

## Fluorescence and zero-field level crossing spectroscopy of the C $2\Sigma^+$ state of NS

Stuart J. Silvers and Chi-Lian Chiu

Citation: *The Journal of Chemical Physics* **61**, 1475 (1974); doi: 10.1063/1.1682075

View online: <http://dx.doi.org/10.1063/1.1682075>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/61/4?ver=pdfcov>

Published by the AIP Publishing

---

### Articles you may be interested in

[Lifetime measurements of the B  \$1\Pi\_u\$  state of K<sub>2</sub> molecules by zero-field level-crossing technique](#)

*J. Chem. Phys.* **69**, 2259 (1978); 10.1063/1.436787

[Comment on the zero-field splitting in the b  \$3\Sigma^-\$  g state of C<sub>2</sub>](#)

*J. Chem. Phys.* **64**, 1245 (1976); 10.1063/1.432274

[Evidence for predissociation in the C  \$2\Sigma^+\$  state of NS](#)

*J. Chem. Phys.* **63**, 1095 (1975); 10.1063/1.431452

[Zero-field level crossing and optical radio-frequency double resonance studies of the A  \$2\Sigma^+\$  states of OH and OD](#)

*J. Chem. Phys.* **58**, 4304 (1973); 10.1063/1.1678987

[Determination of the Rate Constants of the Intersystem Crossing Processes to the Individual Zero-Field Levels of the Lowest Triplet State](#)

*J. Chem. Phys.* **50**, 3113 (1969); 10.1063/1.1671514

---

A promotional banner for AIP Applied Physics Reviews. On the left is a thumbnail image of a journal cover titled 'AIP Applied Physics Reviews' featuring a diagram of a device. The background is a blue gradient with molecular models. The text 'NEW Special Topic Sections' is prominently displayed in white. Below this, 'NOW ONLINE' is written in yellow, followed by 'Lithium Niobate Properties and Applications: Reviews of Emerging Trends' in white. The AIP Applied Physics Reviews logo is in the bottom right corner.

**NEW Special Topic Sections**

**NOW ONLINE**  
Lithium Niobate Properties and Applications:  
Reviews of Emerging Trends

**AIP** Applied Physics Reviews

# Fluorescence and zero-field level crossing spectroscopy of the $C^2\Sigma^+$ state of NS\*

Stuart J. Silvers<sup>†</sup> and Chi-Lian Chiu<sup>†</sup>

Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19174  
(Received 29 May 1973)

Fluorescence and zero-field level crossing (Hanle effect) spectra have been observed for the  $C^2\Sigma^+$  state of NS. The NS radical is generated in a microwave discharge and flowed into a fluorescence cell. Optical excitation is by means of both an NS emission lamp and the Ba II 2304.235 Å atomic line. The latter coincides with absorption lines of the 0-0 band of the  $\gamma$  ( $C^2\Sigma^+ - X^2\Pi$ ) system, exciting fluorescence from apparently several  $N'$  levels. A Hanle effect with this fluorescence is analyzed by making assumptions about the contributions of different  $N'$  levels and their  $g$  values. A radiative lifetime estimate of 6.5 nsec for  $C^2\Sigma^+(v'=0)$  results.

## I. INTRODUCTION

When Fowler and Bakker<sup>1</sup> first detected the band spectrum of the NS free radical, they noted its striking resemblance to that of NO. The similarities reflect the two molecules common number of outer electrons (11). Pursuit of the analogy motivated subsequent NS investigators; correlations can now be made between the known states of NO.<sup>2</sup> But while we understand the states of NO in considerable detail,<sup>3</sup> the states of NS are still relatively unexplored. Thus we apply fluorescence and level crossing methods to the NS molecule with again the aim of improving our comparative understanding of the two molecules. The NS radical is also a suitable choice for level crossing spectroscopy in practical ways; it can readily be generated and flowed in sizable concentrations through a fluorescence cell, and it absorbs and emits radiation in the convenient middle ultraviolet region.

The two band systems originally observed by Fowler and Bakker in a nitrogen and sulphur discharge were named, in analogy to NO,  $\beta$ , and  $\gamma$ . They attributed  $\beta$  to a  $^2\Pi - X^2\Pi$  transition and  $\gamma$  to a  $^2\Sigma$  one. Rotational analyses<sup>4</sup> later confirmed that the  $\gamma$  system originates from a  $C^2\Sigma^+$  state but showed that the  $\beta$  bands are due to an  $A^2\Delta - X^2\Pi$  transition. The search for a low lying  $^2\Pi$  state continued<sup>5</sup> and eventually led to the identification of a state which, though it lies below  $A^2\Delta$ , is called  $B^2\Pi$ .<sup>2,6,7</sup> A fourth assigned state,  $D^2\Sigma$ ,<sup>8</sup> lies just above  $C^2\Sigma^+$ .

Recently high resolution methods have been used to measure the NS ground state fine and hyperfine structure constants and dipole moment. Carrington *et al.*<sup>9</sup> observed the electron paramagnetic spectrum of the  $X^2\Pi_{3/2}$  sublevel by reacting nitrogen atoms with sulphur monochloride in the spectrometer cavity. Uehara and Morino<sup>10</sup> reinvestigated the EPR spectrum and Amano *et al.*<sup>11</sup> have done microwave spectroscopy on both the  $X^2\Pi_{1/2}$  and  $X^2\Pi_{3/2}$  sublevels. These investigators produced NS by discharging a mixture of nitrogen and sulphur monochloride or dichloride before the spectrometer cavity.

We are able to produce NS by a microwave discharge of nitrogen and sulphur dichloride, flow it through a fluorescence cell, and detect fluorescence from the  $C^2\Sigma^+$  state ( $\gamma$  system). Both atomic and molecular emission lamps are used to optically excite the NS molecule.

The Ba II 2304.235 Å line coincides with the  $Q_1$  head of the  $C^2\Sigma^+(v'=0) - X^2\Pi_{1/2}(v''=0)$  sub-band, exciting several  $C$  state rotational ( $N'$ ) levels. With fluorescence from this excitation, a Hanle effect<sup>12</sup> is observed. The width of the signal measures, in the low pressure limit, the product of the excited state's  $g$  value and radiative lifetime. By estimating the fluorescence contributions and  $g$  values of the several  $N'$  levels, we arrive at an estimate for the  $C^2\Sigma^+$  lifetime.

## II. OPTICAL EXCITATION AND FLUORESCENCE

The products of a microwave discharge of nitrogen and sulphur dichloride ( $\text{SCl}_2$ ) are pumped a distance of 20 cm to the fluorescence cell. The cell is made of stainless steel and is similar in design to one shown by Silvers, Bergeman, and Klemperer<sup>13</sup> in their Fig. 4. The formation of a brownish polymer on the walls of the discharge tube and fluorescence cell indicates the presence of NS; the optical windows of the cell are kept clear of this polymer by flowing argon past them.

A microwave discharge like that used to produce NS emits the  $C^2\Sigma^+ - X^2\Pi$  band spectrum. When this emission is used to optically excite NS, it principally populates the  $v'=0$  vibrational level of the  $C$  state by means of the intense 0-0 band. The fluorescence from this excitation, when resolved, is seen to be a  $0-v''$  progression of bands with  $v''$  visible from 0 to 3. Such a molecular lamp populates excited state rotational levels in a way which depends on both the lamp and fluorescence cell temperatures, and the levels contribute to the fluorescence according to their populations.

The multiple excitations of a molecular lamp are not opportune for a Hanle effect experiment. It is necessary to disperse the fluorescence in order to separate the contributions of different rotational levels. This has been done for OH,<sup>14</sup> but for the heavier NS molecule higher resolution is required to separate rotational levels. Our fluorescence intensity is not sufficient to effect this separation. Alternatively the unresolved band Hanle effect can be fit by estimating the contributions of the various rotational levels; this approach has been taken for CO.<sup>15</sup> These problems can be overcome by locating atomic emission lines which excite individual rotational levels. A search did locate an intense barium line (Ba II 2304.235 Å) which falls close to the coincident  $Q_1$  and

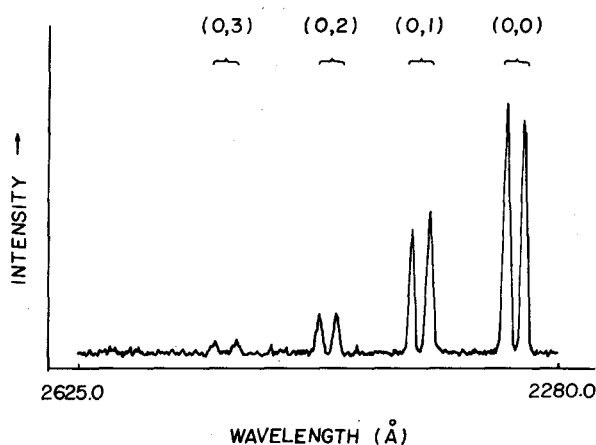


FIG. 1. Medium resolution spectrum of NS fluorescence ( $C \rightarrow X$ ) excited by Ba II 2304 Å. Each band has two components; the longer wavelength one is emission to  $X^2\Pi_{3/2}$ , the shorter to  $X^2\Pi_{1/2}$ .

$Q_{P_{21}}$  heads of the  $C^2\Sigma^+(v'=0) - X^2\Pi_{1/2}(v''=0)$  sub-band.

A hollow cathode lamp with argon carrier gas is used to produce the Ba II line. The lamp design is similar to that shown in Fig. 1 of our previous paper.<sup>16</sup> Barium is placed in the stainless steel cathode cup and care must be taken not to contaminate it. The lamp output, when dispersed, shows that the 2304 Å line is one of only two intense lines throughout the middle ultraviolet region. This lamp excites relatively strong fluorescence from NS with little background scatter from cell surfaces. Using a  $\frac{1}{2}$ -meter grating spectrometer with photoelectric detection to disperse the fluorescence, the same  $0 \rightarrow v''$  progression observed with molecular lamp excitation is detected. Each band is double peaked because of emission to both the  $^2\Pi_{1/2}$  and  $^2\Pi_{3/2}$  ground state fine structure components which are separated by  $223\text{ cm}^{-1}$ . Figure 1 shows this fluorescence spectrum in medium resolution.

Using the spectroscopic constants of Zeeman,<sup>4</sup> four different pairs of molecular transitions calculate to coincide with the Ba II line within  $0.2\text{ cm}^{-1}$ . To the high frequency side by  $0.17\text{ cm}^{-1}$  lie  $Q_1$ ,  $Q_{P_{21}}(\frac{1}{2})$  and  $Q_1$ ,  $Q_{P_{21}}(\frac{3}{2})$ . To the low frequency side by  $0.12\text{ cm}^{-1}$  are  $Q_1$ ,  $Q_{P_{21}}(\frac{9}{2})$  and  $Q_1$ ,  $Q_{P_{21}}(\frac{17}{2})$ . (The excited state doublet levels  $J' = N' + \frac{1}{2}$ ,  $N' - \frac{1}{2}$  are, respectively, excited by the  $Q_1(N' + \frac{1}{2})$  and  $Q_{P_{21}}(N' + \frac{1}{2})$  lines; these lines are optically indistinguishable, implying that the doublet splitting is small.) The barium line is sufficiently close to all these transitions to cause excitation, and consequently we believe that the levels  $v' = 0$ ,  $N' = 3, 4, 8, 9$  all contribute to the fluorescence. An attempt was made to resolve the  $P$  and  $R$  emission of the different levels and thereby obtain information on the extent to which each is excited. The spectrometer was used in second order with a cooled EMI 6256S photomultiplier, but the fluorescence intensity and spectrometer resolution are not quite sufficient to effect the separation. The  $P$ ,  $Q$ , and  $R$  branches are distinguishable and their contours consistent with the hypothesis of quadruple excitation. Figure 2 shows the spectrum. Equally consistent, however,

is the hypothesis that the barium line coincides more exactly with the  $Q_1$  head and pumps  $N' = 5, 6$ , and  $7$ . This alternative interpretation implies some error in Zeeman's spectroscopic constants.

With barium excitation we noticed, when first seeking a Hanle effect, that the fluorescence intensity increases dramatically at higher magnetic field. The size of the increase and its invariance to light polarization rule out a Hanle effect; instead the field improves the near coincidence of atomic and molecular transitions by Zeeman splitting the molecular lines. The splitting is principally of  $^2\Sigma$  levels [ $g_J = 1/(N + \frac{1}{2})$ ], the spin and orbital contributions to the  $^2\Pi_{1/2}$  ground state  $g$  value cancel one another. The fluorescence maximum at 2200 G corresponds to a  $0.1\text{ cm}^{-1}$  displacement of the largest  $M$  sub-level, an amount close to the calculated separations of atomic and molecular lines. As a check on our interpretation, the magnetic effect on fluorescence excited by the molecular lamp was investigated. Here the coincidences are exact, the Zeeman splitting should reduce the overlap of exciting and absorbing lines, and one expects intensity to monotonically decline as field is increased. This is observed and is shown in Fig. 3.

We tentatively assume that the barium line pumps  $N' = 3, 4, 8$ , and  $9$  with equal intensity, bearing in mind the alternative mentioned above. Our attempts to unambiguously determine the pumped levels and their contributions to the fluorescence have not been successful.

### III. THE HANLE EFFECT EXPERIMENT

The experimental arrangement, signal detection, and data handling are essentially the same as that previously described by us.<sup>16</sup> Taking the magnetic field direction to be  $\hat{z}$ , the barium light is incident along  $\hat{y}$  and polarized in the  $\hat{x}$  direction. The fluorescence is detected at  $90^\circ$  to the incident light direction through a  $\hat{y}$  polarizer. The fluorescence is viewed by the photomultiplier through an interference filter whose  $200\text{ Å}$  band pass is centered at  $2300\text{ Å}$ ; this filter reduces the scatter of lamp light from cell surfaces by confining detection to the region of the NS bands.

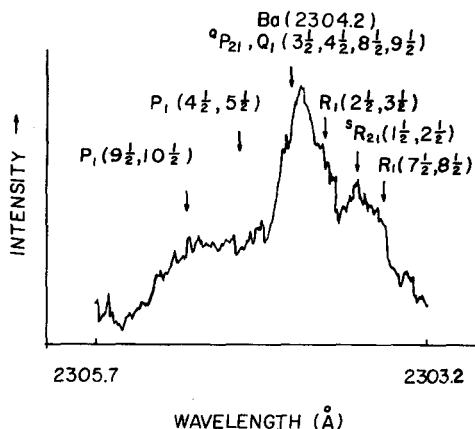


FIG. 2. Higher resolution spectrum of the  $C \rightarrow X^2\Pi_{1/2}$  component of the  $0-0$  band. The positions of the barium exciting and NS emission lines are indicated.

The Hanle effect manifests itself in a change of fluorescence intensity as the excited state  $M$  sublevels are separated by a magnetic field. This change continues until the separation between sublevels with  $\Delta M = 2$  is much greater than the natural linewidth ( $\Gamma$ ). The direction of the intensity change for a  $^2\Sigma$  excited state depends on which emission branch one observes. Each rotational ( $N'$ ) level emits in twelve branches. Since the interference filter passes all branches there is much signal cancellation; the resultant Hanle effect is relatively small. Thus the Zeeman tuning effect described in the previous section at first obscured the Hanle effect. When polarizers were introduced (They increase the percentage change in emission intensity due to the Hanle effect but not that due to tuning.) and lower fields re-examined, the Hanle effect was observed. It vanishes, as expected, when the polarizers are oriented in the  $\hat{z}$  direction; the light cannot then "coherently" excite different  $M$  sublevels. Runs with  $\hat{z}$  polarization also show that the Zeeman tuning effect is not significant compared to the Hanle effect at fields less than 300 G.

Contributors to the total fluorescence cell pressure are nitrogen, sulphur dichloride, their discharge products, and argon. The principal ones are nitrogen and argon. When the combined pressure of these two is varied between 200 and 1000 mtorr, as measured by a McLeod gauge, no change in the Hanle effect curve is noticeable.

#### IV. THE HANLE EFFECT CALCULATION

When more than one excited rotational ( $J$ ) level contributes to the Hanle effect and hyperfine structure is neglected, the fluorescence intensity has the form

$$I = \sum_{J, \alpha, \beta, M, M'} \frac{F_{MM'}(J, \alpha) G_{M'M}(J, \beta)}{\Gamma + i(M - M') \mu_0 g_J H}, \quad (1)$$

where the sum is over all excited  $J$  levels, the excitation ( $\alpha$ ) and emission ( $\beta$ ) branches which connect them to the ground state, and pairs of upper state  $M$  sublevels. The external field is  $H$  and  $\mu_0$  is the Bohr magneton. The excitation or density matrix  $F$  describes the excited  $J$  level prepared by an  $\alpha$  branch transition; for our geometry it is given by

$$F_{MM'}(J, \alpha) = PL(J'', \alpha) \sum_{M''} \langle JM | \mu_x | J''M'' \rangle \langle J''M'' | \mu_x | JM' \rangle,$$

where  $PL$  is a combined ground state ( $J''$ ) population and lamp intensity factor for the transition and  $\mu_x$  is the  $\hat{x}$  component of the dipole moment operator. The emission matrix  $G$  is similarly

$$G_{M'M}(J, \beta) = \sum_{M''} \langle JM' | \mu_y | J''M'' \rangle \langle J''M'' | \mu_y | JM \rangle.$$

It connects  $J$  with  $J''$  through a  $\beta$  branch transition. Noting that  $(M - M')$  can either be 0 or  $\pm 2$ , we in each case sum over  $M$  and obtain from (1)

$$I \propto \sum_{J, \alpha, \beta} [I_0 - cI_0/(1+x^2)], \quad (2)$$

where

$$I_0 = \sum_M F_{MM} G_{MM},$$

$$cI_0 = -2 \sum_M F_{M, M+2} G_{M+2, M},$$

$$x = 2\mu_0 g_J \tau H / \hbar.$$

Each possible excitation-emission path contributes to the sum in (2). A path's contribution to the total intensity ranges from  $I_0 - cI_0$  at zero field to  $I_0$  at infinite field.

We calculate the contributions to (2) using a basis of Hund's Case (a) wavefunctions chosen to have correct parity.<sup>11</sup> Angular momentum techniques<sup>17</sup> are used to evaluate transition moments taking care to be consistent about phase conventions so that the signs of the  $cI_0$  terms are correct. The calculation assumes the  $^2\Pi$  state is pure case (a) in nature and neglects hyperfine structure. General results for the excitation and emission paths involved in our experiment are given in Table I. These expressions then are summed for the eight  $J$  levels ( $N = 3, 4, 8, 9$ ) excited by the barium line assuming that the lamp profile is flat over the levels and the ground state populations are Boltzmann at room temperature. The results, given in Table II, show that  $Q$  branch emission is both most intense and has the largest Hanle effect. The intensity from paths with negative  $cI_0$  factors decreases with field, contrary to the usual positive effect. The overall percentage intensity change,  $\sum cI_0 / \sum (I_0 - cI_0)$ , is thus reduced by cancellation. It calculates to be 9% in the positive direction, which agrees with our observations.

The experimental signal is then fit to (2) by a least squares program. The eight excited  $J$  levels are assigned  $g$  values according to the  $^2\Sigma$  formula  $g_J = 1/(N + \frac{1}{2})$  and their lifetimes ( $\tau$ ) are taken to be equal. The  $I_0$  and  $cI_0$  terms are obtained from Table I and again a flat lamp profile and ground state Boltzmann distribution are assumed. The fit then determines  $\tau(v' = 0)$ . A number of runs at different pressures show no systematic variation in lifetime. The average lifetime for these runs is 6.5 nsec. Figure 4 shows the agreement between an experimental run and the calculated signal.

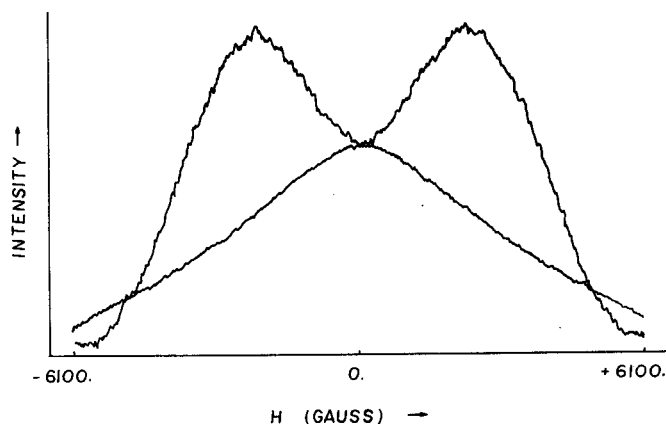


FIG. 3. Effect of a strong magnetic field (Zeeman tuning) on NS fluorescence. Double peaked curve is for Ba II excitation, single peaked curve for molecular lamp excitation.

TABLE I. Contributions to the fluorescence intensity from the possible excitation-emission paths.  $cI_0$  is a path's maximum intensity change due to the Hanle effect and  $I_0$  its intensity at infinite field. Each emission branch is from excited state level  $J$  to both the  $^2\Pi_{1/2}$  and  $^2\Pi_{3/2}$  ground state sublevels. The lamp profile-ground state population factors ( $PL$ ) are all set equal to one;  $\hat{x}, \hat{y}$  light polarization is assumed; and hyperfine structure is neglected.

Excitation branch	Q	Emission R	P
$I_0$	$\frac{(2J+1)^3(4J^2+4J-1)(8J^2+8J-1)}{30(2J)^3(2J+2)^3}$	$\frac{(2J+1)^2(2J-1)(12J^2-8J+1)}{120(2J)^3(2J+2)}$	$\frac{(2J+1)^2(2J+3)(12J^2+32J+21)}{120(2J)(2J+2)^3}$
$Q_1$			
$cI_0$	$\frac{(2J+1)^3(2J+3)(2J-1)(4J^2+4J-1)}{30(2J)^3(2J+2)^3}$	$-\frac{(2J-1)(2J+1)^2(4J^2+4J-3)}{120(2J)^3(2J+2)}$	$-\frac{(2J+1)^2(2J+3)(4J^2+4J-3)}{120(2J)(2J+2)^3}$
$I_0$	$\frac{(2J+1)(4J^2+4J-1)(12J^2+32J+21)}{120(2J)(2J+2)^3}$	$\frac{7(2J-1)^2(2J+3)}{480(2J)(2J+2)}$	$\frac{(2J+3)(28J^3+108J^2+139J+60)}{240(2J+2)^3}$
$Q_{P_{21}}$			
$cI_0$	$-\frac{(2J-1)(2J+1)(2J+3)(4J^2+4J-1)}{120(2J)(2J+2)^3}$	$\frac{(2J-1)^2(2J+3)}{480(2J)(2J+2)}$	$\frac{(2J)(2J+3)^2(2J-1)}{480(2J+2)^3}$

## V. DISCUSSION

The lifetime we measure is apparently uninfluenced by pressure effects such as the entrapment of resonance radiation or collisions. Realizing collisions can shorten the Hanle effect lifetime, but at our working pressures they are unlikely during the time the molecule remains excited. The measured lifetime is thus a radiative one provided no intramolecular nonradiative processes such as predissociation compete with radiation.

The 6.5 nsec value reported here for  $\tau(v'=0)$  contains assumptions about the atomic excitations and the excited state  $g$  values. We assume (1) the barium line equally overlaps the spin and hyperfine components of four  $N'$  levels<sup>18</sup> and (2) Hund's Case (b)  $g$  values, which neglect nuclear spin, apply for these levels. If not all levels are equally excited, the lifetime could be in error by as much as a factor of 2. If Hund's hyperfine coupling Case ( $b_{\beta J}$ ) applies as it does for NO,<sup>19</sup> our  $g$  values are essentially correct.<sup>20</sup> If Case ( $b_{\beta S}$ ) applies, the  $g$  values and hence lifetime are in error by approximately another factor of 2. These error possibilities far outweigh other sources of error in the experiment.

The ground state of NS can be represented according to Mulliken as

$$KKL(\sigma\sigma)^2(\gamma\sigma)^2(x\sigma)^2(w\pi)^4v\pi-X^2\Pi,$$

with the unpaired electron in an antibonding  $\pi$  orbital.

TABLE II. Calculated relative intensity contributions from the various excitation-emission paths to the fluorescence excited by barium.  $cI_0$  is a path's maximum intensity change due to the Hanle effect and  $I_0$  its intensity at infinite field. Hyperfine structure is neglected;  $\hat{x}, \hat{y}$  light polarization is used; and it is assumed that the spin components of  $N'=3, 4, 8$ , and 9 are pumped with equal lamp intensity. Each emission branch is to both the  $^2\Pi_{3/2}$  and  $^2\Pi_{1/2}$  ground state sublevels.

Excitation branch	Q	Emission branch R	P	Total
$Q_1$				
$I_0$	2.88	0.83	1.38	5.09
$cI_0$	1.42	-0.35	-0.35	0.72
$Q_{P_{21}}$				
$I_0$	1.02	0.43	0.73	2.18
$cI_0$	-0.25	0.06	0.06	-0.13

The  $X-C$  transition promotes this electron to a Rydberg type  $\sigma$  orbital leaving a more tightly bound  $1\Sigma^+$  core. Thus the  $C$  state has a smaller  $r_e$  and a larger  $\omega_e$  than the ground state. The lower lying  $A^2\Delta$  and  $B^2\Pi$  states both are weakly bound non-Rydberg types, the result of promoting a bonding electron to an antibonding orbital.

The states of NO are qualitatively similar.<sup>3</sup> The low lying  $A^2\Sigma^+$  state is a Rydberg-type whose lifetime ( $v'=0, 1, 2$ ) is about 180 nsec.<sup>21</sup> This is significantly longer than our NS  $C$  state lifetime even when allowance is made for the approximation we make. It is possible that the two states do not arise from analogous configurations. The non-Rydberg states of NS have term ( $T_e$ ) values  $\frac{1}{3}$  smaller than those of the correlating NO states. If the Rydberg states behave similarly, it is likely that the NO state correlating with the  $C$  state of NS is not the energetically equivalent  $A$  state but rather one of the higher lying  $^2\Sigma^+$  Rydberg levels such as  $D$  (whose  $v'=0$  lifetime has been reported as 20 nsec)<sup>22</sup> or  $E$ . This would imply that NS has lower lying Rydberg states yet unobserved.

Since the  $C$  state of NS lies above Gaydon's<sup>23</sup> recommended ground state dissociation energy, it is possible

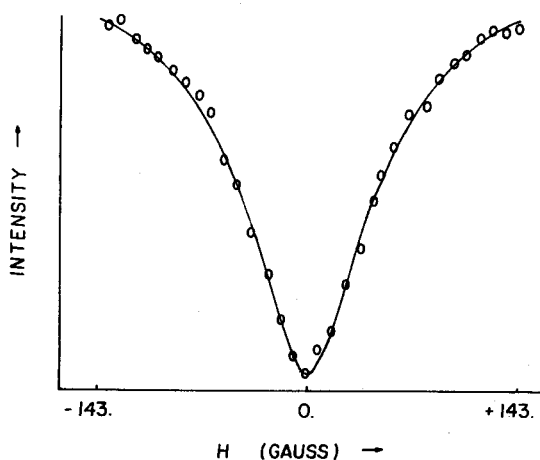


FIG. 4. Fit of the calculated to experimental Hanle effect. Smooth curve is the calculation; circles are experimental points.

that weak predissociation accounts for the relatively short lifetime we report. The Rydberg and non-Rydberg-type states are displaced in  $r_e$ ; their zero order potential curves cross each other giving rise to perturbations and predissociations. A repulsive state arising from ground state atoms, like the  $A'^2\Sigma^+$  state of NO, could either directly or indirectly predissociate the  $C$  state. We are presently pursuing this possibility.

## ACKNOWLEDGMENT

Professor R. M. Hochstrasser has encouraged this work through stimulating discussions and the loan of a spectrometer.

\*This research has been supported by the National Science Foundation under Grant GP 13788.

†Present address: Department of Chemistry, Virginia Commonwealth University, Richmond, VA 23284.

<sup>1</sup>A. Fowler and C. Bakker, *Proc. R. Soc. Lond.* **A136**, 28 (1932).

<sup>2</sup>J. J. Smith and B. Meyer, *J. Mol. Spectrosc.* **14**, 160 (1964).

<sup>3</sup>K. Dressler and E. Miescher, *Astrophys. J.* **141**, 1266 (1965).

<sup>4</sup>P. B. Zeeman, *Can. J. Phys.* **29**, 174 (1951); R. F. Barrow, G. Drummond, and P. B. Zeeman, *Proc. Phys. Soc. A* **67**, 365 (1954).

<sup>5</sup>Barrow *et al.*, Ref. 4, tentatively attributed a number of red-degraded bands in the 2300 Å region to a  $^2\Pi$  state. M. M. Patel, *Z. Phys.* **173**, 347 (1963) added more bands to this assignment. But it can be shown that most of the bands attributed to this state belong to other systems, and thus a  $^2\Pi$  state has not been established in this region.

<sup>6</sup>N. A. Narasimham and K. Srikameswaran, *Proc. Indian Acad. Sci. A* **59**, 227 (1964).

<sup>7</sup>Fowler and Bakker, Ref. 1, originally assigned the letter  $B$  to the upper state in the  $\beta$  system, believing it analogous to the  $B^2\Pi$  state of NO. When Barrow *et al.*, Ref. 4, showed this state to be a  $^2\Delta$  one, they called it the  $A$  state. The  $B$  label then followed the  $\Pi$  state.

<sup>8</sup>N. A. Narasimham and K. Srikameswaran, *Proc. Indian Acad. Sci. A* **56**, 325 (1962). A  $B'^2\Sigma$  state reported by K. C. Joshi,

*Z. Phys.* **191**, 126 (1966), contains vibrationally misassigned bands of the  $D \rightarrow X$  system as pointed out by N. A. Narasimham and T. K. B. Subramanian, *J. Mol. Spectrosc.* **29**, 294 (1969).

<sup>9</sup>A. Carrington and D. H. Levy, *J. Chem. Phys.* **44**, 1298 (1956); A. Carrington and D. H. Levy, *J. Phys. Chem.* **71**, 2 (1967); A. Carrington, B. J. Howard, D. H. Levy, and J. C. Robertson, *Mol. Phys.* **15**, 187 (1968).

<sup>10</sup>H. Uehara and Y. Morino, *Mol. Phys.* **17**, 239 (1969).

<sup>11</sup>T. Amano, S. Saito, E. Hirota, and Y. Morino, *J. Mol. Spectrosc.* **32**, 97 (1969).

<sup>12</sup>For background on the Hanle effect see: B. Budick in *Advances in Atomic and Molecular Physics* (Academic, New York, 1967), Vol. 3, pp. 73–117; R. N. Zare, *J. Chem. Phys.* **45**, 4433 (1966).

<sup>13</sup>S. J. Silvers, T. H. Bergeman, and W. Klemperer, *J. Chem. Phys.* **52**, 4385 (1970).

<sup>14</sup>R. L. De Zafra, A. Marshall, and H. Metcalf, *Phys. Rev. A* **3**, 1557 (1971).

<sup>15</sup>R. L. Burnham, R. C. Isler, and W. C. Wells, *Phys. Rev. A* **6**, 1327 (1972).

<sup>16</sup>S. J. Silvers and C. L. Chiu, *J. Chem. Phys.* **56**, 5663 (1972).

<sup>17</sup>K. Freed, *J. Chem. Phys.* **45**, 4214 (1966).

<sup>18</sup>Since, as Sec. II notes, an alternative possibility is that the barium line excites  $N' = 5, 6$ , and 7, we have also fit the experimental signal assuming that these levels (their spin and hyperfine components) are pumped with equal lamp intensity. The resulting lifetime, 6.5 nsec, is unchanged.

<sup>19</sup>E. M. Weinstock, R. N. Zare, and L. A. Melton, *J. Chem. Phys.* **56**, 3456 (1972).

<sup>20</sup>For Hund's case ( $b_{BJ}$ ) the average of the hyperfine  $g$  values for one  $J$  level is the same as the Case (b) value. In fitting our signal we thus replace the sum of several Lorentz lines of different widths with one such line of average width. This procedure of using an average  $g$  value where hyperfine structure exists has been used for  $\text{Na}_2$  [M. McClintock, W. Demtröder, and R. N. Zare, *J. Chem. Phys.* **51**, 5509 (1969)], for OH (Ref. 14), and for NO (Ref. 19).

<sup>21</sup>This value, reported in Ref. 19, is the result of a Hanle effect measurement.

<sup>22</sup>J. E. Hesser, *J. Chem. Phys.* **48**, 2518 (1968). This measurement is by the phase shift technique.

<sup>23</sup>A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (Chapman and Hall, London, 1968).