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Rotational relaxation in molecular hydrogen and deuterium: Theory versus acoustic experiments

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An explicit formulation of the rotational relaxation time in terms of state-to-state rate coefficients associated to inelastic collisions is reported. The state-to-rate rates needed for the detailed interpretation of relaxation in H₂ and D₂, including isotopic variant mixtures, have been calculated by solving the close-coupling Schrödinger equations using the H₂–H₂ potential energy surface by Diep and Johnson [J. Chem. Phys. 112, 4465 (2000)]. Relaxation related quantities (rotational effective cross section, bulk viscosity, relaxation time, and collision number) calculated from first principles agree reasonably well with acoustic absorption experimental data on H₂ and D₂ between 30 and 293 K. This result confirms at once the proposed formulation, and the validation of the H₂–H₂ potential energy surface employed, since no approximations have been introduced in the dynamics. Accordingly, the state-to-rate rates derived from Diep and Johnson potential energy surface appear to be overestimated by up to 10% for H₂, and up to 30% for D₂ at T = 300 K, showing a better agreement at lower temperatures. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4895398]

I. INTRODUCTION

The interchange of energy between the rotational and translational degrees of freedom of molecules due to inelastic collisions causes a number of physical manifestations usually referred to as “relaxation phenomena.” These have been treated in the frame of a general kinetic theory of transport and relaxation phenomena¹–⁵ based on the generalized Boltzmann equation.⁶–¹⁰ In general, the so derived physical quantities are expressed in terms of complicated integrals involving the state-to-state collision cross sections. For any particular collision process, these cross sections depend only on the collision energy between individual pairs of molecules, a quantity difficult to establish in most experiments. For these two reasons, no simple expressions in terms of more accessible quantities, like the temperature, appear to have been reported for transport and relaxation coefficients. Nonetheless, some of them can be expressed by relative simple expressions in terms of state-to-state rate coefficients (sts-rates, in short). These quantities only depend on the temperature and are better suited than the energy-dependent cross sections for the database tabulations employed in present day astrophysics.

The k(T)ij→ℓm sts-rates account for the probability of the elementary collisional process

\[ M_a(i) + M_b(j) \overset{k(T)ij→ℓm}{\rightarrow} M_a(ℓ) + M_b(m) \]

involving two molecules M_a and M_b of species a and b in a gas at translational temperature T. The two molecules undergo a collision-induced transition from the pre-collisional quantum states i and j into the post-collisional ones ℓ and m. 

Molecular relaxation in H₂ and D₂ is important for several reasons. First, H₂ and D₂ are simple molecules amenable to high level quantum calculations. The H₂–H₂ potential energy surface (PES) has been the subject of a great number of empirical and ab initio methods and is better known than for any other molecule.¹¹–¹⁶ Moreover, since long ago H₂ has been the reference molecule in the development of quantum scattering methods and calculations.¹⁷–⁴⁸ The state-to-state cross-sections and sts-rates for H₂:H₂ and D₂:D₂ inelastic collisions have probably been studied more systematically than for any other molecular system. In addition, due to the low anisotropy of the H₂–H₂ intermolecular PES, transfer of energy between rotational and translational degrees of freedom by H₂:H₂ and D₂:D₂ inelastic collisions has the lowest efficiency among all molecular systems, causing the largest energy non-equilibrium between rotational and translational degrees of freedom. This peculiarity is relevant for the interpretation of gas-dynamic environments like supersonic jets, shock waves, and circumstellar star-forming medium, where H₂ is the most abundant coolant molecule.

In contrast to the many theoretical works, comparatively few experiments on H₂:H₂ and D₂:D₂ inelastic collisions have been conducted so far. Among them, acoustic ultrasonic absorption experiments on H₂ and D₂ isotopomer variants have produced a valuable body of relaxation data at temperatures below 300 K, including relaxation time T between rotational and translational degrees of freedom, rotational relaxation effective cross section σ(0001), bulk viscosity η_V, and collision number Z, quantities which depend on the inelastic collisions.⁴⁹–⁵⁶ Relaxation cross sections and bulk viscosities derived from some of these experiments are summarized in Refs. 4 and 57. An unified theoretical view of these results has

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been reported in terms of tensorial relaxation cross sections, however, a molecular interpretation in terms of elementary inelastic collision processes is still incomplete and far from experimental accuracy in some cases. As shown below, these relaxation related quantities can be expressed explicitly in terms of the \( k_{ij \rightarrow lm} \) rates, providing a tangible link between ultrasonic acoustic experiments, gas dynamic concepts, and advanced quantum scattering calculations of \( k_{ij \rightarrow lm} \) rates based on high-quality intermolecular PESs.

The present paper reports:

1. an explicit description of the rotation-translation relaxation time \( \tau \) for H\(_2\) and D\(_2\) variants in terms of \( k_{ij \rightarrow lm} \) rates,
2. the set of \( k_{ij \rightarrow lm} \) rates for H\(_2\):H\(_2\) and D\(_2\):D\(_2\) inelastic collisions which are relevant in the 20 \( \leq T \leq 300 \) K thermal range, calculated by solving the close-coupling Schrödinger equations from a full \( \textit{ab initio} \) PES,
3. the assessment of the calculated \( k_{ij \rightarrow lm} \) rates by means of experimental data on H\(_2\) and D\(_2\) from ultrasonic absorption experiments,
4. the relaxation time \( \tau \) and the transport coefficients that depend on it (\( \sigma(0001) \), \( \eta_v \), \( Z \)) as calculated from the st rates in the 20 \( \leq T \leq 300 \) K range.

II. THEORY

A. Macroscopic relations

According to the kinetic theory, the rotational relaxation effective cross section \( \sigma(0001) \), the volume viscosity \( \eta_v \), and the collision number \( Z \) are related to the relaxation time \( \tau \) by

\[
\sigma(0001) = (nv_c \tau)^{-1},
\]

\[
\eta_v = \frac{k_B c_{rot}}{c_v} \frac{n k_B T}{\tau} = \frac{k_B c_{rot}}{c_v} \frac{k_B T}{v_c \sigma(0001)},
\]

\[
Z = \tau \tau_{GD} = \frac{\pi d^2}{\sigma(0001)},
\]

where \( k_B \) is Boltzmann constant, \( c_v = (3k_B / 2) + c_{rot} \), and

\[
\tau_{GD} = \frac{1}{4n d^2} \sqrt{\frac{m}{\pi k_B T}}
\]

is the mean time between inelastic collisions for molecules of mass \( m \) and gas-dynamic diameter \( d \) defined by a Lennard-Jones potential,

\[
V_{LL} = 4\epsilon((d/r)^{12} - (d/r)^6).
\]

In this work, we have taken \( d(H_2) = d(D_2) = 2.915 \) Å.

Other quantities in Eqs. (2)–(5) are the number density, \( n \), the average collision velocity between two molecules of reduced mass \( \mu \) in a gas at translational temperature \( T \),

\[
v_c = \sqrt{\frac{8k_B T}{\pi \mu}},
\]

and the rotational heat capacity per molecule, \( c_{rot} \). For a pure molecular gas at rotational temperature \( T_{rot} \), \( c_{rot} \) is given by

\[
c_{rot} = k_B (\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2),
\]

where

\[
\langle \varepsilon^n \rangle = \sum_i \varepsilon_i^n (2J_i + 1) \exp(-\varepsilon_i),
\]

and

\[
Q_{rot} = \sum_i (2J_i + 1) \exp(-\varepsilon_i)
\]

is the rotational partition function; \( J_i \) is the angular momentum quantum number of rotational state \( i \), and \( \varepsilon_i = E_i/(k_B T_{rot}) \), where the energy \( E_i \) is referred to the lowest accessible rotational state of the gas.

B. The relaxation time in H\(_2\) and D\(_2\)

The rotational relaxation time \( \tau \) in a molecular mixture \( M_a + M_b \) refers here to the relaxation of its total rotational energy towards its translational energy. In ultrasonic wave theory, this is formally expressed by a relaxation equation

\[
\frac{dT_{rot}}{dt} = -(T_{rot} - T) \tau^{-1},
\]

in terms of rotational and translational temperatures, \( T_{rot} \) and \( T \), respectively. This definition of rotational relaxation time is only valid if the rotational temperatures of species \( M_a \) and \( M_b \) are similar in the \( M_a + M_b \) gas mixture, i.e., if \( T_{rot,a} \approx T_{rot,b} \). In this case, we shall introduce the approximation

\[
T_{rot,a} \approx T_{rot,b} = T_{rot} \neq T.
\]

Otherwise, if \( T_{rot,a} \neq T_{rot,b} \), different relaxation times \( \tau_a \neq \tau_b \) hold for the relaxation of species \( M_a \) and \( M_b \) in the \( M_a + M_b \) mixture.

It is well established by supersonic jet experiments that the rotational temperatures of \( \text{para-H}_2 \) (pH\(_2\)) and \( \text{ortho-H}_2 \) (oH\(_2\)) are similar in pH\(_2\) + oH\(_2\) mixtures, but differ dramatically from the translational temperature.37,38,62,63 This suggests that a single rotational relaxation time \( \tau \) is a sound physical quantity for describing the relaxation of pH\(_2\) + oH\(_2\) mixtures.

The present derivation of the relaxation time \( \tau \) in terms of elementary collision processes is based on the use of a master equation expressed as a function of \( k_{ij \rightarrow lm} \) rates. Such a master equation has been proposed long ago64 and can be deduced from Boltzmann generalized equation.10

Let us express the rotational contribution to the enthalpy of the \( \alpha_a M_a + \alpha_b M_b \) mixture, with mole fractions \( \alpha_a \) and \( \alpha_b \), and \( \alpha_a + \alpha_b = 1 \), by

\[
H_{rot} = \alpha_a H_{rot,a} + \alpha_b H_{rot,b},
\]

and the rotational contribution to the heat capacity of the mixture by

\[
c_{rot} = \alpha_a c_{rot,a} + \alpha_b c_{rot,b}.
\]
where the contributions of species $M_a$ and $M_b$ are

$$c_{\text{rot},a} = \frac{dH_{\text{rot},a}}{dT_{\text{rot},a}}, \quad \text{and} \quad c_{\text{rot},b} = \frac{dH_{\text{rot},b}}{dT_{\text{rot},b}}. \quad (15)$$

Expressing the time derivative of the contribution of species $M_a$ to the enthalpy as

$$\frac{dH_{\text{rot},a}}{dt} = \frac{dH_{\text{rot},a}}{dT_{\text{rot},a}} \frac{dT_{\text{rot},a}}{dt}, \quad (16)$$

and taking into account the approximation (12), one obtains

$$c_{\text{rot},a} = \frac{dH_{\text{rot},a}}{dt} \frac{dT_{\text{rot},a}}{dt}, \quad (17)$$

and a similar expression for $c_{\text{rot},b}$.

Combining Eqs. (14) and (17) a left-hand-term,

$$\frac{dT_{\text{rot},a}}{dt} = \frac{1}{c_{\text{rot}}} \left( \alpha_a \frac{dH_{\text{rot},a}}{dt} + \alpha_b \frac{dH_{\text{rot},b}}{dt} \right), \quad (18)$$

for the relaxation equation (11) is obtained. The right-hand-side (rhs) of Eq. (18) can be formulated in terms of the elementary collisional processes. This derivation starts expressing the partial enthalpies $H_{\text{rot},a}$ and $H_{\text{rot},b}$ as

$$H_{\text{rot},a} = \sum_i E_{i,a} P_{i,a}, \quad \text{and} \quad H_{\text{rot},b} = \sum_j E_{j,b} P_{j,b}. \quad (19)$$

where $E_{i,a}$ and $E_{j,b}$ are the energies of the rotational levels of species $M_a$ and $M_b$, referred to their respective rotational energy minima, and $P_{i,a}$ and $P_{j,b}$ are the populations of the rotational levels $i$ and $j$ of species $M_a$ and $M_b$, respectively, subject to the normalization condition

$$\sum_i P_{i,a} = 1, \quad \text{and} \quad \sum_j P_{j,b} = 1. \quad (20)$$

The rhs of Eq. (18) is further developed by means of the time derivative of Eqs. (19),

$$\frac{dH_{\text{rot},a}}{dt} = \sum_i E_{i,a} \frac{dP_{i,a}}{dt}, \quad (21)$$

with a similar expression for $dH_{\text{rot},b}/dt$.

At this point it is convenient to label the energy levels of $pH_2$ and $oD_2$ with indices $i, j, \ell, m$ associated to the even rotational quantum numbers $J = 0, 2, 4, \ldots$, reserving the indices $r, s, t, u$ for the odd rotational quantum numbers $J = 1, 3, 5, \ldots$ of $oH_2$ and $pD_2$. Under this tagging Eq. (18) becomes for $pH_2 + oH_2$ or $oD_2 + pD_2$ mixtures

$$\frac{dT_{\text{rot}}}{dt} = \frac{1}{c_{\text{rot}}} \left[ \alpha_a \sum_i E_{i,a} \frac{dP_{i,a}}{dt} + \alpha_b \sum_r E_r \frac{dP_r}{dt} \right], \quad (22)$$

where the time derivatives of rotational populations can be expressed explicitly in terms of $k_{ij \rightarrow \ell m}$ rates by means of the master equation22

$$\frac{dP_i}{dt} = 2n\alpha_a \sum_{j \ell m} \left( -P_j P_{j \ell \ell m} k_{ij \ell \ell m} + P_j P_{m \ell \ell m} k_{ij \ell m \ell} \right)$$

$$+ n\alpha_b \sum_{s \ell t} \left( -P_s P_{s \ell \ell t} k_{ij \ell \ell t} + P_s P_{t \ell \ell t} k_{ij \ell t \ell} \right), \quad (23)$$

and an analogous one for $dP_r/dt$. Superindex $\text{dis}$ indicates that the master equations are formulated so far in terms of collisions between distinguishable molecules, regardless of whether selfcollisions or heterocollisions are considered. The first term of the rhs of Eq. (23) accounts for the $M_a M_a$ selfcollisions to $dP_j/dt$, and the second one for the $M_a M_b$ heterocollisions.

Combining the detailed balance relation between $up$ (excitation) and $down$ (deexcitation) state-to-state rates

$$k_{\ell m \rightarrow ij} = k_{ij \rightarrow \ell m} \frac{(2i+1)(2j+1)}{(2\ell+1)(2m+1)} e^{(E_{i,a} + E_{j,b} - E_{\ell,m})/k_B T}, \quad (24)$$

which holds for all $i, j, \ell, m$ indices, with the relation between rotational populations

$$P_i P_j = P_p P_m \frac{(2i+1)(2j+1)}{(2\ell+1)(2m+1)} e^{(E_{i,a} + E_{j,b} - E_{\ell,m})/k_B T}, \quad (25)$$

the following useful relation:

$$P_i P_j k_{ij \rightarrow \ell m} = P_{\ell} P_{\ell} k_{\ell m \rightarrow ij} e^{-X_{\ell m \rightarrow ij}}, \quad (26)$$

is found, where

$$X = \beta(B(T^{-1} - T_{rot}^{-1})) \quad (27)$$

is the $T_{rot} \neq T$ non-equilibrium parameter, $64 \beta = h c / k_B = 1.43888 \text{ K/cm}^{-1}$, and $B$ is the rotational constant of either $H_2$ or $D_2$. The other term in the exponent of Eq. (26) is

$$A_{ij \rightarrow \ell m} = \ell (\ell + 1) + m(m + 1) - i(i + 1) - j(j + 1). \quad (28)$$

Expressions similar to (26) for other combinations of $i, j, \ell, m, r, s, t, u$ indices permit us expressing Eq. (23) in the form

$$dP_i/dt = 2n\alpha_a \sum_{j \ell m} P_j P_{j \ell \ell m} k_{ij \ell \ell m} (1 - e^{-X_{ij \rightarrow \ell m}})$$

$$+ n\alpha_b \sum_{s \ell t} P_s P_{s \ell \ell t} k_{ij \ell \ell t} (1 - e^{-X_{ij \ell t \ell}}). \quad (29)$$

Substituting (29), and a similar expression for $dP_r/dt$, into Eq. (22), this last equation can be written down as

$$\frac{dT_{\text{rot}}}{dt} = \frac{n}{C_{\text{rot}}} \left[ 2n\alpha_a \sum_{i j \ell m} E_{i,a} P_j P_{j \ell \ell m} k_{ij \ell \ell m} (1 - e^{-X_{ij \rightarrow \ell m}}) \right.$$

$$+ \alpha_a \alpha_b \sum_{i s \ell t} E_{i,a} P_s P_{s \ell \ell t} k_{ij \ell \ell t} (1 - e^{-X_{ij \ell t \ell}})$$

$$+ 2\alpha_a \alpha_b \sum_{i \ell m} E_{i,a} P_{i \ell \ell m} k_{ij \ell \ell m} (1 - e^{-X_{ij \ell m \ell}})$$

$$+ \alpha_b \alpha_a \sum_{r \ell t} E_{r,b} P_{r \ell \ell t} k_{ij \ell \ell t} (1 - e^{-X_{ij \ell t \ell}}) \Big]. \quad (30)$$

For small $T_{rot} \neq T$ breakdown of equilibrium, as is the case in acoustic experiments (but not in supersonic jets of $H_2$ nor $D_2$) the exponential function can be expressed by the first two terms of the power series expansion, leading to

$$1 - e^{-X_{ij \rightarrow \ell m}} \approx X_{ij \rightarrow \ell m}$$

(31)
and similar expressions for the other combinations of indices. By a first permutation of indices \( i \rightleftharpoons j \) and \( l \rightleftharpoons m \) (particle interchange), and a second permutation \( (i, j) \rightleftharpoons (\ell, m) \) (time reversal) in Eq. (30), employing (26) and adding the resulting equations, one obtains eventually

\[
\frac{dT_{rot}}{dt} = -(T_{rot} - T) \\
\times \frac{n k_B}{c_{rot}} \left[ \alpha_a \alpha_a \sum_{ij} \sum_{j} (e_i + e_j - e_\ell - e_m)^2 P_p \sigma_{dis}^{\ell m \rightarrow ij} \\
+ \alpha_a \alpha_b \sum_{i} (e_i - e_u - e_\ell)^2 P_u \sigma_{dis}^{\ell m \rightarrow si} \\
+ \alpha_b \alpha_b \sum_{s} (e_s - e_u - e_\ell)^2 P_u \sigma_{dis}^{\ell m \rightarrow rs} \right] \tag{32}
\]

from which the relaxation time \( \tau \) for the mixture is obtained by identification with the relaxation equation (11).

So far, no restriction has been imposed to the indices in the sums of Eqs. (23)–(32) other than the assignment of \( i, j, \ell, m \) to the quantum states. Likewise, the interchange term \( (i, j) \rightleftharpoons (\ell, m) \) in such sums is written without any qualifications. In practice, however, it makes sense to impose restrictions on such restrictions to avoid double-counting in some processes.

It is advisable to adapt the expression of the relaxation time \( \tau \) to the symmetry requirements of quantum scattering calculations arising from the indistinguishability of the molecules. Accordingly, the \( \text{H}_2: \text{H}_2 \) and the \( \text{O}_2: \text{H}_2 \) collisions should be treated as collisions between indistinguishable molecules in order to satisfy the symmetry of the wavefunction of the colliding pair, while the \( \text{H}_2: \text{H}_2 \) collisions must be treated considering distinguishable molecules. The same criteria hold for \( D_2:D_2 \) collisions.

In a gas of homonuclear diatomic molecules, the relation between cross sections for inelastic collisions where the colliding partners are either distinguishable (\( \text{dis} \)) or indistinguishable (\( \text{ind} \)) is

\[
\sigma_{ij}^{\text{dis}} = \sigma_{ij}^{\text{dis}} + \sigma_{ij}^{\text{dis}} + (\mathcal{W}^+ - \mathcal{W}^-) \sigma_{ij}^{\text{de}}, \tag{33}
\]

where

\[
\mathcal{W}^+ = (I + 1)/(2I + 1) \quad \text{and} \quad \mathcal{W}^- = I/(2I + 1)
\]

are the statistical spin weights of the symmetric and antisymmetric wavefunctions of the colliding partners of nuclear spin \( I \). Since the interchange term \( \sigma_{ij}^{\text{de}} \) seems to be negligible in \( \text{H}_2 \), the relation between the corresponding rates becomes

\[
\kappa_{ij}^{\text{ind}} = \kappa_{ij}^{\text{dis}} + \kappa_{ij}^{\text{dis}}. \tag{35}
\]

Taking this into account, the relaxation time of the \( \alpha_a \alpha_a \text{M}_a \) + \( \alpha_a \alpha_b \text{M}_b \) mixture can be expressed in terms of only \( \text{down} \) stst-

rates as

\[
\tau^{-1} = \frac{n k_B}{c_{rot}} \times \left[ \alpha_a \alpha_a \sum_{ij} \sum_{j} (e_i + e_j - e_\ell - e_m)^2 P_p \sigma_{dis}^{\ell m \rightarrow ij} \\
+ 2 \alpha_a \alpha_b \sum_{i} (e_i - e_u - e_\ell)^2 P_u \sigma_{dis}^{\ell m \rightarrow si} \\
+ \alpha_b \alpha_b \sum_{s} (e_s - e_u - e_\ell)^2 P_u \sigma_{dis}^{\ell m \rightarrow rs} \right] \tag{36}
\]

where the following \( \text{down} \)-restrictions hold:

\[
E_\ell + E_m > E_i + E_j, \\
E_\ell + E_u > E_i + E_s, \tag{37}
\]

The factor

\[
Q_{ij} \equiv [1 + \delta_{ij}(1 - \delta_\ell)(1 - \delta_m)] \\
\times [1 - \delta_\ell(1 - \delta_\ell)] \\
\times [1 - \delta_m(1 - \delta_m)], \tag{38}
\]

in Eq. (36) avoids double-counting in some processes.\textsuperscript{22}

It must be emphasized that, according to Eqs. (36) and (2), neither \( \tau^{-1} \) nor \( \sigma(0001) \) are species-additive quantities, for \( c_{rot} \) is common to the whole mixture. Therefore, \( \sigma(0001) \) for a \( \text{O}_2: \text{H}_2 \) mixture cannot be expressed as a linear combination of the cross sections of pure \( \text{O}_2 \), pure \( \text{H}_2 \), and \( \text{O}_2 \) in \( \text{H}_2 \), and \( \text{H}_2 \) in \( \text{O}_2 \), as assumed in earlier works (e.g., Eq. (11) of Ref. 46).

Following the procedure outlined above, the particular case of the relaxation time of a species \( \alpha_a \text{M}_a \) highly diluted in the \( \alpha_a \text{M}_a + \alpha_a \text{M}_b \) mixture leads to

\[
\tau_a^{-1} = \frac{n k_B}{c_{rot,a}} \sum_{i} (e_i - e_i)(e_\ell + e_u - e_\ell - e_s) P_p \sigma_{dis}^{\ell m \rightarrow is}, \tag{39}
\]

subject to the \( \text{down} \)-restriction \( E_\ell + E_u > E_i + E_s \).
For all cases where acoustic experimental data are available, the relaxation time of H₂ and D₂ can be calculated from Eqs. (36) and (39) using the state-to-state rate coefficients discussed below. The related macroscopic quantities σ(0001), ηV, and Z can be obtained from Eqs. (2)–(4), respectively.

III. THE STATE-TO-STATE RATES FOR H₂:H₂ AND D₂:D₂ INELASTIC COLLISIONS

Due to its relative simplicity, molecular hydrogen has been for decades the reference system for studying inelastic collisions in the frame of quantum scattering theory. Several works aimed at methodological aspects of quantum scattering theory in connection to the H₂–H₂ intermolecular collisions have been reported recently. However, the reported sets of kij→ℓm rates often were not given explicitly and, where given, they were out of the 20 ≤ T ≤ 300 K thermal range of acoustic experiments on H₂ and D₂. These relevant experiments have thus remained underinterpreted to some extent. Although the rotational effective cross section σ(0001) of H₂ variants has been calculated using the M79- and M80-PEES of Diep and Johnson, the H₂–H₂ rigid-rotor ab initio PES of Diep and Johnson.

In the pH 2:pH2, oH 2:oH2, pD 2:pD2, and oD 2:oD2 collisions, the molecules have been considered indistinguishable, with state to state cross sections

\[ \sigma_{ij→ℓm}^{ind} = W^+\sigma_{ij→ℓm}^+ + W^-\sigma_{ij→ℓm}^- \]  

(40)

and weights:

W+(pH₂:pH₂) = 1,  \ W-(pH₂:pH₂) = 0,

W+(oH₂:oH₂) = W+(pD₂:pD₂) = 2/3,

W-(oH₂:oH₂) = W-(pD₂:pD₂) = 1/3,

and averaging over the several nuclear spin combinations,

W+(oD₂:oD₂) = 7/12,  \ W-(oD₂:oD₂) = 5/12.

The σij→ℓm^{ind} cross sections for collisions between indistinguishable molecules, which have been obtained according to Takayanagi’s counting of states, must be multiplied by the factor

\[ F_{ij→ℓm} = \frac{1}{(1 + δ_{ij})(1 + δ_{ℓm})} \]  

(41)

in order to avoid double counting of the collisional process when the initial states of the collision are the same, i.e., i = j, or when the final states are the same (ℓ = m). Proofs in favor of this factor have been provided recently in supersonic jet experiments.

The rate coefficients for collisions between indistinguishable molecules are then obtained by means of the transformation

\[ k_{ij→ℓm}(T) = \frac{v_c}{(k_B T)^2} \int_{E_{min}}^{∞} \frac{F_{ij→ℓm} \sigma_{ij→ℓm}^{ind}}{\exp \left( \frac{E - E_f}{k_B T} \right)} \, dE, \]  

(42)

which averages the cross section weighted with the Boltzmann distribution over a range of energies. This leads to a smooth dependence of kij→ℓm rates on the translational temperature T; E = Et - Ef - Ei is the available precollisional kinetic energy for the molecules in the i and j rotational levels referred to the total energy Et and Em is the minimum kinetic energy for the rotational levels ℓ and m to become accessible. For collisions between distinguishable molecules, the factor F = 1 holds.

The close-coupled Schrödinger equations were solved by means of the hybrid log-derivative-Airy propagator of Alexander and Manolopoulos. The propagation was carried out from a minimum intermolecular distance of 2.01 Å to an intermediate one of 10 Å by means of the log-derivative propagator, and with the Airy method up to 15 Å. Typical step sizes for the log-derivative propagator were about 0.04 Å. Total angular momentum J of the system was increased until the partial cross section for the last four consecutive J’s contributed each with less than 0.005 Å². A total of 14 pairs of rotational levels were included in the close-coupled equations for all H₂:H₂ and D₂:D₂ collision variants, while 20 pairs were included for D₂:D₂. Closed channels were always included for the whole range of temperatures reported in this work. The rotational energies for the H₂ and D₂ monomers were taken from the experiment. The reduced masses employed in the calculations were μ(H₂:H₂) = 1 amu and μ(D₂:D₂) = 2.0141 amu, and the monomer bond length rₑ = 0.7668 Å. Additional computational details are given in Table I. Details on the underlying theory of the collision dynamics of diatomic homonuclear rotors can be found elsewhere.

For the energy range of Table I the convergence of the cross sections is better than 5% for translational temperatures 20 K ≤ T ≤ 300 K. The calculated st = rates for the various H₂:H₂ and D₂:D₂ inelastic collision processes needed for the interpretation of relaxation phenomena in the 20 ≤ T ≤ 300 K range are given in Tables II–VII.

IV. RESULTS

The quantities measured in acoustic absorption experiments are the relaxation time, usually reported in the form τp

| TABLE I. Conditions for the calculation of state-to-state cross sections of H₂:H₂ and D₂:D₂ inelastic collision variants. |
|-----------------|----------------|----------------|
| Grid points     | Energy range   | Step³ (cm⁻¹)  |
| (cm⁻¹)          | (cm⁻¹)         |                |
| pH₂:pH₂         | 621            | 354.34 ≤ Et   | 100 ≤ ΔEt ≤ 1 |
|                 | 905            | 823.75 ≤ Et   | 100 ≤ ΔEt ≤ 1 |
|                 | 906            | 472.82 ≤ Et   | 100 ≤ ΔEt ≤ 1 |
| oH₂:oH₂         | 619            | 182.26 ≤ Et   | 50 ≤ ΔEt ≤ 1  |
|                 | 665            | 424.52 ≤ Et   | 50 ≤ ΔEt ≤ 1  |
|                 | 1223           | 243.10 ≤ Et   | 50 ≤ ΔEt ≤ 1  |
| pD₂:pD₂         | 905            | 823.75 ≤ Et   | 100 ≤ ΔEt ≤ 1 |
|                 | 906            | 472.82 ≤ Et   | 100 ≤ ΔEt ≤ 1 |
| oD₂:oD₂         | 619            | 182.26 ≤ Et   | 50 ≤ ΔEt ≤ 1  |
|                 | 665            | 424.52 ≤ Et   | 50 ≤ ΔEt ≤ 1  |
|                 | 1223           | 243.10 ≤ Et   | 50 ≤ ΔEt ≤ 1  |

³Large step size ΔEt, for small dEt/dτ gradients, and vice versa.
referred to a pressure \( p = 1 \) atm, and the volume viscosity \( \eta_V \). However, in order to compare results from different sources it is convenient to employ the rotational effective cross section \( \sigma \) (0001) and Eqs. (2)–(4), (36), and (39).

In Table VIII, we compare the \( \sigma \) (0001)s calculated here with those from acoustic experiments. Due to some discrepancy with the \( c_{rot} \) employed in other works \(^4,5,7\) we include this datum in the Table VIII as calculated using the rotational energy levels from Ref. \(^70\).

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The agreement of calculated \( \sigma \) (0001)s with experiment is quite good for \( \mathrm{pH}_2 \), \( \mathrm{OH}_2 \), and \( \mathrm{nH}_2 \) and in part for \( \mathrm{oD}_2 \), proving that the dominant st's-rates of Tables II–VII, as well as the equations derived in Sec. II, are globally consistent with the experimental data. The contribution of the individual elementary collision processes to \( \sigma \) (0001) are shown with dashed lines in Figs. 1–4. Their weight in the overall \( \sigma \) (0001) is, however, quite different for each molecular variant. This enables

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identifying which rates can be better assessed by the experiment, and in which thermal range, as discussed below.

Recent calculations of $\sigma(0001)$ resorting on a different approach and potential energy surface\cite{46} are included in Table VIII for comparison. The agreement with the present results, and with experiment, is quite good for $pH_2$, but differs

TABLE VI. Calculated $k_{\text{rot}}^{(0001)}$ (down) rate coefficients for $pD_2:pD_2$ collisions of indistinguishable molecules; units of 10$^{-20}$ m$^3$/s.

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<td>$10B$</td>
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TABLE VIII. Rotational effective cross section of $H_2$ and $D_2$ variants; units of Å$^2$.

<table>
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<th>$T$ (K)</th>
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<td>$pH_2$</td>
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<td>0.307</td>
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<td>$oH_2$</td>
<td>95%</td>
<td>0.955</td>
<td>0.042</td>
<td>0.043</td>
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<tr>
<td>$nH_2$</td>
<td>96%</td>
<td>0.385</td>
<td>0.049</td>
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<td>$oD_2$</td>
<td>77.3</td>
<td>0.091</td>
<td>0.073</td>
<td>0.062</td>
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<tr>
<td>$nD_2$</td>
<td>77.3</td>
<td>1.438</td>
<td>0.087</td>
<td>0.062</td>
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</table>

$\sigma(0001)$ crot (0001) reference from Table 1 of Ref. 46 with the experimental mole fractions.

bReference 54.

aInterpolation from Table 1 of Ref. 46.
Eq. (11) of Ref. 46. As explained in Sec. II B, this quantity is not species-additive.

The bulk viscosity and relaxation time of H$_2$ variants calculated from first principles is shown in Figs. 5–7, jointly with experimental results. Direct comparison with other H$_2$ and D$_2$ experimental values reported in Ref. 57 are given in Tables IX and X. Extended tables with calculated values of rotational effective cross sections, bulk viscosities, relaxation times, and collision numbers are given as the supplementary material.

V. DISCUSSION

It is well established that the sts-rates derived from first principles depend markedly on the accuracy of the PES employed in the calculation. Since the relaxation quantities (\(\sigma(0001), \eta_V, \tau, Z\)) can be expressed in terms of the sts-rates by means of Eqs. (2)–(4), (36), and (39) the comparison with experiment provides a way for validating some sts-rates and, indirectly, the anisotropy of the PES employed in the calculation.

Very few experiments aimed at the validation of sts-rates have been reported so far for H$_2$ and D$_2$. In principle, collision
induced broadening of pure rotational Raman lines bear information on the sts-rates. However, the interpretation of the experimental line broadening parameters of H$_2$ remains inconclusive due to the limited accuracy of the underlying theoretical models.  

Earlier attempts to employ the acoustic relaxation data with the purpose of fixing the anisotropy of the H$_2$–H$_2$ PES, though well oriented, did not provide an overall clear picture of the contribution of the various elementary collision processes to the relaxation. Through the present results, which are to some extent heirs of Ref. 51, we are in better condition to assess some of the calculated sts-rates for

![FIG. 6. Calculated relaxation time of para-H$_2$ versus experiment. See text for the dashed $\rho r_2$ curve.](image)

![FIG. 7. Calculated relaxation time of ortho-H$_2$ versus experiment.](image)

<table>
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<td>oH$_2$</td>
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<td>256 ± 10</td>
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*Reference 54.
H$_2$ and D$_2$ variants, and the quality of the underlying PES.\textsuperscript{15} Figures 1–4, jointly with Table VIII, provide clear criteria for the validation of some of the sts-rates given in Tables II–VII.

As shown in Fig. 1, $\sigma(0001)$ of pH$_2$ depends almost exclusively on the $k_{02\rightarrow00}$ rate in the $20 < T < 120$ K range. At higher temperature, $k_{32\rightarrow02}$ becomes increasingly more important, and at 300 K it dominates over $k_{02\rightarrow00}$, with very little contribution of $k_{22\rightarrow00}$, $k_{04\rightarrow22}$, and other rates. From Fig. 2 we see that $\sigma(0001)$ of oH$_2$ depends largely on $k_{13\rightarrow11}$, providing the validation of this rate in the $15 < T < 300$ K range. Figure 3 provides hints about the $k_{12\rightarrow10}$ rate at 77 K, and again on $k_{13\rightarrow11}$ jointly with $k_{12\rightarrow10}$ at 300 K. According to Eqs. (2) and (39), the $\sigma(0001)$ of pH$_2$ highly diluted in oH$_2$ at 77.3 K given in Table VIII depends almost exclusively on $k_{12\rightarrow10}$, providing a clean validation for this stsrates. The experimental $\sigma(0001)$s for nH$_2$ and nD$_2$ at 77.3 and 293 K on Table VIII confirm this information on $k_{12\rightarrow10}$, tough less accurately due to the mixing with other rates, especially at 293 K.

The remarkable dependence of pH$_2$ low-temperature relaxation on a small amount ($\sim$4%) of pH$_2$ impurity deserves mention. It is shown in Figs. 5 and 7, and is due to the sharp variation of $c_{rot}$ of the impure oH$_2$ with the small amount of the much larger $c_{rot}$ of pH$_2$ impurity, as can be inferred from Table VIII.

Figure 4 shows how strongly oD$_2$ differs from pH$_2$ and oH$_2$ relaxation. While $k_{02\rightarrow00}$ of oD$_2$ is highly consistent with the experiment for $30 < T < 50$ K, and $k_{02\rightarrow00}$ jointly with $k_{22\rightarrow02}$ are consistent with the experiment at $50 < T < 120$ K, non-negligible contributions of $k_{22\rightarrow00}$, $k_{24\rightarrow22}$, and others, appear at $120 < T < 300$ K. This effect is due to the narrower energy gap between the rotational levels of D$_2$. As shown in Table VIII, an overestimation of the calculated $\sigma(0001)$ of up to 40% is evident in this latter thermal range. Due to the several contributions, which are shown in Fig. 4, no validation of the individual rates is possible in this range with the available experimental data. However, since the thermal scaling of H$_2$ with respect to D$_2$ goes approximately with a factor two, a similar overestimation can be expected for the homologous sts-rates of pH$_2$ calculated from the same PES\textsuperscript{15} in the $450 < T < 600$ K range, where no relaxation experimental data appear to be available.

Outside of the mentioned thermal ranges the validation of the sts-rates of Tables II–VII is uncertain. However, the comparison with a small number of sts-rates for H$_2$:H$_2$ collisions reported by other authors is pertinent here. To start with, previous calculations based in the same methodology (MOLSCAT) and PES\textsuperscript{15} agree with Ref. 38 within 5%, but show systematic differences with the sts-rates of Ref. 43, which are 5%–10% smaller than the present ones. We attribute this to the different way how the rotational energies of H$_2$ have been considered in the close-coupling calculation. In the present work, we have employed the experimental ones,\textsuperscript{70} while the homologous rotational energies from Ref. 43 were obtained from a single rotational constant $B$, apparently neglecting centrifugal distortion. This leads to larger energy gaps between rotational levels and, consequently, to smaller ts-rates.

The sts-rates reported by Danby \textit{et al.},\textsuperscript{28} which were calculated from the unpublished M80 PES,\textsuperscript{11} agree better with the present ones than any other sets. In contrast, the $k_{02\rightarrow00}$, $k_{13\rightarrow11}$, $k_{12\rightarrow10}$, and $k_{22\rightarrow10}$ rates for H$_2$:H$_2$ collisions at 100, 200, and 300 K calculated\textsuperscript{29,32} from Schwenke’s H$_2$:H$_2$ PES\textsuperscript{12} are about 25% smaller than the homologous values on Tables II–IV. Although the material for a meaningful comparison with the experiment is limited, present calculation suggests that the sts-rates for H$_2$:H$_2$ collisions derived at $T \leq 300$ K from PES of Diep and Johnson\textsuperscript{15} are overestimated by up to 10%, while those from Schwenke’s PES\textsuperscript{12} are underestimated by a similar amount. A comparison of the above discussed results is shown in Table XI.

No explicit tabulations to compare with appear to be available for sts-rates of D$_2$:D$_2$ collisions, however, relaxation time has been calculated in the two-level approximation employing several PESSs.\textsuperscript{24}

Although no explicit sts-rates have been reported by Schaefer,\textsuperscript{46} the good agreement of the calculated rotational effective cross section $\sigma(0001)$ of pH$_2$ with experiment (see Table VIII) suggests that the PES of Schaefer\textsuperscript{14} might be a good alternative to the PES of Diep and Johnson\textsuperscript{15} and to Schwenke’s PES. However, the poor agreement of the results reported for $\sigma(0001)$ of (95%)oH$_2$ and nH$_2$\textsuperscript{46} indicates some inconsistency in the calculation of the mixtures. Nonetheless, a calculation of $\sigma(0001)$ for oD$_2$:oD$_2$ should confirm the promising PES by Schaefer.\textsuperscript{14}

An open question for the calculation of accurate rates is the influence of non-rigidity of H$_2$ molecule in the H$_2$:H$_2$ PES. Unfortunately, the flexible BMKP-PES\textsuperscript{75} was aimed at dissociation problems and its accuracy has proved
sufficient for the calculation of sts-rates for H₂:H₂ inelastic collisions.\textsuperscript{39,40} It is hoped that the more recent PES by Hinde\textsuperscript{16} can amend this limitation.

### A. Comments on the two-level relaxation model

Earlier attempts to interpret the relaxation time $\tau$ of pH$_2$ in terms of molecular collisions was based on a simplified “two-level” relaxation model with relaxation time $\tau_2$ given by\textsuperscript{1,61}

$$\tau_2^{-1} = n \left( k_{f \rightarrow i}^{eff} + k_{i \rightarrow f}^{eff} \right),$$

where $k_{f \rightarrow i}^{eff}$ and $k_{i \rightarrow f}^{eff}$ are effective rates for the collision-induced transitions between $i = 0$ and $f = 2$ levels of pH$_2$, or $i = 1$ and $f = 3$ levels of oH$_2$. Equation (43) can be derived from Eq. (32) neglecting in $c_{q0}$, the $\langle \epsilon \rangle^2$ term of Eq. (8). This is a good approximation for $T < 100$ K but introduces an increasing error above this threshold.

The relaxation time $\tau_2$, referred to $p = 1$ atm pressure at temperature $T$, becomes

$$\left( p \tau_2 \right)_\text{atm} = \frac{1.363 \times 10^{-28} T}{\left( k_{f \rightarrow i}^{eff} + k_{i \rightarrow f}^{eff} \right)}$$

where $p \tau_2$ is obtained in units of atm s if $T$ is in Kelvin and ($k_{f \rightarrow i}^{eff} + k_{i \rightarrow f}^{eff}$) in m$^3$ s$^{-1}$.

It can be shown from Eqs. (32) and (36) that the effective rates for pure pH$_2$ are related with the true state-to-state rates by

$$k_{2 \rightarrow 0}^{eff} = P_0 \left( P_0 k_{0 \rightarrow 0}^{ind} + P_2 k_{2 \rightarrow 0}^{ind} \right),$$

$$k_{0 \rightarrow 2}^{eff} = P_2 \left( P_0 k_{0 \rightarrow 2}^{ind} + P_2 k_{2 \rightarrow 2}^{ind} \right),$$

and for pure oH$_2$ by

$$k_{3 \rightarrow 1}^{eff} = P_3 \left( P_1 k_{1 \rightarrow 3}^{ind} + P_3 k_{3 \rightarrow 3}^{ind} \right),$$

Comparison of “historical” interpretative results\textsuperscript{51} with the present ones is possible by means of Eq. (46), taking into account the equivalence of the effective cross section

$$\langle Q_{02} \rangle_T = k_{0 \rightarrow 2}^{eff} / v_c.$$

From the $k_{0 \rightarrow 2}^{ind}$ and $k_{2 \rightarrow 2}^{ind}$ sts-rates of Table II, one obtains (in atomic units)

$$\langle Q_{02} \rangle_{300K} = 1.4 \times 10^{-1} a_0^2,$$

$$\langle Q_{02} \rangle_{200K} = 6.5 \times 10^{-2} a_0^2,$$

$$\langle Q_{02} \rangle_{100K} = 4.7 \times 10^{-3} a_0^2,$$

$$\langle Q_{02} \rangle_{50K} = 2.8 \times 10^{-5} a_0^2,$$

in semiquantitative agreement ($\approx$200%) with the values reported in Figure 7 of Ref. 51 for different anisotropy choices.

### TABLE XI. Comparison of H$_2$H$_2$ $k_{\text{ls-r}}$ (down) rates from different close-coupling calculations and PESs; units of $10^{-20}$ m$^3$/s.

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in the PES.\textsuperscript{17–19} Even with the limitations of the two-level relaxation model a parameter $\beta$ accounting for the anisotropy of the H$_2$–H$_2$ intermolecular potential could be fixed for the first time by the experiment, paving the way for the experimental validation of intermolecular potentials on the basis of inelastic collisions.

The two-level relaxation time $\rho \tau_2$ of pH$_2$ is included in Fig. 6 for comparison. It is clear how $\rho \tau_2$ departs from the correct relaxation time for $T > 100$ K. This, however, does not invalidate conceptually the pioneer interpretation of the rotational relaxation in diatomic gases.\textsuperscript{51}

VI. SUMMARY AND CONCLUSIONS

An explicit formulation for the rotational relaxation time of ortho-, para-, and natural- variants of H$_2$ and D$_2$ has been developed in terms of state-to-state rate coefficients for inelastic collisions. This formulation has been tested by means of acoustic ultrasonic absorption experimental data from the literature using the state-to-state rates derived from a full \textit{ab initio} rigid-rotor PES for H$_2$–H$_2$.\textsuperscript{15} The set of sts-rates provided in this work is complete enough for relaxation studies of oH$_2$ + pH$_2$ and oD$_2$ + pD$_2$ mixtures in the $20 < T < 300$ K range.

Although the present formulation is constrained to ortho- and para- variants obeying a common relaxation time, it can be easily generalized to any mixture of gases with different relaxation times.

The agreement of the calculated with the experiment-related observables (relaxation time, rotational effective cross section, bulk viscosity, and collision number) enables the validation of the dominant sts-rates of Tables II–VII and indirectly, of the PES employed in the calculation. However, this validation is somewhat limited due to the small number of acoustic experimental data available, and to the dependence of the calculated sts-rates (up to $\approx 10\%$) on the way how the rotational energies of the fragments are considered in the close-coupling calculation. This source of uncertainty should be carefully considered in future works. On the other hand, a more complete set of acoustic relaxation data including oH$_2$ + pH$_2$, and oD$_2$ + pD$_2$ mixtures with different mole fractions, and H$_2$ + D$_2$ mixtures as well, should contribute to an improved validation of calculated sts-rates and PESs.

We conclude from the present results that the dominant rates of Tables II–VII spanning the $20 < T < 300$ K range are overdetermined up to 10% and 40% for H$_2$ and D$_2$, respectively. Rates derived from Schwenke’s PES\textsuperscript{2} appear to be underestimated by a similar amount, while the sts-rates derived from Schaefer PES\textsuperscript{14} appear to be in between of both. A complete set of sts-rates from this latter PES should be welcome as a guide for future relaxation studies on acoustic, spectral line broadening, and supersonic jet experiments involving H$_2$ and D$_2$. Homologous calculations employing a recent non-rigid H$_2$–H$_2$ PES\textsuperscript{16} should also be considered.

A final comment on the theory underlying the present work is pertinent. Although the formal compatibility of the fundamental equations of Physics of Fluids (Boltzmann equation), and of Quantum Mechanics (Schrödinger equation) is still controversial\textsuperscript{10} the present results, which are based on the joint use of both equations, show that they can be considered compatible within the accuracy limits of the experimental data and of the H$_2$–H$_2$ intermolecular potential employed in the present close-coupling calculations.

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\footnotesize


