

A THEORETICAL REINVESTIGATION OF THE ROTATIONAL AND HYPERFINE LAMBDA DOUBLING SPECTRA OF DIATOMIC MOLECULES WITH A $^2\Pi$ STATE: THE SPECTRUM OF NO

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The third order theory developed in a previous communication for a diatomic molecule in a $^2\Pi$ state is reanalyzed and extended to include contributions due to interactions between rotational levels. The new approach was applied to the rotational and hyperfine Λ -doubling spectrum of ^{14}NO . In contrast to all previous theoretical investigations an excellent agreement is found between the predicted spectrum and the very accurate experimental data.

A new set of rotational and hyperfine structure constants of ^{14}NO was obtained.

1. Introduction

The studies of diatomic open-shell molecules have been performed on a number of molecules in the past years. The rotational and hyperfine Λ -doubling spectra have been investigated mainly for molecules in a $^2\Pi$ state (LiO, NO, OH, SH). However the largest number of transition frequencies, and the most accurate data available for a molecule in a $^2\Pi$ state are known for the NO molecule.

The rotational spectra of NO were observed by Gallagher and Johnson [1] and by Favero et al. [2]. The hyperfine Λ -doubling spectra ($\Delta J = 0$ transitions) of NO were observed by Neumann [3] and by Meerts and Dymanus [4] (further referred to as R1) using the molecular beam electric resonance (MBER) method. The experimental uncertainties of the MBER measurements were typically 1 kHz, but Meerts and Dymanus obtained accuracies of 0.2 kHz for a large number of transitions.

For the interpretation of the MBER spectra Meerts and Dymanus developed a perturbation theory up to third order in fine and hyperfine structure [4]. In this theory the rotational quantum number J is treated as a good quantum number and all interactions off-diagonal in J are neglected. In fact the hyperfine interaction is considered to be a small perturbation on the fine structure. In the Hund's case (a) representation this approach results in a 2×2 secular equation. The agreement between the theoretical and experimental frequencies was found to be rather unsatisfactory. Differences up to 50 kHz were still present. An attempt to include the contributions off-diagonal in J , which only arise from the hyperfine hamiltonian, using a rather tedious perturbation calculation proposed by Freed [5] failed completely. As it turned out later on this perturbation calculation is incorrect.

In the present work the off-diagonal contributions in J are taken into account by setting up a large secular matrix containing all couplings between different J -states and solving the secular problem by a numerical diagonalisation. The maximum dimension of the matrix is $2(2I + 1)$, where I is the nuclear quantum number ($I = 1$ for ^{14}NO). There is no need to introduce extra molecular parameters.

A recalculation of the spectra of ^{14}NO resulted in an excellent agreement between the experimental and the calculated rotational and hyperfine spectra; practically all predicted transitions agree with the observed frequencies within the experimental accuracies.

2. Theory

Only a short review of the applied theory and its implications is given in this section. The hamiltonian for the spectra of open-shell diatomic molecules in the absence of external fields can be written as

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{H}_F + \mathbf{H}_{\text{hf}}, \quad (1)$$

where \mathbf{H}_0 is the non-relativistic hamiltonian for electronic energies in the Born–Oppenheimer approximation, and \mathbf{H}_F and \mathbf{H}_{hf} describe the fine and hyperfine structure contributions, respectively. The explicit form of \mathbf{H}_F and \mathbf{H}_{hf} expressed in terms of operators can be found in a previous paper [6].

The coupling scheme for the electronic and rotational part of the wavefunctions used in the present calculations is the Hund's case (a):

$$|^2\Pi_{\Omega}^{\pm}J\rangle = \frac{1}{\sqrt{2}} [|J\Lambda\Sigma\Omega\rangle \pm (-1)^{J-1/2} |J-\Lambda-\Sigma-\Omega\rangle], \quad (2)$$

where $\Omega = \Lambda + \Sigma$ is taken positive; Λ , Σ , Ω is the projection on the molecular axis of the electronic orbital (L) and spin (S) and of the total angular momentum (J), respectively. The functions of eq. (2) have a well defined symmetry with respect to a reflection (σ_{xz}) of the coordinates and spins of all particles in a plane containing the nuclei [4]:

$$\sigma_{xz} |^2\Pi_{\Omega}^{\pm}J\rangle = \pm |^2\Pi_{\Omega}^{\pm}J\rangle. \quad (3)$$

The definition of the symmetrized functions of eq. (2) is slightly different from the one used in previous papers [4,6]. The present definition simplifies the expressions for the matrix elements which are given below. The total wavefunction $|^2\Pi_{\Omega}^{\pm}JIF\rangle$ including the nuclear part is obtained as a product of the electronic-rotational wavefunctions $|^2\Pi_{\Omega}^{\pm}J\rangle$ and the nuclear spin wavefunctions $|IM_I\rangle$ according to the coupling scheme $F = J + I$. The wavefunctions $|^2\Pi_{\Omega}^{\pm}JIF\rangle$ were used as a basis for a perturbation calculation of the various contributions to the energy. Only the rotational and hyperfine contributions are discussed in this paper.

An extension of the perturbation calculation up to third order in fine and hyperfine structure is performed for NO by Meerts and Dymanus [4]. However, in those calculations the matrix elements between states with different J have been neglected. This is correct for the fine structure effects because all matrix elements of \mathbf{H}_F off-diagonal in J are zero, but it is incorrect for the hyperfine structure. Fortunately no extra coupling constants are required to include these contributions, because they can be described by the major terms of the hyperfine structure containing both second and third order contributions. The relevant molecular parameters defined by Meerts and Dymanus [4,6] are $\chi_1, \chi_2, \chi_3, \chi_4$, for the magnetic hyperfine contributions and ξ_1, ξ_2 , and ξ_3 for the electric quadrupole contributions. The energy contributions via the matrix elements off-diagonal in J of the third order effects are negligibly small and are not considered in the following.

The hyperfine hamiltonian is invariant under σ_{xz} and so matrix elements between states with different symmetry are zero. Obviously the hamiltonian \mathbf{H} is diagonal in F . The general matrix elements of the hyperfine structure can be easily calculated using well known operator techniques. The results are:

$$\begin{aligned} & \langle ^2\Pi_{1/2}^{\pm}J_1IF | \mathbf{H}_{\text{hf}} | ^2\Pi_{1/2}^{\pm}J_2IF \rangle \\ &= G(J_1, J_2, I, F) \left\{ (-1)^{J_2-1/2} \begin{pmatrix} J_1 & 1 & J_2 \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} 2\chi_1 \pm (-1) \begin{pmatrix} J_1 & 1 & J_2 \\ -\frac{1}{2} & 1 & -\frac{1}{2} \end{pmatrix} \sqrt{2}\chi_2 \right\} \\ &+ Q(J_1, J_2, I, F) (-1)^{J_2-1/2} \begin{pmatrix} J_1 & 2 & J_2 \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} \frac{1}{4}\xi_1, \end{aligned} \quad (4)$$

$$\begin{aligned} & \langle {}^2\Pi_{3/2}^{\pm} J_1 IF | \mathbf{H}_{\text{hf}} | {}^2\Pi_{3/2}^{\pm} J_2 IF \rangle \\ & = G(J_1, J_2, I, F) (-1)^{J_2-3/2} \begin{pmatrix} J_1 & 1 & J_2 \\ -\frac{3}{2} & 0 & \frac{3}{2} \end{pmatrix} \frac{2}{3} \chi_3 + Q(J_1, J_2, I, F) (-1)^{J_2-3/2} \begin{pmatrix} J_1 & 2 & J_2 \\ -\frac{3}{2} & 0 & \frac{3}{2} \end{pmatrix} \frac{1}{4} \xi_2, \quad (5) \end{aligned}$$

$$\begin{aligned} & \langle {}^2\Pi_{3/2}^{\pm} J_1 IF | \mathbf{H}_{\text{hf}} | {}^2\Pi_{1/2}^{\pm} J_2 IF \rangle \\ & = G(J_1, J_2, I, F) (-1)^{J_2-1/2} \begin{pmatrix} J_1 & 1 & J_2 \\ -\frac{3}{2} & 1 & \frac{1}{2} \end{pmatrix} \sqrt{2} \chi_4 \pm (-1)^Q Q(J_1, J_2, I, F) \begin{pmatrix} J_1 & 2 & J_2 \\ -\frac{3}{2} & 2 & -\frac{1}{2} \end{pmatrix} \frac{1}{2\sqrt{6}} \xi_3, \quad (6) \end{aligned}$$

where

$$G(J_1, J_2, I, F) = [(2J_1 + 1)(2J_2 + 1)I(I + 1)(2I + 1)]^{1/2} (-1)^{J_1+I+F} \begin{pmatrix} F & J_1 & I \\ 1 & I & J_2 \end{pmatrix},$$

$$Q(J_1, J_2, I, F) = \left(\frac{(2J_1 + 1)(2J_2 + 1)(2I + 3)(2I + 2)(2I + 1)}{2I(2I - 1)} \right)^{1/2} (-1)^{J_1+I+F} \begin{pmatrix} F & J_1 & I \\ 2 & I & J_2 \end{pmatrix}.$$

These equations reduce to the expressions given by Meerts and Dymanus [4,6] if J_1 is set equal to J_2 . The extension of the perturbation theory up to third order was performed following the method of R1. Because the hyperfine hamiltonian mixes states with different J , J is strictly no longer a "good" quantum number. The good quantum numbers are the parity of the state and the F quantum number. This requires two secular equations to be solved for each F value: one for + symmetry and one for - symmetry. The maximum dimension of each secular problem is $2(2I + 1)$. The secular matrix is obtained in three steps: (1) the spin-orbit and rotational contributions, (2) the Λ -doubling up to third order are all taken as in R1 (the matrix elements off-diagonal in J are zero), and (3) the hyperfine structure contributions are included as discussed in this paper. The step (1) requires three molecular parameters: the spin-orbit coupling constant (A_{Π}), and the rotational constant (B_{Π}) for the ${}^2\Pi_{1/2}$ ($B_{\Pi_{1/2}}$) and the ${}^2\Pi_{3/2}$ ($B_{\Pi_{3/2}}$) level. The rotational matrix element between the ${}^2\Pi_{1/2}$ and the ${}^2\Pi_{3/2}$ level is defined by:

$$\langle {}^2\Pi_{3/2}^{\pm} J | \mathbf{H}_{\text{F}} | {}^2\Pi_{1/2}^{\pm} J \rangle = \frac{1}{2} (B_{\Pi_{1/2}} + B_{\Pi_{3/2}}) [(J - \frac{1}{2})(J + \frac{3}{2})]^{1/2}. \quad (7)$$

The centrifugal distortion was included by taking the square of the rotational matrix and multiplying the result by $-D_{\Pi}$ (centrifugal distortion constant). A similar approach was followed by Almy and Horsfall [7] and by Meerts and Dymanus [6] for the Hund's case (a).

The contributions of the Λ -doubling up to third order can be described by four molecular parameters: α_3 , α_7 , α_4 , and α_8 . The last two constants α_4 and α_8 contain only third order effects. In R1 also a fifth Λ -doubling parameter α_5 was obtained, which could be expressed in α_8 by the relation:

$$\alpha_5 = [B_{\Pi}/(B_{\Pi} - B_{\Sigma})] \alpha_8, \quad (8)$$

with B_{Π} and B_{Σ} as the rotational constants of the ${}^2\Pi$ and ${}^2\Sigma$ states, respectively.

The eqs. (4), (5) and (6) were used to include the major hyperfine structure contributions. Of the third order hyperfine terms only those matrix elements, which are diagonal in J are included, using the equations of R1. The following parameters were involved χ_5 , χ_6 , χ_7 , χ_8 , χ_9 , ξ_4 , and ξ_5 . However, as shown in R1 χ_5 and χ_7 could not be determined independently from the spectra, only the linear combination $\chi_5 + \chi_7$.

3. Calculations

The secular matrix was calculated and diagonalized by a computer yielding the eigenvalues and the transition frequencies. The constants were adjusted in a least squares method to fit the available experimental data of ${}^{14}\text{NO}$:

Table 1

Hyperfine Λ -doubling transitions of ^{14}NO in the $^2\Pi_{1/2}$ state as observed with a molecular beam electric resonance spectrometer

J	F_+	F_-	Observed transition (MHz)
9/2	11/2	11/2	1863.878 (1)
11/2	11/2	11/2	2087.217 (1)
11/2	13/2	13/2	2207.877 (2)

Table 2

Molecular parameters of ^{14}NO as obtained in the present calculation ^{a)}

Quantity		
$B_{\Pi_{1/2}}$	(MHz)	50844.97 (16) ^{b)}
$B_{\Pi_{3/2}}$	(MHz)	50850.92 (18)
D_{Π}	(MHz)	0.185 (16)
α_3	(MHz)	89.01234 (4)
α_7	(MHz)	1.4192 (2)
α_4	(kHz)	0.23 (2)
α_8	(kHz)	0.024 (3)
χ_1	(MHz)	46.3300 (2)
χ_2	(MHz)	56.2987 (2)
χ_3	(MHz)	113.659 (8)
χ_4	(MHz)	-20.619 (20)
$\chi_5 + \chi_7$	(kHz)	24.5 (6)
χ_6	(kHz)	0.06 (4)
χ_8	(kHz)	0.0 (3)
χ_9	(kHz)	-1.9 (3)
ξ_1	(MHz)	-1.857 (1)
ξ_2	(MHz)	-1.866 (8)
ξ_3	(MHz)	11.580 (12)
ξ_4	(kHz)	0.0 (2)
ξ_5	(kHz)	0.0 (2)

a) Parameters taken from other sources are $A_{\Pi} = 123.160$ cm [8] and $B_{\Sigma} = 59568.76$ MHz [9].

b) The uncertainties represent three standard deviations.

91 observed transitions in the frequency range from 0.6 MHz to 258 GHz, consisting essentially of four groups:

(a) 20 rotational transitions of the $J = 1/2 \rightarrow 3/2$ and the $J = 3/2 \rightarrow 5/2$ within the $^2\Pi_{1/2}$ state as observed by Gallagher and Johnson [1] with an accuracy of 250 to 500 kHz.

(b) 6 rotational transitions of the $J = 3/2 \rightarrow 5/2$ states in the $^2\Pi_{3/2}$ state. The measurements were performed by Favero et al. [2] with an accuracy of 300 kHz.

(c) 25 hyperfine Λ -doubling transitions ($\Delta J = 0$) of the $J = 1/2$ through $11/2$ states of the $^2\Pi_{1/2}$ state as observed in our laboratory [4]. Three unpublished transitions belonging to this group are given in table 1. The experimental uncertainties of most of these transitions (19) is less or equal to 1 kHz, while 12 of them are accurate within 0.2 kHz.

(d) 40 $\Delta J = 0$ transitions of the $J = 3/2$ through $17/2$ states of the $^2\Pi_{3/2}$ state, all obtained by Meerts and Dymanus [4], most of them with uncertainties of 1 kHz.

A full description of the spectrum required 22 molecular constants. However, two of them — A_{Π} and B_{Σ} — had to be taken from other sources.

The result of the least squares fit is excellent. All but three transitions can be predicted within their experimental errors and a χ^2 value of 50.6 is obtained for those 91 transitions. The χ^2 is defined by

$$\chi^2 = \sum_{i=1}^n (\nu_{\text{exp}}^i - \nu_{\text{calc}}^i)^2 / (\Delta\nu^i)^2, \quad (9)$$

where ν_{calc}^i and ν_{exp}^i are the i th calculated and experimental transition frequency, respectively, and $\Delta\nu^i$ is the experimental uncertainty in the i th frequency.

The confidence level of the fit is 97%. The molecular parameters obtained are given in table 2. The error for

each constant is equal to three standard deviations. One standard deviation is defined in the following way: if we add to or subtract from one of the constants determined in the least squares fit one standard deviation and freely adjust all the other constants the χ^2 value will increase by 1.0. This error definition is checked for each constant and it was found that the positive and negative errors were equal.

The pure third order effects were essential to obtain a satisfactory agreement between the calculated and experimental spectra, a neglect of these contributions resulted in a χ^2 of 8.5×10^4 .

4. Conclusions

The third order perturbation calculation which includes terms off-diagonal in J provides an excellent description of the rotational and hyperfine Λ -doubling spectrum of the NO molecule, for which all the previous treatments failed to calculate the very accurate MBER spectra within their experimental uncertainties. It is expected that this approach is capable of explaining and reproducing the spectra of diatomic $^2\Pi$ molecules to a high degree of reliability. An interpretation of the parameters in terms of molecular properties (e.g., electronic charge distributions) seems to be still rather complicated, because most of the fine and hyperfine structure parameters contain second as well as third order contributions. The third order contributions are a result of the perturbation calculation and connect the ground electronic $^2\Pi$ state with a large number of excited electronic states. The pure second order parameters are of interest because they contain direct information about the electronic charge distribution in the molecule [6]. As can be seen from table 2 the third order contributions although necessary to reproduce the experimental data, are rather small in NO. So the pure second order parts of the parameters can be obtained by neglecting the third order contributions and by increasing the errors somewhat.

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