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Measurements of Collisional Energy Transfer between Rotational Energy Levels in CN†

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A microwave-optical technique which selectively populates a single rotational level of CN and permits the observation of the redistribution of this population was utilized to measure the rates of collisional energy transfer between rotational energy levels of the $B^2\Sigma$ state of CN. CN was formed in the $A\ {}^2\Pi$ state by the addition of CH_2Cl_2 to the afterglow of a nitrogen discharge. The near coincidence of the $K=4$, $v=10$ level of the $A\ {}^2\Pi$ state with the $K=4$, $v=0$ level of the $B\ {}^2\Sigma$ state permits microwave transitions near 10 GHz from the more populated Π level to the Σ level. The increased population in the rotational levels neighboring the $K=4$ level of the $B\ {}^2\Sigma$ state was detected by measuring the increased optical emission due to the $B\ {}^2\Sigma$–$A\ {}^2\Sigma$ transition near 3875 Å. Collisional energy transfer was measured over a pressure range from 0.1 to 5 Torr for changes in rotational quantum number ranging from one to ten. It is shown that rotational transitions having changes in rotational quantum number greater than unity take place with high probability, contrary to the optical selection rule $\Delta K=\pm 1$, and that approximately every gas kinetic collision produces a rotational transition. The relaxation time for the fourth rotational level was found to be 1.2×10^{-7} ($\pm 30\%$) sec at a pressure of 1 Torr.

INTRODUCTION

Collisional energy-transfer rates between rotational energy levels in molecular gases have been measured by two different types of experiments[1]: (1) studies of the bulk properties of the gas which reveal over-all rates of energy relaxation in the low-lying rotational levels and which are made using ultrasonic waves, heat capacity lags, shock waves, and pressure broadening of microwave lines; and (2) studies of the relaxation of individually excited rotational levels of excited electronic states by observation of the fluorescence of molecules in these states. A modification of this latter technique was used in the present experiment.

Earlier experiments have shown that X-band microwave pumping from the K(Ref. 2)$=4$, $v=10$, $A\ {}^2\Pi_{\frac{3}{2}}$ rotational state of CN produces a significant increase in the population of the $K=4$, $v=0$, $B\ {}^2\Sigma$ level.[3] Molecules in this level then undergo inelastic collisions which transfer them to neighboring rotational levels. Increased population in these levels can be determined by observing the increased optical emission from these levels to the ground state ($v=0$, $X\ {}^2\Sigma$). The technique has been found to be sufficiently sensitive that collisionally induced transitions between rotational levels can be observed from the $K=4$ level to all other levels between $K=0$ and $K=15$.

EXPERIMENTAL PROCEDURE

The experimental apparatus was similar to that described in a previous paper[3] in which 13 microwave transitions of CN were detected optically. In the present experiment, the optical emission was scanned with a grating monochromater, while the microwave frequency was fixed at a frequency corresponding to a microwave transition. For most observations a frequency of 9854.9 MHz was used; this frequency corresponds to the transition between the $F=\frac{9}{2}$, $J=\frac{7}{2}$ level of the $A\ {}^2\Pi$ state and the $F=\frac{11}{2}$, $J=\frac{9}{2}$ level of the $B\ {}^2\Sigma$ state. The photomultiplier output of the monochromater was amplified by a 1-kHz narrow band amplifier and the spectrum was displayed on a pen recorder. The monochromator was adjusted to give a resolution of about 0.4 Å, which resolved the individual rotational levels in the R branch. The over-all sensitivity, using a 1-sec time constant, was sufficient to measure the resulting spectrum at pressures from 0.1 to 5.0 Torr. The microwave cavity was excited with about 1 W of power from a klystron and traveling wave amplifier.

METHOD OF ANALYSIS

In the system under consideration, CN molecules are formed predominantly in the $A\ {}^2\Pi$ state by a chemical reaction involving CH_2Cl_2 and the products of an electric discharge in nitrogen. The CN molecules in this $A\ {}^2\Pi$ state are transferred to the $B\ {}^2\Sigma$ state by gas kinetic collisions and by microwave absorption. Optical radiation is observed from both electronic states. The $B\ {}^2\Sigma$ and the perturbed levels of the $A\ {}^2\Pi$ states radiate near 3875 Å directly to the ground electronic and vibrational state, while the $A\ {}^2\Pi$ state radiates at wavelengths greater than 5000 Å to higher vibration levels of the ground electronic state. Since about 98%

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† Preliminary measurements were reported at the 1964 Gaseous Electronics Conference, Bull. Am. Phys. Soc. **10**, 191 (1965).

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[1] T. C. McCoubrey and W. D. McGrath, Quart. Rev. **11**, 87 (1957).

[2] Many workers use N to denote the component of angular momentum here denoted by K. See C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., New York, 1955).

[3] K. M. Evenson, J. L. Dunn, and H. P. Broida, Phys. Rev. **136,** A1566 (1964).

of the gas is molecular nitrogen, exchange of rotational energy of CN occurs largely with the translational and rotational degrees of freedom of N_2. Such processes as collisional quenching of the excited electronic state and collisionally induced transitions between the unperturbed Σ and Π states and between vibrational states have been shown to be less probable than the above-mentioned processes[4] and are neglected here. Thus, the rate of change of population of the xth rotational level, dN_x/dt, may be written

$$dN_x/dt=R_x-N_x/\tau_x+\sum_{y\neq x}P(C_{yx}N_y-C_{xy}N_x), \qquad (1)$$

where x and y are values of the rotational quantum number K, N_x and N_y are the numbers of molecules in the xth and yth rotational level, τ_x is the radiative lifetime of the xth rotational level, C_{xy} is the rate constant for collisionally induced rotational transitions from the xth to the yth level, R_x is the over-all rate of transfer into the xth level by all other processes, and P is the total pressure.

The experiment was performed using square-wave modulated microwave pumping to the fourth rotational level and a phase-sensitive ac detection scheme so that only the increases in the number of molecules in the other levels due to collisions with the increased population of the fourth level were measured.

After equilibration, during the "on" portion of the microwave pumping, Eq. (1) becomes

$$\begin{aligned}0=R_x&-(N_x+\Delta N_x)/\tau_x\\&+\sum_{y\neq x}P(C_{yx}[N_y+\Delta N_y]-C_{xy}[N_x+\Delta N_x]), \qquad (2)\end{aligned}$$

where ΔN_x and ΔN_y are the increases in population due to microwave pumping. Since the modulation frequency was sufficiently low that the CN population was in steady state at all times ($dN_x/dt=0$), the subtraction of Eq. (1) from Eq. (2) yields an expression for the measured ac signal:

$$I_x=\Delta N_x/\tau_x=\sum_{y\neq x}P(C_{yx}I_y\tau_y-C_{xy}I_x\tau_x). \qquad (3)$$

The rate for the collisional depopulation of the fourth level leading to population of the other $B\ {}^2\Sigma$, $v=0$ levels is $\sum_{x\neq4}C_{4x}$, which is approximately

$$\sum_{x\neq4}^{14}C_{4x},$$

owing to very small populations in levels of $x>14$. The

$$\sum_{x\neq4}^{14}C_{4x}$$

can be found under conditions in which $PC_{4x}I_4\tau_4$ is the main term in the summation of Eq. (3) (the conditions are discussed below). Summing this simplified equation from $x=0$ to 14 (omitting $x=4$) gives

$$\sum_{x\neq4}^{14}C_{4x}=\sum_{x\neq4}^{14}\frac{(I_x/I_4)}{\tau_4P}. \qquad (4)$$

One finds the collisional lifetime τ_{coll} at any pressure from

$$\tau_{\text{coll}}=1/\sum_{x\neq4}^{14}PC_{4x}. \qquad (5)$$

To simplify the above Eq. (3), the relationship between C_{xy} and C_{yx} derived by Kondrat'ev[5] is used. Using the principle of detailed balancing, he has shown that

$$\frac{C_{yx}}{C_{xy}}=\frac{(2x+1)}{(2y+1)}\exp\left[\frac{-(E_x-E_y)}{kT}\right]. \qquad (6)$$

Consistent with this expression is the definition of C_{yx}:

$$C_{yx}=6(2x+1)f_{yx}F_{yx}, \qquad (7)$$

where $6(2x+1)$ is the degeneracy of the final state (since the electron spin S is $\frac{1}{2}$ and the nuclear spin I, is 1, the factor 6 results from $(2S+1)(2I+1)$), f_{yx} is an "energetic factor," and F_{yx} is that part of the collisional rate constant independent of the degeneracy and energetic factor. The factor f_{yx} depends on the probability that it is energetically possible for two colliding molecules to give up or receive a quantum of rotational energy.

For a transfer of energy from translational to rotational energy in going from state y to state x ($y<x$), f_{yx} is the probability that two colliding molecules have a relative kinetic energy (E_x-E_y). This probability is

$$f_{yx}=\exp[-(E_x-E_y)/kT], \qquad (y<x). \qquad (8a)$$

For transfers of rotational to translational energy ($y>x$), it is possible for the molecules to carry away any size quantum of rotational energy, hence

$$f_{yx}=1, \qquad (y>x). \qquad (8b)$$

The reason for this definition of the C's in terms of the F's becomes clearer when one substitutes C_{yx} and C_{xy} into Eq. (6) and shows that

$$F_{yx}=F_{xy}. \qquad (9)$$

Now writing Eq. (3) using the f and F factors yields

$$I_x=\sum_{y\neq x}PF_{xy}[(2x+1)f_{yx}I_y\tau_y-(2y+1)f_{xy}I_x\tau_x]. \qquad (10)$$

In equilibrium $I_y\tau_y=N_y=(2y+1)\exp(-E_y/kT)$, and the terms inside the brackets of Eq. (10) cancel. That is, the net number of molecules being transferred by

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

[5] V. N. Kondrat'ev, *Chemical Kinetics of Gas Reactions* (Pergamon Press, Ltd., London, 1964).

collisions between two levels is zero for equilibrium. In these experiments, the intensity of all lines except the $K=4$ line were approximately in equilibrium so that the terms in which x or y were not equal to 4 canceled. The population of the fourth level was greater than ten times that of any other level at low pressures, hence the collisional transfer of molecules from the xth level to the $y=4$ level could be neglected; therefore,

$$I_x/I_4=PF_{4x}(2x+1)f_{4x}\tau_4, \qquad (11)$$

and the values of F_{4x} can be obtained from plots of I_x/I_4 versus pressure at low pressures. A value of 8.5×10^{-8} sec was used for τ of the unperturbed $B\ ^2\Sigma$ levels,[6] and a value 1.14 times this for the fourth level[4] (this longer time is due to the perturbational mixing).

RESULTS AND DISCUSSION

Spectra taken at 0.45 Torr comparing the microwave pumped spectrum having enhancement of the $F=\frac{11}{2}$, $K=4$ level (ac detection), with the CN emission spectrum (dc detection, microwave power off) are shown in Fig. 1. One sees from the ac spectrum that the probability for multiple quantum jumps ($\Delta K>1$) is of the same size as for single quantum jumps ($\Delta K=1$); that is, if only single quantum jumps were allowed, and the probability for jumps between the different levels were of the same order of magnitude, then one would expect a geometrical decrease in the intensities[7] as one moves away from the $K=4$ line. For example, in Fig. 1, the $K=3$ line is $\frac{1}{15}$ of the $K=4$ line; if ΔK were limited to one, then one would expect the intensity of the $K=2$ line to be approximately ($\frac{1}{15}\times\frac{1}{15}$) or $\frac{1}{225}$ of the intensity of the $K=4$ line; however, the $K=2$ line is actually about $\frac{1}{18}$ of the $K=4$ line. The spacing between the rotational levels of the $B\ ^2\Sigma$ state varies from about 5×10^{-4} eV between the zeroth and first level to 72×10^{-4} eV between the 14th and 15th levels; thus, the spacings are quite small with respect to $kT=0.025$ eV. Figure 1 shows the spectral region $K=1$ through $K=16$ of the R branch and $K=0$ and 1 of the P branch. Effects of perturbations between the $B\ ^2\Sigma$ and $A\ ^2\Pi$ are apparent in the enhanced emission in the fourth, seventh, 11th and 15th levels of the dc spectra. The decreases in levels 7 and 15 of the ac spectrum are real and are caused by the combined effect of perturbations in these levels and the depletion of the Π state by the microwave pumping. Depletion of the Π state was also detected in the emission of the red system ($A\ ^2\Pi$–$X\ ^2\Sigma$).

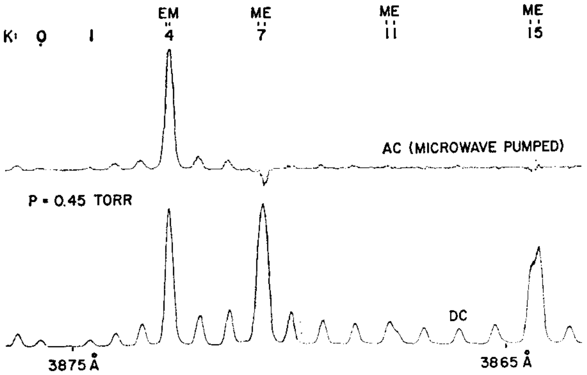

FIG. 1. Spectra of CN at 0.45 Torr which compare the microwave pumped spectrum exciting the $F=11/2$, $K=4$ level, and using ac detection, with the ordinary CN emission spectrum (dc detection, microwave power off). The positions of the extra (E) line (the perturbed $^2\Pi$ line) and the main (M) line (the $^2\Sigma$ line) are shown at the top.

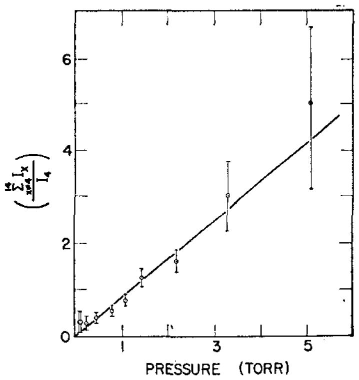

FIG. 2. The sum of the intensity of the $K=0$ through 3 and 5 through 14 lines in the R branch of the $v=0$ $B\ ^2\Sigma\rightarrow v=0$ $X\ ^2\Sigma$ emission divided by the intensity of the $K=4$ line is plotted versus total pressure.

To find the collisional lifetime, one obtains a value for the rate of collisional depopulation with the use of Eq. (3) by making a plot of the sum of the ac intensities of the first 14 lines (except for $K=4$) in the R branch divided by the intensity of the $K=4$ line versus pressure, as is shown in Fig. 2. The collisional lifetime found with the use of Eq. (5) at 1 Torr is 1.2×10^{-7} sec. This value is very near the one of 0.7×10^{-7} sec at 1 Torr found from pressure broadening of the microwave absorption lines[3]; however, it is somewhat smaller than the value of the rotational redistribution time of 6×10^{-7} sec at 1 Torr found by Radford and Broida.[4] The value is also near that of 1.1×10^{-7} sec for the N_2–N_2 collision time[8] at 1 Torr found from viscosity data, revealing that approximately every gas kinetic collision brings about a change in the molecule's rotational energy state (if the CN–N_2 collision frequency is approximately equal to that of N_2–N_2). This is in agreement with experiments on electronically excited NO and OH.[7,9]

Helium at a pressure of 2.32 Torr used as a buffer gas in 0.16 Torr of N_2 and 0.05 Torr of CH_2Cl_2 yielded the same values of τ as did N_2 alone, within the experimental accuracy of about 10%. Thus helium is as effective as N_2 in producing the rotational energy trans-

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[6] R. G. B. Bennett and F. W. Dalby, J. Chem. Phys. **36**, 399 (1962).

[7] H. P. Broida and T. Carrington, J. Chem. Phys. **38**, 136–147 (1963).

[8] E. W. McDaniel, *Collision Phenomena in Ionized Gases* (John Wiley & Sons, Inc., New York, 1964), p. 35.

[9] T. Carrington, (a) J. Chem. Phys. **31**, 1418 (1959); (b) Symp. Combust. 8th Pasedena, California 1961, 257 (1962).

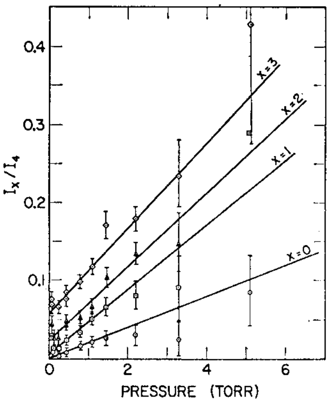

FIG. 3. The ratio of the sum of the intensities of the R and P branch transitions of the $v=0\ B\ ^2\Sigma \rightarrow v=0\ X\ ^2\Sigma$ emission for $K=0$ through 3 divided by the $K=4$ intensity is plotted versus total pressure.

fer. Broida and Carrington[7] found helium only one-half as effective as N_2 for collisional–rotational energy transfer in NO. Changes in the CH_2Cl_2 content by a factor of four produced no changes in the value of τ_{coll} showing that it was not the principle gas responsible for rotational energy transfer.

Relative values of F_{4x} (that part of the collisional rate coefficient independent of degeneracy and the energetic probability factor) between the fourth level and levels 0 through 14 were obtained from slopes of plots of I_x/I_4 versus pressure with the use of Eq. (11). Plots for $x=0$ through 3 are shown in Fig. 3 with excitation of the $J=\frac{9}{2}$, $F=\frac{11}{2}$, $K=4$ level ($\nu=9854.9$ MHz), and values of F_{4x} are shown in Fig. 4. One sees that values of the relative ratio of collisional energy transfer F_{4x} were approximately constant for $x=0$ to 14, but with an indication of a greater probability of energy transfer to rotational levels less than 4. Thus, transitions with $\Delta K>1$ were found to occur with a high degree of probability contrary to the optical selection rule. These results are in agreement with the results of Broida and Carrington[7,9] on NO and OH, and also are in agreement with Fermi's theory[10] as interpreted by Kondrat'ev.[5]

The interesting nonzero intercepts shown in Fig. 3 for Levels 1, 2, 3 and also found for Levels 5 and 6 but not for the other levels indicate an addition to these levels which is pressure independent. This addition may be due to collisions of CN with the walls or with electrons, but no conclusive answer has been found. In calculating F_{4x} it was assumed that these intercepts were constant so that they could be neglected; this assumption may lead to an additional 25% error in the values of F_{4x}, which are shown plotted in Fig. 4. At a pressure of 0.45 Torr, the sum of possible contributions from all lines other than $y=4$ to the xth level [see Eq. (10)], assuming that the F_{xy} are equal, varied from $\frac{1}{3}$ for levels greater than $x=9$ to less than 0.01 for the zeroth level. Thus, the assumption which was used in deriving Eq. (11), that the collisional contributions from molecules in levels other than the fourth level were insignificant, was not completely justified. Therefore, even though the results shown in Fig. 4 probably are not accurate to better than a factor of 2, they do indicate that F_{4x} does not vary rapidly with changes in K.

The experiment was repeated with the excitation at 9354.9 MHz of the $F=\frac{5}{2}$, $J=\frac{7}{2}$, $K=4$ level rather than at 9854.9 MHz of the $F=\frac{11}{2}$, $J=\frac{9}{2}$, $K=4$ level. This was done in order to determine whether or not electron-spin orientation or nuclear-spin orientation are affected (i.e., whether or not $\Delta K=\Delta J$ or $\Delta K=\Delta F$) in these changes of rotational energy. If electron or nuclear-spin orientation were conserved in such collisional transitions, then the ratio of intensities of the lower lying levels to the intensity of the fourth level would be much smaller than in the case of the $F=\frac{11}{2}$, $J=\frac{9}{2}$, $K=4$ level excitation. For example, if $\Delta K=\Delta F$, then, in the case of the $F=\frac{11}{2}$ excitation, the $F=\frac{7}{2}$ level of $K=2$ would be populated by collision, while with $F=\frac{5}{2}$ excitation the $F=\frac{1}{2}$ level of $K=2$ would be populated. From Eq. (9), one sees that the intensity is proportional to the degeneracy $(2y+1)$ if the different F_{xy} are approximately constant. Thus, a much lower relative intensity of the lower lying levels would be expected with the $F=\frac{5}{2}$ rather than with the $F=\frac{11}{2}$ excitation, if transitions with $\Delta K=\Delta F$ and $\Delta K=\Delta J$ were preferred. The only difference in the results of the experiments was that the values of I_x/I_4 average 13% less than with the $F=\frac{11}{2}$ excitation; this is in agreement with an expected 12% difference due to the difference in lifetimes of the $F=\frac{11}{2}$ and $\frac{5}{2}$ levels.[4] Thus, to within the experimental accuracy of about 15%, nuclear or electron spin relaxation is as probable as rotational relaxation in such collisions. This result is in agreement with the measurement of the relaxation of NO due to collisions with NO.[7] However, collisions of NO with argon[7] showed that change in spin orientation was less likely than change in rotation.

SUMMARY

(1) It was found that nearly every collision of CN with N_2 or He can produce a change in the rotational energy of the molecules in the ground vibration level of the $B\ ^2\Sigma^+$ state of CN. At 1 Torr, the value of 1.2×10^{-7} sec for the relaxation of the fourth rotational

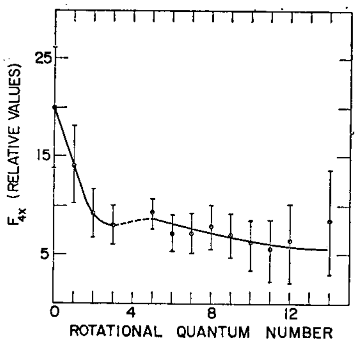

FIG. 4. Values of F_{4x} as calculated from curves such as those in Fig. 3 with the use of Eq. (11) are shown for different values of K.

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[10] E. Fermi, Z. Physik **40**, 399 (1927).

level to the 14 neighboring levels was measured. This value is in good agreement with the value of 0.7×10^{-7} sec obtained from the line broadening of the microwave absorption line.[3]

(2) Values for the relative rates of collisional transfer of rotational energy F_{4x} from the $K=4$ level to the neighboring rotational levels were approximately constant for $x=0$ to 14.

(3) Neither electron nor nuclear-spin orientation was necessarily conserved (i.e., $\Delta K\neq\Delta J$ or $\Delta K\neq\Delta F$) in these transfers of rotational energy.

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