta . \tag{7}$$

From Figure 3a of the paper of HUBER and MIESCHER it can be seen that experimentally for not to small values of N the sum according to (7) is found to be independent of N. (The deperturbed dotted curve for $\Delta\nu_{12}(^2\Pi_d)$ has to be used.) Therefore

$$\xi = \frac{1}{2\sqrt{2}}\,[1{\cdot}5 - (-1{\cdot}1)] = 0{\cdot}92\ \text{cm}^{-1} .$$

Under certain conditions [cf. [2]) p. 348, formula (40)] in a first approximation

$$\xi = \frac{1}{2\sqrt{2}}\,A\,\sqrt{l\,(l + 1)} .$$

HUBER and MIESCHER's considerations indicate $l = 2$, thus $A = 1{\cdot}06\ \text{cm}^{-1}$ is determined. $(C - B)/2$ is known to be $4{\cdot}9\ \text{cm}^{-1}$.

From equations (5b, c), assuming $A = \zeta = 0$

$$(W'_{\Pi_d} - W'_\Sigma)^2 = 32\,\eta^2\,N\,(N + \cdot\,) + (C - B)^2 \qquad (8)$$

results. When this equation (8) is compared with equation (3) in Huber and Miescher's paper $\eta = \alpha/2\sqrt{2} = 1{\cdot}9$ cm^{-1} is obtained ($\alpha = 5{\cdot}4$ cm^{-1}).

Thus all the constants occuring in the equations (6) are determined and the theoretical curves for the doublet splittings $\Delta\,\nu_{12}$ are drawn in Figure 1. The circles indicate the experimental data. It can be seen that the constant doublet splittings of nearly opposite size (1·3 cm^{-1}), observed for $N \gg 1$ in $^2\Pi_d$ and $^2\Sigma$ but not in $^2\Pi_c$ are well interpreted by the theory. The same holds for the rise of the curves for small N observed in $^2\Pi_c$ and $^2\Pi_d$, whereas in $^2\Sigma$ in accordance with theory no rise is observed.
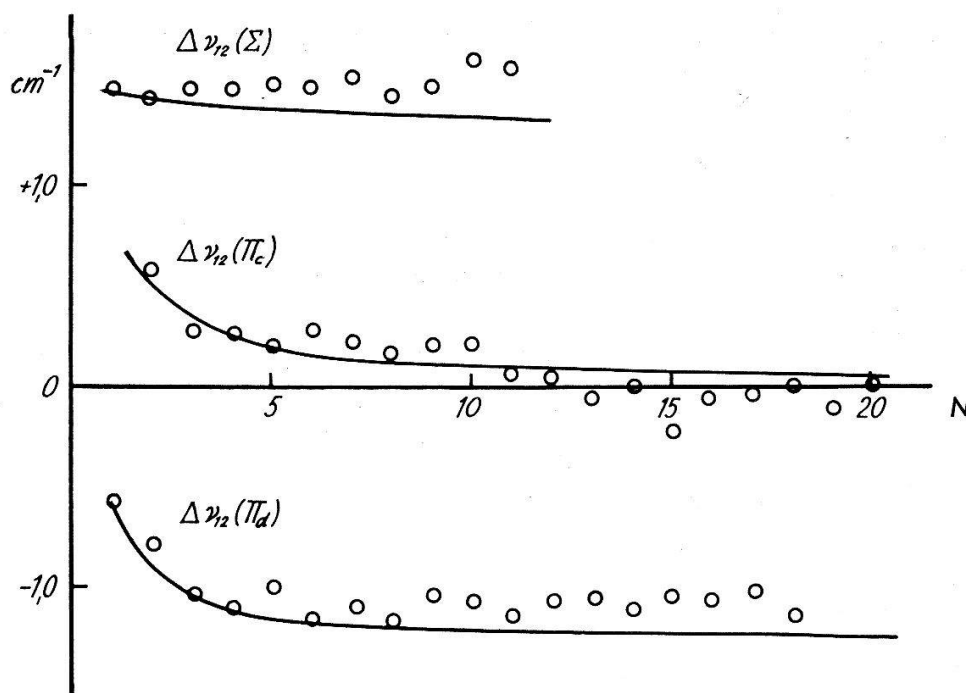

Fig. 1

Curves $\Delta\nu_{12}$ calculated according to equations (6) and experimental values (○), local perturbation $^2\Pi_{c2} - ^2\Pi_{d1}$ eliminated.

The behavior of the doublet splittings $\Delta\nu_{12}$ is even more evident, when the above described $\Sigma - \Pi$ perturbation is eliminated, that is when the values $\Delta\nu_{12}$ obtained theoretically from (6a–c) are subtracted from the actual (not deperturbed) experimental data (full lines in Figure 3a of Huber and Miescher). Then we get Figure 2. From this it can be stated that the $^2\Sigma^+$ state shows a small doublet splitting depending on the rotational quantum number, which, on the basis of the formula $\Delta\nu_{12}(\Sigma) = \gamma\,(N + 1/2)$ results in the value $\gamma = 0{\cdot}022$ cm^{-1}.

The curves $\Delta\nu_{12}$ for the components of the $^2\Pi$ state represent the local mutual interaction involving $^2\Pi_{c2}$ and $^2\Pi_{d1}$. It is treated in the following section IV.
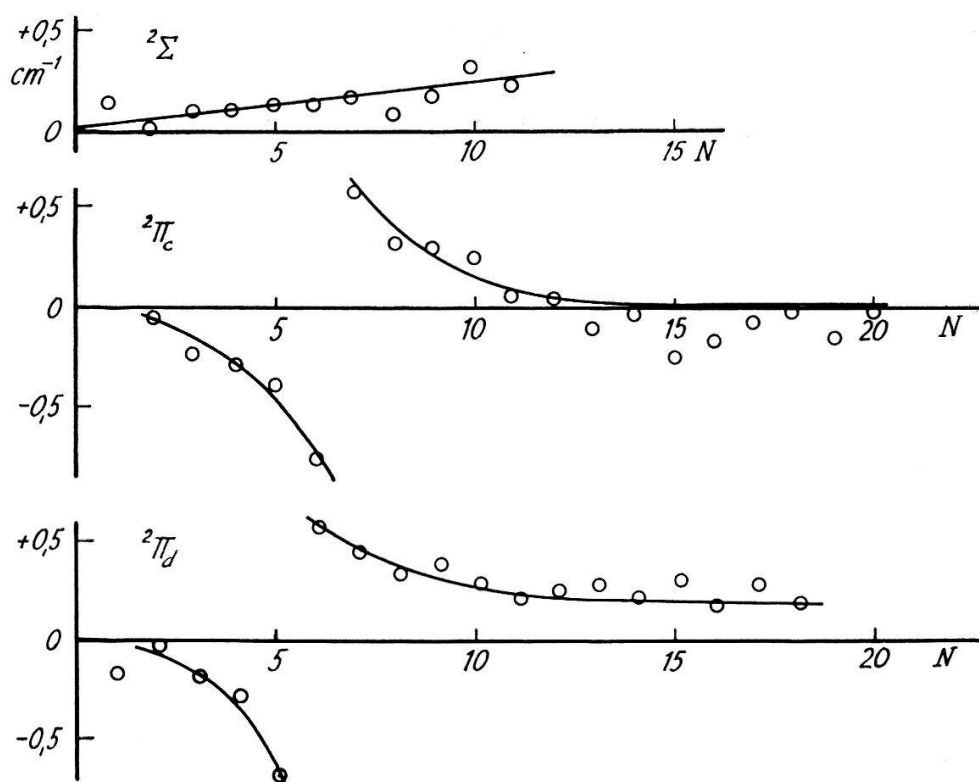
Fig. 2

Difference $\Delta\nu_{12}$(obs.) $-\Delta\nu_{12}$(calc.) between actual experimental and calculated doublet splittings.
$\Sigma-\Pi$ perturbation eliminated.

IV. The Local $H'\,^2\Pi_{c2} - H'\,^2\Pi_{d1}$ Interaction

When in section II the equations (1) were solved the matrix element H_{45} and H_{46} in the determinant (1b) were neglected. This omission is a good approximation as long as the respective solutions $W'_4(^2\Pi_{c2})$ and $W'_5(^2\Pi_{d1})$ do not come too near each other. In the present example of the $H'\,^2\Pi$ state, however, they cross (or avoid crossing).
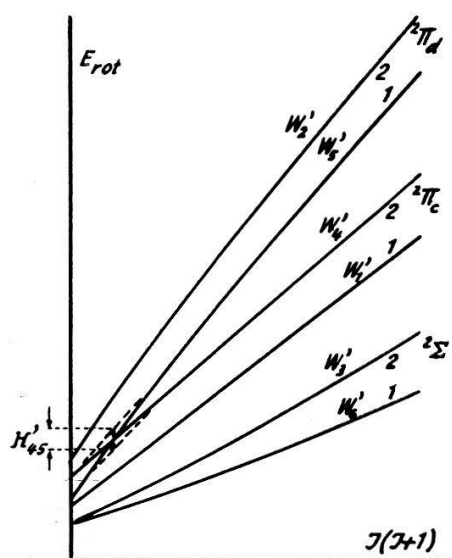

Fig. 3

Rotational energy plotted as function of $J\,(J+1)$. The dotted curves are W''_4 and W''_5 resulting from the interaction where W'_4 and W'_5 cross eachother.

Therefore H_{45} and H_{46} can not be zero and have to be taken into account. With the solutions W' (equations (4)) the part marked by dotted lines of determinant (1b) can be transformed to diagonal form and then takes the following shape:

$$
\begin{matrix} {}^2\Pi_{c2} \\ {}^2\Pi_{d1} \\ {}^2\Sigma_1 \end{matrix}
\quad
\begin{vmatrix} W'_4 - W'' & H'_{45} & H'_{46} \\ H'_{54} & W'_5 - W'' & 0 \\ H'_{64} & 0 & W'_6 - W'' \end{vmatrix} = 0 , \tag{9}
$$

$$
H'_{45} = S_{55} H_{45} + S_{56} H_{46}; \quad H'_{46} = S_{65} H_{45} + S_{66} H_{46},
$$

$$
S_{56} = -S_{65} = \sqrt{\frac{1}{2}\left[1 - \sqrt{1 - \left|\frac{H_{56}}{\Delta_{56}}\right|^2}\right]}; \quad S_{55} = S_{66} = \sqrt{\frac{1}{2}\left[1 + \sqrt{1 - \left|\frac{H_{56}}{\Delta_{56}}\right|^2}\right]},
$$

The form of H_{45}, H_{46} and H_{56} was given in (3a) and (3b), while Δ_{56} means the root-part of (4d). Since H_{56} and Δ_{56}, because of the smallness of C, differ very little even at low quantum numbers, it can be written in a good approximation:

$$
S_{56} = -S_{65} \approx S_{55} = S_{66} \approx \frac{1}{\sqrt{2}}.
$$

Hence the transformed matrix elements are

$$
H'_{45} = \frac{1}{2}\sqrt{\frac{J + \frac{3}{2}}{J + \frac{1}{2}}} \left[\xi + A\sqrt{\frac{J - \frac{1}{2}}{2\left(J + \frac{1}{2}\right)}}\right], \tag{10a}
$$

$$
H'_{46} = \frac{1}{2}\sqrt{\frac{J + \frac{3}{2}}{J + \frac{1}{2}}} \left[\xi - A\sqrt{\frac{J - \frac{1}{2}}{2\left(J + \frac{1}{2}\right)}}\right]. \tag{10b}
$$

Near the intersection of W'_4 and W'_5 the element H'_{46} – which is small anyhow – can be neglected, and thus the solution for W'' is:

$$
\left.\begin{matrix} W''_4 \\ W''_5 \end{matrix}\right| = \frac{W'_4 + W'_5}{2} \pm \sqrt{\left(\frac{W'_4 - W'_5}{2}\right)^2 + |H'_{45}|^2}, \tag{11}
$$

from what

$$
\left.\begin{aligned}
& \left| W''_4({}^2\Pi_{c2}) - W''_5({}^2\Pi_{d1}) \right| \\
& = 2\sqrt{\left(\frac{C - B}{4} - \frac{3A}{8\left(J + \frac{1}{2}\right)} + B\left(J + \frac{1}{2}\right) - \frac{1}{2}\Delta_{56}\right)^2 + \frac{J + \frac{3}{2}}{4\left(J + \frac{1}{2}\right)}\left(\xi + A\sqrt{\frac{J - \frac{1}{2}}{2\left(J + \frac{1}{2}\right)}}\right)^2}.
\end{aligned}\right\} \tag{12}
$$

In Figure 4 a theoretical curve, calculated according to equation (12) is drawn, whereas the circles stand for the experimental data of HUBER and MIESCHER. At the point of intersection ($J = 5^1/_2$) $W''_4 - W''_5$ is just equal to $2 H'_{45}$, for which from (10a), with the values of ξ and A already determined in section III, $H'_{45} = 0.87$ cm^{-1} is calculated. This result agrees exceedingly well with the value found experimentally ($H = 0.89$ cm^{-1} [1]).
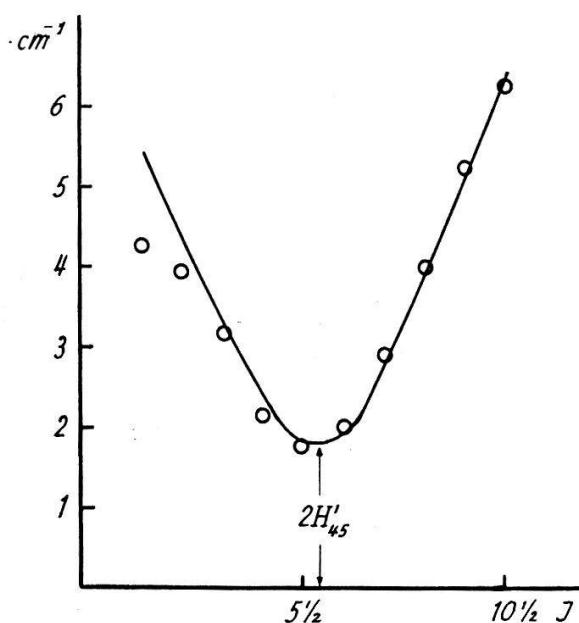

Fig. 4

W''_4 ($^2\Pi_{c2}$) $- W''_5$ ($^2\Pi_{d1}$) according to equation (12) and experimental values (O).

Summarizing, it can be concluded that the unusual doublet splitting, found to be quite independent of the rotational quantum number in the $H\ ^2\Sigma^+$ state of the NO molecule and also the nearly constant doublet splitting appearing in the d-component of the $H'\ ^2\Pi$ state are the result of the fact that, taking into account the spin-orbit interaction, a perturbation of unlike value occurs between the $^2\Sigma_1$ and $^2\Pi_{d1}$ as well as between the $^2\Sigma_2$ and $^2\Pi_{d2}$ components of the two states. Thus, the without perturbation originally coinciding $^2\Sigma_1$ and $^2\Sigma_2$ components as well as $^2\Pi_{d1}$ and $^2\Pi_{d2}$ respectively, are shifted from their original places by different amounts. The local perturbation also, found between the $^2\Pi_{c2}$ and $^2\Pi_{d1}$ components of the $H'\ ^2\Pi$ state, can be interpreted by the spin-orbit interaction, and the theoretically computed perturbation matrix element shows an excellent agreement with the value obtained experimentally.

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