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First measurement of hyperfine structure in N_2^+

S. D. Rosner, T. D. Gaily, and R. A. Holt
The University of Western Ontario, London, Ontario N6A 3K7, Canada

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The hyperfine structure (hfs) of N_2^+ has been resolved for the first time, using Doppler-tuned laser fluorescence spectroscopy. Observations in the region of the (0,1) bandhead of the $B\,^2\Sigma_u^+$-$X\,^2\Sigma_g^+$ first negative system give hfs constants in reasonable agreement with calculations based on the wave functions of Cade *et al.* Preliminary values obtained for the spin-rotation constants are also presented.

INTRODUCTION

The spectrum of N_2^+ has been studied for nearly a century. Its importance for the understanding of auroras, airglows, comet tails, and laboratory discharges and afterglows has long been recognized, but the resolution attained until now has been modest.[1] In the past few years, the $B\,^2\Sigma_u^+$-$X\,^2\Sigma_g^+$ first negative system has been carefully reexamined by several groups[2–6]; one of the results has been the recognition that the published spin-rotation (sr) constants of the B and X states may well be incorrect because of the influence of unresolved hyperfine structure (hfs).[5] Because of the importance of the sr constants as a test of deperturbation methods,[6] and because of the interest in the hfs of molecular ions intrinsically and as a test of molecular wave function calculations, we have undertaken a very-high-resolution study of the first negative system of N_2^+ using Doppler-tuned laser spectroscopy. We report here the observation of *fully resolved* hfs, even at the bandhead, and we list preliminary values for the hfs and sr coupling constants.

THEORY

The theory of the interaction between the electronic spin magnetic moment and the magnetic field due to molecular rotation, first worked out by van Vleck,[7] has been discussed in detail for the case of the B and X states of N_2^+ by Gottscho *et al.*[6] The spin-rotation Hamiltonian is given by $H_{\mathrm{sr}} = \gamma \vec{N} \cdot \vec{S}$, where $\vec{N}$ is the angular momentum of the nuclear rotation, and $\vec{S}$ is the total electronic spin. The coupling constant can be separated into a true sr part, which is generally very small for $^2\Sigma$ states, and a part arising from second-order spin-orbit and rotation-electronic effects. The results of the calculation by Gottscho *et al.* are listed in Table I.

The hfs in a diatomic molecule with nonzero $\vec{S}$ arises predominantly from the magnetic interaction between $\vec{S}$ and the nuclear spins.[8,9] For a Σ state in a homonuclear molecule with one unpaired electron and with total nuclear spin $\vec{I}_T$, the Hamiltonian may be written in spherical tensor form as[10,11]

$$H_{\mathrm{hfs}} = b_F T^{(1)}(\vec{I}_T) \cdot T^{(1)}(\vec{S}) - (10)^{1/2} T^{(1)}(\vec{I}_T) \cdot T^{(1)}(\vec{S}, C^2(\omega)) .$$

The first term is the Fermi-contact interaction, with coupling constant

$$b_F = (8\pi/3) g_e g_n \mu_e \mu_n \langle \delta(\vec{r}) \rangle_\Phi ,$$

where Φ is the electronic wave function of the molecule. The second term represents the dipolar interaction between the electronic and nuclear magnetic moments. The quantity $C^2(\omega)$ is $(4\pi/5)^{1/2}$ times the second rank spherical harmonic tensor whose argument ω gives the angular orientation of the position vector $\vec{r}$ of the unpaired electron relative to one of the nuclei in the coordinate system with the polar axis along the space-fixed z axis. The matrix elements of the dipolar term can be expressed in terms of a reduced matrix element

$$t \equiv g_e g_n \mu_e \mu_n \langle C_0^2(\omega') r^{-3} \rangle_\Phi ,$$

in which ω' is the orientation of $\vec{r}$ with respect to molecule-fixed axes.

Cade, Sales, and Wahl have computed Hartree-Fock-Roothaan (HFR) wave functions, expressed as

TABLE I. Comparison of calculated and measured values of the spin-rotation constants (in units of 10^{-3} cm^{-1}) for the X and B states of N_2^+.

	Theory		Experiment		
	Ref. 6	Ref. 2	Ref. 6	Ref. 5	Present
$\gamma' - \gamma''$		14.6	14.6	14.3	14.8(2)
$\gamma''(v''=1)$	< 12	8.3	9(5)	10[a]	0.2(9)
$\gamma'(v'=0)$	26.3	22.9	24(5)	24	15(1)

[a] This value is for $v''=0$.

TABLE II. Comparison of calculated and measured values of the magnetic hfs constants (in MHz) of the X and B states of N_2^+.

	Theory	Experiment
b_F''	91	39(6)
t''	27	16(6)
b_F'	735	630(9)
t'	7	−21(6)

linear combinations of symmetrized Slater-type orbitals (STO's), for the N_2^+ B and X states.[12] Using these we have calculated the hfs parameters b_F and t, given in Table II. The Fermi-contact constants b_F' and b_F'' are a sensitive measure of the amount of atomic s-orbital contribution to the molecular orbital of the unpaired electron. In the B state this electron is in a σ_u orbital (in the principal configuration) with a large contribution from $\sigma_u 2s$ STO's, whereas in the X state, the electron is in a σ_g orbital whose largest contribution is from $\sigma_g 2p$ STO's.

Calculation of molecular energy levels requires that $\mathcal{H}_{sr}$ and $\mathcal{H}_{hfs}$ be considered together. In the $|NSJIF\rangle$ basis appropriate to Hund's case $b_{\beta J}$,[8] $\mathcal{H}_{sr}$ is diagonal and has matrix elements which increase linearly with N; $\mathcal{H}_{hfs}$ has off-diagonal elements connecting states with $\Delta J = \pm 1$ and $\Delta F = 0$, and *all* its matrix elements become independent of N as $N \rightarrow \infty$. Thus if γ is not large compared to b_F, the $b_{\beta J}$ coupling scheme breaks down for sufficiently small N. For large N, where the scheme is valid, the sr interaction creates $J = N \pm \frac{1}{2}$ spin doublets, and the hfs interaction splits each member into three or six hyperfine components according to whether $I_T = 1$ (N'' odd, N' even) or $I_T = 0, 2$ (N'' even, N' odd). This is the correct picture in the B state for the N' values studied here. In the X state, $\gamma'' \sim b_F''$, and the pattern of levels is irregular; however, the absolute size of the X-state splitting is very small. Furthermore, for pure $b_{\beta J}$ coupling, any B-X transitions which violate $\Delta F = \Delta J = \Delta N$ should be of relative intensity $(2J)^{-2}$ or lower, and thus negligible for the values of N observed here. The optical spectra should therefore have approximately the same doublet structure as the B-state energy levels.

EXPERIMENT

Doppler-tuned laser spectroscopy on an ion beam using fluorescence or collisional detection has been described numerous times.[11,13] Ions were produced in a low-voltage arc source operating with ≈ 50 μm of pure N_2. They were accelerated to 5 kV, focused, and mass filtered to form a beam of N_2^+, which was then deflected electrostatically into collinearity with a laser beam. The typical ion beam current downstream was 600 nA, of which only a small fraction was in the $v'' = 1$ level. Doppler tuning the ions into optical resonance with the laser beam was accomplished in a postacceleration region containing mesh windows to allow the detection of the laser-induced fluorescence by a cooled photomultiplier. To reduce background light arising from collisions of the ions with residual gas, and to block scattered laser light, the photomultiplier was equipped with an interference filter chosen to pass the dominant (0,0) band fluorescence in the neighborhood of 391 nm.

The laser beam at 428 nm was produced by a stabilized cw ring dye laser (Coherent 699-21) using Stilbene 3, and expanded to a $1/e^2$ diameter of ≈ 5 mm. With a laser power of 100 mW, a photomultiplier signal of typically 30 nA was observed, in addition to a background (due to residual gas collisions) of about the same size. As a result of ion-optical effects, the background signal varies in a reproducible way with postacceleration voltage; in the future this effect will be eliminated by up-down counting with a chopped laser beam.

The spectra were obtained by incrementing the postacceleration voltage while recording the digitized photocurrent with a multichannel analyzer. Typical results are shown in Figs. 1 and 2. The $P(10)$ and $P(13)$ lines (Fig. 1) have the predicted structure, except that each member of the $P(10)$ doublet is split into five rather than six components. For reasonable values of the coupling constants, the two components arising from the states with $F = J$ and $I = 0$ or 2 are almost completely overlapped within our

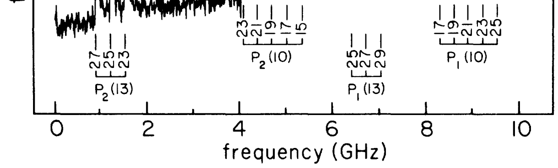

FIG. 1. Fluorescence vs Doppler-shifted laser frequency (with arbitrary origin) for a part of the (0,1) band of the $B\,^2\Sigma_u^+$-$X\,^2\Sigma_g^+$ system of N_2^+. Hyperfine components are labeled by $2F''$. Total data accumulation time was 17 min.

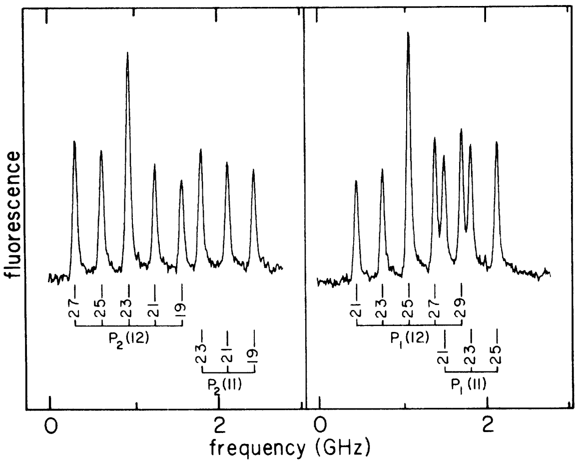

FIG. 2. Fluorescence spectra as in Fig. 1 showing the region at the (0,1) bandhead. Accumulation time was 8.5 min.

resolution. Figure 2 shows the interleaved $P(11)$ and $P(12)$ lines that form the (0,1) bandhead.

The shape of each signal peak reflects the velocity distribution of the ion beam as discussed in previous experiments.[13] We have used least-squares fitting with an asymmetrical Gaussian function to establish the "line center" for each peak; as long as the shape of each line is the same, the peak separations obtained in this manner are independent of the details of the line shape. In order to convert a postacceleration voltage interval ΔE into a frequency interval $\Delta\nu$ using the Doppler formula, we require only an approximate knowledge of the absolute ion beam energy E, because to first order, $\Delta\nu \propto \Delta E/E^{1/2}$. The uncertainty in E, arising from unknown potential distributions in the ion source, contact potentials, charged surfaces, etc., is certaintly well below the 1% level (~ 50 V), thus contributing an error of less than 0.5% to $\Delta\nu$.

The frequency intervals were then used as input data for a least-squares fit to obtain sr and hfs coupling constants. Because $P_1(N'')$-$P_2(N'')$ intervals were measured only in the data of Fig. 1, those data were used to fit all six sr and hfs parameters. The γ' and γ'' constants so obtained were then fixed, and the remaining data (from four other spectra) were used to obtain a second set of values for the four hfs constants, which were entirely consistent with the first set. The results are listed in Tables I and II. The error estimates reflect the statistical uncertainties of the fit and the uncertainty in E. The hfs constants in Table II agree with the theoretical estimates as well as might be expected, considering that other spectroscopic constants predicted from the HFR wave functions are in error by as much as 65%, More data may require the inclusion of the electric quadrupole interaction in the model since it might be of comparable size to the magnetic dipolar interaction.

In general, the difference γ'-γ'' can be determined more accurately than either γ' or γ'' (Ref. 14); Table I shows substantial agreement among all the experimental values of this quantity. We have chosen to quote the results of Coe *et al.*[5] obtained by the method of combination differences because they are less affected by hfs perturbations. The values of γ' and γ'', which they derived from the P- and R-branch doublet splittings *separately*, were inconsistent, and they correctly attributed this to unresolved hfs. Our experimental sr constant γ' disagrees with the theory of Gottscho *et al.*[6]; an attempt to explain this would be premature.

From the fitted values of the constants, it is possible to predict the positions of the satellite lines. Within the limitations of noise and resolution, we see no evidence for such lines, verifying the self-consistency of the analysis. They should appear in spectra of very low N.

CONCLUSIONS

The present experiment has attained a linewidth of 60 MHz, an improvement over previous measurements of nearly an order of magnitude. This has allowed complete resolution of the hfs, and measurement of the differences of the B- and X-state sr and Fermi-contact hfs constants to about 1%. After the background subtraction procedure mentioned above is implemented, we plan to make a systematic study of both the P and R branches, especially the lines of lower N. This should provide a definitive test of the model used, and establish values of the sr and hfs constants with an accuracy of a few MHz. A more elaborate experiment in which the *absolute* wavelengths are measured by a recently introduced technique[13] is also planned. Finally, we expect to be able to measure the X-state constants to kilohertz precision by the laser-fluorescence molecular-beam magnetic resonance method.[15]

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