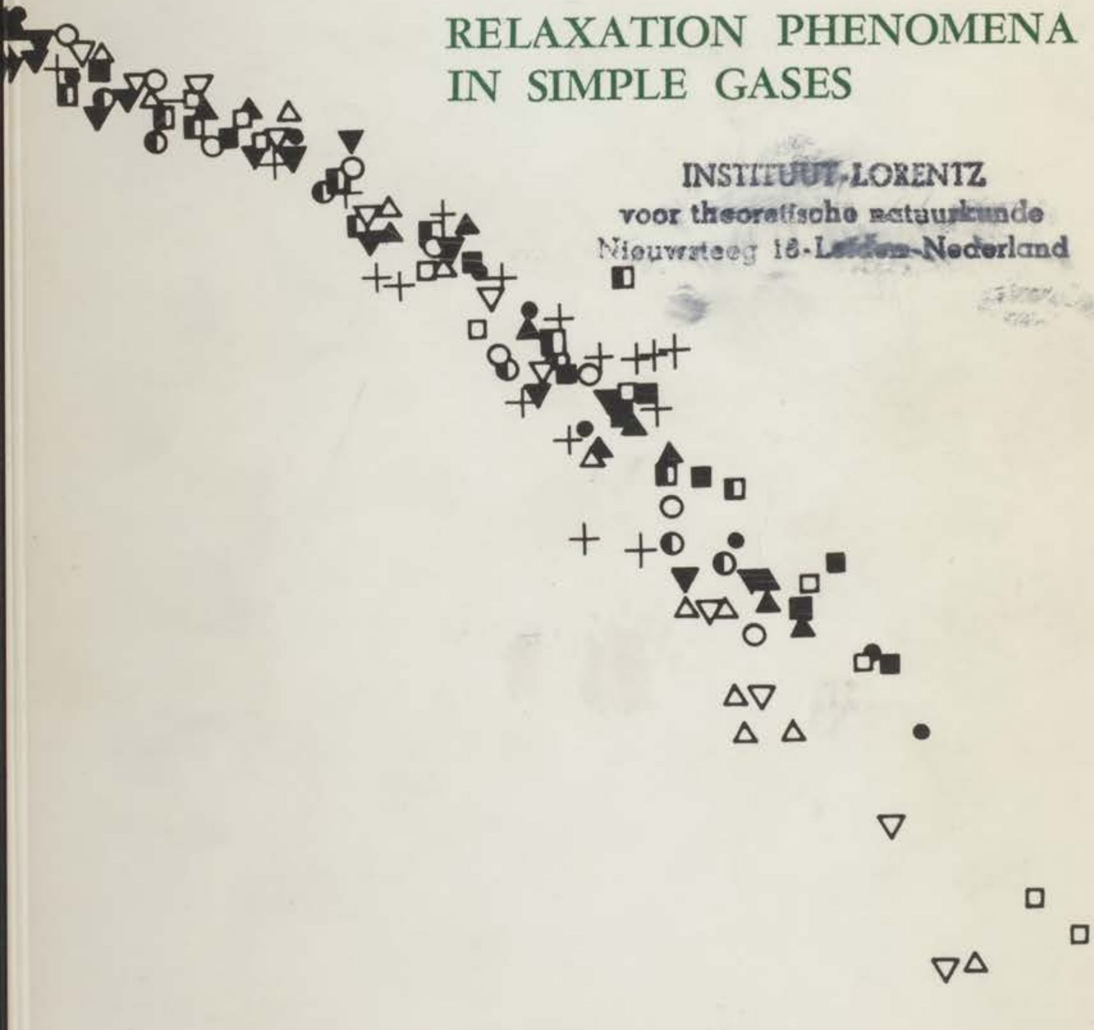
RELAXATION PHENOMENA IN SIMPLE GASES



G. J. PRANGSMA

RELAXATION PHENOMENA IN SIMPLE GASES

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN
DE WISKUNDE EN NATUURWETENSCHAPPEN AAN
DE RIJKSUNIVERSITEIT VAN LEIDEN, OP GEZAG VAN
DE RECTOR MAGNIFICUS DR. W. R. O. GOSLINGS,
HOOGLERAAR IN DE FACULTEIT DER GENEESKUNDE,
TEN OVERSTAAN VAN EEN COMMISSIE UIT
DE SENAAT TE VERDEDIGEN OP WOENSDAG
27 OKTOBER 1971 TE KLOKKE 16.15 UUR

DOOR

GEERT JOHAN PRANGSMA
geboren te Eindhoven in 1941

1971
Drukkerij J. H. Pasmans - 's-Gravenhage

Promotor: Prof. Dr. J.J.M. Beenakker

Dit proefschrift is tot stand gekomen mede onder leiding van Dr. H.F.P. Knaap

STELLINGEN

I

In de theoretische beschrijving van geluidsvoortplanting in zeer verdunde edelgasmengsels komt Goldman tot andere resultaten dan Bramlette en Huang. Voor een goede onderlinge vergelijking van deze theorieën is een numeriek onderzoek naar de invloed van de toegepaste benaderingen gewenst.

E.B. Goldman, J.Acoust.Soc.Amer. 44 (1968) 708.
T.T. Bramlette and A.B. Huang, Phys. Fluids 14 (1971) 34.

II

Dalgarno, Henry en Roberts concluderen ten onrechte, dat de uit de "distorted wave" methode verkregen resultaten voor rotatie-excitatie van H_2-moleculen door H-atomen in overeenstemming zijn met de resultaten van de "modified wave number" benadering.

A. Dalgarno, R.J.W. Henry and C.S. Roberts, Proc.Phys. Soc. 88 (1966) 611.

III

McCourt en Moraal geven in een vergelijking van theorie en experiment voor het "thermomagnetic torque effect" de voorkeur aan het gebruik van approximatieve theoretische relaties boven het gebruik van rechtstreeks gemeten gegevens. Het bezwaar, dat zij aanvoeren tegen deze directe gegevens, is evenzeer aan te voeren tegen de door hen gebruikte benaderingsformule.

F.R. McCourt and H. Moraal, Chem.Phys. Letters 9 (1971) 35.

IV

Het gebruik van een isotrope exchangewisselwerking in de beschrijving van de thermische en magnetische eigenschappen van ceriummagnesiumnitraat is niet realistisch.

V

De bewering van Barker, Bobetic en Pompe, dat zij de Boltzmannvergelijking testen door transporteigenschappen van Ar te berekenen op basis van een uit andere bron verkregen interactiepotentiaal, is onjuist.

J.A. Barker, M.V. Bobetic and A. Pompe, Mol.Phys. 20 (1971) 347.

VI

De coördinaten van het zuurstofatoom in een 4,4'-dichloorbenzofenonkristal, zoals gegeven door Toussaint, zijn onjuist.

J. Toussaint, abstract in: Structure Reports for 1947-1948 Vol. 11 (1951) 676.
Structure Reports for 1952 Vol. 16 (1959) 516.

VII

De energierelaxatie van para H_2 is in botsingen met para H_2 langzamer dan in botsingen met ortho H_2. De verklaring die Crawford hiervoor geeft, is niet overtuigend.

O.H. Crawford, Chem.Phys. Letters 6 (1970) 409.

VIII

De serviceverlening van een rekencentrum kan zonder personeelsuitbreiding verruimd worden door gebruik te maken van de informatieverwerkingscapaciteit van de aanwezige computerinstallatie.

IX

Tegen de wijze, waarop Rijkswaterstaat de fosfaatconcentratie in het Brielse Meer wil reguleren, kunnen op biologische gronden overwegende bezwaren worden ingebracht.

X

De conclusies die Bauer en Kosche trekken uit een vergelijking van acoustisch gemeten botsingsgetallen voor rotatie-overgangen, zijn aanvechtbaar.

H.-J. Bauer and H. Kosche, Acustica 17 (1966) 96.

XI

Bij sommige artikelen over natuurkundige onderwerpen wordt aan het slot de voor de berekeningen benodigde computertijd opgegeven. Zonder voldoende nadere informatie is de waarde van een dergelijke opgave zeer beperkt.

XII

Kerkeraden kunnen veel van hun organisatorische problemen verminderen door de gemeenschapsbeleving onder hun geloofsgenoten op meer dan incidentele schaal te stimuleren. Huisbezoek door een vrijgestelde geestelijke is hiervoor niet het eerst-aangewezen middel.

XIII

Acoustische metingen zijn translatie-invariant.

Dit proefschrift, Hoofdstuk I : K.O.L. kamers 206 en 01.17
Hoofdstuk II : K.O.L. kamers 206 en 10
Hoofdstuk III : K.O.L. kamers 206 en 10
Hoofdstuk V : K.O.L. kamers 206, 01.17 en 10.

Leiden, 27 oktober 1971
G.J. Prangsma.

Aan mijn ouders

Aan Angelique

Het in dit proefschrift beschreven onderzoek werd verricht als onderdeel van het programma van de Werkgemeenschap voor Molecuulfysica van de Stichting voor Fundamenteel Onderzoek der Materie (F.O.M.) met financiele steun van de Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (Z.W.O.).

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CHAPTER IV. A TEST OF APPROXIMATE RELATIONS BETWEEN EFFECTIVE CROSS SECTIONS

Parts of this thesis appeared in Physica:
Chapter I: Physica 48 (1970) 433.
Chapter V: Physica 50 (1970) 323.

PREFACE

In this thesis experiments on a number of relaxation phenomena in dilute gases are reported. Using acoustical techniques, two types of relaxation processes are investigated in detail.

In polyatomic gases the so-called rotational-translational relaxation can be studied. In such gases one considers the rate at which the thermal equilibrium between translational and rotational degrees of freedom is established by the molecular collisions. The gases HD and ortho H_2 have been investigated experimentally to complement earlier Leiden research on rotational relaxation in the hydrogen isotopes. For both gases the temperature range was chosen in such a way that only the two lowest rotational levels (J = 0 and J = 1 in HD and J = 1 and J = 3 in oH_2) were appreciably occupied. Such a situation can be described with a single relaxation time. From the measured relaxation times effective cross sections have been calculated. It is found that the effective cross section for HD (Chapter I) is nearly a constant over the temperature range from 20 to 42 K. Similarly the effective cross section describing the relaxation of HD due to collisions with He is found to be nearly temperature independent.

For a reliably study of the relaxation time for the $J = 1 \rightleftarrows 3$ transition in hydrogen, high purity oH_2 must be available. An apparatus has been constructed, which enriches the oH_2 content of normal H_2 (75% oH_2). This apparatus is described in the first section of Chapter II. From sound absorption measurements in hydrogen with an ortho-concentration of 96% the rotational relaxation time for the $J = 1 \rightleftarrows 3$ transition has been obtained.

At the end of Chapter II the results for rotational relaxation in hydrogenic systems obtained so far in the Kamerlingh Onnes Laboratory are discussed. Special attention is given to comparison of experimental data with theory, both the usefulness and the limitations of the experimental data in such a comparison. It is found that the temperature dependence of the rotational relaxation time is mainly determined by the initial slope of the excitation cross section as a function of energy. The consequences of this observation for concluding uniquely on the exact form of the molecular interaction, are discussed.

In the hydrogen isotopes one has the possibility to perform measurements in a two level system due to the large energy difference between the levels. For most other gases (N_2, CO, etc.) many rotational levels are occupied at experimentally accessible conditions. Under such conditions acoustical techniques cannot distinguish between separate transitions. In the sound absorption one then measures an average over a large number of processes. For the same reason adequate theoretical calculations of excitation cross sections are not yet within reach. It is, however, possible in such cases to derive approximate theoretical relations between different effective cross sections using only the structure of the non-spherical part of the interaction potential.

To provide the experimental data for a test of such relations, rotational relaxation times have been measured for a number of gases. The results are reported in Chapter III and will be used in Chapter IV for a test of some of these relations.

A different type of relaxation process occurs in mixtures of gases with significantly different masses. For an investigation of this phenomenon, occurring when the energy exchange between colliding molecules is obstructed by a large mass difference, mixtures of HD with Ne seem at first glance well-suited. The large amount of rotational energy released upon de-excitation of HD in a collision with Ne cannot be transferred to the heavier Ne atom. It can be shown that this phenomenon alters the rotational relaxation time up to 20%. In the measurements reported in Chapter I, the experimental accuracy is found to be insufficient for a study of this phenomenon in HD-Ne mixtures, due to the large classical absorption.

The effect of such a large mass difference can, however, also be studied under quite different conditions. In a suitably chosen noble gas mixture one can investigate with acoustical techniques the time scale at which the thermal equilibrium between the translational degrees of freedom of the components is established. For such mixtures this time scale can be as great as several times the period between successive collisions. This results in the breakdown of the hydrodynamic description of sound propagation at lower frequencies than is the case for pure gases. This has been experimentally verified for He-Ar mixtures (Chapter V). A comparison with the theory of Goldman shows that further theoretical investigation of such phenomena is needed.

CHAPTER I

ROTATIONAL RELAXATION OF HD BELOW 40 K

Synopsis

Sound absorption measurements are reported for the systems HD, HD–He and HD–Ne at a number of temperatures between 20.4 and 42.6 K. For HD the times for relaxation between the rotational and the translational degrees of freedom through collisions with HD and through collisions with He are derived. For HD–Ne the present method turns out to be inadequate to determine rotational relaxation times. For HD–HD collisions it is found that the collision number, $Z_{\rm rot}$, has a temperature - independent value of about 10, whereas for HD–He collisions $Z_{\rm rot}$ is about 17.

1. *Introduction.* In the investigation of gas dynamics ultrasonic absorption and dispersion provide us with an important tool to obtain experimental information on various processes that can occur upon collisions in the gas – *e.g.*, vibrational and rotational excitation of polyatomic molecules. Especially in the study of inelastic collisions sound absorption measurements give direct information on relaxation times for energy exchange and thus on the collision cross sections for the process under investigation. In the present paper we shall confine our attention to the special case of a two-level rigid rotator, examples of which can be found in the hydrogen isotopes at suitably chosen temperatures. The restriction to a two-level system is suggested by the fact that only in such systems can the relaxation process be rigorously described with one single relaxation time. In such a case the interpretation of the experimental data in terms of a relaxation time is unique and without special difficulties.

According to Herzfeld and Litovitz[1]) the relaxation process in a mixture of a two-level gas, *e.g.* HD, and a noble gas can again be described with a single relaxation time, $\tau_{\rm mix}$. The reciprocal of this relaxation time is given by

$$\frac{1}{\tau_{\rm mix}} = \frac{1 - x_{\rm NG}}{\tau_{\rm HD-HD}} + \frac{x_{\rm NG}}{\tau_{\rm HD-NG}}. \qquad (1)$$

In this equation $\tau_{\rm HD-HD}$ is the relaxation time for HD through collisions with HD and $\tau_{\rm HD-NG}$ the relaxation time for HD through collisions with the noble gas. $x_{\rm NG}$ is the mole fraction of noble gas in the mixture. Eq. (1) applies for the isochoric-isothermal relaxation times for the process studied.

For two of the homonuclear hydrogen molecules – para H_2 and ortho D_2 – measurements have been reported by Sluijter *et al.*[2,3]) and for mixtures of

pH_2 and oD_2 with noble gases by Jonkman *et al.*[4,5]). For the heteronuclear HD molecule rotational relaxation has been studied by Sluijter[2]) at temperatures where more than two levels are appreciably occupied.

It is the purpose of this paper to present experimental data for the rotational relaxation time of HD at temperatures below about 40 K. In this temperature range only the rotational levels $J = 0$ and $J = 1$ are occupied, so that a single relaxation time process results. We shall also report sound absorption measurements in mixtures of HD with He and Ne. From the experimental data for the system HD–He rotational relaxation times for HD can be obtained and compared with eq. (1). For the HD–Ne mixtures, however, it is found that sound absorption is not a reliable means to study rotational relaxation.

Due to the loaded sphere character of HD and to the smaller energy gap between the rotational levels than in the homonuclear hydrogen isotopes, the relaxation time of HD is much shorter than in those isotopes (*cf.* Sluijter[2])). Therefore the maximum of the relaxation absorption will occur at much higher values of the frequency-to-pressure ratio than in H_2 and D_2. This implies that this maximum occurs at f/p values where the absorption due to friction and heat conduction starts to deviate from the well-known Navier–Stokes description. In view of the difficulties involved in a theoretical description of the situation in this regime we prefer to limit our measurements to relatively low f/p values. In section 3 the evaluation of the relaxation time from the experimental data in such situations is described. The experimental setup is outlined in section 2, while section 4 gives a discussion of the results.

2. *Experimental setup*. Sound absorption can be measured by observing the exponential decay of the sound wave intensity as a function of the distance between transmitter and receiver. The same apparatus and temperature control – to reach temperatures between 20 and 40 K – were used as for the earlier research on rotational relaxation of the homonuclear hydrogen isotopes. A detailed description can be found in refs. 4 and 5. To improve the sensitivity of the setup at the necessarily higher f/p values the following changes were made:

a. A power amplifier was constructed which gives an output voltage of more than 50 V (peak value) over a frequency range from 50 kHz to 600 kHz irrespective of the (capacitive) load.

b. The brass backplate in the condensor-type transmitter was replaced with an anodized aluminum backplate following a suggestion of Haebel[6]). As a second condensor plate a 5 μ aluminum foil is used. The aluminum-oxyde dielectricum shows a high breakdown voltage and retains its properties down to 20 K or lower.

c. A new microphone preamplifier was built which, with an amplification factor of more than 200, has a very low noise level and is independent of the frequency in the range 50–600 kHz.

d. The connection between receiver microphone and preamplifier was changed to obtain a better mechanical stiffness and stability. As a result of these measures the spurious electrical pickup by the detector circuit at transmitting frequencies from 100 kHz to 350 kHz was reduced from about 2.5 dB to less than 0.6 dB compared to the (thermal) noise of the receiver.

The HD was prepared through hydrolysis of lithiumaluminumhydride with heavy water in the reaction:

$$\mathrm{LiAlH_4} + 4\,\mathrm{D_2O} \rightarrow \mathrm{LiOD} + \mathrm{Al(OD)_3} + 4\,\mathrm{HD}.$$

The gas obtained in this way was purified by rectification; an isotopic purity of better than 99% was reached.

3. *Evaluation of relaxation times.* From irreversible thermodynamics it is known than an expression for the sound absorption in a relaxing gas (-mixture) can be derived starting from the conservation laws for mass, momentum and energy. In 1943 Meixner[7]) outlined a formalism that generates an equation for the (complex) wave vector, $\boldsymbol{K}$, of the soundwave as a function of the sound frequency, ω. From the imaginary part of this wave vector the sound absorption coefficient, α, is obtained. For the case of a binary mixture of a relaxing gas and a noble gas the following expression for α can be derived by solving Meixner's equation for $\boldsymbol{K}$ and taking the imaginary part of the solution (*cf.* Jonkman[8])):

$$\frac{\alpha}{\omega} = \frac{\alpha_{\mathrm{K}}}{\omega} + \frac{\gamma_\infty}{2V_\infty\gamma_0}\,A\,\frac{\omega\tau_{pS}}{1+\omega^2\tau_{pS}^2}\left[1 - \frac{\gamma_\infty A}{2\gamma_0(1+\omega^2\tau_{pS}^2)}\right.$$
$$+\frac{1}{\tau_{pS}p\gamma_\infty}\left\{2\eta - \frac{(5-\gamma_\infty)(\gamma_\infty-1)}{2\gamma_\infty}\,\frac{M\kappa}{R} + \frac{\gamma_0-1}{\gamma_\infty-1}\,\frac{1-\omega^2\tau_{pS}^2}{1+\omega^2\tau_{pS}^2}\,\rho\mathscr{D}'\right.$$
$$\left.\left. + x_{\mathrm{NG}}(1-x_{\mathrm{NG}})\,\gamma_\infty\tilde{M}^2\rho\mathscr{D}\left(\tfrac{1}{2} + \frac{3-\gamma_\infty}{\gamma_\infty}\,\frac{\alpha_T}{\tilde{M}}\right)\right\}\right], \tag{2}$$

where α_{K} is the classical "Kohler" absorption given by

$$\frac{\alpha_{\mathrm{K}}p}{f^2} = \frac{2\pi^2}{\gamma_\infty V_\infty}\left[\tfrac{4}{3}\eta + \frac{(\gamma_\infty-1)^2}{\gamma_\infty}\,\frac{M\kappa}{R}\right.$$
$$\left. + x_{\mathrm{NG}}(1-x_{\mathrm{NG}})\,\gamma_\infty\tilde{M}^2\rho\mathscr{D}\left(1 - 2\,\frac{\gamma_\infty-1}{\gamma_\infty}\,\frac{\alpha_T}{\tilde{M}}\right)\right], \tag{3}$$

x_{NG} is the mole fraction noble gas, $\tilde{M} = (M_{\mathrm{NG}} - M_{\mathrm{HD}})/M$. $\mathscr{D}'$ is the coefficient describing the selfdiffusion of the relaxing gas in the presence of a noble gas. $\tau_{pS} = [(C_p - C')/C_p]\ \tau_{VT}$ with τ_{VT} the isochoric-isothermal relaxation time. $A = RC'/[C_V(C_p - C')]$ with C' the rotational contribution to the specific heat. The other symbols have their usual meaning. In the derivation of eq. (2) terms in A^2, A/Z_{rot} and $1/Z^2_{\mathrm{rot}}$ have been neglected. The second term in the right-hand side of eq. (2) is the so-called relaxation absorption.

Usually acoustical relaxation times are determined from sound absorption measurements over a f/p range which includes the whole relaxation absorption curve and f/p values where the internal degrees of freedom fail to be excited and where thus the "Kohler" absorption is measured directly. In this way the following experimental checks are obtained on the results:

a. The direct determination of the "Kohler" absorption at high f/p values where the relaxation process no longer contributes to the sound absorption, gives a check on the calculations for $\alpha_{\mathrm{K}}p/f^2$.

b. By studying the shape of the relaxation absorption curve as a function of f/p one may check whether the process under investigation is really a single relaxation time process and whether correct values are inserted for the rotational specific heat, C' (*cf.* eq. (2); see also *e.g.* Jonkman[4])).

These experimental checks, however, cannot be performed for the systems studied in this paper for the following reason. As the relaxation time of HD is only about ten times the average time between two successive elastic collisions, the maximum of the relaxation absorption will occur at such high values of the frequency-to-pressure ratio, that the "Kohler"-absorption, $\alpha_{\mathrm{K}}p/f^2$, is no longer independent of f/p (*cf.* eq. (3)). Therefore it is impossible either to obtain an experimental value for $\alpha_{\mathrm{K}}p/f^2$ or to test the shape of the relaxation absorption curve. Thus the experiments must be restricted to relatively low f/p values where terms in $(\omega\tau_{pS})^2$ can be neglected in eq. (2). This implies that actually the low-frequency value of the volume viscosity is determined, which can be expressed in terms of the isochoric-isothermal relaxation time, τ_{VT} (*cf.* De Groot and Mazur[9])). Neglecting terms in $(\omega\tau_{pS})^2$ – in the experiments we took $\omega\tau_{pS} < 0.1$ – as well as terms in A^2 and A/Z_{rot}, eq. (2) can be rewritten as:

$$\frac{\alpha p}{f^2} = \frac{\alpha_{\mathrm{K}} p}{f^2} + \frac{2\pi^2 A}{V_0}\,\tau_{pS}\,p\,[1 + \text{correction}], \tag{4}$$

with

$$\text{correction} = \frac{1}{\tau_{pS}\,p\,\gamma_\infty}\left\{2\eta - \frac{(5-\gamma_\infty)(\gamma_\infty - 1)}{2\gamma_\infty}\,\frac{M\kappa}{R}\right.$$

$$\left. + \frac{\gamma_\infty - 1}{\gamma_\infty - 1}\,\rho\mathscr{D}' + x_{\mathrm{NG}}(1 - x_{\mathrm{NG}})\,\gamma_\infty \tilde{M}^2 \rho\mathscr{D}\left(\tfrac{1}{2} + \frac{3-\gamma_\infty}{\gamma_\infty}\,\frac{\alpha_T}{\tilde{M}}\right)\right\}. \tag{5}$$

Note that in this approximation $\alpha p/f^2$ is independent of f/p. The correction term is normally neglected, but for HD it can amount to a few percent and can no longer be neglected.

The evaluation of relaxation times from the experimental data is done in the following way. For a number of α values at various f/p values in the proper range (*i.e.* $\omega\tau_{pS} < 0.1$) the quantity $\alpha p/f^2$ is calculated. These values of $\alpha p/f^2$ are averaged to obtain $(\alpha p/f^2)_{\text{av}}$. Using theoretical expressions for the transport coefficients from the book of Hirschfelder *et al.*[10]) and using the quantummechanical collision integrals from the work of Munn *et al.*[11]), $\alpha_{\text{K}}p/f^2$ is calculated from eq. (3) and subtracted from $(\alpha p/f^2)_{\text{av}}$. With eq. (4) this gives a trial value for $\tau_{pS}p$ by omitting the correction. With this trial value the correction is computed. Successive approximations give the correct result for $\tau_{pS}p$, from which the quantity $\tau_{VT}p$ is calculated with

$$\tau_{VT}p = \frac{C_p}{C_p - C'}\,\tau_{pS}p.$$

For pure HD measurements were performed at a number of temperatures ranging from 20.4 to 42.6 K. At the highest temperatures the contribution of the $J = 2$ rotational level to the rotational specific heat is still so small that HD can be treated as a two-level system with one relaxation time. In table I the results for $(\alpha p/f^2)_{\text{av}}$, $\alpha_{\text{K}}p/f^2$ and $\tau_{VT}p$ are shown.

TABLE I

Results for the system HD

T	$\left(\frac{\alpha p}{f^2}\right)_{\text{av}}$	$\frac{\alpha_{\text{K}}p}{f^2}$	$\tau_{VT}p$
(K)	(atm/cm MHz^2)		(10^{-10} s atm)
20.4	0.0178	0.0110	2.1 ± 0.2
27.0	0.0260	0.0130	2.4 ± 0.2
32.1	0.0286	0.0143	2.4 ± 0.2
39.6	0.0330	0.0156	3.0 ± 0.2
39.9	0.0313	0.0157	2.7 ± 0.2
42.6	0.0328	0.0160	3.0 ± 0.2

In mixtures of HD with He and Ne measurements were performed at a number of temperatures and as a function of the mole fractions of the mixtures. The results are shown in table II and table III.

4. *Discussion of the results.* The procedure which had to be used to obtain rotational relaxation times from the sound absorption data (*cf.* section 3)

may under certain conditions lead to relatively large errors in the final results for $\tau_{VT}p$. Since the accuracy of $(\alpha p/f^2)_{\mathrm{av}}$ is about 3% whereas the

TABLE II

Results for the system HD–He

T	x_{He}	$\left(\frac{\alpha p}{f^2}\right)_{\mathrm{av}}$	$\frac{\alpha_K p}{f^2}$	$\tau_{VT}p$
(K)		(atm/cm MHz^2)		(10^{-10} s atm)
27.0	0.000	0.0260	0.0130	2.4 ± 0.2
	0.209	0.0293	0.0174	2.5 ± 0.3
	0.398	0.0318	0.0210	2.6 ± 0.3
	0.498	0.0368	0.0242	3.5 ± 0.5
32.1	0.000	0.0286	0.0143	2.4 ± 0.2
	0.268	0.0348	0.0201	3.0 ± 0.3
	0.416	0.0395	0.0235	3.4 ± 0.3
	0.503	0.0396	0.0257	3.3 ± 0.4
	0.667	0.0428	0.0299	4.0 ± 0.6
	0.668	0.0403	0.0299	3.2 ± 0.6
	0.762	0.0423	0.0325	4.0 ± 0.8
39.9	0.000	0.0313	0.0157	2.7 ± 0.2
	0.232	0.0382	0.0211	3.2 ± 0.3
	0.498	0.0436	0.0270	3.7 ± 0.4
	0.667	0.0454	0.0313	4.1 ± 0.6
	0.747	0.0463	0.0334	4.6 ± 0.8

TABLE III

Results for the system HD–Ne

T	x_{Ne}	$\left(\frac{\alpha p}{f^2}\right)_{\mathrm{av}}$	$\frac{\alpha_K p}{f^2}$	$\tau_{VT}p$
(K)		(atm/cm MHz^2)		(10^{-10} s atm)
32.1	0.000	0.0286	0.0143	2.4 ± 0.2
	0.306	0.112	0.088	(2.9 ± 0.8)
	0.415	0.142	0.099	(5.2 ± 2.8)
	0.594	0.130	0.109	(2.8 ± 0.9)
39.9	0.000	0.0313	0.0157	2.7 ± 0.2
	0.259	0.112	0.089	(2.7 ± 0.7)
	0.509	0.159	0.116	(7.6 ± 4.1)
	0.766	0.144	0.121	(4.0 ± 1.4)

theoretically calculated values for the "Kohler" absorption can be expected to be accurate within about 5% for the investigated systems, the relative error in the resulting relaxation absorption, and thus the relaxation time, rises above 20% when the "Kohler" absorption is more than 75% of the total absorption. This is the case for the investigated HD–Ne mixtures, as

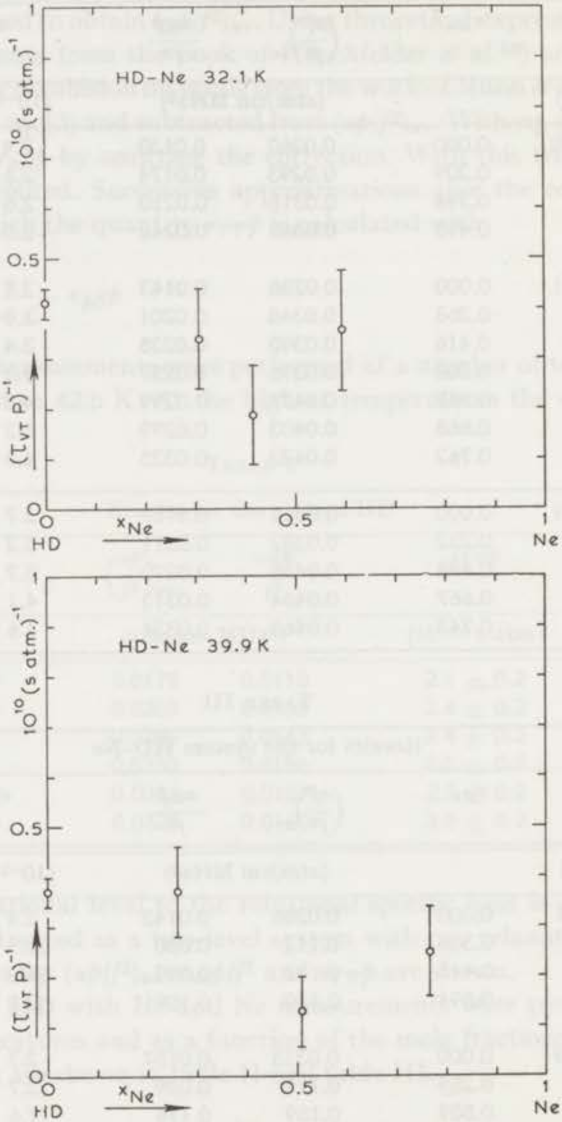

Fig. 1a

Fig. 1b

Fig. 1. $(\tau_{VT}p)^{-1}$ *vs.* x_{Ne} for the system HD–Ne.
a) 32.1 K; b) 39.9 K.

can be seen in table III. As indicated in figs. 1a and 1b, where $(\tau_{VT}p)^{-1}$ is is plotted *versus* the mole fraction Ne, the resulting relaxation times do not allow a reasonable comparison with eq. (1). It is clear that for such mixtures other techniques must be used, which allow a more direct determination of the relaxation time.

A comparison of the data for the system HD–He (*cf.* table II) with eq. (1) on the other hand shows that the expected linear relationship between reciprocal relaxation time and mole fraction is fairly well confirmed. In figs. 2a–c the data of table II are shown together with the line obtained from a least-squares fit of eq. (1) to the experimental points. The final results for $(\tau_{VT}p)_{\text{HD–HD}}$ and $(\tau_{VT}p)_{\text{HD–He}}$ as a function of temperature are given in table IV together with the collision number, Z_{rot}, defined as

$$Z_{\text{rot}} = \frac{\tau_{VT}}{\tau_c}.$$

TABLE IV

Results for HD–HD and HD–He rotational relaxation

System	T (K)	$\tau_{VT}p$ (10^{-10} s atm)	Z_{rot}
HD	20.4	2.1 ± 0.2	11.1
	27.0	2.4 ± 0.1	10.6
	32.1	2.5 ± 0.1	10.4
	39.6	3.0 ± 0.2	11.2
	39.9	2.7 ± 0.1	10.1
	42.6	3.0 ± 0.2	10.6
HD–He	27.0	4.6 ± 1.1	17.3
	32.1	4.8 ± 0.3	16.3
	39.9	5.9 ± 0.2	18.1

The average time between two successive elastic collisions, τ_c, is given by

$$(\tau_c p)^{-1} = \pi\sigma^2\left(\frac{8}{\pi\mu kT}\right)^{\frac{1}{2}}.$$

As an interesting result we see from table IV that Z_{rot} for pure HD is, within the experimental error, about 10 and independent of temperature over the whole range from 20.4 to 42.6 K. Furthermore we see that Z_{rot} for HD–He collisions is about 17, indicating that the transition probability for HD is rather sensitive to the non-sphericity of the interaction potential

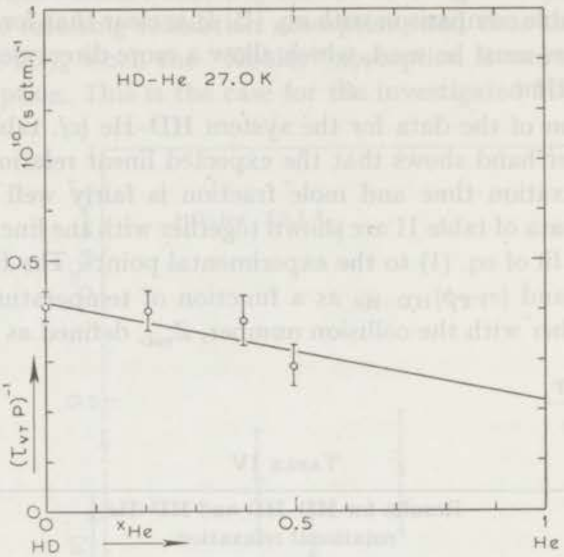
HD-He 27.0 K
1
0.5
0
10^{10} (s atm.)$^{-1}$
$(\tau_{VT}\,p)^{-1}$
0
0.5
1
x_{He}
HD
He

Fig. 2a

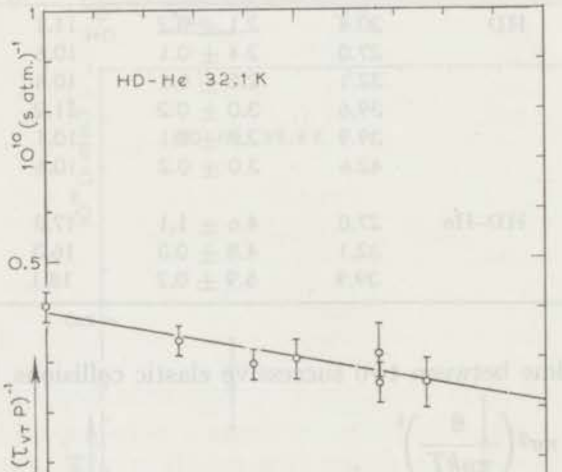
HD-He 32.1 K
0.5
0
10^{10} (s atm.)$^{-1}$
$(\tau_{VT}\,p)^{-1}$
0
0.5
x_{He}
HD
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Fig. 2b

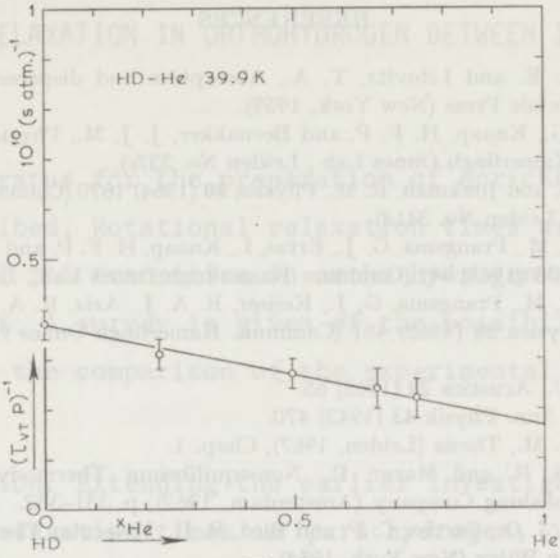

Fig. 2c

Fig. 2. $(\tau_{VT}p)^{-1}$ *vs.* x_{He} for the system HD–He together with the fitted straight line (*cf.* eq. (1)).
a) 27.0 K; b) 32.1 K; c) 39.9 K.

of the colliding molecules. This result is very different from the results for pH_2 and oD_2 where addition of a noble gas leads to smaller values for Z_{rot} than in the pure isotopes (*cf.* Jonkman *et al.*[4,5]). The observed behaviour of Z_{rot} agrees qualitatively with the results in HD–He mixtures for reorientation cross sections (mainly determined by collisions with ($\Delta J = 0$, $\Delta m_J \neq 0$)) as obtained in this laboratory from measurements on the Senftleben–Beenakker effect in the viscosity[12].

Due to the loaded sphere character of HD, the transition probability will be mainly determined by the first term in an expansion of the non-spherical part of the molecular-interaction potential in terms of Legendre polynomials. Truncating this expansion after the P_1 term Takayanagi[13] derived a formula for the transition probability by application of the modified wave-number approximation in the distorted wave method. The obtained values are so high that the perturbation method may not be applied. Even the corrected values proposed by Takayanagi give a wrong prediction for Z_{rot}. Further theoretical work will therefore be needed to clarify the temperature independence of Z_{rot} for pure HD and the increase of Z_{rot} upon addition of He.

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CHAPTER II

ROTATIONAL RELAXATION IN ORTHOHYDROGEN BETWEEN 170 AND 293 K

Synopsis.

An apparatus for the preparation of enriched ortho hydrogen is described. Rotational relaxation times are reported for the $J = 1 \rightleftarrows 3$ transition in ortho hydrogen at 170, 233, 269 and 293 K. A survey is given of the possibilities and limitations in the comparison of the experimental data with theory.

1. *Introduction*. Extending the earlier investigation of the rotational relaxation times in para hydrogen, ortho deuterium, hydrogen deuteride and mixtures of these isotopes with noble gases by means of sound absorption measurements$^{1-5)}$, we have studied the rotational relaxation time of ortho hydrogen. The contribution of the para-component in nH_2 (75% oH_2 - 25% pH_2) to the relaxation absorption is comparable to the contribution of oH_2. Therefore measurements should be performed in pure oH_2, since otherwise the extraction of the relaxation time of oH_2 from the absorption data will be very difficult. To prepare the required enriched oH_2 samples we constructed an apparatus, which is a modified version of the apparatus of Depatie *et al.*$^{6)}$. Our apparatus, in which an enrichment to about 96% oH_2 has been achieved, is described in section 2.

Sound absorption measurements in the ortho-enriched hydrogen samples are reported in section 3 and the procedure to obtain relaxation times from these absorption data is discussed. The results are given in terms of effective cross sections. In section 4 we will outline the present situation of theory and experiment on rotational relaxation of the hydrogen isotopes.

2. *Preparation of enriched ortho hydrogen.* The separation of oH_2 from nH_2 is based on the preferential adsorption of oH_2 on aluminium oxide at 20 K. In a single separation cell an enrichment to 85 - 90% can be achieved, as was reported by Cunningham *et al.*[7]. Depatie and Mills[6] used a single column of about 70 cm length which is drawn out of a liquid hydrogen bath, thus combining the successive stages necessary to obtain a higher enrichment. They reached up to 98% oH_2. The disadvantage of having moving parts in a liquid hydrogen cryostat has been overcome in our apparatus, which is shown schematically in fig. 1. High purity normal hydrogen (75% oH_2) is led into the separation column via valve A. The outgoing gas is pumped away via a pressure regulator, which maintains a pressure of about 50 torr in the column. At regular time intervals a sample of the outgoing gas is taken into the ortho-para analyzer. As soon as the composition of the outflowing gas is stationary, valve A is closed and the column is pumped for half a minute. The desorption is started by forcing the liquid hydrogen downwards out of the space surrounding the Al_2O_3-column. This is achieved by applying an overpressure either by means of He gas or through the evaporation caused by the heating around the column. The lowering of the liquid level is monitored with a capacitance level indicator. The desorption rate is increased by heating of the section above the liquid level.

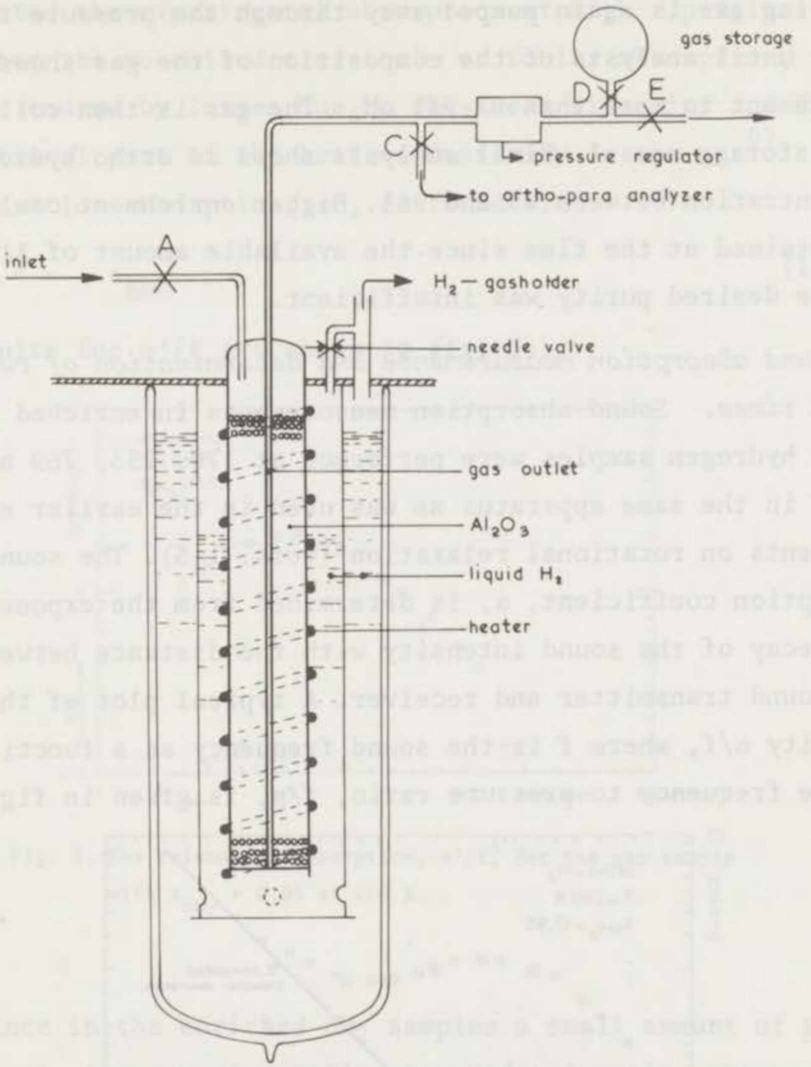

Fig. 1. Diagram of the ortho hydrogen apparatus. For an explanation see text.

The desorbed gas in the cell is forced downwards over the Al_2O_3 where it exchanges with the adsorbed gas, thus achieving an ortho-enrichment of the adsorbed gas layer. The outgoing gas is again pumped away through the pressure regulator until analysis of the composition of the gas shows an enrichment to more than 92-94% oH_2. The gas is then collected in a storage vessel. Final analysis shows an ortho hydrogen concentration between 95 and 96%. Higher enrichment could not be obtained at the time since the available amount of Al_2O_3 of the desired purity was insufficient.

3. *Sound absorption measurements and determination of relaxation times*. Sound absorption measurements in enriched ortho hydrogen samples were performed at 170, 233, 269 and 293 K in the same apparatus as was used in the earlier experiments on rotational relaxation (refs. 1-5). The sound absorption coefficient, α, is determined from the exponential decay of the sound intensity with the distance between the sound transmitter and receiver. A typical plot of the quantity α/f, where f is the sound frequency as a function of the frequency to pressure ratio, f/p, is given in fig. 2.

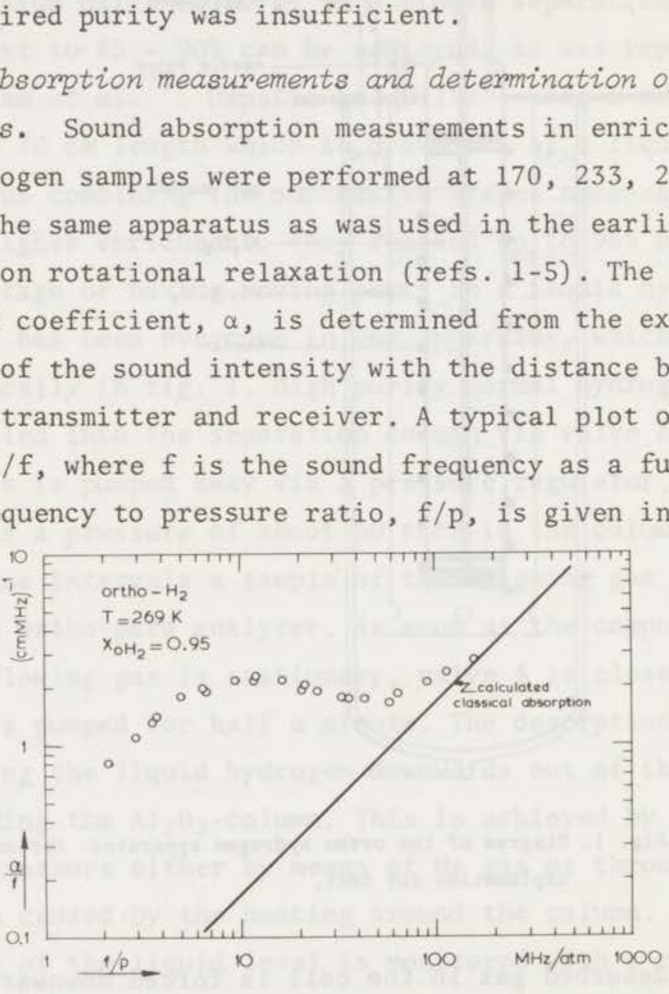

Fig. 2. The total absorption, α/f *vs*. f/p for a sample with x_{oH_2} = 0.95 at 269 K.

As expected the experimental absorption at high f/p-values approaches the so-called classical- or Kohler absorption, which is caused by losses due to the shear viscosity and the translational part of the heat conductivity in the gas[8)].
The relaxation absorption, α', is found with

$$\alpha' = \alpha - \alpha_{Koh} \ . \tag{1}$$

The results for α'/f are shown in fig. 3.

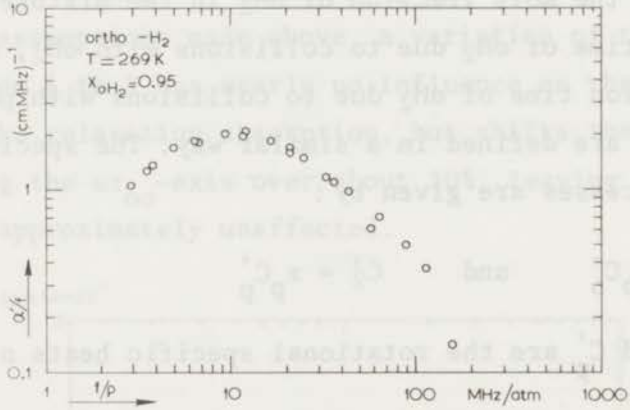

Fig. 3. The relaxation absorption, α'/f, for the gas sample with $x_{oH_2} = 0.95$ at 269 K.

Since in the enriched oH_2 samples a small amount of pH_2 is present, the experimentally observed relaxation absorption contains a contribution from the rotational relaxation of the pH_2. In order to find the relaxation time of oH_2 from the absorption data, we therefore have to establish the relationship between the relaxation absorption and the relaxation times. Under the assumption that simultaneous transitions of two colliding molecules can be ignored, a mixture of oH_2 and pH_2 can be described with two relaxation processes excited in parallel. The relaxation times for these processes can be given by (*cf*. Herzfeld and Litovitz[9]):

$$\frac{1}{\tau_1} = \frac{x_o}{\tau_{oo}} + \frac{x_p}{\tau_{op}} \tag{2}$$

$$\frac{1}{\tau_2} = \frac{x_o}{\tau_{po}} + \frac{x_p}{\tau_{pp}} \tag{3}$$

where x_o is the mole fraction of oH_2 in the mixture, τ_{oo} the relaxation time of oH_2 due to collisions with oH_2, and τ_{op} the relaxation time of oH_2 due to collisions with pH_2. x_p, τ_{pp} and τ_{po} are defined in a similar way. The specific heats for the processes are given by:

$$C_1' = x_o C_o' \quad \text{and} \quad C_2' = x_p C_p' \tag{4}$$

where C_o' and C_p' are the rotational specific heats of pure oH_2 and pH_2.

According to Herzfeld and Litovitz[9] the relaxation absorption can now be given as:

$$\frac{\alpha'}{f} = \left(\frac{V_o}{V}\right)^3 \frac{\pi}{V_o} \frac{R}{C_p(C_V - C')} \left\{ \frac{C_1''\omega\tau_1''}{1+(\omega\tau_1'')^2} + \frac{C_2''\omega\tau_2''}{1+(\omega\tau_2'')^2} \right\} \tag{5}$$

where C_1'', C_2'', τ_1'' and τ_2'' are functions of C_1', C_2', τ_1 and τ_2. The other symbols have their usual meaning. For further details regarding eq. (5) and the quantities involved the reader is referred to ref. 9.

In order to calculate the relaxation absorption from eq. (5) we make use of the fact that τ_{pp} and τ_{po} do not differ by more than a factor 2 (ref. 3). The same is assumed for τ_{op} and τ_{oo}. The terms x_p/τ_{op} and x_p/τ_{pp} in eqs. (2) and (3) can now be ignored since the mole fraction of pH_2 is small. A numerical analysis shows that the error in the relaxation absorption introduced by this approximation is less than about 2%. With this approximation we seek to match eq. (5) to the experimental data by evaluating eq. (5) as a function of $\omega\tau_{oo}$, with the ratio τ_{po}/τ_{oo} as a parameter. A typical result is shown in fig. 4. From this graph we observe that, under the assumptions made above, a variation of the ratio τ_{po}/τ_{oo} from ½ to 2 has nearly no influence on the maximum value of the relaxation absorption, but shifts the whole curve along the $\omega\tau_{oo}$-axis over about 10%, leaving the shape of the curve approximately unaffected.

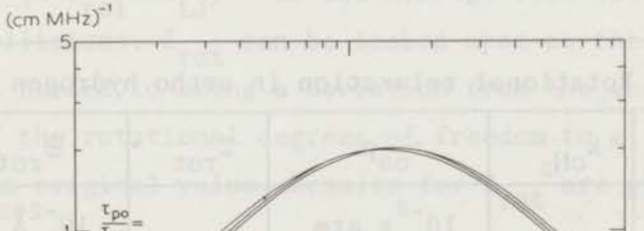

Fig. 4. The calculated relaxation absorption in a mixture with $x_{oH_2} = 0.95$ at 269 K, as a function of $\omega\tau_{oo}$ for several values of the τ_{po}/τ_{oo} - ratio.

The rotational relaxation time is now determined by fitting the theoretical curves (fig. 4) to the experimental data (*cf*. fig. 3). From the f/p-value where $\omega\tau_{oo} = 1$ the relaxation time is then calculated with

$$(\tau_{oo}p)^{-1} = 2\pi\,(f/p)_{\omega\tau_{oo}=1} \;. \tag{6}$$

It will be clear that, since the shape of the α'/f *vs.* $\omega\tau_{oo}$ curve is nearly independent of τ_{po}/τ_{oo}, it is impossible to estimate τ_{po} from the matching procedure. This introduces an uncertainty in $\tau_{oo}p$ which, however, at most temperatures is within the experimental accuracy. In table I the results obtained for $\tau_{oo}p$ are given with the estimated accuracy.

TABLE I

Rotational relaxation in ortho hydrogen

T	x_{oH_2}	$\tau_{oo}p$	Z_{rot}	$\mathfrak{S}_{rot}$
K		10^{-8} s atm		10^{-2} Å^2
170	0.95	2.5 ± 0.5	786	4.9 ± 1.0
233	0.95	1.9 ± 0.2	510	7.6 ± 0.8
269	0.95	2.1 ± 0.2	514	7.3 ± 0.7
293	0.96	2.2 ± 0.2	530	7.3 ± 0.7

In kinetic gas theory the relaxation time is usually written in terms of collision integrals[10)], which involve the scattering cross sections describing the energy transfer from the translational to the rotational degrees of freedom at collisions. The relaxation time can then be given by

$$\frac{1}{\tau_{oo}} = n \langle v_{rel} \rangle \mathfrak{S}_{rot} \qquad (7)$$

where n is the particle density, $\langle v_{rel} \rangle$ the average relative velocity given by and $\mathfrak{S}_{rot}$* is the effective cross section for the inelastic energy transfer between translational and rotational degrees of freedom. Results for $\mathfrak{S}_{rot}$ are shown in table I.

As a useful quantity for qualitative discussions we define the collision number, Z_{rot}

$$Z_{rot} = \tau_{oo}/\tau_c$$

where $\tau_c = (n\langle v_{rel} \rangle \pi\sigma_{LJ}^2)^{-1}$ is the average time between two elastic collisions. Z_{rot} can be looked upon as the number of collisions needed to bring a deviation from the thermal equilibrium of the rotational degrees of freedom to a 1/e-fraction of its original value. Results for Z_{rot} are given in table I.

4. *Discussion*. Before comparing the available experimental material on rotational relaxation of hydrogenic molecules with theory let us briefly resume what steps are involved in such a comparison.

As outlined for example by Sluijter *et al.*[12], in the theoretical approach to two level systems - as the hydrogenic

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* The shorthand notation $\mathfrak{S}_{rot}$ corresponds to the full notation $\mathfrak{S}(0001)$ in more detailed discussions (see *e.g.* table II in Chapter IV of this thesis and Hulsman[11]).

molecules are at low temperatures - one starts from an angle-dependent intermolecular potential, $V(R,\underline{\Omega})$, which is commonly taken to be of the form

$$V(R,\underline{\Omega}) = V_{\mathrm{sph}}(R) + \beta\, V_{\mathrm{non\text{-}sph}}(R,\underline{\Omega})$$

where V_{sph} is the spherical part of the potential and $V_{\mathrm{non\text{-}sph}}$ the angle-dependent part with strength β. With this potential one calculates the cross section for rotational excitation, $\sigma_{J\to J'}(E)$, as a function of the incoming energy, E. An averaging procedure finally gives the theoretical value for the rotational relaxation time, τ_{VT}, as a function of temperature

$$V(R,\underline{\Omega}) \to \sigma_{J\to J'}(E) \to \tau_{VT}(T) .$$

Since $V(R,\underline{\Omega})$ is only approximately known, one would like to invert the above procedure in order to use the experimental data on τ_{VT} to obtain information on $V_{\mathrm{non\text{-}sph}}$. This inversion, however, can in general not be performed directly.

In the actual comparison therefore a clear distinction should be made between the specific tasks of experiment and theory. As far as theory is concerned the computer facilities nowadays available give for the simple cases considered here (the hydrogenic molecules) the possibility to produce adequate numerical results for inelastic scattering cross sections starting from a realistic angle-dependent interaction. The task of the experimentalist is then to select the proper intermolecular potential by a comparison of experimental and theoretical results. It is here no longer his task to use his data to decide on the validity of the approximations adopted in the theory, this now being left for a numerical analysis (see *e.g.* refs. 13, 14, 15).

In view of this it is important to study the possibilities and the limitations of the experimental data in selecting the proper interaction potential. As a starting point we take the expression for the rotational relaxation time, τ_{VT}, in a two level system in terms of the excitation cross section, $\sigma_{J\to J'}(E)$ (*cf.* Sluijter *et al.*$^{12)}$)

$$\frac{1}{\tau_{VT}} = n \, \langle v_{rel} \rangle \left\{ \frac{g_J}{g_{J'}} + \exp\left(-\frac{E_o}{kT}\right) \right\} I(T) \qquad (9)$$

with

$$I(T) = \int_{E_o}^{\infty} \frac{E}{(kT)^2} \exp\left(-\frac{E - E_o}{kT}\right) \sigma_{J\to J'}(E) \, dE \ . \qquad (10)$$

In these expressions g_J and $g_{J'}$ are the statistical weights of the rotational levels J and J' and E_o is the energy difference between these levels. The other symbols have their usual meaning. I(T) is that part of τ_{VT}, that contains the information related to the interaction potential. It can be directly obtained from experimental data.

In order to have a two level system in the experiments, the temperature must be chosen in such a way that $kT/E_o < 0.3$. A lower temperature limit arises from the condition that sufficient relaxation absorption must be present: $0.1 < kT/E_o$. Under these conditions the main contribution to I(T) stems from an energy region of width $\Delta E \simeq E_o$ above the threshold energy.

Calculations of $\sigma_{J\to J'}(E)$ for hydrogenic systems$^{13-16)}$ suggest an overall behaviour over the energy range of interest of the type

$$\sigma_{J\to J'}(E) = b(E - E_o) + c(E - E_o)^2 \quad . \tag{11}$$

Theoretical considerations on the other hand (*cf.* Landau and Lifshitz$^{17)}$) suggest the presence of a contribution with a vertical slope at threshold: $\sim \sqrt{(E - E_o)}$. If the transition to the behaviour given by eq. (11) occurs in a region $(E - E_o)/E_o < 0.1$, such a contribution would show up in our experiments as an additional constant contribution to $\sigma_{J\to J'}(E)$. Hence we use as a trial function the expression

$$\sigma_{J\to J'}(E) = a + b(E - E_o) + c(E - E_o)^2 \quad . \tag{12}$$

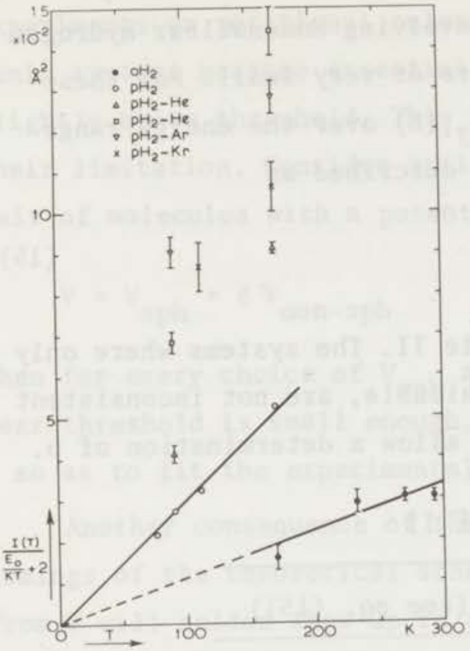
Substitution of eq. (12) in eq. (10) yields after integration

$$I(T) = \frac{a}{kT}(E_o + kT) + b(E_o + 2kT) + 2ckT(E_o + 3kT) \quad . \tag{13}$$

If the term $b(E - E_o)$ gives the dominant contribution to $\sigma_{J\to J'}(E)$ then eq. (13) may be rewritten as

$$\frac{I(T)}{\frac{E_o}{kT} + 2} = (b - \frac{a}{E_o})kT + a + 2c(kT)^2 + \text{small terms} \quad . \tag{14}$$

If this description is indeed valid a plot of the experimental values of $I(T)/(E_o/kT + 2)$ versus temperature will give a straight line. As shown in figs. 5-7 this is in fact the case for most systems studied experimentally. From figs. 5 and 6



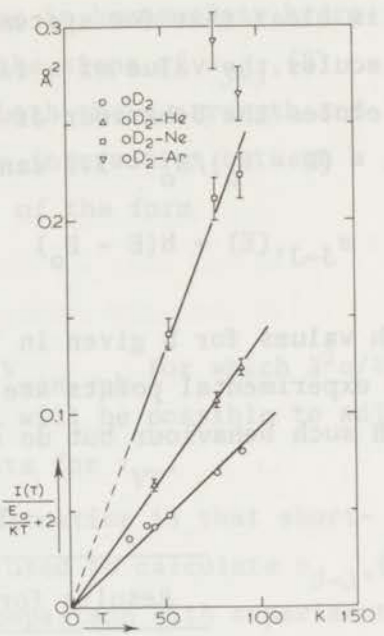


Fig. 5. The quantity $I(T)/\left(\frac{E_o}{kT}+2\right)$ *vs.* temperature for the systems with pH_2 and oH_2.

Fig. 6. The quantity $I(T)/\left(\frac{E_o}{kT}+2\right)$ *vs.* temperature for the systems with oD_2.

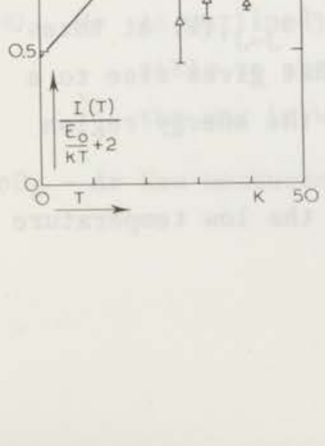


Fig. 7. The quantity $I(T)/\left(\frac{E_o}{kT}+2\right)$ *vs.* temperature for the systems with HD.

it is clear that for systems involving homonuclear hydrogen molecules the value of a is zero or very small. For these molecules the behaviour of $\sigma_{J\to J'}(E)$ over the energy range $0.1 < (E - E_o)/E_o < 1.5$ can be described as

$$\sigma_{J\to J'}(E) = b(E - E_o) \tag{15}$$

with values for b given in table II. The systems where only two experimental points are available, are not inconsistent with such behaviour but do not allow a determination of b.

TABLE II

Results for b (see eq. (15))

System	b
	10^{12} Å^2/erg
pH_2 - pH_2	2.38 ± 0.03
oH_2 - oH_2	0.8 ± 0.1
oD_2 - oD_2	6.1 ± 0.3
oD_2 - He	10.0 ± 0.7
oD_2 - Ne	18 ± 2

The behaviour of systems with HD is, however, quite different, see fig. 7. Here a is significantly different from zero. This suggests that the behaviour of $\sigma_{J\to J'}(E)$ at threshold is characterized by a steep slope that gives rise to a rather large contribution to $\sigma_{J\to J'}(E)$ in the energy region considered.

From the foregoing it is clear that the low temperature experiments on rotational relaxation in homonuclear hydrogenic systems measure essentially the slope of $\sigma_{J\to J'}(E)$ slightly above threshold. This is both their strength and their limitation. Consider again an interaction between a pair of molecules with a potential of the form

$$V = V_{sph} + \beta V_{non\text{-}sph} \; .$$

Then for every choice of V_{sph} and $V_{non\text{-}sph}$ for which $\partial^2\sigma/\partial E^2$ near threshold is small enough, it will be possible to adjust β so as to fit the experimental data for τ_{VT}.

Another consequence of this situation is that shortcomings of the theoretical scheme used to calculate $\sigma_{J\to J'}(E)$ from V will seldom show up in a comparison with experiment. An exception of this is found in the modified wave number approximation as introduced by Takayanagi[18], which introduces a spurious temperature dependence (*cf*. Roberts[15] and Jonkman *et al*.[19]).

So far insufficient calculations are available to be able to use the experimental data to their full advantage.

5. *Suggestions for further experimental work*. From a study of figs. 5-7 it is clear that a number of additional experiments would be helpful. We conclude this Chapter with a short description of the situation in this respect.

HD - He As outlined in ref. 5 it will not readily be possible to obtain data with a better accuracy due to the way in which the experiments must be analysed.

oD_2 - Ar New measurements at more temperatures would be welcome. The temperature range will be limited due to the vapour pressure of Ar at lower temperatures and due to the excitation of the J = 4 level above 100 K. As the reliability of τ_{VT} also depends on an accurate knowledge of the classical absorption, experimental data on the transport coefficients for these systems are required.

oD_2 - Ne Additional measurements at intermediate and somewhat lower temperatures are needed. Here also experimental data on the transport coefficients are lacking.

pH_2 - He, Ne, Ar One or two intermediate temperatures would reduce the uncertainties still present.

pH_2 - Kr In this case the vapour pressure of the Kr is limiting the temperature range. It is questionable whether measurements at an intermediate temperature would change the situation appreciably.

oH_2 and oH_2 - noble gas mixtures. Although more results on these systems would be very welcome, measurements are only worthwhile if ortho-H_2 of a purity better than 99% can be used, due to the occurrence of pH_2 which gives even at low concentrations a relatively large contribution to the relaxation absorption.

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CHAPTER III

ULTRASONIC DETERMINATION OF THE VOLUME VISCOSITY OF N_2, CO, CH_4 AND CD_4 BETWEEN 77 and 300 K

Synopsis

Results are reported for the frequency independent volume viscosity in N_2, CO, CH_4 and CD_4 at temperatures ranging from 77 to 300 K as determined from sound absorption measurements. The closely related rotational relaxation times and the appropriate kinetic cross sections are derived.

1. *Introduction*. In the study of molecular dynamics there is a steady interest in the efficiency of collisional energy transfer between the translational and internal degrees of freedom. From kinetic gas theory it is well known that this energy exchange gives rise to a non-zero volume viscosity of the gas (*cf*. *e.g*. Wang Chang, Uhlenbeck and De Boer[1]), which can be studied experimentally in sound absorption measurements. The expression for the sound absorption in the low frequency region in terms of transport coefficients (see De Groot and Mazur[2]) reads:

$$\frac{\alpha p}{f^2} = \frac{2\pi^2}{\gamma_o V_o} \left[\frac{4}{3}\eta + \frac{(\gamma_o - 1)^2}{\gamma_o} \frac{M\lambda}{R} + \eta_V \right] . \qquad (1)$$

In this expression

α = sound absorption coefficient

p = equilibrium pressure

f = sound wave frequency

γ_o = specific heat ratio at "zero frequency"

V_o = sound velocity at "zero frequency"
η = coefficient of shear viscosity
λ = coefficient of heat conductivity
η_V = coefficient of volume viscosity
M = molecular mass
R = gas constant

The first two terms in eq. (1) are commonly known as the classical absorption, α_{cl}:

$$\frac{\alpha_{cl}p}{f^2} = \frac{2\pi^2}{\gamma_o V_o}\left[\frac{4}{3}\eta + \frac{(\gamma_o - 1)^2}{\gamma_o}\frac{M\lambda}{R}\right] . \qquad (2)$$

Since for the gases N_2, CO, CH_4 and CD_4 absorption data are only available at room temperature and above we performed a series of acoustic experiments at temperatures from room temperature down to 77 K. Data on η_V have an additional importance for testing theoretical relations, involving the volume viscosity, the heat conductivity of polyatomic gases [3] and the Senftleben-Beenakker effect for the viscosity [4]. For this purpose low temperature data are especially interesting. The experimental procedure and results are shown in section 2. The results are compared with other data in section 3. Tests of the relations mentioned above are given in Chapter IV.

2. *Experiments*. For the determination of the sound absorption coefficient, α, we used the apparatus described in earlier papers [5,6]. The experimental method is essentially as follows.

A condensor-type sound transducer transmits plane waves at a steady rate. The waves are detected with a condensor-microphone which moves away from the transmitter at a constant speed. The detected signal is fed to a selective amplifier and plotted on a logarithmic level recorder. The exponential decay of the sound wave amplitude as a function of the distance between sender and receiver produces a straight line on the recorder. The absorption coefficient, α, can be determined from the slope of this line and the quantity $\alpha p/f^2$ (*cf.* eq. (1)) can be computed for a number of frequency and pressure values.

In order to determine the volume viscosity from these data we averaged the $\alpha p/f^2$ values in the frequency-pressure-domain where η_V does not depend on the frequency, and subtracted the classical absorption calculated with eq. (2) using viscosity and heat conductivity data from ref. 7. From the remaining "relaxation" absorption, α', the volume viscosity was computed:

$$\frac{\alpha' p}{f^2} = \frac{2\pi^2}{\gamma_o V_o} \eta_V \quad . \tag{3}$$

As a test of the procedure we performed a run with pure Ne at 77 K. Since in this case $\eta_V = 0$ the sound absorption is given by eq. (2). The results, given in fig. 1, show excellent agreement with the theory (theory: $\alpha_{cl} p/f^2 = 0.142$; experiment: $\alpha_{cl} p/f^2 = 0.143 \pm 0.001$ atm cm^{-1} MHz^{-2}).

Experiments were performed at 77, 180, 260 and 293 K. At 77 K a liquid nitrogen bath was used, whereas the intermediate temperatures (180 and 260 K) were reached by cooling with a liquid nitrogen stream, controlled by a NTC-thermis-

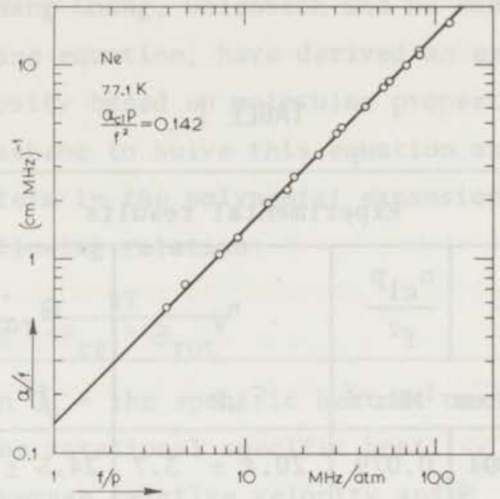

Fig. 1. Results of a test measurement of the absorption of Ne at 77 K together with the theoretical value ($\alpha_{cl}p/f^2 = 0.142$ atm $\mathrm{cm}^{-1}\mathrm{MHz}^{-2}$).

tor mounted on the top flange of the measuring vessel. A temperature stability of better than 0.05 degree was obtained.

The results for $\alpha p/f^2$, $\alpha_{cl}p/f^2$ and η_V are given in table I. A typical example of the experimental data for CO at 180 K is given in fig. 2.

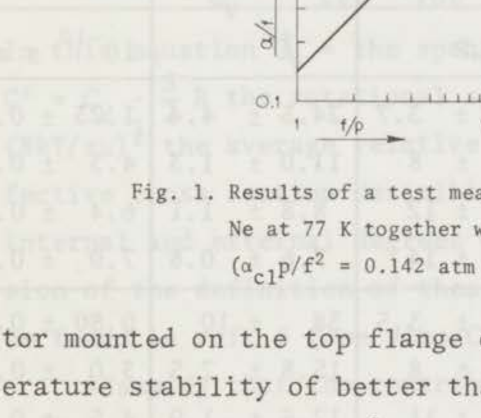

Fig. 2. Typical example of experimental results (CO at 180 K).

TABLE I

Experimental results

Gas	T	$\frac{\alpha p}{f^2}$	$\frac{\alpha_{cl} p}{f^2}$	η_V	$\mathfrak{S}_{rot}$	$\tau_{VT} p$
	K	atm $cm^{-1}MHz^{-2}$		μP	$Å^2$	10^{-10} s atm
N_2	77.1	0.094	0.079	20.4 ± 3.7	24.5 ± 4.4	1.25 ± 0.23
	180	0.148	0.113	69 ± 8	11.0 ± 1.3	4.3 ± 0.5
	260	0.174	0.130	104 ± 12	8.8 ± 1.1	6.4 ± 0.8
	293	0.183	0.132	128 ± 14	7.6 ± 0.8	7.9 ± 0.9
CO	77.1	0.088	0.078	13.0 ± 3.5	38 ± 10	0.80 ± 0.22
	180	0.133	0.108	48 ± 8	15.8 ± 2.5	3.0 ± 0.5
	260	0.155	0.124	73 ± 11	12.5 ± 1.9	4.5 ± 0.7
	293	0.167	0.130	93 ± 13	10.5 ± 1.5	5.7 ± 0.8
CH_4	77.1	0.051	0.035	24.5 ± 2.5	16.0 ± 1.6	1.45 ± 0.14
	180	0.080	0.052	69 ± 6	8.7 ± 0.7	4.1 ± 0.3
	260	0.101	0.061	116 ± 9	6.2 ± 0.5	6.9 ± 0.6
	293	0.111	0.064	144 ± 10	5.3 ± 0.4	8.5 ± 0.6
CD_4	180	0.097	0.065	70 ± 6	9.6 ± 0.9	4.2 ± 0.4
	260	0.120	0.076	113 ± 9	7.2 ± 0.6	6.7 ± 0.5
	293	0.133	0.081	144 ± 12	6.0 ± 0.5	8.5 ± 0.7

3. *Discussion*. Wang Chang, Uhlenbeck and De Boer[1)], starting from the Boltzmann equation, have derived an expression for the volume viscosity based on molecular properties. Using the Chapman-Enskog scheme to solve this equation and keeping only the first term in the polynomial expansion, they arrived at the following relation:

$$[\eta_V]_1 = \frac{RC'}{C_V{}^2} \; \frac{kT}{\langle v_{\mathrm{rel}} \rangle \, \mathfrak{S}_{\mathrm{rot}}} \quad . \tag{4}$$

In this equation C_V = the specific heat at constant volume, $C' = C_V - \frac{3}{2}R$ the rotational specific heat, $\langle v_{\mathrm{rel}} \rangle = (8kT/\pi\mu)^{\frac{1}{2}}$ the average relative velocity and $\mathfrak{S}_{\mathrm{rot}}$* is the effective cross section describing the energy exchange between internal and external degrees of freedom. A detailed discussion of the definition of these effective cross sections can be found in ref. 8 (see also Chapter IV, table II).

Assuming that the contribution of higher order terms to η_V is negligible, we calculated the corresponding effective cross sections from our η_V data (table I). The basis for this assumption is rather weak: it is mainly an extrapolation of the situation for the translational degrees of freedom in monatomic gases and of some calculations performed on hard core classical models. One might hope that for cross sections that are not too strongly dependent on energy the results of these calculations might still be pertinent. The results obtained in this way will be used in two subsequent papers[9)]

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* Note that the shorthand notation, $\mathfrak{S}_{\mathrm{rot}}$, introduced here, corresponds to the full notation $\mathfrak{S}(0001)$ used in more detailed discussions (*e.g.* refs. 8 and 9).

in connection with data from experiments on the heat conductivity of polyatomic gases and from the Senftleben-Beenakker effect in the viscosity, to test a number of theoretical relations.

Although it will be clear from the above that, in general, the volume viscosity is a more fundamental quantity, many authors prefer to present their acoustical data in terms of a relatation time, τ_{VT}, and a collision number defined, for instance, as (*cf*. Herzfeld and Litovitz$^{10)}$):

$$Z_{HL} = \frac{4}{\pi} \frac{\tau_{VT} p}{\eta} . \qquad (5)$$

Such a description starts by postulating a relaxation equation for the internal energy of the form$^{10)}$:

$$- \frac{dE_{int}}{dt} = \frac{1}{\tau_{VT}} (E_{int} - E^{eq}_{int}) , \qquad (6)$$

where E^{eq}_{int} is the internal energy at the equilibrium (translational) temperature.

Such a single-relaxation-time equation corresponds to the first order Sonine approximation in solving the Boltzmann equation$^{1)}$. Higher order approximations yield extra terms with other time scales so that in general one relaxation time is not sufficient to describe the relaxation process. In the first-order approximation, however, the relation between the (measured) volume viscosity and the relaxation time defined by eq. (6) is given by (*cf*. De Groot and Mazur$^{11)}$):

$$\tau_{VT} p = \frac{C_V^{\;2}}{RC'} \eta_V \quad . \qquad (7)$$

Results for $\tau_{VT}p$ are tabulated in table I.

We will now compare our low temperature results with other data obtained at room temperature and above. As can be seen from table I, the classical absorption is a relatively large portion of the sound absorption, especially for N_2 and CO. Thus a small error in α will cause a relatively large error in the volume viscosity (*e.g.* 3% in $\alpha p/f^2$ for N_2 at 293 K leads to an error of 11% in η_V).

For this reason we prefer to perform the comparison on the experimental data for the sound absorption rather than on the derived quantities volume viscosity, relaxation time or collision number, whenever the sound absorption data as such can be taken from the original publications.

Nitrogen. From fig. 3 and table II, where the absorption data from various sources [12-18] are given along with our data, it is clear that although the total spread in the observed sound absorption is not more than about 15%, serious differences in derived quantities will occur.

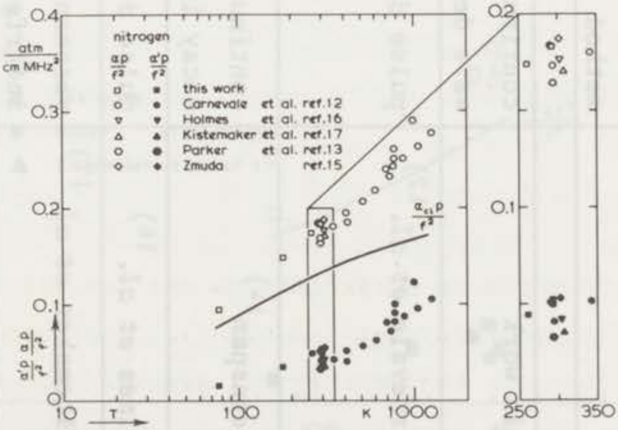

Fig. 3. Comparison of our results for N_2 with data from other sources.

TABLE II

Comparison of sound absorption data for N_2 between 250 and 350 K

Author and reference	Experimental method	Agreement for noble gas	T	$\frac{\alpha p}{f^2}$	$\frac{\alpha_{cl} p}{f^2}$	Z_{HL}
			K	atm $cm^{-1}MHz^{-2}$		
This work	continuous wave decay	yes	260	0.174	0.130	5.1
		yes	293	0.183	0.132	5.8
Carnevale *et al.*[12]	pulse decay	yes	291	0.183	0.132	5.6
			294	0.173	0.132	4.4
			350	0.180	0.139	4.6
Greenspan[14]	continuous wave decay interferometer	yes	300			5.3
Holmes *et al.*[16]	pulse decay	yes	303			4.7
Kistemaker *et al.*[17]	resonant interferometer	yes	307	0.170	0.135	3.9
Parker *et al.*[13]	pulse decay	yes	293	0.164	0.131	3.5
Sessler[18]			294			5.2
Zmuda[15]	resonant interferometer	unknown	302	0.187	0.135	6

From fig. 3 we observe that our absorption data are in reasonable agreement with data of Carnevale *et al.*[12)] as far as the temperature dependence is concerned. However, the absolute values of our data seem to be somewhat higher than the existing data at room temperature. Since literature values for sound absorption in noble gases agree within 3% (*cf.* table II), we cannot explain the differences between the observed data for N_2. In our earlier experiments with hydrogen isotopes (refs. 5 and 19), where classical and relaxation absorption can be determined separately, we have always found excellent agreement between our experimental results and the theoretical values of the maximum in the relaxation absorption, calculated from spectroscopic specific heat data. We feel that this indicates, that our method and our results are reliable. We estimate that there is an error of around 10% in our determinations of η_V.

Carbon monoxide. As illustrated in fig. 4 and table III the

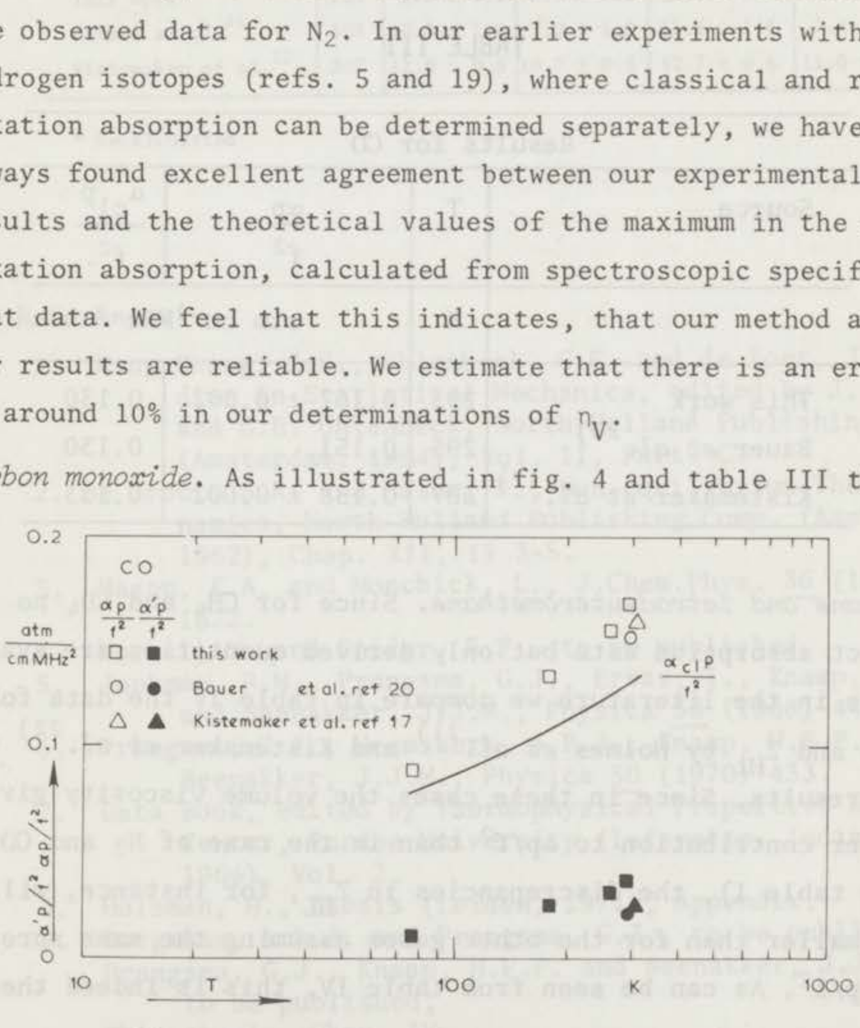

Fig. 4. Results for CO compared with other data.

differences in the derived quantities for CO will be more marked than in the case of N_2, since for CO the classical absorption is a larger portion of the total sound absorption. Again we feel justified in relying on our own data, especially at 260 K and below, where impurities that can influence the effectiveness of the relaxation process will be frozen out.

TABLE III

Results for CO

Source	T	$\frac{\alpha p}{f^2}$	$\frac{\alpha_{cl} p}{f^2}$
	K	atm $cm^{-1}MHz^{-2}$	
This work	293	0.167 ± 0.002	0.130
Bauer *et al.*[20)]	295	0.151	0.130
Kistemaker *et al.*[17)]	307	0.158 ± 0.002	0.133

Methane and tetradeuteromethane. Since for CH_4 and CD_4 no direct absorption data but only derived quantities are available in the literature we compare in table IV the data for $\tau_{VT}p$ and Z_{HL} by Holmes *et al.*[21)] and Kistemaker *et al.*[22)] with our results. Since in these cases the volume viscosity gives a larger contribution to $\alpha p/f^2$ than in the case of N_2 and CO (see table I), the discrepancies in Z_{HL}, for instance, will be smaller than for the other gases assuming the same spread in $\alpha p/f^2$. As can be seen from table IV, this is indeed the case.

TABLE IV

Results for CH_4 and CD_4

	T	$\tau_{VT}p$		Z_{HL}	
	K	10^{-10} s atm			
		CH_4	CD_4	CH_4	CD_4
This work	293	8.5 ± 0.6	8.5 ± 0.7	10.0 ± 0.7	9.0 ± 0.7
Holmes *et al.*[21]	303	10.3 ± 1.6	7.2 ± 1.0	11.8 ± 1.8	7.4 ± 1.0*
Kistemaker *et al.*[22]	307	11.0 ± 0.5	10.7 ± 0.3	12.7 ± 0.6	11.0 ± 0.3

* Recalculated

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CHAPTER IV
A TEST OF APPROXIMATE RELATIONS BETWEEN EFFECTIVE CROSS SECTIONS

Synopsis

Recently obtained results for the effective cross section $\mathfrak{S}(0001)$ will be used to test a number of theoretical approximate relations involving this effective cross section.

1. *Introduction*. To describe transport phenomena in a dilute gas on a molecular basis one starts from the Boltzmann equation. The transport coefficients, such as viscosity or heat conductivity, are then obtained in terms of collision integrals or effective cross sections. In order to obtain numerical values for these quantities, a detailed knowledge of the collisions taking place is needed. This is especially true for polyatomic gases because inelastic collisions are important. As a first step in obtaining information about collisions one needs to calculate (inelastic) scattering cross sections starting from a relaistic intermolecular potential. The second step involves the computation of the collision integral or effective cross section.

At present such complete calculations can be performed only for the homonuclear hydrogen isotopes. For other gases, such as N_2, CO, CH_4 and CD_4, the situation is much less satisfactory. Inelastic scattering cross sections have not been calculated for realistic potentials, but attempts have been made to predict the effective cross sections on a more general basis. An obvious first approach to such calculations is to attempt to find approximate relations between the effective cross sections. In this Chapter we will discuss a number of such relations that involve the effective cross section $\mathfrak{S}(0001)$, which has been obtained from volume viscosity data (see Chapter III).

One such relation has been derived by Mason *et al.*[1,2] on a rather intuitive basis (MM-approximation):

$$\mathfrak{S}(1001) \approx \mathfrak{S}^{(0)}(1001) + \tfrac{1}{2}\mathfrak{S}(0001) \quad . \qquad (1)$$

$\mathfrak{S}(1001)$ occurs in the expression for the heat conductivity (eq. (4)), $\mathfrak{S}^{(0)}(1001)$ is the value of $\mathfrak{S}(1001)$ for a spherical potential and $\mathfrak{S}(0001)$ determines the volume viscosity (eq. (8)). In table II we summarize the definitions of the $\mathfrak{S}$'s occurring in this Chapter. Mason *et al.* used a different notation, but adopting their approximation $-D_{\mathrm{int}} = D_{11}$ - our eq. (1) corresponds to their eq. (10c) in ref. 2.

Recently Moraal and Snider[3,4] derived a number of approximate relations between effective cross sections. They considered a gas that can be described with an interaction potential for which the non-spherical part has the form of a second Legendre-polynomial (P_2 - type angle-dependence). It can be expected that this is the dominant non-spherical part of the potential for homonuclear diatomics and "nearly homonuclear" diatomics such as CO. In a first order distorted wave approximation they found for the nearly classical situation the approximate relations (MS-approximation):

$$\mathfrak{S}(1001) \approx \mathfrak{S}^{(0)}(1001) + \frac{7}{6}\mathfrak{S}(0001) \qquad (2)$$

and

$$\mathfrak{S}(0001) \approx \sqrt{30}\,\mathfrak{S}\begin{pmatrix}2000\\0200\end{pmatrix} \quad . \tag{3}$$

$\mathfrak{S}\begin{pmatrix}2000\\0200\end{pmatrix}$ determines the magnitude of the change of the viscosity in a magnetic field (Senftleben-Beenakker effect).

Since we have recently obtained results for $\mathfrak{S}(0001)$ for a number of gases$^{5)}$, we are now able to test the validity of relations involving this effective cross section (eqs. (1), (2) and (3)).

2. *The relations involving* $\mathfrak{S}(1001)$. The effective cross section $\mathfrak{S}(1001)$ occurs in the expression for the heat conductivity, λ (see *e.g.* Wang Chang, Uhlenbeck and De Boer$^{6)}$)

$$\lambda = \frac{\frac{5}{2}k^2T}{m\langle v_{rel}\rangle}\;\frac{\mathfrak{S}(1001) + 2\sqrt{\frac{2}{5}\frac{c_{int}}{k}}\,\mathfrak{S}\begin{pmatrix}1010\\1001\end{pmatrix} + \frac{2}{5}\frac{c_{int}}{k}\mathfrak{S}(1010)}{\mathfrak{S}(1010)\mathfrak{S}(1001) - \mathfrak{S}\begin{pmatrix}1010\\1001\end{pmatrix}^2} \tag{4}$$

By invoking the exact relations

$$\mathfrak{S}\begin{pmatrix}1010\\1001\end{pmatrix} = \sqrt{\frac{5}{18}\frac{c_{int}}{k}}\,\mathfrak{S}(0001) \tag{5}$$

$$\mathfrak{S}(1010) = \frac{2}{3}\mathfrak{S}(2000) + \frac{5}{9}\frac{c_{int}}{k}\mathfrak{S}(0001) \tag{6}$$

two of the $\mathfrak{S}$'s in eq. (4) can be written in terms of the effective cross sections occurring in the expressions fot the viscosity, η, and the volume viscosity, η_V:

$$\eta = \frac{kT}{\langle v_{rel}\rangle\,\mathfrak{S}(2000)} \tag{7}$$

$$\eta_V = \frac{kT}{\langle v_{rel}\rangle\,\mathfrak{S}(0001)}\;\frac{kc_{int}}{\left(\frac{3}{2}k + c_{int}\right)^2} \quad . \tag{8}$$

Upon substitution of eqs. (5) and (6) into the expression for λ, eq. (4), one has:

$$\lambda = \frac{kT \quad \frac{3}{2}k}{m\langle v_{rel}\rangle \mathfrak{S}(2000)} \; \frac{\frac{5}{2} + \frac{2}{3}\frac{c_{int}}{k}\frac{\mathfrak{S}(2000)}{\mathfrak{S}(1001)} + \frac{5}{3}\frac{c_{int}}{k}\left(1+\frac{c_{int}}{k}\right)\frac{\mathfrak{S}(0001)}{\mathfrak{S}(1001)}}{1 + \frac{5}{6}\frac{c_{int}}{k}\frac{\mathfrak{S}(0001)}{\mathfrak{S}(2000)} - \frac{5}{12}\frac{c_{int}}{k}\frac{\mathfrak{S}(0001)^2}{\mathfrak{S}(2000)\mathfrak{S}(1001)}} \tag{9}$$

Using experimental data for λ, η and η_V one can compute the three effective cross sections $\mathfrak{S}(1001)$, $\mathfrak{S}(2000)$ and $\mathfrak{S}(0001)$ from eqs. (7), (8) and (9).

To test the validity of the approximate relations eqs. (1) and (2) we now proceed as follows. The equations are divided by $\mathfrak{S}(2000)$ giving:

$$\frac{\mathfrak{S}(1001)}{\mathfrak{S}(2000)} \simeq \frac{\mathfrak{S}^{(0)}(1001)}{\mathfrak{S}(2000)} + \chi\,\frac{\mathfrak{S}(0001)}{\mathfrak{S}(2000)} \tag{10}$$

with $\chi = \frac{1}{2}$ for the MM-approximation (eq. (1)) and $\chi = 7/6$ for the MS-approach (see eq. (2)). In this way the first term of the right hand side of the relation eq. (1) is virtually independent of temperature and the potential model; hence a plot of $\mathfrak{S}(1001)/\mathfrak{S}(2000)$ versus $\mathfrak{S}(0001)/\mathfrak{S}(2000)$ will give a straight line with slope χ (see figs. 1 and 2).

Using the additional approximate relation

$$\mathfrak{S}(2000) \simeq \mathfrak{S}^{(0)}(2000) + \psi\,\mathfrak{S}(0001) \tag{11}$$

where $\psi = 0$ in the MM-approach[1,2] and $\psi = 2/15$ according to the MS-approximation3)* the intercept at $\mathfrak{S}(0001)/\mathfrak{S}(2000) = 0$ is given by:

$$\frac{\mathfrak{S}^{(0)}(1001)}{\mathfrak{S}^{(0)}(2000)} = \frac{5}{6}\,\frac{\Omega^{(1,1)*}}{\Omega^{(2,2)*}} \quad . \qquad (12)$$

In fig. 1 the points correspond to the experimental data for N_2 and CO at various temperatures. One observes that the experimental points do extrapolate to the proper intercept.

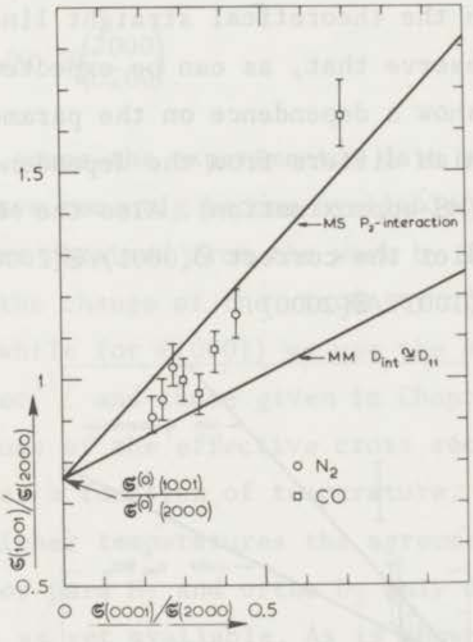

Fig. 1. Comparison of the data for N_2 and CO with the theoretical relation eq. (10).

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* It should be noted that even for $\psi = 2/15$ $\mathfrak{S}(2000)$ differs only a few percent from $\mathfrak{S}^{(0)}(2000)$ for realistic values of $\mathfrak{S}(0001)$.

We see that, although at small values of the parameter $\mathfrak{S}(0001)/\mathfrak{S}(2000)$ the experimental points might still be reconciled with both theoretical lines, there is a definite discrepancy with the MM-approximation at higher values. The MS-approximation (eq. (2)) on the other hand seems to predict somewhat too high values.

In order to see how essential the exact form of the nonsphericity in the potential can be for the form of the approximate relation eq. (1), we plotted in fig. 2 results for CH_4 and CD_4 along with the theoretical straight lines as given by eq. (10). We observe that, as can be expected, the experimental results show a dependence on the parameter $\mathfrak{S}(0001)/\mathfrak{S}(2000)$ which differs from the dependence for a P_2-type interaction (MS-approximation). Also the MM-approximation does not predict the correct $\mathfrak{S}(0001)/\mathfrak{S}(2000)$-dependence of the quantity $\mathfrak{S}(1001)/\mathfrak{S}(2000)$.

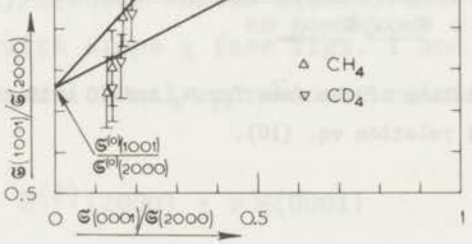

Fig. 2. Comparison of the data for CH_4 and CD_4 with the theoretical relation eq. (10).

It has become common practice to derive collision numbers - essentially the ratio $\mathfrak{S}(2000)/\mathfrak{S}(0001)$ - from heat conductivity data using the MM-approximation, eq. (1), see for example refs. 7 and 8. In view of the failure of this approximation, as illustrated in figs. 1 and 2, such an inverse procedure will lead to erroneous results for $\mathfrak{S}(0001)$, as has already been indicated by *e.g.* Barua *et al.*7).

3. *The relation for* $\mathfrak{S}\begin{pmatrix}2000\\0200\end{pmatrix}$. A second approximate relation involving $\mathfrak{S}(0001)$ has been given by Moraal and Snider3,4)

$$\mathfrak{S}(0001) \approx \sqrt{30}\ \mathfrak{S}\begin{pmatrix}2000\\0200\end{pmatrix} \quad . \qquad (13).$$

For a number of gases the experimental data needed to test this relation have recently become available. The data for $\mathfrak{S}\begin{pmatrix}2000\\0200\end{pmatrix}$ have been obtained from the work by Korving9) and Burgmans10) on the change of the viscosity of gases in a magnetic field*, while for $\mathfrak{S}(0001)$ we use the acoustical results of Sluijter11) and those given in Chapter III. In figs. 3 and 4 the values of the effective cross sections of N_2 and CO are plotted as a function of temperature. We observe that especially at higher temperatures the agreement is quite satisfactory. For para H_2 and ortho D_2 only data at room temperature are as yet available. As is shown in table I, relation eq. (3) seems again to hold quite well. The results for HD, however, where the dominant term in the non-spherical part of the potential is of the P_1-type (first Legendre-poly-

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* Actually in $\Delta\eta$-measurements the absolute magnitude of $\mathfrak{S}\begin{pmatrix}2000\\0200\end{pmatrix}$ is determined. Recent work by Baas14) shows that for N_2 this effective cross section is indeed positive.

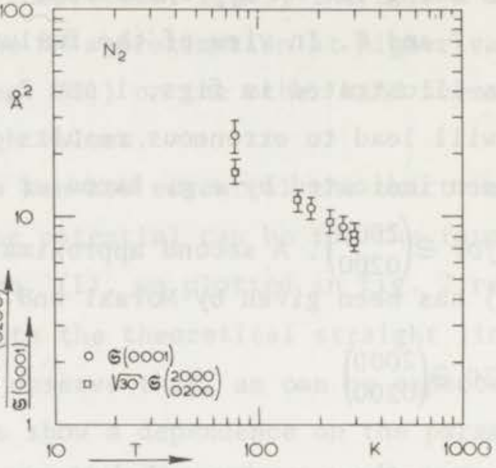

Fig. 3. The relation $\mathfrak{S}(0001) = \sqrt{30}\,\mathfrak{S}\begin{pmatrix}2000\\0200\end{pmatrix}$ tested with experimental data for N_2 ·

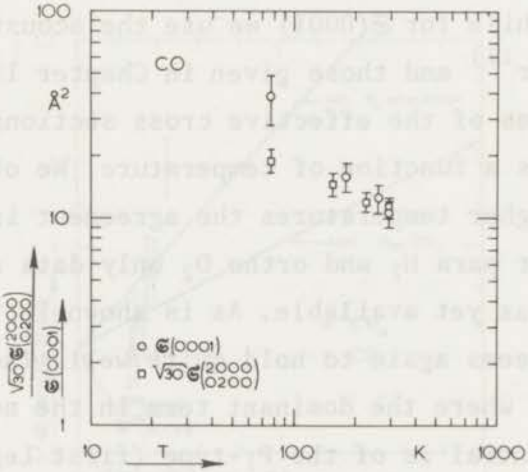

Fig. 4. The relation $\mathfrak{S}(0001) = \sqrt{30}\,\mathfrak{S}\begin{pmatrix}2000\\0200\end{pmatrix}$ tested with experimental data for CO.

TABLE I

Test of the relation $\mathfrak{S}(0001) \approx \sqrt{30}\, \mathfrak{S}\binom{2000}{0200}$
for hydrogen isotopes (see eq. (3))

Gas	T	$\mathfrak{S}(0001)^{11,12)}$	$\sqrt{30}\, \mathfrak{S}\binom{2000}{0200}^{9,10)}$
	K	Å^2	
para H_2	293	0.105	0.110
ortho D_2	293	0.130	0.135
HD	77	2.03	2.59
	293	1.14	1.56

nomial), show significant deviations from relation (3). Also CH_4, not having a P_2-type potential, does not fit the relation eq. (3), which in this case reads: $\mathfrak{S}(0001) \approx (k/c_{int})\, \sqrt{30}\, \mathfrak{S}\binom{2000}{0200}$. This is illustrated in fig. 5 where data from refs. 5 and 10 have been used.

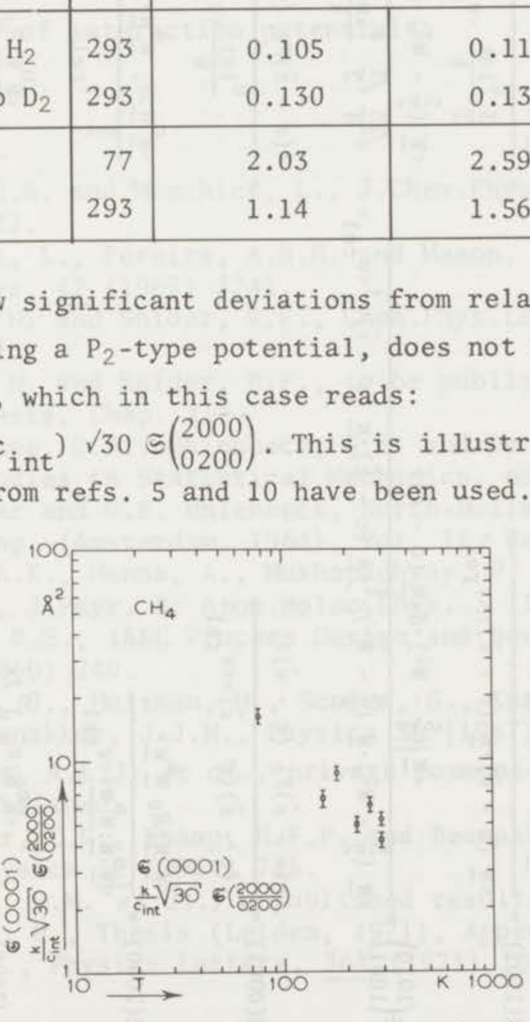

Fig. 5. The relation $\mathfrak{S}(0001) \approx (k/c_{int})\, \sqrt{30}\, \mathfrak{S}\binom{2000}{0200}$ tested with experimental data for CH_4.

TABLE II

Definition of the effective cross sections used in Chapter IV

$$\mathfrak{S}(1010) = \frac{\langle \underline{W}\,(\frac{5}{2} - W^2)\cdot R_0 \underline{W}\,(\frac{5}{2} - W^2)\rangle}{\langle \underline{W}\,(\frac{5}{2} - W^2)\cdot \underline{W}\,(\frac{5}{2} - W^2)\rangle \langle v_{rel}\rangle} = \frac{\langle \underline{W}\,(\frac{5}{2} - W^2)\cdot R_0 \underline{W}\,(\frac{5}{2} - W^2)\rangle}{\frac{15}{4}\,\langle v_{rel}\rangle}$$

$$\mathfrak{S}(1001) = \frac{\langle \underline{W}\,(\varepsilon - \bar{\varepsilon})\cdot R_0 \underline{W}\,(\varepsilon - \bar{\varepsilon})\rangle}{\langle \underline{W}\,(\varepsilon - \bar{\varepsilon})\cdot \underline{W}\,(\varepsilon - \bar{\varepsilon})\rangle \langle v_{rel}\rangle} = \frac{\langle \underline{W}\,(\varepsilon - \bar{\varepsilon})\cdot R_0 \underline{W}\,(\varepsilon - \bar{\varepsilon})\rangle}{\frac{3}{2}\,\frac{c_{int}}{k}\,\langle v_{rel}\rangle}$$

$$\mathfrak{S}\begin{pmatrix}1010\\1001\end{pmatrix} = \frac{\langle \underline{W}\,(\frac{5}{2} - W^2)\cdot R_0 \underline{W}\,(\varepsilon - \bar{\varepsilon})\rangle}{\langle \underline{W}\,(\frac{5}{2} - W^2)\cdot \underline{W}\,(\frac{5}{2} - W^2)\rangle^{\frac{1}{2}} \langle \underline{W}\,(\varepsilon - \bar{\varepsilon})\cdot \underline{W}\,(\varepsilon - \bar{\varepsilon})\rangle^{\frac{1}{2}} \langle v_{rel}\rangle} = \frac{\langle \underline{W}\,(\frac{5}{2} - W^2)\cdot R_0 \underline{W}\,(\varepsilon - \bar{\varepsilon})\rangle}{\sqrt{\frac{15}{4}}\,\sqrt{\frac{3}{2}\,\frac{c_{int}}{k}}\,\langle v_{rel}\rangle}$$

$$\mathfrak{S}(0001) = \frac{\langle (\varepsilon - \bar{\varepsilon}) R_0\,(\varepsilon - \bar{\varepsilon})\rangle}{\langle (\varepsilon - \bar{\varepsilon})(\varepsilon - \bar{\varepsilon})\rangle \langle v_{rel}\rangle} = \frac{\langle (\varepsilon - \bar{\varepsilon}) R_0\,(\varepsilon - \bar{\varepsilon})\rangle}{\frac{c_{int}}{k}\,\langle v_{rel}\rangle}$$

$$\mathfrak{S}(2000) = \frac{\langle \underline{W}^{\circ}\underline{W} : R_0\ \underline{W}^{\circ}\underline{W}\rangle}{\langle \underline{W}^{\circ}\underline{W} : \underline{W}^{\circ}\underline{W}\rangle \langle v_{rel}\rangle} = \frac{\langle \underline{W}^{\circ}\underline{W} : R_0\ \underline{W}^{\circ}\underline{W}\rangle}{\frac{5}{2}\,\langle v_{rel}\rangle}$$

$$\mathfrak{S}\begin{pmatrix}2000\\0200\end{pmatrix} = \frac{\langle \underline{W}^{\circ}\underline{W} : R_0\ \underline{J}^{\circ}\underline{J}\rangle}{\langle \underline{W}^{\circ}\underline{W} : \underline{W}^{\circ}\underline{W}\rangle^{\frac{1}{2}} \langle \underline{J}^{\circ}\underline{J} : \underline{J}^{\circ}\underline{J}\rangle^{\frac{1}{2}} \langle v_{rel}\rangle} = \frac{\langle \underline{W}^{\circ}\underline{W} : R_0\ \underline{J}^{\circ}\underline{J}\rangle}{\sqrt{\frac{5}{2}}\,\sqrt{\frac{2}{3}\,J^4 - \frac{1}{2}\,J^2}\ \langle v_{rel}\rangle}$$

Remarks

1) A more detailed discussion of these effective cross sections is given by Hulsman[13).

2) The numerators are equal to the collision integrals as employed by *e.g.* Wang Chang *et al.*[6) and by Mason *et al.*[1,2).

In conclusion one can state that the approach of Moraal and Snider in which they obtain approximate relations between quite different effective cross sections by using the form of the non-spherical part of the interaction potential is quite succesful. In view of this result it may be hoped that further research in this direction will lead to good results for a variety of interaction potentials.

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CHAPTER V

SOUND ABSORPTION IN MIXTURES IN THE BURNETT REGION

Summary

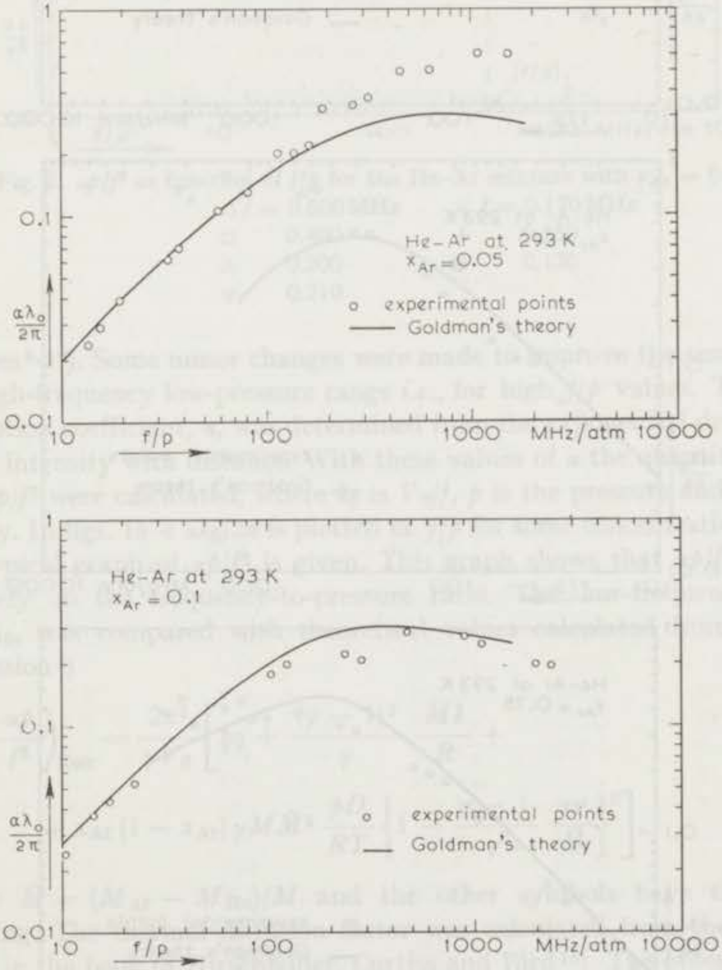
Sound-absorption measurements in gaseous He–Ar mixtures have been performed at 293 K in a frequency range extending from the Navier–Stokes regime far into the transition (Burnett) region. The shape of the absorption curve is found to be independent of the composition of the mixture. An apparent relaxation time is introduced. This relaxation time shows a sharp maximum at low Ar concentration, due to the mass mismatch between He and Ar.

1. *Introduction.* Since the pioneering experiments of Greenspan[1]) in 1950 on sound absorption and dispersion in the Burnett region, there has been a steady interest in the physical aspects of high-frequency sound propagation in gases. At this moment there is reasonable agreement between theory[2]) and experiment[3]) for pure gases, although for higher-order approximations the agreement becomes slightly worse. For binary mixtures the situation is different. In the (low) frequency region where the Navier–Stokes equations are valid the theory was developed by Kohler[4]) and extended by Meixner[5]). This theory is well confirmed by the experimental data of many investigators[6–10]).

At higher frequencies, however, the situation is complicated by the fact that in mixtures collisions between like and between unlike molecules give rise to several different time scales. Furthermore, in mixtures with a large mass mismatch the persistence of velocities will increase, thereby causing more pronounced differences between those various time scales. In these mixtures the deviations from the Navier–Stokes behaviour will occur therefore at lower frequencies than in a pure gas. In 1967 Foch[11]) presented a theory for such mixtures at frequencies where the sound absorption starts to deviate from the Navier–Stokes description.

Recently Goldman[12]) worked out a two-fluid type theory for binary mixtures of gases with a large mass difference assuming that the equilibration of the species (*i.e.* the vanishing of differences in velocity and temperature between the species) is slow as compared to the scale of Maxwellization for each species separately[12,13]). Such a theory should be valid over a wider frequency range. Surprisingly, no experimental data were available for comparison with the theory. For this reason, we undertook the measurement of sound absorption in He–Ar mixtures in a frequency range extending over the Navier–Stokes and Burnett regimes. The results of these investigations are reported in section 2 and will be discussed in section 3.

2. *Experiments.* The measurements were performed at 293 K in the same apparatus as was used earlier to investigate rotational relaxation in hydrogen



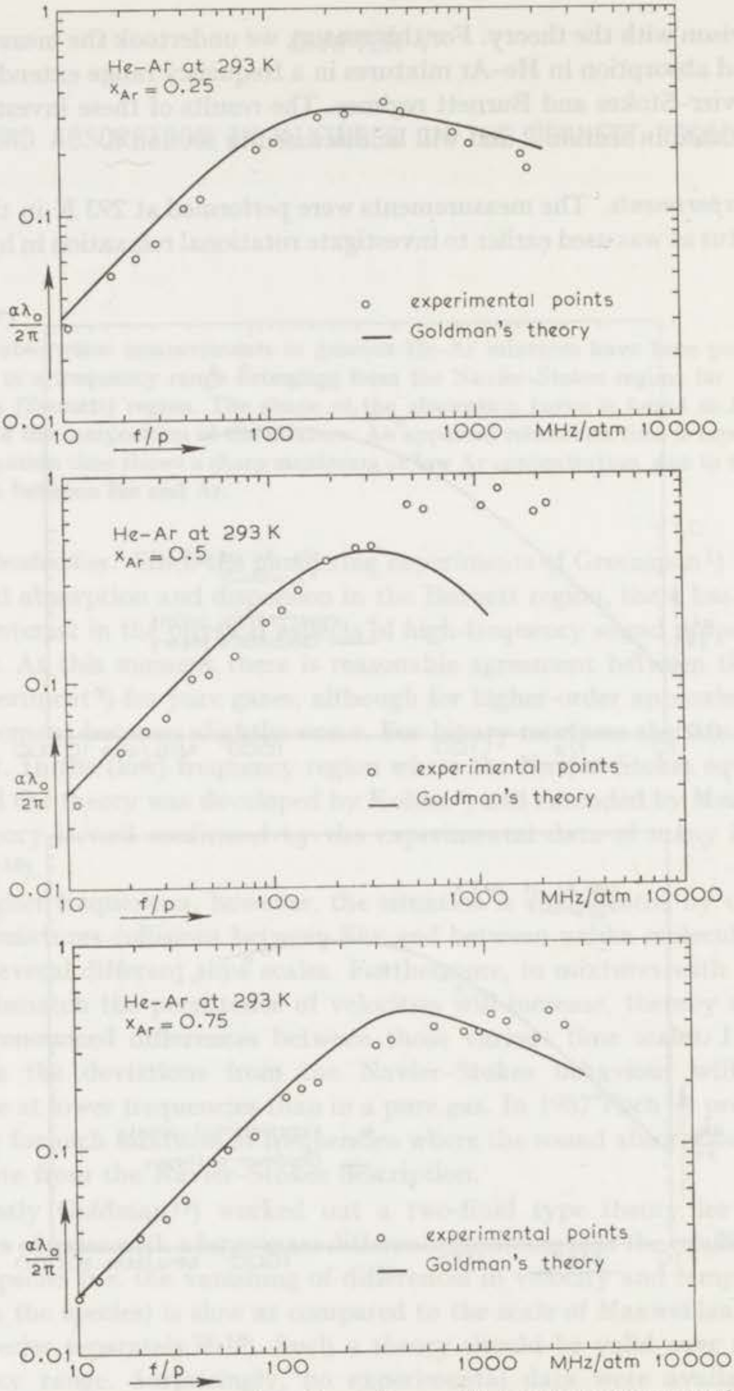


Fig. 1a–c. Absorption per wavelength, $\alpha\lambda_0/2\pi$, *vs.* f/p together with theoretical results of Goldman at various concentrations.

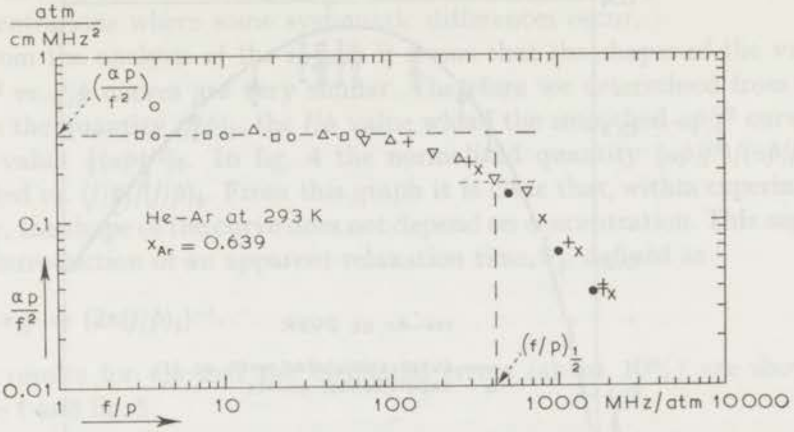


Fig. 2. $\alpha p/f^2$ as function of f/p for the He–Ar mixture with $x_{\text{Ar}} = 0.639$.

○	$f = 0.500$ MHz	×	$f = 0.170$ MHz
□	0.400	+	0.150
△	0.300	●	0.130
▽	0.210		

isotopes[9, 14]. Some minor changes were made to improve the sensitivity in the high-frequency low-pressure range *i.e.*, for high f/p values. The sound absorption coefficient, α, was determined from the exponential decay of the sound intensity with distance. With these values of α the quantities $\alpha\lambda_0/2\pi$ and $\alpha p/f^2$ were calculated, where λ_0 is V_0/f, p is the pressure and f the frequency. In figs. 1a–e $\alpha\lambda_0/2\pi$ is plotted *vs.* f/p for some concentrations. In fig. 2 a typical graph of $\alpha p/f^2$ is given. This graph shows that $\alpha p/f^2$ depends uniquely on the frequency-to-pressure ratio. The low-frequency value, $(\alpha p/f^2)_0$, was compared with theoretical values calculated from Kohler's expression[4])

$$\left(\frac{\alpha p}{f^2}\right)_{\text{Koh}} = \frac{2\pi^2}{\gamma V_0}\left[\tfrac{4}{3}\eta + \frac{(\gamma-1)^2}{\gamma}\,\frac{M\lambda}{R} + x_{\text{Ar}}(1-x_{\text{Ar}})\,\gamma M\tilde{M}^2\,\frac{pD}{RT}\left\{1-\frac{\gamma-1}{\gamma}\,\frac{\alpha_T}{\tilde{M}}\right\}^2\right], \qquad (1)$$

where $\tilde{M} = (M_{\text{Ar}} - M_{\text{He}})/M$ and the other symbols have their usual meaning. The thermal diffusion factor was calculated from the formulae given in the book of Hirschfelder, Curtiss and Bird[15]). The other transport coefficients were taken from experimental data found in the literature[16–19]). The results for $(\alpha p/f^2)_0$ are shown in fig. 3 and in table I together with the corresponding values calculated using the above equation. The experimental

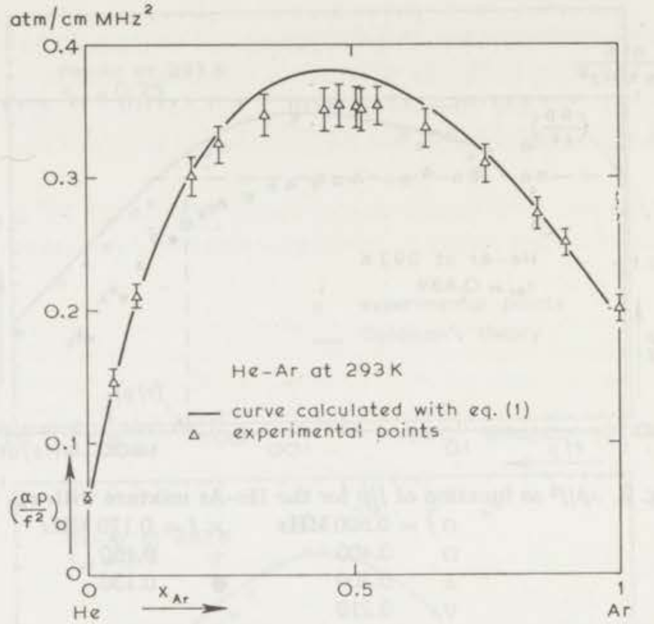


Fig. 3. $(\alpha p/f^2)_0$, the low-frequency value of $\alpha p/f^2$, as function of Ar concentration, compared with the results from Kohler's equation (eq. (1)).

Table I

Experimental results

x_{Ar}	$\left(\frac{\alpha p}{f^2}\right)_0$	$\left(\frac{\alpha p}{f^2}\right)_{Koh}$	$\left(\frac{f}{p}\right)_{\frac{1}{2}}$	$\tau_{\frac{1}{2}}p$
	(atm/cm MHz^2)		(MHz/atm)	(10^{-10} s atm)
0.000	0.059	0.052	600	2.6 ± 0.3
0.051	0.146	0.146	500	3.2 ± 0.3
0.094	0.211	0.208	178	8.9 ± 0.9
0.199	0.302	0.308	217	7.3 ± 0.7
0.249	0.325	0.332	228	7.0 ± 0.7
0.337	0.347	0.366	272	5.8 ± 0.6
0.449	0.351	0.381	450	3.5 ± 0.3
0.476	0.355	0.380	380	4.2 ± 0.4
0.508	0.353	0.379	610	2.6 ± 0.3
0.516	0.351	0.373	520	3.1 ± 0.3
0.548	0.354	0.373	470	3.4 ± 0.3
0.639	0.337	0.356	425	3.8 ± 0.4
0.750	0.310	0.318	360	4.4 ± 0.4
0.848	0.272	0.275	590	2.7 ± 0.3
0.898	0.251	0.249	440	3.6 ± 0.4
1.000	0.201	0.190	420	3.8 ± 0.4

error in $(\alpha p/f^2)_0$ is about 5%. Good agreement is found except at intermediate concentrations where some systematic differences occur.

From the analysis of the results it seems that the shapes of the various $\alpha p/f^2$ *vs.* f/p curves are very similar. Therefore we determined from these plots the quantity $(f/p)_{\frac{1}{2}}$, the f/p value where the smoothed $\alpha p/f^2$ curve has the value $\frac{1}{2}(\alpha p/f^2)_0$. In fig. 4 the normalized quantity $(\alpha p/f^2)/(\alpha p/f^2)_0$ is plotted *vs.* $(f/p)/(f/p)_{\frac{1}{2}}$. From this graph it is clear that, within experimental error, the shape of the curve does not depend on concentration. This suggests the introduction of an apparent relaxation time, $\tau_{\frac{1}{2}}$, defined as

$$\tau_{\frac{1}{2}}p = (2\pi(f/p)_{\frac{1}{2}})^{-1}.$$

The results for $\tau_{\frac{1}{2}}p$ and the estimated errors (about 10%) are shown in table I and fig. 5.

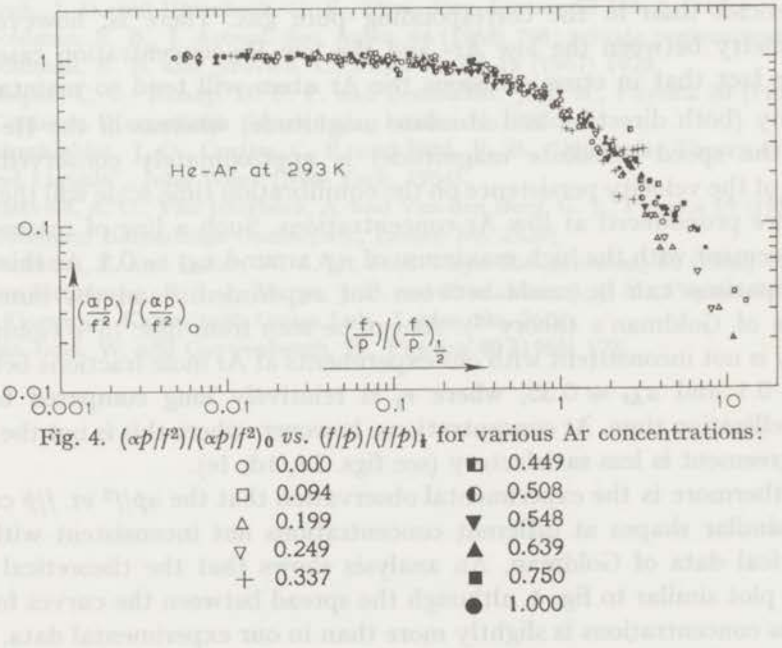


Fig. 4. $(\alpha p/f^2)/(\alpha p/f^2)_0$ *vs.* $(f/p)/(f/p)_{\frac{1}{2}}$ for various Ar concentrations:

○	0.000	◧	0.449
□	0.094	◐	0.508
△	0.199	▼	0.548
▽	0.249	▲	0.639
+	0.337	■	0.750
		●	1.000

3. *Discussion.* From the present data for $\tau_{\frac{1}{2}}p$ (see fig. 5) we observe a sharp increase and a definite maximum at low Ar concentrations, whereas in the high Ar concentration range there seem to be indications that the curve has some structure other than a straight line.

In mixtures with a large mass mismatch the persistence of velocity will – at low concentrations of either component – lead to longer time scales for

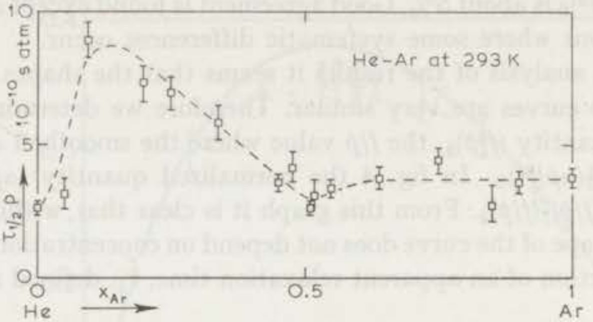


Fig. 5. Results for $\tau_{\frac{1}{2}}p$ as a function of concentration.

the equilibration processes between the species than in the pure gas case. At these concentrations the sound absorption, therefore, will show deviations from the (hydrodynamic) Navier–Stokes behaviour at lower frequencies than in the corresponding pure gas. There is, however, an asymmetry between the low Ar- and the low He-concentration case, due to the fact that in cross collisions the Ar atom will tend to maintain its velocity (both direction and absolute magnitude) whereas of the He atom only the speed (absolute magnitude) is approximately conserved. The effect of the velocity persistence on the equilibration time scale will therefore be more pronounced at low Ar concentrations. Such a line of reasoning is in agreement with the high maximum of $\tau_{\frac{1}{2}}p$ around $x_{\mathrm{Ar}} = 0.1$. At this stage a comparison can be made between our experiments and the numerical results of Goldman's theory¹²). As can be seen from figs. 1a–e Goldman's theory is not inconsistent with our experiments at Ar mole fractions between $x_{\mathrm{Ar}} \approx 0.1$ and $x_{\mathrm{Ar}} \approx 0.35$, where $\tau_{\frac{1}{2}}$ is relatively long compared to the Maxwellization time. At concentrations, however, where this is not the case, the agreement is less satisfactory (see figs. 1a, 1d, 1e).

Furthermore is the experimental observation that the $\alpha p/f^2$ *vs.* f/p curves have similar shapes at different concentrations not inconsistent with the numerical data of Goldman. An analysis shows that the theoretical data give a plot similar to fig. 4, although the spread between the curves for the various concentrations is slightly more than in our experimental data.

Further theoretical work is required in order to elucidate the structure of the $\tau_{\frac{1}{2}}p$ *vs.* x_{Ar} curve.

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SAMENVATTING

In dit proefschrift wordt een aantal onderzoekingen beschreven betreffende relaxatieverschijnselen in verdunde gassen. Met behulp van acoustische technieken is een tweetal relaxatieprocessen in het bijzonder onderzocht.

In meeratomige gassen treedt de zgn. rotatie-translatierelaxatie op. Hierbij bestudeert men de snelheid waarmee het thermisch evenwicht tussen translatie- en rotatie-vrijheidsgraden door middel van moleculaire botsingen wordt ingesteld. Ter afronding van het in Leiden verrichte onderzoek over rotatierelaxatie in de waterstofisotopen, zijn HD en ortho H_2 experimenteel onderzocht. In beide gevallen is een zodanig temperatuurgebied gekozen, dat slechts de twee laagste rotatietoestanden - voor HD $J = 0$ en $J = 1$ en voor oH_2 $J = 1$ en $J = 3$ - in aanzienlijke mate bezet zijn. In een dergelijke situatie is het mogelijk de evenwichtsinstelling met één relaxatietijd te beschrijven. Uit de resultaten zijn effectieve botsingsdoorsneden berekend. De effectieve botsingsdoorsnede voor HD (hoofdstuk I) blijkt in het temperatuurgebied van 20 tot 42 K nagenoeg constant te zijn. Evenzo blijkt de effectieve botsingsdoorsnede, die de relaxatie van HD tengevolge van botsingen met He beschrijft, vrijwel temperatuuronafhankelijk te zijn.

Om de relaxatietijd voor de overgang $J = 1 \rightleftarrows 3$ in waterstof op betrouwbare wijze te kunnen bestuderen, dient men over zeer zuivere oH_2 te beschikken. Een opstelling, waarmee normale waterstof (75% oH_2) verrijkt kan worden, wordt beschreven in het begin van hoofdstuk II. Uit geluidsabsorptie-metingen in waterstof met een ortho-concentratie van 96% is de rotatierelaxatietijd voor de overgang $J = 1 \rightleftarrows 3$ berekend.

Aan het slot van hoofdstuk II worden de in het Kamerlingh Onnes Laboratorium verkregen resultaten voor rotatierelaxatie in para-H_2 ($J = 0 \rightleftarrows 2$), ortho-H_2 ($J = 1 \rightleftarrows 3$), ortho-D_2 ($J = 0 \rightleftarrows 2$) en HD ($J = 0 \rightleftarrows 1$) besproken. Nagegaan wordt, welke mogelijkheden de experimentele gegevens in een vergelijking met de theorie bieden.

Het gedrag van de rotatierelaxatietijd als functie van de temperatuur blijkt in hoofdzaak te worden bepaald door de beginhelling van de curve van de excitatie-cross-sectie als functie van de energie. De consequentie hiervan voor de mogelijkheid om aan de hand van experimentele gegevens uitspraken te doen over de preciese vorm van de moleculaire wisselwerking wordt bediscussieerd.

Bij de waterstofisotopen verkeert men in de situatie, dat het tengevolge van de grote energiesplitsing tussen de rotatieniveau's mogelijk is metingen aan een 2-niveausysteem te verrichten. Bij de meeste andere gassen (N_2, CO, etc.) is evenwel bij experimenteel toegankelijke condities steeds een groot aantal niveau's bezet. Tengevolge hiervan liggen adequate berekeningen van botsingsdoorsneden voorlopig niet in het bereik. In dergelijke gevallen kan men met acoustische technieken geen onderscheid maken tussen afzonderlijke overgangen, doch meet men in de geluidsabsorptie een gemiddelde over een groot aantal processen. Het is echter wel mogelijk om op algemene gronden theoretische relaties tussen verschillende effectieve botsingsdoorsneden af te leiden.

Om de voor een test van dergelijke relaties benodigde experimentele gegevens te verkrijgen zijn voor een aantal gassen de rotatierelaxatietijden gemeten. De resultaten hiervan staan vermeld in hoofdstuk III, terwijl in hoofdstuk IV enkele van de bedoelde relaties besproken worden.

Een ander type relaxatieverschijnsel treedt cp in een mengsel van gassen met een sterk verschillende massa. Voor een bestudering van dit verschijnsel, dat optreedt als de energie-uitwisseling tussen de botsende moleculen bemoeilijkt wordt door het grote massaverschil van de botsingspartners, lijken mengsels van HD met Ne op het eerste gezicht het meest aangewezen. De grote hoeveelheid rotatie-energie die bij de-excitatie van HD in een botsing met Ne vrijkomt, kan nl. niet worden doorgegeven aan het Ne-atoom. Een eenvoudige berekening laat zien, dat dit effect de rotatierelaxatietijd met 10 ã 20% kan veranderen. Bij metingen (vermeld in hoofdstuk I) bleek echter de nauwkeurigheid ontoereikend om dit effect in HD-Ne mengsels te bestuderen. Dit als gevolg van de grote klassieke absorptie.

Het effect van een dergelijk groot massaverschil kan echter ook onder andere condities bestudeerd worden. In een geschikt gekozen edelgasmengsel kan men met acoustische technieken de tijdschaal onderzoeken, waarop het thermisch evenwicht tussen de translatievrijheidsgraden van beide componenten zich instelt. Deze tijdschaal kan in een dergelijk mengsel oplopen tot vele malen de tijd tussen twee opeenvolgende botsingen, hetgeen tot uiting zal komen, doordat de hydrodynamische beschrijving van de geluidsvoortplanting bij een lagere frequentie zijn geldigheid verliest dan voor zuivere gassen het geval is. Dit wordt inderdaad experimenteel gevonden voor He-Ar mengsels (hoofdstuk V). De vergelijking met de theorie van Goldman laat zien dat verder theoretisch onderzoek aan dergelijke verschijnselen noodzakelijk is.

Op verzoek van de faculteit der Wiskunde en Natuurwetenschappen volgt hier een overzicht van mijn studie.

Na mijn Gymnasium-ß opleiding van 1954 tot 1960 aan het Lorentz Lyceum te Eindhoven begon ik in september 1960 mijn studie aan de Rijksuniversiteit te Leiden, waar ik in 1964 het candidaatsexamen aflegde in de Natuurkunde en Wiskunde met bijvak Scheikunde. Sindsdien ben ik op het Kamerlingh Onnes Laboratorium in de werkgroep voor Molecuulfysica onder leiding van Prof.Dr. J.J.M. Beenakker en Dr. H.F.P. Knaap, werkzaam op het gebied van acoustisch onderzoek.

Vanaf 1965 assisteer ik op het natuurkundig practicum voor prae-candidaten. Voorts assisteer ik bij het college Moleculaire Natuurkunde.

In 1967 legde ik het doctoraal examen Experimentele Natuurkunde af, waarna ik begon met het in dit proefschrift beschreven onderzoek op het gebied van relaxatieverschijnselen in eenvoudige, verdunde gassen. Sinds april 1967 ben ik als wetenschappelijk medewerker in dienst van de Stichting voor Fundamenteel Onderzoek der Materie (F.O.M.). Binnen de groep Molecuulfysica had ik een belangrijk aandeel bij het automatiseren van de verwerking van meetgegevens.

In 1965 werkte ik gedurende twee maanden in het "Instituut voor Lage Temperaturen en Technische Fysica" te Leuven.

Bij de experimenten en vrrhuizingen, waarvan de resultaten in dit proefschrift beschreven worden, werd ik achtereenvolgens geassisteerd door Drs. R.A.J. Keijser, Drs. J.P.J. Heemskerk, Drs. J.C.W. Bosschieter, Drs. R.W.C. Brom, L.M.J. Borsboom, A.F. Hengeveld en A.H. Alberga.

De discussies met Dr. C.J.N. van den Meijdenberg met name over hoofdstuk II waren zeer verhelderend. Drs. A.L.J. Burgmans ben ik zeer erkentelijk voor het beschikbaar stellen van nog niet gepubliceerde resultaten ten behoeve van hoofdstuk IV.

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Op verzoek van de Faculteit der Wiskunde en Natuurwetenschappen volgt hier een overzicht van mijn studie.

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