Hyperfine Structure of $N_2\left(B^3Π_g\right.$ and $A^3Σ_u^+)$ from LIF Measurements on a Beam of Metastable N$_2$ Molecules

H. Geisen, D. Neuschäfer, and Ch. Ottinger
Max-Planck-Institut für Strömungsforschung, Göttingen, Federal Republic of Germany

Received July 31, 1986; final version August 22, 1986

Crossing an intense beam of nitrogen molecules in the metastable N$_2$(A) state with the beam from a CW dye laser, laser-induced fluorescence was observed in the first positive system of N$_2$, $B^3Π_g - A^3Σ_u^+$. About 300 lines of the (10, 6) band were studied at sub-Doppler resolution (15 MHz FWHM). From the well-resolved hyperfine structure of the lines, the hyperfine splittings of both the upper and the lower state were derived for a range of rotational quantum numbers up to $J = 12$. Using multiple independent determinations of each splitting via lines belonging to different branches, the hfs could be measured with an accuracy of about 2 MHz. Fitting known theoretical expressions for the hyperfine energies to the data, the following nuclear coupling constants were obtained (in MHz): For the A state, $v = 6$: $\alpha = 12.86$, $\beta = -11.40$, $e^2q_0Q = -2.5$. For the B state, $v = 10$: $K_{11} = 86.46$, $D_{11} = 12.67$, $D_{1-1} = -44.64$, $G_{11} = 69.18$, $Q_{11} = 0.64$, $Q_{1-1} = 1.38$. The hfs is mostly due to nuclear magnetic dipole interactions. For the A state the results are essentially in agreement with hfs constants derived from RF resonance experiments, but are superior as regards the data fit over the entire $J$ range covered. For the B state, the results are new and are interpreted in terms of a simple LCAO model. The Fermi contact coupling constant is in good agreement with unpublished SCF results by V. Staemmler. The striking dependences of the hfs splitting on the fine structure levels, A sublevels and on $J$ are explained both quantitatively and in terms of vector models.

PACS: 33.50; 35.20S

Introduction

The so-called first positive band system of nitrogen, $N_2\left(B^3Π_g - A^3Σ_u^+\right)$, is among the best known of all molecular spectra, being easily excited in electrical discharges through air [1–4]. It also constitutes the most prominent spectral feature in the famous Lewis-Rayleigh nitrogen afterglow, and its origin under these conditions has been the object of much controversy [5–8]. The $N_2(B - A)$ bands appear also in shock-heated nitrogen [9, 10] and play an important role as a means of plasma diagnostics [11]. In nature, this emission occurs in the earth’s airglow and in auroras [12].

The lower of the two electronic states involved, $N_2(A^3Σ_u^+)$, is metastable, having a radiative lifetime of 2.0 s [13]. Lying about 6.2 eV above the electronic ground state of N$_2$, the A state is therefore an important energy carrier in many plasmas [14–16]. Because of its occurrence in the aurora, $N_2(A)$ plays a role in the atmospheric chemistry [17]. Especially with regard to laser development, $N_2(A)$ has received much attention [18–20]. Other practical applications include the determination of trace constituents in gases ("MTES" technique, [21]).

Generally, reaction kinetic studies of $N_2(A)$ have recently experienced a great renaissance; examples for the reaction with O and O$_2$, relevant in the atmosphere [17], are Refs. 22–25. Reactions of $N_2(A)$ with many other molecules have also been studied [26]. While in earlier work the $N_2(A)$ concentration was usually monitored by the $N_2(A-X)$ Vegard-Kaplan emission [22, 24], in recent years laser-induced fluorescence (LIF) in the $N_2(B-A)$ first positive system has been increasingly employed for a highly state specific detection of $N_2(A)$ [23, 25]. Laser excitation in
the N$_2$(B$-$A) system has also been used extensively to prepare N$_2$(B) in specific levels for photochemical studies of that species [27$-$29].

Concomitant with this revival of interest in the N$_2$(B$-$A) transition, improved spectroscopic analyses of the two states involved have been made [30, 31]. The N$_2$(B) lifetime has been redetermined from LIF measurements on N$_2$(A) in a molecular beam, i.e. collision-free [32]. A beam of N$_2$(A) molecules was also used in the first measurement of nuclear hyperfine splittings in this state [33, 34]. This work employed measurements of RF-induced transitions $\Delta M_F$ between Zeeman split levels of some low-J rotational levels of N$_2$(A) [33] as well as direct transitions between hyperfine levels ($\Delta F = \pm 1$) in the presence of a magnetic field [34]. This method is somewhat indirect due to the need to extrapolate the data to zero field, and the experiments were restricted to only a few rotational levels ($J \leq 6$ in [33], $J \leq 2$ in [34]).

The present work is the first measurement of the hyperfine structure (hfs) of the N$_2$(B$-$A) band system. The results were obtained in the course of setting up a molecular beam/LIF apparatus for the study of chemical interactions of N$_2$(A) with complete state specificity. The LIF detection system turned out to give a wealth of high-resolution spectroscopic information, in particular the hyperfine splittings of both the N$_2$(A$^3\Sigma_u^+$) and N$_2$(B$^3\Pi_g$) states. Preliminary results have been communicated [35]. For the A state our measurements extend to much higher rotational levels ($J \leq 12$) than the Rabi-type experiment of [33]. Also, data are obtained in a more direct way, free from the complications by the magnetic field employed in that work. Consequently, more accurate A-state hfs coupling constants are derived in this work. This is an improvement over our first brief communication [35] where we used the original A-state coupling constants from [34] to explain our data. For the N$_2$(B) state the hyperfine splitting had not previously been measured. It shows very interesting, unusual features which were briefly discussed in [35] using an approximative theoretical treatment. In the present work we give, after a full description of the experiment, an improved theoretical analysis and more accurate B-state hyperfine coupling constants. These are also briefly discussed in terms of the electronic structure and compared with ab initio values where available.

The method employed here, sub-Doppler LIF spectroscopy using perpendicularly crossed laser and molecular beams, has been applied to hfs measurements on molecules a number of times (e.g. NO$_2$ [36], I$_2$ [37], Na$_2$ [38], OH [39], NH [40]). However, often only a few or even only one rotational level were investigated, and, to our knowledge, the gradual development of hyperfine structure line splittings with increasing molecular rotation has never been demonstrated systematically through a wide range of $J$ values. We present here complete arrays of hyperfine line profiles for all 27 branches of the N$_2$(B$-$A) system and for virtually all rotational levels up to $J = 12$, a total of 291 rotational lines. We have found these very characteristic splitting patterns extremely useful as aids in the identification of lines of different bands, especially at high vibrational quantum numbers, where the molecular constants given in the literature become unreliable. Therefore we believe that a comprehensive graphical presentation as given below will be valuable for other workers. Also, in many cases it is possible to read qualitatively the characteristic trends of the A and B state level splittings directly from the line splitting patterns, as will be shown below. This we found very informative for a general overview.

All measurements reported here were made on the (10, 6) band of the N$_2$(B$-$A) transition so that the hfs coupling constants given refer specifically to the states N$_2$(A, $v'' = 6$) and N$_2$(B, $v' = 10$). Recently we have extended these measurements to other vibrational levels, ranging from $v' = 5$ to 17 and from $v'' = 1$ to 15. The coupling constants depend only slightly on the molecular vibration, and the line profiles resemble closely those given below for the (10, 6) band. After completion of the analysis the $v$-dependent coupling constants will be published separately.

**Experimental**

A preliminary description of the apparatus used has been given [41]. The vacuum system consists of three separately pumped chambers, I$-$III (Fig. 1). I is a large chamber (50 cm dia.) in which an intense N$_2$ nozzle beam is generated. The effective pumping speed is 6,000 l/s, using a nominally 12,000 l/s oil diffusion pump plus a water-cooled baffle. It is backed by a 500 m$^3$/h Roots and a 180 m$^3$/h rotary pump. With the maximum gas throughput of 5 Torr l/s the pressure in chamber I is 8$\times$10$^{-4}$ Torr, although typically 1.5 Torr l/s were used. Immediately in front of the nozzle a DC discharge burns in the beam itself, exciting a large fraction of molecules into the N$_2$(A) state. The beam then enters the intermediate chamber II, of length 10 cm, which is differentially pumped by a 1,700 l/s oil diffusion pump. This chamber houses electrodes which remove ions from the beam. Also, an efficient low-energy electron gun [42] can be installed here as an alternative to the discharge. III is the main experimental chamber, a large (60 cm $\times$ 70 cm, 80 cm long) aluminium box allowing...