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Line strengths of diatomics: The $b^{1}\Sigma^{+}v'=0 \rightarrow X^{3}\Sigma^{-}v''=0$ transition of the NF radical

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Line intensities in the (0,0) band of NF($b^{1}\Sigma^{+} \rightarrow X^{3}\Sigma^{-}$) spin forbidden emission have been observed in a microwave apparatus. Deduced line strengths of the ${}^{O}P$ and ${}^{S}R$ well resolved branches are shown differently, in contrast with the theoretical prevision, and are interpreted by taking into account some peculiarities of the NF radical. An intermediate (a) and (b) Hund case is seen to apply to ${}^{O}P$ and ${}^{S}R$ in the whole rotational range examined. Accordingly, a reliable value for the effective transition moment μ_{e} is evaluated from the experiment. © 1997 American Institute of Physics. [S0021-9606(97)04431-0]

INTRODUCTION

Nitrogen monohalide radicals in the gas phase are subjects of interest, with the hydride, in an extended area of phenomena such as combustion, astrophysical processes, energy transfer, and in the laser action. Many studies in the last decades have been dedicated to both the formation kinetics¹ and the spectroscopy of these species.² Moreover, in parallel with the development of laser systems, there is increased interest in the chemical kinetics of metastable states.^{3,4} Studies on the contributions of these states to the kinetical and chemical behaviors, on the other hand, may often reveal both experimental and theoretical difficulties, due to relations with long living phenomena. Attempts, however, are easier in the diatomics case, where a simple structure allows emissions to be experimentally well characterized, from both the experimental^{5,6} and the computational^{7,8} standpoints. This is an indicator that a quantitative approach should be suitable, in these cases, for observation of elementary processes active in the low contributions to radiative transitions.

Nitrogen halides have a stronger spin-orbit coupling than the hydride because of higher charges and masses. This is reflected in higher rates in the spin forbidden emissions.⁵ The lowest electronic configuration is an open shell π^2 structure, containing three states, namely ground ${}^{3}\Sigma^{-}$ and metastables ${}^{1}\Delta$ and ${}^{1}\Sigma^{+}$. Perturbations may be allowed among these, and also with the manifold of higher states, 9,10 affecting equilibria both in the energies and in the populations. The theoretical interpretations of the optical transitions of metastables are often used to evaluate the underlying interactions among states. To this aim, the lifetime is an essential datum;^{7,8} however, it should be remembered that the mixing of states, as expressed in the wave functions, is better reflected in the intensities. Actually, lifetime experiments^{5,6} have a rather poor level of discrimination, since only the higher state is fixed, and no decay channels may be either singled out or ruled out. In general, for an understanding of this matter, knowledge is needed of the whole structure of transition, particularly of the rotational manifold. This is achieved with the line strength distributions, where both initial and final nominal states are fixed,⁹⁻¹¹ and influences from parallel nonradiative phenomena are avoided. This kind of spectroscopy is directly related to wave functions, instead of energies, and has been shown as^{12,13} a sensible tool for observation of the configurations active in a forbidden transition. In order to deal with relative intensities, the needed quality of data raises obvious experimental difficulties for a deduction of reliable values of strengths. It has been shown,¹⁴ however, that many of the obstacles connected with detection can be overcome with a suitable control on the experimental conditions related to the signal/noise ratio.

Within nitrogen halides, a peculiar place is taken by the NF radical, as a system isoelectronic with O₂. After initial observations of the $a^1\Delta$ and $b^{-1}\Sigma^+ \rightarrow X^{-3}\Sigma^-$ spin forbidden emissions,¹⁵ the formation¹⁶ and characterization¹⁷ of NF metastables have received considerable interest, particularly for their potential applications as chemical intermediates in lasers. Rather recently,¹⁸ signal intensities from the NF($b^{-1}\Sigma^+v'=0\rightarrow X^{-3}\Sigma^-v''=0$) metastable emission, obtained by Fourier transform spectrometry, have been presented. The somehow analog transition of O₂ has been the first one to be theoretically studied from the point of view of line strengths.¹⁹ Subsequently,²⁰ more general expressions, also suitable for heteronuclear diatomics, have been deduced, and the method itself has developed into an area.¹⁰ In Ref. 18, the data have been applied to well known theoretical

expressions¹¹ in order to obtain a value for the ratio of transition moment components, $\mu_{\parallel}/\mu_{\perp}$. This result has then been used as a reference for rather extended *ab initio* calculations,²¹ within the Breit–Pauli approximation.²² In Ref. 18, however, the comparison with the theory of rotational strength has not been focalized on the single lines, but only limited to an integrated view of the branches.

In this paper new intensity observations of NF($b^{1}\Sigma^{+}v'=0 \rightarrow X^{3}\Sigma^{-}v''=0$) will be presented, with an experimental approach different from Ref. 18. As in previous results,^{12,13} the line strengths' behavior is confirmed to be a peculiarity of the examined molecule. An *ad hoc* interpretation of NF, resolved to the single rotations, is therefore needed. It will be given here, with a few comments on Hund (a) and (b) cases, in relation to both the transition moments ratio and the mixing of states.

EXPERIMENT

The experimental approach that has been adopted for this line strength spectroscopy is based on a rather traditional apparatus, upgraded by a computerized data acquisition and processing branch.

The apparatus has been described elsewhere in a rather detailed way,¹⁴ so it will be only briefly outlined here. Following Douglas and Jones,¹⁵ a flowing afterglow technique has been employed to obtain the NF($b^{1}\Sigma^{+}v' = 0 \rightarrow X^{3}\Sigma^{-}v'' = 0$) emission from a mix of argon (3 Torr) and NF₃ (1.8 mTorr) pure gases by microwave excitation at 2450 MHz. Ar ${}^{3}P_{0,2}$ metastables should be responsible for the NF $b^{1}\Sigma^{+}$ production via dissociative energy transfer.^{3,17} In the present case, direct windowless VUV photolysis of the parent molecule by the argon resonant lines, as employed in previous studies on PH and NH (ND),^{12,13} would generate NF metastables at a rather high vibrational temperature. The present approach, on the other hand, yields the emitting *b* state in its ground vibrational level, with only a small contribution from the v = 1 overtone.

It is known²³ that microwave excitation has no effect on the translational temperature of flowing gas, thus an NF $b^{-1}\Sigma^+$ lifetime of 22 ms¹⁷ allows some 10⁵ collisions before emission, and is widely sufficient to ensure rotational relaxation to the room value. Likewise, a residence time of about 1 s in the viewing volume is clearly enough for emitting species to avoid alterations in the radiation intensity distribution. A peephole allows an adjustment of the emission glow in front of the entrance slit in order to reach a suitable compromise with straylight. The emission is dispersed, with FWHM of about 0.002 nm, by a 1 m Czerny-Turner monochromator (Jarrel-Ash, Model 78-467), equipped with a holographic grating (Jobin-Yvon, special product), and collected by a cooled bialkali photomultiplier (EMI 9924B) with standard noise of a few counts per second. The signal is collected and processed by a computerized branch with software in a multichannel analyzer configuration, settings being related to the sampling frequency and the monochromator scanning speed. Accordingly, an integration is then carried



FIG. 1. (a) NF($b^{-1}\Sigma^+ \rightarrow X^{-3}\Sigma^- v' = v'' = 0$) from Ar ${}^{3}P_{02}$ energy transfer. (b) NF($b^{-1}\Sigma^+ \rightarrow X^{-3}\Sigma^- v' = v'' = 0 - n$) from windowless photolysis.

out for each line, and spurious counts subtracted from the obtained total intensity.

Line strengths are deduced by normalization of intensities on the distribution of population, which is about room temperature.

RESULTS

In Fig. 1(a) the spectrum of the NF($b^{1}\Sigma^{+}\rightarrow X^{3}\Sigma^{-}$) spin forbidden emission is shown, as obtained flowing an NF₃-Ar mixture through the μ w discharge. It is almost completely composed of the (0,0) band, and the (1,1) is visible only at a lower scale. In Fig. 1(b) the emission obtained by VUV photolysis is reported. Hot vibrational distribution makes these data not suitable for deduction of the line strengths of the (0,0) band, because of a superposition of unwanted signal from higher elements of the $\Delta v = 0$ sequence. In Table I, the signal intensities of Fig. 1(a) are reported in counts per second for all assigned lines of the (0,0) band.

The intensity I (photons cm⁻³ s⁻¹) of spontaneously radiated energy in a single rotational line of the transition is expressed by the well known relation²⁰

TABLE I. Wave numbers and emission intensities of observed lines in ^SR and ^OP rotational branches of NF ($b^{-1}\Sigma^+v'=0\rightarrow X^{-3}\Sigma^-v''=0$) transition.

$\Delta N \Delta J_J$	Intensity $(\pm 90 \text{ counts per s})$	${}^{\Delta N}\Delta J_J$	Intensity (±90 counts per s)
${}^{S}R_{4}$	8100	$^{O}P_{1}$	1440
SR_5	8600	$^{O}P_{2}$	2550
SR_6	8820	$^{O}P_{3}$	4025
SR_7	8850	$^{O}P_{4}$	5560
SR_8	9150	$^{O}P_{5}$	6275
SR_9	8880	$^{O}P_{6}$	7370
${}^{S}R_{10}$	9200	$^{O}P_{7}$	8140
${}^{S}R_{11}$	8090	$^{O}P_{8}$	8380
${}^{S}R_{12}$	7920	$^{O}P_{9}$	8830
${}^{S}R_{13}$	6185	$^{O}P_{10}$	8795
${}^{S}R_{14}$	6125	${}^{O}P_{11}$	8580
${}^{S}R_{15}$	5515	${}^{O}P_{12}$	8285
${}^{S}R_{16}$	4575	${}^{O}P_{13}$	7910
${}^{S}R_{17}$	3950	$^{O}P_{14}$	6850
${}^{S}R_{18}$	3440	$^{O}P_{15}$	6540
		$^{O}P_{16}$	5530
		$^{O}P_{17}$	5060
		$^{O}P_{18}^{I}$	4200
		$^{O}P_{19}$	3750
		⁰ P ₂₀	3390

$$I(e'v'J';e''v''J'') = N_{e'v'J'}ch\nu_{J'J''}A(e'v'J';e''v''J''),$$
(1)

where $N_{e'v'J'}$ is the population of emitting state, and e,v,J are labels indicating electronic, vibrational, and rotational quantum numbers, respectively. Single and double primes identify upper and lower molecular levels. The Einstein coefficient for spontaneous emission, $A(s^{-1})$, has the following form¹⁰

$$A(e'v'J';e''v''J'') = (16\pi^{3}/3h\epsilon_{0}g_{J'})\nu_{J'J''}^{3}S_{J'J''}.$$
 (2)

Here, $\nu_{J'J''}$ is the transition frequency (in wave numbers), ϵ_0 is the permittivity of vacuum, and $g_{J'}$ the degree of rotational degeneracy of the emitting state, namely 2J' + 1. A useful expression for *A* is

$$A(e'v'J';e''v''J'') = 3.137 * 10^{-7} \nu_{J'J''}^3 S_{J'J''}(s^{-1}).$$
 (2')

 $S_{J'J''}$ is the line strength which, in the Born–Oppenheimer approximation, can be factorized in vibrational (Franck–Condon), electronic (squared transition moment), and rotational (Hönl–London) terms:²⁴

$$S_{J'J''} = q_{v'v''} R_e^2 \mathscr{S}_{J'J''}.$$
 (3)

Time measurements can only yield an upper limit of the inverse lifetime

$$\tau_{J'}^{-1} = \sum_{J''} A(e'v'J'; e''v''J''), \tag{4}$$

which is the total spontaneous emission coefficient of the (e'v'J') state, from all radiatively allowed channels.¹⁰ In this connection, parallel processes such as quenchings are immaterial for our measurements, unless rotationally selective, and this should be underlined as a different feature of the emission intensity approach.



FIG. 2. Boltzmann plots of ${}^{o}P(\bullet)$, and ${}^{s}R(\bigcirc)$ branches (from Ref. 25). Rotational temperature of emitting population indicated.

The functional dependence of line strength on rotations is extracted from the experiment relying on the following considerations. The intensity (1) of a rotational line, within a band, is essentially determined by the line strength value $S_{j'j''}$ and the Boltzmann factor $\exp(-E_{J'}/kT)$.²⁵ The latter is due to the relative population of the emitting state, which makes the incidence of noise in the deduced line strengths to be exponentially increasing towards the wings of the band. Since a suitably extended comparison is needed between branches²⁶ in order to deduce the transition moments of table of line strengths,¹¹ uniform statistical conditions should be assured to all lines under study. A "quality test" on intensity data can be accomplished in a rather easy way by application on two branches of an approximate method, suggested by Herzberg,²⁵ for the deduction of rotational temperature. The ^{o}P and ^{s}R well resolved lines, which are sharing the same emitting population, must yield very close statistics (Boltzmann plots) and temperatures, in order for the deduced line strengths to be reliable for correlation.

In Fig. 2 the Boltzmann plots of ${}^{o}P$ and ${}^{s}R$ branches of the NF($b {}^{1}\Sigma^{+}v' = 0 \rightarrow X {}^{3}\Sigma^{-}v'' = 0$) emission are reported. Following the method suggested in Ref. 25 (p. 125), the rotational temperature of the emitting population is seen to be close to the room value, as expected. The linearity is acceptable in both branches, and deduced values show a difference of about 3%. This result is a good index of the reliability of data, also in relation to the time drift problems due to single channel detection. Previous data²⁷ on the ${}^{s}R$ branch, from this laboratory, were probably affected by some minor side effects, and are superseded by those presented here.

In Fig. 3 the experimental line strengths of ${}^{o}P$ and ${}^{s}R$ branches in the NF($b \, {}^{1}\Sigma^{+}v' = 0 \rightarrow X \, {}^{3}\Sigma^{-}v'' = 0$) band emission are shown. The values are deduced from data reported in Table I of this work (higher plot), and from Table I of Ref. 18 (lower plot). The lines in the higher plot are theoretical functions for (b) and (a) and (b) Hund cases, to be discussed in the next section. The present experimental re-

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FIG. 3. Experimental line strengths of ${}^{o}P(\bullet)$ and ${}^{s}R(\bigcirc)$ branches. (a): Values evaluated from Table I data (this work); Theoretical line strengths—1 (common): ${}^{o}P$; 2(full line): ${}^{s}R$ for Hund (a)–(b) case; 3(dotted line): ${}^{s}R$ for Hund full (b) case. (b): Values evaluated from data in Table I (Ref. 18).

sults essentially agree with those evaluated from some data in Ref. 18. An improved quality here extends the range of reliability, and is used for a line by line comparison with theory. This must obviously be limited only to regions where the functional dependence of line strengths on the rotational number is very regular, recognizing what could be blurred by experimental inadequacies.

A shift of about two J units between ${}^{o}P$ and ${}^{s}R$ line strengths is clearly distinguishable in both Fig. 3(a) and 3(b) plots, and it is apparent that this behavior is different from what is expected. The theoretical prediction, in fact, claims that the Hund (b) case should thoroughly apply,^{9,11} with a complete coincidence of the line strengths of these branches when the triplet is lower. New assumptions in the theory are thus necessary in order to explain the present behavior.

DISCUSSION

A. Line strength

The line strength of molecules, in Eq. (2), can be expressed in the same general form deduced for atoms²⁸

$$S_{J'J''} = \sum_{M'M''} |\langle \psi_{M'} | \mu | \psi_{M''} \rangle|^2,$$
 (5)

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to the electric dipole, and Ψ are the wave functions, with M labeling all magnetic substates from space fixed components of the total angular momentum J. Attention should be paid to notations and definitions adopted for both atoms and molecules, in order to avoid ambiguities. Some useful recommendations can be found, among others, in Whiting *et al.*,^{24(a)} and will be followed here.

Contrary to the atomic case, body fixed and space fixed frames are not equivalent for molecules, because of moments of inertia of nuclei. For an interpretation of experimental data, it is necessary for (5) to be referred to the laboratory, and be expressed as a function of molecular internal variables, say (x, y, z), defined in a (body fixed) rotating frame. The laboratory uses capital letters (X, Y, Z), and both origins of frames are held fixed in the center of mass of molecules. Since a displacement of function is equivalent to an opposite operation on the frame, it is possible to rely only on the direction cosine matrix between moving frames, briefly $(XYZ) = \phi * (xyz)$. For a quantized system, ϕ can be conveniently expressed with suitable variables by application of the general laws of operators algebra.²⁹ The matrix elements for the fundamental case of symmetric tops have been operationally deduced a few decades ago.³⁰ The employed model is the so-called rigid "dumbbell" rotator.

To follow the arguments in the above calculations, it is necessary to separate the vibronic nonrotational part of energy

$$H = H_{ev} + H_r, \tag{6}$$

where rotations can be considered as perturbations. A suitable form for the basis set is

$$|e,v,r\rangle = |e,v\rangle|r\rangle. \tag{7}$$

Observable trends can thus be evaluated from the angular transformations of a molecule fixed quantity, $\mu_e = \langle e'v' | \mu | e''v'' \rangle$, which is defined as the electric dipole effective transition moment.

According to Hougen's suggestion,⁹ the symmetric top formalism is also applicable to diatomic molecules and radicals, which are considered a special case with the basis set restricted only to functions where k matches Ω . Moreover, since no appreciable change in the equilibrium distance of nuclei is occurring during the NF($b^{1}\Sigma^{+} \rightarrow X^{3}\Sigma$) transition,¹⁷ the $\langle v' | v'' \rangle$ Franck–Condon term, which is unaffected by rotations, may also be factorized in the whole band.

In the case of multiplets, however, nonrotational couplings like spin-orbit (so) and spin-spin (ss) are also present in H_{ev} , which is thus constituted by an unperturbed nonrelativistic Hamiltonian H_{ev}^0 , and an H^s term from the couplings of spin. Thus, the actual total perturbation H^p is of the kind

$$H^p = H^s + H_r \,. \tag{8}$$

If perturbations in (8) can be treated separately, only degeneracies in the vibronic part are thought to be broken to first order. Within this limit, the mixing of $|e,v\rangle$ factors of basis

set (7) leaves rotations diagonal and, for a multiplet state, H_r can be expressed as an effective Hamiltonian³¹ depending on some H^s parameters.⁹ The rotational manifold of a ${}^{3}\Sigma$ state is thus related to three spin vibronic levels affected by rotations only at the second order of perturbation. Intricacies, however, may arise when magnitudes and compositions of the fine structure are comparable with the rotational energy. In general, varied circumstances may happen to occur, which are subdivided into a set of Hund cases.

For triplets, the mixing of basis functions from the rotational perturbation is referred to a couple of splitting coefficients

$$c = \{ [F_2 - F_1] / [F_3 - F_1] \}^{1/2},$$

$$s = \{ [F_3 - F_2] / [F_3 - F_1] \}^{1/2},$$
(9)

which follow the normalization rule $c^2 + s^2 = 1$. Neglecting nuclear spins, it has to be taken into account that spinrotation, spin-orbit, and spin-spin interactions^{10,32} play differently in the transition mechanisms.

With a suitable representation of vector observables of the system, in the space of rotations, one component $(\mu_{e})_{i}$ of the transition moment can be allowed at most,^{9,10,24} with index i=0 or ± 1 , respectively, identifying transitions of parallel and perpendicular character. Moreover, in the case of isotropic and unpolarized emission, and with absence of external electric and magnetic fields, expression (5) can be reduced to only one direction in the space fixed frame, say Z

$$S_{J'J''} = 3(\mu_e)_i^2 \sum_{M'M''} \langle J'M'k' | \mathbf{Z} \cdot \mathbf{i} | J''M''k'' \rangle^2, \qquad (5')$$

 $\mathbf{Z} \cdot \mathbf{i}$ being the cosine of Z with *i*th molecule fixed direction, where transition moment is not vanishing, if any, and (J,M,k) is the H_r set of variables, summarized as r in (7). The elements of the direction cosine matrix, in terms of quantum angular momenta, can be factorized in two "reduced matrix elements," expressed by double bars,³³ where space and body fixed directions are separated. The quantity under summation takes the form

$$\langle r' | \mathbf{Z} \cdot \mathbf{i} | \mathbf{r}'' \rangle = \langle J' M' || \phi_Z || J'' M'' \rangle \langle J' k' || \phi_i || J'' k'' \rangle.$$
(10)

Since in case of internal perturbations only $\Delta J = 0$, $\Delta M = 0$ states can be mixed, the first term of the right-hand side sums up in (5') to a multiplicative factor for each J' - J'' line. On the contrary, the second is depending on the character of transition, which can be either parallel ($\Delta k = 0$) or perpendicular ($\Delta k = \pm 1$). All factors for $\Delta J = 0, \pm 1$ and $\Delta k = 0$, ± 1 transitions, have been tabulated by several authors, 9,10,24b however Di Lauro and Mills have given an exposition suitable for comparison with experiments. Table II of Ref. 33 is readily transformed for diatomics by substitution of k with Ω , as mentioned above.

States may undergo forbidden transitions by channels described at a higher order of approximation, where all possible interactions in the manifold of eigenstates of total Hamiltonian (6) are taken into account. With a proper approximation of the spacing of levels, and use of a well suited basis set, some details may be obtained which are essential in the forbidden transitions. Actually, information which is practically unnoticeable in the energy scale may be deduced from intensities (see, for example, $Zare^{31(c)}$ and $Watson^{31(d)}$).

In the ${}^{1}\Sigma^{+} - {}^{3}\Sigma^{-}$ transition, which is spin forbidden, either parallel and perpendicular transition moments can be present in a single line, with magnitudes depending both on the actual composition of states and type of interactions.³⁴ Table II of Ref. 33, with Ω values for diatomics, displays the direction cosine matrix elements for the linear combinations to be compared with the experiment.

The effective spin rotation Hamiltonian for the ${}^{3}\Sigma$ state is¹¹

$$H_r = B\mathbf{N}^2 + \gamma \mathbf{N} \cdot \mathbf{S} + 2\lambda S_Z^2, \tag{11}$$

where N = J - S, γ is the factor of spin-rotation coupling, and 2λ the separation interval between Σ_0 and $\Sigma_{\pm 1}$, due essentially to second order spin-orbit and first order spin-spin couplings.³⁵ If case (a) basis set is employed, the Watson¹¹ notations $|\Omega, J\rangle$, comprehensive of a factorized term for ${}^{3}\Sigma_{0}$, can be used. The eigenfunctions of H_{r} are expressed by a linear combination of basis functions:

$$|F_{1}(J)\rangle = c_{J}|0,J\rangle + 2^{-1/2}s_{J}\{|1,J\rangle + |-1,J\rangle\},$$

$$|F_{2}(J)\rangle = 2^{-1/2}\{|1,J\rangle\rangle - |-1,J\rangle\},$$

$$|F_{3}(J)\rangle = s_{J}|0,J\rangle - 2^{-1/2}c_{J}\{|1,J\rangle\rangle + |-1,J\rangle\},$$

(12)

where (c_I, s_I) are the mixing coefficients (9) of triplet states for a given J. From transformed Table II of Ref. 33, the general expressions of rotational line strengths are deduced for all ${}^{1}\Sigma^{+} - {}^{3}\Sigma^{-}$ branches

^S
$$R(F_1)_J$$
: $[c_J(J+1)^{1/2}\mu_{\parallel} + s_J J^{1/2}\mu_{\perp}]^2$,
^O $P(F_3)_J$: $[s_J J^{1/2}\mu_{\parallel} + c_J(J+1)^{1/2}\mu_{\perp}]^2$,
^Q $R(F_3)_J$: $[s_J(J+1)^{1/2}\mu_{\parallel} - c_J J^{1/2}\mu_{\perp}]^2$, (13)
^Q $P(F_1)_J$: $[c_J J^{1/2}\mu_{\parallel} - s_J(J+1)^{1/2}\mu_{\perp}]^2$,
^Q $Q(F_2)_J$: $(2J+1)\mu_{\perp}^2$.

This is consistent with that obtained by Watson¹¹ with the same procedure for a reversed order of states, namely with ${}^{1}\Sigma^{+}$ lower. Notations here adopted for parallel and perpendicular transition moments are obvious, and identical to Ref. 9. For a comparison with Ref. 11, $\mu_{\parallel} \equiv \mu_0$, $\mu_{\perp} \equiv -\mu_1$, and J is likewise used instead of J''.

The fine structure displacements are deducible from the eigenvalues of (11). A rather general solution, for a given J, is¹¹

$$F_{1}(J) = BJ(J+1) + (2\lambda - \gamma) + (B - \lambda - \gamma/2) - [(B - \lambda - \gamma/2)^{2} + 4J(J+1)(B - \gamma/2)^{2}]^{1/2},$$

$$F_{2}(J) = BJ(J+1) + (2\lambda - \gamma),$$
(14)
$$F_{3}(J) = BJ(J+1) + (2\lambda - \gamma) + (B - \lambda - \gamma/2) + [(B - \lambda - \gamma/2)^{2} + 4J(J+1)(B - \gamma/2)^{2}]^{1/2}.$$

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In order to evaluate the (c_J, s_J) coefficients from expressions (14), proper approximations on the values of spectroscopic constants may yield an effective dependence from rotations. For example, widely known¹¹ theoretical functions for the line strength have been deduced in the high J or small λ approximation. However, since these limitations plainly indicate a strong spin uncoupling²⁵ from the molecular axis, which is defining a full case (b) configuration, the case (a) basis set may turn out to be inadequate. In a previous study on the PH radical,¹² this circumstance has been seen to apply for increasing rotations, with an initial "regular" behavior of the ${}^{O}P$ and ${}^{S}R$ line strengths followed by a sharp change from J=4 on. This has been put in relation with a simultaneous crossing of the $F_1(N)$ and $F_3(N)$ fine structure terms, due to a transfer in the prevailing energy contribution, from spin-orbit to spin-rotation. A correspondent change in the good quantum number for rotations, from J to N, yields new splitting coefficients and new line strength expressions.

Since it is $(B - \lambda - \gamma/2) \approx 0$ for NF,^{15(b),36} the expressions (14) are easily approximated:

$$F_{1}(J) \approx BJ(J+1) + (2\lambda - \gamma) - 2(B - \gamma/2)(J+1/2),$$

$$F_{2}(J) = BJ(J+1) + (2\lambda - \gamma),$$
(15)

$$F_{3}(J) \approx BJ(J+1) + (2\lambda - \gamma) + 2(B - \gamma/2)(J+1/2),$$

which are valid for a given J. Insertion of (15) into (9) yields

$$c_I = s_I = (1/2)^{1/2},\tag{15'}$$

with J subscripts indicating an intermediate (a)–(b) Hund case, since the $F_{123}(J)$ triplets are rather close to a case (a) configuration. The line strengths for NF are immediately deduced from expressions (13)

^S
$$R(F_1)_J$$
: 1/2[$(J+1)^{1/2}\mu_{\parallel}+J^{1/2}\mu_{\perp}$]²,
^O $P(F_3)_J$: 1/2[$J^{1/2}\mu_{\parallel}+(J+1)^{1/2}\mu_{\perp}$]²,
^Q $R(F_3)_J$: 1/2[$(J+1)^{1/2}\mu_{\parallel}-J^{1/2}\mu_{\perp}$]², (16)
^Q $P(F_1)_J$: 1/2[$J^{1/2}\mu_{\parallel}-(J+1)^{1/2}\mu_{\perp}$]²,
^Q $Q(F_2)_J$: (2J+1) μ_{\perp}^2 .

In a full (b) case, on the contrary, rotations are labeled by N, which is implying a different composition of the triplet. The new functions can be obtained in a direct way by application of standard correspondences: J=N+1 in F_1 ; =N in F_2 ; and =N-1 in F_3 . This should be carried out both in the energy levels (15), in order to deduce the case (b) coefficients from the new functional dependence of term splittings, and in the general line strength expressions (13). For example, the general expressions for ${}^{S}R$ and ${}^{O}P$ line strengths in a full case (b) are

^S
$$R(F_1)_N$$
: $[c_{N+1}(N+2)^{1/2}\mu_{\parallel} + s_{N+1}(N+1)^{1/2}\mu_{\perp}]^2$,
^O $P(F_3)_N$: $[s_{N-1}(N-1)^{1/2}\mu_{\parallel} + c_{N-1}N^{1/2}\mu_{\perp}]^2$.
(13')

Since $B \approx \lambda$, NF could be thought of as a Hund (b) case also in the low rotational levels.⁹ Perturbation techniques, however, are applicable to N triplets only when $N \ge 8$, after a crossing of the $F_1(N)$ and $F_3(N)$ displaced terms. For lower values of N, $F_1(N)$ and $F_3(N)$ approach each other with increasing rotation, therefore N is not a suitable label for the rotational perturbation in this interval. The crossing point of $F_1(N)$ and $F_3(N)$ fine structure levels has been deduced from energy values in Table I of Ref. 18, and is also well reproduced in the general expressions (14).

After application of $F_{123}(J) \leftrightarrow F_{123}(N)$ correspondences, it is seen that the rotational dependence of $F_1(N)$ and $F_3(N)$ displacements from $F_2(N)$ is no longer essentially determined by the *B* constant, but only by the γ spin-rotation coupling.

The perturbation coefficients in the full (b) case are as follows:

$$c_N^2 = (N+3/2)/(2N+1),$$

 $s_N^2 = (N-1/2)/(2N+1),$
(15")

where $F_2(N) - B$ has been used in (9) as an unperturbed level. Substitution of these coefficients in the new general expressions, partially shown in (13'), yields the NF rotational line strength for the full (b) case. Since all states are formally labeled with both J and N, the obtained expressions can be readily transformed into J for a direct comparison with (16), which is applicable to the intermediate (a)–(b) configuration.

In the full (b) case, the line strength of branches takes the following form:

$${}^{S}R(F_{1})_{N}: \quad (2J+1)^{-1}\{[(J+3/2)(J+1)]^{1/2}\mu_{\parallel} \\ +[(J-1/2)J]^{1/2}\mu_{\perp}\}^{2}, \\ {}^{O}P(F_{3})_{N}: \quad (2J+1)^{-1}\{[(J-1/2)J]^{1/2}\mu_{\parallel} \\ +[(J+3/2)(J+1)]^{1/2}\mu_{\perp}\}^{2}, \\ {}^{Q}R(F_{3})_{N}: \quad (2J+1)^{-1}\{[(J-1/2)(J+1)]^{1/2}\mu_{\parallel} \qquad (17) \\ -[(J+3/2)J]^{1/2}\mu_{\perp}\}^{2}, \\ {}^{Q}P(F_{1})_{N}: \quad (2J+1)^{-1}\{[(J+3/2)J]^{1/2}\mu_{\parallel} \\ -[(J-1/2)(J+1)]^{1/2}\mu_{\perp}\}^{2}, \\ {}^{Q}Q(F_{2})_{N}: \quad (2J+1)\mu_{\perp}^{2}, \\ \end{array}$$

where N subscripts remind us that expressions above apply to states where this quantum number is a good one, instead of J.

B. Transition moments

The transition moments ratio, $\mu_{\parallel}/\mu_{\perp}$, is deduced from the experiment by comparing the ratio of integrated branch intensities with theoretical expressions. In order to establish which Hund case applies, if intermediate (a)–(b) or full (b), two values, from (16) and (17), have been deduced for $\mu_{\parallel}/\mu_{\perp}$. By application of both (16) and population distribution, as discussed in the Results section, the following expression holds in the (a)–(b) case for the available branches portion: $76.5464(\mu_{\parallel}/\mu_{\perp})^2 + 153.524(\mu_{\parallel}/\mu_{\perp}) + 77.5406$ $\frac{1}{82.1513(\mu_{\parallel}/\mu_{\perp})^2 - 164.223(\mu_{\parallel}/\mu_{\perp}) + 235.732}$

$$=\frac{I_{\rm EXP}^{\rm NF}({}^{^{S}}R+{}^{^{O}}P)}{I_{\rm EXP}^{\rm NF}({}^{^{O}}P+{}^{^{O}}Q+{}^{^{O}}R)},$$
(18)

where, in the right-hand side, adopted sharing of branches is indicated. Coupled solutions of this second order equation are

(i)
$$\mu_{\parallel}/\mu_{\perp} = -3.79 \pm 0.035;$$

(ii) $\mu_{\parallel}/\mu_{\perp} = -0.044 \pm 0.005,$ (19)

where errors are deduced from identical calculations on several runs of the experiment. It is seen that the error in the (i) value is <1%, whereas in (ii) it is >10%. Thus, from a variational point of view, the (i) value $\mu_{\parallel}/\mu_{\perp} = -3.79$ should be chosen, which is also in very good agreement with that reported in Ref. 18. The same procedure with the (b) case, expressions (17), yields -3.70 ± 0.035 as a solution (with -0.058 ± 0.005). The values of $\mu_{\parallel}/\mu_{\perp}$ here obtained from (16) and (17) refer to the intermediate (a)-(b) and the (b) Hund cases, respectively, and are very similar. Both are also very close to -3.80, which has been proposed in Ref. 18 using theoretical expressions that are inadequate for NF. The reason for these similarities, from this type of evaluation, is that the branches' integrated values are not sensitive to the details of the system, but essentially to asymptotic behaviors that are identical for all expressions. By insertion of -3.79 in ^OP and ^SR line strengths in (16), and -3.70 in (17), linear expressions are deduced which are, respectively, to be expected for NF, if either the (a)-(b) Hund case applies, or the (b). Both cases are plotted in Fig. 3(a), with ^{O}P curves superposed in order to show that different correlations are established between the branches. It is thus immediately recognizable that the (a)-(b) scenario is in complete agreement with the experiment.

Ab initio methods^{21,22} have been used to calculate the NF transition moments, within a microscopic Breit-Pauli (BP) approximation limited to spin orbit. The nonrotational Hamiltonian was

$$H_{\rm ev} = H_{\rm ev}^0 + H^{\rm BP}.\tag{20}$$

Here, $H^{BP} = H^{SO}$ takes the place of H^s in (8), as a microscopic spin-orbit perturbation, also comprising spin-otherorbit coupling (soo). Calculations²¹ have been performed for the NF($b^{1}\Sigma^{+} \rightarrow X^{3}\Sigma^{-}$) transition at different internuclear distances R. Among other results, a couple of values,

-3.75 for R = 1.16 Å and -3.85 for R = 1.30 Å, were obtained for the ratio of the transition moments components. From our value $\mu_{\parallel}/\mu_{\perp} = -3.79$, and taking into account an experimental datum, $\tau = 22.6 \times 10^{-3}$ s.¹⁷ For the $b^{-1}\Sigma^{+}$ state lifetime, the single components are calculated:

$$\mu_{\parallel} = 0.169 * 10^{-2}$$
 a.u.; $\mu_{\perp} = -0.445 * 10^{-3}$ a.u. (21)

The total transition moment $\mu_e(b^{-1}\Sigma^+ \rightarrow X^{-3}\Sigma^-) = (\mu_{\parallel}^2 + 2\mu_{\perp}^2)^{1/2} = 0.18 \times 10^{-2}$ a.u., and the internuclear distance *R* = 1.23 Å is then deduced.

C. General remarks

In a previous investigation on the PH radical in this laboratory,¹² it has been shown that a transition from the intermediate (a)-(b) case to (b) takes place approximately in coincidence with a crossing of the $F_1(N)$ and $F_3(N)$ terms in ${}^{3}\Sigma^{-}$ fine structure. This is due, as said above, because of the spin uncoupling,²⁵ which is inducing N as a good quantum number for rotations instead of J. This is not, on the other hand, the behavior of both NH and ND radicals, where only the (a)-(b) case has been observed.¹³ A preeminent spin-spin contribution, which is indistinguishable from spin-orbit, $^{19(a)}$ to the $^{3}\Sigma$ fine structure of light radicals, as NH(D), was given as an explication. In fact, symmetry decomposition³⁴ of both wave functions and total nonrotational perturbation, spin-orbit+spin-spin, has shown that the $X^{3}\Sigma^{-}$ fine structure, and the $b^{-1}\Sigma^{+} \rightarrow X^{3}\Sigma^{-}$ transition, are uncorrelatable in NH because the liable states are different. An opposite situation should apply to PH, where the essential of $X^{3}\Sigma^{-}$ fine structure is determined by spin-orbit,³⁶ like the transition.

In the present NF case, the fine structure energy curves show a crossing point at about N=8, as discussed above. Nevertheless the system remains in the intermediate (a)-(b)Hund case, also in higher rotational values. As previously mentioned, spin-spin coupling should be taken into account, in addition to spin-orbit, to rationalize the behavior of light radicals. From relative magnitudes of λ_{ss} (=0.985 cm⁻¹) and $\lambda_{so}(=0.296 \text{ cm}^{-1})$, which are effective parameters evaluated for NF by Wayne and Colbourn³⁶ with *ab initio* methods, a situation could be thought of as similar to that of NH(D). In other words, NF rotations should be rather ineffective for the spin uncoupling from the molecular axis, because of a predominant interaction between unpaired spins, which is constituted in any direction of space. A more complete ab initio treatment, like that available for NH,³⁴ seems nonetheless desirable also for the NF radical, to elucidate the actual composition of states and interactions.

The structure of NF $a^1\Delta$ and $b^{-1}\Sigma^+$ metastable states has been the subject of several theoretical studies, 5,21,22,36,37 mainly referring to experimental lifetimes.^{2(a),17} Striking irregularities have been observed when the radiative behaviors of the NF-NCl-NBr sequence were only related to the magnitudes of spin-orbit coupling.⁵ Hund cases, on the other hand, are probably better observed by intensities, where a role can also be forecast for the spin-spin coupling. This, however, has often been neglected in *ab initio* calculations.

CONCLUSIONS

The technique of line strength spectroscopy yields a deeper insight into the rotational manifold of forbidden transitions, and some hints for a description of the effective interactions among states. In the NF(${}^{1}\Sigma^{+} - {}^{3}\Sigma^{-}$) transition, some unexpected features have been shown and interpreted:

Different line strength distributions are obtained for (i) the two ${}^{O}P$ and ${}^{S}R$ branches.

- (ii) Intermediate (a)-(b) Hund case applies all over the examined rotational range.
- (iii) Reliable values for the effective transition moment μ_{e} and the internuclear distance R are obtained.
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