longer be present in the new form, the type of the quantities has not changed substantially in spite of the different starting point. What has changed, however, is their conceptional arrangement.

The advantage of the new concept can be chiefly found in the fact that the abstractness and difficulty [20–22] of the energetic theory of heat and its extended formalism will disappear.

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Viscosity of Ammonia and its Mixtures with Noble Gases in an Electric Field

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The component η_3 of the viscosity of ammonia increases in an electric field. The effect depends on E^2/p and tends to a saturation value close to that found from measurements in a magnetic field. In ammonia-helium mixtures the saturation value of the effect decreases and becomes negative at an ammonia concentration of about 40%.

The viscosity of NH_3, ND_3 and mixtures of NH_3 with helium and argon have been measured in a static, homogeneous, external electric field with methods described elsewhere for other polar gases [1–3]. Ammonia is presented separately because of the very peculiar properties arising from molecular inversion. A consequence of inversion is that the effect depends on field intensity E and pressure p in a very different way from the other polar gases of symmetric top molecules, where it behaves as a function of the ratio E/p.

The component η_3 of viscosity [4] was measured by means of a capillary bridge which was brought out of balance by applying the electric field to two opposite branches, thereby altering their Poiseuille resistance [1]. An Atlas MMM membrane micromanometer was used to read the small pressure difference caused by such unbalance. The main results are the following:

a) the viscosity increases in an electric field (this is in contrast with all other gases studied so far, whose viscosity decreases in an external field, but in agreement with the behaviour of ammonia in a magnetic field [5]);

b) the effect is a function of E^2/p in the pressure range studied (1.3 to 75 Torr for NH_3, 1.2 to 4.4 Torr for ND_3), in agreement with theory [6].

For NH_3, where saturation cannot be reached because of the high fields required, it is possible nevertheless to estimate the saturation value to be .00032, in surprisingly good agreement with the value found by KORVING in a magnetic field [5]. For ND_3, on the other hand, it was possible to measure quite precisely the saturation value, which is .00022, i. e. considerably smaller. The reason why the measurements are easier for heavy ammonia is that the fields required are proportional to the square root of the inversion frequency, which is 23.8 GHz in NH_3 and only 1.6 GHz in ND_3 [7].

The experimental points are shown in Fig. 1, where theoretical curves [6] are also plotted for comparison. Points corresponding to different pressures all fall on the same curve for each species. Since in the magnetic case the situation is much simpler and the relevant cross sections can be extracted directly from the experiments without relying too much on theoretical considerations, the average cross section of 133 Å^2 obtained by KORVING [5] has been used in drawing the theoretical curves. The curves are normalized to the saturation value. The agreement in the field values is good, indicating that the same collision processes are important in the magnetic and the electric problem and also that

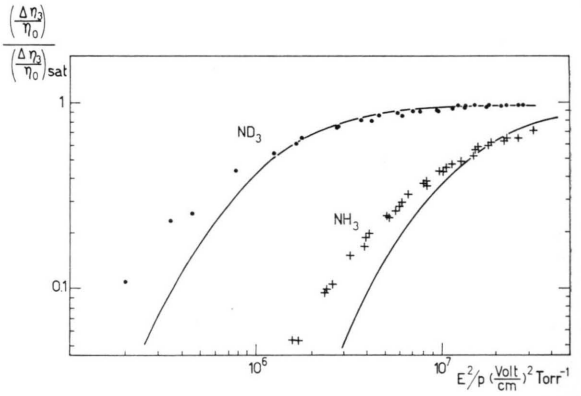

Fig. 1. $\Delta\eta_3/\eta_0$ vs. E^2/p for NH_3 and ND_3. The curves refer to the theory given in Ref. [6].

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the same cross sections can be ascribed to both isotopic species. The disagreement in the shapes is due to an oversimplification of the theory discussed at length in Refs. [2, 6]. The smaller effect in ND_3 can perhaps be ascribed to an increased importance of the negative contribution arising from the term $[\boldsymbol{J}]^{(2)}$ [5, 6]. This contribution is strictly connected with energetically inelastic collisions [8], and strongly quenched in ammonia where such collisions are rare due to the wide spacing of the energy levels [6]. In ND_3 the spacing is smaller and correspondingly the contribution of $[\boldsymbol{J}]^{(2)}$ may be larger.

In Fig. 2 the effect is reported vs. E^2/p for NH_3-He mixtures of several different concentrations. Two double logarithmic plots appear, referring to positive and

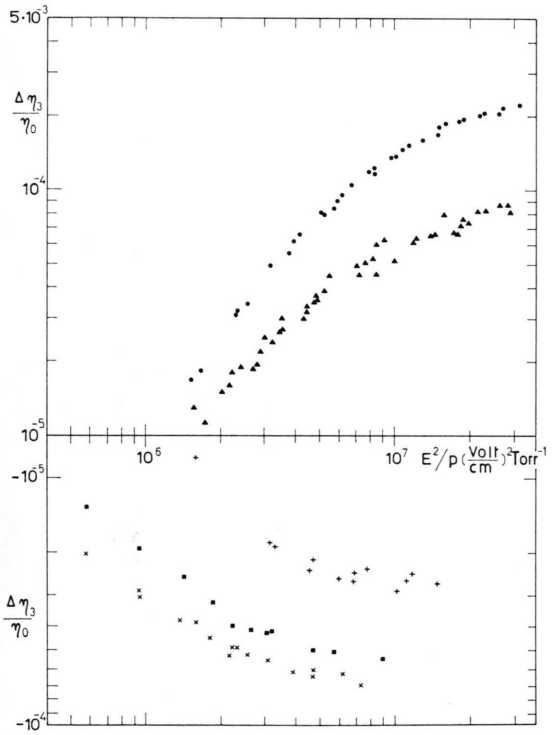

Fig. 2. $\Delta\eta_3/\eta_0$ vs. E^2/p for NH_3 and NH_3-He mixtures. ●: pure ammonia; ▲: $x_{NH_3}=.60$; +: $x_{NH_3}=.31$; ■: $x_{NH_3}=.20$; ×: $x_{NH_3}=.11$.

negative effects respectively, because the viscosity decreases in the field for mixtures with low ammonia content. The effect at saturation and $(E^2/p)_{1/2}$ are reported in Fig. 3 as a function of concentration. The saturation value can be seen to change sign at a concentration just below 40% of ammonia. This can be ascribed to the increased relative importance, at low ammonia concentrations, of the energetically inelastic collisions and of the negative contribution of the term

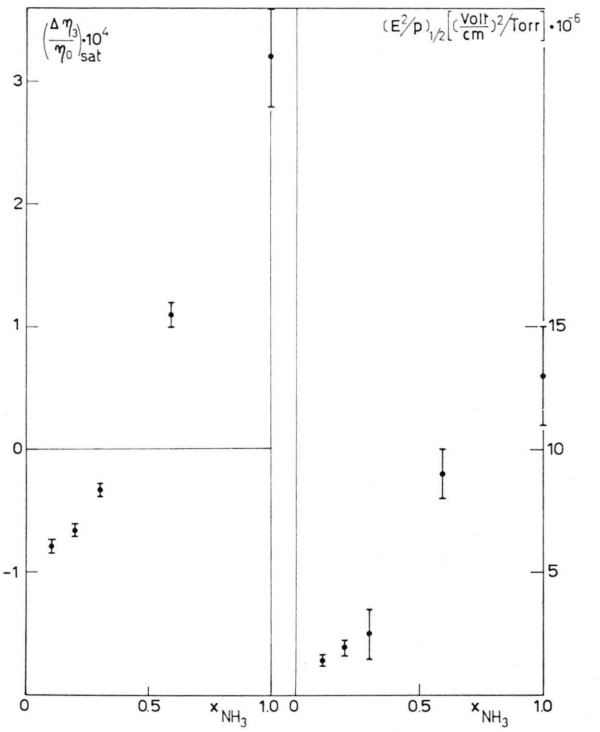

Fig. 3. $(\Delta\eta_3/\eta_0)_{sat}$ and $(E^2/p)_{1/2}$ vs. the ammonia concentration x_{NH_3}.

$[\boldsymbol{J}]^{(2)}$, and maybe also to the decreased importance of the collisions without an inverse which cause the term $\boldsymbol{J}[\boldsymbol{W}]^{(2)}$ to exist (the latter being presumably connected with the dipole-dipole interaction). At the same time, $(E^2/p)_{1/2}$ becomes very small at low ammonia concentrations, because of the smallness of the NH_3-He reorientation cross section. More interesting, the points do not fall on a straight line: this can again be interpreted as corresponding to the presence of two terms (see below, however).

A few measurements have also been performed in NH_3-Ar mixtures, indicating again a change in sign of the effect when the ammonia concentration is decreased below about 40%. Electrical breakdown prevented a thorough study of these mixtures.

A comparison of the present experiments with the thermal conductivity results of DE GROOT et al. [9] shows a very large difference in $(E^2/p)_{1/2}$: this quantity for ND_3 equals about $1.2\cdot10^7$ V²/cm²·Torr for the thermal conductivity, and only $1.2\cdot10^6$ V²/cm²·Torr for the viscosity, exactly a factor of 10 less. This is to be contrasted to CH_3CN, where the situation is reversed [2].

For both gases, the positive effect saturates earlier. The latter seems to be a rather general fact and can be explained as follows [2]. The positive effects are due to terms containing only one $\boldsymbol{J}$ (such as $\boldsymbol{J}\,\boldsymbol{W}$ for λ or

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$\boldsymbol{J}[\boldsymbol{W}]^{(2)}$ for η). Such terms are rather insensitive to purely reorientation collisions which are of paramount importance in strongly polar gases, because $\boldsymbol{J}$ is very nearly a summational invariant due to angular momentum conservation; hence the corresponding cross sections are much smaller than the reorientation cross section. On the other hand, the negative effects are due to terms containing $[\boldsymbol{J}]^{(2)}$ ($[\boldsymbol{J}]^{(2)}\boldsymbol{W}$ for λ, simply $[\boldsymbol{J}]^{(2)}$ for η) and $[\boldsymbol{J}]^{(2)}$ is very sensitive to reorientation, so that the full reorientation cross section appears in this case, which implies short mean free paths and late saturation. The large cross section connected to λ also explains why the thermal conductivity of ND_3 goes over to normal behaviour at relatively low pressures [9].

The behaviour of $(E^2/p)_{1/2}$ in the mixtures, which does not seem to fit well in this picture, is not to be taken as a serious argument against it, because this quantity is of limited significance when two different contributions are present.

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Photoablösung von Elektronen bei Si^- und NH_2^-

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Mit einer bei früheren Messungen [1] erprobten Apparatur wurden die Untersuchungen über die Photoablösung von Elektronen bei stabilen negativen Ionen fortgesetzt. Für Photonenenergien zwischen 0,5 eV und 3,5 eV wurden Größe und Energieabhängigkeit des Wirkungsquerschnittes bei Si^- und NH_2^- bestimmt.

Si^--Ionen wurden aus $SiCl_4$ mit einer Stromstärke von 10^{-9} A erzeugt. Bei Si^- hat der gemessene Wirkungsquerschnitt (Abb. 1) eine niederenergetische Schwelle bei einer korrigierten Photonenenergie von $(0{,}56 \pm 0{,}04)$ eV und einen zweiten Anstieg bei etwa 1,3 eV.

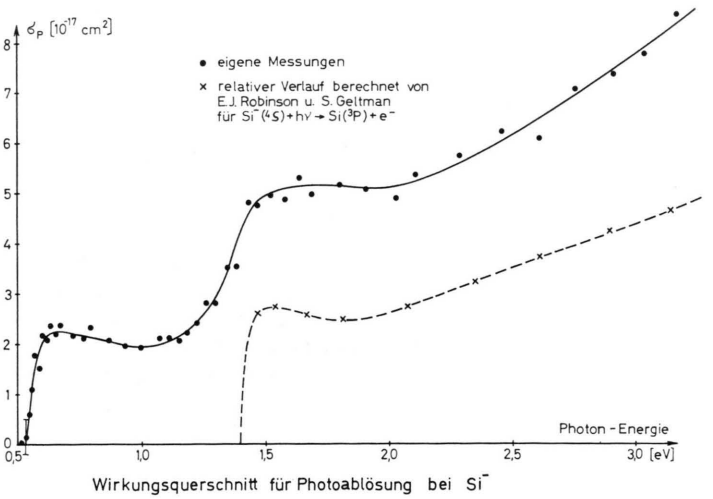
Dieser Verlauf deutet darauf hin, daß der bisher nur theoretisch vorhergesagte [2, 3] metastabile ^2D-Zustand in dem hier erzeugten Si^--Strahl stark bevölkert ist und gegenüber dem ^3P-Grundzustand des neutralen Si eine Bindungsenergie von 0,56 eV hat (Abb. 2).

Der zweite Anstieg des Wirkungsquerschnittes kann durch die folgenden zwei Übergänge erzeugt werden:

1. Die Photoablösung vom ^4S-Grundzustand des negativen Ions zum ^3P-Grundzustand des Atoms. Die erforderliche Minimalenergie sollte nach theoretischen Vorhersagen [2, 3] etwa 1,4 eV betragen.

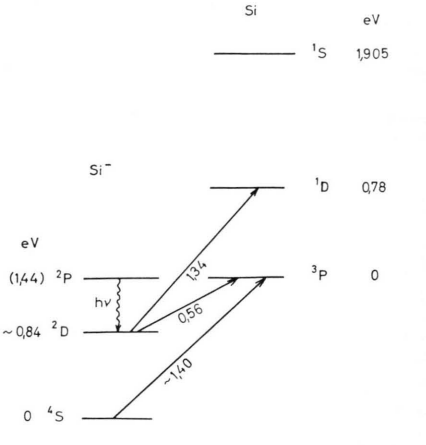
2. Wenn die obige Annahme eines metastabilen ^2D-Zustandes des negativen Ions zutrifft, so sollte bei 1,34 eV minimaler Photonenenergie die Photoablösung von diesem Zustand zum ersten angeregten ^1D-Zustand des Atoms einsetzen.

Die bisher erzielte Meßgenauigkeit ermöglicht noch keine Entscheidung, ob oder wie stark diese beiden



Wirkungsquerschnitt für Photoablösung bei Si^-

Abb. 1.



Niveauschemata von Si^- und Si
Erlaubte Übergänge bei Photoablösung
(Energien in eV)

Abb. 2.

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