THE

PHYSICAL REVIEW

A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. 178, NO. 1 5 FEBRUARY 1969

Microwave Magnetic-Dipole Transitions between Excited Electronic States of CN

K. M. Evenson
National Bureau of Standards, Boulder, Colorado 80302
(Received 3 September 1968)

Eleven microwave transitions in the frequency range from 10.5 to 11.5 GHz have been observed between excited electronic states of CN. These correspond to 11 of 13 allowed magnetic-dipole transitions, $\Delta F=0, \pm 1$, in the $K'=4$ perturbation complex between the three hyperfine levels of the perturbed component of the Λ doublet of the $A^2\Pi_{3/2}{}^+$ $(v=10)$ level and the three hyperfine levels in each of the perturbed and the unperturbed components of the spin doublet of the $B^2\Sigma^+(v=0)$ level. These transitions and the previously measured 13 electric-dipole transitions determine all 12 hyperfine energy levels of this perturbation complex. The experiment is the first microwave measurement of magnetic-dipole transitions between excited electronic states of a molecule. CN was produced predominately in the metastable $A^2\Pi$ state by a chemical reaction when methylene chloride was added to a nitrogen afterglow. Resonant microwave pumping from the Π state increased the population of the three hyperfine levels of each Σ state. The population change was detected by measuring an increase in the intensity of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ (0, 0) violet band of CN near 3875 Å.

INTRODUCTION

Rotational perturbations are observed in the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ violet bands in CN, originating in the $v=0$ level of the $B^2\Sigma^+$ state. Anomalies in the rotational lines were first observed by Herzberg[1] from a flame produced by the chemical reaction between active nitrogen and an organic vapor. Beutler and Fred[2] found the perturbed lines to consist of doublets and proposed that the anomalies in the observed spectra were caused by rotational perturbations between the $v=10$ level of the $A^2\Pi$ state and the $v=0$ level of the $B^2\Sigma$ state. Wager[3,4] obtained measurements of the perturbed line displacements and relative populations. Broida and Golden[5] investigated the pressure dependence of the relative line intensities, and Kiess and Broida[6] obtained precise wavelength measurements of the perturbed lines. Recently, Radford and Broida[7] have discussed the theory of rotational perturbations in diatomic molecules and applied the theory to experimental observations of the Zeeman effect. In addition, they have developed a chemical kinetic theory for the active nitrogen flame[8] to explain the rotational intensity anomalies in the observed spectra.

For a given rotational level, the perturbation is caused by the interaction of one component of the spin doublet of the $B^2\Sigma^+$ state and one component of the Λ doublet of the $A^2\Pi$ state. Thus, for each perturbation, there is a set of four closely spaced levels (each of which is split into three hyperfine components) separated by microwave frequencies: an unperturbed level of the $B^2\Sigma^+$ state, $\Sigma(u)$; a perturbed level which is predominately of Σ character, $\Sigma(p)$; an unperturbed Π level, $\Pi(u)$; and a perturbed level predominately of Π character, $\Pi(p)$. At low pressures, CN is produced predominately in the $A^2\Pi$ state[5,6,8,9] resulting in steady-state population ratios as high as 100 to 1 between these closely spaced levels. Thirteen microwave electric-dipole transitions from the highly populated unperturbed Π levels to the neighboring spin-doublet levels of the Σ state[10,11] and six of the seven allowed electric-dipole transitions between the perturbed and unperturbed Π states[12] have been detected by measuring an increase in the intensity of the corresponding line in the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ violet-band spectrum. An analysis of the hyperfine structure of the $B^2\Sigma^+$ state has been made by Radford[13] in terms of the electronic structure of the $B^2\Sigma$ state of CN. The detection of population increases in rotational levels near the perturbed levels also has provided a means of measuring collisional repopulation rates in these molecular states.[14]

A Zeeman experiment was attempted to gain a knowledge of the Zeeman effect upon such a molecule and also to test the sensitivity of this double resonance technique. The Zeeman pattern was easily observed, but the $2J+1$ lines from each level produced an extremely complicated spectrum. Also, at higher microwave frequencies, other lines appeared. A scan at zero magnetic field yielded several lines of the forbidden $\Pi(p) \to \Sigma(p, u)$ transition. The present paper is a report of precision measurements of these lines and their identification.

EXPERIMENTAL TECHNIQUES

As in earlier experiments,[10,11,12] excited CN molecules were produced from a chemical reaction of active nitrogen and methylene chloride (CH_2Cl_2). The first measurements were performed on the identical apparatus used to detect the 13 electric-dipole transitions, excepting that a higher-order mode of the X-band cavity was used owing to the higher frequencies needed. For final measurements a rectangular cavity operating in the $TE_{1,0,8}$ mode was used; this cavity could be operated in the same mode for the electric-dipole transitions and for the newly found transitions. The cavity was constructed from a 12.5 cm section of X-band waveguide with mica vacuum windows on each end, and with an iris diaphragm and adjustable coupling screw outside the window on one end, and an adjustable short outside the other window. On the broad side of the cavity a 5-mm-wide slot, 6.5 cm long, was cut; a 5-mm-tall "chimney" was soldered on top, and a glass window was attached on top of the chimney with hard wax. This long optical window was used so that the CN optical emission could be observed at various locations along the axis of the cavity. In this way, the electric-dipole transitions could be distinguished from the magnetic-dipole transitions. The frequency and power measuring techniques were identical with those of the previous X-band experiments.

ANALYSIS OF THE SPECTRUM

For the perturbation in the $K'=4$ level, each of the two Λ-doublet levels and the two spin-doublet levels are split into three hyperfine components by magnetic-dipole interaction of the N^{14} nucleus with the total magnetic moment μ_J. The hyperfine components are characterized by the total angular-momentum quantum number $\vec{F}=\vec{J}+\vec{I}$, where $I=1$ for N^{14}; F takes on the values $J+1$, J, $J-1$. From the selection rule for hyperfine structure transitions,[1] $\Delta F=0, \pm 1$, the $\Pi(p) \to \Sigma(p)$ transition is expected to have seven hyperfine components and the $\Pi(p) \to \Sigma(u)$ transition, six components. The $\Pi(p) \to \Sigma(p)$ and $\Pi(p) \to \Sigma(u)$ transitions are forbidden as electric-dipole transitions by the parity selection rule $+ \not\to +$ but are allowed magnetic-dipole transitions. Eleven of these thirteen predicted microwave lines have been observed, and measured frequencies and relative intensities of the lines are listed in Table I and illustrated in Figs. 1 and 2. The transitions were found to occur in the regions of maximum microwave-magnetic-field intensity (every $\lambda_g/2$ or approximately every 2 cm) by moving the photocell lengthways along the microwave cavity. Similarly, electric-dipole transitions were found to occur at regions of maximum electric field, sandwiched between the regions of maximum magnetic-field intensity. Measured relative intensities are good to about 50%; limitations in precision are due to difficulties encountered in holding the microwave-cavity coupling constant during scans over the entire spectrum. At approximately maximum coupling (indicated by no reflected power), the minimum power level at which breakdown was initiated in the gas in the cavity was nearly constant over the entire frequency scan, showing that the energy density was reasonably constant in the cavity over the entire spectrum. Observation of eleven of the thirteen lines plus the knowledge of the spectrum from the earlier measurements allowed an

TABLE I. Frequencies and relative intensities of the observed magnetic-dipole hyperfine transitions of the $K'=4$ rotational level of the $A^2\Pi_{3/2}$ and $B^2\Sigma$ electronic states of CN. Observed relative intensities are the average of 3 scans. $\Delta J=0$ and $\Delta J=+1$ are normalized separately for the calculated relative intensities.

Electronic Transition	Hyperfine Transition $F \to F'$	Frequency (MHz)	Observed Relative Intensity ±50%	Calculated Relative Intensity
$\Pi(p) \to \Sigma(p)$	7/2→9/2	10448[a]	···	4.5
$\Delta J=-1$	9/2→9/2	10462.6 ± 2	62	84
	5/2→7/2	10544 ± 5	12.5	4.5
	7/2→7/2	10558.0 ± 3	62	62
	9/2→7/2	10570.0 ± 5	4.2	4.5
	5/2→5/2	10935.0 ± 2	83	49
	7/2→5/2	10945[a]	···	4.5
$\Pi(p) \to \Sigma(u)$	5/2→7/2	11176.0 ± 1	104	78
$\Delta J=0$	7/2→7/2	11187.0 ± 4	12.5	5.6
	9/2→7/2	11201.0 ± 4	4.2	0.09
	7/2→9/2	11352.0 ± 2	100	100
	9/2→9/2	11365.3 ± 3	5.8	5.6
	9/2→11/2	11503.5 ± 1	83	127

[a]Not observed

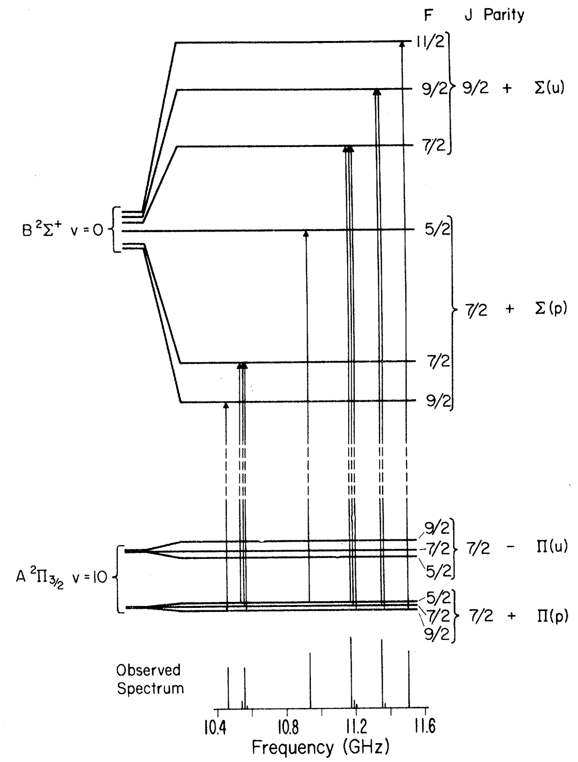

FIG. 1. Energy-level diagram of $B^2\Sigma^+$, $v = 0$, $K' = 4$ and $A^2\Pi_{3/2}$, $v = 10$ states. The observed microwave magnetic-dipole spectrum is shown.

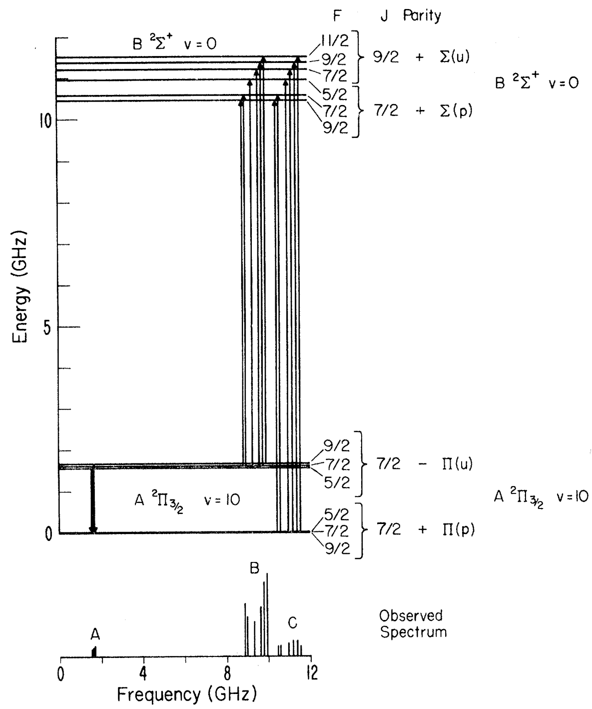

FIG. 2. Energy-level diagram summarizing the major transitions observed in the $K' = 4$ perturbation complex. Three different groups of transitions are illustrated: A, stimulated emission; B, electric-dipole transitions; and C, magnetic-dipole transitions.

unambiguous identification of each line with the particular transition given in the first two columns of Table 1.

Observed and calculated[15] relative intensities are given in the fourth and fifth columns of Table I. Calculated relative intensities have been normalized to agree with measured values at the $F = \frac{7}{2} \rightarrow \frac{7}{2}$ transition for the $\Pi(p) \rightarrow \Sigma(p)$ transitions and at the $F = \frac{7}{2} \rightarrow \frac{9}{2}$ for the $\Pi(p) \rightarrow \Sigma(u)$ series. Agreement between observed and calculated values is quite good on all six of the intense lines and two of the weaker lines, but four of the weaker lines had observed relative intensities that were twice the calculated ones, and one observed value was 50 times larger than the calculated value; similar discrepancies were found in the electric-dipole transitions.[11] These deviations of the weaker line intensities might be attributed to increased transition probabilities caused by the large hyperfine interaction between the nearly degenerate $\Sigma(u)$ and $\Sigma(p)$ levels. Because of this interaction characterized by matrix elements off-diagonal in J, the quantity J is not a good quantum number, and only F and m_F are good quantum numbers.

The electric-dipole lines were approximately 5 times stronger than the magnetic-dipole lines. Since the initial state for the electric-dipole transitions, $\Pi(u)$, is more populated than that for the magnetic-dipole transition, $\Pi(p)$,[7,12] then the electric-dipole transition probability is less than 5 times stronger than that of the magnetic dipole. Hence, the electric-dipole moment of the Π state is less than about 0.01 D.

The frequency differences found from these magnetic-dipole transitions are

$$\Pi(u)\ (F = \tfrac{5}{2}) \rightarrow \Pi(p)\ (F = \tfrac{5}{2}),\quad 1578\ \text{MHz};$$

$$\Pi(p)\ (F = \tfrac{5}{2}) \rightarrow \Pi(p)\ (F = \tfrac{7}{2}),\quad 12.5\ \text{MHz};$$

$$\Pi(p)\ (F = \tfrac{7}{2}) \rightarrow \Pi(p)\ (F = \tfrac{9}{2}),\quad 12.8\ \text{MHz}.$$

The measured spectrum agrees with the number of lines predicted and reveals the previously unknown hyperfine splitting in the $K' = 4$ level of the $A^2\Pi(u)$ state of CN.

The complete energy-level scheme of the $K' = 4$ complex was revealed by comparing the magnetic-dipole lines with the electric dipole lines of previous measurements. It was rather surprising that electric- and magnetic-dipole transitions were of nearly equal intensity.

ACKNOWLEDGMENTS

The author wants to thank Dr. H. E. Radford and Dr. H. P. Broida for their assistance in the interpretation of the spectra and for many helpful and stimulating discussions. He also wishes to thank Dr. Arthur L. Schmeltekopf and Dr. Fred C. Fehsenfeldt for their assistance in measuring the Zeeman spectrum of CN.

[1]G. Herzberg, Z. Physik 49, 512 (1928).
[2]H. Beutler and M. Fred, Phys. Rev. 61, 107 (1942).
[3]A. T. Wager, Phys. Rev. 61, 107 (1942).
[4]A. T. Wager, Phys. Rev. 64, 18 (1943).
[5]H. P. Broida and S. Golden, Can. J. Chem. 38, 1666 (1960).
[6]N. H. Kiess and H. P. Broida, J. Mol. Spec. 7, 194 (1961).
[7]H. E. Radford and H. P. Broida, Phys. Rev. 128, 231 (1962).
[8]H. E. Radford and H. P. Broida, J. Chem. Phys. 38, 644 (1963).
[9]T. Iwai, M. I. Savadatti, and H. P. Broida, J. Chem. Phys. 47, 3861 (1967).
[10]R. L. Barger, H. P. Broida, A. J. Estin, and H. E. Radford, Phys. Rev. Letters 9, 345 (1962).
[11]K. M. Evenson, J. L. Dunn, and H. P. Broida, Phys. Rev. 136, A1566 (1964).
[12]K. M. Evenson, App. Phys. Letters 12, 253 (1968).
[13]H. E. Radford, Phys. Rev. 136, A15 (1964).
[14]K. M. Evenson and H. P. Broida, J. Chem. Phys. 44, 1637 (1966).
[15]C. H. Townes and A. L. Schawlow, Microwave Spectroscopy (McGraw-Hill Book Co., Inc., New York, 1955).

PHYSICAL REVIEW VOLUME 178, NUMBER 1 5 FEBRUARY 1969

Proton Excitation of the Argon Atom*

G. S. Hurst and T. E. Bortner
Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40506
and
T. D. Strickler
Department of Physics, Berea College, Berea, Kentucky
(Received 1 August 1968)

Studies of the excitation of argon with 4-MeV protons have been carried out by making use of a vacuum ultraviolet scanning monochromator and a 6-MeV Van de Graaff accelerator. Protons were directed through the gas and then into a Faraday cup in an arrangement in which the relative intensity of emitted light could be studied over a wide range of gas pressure (1 to 1500 Torr). Four continua near 2100, 1900, 1300, and 1100 Å, respectively, as well as escape radiation originating from the 1048 Å resonance line, were studied as a function of pressure.

Studies of the intensity of the four main continua (per unit of proton power dissipation) as a function of pressure led us to the conclusion that each continuum has a separate atomic precursor. We suggest that the 1300 Å continuum and the 1100 Å continuum are dissociative diatomic continua and originate from the $^1P_1$ (11.83-eV) and the $^3P_1$ (11.62-eV) resonance atomic states, respectively. We tentatively suggest that the continua near 2100 Å and near 1900 Å are recombination spectra involving the formation of argon excimers with binding energies of about 4 eV.

The 1300 and 1100 Å continua have been observed in gas discharges, but these were interpreted as a single continuum originating from the $^3P_1$ state. We believe that the present experimental method, which makes possible gas kinetic observations at spectroscopically defined photon energies, is indeed a powerful tool for the study of atomic and molecular structure and processes.

INTRODUCTION

Continuous emission was observed in helium discharges by Hopfield[1] and reported in 1930. This remarkable work in which a differentially pumped gas-discharge source, vacuum ultraviolet spectrograph, and photographic plates were used to study continuous emission and continuous absorption, has played a classic role in the development of the field of vacuum ultraviolet spectroscopy. Subsequently, continuous emission has been observed in nearly all of the rare gases, and this information has been used to develop continuous light sources for the vacuum ultraviolet region.[2] Reference 2 contains an excellent bibliography of the basic papers as well as a discussion of some of the practical aspects of gas-discharge sources.

In the case of argon a continuum is observed to lie between 1100 and 1600 Å, which we refer to as the 1300 Å continuum. This continuum has been reported by Tanaka[3] using repetitive condensed discharges and quite recently by Wilkinson[4] using microwave excitation. Wilkinson's paper is the first effort to comment in detail on the mechanism