

# Letters to the Editor

**T**HIS section will accept reports of new work, provided these are terse and contain few figures, and especially few half-tone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Managing Editor not later than the 15th of the month preceding that of the issue in which the letter is to appear. No proof will be sent to the authors. The usual publication charge (\$8.00 per page) will not be made and no reprints will be furnished free.

## A Mechanism of Formation of Nitric Oxide in Glow Discharges

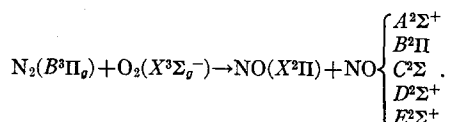
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**I**N an experimental and theoretical investigation of mechanisms of excitation of the triplet bands of nitrogen, at present being carried out here, the well-known excitation of accompanying nitric oxide band systems in nitrogen contaminated with molecular oxygen has also received attention from a theoretical and experimental point of view. In view of the interest in these band systems particularly in terrestrial astrophysics<sup>1</sup> it is the purpose of this note to point out energy resonances existing in a simple mechanism of formation of nitric oxide in such discharges.

It is suggested that in a glow discharge plasma in oxygen contaminated nitrogen, molecules in vibrational levels of the  $B^3\Pi_u$  state (amongst others) may be depopulated by collisions with oxygen ground-state molecules ( $X^3\Sigma_g^-$ ) with the formation of two nitric oxide molecules, one in its ground state ( $X^2\Pi$ ) and the other in any of the vibrational levels of the excited states  $A, B, C, D,$  or  $E$ .<sup>2</sup> This mechanism may be represented by the equation



Such a nonradiative depopulation of  $N_2(B^3\Pi_u)$  and the consequent formation of NO (excited) would cause a diminution in the intensity of bands of the first positive system with the consequent

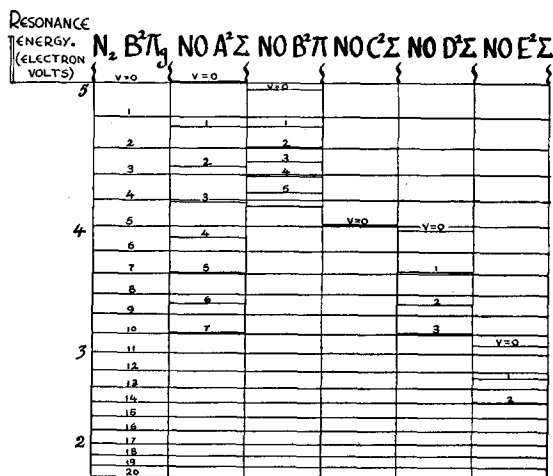


FIG. 1. Energy resonances between  $N_2(B^3\Pi_u)$  and NO ( $A, B, C, D, E$ ).

appearance of bands of the NO systems. This reaction, involving as it does, redistribution both of particles and excitation, is very difficult to analyse by quantum mechanics.<sup>3</sup> However, as has been observed in the quantum-mechanical treatment of similar more simple processes<sup>3</sup> and as may be expected by more general considerations, energy resonance between the systems on either side of the equation is a major criterion in deciding the probability of this mechanism. Accordingly energies appropriate to all the possibilities of vibrational excitation of each side of the equation have been calculated. That is, the difference between energy of excitation of any vibrational level, and the sum of the dissociation energies of the molecules when in the ground state, was calculated for each vibrational possibility for each side of the equation. Comparison between these is shown in Fig. 1 where some quite strong energy resonances are observed.

If an empirical resonance criterion of a few hundredths of an electron volt energy difference be accepted as indicating the probability of the reaction then Table I summarizes the expected

TABLE I. Vibrational levels of  $N_2(B^3\Pi)$  and NO ( $A^2\Sigma, B^2\Pi, C^2\Sigma, D^2\Sigma, E^2\Sigma$ ) which are in near energy resonance.

$N_2$ $B^3\Pi$	$A^2\Sigma$	$B^2\Pi$	NO $C^2\Sigma$	$D^2\Sigma$	$E^2\Sigma$
0	0				
2		2			
3		4			
4	3				
5			0		
7	5			1	
10	7			3	
12					1
14					2

vibrational sequences of the first positive system which will be weakened by the appearance of the indicated vibrational sequences of the nitric oxide systems.

Spectrograms of plates exposed to discharges run in  $N_2/O_2$  mixtures confirm qualitatively the general scope of the above prediction. The appearance of sequences of NO bands other than those specifically quoted above is readily explained by re-excitation of the NO molecules formed in the discharge and less stringent resonance conditions than the arbitrary one above.

Quantitative measurements made on the dependence of the intensity of nitric oxide bands on those of the first positive, to compare with a kinetic analysis which has been made of this mechanism will be the real test of this mechanism. Work has been started here upon such measurements, but in view of the current interest in the spectra of these molecules it has been thought worthwhile to draw attention at this stage to the close energy resonances there existing.

<sup>1</sup> *The Emission Spectra of the Night Sky and Aurorae* (The Physical Society, London, 1948).

<sup>2</sup> A. G. Gaydon, Proc. Phys. Soc. (London) 56, 95, 160 (1944). M. W. Feast, Can. J. Research A28, 488 (1950).

<sup>3</sup> Mott and Massey, *The Theory of Atomic Collisions* (1949), second edition.

## Dipole Moment and Electric Quadrupole Effects in HNCO and HNCS

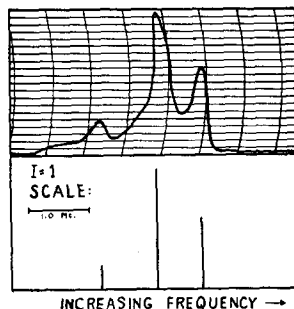
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**I**NTERACTION of the electric quadrupole moment of the nitrogen nucleus with the molecular electric fields of isocyanic and isothiocyanic acids results in a hyperfine splitting of the rotational transitions. The quadrupole coupling constant,  $eQq$ , for each of these molecules has been determined from the splitting of the  $0_0, 0-1_{0,1}$  transition of HNCO at 21,981.7<sup>1</sup> Mc and the  $1_{1,1}-2_{1,2}$  transition of HNCS at 23,499.5 Mc.<sup>2</sup>

FIG. 1. Hyperfine structure of  $0_{0,0}-1_{0,1}$  transition of HNCO. The two lower frequency lines are separated by 0.90 Mc and the two higher frequency lines by 0.60 Mc.



A standard Stark modulation microwave spectroscopy with a lock-in detector and recording meter was used for these measurements. Recording meter traces were compared with the theoretical patterns in order to determine the sign of  $eQq$ . Accurate frequency measurements were made on an oscilloscope. To resolve lines 0.35 Mc apart it was necessary to reduce the pressure to  $10^{-4}$  mm, the temperature to  $-78^{\circ}\text{C}$ , and the klystron cavity sweep rate to 2 cycles per second. Frequencies were reproducible to within 0.02 Mc with HNCO and 0.05 Mc with HNCN.

Figures 1 and 2 compare the observed hyperfine structure of HNCO and HNCN with the theoretical patterns expected on the basis of  $eQq$  equal to  $+2.00 \pm 0.05$  Mc for HNCO and  $+1.2 \pm 0.2$  Mc for HNCN.

TABLE I.  $\text{N}^{14}$  nuclear quadrupole coupling in cyanides and isocyanates.

Molecule	$eQq$ (mc/sec)
HCN	$-4.58^a$
$\text{CH}_3\text{CN}$	$-4.67^b$
CICN	$-3.67^c$
BrCN	$-3.83^c$
ICN	$-3.80^c$
HNCN	$+1.2^d$
HNCO	$+2.00^d$

<sup>a</sup> Simmons, Anderson, and Gordy, Phys. Rev. **77**, 77 (1950).

<sup>b</sup> Kisliuk and Townes, J. Res. Nat. Bur. Stand. **44**, 611 (1950).

<sup>c</sup> Smith, Ring, Smith, and Gordy, Phys. Rev. **74**, 310 (1948) and Townes, Holden, and Merritt, Phys. Rev. **74**, 1113 (1948).

<sup>d</sup> Present work.

Values of  $eQq$  for various compounds containing carbon to nitrogen multiple bonds are given in Table I.

It is interesting to note that compounds in which the nitrogen atom is on the end of the molecule, as in the cyanides, lead to coupling constants of the order of  $-4$  Mc/sec. Isocyanic and isothiocyanic acids, on the other hand, possess small positive coupling constants. The similarity of these values in the two molecules and the difference between these and the  $-\text{C}\equiv\text{N}$  values listed above lead to two qualitative conclusions. (1) Bonds to nitrogen in isocyanic acid are similar to those in isothiocyanic acid, and (2) these bonds are in both cases quite dissimilar to the  $-\text{C}\equiv\text{N}$  bond which would be found if the molecules were HOCN and HSCN. Therefore, the alternative structures HNCO and HNCN are indicated.

FIG. 2. Hyperfine structure of  $1_{1,1}-2_{1,2}$  transition of HNCN. The two large peaks are separated by 0.35 Mc. The frequency of the small peak could not be measured on the oscilloscope.

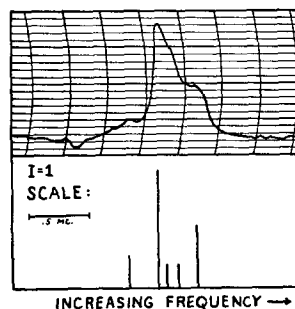


TABLE II. Dipole moment of HNCO and DNCO.

State of molecule	Freq. of $0_{0,0}-1_{0,1}$ transition in Mc/sec.	Dipole moment in Debye units
HNCO: ground state	21,981.7	$1.592 \pm 0.015$
High frequency bending vibration	21,993.0	$1.760 \pm 0.015$
Low frequency bending vibration	22,017.3	$1.620 \pm 0.015$
DNCO: ground state	20,394.7	$1.619 \pm 0.015$

More quantitative calculations of the coupling constants to be expected were made, following the theory of Townes and Dailey.<sup>3</sup> Calculated values correctly predicted in each case the sign of  $eQq$ , but they were only roughly in agreement with the observed magnitudes.

Beard and Dailey<sup>2</sup> have shown from the measured moments of inertia that HNCN is a reasonable structure but HSCN is not. Also, an investigation of the hydrogen stretching frequencies of HNCO and HNCN reported in an earlier paper<sup>1</sup> established that both of these molecules have the proton bonded to the same atom. All of this evidence leads us to the conclusion that the structures are similar and are HNCO and HNCN.

The slight asymmetry of HNCO should result in two, low frequency, nondegenerate vibrations. Two absorption lines, corresponding to molecules in each of these excited vibrational states, were observed. Dependence of intensities upon temperature confirmed the assignment as excited vibrational states; however, the intensity measurements were not sufficiently reproducible to allow a determination of the vibrational frequencies.

Stark splittings were measured as a function of the applied electric field for the  $0_{0,0}-1_{0,1}$  transition of  $\text{HN}^{14}\text{C}^{12}\text{O}^{16}$  and  $\text{DN}^{14}\text{C}^{12}\text{O}^{16}$  in the ground vibrational states, and for  $\text{HN}^{14}\text{C}^{12}\text{O}^{16}$  in the excited vibrational states. Since HNCO is very nearly linear, the theory of the Stark effect in linear molecules was applied in each case and the component of the dipole moment along the principal axis of least moment of inertia was calculated. These values are given in Table II. No satisfactory explanation has been found for the large difference in the change of dipole moment in the two excited vibrational states.

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‡ Contribution from the Gates and Crellin Laboratories of Chemistry.

<sup>1</sup> Jones, Shoolery, Shulman, and Yost, J. Chem. Phys. **18**, 990 (1950).

<sup>2</sup> C. I. Beard and B. P. Dailey, MITRE Tech. Report No. 112 (1949).

<sup>3</sup> C. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 (1949).

## Kinetics of Gas Adsorption as a Method of Area Determination

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TO date, the methods of surface area determination of solids by the adsorption of gases have been based upon appropriate theoretical treatment of the equilibrium measurements.<sup>1,2</sup> Provided there is a significant change in the rate of adsorption when a monolayer is adsorbed, a measurement of gas adsorption kinetics will lead to an independent determination of the surface area of a solid. It appears that no detailed experimental study of adsorption in the multilayer region has been published. We wish to report here the observations on two systems for which the specific rate of