Low-temperature inelastic collisions between hydrogen molecules and helium atoms

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(Received 26 March 2008; accepted 8 May 2008; published online 11 June 2008)

Inelastic H2:He collisions are studied from the experimental and theoretical points of view between 22 and 180 K. State-to-state cross sections and rates are calculated at the converged close-coupling level employing recent potential energy surfaces (PES): The MR-PES [J. Chem. Phys. 100, 4336 (1994)], and the MMR-PES and BMP-PESs [J. Chem. Phys. 119, 3187 (2003)]. The fundamental rates $k_{2-0}$ and $k_{3-1}$ for H2:He collisions are assessed experimentally on the basis of a master equation describing the time evolution of rotational populations of H2 in the vibrational ground state. These populations are measured in the paraxial region of supersonic jets of H2+He mixtures by means of high-sensitivity and high spatial resolution Raman spectroscopy. Good agreement between theory and experiment is found for the $k_{2-0}$ rate derived from the MR-PES, but not for the BMP-PES. For the $k_{3-1}$ rate, which is about one-third to one-half of $k_{2-0}$, the result is less conclusive. The experimental $k_{3-1}$ rate is compatible within experimental error with the values calculated from both PESs. In spite of this uncertainty, the global consistence of experiment and theory in the framework of Boltzmann equation supports the MR-PES and MMR-PESs, and the set of gas-dynamic equations employed to describe the paraxial region of the jet at a molecular level.

I. INTRODUCTION

H2 being the most abundant molecule in the universe, and He its second most-common collision partner in interstellar molecular clouds, inelastic collisions of H2 with He are relevant for the interpretation of spectroscopic observations of such media, as well as for their understanding and physical modeling.1–3 The interaction potential energy surface (PES) involved in H2:He collisions is also relevant in quantum chemistry as the simplest interaction case between a molecule and a closed-shell atom. Therefore, many PESs have been proposed for this system, either on theoretical4–18 or experimental basis.19–21 Since the quality of the state-to-state cross sections and rate coefficients obtained from quantum scattering calculations strongly depends on the potential energy surface employed, experimental validation of these quantities indirectly implies the validation of the PES.

On the other hand, due to its comparative simplicity the H2:He collisional system in the vibrational ground state of H2 is suitable for laboratory experiments aimed at bridging the microscopic (molecular) and the macroscopic versions of gas dynamics on the basis of Boltzmann equation and its generalization to molecular gases.21–24 In molecular astrophysics, as well as in molecular gas dynamics, the relevant quantities to be considered are the state-to-state collisional cross sections and their associated rate coefficients (shorten: “rates”). The collision integral of Boltzmann equation can be expressed in terms of either of them.

Indeed, a major obstacle to the progress of molecular gas dynamics arises from the difficulty to evaluate accurately the cross sections or rates in Boltzmann collision integral. So far, the gap between molecular and macroscopic versions of the gas-dynamic equations has been filled with approximate models, in spite of the well founded molecular descriptions of the transport coefficients derived from Boltzmann collision integral in terms of the state-to-state collisional cross sections.25

The H2:He collisional system has been widely studied from the theoretical viewpoint,1–3,26–44 with more emphasis in the vibrational relaxation problem than in the pure rotational problem constrained to the vibrational ground state of H2. Cold H2:He collisions involving rovibrational excited H2 confers renewed interest to the H2:He system.45–47

Several validation experiments on vibrational relaxation of H2 by He have been reported,48–50 as well as a few rotational relaxation data derived from acoustical measurements.51–53

In this work we report an experimental and theoretical study of H2:He collisions for H2 in the vibrational ground state, in the range of kinetic temperatures 22 K $\leq T \leq 180$ K. The experiment is carried out along the paraxial region of miniature supersonic expansions (length $\approx 1.2$ mm) of H2+He mixtures in stationary regime. In this region Boltzmann equation can be simplified and factorized to the point that the evolution of rotational populations along the supersonic jet can be expressed in terms of state-to-state

inelastic collision rates by means of a master equation. All terms in this master equation, except the rates, are obtained experimentally.

In the H$_2$+He mixtures expanding in the jet H$_2$:H$_2$ self-collisions are present, in addition to the H$_2$:He collisions. The rates for the H$_2$:H$_2$ self-collisions are taken from a recent work, while the reference rates for H$_2$:He collisions are from Balakrishnan et al., being also recalculated here at the converged close-coupled (CCC) level using recent PESs.

Present work is aimed at (a) assessing experimentally the main CCC-calculated rates for H$_2$:He inelastic collisions at low temperature, (b) deciding about the quality of the PESs employed in the CCC calculations, (c) exploring the possibility of deriving the rates for H$_2$:He collisions on the sole basis of the experiment, and (d) testing experimentally the consistency of the gas-dynamic equations of conservation (matter, energy, entropy) as derived from Boltzmann equation, with emphasis on the collision integral term, depending on the rates considered in (a) and (c).

These goals are, of course, not independent. Together they provide a scope which allows us on bridging the molecular and the macroscopic versions of a gas dynamics laboratory experiment. In it, the role of the different elementary collisional processes involving H$_2$ molecules in the vibrational ground state and He atoms can be assessed with unprecedented detail in the low-temperature range.

II. METHODOLOGY

A. The gas-dynamic equations

The experimental environment considered in the present method is the paraxial region of a supersonic free jet of the investigated H$_2$+He gas mixture. For a wide range of conditions the expanded gas behaves in this region as a uniform inviscid one-dimensional flow of variable cross sectional area. This paraxial flow is accepted to be adiabatic and isentropic to a good approximation.

The gas-dynamic equations governing the referred flow have been usually formulated at a macroscopic level in the hypothesis of the continuum. This approach is, however, useless for the present purpose since it ignores a fundamental property of the molecular supersonic flow, namely, the intrinsic breakdown of equilibrium between the internal and the translational degrees of freedom. For a wide range of stagnation conditions, different internal and translational well-defined temperatures ($T_i \neq T_t$) have been verified experimentally in the jet. This means that the local translational and internal thermal equilibria are largely maintained along the jet. It implies that the one-particle position-velocity distribution function for the internal state $i$ can be factorized to a good approximation in the form

$$Q(r,v,t) = \frac{m}{2\pi k_B T_i(r)} \exp\left[-\frac{m}{2k_B T_i(r)} |v-v_0|^2 \right],$$

where $n(r,t)$ is the instantaneous number density at position $r$, $P_i(r,t)$ is the instantaneous population of internal state $i$, and $Q(r,v,t,T_i)$ is the Maxwell–Boltzmann velocity distribution at the local translational temperature $T_i$ in a jet of particles of mass $m$ with local flow velocity $v_0(r)$.

As a practical hint, the entropy invariance in the paraxial region of the jet can be experimentally inferred from the behavior of the internal populations $P_i$ in Eq. (1): The entropy invariance can be expected to be a good approximation if a substantial proportion of the molecules in the paraxial region of the jet, say, $>99\%$, obey a distribution of the form

$$P_i = \frac{g_i \exp(-E_i/k_B T_{int})}{Z_{int}(T_{int})},$$

where $E_i$ is the energy of the internal state $i$, $g_i$ its degeneracy, and $Z_{int}$ the internal partition function at the temperature $T_{int}$. This condition excludes the region of the normal shock and beyond, which departs sharply from distribution (3).

The internal-translational nonequilibrium of the supersonic jet with two temperatures, $T_i$ and $T_{int}$ mimics to some extent the natural status of molecular clouds in the interstellar medium. Thus, it provides appealing possibilities for laboratory studies of molecular collisions of astrophysical interest. In particular, the determination or the validation of state-to-state rates for inelastic collisions at low temperature is a major target in present-day astrophysics.

The gas-dynamic equations accounting for the paraxial supersonic flow at a molecular level, explicitly including the role of molecular collisions and implicitly including the breakdown of equilibrium between internal and translational degrees of freedom, may be derived from the generalized Boltzmann equation,

$$\frac{\partial f_i}{\partial t} + v \cdot \nabla f_i = \left( \frac{\delta f_i}{\partial t} \right)_{\text{coll}}.$$

Degenerate internal states are included in the collision integral ($\delta f_i/\delta t)_{\text{coll}}$ (Ref. 22) under the factorization assumption (1). Such an approach has been proposed elsewhere. An alternative subset of gas-dynamic conservation equations better suited for the present study of inelastic collision rates is

$$\frac{D}{Dt} P_i + P_i \nabla \cdot v_0 = \left( \frac{\delta P_i}{\partial t} \right)_{\text{coll}} \quad \text{(matter)},$$

$$\Delta S = 0 \quad \text{(entropy)},$$

$$\Delta \left( H + \frac{|v_0|^2}{2} \right) = 0 \quad \text{(energy)},$$

where $H$ is the the specific enthalpy. In Eq. (5) $D/Dt = \partial/\partial t + v_0 \cdot \nabla$ stands for the substantial derivative operator, while the right-hand term accounts for the changes of $P_i$ along time due to collisions.
No equations other than Eqs. (5)–(7) are needed here since some of the variables appearing in them are measured experimentally, thus avoiding involved gas-dynamic calculations.

B. The master equation

Equation (5) can still be simplified considering stationary supersonic jets, which provide the simplest and most accurate procedure from the experimental point of view. In such jets the intrinsic term $\delta P_i/\delta \theta$ vanishes, and all the thermodynamic variables in the collision integral $(\delta P_i/\delta \theta)_{coll}$—namely, $P_i(r)$, $n(r)$, $T_i(r)$, and $T_{int}(r)$—become functions of only the position $r$ along the jet axis.

Although the collision integral for molecules $M$ has been formulated originally in terms of state-to-state cross sections $(\sigma's)$ associated with the elementary collision processes involving internal states $i,j,\ell,m$,\textsuperscript{21–23}

$$M(i) + M(j) \rightarrow M(\ell) + M(m),$$

(8)

at well-defined kinetic energy $E$, further simplification is possible by reformulating it in terms of rates associated with the “chemical” reactions,

$$k_{ij-\ell m}$$

(9)

at the local translational temperature $T_i$.

Cross sections and rates are related by

$$k_{ij-\ell m}(T_i) = \frac{\langle \nu \rangle}{(k_BT_i)^2} \int_{E_s}^{\infty} \frac{\sigma_{ij-\ell m}(E)}{E} \exp(E/k_BT_i) E dE,$$  

(10)

where $\langle \nu \rangle = (8k_BT_i/\pi \mu)^{1/2}$ is the mean relative velocity of the colliding partners of reduced mass $\mu$, and $E_s$ is the minimum kinetic energy for the internal states $m$ and $\ell$ to become accessible. Constraining the discussion to collisions between linear molecules at temperatures below 300 K, the internal states are rotational states and $i,j,\ell,m$ may be identified with the rotational quantum number $J$. The rates obey in this case the detailed balance relation

$$k_{\ell m-ij} = k_{ij-\ell m} \frac{(2I + 1)(2J + 1)}{(2\ell + 1)(2m + 1)} \exp(E_{ij} - E_{\ell m}/k_BT_i),$$

(11)

which is consubstantial with the factorized form of Eqs. (1)–(3).

It can be shown that in the paraxial region of a steady molecular (one species) jet expanding along coordinate $z$, Eq. (5) adopts the form of the nonlinear master equation (MEQ),\textsuperscript{61}

$$v_0(z) \frac{dP_i}{dz} = n(z) \sum_{J=0}^{\infty} \left( - P_i(z) P_J(z) k_{ij-\ell m} + P_J(z) P_m(z) k_{\ell m-ij} \right).$$

(12)

This nonlinear differential equation cannot be solved in practice. However, the quantities $P_i$, $dP_i/dz$, and $n$ can be measured point by point along the jet axis as described below, while the translational temperature $T_i$ (implicit in the $k's$) and the flow velocity $v_0$ can also be inferred from the experiment by means of Eqs. (6) and (7), respectively. This way the only unknowns remaining in MEQ (12) are the rates. These may be supplied from models or from high level scattering calculations in order to be assessed by means of MEQ (12) or, in favorable cases, the rates may be derived inverting the MEQ (12). Both options will be explored here.

For jets including atoms in addition to molecules, as in the present work, Eq. (12) must be adapted (see below) in order to account for molecule:atom collisions, which are governed by two-index rates $k_{ij-\ell m}$ in addition to the molecule:molecule collisions governed by the four-index rates $k_{ij-\ell m}$.

III. EXPERIMENT

Inelastic collisions of para-H$_2$ (pH$_2$) and ortho-H$_2$ (oH$_2$) with He atoms are investigated here in the paraxial region of two supersonic jets. These are generated by expanding two mixtures of pH$_2$ and natural-H$_2$ (oH$_2$) with He through a slit nozzle of width $D=130$ $\mu$m and length $L=3$ mm under the following stagnation conditions:

- pH$_2$ (25%) + He (75%): $p_0=408$ mbars, $T_0=295$ K,
- oH$_2$ (27%) + He (73%): $p_0=400$ mbars, $T_0=298$ K.

The pH$_2$ component was prepared in the laboratory from nH$_2$ by means of a cryogenic catalytic converter yielding a purity of pH$_2$ better than 99%, while nH$_2$ and He were high purity (>99.9999%) commercial samples. The pH$_2$ (25%) + He (75%) gas mixture, having less than 1% of oH$_2$ impurity is aimed at studying pH$_2$:He collisions. On the other hand, since oH$_2$ cannot be prepared in our laboratory in sufficient amount and purity, oH$_2$:He collisions have been studied from the nH$_2$ (27%) + He (73%) sample, where oH$_2$ is the dominant species in nH$_2$ in the natural ratio of oH$_2$ to pH$_2$ of 3 to 1.

High-sensitivity Raman spectroscopy (few photons/s) with high spatial resolution (few micrometers) is the quantitative diagnostic technique employed here. Even for the state of the art of the instrumentation available in our laboratory the proportion of the pH$_2$ or nH$_2$ molecular species in the expanded H$_2$+He mixtures can hardly be reduced below $=25\%$ for an acceptable Raman signal to noise ratio. This leads to the undesired contribution of $pH_2$:pH$_2$, pH$_2$:oH$_2$, and oH$_2$:oH$_2$ molecule: molecule self-collisions ($M: M$) accompanying the pH$_2$:He, and oH$_2$:He molecule:atom collisions ($M: A$), which are the goal of present study.

Since the rotational levels of H$_2$ better suited for Raman spectroscopic observation in the present thermal range are $J=0$ and 1, the MEQ (12) adapted to include $M: M$ and $M: A$ collisions can be reduced to the more convenient form

$$\dot{P}_0/n = \alpha_p(M:M)_0 + (1 - \alpha_p)(M:A)_0,$$

(13)

for studying pH$_2$:He collisions in the pH$_2$+He mixture, and

$$\dot{P}_1/n = \alpha_p(M:M)_1 + (1 - \alpha_p)(M:A)_1,$$

(14)

for studying oH$_2$:He collisions in the nH$_2$+He mixture; $\alpha_p=0.25$ and $\alpha_n=0.27$ are the mole fractions of pH$_2$ and nH$_2$, respectively; $P_0=\dot{d}P_0/\dot{d}t$ and $P_1=\dot{d}P_1/\dot{d}t$ are the population rates of $J=0$ and $J=1$ rotational levels of pH$_2$ and nH$_2$.
Self-collisions in H₂ have been studied recently in detail. The mole fractions α₀ and αₚ have been considered to remain constant along the jet, as discussed below.

Detailed balance [Eq. (11)] enables a convenient reformulation of Eqs. (13) and (14) in terms of only “down” rates. The remaining quantities in Eqs. (13)–(14) have been derived from the intensities of the Raman lines of the fundamental H₂ and ortho-H₂ collisions between distinguishable molecules; 54 the only unknowns remaining in Eqs. (13)–(18) are the k₂→₀ and k₁→₀ rates for pH₂+He and oH₂+He collisions, respectively. The remaining quantities in Eqs. (13)–(19) have been determined experimentally as described next.

A. Experimental quantities

All experimental quantities (Pᵢ, Ṗᵢ, n, τᵢ, Tᵢ) in Eqs. (13)–(19) have been derived from the intensities of the Q(0), Q(1), Q(2), Q(3), and Q(4) Raman lines of the fundamental Q branch of H₂ at 4161.2, 4155.3, 4143.5, 4125.9, and 4102.6 cm⁻¹, respectively. These intensities were measured along the axis of the H₂+He jets at steps Δz=50 μm, spanning the range of 50≤z≤1200 μm of axial distances from the nozzle.

Representative Raman spectra of the H₂+He mixtures recorded at z=300 μm on the jet axis are shown in Fig. 1. More details about the high-sensitivity/high spatial resolution Raman spectroscopy employed can be found elsewhere. 58–60,62 The quantities actually measured in the jets were the absolute number density n(z) of H₂+He mixture, and the rotational populations Pᵢ(z) of H₂. They are shown in Figs. 2 and 3. For clarity, Fig. 3 only shows the rotational populations P₀ and P₁, which are the ones better suited for accurate measurements of the dPᵢ/dz gradients. The rotational populations P₂ and P₃ are fixed by the normalization conditions given in Eqs. (A1) and (A2) (Appendix) for P₁ frozen along the expansion at the nozzle exit temperature Tₑ=260 K. The rotational temperatures Tₑ,para and Tₑ,ortho were derived from the ratio of Raman intensities of the Q-lines, I(2)/I(0) and I(3)/I(1), respectively. In turn, Tₑ(z) and v₀(z) were derived from them by means of the conservation Eqs. (6) and (7) as explained below.

The rotational temperature Tₑ(z) was determined on the basis of Eq. (6) imposing the entropy invariance condi-
nuclear spin weights of $S_0$ being the stagnation entropy. Assuming that $S = S_{\text{trans}} + S_{\text{rot}}$, i.e., ignoring the vibrational contribution, which is negligible at $T < 300$ K, and employing the statistical definition of entropy, one obtains

$$T_j(z) = T_0 \left( \frac{n(z)}{n_0} \right)^{2/3} \left[ F \times \prod \left( \frac{P_j(z)}{w_j(2J+1)} \right)^{P_j(z)} \right]^{2a/3},$$

where $F = \prod \left( \frac{P_j^0}{w_j(2J+1)} \right)^{-P_j}$

for the translational temperature at axial distance $z$ in a mixed jet of molecules and atoms, with molecular mole fraction $\alpha$; $w_j = 1$ for $J =$ even and $w_j = 3$ for $J =$ odd are the nuclear spin weights of $pH_2$ and $oH_2$, respectively; $n_0$ is the stagnation number density, and $P_j^0$ are the rotational populations at the stagnation temperature $T_0$. Translational temperatures in the jets are shown in Fig. 4, jointly with the rotational temperatures derived from the measured rotational populations.

The macroscopic flow velocity in the mixed jet is obtained from Eq. (7). The conservation of energy between the source and a point of the jet axis leads to

$$v_0(z) = \left[ \left( 5R(T_0 - T_j(z)) + 2\alpha \int_{T_0}^{T_j(z)} C_{\text{rot}}dT_r \right) / W \right]^{1/2},$$

where $R = 8.31451$ J K$^{-1}$ mol$^{-1}$ is the universal gas constant, $C_{\text{rot}}$ is the molar rotational heat capacity at constant pressure, and

$$W = \alpha W(H_2) + (1 - \alpha) W(He)$$

is the average molar mass of the gas mixture. In the case of hydrogen, $C_{\text{rot}}$ is not a constant but depends on the rotational temperature, and differs for $pH_2$ and $oH_2$ along the expansion. This leads to the slightly different velocities for the two jets shown in Fig. 2.

Finally, the population rates $\dot{P}_0$ and $\dot{P}_1$ along the jets in the left-hand term of MEQs (13) and (14) were obtained from

$$\dot{P}_i = v_0 \frac{dP_i}{dz},$$

where the population gradients $dP_i/dz$ have been measured from the rotational populations $P_i(z)$. These data have been noise filtered by a running average procedure employing a generic function of the form

$$P_i(z) = A + B \exp(-C/z)$$

over consecutive datapoint sets. The gradients $dP_i/dz$ were then obtained deriving the best-fit analytical functions.

Species enrichment due to Mach-number focusing along the jet has been considered. Since He is a Raman-inactive species, enrichment has been measured on a 2:1 mixture of $N_2$ in $H_2$. The largest enrichment of $N_2$ observed along the jet was $\approx 3\%$ for $z > 1$ mm. Since the enrichment is proportional to the mass ratio of species, it can be estimated that the He to $H_2$ enrichment is below 1% in the present experiments. Therefore, the mole fractions $\alpha_p$ and $\alpha_n$ have been taken here as constants.

IV. CALCULATED CROSS SECTIONS AND RATE COEFFICIENTS

Assessment of the $H_2:He$ collisional rates by means of Eqs. (13)–(18) implies two sets of rates, one for the $H_2:He$ self-collisions, and the other for the $H_2:He$ collisions. The former have been reported recently in the low-temperature range. Since the accuracy of $H_2:He$ self-collision rates is $\approx 10\%$, they will be treated here as known data. The most relevant ones are shown in Figs. 5–7, jointly with the $k_{2-0}$ and $k_{3-1}$ rates for $H_2:He$ collisions discussed next.

Cross sections and rates for $H_2:He$ collisions have been calculated by several authors employing different PESs and...
methods.\textsuperscript{2,3,26,29,39,41} Here we consider as a reference the rates reported by Balakrishnan \textit{et al.},\textsuperscript{2} which were calculated using the Muchnick–Russek potential\textsuperscript{17} (MR-PES).

For the sake of completeness, we have calculated at the CCC level the H\textsubscript{2}:He rates using a new H\textsubscript{2}–He potential: the BMP-PES,\textsuperscript{18} which \textit{a priori} should be far superior than the composite semiempirical and \textit{ab initio} MR-PES. The BMP-PES is based on a modern carefully executed set of \textit{ab initio} CI calculations, and includes results from other theoretical calculations.\textsuperscript{16} In order to check consistency, we have repeated the calculation reported by Balakrishnan \textit{et al.},\textsuperscript{2} with the same MR-PES and with a modified version of it, the MMR-PES,\textsuperscript{18} which also includes Tao’s calculations,\textsuperscript{16} and leads to very similar results.

The present CCC calculations have been performed with the full three-dimensional (3D) PESs $V(r,R,\theta)$, where $r$ is the internal coordinate of H\textsubscript{2}, $R$ is the distance between He and the center of mass of H\textsubscript{2}, and $\theta$ is the angle between $\vec{r}$ and $\vec{R}$, which is aligned along the $z$ axis of the body-fixed frame.

The PESs were projected onto five Legendre polynomials $P_{\lambda}$ from $\lambda=0$ to 8 with the help of a 12-point Gauss–Legendre quadrature. Note that, in fact, only half of these points are really needed due to the symmetry of H\textsubscript{2}. The resulting radial coefficients $V_{\lambda}(r,R)$ then allow the vibrational radial coupling terms,

\begin{equation}
V_{\lambda}^{nn}(R) = \int \chi_n(r)V_{\lambda}(r,R)\chi_m(r)dr,
\end{equation}

to be evaluated; $\chi_n(r)$ are wavefunctions of the vibrating H\textsubscript{2} molecule. Although nondiagonal $V_{\lambda}^{nn}(R)$ elements are not relevant for $k_{2\rightarrow0}$ and $k_{3\rightarrow1}$ rates in the investigated thermal range, they were taken into account for solving the set of coupled equations with extended basis sets. These are needed to obtain converged results for higher rates, which will be reported in a forthcoming publication.

We have assessed three approximations. In the first one, we choose the numerical solution of the vibrational Hamiltonian

\begin{equation}
-\frac{\hbar^2}{2\mu_{\text{H}_2}} \frac{d^2}{dr^2} + V_{\text{H}_2}(r) \chi_n(r) = E_n \chi_n(r),
\end{equation}

using a discrete variable representation (DVR) with a basis of sinusoidal functions and the H\textsubscript{2} internal potential of Schwenke.\textsuperscript{64} In the second approximation, we use eigenfunctions of a harmonic oscillator (HO). Eventually, the rigid rotor (RR) approximation is assessed fixing $r$ at the equilibrium bond length $r_e=1.4a_0$. In this case the coupling terms $V_{\lambda}^{nn}(R)$ vanish. The $\alpha_{0\rightarrow2}$ cross sections calculated in the three approximations are given in Table I, where the trend $\sigma(\text{RR})<\sigma(\text{HO})<\sigma(\text{DVR})$ becomes obvious. The same trend holds for other $\sigma_{i\rightarrow j}$’s. In average $\sigma(\text{RR})=0.7\sigma(\text{DVR})$, and $\sigma(\text{HO})=0.85\sigma(\text{DVR})$. These results cast some doubts about the accuracy of cross sections and rates calculated from PESs based in the rigid-rotor approximation.
for the interacting molecules, as is the case with the H$_2$:H$_2$ scattering calculations carried out so far (see Ref. 54 and references therein).

The $\sigma_{2\rightarrow0}$ and $\sigma_{3\rightarrow1}$ cross sections for H$_2$:H$_2$ collisions derived from the MR-PES and the BMP-PES in the DVR approach are shown in Fig. 8. The rotational state-to-state cross sections at total energy $E_r=E_{\text{kin}}+E_{\text{rot}}(J)$ were obtained via the MOLCOL code. The coupled equations were solved with the close-coupling method (Arthur and Dalgarno) and the MOLSCAT code. The propagation for solving the coupled equations was carried out from 2 to 30 $a_0$ with ten points per half wavelength associated with the sum of the total energy and maximum well depth ($\approx$10 cm$^{-1}$). This was done with Johnson’s log-derivative propagator.

The experimental $E_{v,J}$ energy levels of H$_2$ were included in the basis set of the coupled equations. Rovibrational levels up to $v=1$ and $J=2$ were included for energies ranging from 509.95 to 5000 K, and up to $v=1$ and $J=4$ for energies between 5000 and 7000 K. In order to perform the thermal average for the rate coefficients according to Eq. (10), a grid of $\approx$1300 energy points was built using in conjunction the DVR wavefunctions (first approximation) in Eq. (26). Downward as well as upward rate coefficients were calculated independently by means of Eq. (10), their consistency being checked through the detailed balance Eq. (11).

For 10 K $\leq T \leq$ 300 K, our $k_{2\rightarrow0}$ and $k_{3\rightarrow1}$ rates calculated with the MR-PES in the DVR approach differ from those of Balakrishnan et al. by less than 1% and 3%, respectively. Taking into account the different scattering codes, numerical procedures, and approximations employed, this is a remarkable agreement. In turn, the $k_{2\rightarrow0}$ and $k_{3\rightarrow1}$ rates from the MMR-PES are slightly larger than those from the MR-PES, as shown in Figs. 5 and 6.

### V. DISCUSSION

The experimental assessment of the CCC-calculated rates $k_{2\rightarrow0}$ and $k_{3\rightarrow1}$ for H$_2$:H$_2$ collisions shown in Figs. 5 and 6 is based on MEQs (13) and (14), by comparing the left-hand term (LHT) with the right-hand term (RHT) in each MEQ. The LHTs are the pure experimental quantities $\dot{P}_i/n$, while the RHTs are a linear combination of known coefficients and of the calculated $k_{2\rightarrow0}$ or $k_{3\rightarrow1}$ rates, according to Eqs. (15)–(18). The LHTs of MEQs (13) and (14), and their RHT contributions for $k_{2\rightarrow0}$ and $k_{3\rightarrow1}$ calculated rates from MR-PES are shown in Figs. 9 and 10.

#### A. pH$_2$:He collisions

The experimental population rate $\dot{P}_0/n$ of the $J=0$ rotational level (normalized by number density) along the pH$_2$ (25%):He (75%) jet is shown in Fig. 9 (filled circles + error bars), jointly with the pH$_2$:pH$_2$ self-collision contribution (A), the pH$_2$:He contribution (B) depending on the $k_{2\rightarrow0}$ rate calculated from MR-PES and the sum of both (A+B). This sum is close to matching the experimental LHT for the whole thermal range investigated, 22 K $\leq T \leq$ 183 K. Since the pH$_2$:pH$_2$ self-collision contribution (A) is minoritary, and its accuracy is on the order of 10%, one can conclude that the $k_{2\rightarrow0}$ rate derived from MR-PES is slightly too small between 30 and 80 K, but accurate to bet-

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**Table I.** Cross section $\sigma_{n\rightarrow2}$ ($\AA^2$) for pH$_2$:He collisions, calculated from the BMP-PES (Ref. 18) in three approximations.

<table>
<thead>
<tr>
<th>Total energy (K)</th>
<th>DVR$^a$</th>
<th>HO$^b$</th>
<th>RR$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>520</td>
<td>0.003 86</td>
<td>0.003 34</td>
<td>0.002 80</td>
</tr>
<tr>
<td>610</td>
<td>0.025 5</td>
<td>0.022 1</td>
<td>0.018 4</td>
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<td>710</td>
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<td>0.052 8</td>
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<tr>
<td>1000</td>
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<td>0.178</td>
<td>0.149</td>
</tr>
<tr>
<td>1700</td>
<td>0.638</td>
<td>0.551</td>
<td>0.472</td>
</tr>
<tr>
<td>2000</td>
<td>0.826</td>
<td>0.715</td>
<td>0.617</td>
</tr>
<tr>
<td>3500</td>
<td>1.670</td>
<td>1.460</td>
<td>1.300</td>
</tr>
<tr>
<td>4000</td>
<td>1.910</td>
<td>1.670</td>
<td>1.510</td>
</tr>
</tbody>
</table>

$^a$Discrete variable representation.

$^b$Harmonic oscillator.

$^c$Rigid rotor.

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**Figure 8.** CCC-calculated $\sigma_{2\rightarrow0}$ and $\sigma_{3\rightarrow1}$ cross sections for pH$_2$:He and oH$_2$:He collisions from two PESs (Refs. 17 and 18).

**Figure 9.** Assessment of CCC-calculated $k_{2\rightarrow0}$ rate from MR-PES (Ref. 17) in pH$_2$:He collisions (see the text). Vertical figures stand for $T_t(z)$.
ter than 25% according to the experiment. Very minor improvement is obtained for the \( k_{2 \rightarrow 0} \) rate calculated from the MMR-PES.

A similar comparison for the \( k_{2 \rightarrow 0} \) from the BMP-PES (Ref. 18) shows a poor LHT to RHT agreement, suggesting that the calculated rate is too small by about 40%.

As shown in Fig. 9 the \( pH_2:pH_2 \) self-collision term (A) is a minor contribution to the RHT of MEQ (13). Indeed, this is so regardless of the PES employed in the calculation. Thus, it is possible to invert Eq. (13) to obtain \( k_{2 \rightarrow 0} \) from the experiment by assuming the self-collision term (A) to be known within 10% accuracy, which is the case. This is shown in Fig. 11, where the calculated \( k_{2 \rightarrow 0} \)'s are included for comparison, jointly with some experimental rates derived from acoustic measurements at 90.5 and 170 K, and at 300 K. These data permit us to relate the acoustic relaxation time \( \tau \) at pressure \( p \) and temperature \( T_t \), with the up and down rates by \( p \tau T_t = \frac{1.363 \times 10^{-28} T_t}{k_{0-2} + k_{2-0}}, \)

where \( p \tau \) is in atm s, \( T_t \) in kelvin, and \( k's \) in \( 10^{-20} m^3 s^{-1} \).

As shown in Fig. 11, the agreement of the \( k_{2 \rightarrow 0} \) rate calculated from the MR-PES and MMR-PES with the jet experiment is within the experimental error of about 15% in the range from 90 to 180 K. In this range, the calculated \( k_{2 \rightarrow 0} \) is about 5% larger than the two very accurate acoustic data points. Between 30 and 90 K the calculated rate is about 20% smaller than in the jet experiment, the contrast, the \( k_{2 \rightarrow 0} \) calculated from BMP-PES is clearly outside the estimated experimental error.

The inset of Fig. 11 shows the experimental \( k_{2 \rightarrow 0} \) obtained employing the experimental values of \( k_{20-06} \) and \( k_{22-20} \) for the \( pH_2:pH_2 \) self-collisions at \( T_t \leq 110 \) K, instead of the calculated ones. For 30 K \( \leq T_t \leq 110 \) K, there is an improvement of \( \approx 10% \) with respect to the CCC-calculated \( k_{2 \rightarrow 0} \) from MR-PES and MMR-PES. This suggests that the rates for \( pH_2:pH_2 \) collisions, which were calculated from a rigid-rotor PES (Ref. 70) might be underestimated by more than 10%, consistently with the underestimation of the rigid-rotor approximation shown in Table I.

B. \( ohH_2:He \) collisions

The experimental study of \( k_{3 \rightarrow 1} \), which is the main contribution to \( ohH_2:He \) collisions at low temperature, poses additional difficulties compared to \( k_{2 \rightarrow 0} \).

First, the gradient of the rotational population \( P_1 \) along the \( nH_2(27\%) + He(73\%) \) jet is much smaller than that of \( P_0 \) along \( pH_2(25\%) + He(75\%) \) jet, as shown in Fig. 3. This implies that the experimental accuracy of the \( J=1 \) rotational population rate \( \dot{P}_1/n \) shown in Fig. 10 is considerably smaller than of the \( J=0 \) rotational population rate \( \dot{P}_0/n \) in Fig. 9. Also, the small gradient of \( P_1 \) in Fig. 3 indicates that \( k_{3 \rightarrow 1} \) must be significantly smaller than \( k_{2 \rightarrow 0} \), a point confirmed by the CCC calculations shown in Figs. 5 and 6, and by the discussion below.

Second, the contribution of some \( ohH_2:pH_2 \) collisions to the evolution of \( P_1 \) along the \( nH_2(27\%) + He(73\%) \) jet are expected to be comparatively large, as can be inferred from Fig. 7, where the \( k_{30-12} \) and \( k_{41-23} \) rates for ortho:para collisions are about one order of magnitude larger than the \( k_{3 \rightarrow 1} \) rate of \( ohH_2:He \) collisions.

The combination of the above factors leads to a large uncertainty in assessing \( k_{3 \rightarrow 1} \). Figure 10 shows the experimental population rate \( \dot{P}_1/n \) of the \( J=1 \) rotational level along the \( nH_2(27\%) + He(73\%) \) jet, jointly with a large \( ohH_2:ohH_2 \) and \( ohH_2:pH_2 \) self-collision contribution (A), the \( ohH_2:He \) contribution (B) depending on the \( k_{3 \rightarrow 1} \) rate calculated from MR-PES, and the sum of both (A+B), which should match the experimental LHT values of MEQ (14). The \( k_{3 \rightarrow 1} \) rate calculated from either the MR-PES or the MMR-PES are borderline compatible within the experimental uncertainty. A similar comparison employing the B term calculated from the BMP-PES (not shown in Fig. 10) also leads to compatibility with experiment. This ambiguity between the \( k_{3 \rightarrow 1} \) 's derived from MR-PES and BMP-PES's can only be clarified by the experiment by means of \( nH_2 + He \) mixed jets with...
a molar fraction $a \approx 0.05$ of $n_H_2$. However, quantitative Raman spectroscopic measurements in such diluted jets pose a challenge to the present state of the art.

Inversion of MEQ (14) in order to retrieve $k_{3\rightarrow1}$ from experiment reflects the above ambiguity. This is shown in Fig. 12, where the experimental $k_{1\rightarrow1}$ is compatible with both MR- and BMP-PESs. From the experimental point of view the very small value of $k_{3\rightarrow1}$ at $T_s < 100$ K is the result of the difference between two terms of comparable size, with large uncertainties. For $22$ K $\leq$ $T_s$ $\leq$ $40$ K, the only conclusive experimental result is the value $k_{3\rightarrow1} \approx 2 \times 10^{-20}$ m$^3$/s. The only acoustic experimental data known to us on $k_{3\rightarrow1}$ (Ref. 52) is in clear disagreement with the CCC calculations and with the trend of the present jet experiments.

It should be expected that the poor rotational cooling rate of $o_H_2$ by collisions with $He$ shown in Figs. 3 (lower trace) and 4 (upper trace) should still be much less efficient in highly diluted $o_H_2$+$He$ mixtures.

VI. CONCLUSIONS AND COMMENTS

The $k_{2\rightarrow0}$ rate for $H_2$+$He$ collisions in the vibrational ground state$^7$ derived from MR-PES,\textsuperscript{17} or from its variant MMR-PES (Ref. 18) is largely validated for $22$ K $\leq$ $T_s$ $\leq$ $180$ K by the present experiment, as shown in Fig. 9. The corresponding rate from the BMP-PES (Ref. 18) is about $40\%$ too small, and is outside from the estimated experimental uncertainty. This is a surprising result since the BMP-PES is expected to be more accurate than the MR- and MMR-PESs. One must take into account, however, that the experimental results and the calculations to compare with, are sensitive only to the short range of the PES, in particular, to the van der Waals well and the bottom of the repulsive wall. The $V_{20}^0$ term of the PES, which is the main anisotropic component of the PES expanded over Legendre polynomials, is indeed the dominant one for the $\Delta J = 2$ rotational changes involved in $k_{2\rightarrow0}$ and $k_{3\rightarrow1}$ rates. It may happen that the $V_{20}^0$ term of the MR- and MMR-PESs is locally more accurate than the corresponding one from BMP-PES in these regions. This is, however, not in contradiction with a global superiority of the BMP-PES, specially at larger distances and at very short range.\textsuperscript{18} In any case, it seems that in the region probed by our calculations the BMP-PES underestimates the $V_{20}^0$ term by about $20\%$, thus leading to smaller cross sections and to smaller rates than with the MR- and MMR-PESs, and to a poorer agreement with the experiment.

For the $k_{3\rightarrow1}$ rate, the theory-experiment comparison is not conclusive due to the relatively large experimental uncertainty (see Fig. 12), which is compatible with the MR-, MMR-, and BMP-PESs. More experimental work is needed in order to reduce this experimental uncertainty.

The better quality of MR- and MMR-PESs over the BMP-PES in the range of energy $E < 250$ cm$^{-1}$ can be concluded unambiguously from the present rotational relaxation experiments, according to the discussion of Sec. V. This complements the conclusions of Lee et al.\textsuperscript{40} based on the agreement of the vibrational relaxation cross sections calculated from the MR-PES with the experimental results from Audibert et al.\textsuperscript{48,50} and the inability of BMP-PES to properly account for such cross sections.

The feasibility of deriving the $k_{2\rightarrow0}$ and $k_{3\rightarrow1}$ rates for $H_2$+$He$ collisions on the sole basis of the experiment is confirmed here, however, subject to the limitations imposed by the $H_2$+$H_2$ self-collisions in the $H_2$+$He$ mixtures employed. The accuracy of the results shown in Figs. 9–12 can be improved reducing the molar fraction of $H_2$ in the expanded $H_2$+$He$ samples to $a = 0.05$. This should imply data acquisition times for the Raman spectra about five times longer than in the present work, a tedious but probably affordable work from the experimental point of view.

From the expertise gained in this work, a substantial accuracy improvement in determining $k_{2\rightarrow0}$ and $k_{3\rightarrow1}$ can be expected by studying the thermal range $180$ K $\geq$ $T_s$ $\geq$ $20$ K in two adjacent subranges, optimizing the flow conditions by means of the different nozzle, stagnation conditions, and data point distributions given in Table II.

We notice some evidence that the calculated rates\textsuperscript{44} employed in estimating the $p_H_2$:$p_H_2$ self-collisions might be underestimated by $\approx 15\%$ between 30 and 110 K. This should make advisable a recalculation of the $H_2$+$H_2$ inelastic rates on the basis of a new $H_2$+$H_2$ PES including the vibrational degrees of freedom in the $H_2$ colliding partners.

The effect of other $k_{2\rightarrow0}$ ($J \geq 4$) and $k_{3\rightarrow1}$ ($J \geq 5$) rates is undetectable in the range of temperatures and densities investigated in this work. They are expected to be at least one order of magnitude smaller than $k_{2\rightarrow0}$ and $k_{3\rightarrow1}$, respectively.

Taking into account the wide range of the experimental data shown in Figs. 2 and 4, the global agreement between experimental and CCC-calculated rates from the MR-PES and MMR-PESs, can be taken as a consistency proof of the
gas-dynamic conservation Eqs. (5)–(7). These equations provide thus the basis for the experimental investigation of the hitherto elusive inelastic terms of Boltzmann collision integral at a molecular scale.

ACKNOWLEDGMENTS

This work has been supported by the Spanish Ministerio de Educación y Ciencia, research Project Nos. FIS2004-02576 and ESP2004-21006-E, and ASTROCAM network. Thanks are due to J. P. Toennies and the Max-Planck-Institut für Strömungsforschung, Göttingen, for the loan of an nH2 \( \rightarrow p\text{H}_2 \) converter and a diaphragm gas compressor. We also thank Dr. A. Viel, Rennes, for her efficient code for calculating rovibrational H2 wavefunctions using the DVR method.

APPENDIX: MASTER EQUATION COEFFICIENTS

In the thermal range investigated experimentally here, approximately 22 K \( \leq T \leq 180 \) K and 180 K \( \leq T \leq 210 \) K, the rotational levels of \( p\text{H}_2 \) and \( o\text{H}_2 \) whose population \( P_j \) can be measured with sufficient accuracy in the \( \text{pH}_2(25\%) + \text{He}(75\%) \) and \( n\text{H}_2(27\%) + \text{He}(73\%) \) mixtures are \( j = 0, 1 \). The following normalization holds to a good approximation: In the \( \text{pH}_2(25\%) + \text{He}(75\%) \) mixture,

\[
P_0 + P_2 + P_4 = 1, \quad (A1)
\]

and in the \( n\text{H}_2(27\%) + \text{He}(73\%) \) mixture,

\[
P_0 + P_2 + P_4 = 1/4, \quad P_1 + P_3 = 3/4. \quad (A2)
\]

The \( a_{\text{rop}} \) coefficients of Eqs. (15) and (16) are given in the rigid rotor approximation by

\[
a_{012} = (7/15)P_2e^{-4BBT} - P_1P_0, \\
a_{4123} = (27/35)P_2P_3e^{-4BBT} - P_4P_1, \\
a_{2000} = -5P_0e^{-6BBT} + P_2P_0, \\
a_{2202} = -5P_0e^{-6BBT} + P_2P_2, \\
a_{3010} = -(7/3)P_3e^{-10BBT} + P_3P_0, \\
a_{3111} = -(7/3)P_3e^{-10BBT} + P_3P_1, \\
a_{3212} = -(7/3)P_3e^{-10BBT} + P_3P_2, \\
a_{3313} = -(7/3)P_3e^{-10BBT} + P_3P_3. \quad (A3)
\]