

The Raman Spectrum of Arsenic Trichloride

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Citation: [The Journal of Chemical Physics](#) **3**, 754 (1935); doi: 10.1063/1.1749587

View online: <http://dx.doi.org/10.1063/1.1749587>

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LETTERS TO THE EDITOR

On the Disappearance of Hydrogen in the Presence of Positive Ions

Reference is made to a recent letter in this Journal by A. Schechter.¹ It is deemed advisable to discuss briefly some of the points raised therein in order to further clarify this field. Three distinct types of tubes or reaction chambers were used in our investigations: (1) A type which was completely immersed in liquid air,² this type being used both with and without a grid. The experimental results in these tests are therefore independent of the liquid-air level; (2) a tube in which the products were condensed in an attached chamber;³ (3) the tube shown in Fig. 1 with a distance of $7\frac{1}{2}$ cm between anode and collector, in which the reaction chamber was largely immersed in liquid air. This tube gave results similar in every way to those obtained by the other two types.

The liquid-air level, occluded gas, mean free path, possible dissociation of gas, etc., were recognized as factors to be considered and the apparatus was modified from time to time to study them. However, the authors were soon convinced that these factors were secondary in importance to the continued degassing of the hot ion source and the reduction or decomposition of the material composing the ion source. The Pyrex glass apparatus was thoroughly degassed by heating before the tests. The data reproduced in the plot, Fig. 2, of the Schechter letter, and published as curve 1, Fig. 3, were included in our article to show what actually happens in the experiments when a glow discharge is present within the tube. This discharge takes place under conditions similar to the well-known arc and is accompanied by a gaseous clean-up; it is a condition to be avoided in studies of collision experiments where the effect of positive ions as such are to be studied. This curve is therefore not representative of the results obtained. Reference may also be made to Schechter's

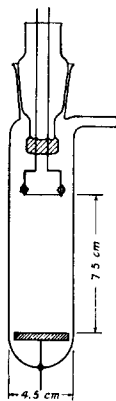


FIG. 1.

results, on the synthesis of ammonia from nitrogen and hydrogen mixtures. A brief account of the results obtained by one of us in a similar experiment⁴ indicated no measurable increase in the rate of decrease in the gas pressure under bombardment of K^+ ions from an iron potassium ammonia catalyst with speeds up to 330 volts. Furthermore in some of these experiments the disappearance of gas in the presence of the nitrogen-hydrogen mixture continued until the decrease in pressure was comparable to the amount of hydrogen present in the original mixture and then ceased, indicating a further reduction of the iron potassium oxides with the formation of water vapor. It was also observed after many hours of operation of the catalyst strip that it became entirely inactive as a clean-up agent in a nitrogen-hydrogen mixture, although the material was still a good emitter of positive ions.

After a further analysis of our experimental data in the light of Schechter's recent letter, we believe our previous conclusions hold although they are not in agreement with the conclusions arrived at by Schechter and his co-workers.

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R. A. NELSON

Bureau of Chemistry and Soils,
U. S. Department of Agriculture,
September 14, 1935.

¹ Schechter, J. Chem. Phys. 3, 433 (1935).

² Kunsman and Nelson, Phys. Rev. 40, 936 (1932).

³ Kunsman and Nelson, J. Chem. Phys. 2, 752 (1934).

⁴ Kunsman, J. Chem. Ed. 6, 629 (1929).

The Raman Spectrum of Arsenic Trichloride

In a recent paper¹ Brodskii and Sack apply Dennison's central force treatment² to the modes of vibration of $AsCl_3$ using the assignment $\omega_1=410$, $\omega_2=159$, $\omega_3=372$, $\omega_4=195$ cm^{-1} . Their calculated bond angle agrees well with electron diffraction results. It seems desirable to point out, however, that polarization experiments³ require another assignment, namely, ω_1 (symmetrical stretching) = 410 ($\rho=0.08$), ω_2 (symmetrical bending) = 195 ($\rho=0.42$), ω_3 (degenerate) = 372 ($\rho=0.86$), ω_4 (degenerate) = 159 ($\rho=0.86$), and that until the polarization theory or experimental results have been shown to be incorrect, one has no reliable criteria for making any other assignment.

On this basis one must still conclude with previous authors⁴ that central forces alone do not suffice for the treatment of the $AsCl_3$ type molecule.

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Gates Chemical Laboratory,
California Institute of Technology,
September 16, 1935.

¹ A. E. Brodskii and A. M. Sack, J. Chem. Phys. 3, 449 (1935).

² D. M. Dennison, Phil. Mag. 1, 195 (1926).

³ J. Cabannes and A. Rousset, Comptes rendus 194, 79 (1931).

⁴ K. W. F. Kohlrausch, *Der Smekal-Raman-Effekt* (Springer, Berlin, 1931); Don M. Yost and J. E. Sherborne, J. Chem. Phys. 2, 125 (1934); Don M. Yost and T. F. Anderson, *ibid.* 2, 624 (1934); J. B. Howard and E. B. Wilson, Jr., *ibid.* 2, 630 (1934).