Perturbations in the C $^3\Pi(v'=1)$ state of AlN studied by laser spectroscopy

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We report the LIF spectrum of the C $^3\Pi(v'=1)\leftarrow$X $^3\Pi(v''=0)$ transition in the AlN molecule. Laser vaporization in combination with supersonic expansion and laser-induced fluorescence are used to produce and detect the AlN molecules. The molecular constants and electronic lifetimes of the C state are determined. Predissociation and an accidental perturbation are discussed and compared to an ab initio potential calculation of the electronic states.

1. Introduction

The first and, to our knowledge, only spectroscopic measurement of the electronic states of the AlN molecule up to now was performed by Simmons and McDonald [1]. They measured two emission bands which they assigned as the $(0\rightarrow0)$ and $(0\rightarrow1)$ bands of a $^3\Pi$–$^3\Pi$ transition. Despite several attempts, Simmons and McDonald were unable to detect the $(1\rightarrow0)$ transition. Rotational constants were determined for both the lower and upper state and a complicated variation of the linewidths throughout the spectrum was explained by unresolved hyperfine structure. An abrupt ending of the rotational structure in the $(0\rightarrow0)$ band was attributed to a predissociation in the upper state. Whether the lower state was the electronic ground state could not be determined.

More recently, two ab initio calculations concerning the electronic state of this molecule were published. Pelissier and Malrieu [2] calculated spectroscopic constants for the six lowest electronic states and assigned the ground electronic level to a $^3\Pi$ state. Langhoff et al. performed a detailed and elaborate study of the electronic states below 35000 cm^{-1} at the state-averaged complete active-space self-consistent-field (SA-CASSCF) and multireference configuration-interaction (MARCI) levels of theory [3]. The aforementioned bands could now be assigned to the C $^3\Pi\rightarrow$X $^3\Pi$ transition. They calculated potential energy curves for the singlet, triplet and quintet states as well as molecular constants and radiative lifetimes. A possible predissociation of the C state by the $(1)^5\Pi$ state was predicted.

The availability of these data, together with our experience that laser vaporization is particularly suitable for the production of diatomic species like AlN, led us to the search for higher vibrations in the C state of this molecule. In this paper, we report the observation of the $v'=1$ state by laser-induced fluorescence.

2. Experimental

The laser-vaporization source has been described in previous papers (see for example ref. [4]). Briefly, 355 nm radiation from a frequency-tripled Nd:YAG laser is focused with a 35 cm focal-length lens onto a rotating aluminum sample inside a short channel in front of a pulsed nozzle. The energy of the vaporizing laser can be varied between 1 and 5 mJ. The delay between opening the nozzle and firing the vaporization laser is chosen so that a maximum number of excited Al atoms is found in the expansion. This corresponds to an optimum production of AlN molecules. The supplied gas is a mixture of 20% NH_3 in Ar at a stagnation pressure of 900 mbar. At 30 mm

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downstream from the vaporization point (flight-time: 32 μs), the free expansion is intersected perpendicularly by the probe laser beam, in this case from a Lambda Physik FL 3002 dye laser (bandwidth 0.2 cm^{-1}) pumped by a Quantel 681C-10 Nd:YAG laser. The laser frequency is calibrated on the lines of the AlN $C\,^3\Pi(v'=0)\leftarrow X\,^3\Pi(v''=0)$ transition as listed by Simmons and McDonald [1]. The fluorescence light is imaged on a photomultiplier via a 1.8 nm bandwidth F/3.7 monochromator. Spectral scans were recorded using a boxcar averager and lifetime measurements were performed with a Lecroy 9400 oscilloscope averaging over some 200 shots.

3. Results and discussion

3.1. General

Similar to the result found by Simard et al. [5] in their study of the VN molecule, NH_3 turned out to be a good N donor in the plasma. An optimum seed ratio for maximum AlN production was not observed. Changing the seed ratio from 1% to 20% NH_3 in Ar only slightly influenced the rotational temperature in the expansion while the density of AlN molecules increased significantly. Attempts with mixtures of NO in Ar or N_2 in Ar were without success: no AlN was detected.

In the spectral region where we measured the AlN $C\,^3\Pi(v'=1)\leftarrow X\,^3\Pi(v'=0)$ transition, we also encountered the strong NH_2 $\tilde{A}\,^2A_1(0,13,0)\leftarrow\tilde{X}\,^2B_1(0,0,0)$ as well as the AlO $B\,^2\Sigma^+(v'=1)\leftarrow X\,^2\Sigma^+(v''=1)$ spectrum. The NH_2 spectrum was well separated in frequency from the AlN spectrum. The AlO spectrum, on the contrary, at first overruled the AlN spectrum completely, but could be separated from it in fluorescence because the vibrational spacings in the electronic ground states of the oxide and the nitride differ slightly. For this purpose, the slitwidths of the monochromator were reduced to 300 μm yielding a 1.8 nm resolution, enough to discriminate between AlN and AlO. The resulting loss in fluorescence signal was partially compensated by the more effective filtering of the (atomic) beam emission, that enabled us to use the photomultiplier at maximum sensitivity.

3.2. Spectroscopic results

The observed spectrum of the C←X transition is shown in fig. 1. The overall structure of the band can be recognized as a spectrum from a $^3\Pi$–$^3\Pi$ transition without intercombination ($\Delta\Omega\neq0$) bands. Because $\Delta\Omega=0$ is forbidden for $\Delta J=0$, two Q branches are expected. In emission, Simmons and McDonald observed two "at best extremely weak, unresolved bands". In our spectrum, however, the Q branches are the strongest features. The reason for this is that the high laser power we use saturates the transition and thereby overcomes the (small) Hönl–London factors. Since the Q lines are not resolved, their individual intensities sum.

The observed linewidths are larger than the instrumental linewidth of the dye laser (0.2 cm^{-1}). They result from both saturation broadening of this electric-dipole-allowed transition and unresolved hyperfine splittings. In the work of Simmons, the magnitude and appearance of these hyperfine splittings are discussed. The laser-power broadening could not be eliminated completely because of the otherwise too large loss in fluorescence signal.

In fig. 1, two distinct perturbations can immediately be seen in the R_3 branch. An apparent accidental degeneracy doubles the $R_3(5)$ and, less clearly, also the $P_3(7)$ line. Secondly, the R_3 band sharply breaks-off after the $R_3(15)$, and the P_3 band after $P_3(17)$. The origin of these perturbations will be treated below.

The measured absolute frequencies of the rotational lines are listed in table 1. Their accuracy is 0.1 cm^{-1}. The $R_3(5)$ and $P_3(7)$ are split up in two lines, 1.0 ± 0.1 cm^{-1} apart. The centers of these symmetric doublets were regarded as the unperturbed frequencies. A least-squares fit of the line frequencies to an effective $^3\Pi$–$^3\Pi$ Hamiltonian (taken from ref. [11]) yields the constants listed in table 2. For comparison, the constants for the $v'=0$ state from the work of Simmons and McDonald have also been included in this table.

Because we only see transitions from the lowest J'' states as a result of the low rotational temperature in the jet (±40 K), the introduction of a centrifugal

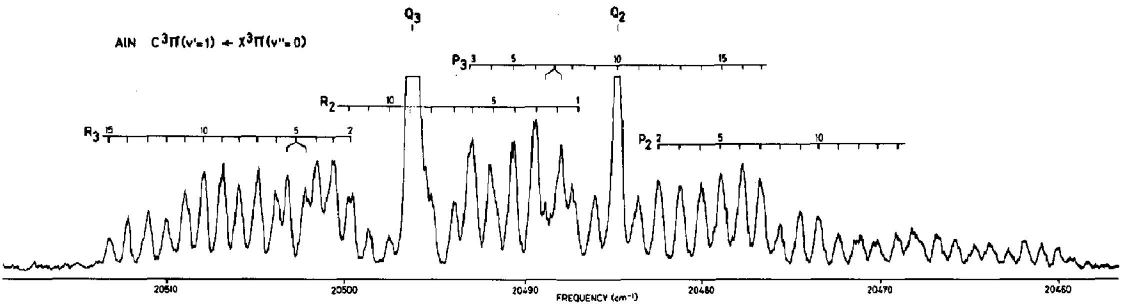

Fig. 1. Excitation spectrum of the C $^3\Pi(v'=1)\leftarrow$X $^3\Pi(v''=0)$ transition.

Table 1
Observed rotational line frequencies for the C $^3\Pi(v'=1)\leftarrow$X $^3\Pi(v''=0)$ transition (cm^{-1})

J''	P_3	Q_3	R_3	P_2	Q_2	R_2
1					20484.75	
2		20496.25	20499.74		484.75	
3	20492.89	496.25	500.67	20481.22	484.75	20489.36
4	491.80	496.25	501.63	480.05	484.75	490.58
5	490.58	496.25	502.77 [a]	478.91	484.75	491.63
6	489.36		503.86	477.70		492.89
7	488.31 [a]		504.95	476.69		493.58
8	487.26		505.96	475.60		495.24
9	486.05		506.93	474.47		
10	484.75		507.94	473.42		497.55
11	483.73		508.95	472.33		498.69
12	482.44		510.00	471.16		
13	481.22		511.10	470.23		
14	480.05		512.23	469.02		
15	478.91		513.24			
16	477.70					
17	476.69					

[a] In the least-squares fit, the center of the doublet does not deviate from the unperturbed line frequency.

distortion constant did not improve the fit. In this fit, the ground-state A''_0 and B''_0 constants were kept fixed at −33.0 and 0.5702 cm^{-1}, respectively. With the additional data now available, B'_e and α'_e, as well as $\Delta G'_{1/2}$, could be calculated. From the Pekeris relation [6],

$$\alpha_e=\frac{6\sqrt{\omega_e x_e B_e^3}}{\omega_e}-\frac{6B_e^2}{\omega_e}\,, \qquad (1)$$

we calculated ω'_e and $\omega_e x'_e$, and with these T_e.

Despite several attempts, we did not succeed in detecting the next ($v'=2$) vibration in the C state. There are two reasons for this: First of all, the Franck–Condon factor is very small for a $\Delta v=2$ transition because the C–X transition is strongly vertical. In fact, when we measured the fluorescence spectrum, the $\Delta v=1$ signal was less than 10% of the $\Delta v=0$ signal and no $\Delta v>1$ transitions could be detected. Secondly, it will be shown in section 3.5, that the $v'=2$ is predissociated by the (1)$^5\Pi$ state.

3.3. Lifetimes

In fig. 2, the lifetimes of the C $^3\Pi_2$, $v'=1$ states are plotted. We measured the fluorescence decay after excitation via the $R_3(2)$–$R_3(15)$ transitions. Except for the $J'=6$ state, a lifetime of 116±6 ns was obtained. For the $v'=0$ state, we excited via the $R_3(4)$ and the $R_2(7)$ transitions and determined a lifetime

Table 2
The $C\,^3\Pi$–$X\,^3\Pi$ transition parameters, molecular constants (cm^{-1}) and lifetimes (ns) for the $C\,^3\Pi$ state

	(1,0)			(0,0) ref. [1]
	this work	ref. [3]		
ν_{10}	20484.71(3)		ν_{00}	19727.32(3)
$A'_1-A''_0$	11.57(4)		$A'_0-A''_0$	10.06(4)
A'_1	−25.8(1.1)		A'_0	−22.98(2.0)
B'_1	0.5723(2)		B'_0	0.5811(2)
B'_e	0.5855(4)	0.5605 [a]	B''_e	0.5730(13) [c]
α'_e	0.0088(4)		α''_e	0.0056(11) [c]
$\Delta G'_{1/2}$	757.39(6)		$\Delta G''_{1/2}$	746.93(9) [c]
T'_e	19718.1(2.4)			
ω'_e	779.4(1.6)	720 [b]	ω''_e	758.4(1.6) [c]
$\omega_e x'_e$	11.0(0.8)		$\omega_e x''_e$	5.7(0.8) [c]
$\tau_{v'=0}$	102(8)	151		
$\tau_{v'=1}$	116(6)	163		

[a] Calculated from MRCI value for $r_e=3.414\,a_0$.

[b] MRCI value.

[c] Calculated using the data of Simmons and McDonald [3].

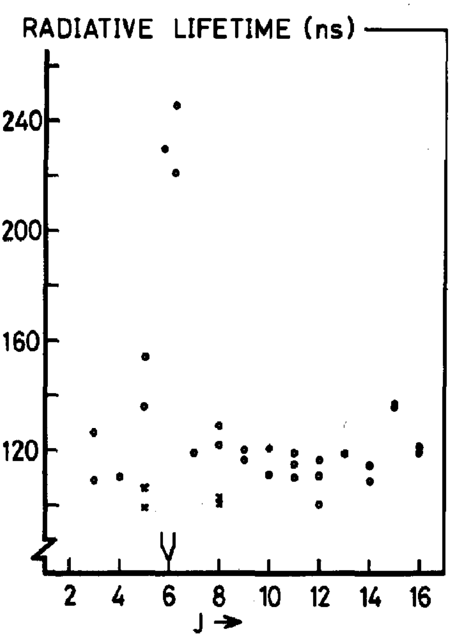

Fig. 2. Lifetimes of the rotational states in the $C\,^3\Pi$, $v'=0$ (crosses) and $v'=1$ (circles).

of 102±8 ns. The errors are based on the statistical spread of the results, originating from the rather poor signal-to-noise ratio we obtained, even after averaging over some 200 shots. The decay after excitation was checked to be single exponential in order to be sure that a flight out of the detection area of the excited molecules did not affect the measurements. From measurements of long lifetimes for other molecules such as CH ($A\,^2\Delta$; 530 ns), we know that the pressure in the jet is low enough to be sure that collisional quenching plays no role of importance.

A comparison between these measured lifetimes with the calculated ones from ref. [3] (see table 2) shows that a tendency towards longer lifetimes for higher vibrational levels seems indeed to be present. Their absolute values, however, differ by some 30%. A strong deviation from the average value is shown for the split $C\,^3\Pi_2$, $v'=1$, $J'=6$ state. For both doublet states, we measured a lifetime of 232±9 ns. The origin of this deviation will be discussed in section 3.4.

3.4. *Accidental perturbation*

The observed perturbation that affects both the frequencies of the transitions to the $C\,^3\Pi_2$, $v'=1$, $J'=6$ state and its lifetime, is most probably due to an accidental degeneracy of this state with a rovibrational level of some other electronic state. Because a complete ab initio calculation of all low-lying singlet, triplet and quintet electronic states has been performed by Langhoff et al., it becomes an interesting question whether we can identify the perturbing state.

This problem can be treated as a mutually interacting pair of rovibronic levels belonging to two different electronic states, $|c\rangle$ and $|p\rangle$ (C state and perturbing state, respectively) (see, for example, ref. [7]).

(i) If $|+\rangle$ and $|-\rangle$ represent the perturbed states (shifted up and down in frequency, respectively) and $|c\rangle$ and $|p\rangle$ the initial unperturbed ones, the equation

$$\frac{1}{\tau_+}+\frac{1}{\tau_-}=\frac{1}{\tau_c}+\frac{1}{\tau_p} \qquad (2)$$

holds. Since $\tau_+=\tau_-=232\pm9$ ns and $\tau_c=116\pm6$ ns, it follows that the lifetime of the perturber must be larger than 1200 ns.

(ii) The interaction matrix element H_{12} can be evaluated using [7],

$$\tfrac{1}{2}|E_+-E_-|=\{[\tfrac{1}{2}(E_c-E_p)]^2+H_{12}^2\}^{1/2}$$
$$-\tfrac{1}{2}|E_c-E_p| \,. \qquad (3)$$

The equal lifetimes of $|+\rangle$ and $|-\rangle$, as well as their symmetrical positions relative to the unperturbed $|c\rangle$ level, suggest that $|+\rangle$ and $|-\rangle$ possess equal $|c\rangle$ and $|p\rangle$ character and that the interaction matrix element can be considered large with respect to $|E_c-E_p|$. Eq. (3) then reduces to

$$H_{12}\approx\tfrac{1}{2}|E_+-E_-| \,. \qquad (4)$$

It follows that H_{12} is equal to about half the observed splitting, i.e. ≈0.5 cm^{-1}. The next rotational level ($J'=7$) is unaffected by this perturbation. The frequencies of the transitions to this state do not deviate from the values calculated in the fit. Also its lifetime equals that of the other unperturbed levels. Stated differently: for this level, $|E_+-E_-|\leqslant0.2$ cm^{-1}. When we substitute this together with $H_{12}=0.5$ cm^{-1} in (2), we get $|E_c-E_p|>2.4$ cm^{-1}, which means $|B_c-B_p|$ must be greater than 0.17 cm^{-1}.

(iii) Each line in the spectrum in fig. 1 actually consists of an unresolved doublet as a result of Λ-doubling. The splitting of the transitions to $J'=6$ indicates that both Λ-doublet levels are perturbed in the same way. From this, we conclude that the perturbing state cannot be a Σ^+ or Σ^- state, since these would only affect one of the $J'=6$ Λ-doublet levels and a triplet splitting would be observed.

The ab initio calculations by Langhoff et al. show that of the bound electronic states, four singlet states: a $^1\Sigma^+$, b $^1\Pi$, c $^1\Delta$ and d $^1\Sigma^+$ and one triplet state: B $^3\Sigma^+$ can be degenerate with the C $^3\Pi$ state. As perturber in our case, the Σ states can be excluded. In both the SA-CASSCF and MRCI calculations of potential curves, the b $^1\Pi$ state lies vertically below the C state whereas the c $^1\Delta$ state shows a significantly larger bond length. Especially for higher vibrations, the B constant of this c state is expected to differ strongly from B_c. The lifetime of the c $^1\Delta$ state is calculated to be 127 μs.

These three considerations led us to the conclusion that the observed accidental perturbation is caused by a vibrationally highly excited level in the c $^1\Delta$ state.

3.5. Predissociation

The observed breaking-off of the rotational structure in the R_3 band at $J'=16$ is probably due to the same predissociation that is responsible for the abrupt ending of the (0,0) band at $J''=47$ observed by Simmons and McDonald. From these two break-off points, the position of the crossing of the effective potential and, thus, the type of curve crossing can be inferred [6]. Taking into account the highest unpredissociated level as well as the first predissociated one in both the $v'=0$ and the $v''=1$ state,

$v'=0$	$J'=48$	21086.60 cm^{-1}
	$J'=49$	21142.89 cm^{-1}
$v'=1$	$J'=15$	20588.46 cm^{-1}
	$J'=16$	20606.17 cm^{-1} ,

we can calculate with

$$\Delta E=BJ_0'(J_0'+1)-BJ_1'(J_1'+1) \,, \qquad (5)$$

where ΔE represents the energy difference between the two break-off points, and with

$$B=h/8\pi^2c\mu R^2 \,, \qquad (6)$$

that the R-value of the crossing of the effective potential curves is 2.75 Å. This is well below twice the equilibrium internuclear distance of the C state, which means that predissociation subcase I(c) applies [6]. Such a predissociation can very well be explained by an outer limb crossing of the C state by the repulsive $(1)^5\Pi$ state, leading to dissociation into two ground-state atoms. This is in agreement with the prediction based on the ab initio calculation of Langhoff et al. [3]. If one assumes a linear dependence of the energies of the breaking-off points on $J(J+1)$ for case I(c) predissociation, extrapolating to zero rotation yields the energy value of the crossing point of the rotationless potential curves. We conclude that the $C\,^3\Pi$ and the $(1)^5\Pi$ states cross at $r=2.75$ Å, 20535 cm^{-1} above the $v=0, J=0$ level of the electronic ground state.

The $v'=2$ state can be calculated to lie at 21220 cm^{-1} above the $v''=0$ state. This is higher than the energy of the crossing of the corresponding effective potential energy curves. This means that the complete (all rotational levels) $v'=2$ state is predissociated by the $(1)^5\Pi$ state.

4. Conclusions

The technique of laser vaporization in combination with supersonic expansion and laser-induced fluorescence is suited for the production and spectroscopic investigation of AlN molecules. The present result represents the first electronic excitation spectrum of AlN. Rotational constants are determined for the $v'=1$ state and two interesting perturbations are studied. An accidental perturbation that causes line splittings and changes the lifetimes is attributed to the interaction with a $^1\Delta$ state. A break-off of the rotational structure caused by predissociation, can be explained by an outer limb crossing of the $C\,^3\Pi$ state by a repulsive $^5\Pi$ state.

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References

[1] J.D. Simmons and J.K. McDonald, J. Mol. Spectry. 41 (1972) 584.

[2] M. Pelissier and J.P. Malrieu, J. Mol. Spectry. 77 (1979) 322.

[3] S.R. Langhoff, C.M. Bauschlicher Jr. and L.G.M. Pettersson, J. Chem. Phys. 89 (1988) 7354.

[4] M. Ebben, G. Meijer and J.J. ter Meulen, Appl. Phys. B 50 (1990) 35.

[5] B. Simard, C. Masoni and P.A. Hackett, J. Mol. Spectry. 136 (1989) 44.

[6] G. Herzberg, Molecular spectra and molecular structure, Vol. 2. Infrared and Raman spectra of polyatomic molecules, 2nd Ed. (Van Nostrand, New York, 1950) p. 431.

[7] H. Lefebvre-Brion and R.W. Field, Perturbations in the spectra of diatomic molecules (Academic Press, New York, 1986) p. 247.