Letters to the Editor

THIS 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 800 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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December 7, 1950

In 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, 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 $B^1Π_u$ state (amongst others) may be depopulated by collisions with oxygen ground-state molecules ($X^1Σ_g^+$) with the formation of two nitric oxide molecules, one in its ground state ($XΠ_u$) and the other in any of the vibrational levels of the excited states $A, B, C, D, E$.

This mechanism may be represented by the equation

$$N_2(B^1Π_u) + O_2(X^1Σ_g^+) \rightarrow NO(XΠ_u) + NO(CΣ_g^+) + NO(DΣ_g^+) + NO(EΣ_g^+)$$

Such a nonradiative depopulation of $N_2(B^1Π_u)$ and the consequent formation of NO (excited) would cause a diminution in the intensity of bands of the first positive system with the consequent appearance of bands of the NO systems. This reaction, involving as it does, redistribution both of particles and excitation, is very difficult to analyze by quantum mechanics. However, as has been observed in the quantum-mechanical treatment of similar more simple processes 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 vibrational sequences of the first positive system which will be weakened by the appearance of the indicated vibrational sequences of the nitric oxide systems.

<table>
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<tr>
<th>$N_2$</th>
<th>$AΣ_g^+$</th>
<th>$BΠ_u$</th>
<th>$No$</th>
<th>$CΣ_g^+$</th>
<th>$DΣ_g^+$</th>
<th>$EΣ_g^+$</th>
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Dipole Moment and Electric Quadrupole Effects in HNCO and HNCS

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November 24, 1950

Interaction 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, $a_q$, for each of these molecules has been determined from the splitting of the $0_a^+ - 1_a^+$ transition of HNCO at 21,981.7 MHz and the $1_{1,1} - 2_{2,1}$ transition of HNCS at 23,499.5 MHz.
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 \( \delta Q \). Accurate frequency measurements were made on an oscilloscope. To resolve lines 0.33 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 HNCS.

Figures 1 and 2 compare the observed hyperfine structure of HNCO and HNCS with the theoretical patterns expected on the basis of \( \delta Q \) equal to \( +2.00 \pm 0.05 \) Mc for HNCO and \( +1.2 \pm 0.2 \) Mc for HNCS.

Table I. \( N^6 \) nuclear quadrupole coupling in cyanides and isocyanates.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( \delta Q ) (Mc/sec)</th>
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<tr>
<td>HCN</td>
<td>-4.58^a</td>
</tr>
<tr>
<td>CHC≡N</td>
<td>-4.67^b</td>
</tr>
<tr>
<td>CIC≡N</td>
<td>-3.67^c</td>
</tr>
<tr>
<td>BrC≡N</td>
<td>-3.83^d</td>
</tr>
<tr>
<td>HNCS</td>
<td>-3.80^e</td>
</tr>
<tr>
<td>HNCO</td>
<td>+2.2^f</td>
</tr>
</tbody>
</table>

^ b Smith, Ring, Smith, and Gordy, Phys. Rev. 74, 310 (1948) and Townes, Holden, and Merritt, Phys. Rev. 74, 1113 (1948).
^ c Present work.

Values of \( \delta Q \) 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 \(-C\equiv N\) 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 \(-C\equiv N\) bond which would be found if the molecules were HOCN and HSCN. Therefore, the alternative structures HNCO and HNCS are indicated.

More quantitative calculations of the coupling constants to be expected were made, following the theory of Townes and Dailey. Calculated values correctly predicted in each case the sign of \( \delta Q \), but they were only roughly in agreement with the observed magnitudes. Bead and Dailey have shown from the measured moments of inertia that HNCS is a reasonable structure but HSCN is not. Also, an investigation of the hydrogen stretching frequencies of HNCO and HNCS reported in an earlier paper 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 HNCS.

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 on 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 \( 0_{01} - 1_{01} \) transition of \( \text{HNCO}^\# \) and \( \text{DN}^\# \) in the ground vibrational states, and for \( \text{HNCO}^\# \) 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.

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

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December 12, 1930

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. 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 of two systems for which the specific rate of