Inelastic collisions in *para*-H₂: Translation-rotation state-to-state rate coefficients and cross sections at low temperature and energy

B. Maté

Instituto de Estructura de la Materia, CSIC Serrano 121, 28006 Madrid, Spain

F. Thibault

*Laboratoire de Physique des Atomes, Lasers, Molecules et Surfaces (UMR-CNRS 6627),
Universite de Rennes I, Campus de Beaulieu, F-35042 Rennes Cedex, France*

G. Tejeda, J. M. Fernández, and S. Montero^{a)}

Instituto de Estructura de la Materia, CSIC Serrano 121, 28006 Madrid, Spain

(Received 26 October 2004; accepted 30 November 2004; published online 3 February 2005)

We report an experimental determination of the $k_{00 \rightarrow 02}$ rate coefficient for inelastic H₂:H₂ collisions in the temperature range from 2 to 110 K based on Raman spectroscopy data in supersonic expansions of *para*-H₂. For this purpose a more accurate method for inverting the master equation of rotational populations is presented. The procedure permits us to reduce the measured $k_{00 \rightarrow 02}$ rate coefficient to the corresponding $\sigma_{00 \rightarrow 02}$ cross section in the range of precollisional energy from 360 to 600 cm⁻¹. Numerical calculations of $\sigma_{00 \rightarrow 02}$ carried out in the frame of the coupled channel method are also reported for different intermolecular potentials of H₂. A good agreement is found between the experimental cross section and the numerical one derived from Diep and Johnson's potential [J. Chem. Phys. **112**, 4465 (2000)]. © 2005 American Institute of Physics.
[DOI: 10.1063/1.1850464]

I. INTRODUCTION

Nonreactive collisions between molecules are relevant in molecular quantum mechanics, gas dynamics, and astrophysics. Due to the large vibrational quantum of H₂, the energy transfer in H₂:H₂ collisions in the gas at room temperature and below is largely described by the rotation-translation state-to-state rate coefficients $k(T)$. At the molecular level, the collision between two single H₂ molecules at relative kinetic energy E is described by the corresponding state-to-state inelastic cross section $\sigma(E)$. These quantities have been the subject of a number of theoretical and computational works,¹⁻⁵ covering, however, the range above 50 K. Below this temperature neither theoretical nor experimental data have been reported as far as we know.

In this paper we report the experimental determination of the dominant state-to-state rate coefficient $k_{00 \rightarrow 02}(T_i)$ of *para*-H₂ (*p*H₂) in the low temperature range, $2 \leq T_i \leq 110$ K, and of its associated inelastic cross section $\sigma_{00 \rightarrow 02}(E)$ in the energy range $360 \leq E \leq 600$ cm⁻¹. These quantities concern the collision induced transitions between the two lowest rotational levels, $J=0$ and $J=2$ of the vibrational ground state ($v=0$), i.e., between a state of pure translational energy and the lowest rotational level accessible by a nonreactive collision. The experimental work is complemented by *ad hoc* scattering calculations.

This paper is structured as follows: in Sec. II the theoretical background of the methodology is described in connection with the physical quantities measured experimentally. Sections III and IV deal with the instrumental aspects

of the experiment and with the measuring procedure of the quantities involved, respectively. In Sec. V the experimental $k_{00 \rightarrow 02}(T_i)$ rate coefficient of *p*H₂ is discussed. The relation between a rate coefficient and the corresponding cross section is also derived in Sec. V as an explicit function of the translational temperature, providing the ground for the experimental determination of the $\sigma_{00 \rightarrow 02}(E)$ cross section of *p*H₂. The discussion is completed in Sec. VI comparing the present experimental rate coefficients and cross sections with the theoretical ones derived using different scattering computational codes and potential energy surfaces of *p*H₂. A brief Sec. VII closes the paper with the main conclusions.

II. METHODOLOGY

The physical foundation of the present experimental method is the spontaneous breakdown of thermal equilibrium between the translational and the rotational degrees of freedom in the core of a steady supersonic expansion of a molecular gas, in this case pure *p*H₂. Such a core, the so-called zone of silence of the expansion, is characterized by a laminar flow of supersonic velocity V , and by a fast decrease of the local number density n and of the translational temperature T_t as the distance z from the nozzle increases. This rarefaction-cooling effect, which is driven by the pressure gradient across the nozzle, causes a progressive reduction of the collisional rate and of the inelastic rate coefficients in the expanding gas. This leads to the gradual breakdown of thermodynamical equilibrium ($T_r \neq T_t$, with $T_r > T_t$) between rotational and translational temperatures.

The above qualitative ideas can be expressed quantitatively by means of a master equation for the energy transfer

^{a)}Electronic mail: emsalvador@iem.cfmac.csic.es

between translational and rotational degrees of freedom considering explicitly the discrete nature of rotational levels. For a gas of diatomic molecules it reads²

$$\frac{dP_i}{dt} = n \sum_{j\ell m} (-P_i P_j k_{ij \rightarrow \ell m} + P_\ell P_m k_{\ell m \rightarrow ij}), \quad (1)$$

describing the time evolution of the population P_i (normalized to unity, i.e., $\sum_i P_i = 1$) of a rotational energy level with quantum number $J=i$, in a gas parcel with instantaneous number density $n(t)$ and translational temperature T_t (averaged over the three translational degrees of freedom). Indices i, j, ℓ , and m span the domain of the rotational quantum number J of the diatomic molecule; $k_{ij \rightarrow \ell m}$ is the translational-rotational state-to-state rate coefficient for the inelastic collision between pairs of molecules in a bath (macroscopic sample) at the translational temperature T_t . The constraint $\{i, j, \ell, m\} = \text{even}$ holds for $p\text{H}_2$.

In order to determine rate coefficients in the environment of a supersonic expansion it is advantageous to transform the master equation (1) from the time domain into the spatial domain, which is directly accessible in the experiment. Since the flow is laminar in the zone of silence of the expansion, in it the rotational populations along the expansion evolve according to

$$P'_i(z) = \frac{n(z)}{V(z)} \sum_{j\ell m} k_{ij \rightarrow \ell m} \times \left(-P_i P_j + P_\ell P_m \frac{(2i+1)(2j+1)}{(2\ell+1)(2m+1)} e^{(E_\ell + E_m - E_i - E_j)/kT_t} \right), \quad (2)$$

where $P'_i(z) = dP_i(z)/dz$; $V(z) = dz/dt$ is the bulk flow velocity of the gas parcel of number density $n(z)$ located at z . For later convenience, Eq. (2) is formulated in terms of only the “upward” rates $k_{ij \rightarrow \ell m}$ by virtue of microscopic reversibility. Upward rates are subject to the constraint $E_i + E_j < E_\ell + E_m$ for the sum of rotational energies before and after the collision.

Under the experimental conditions of this work (see below) the temperature of the expanding gas always remains below the threshold of 250 K. Thus, only the populations of $J=0$ and $J=2$ rotational levels will be considered in the discussion, since the population of the $J=4$ rotational level of $p\text{H}_2$ at 1180 cm^{-1} is hardly detectable. Therefore the expanding $p\text{H}_2$ will be treated here as a two-level system, $J=0$ and $J=2$, of populations P_0 and P_2 described by means of a rotational temperature T_r . The conditions $P_0 + P_2 = 1$ and $P'_0 + P'_2 = 0$ are satisfied within experimental uncertainty.

Since $k_{ij \rightarrow \ell m}$ approximately scales as $\exp[(-E_\ell - E_m + E_i + E_j)/kT_t]$, just the $k_{00 \rightarrow 02}$ and $k_{02 \rightarrow 22}$ rate coefficients of $p\text{H}_2$ are relevant in the range of translational temperatures $2 < T_t < 110\text{ K}$ considered here. In this range upward rate coefficients other than $k_{00 \rightarrow 02}$ and $k_{02 \rightarrow 22}$, either are orders of magnitude smaller (like $k_{00 \rightarrow 22}$) or appear in Eq. (2) weighted with negligible populations (like $k_{04 \rightarrow 24}$), and will therefore be ignored.

A quantity that can be determined experimentally via Eq. (2) is the combination $k_{02} = P_0 k_{00 \rightarrow 02} + P_2 k_{02 \rightarrow 22}$, henceforth referred to as the “reduced” rate coefficient. To this purpose Eq. (2) may be rearranged as

$$k_{02}(T_t, T_r) = \frac{P'_0(z)V(z)}{n(z)P_0(z)} [-1 + e^{X(z)}]^{-1}, \quad (3)$$

a form where all right-hand-term quantities can be determined from the experiment; $X(z) = E_2 \beta [T_t^{-1}(z) - T_r^{-1}(z)]$ accounts for the breakdown of the rotational-translational thermal equilibrium as a function of the distance z from the nozzle; $T_t(z)$ and $T_r(z)$ are, respectively, the local translational and rotational temperatures at z ; $E_2 = 354.38\text{ cm}^{-1}$ is the energy of the $J=2$ rotational level of H_2 , and $\beta = hc/k_B = 1.4388\text{ K/cm}^{-1}$.

For later convenience Eq. (3) will be rewritten as

$$k_{02}(T_t, T_r) = G_{02}(T_t, T_r) e^{-\beta E_2/T_t}, \quad (4)$$

where

$$G_{02}(T_t, T_r) = - \frac{5P'_2(z)V(z)}{P_2(z)n(z)} \Omega \quad (5)$$

is a smooth function of T_t and T_r varying by less than a factor 3 for $2 \leq T_t \leq 110\text{ K}$ and $140 \leq T_r \leq 250\text{ K}$, the thermal domain of present experiment. The factor $\Omega = 1 + (e^X - 1)^{-1}$ varies between ≈ 1.2 at $T_t = 110\text{ K}$ and 1.0 at $T_t \leq 50\text{ K}$.

In Eq. (5), z , $n(z)$, and $P_2(z)$ are measured quantities, while $T_r(z)$, $T_t(z)$, $P'_2(z)$, $V(z)$, and $\Omega(z)$ are inferred from the former data with sufficiently good accuracy. Supersonic expansions of $p\text{H}_2$ under different stagnation conditions show a different evolution of rotational populations and temperature, thus leading to slightly different experimental $G_{02}(T_t, T_r)$ functions and associated $k_{02}(T_t, T_r)$ reduced rate coefficients. From the latter, the $k_{00 \rightarrow 02}(T_t)$ and $k_{02 \rightarrow 22}(T_t)$ rate coefficients can be obtained, as well as their corresponding cross sections, as shown in Sec. V.

The nature and conditions of the experiment, and how the referred quantities have been measured, are described next.

III. EXPERIMENT

All data needed here to determine the mentioned rate coefficients of $p\text{H}_2$ have been retrieved from the intensities of the $Q(0)$ and $Q(2)$ Raman lines measured along the symmetry axis of supersonic expansions of the gas. The spectra were recorded with the apparatus operative at the Instituto de Estructura de la Materia, dedicated to the systematic study of molecular fluid dynamics in the supersonic jets. This instrumentation, based on high sensitivity Raman spectroscopy with very high spatial resolution (few micrometers), has been described elsewhere.⁶ It has been upgraded in several aspects and currently consists of the following parts.

Expansion chamber. The expansion chamber, of $465 \times 440 \times 820\text{ mm}^3$, manufactured in welded aluminum, has 25 mm thick walls, and a 40 mm thick base for optomechanical stability. In order to reduce stray light from the

FIG. 1. Scheme of the Raman scattering excitation for the quantitative investigation of supersonic jets. Raman signal collected along *y* axis.

laser source the interior of the chamber is electrochemically coated in black.

Sample feeding line. Normal H₂ (*n*H₂) of 99.9999% purity was circulated through a cryogenic catalytic converter at a regulated pressure of 1–4 bars to prepare *p*H₂ of purity higher than 99.5%. The purity of *p*H₂ was determined spectroscopically from the ratio of intensities of the (ortho) $Q(1)=4155.25\text{ cm}^{-1}$ to the (para) $Q(0)=4161.18\text{ cm}^{-1}$ Raman lines. The *p*H₂ produced this way was compressed with no intermediate storage, regulated in a second stage to the stagnation pressure p_0 of the experiment, filtered by a 2 μm sintered stainless steel filter, and expanded supersonically into the chamber through a nozzle at $T_0=295\text{ K}$.

Nozzle. An axisymmetric nozzle of diameter $D=50\text{ μm}$ machined in copper has been used in the experiments. This nozzle, installed at the interior of the expansion chamber, is mounted onto a system of three orthogonal micropositioning stages. The point of the expansion flow field to be probed spectroscopically is chosen by moving the nozzle, while the focal spot of the exciting laser beam is maintained fixed for a better optical stability.

Vacuum system. The vacuum in the expansion chamber is provided by a 2000 ℓ/s turbomolecular pump backed by a 400 m³/h roots and a 70 m³/h rotary pumps. In stationary regime the residual pressures were in the range of 10^{-2} – 10^{-3} mbars.

Excitation laser source. A Beamlok 2080 Ar⁺ laser from Spectra Physics was used for excitation of the Raman scattering. Typical excitation power was 2.5 W (single mode) at $\lambda=514.5\text{ nm}$ on a 1.6 mm diameter laser beam.

Excitation/collection optics and micropositioning systems. The required high irradiance at the Raman scattering point of the jet was attained focusing the laser beam by means of a coated lens of $f=35\text{ mm}$ focal length, as shown in the scheme of Fig. 1. Dimension c of $\mathcal{R}$, the region actually “seen” by the spectrometer, is controlled by the entrance slitwidth, and dimension a by the vertical binning system of the charge-coupled device (CCD) detector; $c=5\text{ μm}$ and $a=50\text{ μm}$ are representative values in this work. The Raman signal, collected by a 50 mm $f:0.95$ photographic objective internal to the expansion chamber, was projected onto the

entrance slit of the spectrometer by an external achromat lens of $f=500\text{ mm}$, with total magnifying power $\times 10$. All optical elements within the expansion chamber are positioned by means of high accuracy micropositioning devices actuated by remote control from outside the chamber. Laser stray light from the expansion chamber was further reduced by means of a 514.5 nm notch holographic filter installed in front of the spectrometer slit.

Spectrometer. The very high sensitivity spectrometer is a dedicated instrument which is described in detail elsewhere.⁷ It is equipped with a 2360 lines/mm holographic grating of $102\times 102\text{ mm}^2$ as dispersive element, and with a back-illuminated CCD detector refrigerated by liquid nitrogen. Its active surface has 1340×400 pixels of $20\times 20\text{ μm}^2$. Scanning and data acquisition are fully computerized, employing the home developed software package REGISTRA. Current routine detection limit of this spectrometer at a spectral resolution of 1 cm^{-1} is on the order of 10^{19} molecules/m³.

With the setup described above five supersonic expansions of *p*H₂ have been investigated quantitatively in order to generate the primary data set for obtaining the reduced rate coefficients $k_{02}(T_t, T_r)$ according to Eqs. (4) and (5). In all cases the residual pressure in the expansion chamber was low enough to shape the zone of silence of the expansions larger than $z=300D$. No evidence of normal shock wave was detected in this region, characterized experimentally by a density decay $\propto z^{-2}$ for $z>4D$. This is the best proof of isentropic laminar flow in the investigated region, a condition that must be satisfied for deriving reliable translational temperatures and flow velocities from the experimental number densities and rotational temperatures (see below). For the present purpose a number of Raman spectra of *p*H₂ in the zone 4100 – 4170 cm^{-1} were recorded along the axis of the expansions, starting as close to the nozzle as 25 μm ($z=D/2$).

IV. MEASURED QUANTITIES

For the evaluation of Eqs. (4) and (5) the primary experimental quantities measured along the expansion axis are the distance z from the nozzle, the local number density $n(z)$, and the rotational populations $P_0(z)$ and $P_2(z)$. The remaining quantities $T_r(z)$, $T_t(z)$, $P'_2(z)$, and $V(z)$ were derived from $n(z)$, $P_0(z)$, and $P_2(z)$ as described below.

The distance z was determined from the motion of the nozzle by means of its codified micropositioning stage of nominal precision $\pm 1\text{ μm}$. In turn, $n(z)$, $P_0(z)$, and $P_2(z)$ were derived from the intensities, $I_0(z)$ and $I_2(z)$ of the $Q(0)$ and $Q(2)$ Raman lines of *p*H₂ at 4161.18 and 4143.47 cm^{-1} , respectively. These intensities can be expressed by⁸

$$I_0(z) = Cn(z)P_0(z)\langle 00|\vec{a}|10\rangle^2, \quad (6)$$

$$I_2(z) = Cn(z)P_2(z)\left[\langle 02|\vec{a}|12\rangle^2 + \frac{4}{45}\frac{6}{21}\langle 02|\gamma|12\rangle^2\right], \quad (7)$$

in terms of the rovibrational transition moments of the polarizability invariants, $\langle vJ|\vec{a}|v'J\rangle$ (mean polarizability) and $\langle vJ|\gamma|v'J\rangle$ (anisotropy). The values employed, $\langle 00|\vec{a}|10\rangle \approx \langle 02|\vec{a}|12\rangle = (12.95 \pm 0.1)$ and $\langle 02|\gamma|12\rangle = (11.29 \pm 0.1)$, in units of $10^{-42}\text{ C V}^{-1}\text{ m}^2$, have been derived from a combina-

FIG. 2. Number densities along supersonic expansions of $p\text{H}_2$.

tion of *ab initio* calculations⁹ and additional experimental measurements from our laboratory.

The factor C depends on the exciting irradiance, wavelength, and scattering geometry, and remains constant along the experiment. Here C has been determined from the Raman intensity I_0^{ref} recorded in a static $p\text{H}_2$ sample of known number density and temperature. The corresponding pressure was measured with a high accuracy (0.08%) MKS Baratron pressure gauge. The estimated uncertainties are $\approx 4\%$ for C and $\approx 1\%$ for P_0 .

The experimental number densities determined by means of Eqs. (6) and (7) are shown in Fig. 2. The rotational temperatures associated with the experimental rotational populations $P_0(z)$ and $P_2(z)$ are shown in Fig. 3. Dots stand for the measured data, while continuous lines are the best fits using analytical smoothing functions. For better accuracy the derivative function $P'_2(z)$ was obtained numerically from the smoothed $T_r(z)$'s.

The translational temperature $T_t(z)$ along the expansions has been derived from the smoothed $n(z)$'s and $T_r(z)$'s assuming isentropic flow in the investigated axial region of the jet. The procedure to retrieve $T_t(z)$ is as follows: The entropy $S(z)$ along the expansion is given by

FIG. 3. Rotational and translational temperatures along supersonic expansions of $p\text{H}_2$.

$$S(z) = S_t(z) + S_r(z) + S_v(z), \quad (8)$$

where $S_t(z)$, $S_r(z)$, and $S_v(z)$ are, respectively, the translational, rotational, and vibrational contributions. The latter remains constant since the vibrational cooling of $p\text{H}_2$ is negligible along the expansions. In contrast, the translational and rotational contributions vary with z as

$$S_t(z) = S_t^0 + R \left[\frac{3}{2} \ln T_t(z) - \ln n(z) \right] \quad (9)$$

and

$$S_r(z) = S_r^0 + R \left[\ln Z(z) + T_r(z) \frac{\partial}{\partial T_r(z)} \ln Z(z) \right], \quad (10)$$

respectively, where $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$ is the universal gas constant, and

$$Z(z) \approx 1 + 5e^{-\beta E_2/T_r(z)} \quad (11)$$

stands for the rotational partition function of $p\text{H}_2$ in an approximation good enough if $T_r < 250 \text{ K}$. Imposing the invariance of entropy between the nozzle prechamber of known stagnation conditions and any point of the jet axis, we obtain for the translational temperature

$$T_t(z) = T_0 \left(\frac{n(z)}{n_0} \frac{Z_0}{Z(z)} e^{y_0 - y(z)} \right)^{2/3}, \quad (12)$$

where index zero refers to the stagnation conditions in the nozzle prechamber (not to be confused with those at the nozzle origin $z=0$) and

$$y(z) = P_2(z) \frac{\beta E_2}{T_r(z)}. \quad (13)$$

Since the stagnation conditions (T_0, n_0, p_0) are known for each expansion, and $n(z)$, $T_r(z)$, $Z(z)$, and $y(z)$ are determined from the experiment, the translational temperature $T_t(z)$ along the jet is obtained from Eqs. (12) and (13). This is advantageous compared to an earlier procedure based on the conservation of enthalpy along the expansion axis.¹⁰ Now, the translational temperature at a given point z of the expansion is obtained from the local experimental data $n(z)$ and $T_r(z)$ at the very same point z , according to Eq. (12), and from the stagnation conditions, and there is no need to integrate over the expansion path as in the previous method.¹⁰ Accumulative errors are avoided, overcoming the need for a complete data set between the nozzle exit and the point z .

The translational temperatures determined for the expansions at stagnation pressures $p_0 = 16$ and 1 bars are shown in Fig. 3 (bottom). For $p_0 = 8, 4$, and 2 bars the translational temperatures are between the former ones. The differences among the translational temperatures in the various expansions can be easily understood in terms of Eq. (12). Although the ratio function $n(z)/n_0$ is very nearly invariant in all five expansions, the rotational partition function $Z(z)$ and the $y(z)$ function depend on the rotational temperature, which is specific for each expansion. This leads to significantly different translational temperatures.

FIG. 4. (a) G_{02} functions of $p\text{H}_2$ from expansions at $p_0=4, 8$, and 16 bars. (b) G_{00-02} function of $p\text{H}_2$. Experiment: as obtained from the G_{02} functions assuming $R_{02}=1.54$; error bars are one standard deviation. Theory: MOLSCAT calculation (see the text).

The local flow velocity $V(z)$ along the zone of silence of a supersonic expansion generated at stagnation temperature T_0 can be determined from the conservation of total enthalpy, which leads to

$$V(z) = \left(\frac{R}{W} [7T_0 - 5T_t(z) - 2T_r(z)] \right)^{1/2}, \quad (14)$$

where W is the molar mass of the expanded gas. The estimated error in V is $\leq 1\%$.

A preliminary analysis of the raw experimental number densities and rotational temperatures of the five expansions of $p\text{H}_2$ investigated showed that the $p_0=1$ and 2 bars expansions were thermally too noisy for the present purpose and led to too poor a measure of the $P'_2(z)$'s required in Eq. (5). Thus, only the data from expansions at $p_0=4, 8$, and 16 bars, are considered good enough to determine the $G_{02}(T_t, T_r)$ functions and their corresponding reduced rate coefficients $k_{02}(T_t, T_r)$.

The experimental $G_{02}(T_t, T_r)$'s derived from the $p_0=4, 8$, and 16 bars expansions are depicted in Fig. 4(a). The corresponding reduced rate coefficients $k_{02}(T_t, T_r)$ are given in Table I for selected translational temperatures.

The experimental error of G_{02} 's is mainly determined by $P'_2(z)$ and $n(z)$ errors. While $n(z)$ error is conditioned by the uncertainty of the instrumental constant C , $P'_2(z)$ error strongly depends on the type of function employed for smoothing T_r , specially for T_r approaching asymptotically the terminal rotational temperature, which corresponds to translational temperatures below 10 K as shown in Fig. 3. This is the main reason why $G_{02}(T_t, T_r)$ is expected to be less accurate for $T_t < 10$ K. In order to estimate the accuracy of

TABLE I. Reduced rate coefficient k_{02} of $p\text{H}_2$ measured from three supersonic expansions at stagnation pressure $p_0=16, 8$ and 4 bars, and stagnation temperature $T_0=295$ K. Units of $Q \times \text{m}^3\text{s}^{-1}$.

T_t (K)	16 bars	8 bars	4 bars	Q
110	3.989	4.129	5.028	10^{-20}
100	2.041	2.625	2.992	10^{-20}
50	0.991	1.217	1.298	10^{-22}
20	2.194	2.546	2.733	10^{-29}
10	2.449	2.382	3.893	10^{-40}
5	2.663	2.385	4.270	10^{-62}
2	1.430	1.254	2.397	10^{-128}

k_{02} it is important to realize that T_t must be considered the independent variable, and so error free by definition. Thus, at a fixed T_t the accuracy of the $k_{02}(T_t, T_r)$ determined by means of Eqs. (4) and (5) is sensitive only to the errors of the experimental quantities P_2 , P'_2 , n , V , and T_r at this particular value of T_t . In summary, the accuracy of k_{02} is determined by that of the function G_{02} defined in Eq. (5). In an ideal error-free experiment under the nominal conditions of this work the G_{02} 's from $p_0=16, 8$, and 4 bars measurements should differ by less than 4% . The spread ($\approx 18\%$) of the actual experimental plots shown in Fig. 4(a) thus provides an empirical estimate for the overall experimental uncertainty of G_{02} 's and k_{02} 's.

V. EXPERIMENTAL RATE COEFFICIENTS AND CROSS SECTIONS

From the definition of $k_{02}=P_0k_{00 \rightarrow 02}+P_2k_{02 \rightarrow 22}$ it follows that the $k_{00 \rightarrow 02}$ and $k_{02 \rightarrow 22}$ rate coefficients can in principle be retrieved from the k_{02} 's of Table I, since the rotational populations P_0 and P_2 along the various expansions is known with good accuracy ($\approx 1\%$). However, the system of equations is ill defined due to the experimental errors of about $\pm 18\%$ in k_{02} discussed above, leading to a too poor determination of the ratio

$$R_{20}(T_t) = \frac{k_{02 \rightarrow 22}(T_t)}{k_{00 \rightarrow 02}(T_t)}. \quad (15)$$

We thus conclude that obtaining the $k_{00 \rightarrow 02}$ and $k_{02 \rightarrow 22}$ rates on the sole basis of the reported experiment would require an experimental accuracy about one order of magnitude better than available at present.

In order to overcome this limitation the constraint $R_{20}=1.54 \pm 0.15$, for $2 \leq T_t \leq 110$ K, has been imposed on the basis of the theoretical results discussed below. This way the "experimental" rates of Table II can be compared unambiguously with the theoretical results.

As a further step, we show how the cross sections for inelastic binary collisions at kinetic energy E have been derived from the corresponding experimental rates: the relation between a rate coefficient $k_{ij \rightarrow \ell m}(T_t)$ and its cross section $\sigma_{ij \rightarrow \ell m}(E)$ is given by the weighted average

TABLE II. Rate coefficients $k_{00 \rightarrow 02}$ and $k_{02 \rightarrow 22}$ of $p\text{H}_2$. Units of $Q \times \text{m}^3 \text{s}^{-1}$. Uncertainties in parentheses are one standard deviation.

T_t (K)	$k_{00 \rightarrow 02}$ Experiment ^a	$k_{00 \rightarrow 02}$ Theory ^b	$k_{02 \rightarrow 22}$ Theory ^b	Q
300		1.53	2.58	10^{-18}
200		4.39	7.44	10^{-19}
150		1.44	2.44	10^{-19}
110	3.6(6)	3.29	5.53	10^{-20}
100	2.2(4)	1.92	3.23	10^{-20}
90	1.2(2)	1.02	1.71	10^{-20}
80	5.6(8)	4.64	7.79	10^{-21}
70	2.1(3)	1.73	2.91	10^{-21}
60	6.0(7)	4.75	7.97	10^{-22}
50	1.1(1)	0.81	1.35	10^{-22}
40	7.8(9)	5.90	9.86	10^{-24}
30	1.1(1)	0.80	1.34	10^{-25}
20	2.3(3)	1.63	2.71	10^{-29}
10	2.7(7)	1.65	2.62	10^{-40}
5	2.8(9)	1.63	2.41	10^{-62}
2	1.5(5)	0.89	1.23	10^{-128}

^aThis work, assuming $R_{02} = 1.54 \pm 0.15$.^bThis work, using the PES from Ref. 11.

$$k_{ij \rightarrow \ell m}(T_t) = \frac{\langle v \rangle}{(k_B T_t)^2} \int_{E_s}^{\infty} \frac{\sigma_{ij \rightarrow \ell m}(E)}{\exp(E/k_B T_t)} E dE, \quad (16)$$

under the assumption that the colliding molecules obey a Maxwellian distribution at the translational temperature T_t ; $E = E_{\text{total}} - E_i - E_j$ is the available precollisional kinetic energy for the $J=i$ and $J=j$ rotational levels; E_s is the minimum kinetic energy for the levels $J=\ell$ and $J=m$ to become accessible, and $\langle v \rangle = (8k_B T_t / \pi \mu)^{1/2}$ is the mean relative velocity of the colliding partners of reduced mass μ .

In order to retrieve the $\sigma_{00 \rightarrow 02}$ and $\sigma_{02 \rightarrow 22}$ cross sections of $p\text{H}_2$ from the experimental rate coefficients it will be assumed that the $\sigma_{ij \rightarrow \ell m}$ cross section in Eq. (16) can be described for $E > E_s$ with sufficiently good accuracy by the truncated power series

$$\sigma_{ij \rightarrow \ell m}(E) = \sum_{n=0}^q \sigma_{ij \rightarrow \ell m}^{(n)} E^n, \quad (17)$$

with $q+1$ constant coefficients $\sigma_{ij \rightarrow \ell m}^{(n)}$. With this approximation Eq. (16) can be integrated analytically, and the rate coefficient at the temperature T_t becomes

$$k_{ij \rightarrow \ell m}(T_t) = G_{ij \rightarrow \ell m}(T_t) e^{-\beta E_s / T_t}, \quad (18)$$

with

$$G_{ij \rightarrow \ell m}(T_t) = \langle v \rangle \sum_{n=0}^q \sigma_{ij \rightarrow \ell m}^{(n)} C_n(T_t). \quad (19)$$

The first three $C_n(T)$ coefficients are

$$C_0(T_t) = 1 + \frac{\beta E_s}{T_t}, \quad (20)$$

$$C_1(T_t) = 2E_s + \frac{\beta E_s^2}{T_t} + \frac{2T_t}{\beta}, \quad (21)$$

$$C_2(T_t) = 3E_s^2 + \frac{\beta E_s^3}{T_t} + \frac{6E_s T_t}{\beta} + \frac{6T_t^2}{\beta^2}, \quad (22)$$

where $E_s = (E_\ell + E_m) - (E_i + E_j)$ can be taken as a good approximation. For the particular cases considered here, $k_{00 \rightarrow 02}$ and $k_{02 \rightarrow 22}$, we have $E_s = E_2 = 354.38 \text{ cm}^{-1}$.

For any particular rate coefficient $k_{ij \rightarrow \ell m}(T_t)$ determined experimentally Eq. (18) is a system of r linear equations, one for each translational temperature considered $T_{t1}, T_{t2}, \dots, T_{tr}$, with $q+1$ unknowns $\sigma_{ij \rightarrow \ell m}^{(n)}$. The number $q+1$ of significant $\sigma^{(n)}$'s that can be determined by solving the system depends on the thermal range considered. The higher T_t 's are included the more $\sigma^{(n)}$'s can be determined. The experimental $G_{00 \rightarrow 02}(T_t)$, which carries the information about the $\sigma_{00 \rightarrow 02}^{(n)}$ coefficients according to Eqs. (19)–(22) is shown in Fig. 4(b) jointly with the best theoretical $G_{00 \rightarrow 02}(T_t)$ discussed in the following section.

In the particular case studied here, the solution of the overdetermined system of 13 linear equations for the 13 experimental $k_{00 \rightarrow 02}(T_t)$ data points of Table II, each one for a temperature in the range $2 \leq T_t \leq 110 \text{ K}$, leads to a three-parameter best fit of the cross section

$$\sigma_{00 \rightarrow 02}(E) = \sigma_{00 \rightarrow 02}^{(0)} + \sigma_{00 \rightarrow 02}^{(1)} E + \sigma_{00 \rightarrow 02}^{(2)} E^2, \quad (23)$$

for $360 \leq E \leq 600 \text{ cm}^{-1}$, which is the significant range of pre-collisional energy in Eq. (16) for $T_t \leq 110 \text{ K}$.

Employing the experimental errors of Table II as weighting factors the best fit parameters for the experimental $\sigma_{00 \rightarrow 02}(E)$ are: $\sigma_{00 \rightarrow 02}^{(0)} = 0.0368 \text{ \AA}^2$, $\sigma_{00 \rightarrow 02}^{(1)} = -0.353 376 \times 10^{-3} \text{ \AA}^2 \text{ cm}$, and $\sigma_{00 \rightarrow 02}^{(2)} = 0.809 468 \times 10^{-6} \text{ \AA}^2 \text{ cm}^2$. The $\sigma_{00 \rightarrow 02}(E)$ obtained this way is shown in Fig. 5(b) jointly with the error bars as determined from the errors quoted in Table II.

As an internal consistence test $k_{00 \rightarrow 02}(T_t)$ was recalculated using Eqs. (18) and (19) with the $\sigma_{00 \rightarrow 02}^{(n)}$ constants given above. The results are within 5% of the experimental values of Table II, proving that $k_{00 \rightarrow 02}$ of $p\text{H}_2$ can be interpolated at any temperature $2 \leq T_t \leq 110 \text{ K}$ by means of Eqs. (18)–(22) with reasonably good accuracy.

It deserves mention how the experimental uncertainties of Table II in the domain of temperatures propagate into the domain of energies, shown in Fig. 5(b). While the experimental uncertainty of $k_{00 \rightarrow 02}(T_t)$ is highest at the lowest temperatures investigated, below 10 K, the corresponding uncertainty of $\sigma_{00 \rightarrow 02}(E)$ is almost negligible between about 400 and 450 cm^{-1} , and then increases monotonically for increasing energies. This is due to the truncation of the thermal domain at $T_t = 110 \text{ K}$. On the other hand, the error bar at $E = 360 \text{ cm}^{-1}$ is due to the omission of the resonance at $E_s = 354 \text{ cm}^{-1}$ in Eq. (17). Extending the experimental thermal domain of $k_{00 \rightarrow 02}(T_t)$ above 110 K would lead to a better definition of $\sigma_{00 \rightarrow 02}(E)$ above 600 cm^{-1} . Inclusion of a Gaussian-type function in Eq. (17) should allow for a better definition of $\sigma_{00 \rightarrow 02}(E)$ near the 354 cm^{-1} resonance.

VI. THEORY VERSUS EXPERIMENT

Several calculations of the inelastic state-to-state cross sections and rate coefficients of $p\text{H}_2$ have been reported

FIG. 5. (a) $\sigma_{00 \rightarrow 02}$ cross section calculated from different intermolecular PESs of H₂. (b) Detail and experimental results.

before.¹⁻⁵ Such results depend on the intermolecular potential employed in the calculation, and so far appear to be limited to the thermal range above 50 K. For a meaningful comparison of theory with our experimental results in the range $2 < T_i < 110$ K, we have carried out a number of scattering calculations in the frame of the quantum mechanical coupled channels method, employing two different rigid rotor potential energy surfaces (PESs): Diep and Johnson's (DJ-PES) (Ref. 11), and Schaefer and Köhler's (SK-PES).¹² A grid of total energies from 354.35 to 5000 cm⁻¹ was employed, and at least two closed (i, j) "well-ordered" levels (i.e., with $i \leq j$) were taken into account in addition to the open well-ordered rotational levels.^{1,13} The rotational energy levels were taken from.¹⁴ Comparable calculations reported by Flower⁵ were based on Schwenke's potential (S-PES).¹⁵

The MOLSCAT code¹⁶ was employed considering the *p*H₂ molecules as indistinguishable. Additional test calculations for distinguishable molecules were performed with the MOLCOL code¹⁷ in order to check for quantum interference effects. In this context the cross sections for indistinguishable colliding molecules is expressed as^{1,3}

$$\sigma_{ij \rightarrow \ell m}^{\text{ind}} = \sigma_{ij \rightarrow \ell m}^d + \sigma_{ij \rightarrow \ell m}^e + (W^+ - W^-) \sigma_{ij; \ell m}^{de}, \quad (24)$$

where σ^d and σ^e are the direct and the exchange cross sections for distinguishable molecules; $W^+ = (I+1)/(2I+1) = 1$ and $W^- = I/(2I+1) = 0$ are the boson nuclear spin ($I=0$) statistical weights of the antisymmetric and symmetric wave functions of the *p*H₂-*p*H₂ system; σ^{de} accounts for quantum interference effects.

In Fig. 5(a) (graphs 1 and 2) the quantities $\frac{1}{2} \sigma_{00 \rightarrow 02}^{\text{ind}}$ and $\sigma_{00 \rightarrow 02}^{\text{dis}}$ calculated from the DJ-PES (Ref. 11) are shown for comparison; σ^{ind} was obtained according to Takayanagi's counting of states.^{4,18} Since $\sigma^{\text{dis}} = \sigma^d = \sigma^e$ for distinguishable colliding molecules, we check this way that $\sigma_{00 \rightarrow 02}^{\text{ind}} = 2 \sigma_{00 \rightarrow 02}^{\text{dis}}$, corroborating that interference effects are negligible in *p*H₂ for inelastic cross sections.¹

The $\sigma_{00 \rightarrow 02}$'s calculated by us from SK-PES (Ref. 12) and calculated by Flower⁵ from S-PES (Ref. 15) are included in Fig. 5 (graphs 3 and 4) for comparison. These σ 's are somewhat lower than for the DJ-PES, leading to rate coefficients lower than the experimental ones reported in Table II.

As shown in Fig. 5(b) (graph 1), the best agreement of theory with experiment in the range $400 < E < 600$ cm⁻¹ is found for our calculation based on DJ-PES.¹¹ However, Flower's results (graph 4) as well as our own theoretical results based on SK-PES (Ref. 12) (graph 3) are partially compatible with the experiment since the reported experimental uncertainties are just one standard deviation.

Two discrepancies between experiment and theory deserve mention. First, all the calculated $\sigma_{00 \rightarrow 02}(E)$'s are slightly underestimated with respect to the experiment. Whether this is due to a convergence of theory towards higher σ 's or is caused by systematic errors (of $\approx 10\%$ by excess) in the experimental number densities cannot be decided at present. Second, the experimental $\sigma_{00 \rightarrow 02}(E) \approx 0.014$ Å² determined at $E = 360$ cm⁻¹, near the $E_2 = 354.38$ cm⁻¹ resonance, is significantly overestimated with respect to the theoretical predictions. This may be attributed to neglecting the resonance in the simplified description of $\sigma_{00 \rightarrow 02}(E)$ by the polynomial series of Eq. (17). A resonant term might in principle be considered in Eq. (17). However, experimental data of substantially improved accuracy would be needed to fix such a term.

The calculated cross sections discussed above were transformed to the rate coefficients by means of Eq. (16); the $k_{00 \rightarrow 02}$ and $k_{02 \rightarrow 22}$ resulting from Diep and Johnson's PES (Ref. 11) are reported in Table II and the corresponding $G_{00 \rightarrow 02}$ is shown in Fig. 4(b). In the range where comparison with the experiment is possible, $2 \leq T_i \leq 110$ K, the theoretical prediction is $\approx 15\%$ lower near $T_i \approx 100$ K and $\approx 50\%$ lower for $T \leq 10$ K. However, for $T \leq 10$ K the experimental uncertainty is $\approx 30\%$. Taking into account that the quantities compared span a range larger than 100 orders of magnitude these results are highly encouraging.

VII. SUMMARY AND CONCLUSIONS

We have reported an experimental method substantially improved with respect to our previous works,^{19,20} which allows us to obtain inelastic collisional state-to-state rate coefficients and cross sections as a function of the temperature and collisional energy, respectively. The simplest molecular system *p*H₂ has been employed as a methodological test, reaching temperatures well below the triple point. For the dominant rate coefficient of *p*H₂ at low temperature, $k_{00 \rightarrow 02}$, the agreement with our theoretical calculations employing a recent PES (Ref. 11) as well as with other results from the literature is highly encouraging. The reduction from experi-

mental $k_{00\rightarrow 02}$ of $p\text{H}_2$ to its $\sigma_{00\rightarrow 02}$ has proven successful, with good agreement of this quantity with several theoretical results in the domain of kinetic energy $360 \leq E \leq 600 \text{ cm}^{-1}$.

The reported methodology can be employed with no loss of generality on other molecule-molecule or molecule-atom collisional systems. It also can be extended to a wider thermal range with affordable technical improvements. Experimental information about $\sigma_{00\rightarrow 02}(E)$ of $p\text{H}_2$ in the range up to $E \approx 2000 \text{ cm}^{-1}$ can in principle be obtained by the same method from supersonic expansions spanning the thermal range $2 \leq T_t \leq 300 \text{ K}$ in the jet, which should imply stagnation temperatures above 700 K , a condition beyond the scope of the present work, however, not impossible in a near future. In the light of the expertise developed along this work we judge it feasible to reach an experimental accuracy on the order of 5% in the rate coefficients, a figure which may open appealing options for a rigorous treatment of nonequilibrium problems in the fields of astrophysics and atmospheric physics. It also may provide a firm basis for rarefied gas dynamics models beyond the continuum, as well as a new source of experimental data for the validation of intermolecular potentials in a wide range of energies.

ACKNOWLEDGMENTS

This work was supported by the Spanish Ministerio de Ciencia y Tecnología, Research Project No. BFM2001-2276. The authors wish to thank J. P. Toennies and the Max-Planck-Institut für Strömungsforschung, Göttingen, for the

loan of a $n\text{H}_2 \rightarrow p\text{H}_2$ converter and a membrane gas compressor. They also thank D. R. Flower for providing his calculated cross sections at various energies.

- ¹G. Zarur and H. Rabitz, J. Chem. Phys. **60**, 2057 (1974).
- ²H. Rabitz and S. Lam, J. Chem. Phys. **63**, 3532 (1975).
- ³L. Monchick and J. Schaefer, J. Chem. Phys. **73**, 6153 (1980).
- ⁴G. Danby, D. R. Flower, and T. S. Monteiro, Mon. Not. R. Astron. Soc. **226**, 739 (1987).
- ⁵D. R. Flower, Mon. Not. R. Astron. Soc. **297**, 334 (1998).
- ⁶S. Montero, B. Maté, G. Tejeda, J. M. Fernández, and A. Ramos, in *Atomic and Molecular Beams: The State of the Art 2000*, edited by R. Campargue (Springer, Berlin, 2001), p. 295.
- ⁷G. Tejeda, J. M. Fernández, and S. Montero, Appl. Spectrosc. **51**, 265 (1997).
- ⁸G. Placzek and E. Teller, Z. Phys. **81**, 209 (1933).
- ⁹J. Rychlewski, J. Chem. Phys. **78**, 7252 (1983).
- ¹⁰B. Maté, G. Tejeda, and S. Montero, J. Chem. Phys. **108**, 2676 (1998).
- ¹¹P. Diep and J. K. Johnson, J. Chem. Phys. **112**, 4465 (2000); **113**, 3480 (2000).
- ¹²J. Schaefer and W. E. Köhler, Z. Phys. D: At., Mol. Clusters **13**, 217 (1989).
- ¹³S. Green, J. Chem. Phys. **62**, 2271 (1975).
- ¹⁴C. Schwartz and R. J. Le Roy, J. Mol. Spectrosc. **121**, 420 (1987).
- ¹⁵D. W. Schwenke, J. Chem. Phys. **89**, 2076 (1988).
- ¹⁶J. M. Hutson and S. Green, MOLSCAT version 14, Collaborative Computational Project No. 6 of the UK Science and Engineering Research Council, 1994.
- ¹⁷D. R. Flower, G. Bourhis, and J.-M. Launay, Comput. Phys. Commun. **131**, 187 (2000).
- ¹⁸K. Takayanagi, Adv. At. Mol. Phys. **1**, 149 (1965).
- ¹⁹A. Ramos, G. Tejeda, J. M. Fernández, and S. Montero, Phys. Rev. A **66**, 022702 (2002).
- ²⁰B. Maté, F. Thibault, A. Ramos, G. Tejeda, J. M. Fernández, and S. Montero, J. Chem. Phys. **118**, 4477 (2003).