Optical Detection of Microwave Transitions Between Excited Electronic States of CN and the Identification of the Transitions Involved

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Thirteen microwave transitions in the frequency range from 8800 to 9900 MHz have been observed between excited electronic states of CN. These correspond to all allowed transitions, $\Delta F=0, \pm 1$, in the $K'=4$ perturbation complex between the three hyperfine levels of the unperturbed 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. The identification of all allowed transitions permits a unique determination of nine of the 12 hyperfine energy levels of this perturbation complex. The measured energy separation in this level of the $^2\Sigma$ state is interpreted in terms of the electronic structure of the CN molecule in the following paper. The experiment is the first microwave measurement of the fine and hyperfine structure of an excited electronic state of a molecule and also is the first accurate measurement of the hyperfine structure of a $^2\Sigma$ state. CN was produced predominantly 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 by 0.1 to 5%. 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. A rigid-sphere collision diameter of 4.4 Å was calculated from linewidth measurements of the microwave $\Pi \rightarrow \Sigma$ transition. Collisional population of rotational levels adjacent to $K'=4$ also was observed.

INTRODUCTION

BAND spectra of diatomic molecules show deviations in their rotational structure caused by mutual perturbations of nearly degenerate rotational energy levels of different electronic states. Perturbations occur when Kronig's selection rules[1] are satisfied, the perturbed levels suffering a mutual repulsion, inversely proportional to their unperturbed separation. In addition, each of the two states assumes properties of the other by the mixed character of its eigenfunctions. Thus, the observed spectra of the perturbed lines exhibit three characteristic differences from usual spectra: (1) abnormal intensities, (2) extra lines, and (3) wavelength deviations of the lines from their expected positions.

Some very good examples of rotational perturbations have been 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[2] from a flame produced by the chemical reaction between active nitrogen and an organic vapor. Beutler and Fred[3] 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[4,5] obtained measurements of the perturbed line displacements and relative populations. Broida and Golden[6] investigated the pressure dependence of the relative line intensities and Kiess and Broida[7] obtained precise wavelength measurements of the perturbed lines. Recently, Radford, and Broida[8] 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[9] 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-type 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 predominantly of Σ character, $\Sigma(p)$; an unperturbed Π level, $\Pi(u)$; and a perturbed level predominantly of Π character, $\Pi(p)$ (see Fig. 3). At low pressures, CN is produced predominantly in $A\ ^2\Pi$ state[6,7,9] resulting in steady-state population ratios as high as 10 or 20 to one between these closely spaced levels. Microwave transitions from the highly-populated unperturbed Π level to the neighboring spin doublet levels of the Σ state may be detected by measuring an increase in the intensity of the corresponding line in the $B\ ^2\Sigma^+ \rightarrow X\ ^2\Sigma^+$ violet band spectrum. Rotational levels near the perturbed level in which the microwave transitions are occurring exhibit population increases due to collisions with the other molecules. The detection of these increases provides a

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[1] Kronig's Selection Rules: [G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Princeton, New Jersey, 1950), p. 285]. (1) Both states have the same total angular momentum J. (2) Both states have the same multiplicity $2S+1$. (3) The Λ value may differ by only 0 or ± 1. (4) Both states must have the same parity. (5) For identical nuclei both states must have the same symmetry in their nuclei.

[2] G. Herzberg, Z. Physik **49**, 512 (1928).

[3] H. Beutler and M. Fred, Phys. Rev. **61**, 107 (1942).

[4] A. T. Wager, Phys. Rev. **61**, 107 (1942).

[5] A. T. Wager, Phys. Rev. **64**, 18 (1943).

[6] H. P. Broida and S. Golden, Can. J. Chem. **38**, 1666 (1960).

[7] N. H. Kiess and H. P. Broida, J. Mol. Spectry. **7**, 194 (1961).

[8] H. E. Radford and H. P. Broida, Phys. Rev. **128**, 231 (1962).

[9] H. E. Radford and H. P. Broida, J. Chem. Phys. **38**, 644 (1963).

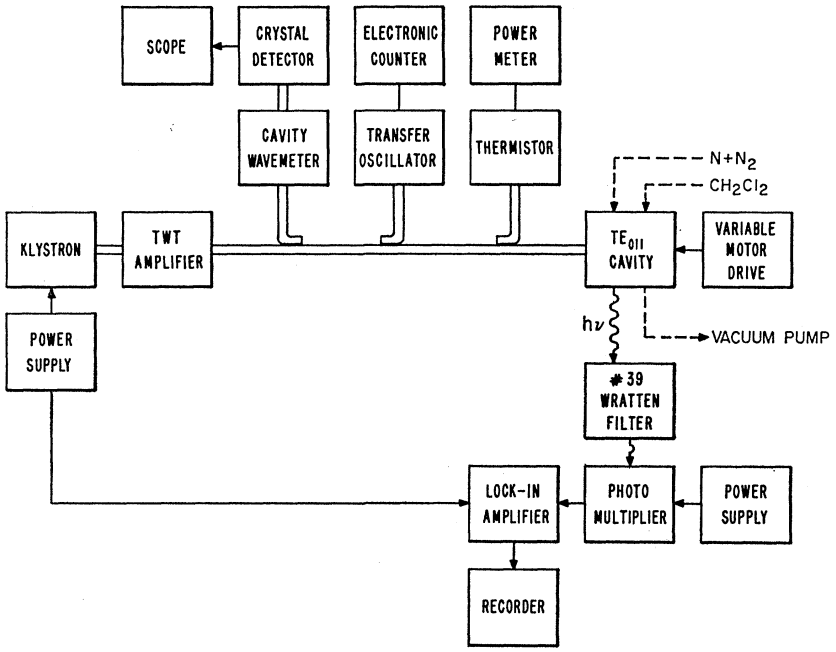

FIG. 1. Block diagram of instrumental arrangement.

method of studying the properties of excited molecular states which display rotational perturbations, provided steady-state population differences and microwave transition probabilities are favorable.

Preliminary measurements[10] have shown that the suggested microwave-optical technique is indeed applicable in the case of the $K'=4$ rotational lines[11] in the $v=0$, $B\,^2\Sigma^+$ state of CN. Increases in the optical line intensity corresponding to three microwave transitions were detected.

The present paper is an extension of the study of the $K'=4$ rotational perturbation. Thirteen microwave transitions were observed and identified in the experiments to be described. The measured energy separation in this level of the $^2\Sigma$ state is interpreted in terms of the electronic structure of the CN molecule in the following paper.[12] The collision diameter for molecular nitrogen was calculated from the slope of the linewidth-versus-pressure curve. The resulting agreement between experiment and theory points out the feasibility of extending this technique to other rotational perturbations in CN and in other species.

EXPERIMENTAL TECHNIQUES

Excited CN was produced from a chemical reaction of active nitrogen and methylene chloride (CH_2Cl_2).[7] The reaction vessel used in the measurements was a silver-plated circular cylindrical X-band cavity with a volume of about 50 cm^3 and with 6-mm-i.d. ports. The cavity was internally coated with Fluoroglide,[13] which was found effective in increasing the nitrogen afterglow intensity. The cavity had a loaded Q of about 12×10^3 and covered the frequency range from 8750 to 10 375 MHz. The adjustment of a small screw transversing the coupling hole to the cavity made possible maximum coupling of the waveguide to the cavity over the entire frequency range of the cavity. Frequency scans at rates from 3 to 30 MHz/min were made by changing the position of one end plate of the cavity by rotating a micrometer screw, coupled to the end plate, with a synchronous motor and speed reducer.

The klystron frequency was maintained at the cavity frequency by manual adjustment of the klystron's mechanical and electronic tuning. Identical reaction cavity and klystron frequencies were indicated on the oscilloscope by a minimum in the reflected microwave signal from the reaction cavity. Active nitrogen was produced in a 2450 MHz discharge cavity (with about 80 W) located on a 10-mm-i.d. quartz tube and placed about 4 cm from the nitrogen inlet port of the reaction cavity. Methylene chloride vapor entered through another port and mixed with the active nitrogen in the cavity. A quartz window was waxed on a third port for observation of the CN emission. The cavity was pumped by a mechanical pump connected to a fourth port. Pressure was measured with a diaphragm-type differential pressure meter connected to a fifth port. Since the CN intensity was found to be dependent upon gas purity, the system was checked for leaks with a helium leak detector.

Although various organic compounds react with active nitrogen to produce the CN flame, the addition

[10] R. L. Barger, H. P. Broida, A. J. Estin, and H. E. Radford, Phys. Rev. Letters **9**, 345 (1962).

[11] Many workers use N to denote the component of angular momentum here denoted by K. See Ref. 15, Sec. 7-2.

[12] H. E. Radford, following paper, Phys. Rev. **136**, A1571 (1964).

[13] "Teflon-like" spray is manufactured by Chemplast Inc., East Newark, N. J.

of 0.1% to 1% methylene chloride has been found to give the greatest CN emission intensity.[7] The stability of this flame and the high intensity of CN emission played an important part in observing the weaker microwave transitions. Fluctuations in the power level of the microwave discharge source were minimized by using rigid mechanical connections in the discharge system. These fluctuations produced a large increase in the noise level at the output. In the pressure range from 0.4- to 1.4-mm Hg total pressure, the flame filled the cavities and appeared equally intense throughout the volume. At pressures below 0.4-mm Hg, the flame intensity was quite weak; however, signals were observable down to pressures as low as 0.09-mm Hg. Raising the pressure above 1.4-mm Hg produced a sharp increase in the emission intensity, corresponding to the diffuse flame changing to an intense localized flame near the input ports. This condition caused a decreased signal-to-noise ratio which limited the maximum pressure at which the signal was observable to about 8-mm Hg.

The experimental arrangement is shown in the block diagram in Fig. 1. It consisted of an X-band reflex klystron whose 1000-Hz square-wave pulsed output was amplified by a medium power traveling-wave tube amplifier. The pulsed signal was then coupled to the circular cylindrical cavity operated in the TE_{011} mode. Frequency and power measurements were made by sampling the input signal to the cavity.

The 1000-cps reference signal for the lock-in amplifier was obtained from the modulation output of the klystron power supply. A violet filter (with 90% peak transmission at 3700 and 1000 Å full width at half-maximum) was used to isolate the $B\,^2\Sigma \rightarrow X\,^2\Sigma$ violet bands of CN. This filtered light was detected with a photomultiplier tube. A monochrometer was used to check the population increases in the individual rotational levels. Changes in the intensity of the optical emission at resonances appeared as a 1000-cps amplitude modulated signal at the output of the photomultiplier. The modulated signal was applied to the signal channel of the lock-in amplifier and the output of the lock-in amplifier, with either an 0.3- or 1.0-sec time constant, was displayed on a recorder.

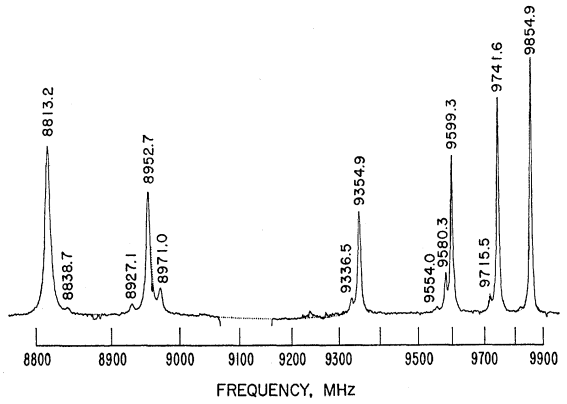

FIG. 2. Recording of microwave spectrum of CN at a pressure of 0.5-mm Hg with 0.3-W microwave power. Corrections for drift in the microwave power and frequency are shown by dotted lines. Deviations from dotted line are due to variations in the klystron's power level and frequency caused by manual readjustment of the various instrumental parameters during the frequency scan. The microwave power was accidentally allowed to nearly double at about 9830 causing the signal-like blip at that frequency.

TABLE I. Frequencies and relative intensities of the observed hyperfine transitions of the $K'=4$ rotational level of the $A\,^2\Pi_{3/2}$ and $B\,^2\Sigma$ electronic state of CN. Observed relative intensities are the average of 7 scans. $\Delta J=0$ and $\Delta J=+1$ are normalized separately for the calculated relative intensities.

Electronic transition	Hyperfine transition ΔF	Frequency MHz	Observed relative intensity ±30%	Calculated relative intensity
$\Pi(u) \rightarrow \Sigma(p)$, $\Delta J=0$	$\frac{9}{2} \rightarrow \frac{9}{2}$	8813.2±0.2	60	60
	$\frac{7}{2} \rightarrow \frac{9}{2}$	8838.7±1.0	1.7	3.2
	$\frac{9}{2} \rightarrow \frac{7}{2}$	8927.1±0.4	3.2	3.2
	$\frac{7}{2} \rightarrow \frac{7}{2}$	8952.7±0.2	48	44
	$\frac{5}{2} \rightarrow \frac{7}{2}$	8971.0±0.4	7	3.2
	$\frac{7}{2} \rightarrow \frac{5}{2}$	9336.5±0.3	6	3.2
	$\frac{5}{2} \rightarrow \frac{5}{2}$	9354.9±0.2	43	35
$\Pi(u) \rightarrow \Sigma(u)$, $\Delta J=+1$	$\frac{9}{2} \rightarrow \frac{7}{2}$	9554.0±0.7	2.5	0.07
	$\frac{7}{2} \rightarrow \frac{7}{2}$	9580.3±0.5	12	4.4
	$\frac{5}{2} \rightarrow \frac{7}{2}$	9599.3±0.2	62	62
	$\frac{9}{2} \rightarrow \frac{9}{2}$	9715.5±0.2	5	4.4
	$\frac{7}{2} \rightarrow \frac{9}{2}$	9741.6±0.2	85	79
	$\frac{9}{2} \rightarrow \frac{11}{2}$	9854.9±0.2	100	100

The microwave frequency measurements, made with a transfer oscillator and electronic counter, could be made with a precision of 1 part in 10^6. Uncertainties in determining the center and half-intensity points of the resonance lines reduced the accuracy by one order of magnitude, i.e., to about 1 part in 10^5. The microwave power level, measured with a thermistor and power meter was maintained constant to about ±5% during the microwave frequency scans by manual adjustment of a variable attenuator located between the traveling-wave amplifier and the cavity. To facilitate easier adjustment of the microwave power level, another attenuator situated between the klystron and traveling-wave amplifier was set so that the traveling-wave amplifier was saturated at the center frequencies of the klystron's mode. This gave a nearly constant power output at different frequencies across the klystron's mode.

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 is split into three hyperfine components by magnetic dipole interaction of the N^{14} nucleus with the total magnetic moment m_J. The hyperfine components are characterized by the total angular-momentum quantum number $F=|J+I|$, where $I=1$ for N^{14}; F takes on the

values $J+1$, J, $J-1$. From the selection rule $\Delta F=0, \pm1$,[1] the $\Pi(u)\rightarrow\Sigma(p)$ transition is expected to have seven hyperfine components and the $\Pi(u)\rightarrow\Sigma(u)$ transition, six components. The $\Pi(p)\rightarrow\Sigma(p)$ and $\Pi(p)\rightarrow\Sigma(p)$ transitions[14] are forbidden as electric dipole transitions by the parity selection rule, $+\not\rightarrow+$. All 13 predicted microwave lines have been observed and are shown in Fig. 2. The ordinate represents the increased emission from the Σ states as detected by the photomultiplier and synchronous detector, and the abscissa is the microwave frequency. In determining center frequencies and linewidths, frequency scans were made at a slower rate over about 100-MHz-wide portions of the spectrum. Measured frequencies and relative intensities of the lines are given in Table I. The relative intensities are good to about 30%; limitations in the precision are due to the 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 maintained in the gas in the cavity was nearly constant over the entire frequency scan, showing that the energy density was constant in the cavity over the entire spectrum. Observation of all 13 lines predicted by the selection rule $\Delta F=\pm1$ or 0 allowed an unambiguous identification of each line with the particular transition given in the first two columns of Table I. The energy-level diagram corresponding to these transitions is shown in Fig. 3, and the energy splittings are listed in Table II.

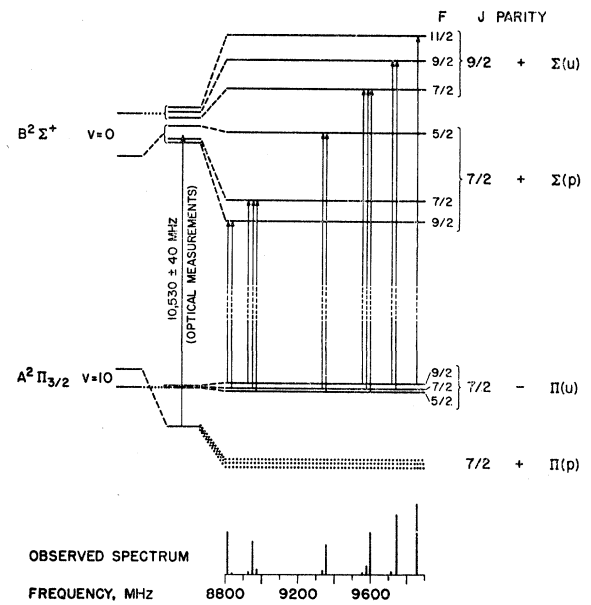

FIG. 3. Energy-level diagram of $B\,^2\Sigma^+$, $v=0$, $K'=4$ and $A\,^2\Pi_{3/2}$, $v=10$, states. The observed microwave spectrum is shown with the transitions identified. The optical measurements were made by R. L. Barger.

[14] Recently we have observed the $\Pi(p)\rightarrow\Sigma(p)$ and $\Pi(p)\rightarrow\Sigma(u)$ magnetic dipole transitions at frequencies from 10.4 to 11.5 GHz with about $\frac{1}{8}$ the intensity of the $\Pi(u)\rightarrow\Sigma(u,p)$ intensities. The $\Pi(u)\rightarrow\Pi(p)$ transitions at frequencies from 1.58 to 1.65 GHz also were observed.

TABLE II. Energy level splittings of the $K'=4$ rotational level of the $A\,^2\Pi_{3/2}$ and $B\,^2\Sigma$ electronic states of CN determined from the experimentally measured transitions.

Electronic state	Hyperfine components F_1–F_2	Frequency difference MHz
$\Sigma(u)$	$\frac{11}{2}-\frac{9}{2}$	139.2±0.5
$\Sigma(u)$	$\frac{9}{2}-\frac{7}{2}$	160.8
$\Sigma(u)(\frac{7}{2})$–$\Sigma(p)(\frac{5}{2})$		244.4
$\Sigma(p)$	$\frac{5}{2}-\frac{7}{2}$	383.7
$\Sigma(p)$	$\frac{7}{2}-\frac{9}{2}$	113.6
$\Sigma(p)(\frac{9}{2})$–$\Pi(u)(\frac{9}{2})$		8813.2
$\Pi(u)$	$\frac{9}{2}-\frac{7}{2}$	25.9
$\Pi(u)$	$\frac{7}{2}-\frac{5}{2}$	18.5

Observed and calculated[15] relative intensities are given in the fourth and fifth columns of Table I. The calculated relative intensities have been normalized to agree with the measured values at the $F=\frac{9}{2}\rightarrow\frac{9}{2}$ transition for the $\Pi(u)\rightarrow\Sigma(p)$ transitions and at the $F=\frac{9}{2}\rightarrow\frac{11}{2}$ for the $\Pi(u)\rightarrow\Sigma(u)$ 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 showed differences as great as a factor of two, and one differed by a factor of 50. This agreement between the predicted and observed intensities is added confirmation for the previous identification of the 13 transitions. These deviations of the weaker line intensities can 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, J is not a good quantum number and only F and m_F are good quantum numbers. It was at first thought that the small vibrational overlap of the $\Pi(u)$ and $\Sigma(u)$ states would lead to a smaller transition probability for these transitions.[8] However, hyperfine mixing is probably partially responsible for the comparable intensities of the $\Pi(u)\rightarrow\Sigma(u)$ and $\Pi(u)\rightarrow\Sigma(p)$ lines. In the following paper[12] the observed hyperfine structure is accounted for with an accuracy of better than 3 MHz.

The signal of the six major lines was found to be a linear function of the microwave flux inside the cavity from 5 W/cm² to the breakdown level of the 100 W/cm². Thus, there was no indication of saturation at pressures near 0.5-mm Hg.

Maximum changes of about 5% in the total light intensity from the six combined levels of the Σ state were measured by observing the dc output of the photomultiplier. The value corresponds to a 30% increase in

[15] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955),

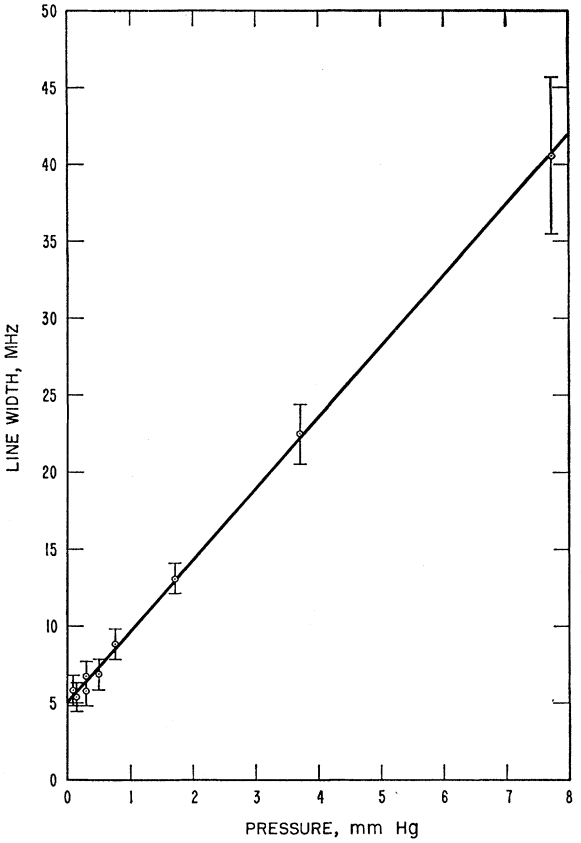

FIG. 4. Graph of the measured full linewidth at one-half maximum intensity, $2\Delta\nu$, as a function of total gas pressure.

an individual hyperfine level at resonance and is the order of magnitude predicted by Radford and Broida.[8]

Earlier attempts[10] at measuring these microwave transitions made use of a monochrometer with dc detection to isolate the $K'=4$ lines at 3878 Å. However, once the transitions were detected, it was found that an ac detection scheme using a detector synchronized to klystron modulation resulted in about a threefold increase in the signal-to-noise ratio. It was then discovered that increases in the optical intensity were not limited to the $K'=4$ level but were present in appreciable amounts (apparently due to collisional population) in the nearby rotational levels with K values differing by as much as 3 or 4 units from $K'=4$. These results on collisional transfer of energy, disobeying the optical selection rule, $\Delta K=\pm 1$, are consistent with rotational transfer found previously in NO.[16] By integrating the light from all of these levels with the use of the violet filter, about an order-of-magnitude increase in the signal-to-noise ratio was obtained. It was this latter arrangement which was utilized in measuring the spectra and linewidths.

[16] H. P. Broida and T. J. Carrington, J. Chem. Phys. **38**, 136 (1963).

LINEWIDTHS

At a pressure of 0.5-mm Hg, the average width of the six major lines was 7.1 ± 0.5 MHz with variations in the widths caused by the nearby smaller lines and by the experimental scatter of 0.2 MHz. Measured full widths at half-maximum of the 9854.9-MHz line are plotted versus pressure in Fig. 4. In the following discussion, the experimental values of the slope of the linewidth-versus-pressure curve, $\delta\Delta\nu/\delta P=2.3$-MHz/mm Hg, where $\Delta\nu$ is the half-width at half-maximum intensity, will be used to calculate the collision diameter, b, for N_2-CN collisions. Extrapolation of the graph of Fig. 4 to zero pressure, $(2\Delta\nu)_{P=0}=5$ MHz gives an indication of a combination of natural linewidths plus the linewidth due to Doppler effect and wall collisions. Since the partial pressures of CN and CH_2Cl_2 are less then 1% of N_2, the broadening of CN lines can be assumed to be due to collision broadening by N_2. The effective hard-sphere collision diameter is given by[17]

$$b=(2\Delta\nu/\sqrt{2}Nv_{\mathrm{av}})^{1/2},$$

where N is the number of molecules per cubic centimeter,

$$v_{\mathrm{av}}=[\tfrac{1}{2}(v^2_{N_2}+v^2_{CN})]^{1/2},$$

and

$$v=(8kT/m\pi)^{1/2}$$

is the individual molecular velocity assuming a Maxwellian distribution. Substituting the values $\delta(\Delta\nu)/\delta p=2.3\times 10^6$—Hz/mm Hg, $N=3.5\times 10^{16}$ molecules/cm^3 at 1-mm Hg pressure and $v_{\mathrm{av}}=4.8\times 10^4$ cm/sec into the above equation, b is found to be $(4.4\pm 0.2)\times 10^{-8}$ cm. This value is in reasonable agreement with the kinetic-theory collision diameter of $b=4.1\times 10^{-8}$ cm.

If it is assumed that the dominant interaction is between the dipole moment of CN and the quadrupole moment of N_2 in $CN-N_2$ collisions, and if the quadrupole moment for nitrogen is taken as the average of several of the experimental values[18–20] ($Q\approx 2.6\times 10^{-26}$ esu), then the dipole moment can be calculated.[21] If the observed broadening is due predominantly to the $^2\Pi$ state, then the calculated dipole moment of this state of CN is about 0.2 D. This value for CN is reasonable when compared with the dipole moment of NO[15] (μ0.16 D). A detailed analysis of the pressure broadening, taking into account the rotational perturbation, should yield a more accurate value for the dipole moment of CN.

The collisional relaxation time for this pressure broadening, $\tau_{cr}=1/2\pi\Delta\nu$, at a pressure of 1-mm Hg is 0.7×10^{-7} sec. This value is in good agreement with the

[17] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 1021.

[18] H. Feeny, W. Madigosky, and B. Winters, J. Chem. Phys. **27**, 898 (1957).

[19] W. S. Benedict and L. D. Kaplan, J. Chem. Phys. **30**, 388 (1959).

[20] Krishnaji and Suresh Chandra, J. Chem. Phys. **38**, 232 (1963).

[21] W. V. Smith and R. Howard, Phys. Rev. **79**, 132 (1950).

kinetic-theory value of about 1×10^{-7} sec and with the characteristic time for rotational redistribution $\simeq3\times10^{-7}$ given by Radford and Broida.[9] This agreement indicates that a large percentage of the collisions result in changes in the rotational state of the molecule.

CONCLUSION

The measured spectrum agrees with the number of lines predicted and reveals a rather large hyperfine splitting in the $B\,^2\Sigma$ state of CN and a relatively small spin splitting. The result is a rather unusual fine and hyperfine structure in the $K'=4$ rotational level, $v=0$, $B\,^2\Sigma$ state of the CN molecule.

Linewidth measurements as a function of pressure show a linear dependence of linewidth on pressure. The collision diameter, calculated from the slope of the linewidth-versus-pressure curve, is in reasonable agreement with the kinetic-theory value.

The results presented have demonstrated that energy levels which cannot be observed by regular optical spectroscopy methods can be found by using a microwave pumping technique. Such techniques are useful only in cases where significant population differences are present. The population increase of about 30% in the individual levels caused by the microwave pumping may have some application for laser action.

The feasibility of this technique applied to excited states of molecules has provided the basis for future work devoted toward other rotational perturbations in CN as well as in other molecules.

ACKNOWLEDGMENTS

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Hyperfine Structure of the $B\,^2\Sigma^+$ State of CN*

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Hyperfine-structure energy formulas are developed for $^2\Sigma$ states of diatomic molecules and are used to analyze some of the results of the microwave-optical experiment on the CN molecule described in the preceding paper. For the excited $B\,^2\Sigma^+$ state the following hyperfine structure constants are derived: $|\Psi^2(0)|=(10.2\pm0.2)\times10^{24}$ cm^{-3}, $\langle(3\cos^2\chi-1)/r^3\rangle_{av}=(7\pm2)\times10^{24}$ cm^{-3}, and $eQq=(-5\pm5)$ MHz. These results are found to be consistent with the valence bond structure :C$\doteq$N:, in which the unpaired electron occupies the σ-bond orbital of the molecule.

INTRODUCTION

EXPLOITING a novel microwave-optical technique, Evenson, Dunn, and Broida[1] have recently determined the hyperfine structure of two rotational levels of the CN molecule, one of which is a spin doublet level of the excited electronic state $B\,^2\Sigma^+$. This is the first precise measurement of magnetic hyperfine structure in a $^2\Sigma$ molecular state, and the results, shown in Table I, fit none of the standard energy formulas[2] In particular, the familiar Interval Rule, which states that the separation between hyperfine structure levels with angular momentum numbers F and F-1 should be proportional to the value of F, is obviously disobeyed. The reason for this becomes evident when one observes that the separations between levels of different F in Table I are as large as the separations between levels of different J; that is, the hyperfine structure is comparable in size with the fine structure. This situation, which may be expected to be typical of $^2\Sigma$ molecular states, corresponds to a thoroughly mixed vector coupling scheme, midway between the limiting cases called $b_{\beta J}$ and $b_{\beta S}$

TABLE I. Hyperfine structure—fine structure intervals in the $B\,^2\Sigma^+$, $v=0$, $K=4$ spin doublet level of CN. All entries in MHz.

J, F[a]	Measured interval[b]	Calculated interval[c]
	$\Delta\nu(J, F\rightarrow J, F-1)$	
$\frac{9}{2}$, $\frac{11}{2}$	139.2	137
$\frac{9}{2}$, $\frac{9}{2}$	160.8	157
$\frac{7}{2}$, $\frac{9}{2}$	−113.6	−117
$\frac{7}{2}$, $\frac{7}{2}$	−383.7	−386
	$\Delta\nu(J, F\rightarrow J-1, F-1)$	
$\frac{9}{2}$, $\frac{7}{2}$	244.4	243

[a] The J values listed are those of the case $b_{\beta J}$ levels which connect with the actual intermediate coupling levels via an adiabatic transformation.
[b] Taken from Table II of Ref. 1 (preceding paper). Experimental uncertainties are ±0.5 MHz.
[c] Calculated from Eqs. (5), (8), and (9), using the values $\delta=497$, $b=467$, $c=60$, $eQq=-5$, all in MHz.

* Supported in part by the U. S. Office of Naval Research.
[1] K. M. Evenson, J. L. Dunn, and H. P. Broida, preceding paper, Phys. Rev. **136**, A1566 (1964). See also, R. L. Barger, H. P. Broida, A. J. Estin, and H. E. Radford, Phys. Rev. Letters **9**, 345 (1962).
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