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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-state rates needed for the detailed interpretation of relaxation in H_2 and D_2 , including isotopic variant mixtures, have been calculated by solving the close-coupling Schrödinger equations using the H_2 – H_2 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 H_2 and D_2 between 30 and 293 K. This result confirms at once the proposed formulation, and the validation of the H_2 – H_2 potential energy surface employed, since no approximations have been introduced in the dynamics. Accordingly, the state-to-state rates derived from Diep and Johnson potential energy surface appear to be overestimated by up to 10% for H_2 , and up to 30% for D_2 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 phenomena^{1–5} 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 data-base tabulations employed in present day astrophysics.

The $k(T)_{ij \rightarrow \ell m}$ sts-rates account for the probability of the elementary collisional process

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 H_2 and D_2 is important for several reasons. First, H_2 and D_2 are simple molecules amenable to high level quantum calculations. The H_2 – H_2 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 H_2 has been the reference molecule in the development of quantum scattering methods and calculations.^{17–48} The state-to-state cross-sections^{21,23–26,46,47} and sts-rates^{27–32,38,42} for H_2 : H_2 and D_2 : D_2 inelastic collisions have probably been studied more systematically than for any other molecular system. In addition, due to the low anisotropy of the H_2 – H_2 intermolecular PES, transfer of energy between rotational and translational degrees of freedom by H_2 : H_2 and D_2 : D_2 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 H_2 is the most abundant coolant molecule.

In contrast to the many theoretical works, comparatively few experiments on H_2 : H_2 and D_2 : D_2 inelastic collisions have been conducted so far. Among them, acoustic ultrasonic absorption experiments on H_2 and D_2 isotopomer variants have produced a valuable body of relaxation data at temperatures below 300 K, including relaxation time τ between rotational and translational degrees of freedom, rotational relaxation effective cross section $\sigma(0001)$, 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,⁵⁸ 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 $k_{ij \rightarrow \ell m}$ sts-rates, providing a tangible link between ultrasonic acoustic experiments, gas dynamic concepts, and advanced quantum scattering calculations of sts-rates based on high-quality intermolecular PESs.

The present paper reports:

- (1) an explicit description of the rotation-translation relaxation time τ for H_2 and D_2 variants in terms of $k_{ij \rightarrow \ell m}$ rates,
- (2) the set of $k_{ij \rightarrow \ell m}$ rates for $\text{H}_2:\text{H}_2$ and $\text{D}_2:\text{D}_2$ 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 *ab initio* PES,¹⁵
- (3) the assessment of the calculated $k_{ij \rightarrow \ell m}$ rates by means of experimental data on H_2 and D_2 from ultrasonic absorption experiments,
- (4) the relaxation time τ and the transport coefficients that depend on it ($\sigma(0001)$, η_V , Z) as calculated from the sts-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 η_V , and the collision number Z are related to the relaxation time τ by^{2,3,5,9}

$$\sigma(0001) = (nv_c\tau)^{-1}, \quad (2)$$

$$\eta_V = \frac{k_B c_{rot}}{c_V^2} n k_B T \tau = \frac{k_B c_{rot}}{c_V^2} \frac{k_B T}{v_c \sigma(0001)}, \quad (3)$$

$$Z = \frac{\tau}{\tau_{GD}} = \frac{\pi d^2}{\sigma(0001)}, \quad (4)$$

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

$$\tau_{GD} = \frac{1}{4nd^2} \sqrt{\frac{m}{\pi k_B T}} \quad (5)$$

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

$$V_{LJ} = 4\epsilon((d/r)^{12} - (d/r)^6). \quad (6)$$

In this work, we have taken $d(\text{H}_2) = d(\text{D}_2) = 2.915 \text{ \AA}$.⁵⁹

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

$$v_c = \sqrt{\frac{8k_B T}{\pi \mu}}, \quad (7)$$

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

$$c_{rot} = k_B(\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2), \quad (8)$$

where

$$\langle \varepsilon^n \rangle = Q_{rot}^{-1} \sum_i \varepsilon_i^n (2J_i + 1) \exp(-\varepsilon_i), \quad (9)$$

and

$$Q_{rot} = \sum_i (2J_i + 1) \exp(-\varepsilon_i) \quad (10)$$

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 τ in a molecular mixture $\text{M}_a + \text{M}_b$ 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 equation⁶¹

$$\frac{dT_{rot}}{dt} = -(T_{rot} - T)\tau^{-1}, \quad (11)$$

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 $\text{M}_a + \text{M}_b$ gas mixture, i.e., if $T_{rot,a} \approx T_{rot,b}$. In this case, we shall introduce the approximation

$$T_{rot,a} \approx T_{rot,b} = T_{rot} \neq T. \quad (12)$$

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 $\text{M}_a + \text{M}_b$ mixture.

It is well established by supersonic jet experiments that the rotational temperatures of *para*- H_2 (pH_2) and *ortho*- H_2 (oH_2) are similar in $\text{pH}_2 + \text{oH}_2$ mixtures, but differ dramatically from the translational temperature.^{37,38,62,63} This suggests that a single rotational relaxation time τ is a sound physical quantity for describing the relaxation of $\text{pH}_2 + \text{oH}_2$ mixtures.

The present derivation of the relaxation time τ in terms of elementary collision processes is based on the use of a master equation expressed as a function of $k_{ij \rightarrow \ell m}$ rates. Such a master equation has been proposed long ago²² and can be deduced from Boltzmann generalized equation.¹⁰

Let us express the rotational contribution to the enthalpy of the $\alpha_a \text{M}_a + \alpha_b \text{M}_b$ mixture, with mole fractions α_a and α_b , and $\alpha_a + \alpha_b = 1$, by

$$H_{rot} = \alpha_a H_{rot,a} + \alpha_b H_{rot,b}, \quad (13)$$

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

$$c_{rot} = \alpha_a c_{rot,a} + \alpha_b c_{rot,b}, \quad (14)$$

where the contributions of species M_a and M_b are

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

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

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

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

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

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

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

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

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 $H_{rot,a}$ and $H_{rot,b}$ as

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

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),

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

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

At this point it is convenient to label the energy levels of pH_2 and oD_2 with indices i, j, ℓ, m associated to the even rotational quantum numbers $J = 0, 2, 4, \dots$, reserving the indices r, s, t, u for the odd rotational quantum numbers $J = 1, 3, 5, \dots$ of oH_2 and pD_2 . Under this tagging Eq. (18) becomes for $\text{pH}_2 + \text{oH}_2$ or $\text{oD}_2 + \text{pD}_2$ mixtures

$$\frac{dT_{rot}}{dt} = \frac{1}{c_{rot}} \left[\alpha_a \sum_i E_i \frac{dP_i}{dt} + \alpha_b \sum_r E_r \frac{dP_r}{dt} \right], \quad (22)$$

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

$$\begin{aligned} \frac{dP_i}{dt} = & 2n\alpha_a \sum_{j\ell m} (-P_i P_j k_{ij \rightarrow \ell m}^{dis} + P_\ell P_m k_{\ell m \rightarrow ij}^{dis}) \\ & + n\alpha_b \sum_{s\ell t} (-P_i P_s k_{is \rightarrow \ell t}^{dis} + P_\ell P_t k_{\ell t \rightarrow is}^{dis}), \end{aligned} \quad (23)$$

and an analogous one for dP_r/dt . Superindex *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 $M_a:M_a$ self-collisions to dP_i/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

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

which holds for all i, j, ℓ, m indices, with the relation between rotational populations

$$P_i P_j = P_\ell P_m \frac{(2i+1)(2j+1)}{(2\ell+1)(2m+1)} e^{(E_\ell + E_m - E_i - E_j)/k_B T_{rot}}, \quad (25)$$

the following useful relation:

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

is found, where

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

is the $T_{rot} \neq T$ non-equilibrium parameter,⁶⁴ $\beta = hc/k_B = 1.4388 \text{ K/cm}^{-1}$, 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

$$\begin{aligned} dP_i/dt = & 2n\alpha_a \sum_{j\ell m} P_\ell P_m k_{\ell m \rightarrow ij}^{dis} (1 - e^{-X A_{ij \rightarrow \ell m}}) \\ & + n\alpha_b \sum_{s\ell t} P_\ell P_t k_{\ell t \rightarrow is}^{dis} (1 - e^{-X A_{is \rightarrow \ell t}}). \end{aligned} \quad (29)$$

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

$$\begin{aligned} \frac{dT_{rot}}{dt} = & \frac{n}{c_{rot}} \left[2\alpha_a \alpha_a \sum_{ij\ell m} E_i P_\ell P_m k_{\ell m \rightarrow ij}^{dis} (1 - e^{-X A_{ij \rightarrow \ell m}}) \right. \\ & + \alpha_a \alpha_b \sum_{is\ell t} E_i P_\ell P_t k_{\ell t \rightarrow is}^{dis} (1 - e^{-X A_{is \rightarrow \ell t}}) \\ & + 2\alpha_b \alpha_b \sum_{rstu} E_r P_t P_u k_{tu \rightarrow rs}^{dis} (1 - e^{-X A_{rs \rightarrow tu}}) \\ & \left. + \alpha_b \alpha_a \sum_{rit\ell} E_r P_t P_\ell k_{\ell t \rightarrow ri}^{dis} (1 - e^{-X A_{ri \rightarrow \ell t}}) \right]. \end{aligned} \quad (30)$$

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

$$(1 - e^{-X A_{ij \rightarrow \ell m}}) \approx X A_{ij \rightarrow \ell m} \quad (31)$$

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

$$\begin{aligned} \frac{dT_{rot}}{dt} = & -(T_{rot} - T) \\ & \times \frac{nk_B}{2c_{rot}} \left[\alpha_a \alpha_a \sum_{ij\ell m} (\varepsilon_i + \varepsilon_j - \varepsilon_\ell - \varepsilon_m)^2 P_\ell P_m k_{\ell m \rightarrow ij}^{dis} \right. \\ & + \alpha_a \alpha_b \sum_{siu\ell} (\varepsilon_s + \varepsilon_i - \varepsilon_u - \varepsilon_\ell)^2 P_u P_\ell k_{u\ell \rightarrow si}^{dis} \\ & \left. + \alpha_b \alpha_b \sum_{rstu} (\varepsilon_r + \varepsilon_s - \varepsilon_t - \varepsilon_u)^2 P_t P_u k_{tu \rightarrow rs}^{dis} \right], \quad (32) \end{aligned}$$

from which the relaxation time τ 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, ℓ, m to pH_2 and r, s, t, u to oH_2 (or to oD_2 and pD_2). Thus, up and $down$ collision processes are included in (32). Since the state-to-state rates of up processes in low temperature H_2 ³⁷ may vary by over 100 orders of magnitude, it is convenient to express Eq. (32) in terms of only $down$ processes, whose rates vary with temperature by less than one order of magnitude within the $20 \leq T \leq 300$ K thermal range investigated here.

It is advisable to adapt the expression of the relaxation time τ to the symmetry requirements of quantum scattering calculations arising from the indistinguishability of the molecules. Accordingly, the $\text{pH}_2:\text{pH}_2$ and the $\text{oH}_2:\text{oH}_2$ collisions should be treated as collisions between indistinguishable molecules in order to satisfy the symmetry of the wavefunction of the colliding pair,⁶⁷ while the $\text{oH}_2:\text{pH}_2$ collisions must be treated considering distinguishable molecules. The same criteria hold for $\text{D}_2:\text{D}_2$ collisions.

In a gas of homonuclear diatomic molecules, the relation between cross sections for inelastic collisions where the colliding partners are either distinguishable (*dis*) or indistinguishable (*ind*) is³⁸

$$\sigma_{ij \rightarrow \ell m}^{ind} = \sigma_{ij \rightarrow \ell m}^{dis} + \sigma_{ij \rightarrow m\ell}^{dis} + (\mathcal{W}^+ - \mathcal{W}^-) \sigma_{ij:\ell m}^{de}, \quad (33)$$

where

$$\mathcal{W}^+ = (I + 1)/(2I + 1) \quad \text{and} \quad \mathcal{W}^- = I/(2I + 1) \quad (34)$$

are the statistical spin weights of the symmetric and antisymmetric wavefunctions of the colliding partners of nuclear spin I . Since the interchange term $\sigma_{ij:\ell m}^{de}$ seems to be negligible in H_2 ,²² the relation between the corresponding rates becomes

$$k_{ij \rightarrow \ell m}^{ind} = k_{ij \rightarrow \ell m}^{dis} + k_{ij \rightarrow m\ell}^{dis}. \quad (35)$$

Taking this into account, the relaxation time of the $\alpha_a M_a + \alpha_b M_b$ mixture can be expressed in terms of only $down$ strates as

$$\begin{aligned} \tau^{-1} = & \frac{nk_B}{c_{rot}} \\ & \times \left[\alpha_a \alpha_a \sum_i \sum_j \sum_{\ell \leq m} \sum_m Q_{ij\ell m} (\varepsilon_i + \varepsilon_j - \varepsilon_\ell - \varepsilon_m)^2 P_\ell P_m k_{\ell m \rightarrow ij}^{ind} \right. \\ & + 2\alpha_a \alpha_b \sum_s \sum_i \sum_u \sum_\ell (\varepsilon_s + \varepsilon_i - \varepsilon_u - \varepsilon_\ell)^2 P_u P_\ell k_{u\ell \rightarrow si}^{dis} \\ & \left. + \alpha_b \alpha_b \sum_r \sum_s \sum_{t \leq u} \sum_u Q_{rstu} (\varepsilon_r + \varepsilon_s - \varepsilon_t - \varepsilon_u)^2 P_t P_u k_{tu \rightarrow rs}^{ind} \right], \quad (36) \end{aligned}$$

where the following *down*-restrictions hold:

$$\begin{aligned} E_\ell + E_m & > E_i + E_j, \\ E_\ell + E_u & > E_i + E_s, \\ E_t + E_u & > E_r + E_s. \end{aligned} \quad (37)$$

The factor

$$\begin{aligned} Q_{ij\ell m} = & [1 + \delta_{ij}(1 - \delta_{\ell i})(1 - \delta_{mi})] \\ & \times [1 - \delta_{\ell i}(1 - \delta_{ij})] \\ & \times [1 - \delta_{mi}(1 - \delta_{ij})], \end{aligned} \quad (38)$$

in Eq. (36) avoids double-counting in some processes.²²

It must be emphasized that, according to Eqs. (36) and (2), neither τ^{-1} nor $\sigma(0001)$ are species-additive quantities, for c_{rot} is common to the whole mixture. Therefore, $\sigma(0001)$ for a $\text{oH}_2 + \text{pH}_2$ mixture cannot be expressed as a linear combination of the cross sections of pure oH_2 , pure pH_2 , oH_2 in pH_2 , and pH_2 in oH_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 M_a highly diluted in the $\alpha_a M_a + \alpha_b M_b$ mixture leads to

$$\tau_a^{-1} = \frac{nk_B}{c_{rot,a}} \sum_{\ell ius} (\varepsilon_\ell - \varepsilon_i)(\varepsilon_\ell + \varepsilon_u - \varepsilon_i - \varepsilon_s) P_\ell P_u k_{\ell u \rightarrow is}^{dis}, \quad (39)$$

subject to the down-restriction $E_\ell + E_u > E_i + E_s$.

For all cases where acoustic experimental data are available,^{49–51,57} 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 $\sigma(0001)$, η_V , 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.^{3,20–29} Several works aimed at methodological aspects of quantum scattering theory in connection to the H₂–H₂ intermolecular PES have been reported recently.^{34–47} However, the reported sets of $k_{ij \rightarrow \ell m}$ rates often were not given explicitly and, where given, they were out of the $20 \leq T \leq 300$ K thermal range of acoustic experiments on H₂ and D₂.^{4,55–57} These relevant experiments have thus remained underinterpreted to some extent. Although the rotational effective cross section $\sigma(0001)$ of H₂ variants has been calculated using the M79- and M80-PESs of H₂–H₂ system,^{3,13,27,46} no calculations on pH₂:oH₂ (highly diluted pH₂), nor oD₂:oD₂ collisions appear to have been reported nor compared with experiment. Moreover, the reported results on nH₂:nH₂⁴⁶ differ significantly from experiment.

In order to test the relaxation time equations (36) and (39), we have calculated here a set of $k_{ij \rightarrow \ell m}$ rates including all *ortho* and *para* variants of H₂ and D₂, which is complete enough for the study of relaxation in the $20 \leq T \leq 300$ K range. This set has been calculated with the MOLSCAT code⁶⁵ employing the H₂–H₂ rigid-rotor *ab initio* PES of Diep and Johnson.¹⁵

In the pH₂:pH₂, oH₂:oH₂, pD₂:pD₂, and oD₂:oD₂ collisions, the molecules have been considered indistinguishable,^{21,23} with state to state cross sections

$$\sigma_{ij \rightarrow \ell m}^{ind} = W^+ \sigma_{ij \rightarrow \ell m}^+ + W^- \sigma_{ij \rightarrow \ell m}^- \quad (40)$$

and weights⁶⁶

$$\begin{aligned} W^+(\text{pH}_2:\text{pH}_2) &= 1, & W^-(\text{pH}_2:\text{pH}_2) &= 0, \\ W^+(\text{oH}_2:\text{oH}_2) &= W^+(\text{pD}_2:\text{pD}_2) = 2/3, \\ W^-(\text{oH}_2:\text{oH}_2) &= W^-(\text{pD}_2:\text{pD}_2) = 1/3, \end{aligned}$$

and averaging over the several nuclear spin combinations,

$$W^+(\text{oD}_2:\text{oD}_2) = 7/12, \quad W^-(\text{oD}_2:\text{oD}_2) = 5/12.$$

The $\sigma_{ij \rightarrow \ell m}^{ind}$ cross sections for collisions between indistinguishable molecules, which have been obtained according to Takayanagi's counting of states,²⁰ must be multiplied by the factor⁶⁷

$$F_{ij\ell m} = \frac{1}{(1 + \delta_{ij})(1 + \delta_{\ell m})}, \quad (41)$$

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 ($\ell = m$). Proofs in favor of this factor have been provided recently in supersonic jet experiments.⁶⁸

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

transformation

$$k_{ij \rightarrow \ell m}^{ind}(T) = \frac{v_c}{(k_B T)^2} \int_{E_{min}}^{\infty} \frac{F_{ij\ell m} \sigma_{ij \rightarrow \ell m}^{ind}}{\exp(E/k_B T)} E dE, \quad (42)$$

which averages the cross section weighted with the Boltzmann distribution over a range of energies. This leads to a smooth dependence of $k_{ij \rightarrow \ell m}$ rates on the translational temperature T ; $E = E_T - E_i - E_j$ is the available precollisional kinetic energy for the molecules in the i and j rotational levels referred to the total energy E_T , and E_{min} 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.⁶⁹ 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 $\mathcal{J}$ of the system was increased until the partial cross section for the last four consecutive $\mathcal{J}$ 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 oD₂:pD₂. 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.⁷⁰ The reduced masses employed in the calculations were $\mu(\text{H}_2:\text{H}_2) = 1$ amu and $\mu(\text{D}_2:\text{D}_2) = 2.0141$ amu, and the monomer bond length $r_e = 0.7668$ 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.⁷¹

For the energy range of Table I the convergence of the cross sections is better than 5% for translational temperatures $20 \text{ K} \leq T \leq 300 \text{ K}$. The calculated sts-rates for the various H₂:H₂ and D₂:D₂ inelastic collision processes needed for the interpretation of relaxation phenomena in the $20 \leq T \leq 300$ 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 (cm ⁻¹)	Step ^a (cm ⁻¹)
pH ₂ :pH ₂	621	354.34 ≤ E _T ≤ 5000	100 ≤ ΔE _T ≤ 1
oH ₂ :oH ₂	905	823.75 ≤ E _T ≤ 5080	100 ≤ ΔE _T ≤ 1
oH ₂ :pH ₂	906	472.82 ≤ E _T ≤ 3292	100 ≤ ΔE _T ≤ 1
oD ₂ :oD ₂	619	182.26 ≤ E _T ≤ 3450	50 ≤ ΔE _T ≤ 1
pD ₂ :pD ₂	665	424.52 ≤ E _T ≤ 3772	50 ≤ ΔE _T ≤ 1
oD ₂ :pD ₂	1223	243.10 ≤ E _T ≤ 2707	50 ≤ ΔE _T ≤ 1

^aLarge step size ΔE_T for small $d\sigma/dE_T$ gradients, and vice versa.

TABLE II. Calculated $k_{\ell m \rightarrow ij}^{ind}$ (down) rate coefficients for $\text{pH}_2\text{:pH}_2$ collisions of indistinguishable molecules; units of $10^{-20} \text{ m}^3/\text{s}$.

$\ell m ij$	0200	2202	0422	2200
Gap	6B	6B	8B	12B
T (K)				
300	167	281	244	4
275	153	258	220	4
250	139	235	196	3
225	126	212	173	3
200	112	189	151	2
180	102	172	133	2
160	92	154	116	2
140	82	137	100	1
120	72	121	85	1
100	63	106	71	1
90	58	98	65	1
80	54	91	58	1
70	50	84	53	1
60	46	78	47	1
50	43	72	42	<1
40	40	67	38	<1
30	38	64	35	<1
20	37	63	33	<1

referred to a pressure $p = 1 \text{ atm}$, and the volume viscosity η_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,^{4,57} we include this datum in the Table VIII as calculated using the rotational energy levels from Ref. 70.

TABLE III. Calculated $k_{tu \rightarrow rs}^{ind}$ (down) rate coefficients for $\text{oH}_2\text{:oH}_2$ collisions of indistinguishable molecules; units of $10^{-20} \text{ m}^3/\text{s}$.

$turs$	1311	3313	3311
Gap	10B	10B	20B
T (K)			
300	160	172	2
275	142	154	2
250	125	136	1
225	109	119	1
200	93	103	1
180	82	90	1
160	71	79	1
140	60	68	<1
120	51	58	<1
100	42	48	<1
90	38	44	<1
80	35	40	<1
70	31	36	<1
60	28	33	<1
50	25	30	<1
40	23	27	<1
30	21	26	<1
20	20	25	<1

TABLE IV. Calculated $k_{u\ell \rightarrow si}^{dis}$ (down) rate coefficients for $\text{oH}_2\text{:pH}_2$ collisions of distinguishable molecules; units of $10^{-20} \text{ m}^3/\text{s}$.

$u\ell si$	3012	1432	1210	3230	3010	3212
Gap	4B	4B	6B	6B	10B	10B
T (K)						
300	849	605	283	290	132	160
275	807	575	259	266	118	142
250	762	543	236	242	105	126
225	715	509	212	218	93	110
200	664	473	189	195	81	95
180	621	442	171	177	71	83
160	576	410	154	159	63	72
140	529	377	136	142	54	62
120	480	342	120	125	47	53
100	429	306	104	109	39	44
90	403	287	96	101	36	40
80	376	269	89	94	33	37
70	351	250	82	87	30	33
60	325	232	76	80	27	30
50	301	215	70	74	25	27
40	278	199	65	69	23	25
30	260	186	61	65	22	23
20	252	180	59	64	21	23

The agreement of calculated $\sigma(0001)$ s with experiment is quite good for pH_2 , oH_2 , and nH_2 and in part for oD_2 , proving that the dominant sts-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

TABLE V. Calculated $k_{\ell m \rightarrow ij}^{ind}$ (down) rate coefficients for $\text{oD}_2\text{:oD}_2$ collisions of indistinguishable molecules; units of $10^{-20} \text{ m}^3/\text{s}$.

$\ell m ij$	0200	2202	2404	0422	2200	0420	2422	4424	2402
Gap	6B	6B	6B	8B	12B	14B	14B	14B	20B
T (K)									
300	192	427	455	550	12	144	158	183	11
275	176	395	420	502	12	127	138	160	9
250	160	363	384	453	9	111	118	139	7
225	145	330	348	404	8	96	100	118	6
200	130	297	312	355	6	82	83	99	5
180	118	270	283	317	5	71	71	85	4
160	106	244	254	277	4	61	59	72	3
140	94	217	226	240	4	51	49	59	3
120	83	191	198	203	3	42	39	48	2
100	72	165	171	167	2	34	31	38	1
90	67	152	157	151	2	30	27	34	1
80	62	140	145	135	2	27	23	30	1
70	57	128	132	119	1	24	20	26	1
60	52	116	120	105	1	20	17	22	1
50	47	105	109	91	1	18	15	19	1
40	43	95	99	79	1	15	13	17	1
30	40	86	91	69	1	13	11	14	<1
20	37	80	86	61	1	12	10	13	<1

TABLE VI. Calculated $k_{tu \rightarrow rs}^{ind}$ (down) rate coefficients for $pD_2:pD_2$ collisions of indistinguishable molecules; units of 10^{-20} m³/s.

<i>turs</i>	1533	1311	3313	3515	1531	3533	3311	3513
Gap	8B	10B	10B	10B	18B	18B	20B	28B
<i>T</i> (K)								
300	383	296	315	339	96	83	6	6
275	350	264	283	304	82	71	5	5
250	316	233	251	269	70	59	4	4
225	282	204	220	236	58	49	4	3
200	248	175	191	203	47	39	3	2
180	220	152	168	178	39	33	2	2
160	193	131	146	154	32	27	2	2
140	167	111	125	132	26	21	1	1
120	141	92	105	110	21	17	1	1
100	116	75	87	91	16	13	1	1
90	104	67	78	82	14	11	1	1
80	93	59	70	73	12	9	1	<1
70	82	52	62	65	10	8	<1	<1
60	72	46	55	57	9	7	<1	<1
50	63	40	48	51	7	6	<1	<1
40	55	34	43	45	6	5	<1	<1
30	48	30	38	40	5	4	<1	<1
20	42	27	35	37	5	4	<1	<1

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 surface⁴⁶ are included in Table VIII for comparison. The agreement with the present results, and with experiment, is quite good for pH_2 , but differs for oH_2 (95%–96% purity) and, specially, for nH_2 (a 75% oH_2 + 25% pH_2 mixture). This discrepancy may be attributed to the additive character of $\sigma(0001)$ assumed for the mixtures in

TABLE VIII. Rotational effective cross section of H_2 and D_2 variants; units of Å².

Species	<i>T</i> (K)	Ref. 57		This work		Ref. 46
		c_{rot}/k_B	$\sigma(0001)$	c_{rot}/k_B	$\sigma(0001)$	
pH_2	77.3	0.307	0.038 ± 0.001	0.293	0.042	0.042^a
	90.5	0.555	0.042 ± 0.005	0.548	0.043	0.043^a
	111.5	0.972	0.045 ± 0.001	0.977	0.049	0.047^a
	170	1.470	0.066 ± 0.001	1.467	0.073	0.068^a
	293	1.107	0.106 ± 0.004	1.111	0.117	0.113^a
pH_2 in oH_2	77.3	0.307	0.068 ± 0.003	0.293	0.069	
oH_2 95% ^b	170	0.385	0.049 ± 0.010	0.442	0.055	0.038^c
95%	233	0.736	0.076 ± 0.008	0.766	0.064	0.050^c
95%	269	0.865	0.074 ± 0.007	0.876	0.070	0.057^c
96%	293	0.922	0.073 ± 0.007	0.922	0.073	0.062^c
nH_2	77.3	0.076	0.050 ± 0.002	0.077	0.061	0.026^c
	293	0.962	0.088 ± 0.007	0.963	0.098	0.062^c
oD_2	31.2	0.091	0.073 ± 0.005	0.088	0.071	
	40.6	0.360	0.071 ± 0.001	0.347	0.068	
	44.5	0.520	0.065 ± 0.001	0.497	0.068	
	52.5	0.850	0.068 ± 0.001	0.827	0.071	
	77.3	1.438	0.087 ± 0.001	1.440	0.097	
	90.5	1.450	0.101 ± 0.002	1.455	0.117	
	130.5	1.178	0.151 ± 0.002	1.184	0.178	
	137.0	1.144	0.152 ± 0.002	1.151	0.186	
	188.5	1.030	0.148 ± 0.001	1.028	0.201	
	243.5	1.010	0.131 ± 0.002	1.009	0.189	
nD_2	293	1.005	0.130 ± 0.005	0.997	0.174	
	295	1.005	0.124 ± 0.002	0.997	0.173	
	77.3	1.050	0.115 ± 0.007	1.053	0.132	
	293	1.003	0.144 ± 0.006	1.001	0.150	

^aInterpolation from Table 1 of Ref. 46.

^bReference 54.

^cFrom Table 1 and Eq. (11) of Ref. 46 with the experimental mole fractions.

TABLE VII. Calculated $k_{ut \rightarrow si}^{dis}$ (down) rate coefficients for $pD_2:oD_2$ collisions of distinguishable molecules; units of 10^{-20} m³/s.

<i>ut si</i>	3012	1432	5234	1210	3230	5250	3010	3212	3414	5032	1412	3432	5030	5232
Gap	4B	4B	4B	6B	6B	6B	10B	10B	10B	12B	14B	14B	18B	18B
<i>T</i> (K)														
300	1478	1055	991	433	446	446	207	288	329	201	170	165	74	82
275	1428	1018	957	400	413	412	188	258	297	177	149	145	64	71
250	1373	977	918	367	379	377	169	228	264	154	129	125	55	60
225	1312	932	876	333	344	341	150	200	232	132	109	107	46	50
200	1245	882	828	299	310	306	131	172	201	111	91	89	38	40
180	1185	837	786	271	282	277	117	151	176	95	78	76	32	34
160	1119	789	741	244	254	249	103	131	153	80	66	64	27	27
140	1046	736	691	216	226	221	89	111	131	66	54	53	22	22
120	965	677	636	189	199	193	76	93	110	53	44	43	18	17
100	876	613	577	162	172	166	64	77	91	42	35	34	14	13
90	828	579	545	149	159	153	58	69	82	37	30	30	12	12
80	778	544	512	136	146	140	53	62	73	32	27	26	10	10
70	726	507	478	123	133	128	47	55	65	28	23	23	9	9
60	671	469	443	111	121	116	42	48	58	24	20	20	8	7
50	616	430	407	100	110	105	38	43	51	20	17	17	7	6
40	560	391	372	90	100	95	33	37	45	17	15	15	6	5
30	506	355	339	81	91	87	30	33	40	15	13	13	5	4
20	459	323	312	74	84	81	27	30	36	13	11	11	4	4

FIG. 1. Calculated rotational effective cross section (solid line) versus experiment, and partial contributions (dashed lines) to $\sigma(0001)$ of *para*-H₂.

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

The bulk viscosity and relaxation time of H₂ variants calculated from first principles is shown in Figs. 5–7, jointly with experimental results. Direct comparison with other H₂ and D₂ 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.⁷²

FIG. 2. Calculated rotational effective cross section (solid lines) versus experiment, and partial contributions (dashed lines) to $\sigma(0001)$ of *ortho*-H₂.

FIG. 3. Calculated rotational effective cross section (solid line) versus experiment, and partial contributions (dashed lines) to $\sigma(0001)$ of *natural*-H₂.

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 ($\sigma(0001)$, η_V , τ , 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 H₂ and D₂. In principle, collision

FIG. 4. Calculated rotational effective cross section (solid line) versus experiment, and partial contributions (dashed lines) to $\sigma(0001)$ of *ortho*-D₂.

FIG. 5. Calculated bulk viscosity of *ortho*-H₂ and *para*-H₂ versus experiment.

induced broadening of pure rotational Raman lines bear information on the sts-rates. However, the interpretation of the experimental line broadening parameters of H₂ remains inconclusive due to the limited accuracy of the underlying theoretical models.^{73,74} Other experiments based on the time evolution of rotational populations of H₂ in supersonic jets have rendered information on the $k_{02 \rightarrow 00}$, $k_{12 \rightarrow 10}$, $k_{30 \rightarrow 12}$, and $k_{13 \rightarrow 11}$ sts-rates of H₂, with reasonably good agreement between theory and experiment.^{37,38}

Earlier attempts to employ the acoustic relaxation data with the purpose of fixing the anisotropy of the H₂-H₂

FIG. 6. Calculated relaxation time of *para*-H₂ versus experiment. See text for the dashed $p\tau_2$ curve.

FIG. 7. Calculated relaxation time of *ortho*-H₂ versus experiment.

PES,⁵¹ 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

TABLE IX. Bulk viscosity of H₂ and D₂ variants; units of 10⁻⁶ Pa s.

Species	<i>T</i> (K)	η_V Ref. 57	η_V This work
pH ₂	77.3	206 ± 8	181
	90.5	278 ± 3	271
	111.5	358 ± 7	322
	170	315 ± 3	282
	293	246 ± 10	225
oH ₂ 95% ^a	170	274 ± 50	260
	233	282 ± 30	335
	269	328 ± 30	343
	293	349 ± 30	352
nH ₂	77.3	53 ± 2	43
	293	296 ± 25	263
oD ₂	31.2	38 ± 2	40
	40.6	125 ± 2	127
	44.5	175 ± 3	157
	52.5	221 ± 3	205
	77.3	225 ± 3	203
	90.5	212 ± 4	182
	130.5	167 ± 3	142
	137.0	170 ± 2	139
	188.5	201 ± 2	147
	243.5	256 ± 4	178
	293	284 ± 11	211
nD ₂	295	299 ± 4	213
	77.3	166 ± 10	145
	293	256 ± 10	245

^aReference 54.

TABLE X. Relaxation time of H₂ variants referred to $p = 1$ atm; units of 10⁻¹⁰ atm s.

Species	T (K)	$(p\tau_E)$ Expt.	$(p\tau_E)$ Calc.
pH ₂	77.3	220 ± 8 ^a 221 ^b	197
	90.5	211 ± 2	205
	111.5	223 ± 4	203
	170	187 ± 2	167
	300	130 ^c	138
pH ₂ in oH ₂	77.3	121 ± 5 ^a	119
nH ₂	77.3	165 ^b	134
oH ₂ 95%	170	250 ± 50 ^d	219
	233	190 ± 20	222
	269	210 ± 20	219
	293	220 ± 20	221
	300	226 ^e	239
oD ₂	31.2	102 ± 5 ^e	105
	40.6	120 ± 2	125
	44.5	136 ± 2	129
	52.5	142 ± 2	135
	77.3	134 ± 2	120
	90.5	126 ± 2	108

^aReference 52.^bReference 56.^cReference 55.^dReference 54.^eReference 53.

H₂ and D₂ variants, and the quality of the underlying PES.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 pH₂ depends almost exclusively on the $k_{02 \rightarrow 00}$ rate in the $20 < T < 120$ K range. At higher temperature, $k_{22 \rightarrow 02}$ becomes increasingly more important, and at 300 K it dominates over $k_{02 \rightarrow 00}$, with very little contribution of $k_{22 \rightarrow 00}$, $k_{04 \rightarrow 22}$, and other rates. From Fig. 2 we see that $\sigma(0001)$ of oH₂ depends largely on $k_{13 \rightarrow 11}$, providing the validation of this rate in the $150 < T < 300$ K range. Figure 3 provides hints about the $k_{12 \rightarrow 10}$ rate at 77 K, and again on $k_{13 \rightarrow 11}$ jointly with $k_{12 \rightarrow 10}$ at 300 K. According to Eqs. (2) and (39), the $\sigma(0001)$ of pH₂ highly diluted in oH₂ at 77.3 K given in Table VIII depends almost exclusively on $k_{12 \rightarrow 10}$, providing a clean validation for this sts-rate. The experimental $\sigma(0001)$ s for nH₂ and nD₂ at 77.3 and 293 K on Table VIII confirm this information on $k_{12 \rightarrow 10}$, though less accurately due to the mixing with other rates, especially at 293 K.

The remarkable dependence of oH₂ low-temperature relaxation on a small amount ($\approx 4\%$) of pH₂ impurity deserves mention. It is shown in Figs. 5 and 7, and is due to the sharp variation of c_{rot} of the impure oH₂ with the small amount of the much larger c_{rot} of pH₂ impurity, as can be inferred from Table VIII.

Figure 4 shows how strongly oD₂ differs from pH₂ and oH₂ relaxation. While $k_{02 \rightarrow 00}$ of oD₂ is highly consistent with the experiment for $30 < T < 50$ K, and $k_{02 \rightarrow 00}$ jointly with $k_{22 \rightarrow 02}$ are consistent with the experiment at $50 < T < 120$ K, non-negligible contributions of $k_{22 \rightarrow 00}$, $k_{24 \rightarrow 22}$, and others,

appear at $120 < T < 300$ K. This effect is due to the narrower energy gap between the rotational levels of D₂. 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 H₂ with respect to D₂ goes approximately with a factor two, a similar overestimation can be expected for the homologous sts-rates of pH₂ calculated from the same PES¹⁵ in the $450 < T < 600$ K range, where no relaxation experimental data appear to be available.

Outside from 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 H₂:H₂ collisions reported by other authors is pertinent here. To start with, previous calculations based in the same methodology (MOLSCAT) and PES¹⁵ 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 H₂ have been considered in the close-coupling calculation. In the present work, we have employed the experimental ones,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 sts-rates.

The sts-rates reported by Danby *et al.*,²⁸ which were calculated from the unpublished M80 PES,¹¹ agree better with the present ones than any other sets. In contrast, the $k_{02 \rightarrow 00}$, $k_{13 \rightarrow 11}$, $k_{12 \rightarrow 10}$, and $k_{30 \rightarrow 10}$ rates for H₂:H₂ collisions at 100, 200, and 300 K calculated^{29,32} from Schwenke's H₂–H₂ PES¹² 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 H₂:H₂ collisions derived at $T \leq 300$ K from PES of Diep and Johnson¹⁵ are overestimated by up to 10%, while those from Schwenke's PES¹² 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 D₂:D₂ collisions, however, relaxation time has been calculated in the two-level approximation employing several PESs.²⁴

Although no explicit sts-rates have been reported by Schaefer,⁴⁶ the good agreement of the calculated rotational effective cross section $\sigma(0001)$ of pH₂ with experiment (see Table VIII) suggests that the PES of Schaefer¹⁴ might be a good alternative to the PES of Diep and Johnson¹⁵ and to Schwenke's¹² PES. However, the poor agreement of the results reported for $\sigma(0001)$ of (95%)oH₂ and nH₂⁴⁶ indicates some inconsistency in the calculation of the mixtures. Nonetheless, a calculation of $\sigma(0001)$ for oD₂:oD₂ should confirm the promising PES by Schaefer.¹⁴

An open question for the calculation of accurate rates is the influence of non-rigidity of H₂ molecule in the H₂–H₂ PES. Unfortunately, the flexible BMKP-PES⁷⁵ was aimed at dissociation problems and its accuracy has proved

TABLE XI. Comparison of $\text{H}_2\text{:H}_2$ $k_{\tau\omega\rightarrow\sigma\rho}$ (down) rates from different close-coupling calculations and PESs; units of 10^{-20} m^3/s .

$\tau\omega\sigma\rho$	0200	0420	1311	3010	1210	1412	5030	5131	Calculation	PES
Gap	6B	14B	10B	10B	6B	14B	18B	18B	Ref.	Ref.
T (K)										
300	167	69	160	132	283	76	29	35	This work	15
	167		164	135	283				38	15
	162	61	151	122	279	67	24	29	43	15
	167	63	143	132	275	72	27	31	28	11
	130	62	130	130	190	65	24	27	29	12
250	139	53	125	105	236	57	22	25	This work	15
	138	47	111	103	227	53	19	21	28	11
200	112	38	93	81	189	40	15	17	This work	15
	112		96	83	189				38	15
	108	33	85	73	185	35	12	14	43	15
	110	33	82	77	181	37	13	14	28	11
	89	33	82	85	130	34	11	12	29	12
150	87	26	65	58	145	27	10	11	This work	15
	86		68	61	145				38	15
	84	22	57	55	137	24	8	9	28	11
100	63	16	42	39	104	17	6	6	This work	15
	63		45	42	104				38	15
	60	14	38	35	100	14	4	5	43	15
	60	13	36	36	97	15	4	5	28	11
	54	14	43	50	78	16	3	4	29	12
50	43	10	25	25	70	10	3	4	This work	15
	43		28	28	70				38	15
	41	8	22	22	67	8	2	3	43	15
	40	7	21	22	64	8	2	3	28	11

insufficient for the calculation of sts-rates for $\text{H}_2\text{:H}_2$ inelastic collisions.^{39,40} It is hoped that the more recent PES by Hinde¹⁶ can amend this limitation.

A. Comments on the two-level relaxation model

Earlier attempts to interpret the relaxation time τ of pH_2 in terms of molecular collisions was based on a simplified “two-level” relaxation model with relaxation time τ_2 given by^{1,61}

$$\tau_2^{-1} = n \left(k_{f \rightarrow i}^{\text{eff}} + k_{i \rightarrow f}^{\text{eff}} \right), \quad (43)$$

where $k_{f \rightarrow i}^{\text{eff}}$ and $k_{i \rightarrow f}^{\text{eff}}$ 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_{rot} 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 τ_2 , referred to $p = 1$ atm pressure at temperature T , becomes

$$(p\tau_2)^{1 \text{ atm}} = \frac{1.363 \times 10^{-28} T}{\left(k_{f \rightarrow i}^{\text{eff}} + k_{i \rightarrow f}^{\text{eff}} \right)}, \quad (44)$$

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

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

$$k_{2 \rightarrow 0}^{\text{eff}} = P_0 (P_0 k_{02 \rightarrow 00}^{\text{ind}} + P_2 k_{22 \rightarrow 02}^{\text{ind}}), \quad (45)$$

$$k_{0 \rightarrow 2}^{\text{eff}} = P_2 (P_0 k_{02 \rightarrow 00}^{\text{ind}} + P_2 k_{22 \rightarrow 02}^{\text{ind}}), \quad (46)$$

and for pure oH_2 by

$$k_{3 \rightarrow 1}^{\text{eff}} = P_1 (P_1 k_{13 \rightarrow 11}^{\text{ind}} + P_3 k_{33 \rightarrow 13}^{\text{ind}}), \quad (47)$$

$$k_{1 \rightarrow 3}^{\text{eff}} = P_3 (P_1 k_{13 \rightarrow 11}^{\text{ind}} + P_3 k_{33 \rightarrow 13}^{\text{ind}}). \quad (48)$$

Comparison of “historical” interpretative results⁵¹ with the present ones is possible by means of Eq. (46), taking into account the equivalence of the effective cross section

$$\langle Q_{02} \rangle_T = k_{0 \rightarrow 2}^{\text{eff}} / v_c. \quad (49)$$

From the $k_{02 \rightarrow 00}^{\text{ind}}$ and $k_{22 \rightarrow 02}^{\text{ind}}$ sts-rates of Table II, one obtains (in atomic units)

$$\langle Q_{02} \rangle_{300\text{K}} = 1.4 \times 10^{-1} a_0^2, \quad (50)$$

$$\langle Q_{02} \rangle_{200\text{K}} = 6.5 \times 10^{-2} a_0^2, \quad (51)$$

$$\langle Q_{02} \rangle_{100\text{K}} = 4.7 \times 10^{-3} a_0^2, \quad (52)$$

$$\langle Q_{02} \rangle_{50\text{K}} = 2.8 \times 10^{-5} a_0^2, \quad (53)$$

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

in the PES.^{17–19} Even with the limitations of the two-level relaxation model a parameter β accounting for the anisotropy of the $\text{H}_2\text{--H}_2$ 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 $p\tau_2$ of pH_2 is included in Fig. 6 for comparison. It is clear how $p\tau_2$ 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.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 *ab initio* rigid-rotor PES for $\text{H}_2\text{--H}_2$.¹⁵ The set of sts-rates provided in this work is complete enough for relaxation studies of $\text{oH}_2 + \text{pH}_2$ and $\text{oD}_2 + \text{pD}_2$ 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 $\text{oH}_2 + \text{pH}_2$, and $\text{oD}_2 + \text{pD}_2$ mixtures with different mole fractions, and $\text{H}_2 + \text{D}_2$ 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 PES¹² appear to be underestimated by a similar amount, while the sts-rates derived from Schaefer PES¹⁴ 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 $\text{H}_2\text{--H}_2$ PES¹⁶ 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 controversial¹⁰ 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 $\text{H}_2\text{--H}_2$ intermolecular potential employed in the present close-coupling calculations.

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