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Citation: *The Journal of Chemical Physics* **143**, 214303 (2015); doi: 10.1063/1.4936417

View online: <http://dx.doi.org/10.1063/1.4936417>

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# Influence of a magnetic field on the viscosity of a dilute gas consisting of linear molecules

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(Received 10 October 2015; accepted 12 November 2015; published online 1 December 2015)

The viscomagnetic effect for two linear molecules, N<sub>2</sub> and CO<sub>2</sub>, has been calculated in the dilute-gas limit directly from the most accurate *ab initio* intermolecular potential energy surfaces presently available. The calculations were performed by means of the classical trajectory method in the temperature range from 70 K to 3000 K for N<sub>2</sub> and 100 K to 2000 K for CO<sub>2</sub>, and agreement with the available experimental data is exceptionally good. Above room temperature, where no experimental data are available, the calculations provide the first quantitative information on the magnitude and the behavior of the viscomagnetic effect for these gases. In the presence of a magnetic field, the viscosities of nitrogen and carbon dioxide decrease by at most 0.3% and 0.7%, respectively. The results demonstrate that the viscomagnetic effect is dominated by the contribution of the  $\underline{jj}$  polarization at all temperatures, which shows that the alignment of the rotational axes of the molecules in the presence of a magnetic field is primarily responsible for the viscomagnetic effect. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4936417>]

## I. INTRODUCTION

It has been known for some time that the shear viscosity  $\eta$  of a dilute gas consisting of polyatomic molecules is influenced by the presence of a magnetic field.<sup>1,2</sup> During the 1960s, it was established experimentally that this effect is small, but measurable in carefully designed viscometers. Numerous measurements have been performed,<sup>3,4</sup> and the kinetic theory has been developed<sup>3</sup> that illustrates that the viscomagnetic effect can provide a sensitive probe for the anisotropy of the intermolecular potential. Calculations of the viscomagnetic effect have lagged behind the other developments, as for a long time it proved computationally very expensive and nearly intractable to perform them. Most treatments relied on simplifying the molecular interactions, a rough-sphere model being the most advanced.<sup>5</sup> The advent of classical trajectory (CT) calculations and recent developments<sup>6–13</sup> that have established it as the method of choice for computing transport properties of dilute gases consisting of small polyatomic molecules have radically changed the situation. We are now in the position to perform calculations of the viscomagnetic effect directly from the intermolecular potential. In this work, we have taken advantage of generalized cross sections for N<sub>2</sub> and CO<sub>2</sub> recently evaluated by means of classical trajectories using highly accurate *ab initio* potentials<sup>9,12</sup> to calculate the viscomagnetic effect for these two gases. This supplements our work on the viscomagnetic effect in methane<sup>6</sup> and building on earlier attempts to analyze the viscomagnetic effect in N<sub>2</sub> and CO<sub>2</sub>.<sup>14,15</sup>

The present calculations allow for a stringent test of the kinetic theory expressions and different approximations,

provide values of the viscomagnetic effect at temperatures where no experiments have been carried out, improve our understanding of the dominant collisional effects, and allow for the quantification of the different contributions that make up the viscomagnetic effect. Furthermore, the comparison with the available experimental data allows for further validation of the anisotropy of the proposed *ab initio* potentials. The choice of N<sub>2</sub> and CO<sub>2</sub> is not only driven by the existence of accurate values of generalized cross sections but also by the fact that for linear molecules, the theory for the viscomagnetic effect is well established.<sup>3</sup>

Linear diamagnetic molecules, such as nitrogen and carbon dioxide, can undergo inelastic collisions and possess a finite magnetic moment due to their rotation. In any kinetic theory treatment, one has to consider not only the distribution of the reduced peculiar velocities  $\mathbf{W}$  of the molecules but also the distribution of their rotational angular momenta  $\mathbf{j}$ . Application of an external macroscopic velocity field will cause, through collisions, an anisotropy (polarization) in both distributions. At the macroscopic level, the polarization is manifested as the gas viscosity. In the presence of a magnetic field, precession of the magnetic moments will occur, thus altering the polarizations that have been established as a result of the macroscopic velocity gradient and the molecular collisions. In the direction of the magnetic field (longitudinal effect), this will result in a reduction of the viscosity of a dilute diamagnetic gas. The longitudinal viscomagnetic effect is only a function of  $B/P$ , the ratio of the magnetic flux density  $B$  and the pressure  $P$ , and at high ratios it will reach a saturation level. In addition, the presence of the magnetic field will induce a viscomagnetic effect in the gas perpendicular to the field (transverse effect), which is also a function of  $B/P$ , but exhibits a maximum and decays to zero at high values of the  $B/P$  ratio.

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The shear viscosity of a dilute polyatomic gas is obtained formally by solving the Waldmann-Snyder equation<sup>16–18</sup> (generalized Boltzmann equation) with respect to the perturbation of the distribution function from the local equilibrium.<sup>3,19–22</sup> The expansion is performed in terms of irreducible tensors containing  $\mathbf{W}$  and  $\mathbf{j}$ . The viscosity is primarily determined by the second rank tensor  $\overline{\mathbf{W}\mathbf{W}}$ . However, for a polyatomic gas, it is important to also include the polarizations that depend on  $\mathbf{j}$ . Traditionally, this involved polarizations of the type  $\overline{\mathbf{j}\mathbf{j}}$ ,  $\overline{\mathbf{W}\mathbf{W}\mathbf{j}}$ , and  $\overline{\mathbf{W}\mathbf{W}\mathbf{j}\mathbf{j}}$ .<sup>3,20,23,24</sup> The inclusion of an odd-in- $\mathbf{j}$  polarization is especially interesting, as it indicates, in the classical picture, the absence of inverse collisions and lack of preserving detailed balance.<sup>23</sup> It can be seen quantum-mechanically as a measure of how much the degeneracy of the rotational states influences the viscomagnetic effect. For linear molecules, the expressions for the contributions of each of the three polarizations to the viscomagnetic effect are available, but to the best of our knowledge, the expressions arising from the  $\overline{\mathbf{W}\mathbf{W}\mathbf{j}}$  and  $\overline{\mathbf{W}\mathbf{W}\mathbf{j}\mathbf{j}}$  polarizations are only available in the so-called spherical approximation (see Chap. 5.2.2 of Ref. 3). As part of the expansion of the distribution function, basis functions are constructed by multiplying each polarization tensor by Laguerre polynomials in  $W^2$  and  $j^2$ . Traditionally, such an expansion was only performed for the dominant  $\overline{\mathbf{W}\mathbf{W}}$  polarization<sup>3</sup> and resulted in the higher-order correction factors  $f^{(n)}$ , which are also familiar from the treatment of monatomic species.<sup>25</sup> The recent work on  $\text{N}_2$  and  $\text{CO}_2$  indicates that contributions of higher-order correction factors for shear viscosity are, at most,  $+(1-2)\%$ .<sup>9,12,15</sup> Moraal *et al.*<sup>5</sup> also studied the inclusion of higher-order correction factors in the  $\overline{\mathbf{j}\mathbf{j}}$  polarization and concluded, based on the rough-sphere model, that they are much smaller than the analogous velocity ones. Hence, for the purpose of this work, only the results in the first-order approximation will be discussed further.

All the experimental evidence so far<sup>3</sup> points to the dominance of the  $\overline{\mathbf{j}\mathbf{j}}$  contribution in determining the viscomagnetic effect, and all the analyses of the experimental data to extract the appropriate generalized cross sections have been performed on this basis. Furthermore, the cross sections obtained in this manner were used in previous CT studies of linear molecules as the basis for comparison.<sup>14,15,26</sup> We are now in a position to assess the validity of this assumption by calculating the contributions from the other two polarizations and hence can test the validity of the experimental analyses based solely on the  $\overline{\mathbf{j}\mathbf{j}}$  contribution.

In Sec. II, we briefly describe the kinetic theory approach used to calculate the viscomagnetic effect. In Sec. III, we compare with experimental data and discuss the contributions of different polarizations and the temperature dependence of the viscomagnetic effect. A summary and conclusions are given in Sec. IV.

## II. THEORY

In the presence of a magnetic field, the changes in the viscosity  $\eta$ , which is now a tensorial quantity, can be described in terms of five nonzero independent coefficients, three  $\Delta\eta_i^+/\eta$  with  $i = 0, 1, 2$  describing the longitudinal effects

and two  $\eta_i^-/\eta$  with  $i = 1, 2$  describing the transverse effects.<sup>3</sup> For linear molecules, assuming that only the  $\overline{\mathbf{j}\mathbf{j}}$ ,  $\overline{\mathbf{W}\mathbf{W}\mathbf{j}}$ , and  $\overline{\mathbf{W}\mathbf{W}\mathbf{j}\mathbf{j}}$  polarizations contribute, one can express the five viscomagnetic coefficients in the first-order approximation, using the latest notation, as follows:

$$\frac{\Delta\eta_0^+}{\eta} = +\frac{3}{2}\psi_{21}f(\xi_{21}) - \frac{1}{24}\psi_{22}[2f(\xi_{22}) + 8f(2\xi_{22})], \quad (1)$$

$$\frac{\Delta\eta_1^+}{\eta} = -\psi_{02}f(\xi_{02}) + \frac{5}{4}\psi_{21}f(\xi_{21}) - \frac{1}{24}\psi_{22}[7f(\xi_{22}) + 6f(2\xi_{22})], \quad (2)$$

$$\frac{\Delta\eta_2^+}{\eta} = -\psi_{02}f(2\xi_{02}) + \frac{1}{2}\psi_{21}f(\xi_{21}) - \frac{1}{24}\psi_{22}[6f(\xi_{22}) + 4f(2\xi_{22})], \quad (3)$$

$$\frac{\eta_1^-}{\eta} = -\psi_{02}g(\xi_{02}) + \frac{1}{4}\psi_{21}g(\xi_{21}) - \frac{1}{24}\psi_{22}[-5g(\xi_{22}) + 6g(2\xi_{22})], \quad (4)$$

$$\frac{\eta_2^-}{\eta} = -\psi_{02}g(2\xi_{02}) + \frac{1}{2}\psi_{21}g(\xi_{21}) - \frac{1}{24}\psi_{22}[6g(\xi_{22}) + 4g(2\xi_{22})], \quad (5)$$

where  $f(x) = x^2/(1+x^2)$ ,  $g(x) = x/(1+x^2)$ , and the dimensionless field parameter  $\xi_{pq}$  is given by

$$\xi_{pq} = \frac{g_{\text{rot}}\mu_{\text{N}}k_{\text{B}}T}{\hbar\langle v \rangle_0} \frac{1}{\Xi(pq00)^{(0)}} \frac{B}{P}. \quad (6)$$

Here,  $g_{\text{rot}}$  is the rotational  $g$ -factor specific to each molecular species,<sup>3</sup>  $\mu_{\text{N}}$  is the nuclear magneton,  $\hbar$  is Planck's constant,  $k_{\text{B}}$  is Boltzmann's constant,  $T$  is the temperature, and  $\langle v \rangle_0 = 4(k_{\text{B}}T/\pi m)^{1/2}$  is the average relative thermal speed with  $m$  being the molecular mass. The quantity  $\psi_{pq}$ , which largely governs the magnitude of the contribution from each polarization, is given as

$$\psi_{pq} = \frac{\Xi\left(\begin{smallmatrix} pq00 \\ 2000 \end{smallmatrix}\right)^2}{\Xi(2000)\Xi(pq00)^{(0)}}. \quad (7)$$

The customary notation  $\Xi\left(\begin{smallmatrix} p & q & s & t \\ p' & q' & s' & t' \end{smallmatrix}\right)^{(k)}$  is employed in labeling the temperature-dependent generalized cross sections, which include details of the dynamics of the binary encounters in the pure gas with appropriate statistical averaging over the internal states and translational energy.<sup>3</sup> The indices  $p, p'$  and  $q, q'$  denote the tensorial ranks in  $\mathbf{W}$  and  $\mathbf{j}$ , respectively, while  $k$  is the total tensorial rank of the basis functions underlying the generalized cross sections. The cross sections used in the present work are referred to as barred cross sections.<sup>3,4</sup> Unbarred cross sections<sup>3,27</sup> differ from the respective barred ones only when both  $p$  and  $q$  or both  $p'$  and  $q'$  are nonzero. We do not indicate the bar when the barred and unbarred cross sections are identical. The unbarred cross section  $\Xi(pq00)^{(0)}$  in Eqs. (6) and (7) can be calculated as a weighted average of the related barred cross sections, see Eqs. (5.2-11) of Ref. 3. For notational convenience, when  $p'q's't' = pqst$ , just one row is retained, and if the value of  $k$  is unique, it is omitted. Diagonal

and off-diagonal cross sections are referred to as transport (those  $\Xi(pqst)^{(k)}$  with  $p \neq 0$ ) or relaxation [ $\Xi(0qst)$ ] and production or coupling cross sections, respectively. Transport and relaxation cross sections are always positive, so that  $\psi_{pq}$  is positive as well. The cross section  $\Xi(2000)$  is usually referred to as the viscosity cross section since the field-free viscosity is given in the first-order approximation (which accounts only for the dominant **WW** polarization) by

$$\eta = \frac{k_B T}{\langle v \rangle_0 \Xi(2000)}. \quad (8)$$

It is interesting to observe [see Eqs. (1)–(5)] that while the **jj** and **WWjj** polarizations lead to a negative longitudinal viscomagnetic effect, the odd-in-**j** **WWj** polarization leads to a positive one.

The generalized cross sections for nitrogen and carbon dioxide were computed using of a modified version of the **TRAJECT** software code.<sup>28</sup> Classical trajectories describing the collision process of two molecules were obtained for a given total energy,  $E = E_{tr} + E_{rot}$ , by integrating Hamilton's equations for linear rigid rotors from pre- to post-collisional values (initial and final separation: 500 Å) using the highly accurate *ab initio* pair potentials of Refs. 9 and 12 for N<sub>2</sub> and CO<sub>2</sub>, respectively. The total-energy-dependent generalized cross sections can be represented as nine-dimensional integrals over the initial states. They were calculated for 33 values of  $E$ , ranging from 15 K to 60 000 K for N<sub>2</sub> and 60 K to 60 000 K for CO<sub>2</sub>, by means of a simple Monte Carlo procedure, in which the initial states were generated utilizing quasi-random numbers. Up to  $8 \times 10^6$  trajectories for N<sub>2</sub> and  $4 \times 10^6$  trajectories for CO<sub>2</sub> were computed at each energy. For low energies, the number of trajectories had to be reduced significantly because the computational demand to achieve a sufficient accuracy for a particular trajectory increases as the energy decreases. The final integration over the total energy to obtain temperature-dependent generalized cross sections was performed using Chebyshev quadrature. We estimate the standard uncertainty of the computed cross sections due to the Monte Carlo integration to be of the order of 0.1% for  $\Xi(2000)$ ,  $\Xi(0200)$ ,  $\Xi(2100)^{(0)}$ , and  $\Xi(2200)^{(0)}$ , 1% for  $\Xi\left(\begin{smallmatrix} 0200 \\ 2000 \end{smallmatrix}\right)$ , and 5% for  $\Xi\left(\begin{smallmatrix} 2100 \\ 2000 \end{smallmatrix}\right)$  and  $\Xi\left(\begin{smallmatrix} 2200 \\ 2000 \end{smallmatrix}\right)$ .

The present sets of generalized cross sections for N<sub>2</sub> and CO<sub>2</sub> have already been utilized in Refs. 12 and 13 for the calculation of traditional, field-free transport properties of dilute CO<sub>2</sub> gas and CH<sub>4</sub>-N<sub>2</sub> gas mixtures. The computed viscosities were found to be in excellent agreement with the best experimental data. Average deviations from the data of Vogel and co-workers,<sup>29–31</sup> which have an uncertainty of about 0.2%, are only -0.55% for carbon dioxide<sup>12</sup> and -0.24% for nitrogen,<sup>13</sup> thus confirming the high quality of the *ab initio* pair potentials<sup>9,12</sup> and their suitability for the present study.

### III. RESULTS

#### A. Comparison with experiment

##### 1. Nitrogen

Beenakker *et al.*<sup>2</sup> were the first to report a viscomagnetic effect for nitrogen in their seminal work that established

that the viscosity of diamagnetic molecules can decrease in the presence of a magnetic field. Previous experimental work<sup>32,33</sup> reported no such effect. Since the early 1960s, eight independent measurements of viscomagnetic coefficients in nitrogen, carried out in three different laboratories, have been performed using capillary viscometers operating in a null mode. As a continuation of the measurements of Beenakker *et al.*,<sup>2</sup> Korving *et al.*<sup>34</sup> reported a first set of accurate measurements for nitrogen that clearly exhibited a viscomagnetic effect. They carried out measurements of the average of two longitudinal coefficients,  $-(\Delta\eta_1^+ + \Delta\eta_2^+)/2\eta$ , by taking advantage of the cylindrical symmetry of their circular cross-sectional capillary and positioning the field perpendicular to the flow. The measurements were performed at room temperature at  $B/P$  values of up to 0.0035 T/Pa (4.7 kOe/Torr). Korving followed this work with more extensive measurements<sup>35</sup> of two different longitudinal coefficients,  $-(\Delta\eta_2^+ - \Delta\eta_1^+)/\eta$  and  $-\Delta\eta_1^+/\eta$ , also at room temperature but with a stronger magnet, which allowed him to reach values of  $B/P$  as high as 0.031 T/Pa (41 kOe/Torr). The transverse coefficient  $\eta_2^-/\eta$  was first measured by Kikoin *et al.*<sup>36</sup> This was followed by work of Hulsman and co-workers,<sup>37,38</sup> who measured both transverse viscomagnetic coefficients,  $\eta_1^-/\eta$  and  $\eta_2^-/\eta$ , at room temperature using an experimental setup with an adjustable magnet orientation, which allowed for the determination of both coefficients with lower uncertainty. Subsequently, Hulsman *et al.*<sup>37,39</sup> reported a further set of measurements to evaluate the longitudinal coefficients at room temperature in the  $B/P$  range up to 0.007 T/Pa (9.5 kOe/Torr). They used an experimental arrangement with an electromagnet that could be rotated to realize different orientations between the magnetic field and the flow. Measurements at three different orientations allowed them to evaluate  $-\Delta\eta_1^+/\eta$ ,  $-(\Delta\eta_2^+ + \Delta\eta_0^+)/2\eta$  and  $-\Delta\eta_0^+/\eta$ . Finally, Burgmans *et al.*<sup>40</sup> measured the sum of two longitudinal coefficients,  $-(\Delta\eta_1^+ + \Delta\eta_2^+)/2\eta$ , at four temperatures, 77.4, 156, 223, and 293 K, and their difference,  $-(\Delta\eta_2^+ - \Delta\eta_1^+)/\eta$ , at a single temperature of 77.4 K for  $B/P$  strengths up to 0.023 T/Pa (31 kOe/Torr). Three more sets of measurements<sup>41,42</sup> are available at room temperature for  $\Delta\eta_1^+/\eta$ ,<sup>41</sup>  $\Delta\eta_2^+/\eta$ ,<sup>41</sup> and  $\eta_1^-/\eta$ .<sup>42</sup> They were specifically generated to validate the correct functioning of the apparatus, and they agree with the data of Hulsman *et al.*,<sup>38,39</sup> which were used as reference values. Therefore, these data sets are only partially used in our comparison.

In Figs. 1–4, the calculated values of the viscomagnetic coefficients are compared with the available experimental data (read from the published figures). No uncertainty estimate was given by the authors for the experimental data, although it was stated<sup>34</sup> that relative viscosity changes of  $2 \times 10^{-6}$  could be detected. We start by comparing the calculated values to the measured ones for the longitudinal viscomagnetic coefficients. Figure 1 shows the comparison with the data of Burgmans *et al.*,<sup>40</sup> who measured  $-(\Delta\eta_1^+ + \Delta\eta_2^+)/2\eta$  as a function of  $B/P$  at four different temperatures. We have also included the experimental data of Korving *et al.*<sup>34</sup> and the data calculated from the coefficients  $-\Delta\eta_1^+/\eta$  and  $-\Delta\eta_2^+/\eta$  quoted by Hulsman *et al.*<sup>39</sup> to illustrate the consistency of the experimental data at 293 K. The agreement between

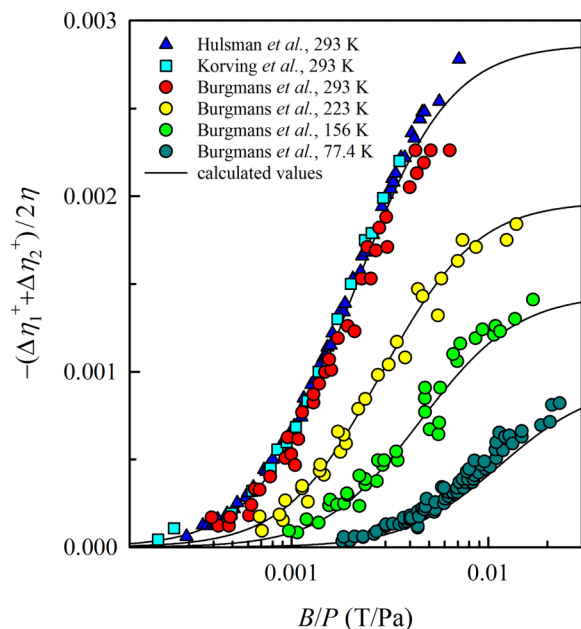


FIG. 1. Experimental data and calculated values for an average of two viscomagnetic coefficients,  $-(\Delta\eta_1^+ + \Delta\eta_2^+)/2\eta$ , for  $N_2$  as a function of the ratio of magnetic flux density  $B$  and pressure  $P$ . For clarity, the data of Burgmans *et al.*<sup>40</sup> at  $T = 77.4$  K,  $T = 156$  K, and  $T = 223$  K and the corresponding calculated values have been divided by 2, 2, and 1.5, respectively.

the calculated and measured values of  $-(\Delta\eta_1^+ + \Delta\eta_2^+)/2\eta$  is excellent. At the lowest temperature of 77.4 K, the calculated values underestimate the experimental ones somewhat.

Figure 2 shows the calculated and measured values for the coefficients  $-\Delta\eta_1^+/\eta$  and  $-\Delta\eta_2^+/\eta$  at  $T = 293$  K. For  $-\Delta\eta_1^+/\eta$ , two sets of data, which are in very good agreement, are available,<sup>35,39</sup> while for  $-\Delta\eta_2^+/\eta$ , the data of Hulsman,<sup>39</sup> reported as  $-(\Delta\eta_2^+ + \Delta\eta_0^+)/2\eta$  and  $-\Delta\eta_0^+/\eta$ , were used to

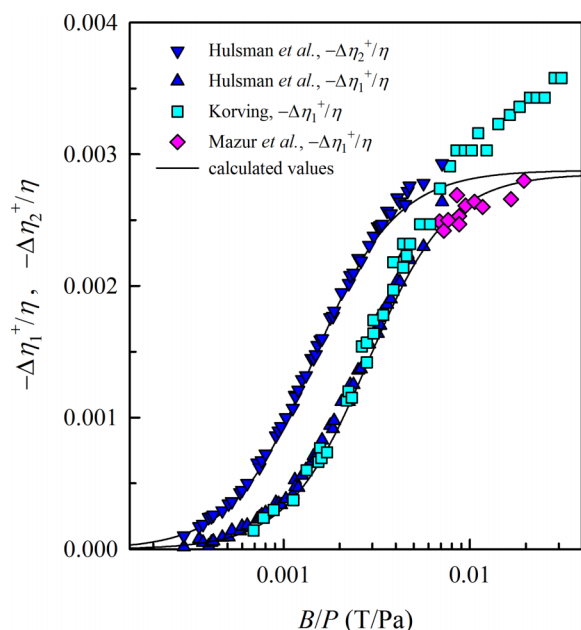


FIG. 2. Experimental data and calculated values for the viscomagnetic coefficients  $-\Delta\eta_1^+/\eta$  and  $-\Delta\eta_2^+/\eta$  for  $N_2$  at  $T = 293$  K as a function of the ratio of magnetic flux density  $B$  and pressure  $P$ .

generate it. Considering that the values of  $-\Delta\eta_0^+/\eta$  are two orders of magnitude smaller than those of  $-\Delta\eta_2^+/\eta$ , the uncertainty introduced by calculating the “experimental”  $-\Delta\eta_2^+/\eta$  coefficient in this manner is low. Figure 2 illustrates that the agreement between the calculated and experimental values is excellent up to  $B/P$  values that correspond to the extent of the data of Hulsman *et al.*,<sup>39</sup> with only a slight underestimation of the  $-\Delta\eta_2^+/\eta$  coefficient. At  $B/P$  values higher than  $7 \times 10^{-3}$  T/Pa, Korving’s  $-\Delta\eta_1^+/\eta$  data<sup>35</sup> are systematically underestimated. A similar underestimation at high  $B/P$  ratios of data generated by Korving using the same apparatus was observed for  $CH_4$ .<sup>6</sup> Mazur *et al.*<sup>41</sup> also measured the values of  $-\Delta\eta_1^+/\eta$  and  $-\Delta\eta_2^+/\eta$  for nitrogen in order to validate their new apparatus that was subsequently used to measure the viscomagnetic effect for symmetric-top molecules. Their measurements for nitrogen extend to higher  $B/P$  values (up to 0.02 T/Pa) than those of Hulsman *et al.*,<sup>39</sup> and we have included their high  $B/P$  data for the viscomagnetic coefficient  $-\Delta\eta_1^+/\eta$  in Fig. 2. As can be observed, the data of Mazur *et al.* lie below the data of Korving and are in good agreement with the calculated viscomagnetic coefficient. It is interesting to note that Korving gave more weight to his data at lower  $B/P$  values when fitting the dominant  $\bar{j}j$  polarization, and consequently his fitted curve also underestimates his measured data at high  $B/P$  values. Furthermore, we have tried to vary the values of the cross sections that enter Eq. (2), but no reasonable combination of cross sections gave a good overall fit to the measured  $-\Delta\eta_1^+/\eta$  data. There is thus sufficient evidence to indicate that the data of Korving<sup>35</sup> at high  $B/P$  values suffer from a systematic bias.

In Fig. 3, we compare with the data of Burgmans *et al.*<sup>40</sup> and Korving<sup>35</sup> for the difference between two longitudinal coefficients,  $-(\Delta\eta_2^+ - \Delta\eta_1^+)/\eta$ , as a function of

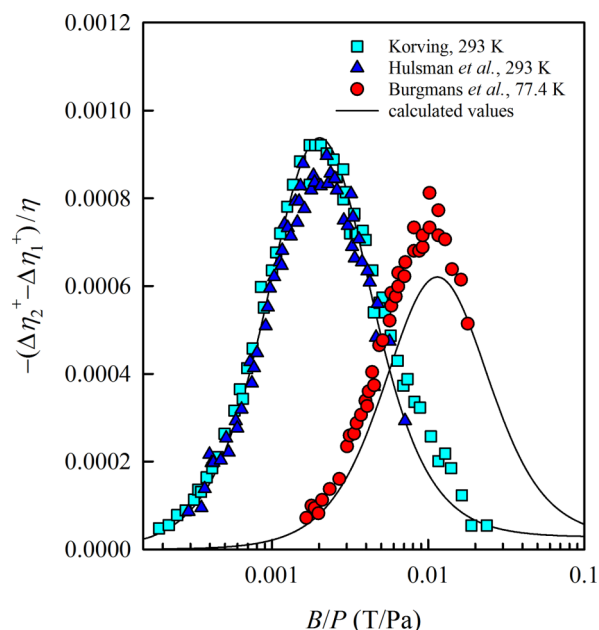


FIG. 3. Experimental data and calculated values for a difference of two viscomagnetic coefficients,  $-(\Delta\eta_2^+ - \Delta\eta_1^+)/\eta$ , for  $N_2$  as a function of the ratio of magnetic flux density  $B$  and pressure  $P$ .

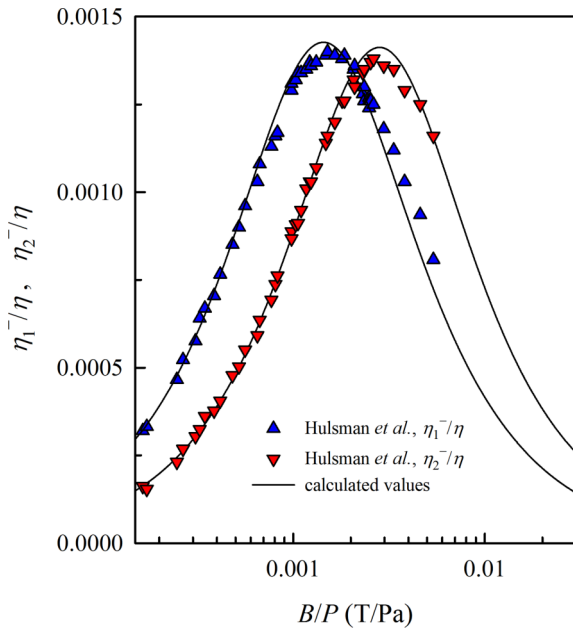


FIG. 4. Experimental data and calculated values for the viscomagnetic coefficients  $\eta_1^-/\eta$  and  $\eta_2^-/\eta$  for  $N_2$  at  $T = 293$  K as a function of the ratio of magnetic flux density  $B$  and pressure  $P$ .

$B/P$  at two different temperatures. We have also included the data calculated from the coefficients  $-\Delta\eta_1^+/\eta$  and  $-\Delta\eta_2^+/\eta$  given by Hulsman *et al.*<sup>38</sup> to show the consistency of the experimental data at 293 K. As in the case of the coefficient  $-(\Delta\eta_1^+ + \Delta\eta_2^+)/2\eta$  (see Fig. 1), the agreement between the calculated values and the experimental data at 293 K is excellent, while at 77.4 K, the calculated values underestimate the data of Burgmans *et al.*<sup>40</sup> The differences observed for  $-(\Delta\eta_1^+ + \Delta\eta_2^+)/2\eta$  and  $-(\Delta\eta_2^+ - \Delta\eta_1^+)/\eta$  at 77.4 K are understandable. At such low temperatures, the uncertainties of both the calculated values and the measured data are higher than at room temperature. We have performed a simple sensitivity analysis by assuming that all the difference can be ascribed to the uncertainty in the classical trajectory calculations. We obtain perfect agreement between the measured and calculated values for both  $-(\Delta\eta_1^+ + \Delta\eta_2^+)/2\eta$  and  $-(\Delta\eta_2^+ - \Delta\eta_1^+)/\eta$  by increasing the temperature to 82 K or by decreasing the  $\Xi(0200)$  cross section by 9%. Although this is far outside the standard uncertainty of the calculated  $\Xi(0200)$  cross section due to the Monte Carlo integration ( $\approx 0.1\%$ ), it is possible, although unlikely, that systematic errors due to deficiencies in the pair potential, the use of the rigid-rotor approximation, and the restriction to classical mechanics are primarily responsible for the observed discrepancy. We note that a more plausible explanation is that the temperature control in the experimental setup of Burgmans *et al.*<sup>40</sup> is not as good as claimed. The 77.4 K measurements were performed in an apparatus with a much smaller vacuum jacket than was used for the measurements at higher temperatures, and the actual temperature was measured at the vacuum jacket rather than in the middle of the gas. Furthermore, Burgmans *et al.*<sup>40</sup> have stated that it was “difficult to achieve a temperature stability good enough to successfully operate the apparatus below 77 K.”

Only Hulsman *et al.*<sup>39</sup> performed measurements that allowed for a value of the coefficient  $-\Delta\eta_0^+/\eta$  to be calculated. This is the only viscomagnetic coefficient that has no contribution from the dominant  $\mathbf{j}\mathbf{j}$  polarization and is consequently expected to be much smaller than the other coefficients. The values of  $-\Delta\eta_0^+/\eta$  evaluated by Hulsman *et al.*<sup>39</sup> at  $T = 293$  K increase from zero at low  $B/P$  values to a plateau of  $5 \times 10^{-5}$  at the highest magnetic field strengths measured,  $B/P = (2.8-7.0) \times 10^{-3}$  T/Pa. As the calculation performed by Hulsman *et al.*<sup>39</sup> involved a subtraction of two large numbers, the reproducibility is low and the scatter of the quoted  $-\Delta\eta_0^+/\eta$  data at the observed plateau is  $\pm 2 \times 10^{-5}$ . Our calculated values indicate that in the range of  $B/P$  where Hulsman *et al.*<sup>39</sup> observed a plateau,  $-\Delta\eta_0^+/\eta$  decreases from  $2.0 \times 10^{-5}$  to  $1.3 \times 10^{-5}$  before reaching a plateau of  $-1.5 \times 10^{-5}$  at  $B/P$  ratios greater than 0.2 T/Pa. Although the calculated values are roughly one third of those determined experimentally, the agreement is reasonable considering the large uncertainty associated with the experimental determination of  $-\Delta\eta_0^+/\eta$ . A more detailed discussion of the behavior of the  $-\Delta\eta_0^+/\eta$  coefficient will be presented in Sec. III B 2.

Figure 4 shows the calculated values and the experimental data of Hulsman *et al.*<sup>38</sup> for the two transverse viscomagnetic coefficients,  $\eta_1^-/\eta$  and  $\eta_2^-/\eta$ , at  $T = 293$  K. The agreement is excellent, and both the position and the magnitude of the maximum are reproduced rather well. The measurements of  $\eta_2^-/\eta$  by Kikoin *et al.*,<sup>36</sup> which are not included in Fig. 4, exhibit a maximum of  $1.0 \times 10^{-3}$  at a  $B/P$  value of about  $3 \times 10^{-3}$  T/Pa, and although the position of the maximum agrees with that of Hulsman *et al.*<sup>38</sup> and that of the calculated value, the magnitude of the measured transverse effect is  $\approx 27\%$  smaller.

## 2. Carbon dioxide

Measurements of the viscomagnetic effect in  $CO_2$  are scarce. Korving and co-workers<sup>34,35</sup> reported measurements of  $-(\Delta\eta_1^+ + \Delta\eta_2^+)/2\eta$ ,  $-(\Delta\eta_2^+ - \Delta\eta_1^+)/\eta$ , and  $-\Delta\eta_1^+/\eta$  employing the already described viscometers used to measure the viscomagnetic effect for nitrogen. The measurements were carried out at room temperature at  $B/P$  values of up to 0.053 T/Pa (71 kOe/Torr). The only other measurements are those of van Ditzhuyzen *et al.*<sup>24</sup> using a capillary viscometer with a superconducting magnet capable of generating very high fields strengths, which was arranged either perpendicular to the flow or at an angle of  $45^\circ$ . The apparatus was used to perform measurements of the longitudinal coefficient  $-\Delta\eta_2^+/\eta$  and the combination  $-(\Delta\eta_2^+ + 3\Delta\eta_0^+)/4\eta$  at  $T = 293$  K and values of  $B/P$  as high as 0.073 T/Pa (97 kOe/Torr).

In Fig. 5, the calculated and measured values of the longitudinal viscomagnetic coefficients  $-\Delta\eta_1^+/\eta$  and  $-\Delta\eta_2^+/\eta$  and their difference,  $-(\Delta\eta_2^+ - \Delta\eta_1^+)/\eta$ , are shown for  $T = 293$  K. The agreement with the data of van Ditzhuyzen *et al.*<sup>24</sup> is excellent. Only the  $-\Delta\eta_2^+/\eta$  coefficient of van Ditzhuyzen *et al.* is shown in the figure, as due to the small magnitude of the  $-\Delta\eta_0^+/\eta$  term, the good agreement we observed for the  $-(\Delta\eta_2^+ + 3\Delta\eta_0^+)/4\eta$  coefficient is to be expected. The data of Korving<sup>34,35</sup> agree well for  $B/P$  values below 0.016 T/Pa,

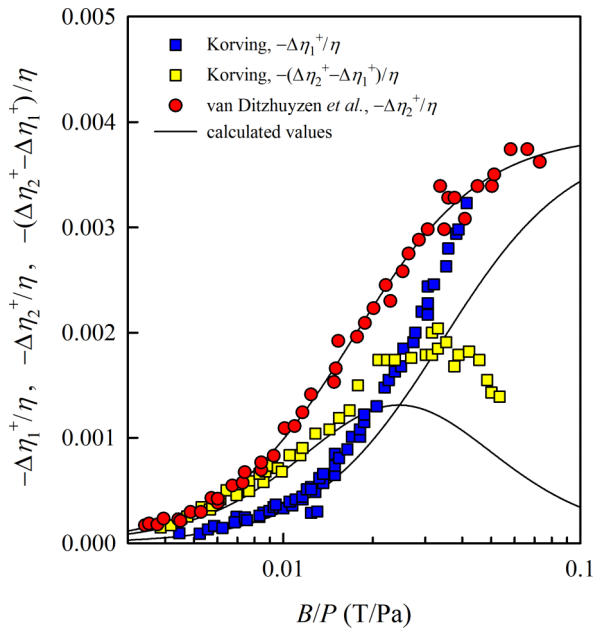


FIG. 5. Experimental data and calculated values for the two viscomagnetic coefficients  $-\Delta\eta_1^+/\eta$  and  $-\Delta\eta_2^+/\eta$  and the difference between them for  $\text{CO}_2$  at  $T = 293$  K as a function of the ratio of magnetic flux density  $B$  and pressure  $P$ .

while above that the calculated values underestimate the measured ones.<sup>35</sup> In order to compare the two sets of experimental data, we have used the  $-(\Delta\eta_2^+ - \Delta\eta_1^+)/\eta$  and  $-\Delta\eta_1^+/\eta$  data measured by Korving<sup>35</sup> to calculate the values of  $-\Delta\eta_2^+/\eta$ . At high values of  $B/P$ , these data are up to 40% higher than the data measured by van Ditzhuyzen and co-workers. Disagreement between the data of Korving<sup>35</sup> and other workers at high  $B/P$  values has already been noted when discussing the measurements for nitrogen and methane.<sup>6</sup> For measurements on  $\text{CO}_2$ , higher  $B/P$  values than those used for  $\text{N}_2$  had to be attained because of the smaller magnetic moment. As the same magnet was used by Korving, this required performing the measurements at much lower pressure, where the experimental uncertainty is higher. In the experimental setup of van Ditzhuyzen *et al.*, which was specifically designed to carry out measurements for molecules with a low magnetic moment, the need to go to lower pressures was eliminated by making use of a much stronger magnet. Thus, the analysis of the measurements for  $\text{CO}_2$  supports the overwhelming evidence already presented for  $\text{N}_2$  that the measurements of Korving and co-workers at high  $B/P$  values have a much larger uncertainty than assumed at the time.

## B. Behavior of the field effect

### 1. Contributions by different polarizations

The magnitude of each polarization is primarily determined by the value of  $\psi_{pq}$  as already discussed in Sec. II. As  $\psi_{pq}$  is a ratio of cross sections, see Eq. (7), we first examine the behavior of the cross sections governing the viscomagnetic effect as a function of temperature. The transport and relaxation cross sections  $\Xi(2000)$ ,  $\Xi(0200)$ ,  $\Xi(2100)^{(0)}$ , and  $\Xi(2200)^{(0)}$  exhibit a monotonic decrease with

temperature, which follows approximately a  $1/T$  dependence. The cross sections  $\Xi(2100)^{(0)}$  and  $\Xi(2200)^{(0)}$  are similar in magnitude; the differences between them do not exceed 8% for either molecule. The viscosity transport cross section,  $\Xi(2000)$ , and the relaxation cross section,  $\Xi(0200)$ , are of similar magnitude, but smaller than  $\Xi(2100)^{(0)}$  and  $\Xi(2200)^{(0)}$ . At low temperatures, for both molecules  $\Xi(0200)$  is larger than  $\Xi(2000)$ , while at higher temperatures, the reverse is true. For  $\text{N}_2$ , the change already occurs at around 95 K, while for  $\text{CO}_2$ , it only occurs at 830 K. Broadly speaking, this indicates that for  $\text{N}_2$ , the exchange of linear momentum is more favorable than the relaxation of angular momentum over most of the temperature range, while for  $\text{CO}_2$ , this is only true at high temperatures.

The production cross sections  $\Xi\left(\begin{smallmatrix} 0200 \\ 2000 \end{smallmatrix}\right)$ ,  $\Xi\left(\begin{smallmatrix} 2100 \\ 2000 \end{smallmatrix}\right)$ , and  $\Xi\left(\begin{smallmatrix} 2200 \\ 2000 \end{smallmatrix}\right)$  for both molecules are at least an order of magnitude smaller than  $\Xi(2000)$ . The largest of these three cross sections is  $\Xi\left(\begin{smallmatrix} 0200 \\ 2000 \end{smallmatrix}\right)$ . Above 65 K for  $\text{N}_2$  and 180 K for  $\text{CO}_2$ , it monotonically decreases with temperature. Nevertheless, its relative magnitude compared to  $\Xi(2000)$  or  $\Xi(0200)$  indicates that for both molecules the collisions are ineffective in coupling the angular-momentum polarization to that in velocity at all temperatures. The other two production cross sections,  $\Xi\left(\begin{smallmatrix} 2100 \\ 2000 \end{smallmatrix}\right)$  and  $\Xi\left(\begin{smallmatrix} 2200 \\ 2000 \end{smallmatrix}\right)$ , exhibit a more complex temperature dependence, which in some cases involves a change in sign. This is especially true for the cross section  $\Xi\left(\begin{smallmatrix} 2100 \\ 2000 \end{smallmatrix}\right)$ , which increases with temperature from a negative value, changing sign at around 125 K for  $\text{N}_2$  and 510 K for  $\text{CO}_2$ . A similar behavior for this cross section was already observed for the spherical-top molecule methane.<sup>6</sup>

In order to compare the contributions of each polarization to the viscomagnetic effect, we first examine the dimensionless ratios  $\psi_{21}/\psi_{02}$  and  $\psi_{22}/\psi_{02}$ . Figure 6 illustrates the temperature dependence of these two ratios for both  $\text{N}_2$  and  $\text{CO}_2$ . The ratio  $\psi_{21}/\psi_{02}$  exhibits a minimum at the point where the cross section  $\Xi\left(\begin{smallmatrix} 2100 \\ 2000 \end{smallmatrix}\right)$  changes sign. Its value never exceeds 0.1, indicating that for both gases, the  $\overline{\mathbf{W}\mathbf{W}\mathbf{j}}$  polarization is small compared to the  $\overline{\mathbf{j}\mathbf{j}}$  polarization. This behavior is similar to that observed for methane.<sup>6</sup> The increase of the contribution of the odd-in- $\mathbf{j}$   $\overline{\mathbf{W}\mathbf{W}\mathbf{j}}$  polarization with temperature relative to the  $\overline{\mathbf{j}\mathbf{j}}$  polarization can be interpreted quantum-mechanically

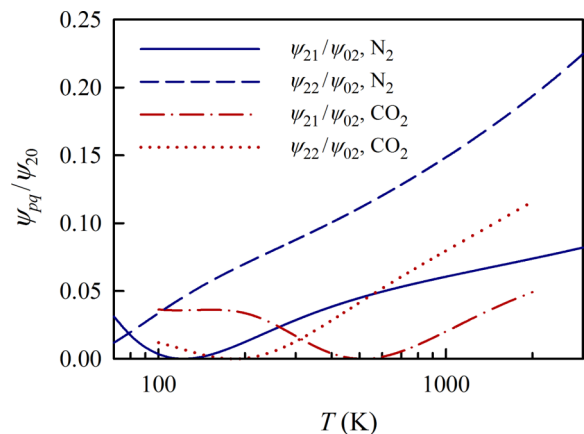


FIG. 6. Ratio of  $\psi_{pq}$  ( $pq = 21, 22$ ) and  $\psi_{02}$  as a function of temperature  $T$ .

as being due to the increase in the degeneracy of the rotational states, which would favor non-inverse collisions. The quantum-mechanical collision behavior should be close to the classical one at all temperatures considered in this work.

As can be seen in Fig. 6, the ratio  $\psi_{22}/\psi_{02}$  is much larger for both molecules than the ratio  $\psi_{21}/\psi_{02}$ , reaching a value of 0.225 for  $N_2$  at 3000 K, the highest temperature investigated. Hence, for the linear molecules  $N_2$  and  $CO_2$ , the impact of the  $\overline{WW}\overline{jj}$  polarization at high temperatures is stronger than that of the  $\overline{WW}\overline{j}$  polarization, but still weak compared to that of the  $\overline{jj}$  polarization. Here we observe significant differences compared to the  $CH_4$  molecule, where the contribution of the  $\overline{WW}\overline{jj}$  polarization at high temperatures was negligible.<sup>6</sup> For all three molecules, the  $\mathfrak{S}\left(\begin{smallmatrix} 2200 \\ 2000 \end{smallmatrix}\right)$  cross section tends to essentially a constant value at high temperatures, probably indicating that the features of the anisotropy of the intermolecular potential specifically responsible for generating the  $\overline{WW}\overline{jj}$  polarization remain nearly constant as we probe higher into the repulsive wall. For the two linear molecules, this high-temperature limit of  $\mathfrak{S}\left(\begin{smallmatrix} 2200 \\ 2000 \end{smallmatrix}\right)$  is positive and two times larger for  $CO_2$  than for  $N_2$ , whereas for  $CH_4$ , it is negative and two orders of magnitude smaller than for  $CO_2$ ,<sup>6</sup> thus implying that for  $CH_4$ , the anisotropy of the repulsive wall of the intermolecular potential is too weak to generate a significant contribution from the  $\overline{WW}\overline{jj}$  polarization. However, for the cross section  $\mathfrak{S}\left(\begin{smallmatrix} 0200 \\ 2000 \end{smallmatrix}\right)$ , we do not observe such a discrepancy between methane and the other two gases. Based on the analysis carried out so far, it would seem that the shape of the molecule, spherical top vs linear, seems to be a dominant factor in determining the magnitude of the contribution from the  $\overline{WW}\overline{jj}$  polarization. It is interesting to note that Moraal *et al.*<sup>5</sup> estimated that the upper limit of the ratio  $\psi_{22}/\psi_{02}$  will not exceed 0.1 based on the rough sphere model. As can be seen from Fig. 6, this is a reasonable assumption for  $CO_2$ , but not for  $N_2$ , where this ratio reaches a value of 0.225 at 3000 K. Thus, for nitrogen at high temperatures, we are observing a stronger coupling between the  $\overline{WW}$  and  $\overline{WW}\overline{jj}$  tensors than we would expect from the rough sphere model.

We next consider the influence of different polarizations on the overall viscomagnetic effect. For the longitudinal viscomagnetic coefficients  $-\Delta\eta_1^+/\eta$  and  $-\Delta\eta_2^+/\eta$ , the largest contribution of the  $\overline{WW}\overline{j}$  and  $\overline{WW}\overline{jj}$  polarizations is at saturation with respect to the  $B/P$  ratio. Figure 7 illustrates the relative combined contribution of the two polarizations at saturation as a function of temperature. It is clear that for both molecules, the dominant contribution is due to the  $\overline{jj}$  polarization, hence indicating that the alignment of the rotational axes of the molecules in the presence of a magnetic field is primarily responsible for the viscomagnetic effect. The same is true for the two transverse coefficients,  $\eta_1^-/\eta$  and  $\eta_2^-/\eta$ . The combined contribution of the  $\overline{WW}\overline{j}$  and  $\overline{WW}\overline{jj}$  polarizations is highest for  $N_2$  at the highest temperature studied (3000 K), where it increases the maximum in  $\eta_2^-/\eta$  by 2.3% and shifts its position on the  $B/P$  axis by +2%.

The influence of the secondary  $\overline{WW}\overline{j}$  and  $\overline{WW}\overline{jj}$  polarizations compared to the dominant  $\overline{jj}$  polarization is small

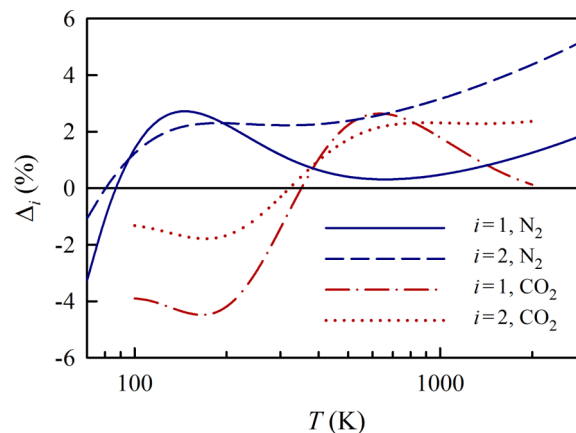


FIG. 7. Relative deviations  $\Delta_i$  of the viscomagnetic coefficients  $-(\Delta\eta_i^+/\eta)_{\text{sat}}$  ( $i = 1, 2$ ) from the corresponding coefficients obtained if only the dominant  $\overline{jj}$  polarization is considered, as a function of temperature  $T$ .

not only because the relative magnitude of each polarization is small but also because their contributions to the overall viscomagnetic effect are of different sign, see Eqs. (1)–(5). This also partly explains the shape of the curves at high temperatures observed in Fig. 7. For  $CO_2$ , the  $\overline{WW}\overline{j}$  and  $\overline{WW}\overline{jj}$  polarizations increase at approximately the same rate as can be seen in Fig. 6, and the cancellation leads to an approximately constant contribution to the  $\Delta\eta_2^+/\eta$  coefficient at high temperatures, see Fig. 7. For  $N_2$ , the  $\overline{WW}\overline{jj}$  polarization increases much more rapidly than the  $\overline{WW}\overline{j}$  polarization, and consequently the combined contribution of the two polarizations to  $\Delta\eta_2^+/\eta$  increases gradually with temperature, see Figs. 6 and 7. It is interesting to observe that the contribution of the odd-in- $j$   $\overline{WW}\overline{j}$  polarization to the viscomagnetic effect never exceeds 4%, which gives us a measure of how well detailed balance is maintained during the collisions.<sup>23</sup>

## 2. Temperature dependence of the viscomagnetic effect

The experimental work carried out so far has enabled the assessment of the viscomagnetic effect in a relatively narrow range of temperatures. The calculations performed as part of the present work allow for enhancing our understanding of the viscomagnetic effect over a much wider range of temperatures. We will specifically consider the temperature behavior of the saturation values of the longitudinal coefficients and of the maximum values of the transverse coefficients.

If only the  $\overline{jj}$  polarization is considered, it follows from Eqs. (2)–(5) for molecules with a negative value of  $g_{\text{rot}}$ , such as  $N_2$  and  $CO_2$ , that

$$-\left(\frac{\Delta\eta_1^+}{\eta}\right)_{\text{sat}} = -\left(\frac{\Delta\eta_2^+}{\eta}\right)_{\text{sat}} = 2\left(\frac{\eta_1^-}{\eta}\right)_{\text{max}} = 2\left(\frac{\eta_2^-}{\eta}\right)_{\text{max}} = \psi_{02}. \quad (9)$$

As the  $\overline{jj}$  polarization is dominant, it is thus sufficient to examine only one of the coefficients. Figure 8 illustrates the behavior of  $-(\Delta\eta_2^+/\eta)_{\text{sat}}$  for  $N_2$  and  $CO_2$ . For both gases, we observe an increase in the saturation value with increasing



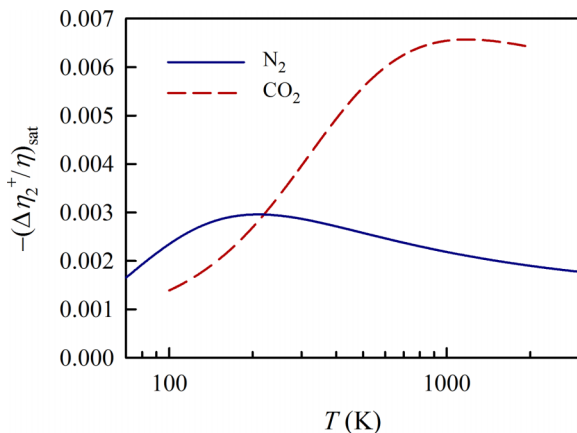


FIG. 8. Viscomagnetic coefficient  $-(\Delta\eta_2^+/\eta)_{\text{sat}}$  as a function of temperature  $T$ .

temperature, followed by a slow decrease as the influence of the repulsive part of the potential becomes dominant. The coefficient for  $\text{CO}_2$  is approximately three times larger than that for  $\text{N}_2$  at high temperatures. It is interesting to note that the saturation value for  $\text{CH}_4$  shows the same qualitative behavior, with a maximum value of  $-(\Delta\eta_2^+/\eta)_{\text{sat}} \approx 0.9 \times 10^{-3}$  occurring at 340 K.<sup>6</sup> Thus, for all three molecules, a magnetic field lowers the viscosity of the gas in the direction of the field at all temperatures. This is not only true at saturation but for all  $B/P$  ratios. However, in contrast to  $\text{CH}_4$ , the transverse viscomagnetic effect for  $\text{N}_2$  and  $\text{CO}_2$  is positive as a direct result of the negative value of the rotational  $g$ -factor for both molecules.

Figure 9 shows the behavior of  $(\Delta\eta_0^+/\eta)_{\text{sat}}$  for  $\text{N}_2$  and  $\text{CO}_2$ . This viscomagnetic coefficient has no contribution from the  $\overline{\mathbf{j}\mathbf{j}}$  polarization, so it is in essence another measure of how important the other polarizations are. For both gases, the magnitude is small; the absolute value does not exceed  $0.16 \times 10^{-3}$  in the temperature range studied, supporting the earlier conclusion that the contributions of the  $\overline{\mathbf{W}\mathbf{W}\mathbf{j}}$  and  $\overline{\mathbf{W}\mathbf{W}\mathbf{j}\mathbf{j}}$  polarizations are indeed almost negligible. The different temperature dependence observed for the two gases can be ascribed to the opposite signs of the two polarizations and the resulting cancellations, see Eq. (1).

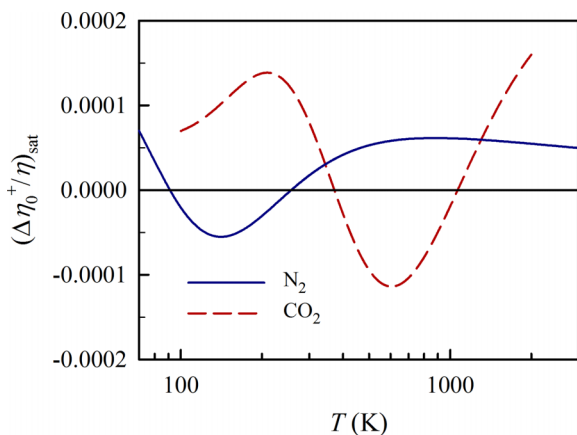


FIG. 9. Viscomagnetic coefficient  $(\Delta\eta_0^+/\eta)_{\text{sat}}$  as a function of temperature  $T$ .

#### IV. SUMMARY AND CONCLUSIONS

The viscomagnetic effect has been calculated for the linear molecules nitrogen and carbon dioxide in the dilute-gas limit over a wide range of temperatures using state-of-the-art *ab initio* pair potentials. The agreement with experimental data, which are only available up to room temperature, is excellent and further validates the kinetic theory approach for calculating the viscomagnetic effect and the high accuracy of the pair potentials. The contributions from the  $\overline{\mathbf{j}\mathbf{j}}$ ,  $\overline{\mathbf{W}\mathbf{W}\mathbf{j}}$ , and  $\overline{\mathbf{W}\mathbf{W}\mathbf{j}\mathbf{j}}$  polarizations have been investigated, and the results clearly show that the  $\overline{\mathbf{j}\mathbf{j}}$  polarization is dominant at all temperatures, which is partially due to the cancellation of the contributions from the  $\overline{\mathbf{W}\mathbf{W}\mathbf{j}}$  and  $\overline{\mathbf{W}\mathbf{W}\mathbf{j}\mathbf{j}}$  polarizations. However, at high temperatures the relative contributions of the  $\overline{\mathbf{W}\mathbf{W}\mathbf{j}}$  and  $\overline{\mathbf{W}\mathbf{W}\mathbf{j}\mathbf{j}}$  polarizations increase, indicating that the anisotropy of the repulsive wall is favorable for the creation of these polarizations.

The longitudinal viscomagnetic coefficients  $\Delta\eta_1^+/\eta$  and  $\Delta\eta_2^+/\eta$  are always negative. Their almost identical absolute values at saturation increase with increasing temperature, followed by a slow decrease as the repulsive part of the potential becomes more and more dominant. The longitudinal viscomagnetic coefficient  $\Delta\eta_0^+/\eta$ , which contains no contribution from the  $\overline{\mathbf{j}\mathbf{j}}$  polarization, is always much smaller in magnitude than the other two coefficients. The two transverse viscomagnetic coefficients,  $\eta_1^-/\eta$  and  $\eta_2^-/\eta$ , which are positive for both gases and vanish at saturation, are at most half the absolute value of the longitudinal coefficients  $\Delta\eta_1^+/\eta$  and  $\Delta\eta_2^+/\eta$  at saturation.

#### ACKNOWLEDGMENTS

R.H. gratefully acknowledges financial support by the Deutsche Forschungsgemeinschaft (DFG) through Grant No. HE 6155/1-1.

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